Supporting Information

Nickel-Catalyzed Ligand-Controlled Switchable Skeletal Rearrangements: Divergent Synthesis of Cyclohexenols, Cycloheptenols, and 2-Benzazepin-5-ones

Yongli Liu, Yuanyuan Ping,* Wangqing Kong*

The Institute for Advanced Studies (IAS), Wuhan University, Wuhan, P. R. China.

Email: wqkong@whu.edu.cn

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1. General Information

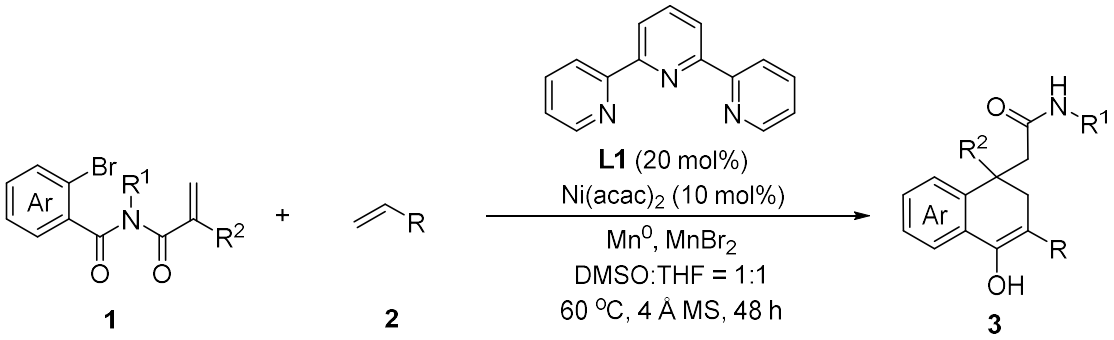
Nuclear magnetic resonance (NMR) spectroscopy measurements were carried out at room temperature. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, HSQC, HMBC, COSY and NOESY experiments were carried out using Bruker ADVANCE III (600 MHz) or JNM-ECZ400S/L1 (400 MHz) spectrometers. Chemical shifts (δ) are reported in ppm relative to the residual solvent peak with corresponding coupling constants (*J*) in Hertz (Hz) and multiplicities (s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet and combinations of these and app.: apparent multiplicities). Gas chromatography were determined with a SHIMADZU Nexis GC 2030 gas chromatography instrument with a FID detector. High-resolution mass spectra (HRMS) were recorded on Thermo Fisher Orbitrap Elite mass spectrometer. Column and elution details were specified in each entry.

Materials and Methods:

Unless otherwise stated, starting materials were purchased from commercial suppliers (Stream, Leyan.com, Energy Chemical and so on). All reactions dealing with air- or moisture-sensitive compounds were performed in the argon-filled glove box or by standard Schlenk techniques in oven-dried reaction vessels under argon atmosphere. Solvents were purchased in HPLC quality, degassed by purging thoroughly with argon and dried over activated molecular sieves of appropriate size. More sensitive compounds were stored in a desiccator or in a glove-box if required. Reactions were monitored by thin layer chromatography (TLC) using glass 0.25 mm silica gel plates. Compounds were visualized by UV-light at 254 nm and by dipping the plates in an aqueous potassium permanganate solution followed by heating. Flash column chromatography was performed over silica gel (200-400 mesh).

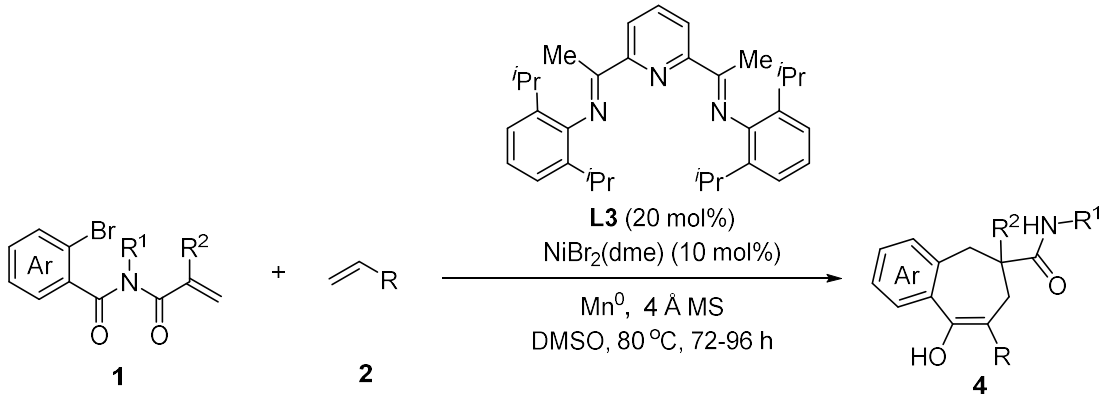
2. General Procedures

2.1 General procedure for the synthesis of products 3



An oven-dried sealed tube equipped with a PTFE-coated stir bar was charged with $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 4.6 mg), aryl bromide **1** (0.1 mmol, 1 equiv), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), alkene **2** (0.3 mmol), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL). The sealed tube was sealed and removed from the glovebox. Then the reaction was stirred at 60 °C until the reaction was complete (monitored by TLC). The resulting mixture was quenched with saturated NH_4Cl solution (5 mL) and further diluted with water (10 mL). The aqueous layer was extracted with EtOAc and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by chromatography on silica gel, eluting with petroleum ether/EtOAc (10/1~1/1) to afford the desired products **3**.

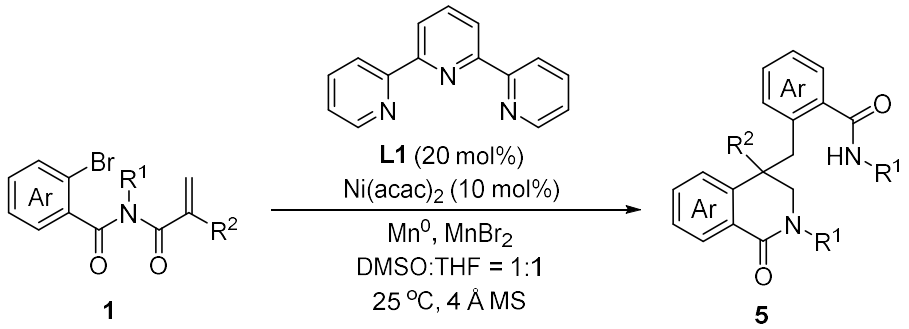
2.2 General procedure for the synthesis of products 4



An oven-dried sealed tube equipped with a PTFE-coated stir bar was charged with $NiBr_2(dme)$ (10 mol%, 3.1 mg), **L3** (20 mol%, 9.6 mg), aryl bromide **1** (0.1 mmol, 1 equiv), Mn^0 (0.3 mmol, 16.5 mg), alkene **2** (0.3 mmol), 4 Å molecular sieves (30 mg) and anhydrous DMSO (2 mL).

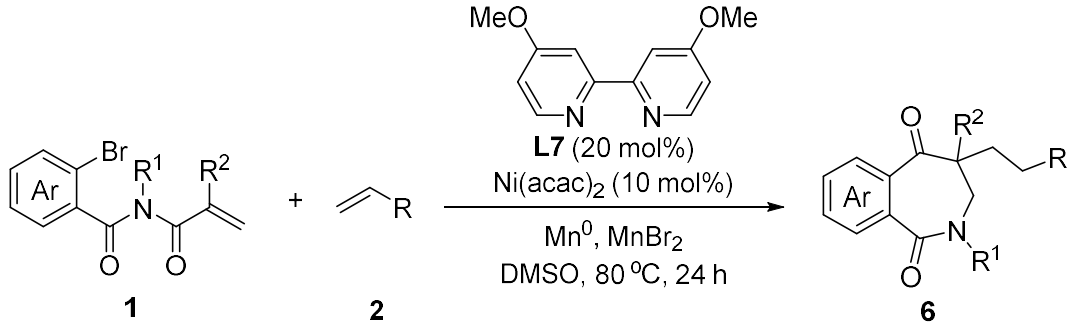
The sealed tube was sealed and removed from the glovebox. Then the reaction was stirred at 80 °C in an aluminium bead bath until the reaction was complete (monitored by TLC). The resulting mixture was quenched with saturated NH_4Cl solution (5 mL) and further diluted with water (10 mL). The aqueous layer was extracted with EtOAc and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by chromatography on silica gel, eluting with petroleum ether/EtOAc (10/1~1/1) to afford the desired products **4**.

2.3 General procedure for the synthesis of products 5



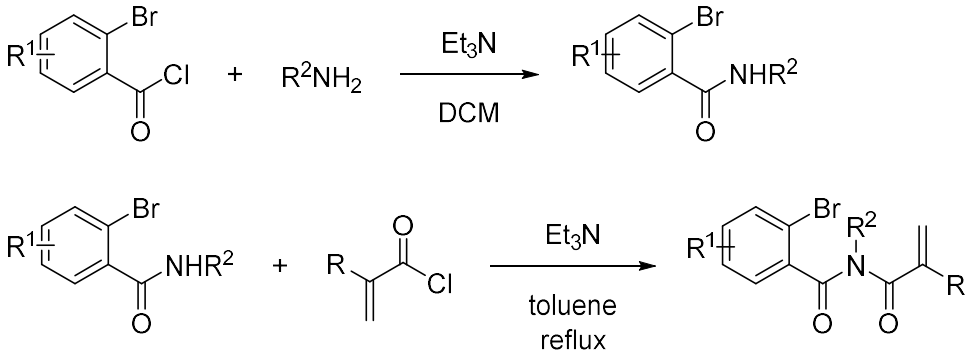
An oven-dried sealed tube equipped with a PTFE-coated stir bar was charged with $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 4.6 mg), aryl bromide **1** (0.1 mmol, 1 equiv), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL). The sealed tube was sealed and removed from the glovebox. Then the reaction was stirred at 60 °C until the reaction was complete (monitored by TLC). The resulting mixture was quenched with saturated NH_4Cl solution (5 mL) and further diluted with water (10 mL). The aqueous layer was extracted with EtOAc and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by chromatography on silica gel, eluting with petroleum ether/EtOAc (5/1~1/1) to afford the desired products **5**.

2.4 General procedure for the synthesis of products 6



An oven-dried sealed tube equipped with a PTFE-coated stir bar was charged with $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), aryl bromide **1** (0.1 mmol, 1 equiv), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), alkene **2** (0.3 mmol) and anhydrous DMSO (2 mL). The sealed tube was sealed and removed from the glovebox. Then the reaction was stirred at 80 °C until the reaction was complete (monitored by TLC). The resulting mixture was quenched with saturated NH_4Cl solution (5 mL) and further diluted with water (10 mL). The aqueous layer was extracted with EtOAc and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by chromatography on silica gel, eluting with petroleum ether/EtOAc (10/1~1/1) to afford the desired products **6**.

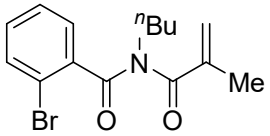
3. Synthesis and Characterization of Starting Materials



To a solution of amine (20 mmol, 1 equiv) and triethylamine (2 equiv) in DCM (40 mL) at 0 ℃ was added dropwise a solution of 2-bromobenzoyl chloride (1.2 equiv) in DCM (10 mL) over 15 min. After stirring for another 30 min, the mixture was warmed to room temperature and stirred until the amine was consumed completely (monitored by TLC). The resulting solution was concentrated, and the residue was dissolved in EtOAc (50 mL) and filtered. The organic layer was washed with saturated $NaHCO_3$ solution (50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue substituted 2-bromobenzamide was used for the next step without further purification.

Methacryloyl chloride (2 equiv) in toluene (0.1 M) was added to the mixture of substituted 2-bromobenzamide (1 equiv), triethylamine (2 equiv) and DMAP (0.1 equiv) in toluene (0.1 M). The mixture was stirred overnight at reflux. The reaction was quenched with saturated aqueous Na_2CO_3 (5 mL), then the mixture was extracted with dichloromethane (3 × 5 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel affording the corresponding product.

2-bromo-*N*-butyl-*N*-methacryloylbenzamide (1a)

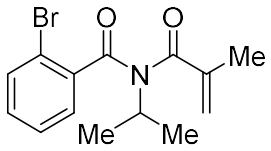


Chemical Formula: $C_{15}H_{18}BrNO_2$
Exact Mass: 323.0521

Compound **1a** was prepared according to General Procedure **3**. ^1H NMR (400 MHz, $CDCl_3$) δ

7.58 (dd, J = 7.9, 1.1 Hz, 1H), 7.34 – 7.29 (m, 1H), 7.23 (dd, J = 7.7, 1.8 Hz, 1H), 7.18 (dd, J = 7.5, 1.8 Hz, 1H), 5.44 – 5.40 (m, 1H), 5.20 (d, J = 1.5 Hz, 1H), 3.93 – 3.84 (m, 2H), 1.75 – 1.64 (m, 3H), 1.49 – 1.36 (m, 6H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.4, 171.0, 143.3, 139.1, 134.2, 131.6, 129.4, 127.2, 121.8, 121.6, 45.7, 30.7, 20.4, 18.1, 13.9. HRMS: (ESI) calcd for $C_{15}H_{19}BrNO_2^+[M+H]^+$ 324.0594; found 324.0594.

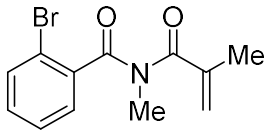
2-bromo-*N*-isopropyl-*N*-methacryloylbenzamide (1b)



Chemical Formula: $C_{14}H_{16}BrNO_2$
Exact Mass: 309.0364

Compound **1b** was prepared according to General Procedure **3**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 1H), 7.35 – 7.28 (m, 1H), 7.25 – 7.20 (m, 1H), 7.20 – 7.16 (m, 1H), 5.47 (d, J = 1.2 Hz, 1H), 5.27 (d, J = 1.5 Hz, 1H), 4.90 – 4.77 (m, 1H), 1.46 (d, J = 6.9 Hz, 6H), 1.32 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.6, 170.0, 144.3, 139.2, 134.1, 131.4, 129.2, 127.1, 122.0, 121.9, 49.1, 17.4; HRMS: (ESI) calcd for $C_{14}H_{17}BrNO_2^+[M+H]^+$ 310.0437; found 310.0432.

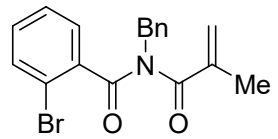
2-bromo-*N*-methacryloyl-*N*-methylbenzamide (1c)



Chemical Formula: $C_{12}H_{12}BrNO_2$
Exact Mass: 281.0051

Compound **1c** was prepared according to General Procedure **3**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 1H), 7.35 – 7.30 (m, 1H), 7.28 – 7.24 (m, 1H), 7.22 – 7.20 (m, 1H), 5.44 (d, J = 1.0 Hz, 1H), 5.23 (d, J = 1.6 Hz, 1H), 3.37 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.0, 171.1, 142.3, 138.7, 133.7, 131.4, 129.3, 127.2, 121.6, 120.8, 32.6, 18.2; HRMS: (ESI) calcd for $C_{12}H_{13}BrNO_2^+[M+H]^+$ 282.0124; found 282.0125.

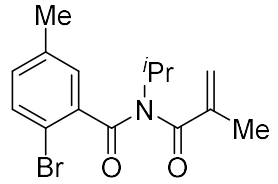
_N_-benzyl-2-bromo-_N_-methacryloylbenzamide (1d)



Chemical Formula: $C_{18}H_{16}BrNO_2$
Exact Mass: 357.0364

Compound **1d** was prepared according to General Procedure **3**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.49 (d, *J* = 7.0 Hz, 2H), 7.36 – 7.30 (m, 2H), 7.30 – 7.26 (m, 2H), 7.23 (td, *J* = 7.6, 1.9 Hz, 1H), 7.06 (dd, *J* = 7.3, 1.9 Hz, 1H), 5.29 (s, 1H), 5.15 (d, *J* = 1.5 Hz, 1H), 5.08 (s, 2H), 1.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.0, 170.8, 143.1, 138.8, 137.0, 134.2, 131.7, 129.3, 129.3, 128.7, 127.9, 127.2, 121.9, 121.8, 48.9, 18.0. HRMS: (ESI) calcd for $C_{18}H_{17}BrNO_2^+$[M+H]$^+$ 358.0437; found 358.0437.

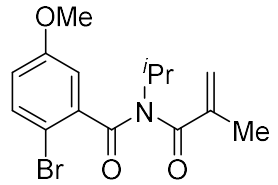
2-bromo-_N_-isopropyl-_N_-methacryloyl-5-methylbenzamide (1e)



Chemical Formula: $C_{15}H_{18}BrNO_2$
Exact Mass: 323.0521

Compound **1e** was prepared according to General Procedure **3**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.1 Hz, 1H), 7.05 – 7.01 (m, 1H), 6.96 (s, 1H), 5.45 (s, 1H), 5.27 – 5.23 (m, 1H), 4.88 – 4.79 (m, 1H), 2.29 (s, 3H), 1.46 (d, *J* = 6.8 Hz, 6H), 1.35 – 1.31 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.3, 170.7, 144.8, 139.6, 137.9, 134.5, 132.7, 130.3, 122.5, 119.1, 49.6, 21.3, 18.0. HRMS: (ESI) calcd for $C_{15}H_{19}BrNO_2^+$[M+H]$^+$ 324.0594; found 324.0595.

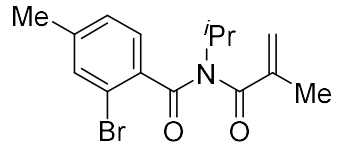
2-bromo-_N_-isopropyl-_N_-methacryloyl-5-methoxybenzamide (1f)



Chemical Formula: $C_{15}H_{18}BrNO_3$
Exact Mass: 339.0470

Compound **1f** was prepared according to General Procedure **3**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.8 Hz, 1H), 6.81 – 6.75 (m, 1H), 6.70 (d, *J* = 2.8 Hz, 1H), 5.47 (s, 1H), 5.29 (s, 1H), 4.88 – 4.75 (m, 1H), 3.77 (s, 3H), 1.46 (d, *J* = 6.8 Hz, 6H), 1.41 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 170.4, 159.2, 144.7, 140.3, 135.4, 122.8, 117.5, 115.8, 112.5, 56.3, 49.8, 18.2. HRMS: (ESI) calcd for $C_{15}H_{19}BrNO_3^+[M+H]^+$ 340.0543; found 340.0538.

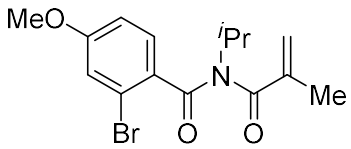
2-bromo-*N*-isopropyl-*N*-methacryloyl-4-methylbenzamide (1g)



Chemical Formula: $C_{15}H_{18}BrNO_2$
Exact Mass: 323.0521

Compound **1g** was prepared according to General Procedure **3**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.12 – 7.04 (m, 2H), 5.44 (s, 1H), 5.25 (d, *J* = 1.5 Hz, 1H), 4.88 – 4.76 (m, 1H), 2.34 – 2.30 (m, 3H), 1.45 (d, *J* = 6.9 Hz, 6H), 1.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 170.9, 145.0, 142.8, 137.1, 135.3, 129.8, 128.3, 122.4, 122.2, 49.6, 21.6, 18.1. HRMS: (ESI) calcd for $C_{15}H_{19}BrNO_2^+[M+H]^+$ 324.0594; found 324.0595.

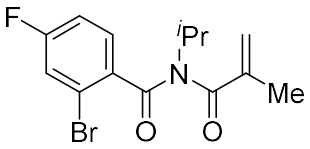
2-bromo-*N*-isopropyl-*N*-methacryloyl-4-methoxybenzamide (1h)



Chemical Formula: $C_{15}H_{18}BrNO_3$
Exact Mass: 339.0470

Compound **1h** was prepared according to General Procedure **3**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.09 (m, 2H), 6.83 – 6.75 (m, 1H), 5.40 (s, 1H), 5.25 (d, *J* = 1.5 Hz, 1H), 4.88 – 4.78 (m, 1H), 3.81 (s, 3H), 1.45 (d, *J* = 6.9 Hz, 6H), 1.39 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 170.9, 161.8, 145.2, 132.5, 131.2, 123.7, 121.8, 120.4, 56.3, 49.7, 18.3. HRMS: (ESI) calcd for $C_{15}H_{19}BrNO_3^+[M+H]^+$ 340.0543; found 340.0538.

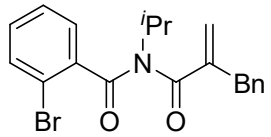
2-bromo-4-fluoro-*N*-isopropyl-*N*-methacryloylbenzamide (1i)



Chemical Formula: $C_{14}H_{15}BrFNO_2$
Exact Mass: 327.0270

Compound **1i** was prepared according to General Procedure **3**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 1H), 7.21 – 7.15 (m, 1H), 7.06 – 7.00 (m, 1H), 5.48 – 5.44 (m, 1H), 5.32 – 5.28 (m, 1H), 4.86 – 4.77 (m, 1H), 1.45 (dd, *J* = 6.8, 2.7 Hz, 6H), 1.41 – 1.38 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.0, 169.8, 163.4 (d, *J* = 256.2 Hz), 144.9, 136.3, 136.3, 131.2 (d, *J* = 8.9 Hz), 123.5, 123.4, 122.8, 122.3 (d, *J* = 24.8 Hz), 114.9 (d, *J* = 21.6 Hz), 49.9, 18.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.90 (q, *J* = 7.4 Hz). HRMS: (ESI) calcd for $C_{15}H_{16}BrFNO_2^+[M+H]^+$ 328.0343; found 328.0339.

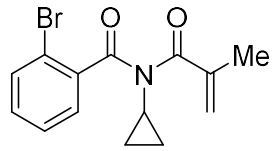
***N*-(2-benzylacryloyl)-2-bromo-*N*-isopropylbenzamide (1j)**



Chemical Formula: $C_{20}H_{20}BrNO_2$
Exact Mass: 385.0677

Compound **1j** was prepared according to General Procedure **3**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.63 (m, 1H), 7.37 – 7.28 (m, 2H), 7.25 – 7.14 (m, 4H), 6.71 – 6.66 (m, 2H), 5.62 (t, *J* = 1.4 Hz, 1H), 4.91 (t, *J* = 1.9 Hz, 1H), 4.90 – 4.81 (m, 1H), 3.00 (s, 2H), 1.48 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.3, 170.2, 148.6, 139.5, 136.9, 134.4, 131.7, 129.7, 129.5, 128.6, 127.5, 126.6, 123.1, 122.2, 49.5, 37.3. HRMS: (ESI) calcd for $C_{20}H_{21}BrNO_2^+[M+H]^+$ 386.0750; found 386.0750.

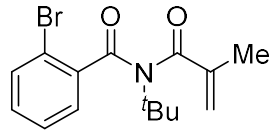
2-bromo-*N*-cyclopropyl-*N*-methacryloylbenzamide (1k)



Chemical Formula: $C_{14}H_{14}BrNO_2$
Exact Mass: 307.0208

Compound **1k** was prepared according to General Procedure **3**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 1H), 7.36 – 7.29 (m, 1H), 7.27 – 7.18 (m, 2H), 5.55 (s, 1H), 5.41 (d, J = 1.6 Hz, 1H), 3.01 – 2.80 (m, 1H), 1.67 (s, 3H), 1.03 – 0.79 (m, 2H), 0.75 – 0.56 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.4, 170.7, 142.4, 138.9, 133.3, 130.9, 128.2, 127.1, 122.6, 120.0, 28.7, 17.9, 8.6; HRMS: (ESI) calcd for $C_{14}H_{15}BrNO_2^+[M+H]^+$ 308.0281; found 308.0280.

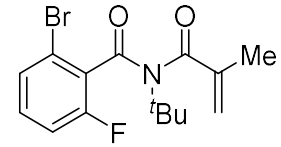
2-bromo-*N*-(tert-butyl)-*N*-methacryloylbenzamide (1l)



Chemical Formula: $C_{15}H_{18}BrNO_2$
Exact Mass: 323.0521

Compound **1l** was prepared according to General Procedure **3**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 – 7.33 (m, 1H), 7.29 – 7.24 (m, 1H), 7.19 – 7.12 (m, 2H), 5.91 (s, 1H), 5.59 (s, 1H), 1.62 (s, 9H), 1.27 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 167.0, 144.2, 139.0, 133.5, 130.5, 129.6, 126.7, 126.4, 121.4, 59.6, 28.6, 16.9; HRMS: (ESI) calcd for $C_{15}H_{19}BrNO_2S^+[M+H]^+$ 324.0594; found 324.0582.

2-bromo-*N*-(*tert*-butyl)-6-fluoro-*N*-methacryloylbenzamide (1m)

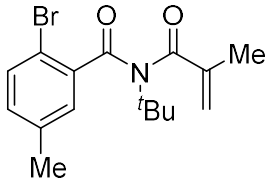


Chemical Formula: $C_{15}H_{17}BrFNO_2$
Exact Mass: 341.0427

Compound **1m** was prepared according to General Procedure **3**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 1H), 7.21 – 7.13 (m, 1H), 7.01 – 6.93 (m, 1H), 5.96 (s, 1H), 5.65 (d, J = 1.5 Hz, 1H), 1.61 (s, 9H), 1.34 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.8, 162.1, 158.3 (d, J = 253.5

Hz), 143.0, 131.6 (d, J = 9.0 Hz), 128.7 (d, J = 3.5 Hz), 128.4 (d, J = 20.8 Hz), 126.9 (d, J = 2.4 Hz), 114.7 (d, J = 21.7 Hz), 59.9, 28.3, 16.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ -108.2; HRMS: (ESI) calcd for $C_{15}H_{18}BrFNO_2^+[M+H]^+$ 342.0500; found 342.0487.

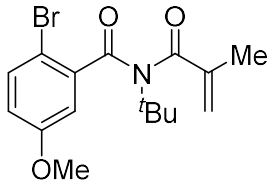
2-bromo-*N*-(*tert*-butyl)-*N*-methacryloyl-5-methylbenzamide (1n)



Chemical Formula: $C_{16}H_{20}BrNO_2$
Exact Mass: 337.0677

Compound **1n** was prepared according to General Procedure **3**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 1H), 7.03 – 6.91 (m, 2H), 5.88 (d, J = 0.9 Hz, 1H), 5.57 (d, J = 1.6 Hz, 1H), 2.26 (s, 3H), 1.61 (s, 9H), 1.27 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.8, 167.2, 144.2, 138.7, 136.9, 133.2, 131.2, 130.1, 126.1, 117.9, 59.5, 28.6, 20.7, 16.9; HRMS: (ESI) calcd for $C_{16}H_{21}BrNO_2^+[M+H]^+$ 338.0750; found 338.0740.

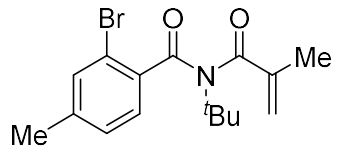
2-bromo-*N*-(*tert*-butyl)-*N*-methacryloyl-5-methoxybenzamide (1o)



Chemical Formula: $C_{16}H_{20}BrNO_3$
Exact Mass: 353.0627

Compound **1o** was prepared according to General Procedure **3**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 1H), 6.73 – 6.69 (m, 2H), 5.91 (s, 1H), 5.61 (s, 1H), 3.75 (s, 3H), 1.61 (s, 9H), 1.35 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.6, 166.7, 158.2, 144.1, 139.5, 134.2, 126.6, 116.8, 115.1, 111.6, 59.5, 55.7, 28.6, 17.0; HRMS: (ESI) calcd for $C_{16}H_{21}BrNO_3^+[M+H]^+$ 354.0699; found 354.0690.

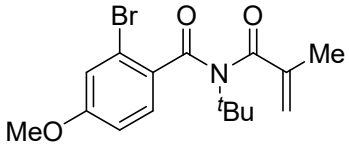
2-bromo-*N*-(*tert*-butyl)-*N*-methacryloyl-4-methylbenzamide (1p)



Chemical Formula: $C_{16}H_{20}BrNO_2$
Exact Mass: 337.0677

Compound **1p** was prepared according to General Procedure **3**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 1H), 7.10 – 6.97 (m, 2H), 5.86 (s, 1H), 5.57 (s, 1H), 2.29 (s, 3H), 1.61 (s, 9H), 1.29 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.6, 167.4, 144.3, 141.2, 136.3, 134.0, 129.5, 127.3, 125.9, 121.3, 59.5, 28.7, 20.9, 17.0; HRMS: (ESI) calcd for $C_{16}H_{21}BrNO_2^+[M+H]^+$ 338.0750; found 338.0744.

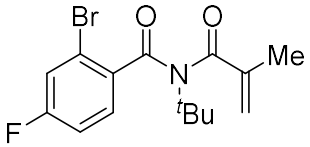
2-bromo-*N*-(tert-butyl)-*N*-methacryloyl-4-methoxybenzamide (1q)



Chemical Formula: $C_{16}H_{20}BrNO_3$
Exact Mass: 353.0627

Compound **1q** was prepared according to General Procedure **3**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 – 7.01 (m, 2H), 6.82 – 6.71 (m, 1H), 5.81 (s, 1H), 5.56 (s, 1H), 3.78 (s, 3H), 1.61 (s, 9H), 1.33 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.5, 167.6, 160.5, 144.5, 131.8, 130.9, 125.3, 122.6, 119.2, 112.2, 59.5, 55.6, 28.8, 17.2; HRMS: (ESI) calcd for $C_{16}H_{21}BrNO_3^+[M+H]^+$ 354.0699; found 354.0686.

2-bromo-*N*-(*tert*-butyl)-4-fluoro-*N*-methacryloylbenzamide (1r)

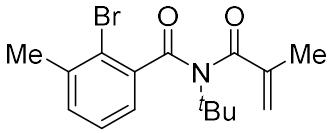


Chemical Formula: $C_{15}H_{17}BrFNO_2$
Exact Mass: 341.0427

Compound **1r** was prepared according to General Procedure **3**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 1H), 7.16 – 7.10 (m, 1H), 7.01 – 6.94 (m, 1H), 5.92 (s, 1H), 5.64 (d, J = 1.6 Hz, 1H), 1.60 (s, 9H), 1.36 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.5, 166.2, 162.2 (d, J = 254.6

Hz), 144.2, 135.4 (d, J = 3.8 Hz), 130.9 (d, J = 8.8 Hz), 126.8, 122.3 (d, J = 9.7 Hz), 121.0 (d, J = 24.5 Hz), 113.9 (d, J = 21.3 Hz), 59.7, 28.6, 17.0; ^{19}F NMR (565 MHz, $CDCl_3$) δ -108.4 (m); HRMS: (ESI) calcd for $C_{15}H_{18}BrFNO_2^+[M+H]^+$ 342.0500; found 342.0487.

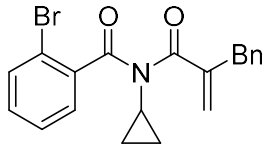
2-bromo-*N*-(*tert*-butyl)-*N*-methacryloyl-3-methylbenzamide (1s)



Chemical Formula: $C_{16}H_{20}BrNO_2$
Exact Mass: 337.0677

Compound **1s** was prepared according to General Procedure **3**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 – 7.11 (m, 2H), 6.98 – 6.92 (m, 1H), 5.91 (s, 1H), 5.55 (d, J = 1.3 Hz, 1H), 2.37 (s, 3H), 1.61 (s, 9H), 1.26 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.8, 167.3, 144.0, 139.49, 139.51, 131.2, 127.2, 126.5, 126.2, 123.4, 59.4, 28.6, 23.4, 16.9; HRMS: (ESI) calcd for $C_{16}H_{21}BrNO_2^+[M+H]^+$ 338.0750; found 338.0751.

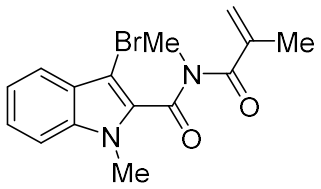
***N*-(2-benzylacryloyl)-2-bromo-*N*-cyclopropylbenzamide (1t)**



Chemical Formula: $C_{20}H_{18}BrNO_2$
Exact Mass: 383.0521

Compound **1t** was prepared according to General Procedure **3**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, J = 7.9, 1.2 Hz, 1H), 7.32 (td, J = 7.4, 1.4 Hz, 1H), 7.28 (dd, J = 7.7, 2.0 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.22 – 7.19 (m, 1H), 7.16 (dd, J = 7.2, 2.1 Hz, 1H), 6.96 (d, J = 6.6 Hz, 2H), 5.69 (t, J = 1.0 Hz, 1H), 5.18 (t, J = 1.7 Hz, 1H), 3.39 (s, 2H), 2.88 (ddd, J = 10.9, 7.1, 3.9 Hz, 1H), 0.95 – 0.82 (m, 2H), 0.62 – 0.50 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.8, 170.7, 146.4, 138.9, 137.2, 133.3, 130.9, 129.5, 128.5, 128.1, 127.2, 126.6, 123.4, 120.0, 37.9, 28.9, 8.7; HRMS: (ESI) calcd for $C_{20}H_{19}BrNO_2^+[M+H]^+$ 384.0594; found 384.0581.

3-bromo-*N*-methacryloyl-*N*,1-dimethyl-1*H*-indole-2-carboxamide (1u)

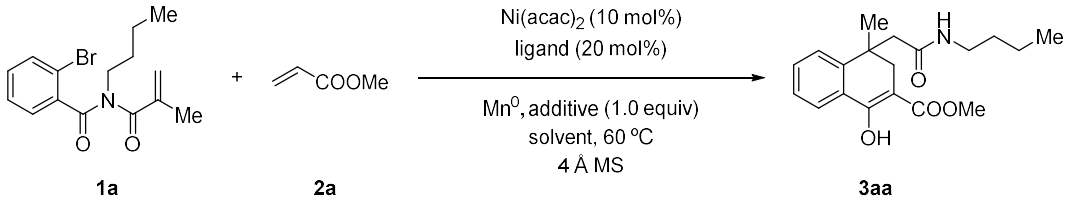


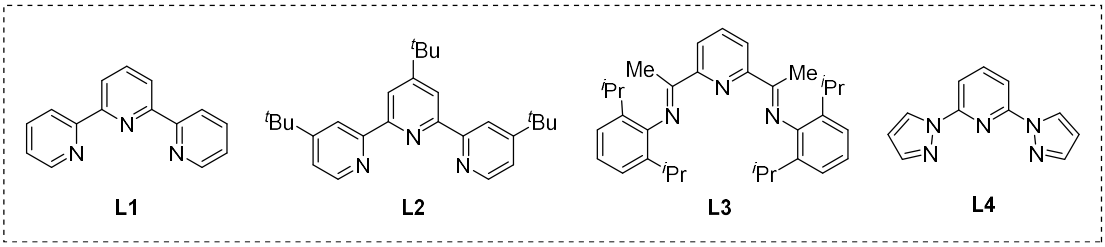
Chemical Formula: $C_{15}H_{15}BrN_2O_2$
Exact Mass: 334.0317

Compound **1u** was prepared according to General Procedure **3**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 1H), 7.41 – 7.37 (m, 1H), 7.35 – 7.33 (m, 1H), 7.24 – 7.21 (m, 1H), 5.20 (s, 1H), 5.08 (s, 1H), 3.78 (s, 3H), 3.45 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.7, 166.2, 144.7, 137.7, 132.7, 125.9, 125.8, 121.5, 120.9, 118.3, 110.1, 93.8, 32.0, 31.4, 18.7; HRMS: (ESI) calcd for $C_{15}H_{16}BrN_2O_2^{+}$[M+H]$^{+}$ 335.0390; found 335.0380.

4. Optimization of Reaction Conditions

Table S1: Optimization of Reaction Conditions for preparing 3aa

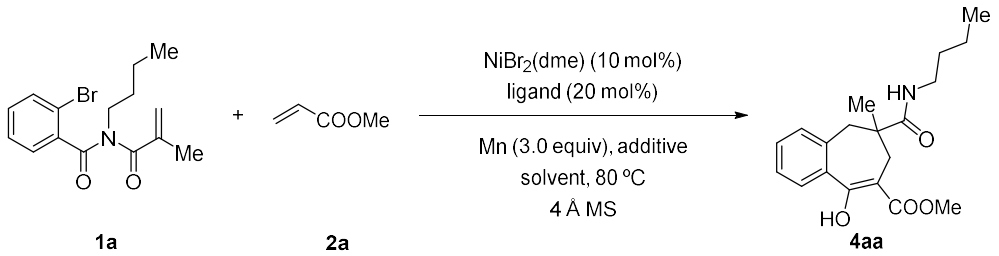


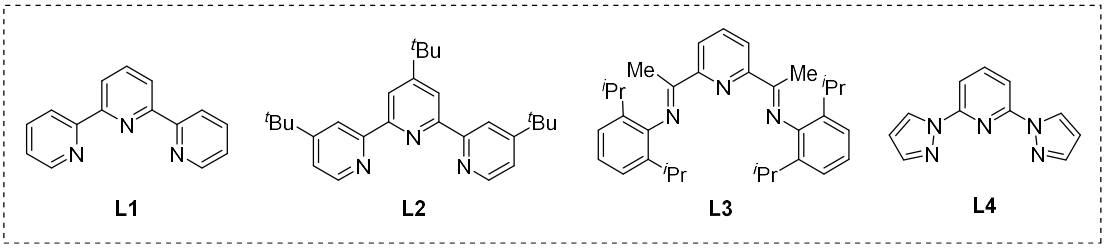


entry	ligand	additive	solvent	yield of **3aa** (%)
1	**L1**	$MgBr_2$	DMSO	48
2	**L1**	$MgCl_2$	DMSO	33
3	**L1**	$MnBr_2$	DMSO	70
4	**L2**	$MnBr_2$	DMSO	67
5	**L3**	$MnBr_2$	DMSO	trace
6	**L4**	$MnBr_2$	DMSO	trace
7[a]	**L1**	$MnBr_2$	DMSO	28
8[b]	**L1**	$MnBr_2$	DMSO	51
9	**L1**	**$MnBr_2$**	**DMSO:THF=1:1**	**74**

Reactions were carried out with **1a** (0.1 mmol), **2a** (0.3 mmol), $Ni(acac)_2$ (10 mol%), ligand (20 mol%), additive (0.1 mmol, 1 equiv), Mn (0.3 mmol, 3 equiv), 4 Å MS (30 mg) in 2 mL DMSO at 60 °C. [a]The reaction was carried out at 40 °C. [b]The reaction was carried out at 80 °C.

Table S2: Optimization of Reaction Conditions for preparing 4aa



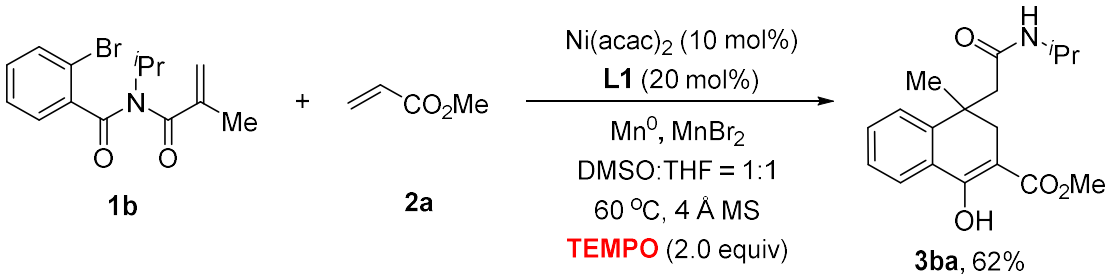


entry	ligand	additive	solvent	yield of **4aa** (%)
1	**L1**	$MnBr_2$	DMSO	trace
2	**L2**	$MnBr_2$	DMSO	trace
3	**L3**	$MnBr_2$	DMSO	57
4	**L4**	$MnBr_2$	DMSO	36
5	**L3**	-	**DMSO**	**65**
6	**L3**	-	DMA	51
7	**L3**	-	DMF	48

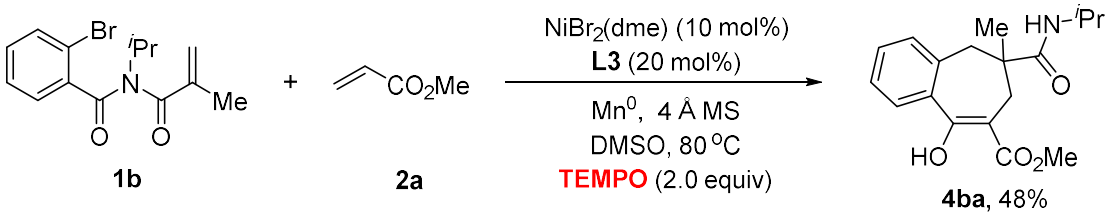
Reactions were carried out with **1a** (0.1 mmol), **2a** (0.3 mmol), $NiBr_2$(dme) (10 mol%), ligand (20 mol%), additive (0.1 mmol, 1 equiv), Mn (0.3 mmol, 3 equiv), 4 Å MS (30 mg) in 2 mL solvent at 80 °C.

5. Mechanistic Studies

5.1 Radical Trapping experiments



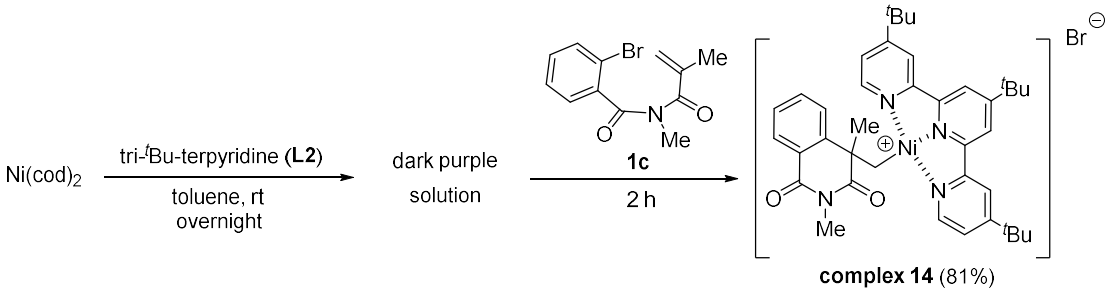
An oven-dried sealed tube equipped with a PTFE-coated stir bar was charged with $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 9.6 mg), **1b** (0.1 mmol, 30.9 mg), $MnBr_2$ (0.2 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), **2a** (0.3 mmol, 25.8 mg), 4 Å molecular sieves (30 mg), TEMPO (0.2 mmol, 31.3 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL). The sealed tube was sealed and removed from the glovebox. Then the reaction was stirred at 60 °C in an aluminium bead bath until the reaction was complete (monitored by TLC). The resulting mixture was quenched with saturated NH_4Cl solution (5 mL) and further diluted with water (10 mL). The aqueous layer was extracted with EtOAc and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by chromatography on silica gel, eluting with petroleum ether/EtOAc (10/1~2/1) to afford the desired product **3ba** (19.7 mg, 62%).



An oven-dried sealed tube equipped with a PTFE-coated stir bar was charged with $Ni(dme)_2$ (10 mol%, 3.1 mg), terpyridine **L3** (20 mol%, 9.6 mg), **1b** (0.1 mmol, 30.9 mg), Mn^0 (0.3 mmol, 16.5 mg), **2a** (0.3 mmol, 25.8 mg), 4 Å molecular sieves (30 mg), TEMPO (0.2 mmol, 31.3 mg), and anhydrous DMSO (2 mL). The sealed tube was sealed and removed from the glovebox. Then the reaction was stirred at 80 °C in an aluminium bead bath until the reaction was complete (monitored by TLC). The resulting mixture was quenched with saturated NH_4Cl solution (5 mL) and further diluted with water (10 mL). The aqueous layer was extracted with EtOAc and the

combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by chromatography on silica gel, eluting with petroleum ether/EtOAc (10/1~2/1) to afford the desired monofluorinated tricyclic indanones **4ba** (15.2 mg, 48%).

5.2 Synthesis of the *σ*-alkyl-Ni(II) complex 14

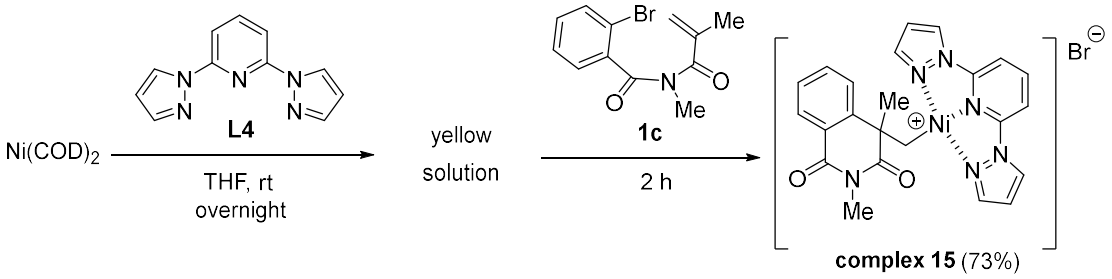


complex 14 (81%)

The synthesis of complex **14** followed the procedure we reported previously.[1]

In a nitrogen-filled glove-box, a 50 mL round bottom flask containing a PTFE-coated stirring bar was charged with $Ni(cod)_2$ (0.5 mmol, 136 mg), tri-^{t}Bu-terpyridine **L2** (0.5 mmol, 200.6 mg) and dry toluene (15 mL). The resulting dark purple mixture was stirred at room temperature for overnight. **1c** (1.1 equiv, 154 mg) was then added and stirred for additional 2 hours. Dry *n*-hexane (30 mL) was added to the yellow-green mixture and filtered. The resulting participate was washed with *n*-hexane (5 × 20 mL) to remove residual cyclooctadiene and **1c**, dried under vacuum to give the complex **14** as a golden yellow solid (299.7 mg, 81% yield). ^{1}H NMR (600 MHz, CD_3CN) δ 8.33 (s, 2H), 8.21 (s, 2H), 7.90 (s, 2H), 7.68 (d, J = 7.7 Hz, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.41 (s, 2H), 7.29 (t, J = 7.6 Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H), 2.50 (s, 3H), 1.84 (s, 3H), 1.56 (s, 9H), 1.44 (s, 18H), 1.21 – 1.16 (m, 1H), 1.10 (s, 1H); ^{13}C NMR (151 MHz, CD_3CN) δ 177.6, 168.2, 166.6, 165.4, 156.6, 152.4, 151.9, 146.7, 134.3, 128.1, 127.6, 126.8, 126.2, 124.8, 121.4, 120.6, 51.5, 37.5, 36.5, 30.7, 30.2, 26.6, 26.4, 15.9.

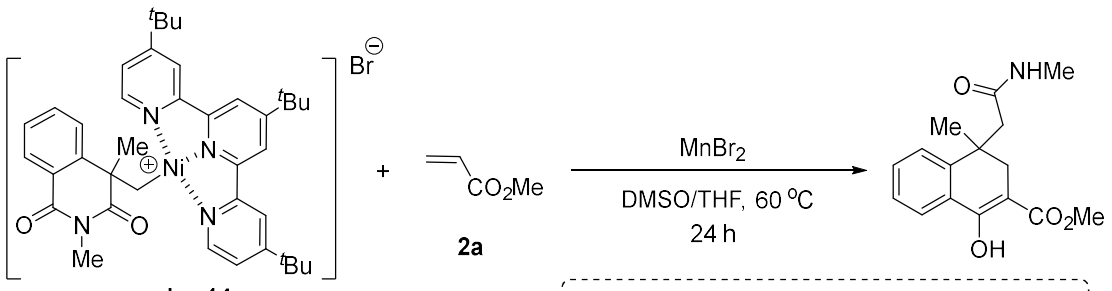
5.3 Synthesis of the σ-alkyl-Ni(II) complex 15



The synthesis of complex **15** followed the procedure we reported previously.[1]

In a nitrogen-filled glove-box, a 50 mL round bottom flask containing a PTFE-coated stirring bar was charged with $Ni(cod)_2$ (0.25 mmol, 68.8 mg), 2,6-di(1*H*-pyrazol-1-yl)pyridine **L4** (0.25 mmol, 52.7 mg) and dry THF (8 mL). The resulting yellow solution was then stirred at room temperature for overnight. **1c** (2 equiv, 141.1 mg) was then added to the mixture and stirred for additional 2 hours. Dry *n*-hexane (30 mL) was added to the yellow colored mixture and filtered. The resulting participate was washed with *n*-hexane (5 × 20 mL) to remove residual cyclooctadiene and **1c**, dried under vacuum to give the complex **15** as a golden yellow solid (100.4 mg, 73% yield). ^{1}H NMR (600 MHz, CD_3CN) δ 8.53 (s, 2H), 8.35 (t, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.20 (s, 2H), 6.58 (s, 2H), 2.84 (s, 3H), 1.86 (s, 3H), 1.67 (d, *J* = 8.7 Hz, 1H), 1.58 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (151 MHz, CD_3CN) δ 177.4, 165.6, 146.9, 146.5, 145.4, 134.3, 133.1, 128.4, 127.8, 127.1, 126.1, 112.0, 108.8, 51.2, 27.1, 25.3.

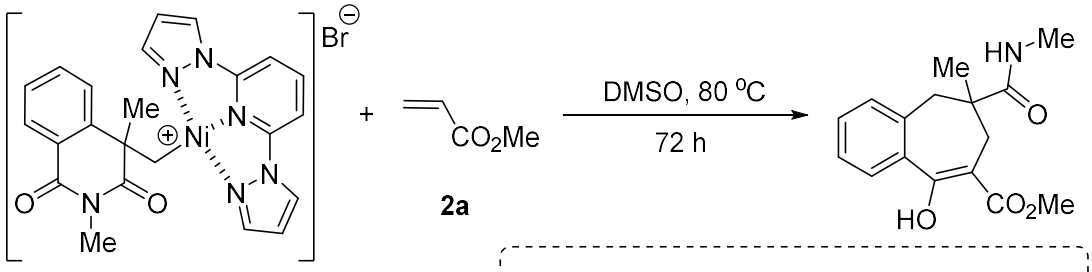
5.4 Control Experiments



reducing agent	yield of **3ca** (%)
-	trace
Mn (3 equiv)	47

An oven-dried sealed tube equipped with a PTFE-coated stir bar was charged with complex **14**

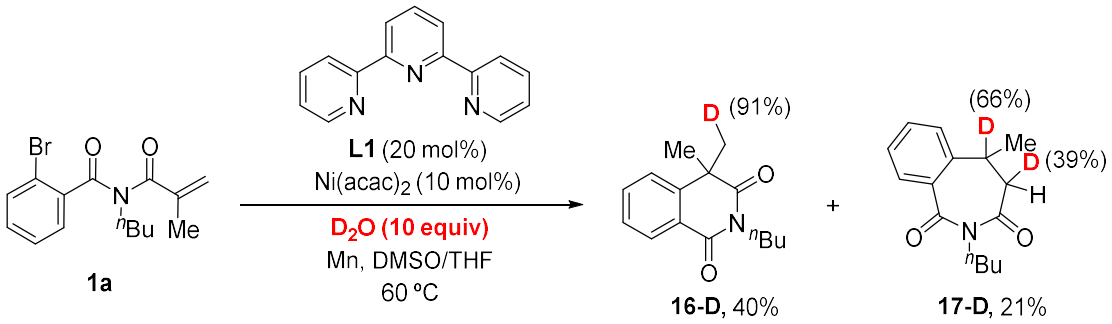
(0.027 mmol, 20 mg), **2a** (2 equiv, 2.3 mg), Mn (3 equiv, 4.5 mg), $MnBr_2$ (1 equiv, 5.8 mg), anhydrous DMSO (0.3 mL) and anhydrous THF (0.3 mL). This reaction mixture was stirred at 60 ºC until the reaction was complete (monitored by TLC). The resulting mixture was quenched with saturated NH_4Cl solution (5 mL). The aqueous layer was extracted with EtOAc (3 × 5 mL) and the combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with petroleum ether/EtOAc (5/1~1/1) to afford **3ca** (4.2 mg, 47%).



reducing agent	yield of **4ca** (%)
-	trace
Mn (3 equiv)	19

An oven-dried sealed tube equipped with a PTFE-coated stir bar was charged with complex **15** (0.04 mmol, 22 mg), **2a** (3 equiv, 23.7 mg), Mn (3 equiv, 6.6 mg), anhydrous DMSO (0.6 mL). This reaction mixture was stirred at 80 ºC until the reaction was complete (monitored by TLC). The resulting mixture was quenched with saturated NH_4Cl solution (5 mL). The aqueous layer was extracted with EtOAc (3 × 5 mL) and the combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with petroleum ether/EtOAc (5/1~1/1) to afford **4ca** (2.5 mg, 19% yield).

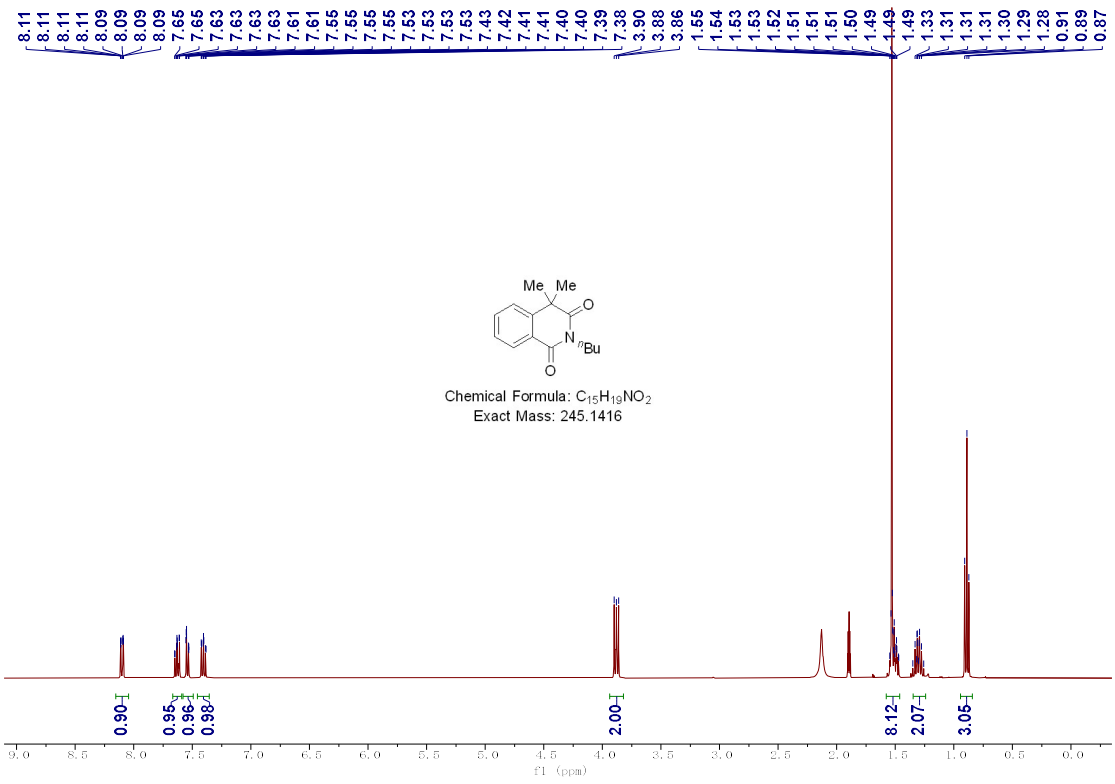
5.5 Deuterium-labelling experiments



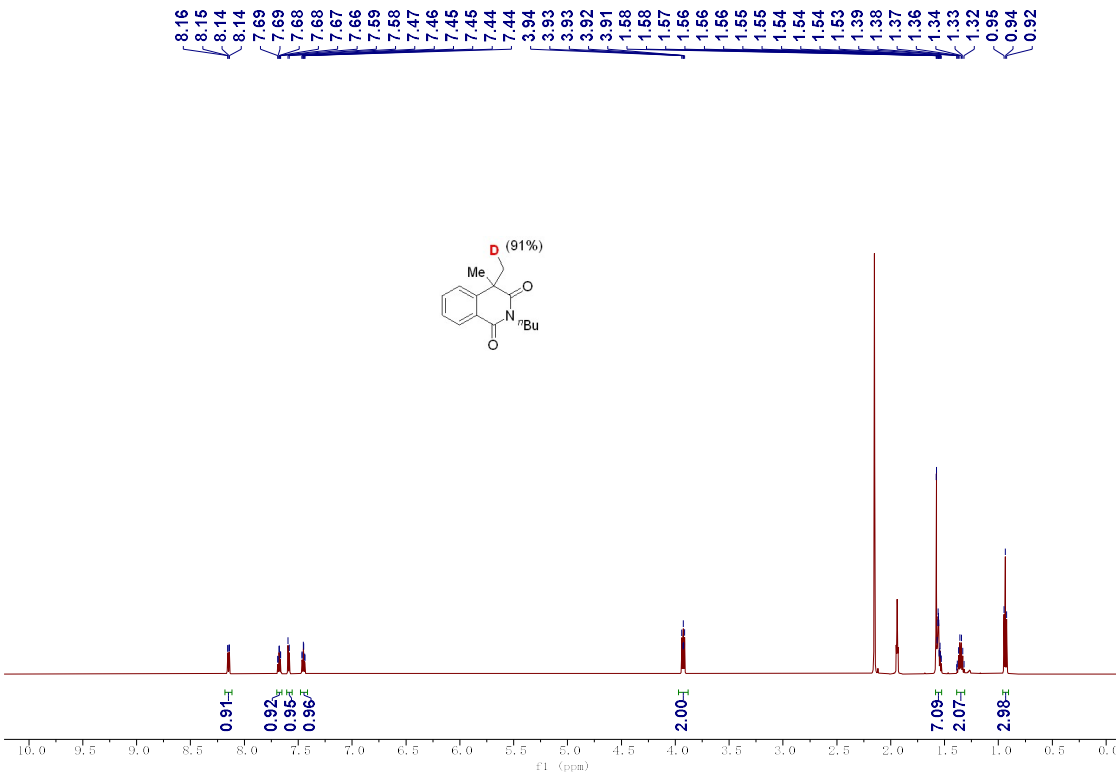
An oven-dried sealed tube equipped with a PTFE-coated stir bar was charged with $Ni(acac)_2$ (0.01 mmol, 2.5 mg), terpyridine **L1** (0.02 mmol, 4.6 mg), Mn (0.3 mmol, 16.5 mg) and **1a** (0.1 mmol, 32.4 mg). The sealed tube was evacuated and backfilled with argon (this process was repeated for three times) and then DMSO (1 mL), THF (1 mL), and D_2O (1 mmol, 20 mg) was added. This reaction mixture was stirred at room temperature until the reaction was complete (monitored by TLC). The resulting mixture was quenched with saturated NH_4Cl solution (5 mL) and further diluted with water (10 mL). The aqueous layer was extracted with EtOAc (3 × 15 mL) and the combined organic layers were washed with brine (2 × 20 mL), dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with petroleum ether/EtOAc (30/1~15/1) to afford the corresponding product **16-D** (9.8 mg, 40% yield, 91% D incorporation) and **17-D** (5.2 mg, 21% yield, 66% D and 39% D).

The ^1H NMR spectra of **16-D** and **17-D** were shown as below.

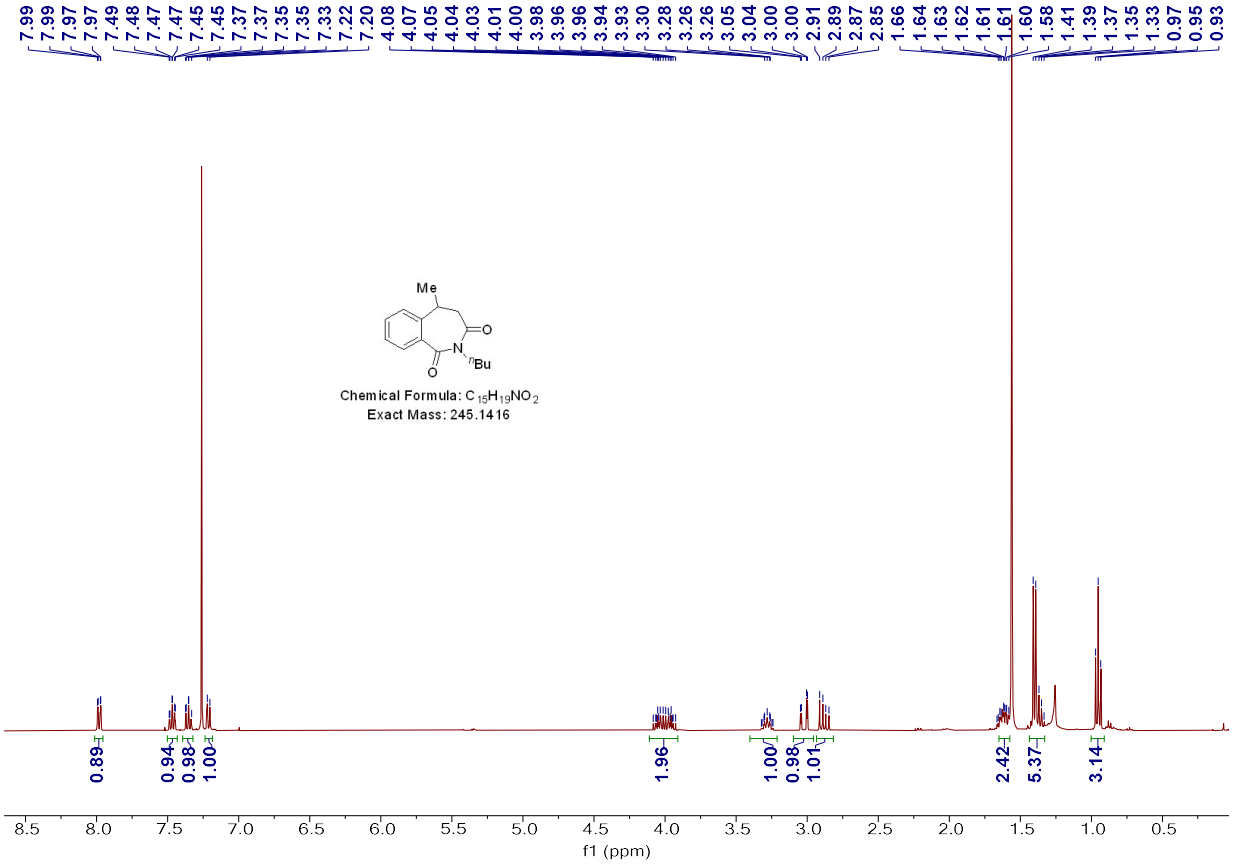
16


Me Me
O
N nBu
O
Chemical Formula: C15H19NO2
Exact Mass: 245.1416
0.90
0.95
0.96
0.98
2.00
8.12
2.07
3.05
f1 (ppm)

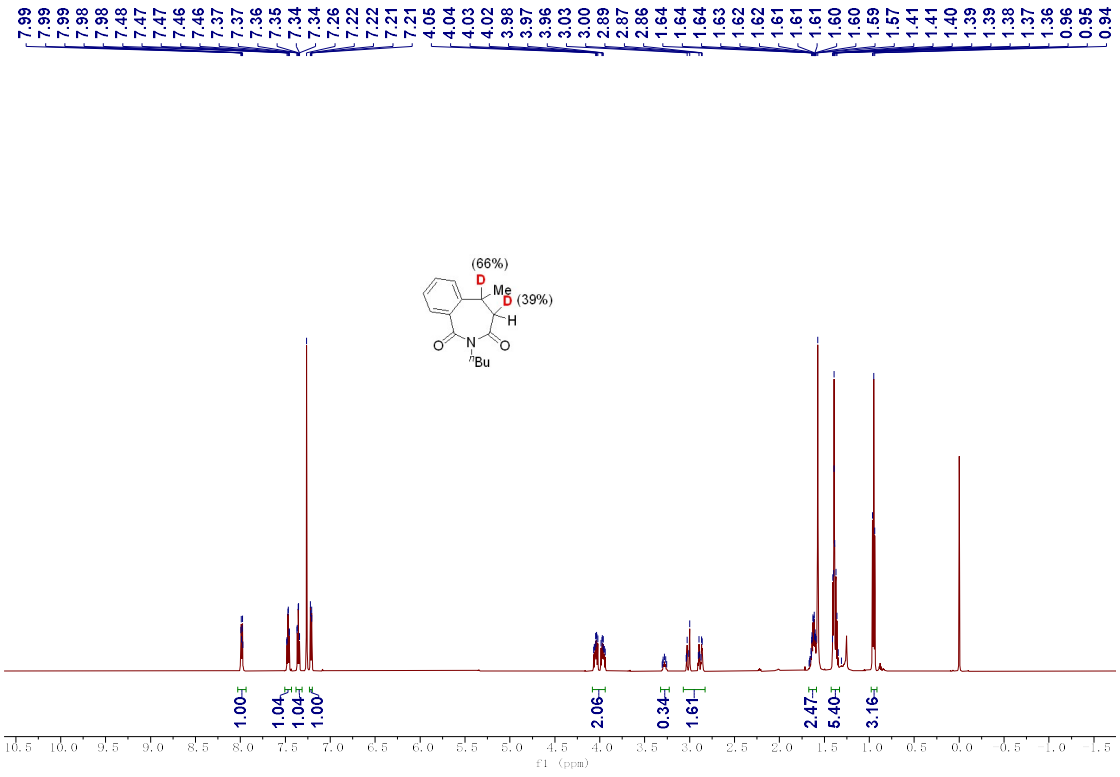
16-D

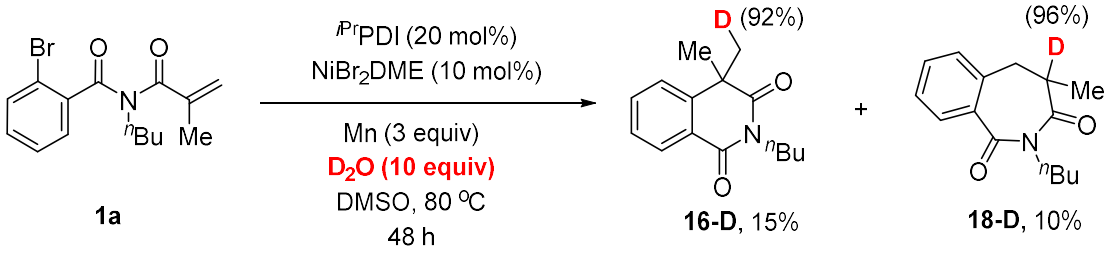

D (91%)
Me
O
N nBu
O
0.91
0.92
0.95
0.96
2.00
7.09
2.07
2.98
f1 (ppm)

17


Me
O
N
O
nBu
Chemical Formula: C15H19NO2
Exact Mass: 245.1416
f1 (ppm)

17-D

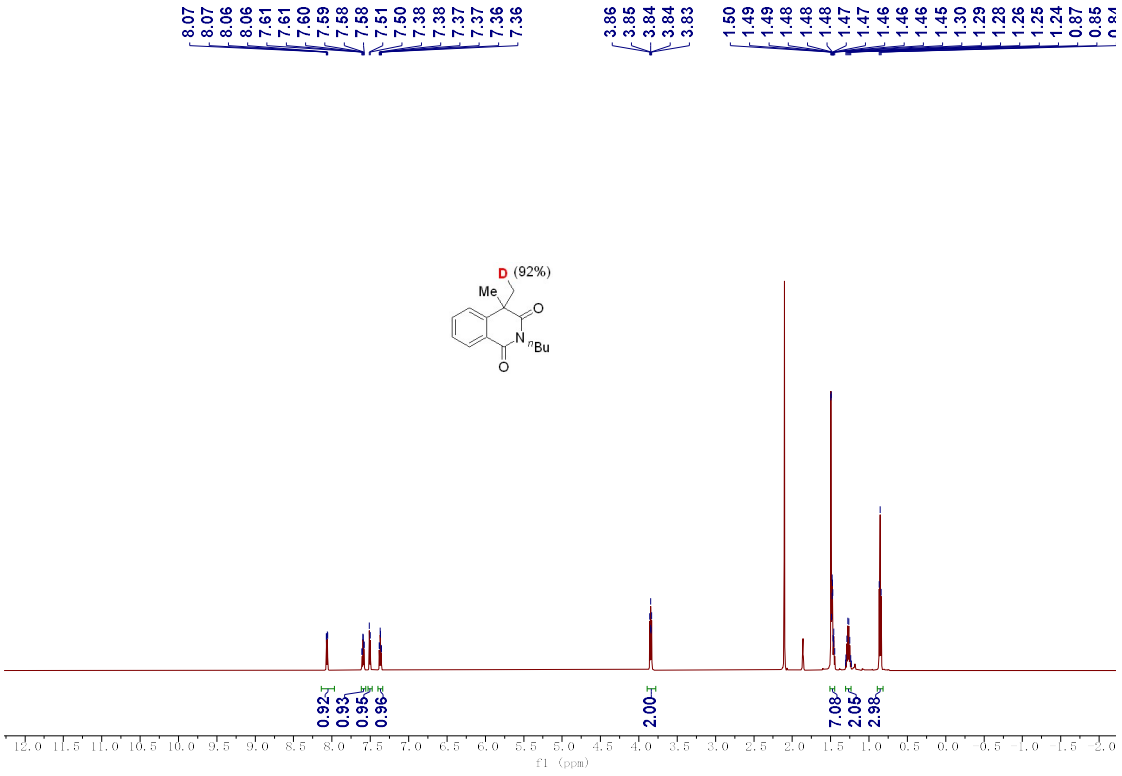

(66%)
D
Me
D (39%)
H
O
N
O
nBu
f1 (ppm)



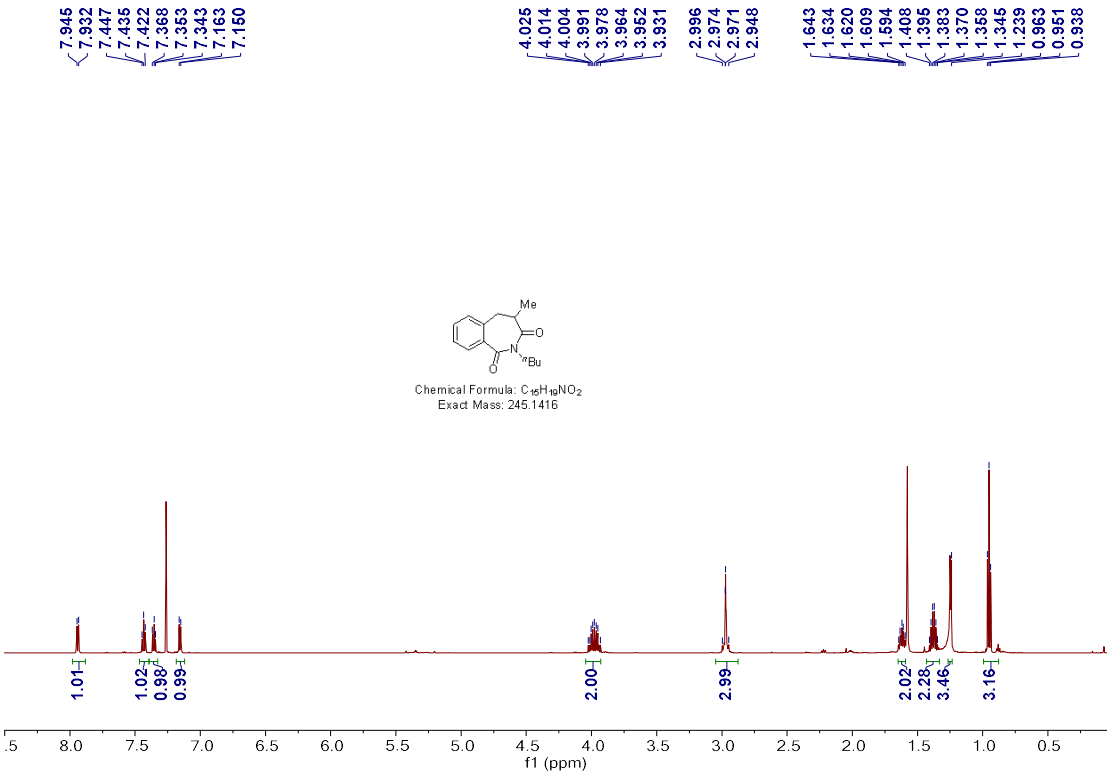
An oven-dried sealed tube equipped with a PTFE-coated stir bar was charged with $NiBr_2DME$ (0.01 mmol, 3.1 mg), ^{iPr}PDI (**L3**) (0.02 mmol, 9.6 mg), Mn (0.3 mmol, 16.5 mg) and **1a** (0.1 mmol, 32.4 mg). The sealed tube was evacuated and backfilled with argon (this process was repeated for three times) and then DMSO (2 mL) and D_2O (1 mmol, 20 mg) was added. This reaction mixture was stirred at 80 °C until the reaction was complete (monitored by TLC). The resulting mixture was quenched with saturated NH_4Cl solution (5 mL) and further diluted with water (10 mL). The aqueous layer was extracted with EtOAc (3 × 15 mL) and the combined organic layers were washed with brine (2 × 20 mL), dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with petroleum ether/EtOAc (30/1~15/1) to afford the corresponding product **16-D** (3.7 mg, 15% yield, 92% D incorporation) and **18-D** (2.5 mg, 10% yield, 96% D incorporation).

The ^{1}H NMR spectra of **16-D** and **18-D** were shown as below.

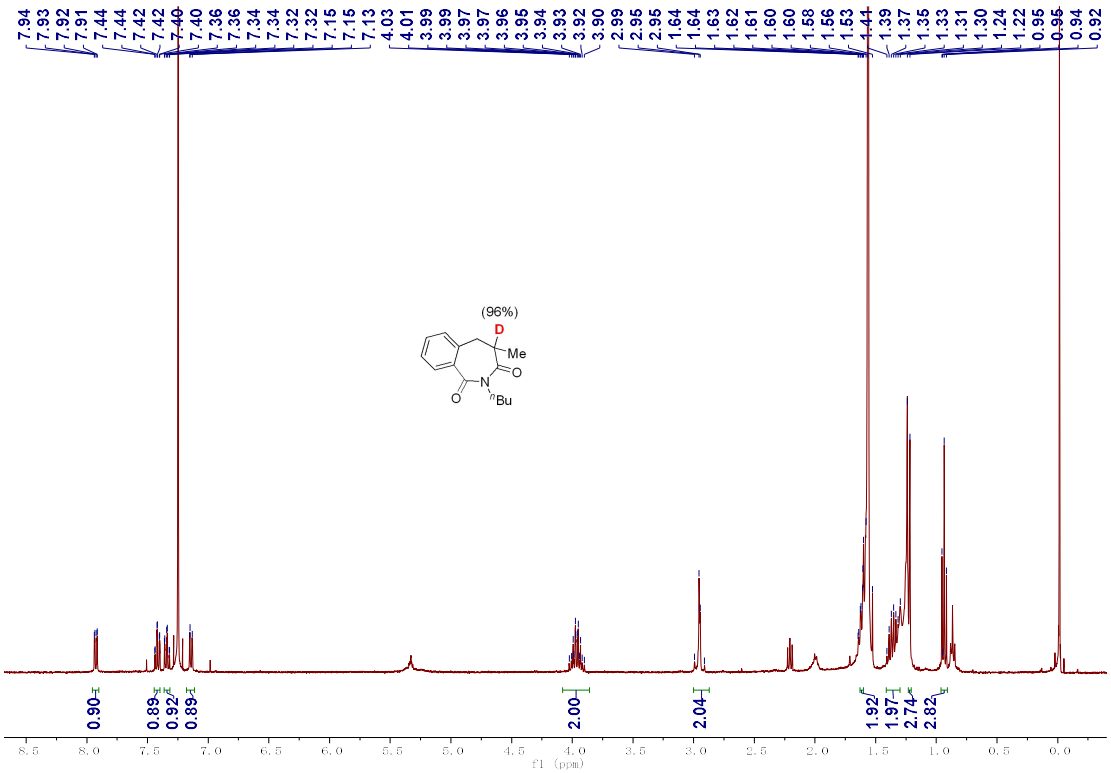
16-D


8.07
8.07
8.06
8.06
7.61
7.61
7.60
7.59
7.58
7.58
7.51
7.50
7.38
7.37
7.37
7.36
7.36
3.86
3.85
3.84
3.84
3.83
1.50
1.49
1.49
1.48
1.48
1.48
1.47
1.47
1.46
1.46
1.46
1.45
1.30
1.29
1.28
1.26
1.25
1.24
0.87
0.85
D (92%)
Me
O
N
nBu
O
0.92
0.93
0.95
0.96
2.00
7.08
2.05
2.98
f1 (ppm)

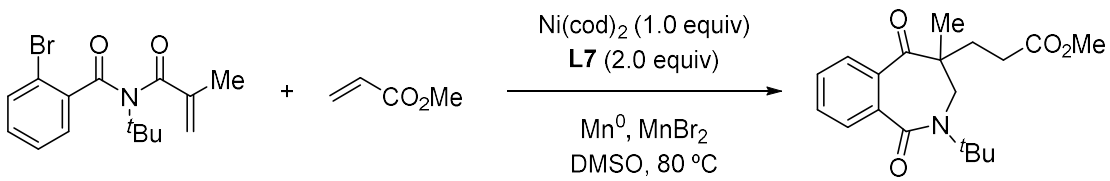
18


7.945
7.932
7.447
7.435
7.422
7.368
7.353
7.343
7.163
7.150
4.025
4.014
4.004
3.991
3.978
3.964
3.952
3.931
2.996
2.974
2.971
2.948
1.643
1.634
1.620
1.609
1.594
1.408
1.395
1.383
1.370
1.358
1.345
1.239
0.963
0.951
0.938
Me
O
N
nBu
O
Chemical Formula: C15H19NO2
Exact Mass: 245.1416
1.01
1.02
0.98
0.99
2.00
2.99
2.02
2.28
3.46
3.16
f1 (ppm)

18-D


7.94
7.93
7.92
7.91
7.44
7.44
7.42
7.42
7.40
7.40
7.36
7.36
7.34
7.34
7.32
7.32
7.15
7.15
7.13
4.03
4.01
3.99
3.99
3.97
3.97
3.96
3.95
3.94
3.93
3.92
3.90
2.99
2.95
2.95
1.64
1.64
1.63
1.62
1.61
1.60
1.60
1.58
1.56
1.53
1.44
1.39
1.37
1.35
1.33
1.31
1.30
1.24
1.22
0.95
0.96
0.94
0.92
(96%)
D
Me
O
O
N
nBu
0.90
0.89
0.92
0.89
2.00
2.04
1.92
1.97
2.74
2.82
f1 (ppm)

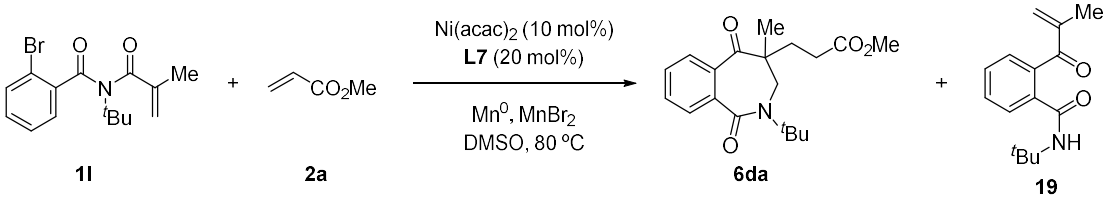
5.6 The reaction with stoichiometric Ni(cod)$_2$.



1l **2a** **6da,** 45%

An oven-dried sealed tube equipped with a PTFE-coated stir bar was charged with Ni(cod)$_2$ (1.0 equiv, 26.5 mg), **L7** (2.0 equiv, 43.2 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), **1l** (0.1 mmol, 32.3 mg) and methyl acrylate (0.3 mmol, 25.8 mg) and anhydrous DMSO (2 mL). The sealed tube was sealed and removed from the glovebox. Then the reaction was stirred at 80 ºC until the reaction was complete (monitored by TLC). The resulting mixture was quenched with saturated NH_4Cl solution (5 mL) and further diluted with water (10 mL). The aqueous layer was extracted with EtOAc and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by chromatography on silica gel, eluting with petroleum ether/EtOAc (10/1~2/1) to afford the desired products **6da** (14.9 mg, 45% yield).

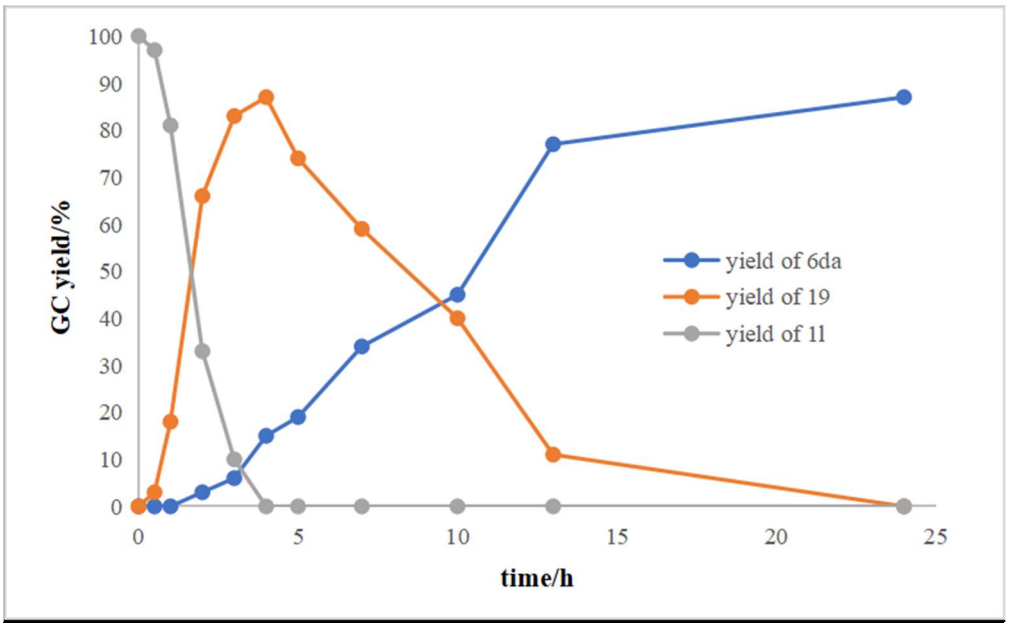
5.7 Kinetic profile of the cyclization/coupling reaction of 1l and 2a using L7 as the ligand



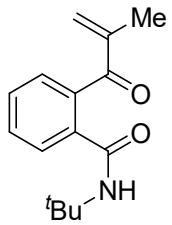
Ten experiments were set up in parallel: An oven-dried sealed tube equipped with a PTFE-coated stir bar was charged with $Ni(acac)_2$ (10 mol%, 2.6 mg), **L7** (20 mol%, 4.6 mg), alkene-tethered aryl bromide **1l** (0.1 mmol, 1 equiv), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), methyl acrylate **2a** (0.3 mmol, 25.8 mg) and anhydrous DMSO (2 mL). The sealed tube was sealed and removed from the glovebox. The reaction was then stirred at 80 °C and quenched at the set time.

Table S3: Kinetic profile of the cyclization/coupling reaction of 1d and 2a

entry	time (hour)	yield of **1l** (%)	yield of **6da** (%)	yield of **19** (%)
1	0	100	0	0
2	0.5	97	0	3
3	1	81	0	18
4	2	33	3	66
5	3	10	6	83
6	4	0	15	87
7	5	0	19	74
8	7	0	34	59
9	10	0	45	40
10	13	0	77	11
11	24	0	87	0



***N*-(*tert*-butyl)-2-methacryloylbenzamide (19)**



Chemical Formula: $C_{15}H_{19}NO_2$
Exact Mass: 245.1416

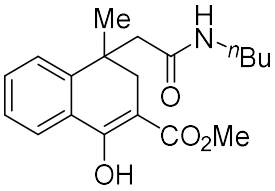
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 1H), 7.48 – 7.44 (m, 2H), 7.37 – 7.34 (m, 1H), 5.90 – 5.83 (m, 1H), 5.73 (s, 1H), 5.49 – 5.38 (m, 1H), 2.06 (t, J = 1.2 Hz, 3H), 1.38 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 199.7, 167.4, 145.4, 139.1, 136.9, 130.0, 129.8, 128.7, 128.2, 126.9, 52.0, 28.6, 17.6.

HRMS: (ESI) calcd for $C_{15}H_{20}NO_2^+$[M+H]$^+$ 246.1489; found 246.1496.

6. Characterization Data of Products

methyl 4-(2-(butylamino)-2-oxoethyl)-1-hydroxy-4-methyl-3,4-dihydronaphthalene-2-carboxylate (3aa)



Chemical Formula: $C_{19}H_{25}NO_4$
Exact Mass: 331.1784

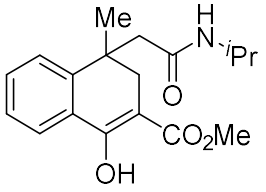
3aa was prepared according to general procedure **2.1** using 2-bromo-*N*-butyl-*N*-methacryloylbenzamide (0.1 mmol, 32.3 mg), methyl acrylate (0.3 mmol, 25.8 mg), $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 4.6 mg), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **3aa** (24.6 mg, 74% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.37 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 8.2 Hz, 1H), 7.36 – 7.31 (m, 2H), 4.88 (s, 1H), 3.84 (s, 3H), 3.03 (dd, *J* = 12.4, 7.0 Hz, 2H), 2.61 (dd, *J* = 171.2, 16.0 Hz, 2H), 2.40 – 2.24 (m, 2H), 1.58 (s, 3H), 1.28 – 1.21 (m, 2H), 1.21 – 1.14 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.0, 170.3, 164.2, 145.0, 131.2, 128.4, 126.9, 125.1, 124.9, 95.0, 51.8, 39.1, 36.4, 33.9, 31.4, 25.2, 19.9, 13.7.

HRMS: (ESI) calcd for $C_{19}H_{26}NO_4^+$ $[M+H]^+$ 332.1856; found 332.1859.

methyl 1-hydroxy-4-(2-(isopropylamino)-2-oxoethyl)-4-methyl-3,4-dihydronaphthalene-2-carboxylate (3ba)



Chemical Formula: $C_{18}H_{23}NO_4$
Exact Mass: 317.1627

3ba was prepared according to general procedure **2.1** using 2-bromo-*N*-isopropyl-*N*-

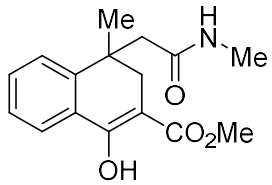
methacryloylbenzamide (0.1 mmol, 30.9 mg), methyl acrylate (0.3 mmol, 25.8 mg), $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 4.6 mg), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **3ba** (25.7 mg, 81% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.37 (s, 1H), 7.85 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.34 – 7.29 (m, 2H), 4.72 (d, *J* = 7.8 Hz, 1H), 3.90 – 3.84 (m, 1H), 3.82 (s, 3H), 2.59 (dd, *J* = 171.7, 16.0 Hz, 2H), 2.26 (dd, *J* = 67.0, 13.4 Hz, 2H), 1.57 (s, 3H), 0.99 (d, *J* = 6.5 Hz, 3H), 0.86 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.0, 169.4, 164.3, 144.9, 131.2, 128.4, 126.8, 125.3, 124.9, 95.0, 51.8, 46.7, 41.0, 36.3, 33.9, 25.1, 22.5, 22.4.

HRMS: (ESI) calcd for $C_{18}H_{24}NO_4^+$ $[M+H]^+$ 318.1700; found 318.1694.

methyl 1-hydroxy-4-methyl-4-(2-(methylamino)-2-oxoethyl)-3,4-dihydronaphthalene-2-carboxylate (3ca)



Chemical Formula: $C_{16}H_{19}NO_4$
Exact Mass: 289.1314

3ca was prepared according to general procedure **2.1** using 2-bromo-*N*-methacryloyl-*N*-methylbenzamide (0.1 mmol, 28.1 mg), methyl acrylate (0.3 mmol, 25.8 mg), $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 4.6 mg), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~1/1) to obtain **3ca** (14.2 mg, 49% yield).

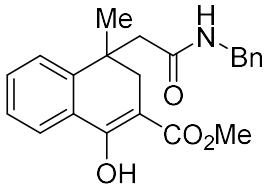
^{1}H NMR (600 MHz, $CDCl_3$) δ 12.36 (s, 1H), 7.87 (d, *J* = 9.4 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.36 – 7.30 (m, 2H), 4.84 (s, 1H), 3.84 (s, 3H), 2.75 (d, *J* = 15.9 Hz, 1H), 2.57 (d, *J* = 4.9 Hz, 3H), 2.46 (d, *J* = 16.0 Hz, 1H), 2.37 (d, *J* = 13.1 Hz, 1H), 2.26 (d, *J* = 13.1 Hz, 1H), 1.57 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.0, 171.1, 164.2, 145.0, 131.1, 128.4, 126.9, 125.02, 124.97,

95.1, 51.8, 46.6, 36.4, 33.8, 26.1, 25.2.

HRMS: (ESI) calcd for $C_{16}H_{20}NO_4^+[M+H]^+$ 290.1387; found 290.1387.

methyl 4-(2-(benzylamino)-2-oxoethyl)-1-hydroxy-4-methyl-3,4-dihydronaphthalene-2-carboxylate (3da)



Chemical Formula: $C_{22}H_{23}NO_4$
Exact Mass: 365.1627

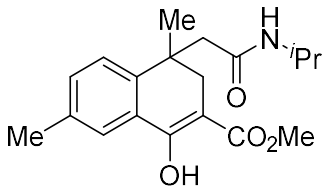
3da was prepared according to general procedure **2.1** using 2-bromo-*N*-benzyl-*N*-methacryloylbenzamide (0.1 mmol, 35.7 mg), methyl acrylate (0.3 mmol, 25.8 mg), $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 4.6 mg), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **3da** (25.6 mg, 70% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.35 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.26 (m, 6H), 7.08 (d, *J* = 6.6 Hz, 2H), 5.16 (s, 1H), 4.28 – 4.18 (m, 2H), 3.77 (s, 3H), 2.77 (d, *J* = 16.0 Hz, 1H), 2.48 (d, *J* = 16.0 Hz, 1H), 2.43 (d, *J* = 13.2 Hz, 1H), 2.33 (d, *J* = 13.2 Hz, 1H), 1.60 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.0, 170.2, 164.3, 144.8, 137.9, 131.3, 128.6, 128.4, 127.9, 127.5, 126.9, 125.1, 125.0, 95.0, 51.8, 46.5, 43.6, 36.4, 34.0, 25.2.

HRMS: (ESI) calcd for $C_{22}H_{24}NO_4^+[M+H]^+$ 366.1699; found 366.1698.

methyl 1-hydroxy-4-(2-(isopropylamino)-2-oxoethyl)-4,7-dimethyl-3,4-dihydronaphthalene-2-carboxylate (3ea)



Chemical Formula: $C_{19}H_{25}NO_4$
Exact Mass: 331.1784

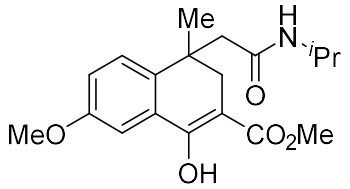
3ea was prepared according to general procedure **2.1** using 2-bromo-*N*-isopropyl-*N*-methacryloyl-5-methylbenzamide (0.1 mmol, 32.3 mg), methyl acrylate (0.3 mmol, 25.8 mg), $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 4.6 mg), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **3ea** (21.8 mg, 66% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.40 (s, 1H), 7.71 – 7.64 (m, 1H), 7.25 – 7.20 (m, 2H), 4.67 (d, *J* = 7.6 Hz, 1H), 3.94 – 3.86 (m, 1H), 3.83 (s, 3H), 2.58 (dd, *J* = 177.3, 16.0 Hz, 2H), 2.36 (s, 3H), 2.25 (dd, *J* = 58.4, 12.4 Hz, 2H), 1.56 (s, 3H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.89 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.1, 169.5, 164.6, 142.1, 136.6, 132.0, 128.2, 125.4, 125.3, 95.0, 51.8, 46.8, 41.0, 36.1, 34.0, 25.2, 22.6, 22.4, 21.0.

HRMS: (ESI) calcd for $C_{19}H_{26}NO_4^+$ $[M+H]^+$ 332.1856; found 332.1847.

methyl 1-hydroxy-4-(2-(isopropylamino)-2-oxoethyl)-7-methoxy-4-methyl-3,4-dihydronaphthalene-2-carboxylate (3fa)



Chemical Formula: $C_{19}H_{25}NO_5$
Exact Mass: 347.1733

3fa was prepared according to general procedure **2.1** using 2-bromo-*N*-isopropyl-*N*-methacryloyl-5-methoxybenzamide (0.1 mmol, 33.9 mg), methyl acrylate (0.3 mmol, 25.8 mg), $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 4.6 mg), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **3fa** (20.1 mg, 58% yield).

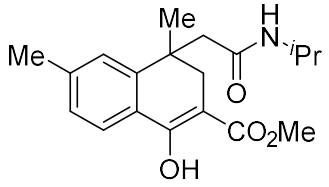
^{1}H NMR (600 MHz, $CDCl_3$) δ 12.40 (s, 1H), 7.39 (d, *J* = 2.9 Hz, 1H), 7.24 (d, *J* = 8.6 Hz, 1H), 6.93 (dd, *J* = 8.6, 2.9 Hz, 1H), 4.72 (d, *J* = 7.8 Hz, 1H), 3.92 – 3.86 (m, 1H), 3.83 (s, 6H), 2.57 (dd, *J* = 180.9, 16.0 Hz, 2H), 2.24 (dd, *J* = 62.9, 11.9 Hz, 2H), 1.54 (s, 3H), 1.00 (d, *J* = 6.6 Hz,

3H), 0.90 (d, J = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.1, 169.5, 164.1, 158.4, 137.2, 129.5, 126.5, 117.3, 109.3, 95.5, 55.4, 51.8, 46.9, 41.0, 35.9, 34.2, 25.3, 22.6, 22.5.

HRMS: (ESI) calcd for $C_{19}H_{26}NO_4^+$ $[M+H]^+$ 348.1805; found 348.1798.

methyl 1-hydroxy-4-(2-(isopropylamino)-2-oxoethyl)-4,6-dimethyl-3,4-dihydronaphthalene-2-carboxylate (3ga)



Chemical Formula: $C_{19}H_{25}NO_4$
Exact Mass: 331.1784

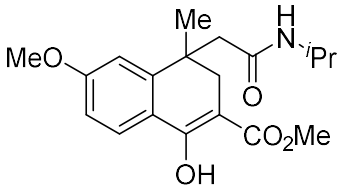
3ga was prepared according to general procedure **2.1** using 2-bromo-*N*-isopropyl-*N*-methacryloyl-4-methylbenzamide (0.1 mmol, 32.3 mg), methyl acrylate (0.3 mmol, 25.8 mg), $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 4.6 mg), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **3ga** (20.2 mg, 61% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.39 (s, 1H), 7.76 (d, J = 8.3 Hz, 1H), 7.15 – 7.12 (m, 2H), 4.61 (d, J = 7.9 Hz, 1H), 3.92 – 3.85 (m, 1H), 3.83 (s, 3H), 2.57 (dd, J = 156.5, 15.9 Hz, 2H), 2.37 (s, 3H), 2.26 (dd, J = 90.9, 12.9 Hz, 2H), 1.57 (s, 3H), 0.99 (d, J = 6.6 Hz, 3H), 0.85 (d, J = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.1, 169.5, 164.7, 144.9, 141.7, 127.6, 126.1, 125.7, 125.0, 94.2, 51.7, 46.8, 41.0, 36.4, 34.3, 25.0, 22.5, 22.4, 21.8.

HRMS: (ESI) calcd for $C_{19}H_{26}NO_4^+$ $[M+H]^+$ 332.1856; found 332.1848.

methyl 1-hydroxy-4-(2-(isopropylamino)-2-oxoethyl)-6-methoxy-4-methyl-3,4-dihydronaphthalene-2-carboxylate (3ha)



Chemical Formula: $C_{19}H_{25}NO_5$
Exact Mass: 347.1733

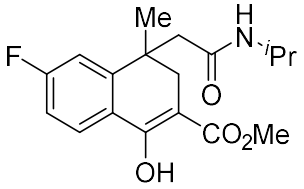
3ha was prepared according to general procedure **2.1** using 2-bromo-*N*-isopropyl-*N*-methacryloyl-4-methoxybenzamide (0.1 mmol, 33.9 mg), methyl acrylate (0.3 mmol, 25.8 mg), $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 4.6 mg), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **3ha** (19.8 mg, 57% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.43 (s, 1H), 7.82 (d, *J* = 8.6 Hz, 1H), 6.86 (d, *J* = 2.5 Hz, 1H), 6.83 (dd, *J* = 8.5, 2.5 Hz, 1H), 4.69 (d, *J* = 7.4 Hz, 1H), 3.95 – 3.88 (m, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 2.57 (dd, *J* = 164.9, 15.8 Hz, 2H), 2.25 (dd, *J* = 68.7, 13.2 Hz, 2H), 1.57 (s, 3H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.89 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.1, 169.4, 164.8, 162.2, 147.5, 127.0, 121.2, 111.7, 111.5, 92.9, 55.4, 51.7, 46.7, 41.1, 36.7, 34.0, 25.0, 22.6, 22.4.

HRMS: (ESI) calcd for $C_{19}H_{26}NO_5^+$ $[M+H]^+$ 348.1806; found 348.1808.

methyl 6-fluoro-1-hydroxy-4-(2-(isopropylamino)-2-oxoethyl)-4-methyl-3,4-dihydronaphthalene-2-carboxylate (3ia)



Chemical Formula: $C_{18}H_{22}FNO_4$
Exact Mass: 335.1533

3ia was prepared according to general procedure **2.1** using 2-bromo-4-fluoro-*N*-isopropyl-*N*-methacryloylbenzamide (0.1 mmol, 32.7 mg), methyl acrylate (0.3 mmol, 25.8 mg), $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 4.6 mg), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF

(1 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **3ia** (16.5 mg, 49% yield).

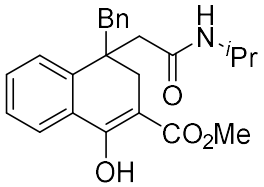
^{1}H NMR (600 MHz, $CDCl_3$) δ 12.39 (s, 1H), 7.86 (dd, *J* = 8.6, 5.9 Hz, 1H), 7.03 (dd, *J* = 10.0, 2.6 Hz, 1H),7.04 – 6.98 (m, 1H), 4.75 (d, *J* = 8.0 Hz, 1H), 3.93 – 3.83 (m, 1H), 3.83 (s, 3H), 2.60 (dd, *J* = 185.5, 16.0 Hz, 2H), 2.25 (dd, *J* = 53.8, 13.2 Hz, 2H), 1.56 (s, 3H), 1.02 (d, *J* = 6.6 Hz, 3H), 0.91 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.0, 169.0, 164.7 (d, *J* = 267.3 Hz), 163.7, 148.30, 148.25, 127.4, 127.3, 124.7 (d, *J* = 2.7 Hz), 113.8 (d, *J* = 21.8 Hz), 112.9 (d, *J* = 22.9 Hz), 94.4, 51.9, 46.4, 41.1, 36.6, 33.7, 25.0, 22.6, 22.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -107.27 (q, *J* = 8.3, 7.9 Hz).

HRMS: (ESI) calcd for $C_{18}H_{23}FNO_4^+$ $[M+H]^+$ 336.1605; found 336.1600.

methyl 4-benzyl-1-hydroxy-4-(2-(isopropylamino)-2-oxoethyl)-3,4-dihydronaphthalene-2-carboxylate (3ja)



Chemical Formula: $C_{24}H_{27}NO_4$
Exact Mass: 393.1940

3ja was prepared according to general procedure **2.1** using *N*-(2-benzylacryloyl)-2-bromo-*N*-isopropylbenzamide (0.1 mmol, 38.5 mg), methyl acrylate (0.3 mmol, 25.8 mg), $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 4.6 mg), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **3ja** (13.8 mg, 35% yield).

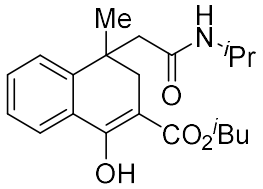
^{1}H NMR (600 MHz, $CDCl_3$) δ 12.40 (s, 1H), 7.93 – 7.90 (m, 1H), 7.36 – 7.31 (m, 2H), 7.23 – 7.18 (m, 3H), 7.14 – 7.12 (m, 1H), 7.10 – 7.06 (m, 2H), 4.84 (d, *J* = 7.9 Hz, 1H), 3.97 – 3.87 (m, 1H), 3.79 (s, 3H), 3.22 (dd, *J* = 288.6, 13.2 Hz, 2H), 2.61 (dd, *J* = 84.4, 16.0 Hz, 2H), 2.43 (dd, *J* = 43.5, 13.4 Hz, 2H), 1.00 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.1, 169.6, 163.9, 143.3, 137.4, 131.3, 130.7, 128.8, 127.7,

126.9, 126.2, 126.1, 125.0, 94.8, 51.7, 42.9, 42.3, 41.1, 40.4, 31.2, 22.6, 22.4.

HRMS: (ESI) calcd for $C_{24}H_{28}NO_4^+$ $[M+H]^+$ 394.2013; found 394.2009.

methyl 1-hydroxy-4-(2-(isopropylamino)-2-oxoethyl)-4-methyl-3,4-dihydronaphthalene-2-carboxylate (3bb)



Chemical Formula: $C_{21}H_{29}NO_4$
Exact Mass: 359.2097

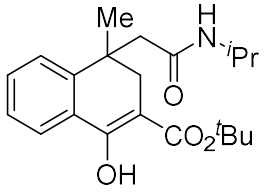
3bb was prepared according to general procedure **2.1** using 2-bromo-*N*-isopropyl-*N*-methacryloylbenzamide (0.1 mmol, 30.9 mg), isobutyl acrylate (0.3 mmol, 38.4 mg), $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 4.6 mg), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **3bb** (27.7 mg, 77% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.46 (s, 1H), 7.87 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.36 – 7.31 (m, 2H), 4.58 (d, *J* = 7.3 Hz, 1H), 4.10 – 3.94 (m, 2H), 3.89 – 3.82 (m, 1H), 2.60 (dd, *J* = 131.9, 16.0 Hz, 2H), 2.30 (dd, *J* = 134.4, 13.1 Hz, 2H), 2.07 – 1.98 (m, 1H), 1.60 (s, 3H), 0.99 – 0.97 (m, 9H), 0.84 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.7, 169.5, 164.1, 144.7, 131.1, 128.6, 126.9, 125.5, 124.9, 95.4, 70.7, 46.8, 41.0, 36.4, 34.4, 27.8, 25.2, 22.6, 22.4, 19.1.

HRMS: (ESI) calcd for $C_{21}H_{30}NO_4^+$ $[M+H]^+$ 360.2169; found 360.2169.

***tert*-butyl 1-hydroxy-4-(2-(isopropylamino)-2-oxoethyl)-4-methyl-3,4-dihydronaphthalene-2-carboxylate (3bc)**



Chemical Formula: $C_{21}H_{29}NO_4$
Exact Mass: 359.2097

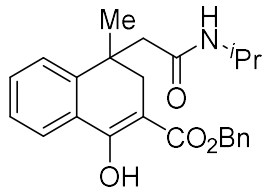
3bc was prepared according to general procedure **2.1** using 2-bromo-*N*-isopropyl-*N*-methacryloylbenzamide (0.1 mmol, 30.9 mg), *tert*-butyl acrylate (0.3 mmol, 38.4 mg), $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 4.6 mg), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **3bc** (27.8 mg, 77% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.63 (s, 1H), 7.85 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.34 – 7.29 (m, 2H), 4.58 (d, *J* = 7.9 Hz, 1H), 3.89 – 3.81 (m, 1H), 2.59 (d, *J* = 16.1 Hz, 1H), 2.45 – 2.40 (m, 2H), 2.18 (d, *J* = 13.0 Hz, 1H), 1.58 (s, 3H), 1.55 (s, 9H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.84 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.6, 169.5, 163.6, 144.5, 130.8, 128.8, 126.8, 125.4, 124.7, 96.5, 81.7, 46.8, 41.0, 36.4, 35.0, 28.4, 25.2, 22.7, 22.4.

HRMS: (ESI) calcd for $C_{21}H_{30}NO_4^+$ $[M+H]^+$ 360.2169; found 360.2175.

benzyl 1-hydroxy-4-(2-(isopropylamino)-2-oxoethyl)-4-methyl-3,4-dihydronaphthalene-2-carboxylate (3bd)



Chemical Formula: $C_{24}H_{27}NO_4$
Exact Mass: 393.1940

3bd was prepared according to general procedure **2.1** using 2-bromo-*N*-isopropyl-*N*-methacryloylbenzamide (0.1 mmol, 30.9 mg), benzyl acrylate (0.3 mmol, 48.6 mg), $Ni(acac)_2$

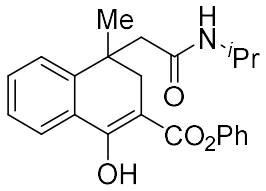
(10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 4.6 mg), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **3bd** (23.6 mg, 60% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.39 (s, 1H), 7.87 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.42 – 7.30 (m, 8H), 5.36 – 5.21 (m, 2H), 4.62 (d, *J* = 7.8 Hz, 1H), 3.89 – 3.80 (m, 1H), 2.62 (dd, *J* = 154.3, 16.1 Hz, 2H), 2.29 (dd, *J* = 110.7, 13.0 Hz, 2H), 1.58 (s, 3H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.83 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.4, 169.4, 164.6, 144.8, 135.7, 131.3, 128.6, 128.4, 128.3, 128.0, 126.9, 125.4, 124.9, 95.1, 66.3, 46.8, 41.0, 36.4, 34.2, 25.2, 22.5, 22.3.

HRMS: (ESI) calcd for $C_{24}H_{28}NO_4^+$ $[M+H]^+$ 394.2013; found 394.2009.

phenyl 1-hydroxy-4-(2-(isopropylamino)-2-oxoethyl)-4-methyl-3,4-dihydronaphthalene-2-carboxylate (3be)



Chemical Formula: $C_{23}H_{25}NO_4$
Exact Mass: 379.1784

3be was prepared according to general procedure **2.1** using 2-bromo-*N*-isopropyl-*N*-methacryloylbenzamide (0.1 mmol, 30.9 mg), phenyl acrylate (0.3 mmol, 42.9 mg), $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 4.6 mg), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **3be** (20.8 mg, 55% yield).

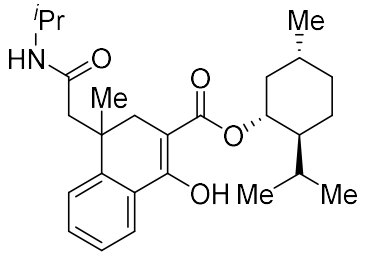
^{1}H NMR (600 MHz, $CDCl_3$) δ 12.23 (s, 1H), 7.90 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.47 – 7.38 (m, 4H), 7.37 – 7.32 (m, 1H), 7.29 – 7.26 (m, 1H), 7.18 – 7.16 (m, 2H), 4.73 (d, *J* = 7.9 Hz, 1H), 3.95 – 3.78 (m, 1H), 2.81 (dd, *J* = 179.2, 16.0 Hz, 2H), 2.38 (dd, *J* = 86.1, 13.1 Hz, 2H), 1.64 (s, 3H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 169.3, 166.1, 150.3, 145.1, 131.7, 129.5, 128.3, 127.0,

126.0, 125.5, 125.1, 121.7, 94.7, 46.9, 41.1, 36.5, 34.3, 25.3, 22.6, 22.4.

HRMS: (ESI) calcd for $C_{23}H_{26}NO_4^+$ $[M+H]^+$ 380.1856; found 380.1860.

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 1-hydroxy-4-(2-(isopropylamino)-2-oxoethyl)-4-methyl-3,4-dihydronaphthalene-2-carboxylate (3bf)



Chemical Formula: $C_{27}H_{39}NO_4$
Exact Mass: 441.2879

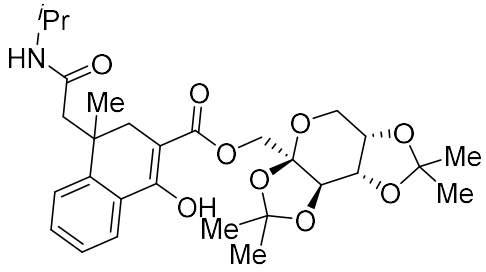
3bf was prepared according to general procedure **2.1** using 2-bromo-*N*-isopropyl-*N*-methacryloylbenzamide (0.1 mmol, 30.9 mg), (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl acrylate (0.3 mmol, 63.2 mg), $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 4.6 mg), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **3bf** (26.5 mg, 60% yield, dr = 1:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.59 (s, 1H), 7.86 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.35 – 7.30 (m, 2H), 4.88 – 4.80 (m, 1H), 4.57 (d, *J* = 7.9 Hz, 1H), 3.92 – 3.75 (m, 1H), 2.57 (dd, *J* = 134.0, 16.1 Hz, 2H), 2.31 (dd, *J* = 138.6, 13.1 Hz, 2H), 2.13 – 2.07 (m, 1H), 1.87 – 1.81 (m, 1H), 1.74 – 1.69 (m, 2H), 1.60 (s, 3H), 1.51 – 1.45 (m, 1H), 1.14 – 1.07 (m, 2H), 1.05 – 1.01 (m, 1H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H), 0.83 (d, *J* = 6.5 Hz, 3H), 0.82 – 0.78 (m, 1H), 0.77 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.4, 169.5, 164.0, 144.6, 131.1, 128.6, 126.9, 125.5, 124.8, 95.5, 74.8, 47.0, 46.7, 41.2, 41.0, 36.4, 34.5, 34.2, 31.5, 26.5, 25.2, 23.7, 22.7, 22.4, 22.0, 20.6, 16.6.

HRMS: (ESI) calcd for $C_{27}H_{40}NO_4^+$ $[M+H]^+$ 442.2952; found 442.2937.

(2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl 1-hydroxy-4-(2-(isopropylamino)-2-oxoethyl)-4-methyl-3,4-dihydronaphthalene-2-carboxylate (3bg)



Chemical Formula: $C_{29}H_{39}NO_9$
Exact Mass: 545.2625

3bg was prepared according to general procedure **2.1** using 2-bromo-*N*-isopropyl-*N*-methacryloylbenzamide (0.1 mmol, 30.9 mg), ((3a*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 1-hydroxy-4-(2-(isopropylamino)-2-oxoethyl)-4-methyl-3,4-dihydronaphthalene-2-carboxylate (0.3 mmol, 141.3 mg), $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 4.6 mg), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~1/1) to obtain **3bg** (26.2 mg, 48% yield, dr = 1:1).

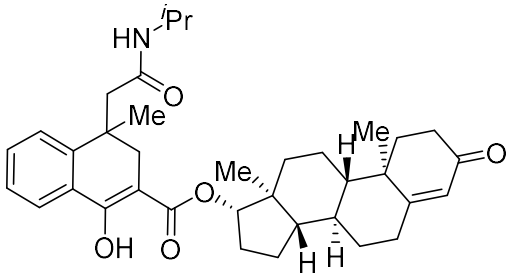
^{1}H NMR (600 MHz, $CDCl_3$) δ 12.35 (s, 1H), 7.86 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.32 (q, *J* = 6.8, 5.7 Hz, 2H), 4.63 (td, *J* = 8.1, 2.6 Hz, 1H), 4.63 (dd, *J* = 157.9, 11.8 Hz, 1H), 4.68 – 4.53 (m, 1H), 4.38 (dd, *J* = 39.3, 2.7 Hz, 1H), 4.25 (dd, *J* = 7.9, 1.7 Hz, 1H), 4.17 (dd, *J* = 119.1, 11.8 Hz, 1H), 3.96 – 3.91 (m, 1H), 3.86 – 3.79 (m, 1H), 3.79 – 3.75 (m, 1H), 2.72 (dd, *J* = 30.1, 15.9 Hz, 1H), 2.53 – 2.46 (m, 1H), 2.39 (dd, *J* = 34.4, 13.0 Hz, 1H), 2.14 (dd, *J* = 48.2, 13.0 Hz, 1H), 1.57 (d, *J* = 1.6 Hz, 3H), 1.53 (d, *J* = 12.8 Hz, 3H), 1.49 (d, *J* = 2.3 Hz, 3H), 1.41 – 1.32 (m, 6H), 0.96 (dd, *J* = 13.3, 6.6 Hz, 3H), 0.81 (dd, *J* = 31.8, 6.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.8 (d, *J* = 15.4 Hz), 169.2 (d, *J* = 4.7 Hz), 164.9 (d, *J* = 8.8 Hz), 144.5 (d, *J* = 57.7 Hz), 131.3 (d, *J* = 6.3 Hz), 128.3 (d, *J* = 13.0 Hz), 126.9, 125.5 (d, *J* = 36.0 Hz), 125.0 (d, *J* = 6.2 Hz), 109.1 (d, *J* = 4.3 Hz), 108.9 (d, *J* = 2.4 Hz), 101.3 (d, *J* = 8.9 Hz), 94.6 (d, *J* = 5.6 Hz), 70.8 (d, *J* = 3.2 Hz), 70.2 (d, *J* = 3.9 Hz), 70.0 (d, *J* = 3.6 Hz), 64.2 (d, *J* = 71.8 Hz), 61.3 (d, *J* = 6.7 Hz), 46.7, 41.0 (d, *J* = 5.3 Hz), 36.4, 34.7 (d, *J* = 75.4 Hz),

26.5, 25.8 (d, J = 3.1 Hz), 25.5 (d, J = 37.0 Hz), 25.2 (d, J = 4.2 Hz), 24.0, 22.5 (d, J = 33.4 Hz), 22.4 (d, J = 32.7 Hz).

HRMS: (ESI) calcd for $C_{29}H_{40}NO_9^+$ $[M+H]^+$ 546.2698; found 546.2698.

(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-17-yl 1-hydroxy-4-(2-(isopropylamino)-2-oxoethyl)-4-methyl-3,4-dihydronaphthalene-2-carboxylate (3bh)



Chemical Formula: $C_{36}H_{47}NO_5$
Exact Mass: 573.3454

3bh was prepared according to general procedure **2.1** using 2-bromo-*N*-isopropyl-*N*-methacryloylbenzamide (0.1 mmol, 30.9 mg), (8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl acrylate (0.3 mmol, 103.0 mg), $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 4.6 mg), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~1/1) to obtain **3bh** (32.2 mg, 56% yield, dr = 1:1).

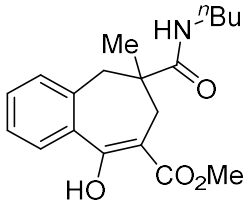
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.43 (d, J = 8.1 Hz, 1H), 7.85 (dd, J = 7.9, 1.6 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.34 – 7.27 (m, 2H), 5.72 (s, 1H), 4.79 – 4.71 (m, 1H), 4.55 (dd, J = 30.3, 7.8 Hz, 1H), 3.88 – 3.76 (m, 1H), 2.66 (dd, J = 16.1, 3.4 Hz, 1H), 2.51 – 2.12 (m, 10H), 2.06 – 1.80 (m, 4H), 1.66 (s, 3H), 1.59 – 1.57 (m, 3H), 1.45 – 1.36 (m, 2H), 1.19 (d, J = 4.3 Hz, 2H), 1.16 – 1.07 (m, 2H), 1.06 – 0.98 (m, 2H), 0.95 (t, J = 7.0 Hz, 3H), 0.88 (d, J = 8.3 Hz, 3H), 0.84 – 0.79 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 199.5, 171.0, 169.5, 131.1, 131.0, 128.62, 128.57, 127.0, 126.9, 125.7, 125.5, 124.9, 124.0, 95.6, 95.5, 82.8, 82.7, 53.73, 53.71, 50.30, 50.27, 46.92, 46.87, 42.9,

42.9, 41.1, 41.0, 38.6, 36.7, 36.40, 36.38, 35.7, 35.4, 35.0, 34.5, 33.9, 32.7, 31.5, 29.7, 27.80, 27.75, 25.3, 23.6, 22.65, 22.60, 22.4, 20.6, 20.5, 17.4, 12.25, 12.21.

HRMS: (ESI) calcd for $C_{36}H_{48}NO_5^+$ $[M+H]^+$ 574.3527; found 574.3518.

methyl 6-(butylcarbamoyl)-9-hydroxy-6-methyl-6,7-dihydro-5*H*-benzo[7]annulene-8-carboxylate (4aa)



Chemical Formula: $C_{19}H_{25}NO_4$
Exact Mass: 331.1784

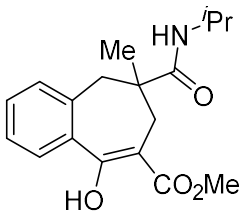
4aa was prepared according to general procedure **2.2** using 2-bromo-*N*-butyl-*N*-methacryloylbenzamide (0.1 mmol, 32.3 mg), methyl acrylate (0.3 mmol, 25.8 mg , $NiBr_2$(dme) (10 mol%, 3.1 mg), **L3** (20 mol%, 9.6 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg) and anhydrous DMSO (2 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **4aa** (21.3 mg, 64% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.73 (s, 1H), 7.65 (dd, *J* = 7.1, 2.0 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.27 (dd, *J* = 7.0, 1.9 Hz, 1H), 6.02 (s, 1H), 3.86 (s, 3H), 3.29 – 3.20 (m, 2H), 2.79 (dd, *J* = 261.1, 13.4 Hz, 2H), 2.21 (dd, *J* = 256.0, 14.9 Hz, 2H), 1.50 – 1.44 (m, 2H), 1.38 – 1.29 (m, 2H), 1.22 (s, 3H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.8, 173.1, 172.3, 139.2, 135.5, 130.84, 130.82, 127.6, 127.2, 98.5, 55.9, 52.4, 42.1, 39.8, 32.5, 32.0, 24.9, 20.5, 14.2.

HRMS: (ESI) calcd for $C_{19}H_{26}NO_4^+$ $[M+H]^+$ 332.1856; found 332.1857.

methyl 9-hydroxy-6-(isopropylcarbamoyl)-6-methyl-6,7-dihydro-5*H*-benzo[7]annulene-8-carboxylate (4ba)



Chemical Formula: $C_{18}H_{23}NO_4$
Exact Mass: 317.1627

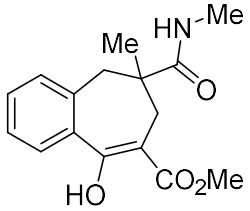
4ba was prepared according to general procedure **2.2** using 2-bromo-*N*-isopropyl-*N*-methacryloylbenzamide (0.1 mmol, 30.9 mg), methyl acrylate (0.3 mmol, 25.8 mg), $NiBr_2$(dme) (10 mol%, 3.1 mg), **L3** (20 mol%, 9.6 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg) and anhydrous DMSO (2 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **4ba** (22.6 mg, 71% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.74 (s, 1H), 7.65 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.27 (d, *J* = 1.7 Hz, 1H), 5.86 (s, 1H), 4.14 – 4.01 (m, 1H), 3.86 (s, 3H), 2.78 (dd, *J* = 247.1, 13.4 Hz, 2H), 2.20 (dd, *J* = 299.0, 14.9 Hz, 2H), 1.20 (s, 3H), 1.15 (d, *J* = 6.5 Hz, 3H), 1.12 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.5, 172.7, 171.9, 138.8, 135.1, 130.5, 130.4, 127.2, 126.8, 98.2, 55.4, 52.0, 41.7, 41.3, 32.1, 24.4, 22.7.

HRMS: (ESI) calcd for $C_{19}H_{24}NO_4^+$ $[M+H]^+$ 318.1700; found 318.1701.

methyl 9-hydroxy-6-methyl-6-(methylcarbamoyl)-6,7-dihydro-5*H*-benzo[7]annulene-8-carboxylate (4ca)



Chemical Formula: $C_{16}H_{19}NO_4$
Exact Mass: 289.1314

4ca was prepared according to general procedure **2.2** using 2-bromo-*N*-methacryloyl-*N*-methylbenzamide (0.1 mmol, 28.2 mg), methyl acrylate (0.3 mmol, 25.8 mg), $NiBr_2$(dme) (10 mol%, 3.1 mg), **L3** (20 mol%, 9.6 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg) and anhydrous DMSO (2 mL) and was purified by silica gel column chromatography

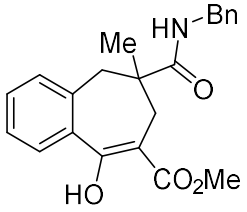
(petroleum ether/ethyl acetate = 5/1~1/1) to obtain **4ca** (19.1 mg, 66% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.69 (s, 1H), 7.67 – 7.62 (m, 1H), 7.40 – 7.34 (m, 2H), 7.28 (dd, *J* = 7.1, 1.8 Hz, 1H), 6.08 (s, 1H), 3.87 (s, 3H), 3.02 (d, *J* = 13.4 Hz, 1H), 2.80 (d, *J* = 4.7 Hz, 3H), 2.56 (d, *J* = 13.3 Hz, 1H), 2.21 (dd, *J* = 238.0, 14.7 Hz, 2H), 1.22 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 177.1, 172.7, 171.8, 138.8, 135.1, 130.49, 130.47, 127.2, 126.8, 98.1, 55.6, 52.0, 41.7, 32.2, 26.5, 24.5.

HRMS: (ESI) calcd for $C_{16}H_{20}NO_4^+$ $[M+H]^+$ 290.1387; found 290.1388.

methyl 6-(benzylcarbamoyl)-9-hydroxy-6-methyl-6,7-dihydro-5*H*-benzo[7]annulene-8-carboxylate (4da)



Chemical Formula: $C_{22}H_{23}NO_4$
Exact Mass: 365.1627

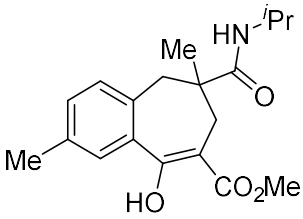
4da was prepared according to general procedure **2.2** using 2-bromo-*N*-benzyl-*N*-methacryloylbenzamide (0.1 mmol, 35.7 mg), methyl acrylate (0.3 mmol, 25.8 mg), $NiBr_2$(dme) (10 mol%, 3.1 mg), **L9** (20 mol%, 9.6 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg) and anhydrous DMSO (2 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **4da** (23.2 mg, 63% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.76 (s, 1H), 7.65 (d, *J* = 7.1 Hz, 1H), 7.40 – 7.27 (m, 8H), 6.46 (s, 1H), 4.53 – 4.37 (m, 2H), 3.50 (s, 3H), 2.84 (dd, *J* = 208.9, 13.4 Hz, 2H), 2.22 (dd, *J* = 331.3, 15.1 Hz, 2H), 1.26 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.6, 172.7, 172.3, 138.7, 138.4, 135.2, 130.8, 130.7, 128.9, 128.1, 127.8, 127.4, 127.0, 98.2, 55.8, 51.8, 44.1, 42.0, 32.0, 24.8.

HRMS: (ESI) calcd for $C_{22}H_{24}NO_4^+$ $[M+H]^+$ 366.1700; found 366.1704.

methyl 9-hydroxy-6-(isopropylcarbamoyl)-2,6-dimethyl-6,7-dihydro-5*H*-benzo[7]annulene-8-carboxylate (4ea)



Chemical Formula: $C_{19}H_{25}NO_4$
Exact Mass: 331.1784

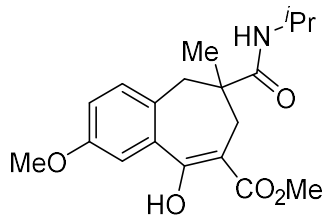
4ea was prepared according to general procedure **2.2** using 2-bromo-*N*-isopropyl-*N*-methacryloyl-5-methylbenzamide (0.1 mmol, 32.3 mg), methyl acrylate (0.3 mmol, 25.8 mg), $NiBr_2$(dme) (10 mol%, 3.1 mg), **L3** (20 mol%, 9.6 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg) and anhydrous DMSO (2 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **4ea** (18.6 mg, 56% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.76 (s, 1H), 7.47 – 7.46 (m, 1H), 7.19 (dd, *J* = 7.8, 2.4 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 5.86 (s, 1H), 4.10 – 4.03 (m, 1H), 3.86 (s, 3H), 2.73 (dd, *J* = 233.7, 13.5 Hz, 2H), 2.37 (s, 3H), 2.19 (dd, *J* = 290.2, 13.8 Hz, 2H), 1.19 (s, 3H), 1.14 (d, *J* = 6.5 Hz, 3H), 1.12 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.7, 172.8, 172.2, 136.6, 135.7, 134.9, 131.3, 130.4, 127.7, 98.1, 55.2, 51.9, 41.3, 41.2, 32.2, 24.4, 22.7, 21.0.

HRMS: (ESI) calcd for $C_{19}H_{26}NO_4^+$ $[M+H]^+$ 332.1856; found 332.1855.

methyl 9-hydroxy-6-(isopropylcarbamoyl)-2-methoxy-6-methyl-6,7-dihydro-5*H*-benzo[7]annulene-8-carboxylate (4fa)



Chemical Formula: $C_{19}H_{25}NO_5$
Exact Mass: 347.1733

4fa was prepared according to general procedure **2.2** using 2-bromo-*N*-isopropyl-*N*-methacryloyl-4-methoxybenzamide (0.1 mmol, 33.9 mg), methyl acrylate (0.3 mmol, 25.8 mg), $NiBr_2$(dme) (10 mol%, 3.1 mg), **L3** (20 mol%, 9.6 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg) and anhydrous DMSO (2 mL) and was purified by silica gel column

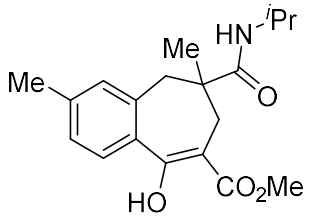
chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **4fa** (13.2 mg, 38% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.77 (s, 1H), 7.18 (d, *J* = 2.8 Hz, 1H), 7.17 (d, *J* = 8.3 Hz, 1H), 6.93 (dd, *J* = 8.3, 2.8 Hz, 1H), 5.82 (d, *J* = 6.6 Hz, 1H), 4.12 – 4.02 (m, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 2.71 (dd, *J* = 241.6, 13.6 Hz, 2H), 2.19 (dd, *J* = 276.9, 14.9 Hz, 2H), 1.18 (s, 3H), 1.14 (d, *J* = 6.5 Hz, 3H), 1.12 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.6, 172.8, 171.7, 158.5, 135.9, 131.6, 131.0, 116.8, 111.8, 98.4, 55.4, 55.2, 52.0, 41.2, 40.9, 32.2, 24.3, 22.7.

HRMS: (ESI) calcd for $C_{19}H_{26}NO_5^+$ $[M+H]^+$ 348.1806; found 348.1796.

methyl 9-hydroxy-6-(isopropylcarbamoyl)-3,6-dimethyl-6,7-dihydro-5*H*-benzo[7]annulene-8-carboxylate (4ga)



Chemical Formula: $C_{19}H_{25}NO_4$
Exact Mass: 331.1784

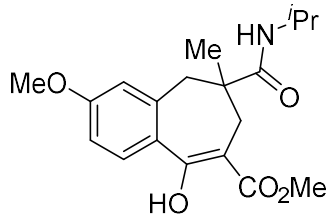
4ga was prepared according to general procedure **2.2** using 2-bromo-*N*-isopropyl-*N*-methacryloyl-4-methylbenzamide (0.1 mmol, 32.3 mg), methyl acrylate (0.3 mmol, 25.8 mg), $NiBr_2$(dme) (10 mol%, 3.1 mg), **L3** (20 mol%, 9.6 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg) and anhydrous DMSO (2 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **4ga** (17.6 mg, 53% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.74 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 8.7 Hz, 1H), 7.08 (s, 1H), 5.89 (s, 1H), 4.11 – 4.04 (m, 1H), 3.85 (s, 3H), 2.74 (dd, *J* = 235.8, 13.4 Hz, 2H), 2.38 (s, 3H), 2.20 (dd, *J* = 294.1, 14.8 Hz, 2H), 1.20 (s, 3H), 1.14 (d, *J* = 6.6 Hz, 3H), 1.12 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.7, 172.8, 172.3, 140.8, 138.7, 132.3, 131.2, 127.6, 127.2, 97.7, 55.3, 51.9, 41.7, 41.2, 32.2, 24.5, 22.7, 21.5.

HRMS: (ESI) calcd for $C_{19}H_{26}NO_4^+$ $[M+H]^+$ 332.1856; found 332.1853.

methyl 9-hydroxy-6-(isopropylcarbamoyl)-3-methoxy-6-methyl-6,7-dihydro-5*H*-benzo[7]annulene-8-carboxylate (4ha)



Chemical Formula: $C_{19}H_{25}NO_5$
Exact Mass: 347.1733

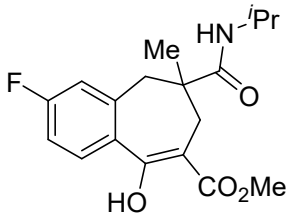
4ha was prepared according to general procedure **2.2** using 2-bromo-*N*-isopropyl-*N*-methacryloyl-4-methoxybenzamide (0.1 mmol, 33.9 mg), methyl acrylate (0.3 mmol, 25.8 mg), $NiBr_2$(dme) (10 mol%, 3.1 mg), **L3** (20 mol%, 9.6 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg) and anhydrous DMSO (2 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **4ha** (18.7 mg, 54% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.76 (s, 1H), 7.60 (d, *J* = 8.6 Hz, 1H), 6.87 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.79 (d, *J* = 2.6 Hz, 1H), 5.93 (s, 1H), 4.17 – 4.03 (m, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 2.75 (dd, *J* = 237.0, 13.3 Hz, 2H), 2.21 (dd, *J* = 313.4, 14.9 Hz, 2H), 1.21 (s, 3H), 1.15 (d, *J* = 6.6 Hz, 3H), 1.13 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.6, 172.8, 172.3, 161.2, 140.9, 129.0, 127.6, 115.9, 112.2, 97.1, 55.4, 55.2, 51.9, 42.2, 41.2, 32.3, 29.7, 24.6, 22.8.

HRMS: (ESI) calcd for $C_{19}H_{26}NO_5^+$ $[M+H]^+$ 348.1805; found 348.1801.

methyl 3-fluoro-9-hydroxy-6-(isopropylcarbamoyl)-6-methyl-6,7-dihydro-5*H*-benzo[7]annulene-8-carboxylate (4ia)



Chemical Formula: $C_{18}H_{22}FNO_4$
Exact Mass: 335.1533

4ia was prepared according to general procedure **2.2** using 2-bromo-4-fluoro-*N*-isopropyl-*N*-methacryloylbenzamide (0.1 mmol, 32.7 mg), methyl acrylate (0.3 mmol, 25.8 mg), $NiBr_2$(dme)

(10 mol%, 3.1 mg), **L9** (20 mol%, 9.6 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg) and anhydrous DMSO (2 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **4ia** (18.5 mg, 55% yield).

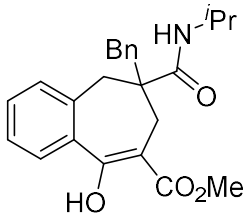
^{1}H NMR (600 MHz, $CDCl_3$) δ 12.73 (s, 1H), 7.64 (dd, *J* = 8.5, 5.8 Hz, 1H), 7.07 – 7.02 (m, 1H), 7.00 (dd, *J* = 9.2, 2.6 Hz, 1H), 5.82 (s, 1H), 4.12 – 4.03 (m, 1H), 3.86 (s, 3H), 2.77 (dd, *J* = 291.9, 13.3 Hz, 2H), 2.20 (dd, *J* = 300.1, 14.9 Hz, 2H), 1.21 (s, 3H), 1.16 (d, *J* = 6.5 Hz, 3H), 1.13 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.2, 172.7, 171.1, 163.5 (d, *J* = 251.8 Hz), 141.8 (d, *J* = 8.7 Hz), 131.2 (d, *J* = 4.4 Hz), 129.4 (d, *J* = 8.7 Hz), 117.4 (d, *J* = 21.8 Hz), 113.9 (d, *J* = 21.8 Hz), 98.1, 55.4, 52.0, 41.7, 41.3, 32.2, 24.5, 22.73, 22.71.

^{19}F NMR (565 MHz, $CDCl_3$) δ -109.4 – -109.6 (m).

HRMS: (ESI) calcd for $C_{18}H_{23}FNO_4^+$ $[M+H]^+$ 336.1605; found 336.1603.

methyl 6-benzyl-9-hydroxy-6-(isopropylcarbamoyl)-6,7-dihydro-5*H*-benzo[7]annulene-8-carboxylate (4ja)



Chemical Formula: $C_{24}H_{27}NO_4$
Exact Mass: 393.1940

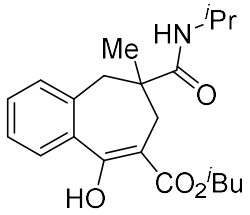
4ja was prepared according to general procedure **2.2** using *N*-(2-benzylacryloyl)-2-bromo-*N*-isopropylbenzamide (0.1 mmol, 38.5 mg), methyl acrylate (0.3 mmol, 25.8 mg), $NiBr_2$(dme) (10 mol%, 3.1 mg), **L3** (20 mol%, 9.6 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg) and anhydrous DMSO (2 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **4ja** (23.6 mg, 60% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.81 (s, 1H), 7.70 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.34 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.24 – 7.17 (m, 3H), 7.12 – 7.09 (m, 2H), 6.00 (s, 1H), 4.10 – 4.01 (m, 1H), 3.83 (s, 3H), 3.19 (d, *J* = 13.1 Hz, 1H), 2.91 – 2.82 (m, 2H), 2.71 – 2.25 (m, 2H), 1.97 (d, *J* = 15.4 Hz, 1H), 1.03 (d, *J* = 6.5 Hz, 3H), 1.00 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.8, 172.4, 138.3, 137.3, 135.1, 130.7, 130.6, 130.1, 128.0, 127.4, 127.0, 126.5, 97.7, 60.5, 52.0, 44.0, 41.5, 41.3, 29.8, 22.7, 22.6.

HRMS: (ESI) calcd for $C_{24}H_{28}NO_4^+$ $[M+H]^+$ 394.2013; found 394.2014.

isobutyl 9-hydroxy-6-(isopropylcarbamoyl)-6-methyl-6,7-dihydro-5*H*-benzo[7]annulene-8-carboxylate (4bb)



Chemical Formula: $C_{21}H_{29}NO_4$
Exact Mass: 359.2097

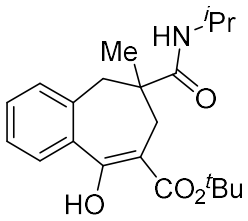
4bb was prepared according to general procedure **2.2** using 2-bromo-*N*-isopropyl-*N*-methacryloylbenzamide (0.1 mmol, 30.9 mg), isobutyl acrylate (0.3 mmol, 38.4 mg), $NiBr_2$(dme) (10 mol%, 3.1 mg), **L3** (20 mol%, 9.6 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg) and anhydrous DMSO (2 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **4bb** (25.5 mg, 71% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.82 (s, 1H), 7.68 – 7.61 (m, 1H), 7.39 – 7.33 (m, 2H), 7.27 – 7.24 (m, 1H), 5.63 (s, 1H), 4.18 (dd, *J* = 10.5, 6.9 Hz, 1H), 4.10 – 4.03 (m, 1H), 3.92 (dd, *J* = 10.7, 6.5 Hz, 1H), 2.75 (dd, *J* = 260.7, 13.4 Hz, 2H), 2.23 (dd, *J* = 93.7, 14.5 Hz, 2H), 2.08 – 2.00 (m, 1H), 1.24 (s, 3H), 1.12 (t, *J* = 6.5 Hz, 6H), 1.00 (d, *J* = 1.3 Hz, 3H), 0.99 (d, *J* = 1.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.5, 172.6, 171.5, 138.8, 135.3, 130.4, 130.2, 127.2, 126.9, 98.4, 71.0, 55.4, 42.1, 41.3, 32.0, 27.8, 24.3, 22.7, 19.21, 19.16.

HRMS: (ESI) calcd for $C_{21}H_{30}NO_4^+$ $[M+H]^+$ 360.2169; found 360.2170.

***tert*-butyl 9-hydroxy-6-(isopropylcarbamoyl)-6-methyl-6,7-dihydro-5*H*-benzo[7]annulene-8-carboxylate (4bc)**



Chemical Formula: $C_{21}H_{29}NO_4$
Exact Mass: 359.2097

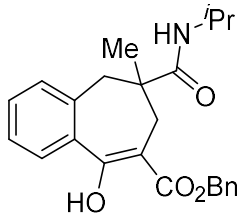
4bc was prepared according to general procedure **2.2** using 2-bromo-*N*-isopropyl-*N*-methacryloylbenzamide (0.1 mmol, 30.9 mg), *tert*-butyl acrylate (0.3 mmol, 38.4 mg), $NiBr_2$(dme) (10 mol%, 3.1 mg), **L3** (20 mol%, 9.6 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg) and anhydrous DMSO (2 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **4bc** (23.1 mg, 64% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.81 (s, 1H), 7.65 – 7.63 (m, 1H), 7.37 – 7.33 (m, 2H), 7.25 – 7.22 (m, 1H), 5.61 (s, 1H), 4.10 – 4.03 (m, 1H), 2.74 (dd, *J* = 256.3, 13.4 Hz, 2H), 2.25 – 2.09 (m, 2H), 1.58 (s, 9H), 1.23 (s, 3H), 1.13 (d, *J* = 4.0 Hz, 3H), 1.12 (d, *J* = 4.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.7, 138.8, 135.6, 130.14, 130.12, 127.2, 126.8, 99.7, 82.2, 55.5, 42.1, 41.3, 32.4, 28.4, 24.3, 22.7.

HRMS: (ESI) calcd for $C_{21}H_{30}NO_4^+$ $[M+H]^+$ 360.2169; found 360.2169.

benzyl 9-hydroxy-6-(isopropylcarbamoyl)-6-methyl-6,7-dihydro-5*H*-benzo[7]annulene-8-carboxylate (4bd)



Chemical Formula: $C_{24}H_{27}NO_4$
Exact Mass: 393.1940

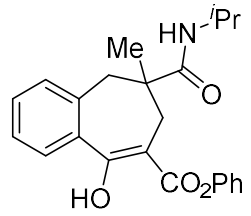
4bd was prepared according to general procedure **2.2** using 2-bromo-*N*-isopropyl-*N*-methacryloylbenzamide (0.1 mmol, 30.9 mg), benzyl acrylate (0.3 mmol, 48.6 mg), $NiBr_2$(dme) (10 mol%, 3.1 mg), **L3** (20 mol%, 9.6 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg) and anhydrous DMSO (2 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **4bd** (30.9 mg, 78% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.76 (s, 1H), 7.65 (dd, *J* = 7.1, 2.0 Hz, 1H), 7.43 – 7.34 (m, 7H), 7.27 – 7.24 (m, 1H), 5.64 (s, 1H), 5.31 (dd, *J* = 137.2, 12.4 Hz, 2H), 4.05 – 3.97 (m, 1H), 2.77 (dd, *J* = 283.3, 13.4 Hz, 2H), 2.24 (dd, *J* = 163.7, 14.7 Hz, 2H), 1.20 (s, 3H), 1.04 (s, 3H), 1.03 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.8, 172.7, 172.4, 139.2, 135.9, 135.5, 130.82, 130.77, 130.7, 129.1, 128.8, 128.5, 127.6, 127.2, 98.6, 67.0, 55.7, 42.2, 41.7, 32.5, 24.7, 23.00, 22.96.

HRMS: (ESI) calcd for $C_{24}H_{28}NO_4^+$ $[M+H]^+$ 394.2013; found 394.2008.

phenyl 9-hydroxy-6-(isopropylcarbamoyl)-6-methyl-6,7-dihydro-5*H*-benzo[7]annulene-8-carboxylate (4be)



Chemical Formula: $C_{23}H_{25}NO_4$
Exact Mass: 379.1784

4be was prepared according to general procedure **2.2** using 2-bromo-*N*-isopropyl-*N*-methacryloylbenzamide (0.1 mmol, 30.9 mg), phenyl acrylate (0.3 mmol, 44.4 mg), $NiBr_2$(dme) (10 mol%, 3.1 mg), **L3** (20 mol%, 9.6 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg) and anhydrous DMSO (2 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **4be** (25.4 mg, 67% yield).

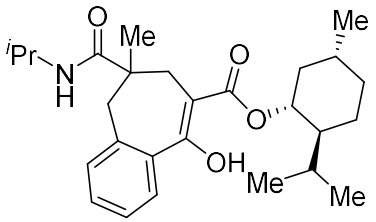
^{1}H NMR (600 MHz, $CDCl_3$) δ 12.58 (s, 1H), 7.69 – 7.66 (m, 1H), 7.46 – 7.42 (m, 2H), 7.42 – 7.36 (m, 2H), 7.32 – 7.28 (m, 2H), 7.19 – 7.16 (m, 2H), 5.62 (d, *J* = 7.7 Hz, 1H), 4.11 – 4.04 (m, 1H), 2.88 (dd, *J* = 382.6, 13.5 Hz, 2H), 2.40 (dd, *J* = 150.4, 14.6 Hz, 2H), 1.33 (s, 3H), 1.10 (d, *J* = 6.6 Hz, 3H), 1.06 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.3, 171.2, 150.2, 130.8, 130.5, 129.65, 129.57, 127.3, 126.9, 126.2, 121.8, 115.3, 98.0, 60.4, 55.4, 41.4, 32.8, 24.4, 22.7, 21.1, 14.2.

HRMS: (ESI) calcd for $C_{23}H_{26}NO_4^+$ $[M+H]^+$ 380.1856; found 380.1846.

2-isopropyl-5-methylcyclohexyl 9-hydroxy-6-(isopropylcarbamoyl)-6-methyl-6,7-

dihydro-5*H*-benzo[7]annulene-8-carboxylate (4bf)



Chemical Formula: $C_{27}H_{39}NO_4$
Exact Mass: 441.2879

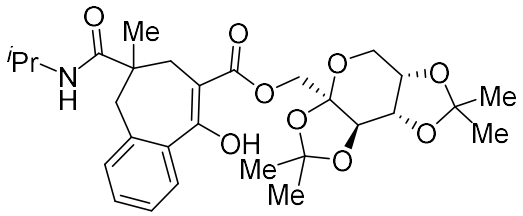
4bf was prepared according to general procedure **2.2** using 2-bromo-*N*-isopropyl-*N*-methacryloylbenzamide (0.1 mmol, 30.9 mg), (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl acrylate (0.3 mmol, 63.1 mg), $NiBr_2$(dme) (10 mol%, 3.1 mg), **L3** (20 mol%, 9.6 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg) and anhydrous DMSO (2 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **4bf** (31.3 mg, 71% yield, dr = 1:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.86 (s, 1H), 7.67 – 7.63 (m, 1H), 7.39 – 7.33 (m, 2H), 7.24 (q, *J* = 4.7 Hz, 1H), 5.48 (d, *J* = 61.8 Hz, 1H), 4.94 – 4.86 (m, 1H), 4.09 – 4.02 (m, 1H), 2.97 (dd, *J* = 36.6, 13.5 Hz, 1H), 2.50 (dd, *J* = 13.6, 10.5 Hz, 1H), 2.22 (d, *J* = 6.5 Hz, 1H), 2.10 (d, *J* = 13.4 Hz, 1H), 2.02 – 1.81 (m, 2H), 1.72 (dd, *J* = 14.5, 2.9 Hz, 2H), 1.59 – 1.52 (m, 1H), 1.52 – 1.43 (m, 2H), 1.23 (d, *J* = 12.7 Hz, 3H), 1.14 – 1.10 (m, 6H), 1.08 – 1.05 (m, 1H), 0.93 (dd, *J* = 6.5, 2.9 Hz, 3H), 0.91 (s, 3H), 0.80 (dd, *J* = 6.9, 1.8 Hz, 3H), 0.77 – 0.72 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.7, 175.6, 172.35, 172.33, 170.89, 170.86, 139.1, 138.9, 135.5, 130.3, 130.1, 130.0, 127.3, 127.2, 126.9, 126.8, 98.7, 98.6, 75.1, 74.8, 55.5, 55.4, 47.1, 47.0, 42.3, 41.9, 41.4, 41.3, 41.1, 41.0, 34.18, 34.15, 32.2, 32.0, 31.5, 31.4, 26.3, 26.0, 24.3, 24.1, 23.4, 23.0, 22.8, 22.73, 22.70, 22.03, 22.01, 20.9, 20.8, 16.3, 15.9.

HRMS: (ESI) calcd for $C_{27}H_{40}NO_4^+$ $[M+H]^+$ 442.2952; found 442.2951.

((3a*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 9-hydroxy-6-(isopropylcarbamoyl)-6-methyl-6,7-dihydro-5*H*-benzo[7]annulene-8-carboxylate (4bg)



Chemical Formula: $C_{29}H_{39}NO_9$
Exact Mass: 545.2625

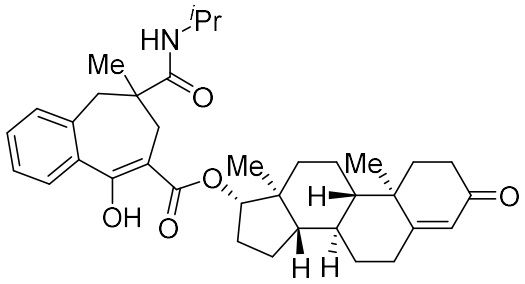
4bg was prepared according to general procedure **2.2** using 2-bromo-*N*-isopropyl-*N*-methacryloylbenzamide (0.1 mmol, 30.9 mg), ((3aR,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 1-hydroxy-4-(2-(isopropylamino)-2-oxoethyl)-4-methyl-3,4-dihydronaphthalene-2-carboxylate (0.3 mmol, 141.3 mg), $NiBr_2$(dme) (10 mol%, 3.1 mg), **L3** (20 mol%, 9.6 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg) and anhydrous DMSO (2 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~1/1) to obtain **4bg** (25.5 mg, 47% yield, dr = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.54 (s, 1H), 7.63 (dd, *J* = 7.2, 1.9 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.27 – 7.23 (m, 1H), 5.79 (d, *J* = 17.5 Hz, 1H), 4.64 – 4.59 (m, 1H), 4.43 (d, *J* = 4.3 Hz, 1H), 4.33 (dd, *J* = 33.1, 2.6 Hz, 1H), 4.26 – 4.18 (m, 2H), 4.14 – 4.00 (m, 1H), 3.96 – 3.74 (m, 2H), 2.96 (t, *J* = 12.8 Hz, 1H), 2.62 (s, 3H), 2.59 – 2.34 (m, 2H), 2.02 (dd, *J* = 75.6, 14.8 Hz, 1H), 1.48 (d, *J* = 8.2 Hz, 3H), 1.38 – 1.33 (m, 6H), 1.21 (d, *J* = 12.5 Hz, 3H), 1.14 – 1.09 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.6, 175.3, 171.6, 171.4, 138.9, 138.6, 135.2, 135.1, 130.5, 130.5, 130.4, 127.2, 126.9, 109.2, 109.2, 108.9, 108.9, 101.3, 101.3, 98.2, 97.9, 70.8, 70.7, 70.6, 70.0, 70.0, 65.6, 65.1, 61.4, 61.4, 55.4, 55.2, 42.0, 41.7, 41.4, 41.3, 32.2, 31.8, 26.6, 25.9, 25.9, 25.6, 25.5, 24.5, 24.4, 24.0, 24.0, 22.8, 22.7, 22.7.

HRMS: (ESI) calcd for $C_{29}H_{40}NO_9^+$ $[M+H]^+$ 546.2698; found 546.2699.

(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl 9-hydroxy-6-(isopropylcarbamoyl)-6-methyl-6,7-dihydro-5*H*-benzo[7]annulene-8-carboxylate (4bh)



Chemical Formula: $C_{36}H_{47}NO_5$
Exact Mass: 573.3454

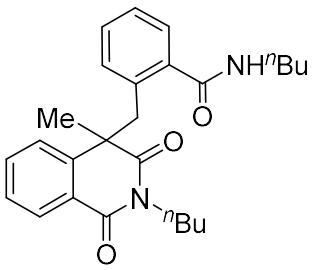
4bh was prepared according to general procedure **2.2** using 2-bromo-*N*-isopropyl-*N*-methacryloylbenzamide (0.1 mmol, 30.9 mg), (8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl acrylate (0.3 mmol, 103.0 mg), $NiBr_2$(dme) (10 mol%, 3.1 mg), **L3** (20 mol%, 9.6 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg) and anhydrous DMSO (2 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~1/1) to obtain **4bh** (22.3 mg, 39% yield, dr = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.82 (s, 1H), 7.67 – 7.61 (m, 1H), 7.38 – 7.33 (m, 2H), 7.22 (dt, *J* = 5.0, 3.1 Hz, 1H), 5.73 (d, *J* = 1.6 Hz, 1H), 5.42 (s, 1H), 4.82 – 4.69 (m, 1H), 4.11 – 3.99 (m, 1H), 2.99 – 2.87 (m, 1H), 2.51 – 2.15 (m, 8H), 2.06 – 1.98 (m, 1H), 1.90 – 1.81 (m, 2H), 1.77 – 1.56 (m, 6H), 1.48 – 1.34 (m, 2H), 1.24 (s, 3H), 1.19 (s, 3H), 1.13 – 1.08 (m, 6H), 1.04 – 0.93 (m, 2H), 0.93 – 0.89 (m, 3H), 0.89 – 0.79 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.5, 172.7, 171.9, 138.8, 135.1, 130.5, 130.4, 127.2, 126.8, 98.2, 55.4, 52.0, 41.7, 41.3, 32.1, 24.4, 22.7.

HRMS: (ESI) calcd for $C_{36}H_{48}NO_5^+$ $[M+H]^+$ 574.3527; found 574.3518.

_N_-butyl-2-((2-butyl-4-methyl-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)methyl)benzamide (5a)



Chemical Formula: $C_{26}H_{32}N_2O_3$
Exact Mass: 420.2413

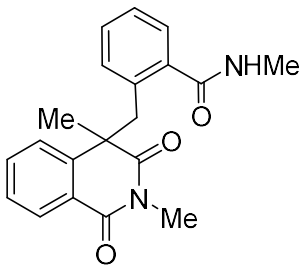
5a was prepared according to general procedure **2.3** using 2-bromo-*N*-butyl-*N*-methacryloylbenzamide (0.1 mmol, 32.3 mg), $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 4.6 mg), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~1/1) to obtain **5a** (9.2 mg, 44% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 6.9 Hz, 1H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 7.1 Hz, 1H), 7.07 (t, *J* = 7.0 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 1H), 5.88 (s, 1H), 3.87 – 3.73 (m, 3H), 3.63 (d, *J* = 14.1 Hz, 1H), 3.43 (dq, *J* = 13.7, 7.0 Hz, 1H), 3.12 – 3.02 (m, 1H), 1.77 (s, 3H), 1.59 – 1.53 (m, 2H), 1.43 (dt, *J* = 14.9, 7.4 Hz, 2H), 1.35 – 1.30 (m, 2H), 1.20 (dq, *J* = 14.7, 7.3 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 169.5, 163.7, 143.0, 137.3, 134.3, 133.8, 129.8, 129.4, 128.5, 127.6, 127.3, 127.0, 126.6, 125.1, 49.0, 44.4, 40.3, 39.8, 31.4, 29.8, 29.0, 20.2, 20.1, 13.79, 13.76.

HRMS: (ESI) calcd for $C_{26}H_{33}N_2O_3^+$ $[M+H]^+$ 421.2486; found 421.2485.

2-((2,4-dimethyl-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)methyl)-*N*-methylbenzamide (5b)



Chemical Formula: $C_{20}H_{20}N_2O_3$
Exact Mass: 336.1474

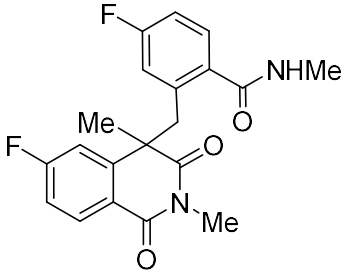
5b was prepared according to general procedure **2.3** using 2-bromo-*N*-methacryloyl-*N*-methylbenzamide (0.1 mmol, 28.2 mg), $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 4.6 mg), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1~1/1) to obtain **5b** (6.1 mg, 36% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.9 Hz, 1H), 7.68 – 7.62 (m, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.36 (m, 1H), 7.20 – 7.06 (m, 3H), 6.85 (d, *J* = 8.5 Hz, 1H), 5.28 – 5.24 (m, 1H), 3.94 (d, *J* = 13.5 Hz, 1H), 3.51 (d, *J* = 13.5 Hz, 1H), 3.15 (s, 3H), 2.69 (d, *J* = 4.9 Hz, 3H), 1.82 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.3, 170.0, 163.9, 142.3, 136.6, 134.4, 133.6, 130.7, 129.5, 128.1, 127.3, 127.2, 127.1, 126.8, 125.1, 49.5, 45.6, 27.1, 26.9, 26.8.

HRMS: (ESI) calcd for $C_{20}H_{21}N_2O_3^+$ $[M+H]^+$ 337.1547; found 337.1545.

4-fluoro-2-((6-fluoro-2,4-dimethyl-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)methyl)-*N*-methylbenzamide (5c)



Chemical Formula: $C_{20}H_{18}F_2N_2O_3$
Exact Mass: 372.1285

5c was prepared according to general procedure **2.3** using 2-bromo-4-fluoro-*N*-methacryloyl-*N*-methylbenzamide (0.1 mmol, 29.8 mg), $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20

mol%, 4.6 mg), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~1/1) to obtain **5c** (8.4 mg, 45% yield).

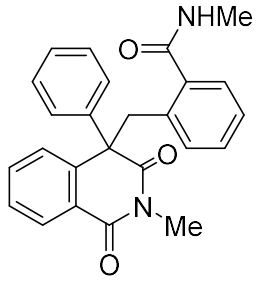
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.7, 5.9 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.18 – 7.05 (m, 2H), 6.81 (td, *J* = 8.2, 2.6 Hz, 1H), 6.65 – 6.55 (m, 1H), 5.39 (s, 1H), 4.02 (d, *J* = 13.7 Hz, 1H), 3.51 (d, *J* = 13.7 Hz, 1H), 3.27 – 3.17 (m, 3H), 2.78 (d, *J* = 4.9 Hz, 3H), 1.79 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.6, 168.9, 166.3 (d, *J* = 255.8 Hz), 162.9, 162.8 (d, *J* = 250.7 Hz), 145.1 (d, *J* = 8.7 Hz), 137.8 (d, *J* = 7.7 Hz), 132.7 (d, *J* = 3.3 Hz), 131.3 (d, *J* = 9.4 Hz), 129.3 (d, *J* = 8.7 Hz), 121.5 (d, *J* = 2.6 Hz), 117.5 (d, *J* = 21.8 Hz), 115.3 (d, *J* = 22.1 Hz), 114.1 (d, *J* = 21.2 Hz), 113.7 (d, *J* = 23.3 Hz), 49.6, 44.7, 27.6, 27.0, 26.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -102.12 – -102.61 (m), -109.28 – -109.89 (m).

HRMS: (ESI) calcd for $C_{20}H_{19}F_2N_2O_3^+$ $[M+H]^+$ 373.1358; found 373.1355.

_N_-methyl-2-((2-methyl-1,3-dioxo-4-phenyl-1,2,3,4-tetrahydroisoquinolin-4-yl)methyl)benzamide (5d)



Chemical Formula: $C_{25}H_{22}N_2O_3$
Exact Mass: 398.1630

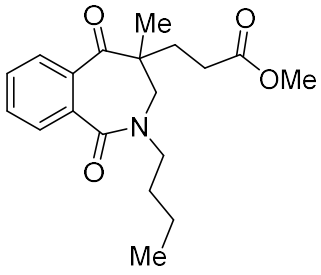
5d was prepared according to general procedure **2.3** using 2-bromo-*N*-methyl-*N*-(2-phenylacryloyl)benzamide (0.1 mmol, 34.3 mg), $Ni(acac)_2$ (10 mol%, 2.6 mg), terpyridine **L1** (20 mol%, 4.6 mg), $MnBr_2$ (0.1 mmol, 21.4 mg), Mn^0 (0.3 mmol, 16.5 mg), 4 Å molecular sieves (30 mg), anhydrous DMSO (1 mL) and anhydrous THF (1 mL) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~1/1) to obtain **5d** (8.4 mg, 42% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 9.2 Hz, 1H), 7.56 – 7.46 (m, 1H), 7.38 – 7.27 (m, 4H), 7.25 (d, *J* = 5.2 Hz, 2H), 7.23 – 7.15 (m, 1H), 7.16 – 7.08 (m, 3H), 6.95 (d, *J* = 7.3 Hz, 1H), 5.20 (s, 1H), 4.55 (d, *J* = 12.9 Hz, 1H), 4.17 (d, *J* = 13.0 Hz, 1H), 3.18 (s, 3H), 2.67 (d, *J* = 4.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.3, 169.9, 163.9, 143.6, 142.6, 137.0, 134.2, 133.4, 131.0, 129.9, 129.6, 128.8, 127.8, 127.71, 127.66, 127.4, 127.3, 127.2, 125.4, 58.0, 41.5, 27.0, 26.8.

HRMS: (ESI) calcd for $C_{25}H_{23}N_2O_3^+$ $[M+H]^+$ 399.1703; found 399.1698.

methyl 3-(2-butyl-4-methyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)propanoate (6aa)



Chemical Formula: $C_{19}H_{25}NO_4$
Exact Mass: 331.1784

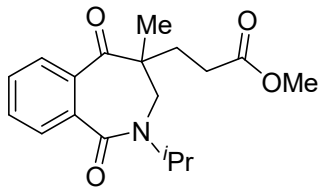
6aa was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-butyl-*N*-methacryloylbenzamide (0.1 mmol, 32.3 mg) and methyl acrylate (0.3 mmol, 25.8 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~2/1) to obtain **6aa** (17.6 mg, 53% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.57 – 7.53 (m, 1H), 7.44 (dd, *J* = 7.6, 1.5 Hz, 1H), 3.93 (s, 1H), 3.72 – 3.65 (m, 4H), 3.20 (d, *J* = 15.0 Hz, 2H), 2.43 – 2.33 (m, 2H), 1.95 – 1.78 (m, 2H), 1.68 – 1.61 (m, 1H), 1.42 – 1.35 (m, 2H), 1.29 (s, 3H), 0.97 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.7, 173.3, 168.5, 137.2, 133.7, 132.1, 131.4, 128.9, 127.3, 54.7, 54.5, 51.9, 49.4, 31.4, 29.7, 28.6, 20.2, 19.4, 13.9.

HRMS: (ESI) calcd for $C_{19}H_{26}NO_4^+$ $[M+H]^+$ 332.1856; found 332.1859.

methyl 3-(2-isopropyl-4-methyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)propanoate (6ba)



Chemical Formula: $C_{18}H_{23}NO_4$
Exact Mass: 317.1627

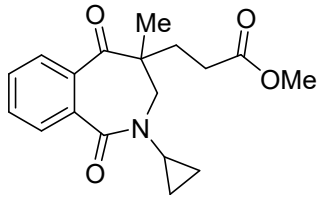
6ba was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-isopropyl-*N*-methacryloylbenzamide (0.1 mmol, 30.9 mg) and methyl acrylate (0.3 mmol, 25.8 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~2/1) to obtain **6ba** (18.1 mg, 57% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.56 – 7.50 (m, 1H), 7.39 (dd, *J* = 7.4, 1.4 Hz, 1H), 4.51 – 4.37 (m, 1H), 3.66 (s, 3H), 3.37 (dd, *J* = 176.1, 15.1 Hz, 2H), 2.35 (dd, *J* = 8.9, 7.4 Hz, 2H), 1.90 – 1.67 (m, 2H), 1.35 – 1.28 (m, 9H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.3, 173.3, 169.8, 136.4, 133.5, 131.9, 131.5, 130.0, 127.4, 77.3, 77.1, 76.9, 54.0, 52.0, 51.9, 50.0, 31.6, 28.7, 20.4, 20.3, 19.1;

HRMS: (ESI) calcd for $C_{18}H_{23}NO_4^+$[M+H]$^+$ 318.1700; found 318.1692.

methyl 3-(2-cyclopropyl-4-methyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)propanoate (6ca)



Chemical Formula: $C_{18}H_{21}NO_4$
Exact Mass: 315.1471

6ca was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol,

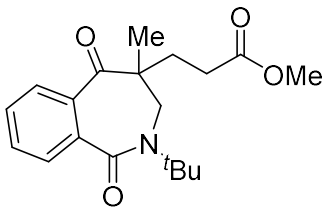
16.5 mg), 2-bromo-*N*-cyclopropyl-*N*-methacryloylbenzamide (0.1 mmol, 30.7 mg) and methyl acrylate (0.3 mmol, 25.8 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~2/1) to obtain **6ca** (14.2 mg, 45% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.63 – 7.56 (m, 1H), 7.56 – 7.50 (m, 1H), 7.45 (dd, *J* = 7.6, 1.5 Hz, 1H), 3.70 – 3.61 (m, 4H), 3.27 (d, *J* = 15.1 Hz, 1H), 3.00 – 2.91 (m, 1H), 2.38 (t, *J* = 8.2 Hz, 2H), 2.00 – 1.78 (m, 2H), 1.28 (s, 3H), 1.04 – 0.90 (m, 2H), 0.89 – 0.68 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.4, 173.4, 170.3, 136.3, 133.8, 132.3, 131.5, 129.5, 127.7, 55.2, 54.2, 52.0, 32.3, 31.6, 28.8, 19.9, 8.3, 7.8;

HRMS: (ESI) calcd for $C_{18}H_{23}NO_4^+$[M+H]$^+$ 316.1543; found 316.1534.

methyl 3-(2-(*tert*-butyl)-4-methyl-1,5-dioxo-2,3,4,5-tetrahydro-1H-benzo[*c*]azepin-4-yl)propanoate (6da)



Chemical Formula: $C_{19}H_{25}NO_4$
Exact Mass: 331.1784

6da was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-(*tert*-butyl)-*N*-methacryloylbenzamide (0.1 mmol, 32.3 mg) and methyl acrylate (0.3 mmol, 25.8 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~2/1) to obtain **6da** (24.2 mg, 73% yield).

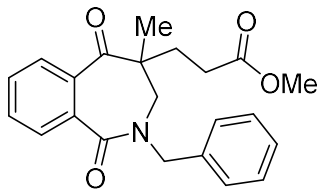
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.53 – 7.47 (m, 1H), 7.37 (dd, *J* = 7.6, 1.5 Hz, 1H), 3.70 – 3.60 (m, 4H), 3.47 (d, *J* = 15.7 Hz, 1H), 2.43 – 2.22 (m, 2H), 1.75 – 1.64 (m, 2H), 1.54 (s, 9H), 1.33 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.1, 173.2, 169.8, 135.8, 135.2, 131.8, 130.8, 129.6, 126.7,

58.3, 54.1, 51.8, 51.3, 31.8, 28.9, 28.5, 18.8;

HRMS: (ESI) calcd for $C_{19}H_{26}NO_4^+[M+H]^+$ 332.1856; found 332.1857.

methyl 3-(2-benzyl-4-methyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)propanoate (6ea)



Chemical Formula: $C_{22}H_{23}NO_4$
Exact Mass: 365.1627

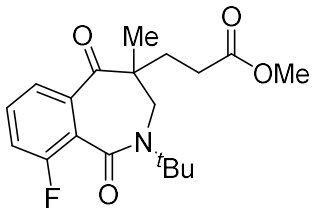
6ea was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), *N*-benzyl-2-bromo-*N*-methacryloylbenzamide (0.1 mmol, 35.7 mg) and methyl acrylate (0.3 mmol, 25.8 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~2/1) to obtain **6ea** (17.5 mg, 48% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.68 – 7.61 (m, 1H), 7.61 – 7.54 (m, 1H), 7.45 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.39 – 7.27 (m, 5H), 5.35 – 4.39 (m, 2H), 3.65 (s, 3H), 3.38 (dd, *J* = 169.1, 15.2 Hz, 2H), 2.43 – 2.25 (m, 2H), 2.00 – 1.72 (m, 2H), 1.28 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.5, 173.3, 169.3, 136.8, 136.7, 132.6, 132.3, 131.9, 130.1, 129.0, 128.2, 127.9, 54.5, 53.7, 52.03, 51.97, 31.3, 28.7, 19.7;

HRMS: (ESI) calcd for $C_{22}H_{23}NO_4^+[M+H]^+$ 366.1700; found 366.1714.

methyl 3-(2-(*tert*-butyl)-9-fluoro-4-methyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)propanoate (6fa)



Chemical Formula: $C_{19}H_{24}FNO_4$
Exact Mass: 349.1689

6fa was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-(*tert*-butyl)-6-fluoro-*N*-methacryloylbenzamide (0.1 mmol, 34.1 mg) and methyl acrylate (0.3 mmol, 25.8 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~2/1) to obtain **6fa** (17.8 mg, 51% yield).

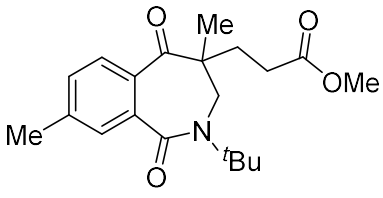
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (ddd, *J* = 8.4, 7.6, 4.9 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.13 (dd, *J* = 7.6, 1.2 Hz, 1H), 3.68 (d, *J* = 11.9 Hz, 1H), 3.65 (s, 3H), 3.47 (d, *J* = 15.9 Hz, 1H), 2.34 – 2.26 (m, 2H), 1.69 – 1.59 (m, 2H), 1.55 (s, 9H), 1.31 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 205.8 (d, *J* = 2.8 Hz), 173.3, 164.9 (d, *J* = 2.1 Hz), 159.9 (d, *J* = 257.2 Hz), 136.8, 131.9 (d, *J* = 9.0 Hz), 124.3 (d, *J* = 13.0 Hz), 122.2 (d, *J* = 3.7 Hz), 120.0 (d, *J* = 22.7 Hz), 58.7, 54.7, 52.0, 51.6, 29.2, 29.1, 28.6, 18.7;

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.10 – -113.17 (m);

HRMS: (ESI) calcd for $C_{19}H_{25}FNO_4^+[M+H]^+$ 350.1762; found 350.1761.

methyl 3-(2-(*tert*-butyl)-4,8-dimethyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)propanoate (6ga)



Chemical Formula: $C_{20}H_{27}NO_4$
Exact Mass: 345.1940

6ga was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol,

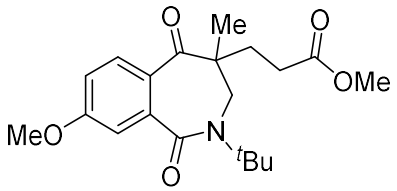
16.5 mg), 2-bromo-*N*-(*tert*-butyl)-*N*-methacryloyl-5-methylbenzamide (0.1 mmol, 33.7 mg) and methyl acrylate (0.3 mmol, 25.8 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~2/1) to obtain **6ga** (24.2 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 1H), 7.32 – 7.27 (m, 2H), 3.64 (s, 3H), 3.64 (d, *J* = 15.8 Hz, 1H), 3.45 (d, *J* = 15.7 Hz, 1H), 2.41 (s, 3H), 2.35 – 2.26 (m, 2H), 1.73 – 1.65 (m, 2H), 1.53 (s, 9H), 1.31 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.2, 173.5, 170.1, 142.8, 135.9, 132.8, 131.8, 130.2, 127.2, 58.5, 54.0, 52.0, 51.4, 32.3, 29.1, 28.7, 21.5, 19.2;

HRMS: (ESI) calcd for $C_{20}H_{28}NO_4^+$[M+H]$^+$ 346.2013; found 346.2006.

methyl 3-(2-(*tert*-butyl)-8-methoxy-4-methyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)propanoate (6ha)



Chemical Formula: $C_{20}H_{27}NO_5$
Exact Mass: 361.1889

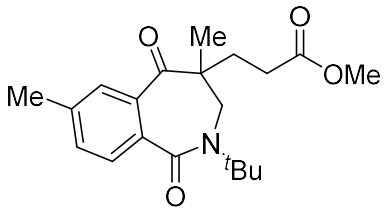
6ha was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-(*tert*-butyl)-*N*-methacryloyl-5-methoxybenzamide (0.1 mmol, 35.3 mg) and methyl acrylate (0.3 mmol, 25.8 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~2/1) to obtain **6ha** (18.1 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.5 Hz, 1H), 7.31 (d, *J* = 2.6 Hz, 1H), 7.00 (dd, *J* = 8.5, 2.6 Hz, 1H), 3.88 (s, 3H), 3.70 – 3.62 (d, *J* = 16.5 Hz, 1H), 3.64 (s, 3H), 3.46 (d, *J* = 15.7 Hz, 1H), 2.38 – 2.24 (m, 2H), 1.76 – 1.71 (m, 2H), 1.54 (s, 9H), 1.31 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 206.3, 173.5, 169.6, 162.7, 138.1, 129.5, 128.3, 117.9, 113.7, 58.6, 55.8, 53.7, 51.9, 51.2, 32.7, 29.0, 28.7, 19.5;

HRMS: (ESI) calcd for $C_{20}H_{28}NO_5^+[M+H]^+$ 362.1958; found 362.1962.

methyl 3-(2-(*tert*-butyl)-4,7-dimethyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)propanoate (6ia)



Chemical Formula: $C_{20}H_{27}NO_4$
Exact Mass: 345.1940

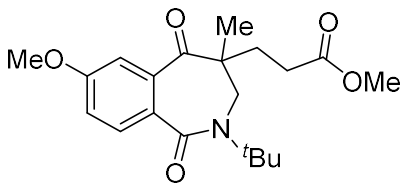
6ia was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-(*tert*-butyl)-*N*-methacryloyl-4-methylbenzamide (0.1 mmol, 33.7 mg) and methyl acrylate (0.3 mmol, 25.8 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~2/1) to obtain **6ia** (21.7 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.38 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.16 (s, 1H), 3.67 (s, 3H), 3.63 (d, *J* = 6.7 Hz, 1H), 3.46 (d, *J* = 15.7 Hz, 1H), 2.40 (s, 3H), 2.36 – 2.28 (m, 2H), 1.77 – 1.65 (m, 2H), 1.54 (s, 9H), 1.32 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.4, 173.3, 170.0, 141.4, 135.3, 133.2, 132.7, 129.8, 127.0, 58.3, 54.1, 51.8, 51.3, 32.0, 29.0, 28.6, 21.2, 18.9;

HRMS: (ESI) calcd for $C_{20}H_{28}NO_4^+[M+H]^+$ 346.2013; found 346.2024.

methyl 3-(2-(*tert*-butyl)-7-methoxy-4-methyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)propanoate (6ja)



Chemical Formula: $C_{20}H_{27}NO_5$
Exact Mass: 361.1889

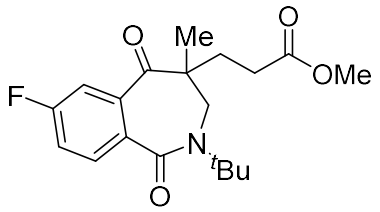
6ja was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-(*tert*-butyl)-*N*-methacryloyl-4-methoxybenzamide (0.1 mmol, 35.3 mg) and methyl acrylate (0.3 mmol, 25.8 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~2/1) to obtain **6ja** (17.7 mg, 49% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.7 Hz, 1H), 7.08 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.83 (d, *J* = 2.7 Hz, 1H), 3.85 (s, 3H), 3.67 – 3.63 (m, 4H), 3.46 (d, *J* = 15.7 Hz, 1H), 2.35 – 2.29 (m, 2H), 1.74 – 1.68 (m, 2H), 1.52 (s, 9H), 1.31 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.2, 173.4, 170.0, 161.5, 137.0, 132.1, 128.6, 118.2, 111.0, 58.4, 55.7, 54.2, 52.0, 51.4, 32.1, 29.1, 28.7, 19.1;

HRMS: (ESI) calcd for $C_{20}H_{28}NO_5^+[M+H]^+$ 362.1962; found 362.1953.

methyl 3-(2-(*tert*-butyl)-7-fluoro-4-methyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)propanoate (6ka)



Chemical Formula: $C_{19}H_{24}FNO_4$
Exact Mass: 349.1689

6ka was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-(*tert*-butyl)-4-fluoro-*N*-methacryloylbenzamide (0.2 mmol, 34.1 mg) and methyl acrylate (0.3 mmol, 25.8 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~2/1) to obtain **6ka** (20.9 mg, 60% yield).

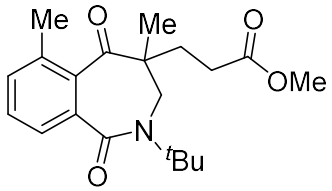
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.7, 5.3 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.07 (dd, *J* = 8.3, 2.7 Hz, 1H), 3.66 (s, 3H), 3.63 (d, *J* = 8.4 Hz, 1H), 3.48 (d, *J* = 15.7 Hz, 1H), 2.37 – 2.27 (m, 2H), 1.77 – 1.65 (m, 2H), 1.53 (s, 9H), 1.32 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 205.8, 173.1, 168.9, 163.8 (d, *J* = 253.5 Hz), 137.3 (d, *J* = 6.6 Hz), 132.8 (d, *J* = 8.2 Hz), 132.1 (d, *J* = 3.6 Hz), 119.1 (d, *J* = 21.5 Hz), 113.6 (d, *J* = 23.3 Hz), 58.6, 54.1, 51.9, 51.4, 31.8, 28.9, 28.5, 18.9;

^{19}F NMR (376 MHz, $CDCl_3$) δ -107.98 – -108.09 (m).

HRMS: (ESI) calcd for $C_{19}H_{25}FNO_4^+$[M+H]$^+$ 350.1762; found 350.1762.

methyl 3-(2-(*tert*-butyl)-4,6-dimethyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)propanoate (6la)



Chemical Formula: $C_{20}H_{27}NO_4$
Exact Mass: 345.1940

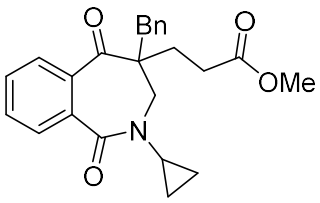
6la was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-(*tert*-butyl)-*N*-methacryloyl-3-methylbenzamide (0.1 mmol, 33.7 mg) and methyl acrylate (0.3 mmol, 25.8 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~2/1) to obtain **6la** (16.9 mg, 49% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 3.65 (s, 3H), 3.53 (d, *J* = 15.6 Hz, 1H), 3.40 (d, *J* = 15.5 Hz, 1H), 2.36 (t, *J* = 8.3 Hz, 2H), 2.26 (s, 3H), 1.70 – 1.56 (m, 2H), 1.50 (s, 9H), 1.25 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.1, 173.4, 170.4, 136.5, 134.8, 134.4, 133.0, 130.4, 126.9, 58.3, 55.8, 52.0, 51.5, 29.7, 29.0, 28.8, 19.4, 17.5;

HRMS: (ESI) calcd for $C_{20}H_{28}NO_4^+$[M+H]$^+$ 346.2013; found 346.2014.

methyl 3-(4-benzyl-2-cyclopropyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)propanoate (6ma)



Chemical Formula: $C_{24}H_{25}NO_4$
Exact Mass: 391.1784

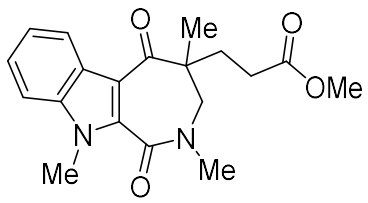
6ma was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-cyclopropyl-*N*-methacryloylbenzamide (0.1 mmol, 38.3 mg) and methyl acrylate (0.3 mmol, 25.8 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~2/1) to obtain **6ma** (17.6 mg, 45% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.53 – 7.46 (m, 1H), 7.43 – 7.37 (m, 1H), 7.34 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.22 – 7.12 (m, 3H), 7.09 – 7.02 (m, 2H), 3.79 (d, *J* = 15.4 Hz, 1H), 3.68 (s, 3H), 3.35 (d, *J* = 15.4 Hz, 1H), 3.15 (d, *J* = 13.5 Hz, 1H), 2.97 – 2.85 (m, 1H), 2.77 (d, *J* = 13.5 Hz, 1H), 2.65 – 2.58 (m, 2H), 2.36 – 1.99 (m, 2H), 1.16 – 0.86 (m, 2H), 0.85 – 0.63 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 206.7, 173.4, 169.6, 136.3, 135.3, 133.7, 132.4, 131.1, 130.4, 129.3, 128.5, 128.2, 127.1, 58.0, 53.0, 52.0, 42.2, 32.4, 29.9, 29.2, 10.3, 7.5;

HRMS: (ESI) calcd for $C_{24}H_{26}NO_4^+$[M+H]$^+$ 392.1856; found 392.1857.

methyl 3-(2,4,10-trimethyl-1,5-dioxo-1,2,3,4,5,10-hexahydroazepino[3,4-*b*]indol-4-yl)propanoate (6na)



Chemical Formula: $C_{19}H_{22}N_2O_4$
Exact Mass: 342.1580

6na was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol,

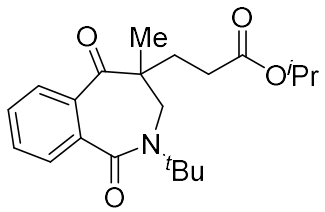
16.5 mg), 5-bromo-*N*-methacryloyl-*N*,1-dimethyl-1*H*-indole-6-carboxamide (0.1 mmol, 33.4 mg) and methyl acrylate (0.3 mmol, 25.8 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~1/1) to obtain **6na** (13.7 mg, 40% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.1 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.35 – 7.31 (m, 1H), 4.06 (s, 3H), 3.63 (s, 3H), 3.30 (s, 3H), 2.37 (t, *J* = 8.0 Hz, 2H), 2.24 – 1.88 (m, 2H), 1.27 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 199.7, 173.7, 161.7, 138.5, 133.5, 125.7, 125.5, 123.7, 123.6, 115.8, 110.3, 57.0, 51.9, 51.8, 37.8, 32.8, 29.8, 29.2, 21.6;

HRMS: (ESI) calcd for $C_{19}H_{23}N_2O_4^+$[M+H]$^+$ 343.1652; found 343.1652.

isopropyl 3-(2-(*tert*-butyl)-4-methyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)propanoate (6db)



Chemical Formula: $C_{21}H_{29}NO_4$
Exact Mass: 359.2097

6db was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-(*tert*-butyl)-*N*-methacryloylbenzamide (0.1 mmol, 32.3 mg) and isopropyl acrylate (0.2 mmol, 22.8 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~2/1) to obtain **6db** (21.2 mg, 59% yield).

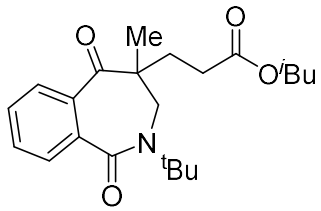
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.54 – 7.47 (m, 1H), 7.38 (dd, *J* = 7.5, 1.5 Hz, 1H), 5.07 – 4.87 (m, 1H), 3.65 (d, *J* = 15.7 Hz, 1H), 3.47 (d, *J* = 15.7 Hz, 1H), 2.31 – 2.23 (m, 2H), 1.76 – 1.68 (m, 2H), 1.54 (s, 9H), 1.32 (s, 3H), 1.21 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.3, 172.4, 169.9, 135.8, 135.3, 131.9, 131.0, 129.6, 126.8,

68.1, 58.4, 54.2, 51.3, 31.9, 29.2, 29.0, 21.8, 18.9;

HRMS: (ESI) calcd for $C_{21}H_{30}NO_4^+$[M+H]$^+$ 360.2169; found 360.2168.

isobutyl 3-(2-(*tert*-butyl)-4-methyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)propanoate (6dc)



Chemical Formula: $C_{22}H_{31}NO_4$
Exact Mass: 373.2253

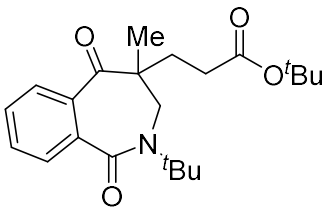
6dc was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-(*tert*-butyl)-*N*-methacryloylbenzamide (0.1 mmol, 32.3 mg) and butyl acrylate (0.3 mmol, 38.4 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~2/1) to obtain **6dc** (27.7 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.61 – 7.53 (m, 1H), 7.53 – 7.45 (m, 1H), 7.36 (dd, *J* = 7.6, 1.4 Hz, 1H), 3.82 (d, *J* = 6.7 Hz, 2H), 3.64 (d, *J* = 15.8 Hz, 1H), 3.47 (d, *J* = 15.7 Hz, 1H), 2.41 – 2.23 (m, 2H), 1.97 – 1.82 (m, 1H), 1.78 – 1.63 (m, *J* = 6.8 Hz, 1H), 1.53 (s, 9H), 1.32 (s, 3H), 0.95 – 0.91 (m, 1H), 0.91 (s, 3H), 0.89 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.4, 173.0, 170.0, 135.9, 135.4, 132.0, 131.0, 129.7, 126.8, 71.0, 58.5, 54.3, 51.5, 32.0, 29.0, 28.9, 27.7, 19.2, 19.0;

HRMS: (ESI) calcd for $C_{22}H_{32}NO_4^+$[M+H]$^+$ 374.2326; found 374.2334.

***tert*-butyl 3-(2-(*tert*-butyl)-4-methyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)propanoate (6dd)**



Chemical Formula: $C_{22}H_{31}NO_4$
Exact Mass: 373.2253

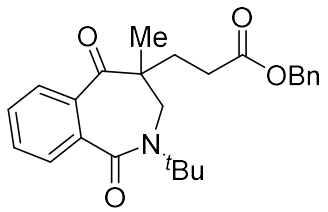
6dd was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-(*tert*-butyl)-*N*-methacryloylbenzamide (0.1 mmol, 32.3 mg) and *tert*-butyl acrylate (0.3 mmol, 38.4 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~2/1) to obtain **6dd** (27.6 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.61 – 7.53 (m, 1H), 7.53 – 7.45 (m, 1H), 7.36 (dd, *J* = 7.5, 1.4 Hz, 1H), 3.63 (d, *J* = 15.7 Hz, 1H), 3.46 (d, *J* = 15.8 Hz, 1H), 2.29 – 2.11 (m, 2H), 1.70 – 1.62 (m, 2H), 1.53 (s, 9H), 1.40 (s, 9H), 1.31 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.4, 172.2, 170.0, 135.9, 135.5, 131.9, 131.0, 129.7, 126.9, 80.9, 58.5, 54.3, 51.4, 32.1, 30.1, 29.1, 28.1, 19.0;

HRMS: (ESI) calcd for $C_{22}H_{32}NO_4^+[M+H]^+$ 374.2326; found 374.2324.

benzyl 3-(2-(*tert*-butyl)-4-methyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)propanoate (6de)



Chemical Formula: $C_{25}H_{29}NO_4$
Exact Mass: 407.2097

6de was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-(*tert*-butyl)-*N*-methacryloylbenzamide (0.1 mmol, 32.3 mg) and benzyl acrylate (0.3 mmol, 48.6 mg) and anhydrous DMSO (2 mL). The residue was purified by silica

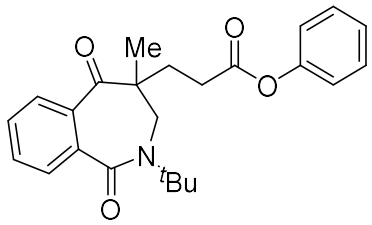
gel column chromatography (petroleum ether/ethyl acetate = 10/1~2/1) to obtain **6de** (20.4 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.52 – 7.45 (m, 1H), 7.40 – 7.30 (m, 6H), 5.09 (s, 2H), 3.63 (d, *J* = 15.7 Hz, 1H), 3.46 (d, *J* = 15.7 Hz, 1H), 2.46 – 2.29 (m, 2H), 1.82 – 1.65 (m, 2H), 1.53 (s, 9H), 1.32 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.3, 172.8, 170.0, 135.9, 135.7, 135.3, 132.0, 131.1, 129.7, 128.7, 128.5, 128.4, 126.9, 66.7, 58.5, 54.2, 51.4, 32.0, 29.0, 28.9, 19.0;

HRMS: (ESI) calcd for $C_{25}H_{30}NO_4^+$[M+H]$^+$ 408.2169; found 408.2179.

phenyl 3-(2-(*tert*-butyl)-4-methyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)propanoate (6df)



Chemical Formula: $C_{24}H_{27}NO_4$
Exact Mass: 393.1940

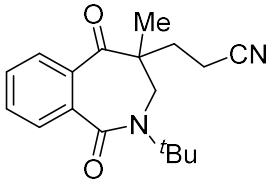
6df was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-(*tert*-butyl)-*N*-methacryloylbenzamide (0.1 mmol, 32.3 mg) and phenyl acrylate (0.3 mmol, 42.9 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~2/1) to obtain **6df** (12.2 mg, 31% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.65 – 7.47 (m, 2H), 7.45 – 7.32 (m, 3H), 7.25 – 7.20 (m, 1H), 7.08 – 7.03 (m, 2H), 3.84 – 3.45 (m, 2H), 2.68 – 2.50 (m, 2H), 1.98 – 1.69 (m, 2H), 1.56 (s, 9H), 1.39 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.6, 171.8, 170.2, 150.8, 136.2, 135.5, 132.4, 131.4, 130.1, 129.8, 127.2, 126.3, 121.8, 58.8, 54.5, 51.8, 32.1, 29.3, 19.4;

HRMS: (ESI) calcd for $C_{24}H_{27}NO_4^+$[M+H]$^+$ 394.2013; found 394.2013.

3-(2-(*tert*-butyl)-4-methyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)propanenitrile (6dg)



Chemical Formula: $C_{18}H_{22}N_2O_2$
Exact Mass: 298.1681

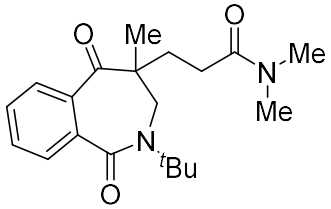
6dg was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-(*tert*-butyl)-*N*-methacryloylbenzamide (0.1 mmol, 32.3 mg) and acrylonitrile (0.3 mmol, 16.1 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~2/1) to obtain **6dg** (17.0 mg, 57% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.66 – 7.59 (m, 1H), 7.57 – 7.51 (m, 1H), 7.40 (dd, *J* = 7.6, 1.4 Hz, 1H), 3.65 (d, *J* = 15.7 Hz, 1H), 3.52 (d, *J* = 15.8 Hz, 1H), 2.49 – 2.35 (m, 2H), 1.88 – 1.66 (m, 2H), 1.55 (s, 9H), 1.35 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 206.7, 169.9, 136.1, 134.7, 132.7, 131.4, 130.2, 127.0, 119.4, 58.8, 54.1, 51.4, 32.6, 29.2, 19.1, 12.6;

HRMS: (ESI) calcd for $C_{18}H_{23}N_2O_2^+[M+H]^+$ 299.1754; found 299.1749.

3-(2-(*tert*-butyl)-4-methyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)-*N*,*N*-dimethylpropanamide (6dh)



Chemical Formula: $C_{20}H_{28}N_2O_3$
Exact Mass: 344.2100

6dh was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol,

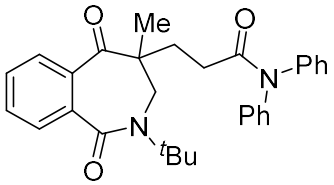
16.5 mg), 2-bromo-*N*-(*tert*-butyl)-*N*-methacryloylbenzamide (0.1 mmol, 32.3 mg) and *N*,*N*-dimethylacrylamide (0.3 mmol, 29.7 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~1/1) to obtain **6dh** (17.9 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.60 – 7.53 (m, 1H), 7.51 – 7.44 (m, 1H), 7.34 (dd, *J* = 7.6, 1.4 Hz, 1H), 3.67 (d, *J* = 15.8 Hz, 1H), 3.49 (d, *J* = 15.8 Hz, 1H), 2.99 (s, 3H), 2.92 (s, 3H), 2.41 – 2.17 (m, 2H), 1.71 (t, *J* = 8.1 Hz, 2H), 1.54 (s, 9H), 1.34 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.9, 171.9, 170.0, 136.0, 135.5, 132.0, 131.0, 129.7, 126.7, 58.5, 54.5, 52.0, 37.3, 35.7, 32.3, 29.1, 27.6, 19.0;

HRMS: (ESI) calcd for $C_{20}H_{29}N_2O_3^+$[M+H]$^+$ 345.2173; found 345.2174.

3-(2-(*tert*-butyl)-4-methyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)-*N*,*N*-diphenylpropanamide (6di)



Chemical Formula: $C_{30}H_{32}N_2O_3$
Exact Mass: 468.2413

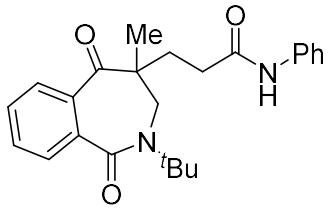
6di was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-(*tert*-butyl)-*N*-methacryloylbenzamide (0.1 mmol, 32.3 mg) and *N*,*N*-diphenylacrylamide (0.3 mmol, 72.9 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~1/1) to obtain **6di** (30.0 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.58 – 7.50 (m, 1H), 7.46 – 7.33 (m, 6H), 7.24 (d, *J* = 7.7 Hz, 5H), 7.11 (dd, *J* = 7.6, 1.4 Hz, 1H), 3.61 (d, *J* = 15.7 Hz, 1H), 3.41 (d, *J* = 15.7 Hz, 1H), 2.23 (t, *J* = 7.8 Hz, 2H), 1.88 – 1.67 (m, 2H), 1.51 (s, 9H), 1.23 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.6, 172.0, 169.9, 142.6, 135.8, 135.5, 131.8, 130.9, 129.6, 126.8, 58.4, 54.3, 51.4, 33.1, 29.8, 29.0, 19.3;

HRMS: (ESI) calcd for $C_{30}H_{33}N_2O_3^+$[M+H]$^+$ 469.2486; found 469.2478.

3-(2-(*tert*-butyl)-4-methyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)-*N*-phenylpropanamide (6dj)



Chemical Formula: $C_{24}H_{28}N_2O_3$
Exact Mass: 392.2100

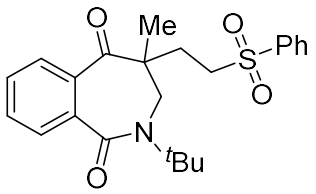
6dj was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-(*tert*-butyl)-*N*-methacryloylbenzamide (0.1 mmol, 32.3 mg) and *N*-phenylacrylamide (0.3 mmol, 41.1 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~1/1) to obtain **6dj** (30.2 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.80 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.60 – 7.52 (m, 1H), 7.49 – 7.41 (m, 3H), 7.34 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 3.65 (d, *J* = 15.7 Hz, 1H), 3.49 (d, *J* = 15.8 Hz, 1H), 2.47 – 2.25 (m, 2H), 1.85 – 1.72 (m, 2H), 1.54 (s, 9H), 1.33 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.0, 169.4, 169.0, 137.0, 134.9, 134.3, 131.1, 130.1, 128.7, 128.1, 125.7, 123.4, 118.9, 57.6, 53.6, 50.8, 31.1, 30.8, 28.0, 17.9;

HRMS: (ESI) calcd for $C_{24}H_{29}N_2O_3^+$[M+H]$^+$ 393.2173; found 393.2174.

2-(*tert*-butyl)-4-methyl-4-(2-(phenylsulfonyl)ethyl)-3,4-dihydro-1*H*-benzo[*c*]azepine-1,5(2*H*)-dione (6dk)



Chemical Formula: $C_{23}H_{27}NO_4S$
Exact Mass: 413.1661

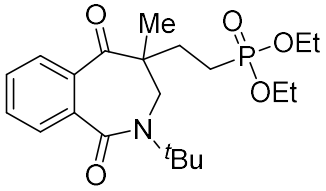
6dk was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-(*tert*-butyl)-*N*-methacryloylbenzamide (0.1 mmol, 32.3 mg) and (vinylsulfonyl)benzene (0.3 mmol, 50.4 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~1/1) to obtain **6dk** (25.2 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 2H), 7.79 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.72 – 7.65 (m, 1H), 7.61 – 7.53 (m, 3H), 7.47 – 7.40 (m, 1H), 7.12 (dd, *J* = 7.6, 1.3 Hz, 1H), 3.59 (d, *J* = 15.8 Hz, 1H), 3.47 (d, *J* = 15.8 Hz, 1H), 3.17 – 3.10 (m, 2H), 1.83 – 1.72 (m, 2H), 1.50 (s, 9H), 1.25 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 206.7, 169.9, 138.8, 135.9, 134.6, 134.1, 132.4, 131.2, 129.9, 129.6, 128.2, 126.7, 58.7, 53.7, 51.7, 51.6, 29.1, 29.0, 18.9;

HRMS: (ESI) calcd for $C_{23}H_{28}NO_4S^+[M+H]^+$ 414.1735; found 414.1731.

diethyl (2-(2-(*tert*-butyl)-4-methyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)ethyl)phosphonate (6dl)



Chemical Formula: $C_{21}H_{32}NO_5P$
Exact Mass: 409.2018

6dl was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-(*tert*-butyl)-*N*-methacryloylbenzamide (0.1 mmol, 32.3 mg) and diethyl

vinylphosphonate (0.3 mmol, 49.2 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1~2/1) to obtain **6dl** (20.5 mg, 50% yield).

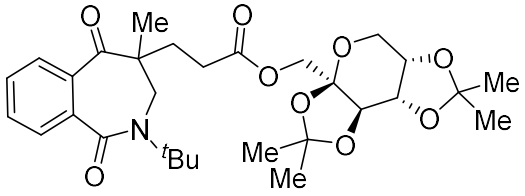
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 4.08 – 4.02 (m, 4H), 3.62 (d, *J* = 15.8 Hz, 1H), 3.46 (d, *J* = 15.8 Hz, 1H), 1.70 – 1.65 (m, 2H), 1.53 (s, 9H), 1.46 – 1.39 (m, 2H), 1.31 (s, 3H), 1.29 (t, *J* = 6.6 Hz, 3H), 1.26 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.1, 169.9, 135.9, 135.3, 132.1, 131.1, 129.8, 126.7, 58.6, 51.3, 29.0, 20.9, 19.9, 18.8;

^{31}P NMR (243 MHz, $CDCl_3$) δ 30.95;

HRMS: (ESI) calcd for $C_{21}H_{33}NO_5P^+[M+H]^+$ 410.2091; found 410.2088.

(2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl 3-(2-(*tert*-butyl)-4-methyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)propanoate (6dm)



Chemical Formula: $C_{30}H_{41}NO_9$
Exact Mass: 559.2781

6dm was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-(*tert*-butyl)-*N*-methacryloylbenzamide (0.1 mmol, 32.3 mg) and ((3a*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-b:4',5'-*d*]pyran-3a-yl)methyl acrylate (0.3 mmol, 94.2 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~2/1) to obtain **6dm** (31.3 mg, 56% yield, dr = 1:1).

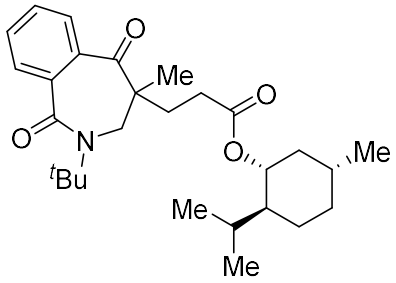
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.33 (dd, *J* = 12.7, 6.9 Hz, 1H), 4.62 – 4.53 (m, 1H), 4.36 (dd, *J* = 16.1, 11.7 Hz, 1H),

4.25 (t, *J* = 2.6 Hz, 1H), 4.22 (dd, *J* = 7.9, 1.8 Hz, 1H), 4.00 (dd, *J* = 15.6, 11.7 Hz, 1H), 3.90 – 3.84 (m, 1H), 3.74 (d, *J* = 13.0 Hz, 1H), 3.63 (dd, *J* = 15.8, 5.7 Hz, 1H), 3.45 (dd, *J* = 15.8, 3.7 Hz, 1H), 2.44 – 2.28 (m, 2H), 1.77 – 1.63 (m, 2H), 1.52 (s, 9H), 1.51 (s, 3H), 1.45 (s, 3H), 1.37 (d, *J* = 16.2 Hz, 3H), 1.32 (s, 3H), 1.31 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.3, 207.2, 172.3, 169.93, 169.91, 135.92, 135.90, 135.3, 132.0, 131.03, 131.01, 129.7, 126.9, 126.7, 109.2, 108.9, 108.8, 101.4, 77.4, 77.2, 76.9, 70.77, 70.75, 70.64, 70.58, 70.0, 65.74, 65.65, 61.3, 58.5, 54.2, 54.1, 51.5, 31.9, 29.0, 28.71, 28.66, 26.55, 26.53, 25.9, 25.31, 25.29, 24.1, 19.0, 18.9;

HRMS: (ESI) calcd for $C_{30}H_{42}NO_9^+[M+H]^+$ 560.2854; found 560.2852.

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 3-(2-(*tert*-butyl)-4-methyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)propanoate (6dn)



Chemical Formula: $C_{28}H_{41}NO_4$
Exact Mass: 455.3036

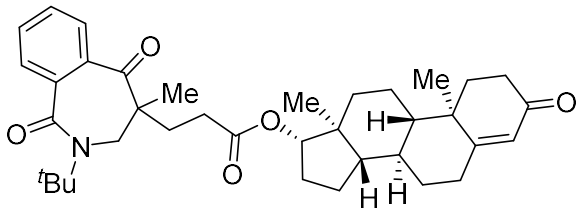
6dn was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-(*tert*-butyl)-*N*-methacryloylbenzamide (0.1 mmol, 32.3 mg) and (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl acrylate (0.3 mmol, 63.0 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~2/1) to obtain **6dn** (24.1 mg, 53% yield, dr = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.52 – 7.47 (m, 1H), 7.37 (dt, *J* = 7.7, 1.0 Hz, 1H), 4.68 – 4.56 (m, 1H), 3.67 – 3.44 (m, 2H), 2.35 – 2.21 (m, 2H), 1.96 – 1.88 (m, 1H), 1.83 – 1.62 (m, 6H), 1.53 (s, 9H), 1.38 – 1.32 (m, 2H), 1.31 (s, 3H), 1.04 – 0.98 (m, 1H), 0.98 – 0.93 (m, 1H), 0.89 – 0.84 (m, 12H), 0.71 (dd, *J* = 6.9, 5.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.36, 207.28, 172.5, 172.4, 169.91, 169.88, 135.9, 135.4, 135.3, 131.89, 131.86, 130.9, 129.7, 129.6, 126.8, 74.6, 58.4, 54.3, 54.2, 51.3, 51.2, 47.0, 46.9, 40.9, 34.2, 31.4, 29.2, 29.1, 29.0, 28.8, 26.3, 26.2, 23.4, 22.0, 20.8, 19.1, 18.9, 16.30, 16.27.

HRMS: (ESI) calcd for $C_{28}H_{42}NO_4^+$ $[M+H]^+$ 456.3108; found 456.3109.

(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl 3-(2-(*tert*-butyl)-4-methyl-1,5-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepin-4-yl)propanoate (6do)



Chemical Formula: $C_{37}H_{49}NO_5$
Exact Mass: 587.3611

6do was prepared according to general procedure **2.4** using $Ni(acac)_2$ (10 mol%, 2.6 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 4.3 mg), $MnBr_2$ (0.2 mmol, 42.8 mg), Mn^0 (0.3 mmol, 16.5 mg), 2-bromo-*N*-(*tert*-butyl)-*N*-methacryloylbenzamide (0.1 mmol, 32.3 mg) and (8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl acrylate (0.3 mmol, 102.6 mg) and anhydrous DMSO (2 mL). The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~1/1) to obtain **6do** (26.5 mg, 45% yield, dr = 1:1).

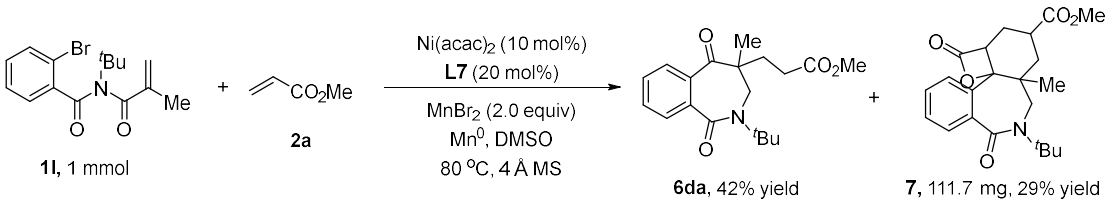
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.51 – 7.46 (m, 1H), 7.37 – 7.33 (m, 1H), 5.70 (d, *J* = 1.7 Hz, 1H), 4.55 (dd, *J* = 9.2, 7.7 Hz, 1H), 3.66 – 3.42 (m, 2H), 2.45 – 2.21 (m, 8H), 2.21 – 2.05 (m, 1H), 2.04 – 1.94 (m, 1H), 1.86 – 1.78 (m, 1H), 1.77 – 1.67 (m, 4H), 1.67 – 1.61 (m, 1H), 1.59 – 1.54 (m, 1H), 1.54 – 1.51 (m, 9H), 1.49 – 1.32 (m, 2H), 1.31 (s, 3H), 1.17 (s, 3H), 1.11 – 0.84 (m, 4H), 0.79 (d, *J* = 4.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.3, 199.5, 172.9, 170.9, 169.9, 135.8, 135.3, 131.9, 130.9, 129.7, 126.7, 124.0, 82.83, 82.80, 81.6, 58.4, 54.2, 53.7, 51.41, 51.37, 50.2, 42.5, 38.6, 36.6, 36.6, 35.7, 35.4, 33.9, 32.7, 31.5, 29.0, 27.5, 23.5, 20.5, 18.9, 17.4, 12.10, 12.08.

HRMS: (ESI) calcd for $C_{37}H_{50}NO_5^+$ $[M+H]^+$ 588.3684; found 588.3672.

7. Synthetic Transformation

Synthesis of methyl 2-(*tert*-butyl)-12a-methyl-3,9-dioxo-2,3,9,9a,10,11,12,12a-octahydro-1*H*-benzo[*c*]oxeto[2',3':1,6]benzo[1,2-e]azepine-11-carboxylate (7)



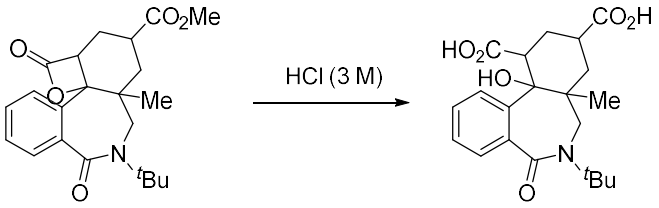
7 was prepared according to general procedure **2.4** using 2-bromo-*N*-(*tert*-butyl)-*N*-methacryloylbenzamide (1 mmol, 324 mg), methyl acrylate **2a** (4 mmol, 344 mg), $Ni(acac)_2$ (10 mol%, 26 mg), 4,4'-dimethoxy-2,2'-bipyridine **L7** (20 mol%, 43 mg), $MnBr_2$ (2 mmol, 428 mg), Mn^0 (3 mmol, 165 mg), 4 Å MS (150 mg) and anhydrous DMSO (2 mL). The sealed tube was sealed and removed from the glovebox. Then the reaction was stirred at 80 °C until the reaction was complete (monitored by TLC). The resulting mixture was quenched with saturated NH_4Cl solution (5 mL) and further diluted with water (10 mL). The aqueous layer was extracted with EtOAc and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by chromatography on silica gel, eluting with petroleum ether/EtOAc (10/1~1/1) to afford the compound **7** (111.7 mg, 29% yield) and **6da** (139 mg, 42% yield).

^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.45 (td, *J* = 7.6, 1.6 Hz, 1H), 7.39 (td, *J* = 7.5, 1.4 Hz, 1H), 3.93 (dd, *J* = 10.4, 5.9 Hz, 1H), 3.37 (d, *J* = 15.9 Hz, 1H), 3.15 (s, 3H), 3.00 (d, *J* = 16.0 Hz, 1H), 2.96 (dd, *J* = 5.5, 2.8 Hz, 1H), 2.41 – 2.30 (m, 1H), 2.21 – 2.05 (m, 2H), 1.80 (ddd, *J* = 12.8, 5.6, 2.7 Hz, 1H), 1.59 (s, 9H), 0.68 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.3, 171.7, 171.68, 135.4, 132.6, 130.3, 129.9, 128.2, 124.3, 86.0, 57.7, 51.7, 51.1, 46.3, 43.3, 36.5, 34.0, 29.4, 29.0, 23.4.

HRMS: (ESI) calcd for $C_{22}H_{28}NO_5^+[M+H]^+$ 386.1962; found 386.1972.

Synthesis of 6-(*tert*-butyl)-11b-hydroxy-4a-methyl-7-oxo-2,3,4,4a,5,6,7,11b-octahydro-1*H*-dibenzo[c,e]azepine-1,3-dicarboxylic acid (8)

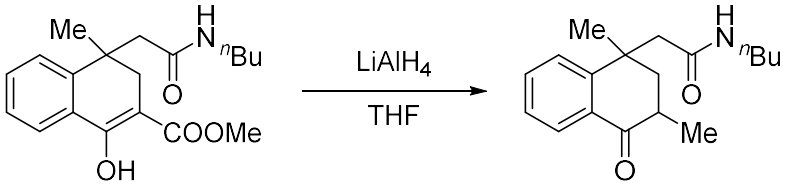


7 **8**, 99% yield

To a solution of **7** (0.1 mmol) in THF (2 mL) was added HCl (3 M, 2mL) in portions at 25 °C. Then stirred at 80 °C for 12 hours, the mixture was quenched with ice H_2O and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by flash column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (3/1~1/3) to afford **8** (37.9 mg, 99% yield). The structure of product **8** can be confirmed by X-ray crystallography and high-resolution mass spectra.

HRMS: (ESI) calcd for $C_{21}H_{28}NO_6^+[M+H]^+$ 390.1911; found 390.1920.

Synthesis of *N*-butyl-2-(1,3-dimethyl-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)acetamide (9)



3aa **9**, 73% yield

To a solution of **3aa** (0.1 mmol, 33.1 mg) in THF (4 mL) was added $LiAlH_4$ (0.5 mmol, 19.0 mg) at 0 °C, and the reaction mixture was stirred at room temperature for 16 hours, the mixture was quenched with ice H_2O and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by flash column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (5/1~1/1) to afford **9** (20.9 mg, 73% yield).

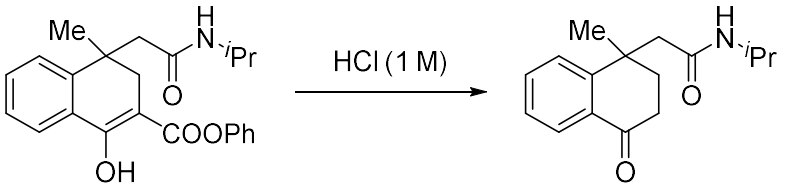
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (dd, J = 7.9, 1.5 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.40 (dd, J = 8.0, 1.3 Hz, 1H), 7.36 – 7.32 (m, 1H), 5.16 (s, 1H), 3.22 – 3.13 (m, 2H), 2.91 – 2.84 (m, 1H),

2.55 (d, J = 13.4 Hz, 1H), 2.38 – 2.33 (m, 2H), 1.83 (t, J = 13.8 Hz, 1H), 1.56 (s, 3H), 1.40 – 1.34 (m, 2H), 1.28 – 1.22 (m, 5H), 0.89 (t, J = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 200.6, 170.1, 150.1, 133.5, 131.4, 127.8, 127.0, 126.3, 48.1, 43.3, 39.3, 38.4, 36.9, 31.6, 27.8, 20.0, 15.7, 13.7.

HRMS: (ESI) calcd for $C_{18}H_{26}NO_2^+$ $[M+H]^+$ 288.1958; found 288.1957.

Synthesis of *N*-isopropyl-2-(1-methyl-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)acetamide (10)



3be **10**, 81% yield

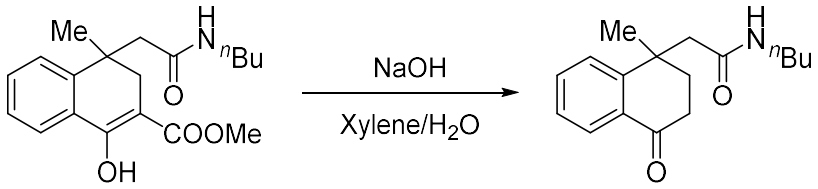
To a solution of **3be** (0.1 mmol, 38.1 mg) in MeOH (1 mL) was added HCl (2 mL, 1 M) at room temperature, and the reaction mixture was stirred at 25 °C for 12 hours. The resulting mixture was quenched with saturated NH_4Cl solution (5 mL) and further diluted with water (10 mL). The aqueous layer was extracted with EtOAc and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by chromatography on silica gel, eluting with petroleum ether/EtOAc (3/1~2/1) to afford **10** (21.0 mg, 81% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (dd, J = 7.8, 1.6 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.41 (dd, J = 8.0, 1.3 Hz, 1H), 7.36 – 7.33 (m, 1H), 4.92 (d, J = 7.8 Hz, 1H), 4.01 – 3.94 (m, 1H), 2.86 – 2.69 (m, 2H), 2.55 – 2.38 (m, 2H), 2.36 – 2.04 (m, 2H), 1.56 (s, 3H), 1.01 (d, J = 3.3 Hz, 3H), 1.00 (d, J = 3.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.0, 169.1, 150.0, 133.8, 131.6, 127.8, 126.9, 126.2, 48.3, 41.3, 36.7, 34.8, 34.3, 27.6, 22.65, 22.60.

HRMS: (ESI) calcd for $C_{16}H_{22}NO_2^+$ $[M+H]^+$ 260.1645; found 260.1643.

Synthesis of *N*-butyl-2-(1-methyl-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)acetamide (11)



3aa **11**, 87% yield

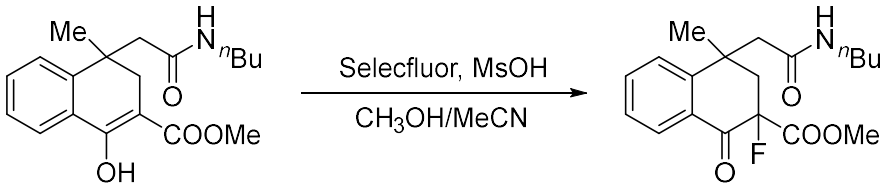
To a solution of **3aa** (0.1 mmol, 33.1 mg), NaOH (0.7 mmol, 28 mg) in Xylene (2 mL) was added H_2O (2 mL) at room temperature, and the reaction mixture was stirred at 90 °C for 8 hours, the mixture was quenched with ice H_2O and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by flash column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (5/1~1/1) to afford **11** (23.8 mg, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.40 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.35 – 7.30 (m, 1H), 5.28 (s, 1H), 3.17 – 3.10 (m, 2H), 2.85 – 2.65 (m, 2H), 2.59 – 2.40 (m, 2H), 2.38 – 2.30 (m, 1H), 2.09 – 2.02 (m, 1H), 1.55 (s, 3H), 1.37 – 1.28 (m, 2H), 1.26 – 1.15 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.0, 170.0, 150.1, 133.8, 130.5, 127.7, 126.9, 126.1, 48.0, 39.2, 36.7, 34.8, 34.2, 31.5, 27.6, 20.0, 13.7.

HRMS: (ESI) calcd for $C_{17}H_{24}NO_2^+$ $[M+H]^+$ 274.1802; found 274.1812.

Synthesis of methyl 4-(2-(butylamino)-2-oxoethyl)-2-fluoro-4-methyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (12)

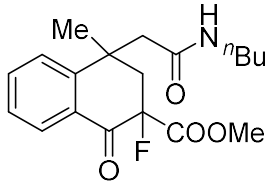


3aa **12**, 94% yield (dr = 2:1)

The synthesis of **12** followed the procedure reported previously.[2]

To a solution of **3aa** (0.1 mmol, 33.1 mg), Selecfluor (0.11 mmol, 38.9 mg) in CH_3OH (2 mL) MeCN (2 mL) was added methanesulfonic acid (0.02 mmol, 2.0 mg) at room temperature, and the reaction mixture was stirred at 60 °C for 12 hours. The mixture was concentrated and the

residue was purified by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (5/1~1/1) to afford **12** (32.8 mg, 94% yield, dr = 2:1).



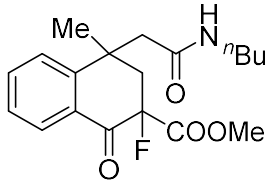
Chemical Formula: $C_{19}H_{24}FNO_4$
Exact Mass: 349.1689
dr = 2:1 (major)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.44 – 7.37 (m, 2H), 5.41 (s, 1H), 3.85 (s, 3H), 3.33 (dd, *J* = 39.1, 15.4 Hz, 1H), 3.23 – 3.05 (m, 2H), 2.72 – 2.55 (m, 2H), 2.49 (t, *J* = 15.2 Hz, 1H), 1.57 (d, *J* = 1.7 Hz, 3H), 1.38 – 1.30 (m, 2H), 1.27 – 1.17 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 188.0 (d, *J* = 19.6 Hz), 169.3, 168.5 (d, *J* = 27.1 Hz), 149.5, 135.0, 129.3, 129.1, 127.4, 125.9, 93.0 (d, *J* = 191.8 Hz), 53.2, 48.7, 40.7 (d, *J* = 20.4 Hz), 39.2, 36.1, 31.84, 31.8 (d, *J* = 4.3 Hz), 20.0, 13.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -155.73 (dd, *J* = 39.0, 14.8 Hz).

HRMS: (ESI) calcd for $C_{19}H_{25}FNO_4^+$ $[M+H]^+$ 350.1762; found 350.1765.



Chemical Formula: $C_{19}H_{24}FNO_4$
Exact Mass: 349.1689
dr = 2:1 (minor)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.69 – 7.64 (m, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.45 – 7.40 (m, 1H), 5.41 (s, 1H), 3.85 (s, 3H), 3.26 – 3.10 (m, 2H), 2.80 (t, *J* = 15.7 Hz, 1H), 2.75 – 2.56 (m, 1H), 2.56 – 2.40 (m, 2H), 1.69 (s, 3H), 1.44 – 1.36 (m, 2H), 1.33 – 1.22 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H).

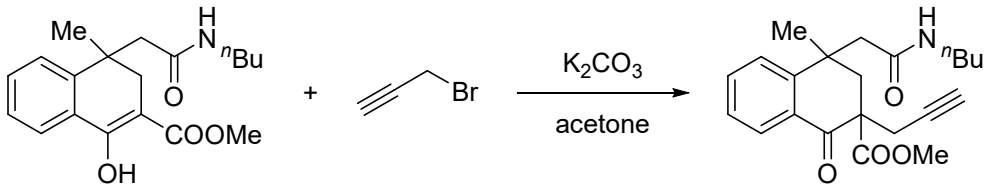
^{13}C NMR (151 MHz, $CDCl_3$) δ 187.8 (d, *J* = 19.7 Hz), 169.4, 168.1 (d, *J* = 26.3 Hz), 150.2, 135.4, 129.0, 128.7, 127.6, 126.6, 93.1 (d, *J* = 189.7 Hz), 53.3, 49.8 (d, *J* = 4.3 Hz), 41.2 (d, *J*

= 20.6 Hz), 39.2, 35.5, 31.6, 27.4, 20.0, 13.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -155.89 (dd, *J* = 42.0, 16.0 Hz).

HRMS: (ESI) calcd for $C_{19}H_{25}FNO_4^+$ $[M+H]^+$ 350.1762; found 350.1765.

Synthesis of methyl 4-(2-(butylamino)-2-oxoethyl)-4-methyl-1-oxo-2-(prop-2-yn-1-yl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (13)



3aa **13**, 86% yield

The synthesis of **13** followed the procedure reported previously.[3]

To a solution of **3aa** (0.1 mmol, 33.1 mg), K_2CO_3 (0.12 mmol, 16.6 mg) in acetone (4 mL) was added 3-bromoprop-1-yne (0.2 mmol, 23.6 mg) at room temperature, and the reaction mixture was stirred at 60 ºC for 5 hours. The mixture was concentrated and the residue was purified by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (5/1~1/1) to afford **13** (31.7 mg, 86% yield).

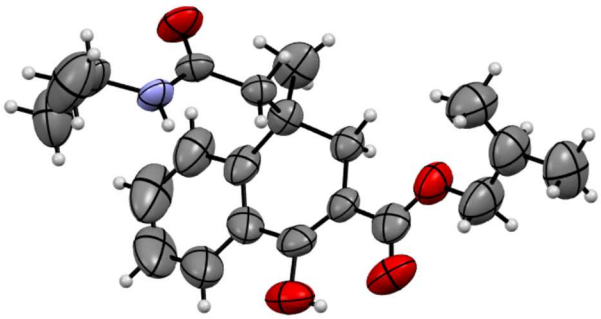
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.48 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.38 – 7.33 (m, 1H), 6.45 (s, 1H), 3.69 (s, 3H), 3.38 – 3.14 (m, 2H), 2.98 – 2.80 (m, 3H), 2.45 – 2.36 (m, 2H), 2.25 (dd, *J* = 15.1, 0.8 Hz, 1H), 2.04 (t, *J* = 2.7 Hz, 1H), 1.52 (d, *J* = 15.1 Hz, 5H), 1.43 – 1.33 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 193.3, 173.7, 169.5, 149.6, 134.5, 130.8, 128.1, 127.1, 79.1, 71.9, 54.9, 53.5, 48.0, 40.3, 39.3, 35.8, 31.6, 30.0, 27.0, 20.2, 13.8.

HRMS: (ESI) calcd for $C_{22}H_{28}NO_4^+$ $[M+H]^+$ 370.2013; found 370.2016.

8. X-Ray Crystallographic Data

8.1 X-Ray Crystallographic Analysis of Compound 3bb



CCDC: 2375726

Table S4: Crystal data and structure refinement for 3bb.

Empirical formula	$C_{21}H_{29}NO_4$
Formula weight	359.45
Temperature/K	300.2(4)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	29.1328(15)
b/Å	14.8670(8)
c/Å	9.7039(4)
α/°	90
β/°	97.610(4)
γ/°	90
Volume/Å^3	4165.9(4)
Z	8
ρ_{calc}g/cm^3	1.146
μ/mm^{-1}	0.633
F(000)	1552.0
Crystal size/mm^3	0.1 × 0.03 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.122 to 133.184
Index ranges	$-34 \leq h \leq 32$, $-17 \leq k \leq 16$, $-11 \leq l \leq 11$
Reflections collected	26253
Independent reflections	7326 [R_{int} = 0.0701, R_{sigma} = 0.0638]
Data/restraints/parameters	7326/36/501
Goodness-of-fit on F^2	1.113
Final R indexes [I>=2σ (I)]	R_1 = 0.1277, wR_2 = 0.3062
Final R indexes [all data]	R_1 = 0.1860, wR_2 = 0.3363
Largest diff. peak/hole / e Å^{-3}	0.36/-0.27

Table S5: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3bb. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O001	5362.5(14)	6742(3)	4690(4)	73.3(11)
O002	8558.3(16)	7447(3)	716(4)	86.2(14)
O003	4978.1(16)	6177(3)	2714(4)	82.4(13)
O004	3549.3(15)	7479(3)	8220(4)	84.7(14)
N005	8351.0(16)	7734(3)	2803(4)	65.0(13)
O006	4184.5(16)	5452(3)	2834(4)	83.9(13)
O007	10397.4(16)	6713(3)	5649(5)	91.4(14)
N008	3325.6(17)	7680(4)	5940(4)	72.8(14)
O009	9219.2(18)	5559(3)	6734(5)	96.6(15)
O00A	10024.9(19)	6216(3)	7371(5)	100.2(16)
C00B	3636.8(19)	7462(3)	6997(5)	53.8(13)
C00C	8653(2)	7466(4)	1988(5)	58.8(14)
C00D	4282.7(18)	6270(3)	7037(5)	51.1(12)
C00E	4727(2)	6122(4)	6401(6)	62.6(15)
C00F	5010(2)	6299(4)	3987(7)	65.1(15)
C00G	4108.1(18)	7226(3)	6652(5)	53.0(13)
C00H	3914.1(19)	5599(3)	6406(6)	56.5(13)
C00I	4663.4(19)	6017(4)	4837(6)	58.8(14)
C00J	10047(3)	6318(4)	6092(8)	78.6(18)
C00K	9682(2)	6053(4)	5042(6)	59.1(14)
C00L	4269(2)	5618(4)	4228(6)	65.6(16)
C00M	3906(2)	5338(4)	5006(6)	63.7(15)
C00N	9281(2)	6241(4)	2544(6)	62.4(15)
C00O	9124.1(18)	7217(3)	2704(5)	54.6(13)
C00P	9740.3(19)	6116(4)	3492(6)	63.2(15)
C00Q	8906(2)	5406(4)	4369(8)	78.6(19)
C00R	9299(2)	5699(4)	5388(7)	74.1(17)
C00S	3561(2)	5313(4)	7115(7)	78.2(18)
C00T	8913(2)	5627(4)	2959(7)	74.2(17)
C00U	4400(2)	6167(4)	8605(5)	70.3(16)

Table S5: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3bb. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C00V	5715(2)	7060(5)	3881(7)	83.9(19)
C00W	9381(3)	6072(5)	1026(6)	93(2)
C00X	7880(2)	8032(6)	2292(6)	87(2)
C00Y	3536(3)	4802(5)	4402(8)	87(2)
C00Z	6015(2)	7718(5)	4736(7)	82.2(19)
C010	2853(2)	7929(5)	6077(7)	96(2)
C011	8541(3)	5318(5)	2012(9)	103(3)
C012	5752(3)	8542(5)	5060(8)	105(2)
C013	3208(3)	4790(5)	6499(10)	101(2)
C014	11028(3)	7717(6)	6250(9)	109(3)
C015	3193(3)	4532(5)	5131(10)	105(3)
C016	8541(3)	4940(6)	4773(11)	114(3)
C017	6424(3)	7963(6)	3973(9)	115(3)
C018	8181(4)	4656(7)	3806(17)	148(4)
C019	11453(3)	7926(7)	7304(9)	129(3)
C01A	10767(3)	7017(6)	6714(9)	119(3)
C01B	10785(3)	8546(6)	5684(9)	123(3)
C01C	8183(3)	4854(6)	2403(15)	143(4)
C01D	7749(3)	8821(7)	3143(10)	148(4)
C01E	7545(3)	7272(7)	2356(11)	137(3)
C1	2511(5)	7654(12)	4809(13)	83(4)
C2	2804(6)	8906(8)	6460(20)	118(6)
C1A	2528(8)	7222(14)	5350(30)	157(10)
C2A	2839(9)	8886(9)	5460(20)	171(10)

Table S6: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3bb. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O001	72(3)	77(3)	74(3)	-2(2)	20(2)	-2(2)
O002	112(4)	109(3)	35(2)	-1(2)	-1(2)	17(3)
O003	103(3)	83(3)	64(3)	-6(2)	22(2)	14(3)
O004	97(3)	116(4)	42(2)	1(2)	14(2)	23(3)
N005	72(3)	87(3)	33(2)	4(2)	-1(2)	10(3)
O006	108(4)	75(3)	65(3)	-22(2)	-2(2)	3(3)
O007	79(3)	94(3)	91(3)	6(3)	-22(3)	-8(3)
N008	87(4)	98(4)	35(2)	4(2)	14(2)	25(3)
O009	128(4)	83(3)	82(3)	26(3)	27(3)	12(3)
O00A	134(4)	93(3)	68(3)	8(3)	-9(3)	20(3)
C00B	75(4)	54(3)	34(3)	2(2)	13(2)	5(3)
C00C	77(4)	61(3)	39(3)	4(3)	9(3)	3(3)
C00D	59(3)	42(3)	50(3)	5(2)	-1(2)	-4(2)
C00E	70(4)	49(3)	66(4)	-9(3)	-2(3)	1(3)
C00F	68(4)	53(3)	74(4)	-2(3)	7(3)	17(3)
C00G	68(3)	46(3)	45(3)	-1(2)	7(2)	-3(3)
C00H	66(4)	43(3)	61(3)	-4(2)	6(3)	-3(3)
C00I	60(4)	48(3)	65(3)	-7(3)	-2(3)	10(3)
C00J	81(5)	53(4)	100(6)	5(4)	4(4)	8(3)
C00K	60(4)	49(3)	65(4)	6(3)	-4(3)	7(3)
C00L	85(4)	49(3)	61(4)	-14(3)	3(3)	16(3)
C00M	74(4)	40(3)	74(4)	-9(3)	-3(3)	3(3)
C00N	66(4)	62(3)	58(3)	-8(3)	4(3)	2(3)
C00O	63(3)	50(3)	51(3)	0(2)	7(2)	-3(3)
C00P	64(4)	53(3)	71(4)	3(3)	2(3)	5(3)
C00Q	69(4)	56(4)	110(6)	20(4)	10(4)	-7(3)
C00R	87(5)	59(4)	76(4)	22(3)	11(4)	12(3)
C00S	74(4)	67(4)	92(5)	0(4)	6(4)	-10(3)
C00T	74(4)	46(3)	97(5)	7(3)	-9(3)	4(3)
C00U	80(4)	70(4)	58(3)	14(3)	-4(3)	2(3)
C00V	81(5)	87(5)	90(5)	0(4)	32(4)	3(4)

Table S6: Anisotropic Displacement Parameters ($Å^2×10^3$) for 3bb. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C00W	114(6)	94(5)	71(4)	-31(4)	8(4)	20(4)
C00X	84(5)	128(6)	46(3)	7(4)	-2(3)	32(5)
C00Y	92(5)	70(4)	95(5)	-14(4)	-11(4)	-16(4)
C00Z	75(4)	98(5)	73(4)	7(4)	9(3)	1(4)
C010	102(5)	131(6)	59(4)	6(4)	18(3)	44(5)
C011	93(6)	74(5)	130(7)	0(5)	-31(5)	-15(4)
C012	119(6)	94(6)	105(6)	-14(5)	24(5)	-16(5)
C013	85(5)	93(6)	124(7)	4(5)	7(5)	-23(4)
C014	91(6)	113(7)	113(6)	-11(5)	-17(5)	-20(5)
C015	89(6)	89(6)	129(7)	-13(5)	-16(5)	-30(4)
C016	92(6)	97(6)	153(8)	42(6)	19(6)	-6(5)
C017	101(6)	120(7)	133(7)	-6(6)	43(5)	-21(5)
C018	93(7)	101(7)	244(14)	54(8)	8(8)	-37(5)
C019	105(6)	142(8)	132(7)	-35(6)	-15(5)	-33(6)
C01A	106(6)	117(7)	119(7)	13(6)	-42(5)	-19(6)
C01B	142(8)	105(7)	116(7)	13(5)	-7(6)	-9(6)
C01C	99(7)	76(6)	237(14)	15(7)	-44(8)	-36(5)
C01D	140(8)	162(9)	134(8)	-27(7)	-12(6)	74(7)
C01E	82(6)	145(9)	179(10)	-15(7)	4(6)	-9(6)
C1	60(8)	107(11)	83(9)	10(8)	9(6)	-3(8)
C2	96(11)	115(12)	143(13)	-48(10)	18(10)	34(9)
C1A	133(15)	148(17)	195(18)	-5(14)	38(14)	-22(13)
C2A	160(16)	177(17)	179(17)	-44(14)	34(14)	73(13)

Table S7: Bond Lengths for 3bb.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O001	C00F	1.330(7)	C00L	C00M	1.441(8)
O001	C00V	1.452(7)	C00M	C00Y	1.404(8)
O002	C00C	1.230(6)	C00N	C00O	1.535(7)
O003	C00F	1.240(7)	C00N	C00P	1.532(8)
O004	C00B	1.247(6)	C00N	C00T	1.503(8)
N005	C00C	1.320(7)	C00N	C00W	1.560(8)
N005	C00X	1.465(7)	C00Q	C00R	1.475(9)
O006	C00L	1.365(6)	C00Q	C00T	1.410(9)
O007	C00J	1.299(8)	C00Q	C016	1.368(10)
O007	C01A	1.460(8)	C00S	C013	1.363(9)
N008	C00B	1.316(7)	C00T	C011	1.402(9)
N008	C010	1.450(8)	C00V	C00Z	1.489(9)
O009	C00R	1.373(7)	C00X	C01D	1.512(10)
O00A	C00J	1.260(8)	C00X	C01E	1.500(11)
C00B	C00G	1.497(7)	C00Y	C015	1.358(10)
C00C	C00O	1.500(7)	C00Z	C012	1.500(10)
C00D	C00E	1.523(7)	C00Z	C017	1.527(9)
C00D	C00G	1.539(7)	C010	C1	1.532(8)
C00D	C00H	1.533(7)	C010	C2	1.510(8)
C00D	C00U	1.523(7)	C010	C1A	1.525(9)
C00E	C00I	1.512(7)	C010	C2A	1.540(9)
C00F	C00I	1.448(8)	C011	C01C	1.345(12)
C00H	C00M	1.409(7)	C013	C015	1.377(11)
C00H	C00S	1.377(8)	C014	C019	1.529(10)
C00I	C00L	1.357(8)	C014	C01A	1.399(11)
C00J	C00K	1.429(9)	C014	C01B	1.490(11)
C00K	C00P	1.539(8)	C016	C018	1.379(13)
C00K	C00R	1.316(8)	C018	C01C	1.394(14)

Table S8: Bond Angles for 3bb.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C00F	O001	C00V	116.0(5)	C00P	C00N	C00W	106.8(5)
C00C	N005	C00X	123.9(5)	C00T	C00N	C00O	108.3(5)
C00J	O007	C01A	116.3(6)	C00T	C00N	C00P	111.3(5)
C00B	N008	C010	123.8(5)	C00T	C00N	C00W	112.6(5)
O004	C00B	N008	122.0(5)	C00C	C00O	C00N	116.9(4)
O004	C00B	C00G	121.8(5)	C00N	C00P	C00K	113.1(5)
N008	C00B	C00G	116.2(4)	C00T	C00Q	C00R	118.2(6)
O002	C00C	N005	121.9(5)	C016	C00Q	C00R	121.4(7)
O002	C00C	C00O	122.0(5)	C016	C00Q	C00T	120.4(7)
N005	C00C	C00O	116.1(4)	O009	C00R	C00Q	112.3(6)
C00E	C00D	C00G	107.8(4)	C00K	C00R	O009	124.0(6)
C00E	C00D	C00H	109.4(4)	C00K	C00R	C00Q	123.7(6)
C00H	C00D	C00G	108.2(4)	C013	C00S	C00H	121.8(7)
C00U	C00D	C00E	107.5(4)	C00Q	C00T	C00N	120.2(5)
C00U	C00D	C00G	111.0(4)	C011	C00T	C00N	122.7(7)
C00U	C00D	C00H	112.7(4)	C011	C00T	C00Q	116.8(7)
C00I	C00E	C00D	115.0(5)	O001	C00V	C00Z	108.5(5)
O001	C00F	C00I	113.6(5)	N005	C00X	C01D	110.0(6)
O003	C00F	O001	122.3(6)	N005	C00X	C01E	110.1(6)
O003	C00F	C00I	124.0(6)	C01E	C00X	C01D	110.5(7)
C00B	C00G	C00D	116.4(4)	C015	C00Y	C00M	121.8(7)
C00M	C00H	C00D	119.0(5)	C00V	C00Z	C012	112.1(6)
C00S	C00H	C00D	122.1(5)	C00V	C00Z	C017	108.9(6)
C00S	C00H	C00M	118.5(5)	C012	C00Z	C017	111.0(7)
C00F	C00I	C00E	122.6(5)	N008	C010	C1	112.5(8)
C00L	C00I	C00E	117.8(5)	N008	C010	C2	112.9(9)
C00L	C00I	C00F	119.5(5)	N008	C010	C1A	108.6(12)
O007	C00J	C00K	115.6(7)	N008	C010	C2A	100.2(10)
O00A	C00J	O007	121.7(7)	C2	C010	C1	112.6(12)
O00A	C00J	C00K	122.6(7)	C1A	C010	C2A	118.3(15)
C00J	C00K	C00P	120.8(6)	C01C	C011	C00T	122.9(9)
C00R	C00K	C00J	120.3(6)	C00S	C013	C015	120.5(8)
C00R	C00K	C00P	118.8(5)	C01A	C014	C019	111.3(8)
O006	C00L	C00M	114.7(5)	C01A	C014	C01B	118.8(8)
C00I	C00L	O006	122.8(6)	C01B	C014	C019	112.4(8)
C00I	C00L	C00M	122.4(5)	C00Y	C015	C013	119.2(7)
C00H	C00M	C00L	120.4(5)	C00Q	C016	C018	120.7(9)
C00Y	C00M	C00H	118.2(6)	C016	C018	C01C	119.9(9)
C00Y	C00M	C00L	121.4(6)	C014	C01A	O007	112.6(7)
C00O	C00N	C00W	110.1(5)	C011	C01C	C018	119.2(9)
C00P	C00N	C00O	107.6(4)				

Table S9: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3bb.

Atom	*x*	*y*	*z*	U(eq)
H005	8435.81	7733.98	3686.13	78
H006	4407.41	5614.5	2462.67	126
H008	3407.58	7674.2	5120.59	87
H009	9453.61	5682.59	7265.5	145
H00A	4932.51	6627.27	6647.59	75
H00B	4879.24	5586.98	6812.5	75
H00C	4328.34	7651.76	7119.83	64
H00D	4107.56	7306.85	5659.76	64
H00J	9132.08	7340.41	3688.14	66
H00K	9349.22	7609.24	2358.57	66
H00L	9942.54	6618.27	3358.63	76
H00M	9889.05	5572.03	3221.65	76
H00S	3564.53	5480.71	8039.69	94
H00E	4509.76	5567.33	8818.9	105
H00F	4127.63	6275.62	9040.2	105
H00G	4635.91	6591.69	8946.14	105
H00H	5571.14	7344.86	3033.89	101
H00I	5900.19	6558.02	3629.2	101
H00N	9120.02	6262.93	384.52	140
H00O	9434.69	5441.94	898.2	140
H00P	9650.41	6406.26	861.18	140
H00X	7869.47	8223.7	1322.24	105
H00Y	3525.73	4626.39	3478.6	105
H00Z	6136.64	7427.21	5615.84	99
H010	2767.43	7579.41	6860.31	116
H01A	2812.6	7957.86	7062.86	116
H011	8541.11	5439.1	1071.8	124
H01B	5654.64	8866.07	4216.28	158
H01C	5948.62	8919.6	5688.85	158
H01D	5485.93	8368.2	5481.87	158
H013	2975.19	4607.24	7005.71	122
H014	11157.13	7459.67	5454.1	130
H015	2951.64	4176.25	4711.15	126
H016	8536.82	4813.44	5709.73	137
H01E	6598.13	7430.09	3832.38	173
H01F	6619.34	8386.74	4517.4	173
H01G	6310.83	8224.92	3088.76	173
H018	7936.59	4333.05	4090.11	177
H01H	11355.55	8200.74	8112.05	193

Table S9: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3bb.

Atom	*x*	*y*	*z*	U(eq)
H01I	11653.45	8329.2	6894.33	193
H01J	11615.56	7377.7	7566.37	193
H01K	10631.2	7219.07	7520.95	143
H01L	10969.47	6514.62	6997.98	143
H01M	10697.51	8898.99	6434.86	185
H01N	10513.78	8383.01	5063.34	185
H01O	10988.84	8891.64	5187.55	185
H01P	7940.25	4667.46	1745.21	172
H01Q	7778.28	8653.24	4106.13	221
H01R	7434.6	8992.7	2832.2	221
H01S	7950.9	9318.63	3031.61	221
H01T	7620.78	6791.19	1765.26	205
H01U	7236.07	7478.82	2047.66	205
H01V	7562.94	7058.71	3295.42	205
H1A	2521.98	8084.6	4077.57	125
H1B	2203.33	7633.04	5060.92	125
H1C	2593.43	7070.61	4495	125
H2A	2948.49	9001.24	7399.07	177
H2B	2481.74	9058.85	6393.15	177
H2C	2951.25	9277.42	5841.08	177
H1AA	2616.11	7096.48	4445.74	236
H1AB	2215.82	7442.95	5240.1	236
H1AC	2548.15	6680.53	5889.39	236
H2AA	3125.89	9186.36	5765.58	256
H2AB	2588.33	9216.51	5772.93	256
H2AC	2792.56	8851.35	4465.77	256

Table S10: Atomic Occupancy for 3bb.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
H010	0.5	H01A	0.5	C1	0.5
H1A	0.5	H1B	0.5	H1C	0.5
C2	0.5	H2A	0.5	H2B	0.5
H2C	0.5	C1A	0.5	H1AA	0.5
H1AB	0.5	H1AC	0.5	C2A	0.5
H2AA	0.5	H2AB	0.5	H2AC	0.5

Crystal structure determination of [3bb]

Crystal Data for $C_{21}H_{29}NO_4$ (M =359.45 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 29.1328(15) Å, b = 14.8670(8) Å, c = 9.7039(4) Å, β = 97.610(4)°, V = 4165.9(4) Å^3, Z = 8, T = 300.2(4) K, μ(Cu Kα) = 0.633 mm^{-1}, *Dcalc* = 1.146 g/cm^3, 26253 reflections measured (6.122° ≤ 2Θ ≤ 133.184°), 7326 unique (R_{int} = 0.0701, R_{sigma} = 0.0638) which were used in all calculations. The final R_1 was 0.1277 (I > 2σ(I)) and wR_2 was 0.3363 (all data).

8.2 X-Ray Crystallographic Analysis of Compound 4bd

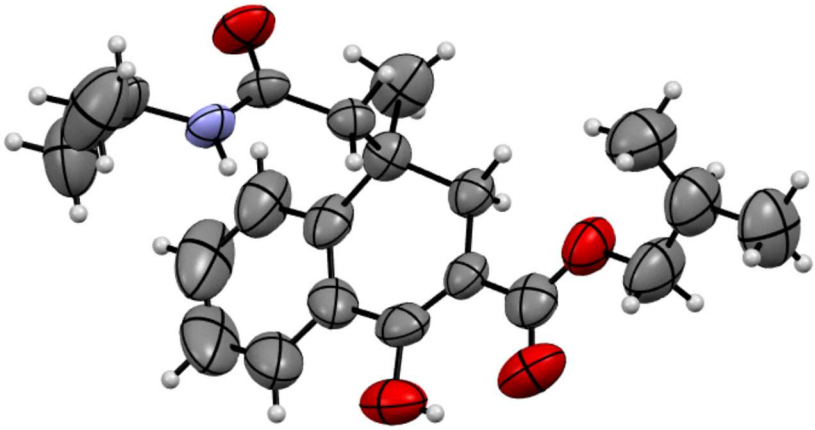


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Table S11: Crystal data and structure refinement for 4bd.

Identification code	**4bd**
Empirical formula	$C_{24}H_{26}NO_4$
Formula weight	392.46
Temperature/K	299.87(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.4689(11)
b/Å	17.7794(13)
c/Å	10.0344(8)
α/°	90
β/°	98.643(7)
γ/°	90
Volume/Å^3	2199.3(3)
Z	4
ρ_{calc}g/cm^3	1.185
μ/mm^{-1}	0.648
F(000)	836.0
Crystal size/mm^3	0.15 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.17 to 140.14
Index ranges	$-15 \leq h \leq 12$, $-21 \leq k \leq 21$, $-12 \leq l \leq 12$
Reflections collected	29037
Independent reflections	4147 [R_{int} = 0.0663, R_{sigma} = 0.0288]
Data/restraints/parameters	4147/0/267
Goodness-of-fit on F^2	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0566, wR_2 = 0.1641
Final R indexes [all data]	R_1 = 0.0769, wR_2 = 0.1936
Largest diff. peak/hole / e Å^{-3}	0.46/-0.19

Table S12: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 4bd. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O27	1719.0(13)	7125.3(8)	2221.4(13)	75.5(5)
O13	5128.0(13)	5587.2(8)	3065.3(16)	81.5(5)
O28	3742.5(14)	4174.0(8)	52.1(18)	86.8(5)
O15	5248.9(14)	4532.7(9)	1899.3(19)	90.2(5)
N23	1488.3(14)	7574.2(9)	94.8(16)	68.5(5)
C22	1967.4(15)	7119.0(10)	1072.2(17)	56.5(5)
C1	3677.5(17)	5292.5(11)	1359(2)	64.6(5)
C2	3022.4(16)	5951.0(11)	1740.9(19)	61.4(5)
C3	2873.5(16)	6606.1(10)	711.3(19)	59.4(5)
C5	1824.4(19)	5631.2(11)	-895.1(19)	65.9(5)
C11	3245.4(18)	4807.2(11)	364(2)	69.0(6)
C4	2614.7(18)	6278.3(11)	-729.9(19)	65.3(5)
C10	2163.6(19)	4913.5(11)	-438(2)	68.5(6)
C12	4729.2(19)	5102.5(12)	2102(2)	72.6(6)
C16	6553.4(17)	6017.0(13)	4767(2)	74.4(6)
C24	654(2)	8125.5(12)	276(2)	76.2(6)
C6	767(2)	5708.7(14)	-1577(2)	78.8(6)
C9	1480(2)	4296.8(13)	-736(2)	80.2(6)
C29	3911.7(19)	7080.6(13)	826(3)	81.8(7)
C8	448(2)	4389.2(15)	-1424(3)	88.9(7)
C7	89(2)	5093.1(16)	-1831(2)	89.3(7)
C21	6336(2)	6762.1(15)	4479(3)	99.9(9)
C17	7162(2)	5842.8(16)	5973(3)	100.0(9)
C26	1065(3)	8904.8(14)	30(3)	102.7(9)
C14	6200(2)	5401.7(16)	3773(3)	99.6(9)
C19	7317(3)	7113(2)	6608(4)	119.0(11)
C20	6712(2)	7309.4(16)	5405(4)	118.0(12)
C25	-383(2)	7934(2)	-665(3)	112.4(10)
C18	7559(3)	6381(2)	6886(3)	119.4(11)

Table S13: Anisotropic Displacement Parameters ($Å^2×10^3$) for 4bd. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O27	100.5(12)	75.6(9)	54.1(8)	5.1(6)	23.9(7)	19.3(8)
O13	72.1(10)	78.8(10)	88.7(11)	-10.7(8)	-3.8(8)	16.7(7)
O28	95.9(13)	59.9(8)	104.9(13)	-13.9(8)	15.6(9)	11.7(8)
O15	83.2(11)	75.2(10)	111.9(13)	-7.6(9)	13.7(9)	21.2(8)
N23	83.9(12)	66.7(10)	58.2(9)	6.2(7)	21.1(8)	17.7(9)
C22	66.3(12)	51.1(9)	53.3(10)	-3.4(7)	13.2(8)	-3.2(8)
C1	68.5(13)	56.8(10)	69.3(12)	-0.2(9)	12.9(9)	4.5(9)
C2	64.9(12)	59.1(10)	60.5(11)	-1.9(8)	10.6(9)	3.0(9)
C3	64.1(12)	55.8(10)	60.5(10)	-0.5(8)	16.6(8)	-0.3(8)
C5	81.2(14)	65.2(11)	53.0(10)	-4.2(8)	15.6(9)	3.3(10)
C11	77.7(15)	53.4(10)	78.3(13)	-0.3(9)	19.4(11)	3.4(9)
C4	80.6(14)	59.4(11)	60.1(11)	0.9(8)	24.5(9)	6.3(9)
C10	83.6(15)	60.9(11)	61.9(11)	-6.9(9)	14.0(10)	-0.8(10)
C12	73.9(15)	63.8(12)	80.3(14)	0.5(10)	12.5(11)	7.9(10)
C16	64.5(13)	73.8(13)	83.7(14)	3.0(11)	7.4(10)	8.7(10)
C24	98.2(17)	69.7(12)	65.5(12)	5.1(10)	27.5(11)	23.6(11)
C6	94.7(18)	83.1(14)	56.7(11)	-4.6(10)	5.4(11)	7.7(12)
C9	97.6(18)	67.6(13)	74.9(14)	-9.9(10)	11.6(12)	-7.9(12)
C29	69.5(15)	77.8(14)	101.1(17)	1.8(12)	22.8(12)	-8.3(11)
C8	96.5(19)	89.5(17)	78.8(15)	-18.0(13)	6.8(13)	-17.3(14)
C7	90.1(18)	103.5(19)	69.6(14)	-15.7(13)	-4.0(12)	-5.5(15)
C21	85.1(18)	79.8(16)	125(2)	14.5(15)	-14.8(15)	9.2(13)
C17	120(2)	83.5(16)	89.4(17)	17.9(13)	-6.8(16)	2.5(15)
C26	153(3)	68.4(14)	89.3(17)	0.6(12)	27.4(17)	14.1(16)
C14	78.3(17)	97.4(18)	114(2)	-12.4(15)	-15.2(15)	25.2(14)
C19	96(2)	125(3)	135(3)	-43(2)	10.4(19)	-0.2(19)
C20	82.2(19)	73.2(16)	191(4)	-7.2(19)	-3(2)	6.1(14)
C25	90(2)	128(3)	121(2)	12.1(19)	21.2(17)	21.8(17)
C18	143(3)	123(3)	84.5(19)	1.9(18)	-8.6(18)	-5(2)

Table S14: Bond Lengths for 4bd.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O27	C22	1.238(2)	C5	C6	1.398(3)
O13	C12	1.334(3)	C11	C10	1.476(3)
O13	C14	1.454(3)	C10	C9	1.394(3)
O28	C11	1.345(2)	C16	C21	1.374(3)
O15	C12	1.236(3)	C16	C17	1.364(3)
N23	C22	1.341(2)	C16	C14	1.501(3)
N23	C24	1.461(3)	C24	C26	1.511(4)
C22	C3	1.537(3)	C24	C25	1.521(4)
C1	C2	1.510(3)	C6	C7	1.383(3)
C1	C11	1.367(3)	C9	C8	1.375(4)
C1	C12	1.448(3)	C8	C7	1.371(4)
C2	C3	1.549(3)	C21	C20	1.378(4)
C3	C4	1.548(3)	C17	C18	1.366(4)
C3	C29	1.535(3)	C19	C20	1.369(5)
C5	C4	1.508(3)	C19	C18	1.356(5)
C5	C10	1.400(3)			

Table S15: Bond Angles for 4bd.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C12	O13	C14	115.00(17)	C5	C10	C11	120.12(19)
C22	N23	C24	124.14(17)	C9	C10	C5	120.1(2)
O27	C22	N23	121.97(17)	C9	C10	C11	119.7(2)
O27	C22	C3	121.36(16)	O13	C12	C1	115.64(18)
N23	C22	C3	116.64(16)	O15	C12	O13	120.1(2)
C11	C1	C2	120.39(18)	O15	C12	C1	124.3(2)
C11	C1	C12	117.13(18)	C21	C16	C14	122.3(2)
C12	C1	C2	122.19(18)	C17	C16	C21	118.1(2)
C1	C2	C3	115.39(16)	C17	C16	C14	119.5(2)
C22	C3	C2	107.92(15)	N23	C24	C26	109.2(2)
C22	C3	C4	112.72(16)	N23	C24	C25	109.1(2)
C4	C3	C2	109.10(15)	C26	C24	C25	112.4(2)
C29	C3	C22	107.32(15)	C7	C6	C5	121.2(2)
C29	C3	C2	110.35(17)	C8	C9	C10	120.6(2)
C29	C3	C4	109.41(17)	C7	C8	C9	119.9(2)
C10	C5	C4	120.0(2)	C8	C7	C6	120.3(2)
C6	C5	C4	122.10(19)	C16	C21	C20	120.2(3)
C6	C5	C10	117.8(2)	C16	C17	C18	122.3(3)
O28	C11	C1	123.6(2)	O13	C14	C16	108.41(19)
O28	C11	C10	113.31(18)	C18	C19	C20	120.2(3)
C1	C11	C10	123.04(18)	C19	C20	C21	120.1(3)
C5	C4	C3	115.54(16)	C19	C18	C17	119.2(3)

Table S16: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 4bd.

Atom	*x*	*y*	*z*	U(eq)
H28	4270.93	4093.07	625.89	130
H2A	3371.48	6146.46	2600.17	74
H2B	2310.75	5769.81	1866.77	74
H4A	2325.37	6678.53	-1336.36	78
H4B	3288.24	6111.88	-1007.77	78
H24	509.1	8096.28	1208.38	91
H6	515.2	6182.6	-1865.46	95
H9	1723.27	3818.09	-466.62	96
H29A	3846.71	7438.84	102.92	123
H29B	4521.46	6757.97	775.06	123
H29C	4016.28	7341.85	1673.37	123
H8	-4.76	3975	-1612.71	107
H7	-614.24	5157.09	-2279.67	107
H21	5933.92	6897.46	3657.22	120
H17	7311.83	5340.28	6179.97	120
H26A	1706.95	9005.64	661.86	154
H26B	517.19	9268.62	144.2	154
H26C	1232.7	8935.47	-870.96	154
H14A	6709.4	5355.98	3136.55	120
H14B	6176.51	4925.62	4240.37	120
H19	7562.62	7483.14	7235.42	143
H20	6554.89	7812.67	5212.58	142
H25A	-235.39	7915.03	-1576.64	169
H25B	-920	8312.72	-592.32	169
H25C	-647.63	7454.09	-421.83	169
H18	7990.04	6247.42	7689.71	143

Crystal structure determination of [4bd]

Crystal Data for $C_{24}H_{26}NO_4$ (M =392.46 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 12.4689(11) Å, b = 17.7794(13) Å, c = 10.0344(8) Å, β = 98.643(7)°, V = 2199.3(3) Å^3, Z = 4, T = 299.87(10) K, μ(Cu Kα) = 0.648 mm^{-1}, *Dcalc* = 1.185 g/cm^3, 29037 reflections measured (7.17° ≤ 2Θ ≤ 140.14°), 4147 unique (R_{int} = 0.0663, R_{sigma} = 0.0288) which were used in all calculations. The final R_1 was 0.0566 (I > 2σ(I)) and wR_2 was 0.1936 (all data).

8.3 X-Ray Crystallographic Analysis of Compound 5d

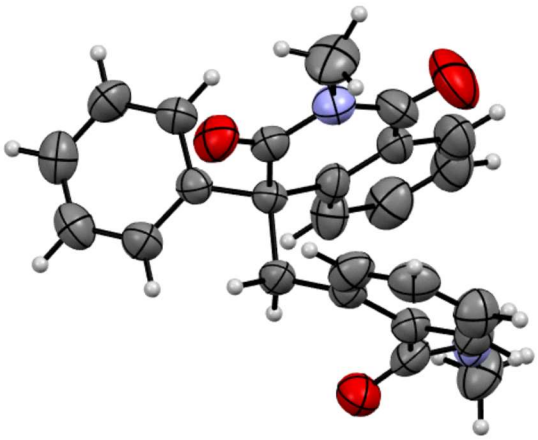

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Table S17: Crystal data and structure refinement for 5d.

Identification code	5d
Empirical formula	$C_{25}H_{22}N_2O_3$
Formula weight	398.44
Temperature/K	296(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.310(11)
b/Å	10.423(14)
c/Å	23.48(3)
α/°	90
β/°	98.79(2)
γ/°	90
Volume/Å^3	2010(5)
Z	4
ρ_{calc}g/cm^3	1.317
μ/mm^{-1}	0.087
F(000)	840.0
Crystal size/mm^3	0.160 × 0.150 × 0.130
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.51 to 50.496
Index ranges	$-9 \le h \le 9$, $-12 \le k \le 12$, $-21 \le l \le 28$
Reflections collected	10370
Independent reflections	3618 [R_{int} = 0.0834, R_{sigma} = 0.0979]
Data/restraints/parameters	3618/0/277
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0648, wR_2 = 0.1254
Final R indexes [all data]	R_1 = 0.1724, wR_2 = 0.1624
Largest diff. peak/hole / e Å^{-3}	0.26/-0.18

Table S18: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 5d. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O(1)	3593(3)	3845(3)	5039.9(12)	72.1(9)
O(2)	4078(5)	119(3)	5974.2(14)	115.2(13)
O(3)	7818(3)	4714(3)	7318.9(12)	72.9(9)
N(1)	7695(4)	2723(4)	7673.4(15)	60.2(10)
N(2)	3719(4)	1979(4)	5511.4(15)	63.3(10)
C(1)	7595(5)	3173(4)	8245.9(17)	81.6(14)
C(2)	7799(4)	3550(5)	7244.3(18)	57.6(11)
C(3)	7963(4)	2952(4)	6674.8(17)	49.6(10)
C(4)	9055(5)	1967(4)	6669.0(19)	64.2(12)
C(5)	9365(5)	1428(4)	6159(2)	72.9(13)
C(6)	8578(5)	1912(4)	5650(2)	68.9(13)
C(7)	7485(5)	2895(4)	5657.7(18)	63.2(12)
C(8)	7132(4)	3427(4)	6158.3(17)	46.7(10)
C(9)	5895(4)	4486(3)	6123.7(15)	50.1(10)
C(10)	4074(4)	4032(3)	6059.2(15)	44.8(10)
C(11)	2906(4)	5166(4)	5993.2(14)	46.5(10)
C(12)	1248(5)	4923(4)	5888.7(16)	62.1(12)
C(13)	133(5)	5890(5)	5803.9(18)	72.6(13)
C(14)	647(6)	7142(5)	5839.1(17)	70.4(13)
C(15)	2251(6)	7391(4)	5946.6(17)	68.7(12)
C(16)	3393(5)	6421(4)	6022.1(16)	59.5(11)
C(17)	3847(4)	3250(4)	6581.2(17)	50.8(10)
C(18)	3869(4)	1932(4)	6554.8(18)	56.2(11)
C(19)	3787(5)	1210(4)	7033(2)	76.7(14)
C(20)	3634(5)	1791(5)	7541(2)	77.4(15)
C(21)	3558(5)	3097(5)	7569.6(19)	79.1(14)
C(22)	3709(5)	3842(4)	7093.7(17)	63.6(12)
C(23)	3915(5)	1287(5)	6008(2)	69.6(13)
C(24)	3750(4)	3290(4)	5496.7(18)	52.8(11)
C(25)	3548(6)	1324(4)	4947.0(18)	92.4(16)

Table S19: Anisotropic Displacement Parameters ($Å^2×10^3$) for 5d. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	79(2)	87(2)	48.2(18)	10.4(17)	1.8(16)	0.2(17)
O(2)	179(4)	51(2)	115(3)	-4(2)	19(2)	-13(2)
O(3)	85(2)	58(2)	71(2)	-4.2(17)	-2.7(16)	-5.2(17)
N(1)	68(2)	63(3)	48(2)	5(2)	5.8(18)	7(2)
N(2)	66(2)	62(3)	58(2)	-3(2)	-1.2(19)	-4(2)
C(1)	93(4)	97(4)	50(3)	4(3)	-1(3)	14(3)
C(2)	46(3)	70(3)	53(3)	4(3)	-5(2)	3(2)
C(3)	42(2)	52(3)	54(3)	2(2)	5(2)	-2(2)
C(4)	55(3)	68(3)	67(3)	11(2)	2(2)	2(2)
C(5)	69(3)	75(3)	78(4)	0(3)	20(3)	10(2)
C(6)	58(3)	83(4)	69(3)	-8(3)	20(3)	-11(3)
C(7)	47(3)	84(3)	58(3)	7(3)	9(2)	-3(2)
C(8)	39(2)	52(3)	49(2)	7(2)	6(2)	-10.6(19)
C(9)	41(2)	55(3)	54(3)	13(2)	5.1(19)	-7(2)
C(10)	41(2)	45(2)	47(2)	4.5(19)	1.7(18)	-6.5(19)
C(11)	49(2)	49(3)	42(2)	6.5(19)	6.1(19)	-7(2)
C(12)	51(3)	55(3)	78(3)	6(2)	2(2)	-8(2)
C(13)	47(3)	74(3)	93(4)	5(3)	2(2)	7(3)
C(14)	78(4)	67(4)	68(3)	12(3)	16(3)	18(3)
C(15)	84(4)	48(3)	75(3)	-2(2)	16(3)	-2(3)
C(16)	54(3)	59(3)	65(3)	7(2)	8(2)	-8(2)
C(17)	46(2)	55(3)	52(3)	15(2)	8(2)	5(2)
C(18)	50(3)	54(3)	63(3)	15(2)	2(2)	-5(2)
C(19)	71(3)	71(4)	88(4)	27(3)	13(3)	-6(3)
C(20)	74(3)	94(4)	65(3)	35(3)	14(3)	-5(3)
C(21)	79(3)	101(4)	61(3)	11(3)	18(3)	5(3)
C(22)	78(3)	68(3)	48(3)	18(2)	18(2)	11(2)
C(23)	76(3)	51(3)	79(4)	3(3)	2(3)	-18(3)
C(24)	42(2)	53(3)	62(3)	1(2)	4(2)	-1(2)
C(25)	111(4)	89(4)	69(3)	-34(3)	-13(3)	11(3)

Table S20: Bond Lengths for 5d.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O(1)	C(24)	1.208(4)	C(10)	C(17)	1.507(5)
O(2)	C(23)	1.229(5)	C(10)	C(24)	1.518(5)
O(3)	C(2)	1.226(5)	C(10)	C(11)	1.522(5)
N(1)	C(2)	1.339(5)	C(11)	C(16)	1.368(5)
N(1)	C(1)	1.438(5)	C(11)	C(12)	1.385(5)
N(2)	C(23)	1.359(5)	C(12)	C(13)	1.363(5)
N(2)	C(24)	1.368(5)	C(13)	C(14)	1.372(5)
N(2)	C(25)	1.478(5)	C(14)	C(15)	1.344(6)
C(2)	C(3)	1.500(5)	C(15)	C(16)	1.379(5)
C(3)	C(4)	1.372(5)	C(17)	C(22)	1.373(5)
C(3)	C(8)	1.391(5)	C(17)	C(18)	1.376(5)
C(4)	C(5)	1.382(5)	C(18)	C(19)	1.361(5)
C(5)	C(6)	1.368(5)	C(18)	C(23)	1.456(6)
C(6)	C(7)	1.371(5)	C(19)	C(20)	1.362(6)
C(7)	C(8)	1.371(5)	C(20)	C(21)	1.365(6)
C(8)	C(9)	1.502(5)	C(21)	C(22)	1.382(5)
C(9)	C(10)	1.571(5)			

Table S21: Bond Angles for 5d.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(2)	N(1)	C(1)	120.9(4)	C(16)	C(11)	C(12)	117.5(4)
C(23)	N(2)	C(24)	123.5(4)	C(16)	C(11)	C(10)	123.9(4)
C(23)	N(2)	C(25)	120.4(4)	C(12)	C(11)	C(10)	118.5(4)
C(24)	N(2)	C(25)	116.0(4)	C(13)	C(12)	C(11)	121.7(4)
O(3)	C(2)	N(1)	122.1(4)	C(12)	C(13)	C(14)	119.7(4)
O(3)	C(2)	C(3)	122.5(4)	C(15)	C(14)	C(13)	119.1(4)
N(1)	C(2)	C(3)	115.4(4)	C(14)	C(15)	C(16)	121.7(4)
C(4)	C(3)	C(8)	119.9(4)	C(11)	C(16)	C(15)	120.2(4)
C(4)	C(3)	C(2)	118.0(4)	C(22)	C(17)	C(18)	119.5(4)
C(8)	C(3)	C(2)	121.9(4)	C(22)	C(17)	C(10)	120.5(4)
C(3)	C(4)	C(5)	121.6(4)	C(18)	C(17)	C(10)	119.9(4)
C(6)	C(5)	C(4)	118.7(4)	C(19)	C(18)	C(17)	120.8(4)
C(5)	C(6)	C(7)	119.6(4)	C(19)	C(18)	C(23)	118.9(4)
C(6)	C(7)	C(8)	122.8(4)	C(17)	C(18)	C(23)	120.2(4)
C(7)	C(8)	C(3)	117.4(4)	C(18)	C(19)	C(20)	120.0(5)
C(7)	C(8)	C(9)	119.0(4)	C(19)	C(20)	C(21)	119.8(4)
C(3)	C(8)	C(9)	123.5(4)	C(20)	C(21)	C(22)	120.7(5)
C(8)	C(9)	C(10)	115.1(3)	C(17)	C(22)	C(21)	119.1(4)
C(17)	C(10)	C(24)	113.8(3)	O(2)	C(23)	N(2)	118.1(5)
C(17)	C(10)	C(11)	110.2(3)	O(2)	C(23)	C(18)	122.2(5)
C(24)	C(10)	C(11)	106.3(3)	N(2)	C(23)	C(18)	119.7(4)
C(17)	C(10)	C(9)	108.9(3)	O(1)	C(24)	N(2)	120.1(4)
C(24)	C(10)	C(9)	106.1(3)	O(1)	C(24)	C(10)	120.6(4)
C(11)	C(10)	C(9)	111.5(3)	N(2)	C(24)	C(10)	119.2(4)

Table S22: Torsion Angles for 5d.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C(1)	N(1)	C(2)	O(3)	0.2(6)	C(24)	C(10)	C(17)	C(22)	-164.3(3)
C(1)	N(1)	C(2)	C(3)	177.6(3)	C(11)	C(10)	C(17)	C(22)	-45.0(5)
O(3)	C(2)	C(3)	C(4)	131.8(4)	C(9)	C(10)	C(17)	C(22)	77.6(4)
N(1)	C(2)	C(3)	C(4)	-45.7(5)	C(24)	C(10)	C(17)	C(18)	19.4(5)
O(3)	C(2)	C(3)	C(8)	-43.7(6)	C(11)	C(10)	C(17)	C(18)	138.7(4)
N(1)	C(2)	C(3)	C(8)	138.8(4)	C(9)	C(10)	C(17)	C(18)	-98.7(4)
C(8)	C(3)	C(4)	C(5)	0.3(6)	C(22)	C(17)	C(18)	C(19)	-1.3(6)
C(2)	C(3)	C(4)	C(5)	-175.2(4)	C(10)	C(17)	C(18)	C(19)	175.1(3)
C(3)	C(4)	C(5)	C(6)	1.2(6)	C(22)	C(17)	C(18)	C(23)	176.3(4)
C(4)	C(5)	C(6)	C(7)	-1.3(6)	C(10)	C(17)	C(18)	C(23)	-7.4(6)
C(5)	C(6)	C(7)	C(8)	-0.1(6)	C(17)	C(18)	C(19)	C(20)	1.9(6)
C(6)	C(7)	C(8)	C(3)	1.6(6)	C(23)	C(18)	C(19)	C(20)	-175.7(4)
C(6)	C(7)	C(8)	C(9)	-179.0(3)	C(18)	C(19)	C(20)	C(21)	0.2(7)
C(4)	C(3)	C(8)	C(7)	-1.7(5)	C(19)	C(20)	C(21)	C(22)	-3.0(7)
C(2)	C(3)	C(8)	C(7)	173.7(3)	C(18)	C(17)	C(22)	C(21)	-1.4(6)
C(4)	C(3)	C(8)	C(9)	178.9(3)	C(10)	C(17)	C(22)	C(21)	-177.8(3)
C(2)	C(3)	C(8)	C(9)	-5.7(5)	C(20)	C(21)	C(22)	C(17)	3.6(6)
C(7)	C(8)	C(9)	C(10)	84.1(4)	C(24)	N(2)	C(23)	O(2)	-170.7(4)
C(3)	C(8)	C(9)	C(10)	-96.5(4)	C(25)	N(2)	C(23)	O(2)	5.8(6)
C(8)	C(9)	C(10)	C(17)	61.5(4)	C(24)	N(2)	C(23)	C(18)	11.5(6)
C(8)	C(9)	C(10)	C(24)	-61.4(4)	C(25)	N(2)	C(23)	C(18)	-172.0(4)
C(8)	C(9)	C(10)	C(11)	-176.8(3)	C(19)	C(18)	C(23)	O(2)	-8.8(7)
C(17)	C(10)	C(11)	C(16)	117.3(4)	C(17)	C(18)	C(23)	O(2)	173.6(4)
C(24)	C(10)	C(11)	C(16)	-118.9(4)	C(19)	C(18)	C(23)	N(2)	168.9(4)
C(9)	C(10)	C(11)	C(16)	-3.7(5)	C(17)	C(18)	C(23)	N(2)	-8.7(6)
C(17)	C(10)	C(11)	C(12)	-63.8(4)	C(23)	N(2)	C(24)	O(1)	178.8(4)
C(24)	C(10)	C(11)	C(12)	60.0(4)	C(25)	N(2)	C(24)	O(1)	2.2(6)
C(9)	C(10)	C(11)	C(12)	175.3(3)	C(23)	N(2)	C(24)	C(10)	2.1(6)
C(16)	C(11)	C(12)	C(13)	1.5(6)	C(25)	N(2)	C(24)	C(10)	-174.5(3)
C(10)	C(11)	C(12)	C(13)	-177.6(4)	C(17)	C(10)	C(24)	O(1)	166.3(3)
C(11)	C(12)	C(13)	C(14)	-2.0(6)	C(11)	C(10)	C(24)	O(1)	44.8(5)
C(12)	C(13)	C(14)	C(15)	1.2(7)	C(9)	C(10)	C(24)	O(1)	-74.0(4)
C(13)	C(14)	C(15)	C(16)	0.0(7)	C(17)	C(10)	C(24)	N(2)	-17.0(5)
C(12)	C(11)	C(16)	C(15)	-0.2(6)	C(11)	C(10)	C(24)	N(2)	-138.5(3)
C(10)	C(11)	C(16)	C(15)	178.8(4)	C(9)	C(10)	C(24)	N(2)	102.7(4)
C(14)	C(15)	C(16)	C(11)	-0.5(6)					

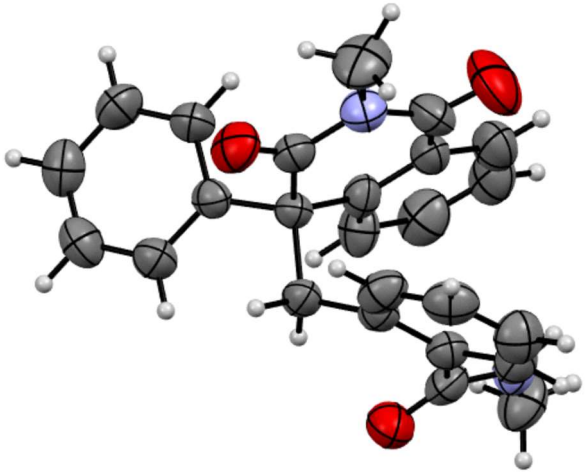
Table S23: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 5d.

Atom	*x*	*y*	*z*	U(eq)
H(1A)	8579.4	3618.82	8395.94	122
H(1B)	7454.11	2454.95	8489.83	122
H(1C)	6684.65	3744.21	8234.12	122
H(4)	9600.1	1653.88	7016.68	77
H(5)	10093.19	749.77	6161.65	87
H(6)	8782.48	1576.12	5301.13	83
H(7)	6960.34	3214.54	5308.22	76
H(9A)	6019.84	5029.12	5797.77	60
H(9B)	6130.62	5006.34	6468.96	60
H(12)	885.81	4077.34	5875.96	74
H(13)	-972.48	5701.21	5722.62	87
H(14)	-104.17	7809.17	5789.2	85
H(15)	2601.04	8239.58	5970.65	82
H(16)	4495.9	6620.43	6092.89	71
H(19)	3835.87	320.53	7011.58	92
H(20)	3581.28	1298.41	7868.48	93
H(21)	3402.42	3489.58	7912.7	95
H(22)	3716.48	4732.73	7120.4	76
H(25A)	3057.9	1898.49	4650.78	139
H(25B)	2873.18	578.68	4954.44	139
H(25C)	4603.53	1069.48	4869.05	139
H(1E)	7600(50)	1830(40)	7575(18)	106(18)

Crystal structure determination of [5d]

Crystal Data for $C_{25}H_{22}N_2O_3$ (M =398.44 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 8.310(11) Å, b = 10.423(14) Å, c = 23.48(3) Å, β = 98.79(2)°, V = 2010(5) Å^3, Z = 4, T = 296(2) K, μ(MoKα) = 0.087 mm^{-1}, *Dcalc* = 1.317 g/cm^3, 10370 reflections measured (3.51° ≤ 2Θ ≤ 50.496°), 3618 unique (R_{int} = 0.0834, R_{sigma} = 0.0979) which were used in all calculations. The final R_1 was 0.0648 (I > 2σ(I)) and wR_2 was 0.1624 (all data).

8.4 X-Ray Crystallographic Analysis of Compound 6ka



CCDC: 2375729

Table S24: Crystal data and structure refinement for 6ka.

Empirical formula	$C_{19}H_{24}FNO_4$
Formula weight	349.39
Temperature/K	296(2)
Crystal system	monoclinic
Space group	Cc
a/Å	10.190(3)
b/Å	30.800(10)
c/Å	7.169(2)
α/°	90
β/°	124.509(4)
γ/°	90
Volume/Å^3	1854.0(10)
Z	4
ρ_{calc}g/cm^3	1.252
μ/mm^{-1}	0.094
F(000)	744.0
Crystal size/mm^3	0.180 × 0.160 × 0.100
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.644 to 55.112
Index ranges	-7 ≤ h ≤ 13, -40 ≤ k ≤ 40, -9 ≤ l ≤ 8
Reflections collected	5763
Independent reflections	2851 [R_{int} = 0.0263, R_{sigma} = 0.0407]
Data/restraints/parameters	2851/2/231
Goodness-of-fit on F^2	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0408, wR_2 = 0.1039
Final R indexes [all data]	R_1 = 0.0512, wR_2 = 0.1109
Largest diff. peak/hole / e Å^{-3}	0.15/-0.19
Flack parameter	0.9(9)

Table S25: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 6ka. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F(1)	8025(3)	6554.6(9)	12457(4)	101.3(8)
O(1)	2039(3)	7050.7(7)	3170(4)	75.3(7)
O(2)	3831(3)	5608.1(6)	5817(4)	60.5(6)
O(3)	8379(3)	4698.8(7)	6676(4)	71.4(7)
O(4)	9262(3)	5370.9(9)	7142(6)	97.2(10)
N(2)	2894(3)	6572.4(7)	1653(4)	47.9(6)
C(1)	6201(3)	6245.6(10)	8917(5)	50.3(7)
C(2)	6861(4)	6608.6(12)	10241(5)	62.1(9)
C(3)	6375(5)	7018.4(11)	9405(6)	68.9(10)
C(4)	5148(4)	7068.4(9)	7165(6)	60.5(8)
C(5)	4461(3)	6709.8(8)	5749(5)	46.0(6)
C(6)	5011(3)	6296.4(7)	6652(4)	39.4(6)
C(7)	4308(3)	5897.7(7)	5213(4)	39.2(6)
C(8)	4400(3)	5862.1(8)	3184(4)	40.9(6)
C(9)	4276(3)	6312.1(8)	2163(5)	46.0(6)
C(10)	3031(4)	6791.6(8)	3394(5)	48.5(7)
C(11)	1535(4)	6680.7(11)	-748(5)	62.1(9)
C(12)	1645(6)	7163.3(16)	-1165(8)	101.2(15)
C(13)	-31(4)	6573.4(16)	-1057(7)	84.7(12)
C(14)	1635(6)	6414.5(19)	-2461(6)	96.9(15)
C(15)	3150(4)	5546.1(10)	1448(5)	60.0(8)
C(16)	6111(3)	5693.9(8)	4137(5)	44.8(6)
C(17)	6469(3)	5244.5(9)	5181(5)	50.1(7)
C(18)	8182(4)	5123.9(9)	6419(5)	49.2(6)
C(19)	10002(5)	4540.6(13)	7968(8)	86.6(12)

Table S26: Anisotropic Displacement Parameters ($Å^2×10^3$) for 6ka. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F(1)	87.3(16)	129.4(19)	46.2(12)	-13.8(12)	13.1(11)	-12.5(14)
O(1)	79.1(17)	59.0(13)	80.1(16)	10.9(11)	40.5(14)	33.3(11)
O(2)	70.9(14)	45.6(10)	86.3(16)	-0.7(10)	57.2(13)	-10.4(10)
O(3)	44.0(12)	53.7(11)	94.3(18)	6.2(10)	26.0(13)	11.8(9)
O(4)	42.6(13)	67.5(14)	130(2)	11.0(15)	17.6(14)	-0.8(12)
N(2)	40.0(12)	54.4(12)	43.9(14)	12.7(10)	20.5(11)	11.1(10)
C(1)	48.0(15)	56.3(15)	45.5(16)	4.3(12)	25.9(13)	0.3(13)
C(2)	54.5(19)	84(2)	39.8(18)	-9.3(14)	22.0(15)	-12.9(16)
C(3)	71(2)	65(2)	67(2)	-24.2(16)	38(2)	-21.9(17)
C(4)	74(2)	38.6(14)	72(2)	-7.9(13)	43.4(19)	-8.9(13)
C(5)	50.6(16)	38.3(12)	52.7(17)	-1.6(11)	31.5(14)	-2.6(11)
C(6)	40.3(13)	39.4(12)	42.2(14)	1.1(10)	25.6(12)	-2.0(10)
C(7)	32.7(12)	35.0(11)	48.1(15)	2.7(10)	21.8(11)	1.7(10)
C(8)	31.2(12)	43.2(12)	41.5(14)	-3.2(10)	16.6(11)	1.3(10)
C(9)	37.1(13)	56.9(15)	44.0(14)	4.6(12)	23.0(11)	4.6(12)
C(10)	49.7(15)	37.2(12)	56.1(18)	7.3(12)	28.5(14)	5.6(12)
C(11)	46.5(18)	79(2)	48.9(19)	20.1(15)	19.7(15)	14.1(15)
C(12)	103(4)	101(3)	86(3)	55(2)	46(3)	20(3)
C(13)	46.5(19)	115(3)	73(3)	14(2)	22.5(19)	7.9(19)
C(14)	75(3)	151(4)	42(2)	13(2)	19.3(19)	30(3)
C(15)	41.4(16)	63.5(17)	53.6(19)	-14.8(14)	14.1(14)	-4.2(13)
C(16)	37.1(13)	51.7(14)	45.6(15)	-1.7(11)	23.4(12)	4.0(11)
C(17)	41.5(14)	50.7(15)	57.1(18)	-2.9(12)	27.2(13)	2.9(12)
C(18)	45.0(15)	49.1(14)	46.8(16)	-2.0(11)	22.0(13)	3.4(12)
C(19)	51(2)	85(2)	104(3)	16(2)	32(2)	28.2(19)

Table S27: Bond Lengths for 6ka.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F(1)	C(2)	1.350(4)	C(4)	C(5)	1.391(4)
O(1)	C(10)	1.225(4)	C(5)	C(6)	1.394(3)
O(2)	C(7)	1.207(3)	C(5)	C(10)	1.500(4)
O(3)	C(18)	1.322(3)	C(6)	C(7)	1.499(3)
O(3)	C(19)	1.447(4)	C(7)	C(8)	1.514(4)
O(4)	C(18)	1.188(4)	C(8)	C(15)	1.524(4)
N(2)	C(10)	1.355(4)	C(8)	C(9)	1.539(4)
N(2)	C(9)	1.475(4)	C(8)	C(16)	1.557(3)
N(2)	C(11)	1.513(4)	C(11)	C(13)	1.519(5)
C(1)	C(2)	1.371(5)	C(11)	C(14)	1.527(6)
C(1)	C(6)	1.379(4)	C(11)	C(12)	1.532(6)
C(2)	C(3)	1.364(5)	C(16)	C(17)	1.516(4)
C(3)	C(4)	1.375(5)	C(17)	C(18)	1.489(4)

Table S28: Bond Angles for 6ka.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(18)	O(3)	C(19)	116.8(3)	C(7)	C(8)	C(9)	111.0(2)
C(10)	N(2)	C(9)	117.2(2)	C(15)	C(8)	C(9)	112.4(2)
C(10)	N(2)	C(11)	119.3(2)	C(7)	C(8)	C(16)	105.4(2)
C(9)	N(2)	C(11)	122.1(2)	C(15)	C(8)	C(16)	110.8(2)
C(2)	C(1)	C(6)	118.8(3)	C(9)	C(8)	C(16)	106.2(2)
F(1)	C(2)	C(3)	119.3(3)	N(2)	C(9)	C(8)	114.7(2)
F(1)	C(2)	C(1)	118.3(3)	O(1)	C(10)	N(2)	123.9(3)
C(3)	C(2)	C(1)	122.4(3)	O(1)	C(10)	C(5)	117.4(3)
C(2)	C(3)	C(4)	118.7(3)	N(2)	C(10)	C(5)	118.7(2)
C(3)	C(4)	C(5)	120.8(3)	N(2)	C(11)	C(13)	109.0(3)
C(4)	C(5)	C(6)	118.9(3)	N(2)	C(11)	C(14)	111.2(3)
C(4)	C(5)	C(10)	117.0(2)	C(13)	C(11)	C(14)	108.0(3)
C(6)	C(5)	C(10)	123.7(2)	N(2)	C(11)	C(12)	108.3(3)
C(1)	C(6)	C(5)	120.3(2)	C(13)	C(11)	C(12)	111.6(3)
C(1)	C(6)	C(7)	118.4(2)	C(14)	C(11)	C(12)	108.6(4)
C(5)	C(6)	C(7)	121.3(2)	C(17)	C(16)	C(8)	114.7(2)
O(2)	C(7)	C(6)	119.4(2)	C(18)	C(17)	C(16)	113.3(2)
O(2)	C(7)	C(8)	123.2(2)	O(4)	C(18)	O(3)	123.0(3)
C(6)	C(7)	C(8)	117.1(2)	O(4)	C(18)	C(17)	125.7(3)
C(7)	C(8)	C(15)	110.7(2)	O(3)	C(18)	C(17)	111.4(2)

Table S29: Torsion Angles for 6ka.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C(6)	C(1)	C(2)	F(1)	180.0(3)	C(7)	C(8)	C(9)	N(2)	-52.1(3)
C(6)	C(1)	C(2)	C(3)	0.5(5)	C(15)	C(8)	C(9)	N(2)	72.5(3)
F(1)	C(2)	C(3)	C(4)	-177.6(3)	C(16)	C(8)	C(9)	N(2)	-166.2(2)
C(1)	C(2)	C(3)	C(4)	1.9(5)	C(9)	N(2)	C(10)	O(1)	172.9(3)
C(2)	C(3)	C(4)	C(5)	-2.9(6)	C(11)	N(2)	C(10)	O(1)	6.5(4)
C(3)	C(4)	C(5)	C(6)	1.5(5)	C(9)	N(2)	C(10)	C(5)	-8.3(3)
C(3)	C(4)	C(5)	C(10)	174.4(3)	C(11)	N(2)	C(10)	C(5)	-174.6(3)
C(2)	C(1)	C(6)	C(5)	-1.9(4)	C(4)	C(5)	C(10)	O(1)	-41.3(4)
C(2)	C(1)	C(6)	C(7)	179.4(3)	C(6)	C(5)	C(10)	O(1)	131.1(3)
C(4)	C(5)	C(6)	C(1)	0.9(4)	C(4)	C(5)	C(10)	N(2)	139.7(3)
C(10)	C(5)	C(6)	C(1)	-171.4(3)	C(6)	C(5)	C(10)	N(2)	-47.8(4)
C(4)	C(5)	C(6)	C(7)	179.5(3)	C(10)	N(2)	C(11)	C(13)	-63.7(4)
C(10)	C(5)	C(6)	C(7)	7.2(4)	C(9)	N(2)	C(11)	C(13)	130.7(3)
C(1)	C(6)	C(7)	O(2)	51.6(3)	C(10)	N(2)	C(11)	C(14)	177.3(3)
C(5)	C(6)	C(7)	O(2)	-127.1(3)	C(9)	N(2)	C(11)	C(14)	11.7(4)
C(1)	C(6)	C(7)	C(8)	-122.0(3)	C(10)	N(2)	C(11)	C(12)	58.0(4)
C(5)	C(6)	C(7)	C(8)	59.3(3)	C(9)	N(2)	C(11)	C(12)	-107.6(4)
O(2)	C(7)	C(8)	C(15)	27.8(4)	C(7)	C(8)	C(16)	C(17)	63.5(3)
C(6)	C(7)	C(8)	C(15)	-158.8(2)	C(15)	C(8)	C(16)	C(17)	-56.2(3)
O(2)	C(7)	C(8)	C(9)	153.4(3)	C(9)	C(8)	C(16)	C(17)	-178.6(2)
C(6)	C(7)	C(8)	C(9)	-33.3(3)	C(8)	C(16)	C(17)	C(18)	-170.2(2)
O(2)	C(7)	C(8)	C(16)	-92.1(3)	C(19)	O(3)	C(18)	O(4)	2.0(5)
C(6)	C(7)	C(8)	C(16)	81.3(3)	C(19)	O(3)	C(18)	C(17)	-176.6(3)
C(10)	N(2)	C(9)	C(8)	81.6(3)	C(16)	C(17)	C(18)	O(4)	21.3(5)
C(11)	N(2)	C(9)	C(8)	-112.4(3)	C(16)	C(17)	C(18)	O(3)	-160.1(2)

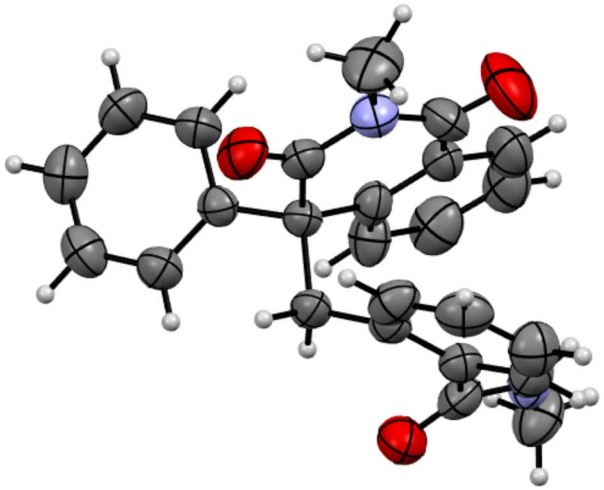
Table S30: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 6ka.

Atom	*x*	*y*	*z*	U(eq)
H(1)	6550.24	5970.01	9535.81	60
H(3)	6864.69	7259.24	10331.12	83
H(4)	4773.15	7345.23	6588.93	73
H(9A)	5239.83	6473.69	3211.1	55
H(9B)	4220.22	6273.78	776.79	55
H(12A)	729.87	7244.83	-2624.07	152
H(12B)	2593.47	7214.01	-1114.89	152
H(12C)	1678.63	7333.25	-15.45	152
H(13A)	-899.55	6651.66	-2560.14	127
H(13B)	-109.74	6732.89	26.31	127
H(13C)	-74.8	6267.84	-833.29	127
H(14A)	715.31	6471.64	-3958.4	145
H(14B)	1672.49	6111.11	-2126.61	145
H(14C)	2579.33	6493.29	-2375.01	145
H(15A)	2109.07	5669.57	768.9	90
H(15B)	3217.28	5278.38	2183.19	90
H(15C)	3336.1	5491.31	297.55	90
H(16A)	6263.67	5690.88	2919.34	54
H(16B)	6873.32	5896.72	5274.26	54
H(17A)	6147.63	5231.78	6220.36	60
H(17B)	5840.44	5033.32	3992.94	60
H(19A)	9998.49	4229.83	7861.19	130
H(19B)	10523.59	4623.76	9524.69	130
H(19C)	10560.58	4663.2	7374.73	130

Crystal structure determination of [6ka]

Crystal Data for $C_{19}H_{24}FNO_4$ (M =349.39 g/mol): monoclinic, space group Cc (no. 9), a = 10.190(3) Å, b = 30.800(10) Å, c = 7.169(2) Å, β = 124.509(4)°, V = 1854.0(10) Å^3, Z = 4, T = 296(2) K, μ(MoKα) = 0.094 mm^{-1}, *Dcalc* = 1.252 g/cm^3, 5763 reflections measured (2.644° ≤ 2Θ ≤ 55.112°), 2851 unique (R_{int} = 0.0263, R_{sigma} = 0.0407) which were used in all calculations. The final R_1 was 0.0408 (I > 2σ(I)) and wR_2 was 0.1109 (all data).

8.5 X-Ray Crystallographic Analysis of Compound 8



CCDC: 2375730

Table S31: Crystal data and structure refinement for 8.

Empirical formula	$C_{21}H_{27}NO_6$
Formula weight	389.43
Temperature/K	296(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.489(4)
b/Å	10.046(5)
c/Å	13.050(6)
α/°	82.159(7)
β/°	81.441(8)
γ/°	70.155(7)
Volume/Å^3	1030.8(9)
Z	2
ρ_{calc}g/cm^3	1.255
μ/mm^{-1}	0.092
F(000)	416.0
Crystal size/mm^3	0.16 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.17 to 54.91
Index ranges	-10 ≤ h ≤ 6, -12 ≤ k ≤ 12, -16 ≤ l ≤ 16
Reflections collected	6419
Independent reflections	4545 [R_{int} = 0.0450, R_{sigma} = 0.1220]
Data/restraints/parameters	4545/3/257
Goodness-of-fit on F^2	1.011
Final R indexes [I>=2σ (I)]	R_1 = 0.0809, wR_2 = 0.1756
Final R indexes [all data]	R_1 = 0.1648, wR_2 = 0.2182
Largest diff. peak/hole / e Å^{-3}	0.62/-0.27

Table S32: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 8. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	2941(3)	2989(3)	668.5(18)	41.2(7)
O2	9257(4)	1662(3)	4400(3)	68.5(10)
O3	8454(4)	-189(3)	4318(2)	61.8(9)
O4	5504(4)	6533(3)	1816(2)	58.1(9)
O5	6620(4)	4940(3)	672.1(19)	51.2(8)
O6	4294(3)	5588(3)	3717.0(18)	40.3(7)
N1	3253(4)	2173(3)	2369(2)	33.6(8)
C1	3973(5)	4653(4)	3104(3)	31.6(9)
C2	2389(5)	5397(4)	2563(3)	32.7(9)
C3	1417(5)	6780(4)	2736(3)	48.1(11)
C4	-34(6)	7463(5)	2266(4)	66.0(14)
C5	-557(6)	6781(5)	1598(4)	60.4(13)
C6	376(5)	5422(4)	1407(3)	48.1(11)
C7	1854(5)	4705(4)	1887(3)	34.5(9)
C8	2741(5)	3216(4)	1601(3)	32.3(9)
C9	2749(5)	257ÅaÅ6(4)	3453(2)	35.9(9)
C10	3678(5)	3426(4)	3893(3)	32.2(9)
C11	5335(5)	2487(4)	4321(3)	35.9(9)
C12	6857(5)	2007(4)	3506(3)	34.4(9)
C13	7128(5)	3285(4)	2846(3)	36.7(9)
C14	5552(4)	4111(3)	2307(3)	29.1(8)
C15	8333(5)	1135(4)	4095(3)	40.1(10)
C16	5847(5)	5335(4)	1587(3)	33.7(9)
C17	2461(5)	4057(4)	4842(3)	47.1(11)
C18	3919(6)	627(4)	2111(3)	45.4(11)
C19	2509(6)	278(4)	1697(4)	64.5(14)
C20	5512(6)	401(4)	1326(3)	59.2(13)
C21	4396(6)	-395(4)	3092(3)	60.3(14)

Table S33: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 8. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	60.7(19)	39.5(15)	24.5(13)	1.8(11)	-7.6(13)	-18.1(14)
O2	63(2)	57(2)	93(2)	27.6(18)	-43(2)	-28.3(18)
O3	65(2)	41.1(17)	75(2)	8.2(15)	-37.7(18)	-5.0(16)
O4	83(2)	36.3(16)	55.3(18)	-6.9(14)	11.6(17)	-26.2(16)
O5	78(2)	44.5(16)	29.9(15)	5.5(12)	-0.1(15)	-24.2(16)
O6	51.1(18)	38.3(15)	35.0(14)	-9.7(12)	-8.0(13)	-15.4(13)
N1	46(2)	28.4(16)	24.9(15)	0.3(13)	-3.6(14)	-12.0(15)
C1	34(2)	32.4(19)	27.9(19)	-6.0(15)	-5.9(16)	-8.5(17)
C2	32(2)	30.4(19)	32.1(19)	-0.8(16)	-4.5(17)	-5.5(17)
C3	42(3)	41(2)	59(3)	-14(2)	-13(2)	-5(2)
C4	51(3)	41(3)	94(4)	-18(3)	-16(3)	8(2)
C5	46(3)	51(3)	78(3)	-5(3)	-24(3)	-1(2)
C6	45(3)	44(2)	58(3)	1(2)	-21(2)	-15(2)
C7	41(2)	33(2)	28.2(19)	3.0(16)	-6.1(17)	-11.4(18)
C8	37(2)	34(2)	27(2)	2.2(16)	-3.8(17)	-15.6(18)
C9	44(2)	39(2)	21.6(18)	-0.4(16)	3.1(17)	-13.3(19)
C10	35(2)	36(2)	22.9(18)	-2.5(15)	-0.8(16)	-9.1(18)
C11	40(2)	43(2)	22.0(18)	3.0(16)	-6.8(16)	-10.0(19)
C12	38(2)	33(2)	26.4(19)	3.3(16)	-7.5(17)	-5.2(18)
C13	35(2)	38(2)	33(2)	2.2(17)	-2.1(17)	-8.1(18)
C14	33(2)	25.8(18)	27.5(18)	1.0(15)	-4.0(16)	-8.5(16)
C15	43(3)	36(2)	38(2)	2.7(18)	-4.1(19)	-9(2)
C16	36(2)	34(2)	31(2)	1.4(17)	-7.4(17)	-12.0(18)
C17	47(3)	60(3)	31(2)	-13.7(19)	5.5(19)	-13(2)
C18	73(3)	25(2)	38(2)	0.3(17)	-10(2)	-14(2)
C19	95(4)	50(3)	65(3)	-1(2)	-25(3)	-39(3)
C20	70(3)	50(3)	46(3)	-14(2)	-4(2)	-1(2)
C21	98(4)	34(2)	46(3)	9.7(19)	-18(3)	-18(2)

Table S34: Bond Lengths for 8.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C8	1.245(4)	C4	C5	1.382(6)
O2	C15	1.219(5)	C5	C6	1.361(5)
O3	C15	1.294(5)	C6	C7	1.408(5)
O4	C16	1.207(4)	C7	C8	1.499(5)
O5	C16	1.317(4)	C9	C10	1.551(5)
O6	C1	1.429(4)	C10	C11	1.539(5)
N1	C8	1.351(4)	C10	C17	1.547(5)
N1	C9	1.486(4)	C11	C12	1.530(5)
N1	C18	1.529(4)	C12	C13	1.511(5)
C1	C2	1.523(5)	C12	C15	1.512(5)
C1	C10	1.558(5)	C13	C14	1.530(5)
C1	C14	1.555(5)	C14	C16	1.510(5)
C2	C3	1.384(5)	C18	C19	1.542(6)
C2	C7	1.403(5)	C18	C20	1.540(6)
C3	C4	1.379(6)	C18	C21	1.540(5)

Table S35: Bond Angles for 8.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	N1	C9	116.6(3)	C11	C10	C9	113.6(3)
C8	N1	C18	119.1(3)	C11	C10	C17	106.1(3)
C9	N1	C18	122.5(3)	C17	C10	C1	109.5(3)
O6	C1	C2	111.2(3)	C17	C10	C9	103.5(3)
O6	C1	C10	105.3(3)	C12	C11	C10	115.6(3)
O6	C1	C14	107.7(3)	C13	C12	C11	109.9(3)
C2	C1	C10	108.9(3)	C13	C12	C15	113.7(3)
C2	C1	C14	111.6(3)	C15	C12	C11	106.6(3)
C14	C1	C10	112.0(3)	C12	C13	C14	109.5(3)
C3	C2	C1	120.7(3)	C13	C14	C1	111.9(3)
C3	C2	C7	117.8(3)	C16	C14	C1	110.6(3)
C7	C2	C1	121.5(3)	C16	C14	C13	110.1(3)
C4	C3	C2	121.5(4)	O2	C15	O3	122.8(4)
C3	C4	C5	120.7(4)	O2	C15	C12	122.4(4)
C6	C5	C4	119.4(4)	O3	C15	C12	114.5(4)
C5	C6	C7	120.7(4)	O4	C16	O5	122.4(3)
C2	C7	C6	120.0(3)	O4	C16	C14	125.3(3)
C2	C7	C8	125.5(3)	O5	C16	C14	112.2(3)
C6	C7	C8	114.5(3)	N1	C18	C19	108.8(3)
O1	C8	N1	122.8(3)	N1	C18	C20	109.3(3)
O1	C8	C7	118.6(3)	N1	C18	C21	111.0(3)
N1	C8	C7	118.6(3)	C20	C18	C19	112.7(3)
N1	C9	C10	119.4(3)	C21	C18	C19	107.0(3)
C9	C10	C1	112.9(3)	C21	C18	C20	108.1(4)
C11	C10	C1	110.7(3)				

Table S36: Torsion Angles for 8.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O6	C1	C2	C3	-3.2(5)	C8	N1	C18	C19	-61.2(4)
O6	C1	C2	C7	177.7(3)	C8	N1	C18	C20	62.2(5)
O6	C1	C10	C9	161.1(3)	C8	N1	C18	C21	-178.7(4)
O6	C1	C10	C11	-70.3(3)	C9	N1	C8	O1	-172.9(4)
O6	C1	C10	C17	46.4(4)	C9	N1	C8	C7	5.5(5)
O6	C1	C14	C13	61.1(4)	C9	N1	C18	C19	103.5(4)
O6	C1	C14	C16	-62.0(3)	C9	N1	C18	C20	-133.1(4)
N1	C9	C10	C1	43.4(4)	C9	N1	C18	C21	-14.0(5)
N1	C9	C10	C11	-83.6(4)	C9	C10	C11	C12	79.9(4)
N1	C9	C10	C17	161.7(3)	C10	C1	C2	C3	112.4(4)
C1	C2	C3	C4	-179.0(4)	C10	C1	C2	C7	-66.8(4)
C1	C2	C7	C6	179.5(3)	C10	C1	C14	C13	-54.2(4)
C1	C2	C7	C8	-1.1(6)	C10	C1	C14	C16	-177.3(3)
C1	C10	C11	C12	-48.3(4)	C10	C11	C12	C13	55.2(4)
C1	C14	C16	O4	31.2(5)	C10	C11	C12	C15	178.8(3)
C1	C14	C16	O5	-152.1(3)	C11	C12	C13	C14	-59.2(4)
C2	C1	C10	C9	41.8(4)	C11	C12	C15	O2	-90.1(5)
C2	C1	C10	C11	170.4(3)	C11	C12	C15	O3	84.8(4)
C2	C1	C10	C17	-72.9(4)	C12	C13	C14	C1	60.4(4)
C2	C1	C14	C13	-176.6(3)	C12	C13	C14	C16	-176.2(3)
C2	C1	C14	C16	60.3(4)	C13	C12	C15	O2	31.2(5)
C2	C3	C4	C5	-0.4(7)	C13	C12	C15	O3	-154.0(3)
C2	C7	C8	O1	-134.1(4)	C13	C14	C16	O4	-92.9(5)
C2	C7	C8	N1	47.5(5)	C13	C14	C16	O5	83.7(4)
C3	C2	C7	C6	0.3(5)	C14	C1	C2	C3	-123.5(4)
C3	C2	C7	C8	179.8(3)	C14	C1	C2	C7	57.3(4)
C3	C4	C5	C6	0.1(7)	C14	C1	C10	C9	-82.1(4)
C4	C5	C6	C7	0.4(7)	C14	C1	C10	C11	46.5(4)
C5	C6	C7	C2	-0.6(6)	C14	C1	C10	C17	163.2(3)
C5	C6	C7	C8	179.9(4)	C15	C12	C13	C14	-178.6(3)
C6	C7	C8	O1	45.5(5)	C17	C10	C11	C12	-167.1(3)
C6	C7	C8	N1	-133.0(4)	C18	N1	C8	O1	-7.4(6)
C7	C2	C3	C4	0.2(6)	C18	N1	C8	C7	171.0(3)
C8	N1	C9	C10	-75.7(4)	C18	N1	C9	C10	119.3(4)

Table S37: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 8.

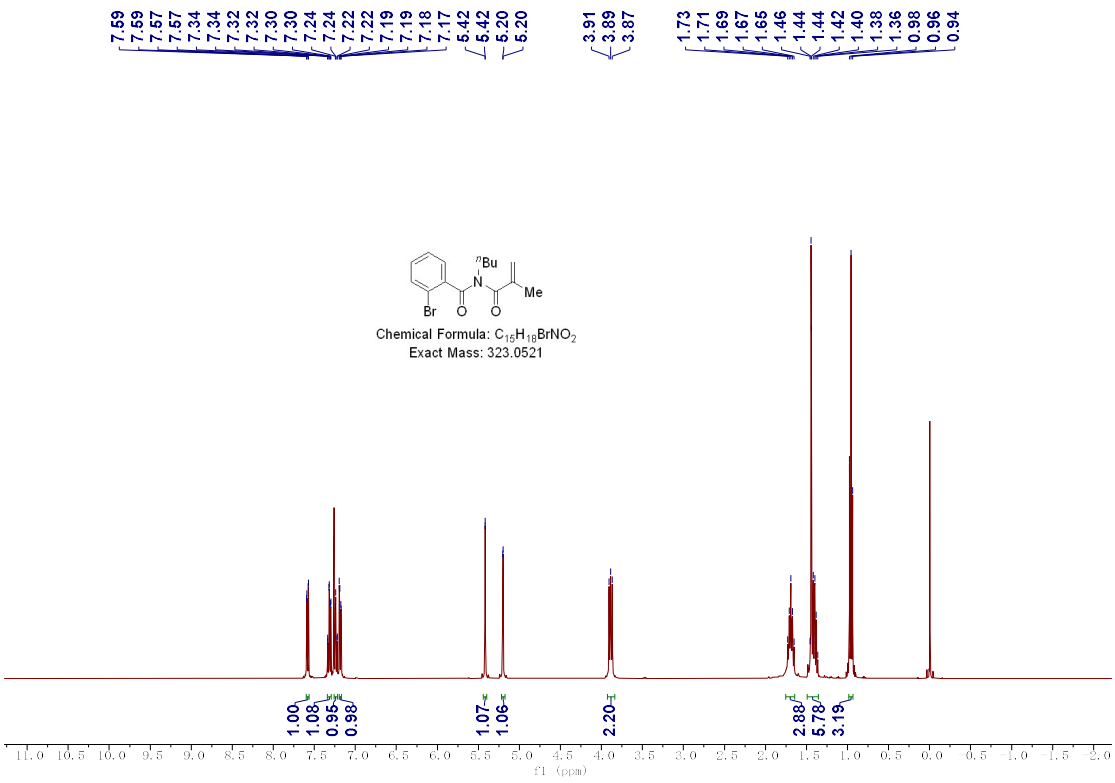
Atom	*x*	*y*	*z*	U(eq)
H3	1749.41	7260.57	3179.98	58
H4	-667.84	8390.52	2399.63	79
H5	-1535.39	7246.68	1281.85	72
H6	32.07	4961.51	954.6	58
H9A	2864.66	1708.48	3908.62	43
H9B	1559.75	3128.71	3508.41	43
H11A	5606.01	3006.73	4805.65	43
H11B	5150.81	1648.34	4710.1	43
H12	6637.16	1398.08	3056.4	41
H13A	8090.28	2977.55	2327.96	44
H13B	7356.61	3893.41	3279.92	44
H14	5338.2	3468.19	1884.28	35
H17A	2201.45	3307.31	5297.64	71
H17B	1442.4	4727.35	4608.46	71
H17C	2985.6	4529.53	5209.55	71
H19A	2886.2	-710.38	1580.65	97
H19B	2233.36	847.04	1054.8	97
H19C	1528.07	478.62	2198.67	97
H20A	5934.89	-570.29	1164.13	89
H20B	6355.29	617.72	1622.71	89
H20C	5237.82	1015.67	700.99	89
H21A	4891.2	-1351.56	2902.66	90
H21B	3402.69	-323.84	3572.06	90
H21C	5189.99	-145.82	3414.52	90
H3D	9315.91	-595.73	4683.68	72
H5D	6516.33	5713.53	280.11	72
H6D	4470.41	6218.2	3292.41	72

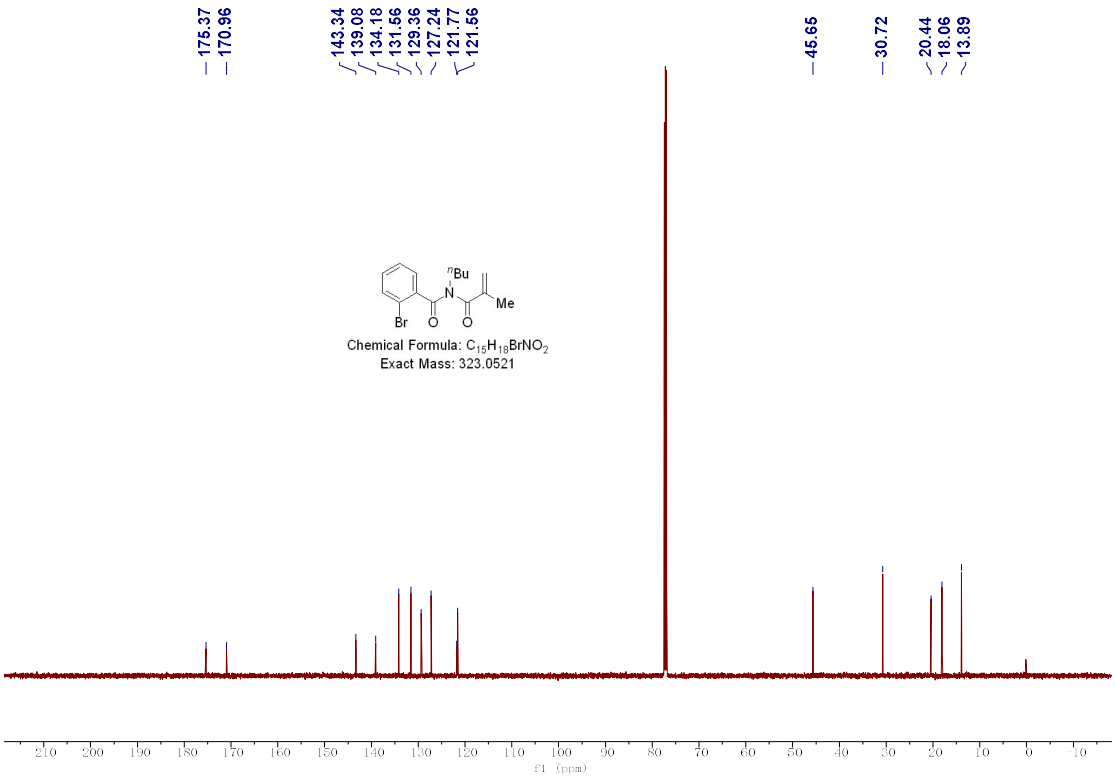
Crystal structure determination of [8]

Crystal Data for $C_{21}H_{27}NO_6$ (M =389.43 g/mol): triclinic, space group P-1 (no. 2), a = 8.489(4) Å, b = 10.046(5) Å, c = 13.050(6) Å, α = 82.159(7)°, β = 81.441(8)°, γ = 70.155(7)°, V = 1030.8(9) Å^3, Z = 2, T = 296(2) K, μ(MoKα) = 0.092 mm^{-1}, *Dcalc* = 1.255 g/cm^3, 6419 reflections measured (3.17° ≤ 2Θ ≤ 54.91°), 4545 unique (R_{int} = 0.0450, R_{sigma} = 0.1220) which were used in all calculations. The final R_1 was 0.0809 (I > 2σ(I)) and wR_2 was 0.2182 (all data).

9. NMR Spectra

1a





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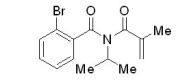
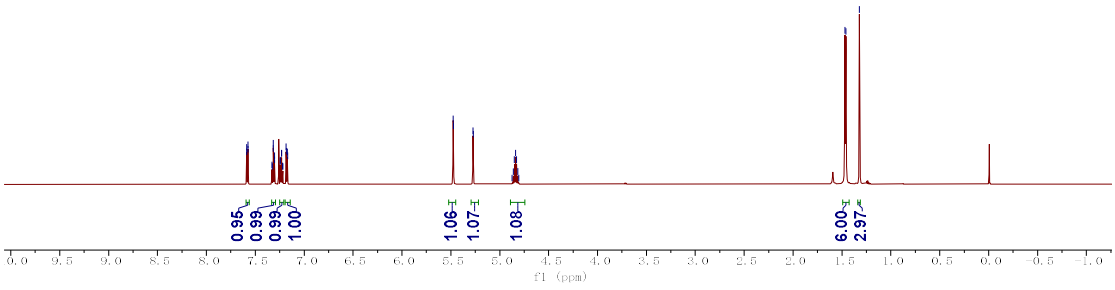
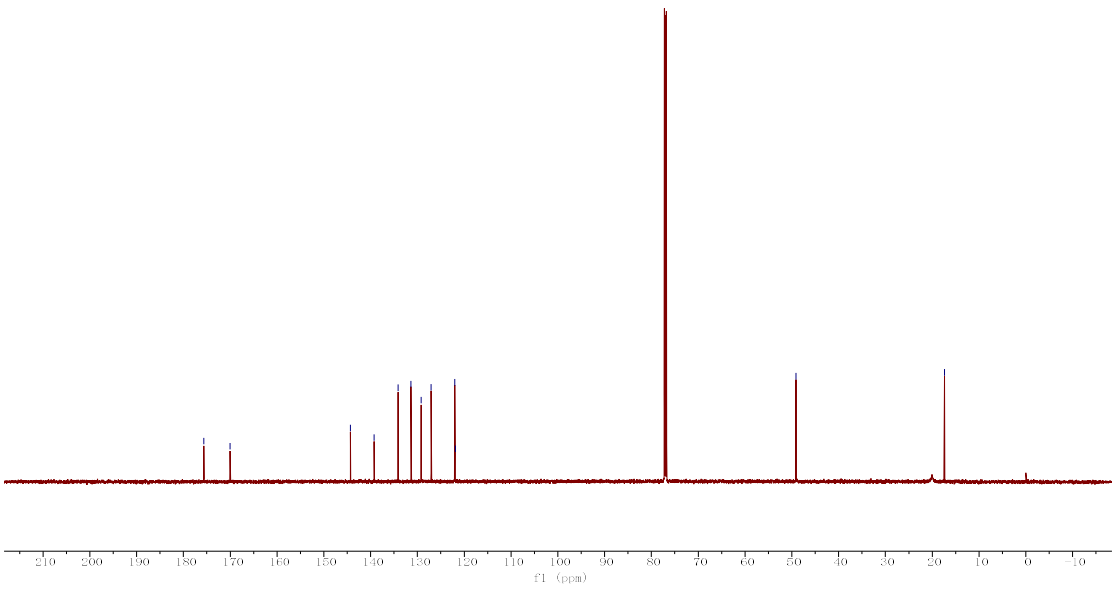


Chemical Formula: $C_{14}H_{16}BrNO_2$
Exact Mass: 309.0364





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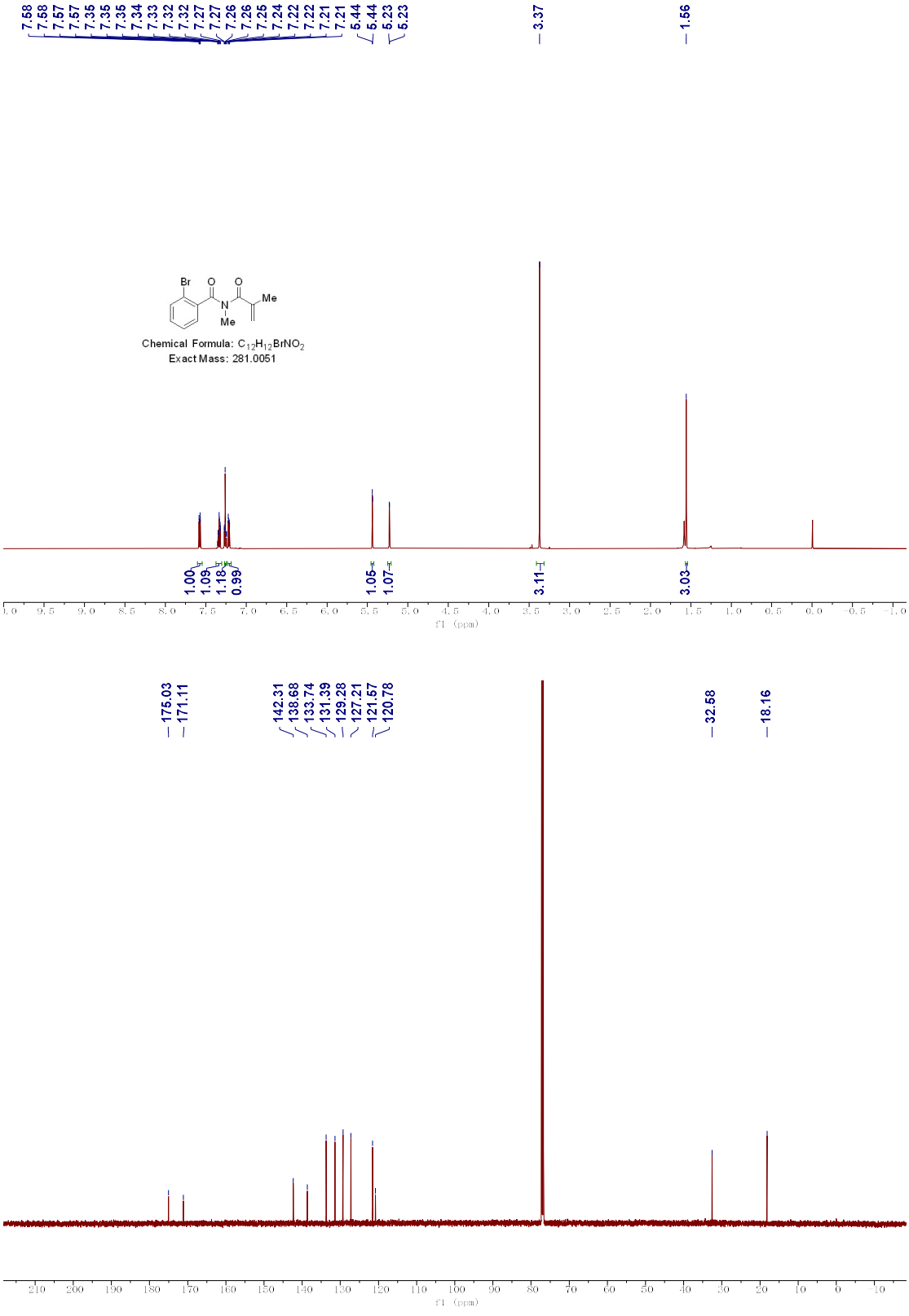
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7.21
7.21
5.44
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5.23
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Me
Me
Me
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3.11
3.03
f1 (ppm)
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171.11
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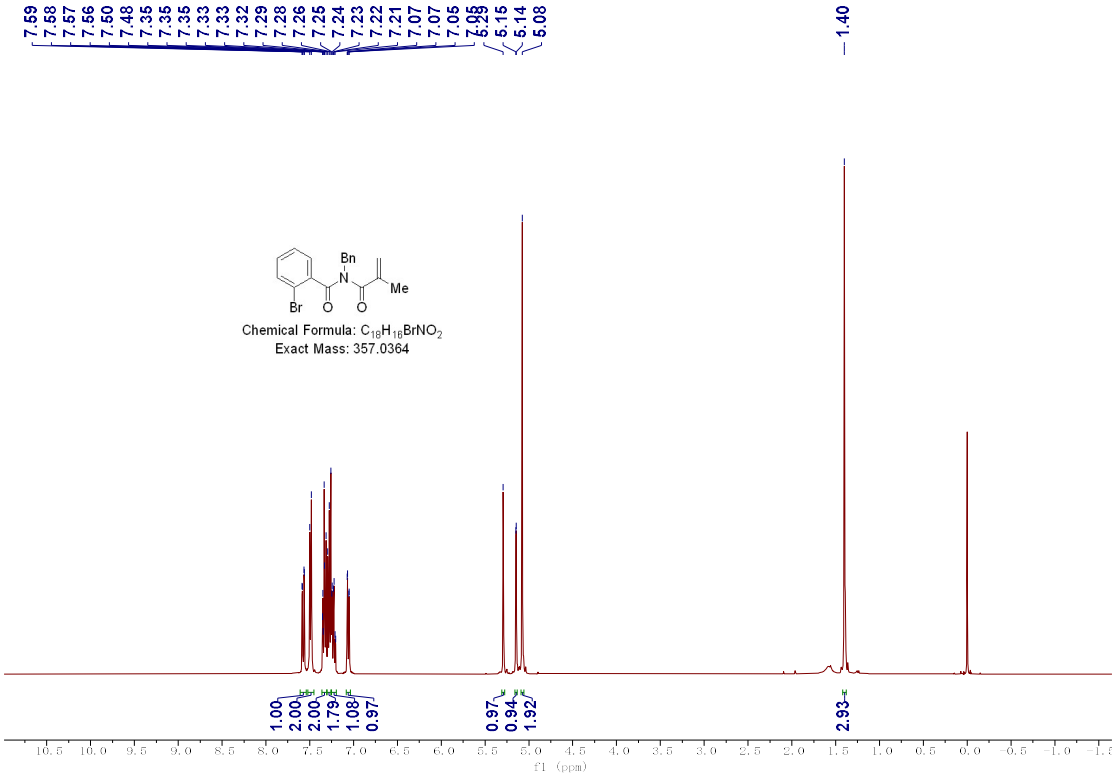
f1 (ppm)

1d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7.23
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7.07
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Me
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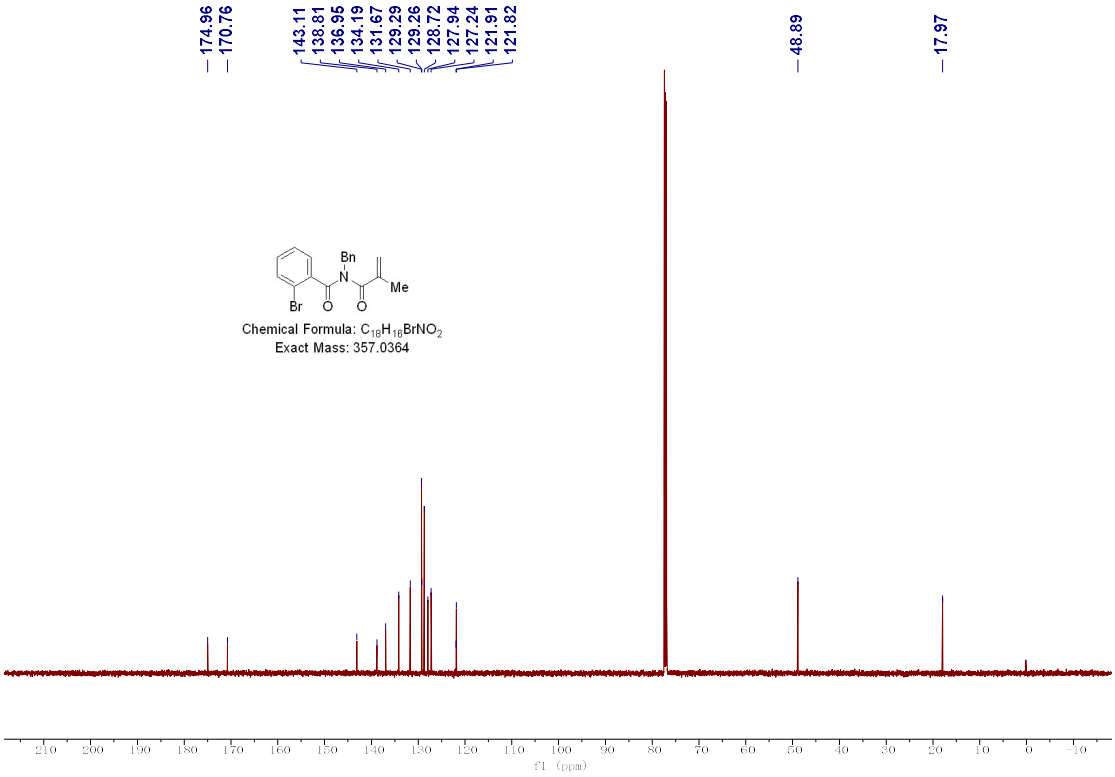
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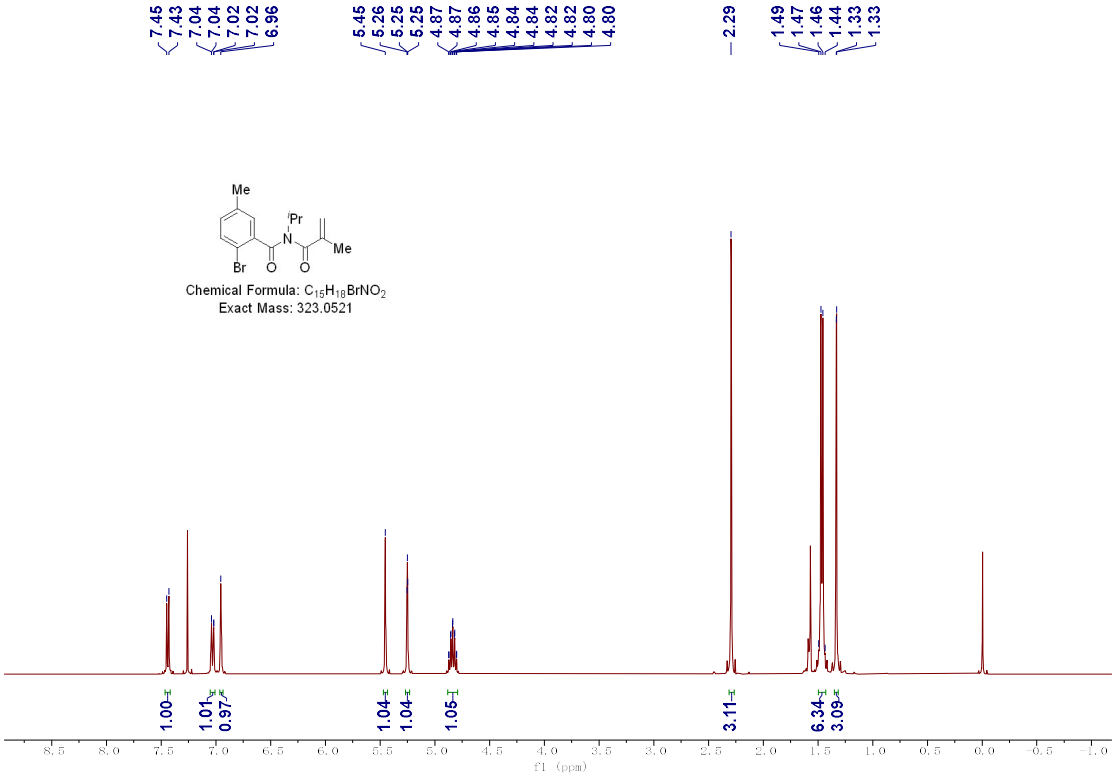
Exact Mass: 357.0364
f1 (ppm)

1e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4.86
4.85
4.84
4.84
4.82
4.82
4.80
4.80
2.29
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1.47
1.46
1.44
1.33
1.33
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Pr
N
Me
Br
O
O
Chemical Formula: C15H18BrNO2
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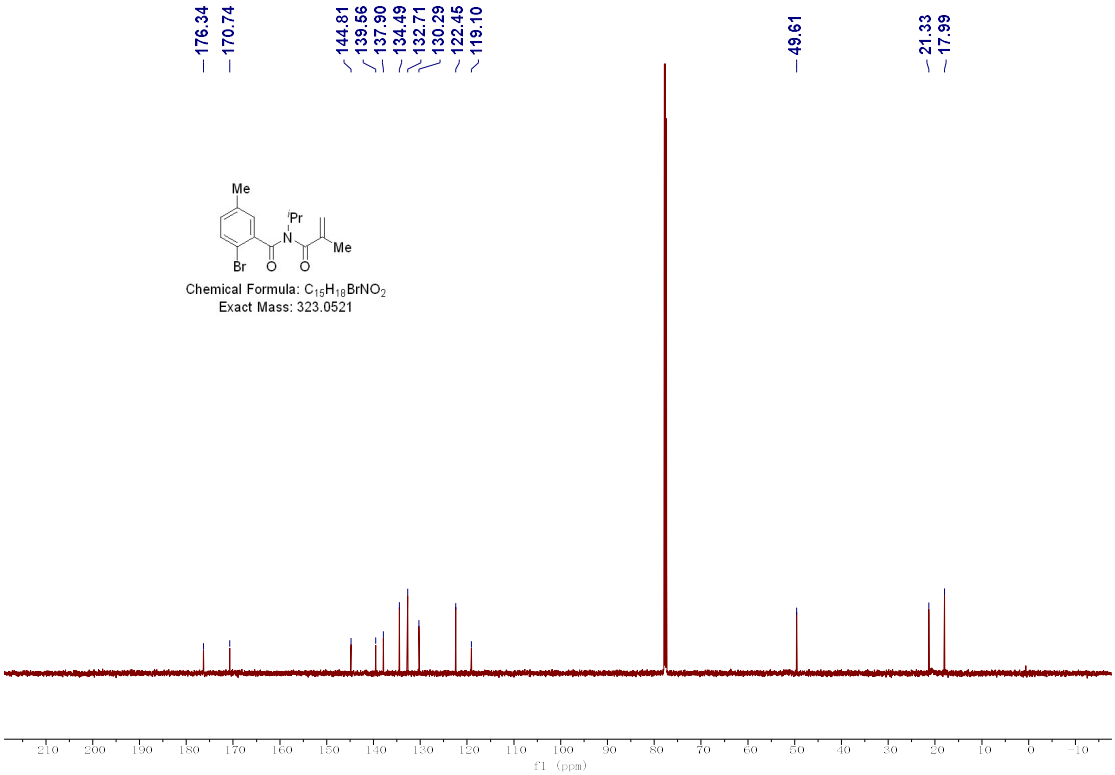
f1 (ppm)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49.61
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17.99
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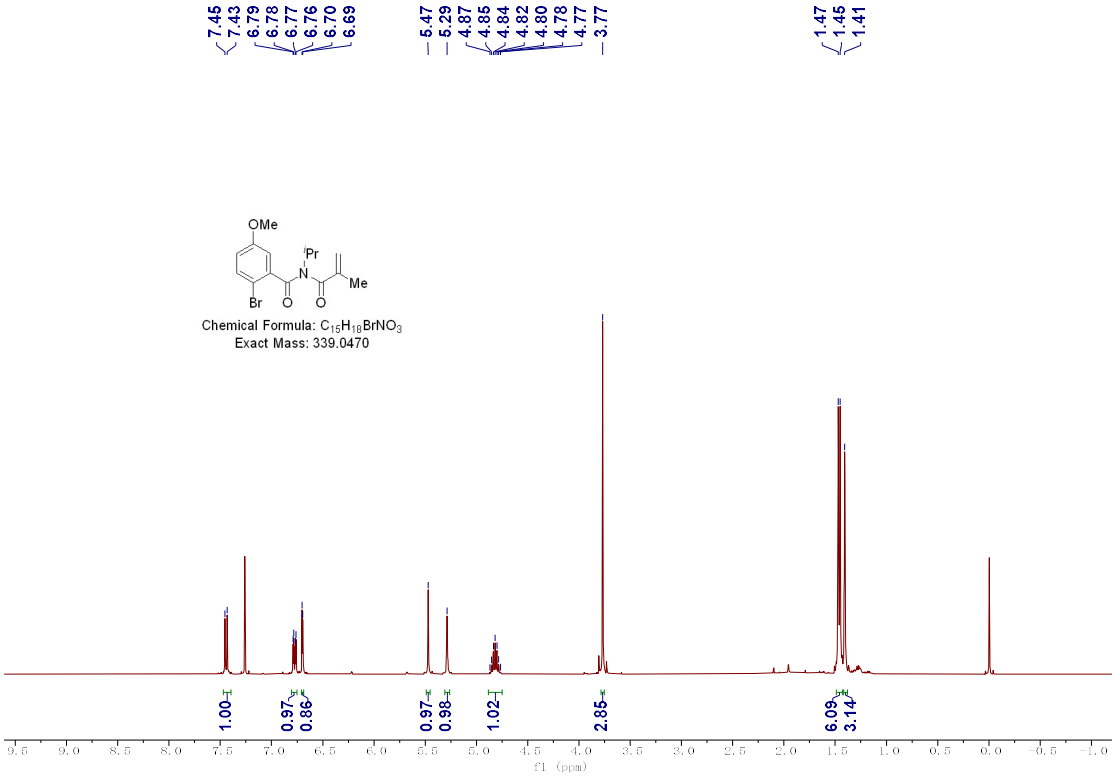
Me
Br
O
O
Chemical Formula: C15H18BrNO2
Exact Mass: 323.0521
f1 (ppm)

1f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Me
Br
O
O
Chemical Formula: C15H18BrNO3
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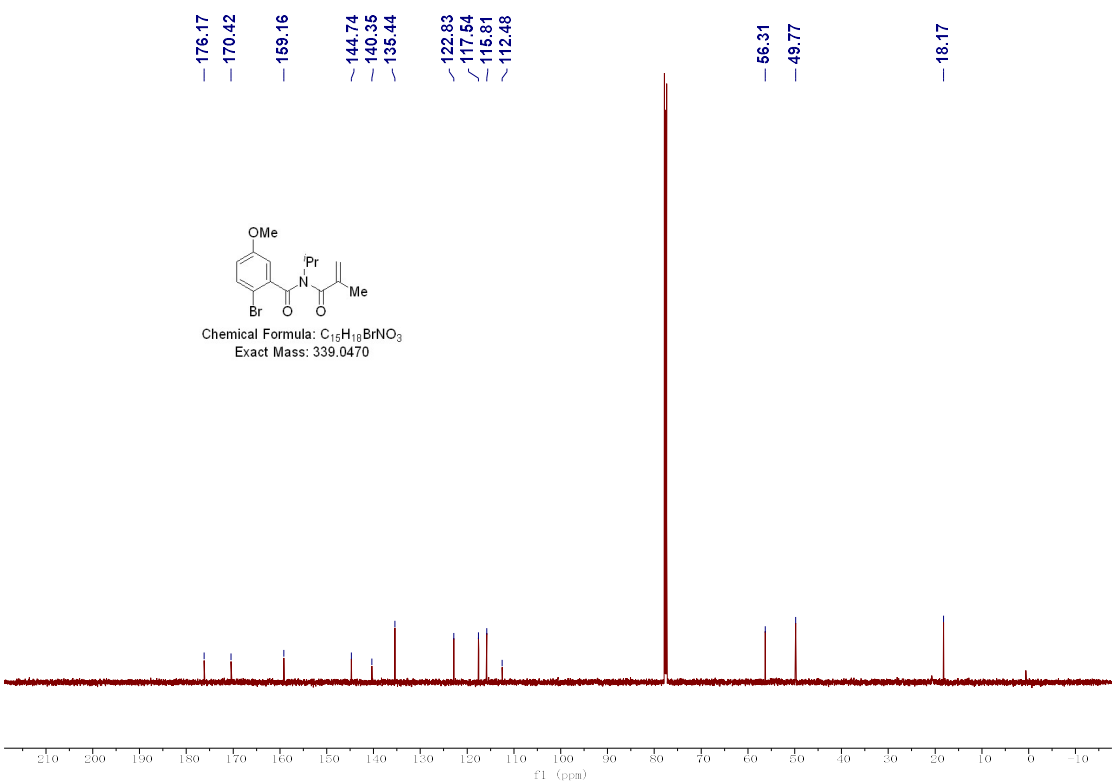
f1 (ppm)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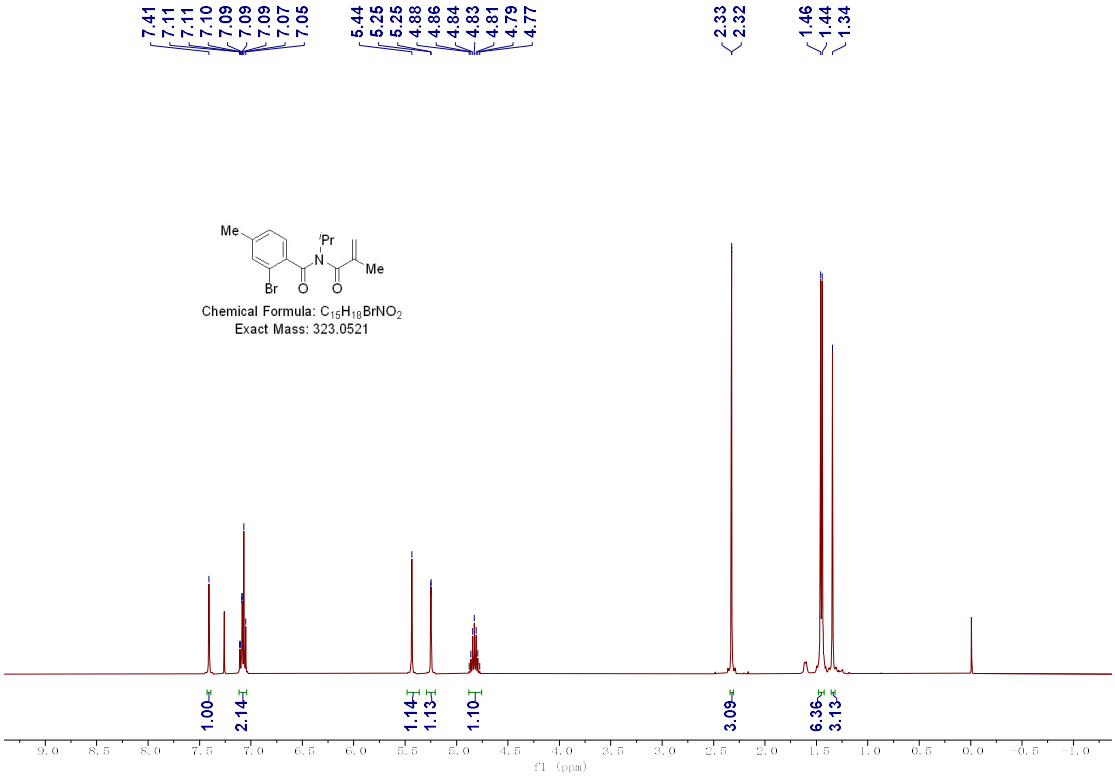
Me
Br
O
O
Chemical Formula: C15H18BrNO3
Exact Mass: 339.0470
f1 (ppm)

1g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4.84
4.83
4.81
4.79
4.77
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2.32
1.46
1.44
1.34
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iPr
N
Me
Br
O
O
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1.10
3.09
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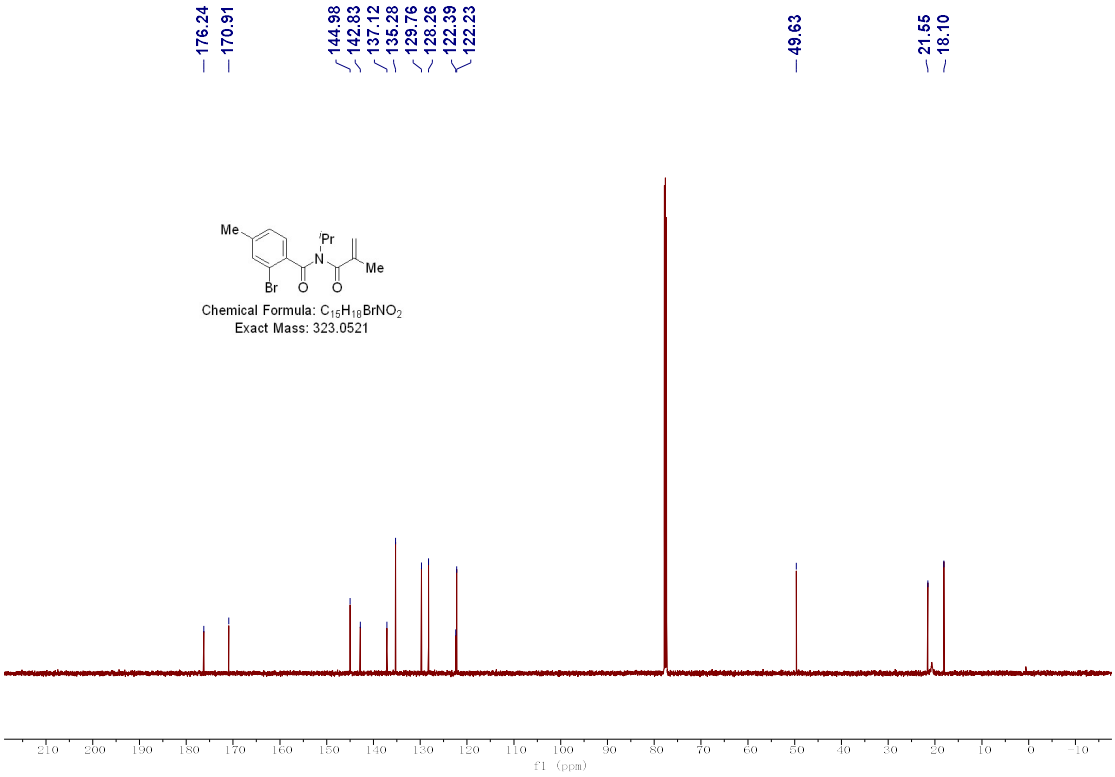
f1 (ppm)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122.23
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21.55
18.10
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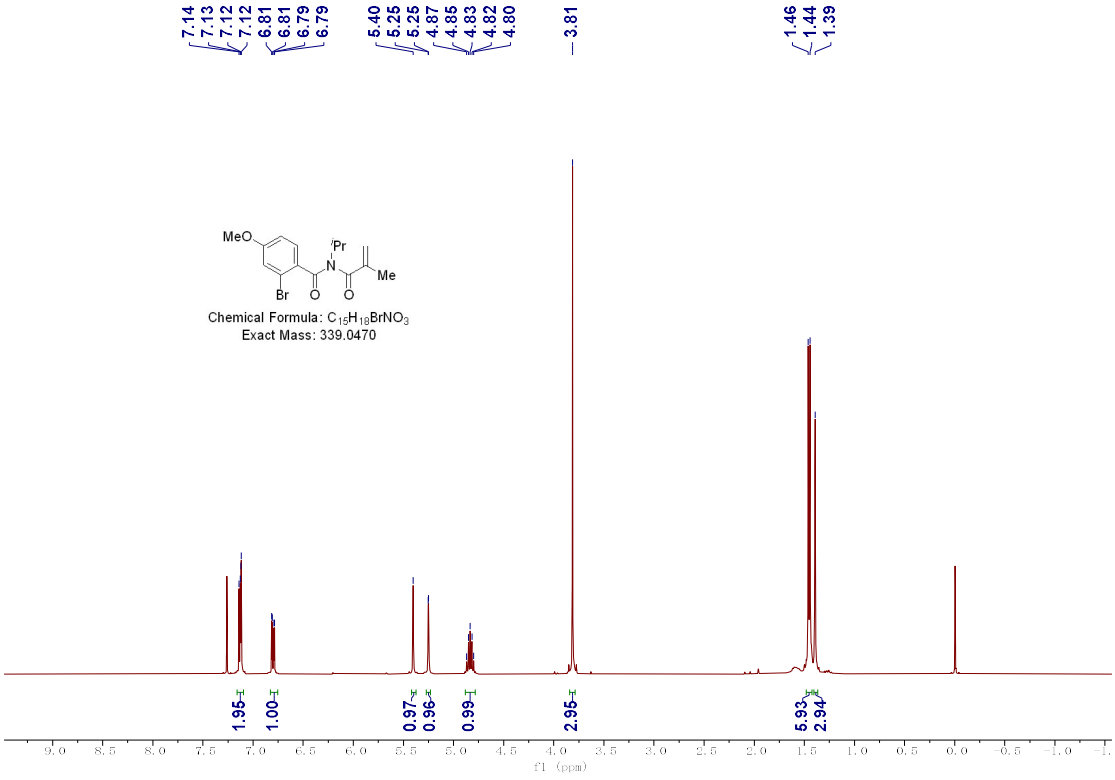
iPr
N
Me
Br
O
O
Chemical Formula: C15H18BrNO2
Exact Mass: 323.0521
f1 (ppm)

1h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5.25
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4.83
4.82
4.80
3.81
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1.44
1.39
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Br
N
/Pr
Me
O
O
Chemical Formula: C15H18BrNO3
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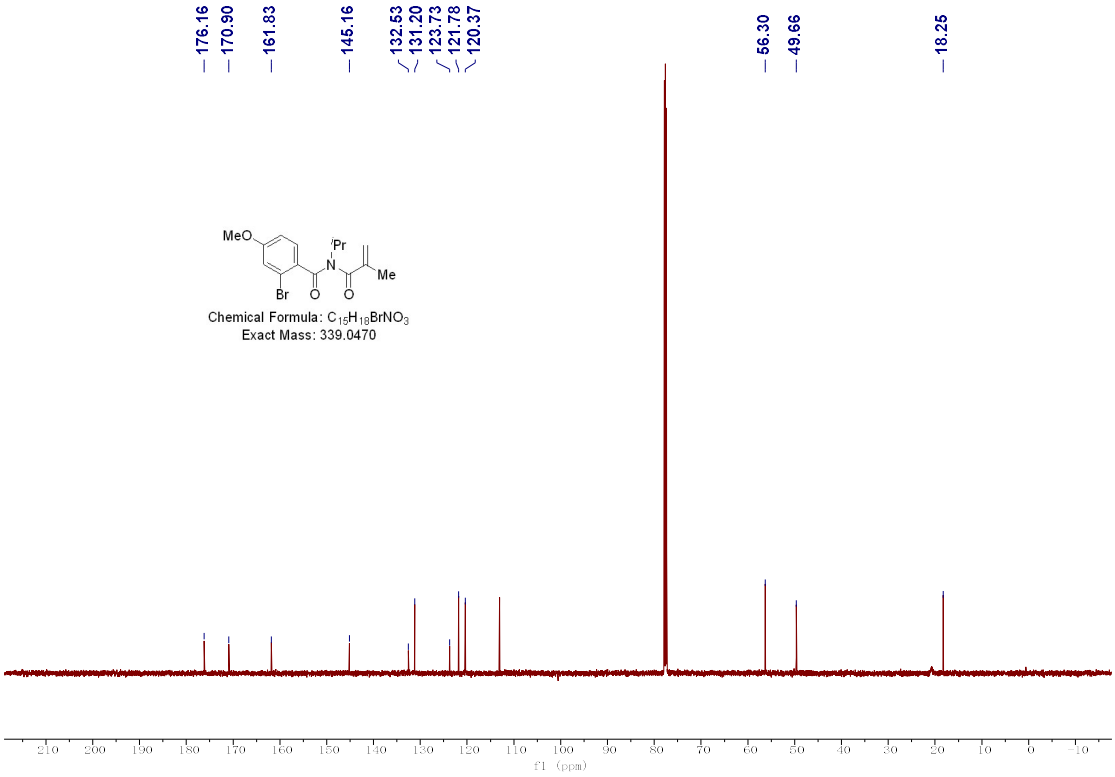
f1 (ppm)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O
O
Chemical Formula: C15H18BrNO3
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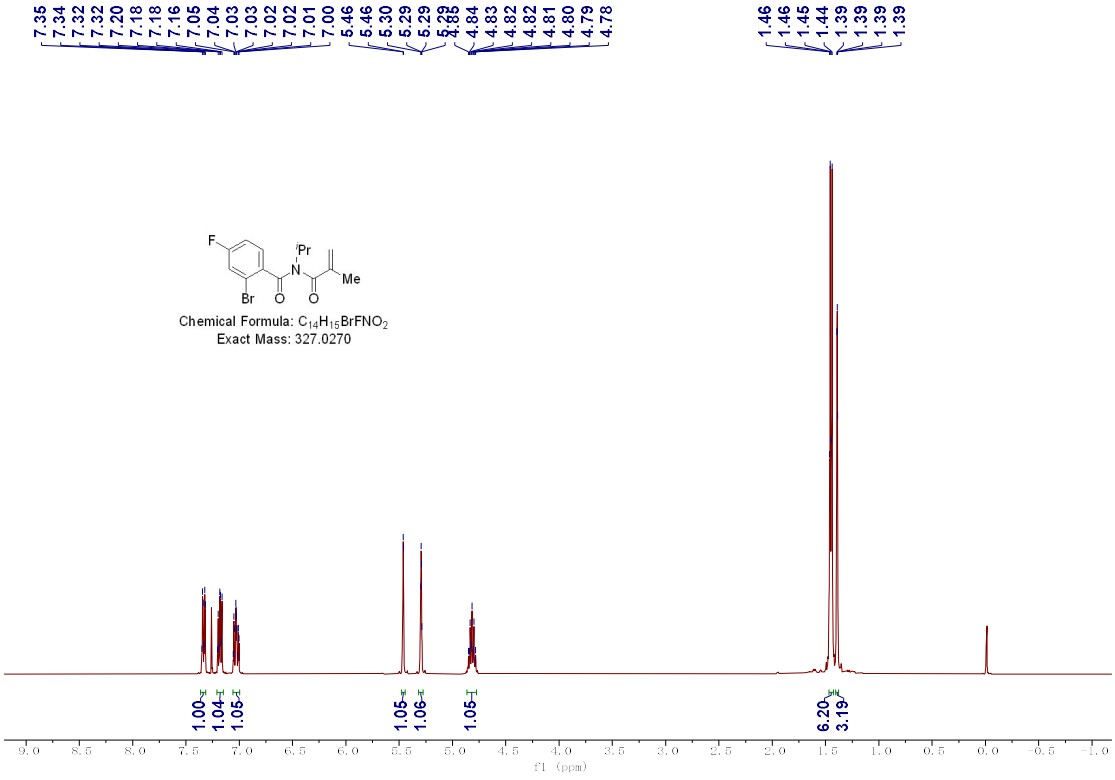
f1 (ppm)

1i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4.81
4.80
4.79
4.78
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1.46
1.45
1.44
1.39
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N
Me
Br
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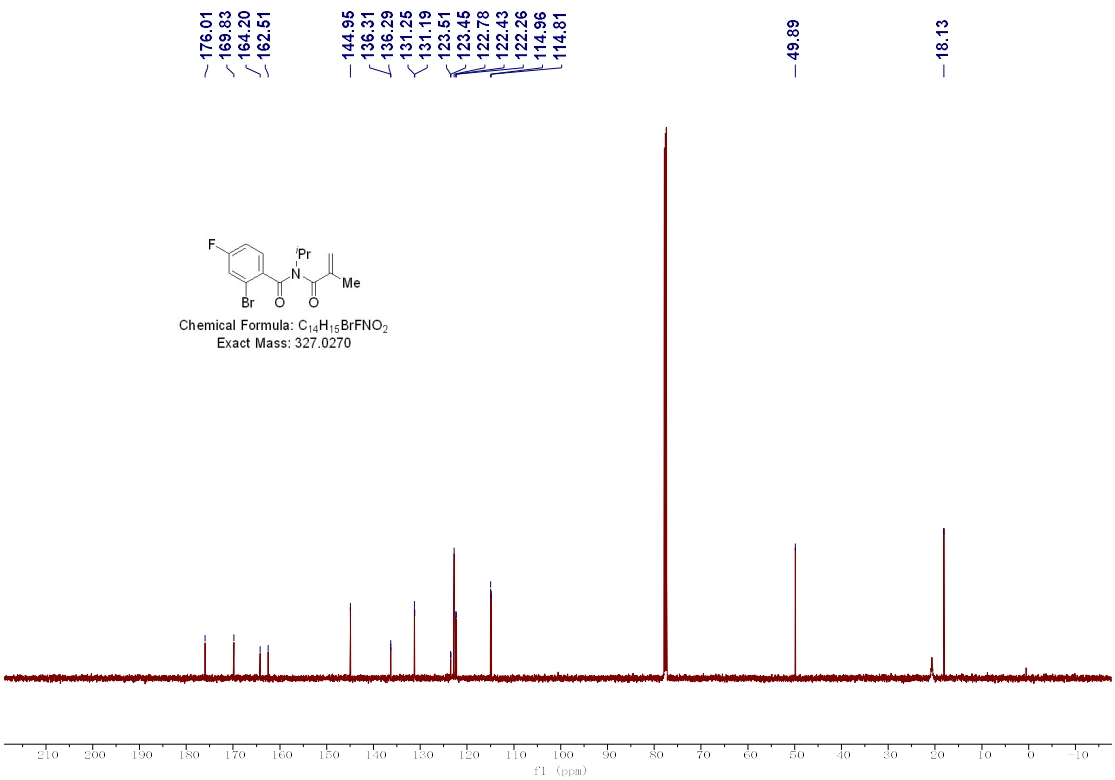
f1 (ppm)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122.43
122.26
114.96
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N
Me
Br
O
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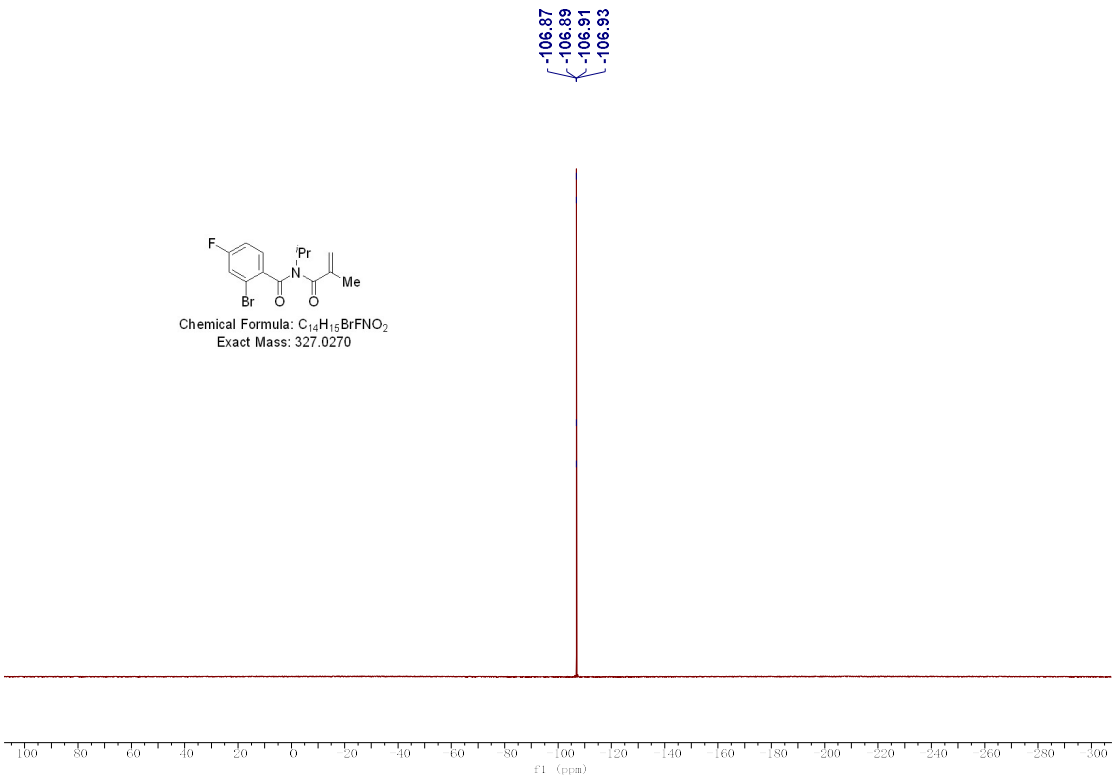
f1 (ppm)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60
40
20
0
-20
-40
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-140
-160
-180
-200
-220
-240
-260
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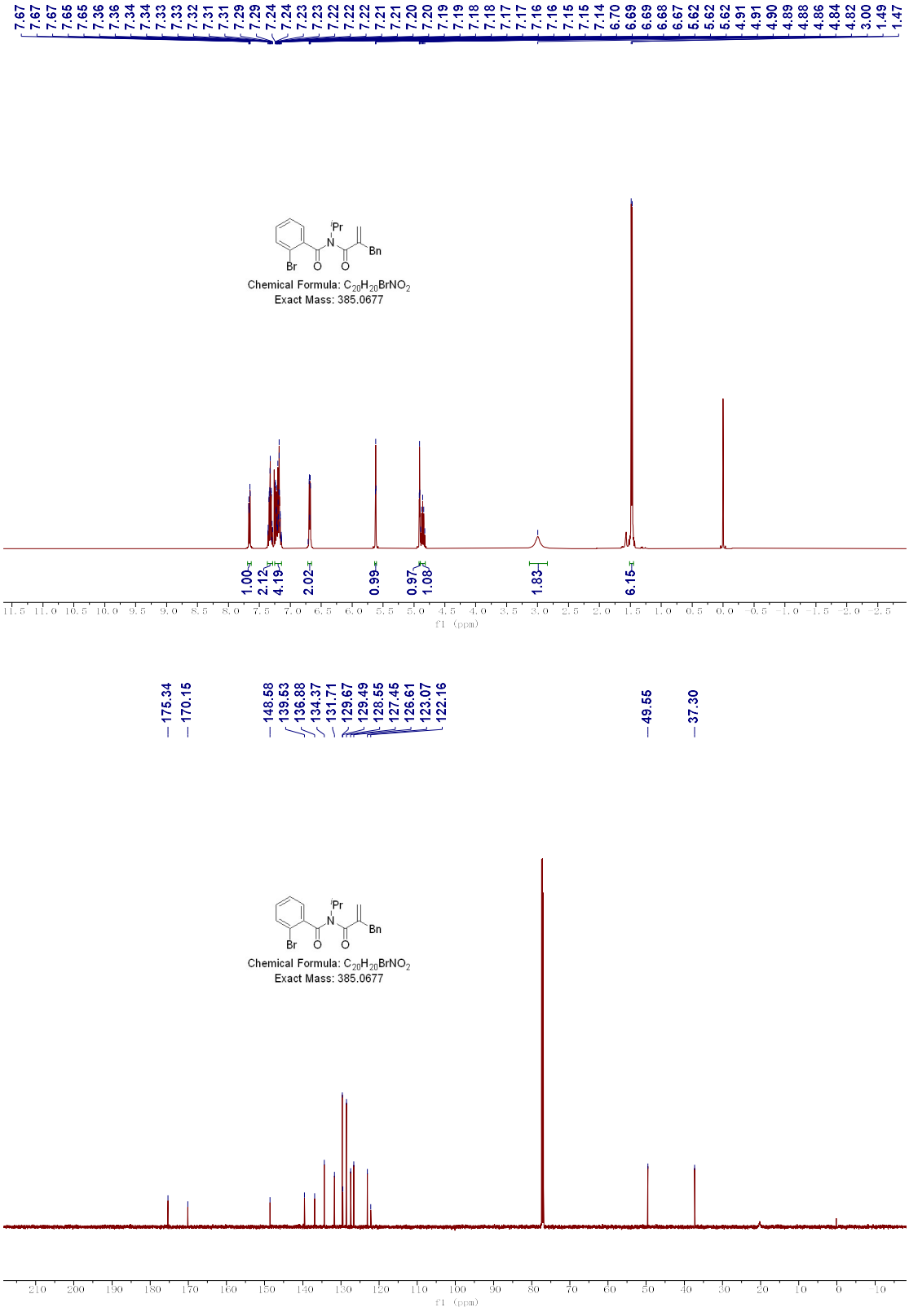
-300
f1 (ppm)

1j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iPr
N
Br
O
O
Bn
Chemical Formula: C20H20BrNO2
Exact Mass: 385.0677
1.00 2.12 4.19 2.02 0.99 0.97 1.08 1.83 6.15
f1 (ppm)
175.34 170.15 148.58 139.53 136.88 134.37 131.71 129.67 129.49 128.55 127.45 126.61 123.07 122.16 49.55 37.30
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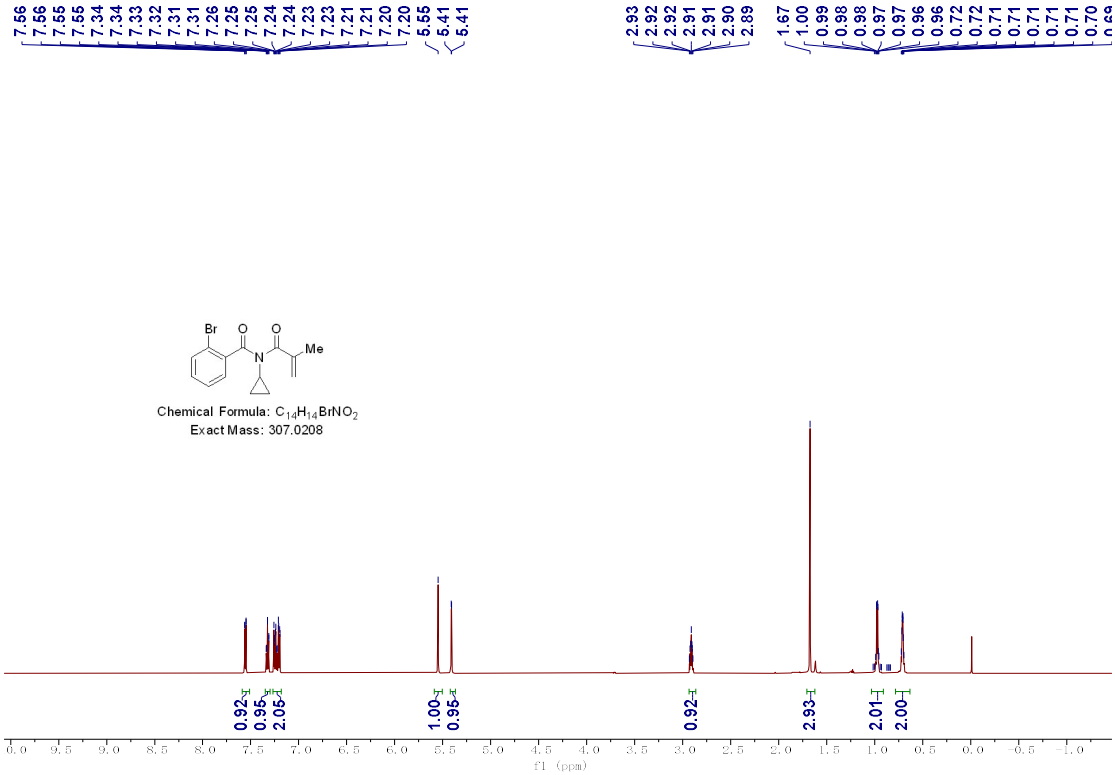
Br
O
O
Bn
Chemical Formula: C20H20BrNO2
Exact Mass: 385.0677
f1 (ppm)

1k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7.21
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5.41
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2.92
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2.90
2.89
1.67
1.00
0.99
0.98
0.98
0.97
0.97
0.96
0.96
0.72
0.72
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0.71
0.71
0.71
0.71
0.70
Br
O
O
N
Me
Chemical Formula: C14H14BrNO2
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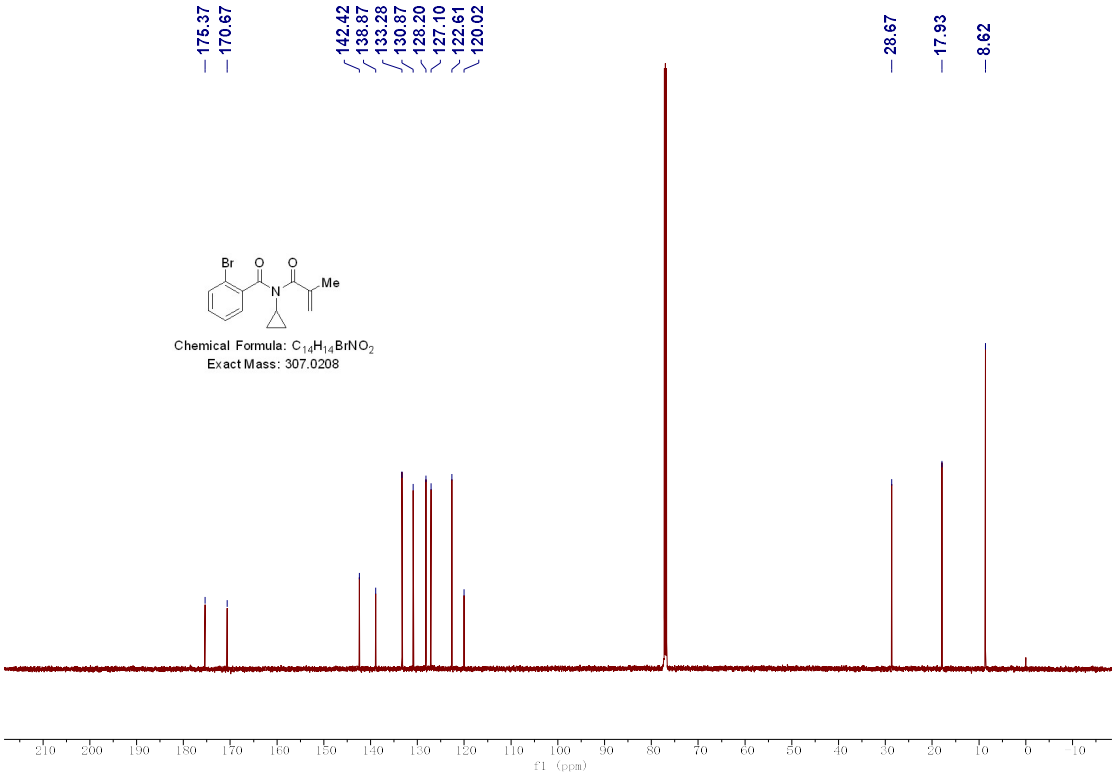
2.00
f1 (ppm)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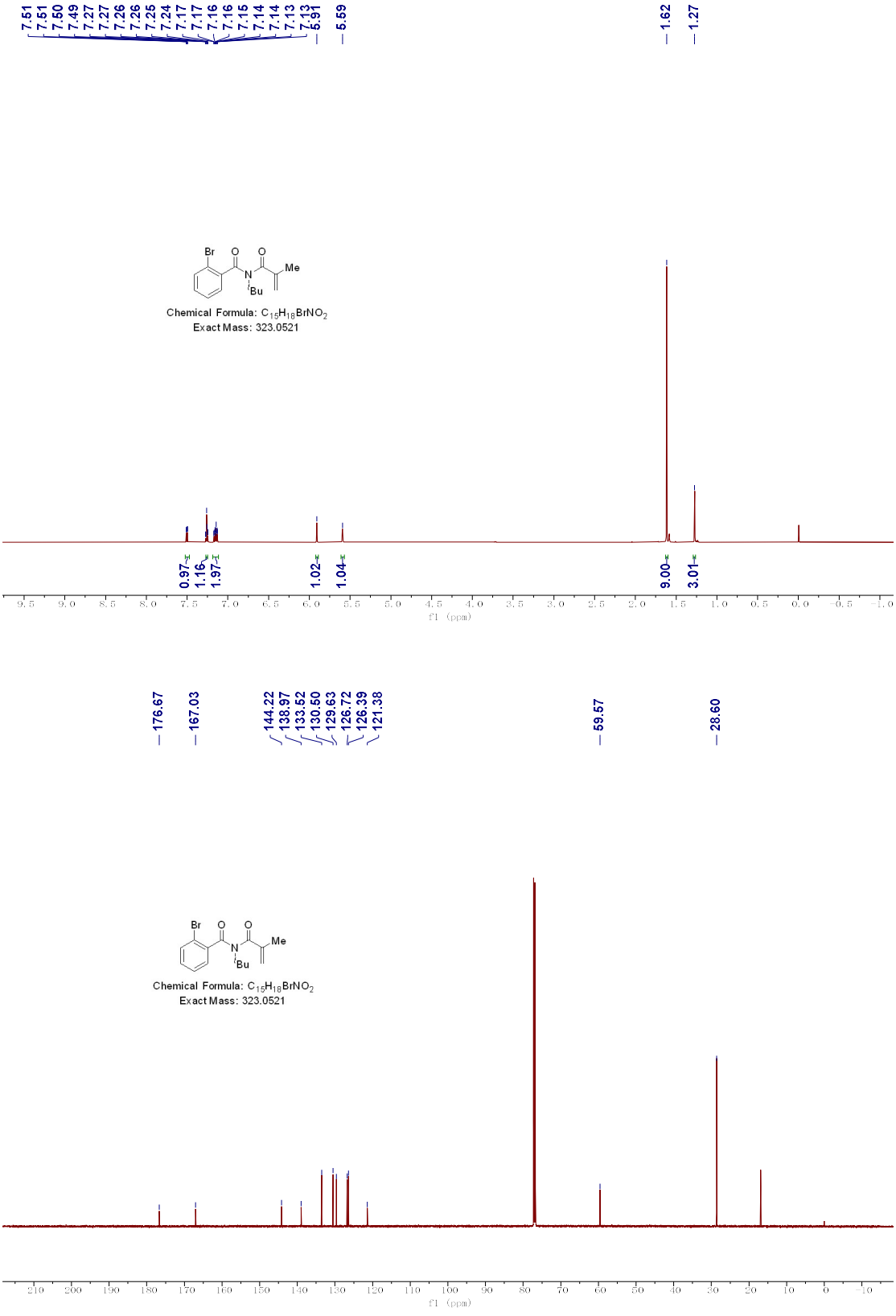
Chemical Formula: C14H14BrNO2
Exact Mass: 307.0208
f1 (ppm)

1l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6.91
5.59
1.62
1.27
Br
O
O
N
Me
tBu
Chemical Formula: C15H18BrNO2
Exact Mass: 323.0521
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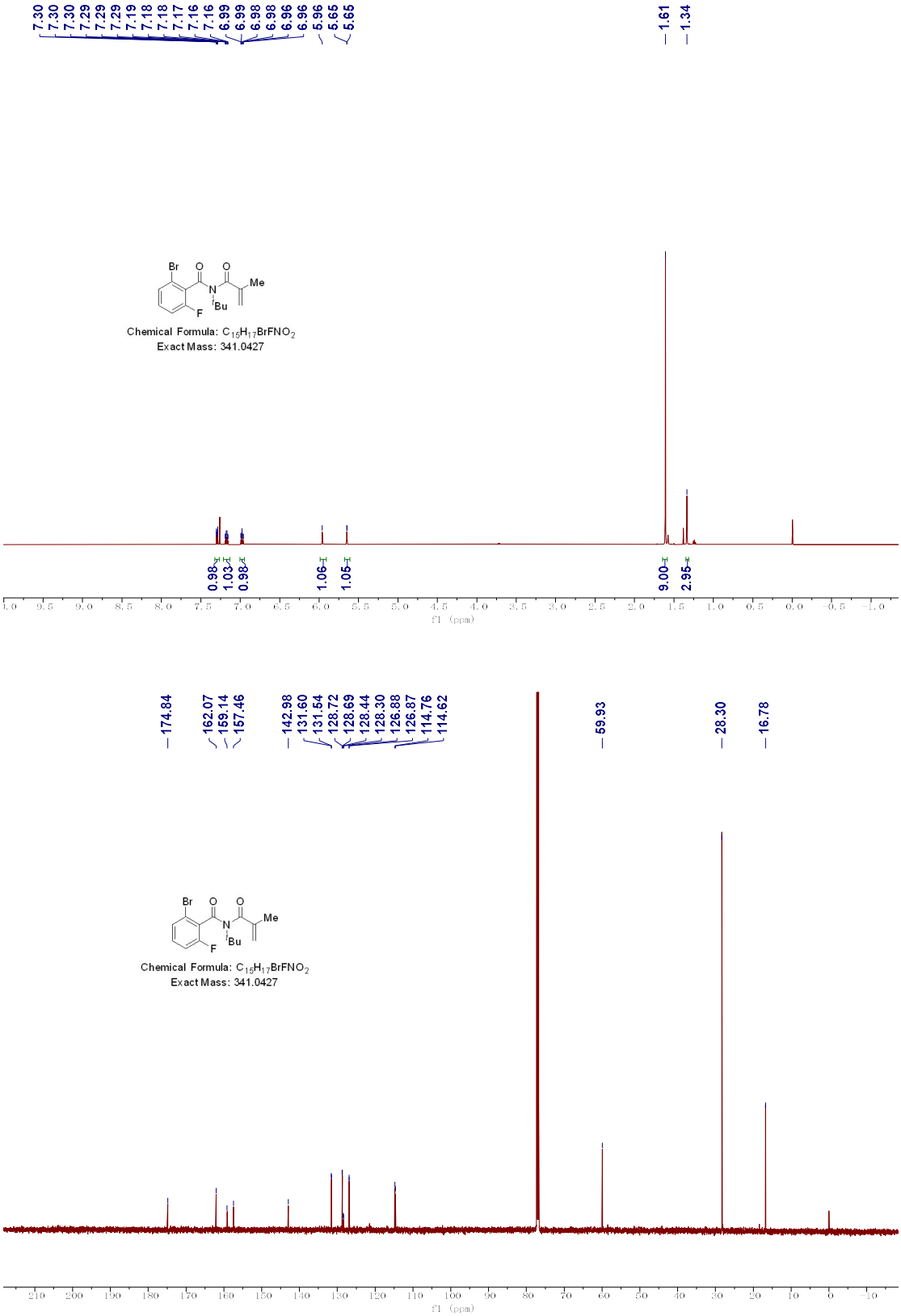
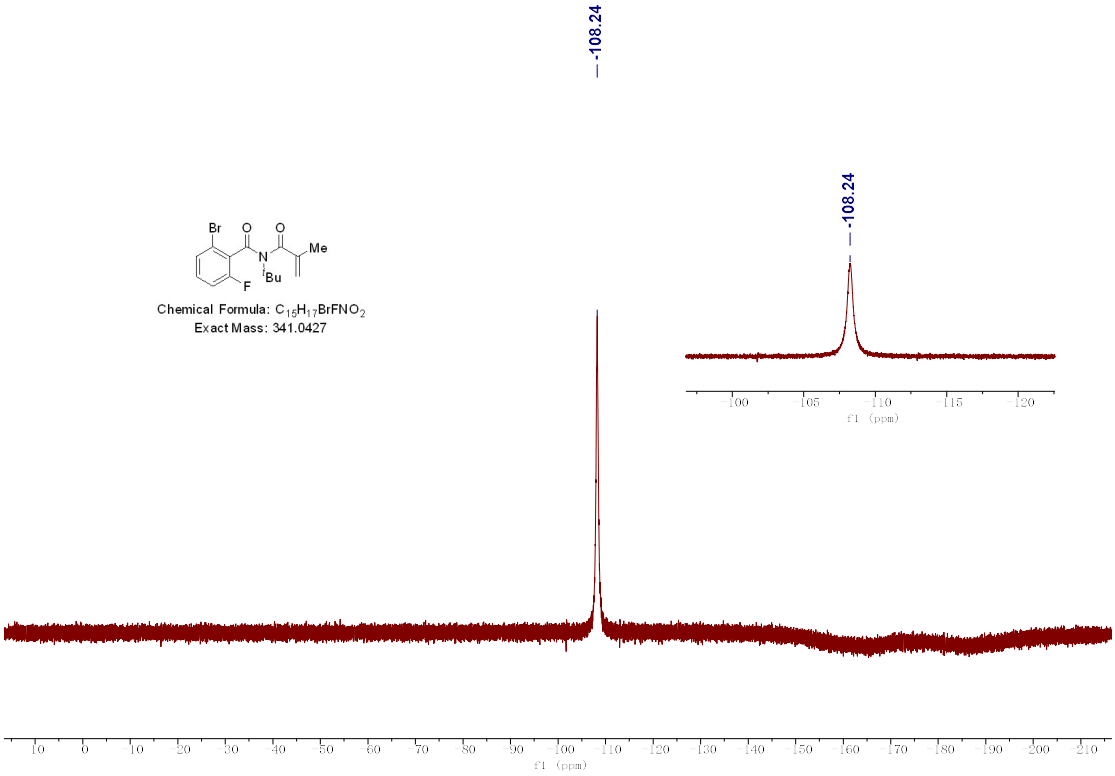
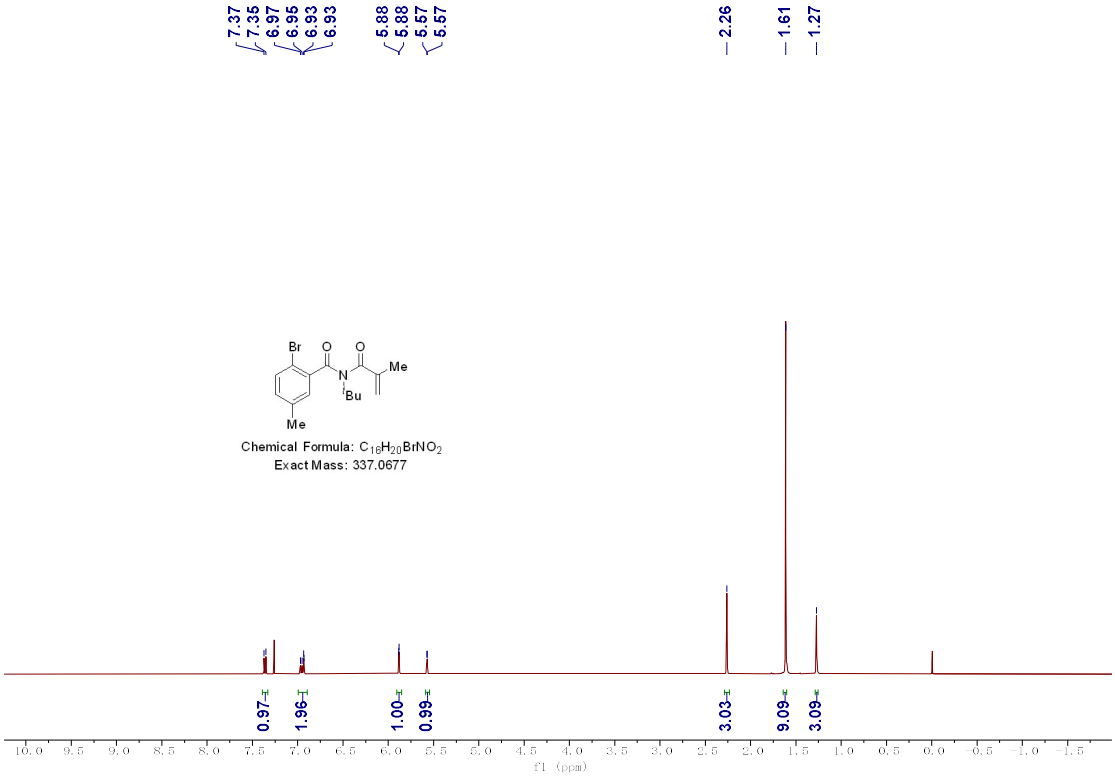
1.97
1.02
1.04
9.00
3.01
f1 (ppm)
176.67
167.03
144.22
138.97
133.52
130.50
129.63
126.72
126.39
121.38
59.57
28.60
Br
O
O
N
Me
tBu
Chemical Formula: C15H18BrNO2
Exact Mass: 323.0521
f1 (ppm)

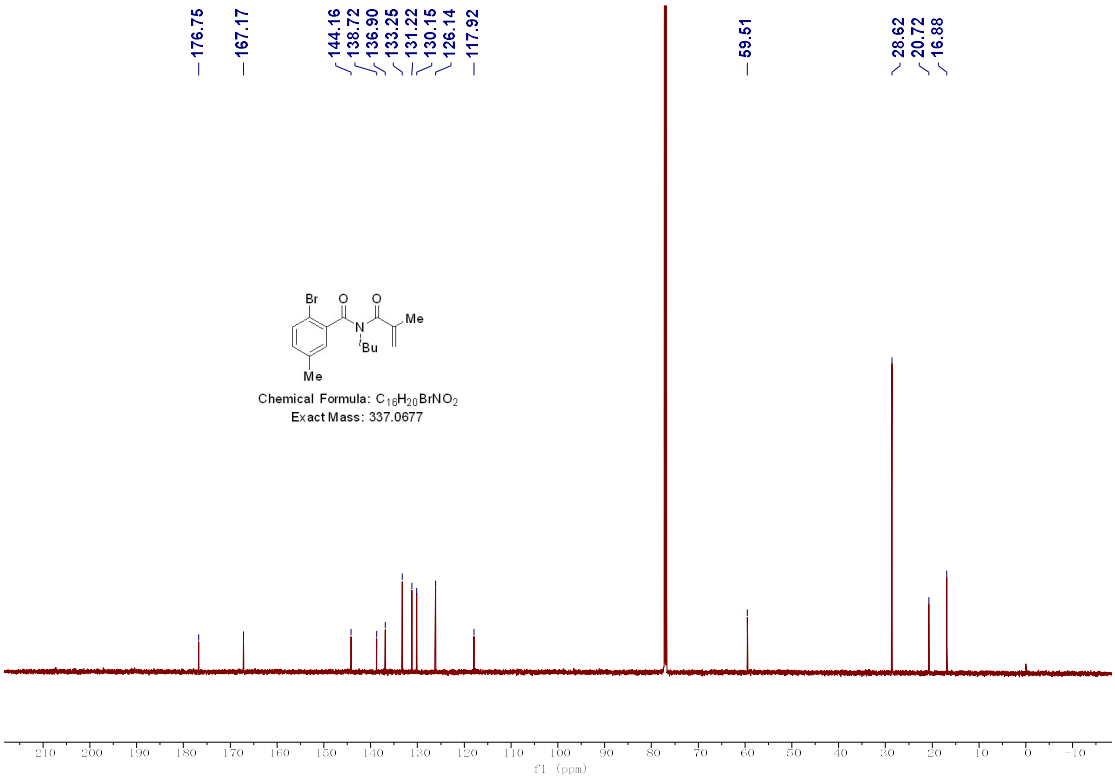
1m


7.30
7.30
7.30
7.29
7.29
7.29
7.19
7.18
7.18
7.17
7.16
7.16
6.99
6.99
6.98
6.98
6.96
6.96
5.96
5.65
5.65
1.61
1.34
Br
O
O
N
Me
iBu
F
Chemical Formula: C15H17BrFNO2
Exact Mass: 341.0427
0.98
1.03
0.98
1.06
1.05
9.00
2.95
f1 (ppm)
174.84
162.07
159.14
157.46
142.98
131.60
131.54
128.72
128.69
128.44
128.30
126.88
126.87
114.76
114.62
59.93
28.30
16.78
Br
O
O
N
Me
iBu
F
Chemical Formula: C15H17BrFNO2
Exact Mass: 341.0427
f1 (ppm)

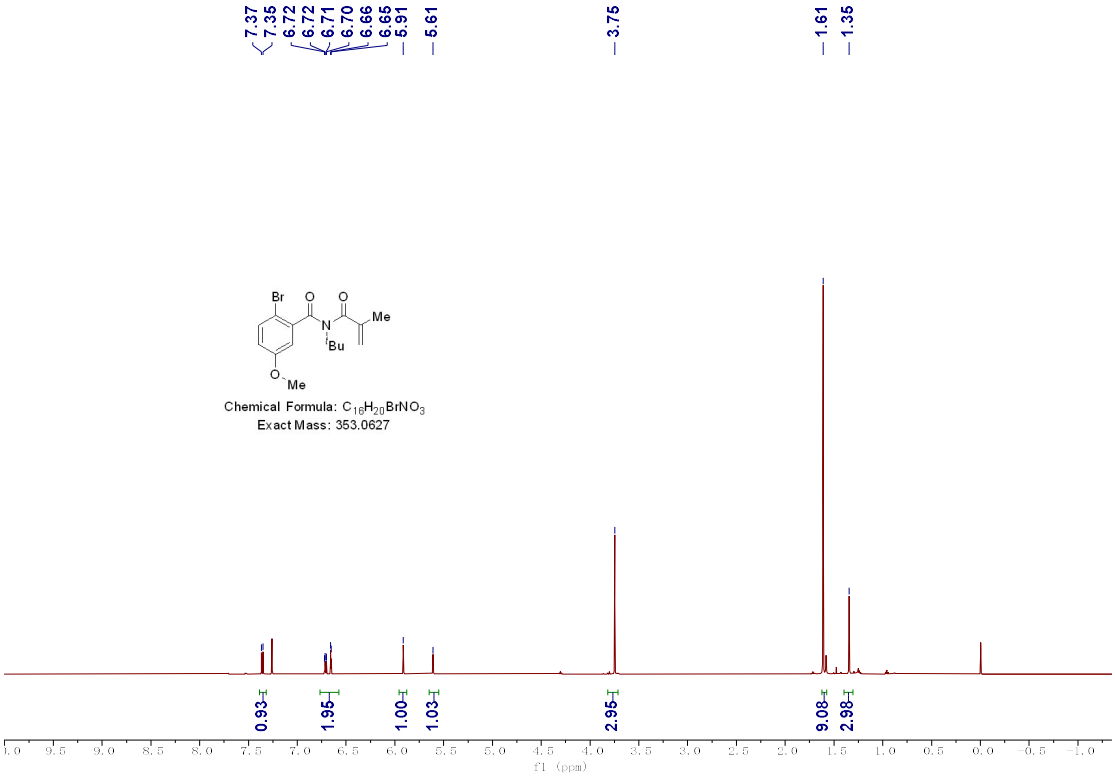

-108.24
Br
O
O
N
Me
Bu
F
Chemical Formula: C15H17BrFNO2
Exact Mass: 341.0427
-108.24
100
105
110
115
120
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

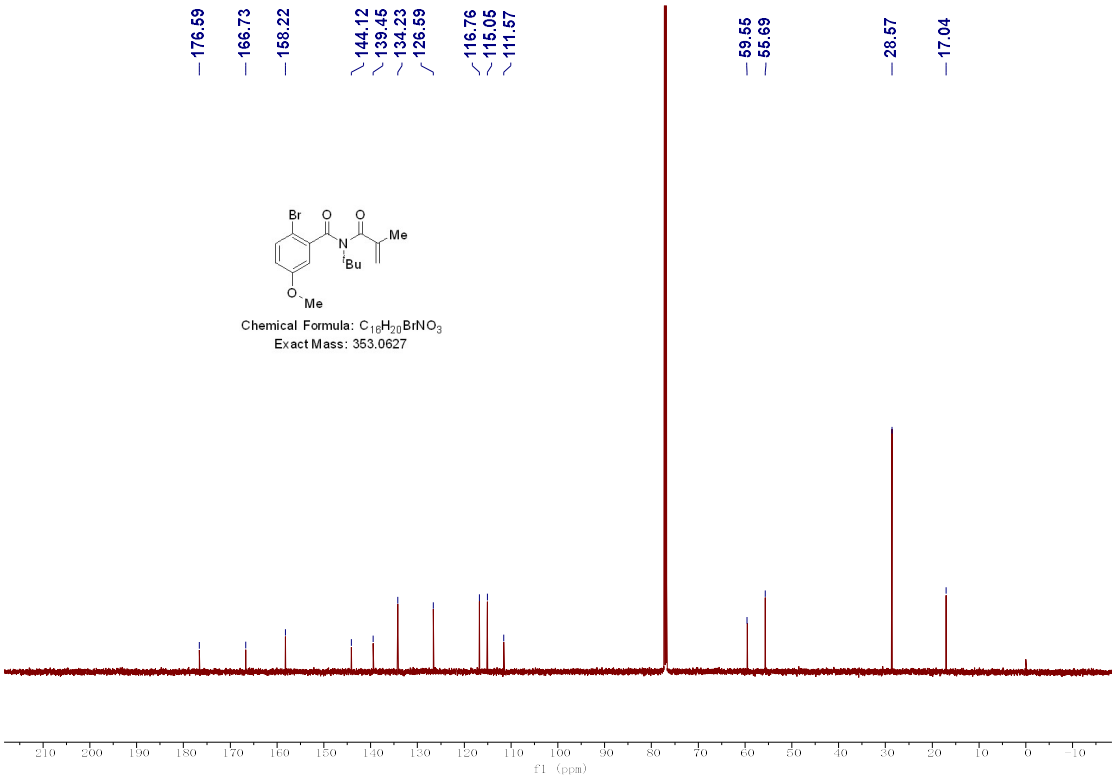
1n


7.37
7.35
6.97
6.95
6.93
6.93
5.88
5.88
5.57
5.57
2.26
1.61
1.27
Br
O
O
N
Me
Bu
Me
Chemical Formula: C16H20BrNO2
Exact Mass: 337.0677
0.97
1.96
1.00
0.99
3.03
9.09
3.09
f1 (ppm)

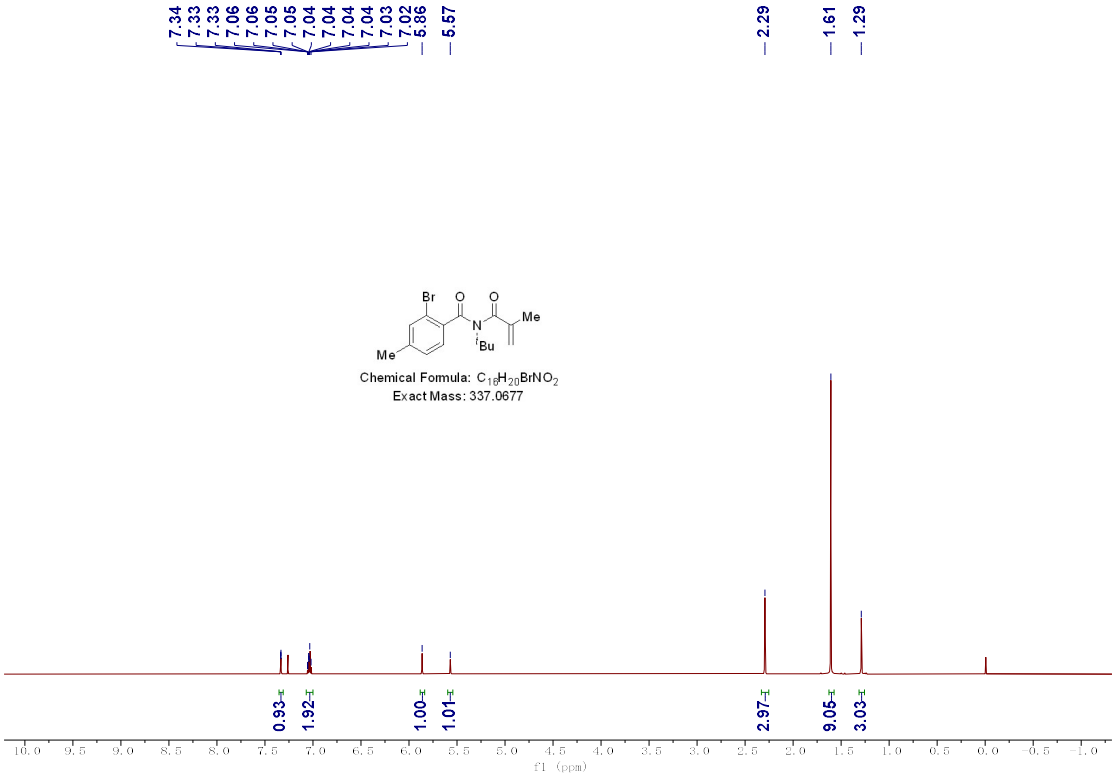

176.75
167.17
144.16
138.72
136.90
133.25
131.22
130.15
126.14
117.92
59.51
28.62
20.72
16.88
Br
O
O
N
Me
Bu
Me
Chemical Formula: C16H20BrNO2
Exact Mass: 337.0677
f1 (ppm)

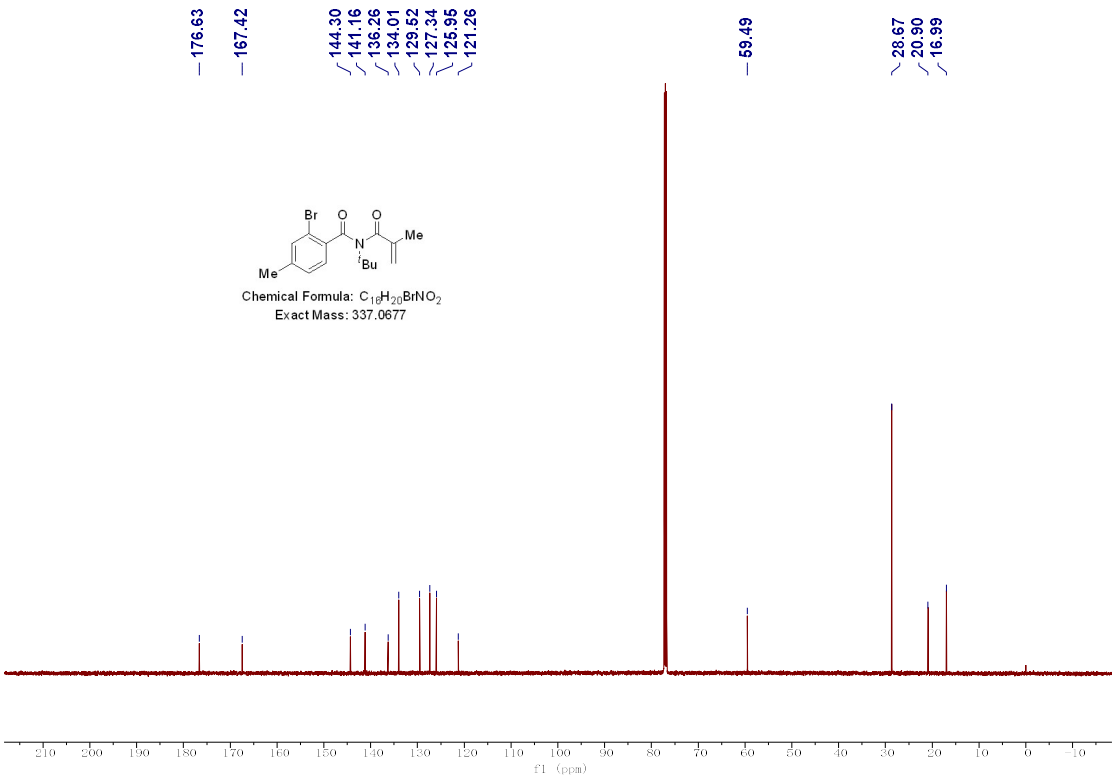
1o


7.37
7.35
6.72
6.72
6.71
6.70
6.66
6.65
5.91
5.61
3.75
1.61
1.35
Br
O
O
N
Me
tBu
O
Me
Chemical Formula: C18H20BrNO3
Exact Mass: 353.0627
0.93
1.95
1.00
1.03
2.95
9.08
2.98
f1 (ppm)

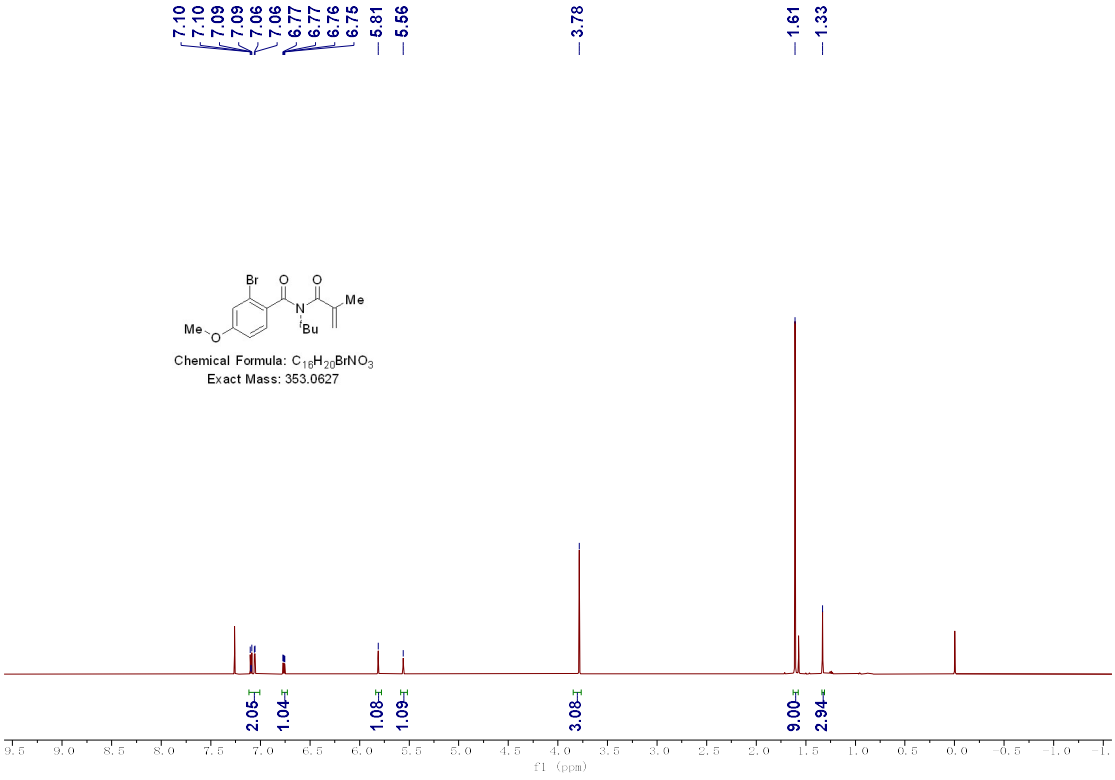

176.59
166.73
158.22
144.12
139.45
134.23
126.59
116.76
115.05
111.57
59.55
55.69
28.57
17.04
Br
O
O
N
Me
tBu
O
Me
Chemical Formula: C18H20BrNO3
Exact Mass: 353.0627
f1 (ppm)

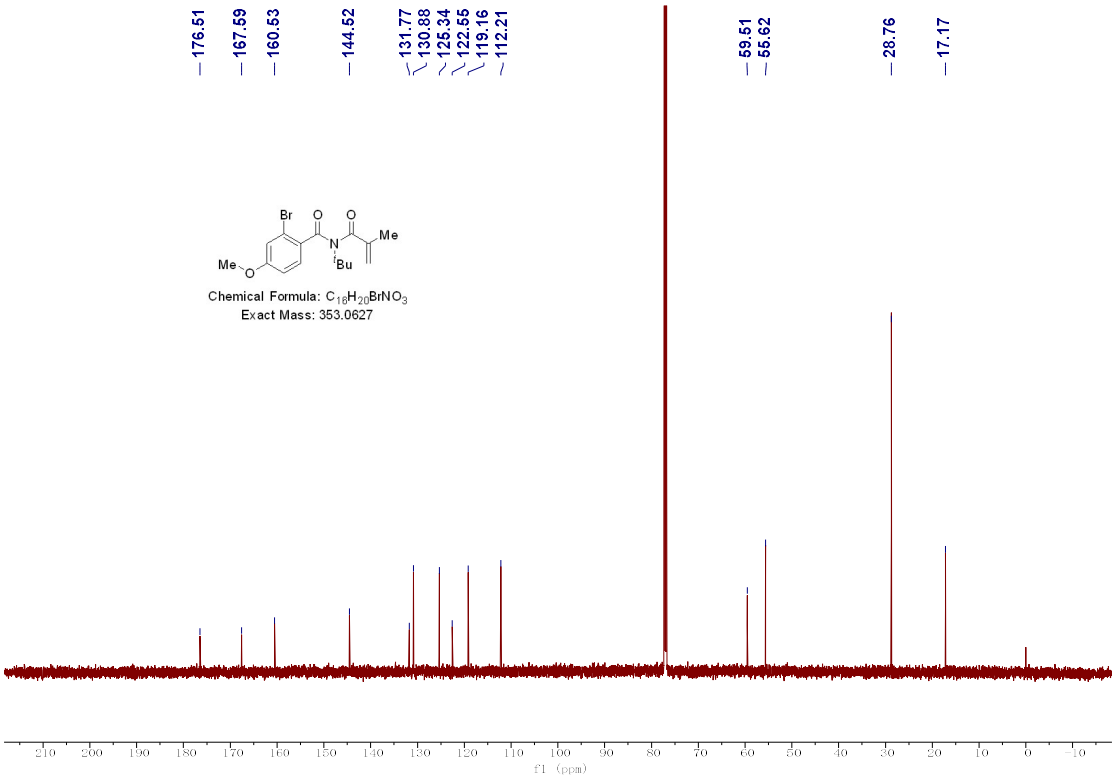
1p


7.34
7.33
7.33
7.06
7.06
7.05
7.05
7.04
7.04
7.04
7.04
7.03
7.02
6.86
6.57
2.29
1.61
1.29
Br
O
O
N
Me
iBu
Me
Chemical Formula: C18H20BrNO2
Exact Mass: 337.0677
0.93
1.92
1.00
1.01
2.97
9.05
3.03
f1 (ppm)

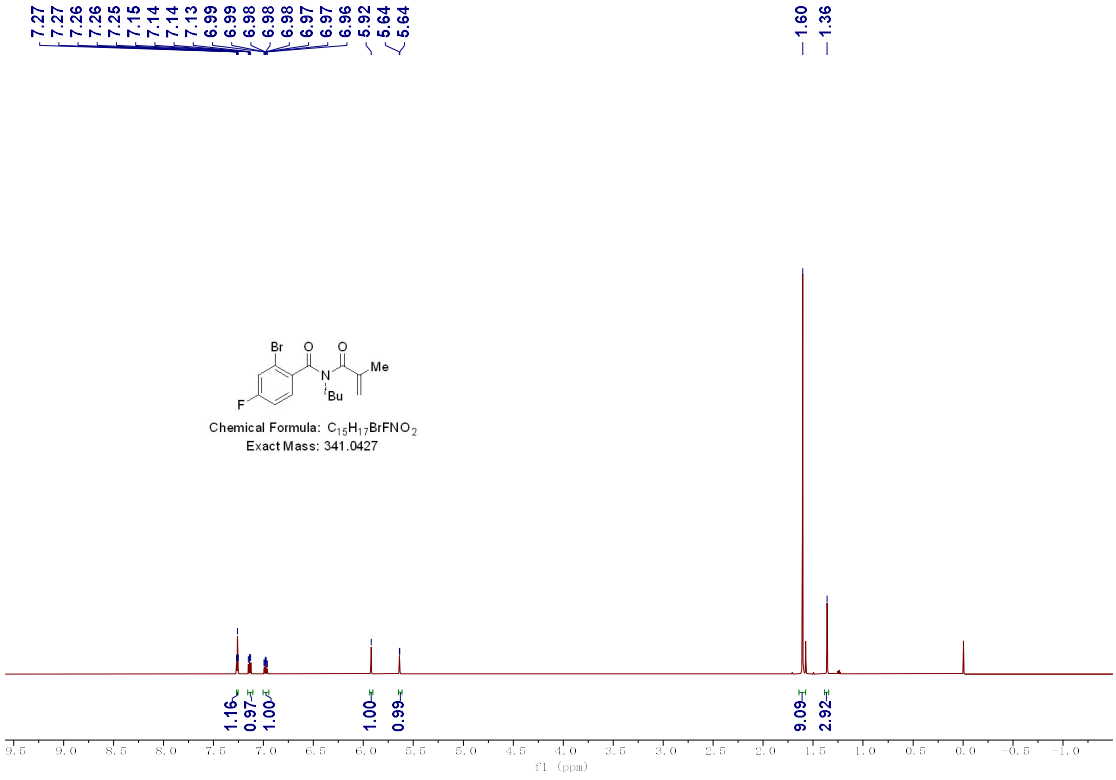

176.63
167.42
144.30
141.16
136.26
134.01
129.52
127.34
125.95
121.26
59.49
28.67
20.90
16.99
Br
O
O
N
Me
iBu
Me
Chemical Formula: C18H20BrNO2
Exact Mass: 337.0677
f1 (ppm)

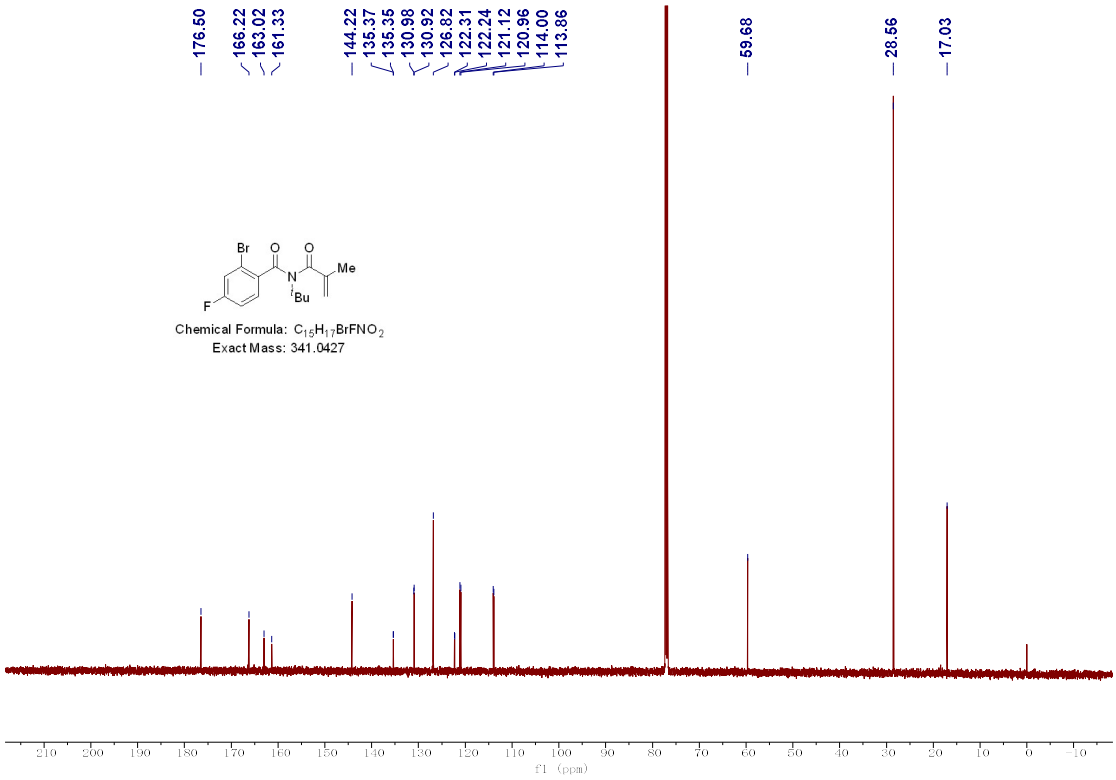
1q

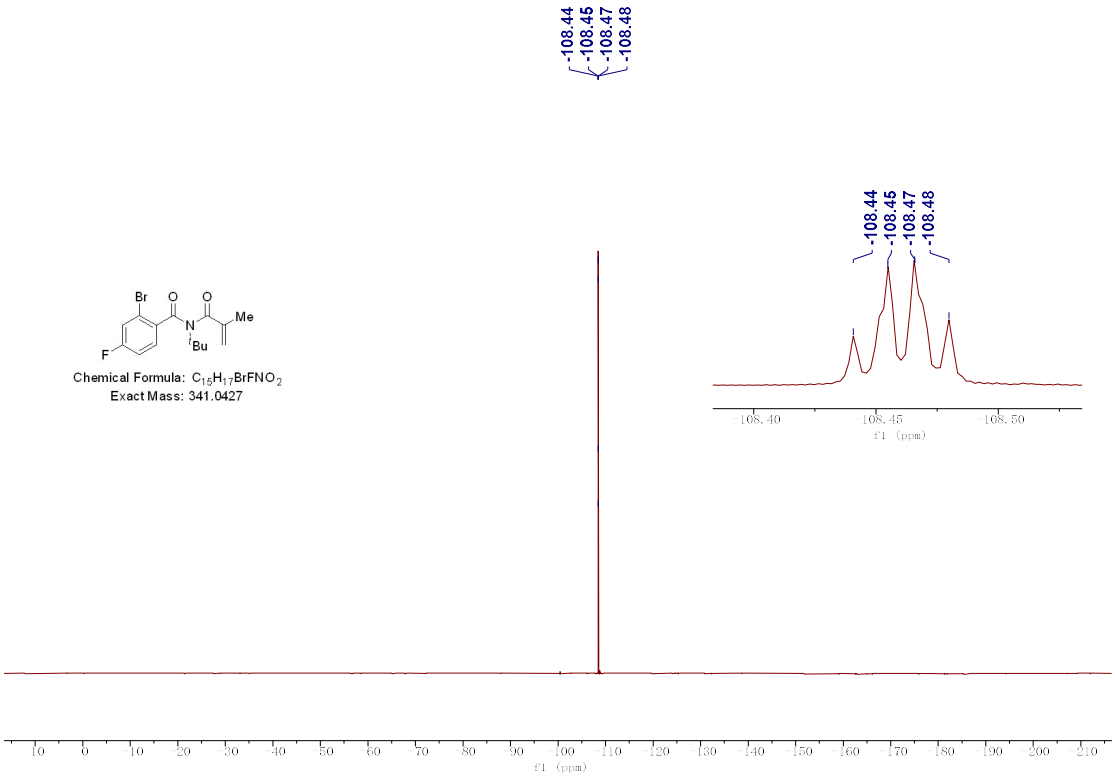

7.10
7.10
7.09
7.09
7.06
7.06
6.77
6.77
6.76
6.75
5.81
5.56
3.78
1.61
1.33
Br
O
O
N
Me
Me
O
tBu
Chemical Formula: C18H20BrNO3
Exact Mass: 353.0627
2.05
1.04
1.08
1.09
3.08
9.00
2.94
f1 (ppm)


176.51
167.59
160.53
144.52
131.77
130.88
125.34
122.55
119.16
112.21
59.51
55.62
28.76
17.17
Br
O
O
N
Me
Me
O
tBu
Chemical Formula: C18H20BrNO3
Exact Mass: 353.0627
f1 (ppm)

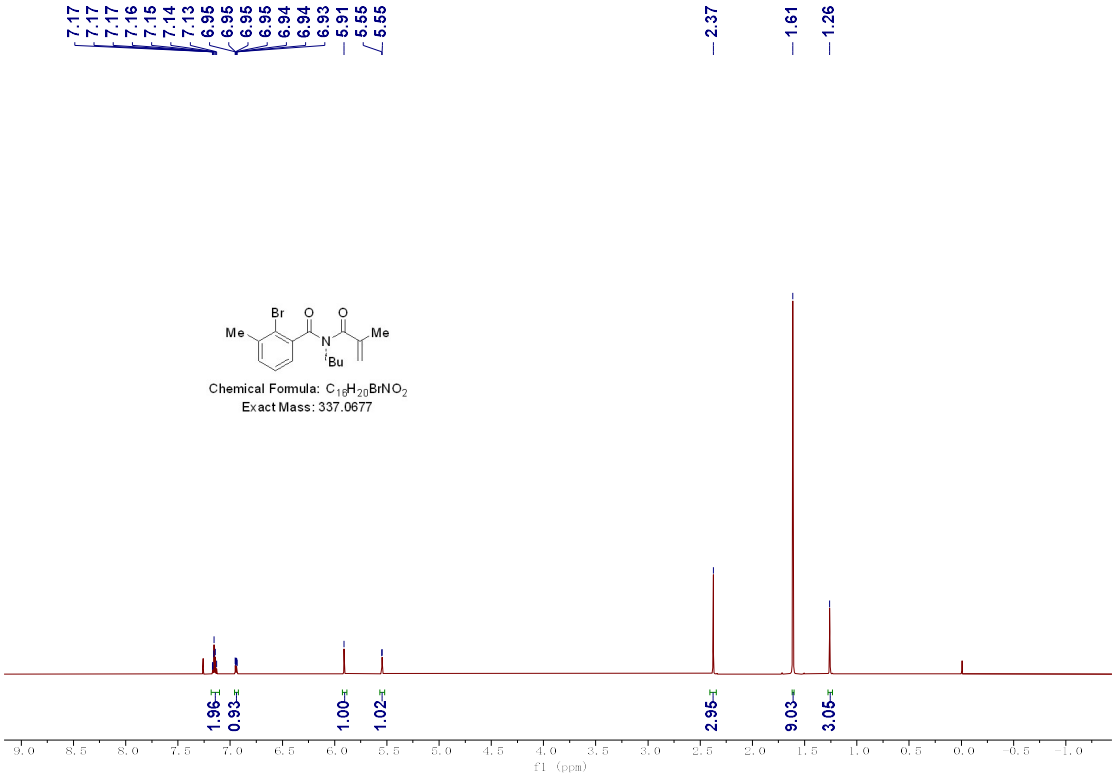
1r

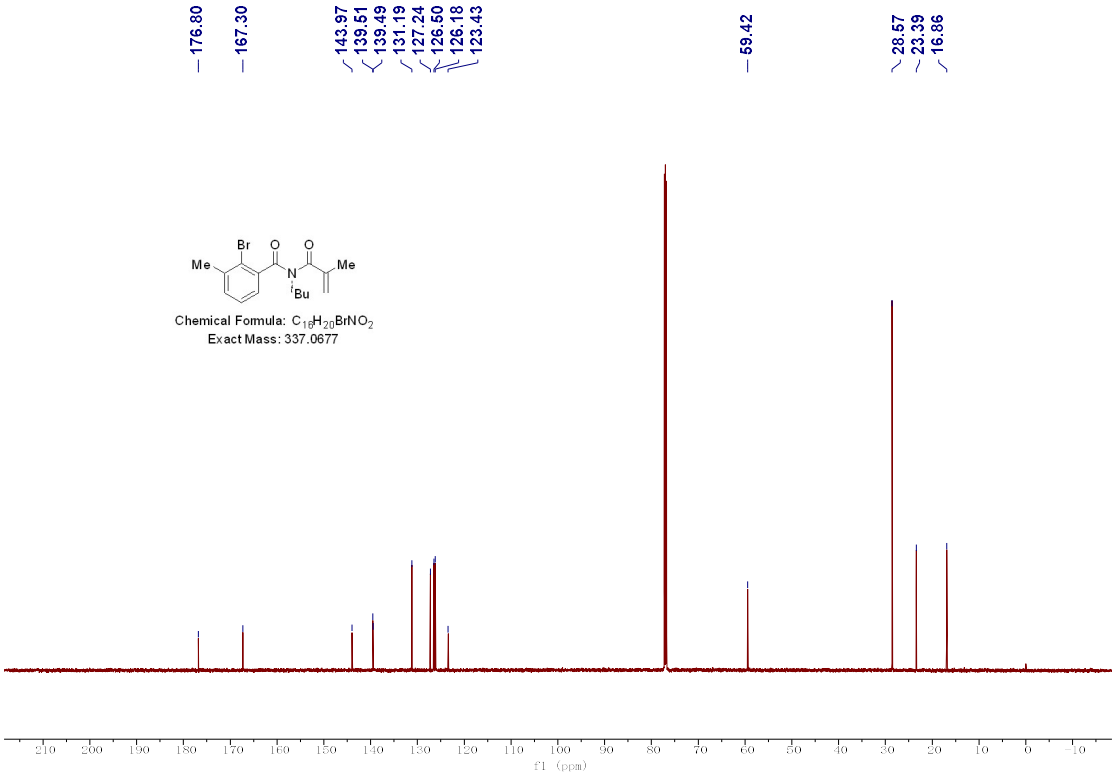

7.27
7.27
7.26
7.26
7.25
7.15
7.14
7.14
7.13
6.99
6.99
6.98
6.98
6.98
6.97
6.97
6.96
5.92
5.64
5.64
1.60
1.36
Br
O
O
N
Me
iBu
F
Chemical Formula: C15H17BrFNO2
Exact Mass: 341.0427
1.16
0.97
1.00
1.00
0.99
9.09
2.92
f1 (ppm)


176.50
166.22
163.02
161.33
144.22
135.37
135.35
130.98
130.92
126.82
122.31
122.24
121.12
120.96
114.00
113.86
59.68
28.56
17.03
Br
O
O
N
Me
iBu
F
Chemical Formula: C15H17BrFNO2
Exact Mass: 341.0427
f1 (ppm)

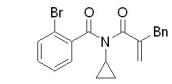

-108.44
-108.45
-108.47
-108.48
Br
O
O
N
Me
iBu
F
Chemical Formula: C15H17BrFNO2
Exact Mass: 341.0427
-108.44
-108.45
-108.47
-108.48
108.40
108.45
108.50
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

1s

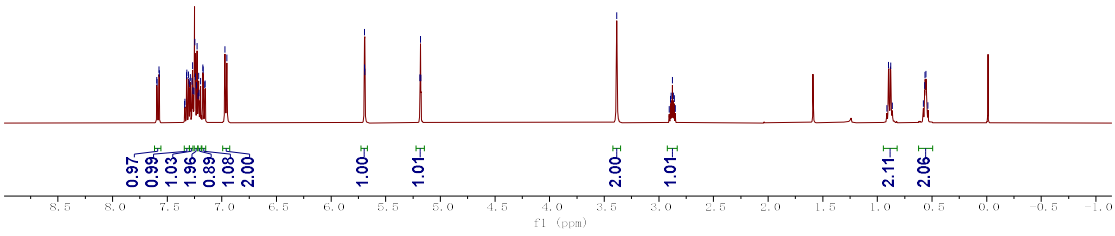

7.17
7.17
7.17
7.16
7.15
7.14
7.13
6.95
6.95
6.95
6.95
6.94
6.94
6.93
5.91
5.55
5.55
2.37
1.61
1.26
Br
O
O
Me
N
Me
iBu
Chemical Formula: C18H20BrNO2
Exact Mass: 337.0677
1.96
0.93
1.00
1.02
2.95
9.03
3.05
f1 (ppm)

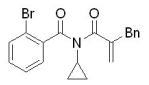

176.80
167.30
143.97
139.51
139.49
131.19
127.24
126.50
126.18
123.43
59.42
28.57
23.39
16.86
Br
O
O
Me
N
Me
iBu
Chemical Formula: C18H20BrNO2
Exact Mass: 337.0677
f1 (ppm)

1t



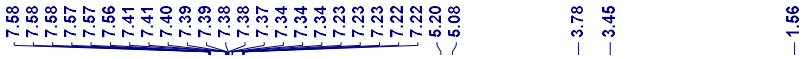
Chemical Formula: $C_{20}H_{18}BrNO_2$
Exact Mass: 383.0521

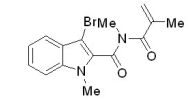




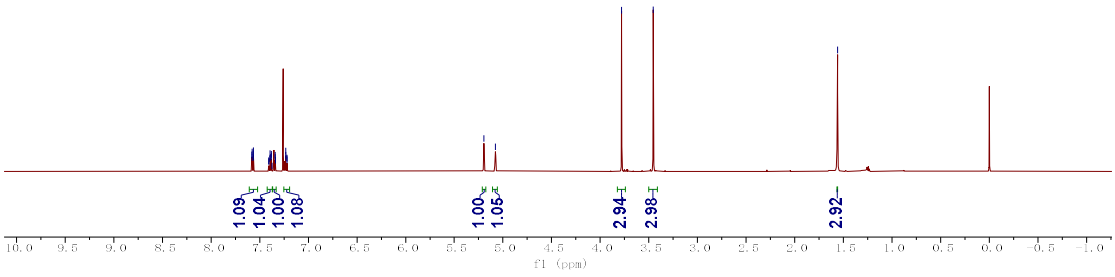
Chemical Formula: $C_{20}H_{18}BrNO_2$
Exact Mass: 383.0521

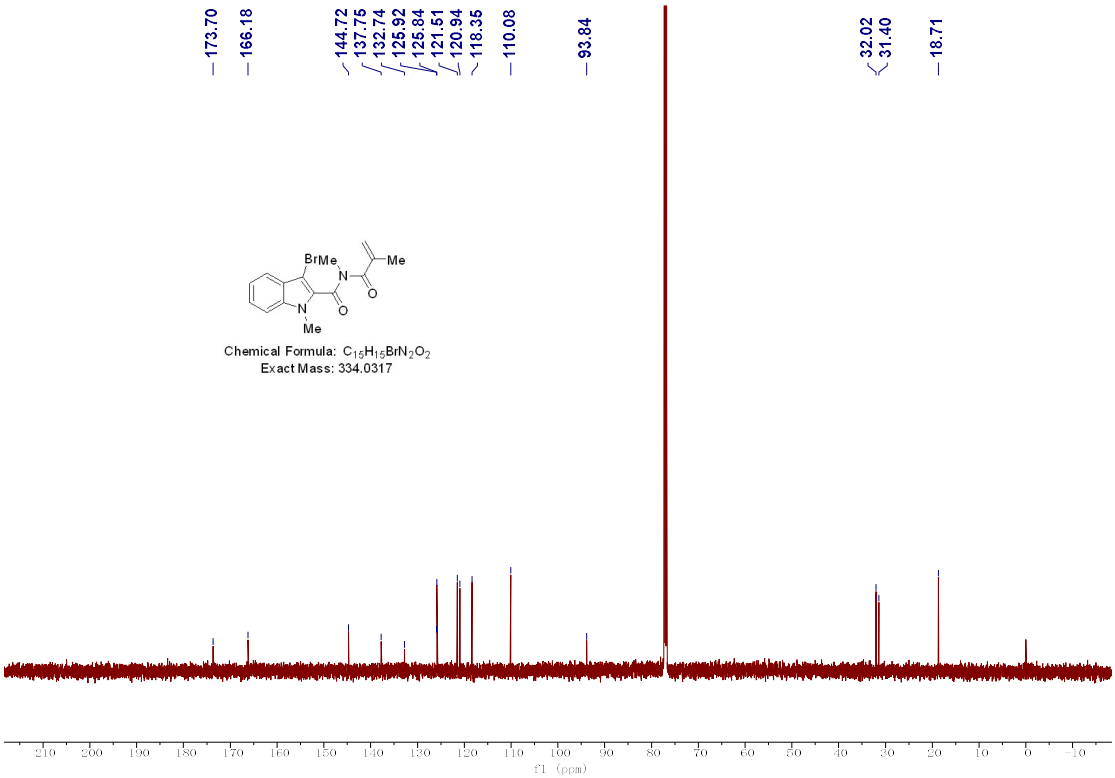
1u





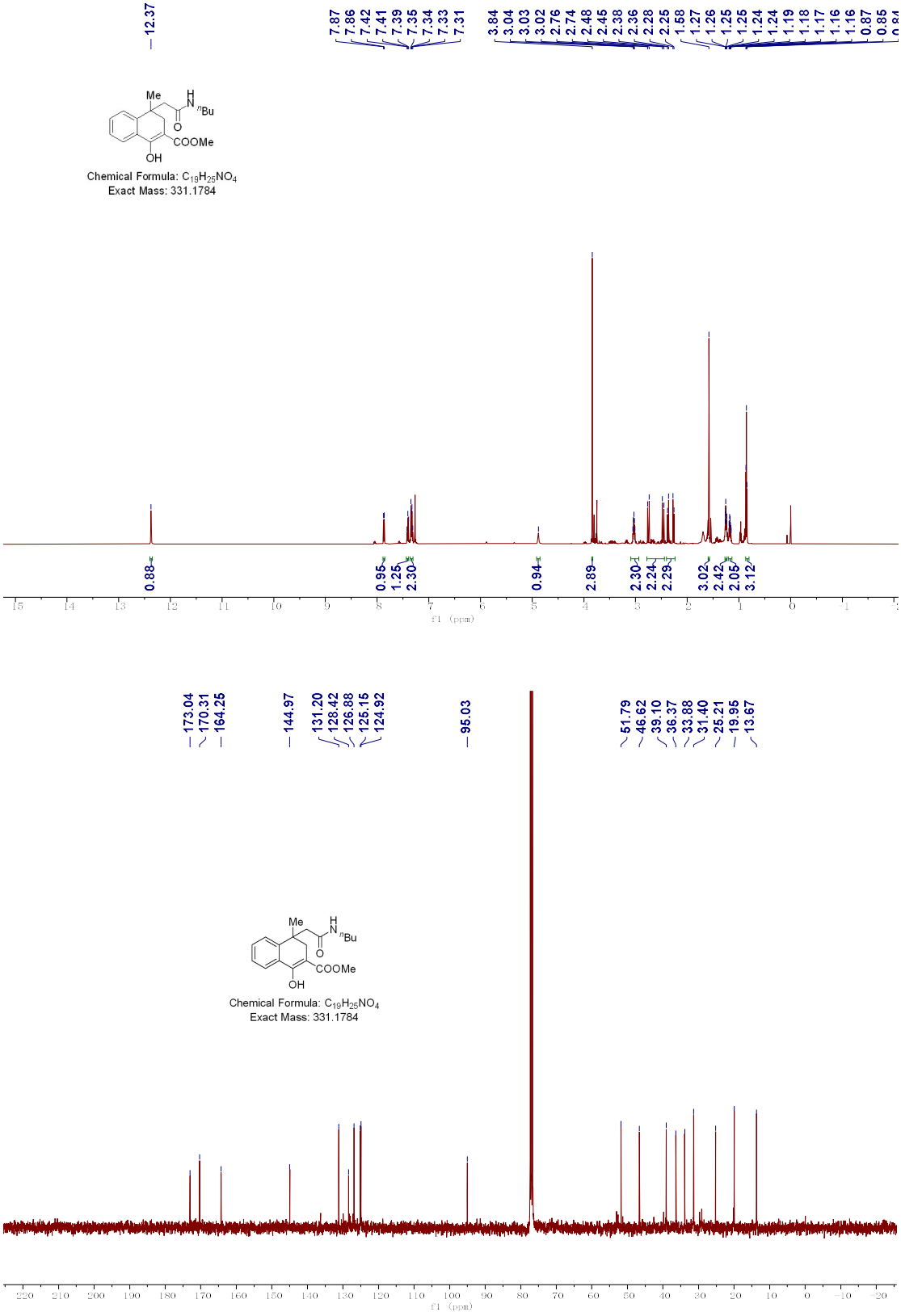
Chemical Formula: $C_{15}H_{16}BrN_2O_2$
Exact Mass: 334.0317



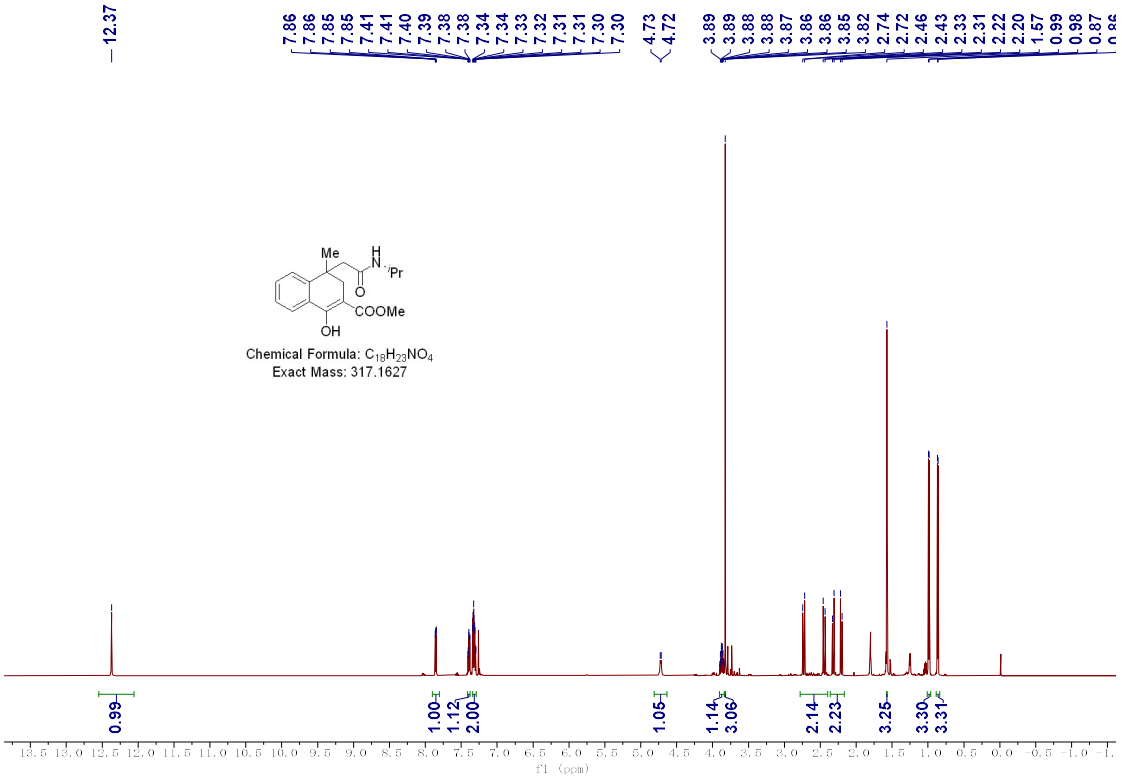


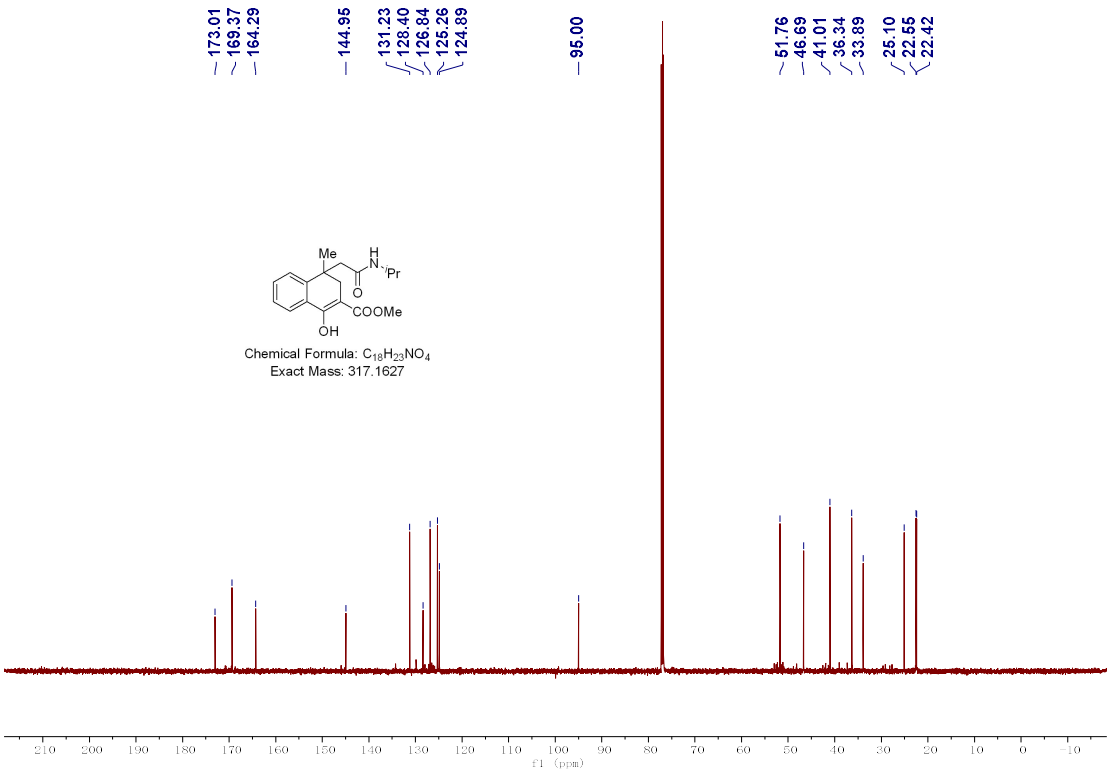
Chemical Formula: $C_{15}H_{16}BrN_2O_2$
Exact Mass: 334.0317

3aa

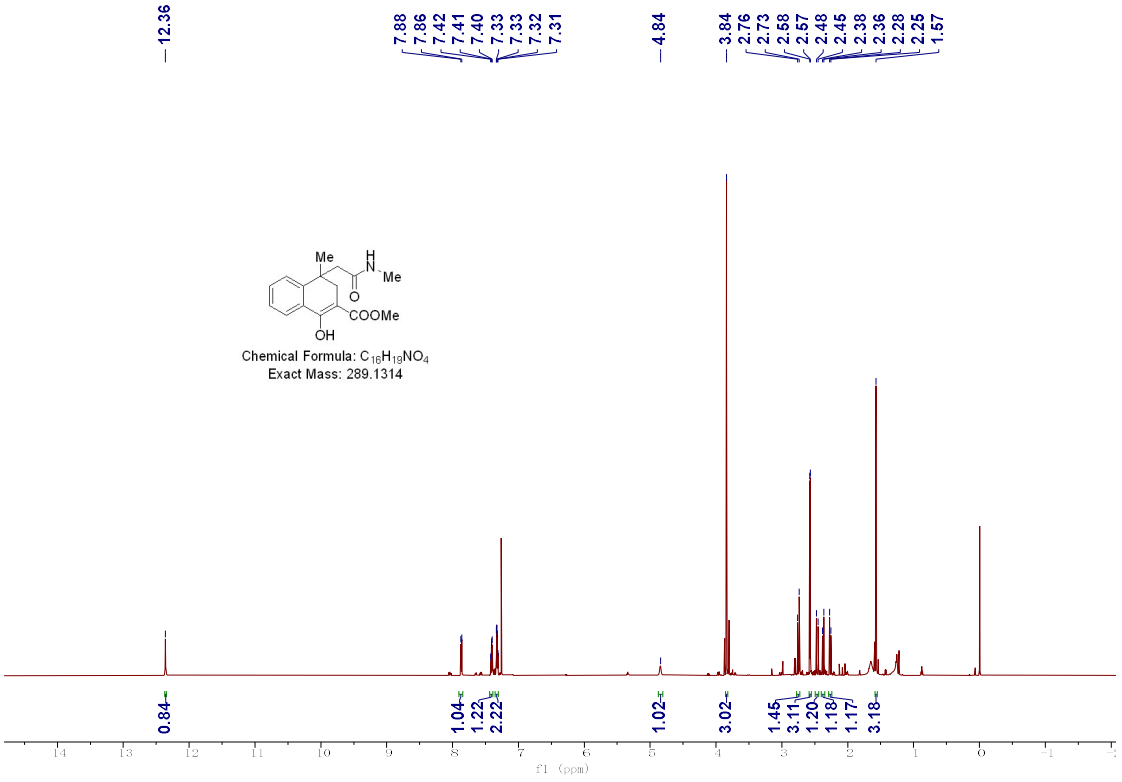

12.37
7.87
7.86
7.42
7.41
7.39
7.35
7.34
7.33
7.31
3.84
3.04
3.03
3.02
2.76
2.74
2.48
2.45
2.38
2.36
2.28
2.25
1.58
1.27
1.26
1.25
1.25
1.24
1.24
1.19
1.18
1.17
1.16
1.16
0.87
0.85
Me
H
N
nBu
O
COOMe
OH
Chemical Formula: C19H25NO4
Exact Mass: 331.1784
0.88
0.95
1.25
2.30
0.94
2.89
2.30
2.24
2.29
3.02
2.42
2.05
3.12
f1 (ppm)
173.04
170.31
164.25
144.97
131.20
128.42
126.88
126.15
124.92
95.03
51.79
46.62
39.10
36.37
33.88
31.40
26.21
19.95
13.67
Me
H
N
nBu
O
COOMe
OH
Chemical Formula: C19H25NO4
Exact Mass: 331.1784
f1 (ppm)

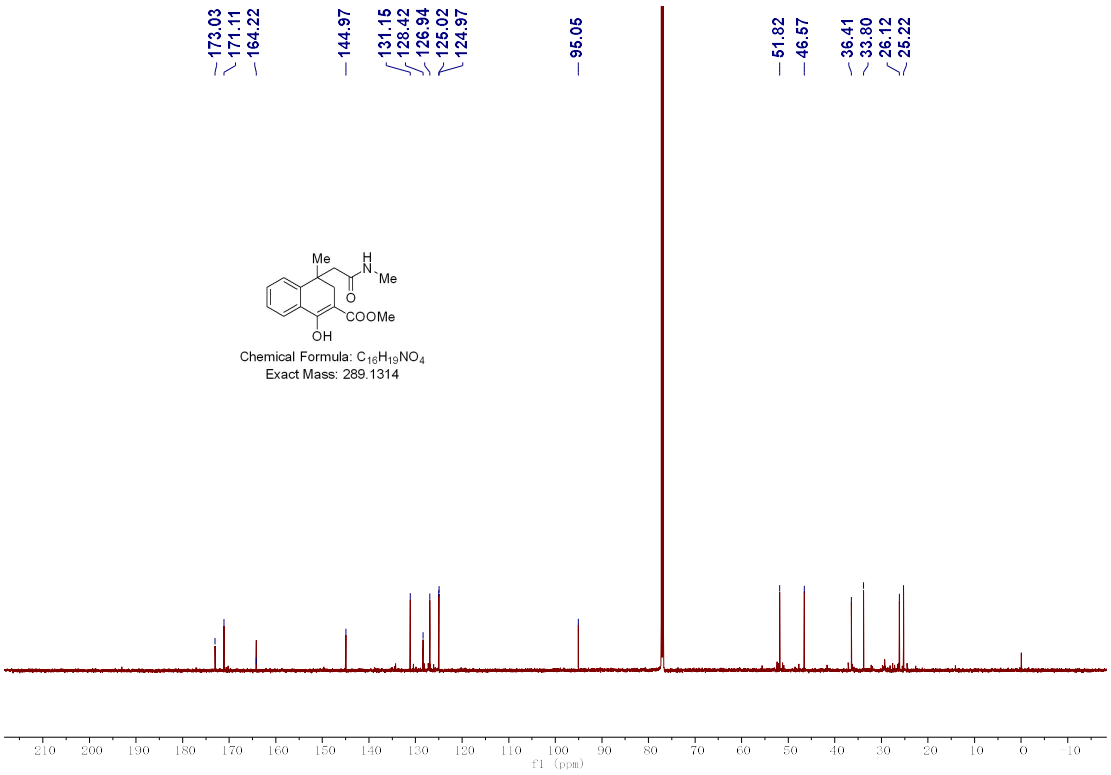
3ba


12.37
7.86
7.86
7.85
7.85
7.41
7.40
7.39
7.38
7.38
7.34
7.34
7.33
7.32
7.31
7.31
7.30
7.30
4.73
4.72
3.89
3.89
3.88
3.88
3.87
3.86
3.86
3.85
3.82
2.74
2.72
2.46
2.43
2.33
2.31
2.22
2.20
1.57
0.99
0.98
0.87
Me
H
N
iPr
O
COOMe
OH
Chemical Formula: C18H23NO4
Exact Mass: 317.1627
0.99
1.00
1.12
2.00
1.05
1.14
3.06
2.14
2.23
3.25
3.30
3.31
f1 (ppm)

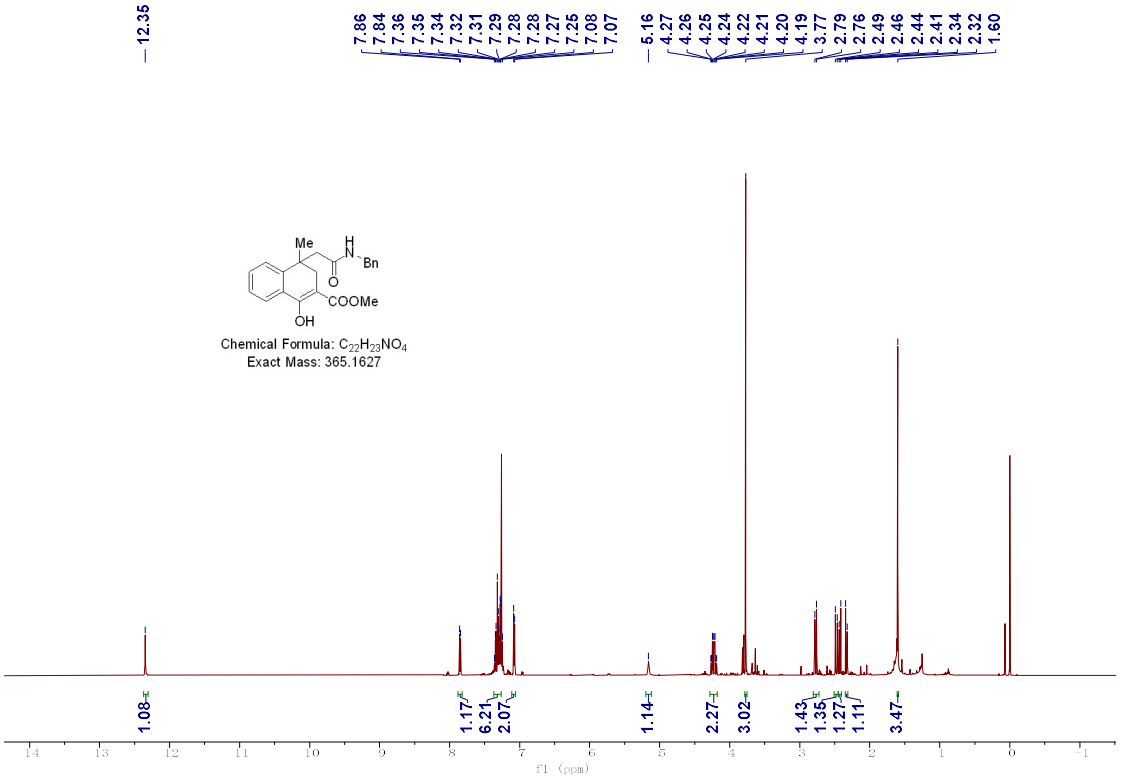

173.01
169.37
164.29
144.95
131.23
128.40
126.84
125.26
124.89
95.00
51.76
46.69
41.01
36.34
33.89
25.10
22.55
22.42
Me
H
N
iPr
O
COOMe
OH
Chemical Formula: C18H23NO4
Exact Mass: 317.1627
f1 (ppm)

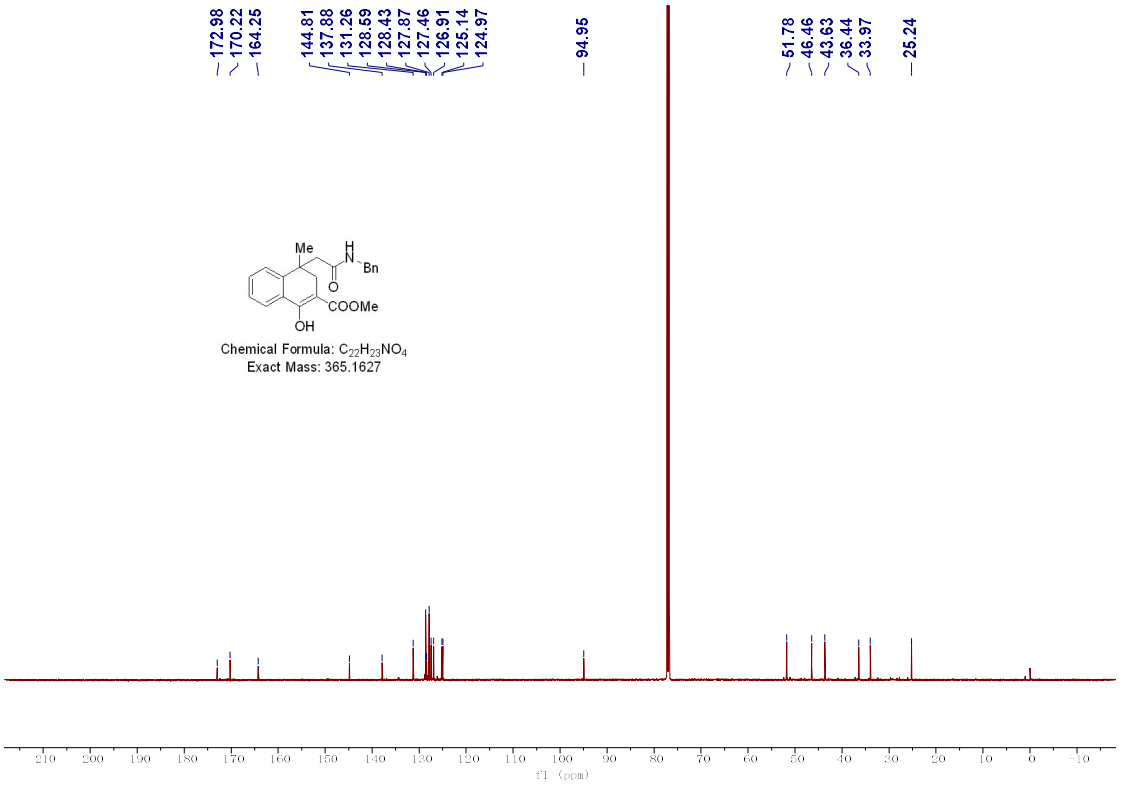
3ca


12.36
7.88
7.86
7.42
7.41
7.40
7.33
7.33
7.32
7.31
4.84
3.84
2.76
2.73
2.58
2.57
2.48
2.45
2.38
2.36
2.28
2.25
1.57
Me
H
N
Me
O
COOMe
OH
Chemical Formula: C16H19NO4
Exact Mass: 289.1314
0.84
1.04
1.22
2.22
1.02
3.02
1.45
3.11
1.20
1.18
1.17
3.18
f1 (ppm)

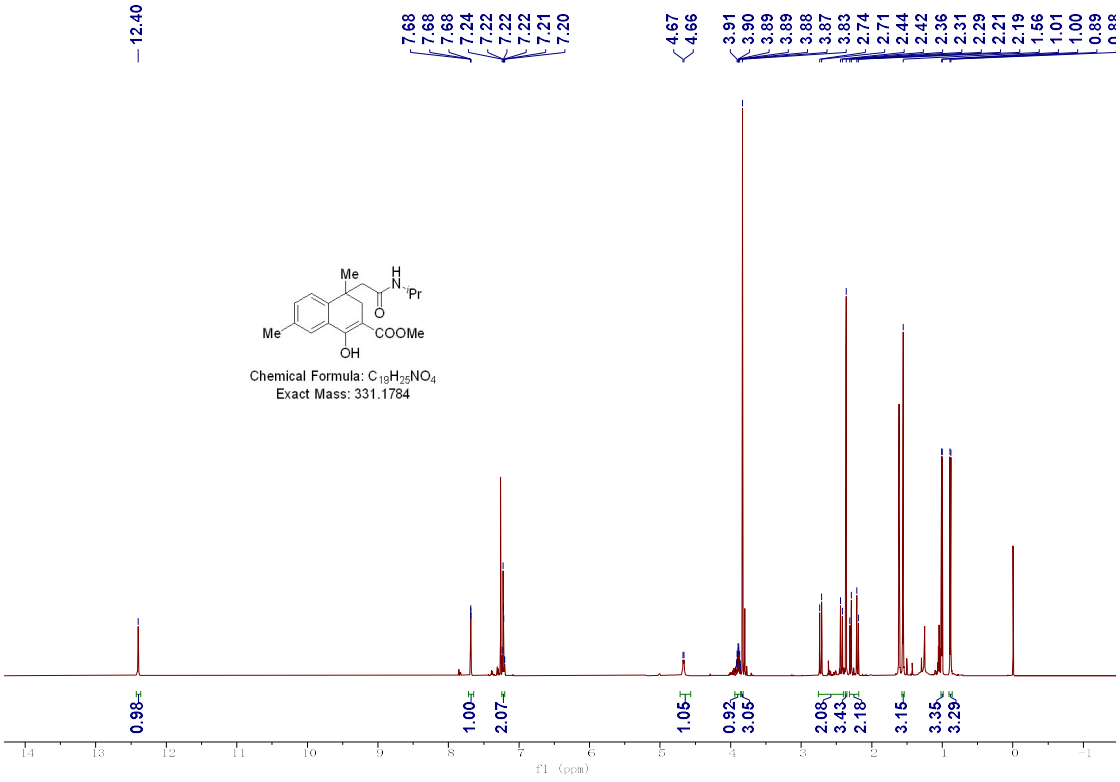

173.03
171.11
164.22
144.97
131.15
128.42
126.94
125.02
124.97
95.05
51.82
46.57
36.41
33.80
26.12
25.22
Me
H
N
Me
O
COOMe
OH
Chemical Formula: C16H19NO4
Exact Mass: 289.1314
f1 (ppm)

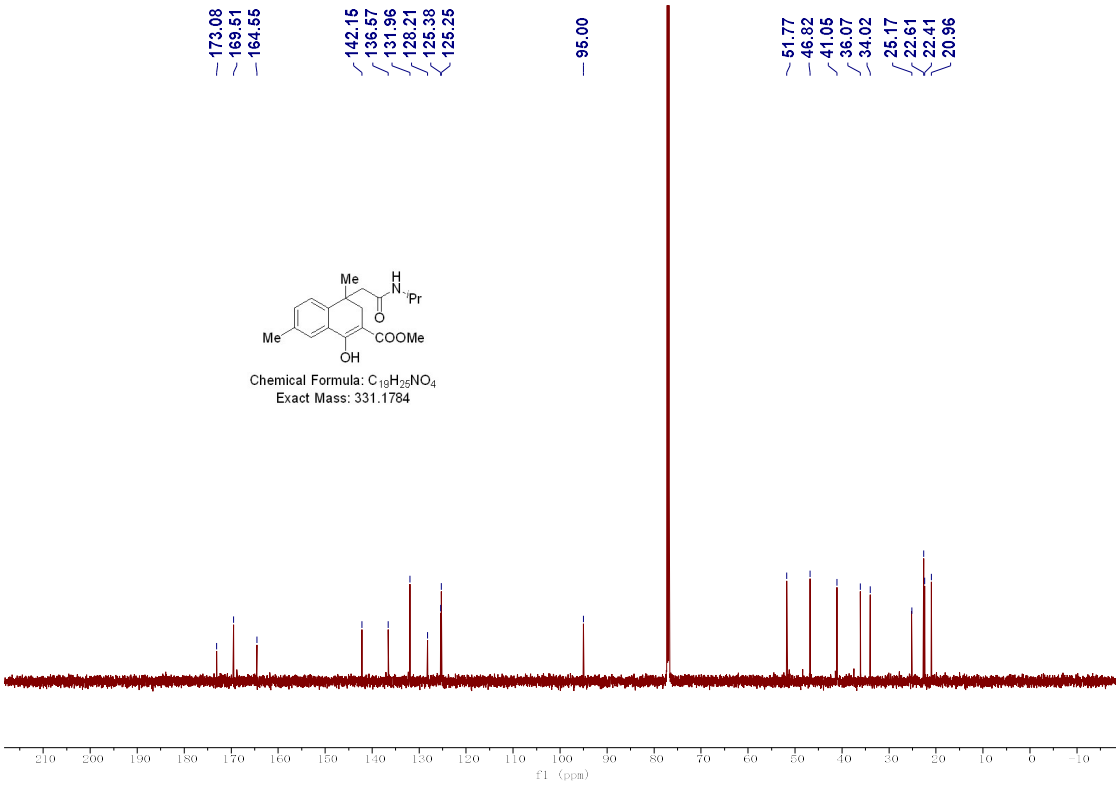
3da


12.35
7.86
7.84
7.36
7.35
7.34
7.32
7.31
7.29
7.28
7.28
7.27
7.25
7.08
7.07
5.16
4.27
4.26
4.25
4.24
4.22
4.21
4.20
4.19
3.77
2.79
2.76
2.49
2.46
2.44
2.41
2.34
2.32
1.60
Me
H
N
Bn
O
COOMe
OH
Chemical Formula: C22H23NO4
Exact Mass: 365.1627
1.08
1.17
6.21
2.07
1.14
2.27
3.02
1.43
1.35
1.27
1.11
3.47
f1 (ppm)

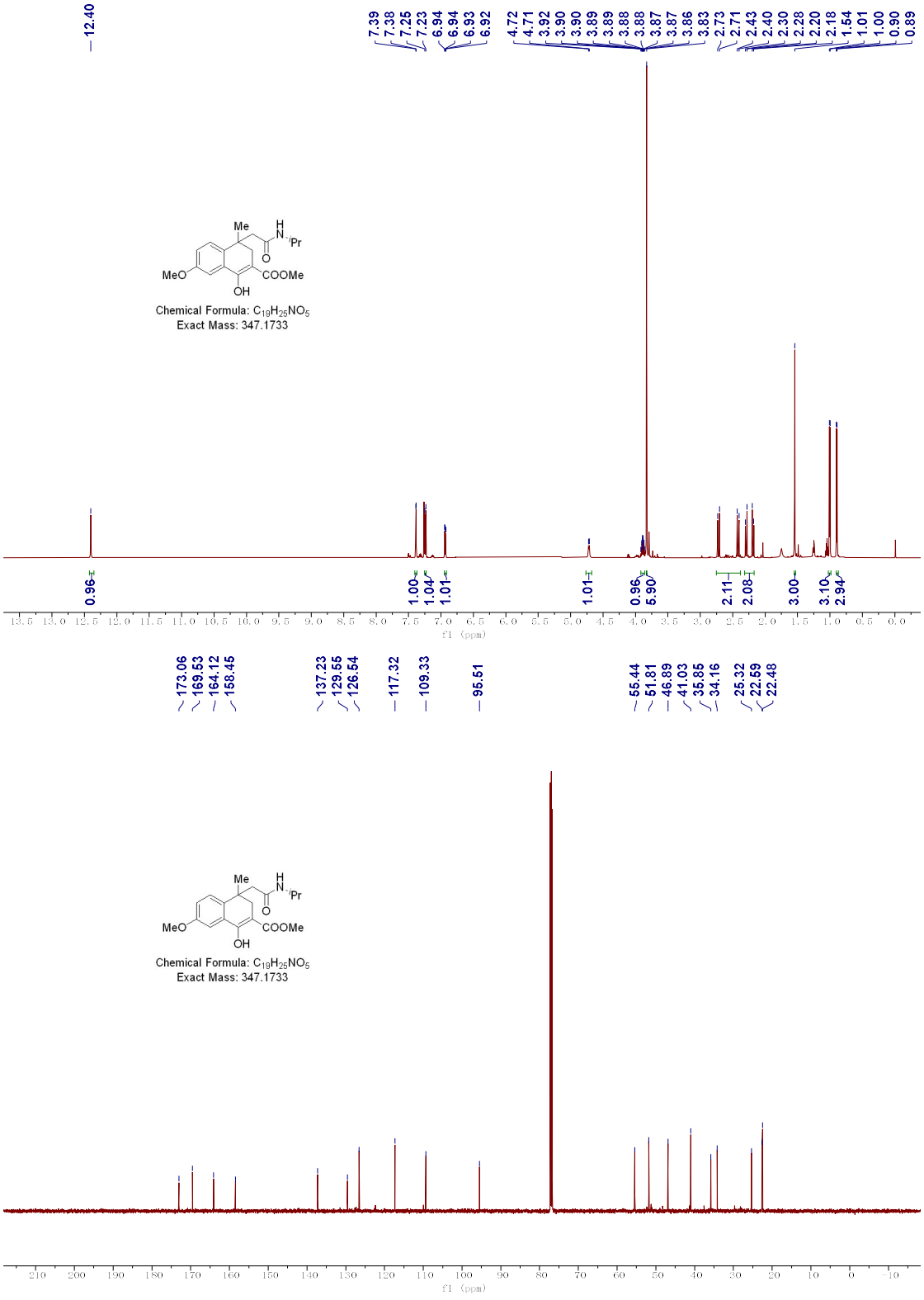

172.98
170.22
164.25
144.81
137.88
131.26
128.59
128.43
127.87
127.46
126.91
125.14
124.97
94.95
51.78
46.46
43.63
36.44
33.97
25.24
Me
H
N
Bn
O
COOMe
OH
Chemical Formula: C22H23NO4
Exact Mass: 365.1627
f1 (ppm)

3ea

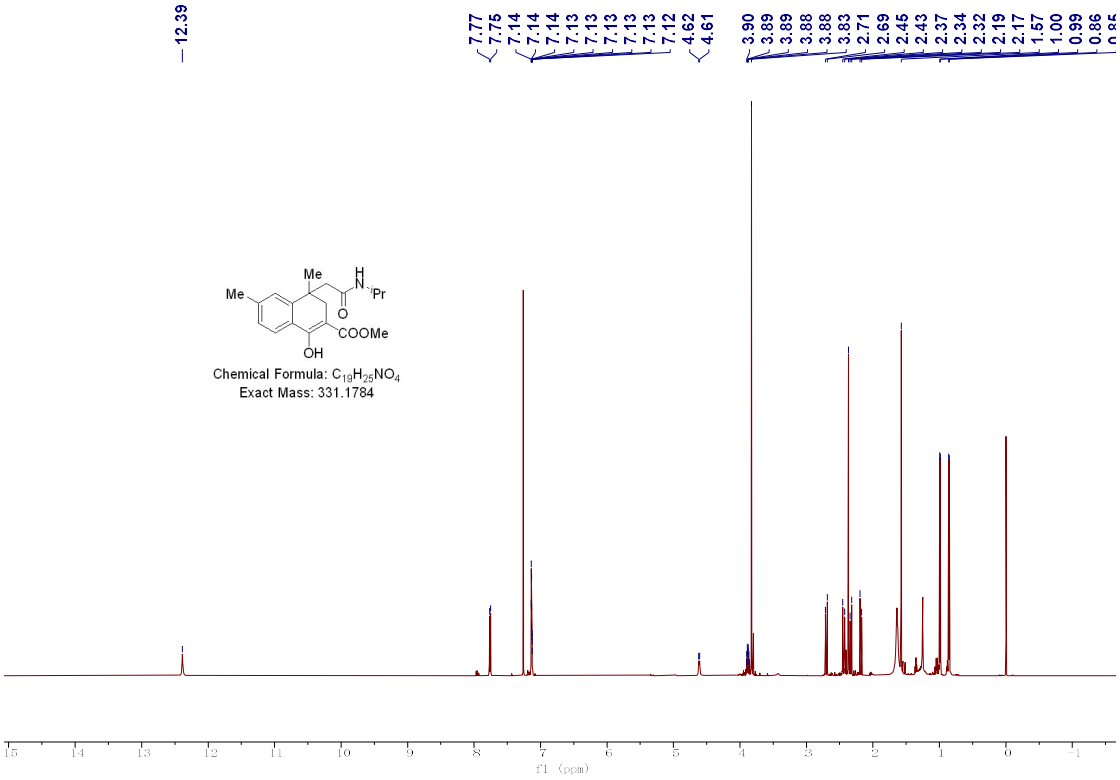

12.40
7.68
7.68
7.68
7.24
7.22
7.22
7.22
7.21
7.20
4.67
4.66
3.91
3.90
3.89
3.89
3.88
3.87
3.83
2.74
2.71
2.44
2.42
2.36
2.31
2.29
2.21
2.19
1.56
1.01
1.00
0.89
Me
H
N
iPr
O
Me
COOMe
OH
Chemical Formula: C19H25NO4
Exact Mass: 331.1784
0.98
1.00
2.07
1.05
0.92
3.05
2.08
3.43
2.18
3.15
3.35
3.29
f1 (ppm)

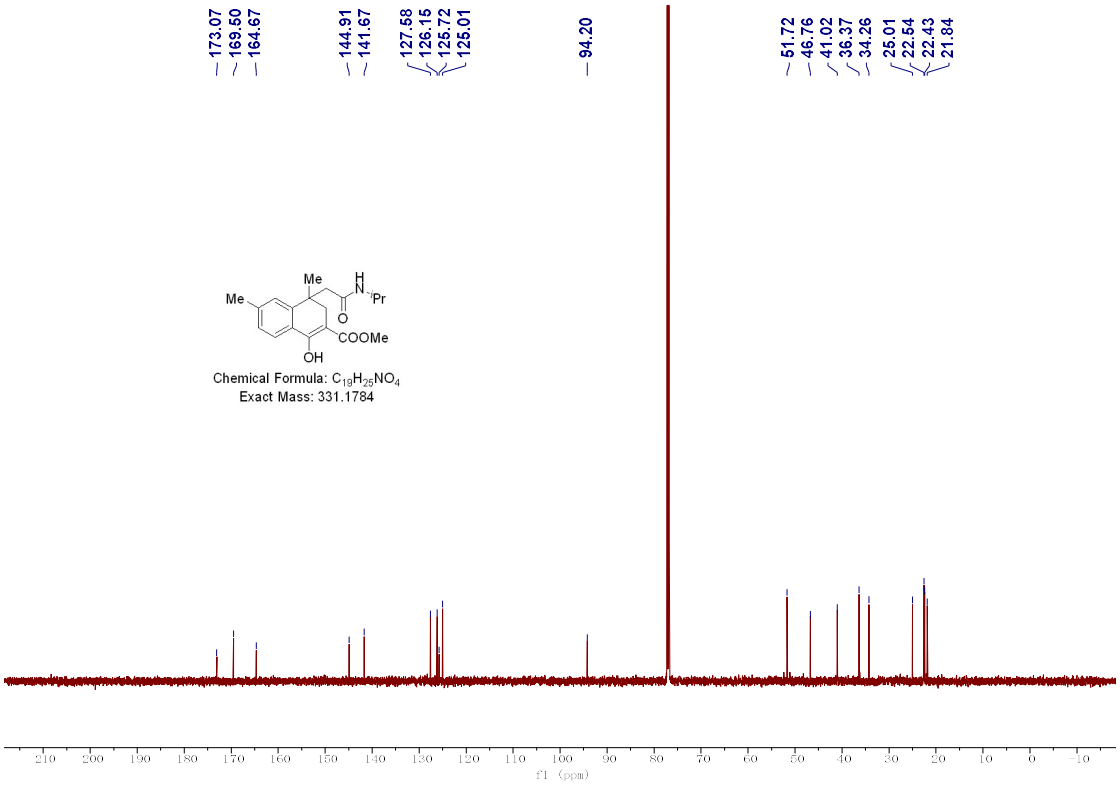

173.08
169.51
164.55
142.15
136.57
131.96
128.21
126.38
125.25
95.00
51.77
46.82
41.05
36.07
34.02
25.17
22.61
22.41
20.96
Me
H
N
iPr
O
Me
COOMe
OH
Chemical Formula: C19H25NO4
Exact Mass: 331.1784
f1 (ppm)

3fa

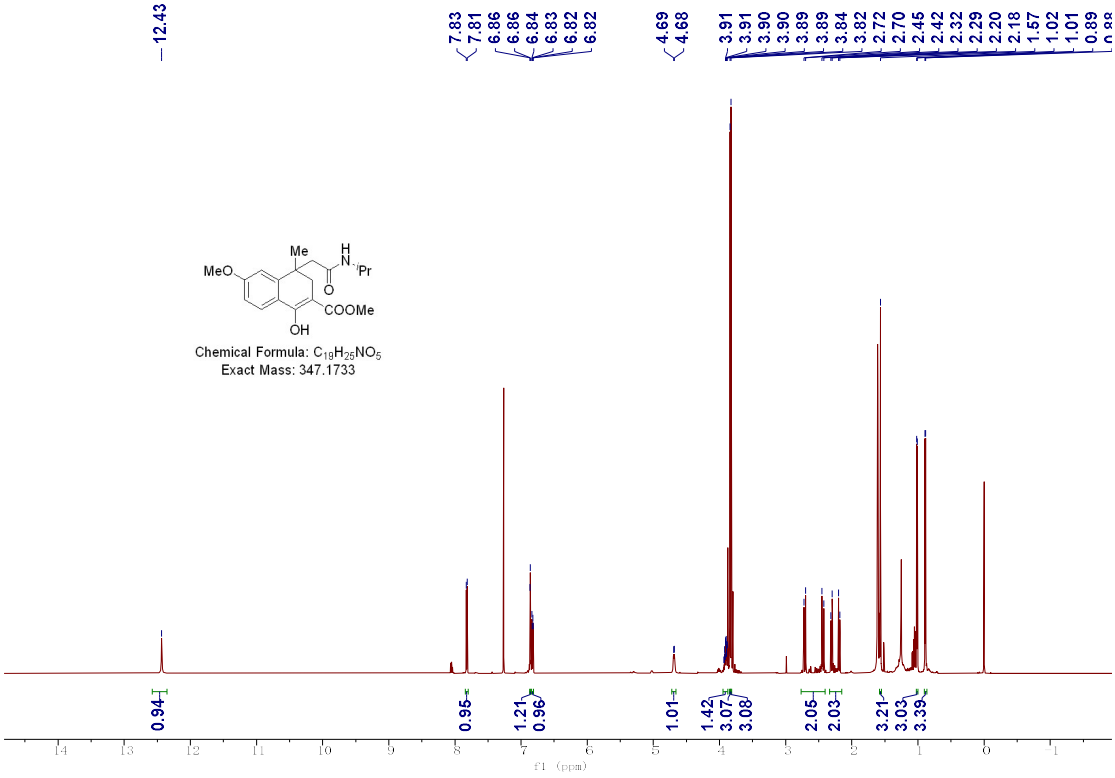

12.40
7.39
7.38
7.25
7.23
6.94
6.94
6.93
6.92
4.72
4.71
3.92
3.90
3.90
3.89
3.89
3.88
3.88
3.87
3.87
3.86
3.83
2.73
2.71
2.43
2.40
2.30
2.28
2.20
2.18
1.54
1.01
1.00
0.90
0.89
Me
H
N
iPr
O
MeO
COOMe
OH
Chemical Formula: C18H25NO5
Exact Mass: 347.1733
0.96
1.00
1.04
1.01
1.01
0.96
5.90
2.11
2.08
3.00
3.10
2.94
f1 (ppm)
173.06
169.53
164.12
158.45
137.23
129.55
126.54
117.32
109.33
95.51
55.44
51.81
46.89
41.03
35.85
34.16
25.32
22.59
22.48
Me
H
N
iPr
O
MeO
COOMe
OH
Chemical Formula: C18H25NO5
Exact Mass: 347.1733
f1 (ppm)

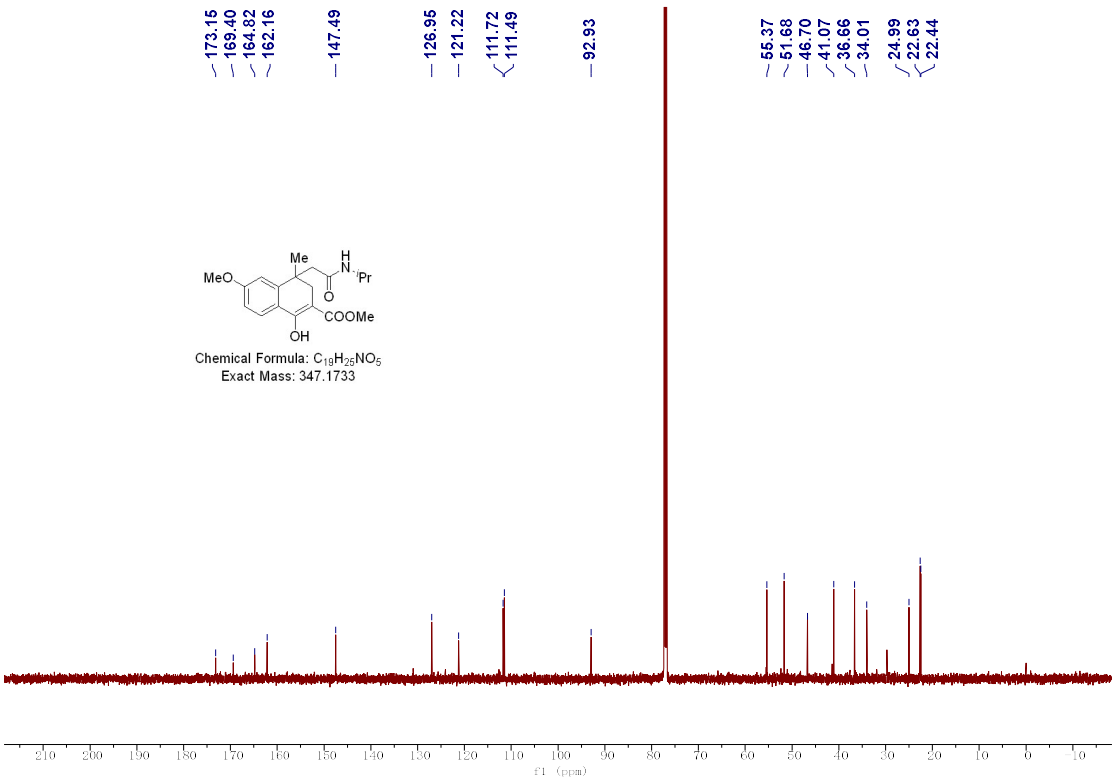
3ga


12.39
7.77
7.75
7.14
7.14
7.13
7.13
7.13
7.13
7.12
4.62
4.61
3.90
3.89
3.89
3.88
3.88
3.83
2.71
2.69
2.45
2.43
2.37
2.34
2.32
2.19
2.17
1.57
1.00
0.99
0.86
Me
Me
H
N
iPr
O
COOMe
OH
Chemical Formula: C19H25NO4
Exact Mass: 331.1784
f1 (ppm)

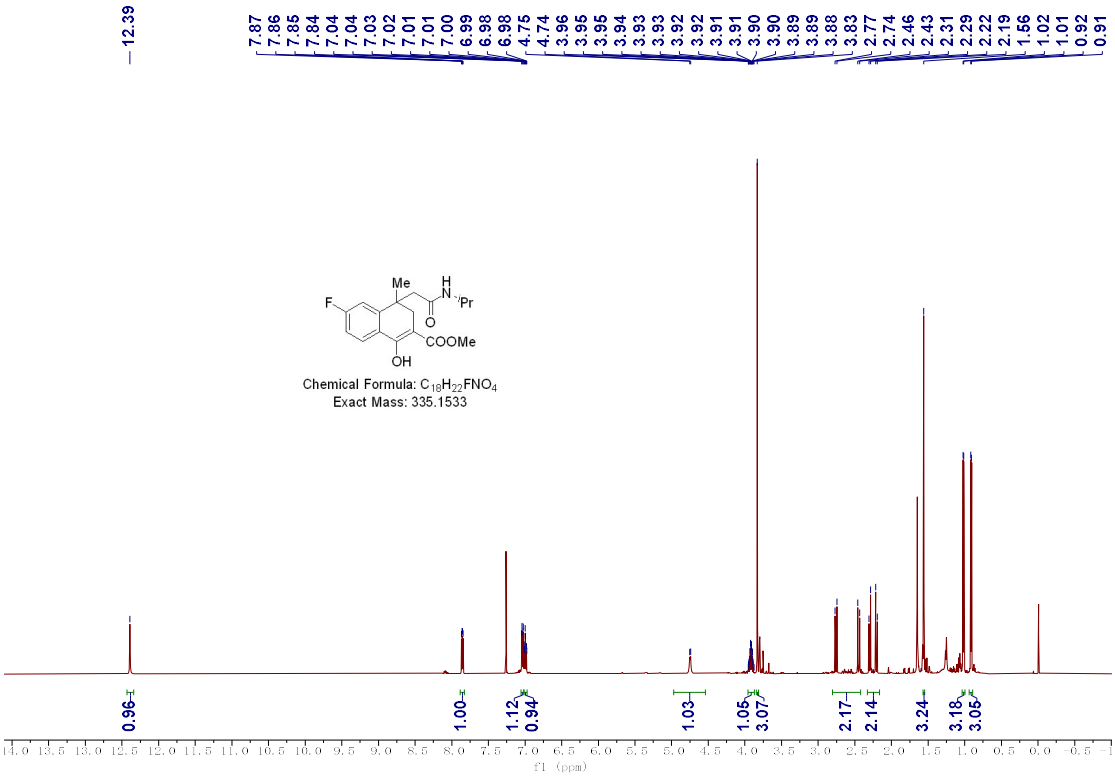

173.07
169.50
164.67
144.91
141.67
127.58
126.15
125.72
125.01
94.20
51.72
46.76
41.02
36.37
34.26
25.01
22.54
22.43
21.84
Me
Me
H
N
iPr
O
COOMe
OH
Chemical Formula: C19H25NO4
Exact Mass: 331.1784
f1 (ppm)

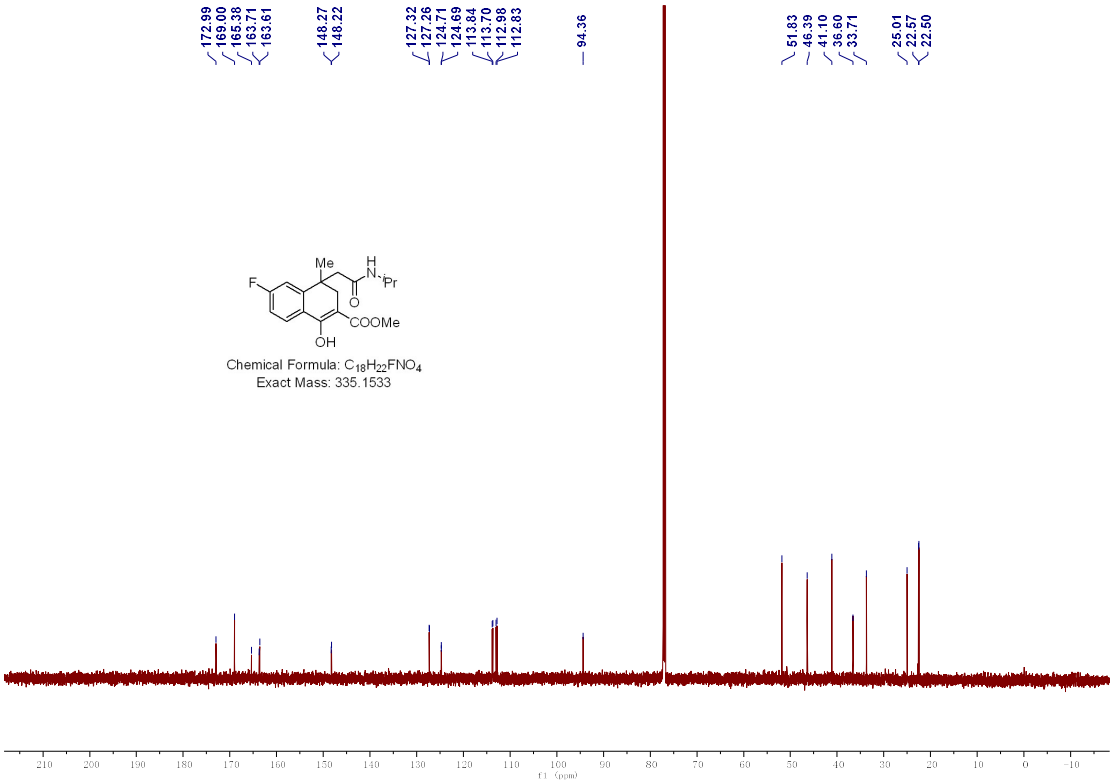
3ha


12.43
7.83
7.81
6.86
6.86
6.84
6.83
6.82
6.82
4.69
4.68
3.91
3.91
3.90
3.90
3.89
3.89
3.84
3.82
2.72
2.70
2.45
2.42
2.32
2.29
2.20
2.18
1.57
1.02
1.01
0.89
Me
H
N
iPr
MeO
O
COOMe
OH
Chemical Formula: C18H25NO5
Exact Mass: 347.1733
0.94
0.95
1.21
0.96
1.01
1.42
3.07
3.08
2.05
2.03
3.21
3.03
3.39
f1 (ppm)


173.15
169.40
164.82
162.16
147.49
126.95
121.22
111.72
111.49
92.93
55.37
51.68
46.70
41.07
36.66
34.01
24.99
22.63
22.44
Me
H
N
iPr
MeO
O
COOMe
OH
Chemical Formula: C18H25NO5
Exact Mass: 347.1733
f1 (ppm)

3ia


12.39
7.87
7.86
7.85
7.84
7.04
7.04
7.03
7.02
7.01
7.01
7.00
6.99
6.98
6.98
4.75
4.74
3.96
3.95
3.95
3.94
3.93
3.93
3.92
3.92
3.91
3.91
3.90
3.90
3.89
3.89
3.88
3.83
2.77
2.74
2.46
2.43
2.31
2.29
2.22
2.19
1.56
1.02
1.01
0.92
0.91
Me
H
N
iPr
F
O
COOMe
OH
Chemical Formula: C18H22FNO4
Exact Mass: 335.1533
0.96
1.00
1.12
0.94
1.03
1.05
3.07
2.17
2.14
3.24
3.18
3.05
f1 (ppm)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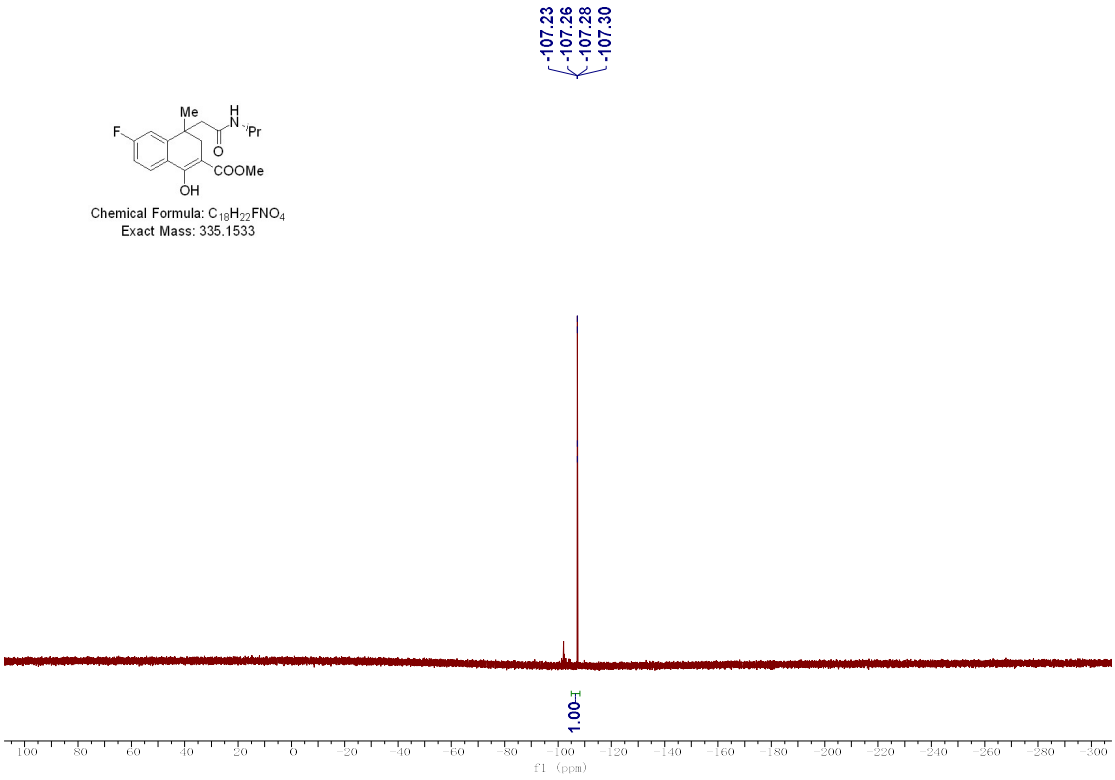
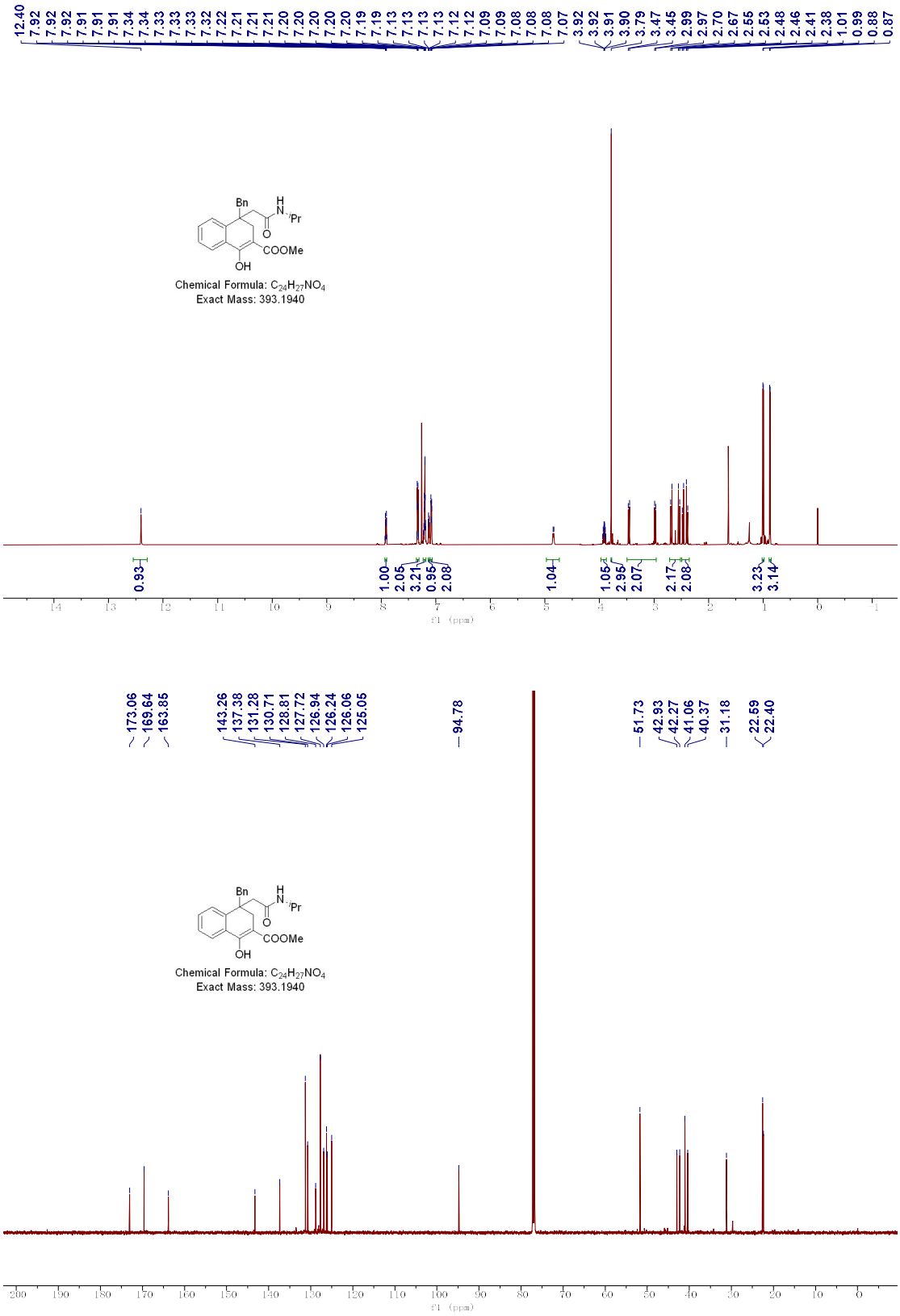
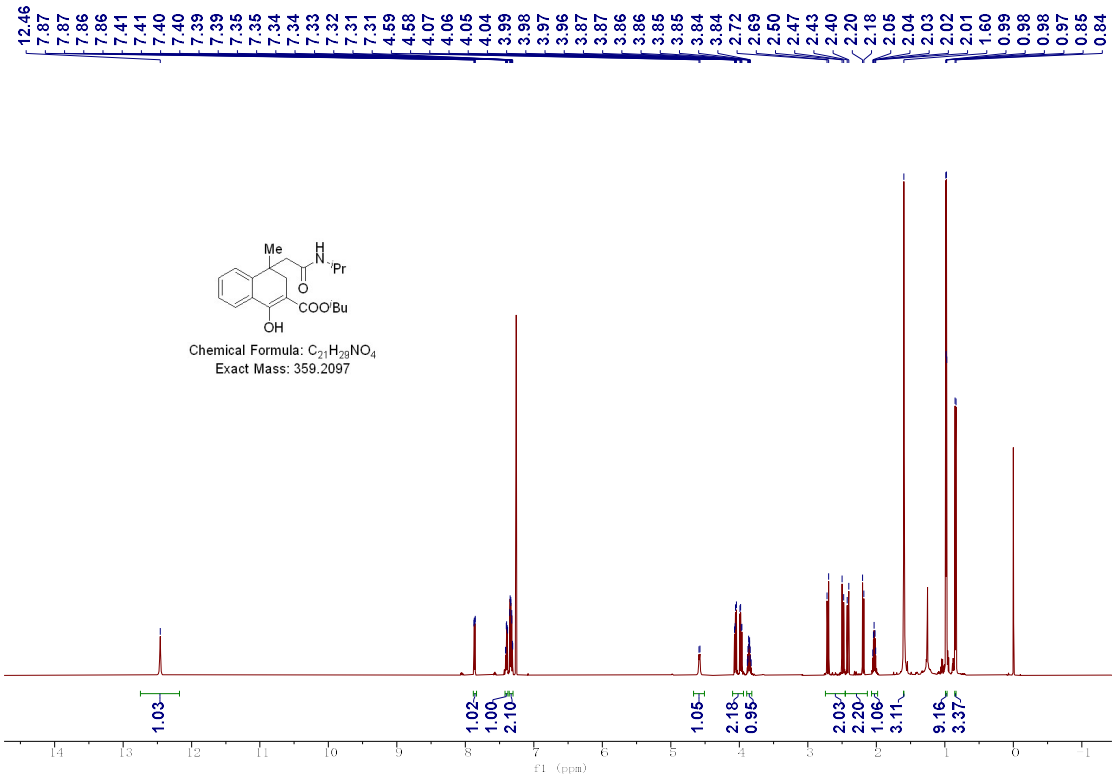
169.00
165.38
163.71
163.61
148.27
148.22
127.32
127.26
124.71
124.69
113.84
113.70
112.98
112.83
94.36
51.83
46.39
41.10
36.60
33.71
25.01
22.57
22.50
Me
H
N
iPr
F
O
COOMe
OH
Chemical Formula: C18H22FNO4
Exact Mass: 335.1533
f1 (ppm)

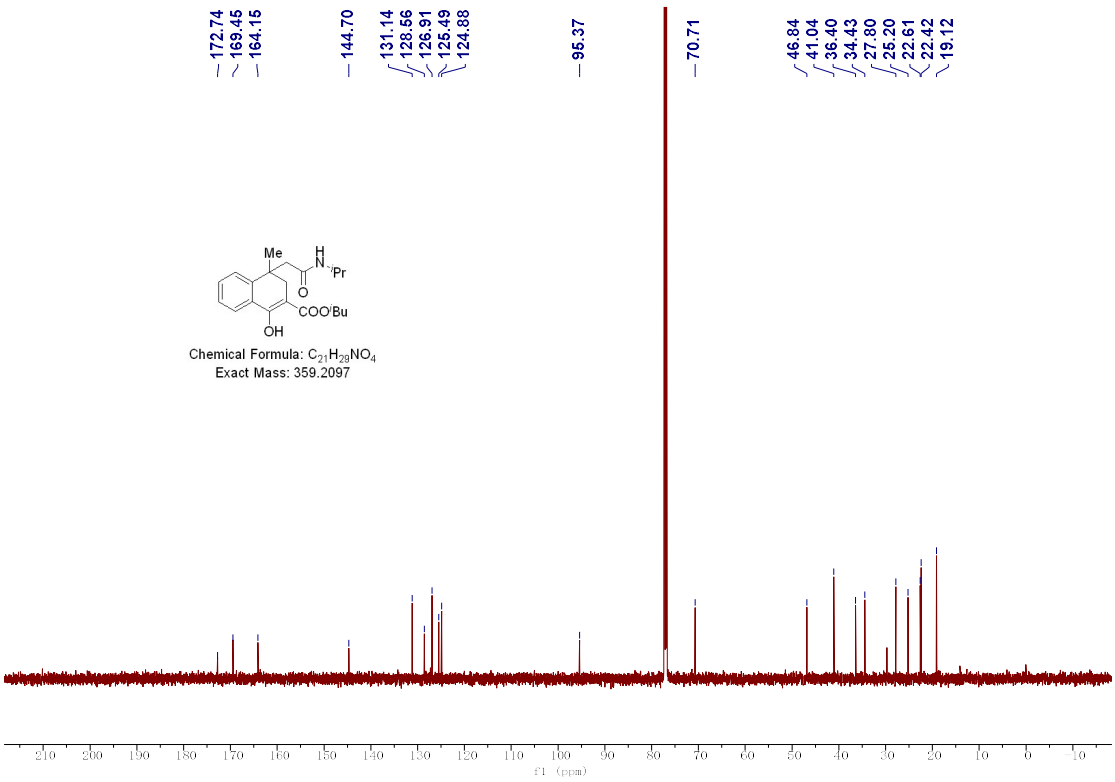

-107.23
-107.26
-107.28
-107.30
Me
H
N
iPr
F
O
COOMe
OH
Chemical Formula: C18H22FNO4
Exact Mass: 335.1533
1.00
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-300
f1 (ppm)

3ja

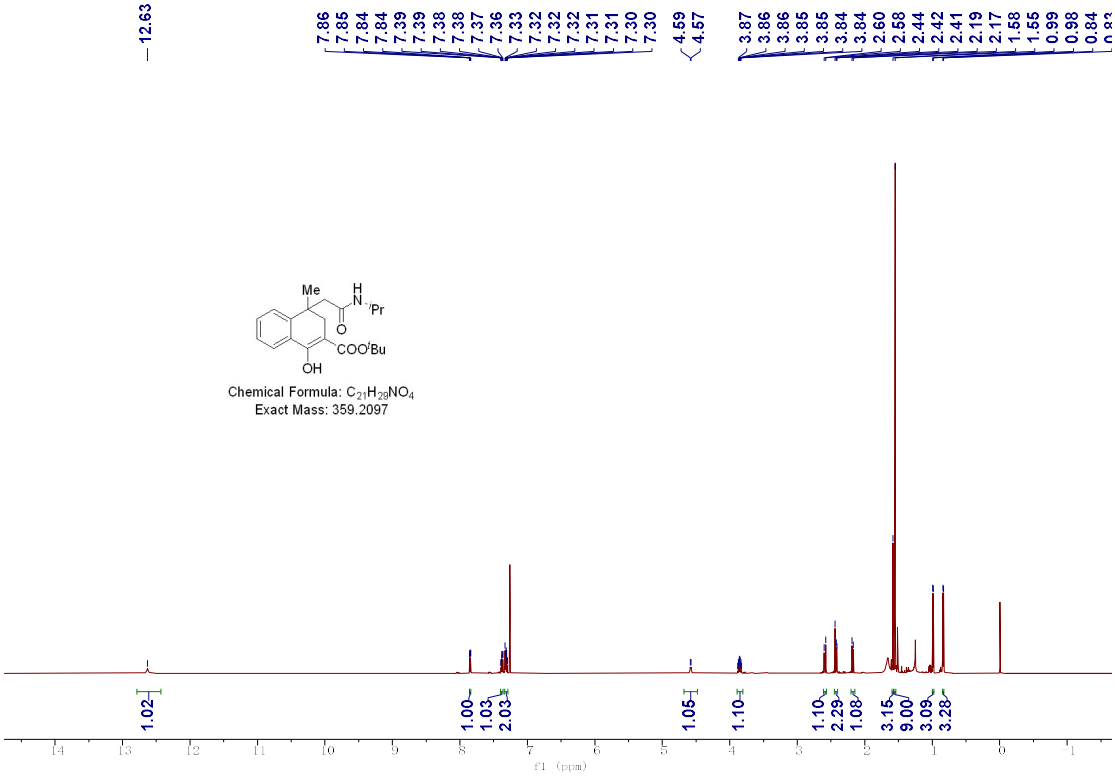

12.40
7.92
7.92
7.92
7.91
7.91
7.91
7.34
7.34
7.33
7.33
7.33
7.32
7.22
7.21
7.21
7.21
7.20
7.20
7.20
7.20
7.20
7.19
7.19
7.13
7.13
7.13
7.12
7.12
7.09
7.09
7.08
7.08
7.08
7.07
3.92
3.92
3.91
3.90
3.79
3.47
3.45
2.99
2.97
2.70
2.67
2.55
2.53
2.48
2.46
2.41
2.38
1.01
0.99
0.88
0.87
Bn
H
N
iPr
O
COOMe
OH
Chemical Formula: C24H27NO4
Exact Mass: 393.1940
0.93
1.00
2.05
3.21
0.95
2.08
1.04
1.05
2.95
2.07
2.17
2.08
3.23
3.14
f1 (ppm)
173.06
169.64
163.85
143.26
137.38
131.28
130.71
128.81
127.72
126.94
126.24
126.06
125.05
94.78
51.73
42.93
42.27
41.06
40.37
31.18
22.59
22.40
Bn
H
N
iPr
O
COOMe
OH
Chemical Formula: C24H27NO4
Exact Mass: 393.1940
f1 (ppm)

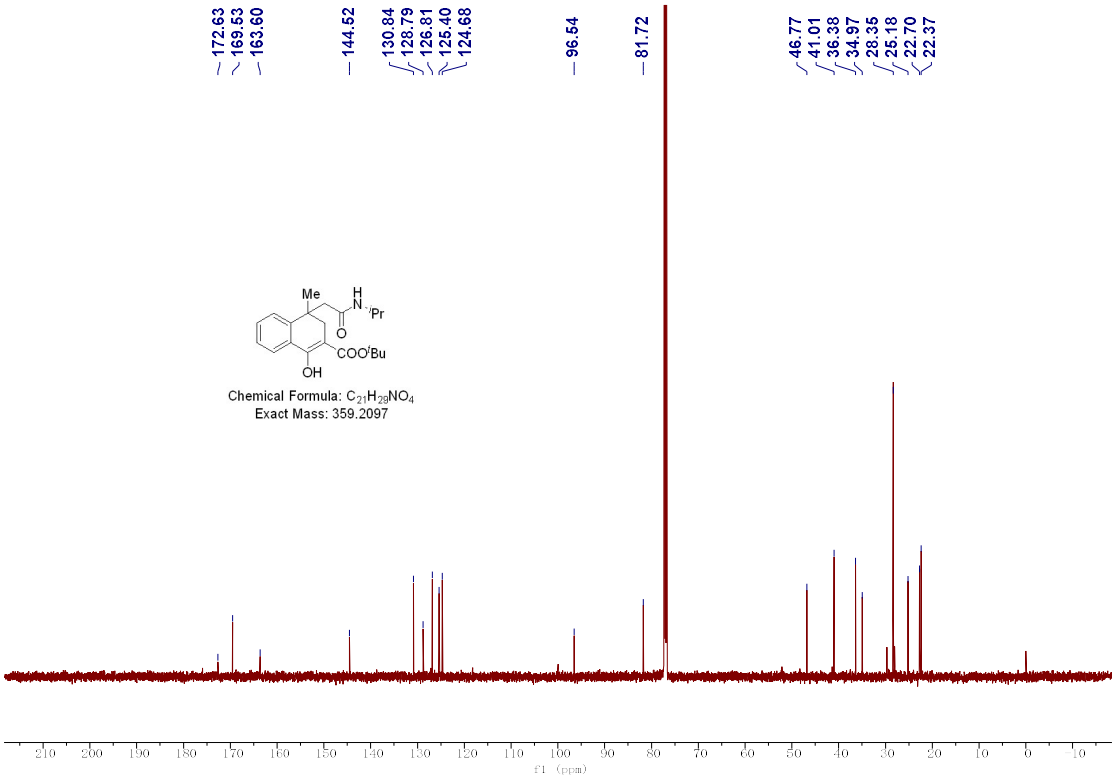
3bb


12.46
7.87
7.87
7.86
7.86
7.41
7.41
7.40
7.40
7.39
7.39
7.35
7.35
7.34
7.34
7.33
7.32
7.31
7.31
4.59
4.58
4.07
4.06
4.05
4.04
3.99
3.98
3.97
3.96
3.87
3.87
3.86
3.86
3.85
3.85
3.84
3.84
2.72
2.69
2.50
2.47
2.43
2.40
2.20
2.18
2.05
2.04
2.03
2.02
2.01
1.60
0.99
0.98
0.98
0.97
0.85
0.84
Me
H
N
iPr
O
COO
tBu
OH
Chemical Formula: C21H29NO4
Exact Mass: 359.2097
1.03
1.02
1.00
2.10
1.05
2.18
0.95
2.03
2.20
1.06
3.11
9.16
3.37
f1 (ppm)

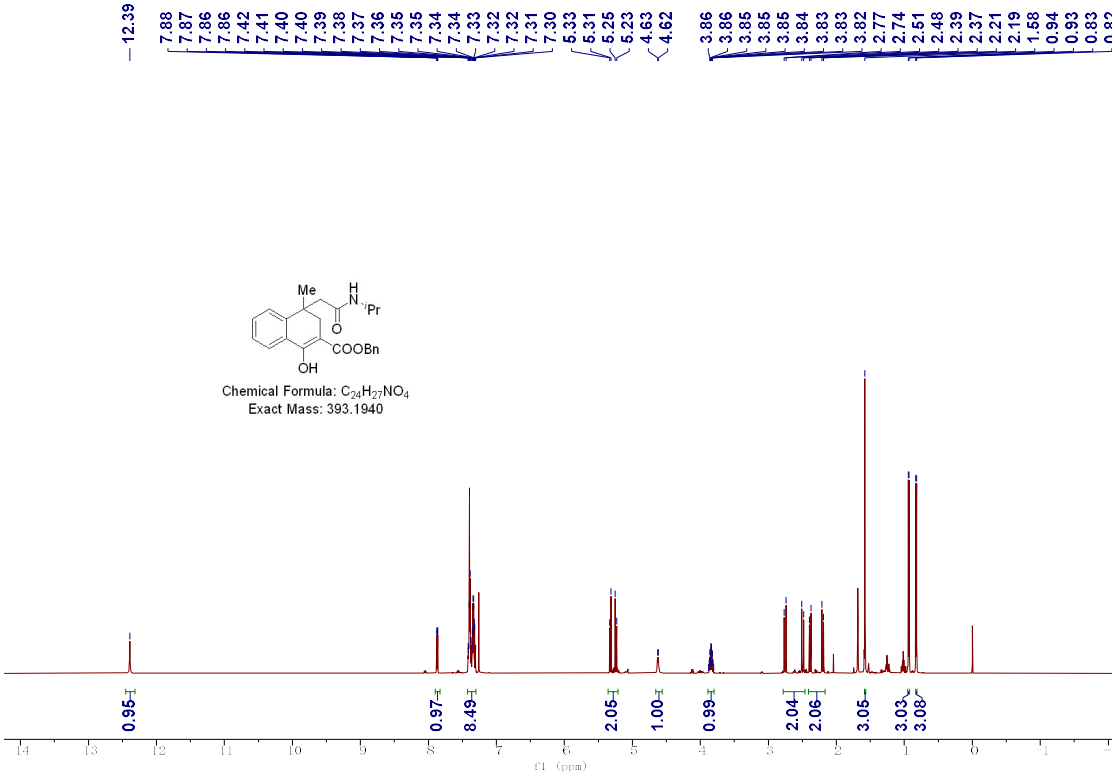

172.74
169.45
164.15
144.70
131.14
128.56
126.91
125.49
124.88
95.37
70.71
46.84
41.04
36.40
34.43
27.80
25.20
22.61
22.42
19.12
Me
H
N
iPr
O
COO
tBu
OH
Chemical Formula: C21H29NO4
Exact Mass: 359.2097
f1 (ppm)

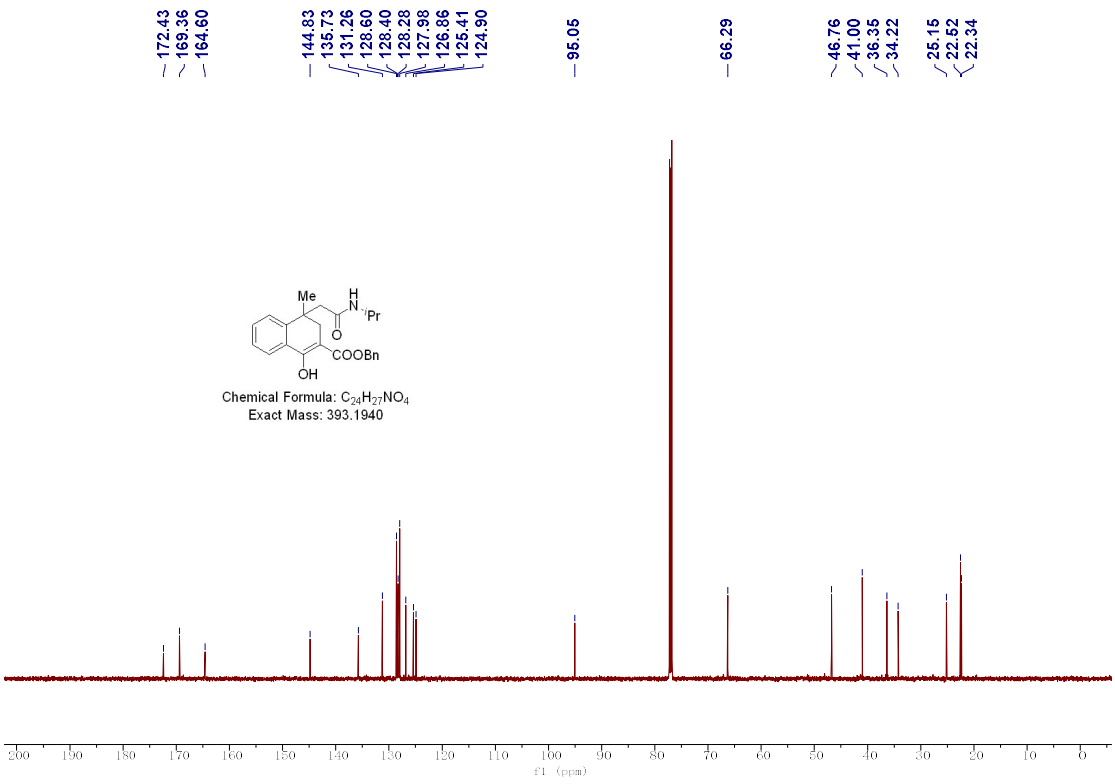
3bc


12.63
7.86
7.85
7.84
7.84
7.39
7.39
7.38
7.38
7.37
7.36
7.33
7.32
7.32
7.31
7.31
7.30
7.30
4.59
4.57
3.87
3.86
3.86
3.85
3.85
3.84
3.84
2.60
2.58
2.44
2.42
2.41
2.19
2.17
1.58
1.55
0.99
0.98
0.84
Me
H
N
iPr
O
COOtBu
OH
Chemical Formula: C21H29NO4
Exact Mass: 359.2097
1.02
1.00
1.03
2.03
1.05
1.10
1.10
2.29
1.08
3.15
9.00
3.09
3.28
f1 (ppm)

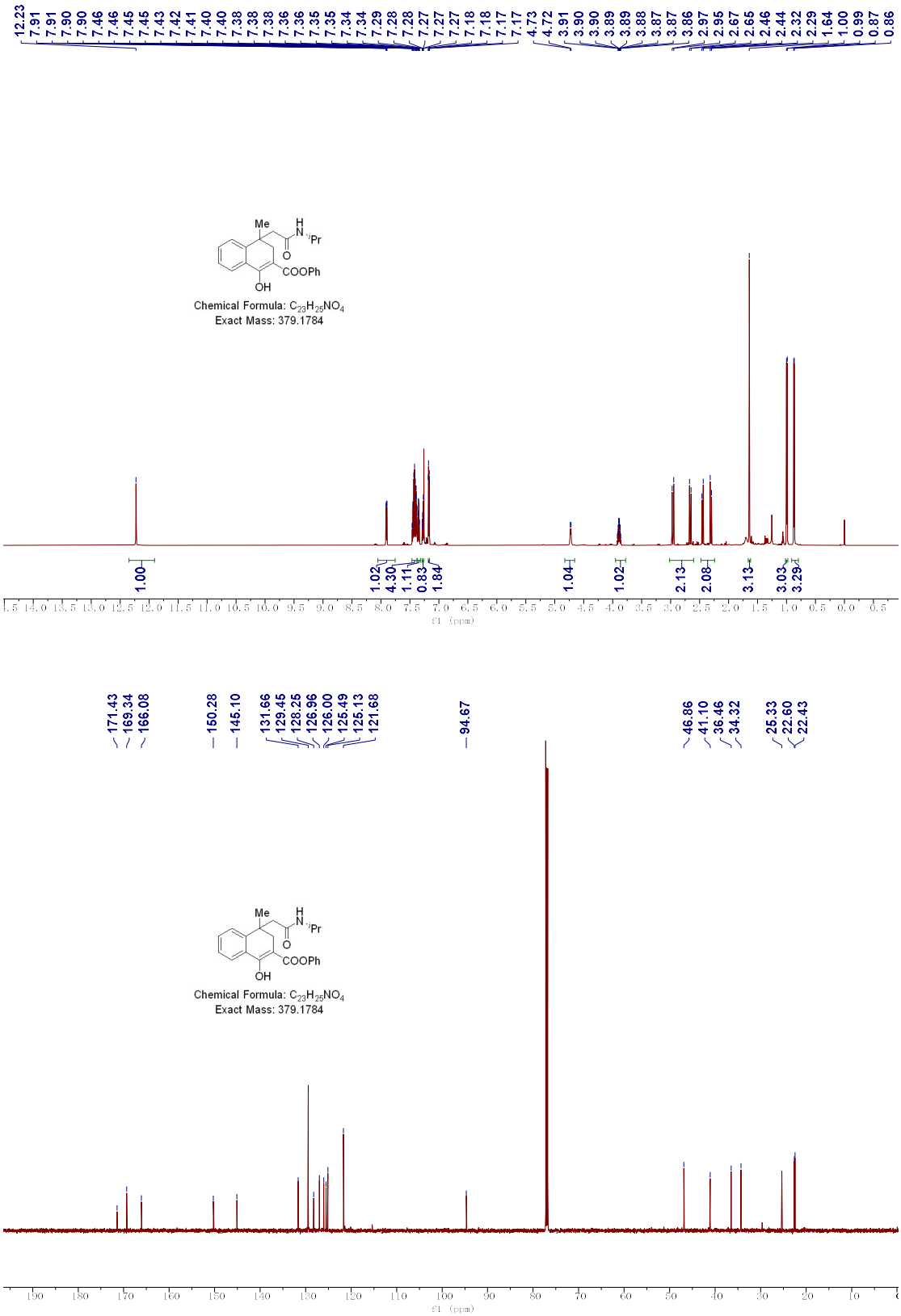

172.63
169.53
163.60
144.52
130.84
128.79
126.81
125.40
124.68
96.54
81.72
46.77
41.01
36.38
34.97
28.35
25.18
22.70
22.37
Me
H
N
iPr
O
COOtBu
OH
Chemical Formula: C21H29NO4
Exact Mass: 359.2097
f1 (ppm)

3bd

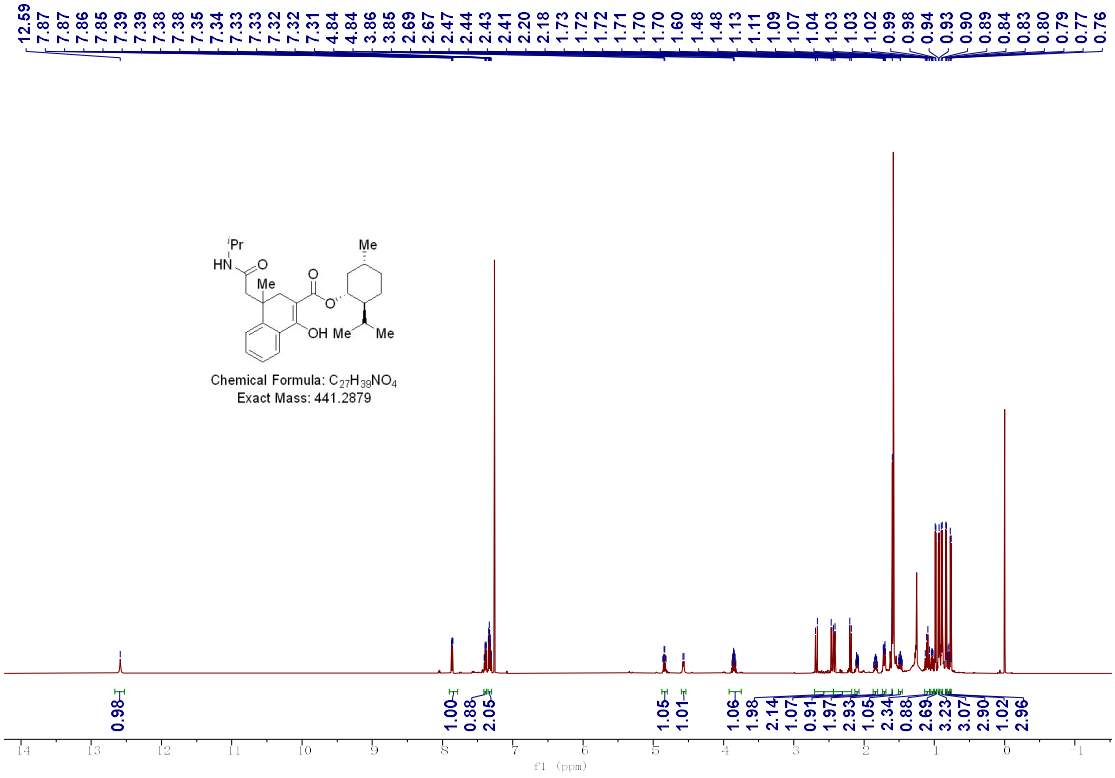

12.39
7.88
7.87
7.86
7.86
7.42
7.41
7.40
7.40
7.39
7.38
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.30
5.33
5.31
5.25
5.23
4.63
4.62
3.86
3.86
3.85
3.85
3.85
3.84
3.83
3.83
3.82
2.77
2.74
2.51
2.48
2.39
2.37
2.21
2.19
1.58
0.94
0.93
0.83
Me
NH
iPr
O
COOBn
OH
Chemical Formula: C24H27NO4
Exact Mass: 393.1940
0.95
0.97
8.49
2.05
1.00
0.99
2.04
2.06
3.05
3.03
3.08
f1 (ppm)

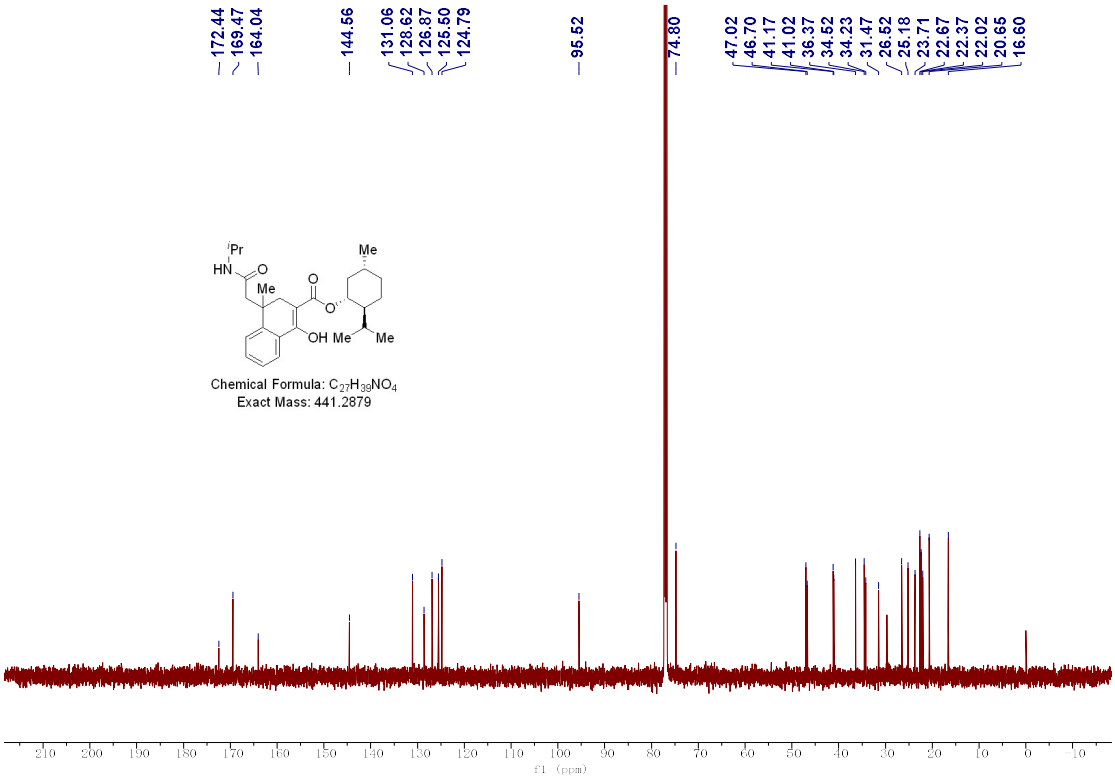

172.43
169.36
164.60
144.83
135.73
131.26
128.60
128.40
128.28
127.98
126.86
125.41
124.90
95.05
66.29
46.76
41.00
36.35
34.22
25.15
22.52
22.34
Me
NH
iPr
O
COOBn
OH
Chemical Formula: C24H27NO4
Exact Mass: 393.1940
f1 (ppm)

3be

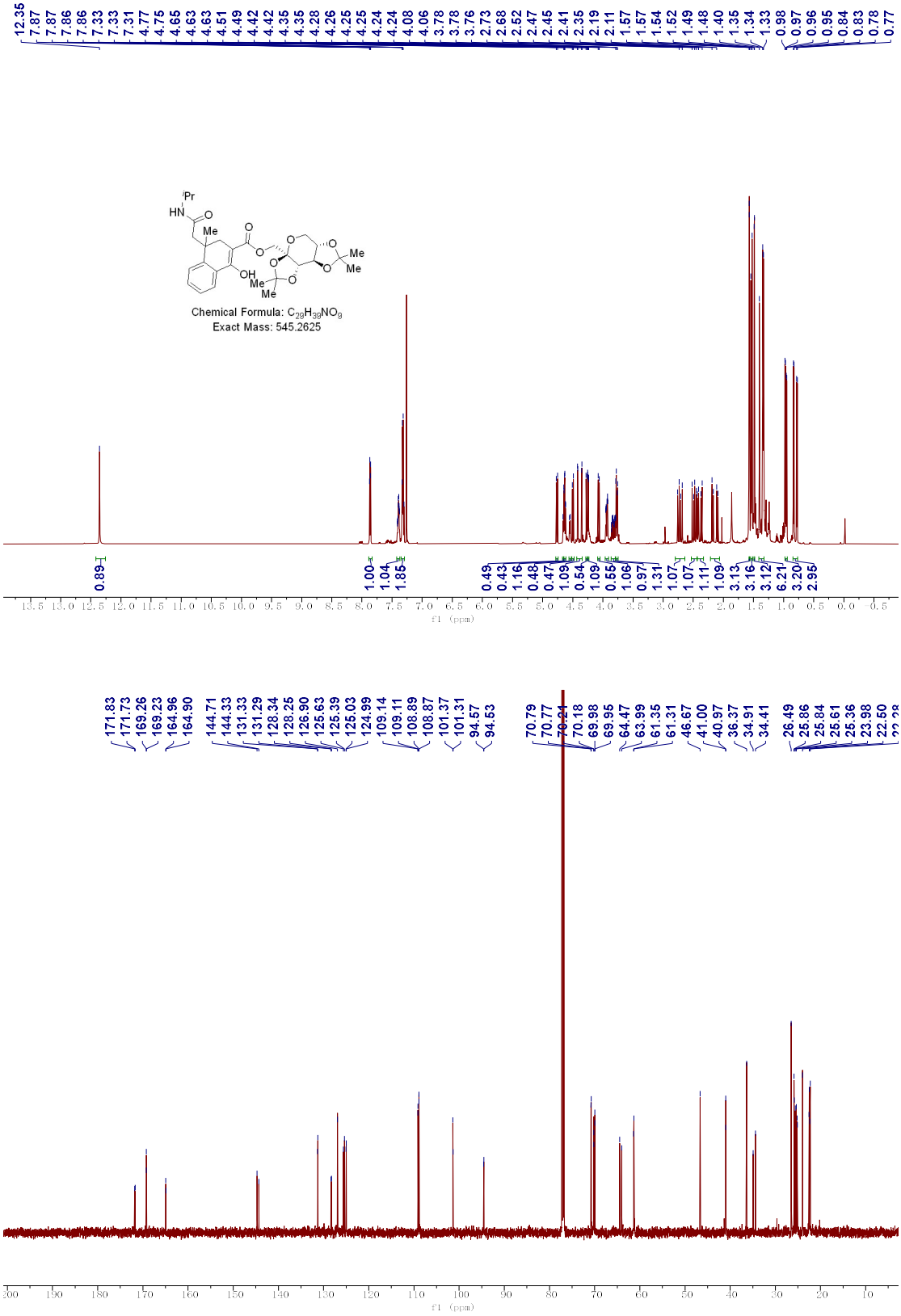

12.23
7.91
7.91
7.90
7.90
7.46
7.46
7.45
7.45
7.43
7.42
7.41
7.40
7.40
7.38
7.38
7.38
7.36
7.36
7.35
7.35
7.34
7.34
7.29
7.28
7.28
7.27
7.27
7.27
7.18
7.18
7.17
7.17
4.73
4.72
3.91
3.90
3.90
3.89
3.89
3.88
3.87
3.86
2.97
2.95
2.67
2.65
2.46
2.44
2.32
2.29
1.64
1.00
0.99
0.87
0.86
Me
H
N
iPr
O
COOPh
OH
Chemical Formula: C23H25NO4
Exact Mass: 379.1784
1.00
1.02
4.30
1.11
0.83
1.84
1.04
1.02
2.13
2.08
3.13
3.03
3.29
f1 (ppm)
171.43
169.34
166.08
150.28
145.10
131.66
129.45
128.25
126.96
126.00
125.49
125.13
121.68
94.67
46.86
41.10
36.46
34.32
25.33
22.60
22.43
Me
H
N
iPr
O
COOPh
OH
Chemical Formula: C23H25NO4
Exact Mass: 379.1784
f1 (ppm)

3bf

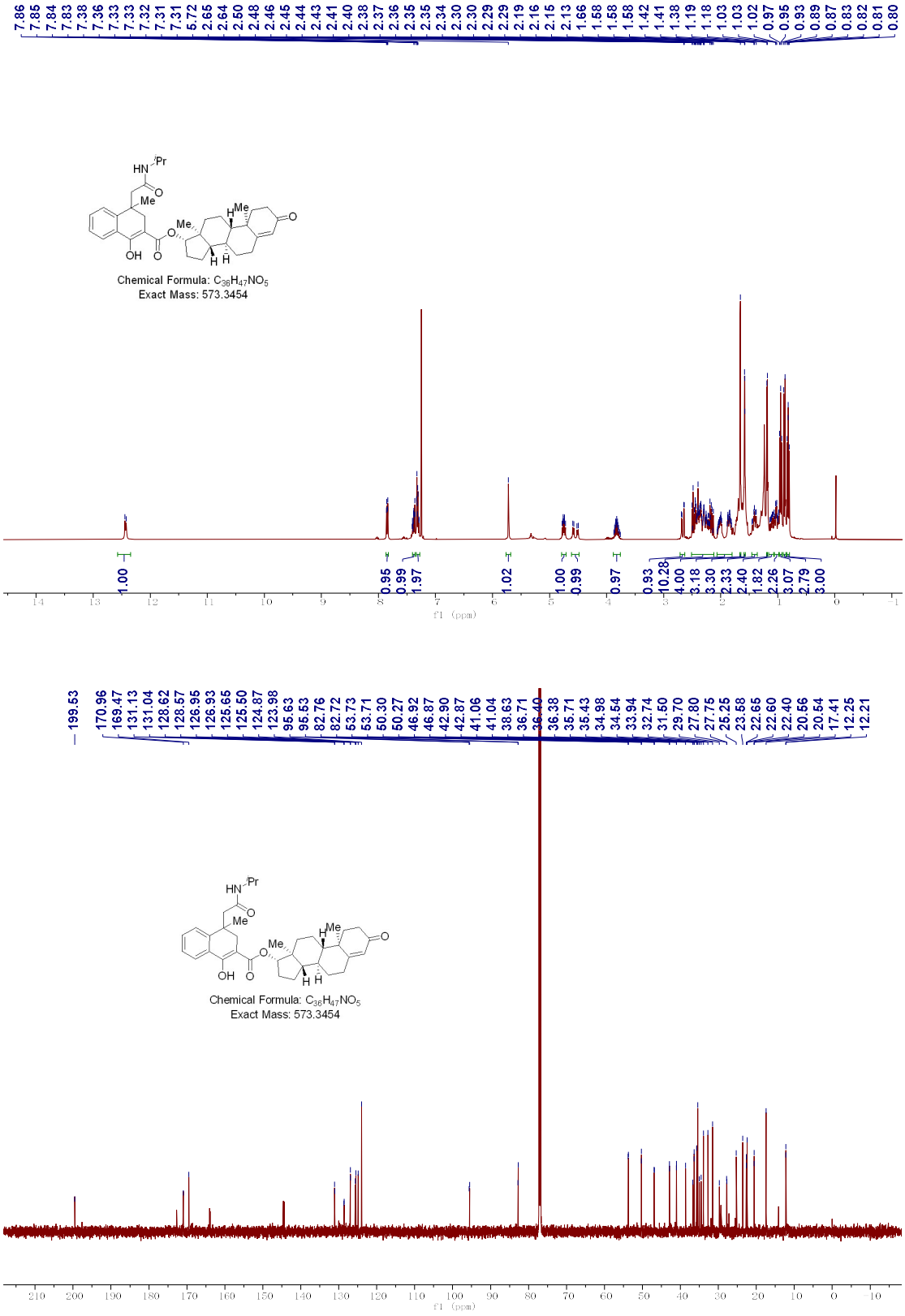

12.59
7.87
7.87
7.86
7.85
7.39
7.39
7.38
7.38
7.35
7.34
7.33
7.33
7.32
7.32
7.31
4.84
4.84
3.86
3.85
2.69
2.67
2.47
2.44
2.43
2.41
2.20
2.18
1.73
1.72
1.72
1.71
1.70
1.70
1.60
1.48
1.48
1.13
1.11
1.09
1.07
1.04
1.03
1.03
1.02
0.99
0.98
0.94
0.93
0.90
0.89
0.84
0.83
0.80
0.79
0.77
0.76
iPr
HN
O
Me
O
O
Me
OH Me
Me
Chemical Formula: C27H39NO4
Exact Mass: 441.2879
0.98
1.00
0.88
2.05
1.05
1.01
1.06
1.98
2.14
1.07
0.91
1.97
2.93
1.05
2.34
0.88
2.69
3.23
3.07
2.90
1.02
2.96
f1 (ppm)


172.44
169.47
164.04
144.56
131.06
128.62
126.87
125.50
124.79
95.52
74.80
47.02
46.70
41.17
41.02
36.37
34.52
34.23
31.47
26.52
25.18
23.71
22.67
22.37
22.02
20.65
16.60
iPr
HN
O
Me
O
O
Me
OH Me
Me
Chemical Formula: C27H39NO4
Exact Mass: 441.2879
f1 (ppm)

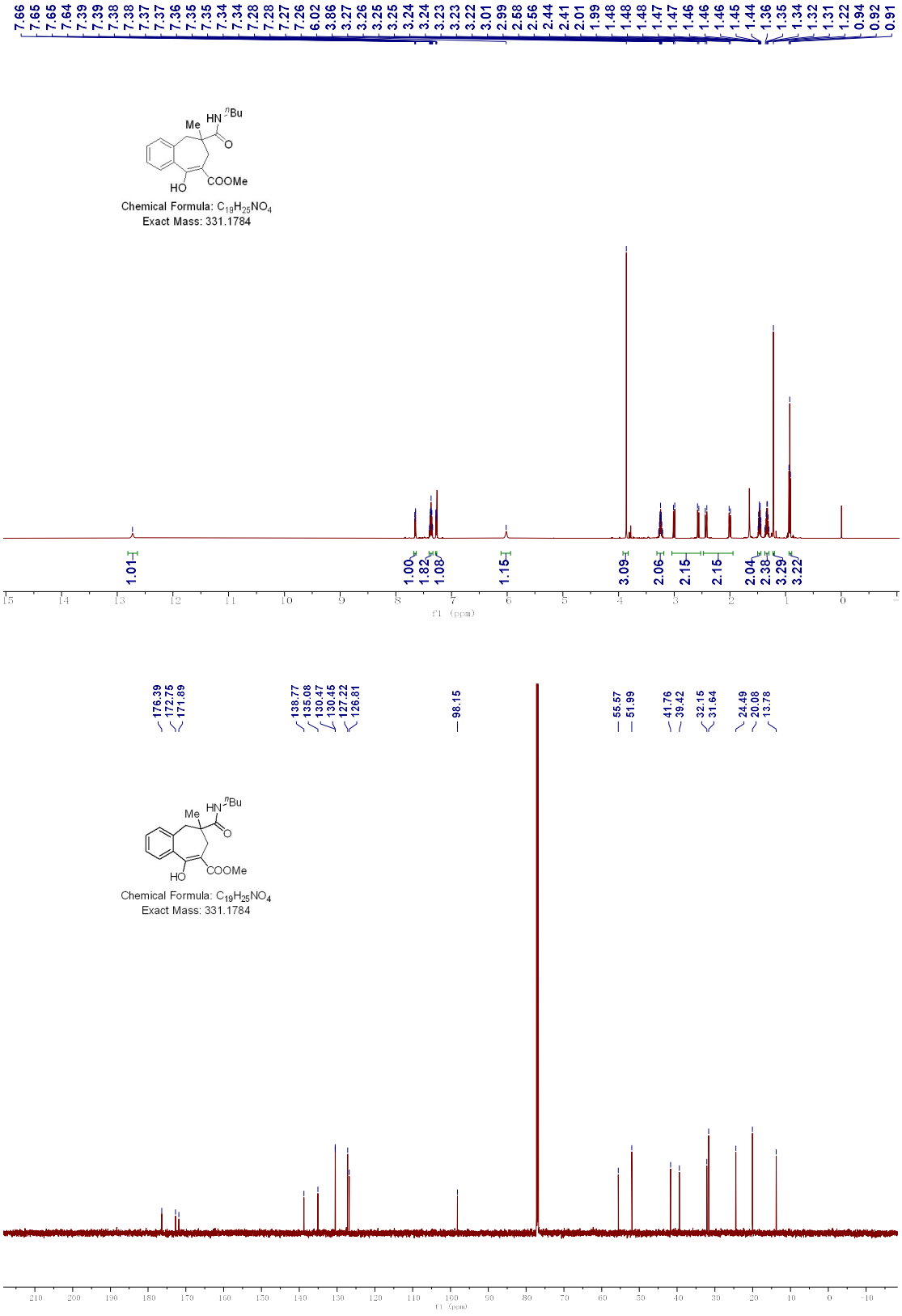
3bg



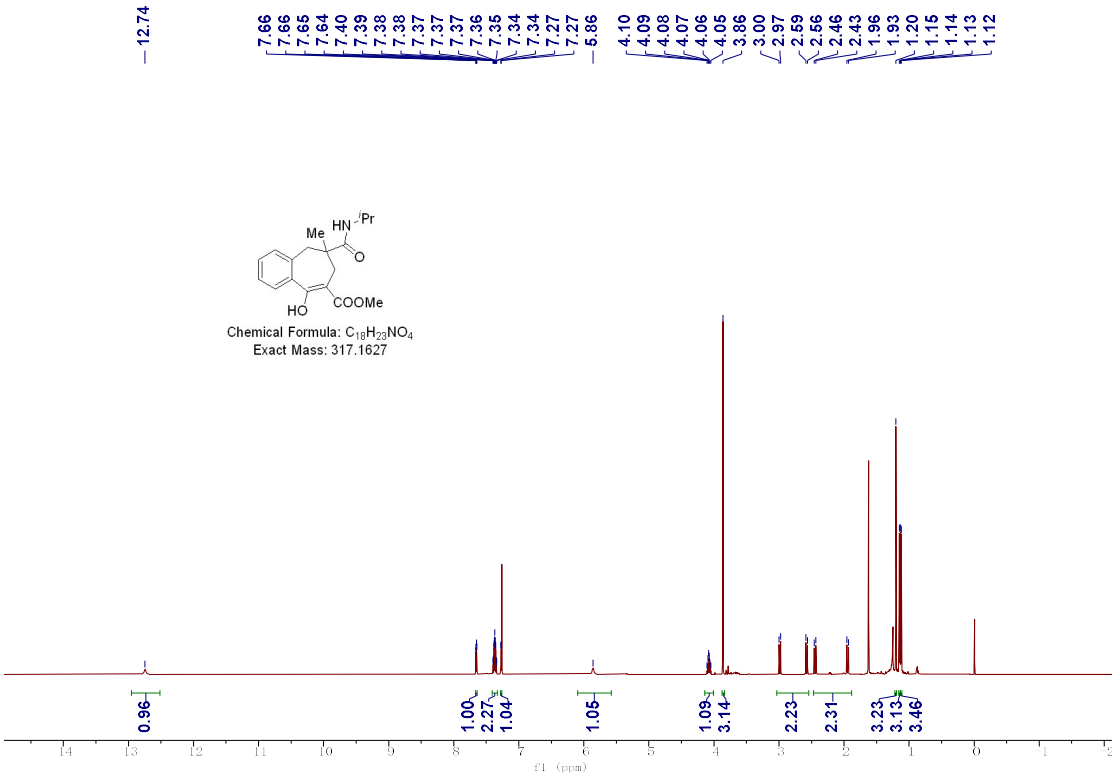
3bh

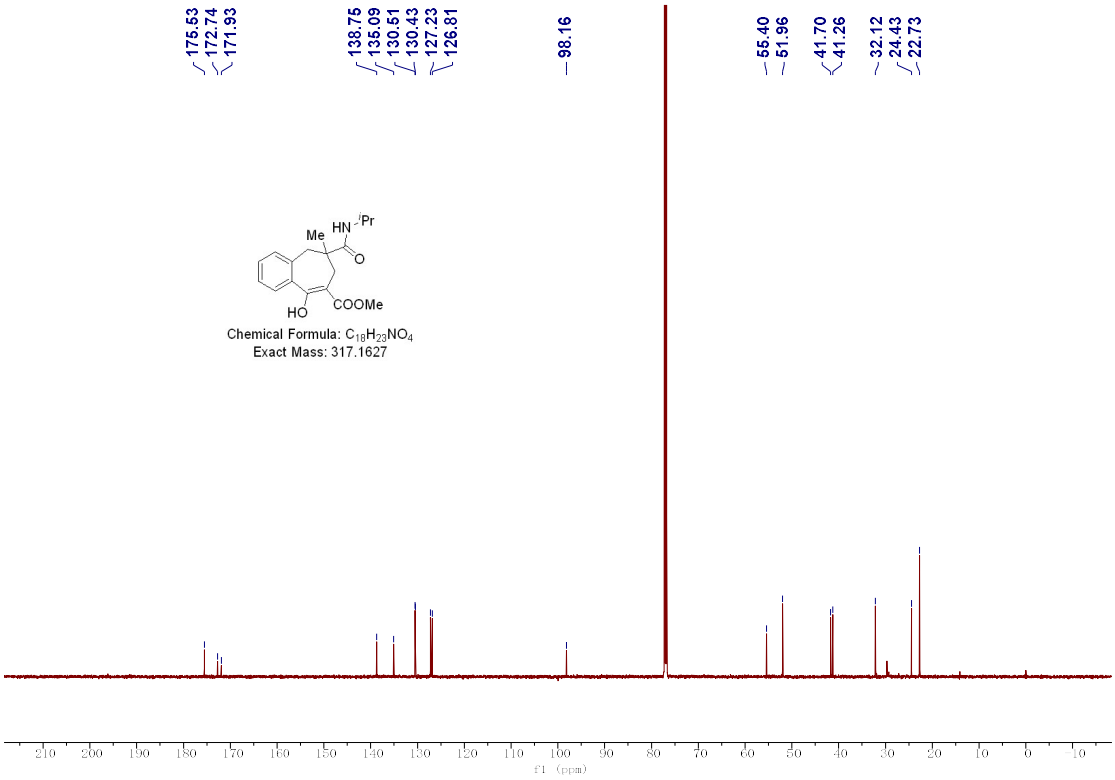

Chemical Formula: C36H47NO5
Exact Mass: 573.3454
Chemical Formula: C36H47NO5
Exact Mass: 573.3454

4aa

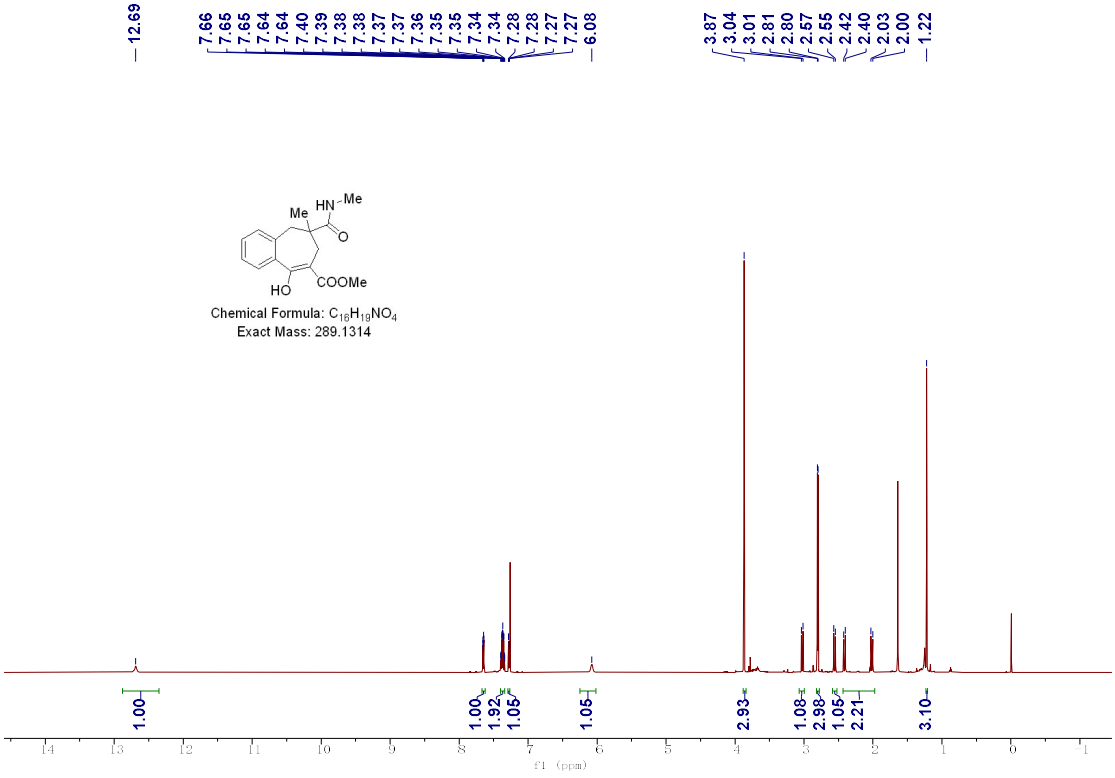

7.66 7.65 7.65 7.64 7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.35 7.35 7.34 7.34 7.28 7.28 7.27 7.26 6.02 3.86 3.27 3.26 3.25 3.25 3.24 3.24 3.23 3.23 3.22 3.01 2.99 2.58 2.56 2.44 2.41 2.01 1.99 1.48 1.48 1.48 1.47 1.47 1.46 1.46 1.46 1.45 1.44 1.36 1.35 1.34 1.32 1.31 1.22 0.94 0.92 0.91
Me
HN
nBu
O
HO
COOMe
Chemical Formula: C18H25NO4
Exact Mass: 331.1784
1.01 1.00 1.82 1.08 1.15 3.09 2.06 2.15 2.15 2.04 2.38 3.29 3.22
f1 (ppm)
176.39 172.75 171.89 138.77 135.08 130.47 130.45 127.22 126.81 98.15 55.57 51.99 41.76 39.42 32.15 31.64 24.49 20.08 13.78
Me
HN
nBu
O
HO
COOMe
Chemical Formula: C19H25NO4
Exact Mass: 331.1784
f1 (ppm)

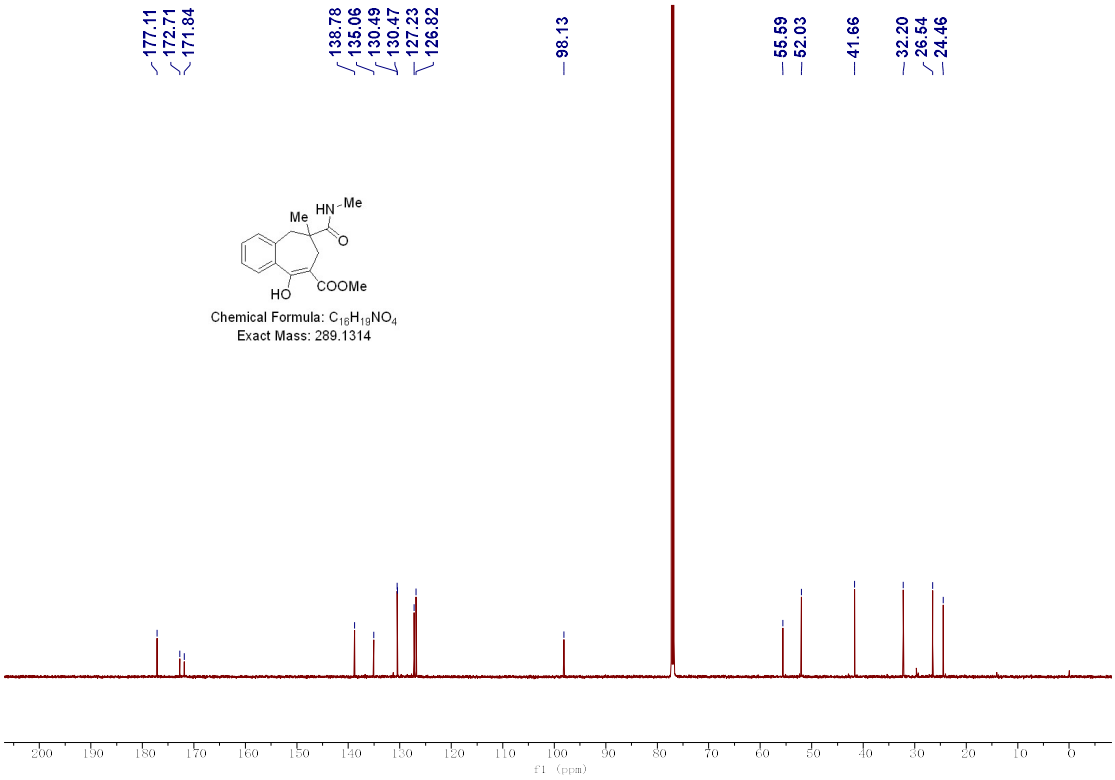
4ba


12.74
7.66
7.66
7.65
7.64
7.40
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.35
7.34
7.34
7.27
7.27
5.86
4.10
4.09
4.08
4.07
4.06
4.05
3.86
3.00
2.97
2.59
2.56
2.46
2.43
1.96
1.93
1.20
1.15
1.14
1.13
1.12
Me
HN
iPr
O
HO
COOMe
Chemical Formula: C18H23NO4
Exact Mass: 317.1627
0.96
1.00
2.27
1.04
1.05
1.09
3.14
2.23
2.31
3.23
3.13
3.46
f1 (ppm)

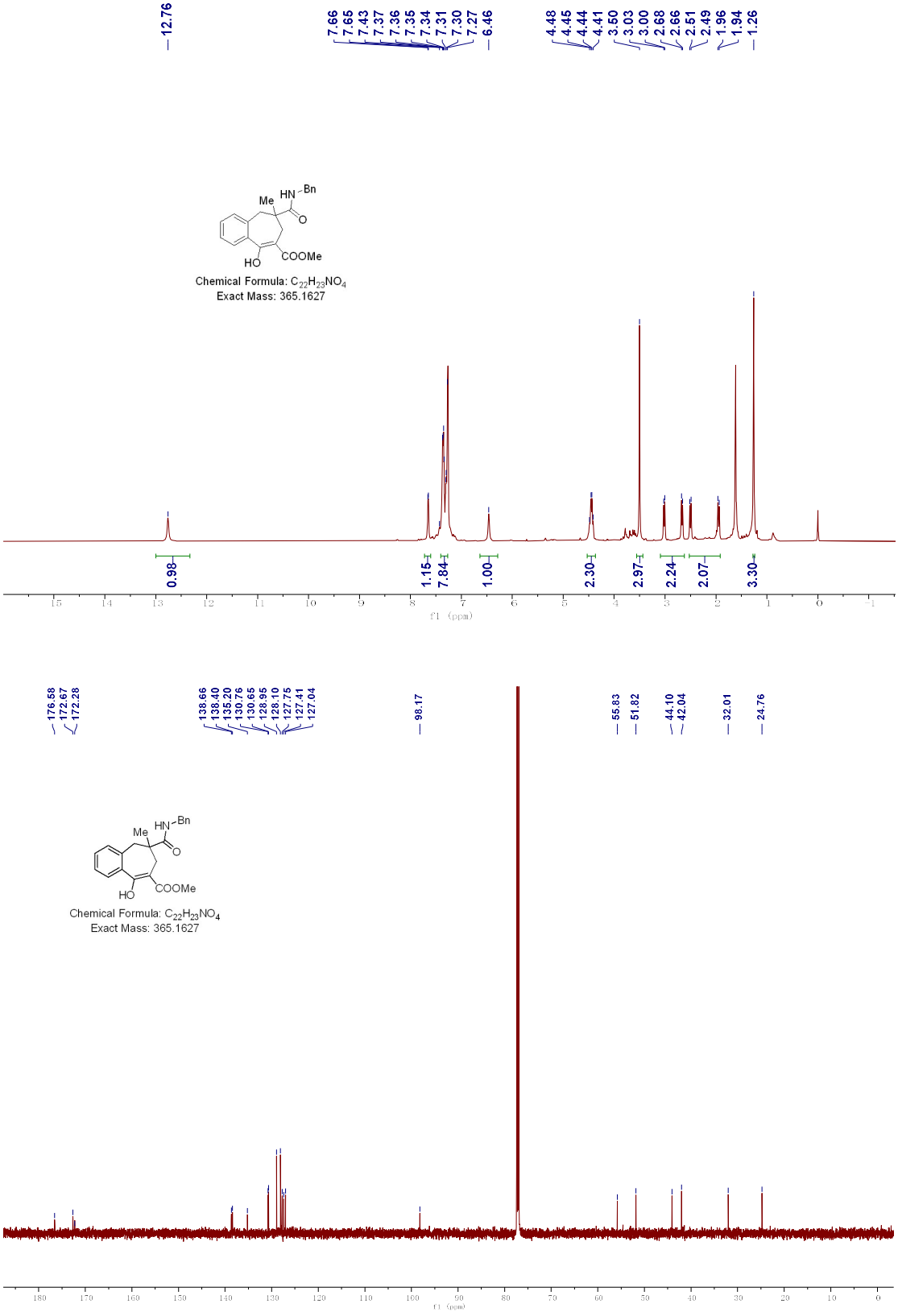

175.53
172.74
171.93
138.75
135.09
130.61
130.43
127.23
126.81
98.16
55.40
51.96
41.70
41.26
32.12
24.43
22.73
Me
HN
iPr
O
HO
COOMe
Chemical Formula: C18H23NO4
Exact Mass: 317.1627
f1 (ppm)

4ca

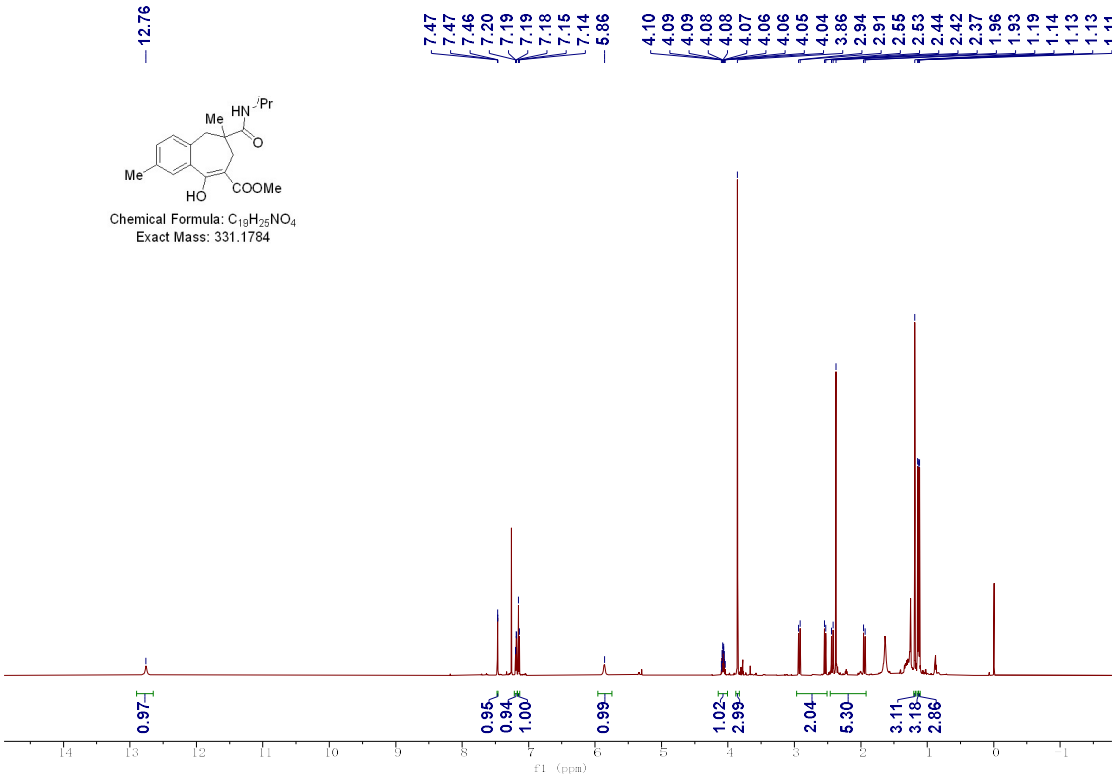

12.69
7.66
7.65
7.65
7.64
7.64
7.40
7.39
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.34
7.28
7.28
7.27
7.27
6.08
3.87
3.04
3.01
2.81
2.80
2.57
2.55
2.42
2.40
2.03
2.00
1.22
Me
HN
Me
O
HO
COOMe
Chemical Formula: C16H19NO4
Exact Mass: 289.1314
1.00
1.00
1.92
1.05
1.05
2.93
1.08
2.98
1.05
2.21
3.10
f1 (ppm)

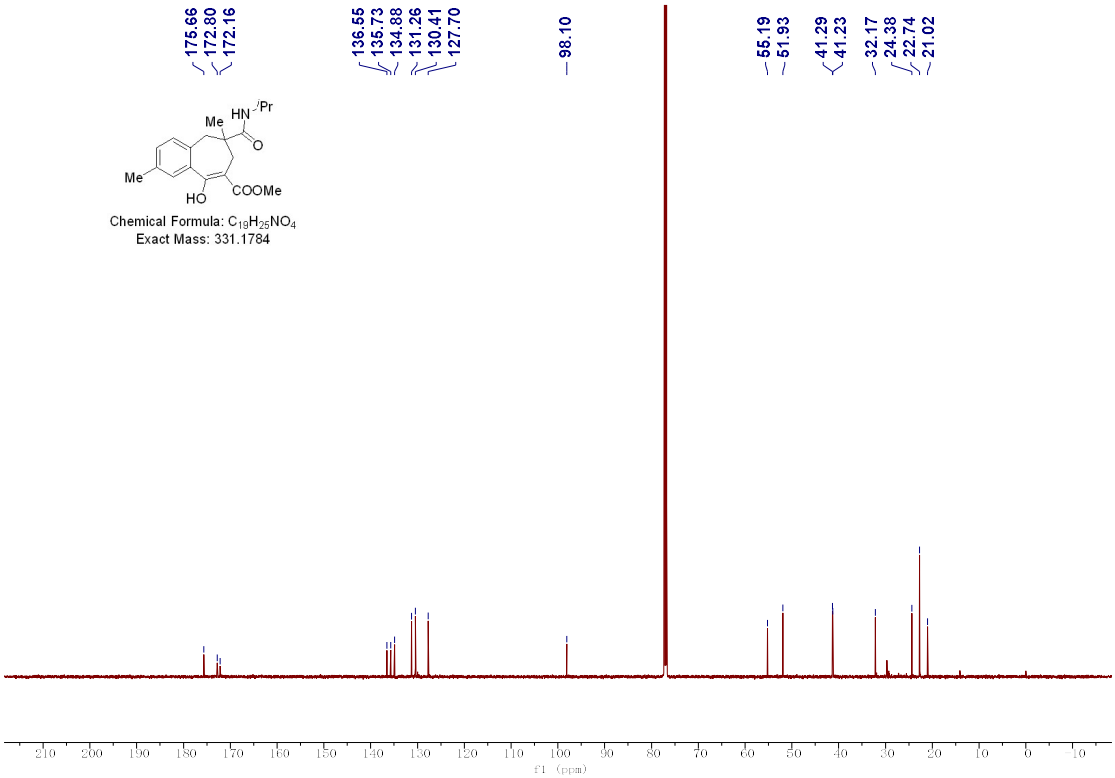

177.11
172.71
171.84
138.78
135.06
130.49
130.47
127.23
126.82
98.13
55.59
52.03
41.66
32.20
26.54
24.46
Me
HN
Me
O
HO
COOMe
Chemical Formula: C16H19NO4
Exact Mass: 289.1314
f1 (ppm)

4da

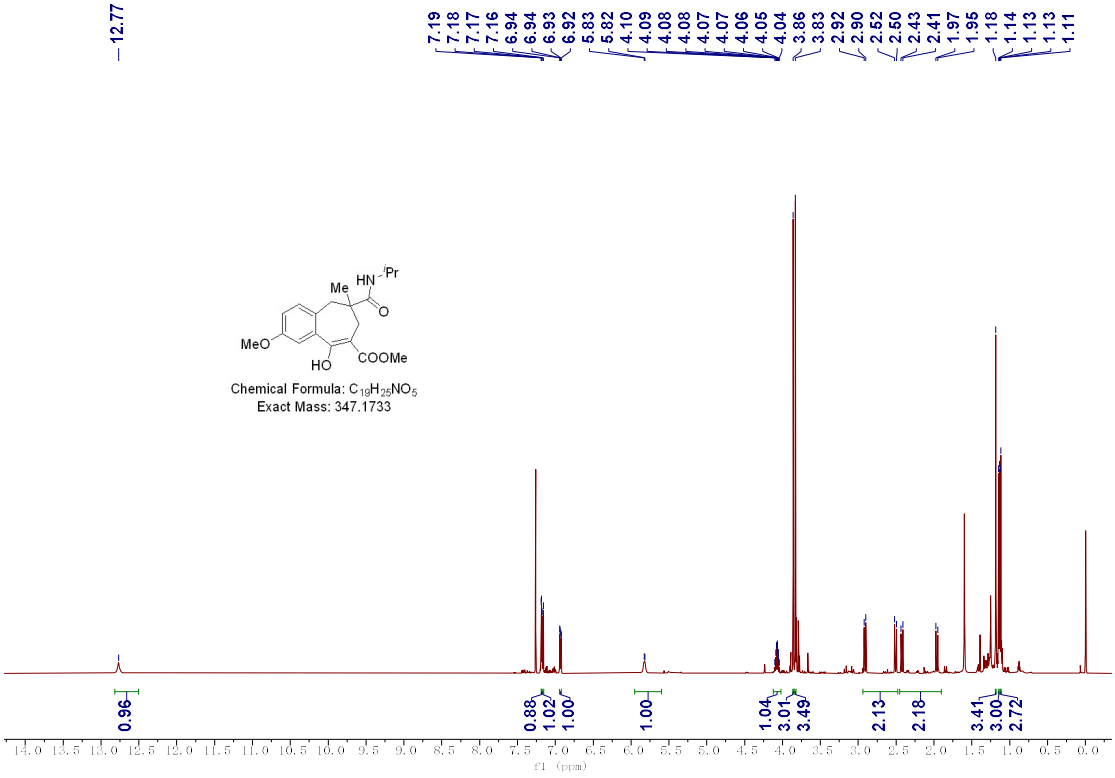

12.76
7.66
7.65
7.43
7.37
7.36
7.35
7.34
7.31
7.30
7.27
6.46
4.48
4.45
4.44
4.41
3.50
3.03
3.00
2.68
2.66
2.51
2.49
1.96
1.94
1.26
Me
HN
Bn
O
COOMe
HO
Chemical Formula: C22H23NO4
Exact Mass: 365.1627
0.98
1.15
7.84
1.00
2.30
2.97
2.24
2.07
3.30
f1 (ppm)
176.58
172.67
172.28
138.66
138.40
135.20
130.76
130.65
128.95
128.10
127.75
127.41
127.04
98.17
55.83
51.82
44.10
42.04
32.01
24.76
Chemical Formula: C22H23NO4
Exact Mass: 365.1627
f1 (ppm)

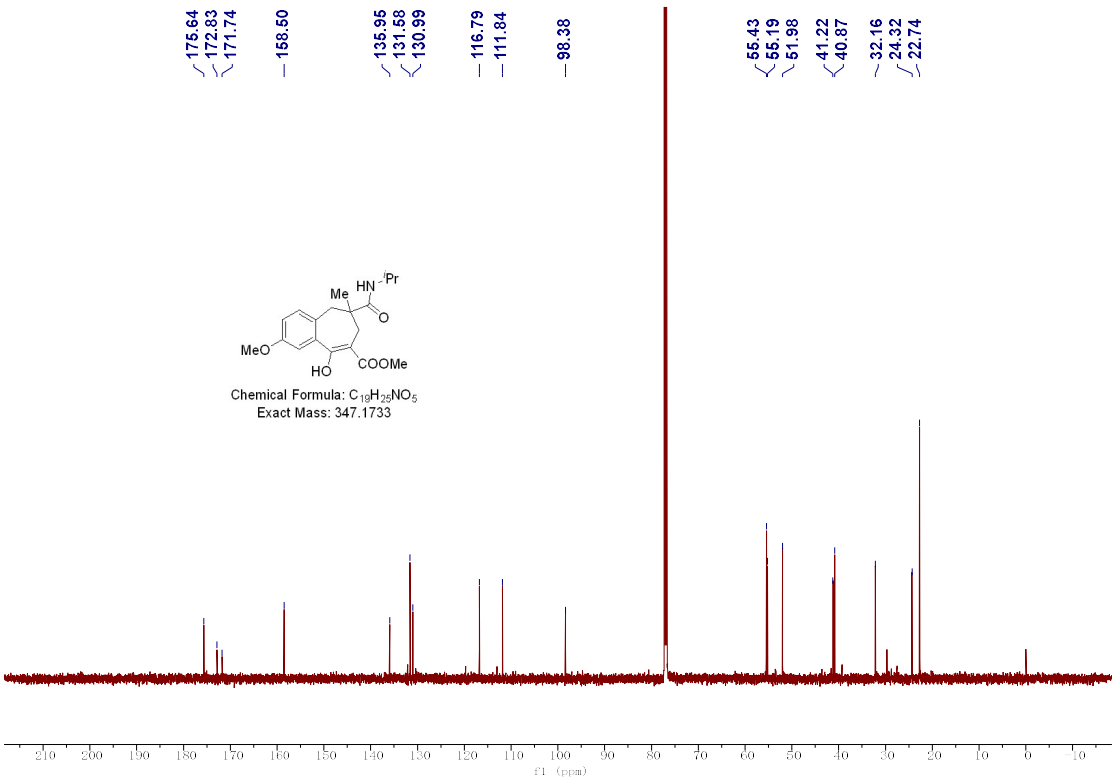
4ea


12.76
7.47
7.47
7.46
7.20
7.19
7.19
7.18
7.15
7.14
5.86
4.10
4.09
4.09
4.08
4.08
4.07
4.06
4.06
4.05
4.04
3.86
2.94
2.91
2.55
2.53
2.44
2.42
2.37
1.96
1.93
1.19
1.14
1.13
1.13
Me
HN
iPr
O
Me
HO
COOMe
Chemical Formula: C19H25NO4
Exact Mass: 331.1784
0.97
0.95
0.94
1.00
0.99
1.02
2.99
2.04
5.30
3.11
3.18
2.86
f1 (ppm)

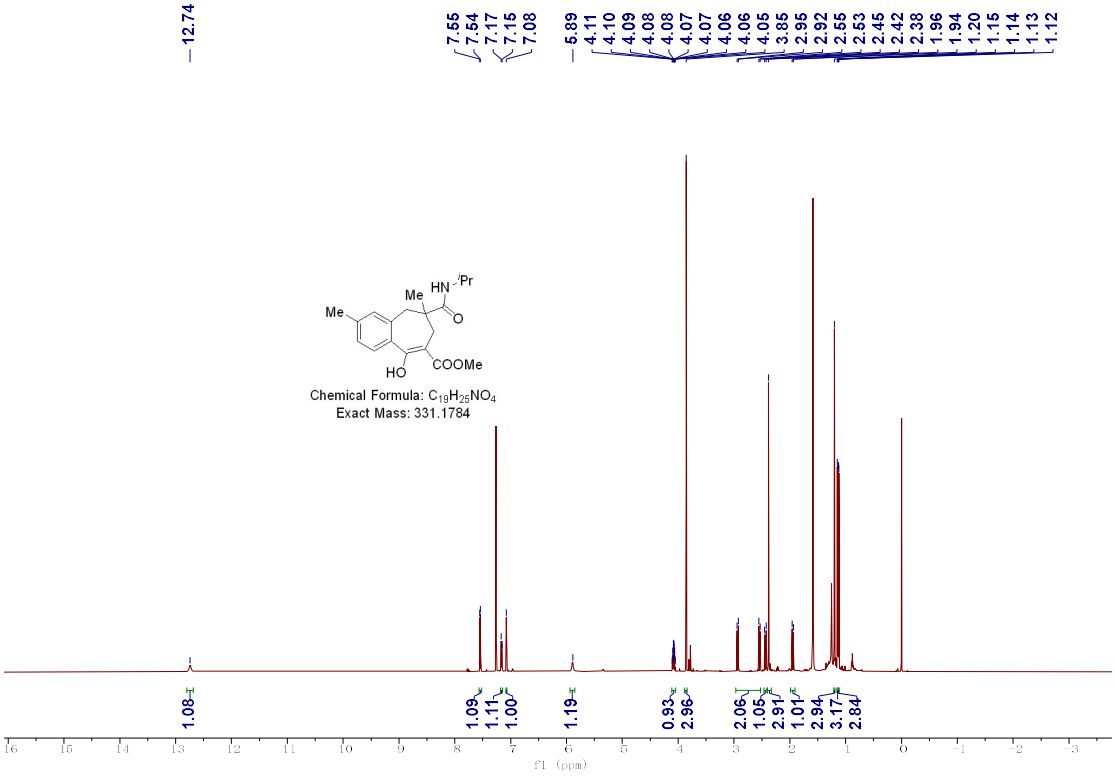

175.66
172.80
172.16
136.55
135.73
134.88
131.26
130.41
127.70
98.10
55.19
51.93
41.29
41.23
32.17
24.38
22.74
21.02
Me
HN
iPr
O
Me
HO
COOMe
Chemical Formula: C19H25NO4
Exact Mass: 331.1784
f1 (ppm)

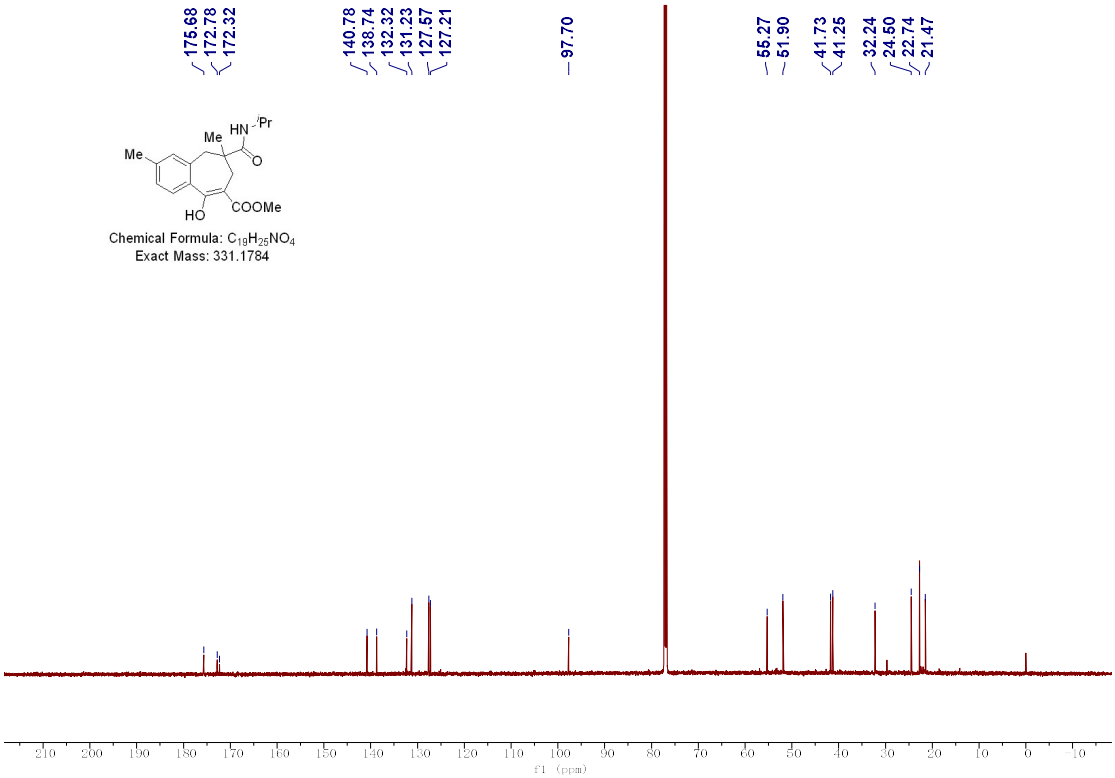
4fa


12.77
7.19
7.18
7.17
7.16
6.94
6.94
6.93
6.92
5.83
5.82
4.10
4.09
4.08
4.08
4.07
4.07
4.06
4.05
4.04
3.86
3.83
2.92
2.90
2.52
2.50
2.43
2.41
1.97
1.95
1.18
1.14
1.13
1.13
1.11
Me
HN
iPr
O
MeO
HO
COOMe
Chemical Formula: C19H25NO5
Exact Mass: 347.1733
0.96
0.88
1.02
1.00
1.00
1.04
3.01
3.49
2.13
2.18
3.41
3.00
2.72
f1 (ppm)

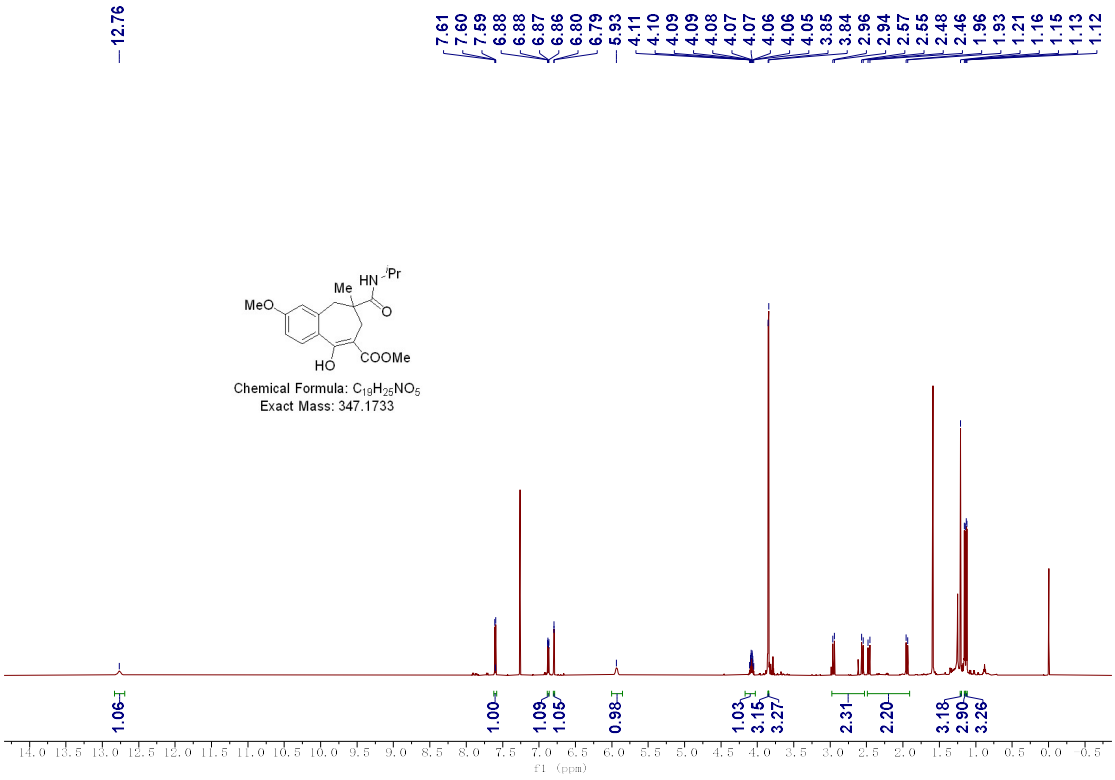

175.64
172.83
171.74
158.50
135.95
131.58
130.99
116.79
111.84
98.38
55.43
55.19
51.98
41.22
40.87
32.16
24.32
22.74
Me
HN
iPr
O
MeO
HO
COOMe
Chemical Formula: C19H25NO5
Exact Mass: 347.1733
f1 (ppm)

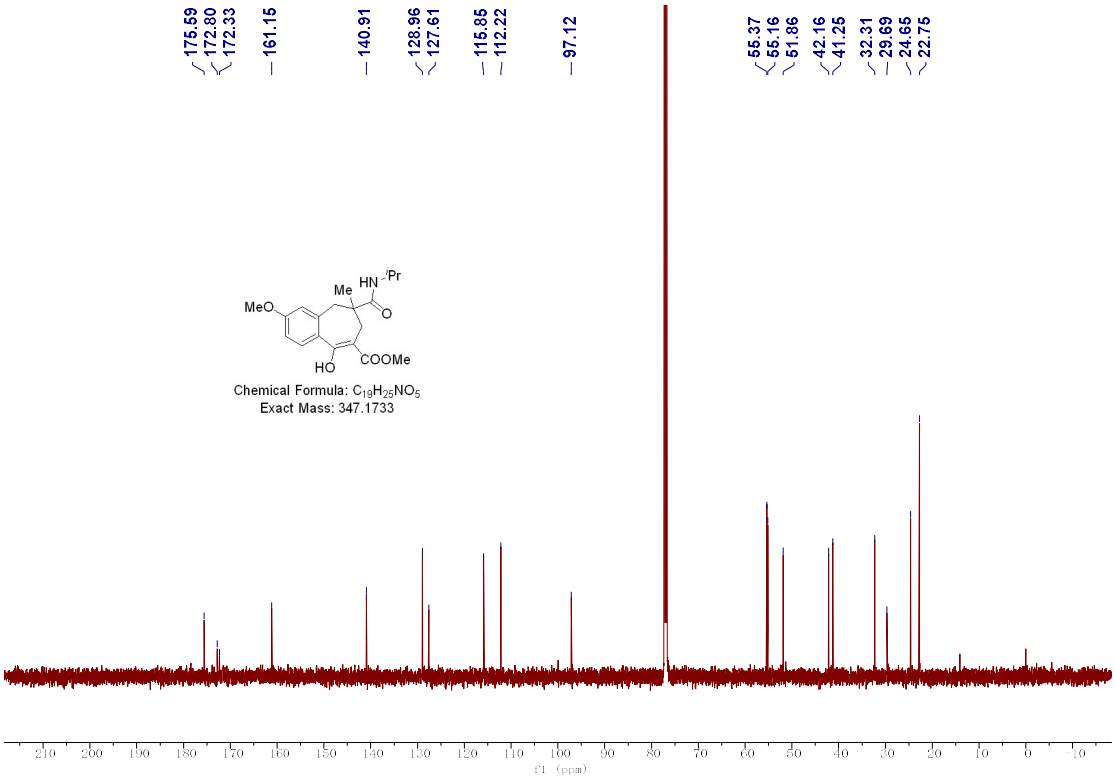
4ga


12.74
7.55
7.54
7.17
7.15
7.08
5.89
4.11
4.10
4.09
4.08
4.08
4.07
4.07
4.06
4.06
4.05
3.85
2.95
2.92
2.55
2.53
2.45
2.42
2.38
1.96
1.94
1.20
1.15
1.14
1.13
1.12
Me
HN
iPr
O
HO
COOMe
Chemical Formula: C19H25NO4
Exact Mass: 331.1784
1.08
1.09
1.11
1.00
1.19
0.93
2.96
2.06
1.05
2.91
1.01
2.94
3.17
2.84
f1 (ppm)

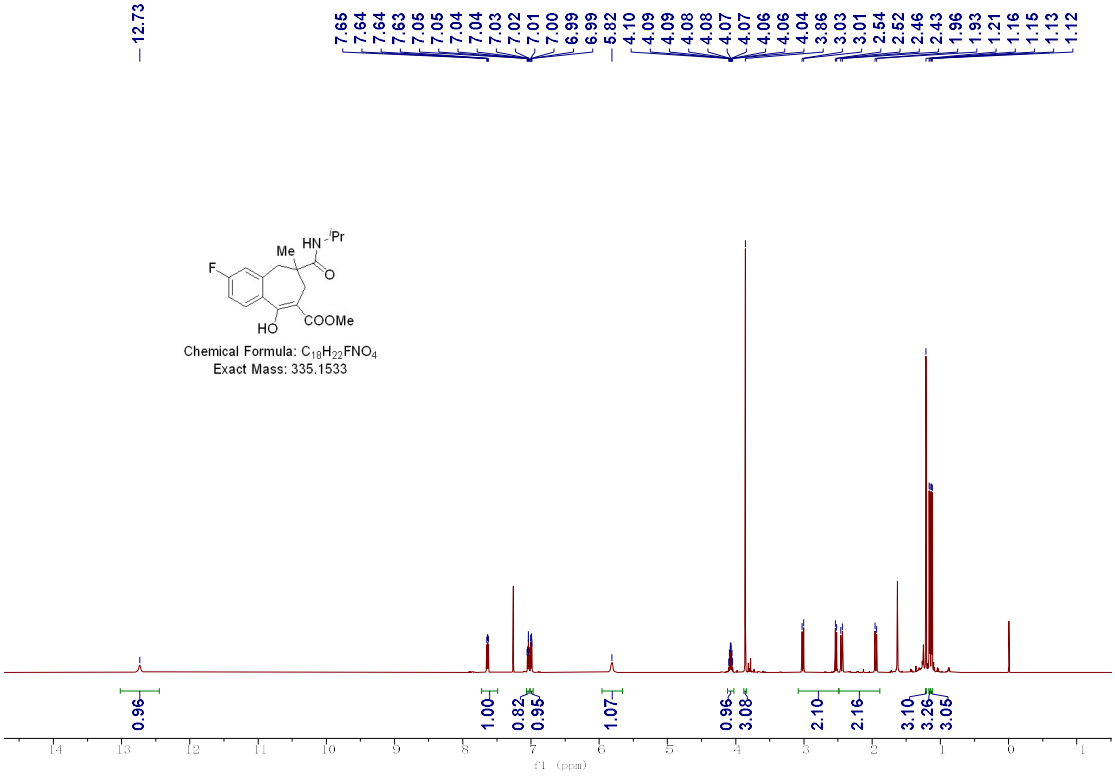

175.68
172.78
172.32
140.78
138.74
132.32
131.23
127.57
127.21
97.70
55.27
51.90
41.73
41.25
32.24
24.50
22.74
21.47
Me
HN
iPr
O
HO
COOMe
Chemical Formula: C19H25NO4
Exact Mass: 331.1784
f1 (ppm)

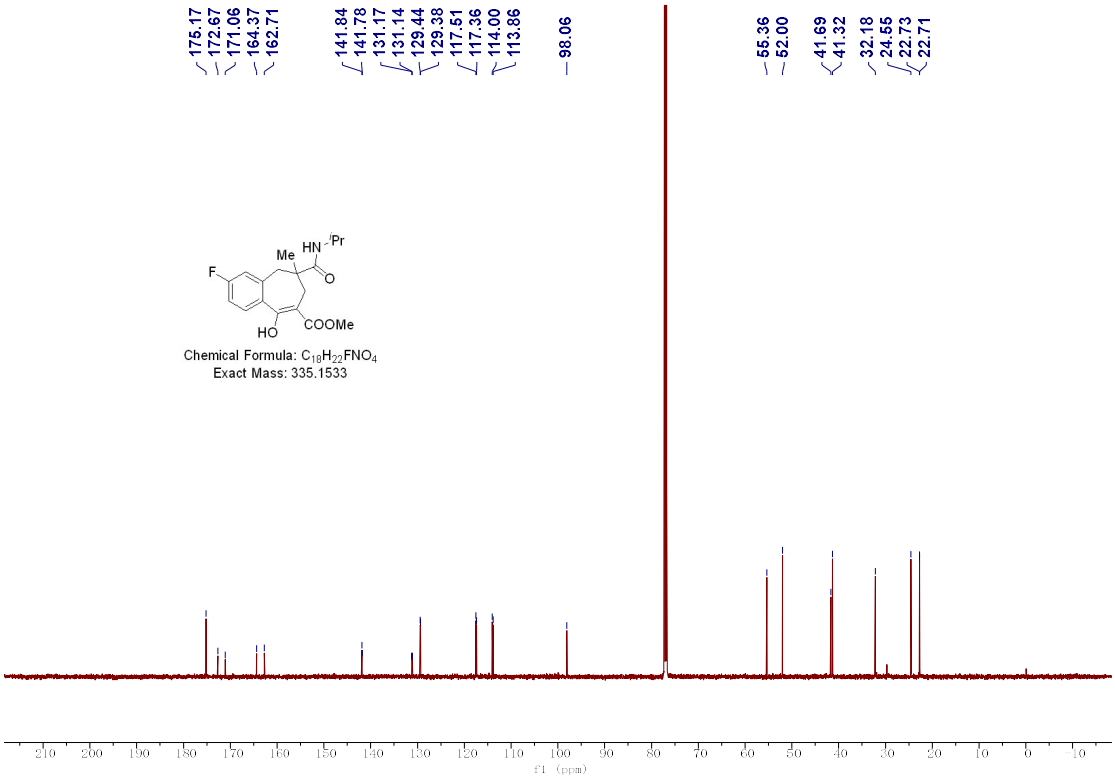
4ha

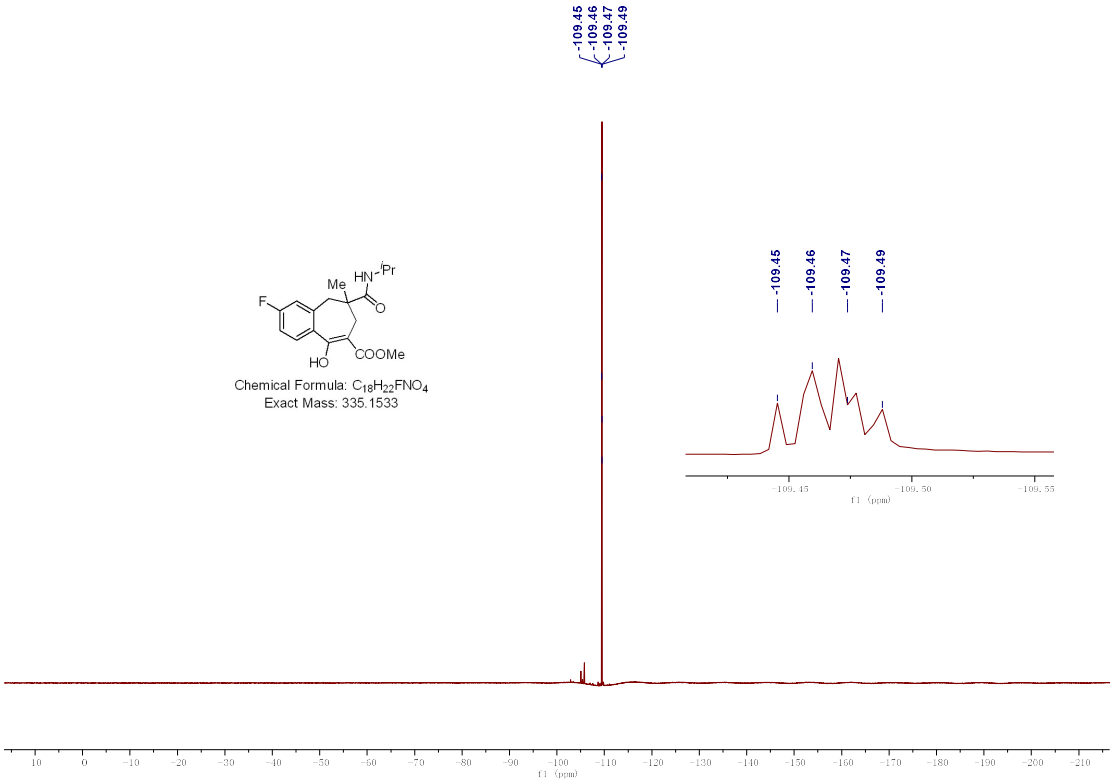

12.76
7.61
7.60
7.59
6.88
6.87
6.86
6.80
6.79
5.93
4.11
4.10
4.09
4.09
4.08
4.07
4.07
4.06
4.06
4.05
3.85
3.84
2.96
2.94
2.57
2.55
2.48
2.46
1.96
1.93
1.21
1.16
1.15
1.13
1.12
MeO
Me
HN
iPr
O
HO
COOMe
Chemical Formula: C19H25NO5
Exact Mass: 347.1733
1.06
1.00
1.09
1.05
0.98
1.03
3.15
3.27
2.31
2.20
3.18
2.90
3.26
f1 (ppm)


175.59
172.80
172.33
161.15
140.91
128.96
127.61
115.85
112.22
97.12
55.37
55.16
51.86
42.16
41.25
32.31
29.69
24.65
22.75
MeO
Me
HN
iPr
O
HO
COOMe
Chemical Formula: C19H25NO5
Exact Mass: 347.1733
f1 (ppm)

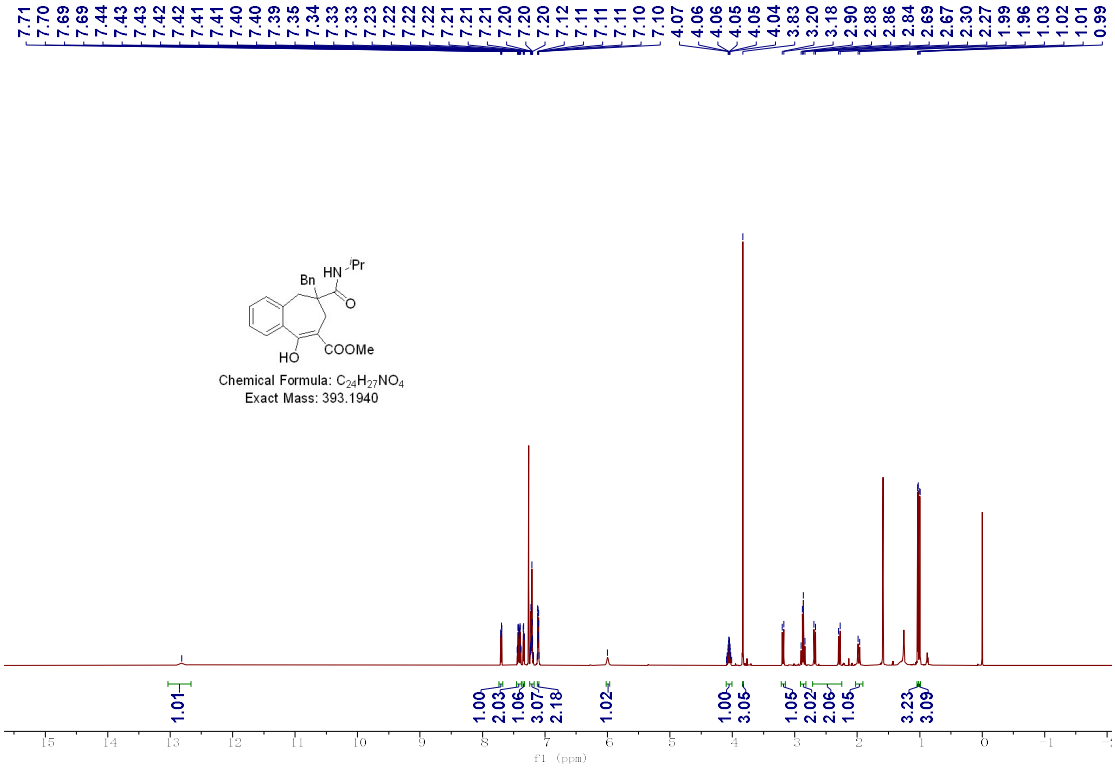
4ia

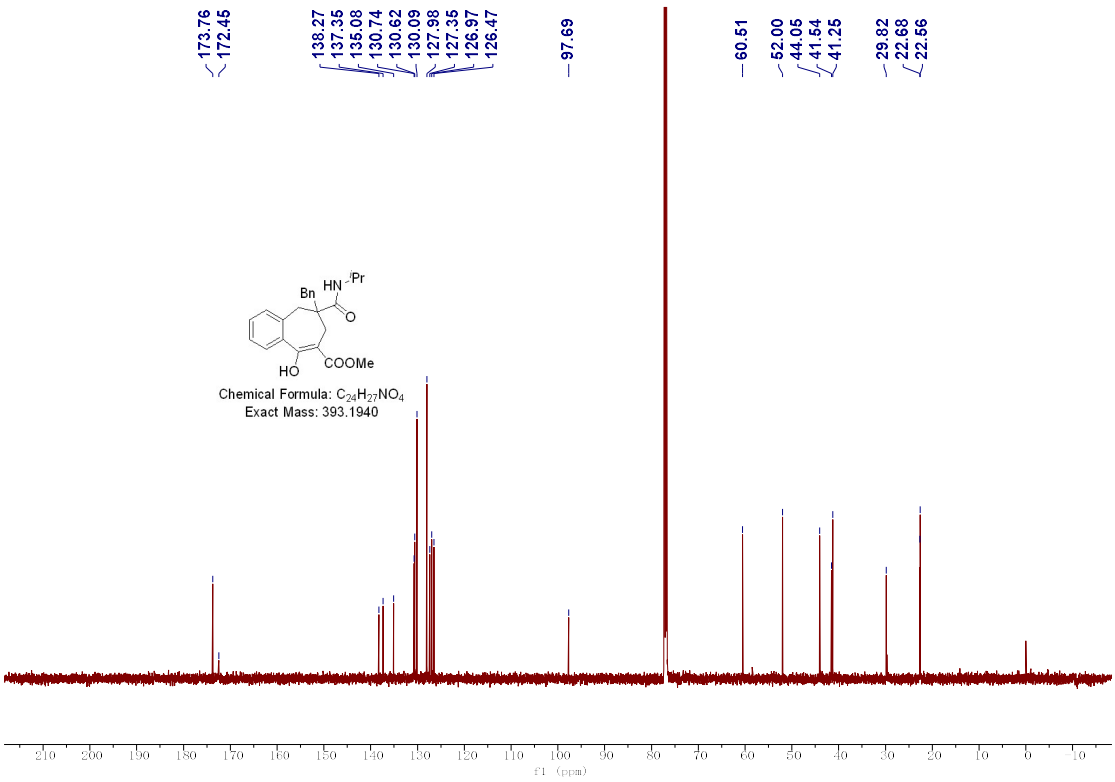

12.73
7.65
7.64
7.64
7.63
7.05
7.05
7.04
7.04
7.03
7.02
7.01
7.00
6.99
6.99
5.82
4.10
4.09
4.09
4.08
4.08
4.07
4.07
4.06
4.06
4.04
3.86
3.03
3.01
2.54
2.52
2.46
2.43
1.96
1.93
1.21
1.16
1.15
1.13
1.12
Me
HN
iPr
F
O
COOMe
HO
Chemical Formula: C18H22FNO4
Exact Mass: 335.1533
0.96
1.00
0.82
0.95
1.07
0.96
3.08
2.10
2.16
3.10
3.26
3.05
f1 (ppm)


175.17
172.67
171.06
164.37
162.71
141.84
141.78
131.17
131.14
129.44
129.38
117.51
117.36
114.00
113.86
98.06
55.36
52.00
41.69
41.32
32.18
24.55
22.73
22.71
Me
HN
iPr
F
O
COOMe
HO
Chemical Formula: C18H22FNO4
Exact Mass: 335.1533
f1 (ppm)

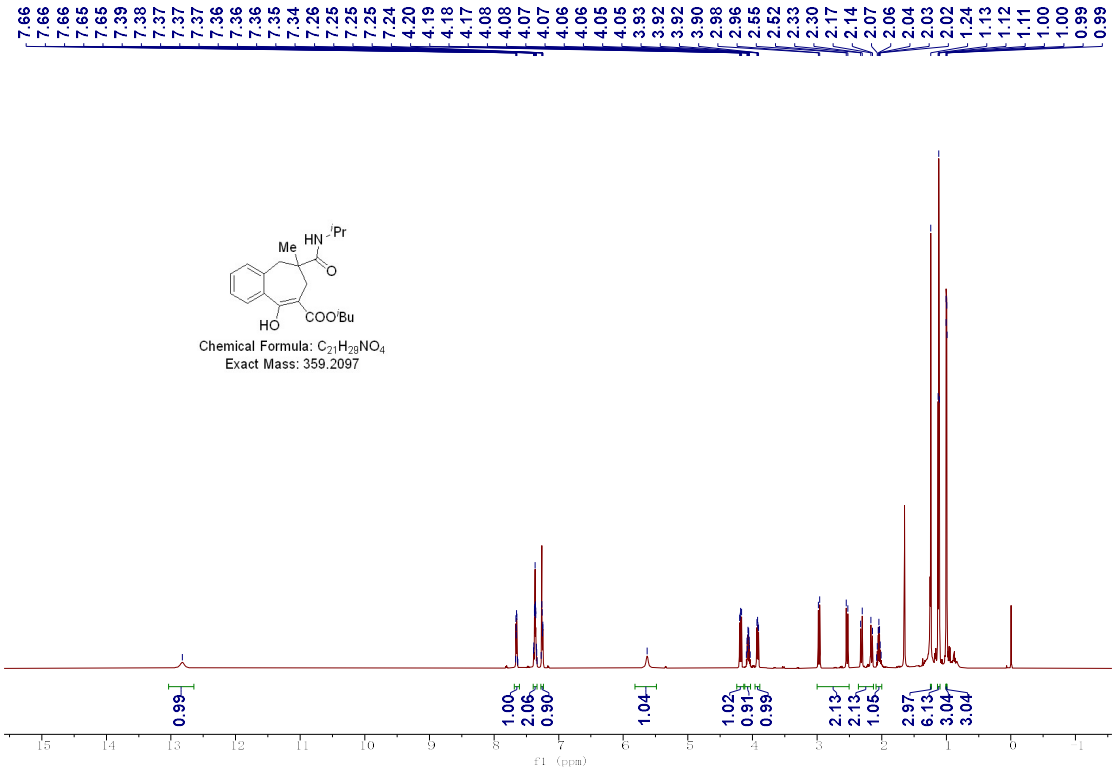

-109.45
-109.46
-109.47
-109.49
Me
HN
iPr
O
F
HO
COOMe
Chemical Formula: C18H22FNO4
Exact Mass: 335.1533
-109.45
-109.46
-109.47
-109.49
-109.45
-109.50
-109.55
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

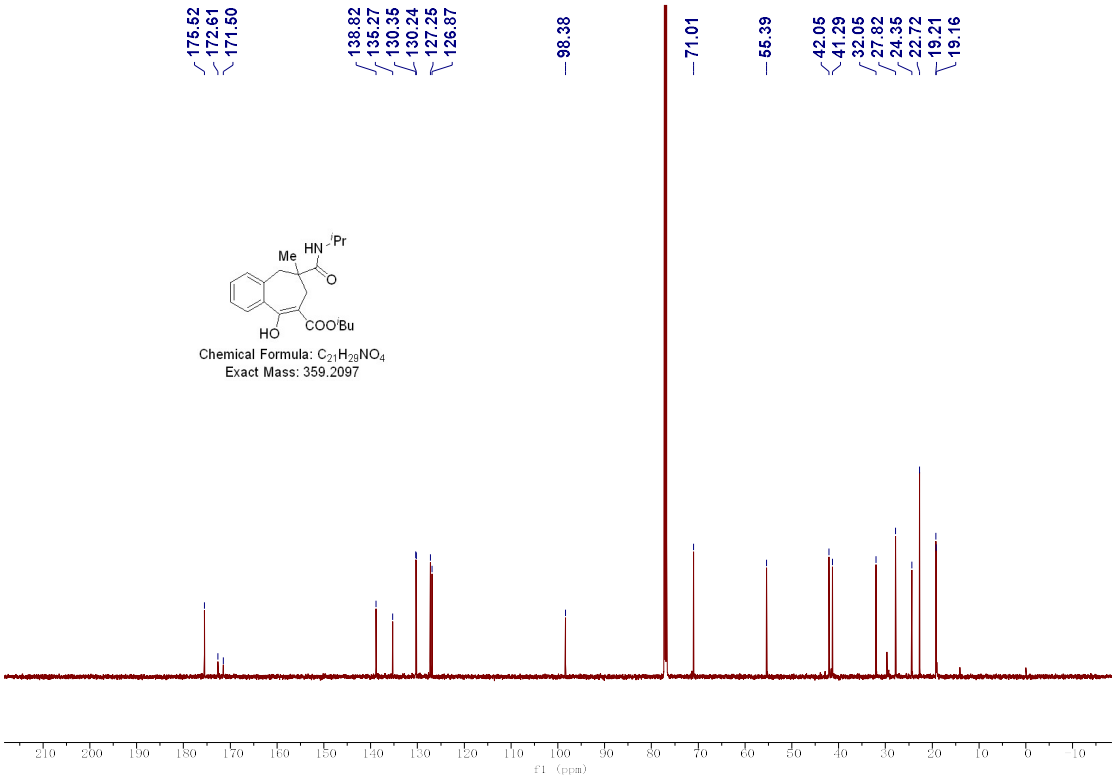
4ja


7.71 7.70 7.69 7.69 7.44 7.43 7.43 7.42 7.42 7.41 7.41 7.40 7.40 7.39 7.35 7.34 7.33 7.33 7.23 7.22 7.22 7.22 7.21 7.21 7.21 7.20 7.20 7.20 7.12 7.11 7.11 7.11 7.10 7.10 4.07 4.06 4.06 4.05 4.05 4.04 3.83 3.20 3.18 2.90 2.88 2.86 2.84 2.69 2.67 2.30 2.27 1.99 1.96 1.03 1.02 1.01 0.99
Bn
HN
iPr
O
HO
COOMe
Chemical Formula: C24H27NO4
Exact Mass: 393.1940
1.01 1.00 2.03 1.06 3.07 2.18 1.02 1.00 3.05 1.05 2.02 2.06 1.05 3.23 3.09
f1 (ppm)

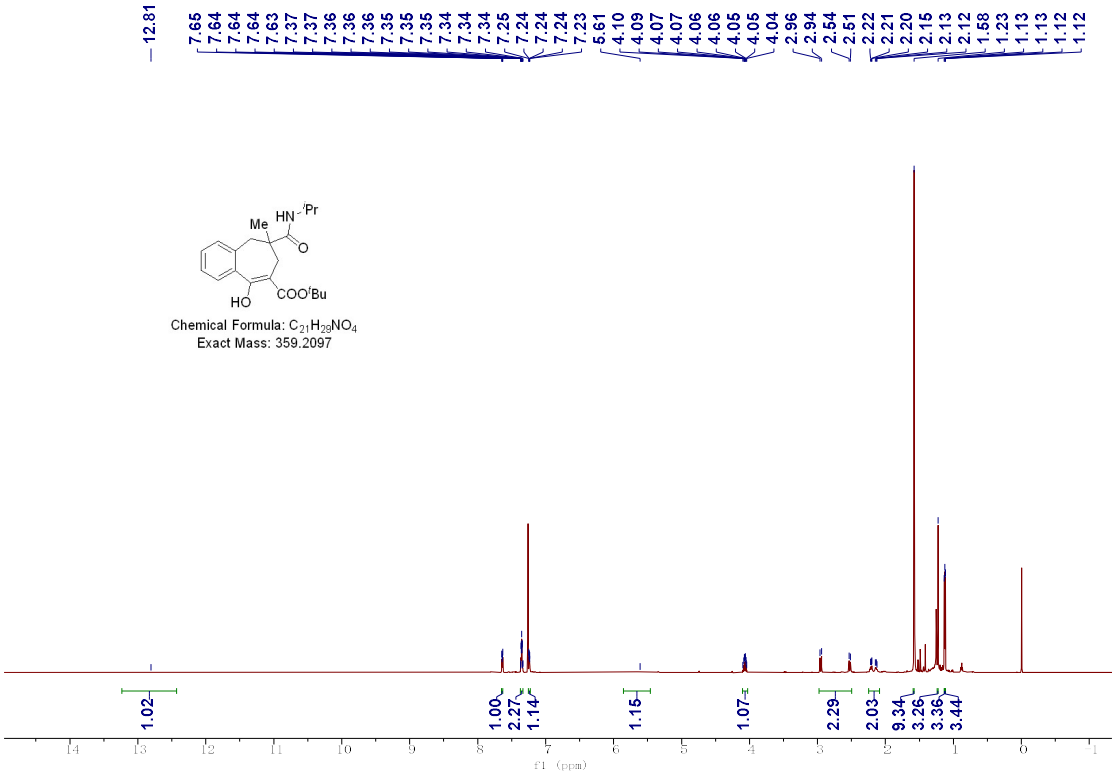

173.76 172.45 138.27 137.35 135.08 130.74 130.62 130.09 127.98 127.35 126.97 126.47 97.69 60.51 52.00 44.05 41.54 41.25 29.82 22.68 22.56
Bn
HN
iPr
O
HO
COOMe
Chemical Formula: C24H27NO4
Exact Mass: 393.1940
f1 (ppm)

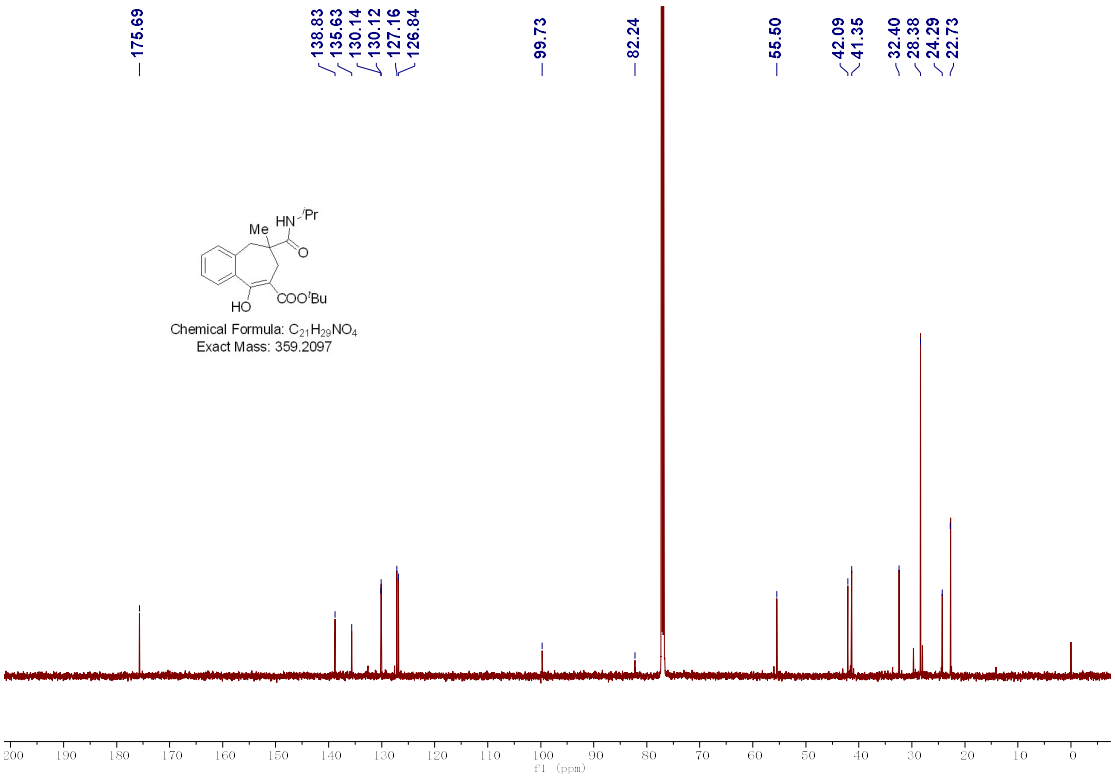
4bb


7.66 7.66 7.66 7.65 7.65 7.39 7.38 7.37 7.37 7.37 7.36 7.36 7.35 7.34 7.26 7.25 7.25 7.24 4.20 4.19 4.18 4.17 4.08 4.08 4.07 4.07 4.06 4.06 4.05 4.05 3.93 3.92 3.92 3.90 2.98 2.96 2.55 2.52 2.33 2.30 2.17 2.14 2.07 2.06 2.04 2.03 2.02 1.24 1.13 1.12 1.11 1.00 1.00 0.99 0.99
Me
HN
iPr
O
HO
COOtBu
Chemical Formula: C21H28NO4
Exact Mass: 359.2097
0.99
1.00
2.06
0.90
1.04
1.02
0.91
0.99
2.13
2.13
1.05
2.97
6.13
3.04
3.04
f1 (ppm)

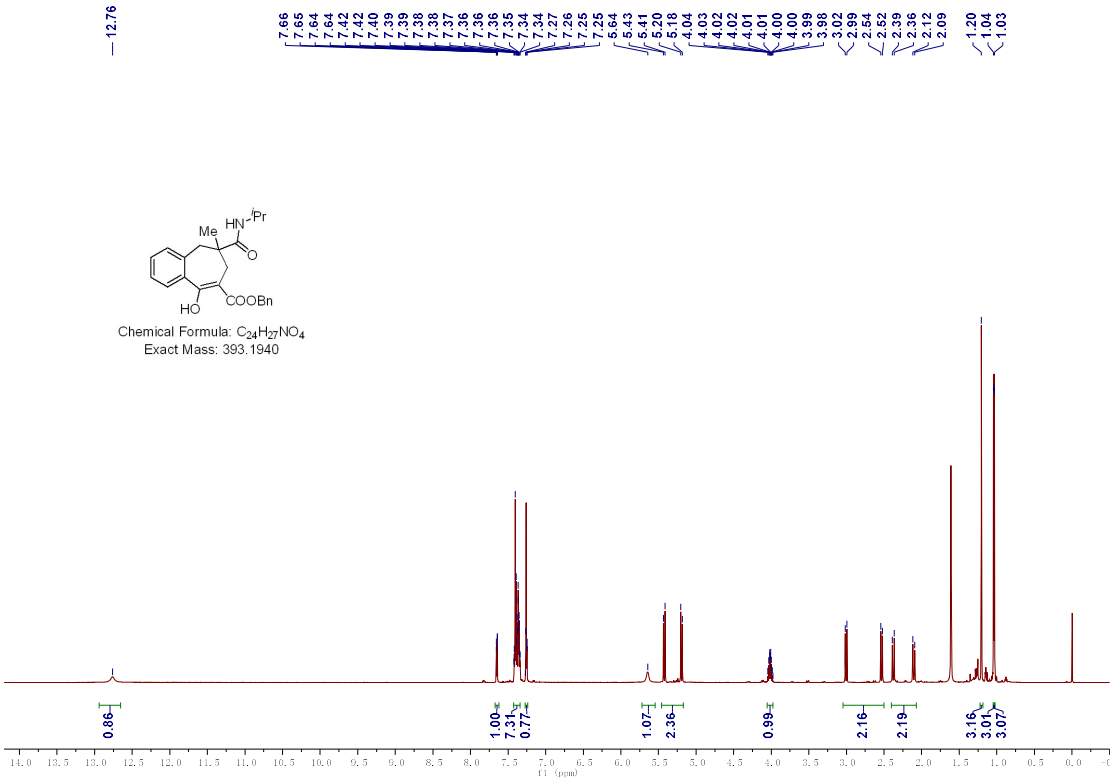

176.52
172.61
171.50
138.82
135.27
130.35
130.24
127.25
126.87
98.38
71.01
55.39
42.05
41.29
32.05
27.82
24.35
22.72
19.21
19.16
Me
HN
iPr
O
HO
COOtBu
Chemical Formula: C21H28NO4
Exact Mass: 359.2097
f1 (ppm)

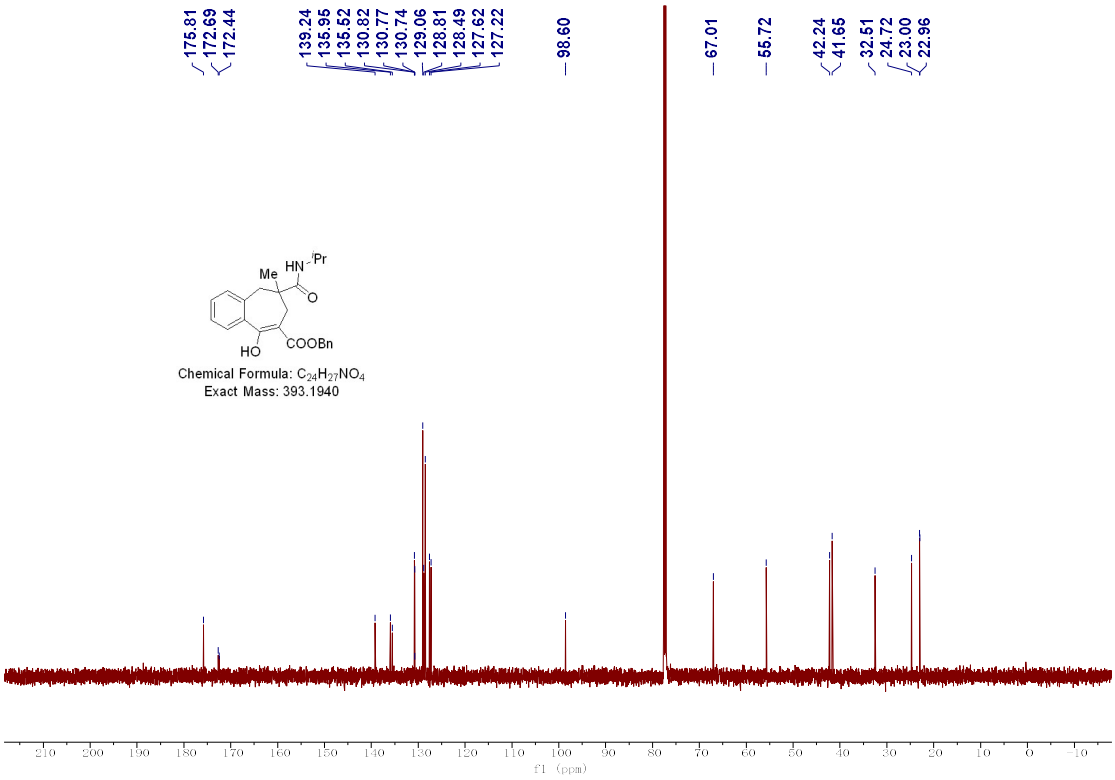
4bc


12.81
7.65 7.64 7.64 7.64 7.63 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.34 7.25 7.24 7.24 7.24 7.23
5.61
4.10 4.09 4.07 4.07 4.06 4.06 4.05 4.05 4.04
2.96 2.94 2.54 2.51
2.22 2.21 2.20 2.15 2.13 2.12 1.58 1.23 1.13 1.13 1.12 1.12
Me
HN
iPr
O
HO
COOtBu
Chemical Formula: C21H29NO4
Exact Mass: 359.2097
1.02
1.00 2.27 1.14 1.15 1.07 2.29 2.03 9.34 3.26 3.36 3.44
f1 (ppm)

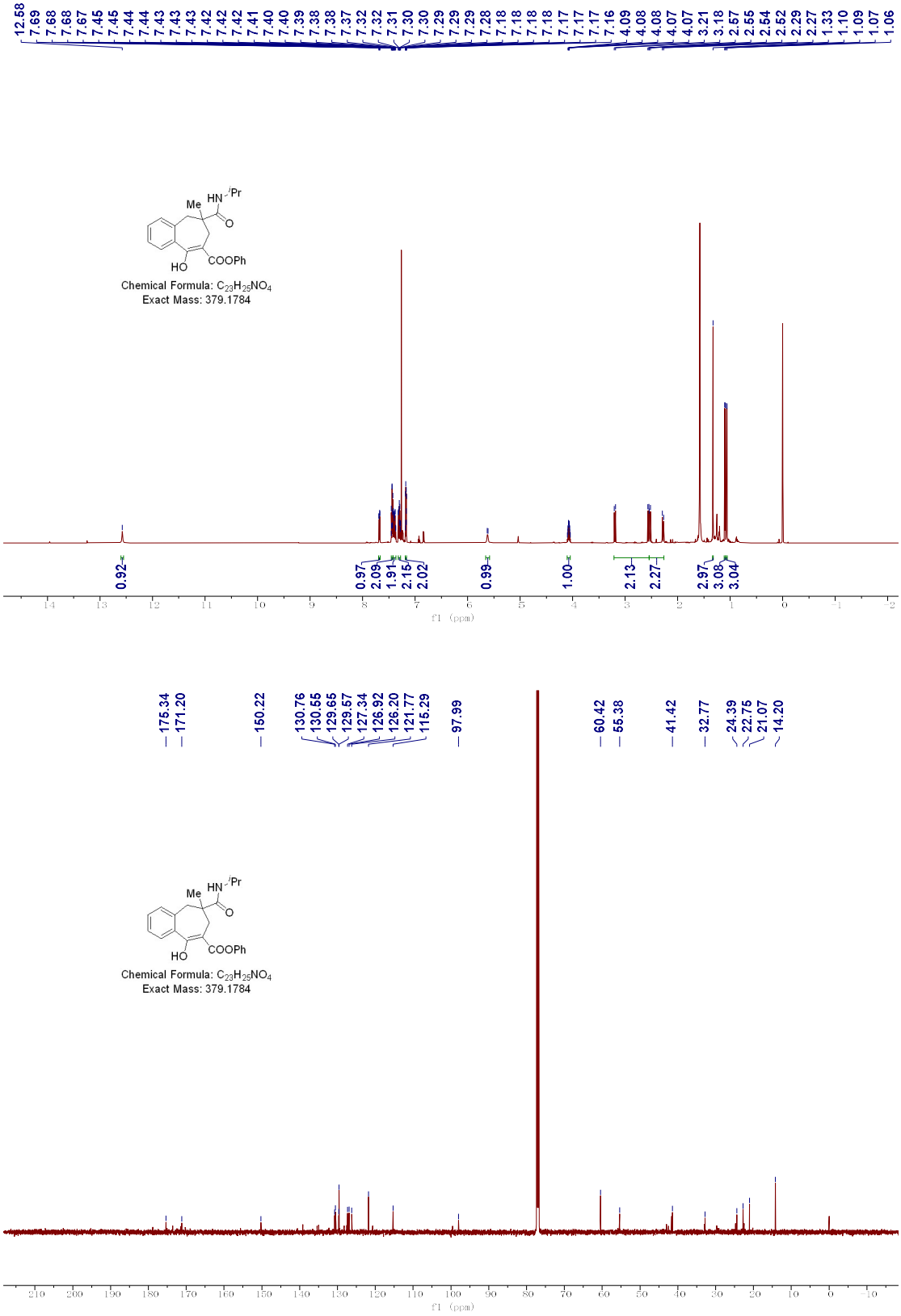

175.69
138.83 135.63 130.14 130.12 127.16 126.84
99.73
82.24
55.50
42.09 41.35
32.40 28.38 24.29 22.73
Me
HN
iPr
O
HO
COOtBu
Chemical Formula: C21H29NO4
Exact Mass: 359.2097
f1 (ppm)

4bd

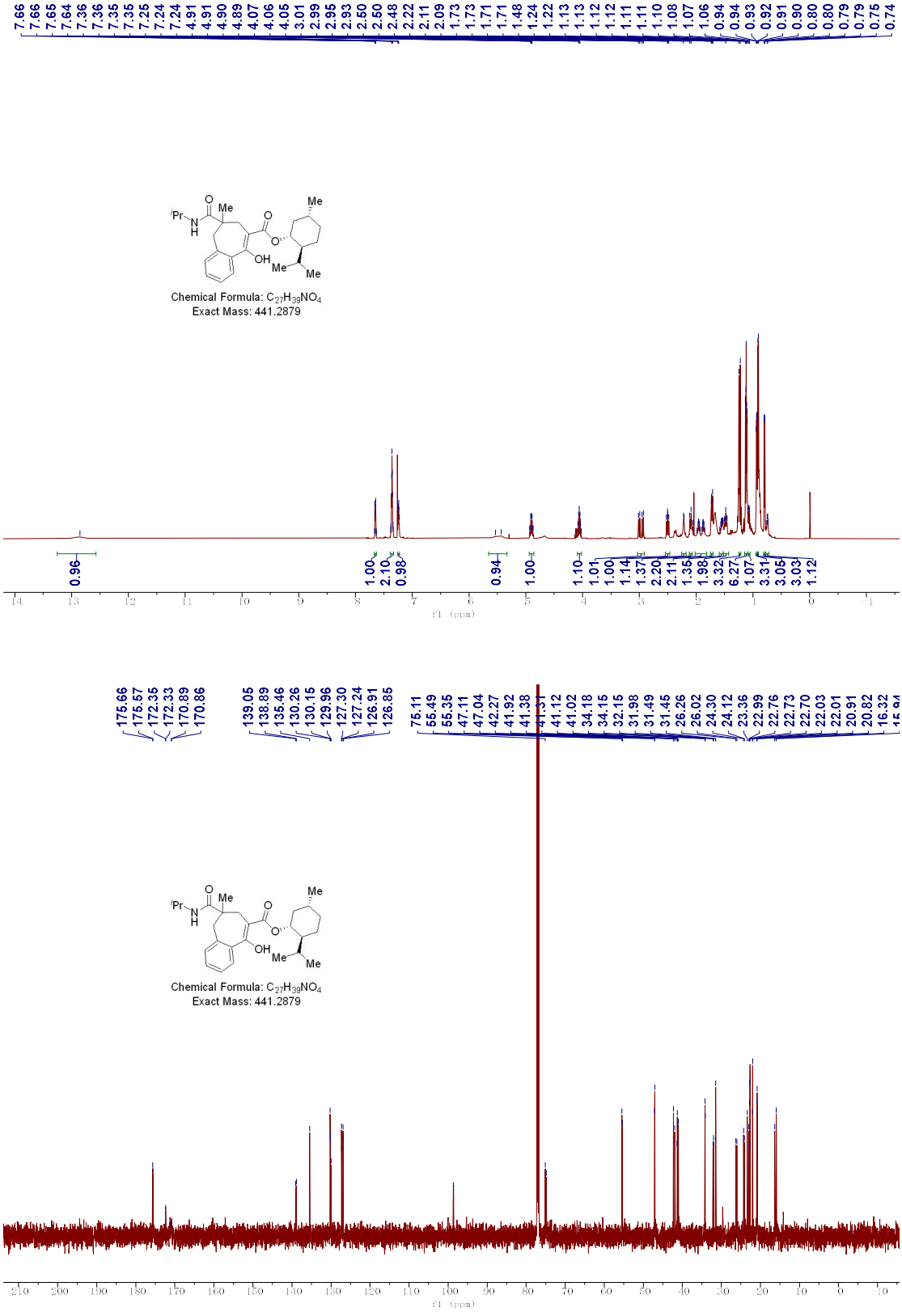

12.76
7.66 7.65 7.64 7.64 7.42 7.40 7.39 7.39 7.38 7.38 7.37 7.36 7.36 7.36 7.35 7.34 7.34 7.27 7.26 7.25 7.25 5.64 5.43 5.41 5.20 5.18 4.04 4.03 4.02 4.02 4.01 4.01 4.00 4.00 3.99 3.98 3.02 2.99 2.54 2.52 2.39 2.36 2.12 2.09 1.20 1.04 1.03
Me
HN
iPr
O
HO
COOBn
Chemical Formula: C24H27NO4
Exact Mass: 393.1940
0.86 1.00 7.31 0.77 1.07 2.36 0.99 2.16 2.19 3.16 3.01 3.07
f1 (ppm)


175.81 172.69 172.44 139.24 135.95 135.52 130.82 130.77 130.74 129.06 128.81 128.49 127.62 127.22 98.60 67.01 55.72 42.24 41.65 32.51 24.72 23.00 22.96
Me
HN
iPr
O
HO
COOBn
Chemical Formula: C24H27NO4
Exact Mass: 393.1940
f1 (ppm)

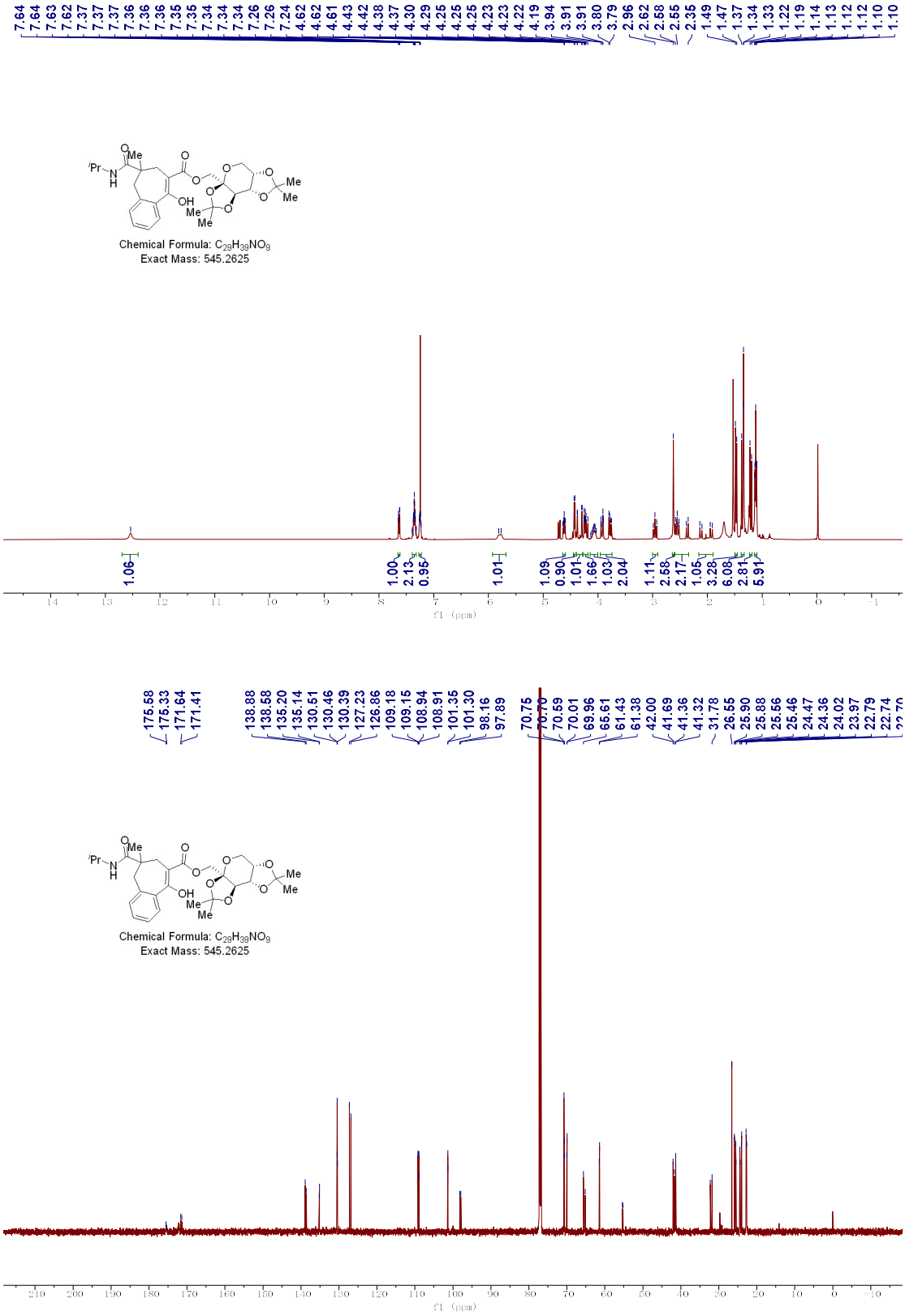
4be


12.58
7.69
7.68
7.68
7.67
7.45
7.45
7.44
7.44
7.43
7.43
7.43
7.42
7.42
7.42
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.32
7.31
7.30
7.30
7.29
7.29
7.29
7.28
7.18
7.18
7.18
7.18
7.17
7.17
7.17
7.16
4.09
4.08
4.08
4.07
4.07
3.21
3.18
2.57
2.55
2.54
2.52
2.29
2.27
1.33
1.10
1.09
1.07
1.06
Me
HN
iPr
O
HO
COOPh
Chemical Formula: C23H25NO4
Exact Mass: 379.1784
0.92
0.97
2.09
1.91
2.15
2.02
0.99
1.00
2.13
2.27
2.97
3.08
3.04
f1 (ppm)
175.34
171.20
150.22
130.76
130.55
129.65
129.57
127.34
126.92
126.20
121.77
115.29
97.99
60.42
56.38
41.42
32.77
24.39
22.75
21.07
14.20
Me
HN
iPr
O
HO
COOPh
Chemical Formula: C23H25NO4
Exact Mass: 379.1784
f1 (ppm)

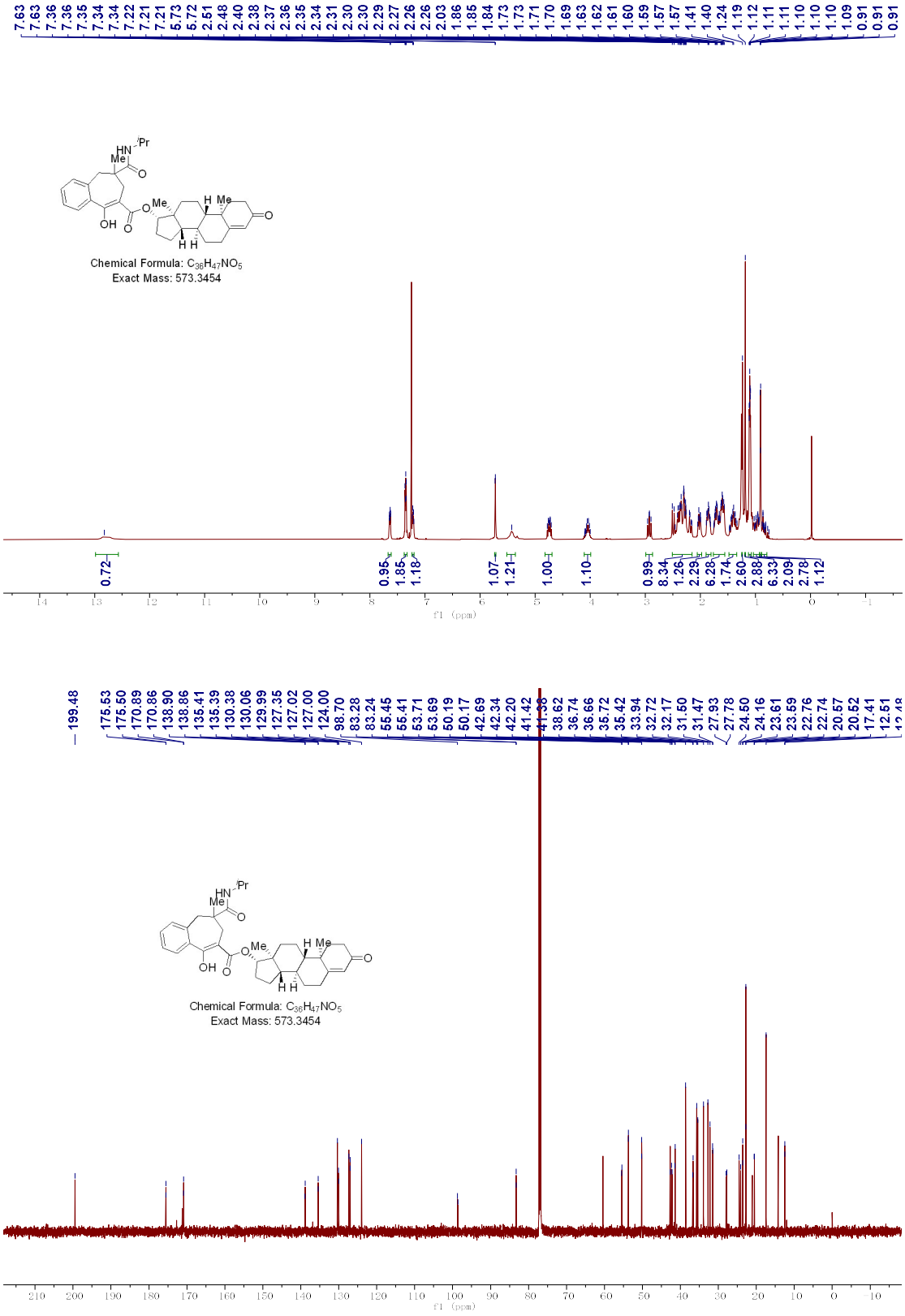
4bf


Chemical Formula: C27H38NO4
Exact Mass: 441.2879
Chemical Formula: C27H38NO4
Exact Mass: 441.2879

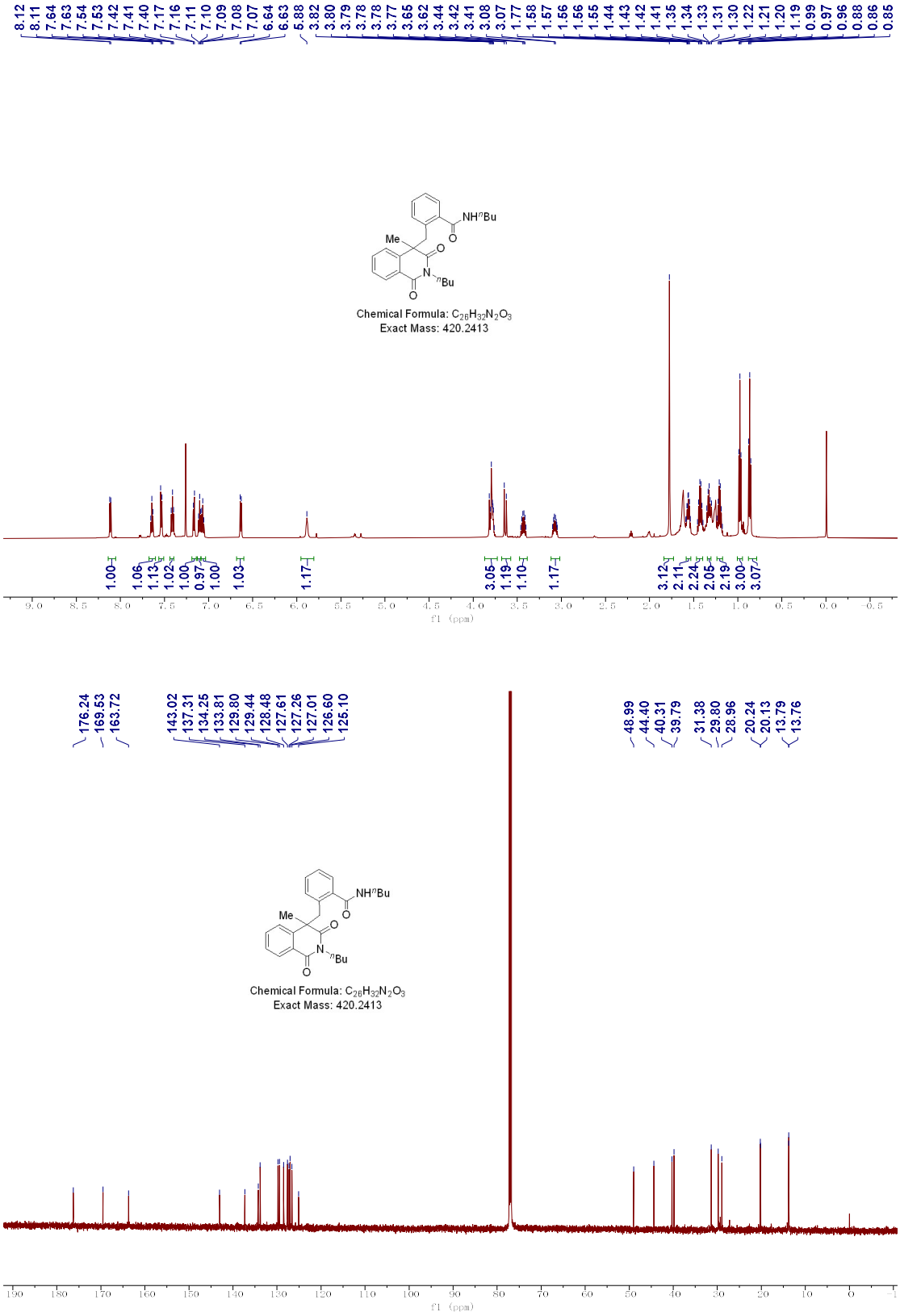
4bg


Chemical Formula: C29H38NO9
Exact Mass: 545.2625
f1 (ppm)
Chemical Formula: C29H38NO9
Exact Mass: 545.2625
f1 (ppm)

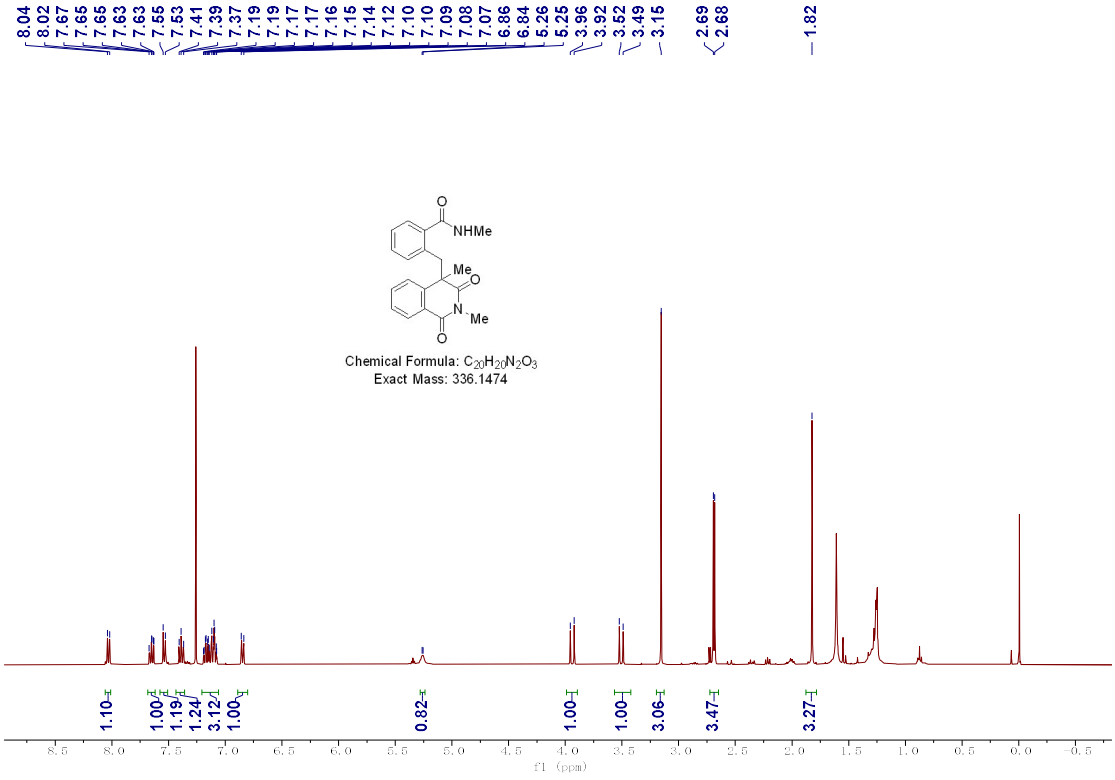
4bh

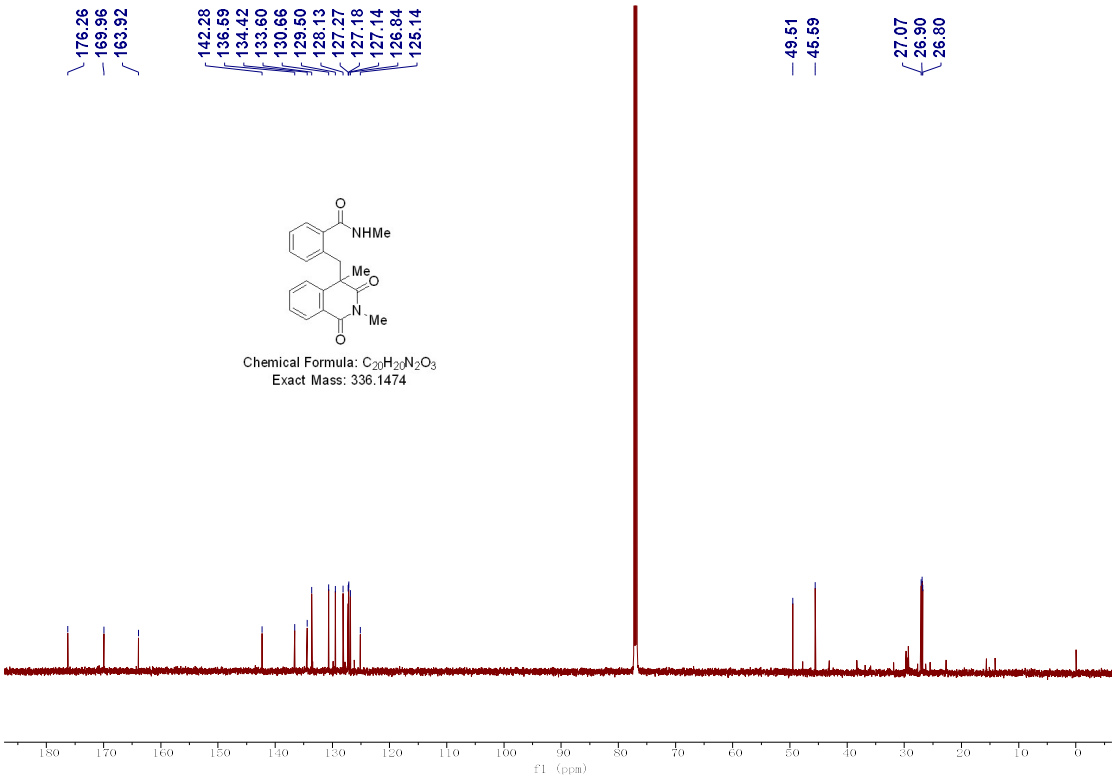

Chemical Formula: C36H47NO5
Exact Mass: 573.3454
f1 (ppm)
Chemical Formula: C36H47NO5
Exact Mass: 573.3454
f1 (ppm)

5a

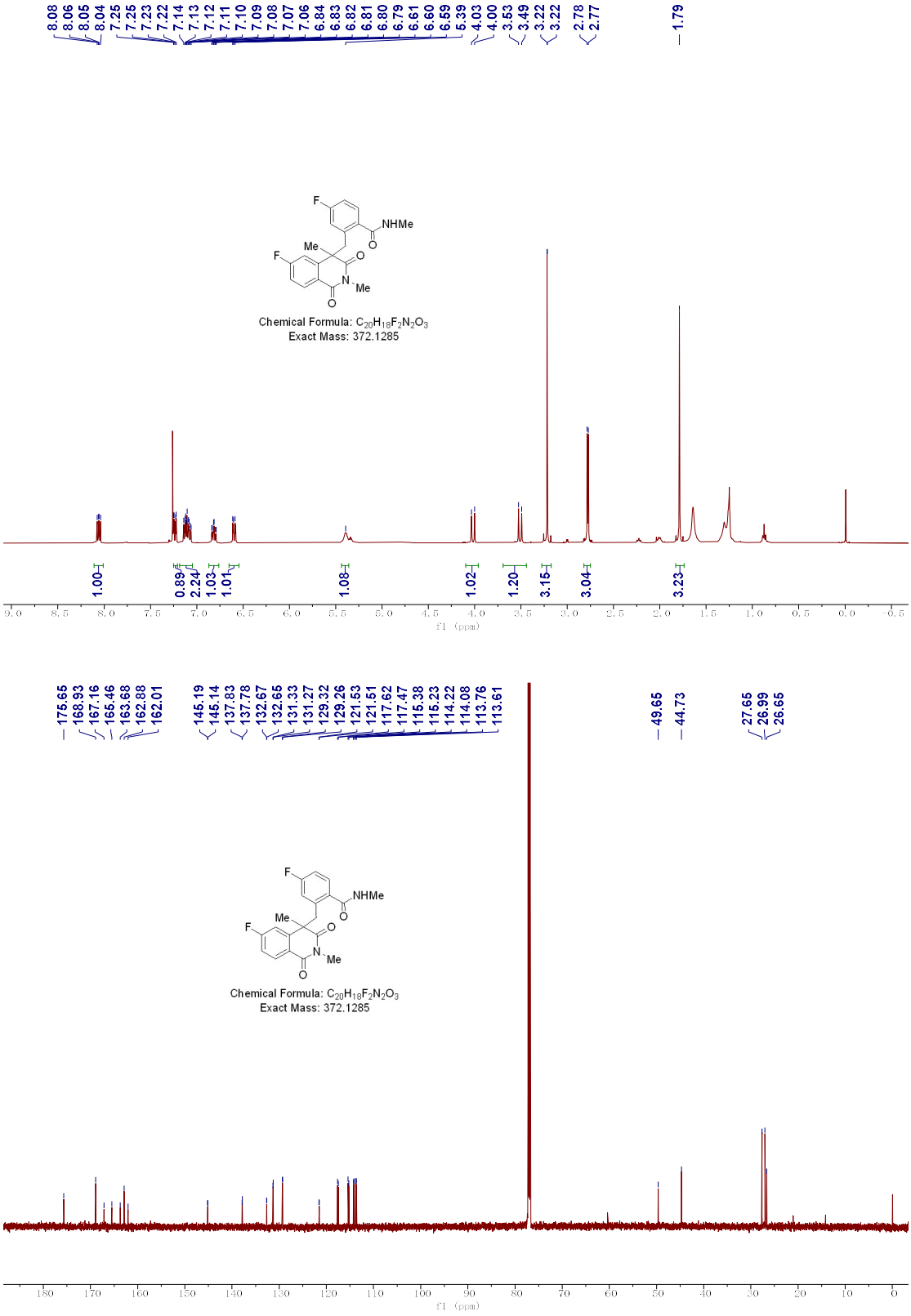

8.12 8.11 7.64 7.63 7.54 7.53 7.42 7.41 7.40 7.17 7.16 7.11 7.10 7.09 7.08 7.07 6.64 6.63 5.88 3.82 3.80 3.79 3.78 3.78 3.77 3.65 3.62 3.44 3.42 3.41 3.08 3.07 1.77 1.58 1.57 1.56 1.56 1.55 1.44 1.43 1.42 1.41 1.35 1.34 1.33 1.31 1.30 1.22 1.21 1.20 1.19 0.99 0.97 0.96 0.88 0.86 0.85
NHⁿBu
Me
O
N
ⁿBu
O
Chemical Formula: C26H32N2O3
Exact Mass: 420.2413
1.00 1.06 1.13 1.02 1.00 0.97 1.00 1.03 1.17 3.05 1.19 1.10 1.17 3.12 2.11 2.24 2.05 2.19 3.00 3.07
f1 (ppm)
176.24 169.53 163.72 143.02 137.31 134.25 133.81 129.80 129.44 128.48 127.61 127.26 127.01 126.60 125.10 48.99 44.40 40.31 39.79 31.38 29.80 28.96 20.24 20.13 13.79 13.76
NHⁿBu
Me
O
N
ⁿBu
O
Chemical Formula: C26H32N2O3
Exact Mass: 420.2413
f1 (ppm)

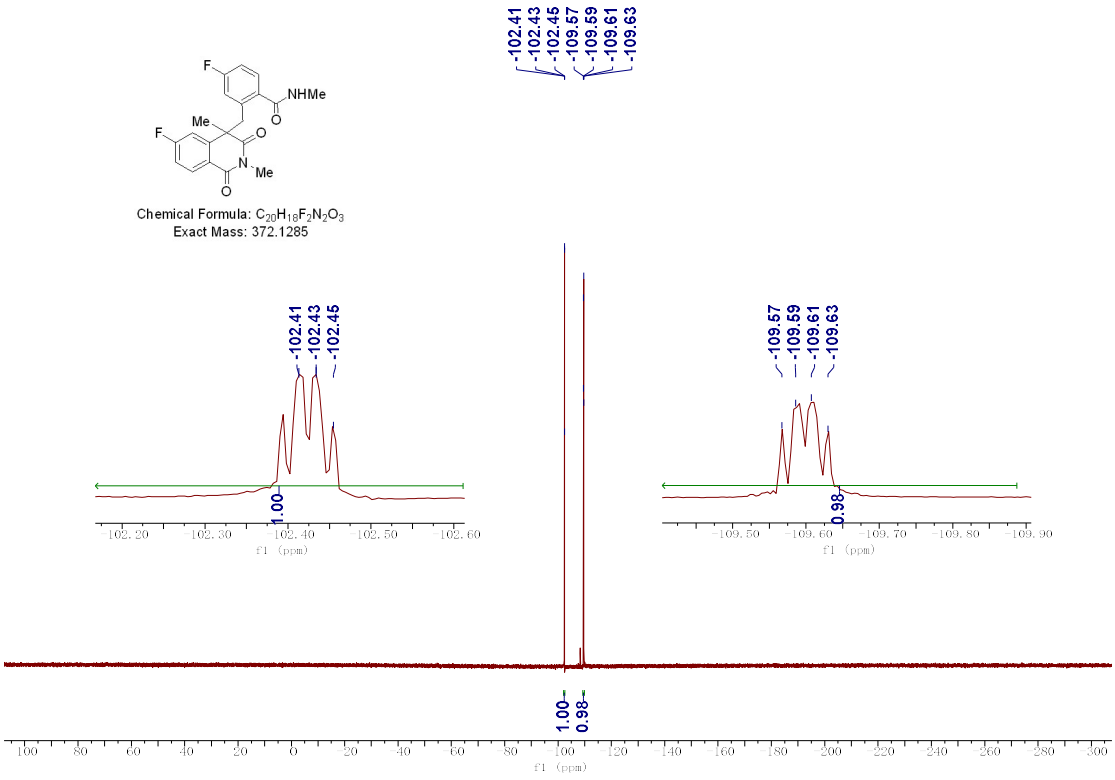
5b


8.04
8.02
7.67
7.65
7.65
7.63
7.63
7.55
7.53
7.41
7.39
7.37
7.19
7.19
7.17
7.17
7.16
7.15
7.14
7.12
7.10
7.10
7.09
7.08
7.07
6.86
6.84
5.26
5.25
3.96
3.92
3.52
3.49
3.15
2.69
2.68
1.82
NHMe
Me
O
N
Me
O
Chemical Formula: C20H20N2O3
Exact Mass: 336.1474
1.10
1.00
1.19
1.24
3.12
1.00
0.82
1.00
1.00
3.06
3.47
3.27
f1 (ppm)

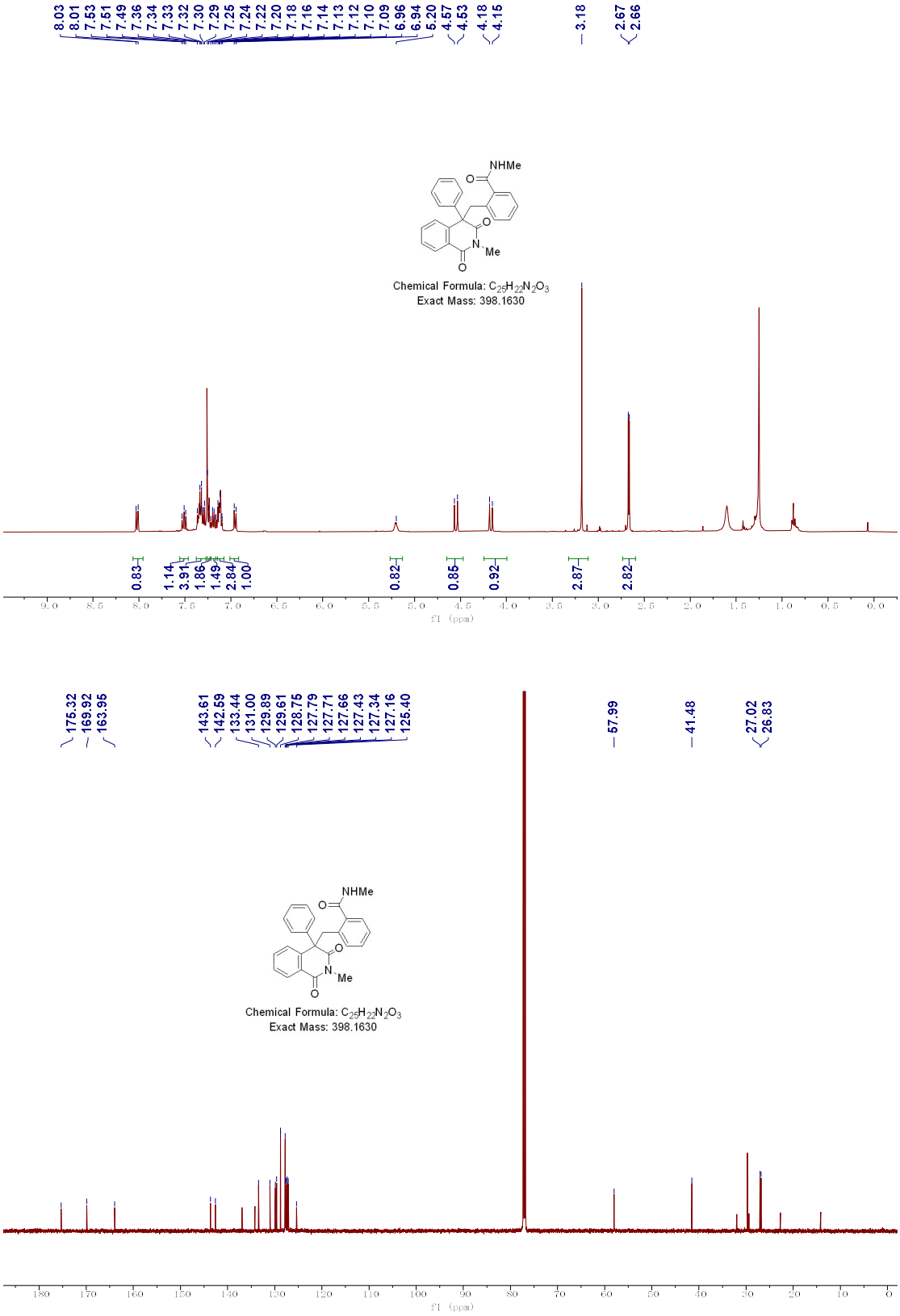

176.26
169.96
163.92
142.28
136.59
134.42
133.60
130.66
129.50
128.13
127.27
127.18
127.14
126.84
125.14
49.51
45.59
27.07
26.90
26.80
NHMe
Me
O
N
Me
O
Chemical Formula: C20H20N2O3
Exact Mass: 336.1474
f1 (ppm)

5c

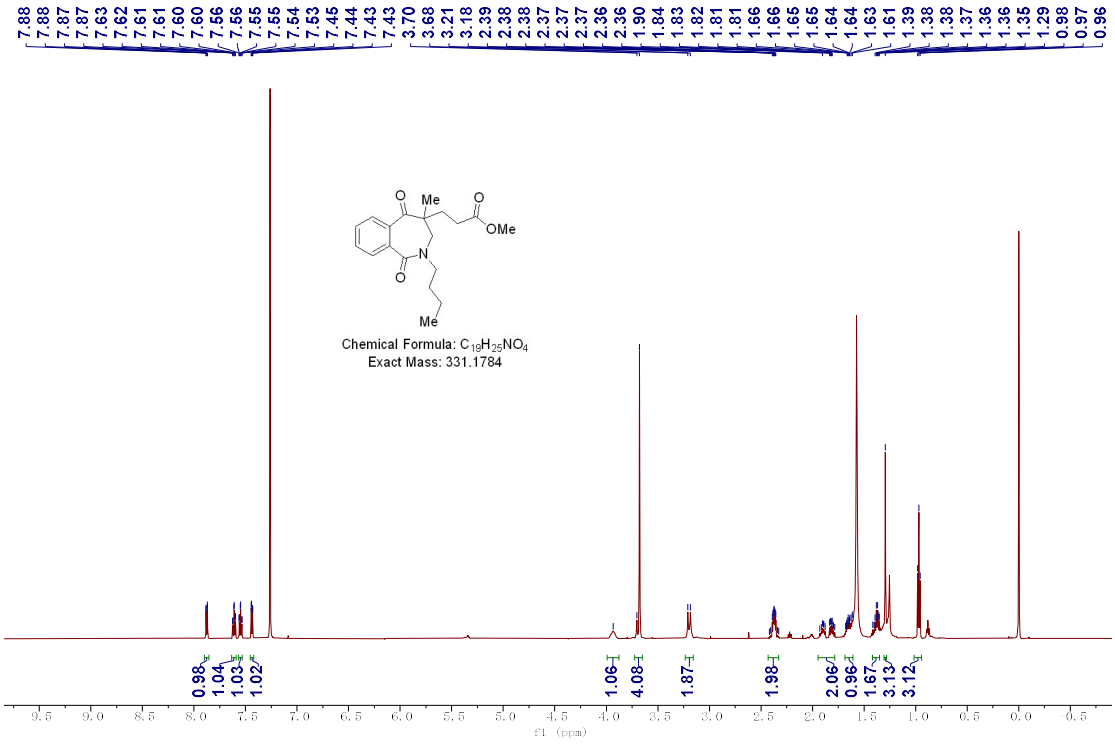

8.08
8.06
8.05
8.04
7.25
7.23
7.22
7.14
7.13
7.12
7.11
7.10
7.09
7.08
7.07
7.06
6.84
6.83
6.82
6.81
6.80
6.79
6.61
6.60
6.59
5.39
4.03
4.00
3.53
3.49
3.22
3.22
2.78
2.77
1.79
F
NHMe
O
Me
F
O
N
Me
O
Chemical Formula: C20H18F2N2O3
Exact Mass: 372.1285
1.00
0.89
2.24
1.03
1.01
1.08
1.02
1.20
3.15
3.04
3.23
f1 (ppm)
175.65
168.93
167.16
165.46
163.68
162.88
162.01
145.19
145.14
137.83
137.78
132.67
132.65
131.33
131.27
129.32
129.26
121.53
121.51
117.62
117.47
115.38
115.23
114.22
114.08
113.76
113.61
49.65
44.73
27.65
26.99
26.65
F
NHMe
O
Me
F
O
N
Me
O
Chemical Formula: C20H18F2N2O3
Exact Mass: 372.1285
f1 (ppm)

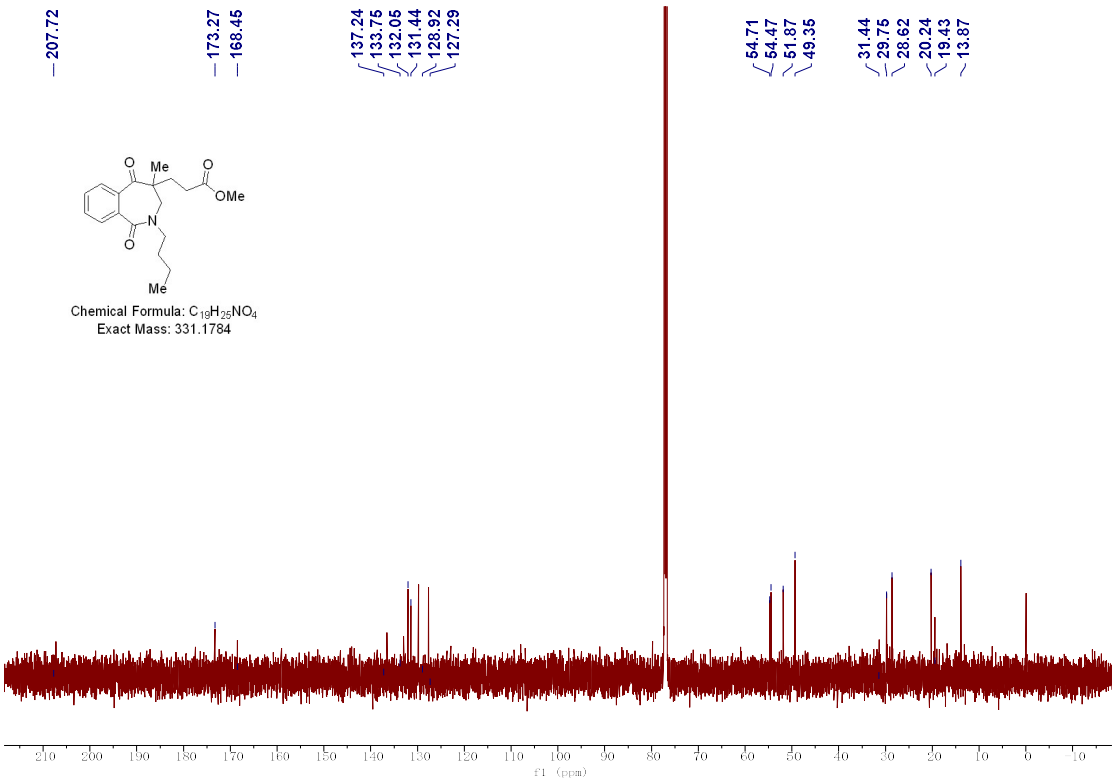

-102.41
-102.43
-102.45
-109.57
-109.59
-109.61
-109.63
F
NHMe
O
Me
F
O
N
Me
O
Chemical Formula: C20H18F2N2O3
Exact Mass: 372.1285
-102.41
-102.43
-102.45
1.00
-102.20
-102.30
-102.40
-102.50
-102.60
f1 (ppm)
-109.57
-109.59
-109.61
-109.63
0.98
-109.50
-109.60
-109.70
-109.80
-109.90
f1 (ppm)
1.00
0.98
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-300
f1 (ppm)

5d

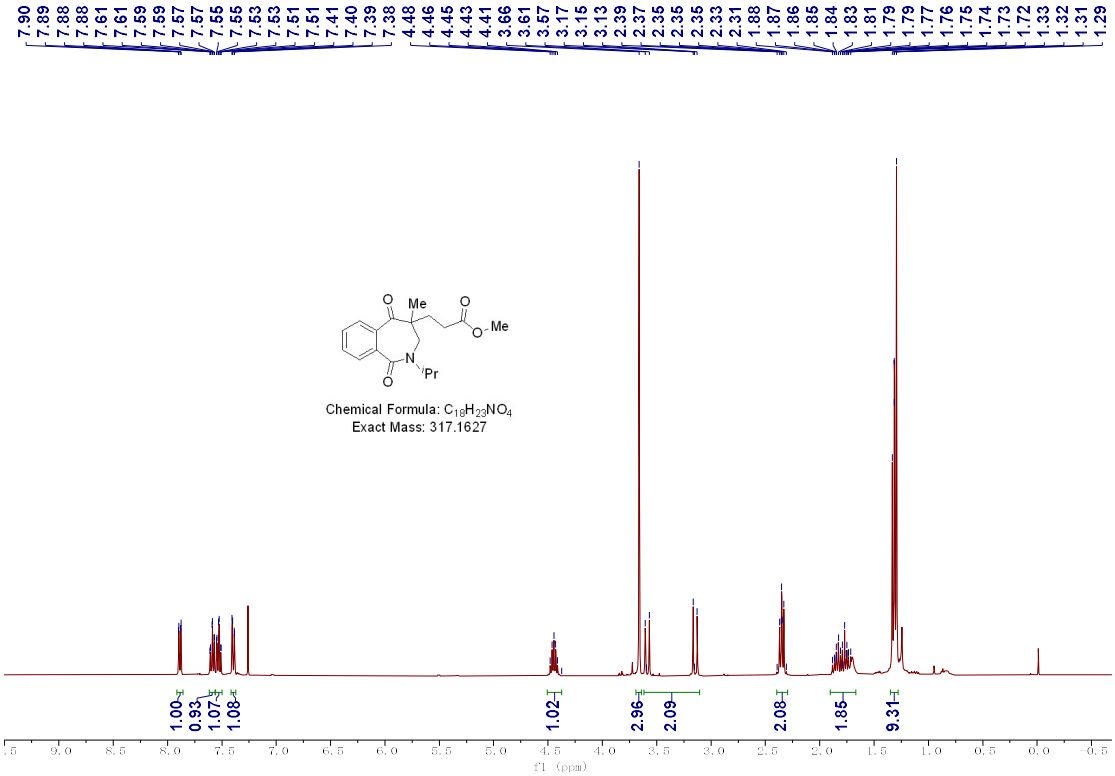

8.03
8.01
7.53
7.51
7.49
7.36
7.34
7.33
7.32
7.30
7.29
7.25
7.24
7.22
7.20
7.18
7.16
7.14
7.13
7.12
7.10
7.09
6.96
6.94
5.20
4.57
4.53
4.18
4.15
3.18
2.67
2.66
NHMe
O
O
N
Me
O
Chemical Formula: C25H22N2O3
Exact Mass: 398.1630
0.83
1.14
3.91
1.86
1.49
2.84
1.00
0.82
0.85
0.92
2.87
2.82
f1 (ppm)
175.32
169.92
163.95
143.61
142.59
133.44
131.00
129.89
129.61
128.75
127.79
127.71
127.66
127.43
127.34
127.16
125.40
57.99
41.48
27.02
26.83
NHMe
O
O
N
Me
O
Chemical Formula: C25H22N2O3
Exact Mass: 398.1630
f1 (ppm)

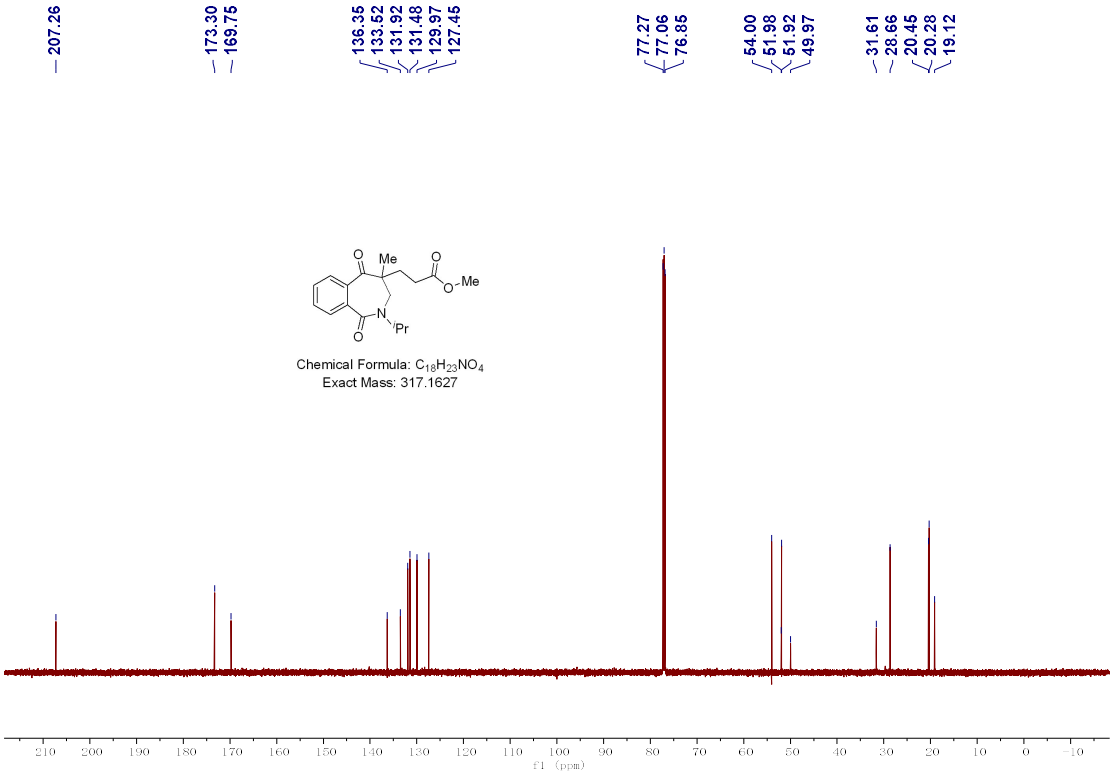
6aa


7.88 7.88 7.87 7.87 7.63 7.62 7.61 7.61 7.60 7.60 7.56 7.56 7.55 7.55 7.54 7.53 7.45 7.44 7.43 7.43 3.70 3.68 3.21 3.18 2.39 2.38 2.38 2.37 2.37 2.36 2.36 1.90 1.84 1.83 1.82 1.81 1.81 1.66 1.66 1.65 1.65 1.64 1.64 1.63 1.61 1.39 1.38 1.38 1.37 1.36 1.36 1.35 1.29 0.98 0.97 0.96
Me
O
OMe
N
Me
Chemical Formula: C18H25NO4
Exact Mass: 331.1784
0.98 1.04 1.03 1.02 1.06 4.08 1.87 1.98 2.06 0.96 1.67 3.13 3.12
f1 (ppm)

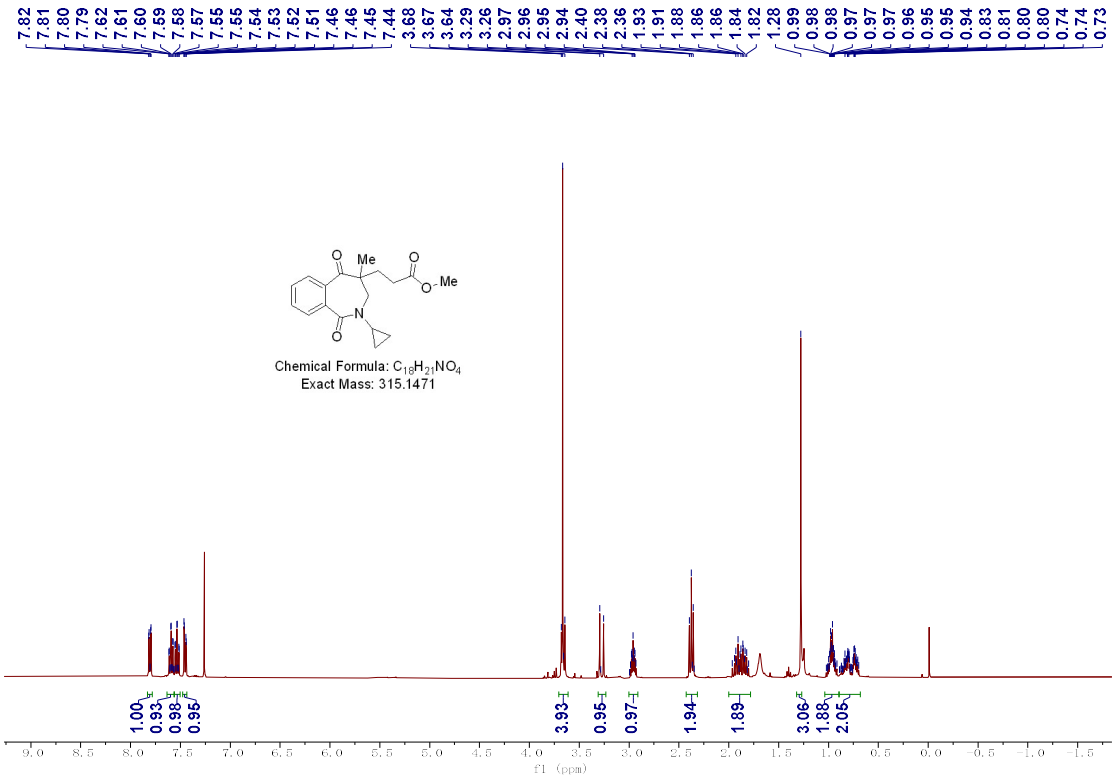

207.72 173.27 168.45 137.24 133.75 132.05 131.44 128.92 127.29 54.71 54.47 51.87 49.35 31.44 29.75 28.62 20.24 19.43 13.87
Me
O
OMe
N
Me
Chemical Formula: C18H25NO4
Exact Mass: 331.1784
f1 (ppm)

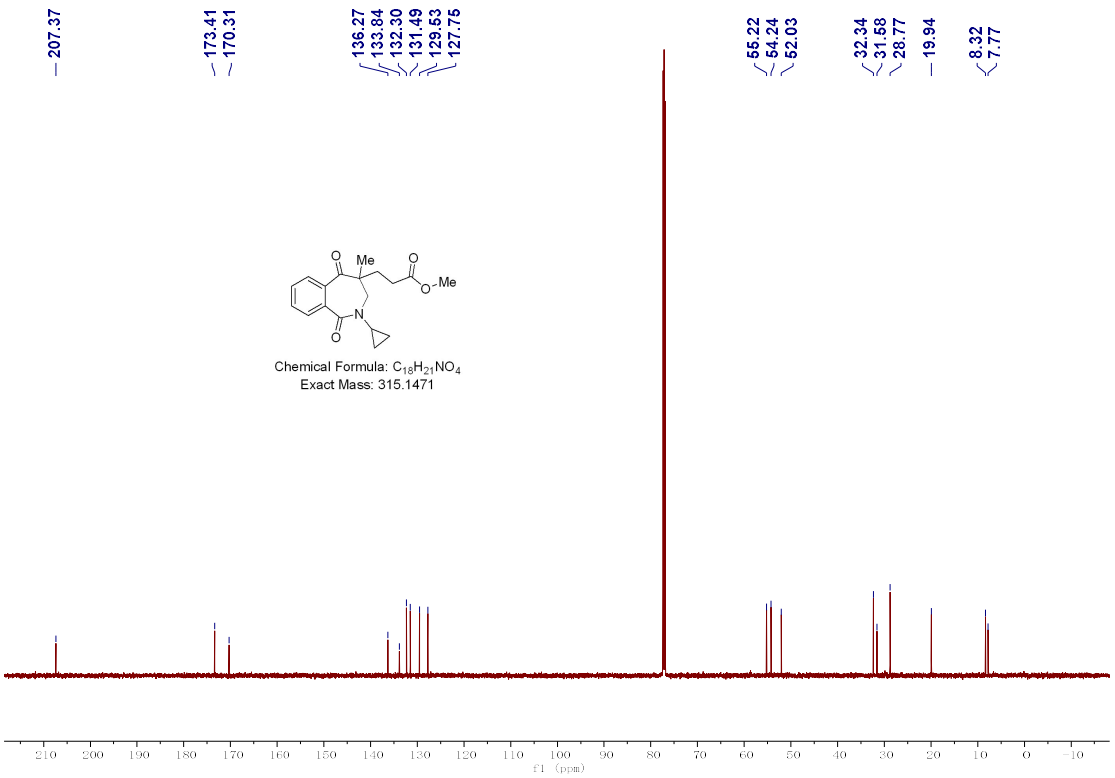
6ba


7.90 7.89 7.88 7.88 7.61 7.61 7.59 7.59 7.57 7.57 7.55 7.55 7.53 7.53 7.51 7.51 7.41 7.40 7.39 7.38
4.48 4.46 4.45 4.43 4.41 3.66 3.61 3.57 3.17 3.15 3.13 2.39 2.37 2.35 2.35 2.35 2.33 2.31 1.88 1.87 1.86 1.85 1.84 1.83 1.81 1.79 1.79 1.77 1.76 1.75 1.74 1.73 1.72 1.33 1.32 1.31 1.29
Me
O
O
Me
N
iPr
O
Chemical Formula: C18H23NO4
Exact Mass: 317.1627
1.00 0.93 1.07 1.08 1.02 2.96 2.09 2.08 1.85 9.31
f1 (ppm)

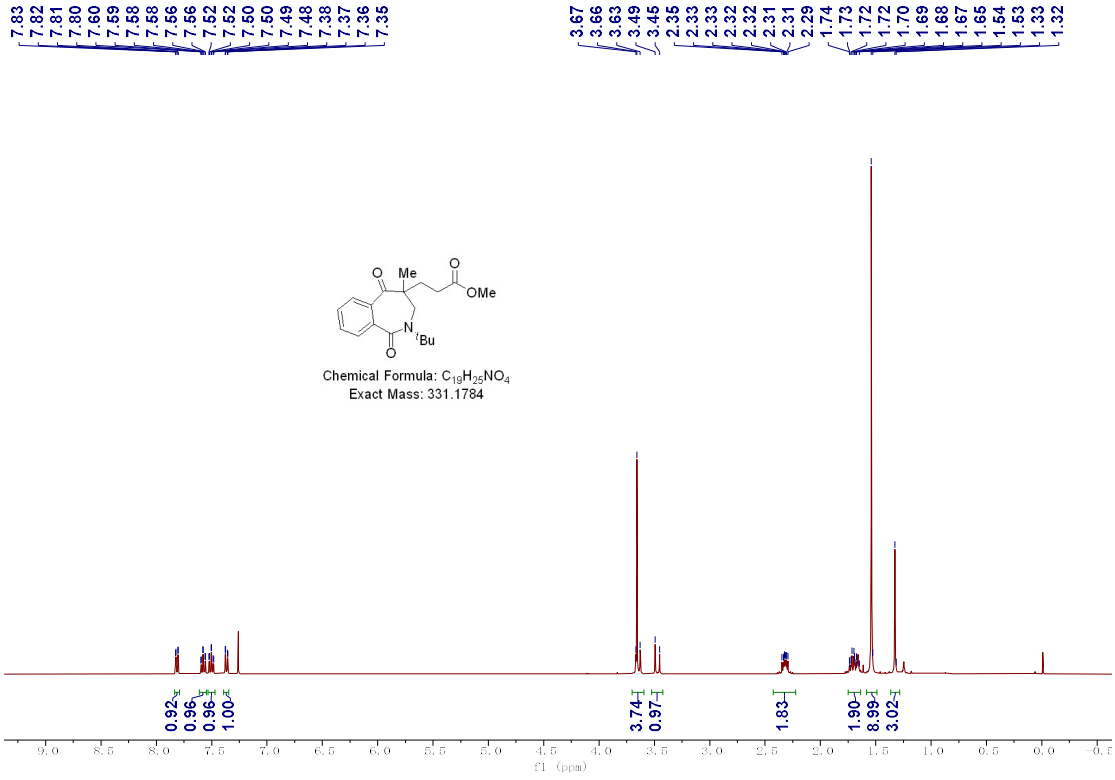

207.26
173.30 169.75
136.35 133.52 131.92 131.48 129.97 127.45
77.27 77.06 76.85
54.00 51.98 51.92 49.97
31.61 28.66 20.45 20.28 19.12
Me
O
O
Me
N
iPr
O
Chemical Formula: C18H23NO4
Exact Mass: 317.1627
f1 (ppm)

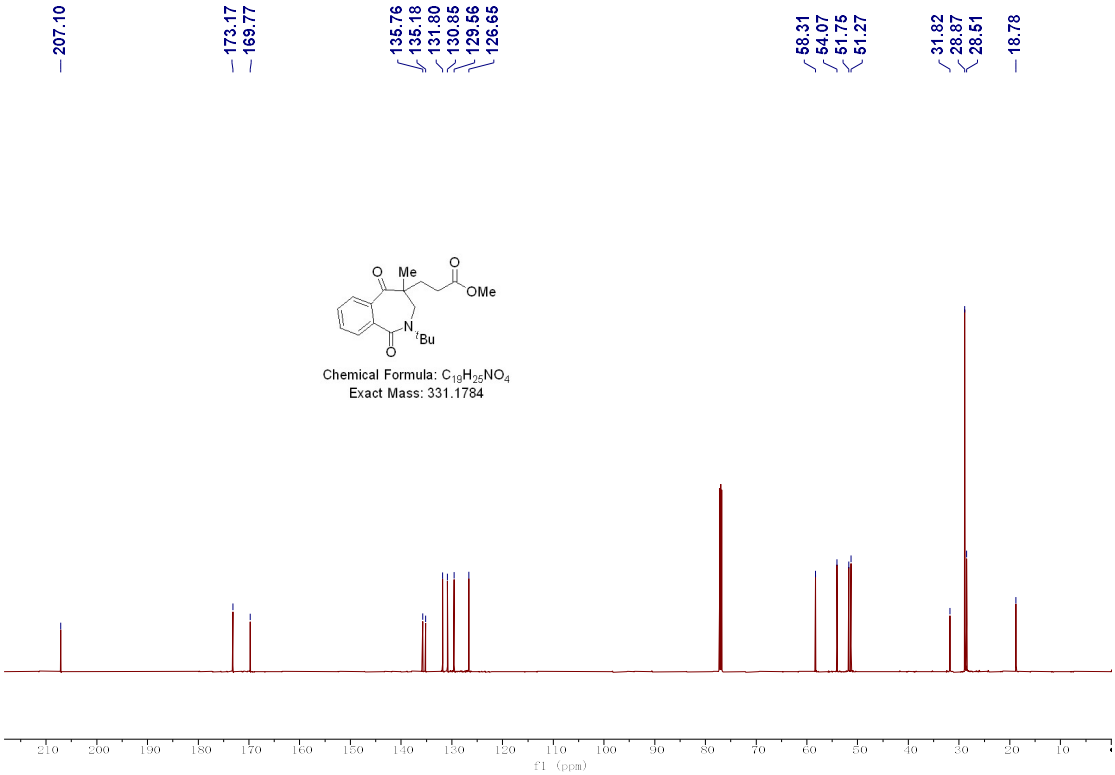
6ca


7.82 7.81 7.80 7.79 7.62 7.61 7.60 7.59 7.58 7.57 7.55 7.55 7.54 7.53 7.52 7.51 7.46 7.45 7.44
3.68 3.67 3.64 3.29 3.26 2.97 2.96 2.95 2.94 2.40 2.38 2.36 1.93 1.91 1.88 1.86 1.86 1.84 1.82 1.28 0.99 0.98 0.98 0.97 0.97 0.97 0.96 0.95 0.95 0.94 0.83 0.81 0.80 0.80 0.74 0.74 0.73
Me
O
O
O
Me
N
O
Chemical Formula: C18H21NO4
Exact Mass: 315.1471
1.00 0.93 0.98 0.95 3.93 0.95 0.97 1.94 1.89 3.06 1.88 2.05
f1 (ppm)

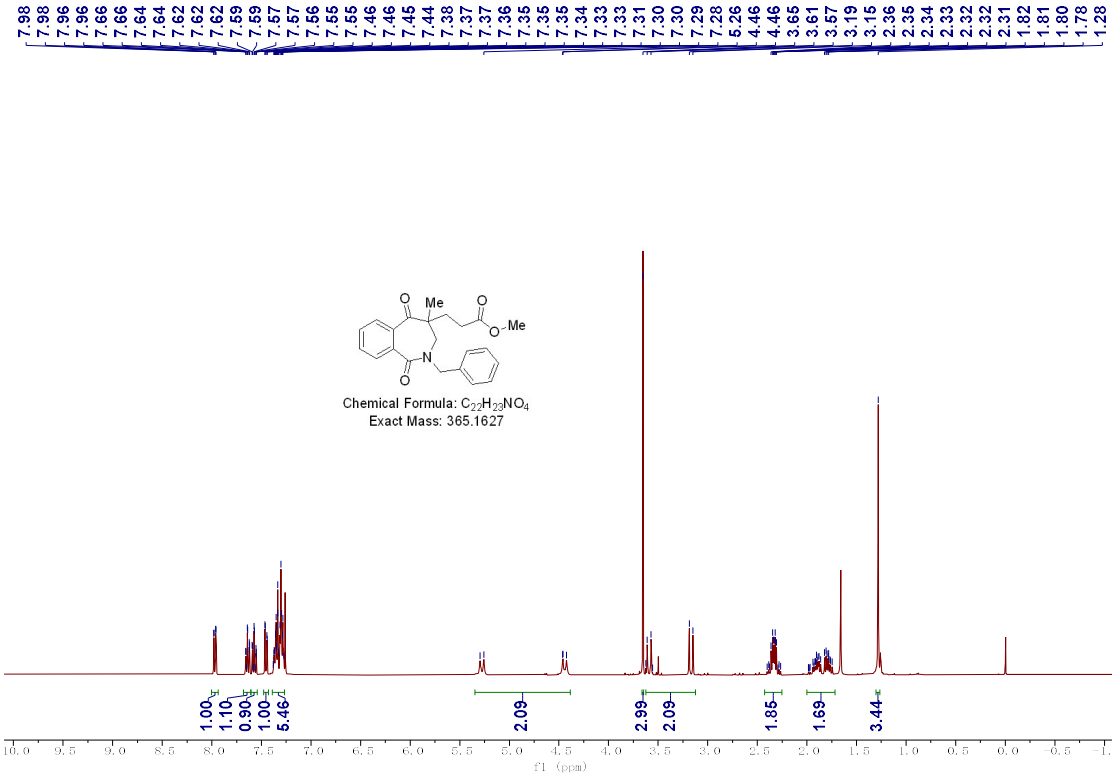

207.37
173.41 170.31
136.27 133.84 132.30 131.49 129.53 127.75
55.22 54.24 52.03
32.34 31.58 28.77 19.94 8.32 7.77
Me
O
O
O
Me
N
O
Chemical Formula: C18H21NO4
Exact Mass: 315.1471
f1 (ppm)

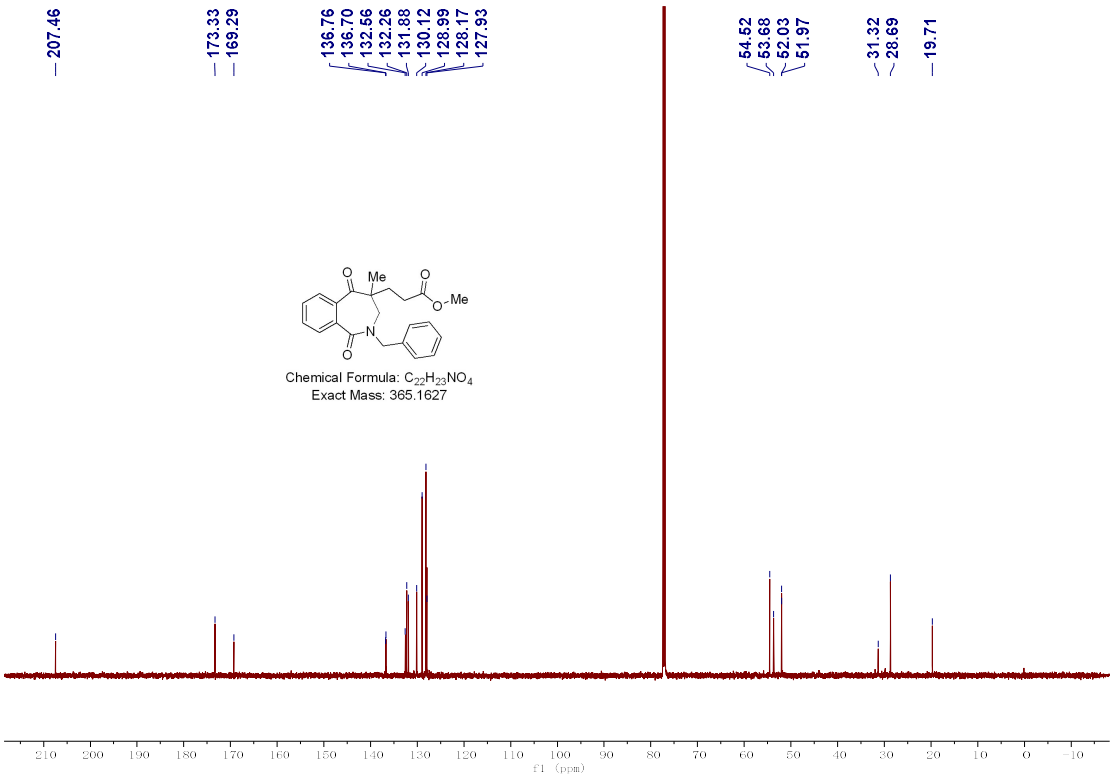
6da


7.83
7.82
7.81
7.80
7.60
7.59
7.58
7.58
7.56
7.56
7.52
7.52
7.50
7.50
7.49
7.48
7.38
7.37
7.36
7.35
3.67
3.66
3.63
3.49
3.45
2.35
2.33
2.33
2.32
2.32
2.31
2.31
2.29
1.74
1.73
1.72
1.72
1.70
1.69
1.68
1.67
1.65
1.54
1.53
1.33
1.32
Me
OMe
tBu
Chemical Formula: C19H25NO4
Exact Mass: 331.1784
0.92
0.96
0.96
1.00
3.74
0.97
1.83
1.90
8.99
3.02
f1 (ppm)

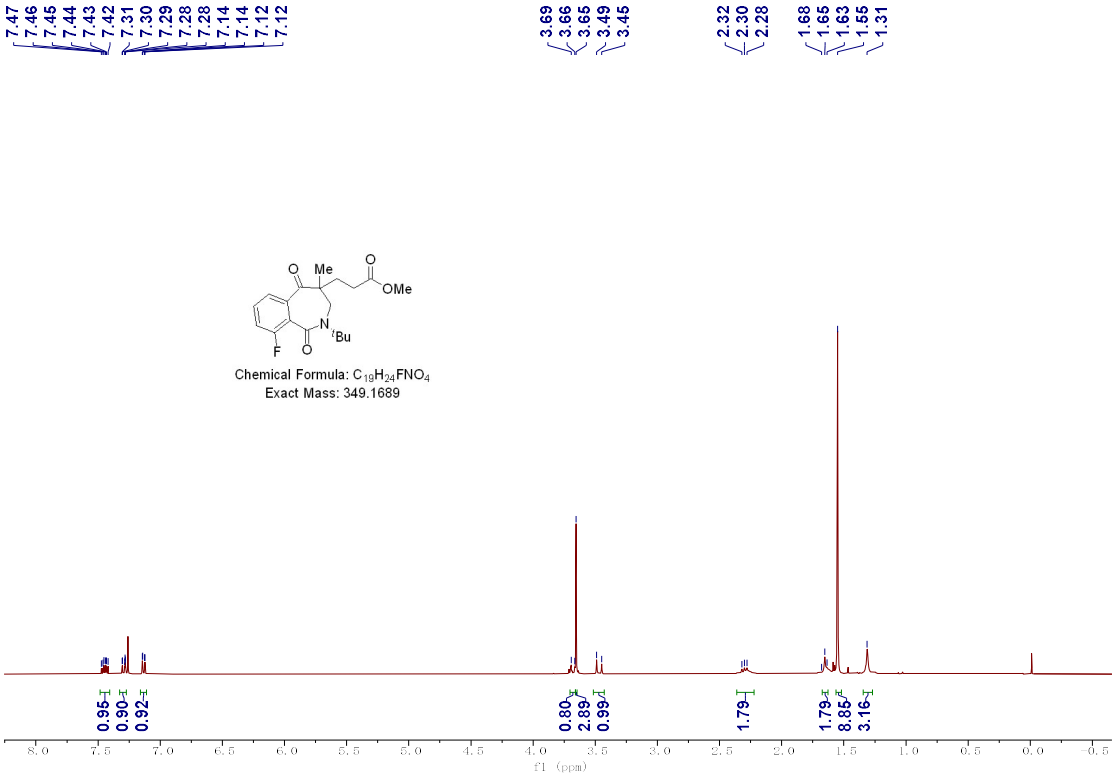

207.10
173.17
169.77
135.76
135.18
131.80
130.85
129.56
126.65
58.31
54.07
51.75
51.27
31.82
28.87
28.51
18.78
Me
OMe
tBu
Chemical Formula: C19H25NO4
Exact Mass: 331.1784
f1 (ppm)

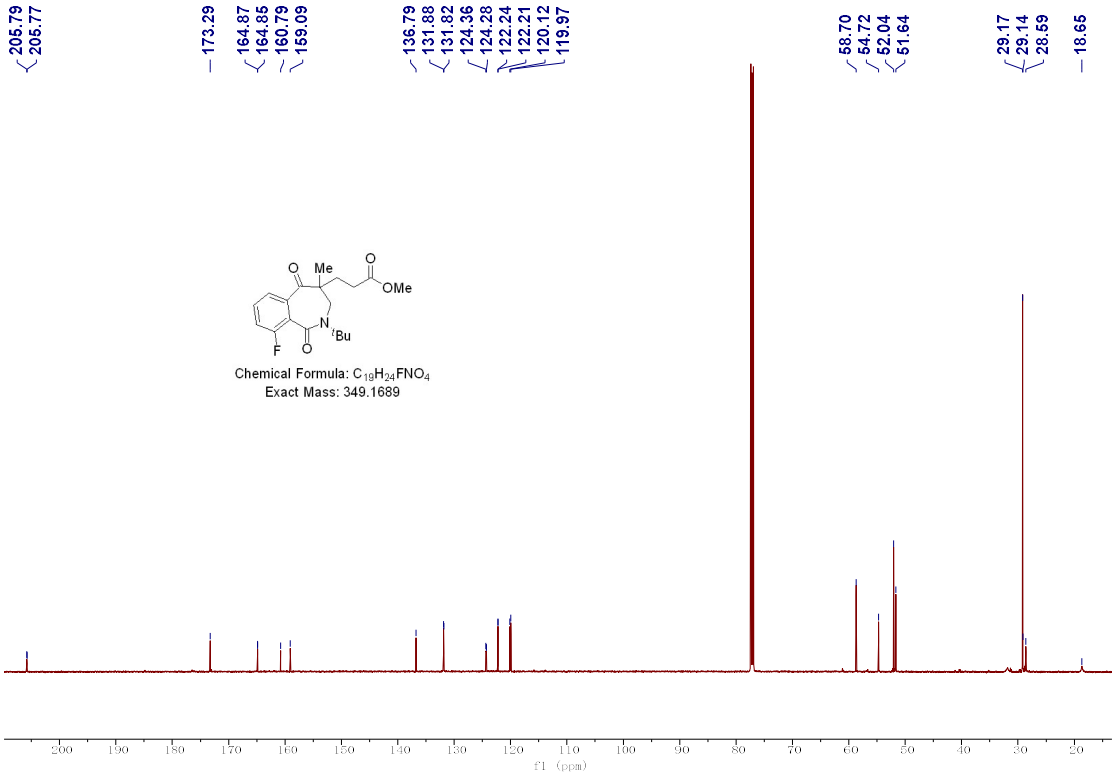
6ea

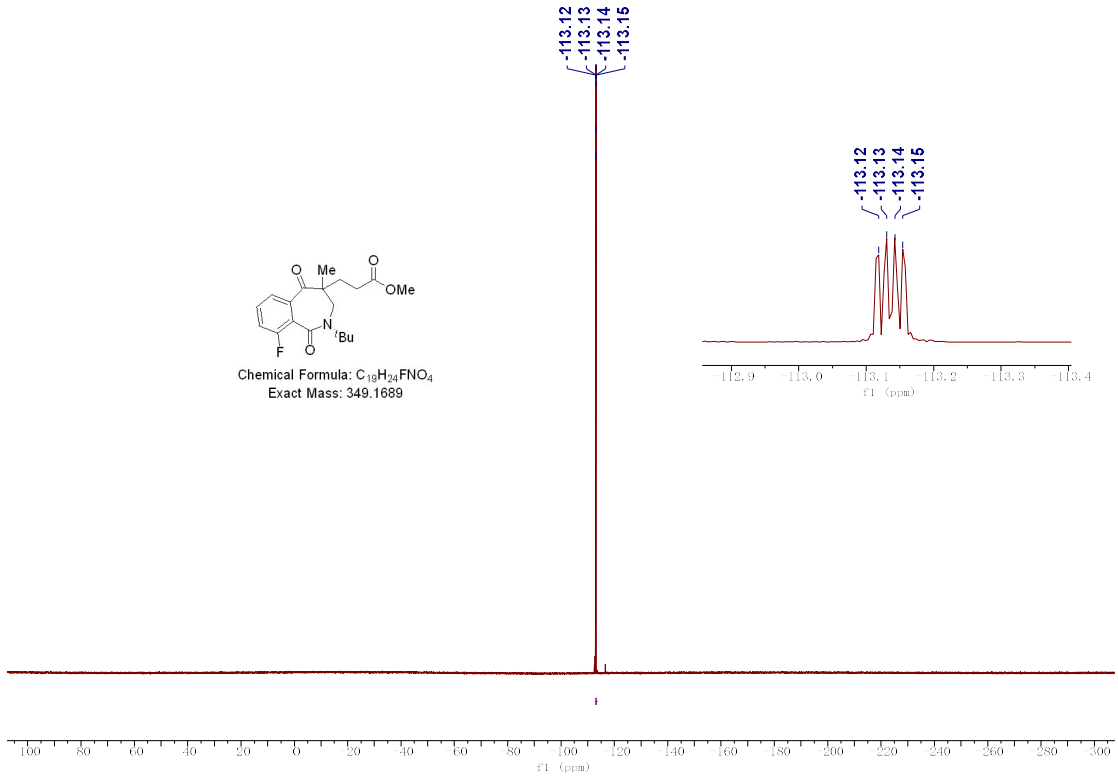

7.98 7.98 7.96 7.96 7.66 7.66 7.64 7.64 7.62 7.62 7.62 7.59 7.59 7.57 7.57 7.56 7.55 7.55 7.46 7.46 7.45 7.44 7.38 7.37 7.37 7.36 7.35 7.35 7.35 7.34 7.33 7.33 7.31 7.30 7.30 7.29 7.28 5.26 4.46 4.46 3.65 3.61 3.57 3.19 3.15 2.36 2.35 2.34 2.33 2.32 2.32 2.31 1.82 1.81 1.80 1.78 1.28
Me
O
O
O-Me
N
O
Chemical Formula: C22H23NO4
Exact Mass: 365.1627
1.00 1.10 0.90 1.00 5.46 2.09 2.99 2.09 1.85 1.69 3.44
f1 (ppm)


207.46
173.33
169.29
136.76
136.70
132.56
132.26
131.88
130.12
128.99
128.17
127.93
54.52
53.68
52.03
51.97
31.32
28.69
19.71
Me
O
O
O-Me
N
O
Chemical Formula: C22H23NO4
Exact Mass: 365.1627
f1 (ppm)

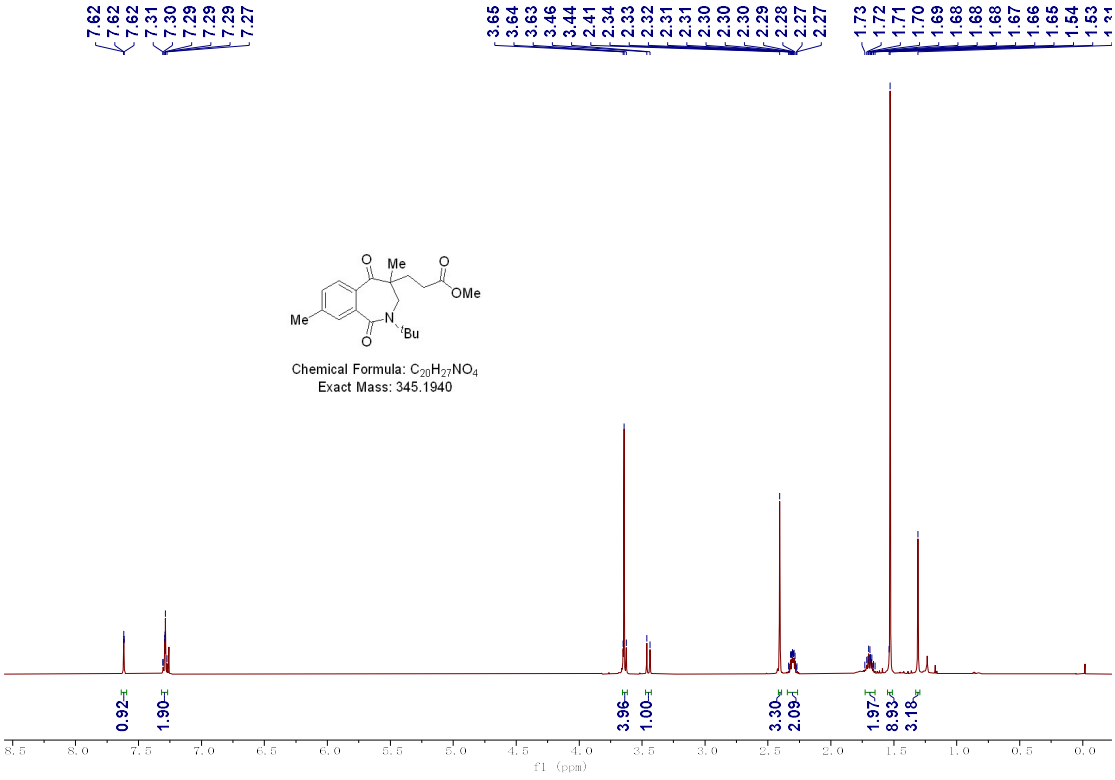
6fa

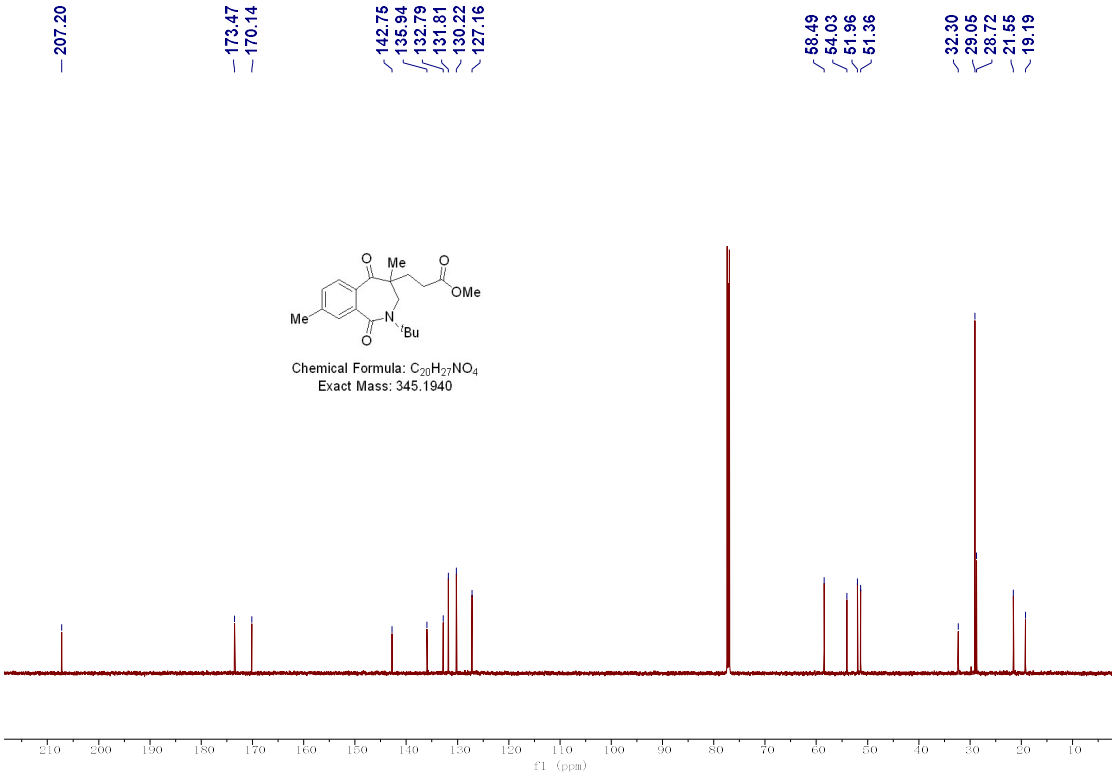

7.47
7.46
7.45
7.44
7.43
7.42
7.31
7.30
7.29
7.28
7.28
7.14
7.12
7.12
3.69
3.66
3.65
3.49
3.45
2.32
2.30
2.28
1.68
1.65
1.63
1.55
1.31
Me
O
OMe
N
tBu
F
Chemical Formula: C19H24FNO4
Exact Mass: 349.1689
0.95
0.90
0.92
0.80
2.89
0.99
1.79
1.79
8.85
3.16
f1 (ppm)


205.79
205.77
173.29
164.87
164.85
160.79
159.09
136.79
131.88
131.82
124.36
124.28
122.24
122.21
120.12
119.97
58.70
54.72
52.04
51.64
29.17
29.14
28.59
18.65
Me
O
OMe
N
tBu
F
Chemical Formula: C19H24FNO4
Exact Mass: 349.1689
f1 (ppm)

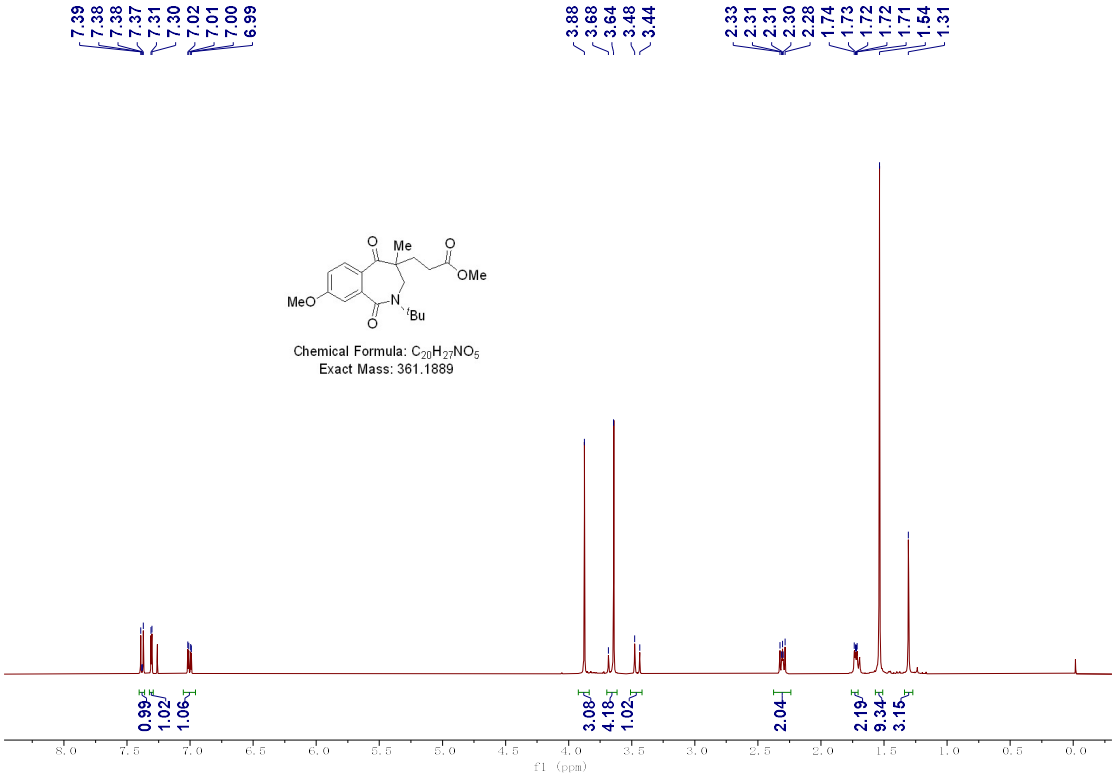

-113.12
-113.13
-113.14
-113.15
O
Me
O
OMe
N
tBu
O
F
Chemical Formula: C19H24FNO4
Exact Mass: 349.1689
-113.12
-113.13
-113.14
-113.15
112.9
113.0
113.1
113.2
113.3
113.4
f1 (ppm)
100
80
60
40
20
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
f1 (ppm)

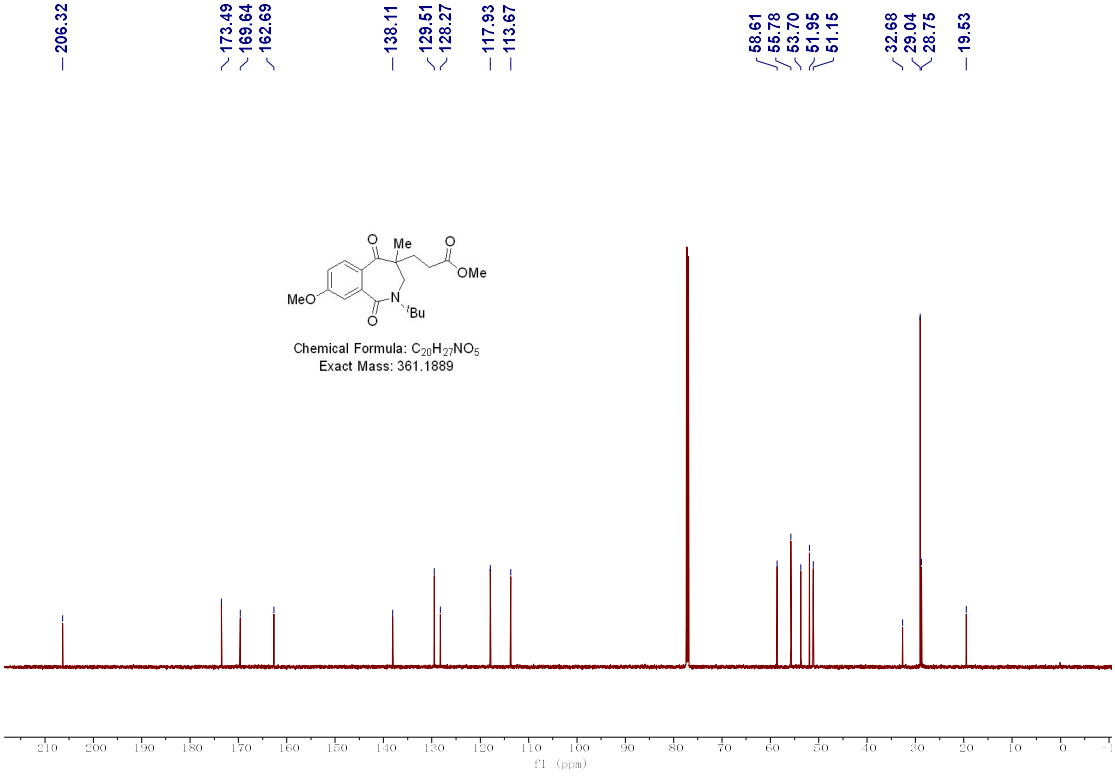
6ga


7.62
7.62
7.62
7.31
7.30
7.29
7.29
7.29
7.27
3.65
3.64
3.63
3.46
3.44
2.41
2.34
2.33
2.32
2.31
2.31
2.30
2.30
2.30
2.29
2.28
2.27
2.27
1.73
1.72
1.71
1.70
1.69
1.68
1.68
1.68
1.67
1.66
1.65
1.54
1.53
Me
O
O
OMe
Me
N
tBu
O
Chemical Formula: C20H27NO4
Exact Mass: 345.1940
0.92
1.90
3.96
1.00
3.30
2.09
1.97
8.93
3.18
f1 (ppm)

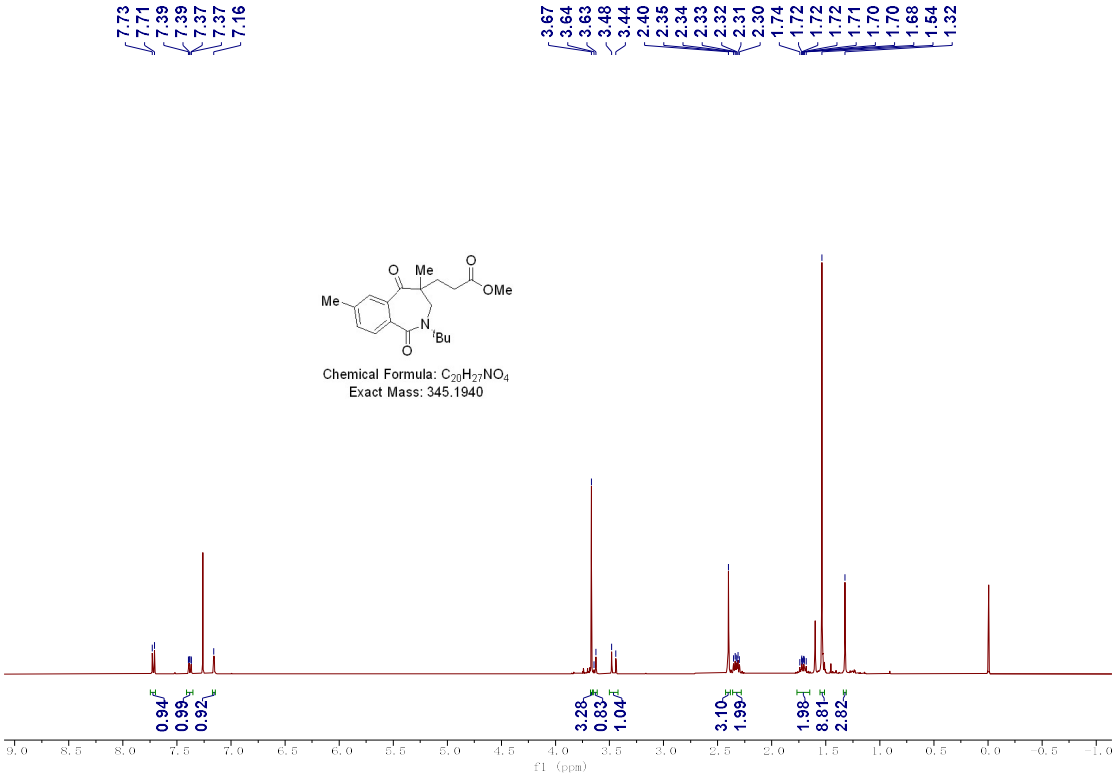

207.20
173.47
170.14
142.75
135.94
132.79
131.81
130.22
127.16
58.49
54.03
51.96
51.36
32.30
29.05
28.72
21.55
19.19
Me
O
O
OMe
Me
N
tBu
O
Chemical Formula: C20H27NO4
Exact Mass: 345.1940
f1 (ppm)

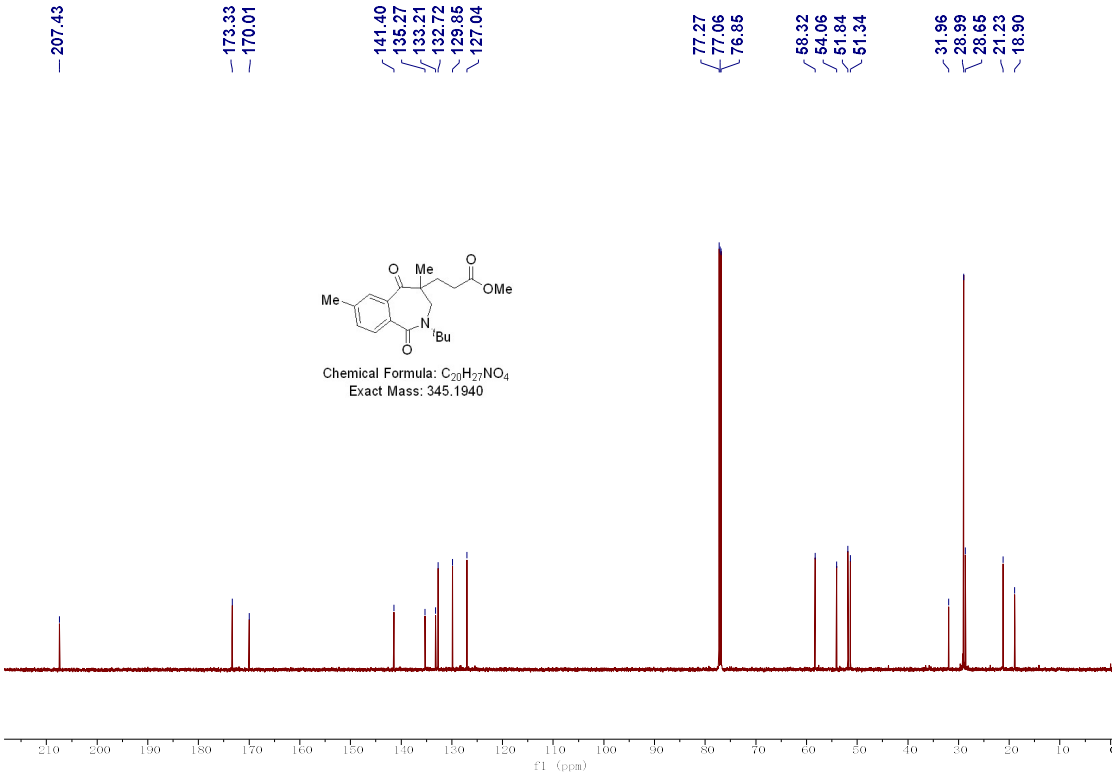
6ha


7.39
7.38
7.38
7.37
7.31
7.30
7.02
7.01
7.00
6.99
3.88
3.68
3.64
3.48
3.44
2.33
2.31
2.31
2.30
2.28
1.74
1.73
1.72
1.72
1.71
1.54
1.31
Me
O
OMe
MeO
N
tBu
Chemical Formula: C20H27NO5
Exact Mass: 361.1889
0.99
1.02
1.06
3.08
4.18
1.02
2.04
2.19
9.34
3.15
f1 (ppm)

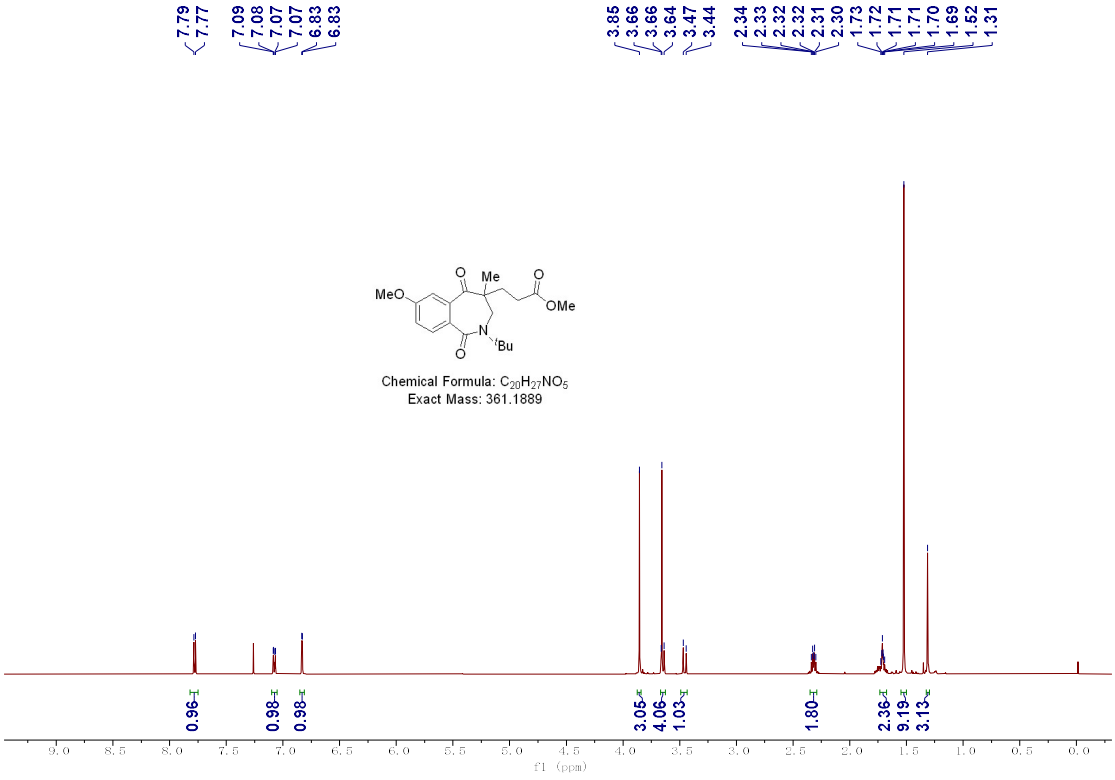

206.32
173.49
169.64
162.69
138.11
129.51
128.27
117.93
113.67
58.61
55.78
53.70
51.95
51.15
32.68
29.04
28.75
19.53
Me
O
OMe
MeO
N
tBu
Chemical Formula: C20H27NO5
Exact Mass: 361.1889
f1 (ppm)

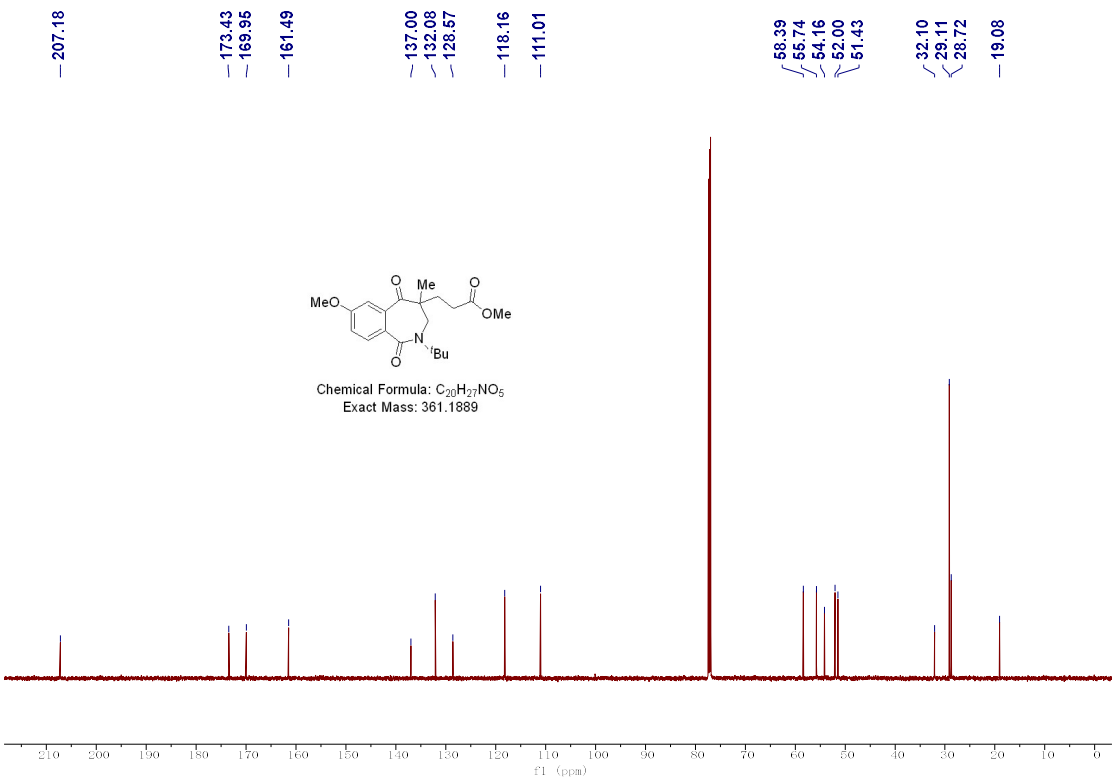
6ia


7.73
7.71
7.39
7.39
7.37
7.37
7.16
3.67
3.64
3.63
3.48
3.44
2.40
2.35
2.34
2.33
2.32
2.31
2.30
1.74
1.72
1.72
1.72
1.71
1.70
1.70
1.68
1.54
1.32
Me
O
Me
O
OMe
N
tBu
O
Chemical Formula: C20H27NO4
Exact Mass: 345.1940
0.94
0.99
0.92
3.28
0.83
1.04
3.10
1.99
1.98
8.81
2.82
f1 (ppm)

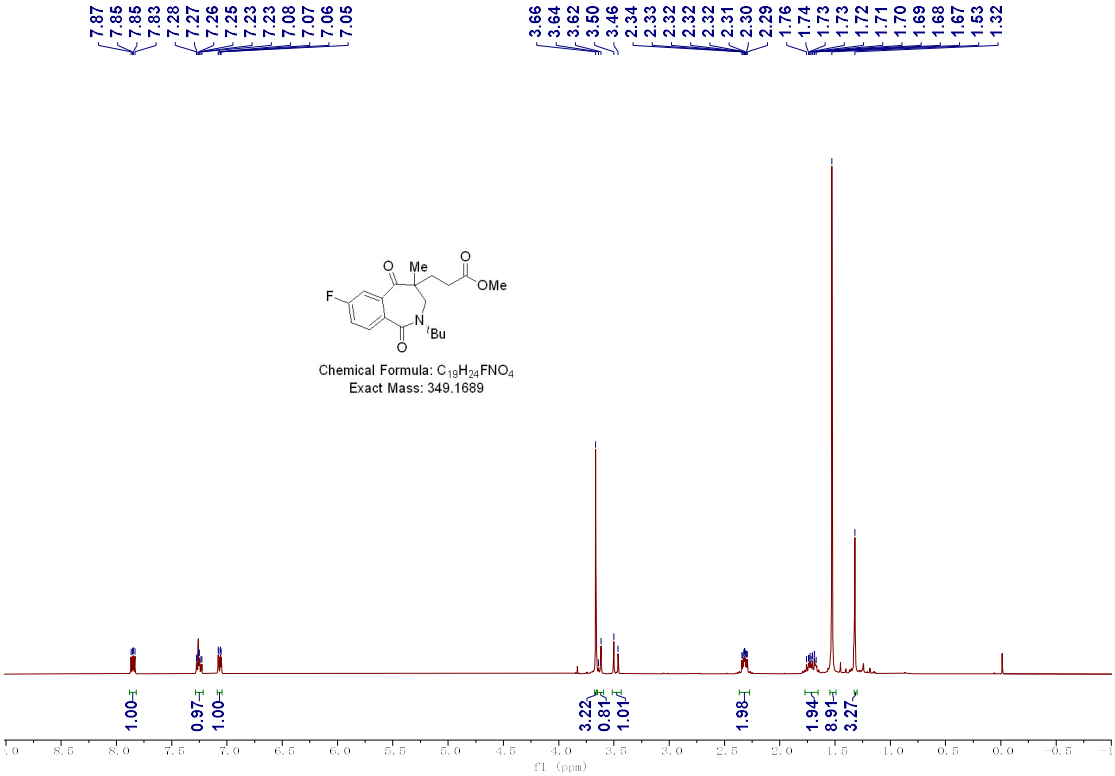

207.43
173.33
170.01
141.40
135.27
133.21
132.72
129.85
127.04
77.27
77.06
76.85
58.32
54.06
51.84
51.34
31.96
28.99
28.65
21.23
18.90
Me
O
Me
O
OMe
N
tBu
O
Chemical Formula: C20H27NO4
Exact Mass: 345.1940
f1 (ppm)

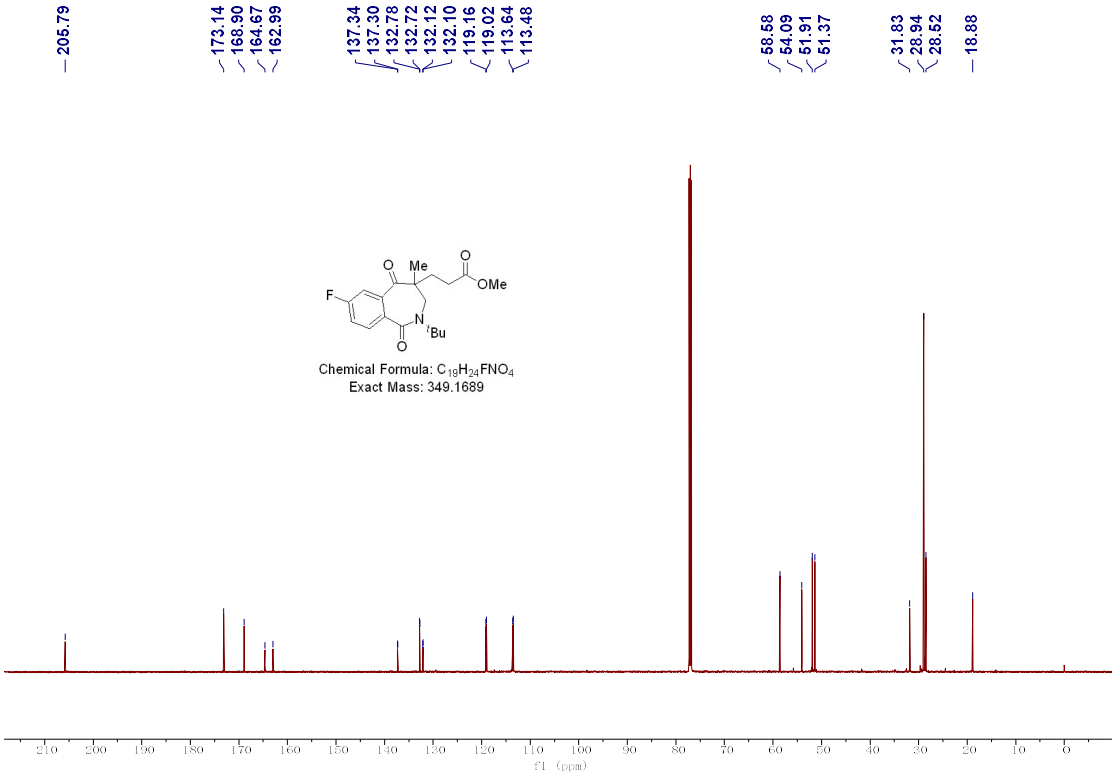
6ja

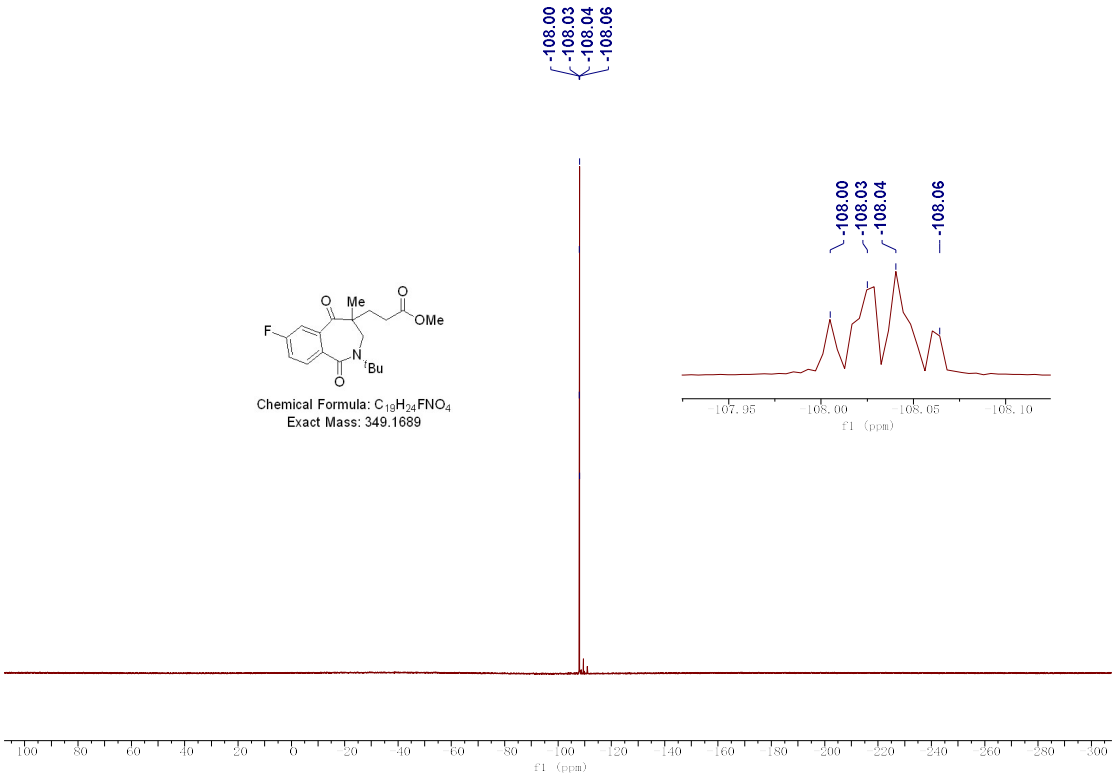

7.79
7.77
7.09
7.08
7.07
7.07
6.83
6.83
3.85
3.66
3.66
3.64
3.47
3.44
2.34
2.33
2.32
2.32
2.31
2.30
1.73
1.72
1.71
1.71
1.70
1.69
1.52
1.31
MeO
Me
O
OMe
N
tBu
Chemical Formula: C20H27NO5
Exact Mass: 361.1889
0.96
0.98
0.98
3.05
4.06
1.03
1.80
2.36
9.19
3.13
f1 (ppm)


207.18
173.43
169.95
161.49
137.00
132.08
128.57
118.16
111.01
58.39
55.74
54.16
52.00
51.43
32.10
29.11
28.72
19.08
MeO
Me
O
OMe
N
tBu
Chemical Formula: C20H27NO5
Exact Mass: 361.1889
f1 (ppm)

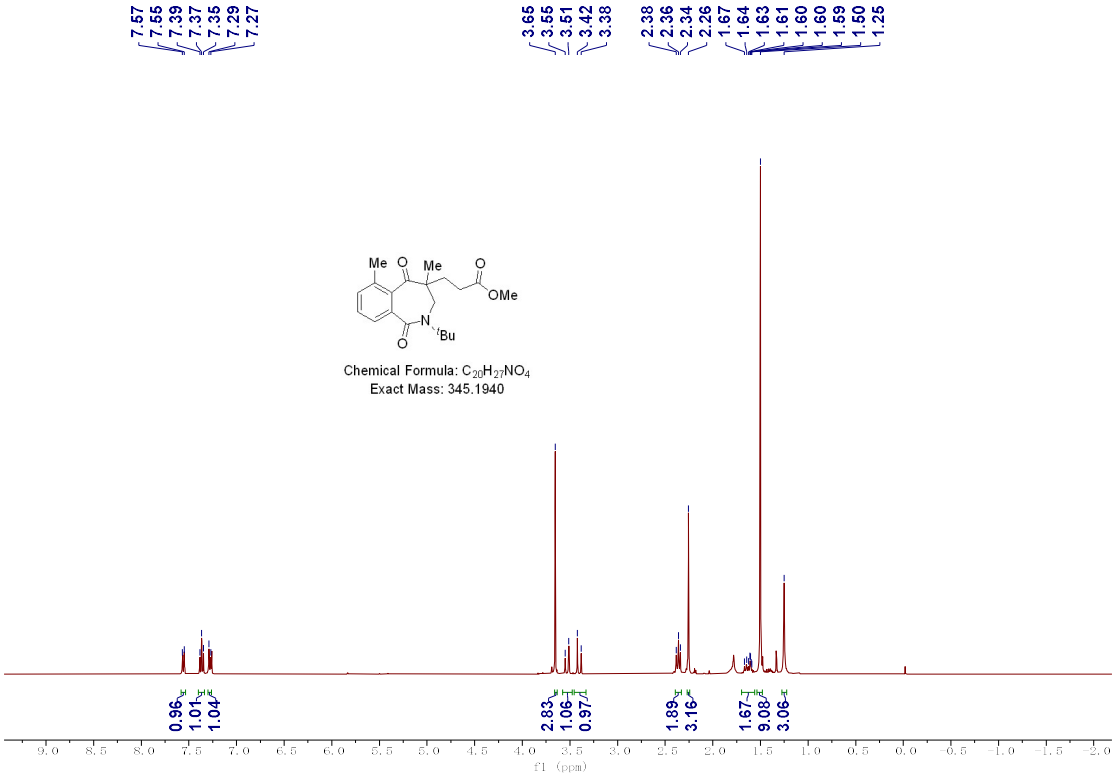
6ka

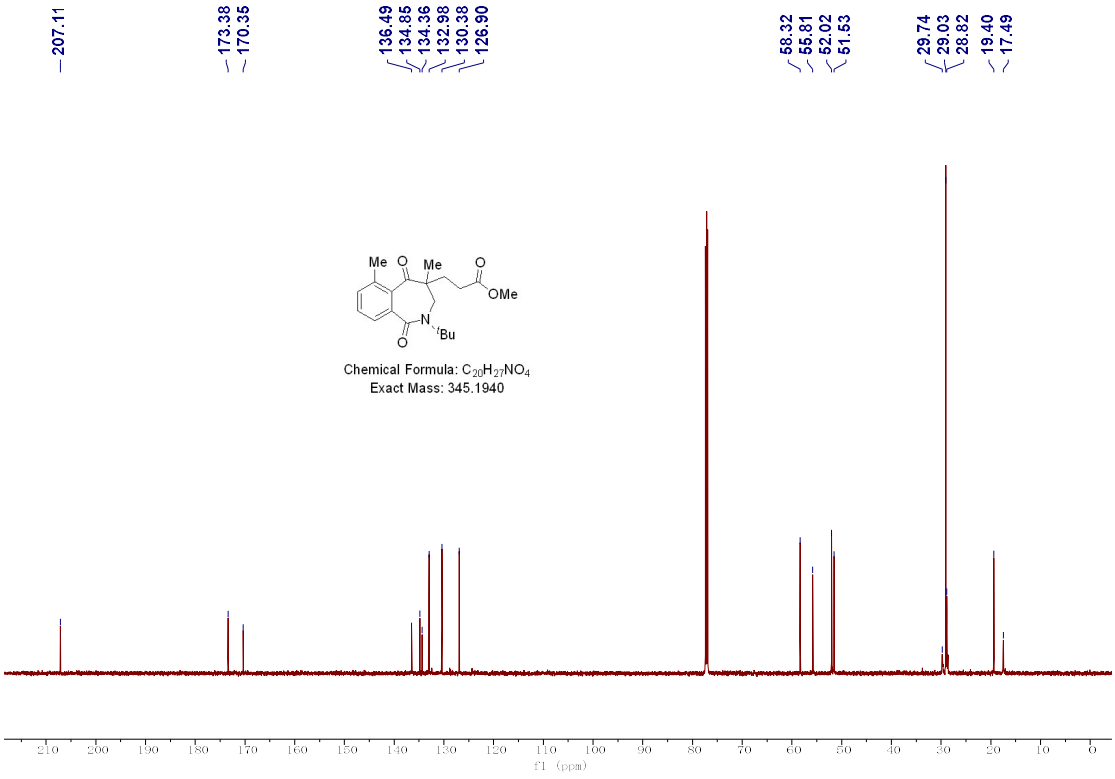

7.87
7.85
7.85
7.83
7.28
7.27
7.26
7.25
7.23
7.23
7.08
7.07
7.06
7.05
3.66
3.64
3.62
3.50
3.46
2.34
2.33
2.32
2.32
2.32
2.31
2.30
2.29
1.76
1.74
1.73
1.73
1.72
1.71
1.70
1.69
1.68
1.67
1.53
1.32
Me
O
OMe
F
N
tBu
Chemical Formula: C19H24FNO4
Exact Mass: 349.1689
1.00
0.97
1.00
3.22
0.81
1.01
1.98
1.94
8.91
3.27
f1 (ppm)


205.79
173.14
168.90
164.67
162.99
137.34
137.30
132.78
132.72
132.12
132.10
119.16
119.02
113.64
113.48
58.58
54.09
51.91
51.37
31.83
28.94
28.52
18.88
Me
O
OMe
F
N
tBu
Chemical Formula: C19H24FNO4
Exact Mass: 349.1689
f1 (ppm)

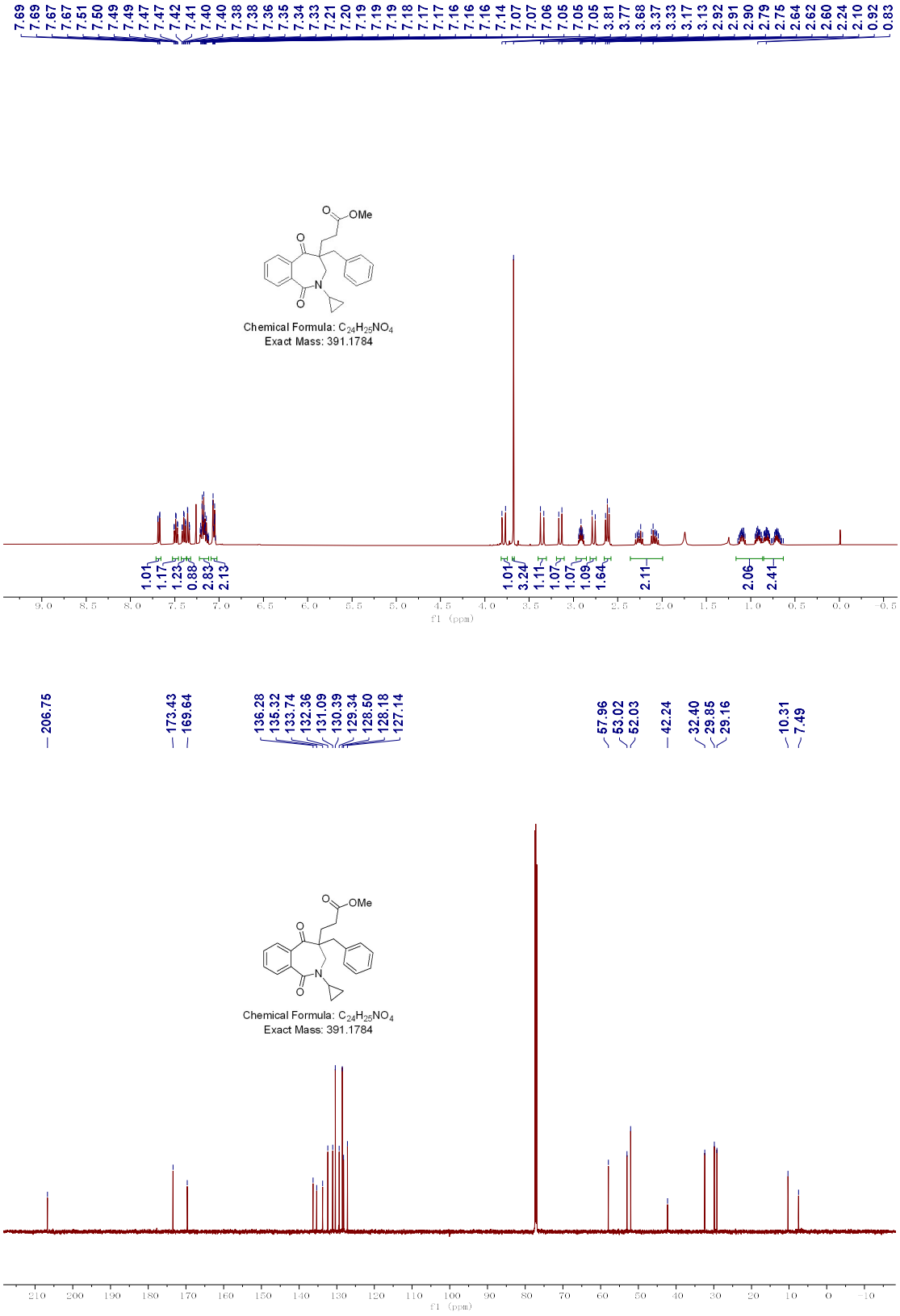

-108.00
-108.03
-108.04
-108.06
Me
O
O
OMe
F
N
tBu
O
Chemical Formula: C19H24FNO4
Exact Mass: 349.1689
-107.95
-108.00
-108.05
-108.10
f1 (ppm)
100
80
60
40
20
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
f1 (ppm)

6la

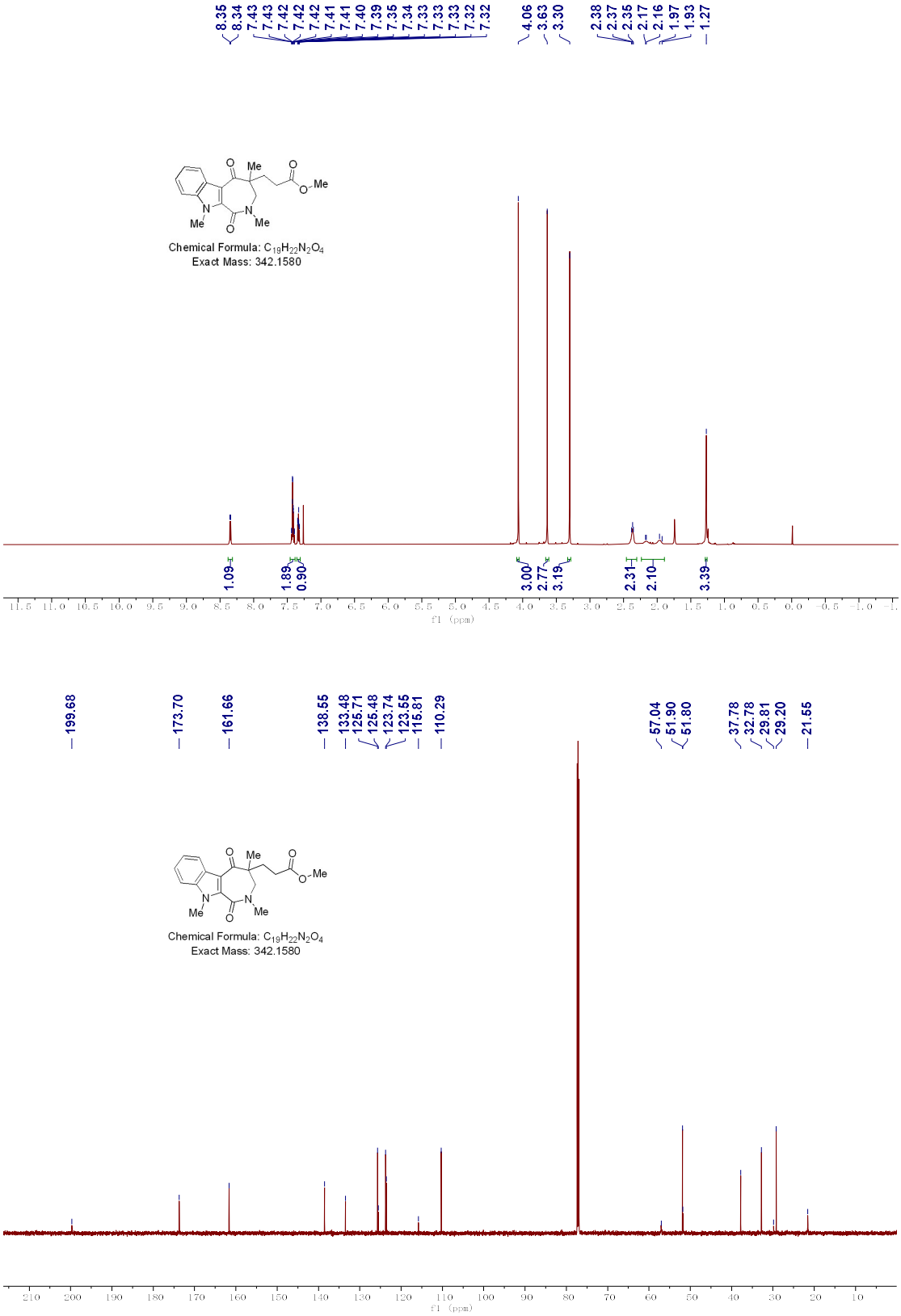

7.57
7.55
7.39
7.37
7.35
7.29
7.27
3.65
3.55
3.51
3.42
3.38
2.38
2.36
2.34
2.26
1.67
1.64
1.63
1.61
1.60
1.60
1.59
1.50
1.25
Me
O
Me
O
OMe
N
tBu
O
Chemical Formula: C20H27NO4
Exact Mass: 345.1940
0.96
1.01
1.04
2.83
1.06
0.97
1.89
3.16
1.67
9.08
3.06
f1 (ppm)


207.11
173.38
170.35
136.49
134.85
134.36
132.98
130.38
126.90
58.32
55.81
52.02
51.53
29.74
29.03
28.82
19.40
17.49
Me
O
Me
O
OMe
N
tBu
O
Chemical Formula: C20H27NO4
Exact Mass: 345.1940
f1 (ppm)

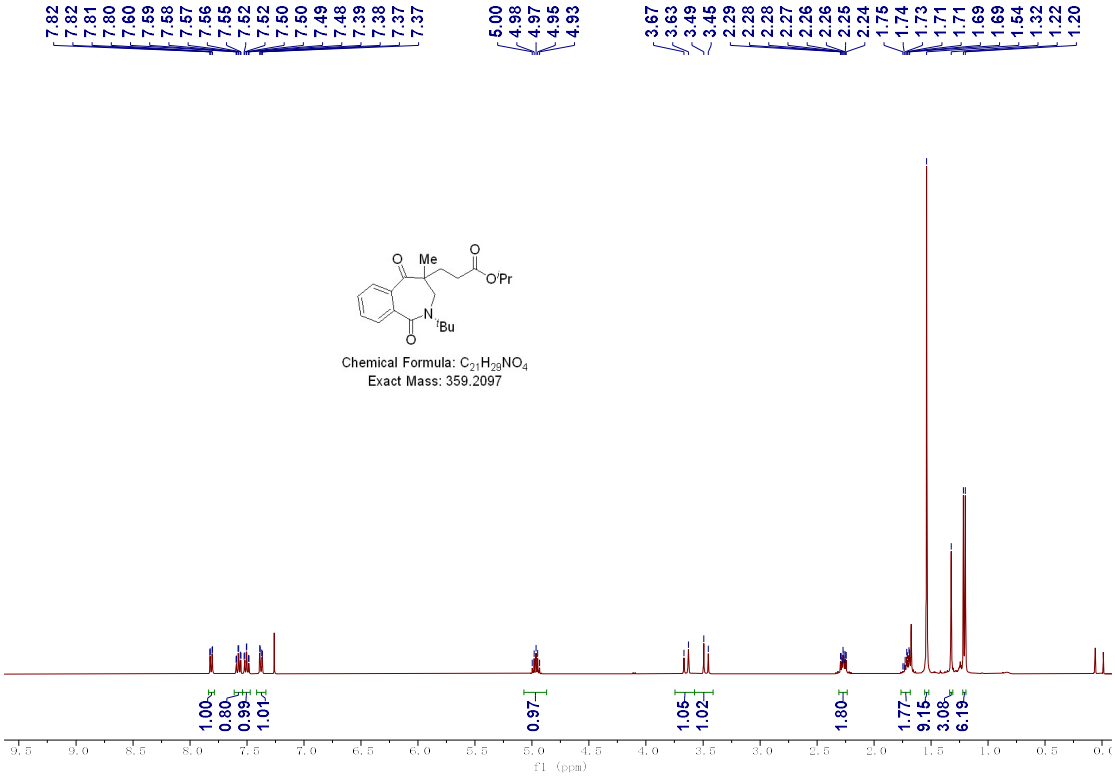
6ma

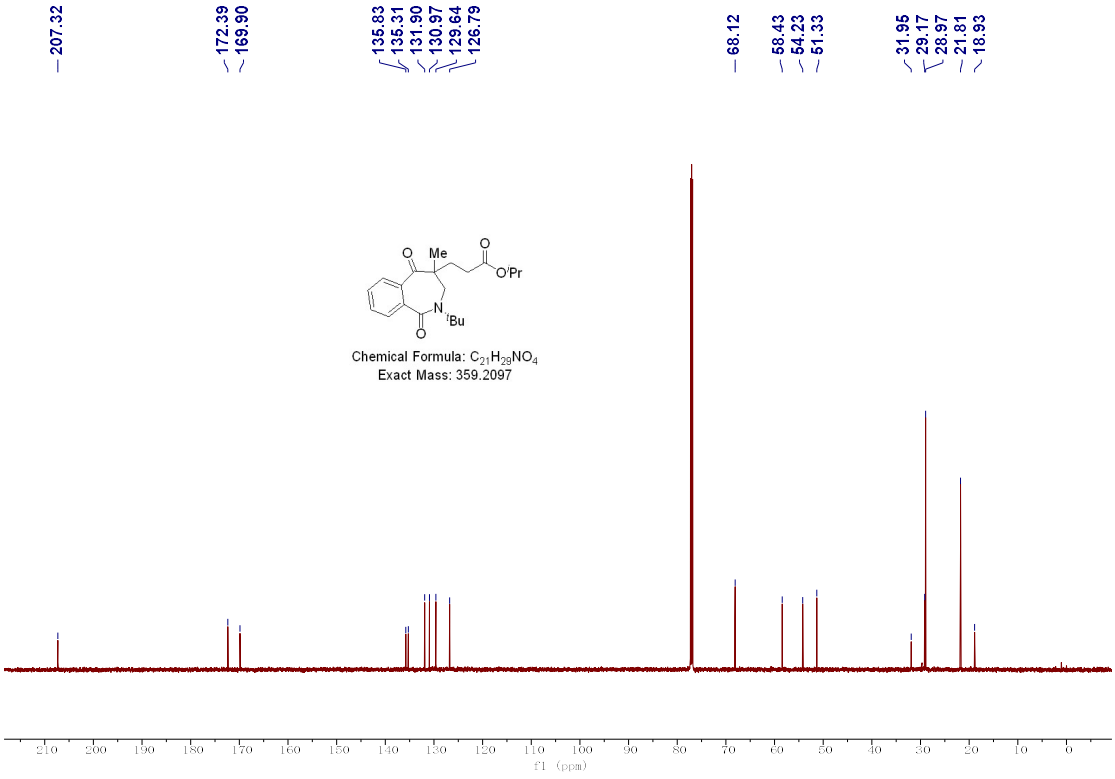

7.69 7.69 7.67 7.67 7.51 7.50 7.49 7.49 7.47 7.47 7.42 7.41 7.40 7.40 7.38 7.38 7.36 7.35 7.34 7.33 7.21 7.20 7.19 7.19 7.19 7.18 7.17 7.17 7.16 7.16 7.16 7.14 7.07 7.07 7.06 7.05 7.05 7.05 3.81 3.77 3.68 3.37 3.33 3.17 3.13 2.92 2.91 2.90 2.79 2.75 2.64 2.62 2.60 2.24 2.10 0.92 0.83
OMe
Chemical Formula: C24H25NO4
Exact Mass: 391.1784
1.01 1.17 1.23 0.88 2.83 2.13 1.01 3.24 1.11 1.07 1.07 1.09 1.64 2.11 2.06 2.41
f1 (ppm)
206.75 173.43 169.64 136.28 135.32 133.74 132.36 131.09 130.39 129.34 128.50 128.18 127.14 57.96 53.02 52.03 42.24 32.40 29.85 29.16 10.31 7.49
OMe
Chemical Formula: C24H25NO4
Exact Mass: 391.1784
f1 (ppm)

6na

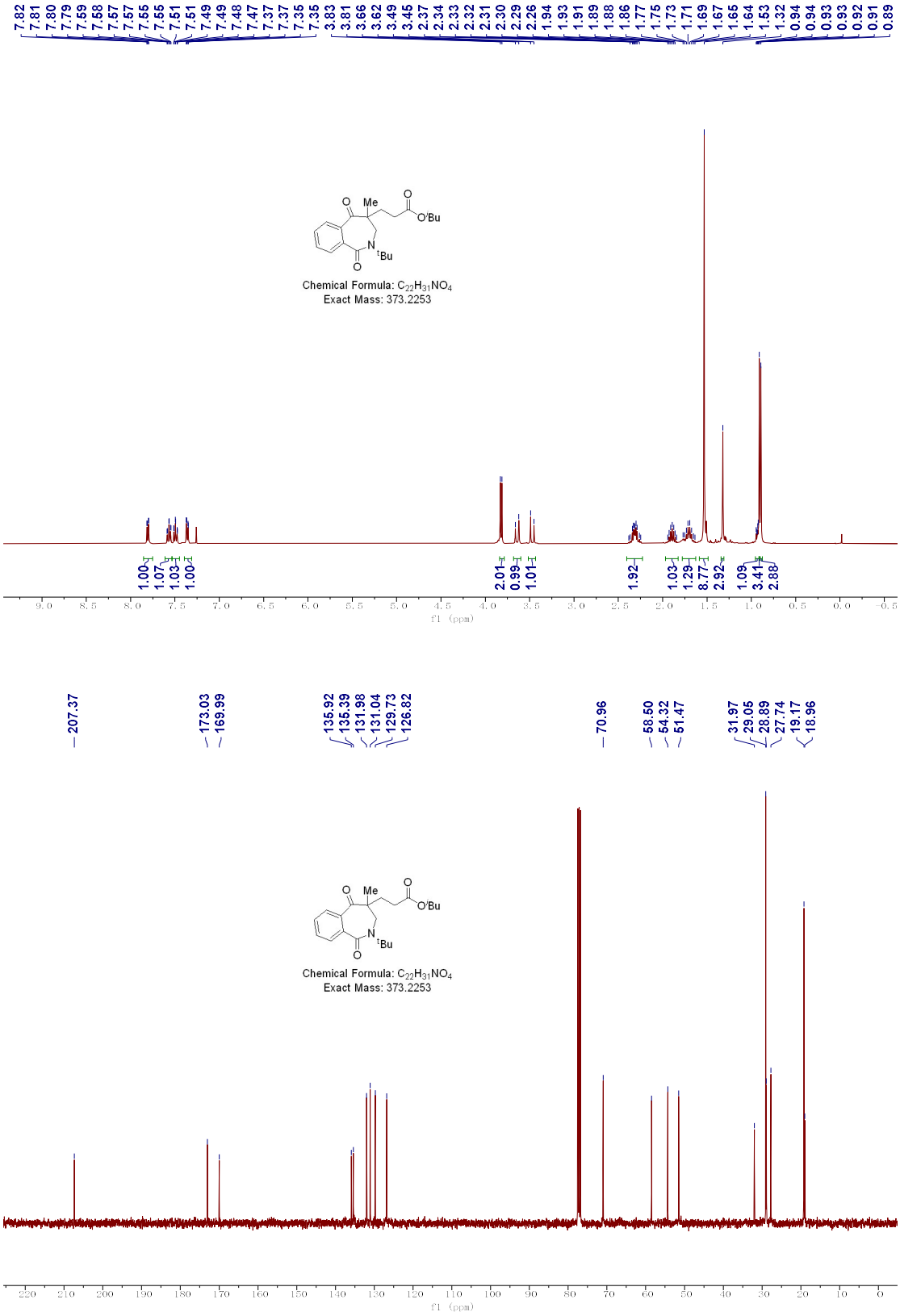

8.35
8.34
7.43
7.43
7.42
7.42
7.42
7.42
7.41
7.41
7.40
7.39
7.35
7.34
7.33
7.33
7.33
7.32
7.32
4.06
3.63
3.30
2.38
2.37
2.35
2.17
2.16
1.97
1.93
1.27
Me
Me
Me
Me
Me
Chemical Formula: C19H22N2O4
Exact Mass: 342.1580
1.09
1.89
0.90
3.00
2.77
3.19
2.31
2.10
3.39
f1 (ppm)
199.68
173.70
161.66
138.55
133.48
125.71
125.48
123.74
123.55
115.81
110.29
57.04
51.90
51.80
37.78
32.78
29.81
29.20
21.55
Chemical Formula: C19H22N2O4
Exact Mass: 342.1580
f1 (ppm)

6db

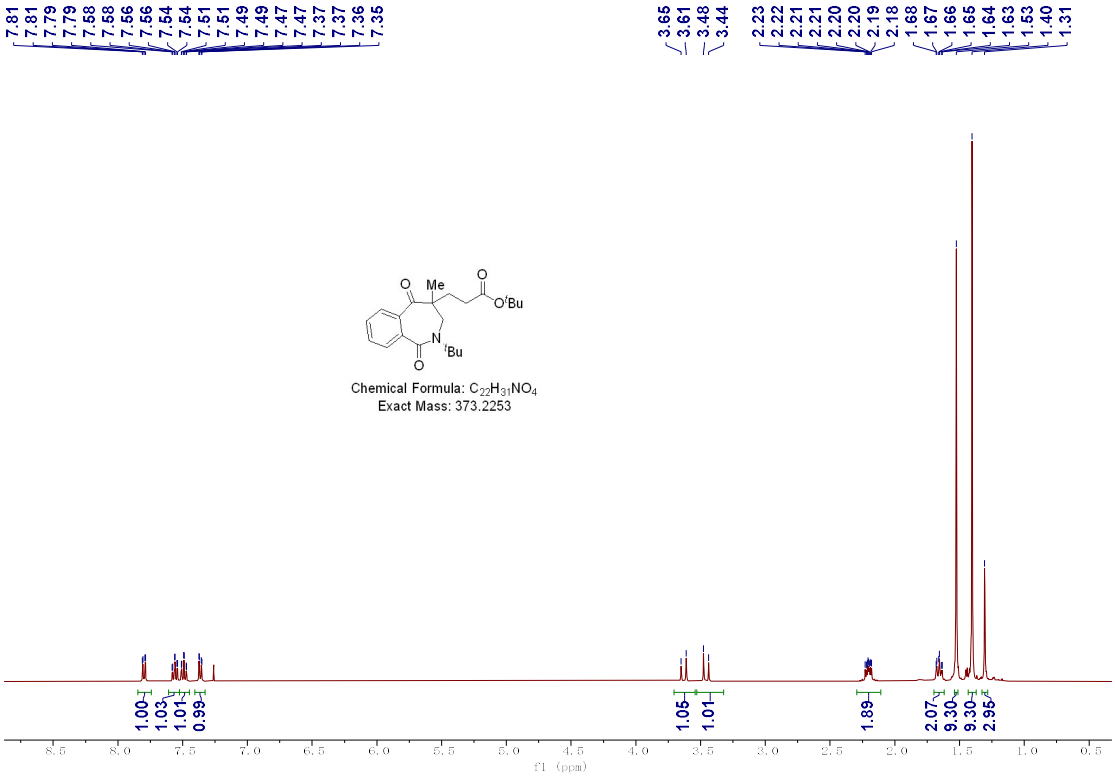

7.82
7.82
7.81
7.80
7.60
7.59
7.58
7.57
7.56
7.55
7.52
7.52
7.50
7.50
7.49
7.48
7.39
7.38
7.37
7.37
5.00
4.98
4.97
4.95
4.93
3.67
3.63
3.49
3.45
2.29
2.28
2.28
2.27
2.26
2.26
2.25
2.24
1.75
1.74
1.73
1.71
1.71
1.69
1.69
1.54
1.32
1.22
1.20
Me
O
O
O
iPr
N
tBu
O
Chemical Formula: C21H28NO4
Exact Mass: 359.2097
1.00
0.80
0.99
1.01
0.97
1.05
1.02
1.80
1.77
9.15
3.08
6.19
f1 (ppm)

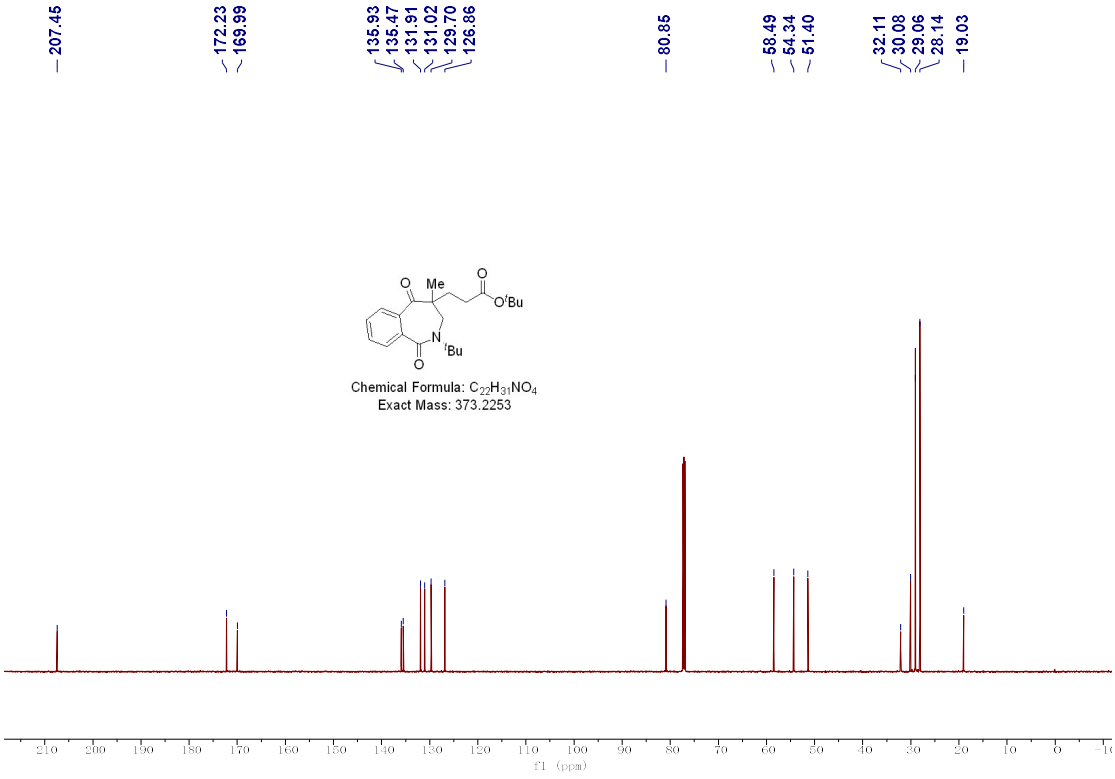

207.32
172.39
169.90
135.83
135.31
131.90
130.97
129.64
126.79
68.12
58.43
54.23
51.33
31.95
29.17
28.97
21.81
18.93
Me
O
O
O
iPr
N
tBu
O
Chemical Formula: C21H28NO4
Exact Mass: 359.2097
f1 (ppm)

6dc

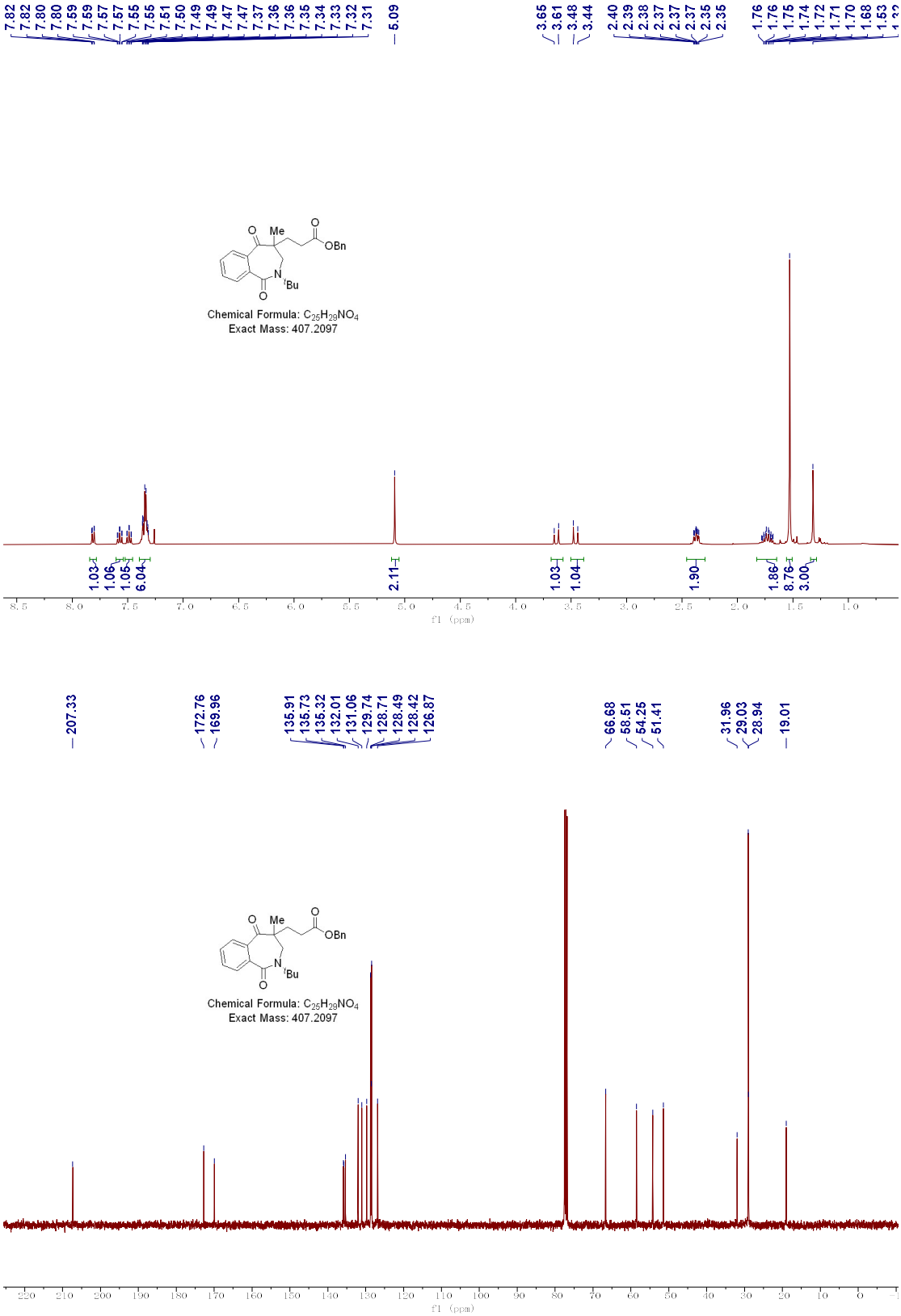

7.82 7.81 7.80 7.79 7.59 7.58 7.57 7.57 7.56 7.55 7.51 7.51 7.49 7.49 7.48 7.47 7.37 7.37 7.35 7.35 3.83 3.81 3.66 3.62 3.49 3.45 2.37 2.34 2.33 2.32 2.31 2.30 2.29 2.26 1.94 1.93 1.91 1.89 1.88 1.86 1.77 1.75 1.73 1.71 1.69 1.67 1.65 1.64 1.53 1.32 0.94 0.94 0.93 0.93 0.92 0.91 0.89
Me
O'Bu
tBu
Chemical Formula: C22H31NO4
Exact Mass: 373.2253
1.00 1.07 1.03 1.00 2.01 0.99 1.01 1.92 1.03 1.29 8.77 2.92 1.09 3.41 2.88
f1 (ppm)
207.37 173.03 169.99 135.92 135.39 131.98 131.04 129.73 126.82 70.96 58.50 54.32 51.47 31.97 29.05 28.89 27.74 19.17 18.96
Me
O'Bu
tBu
Chemical Formula: C22H31NO4
Exact Mass: 373.2253
f1 (ppm)

6dd

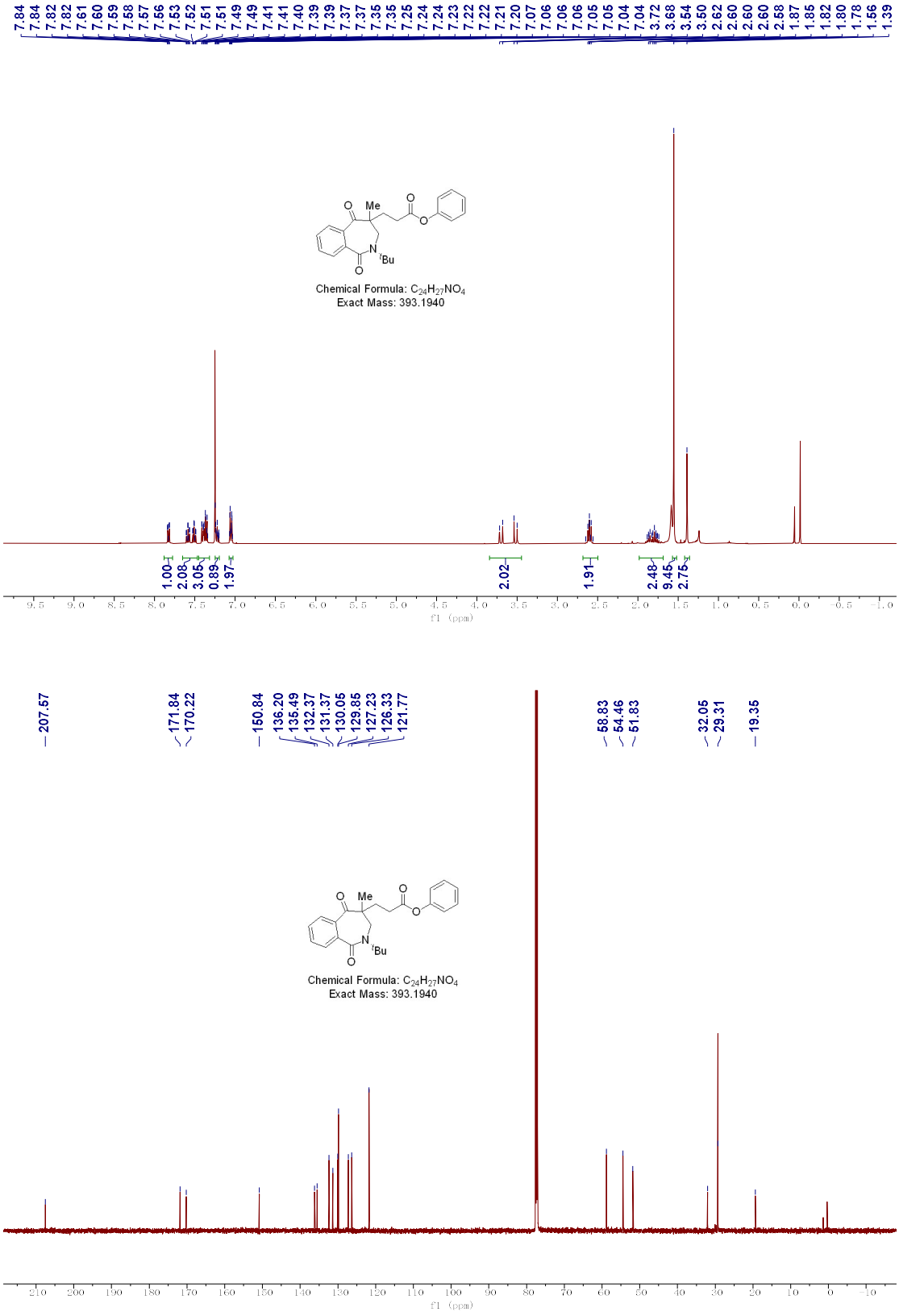

7.81 7.81 7.79 7.79 7.58 7.58 7.56 7.56 7.54 7.54 7.51 7.51 7.49 7.49 7.47 7.47 7.37 7.37 7.36 7.35
3.65 3.61 3.48 3.44
2.23 2.22 2.21 2.21 2.20 2.20 2.19 2.18 1.68 1.67 1.66 1.65 1.64 1.63 1.53 1.40 1.31
Me
O
O
O
O
O
N
tBu
tBu
Chemical Formula: C22H31NO4
Exact Mass: 373.2253
1.00 1.03 1.01 0.99 1.05 1.01 1.89 2.07 9.30 9.30 2.95
f1 (ppm)


207.45
172.23 169.99
135.93 135.47 131.91 131.02 129.70 126.86
80.85
58.49 54.34 51.40
32.11 30.08 29.06 28.14 19.03
Me
O
O
O
O
O
N
tBu
tBu
Chemical Formula: C22H31NO4
Exact Mass: 373.2253
f1 (ppm)

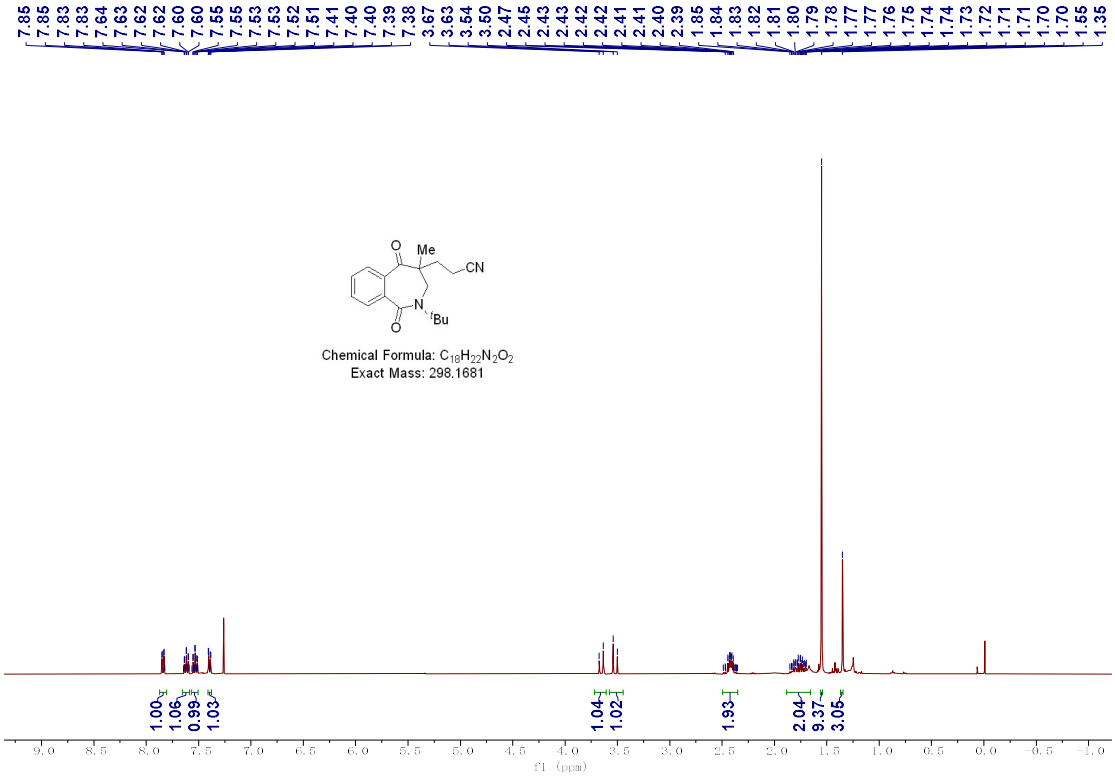
6de

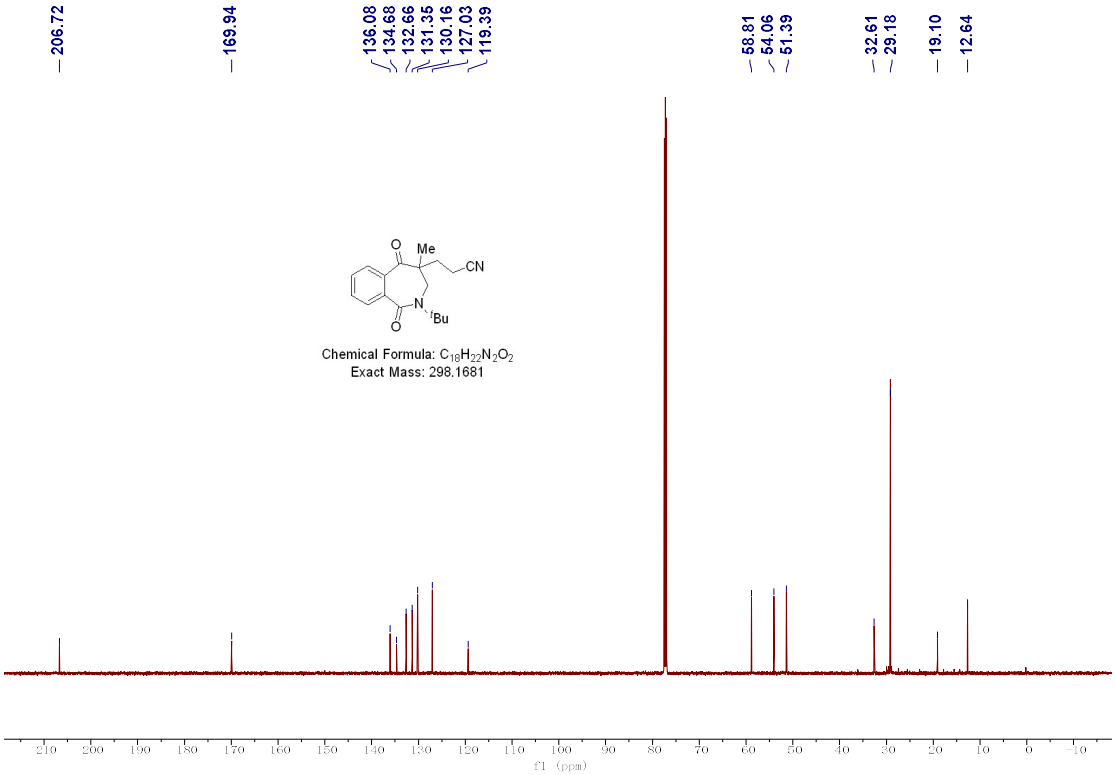

7.82
7.82
7.80
7.80
7.59
7.59
7.57
7.57
7.55
7.55
7.51
7.50
7.49
7.49
7.47
7.47
7.37
7.36
7.36
7.35
7.34
7.33
7.32
7.31
5.09
3.65
3.61
3.48
3.44
2.40
2.39
2.38
2.37
2.37
2.37
2.35
2.35
1.76
1.76
1.75
1.74
1.72
1.71
1.70
1.68
1.53
Me
O
OBn
N
tBu
Chemical Formula: C25H29NO4
Exact Mass: 407.2097
1.03
1.06
1.05
6.04
2.11
1.03
1.04
1.90
1.86
8.76
3.00
f1 (ppm)
207.33
172.76
169.96
135.91
135.73
135.32
132.01
131.06
129.74
128.71
128.49
128.42
126.87
66.68
58.51
54.25
51.41
31.96
29.03
28.94
19.01
Chemical Formula: C25H29NO4
Exact Mass: 407.2097
f1 (ppm)

6df

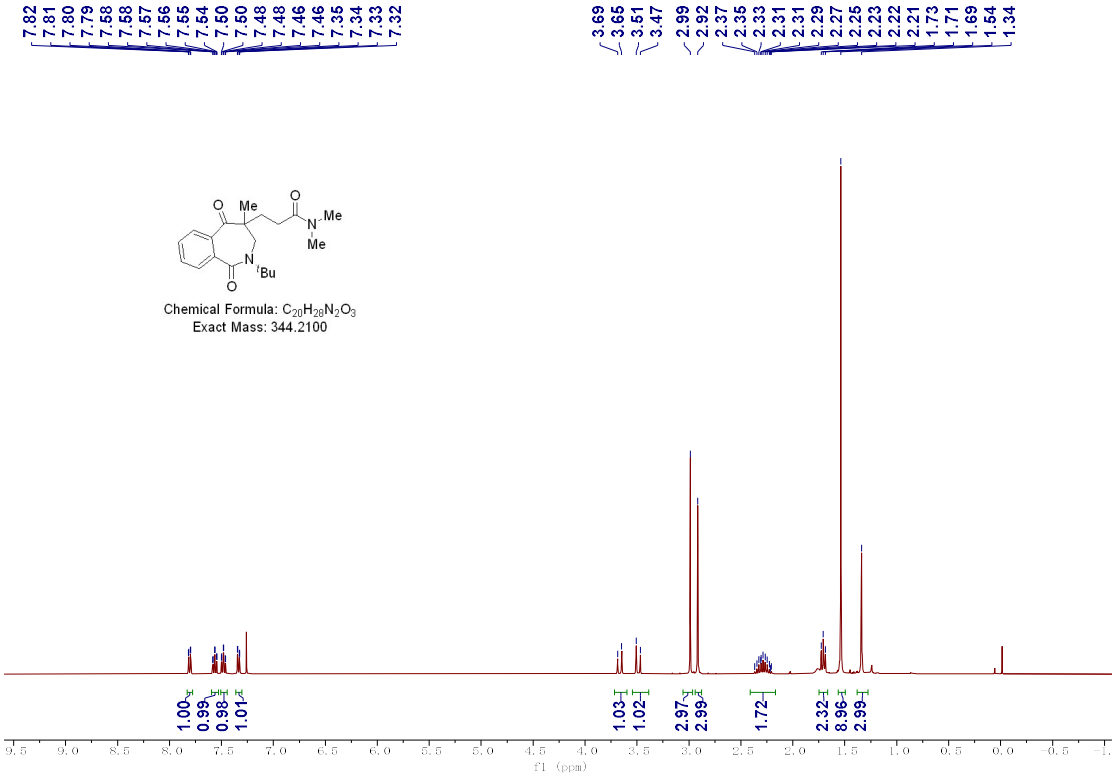

7.84 7.84 7.82 7.82 7.61 7.60 7.59 7.58 7.57 7.56 7.53 7.52 7.51 7.51 7.49 7.49 7.41 7.41 7.40 7.39 7.39 7.37 7.37 7.35 7.35 7.25 7.24 7.24 7.23 7.22 7.22 7.21 7.20 7.07 7.06 7.06 7.06 7.05 7.05 7.04 7.04 3.72 3.68 3.54 3.50 2.62 2.60 2.60 2.60 2.58 1.87 1.85 1.82 1.80 1.78 1.56 1.39
Me
tBu
Chemical Formula: C24H27NO4
Exact Mass: 393.1940
1.00 2.08 3.05 0.89 1.97 2.02 1.91 2.48 9.45 2.75
f1 (ppm)
207.57 171.84 170.22 150.84 136.20 135.49 132.37 131.37 130.05 129.85 127.23 126.33 121.77 58.83 54.46 51.83 32.05 29.31 19.35
Me
tBu
Chemical Formula: C24H27NO4
Exact Mass: 393.1940
f1 (ppm)

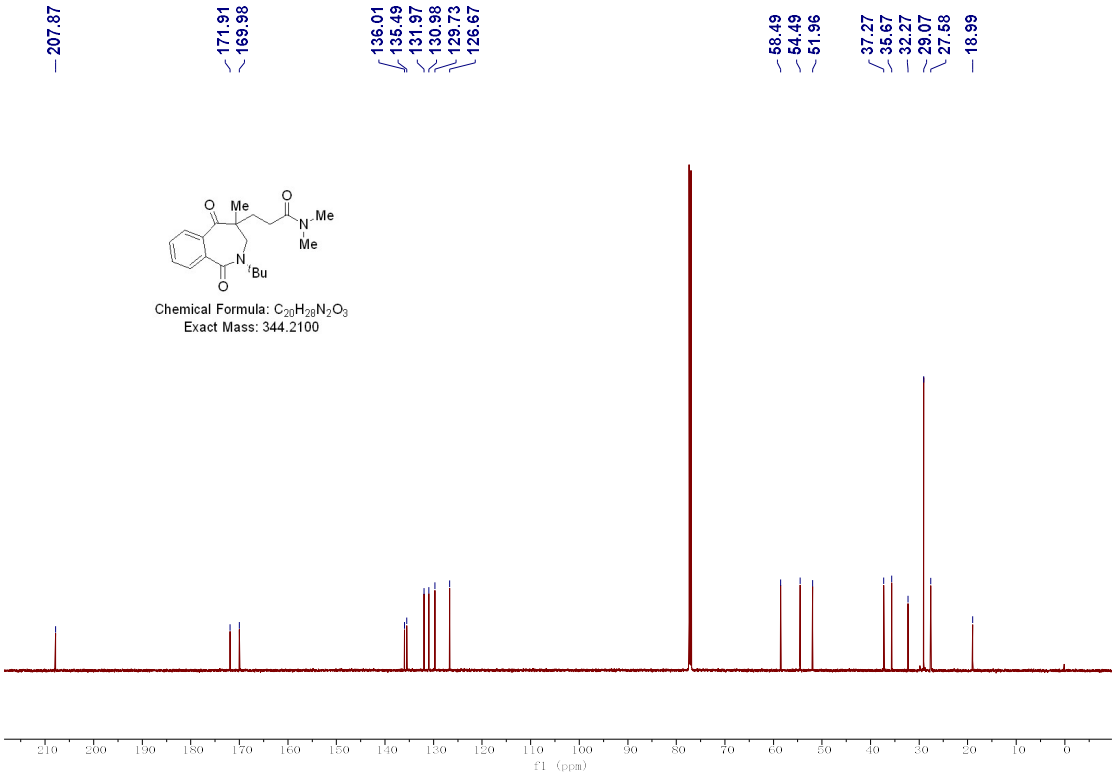
6dg


7.85 7.85 7.83 7.83 7.64 7.63 7.62 7.62 7.60 7.60 7.55 7.55 7.53 7.53 7.52 7.51 7.41 7.40 7.40 7.39 7.38
3.67 3.63 3.54 3.50 2.47 2.45 2.43 2.43 2.42 2.42 2.41 2.41 2.40 2.39 1.85 1.84 1.83 1.82 1.81 1.80 1.79 1.78 1.77 1.77 1.76 1.75 1.74 1.74 1.73 1.72 1.71 1.71 1.70 1.70 1.55 1.35
O
Me
CN
N
tBu
O
Chemical Formula: C18H22N2O2
Exact Mass: 298.1681
1.00 1.06 0.99 1.03 1.04 1.02 1.93 2.04 9.37 3.05
f1 (ppm)

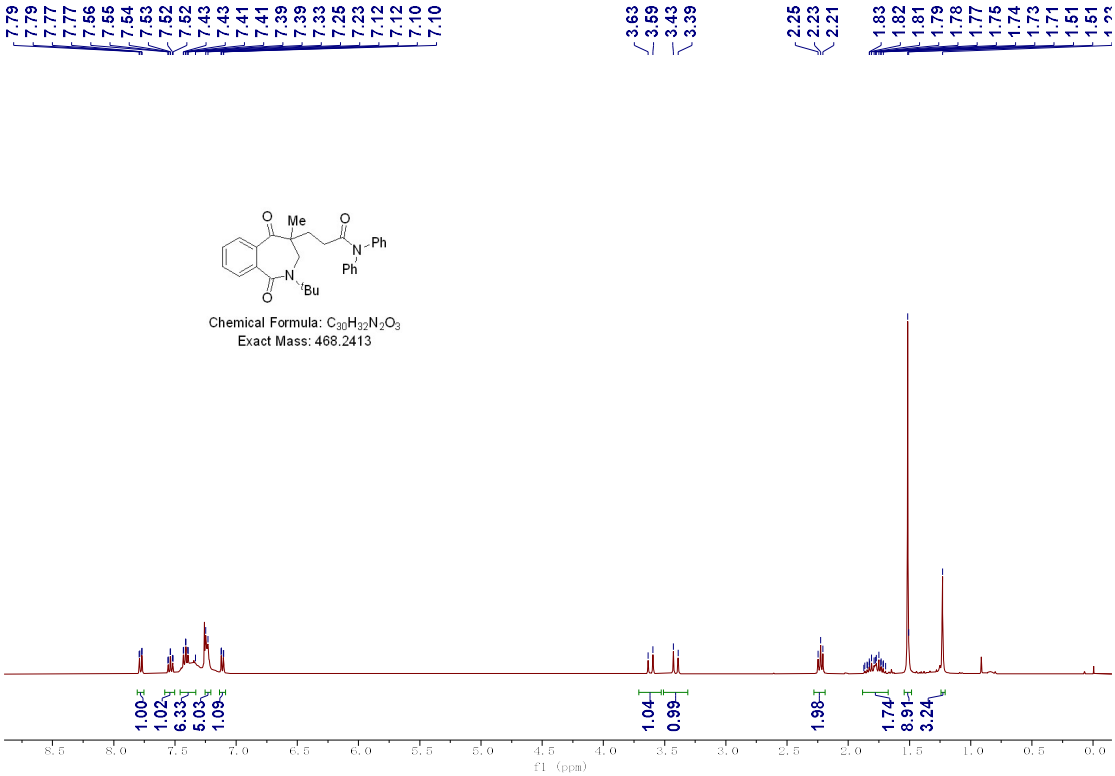

206.72
169.94
136.08 134.68 132.66 131.35 130.16 127.03 119.39
58.81 54.06 51.39
32.61 29.18
19.10
12.64
O
Me
CN
N
tBu
O
Chemical Formula: C18H22N2O2
Exact Mass: 298.1681
f1 (ppm)

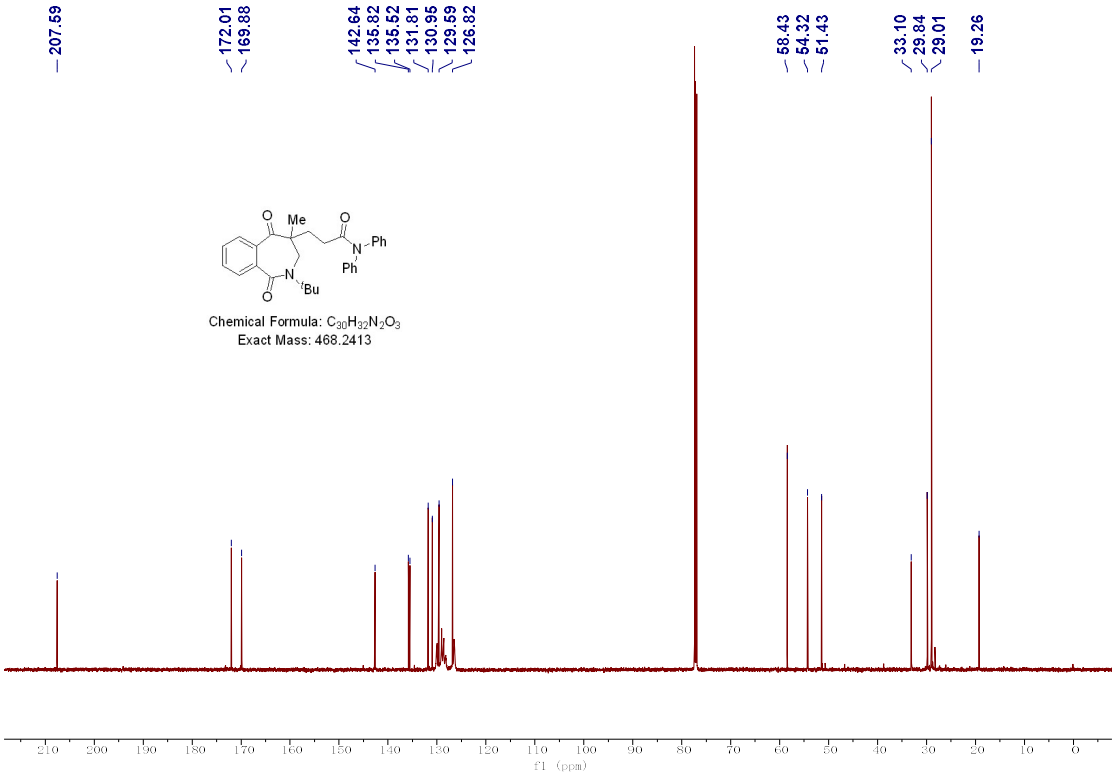
6dh


7.82
7.81
7.80
7.79
7.58
7.58
7.57
7.56
7.55
7.54
7.50
7.50
7.48
7.48
7.46
7.46
7.35
7.34
7.33
7.32
3.69
3.65
3.51
3.47
2.99
2.92
2.37
2.35
2.33
2.31
2.31
2.29
2.27
2.25
2.23
2.22
2.21
1.73
1.71
1.69
1.54
1.34
Me
O
N
Me
Me
O
N
tBu
O
Chemical Formula: C20H28N2O3
Exact Mass: 344.2100
1.00
0.99
0.98
1.01
1.03
1.02
2.97
2.99
1.72
2.32
8.96
2.99
f1 (ppm)

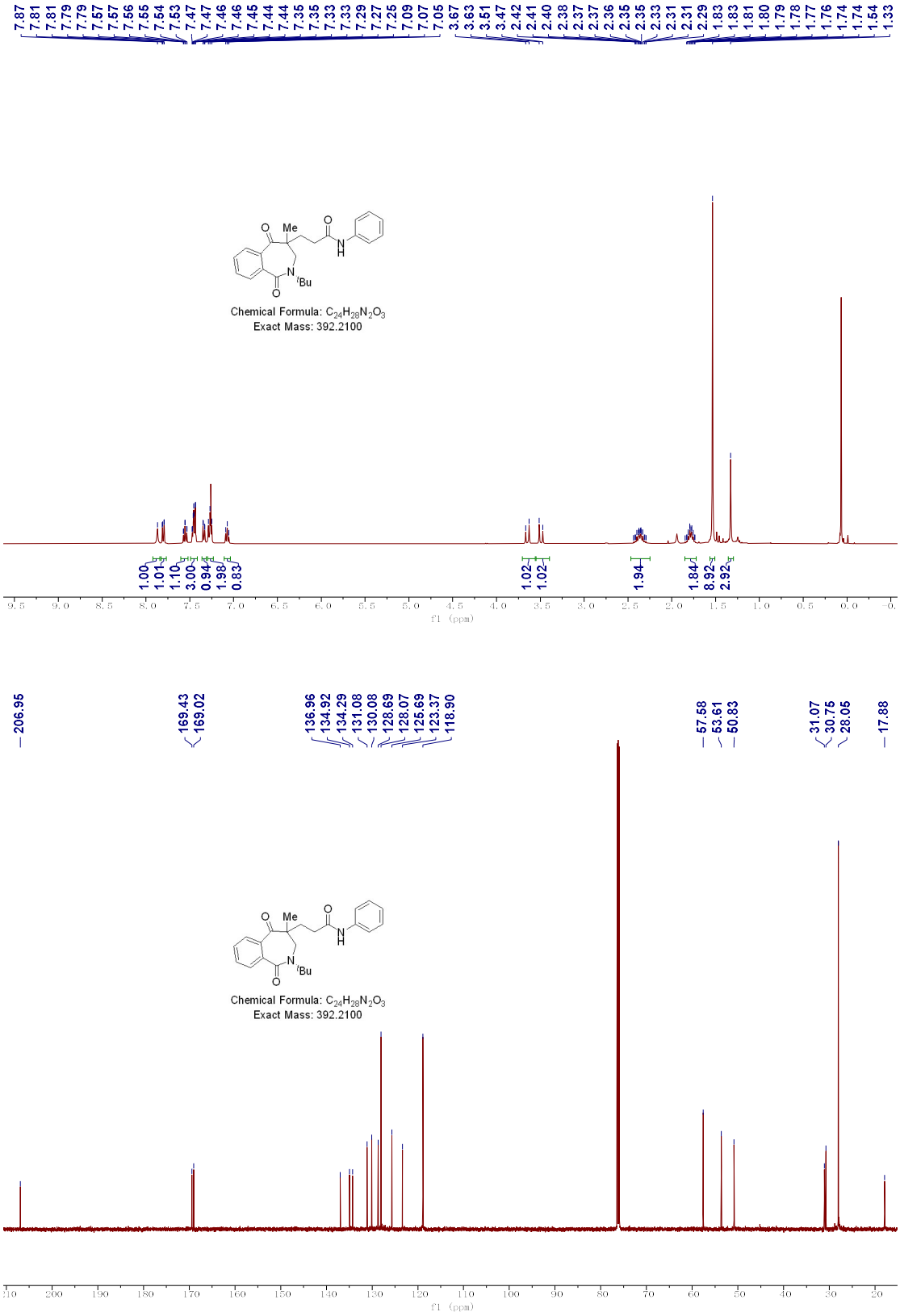

207.87
171.91
169.98
136.01
135.49
131.97
130.98
129.73
126.67
58.49
54.49
51.96
37.27
35.67
32.27
29.07
27.58
18.99
Me
O
N
Me
Me
O
N
tBu
O
Chemical Formula: C20H28N2O3
Exact Mass: 344.2100
f1 (ppm)

6di

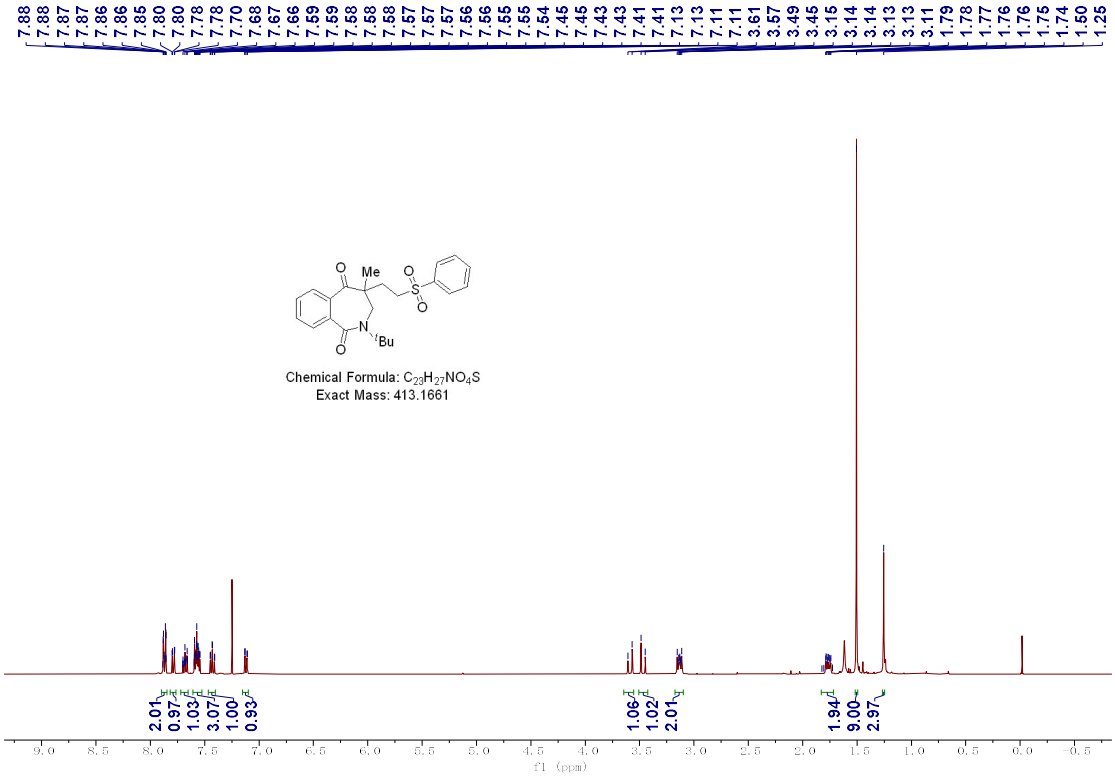

7.79
7.79
7.77
7.77
7.56
7.55
7.54
7.53
7.52
7.52
7.43
7.43
7.41
7.41
7.39
7.39
7.33
7.25
7.23
7.12
7.12
7.10
7.10
3.63
3.59
3.43
3.39
2.25
2.23
2.21
1.83
1.82
1.81
1.79
1.78
1.77
1.75
1.74
1.73
1.71
1.51
1.51
Me
O
O
N
Ph
Ph
N
tBu
O
Chemical Formula: C30H32N2O3
Exact Mass: 468.2413
1.00
1.02
6.33
5.03
1.09
1.04
0.99
1.98
1.74
8.91
3.24
f1 (ppm)

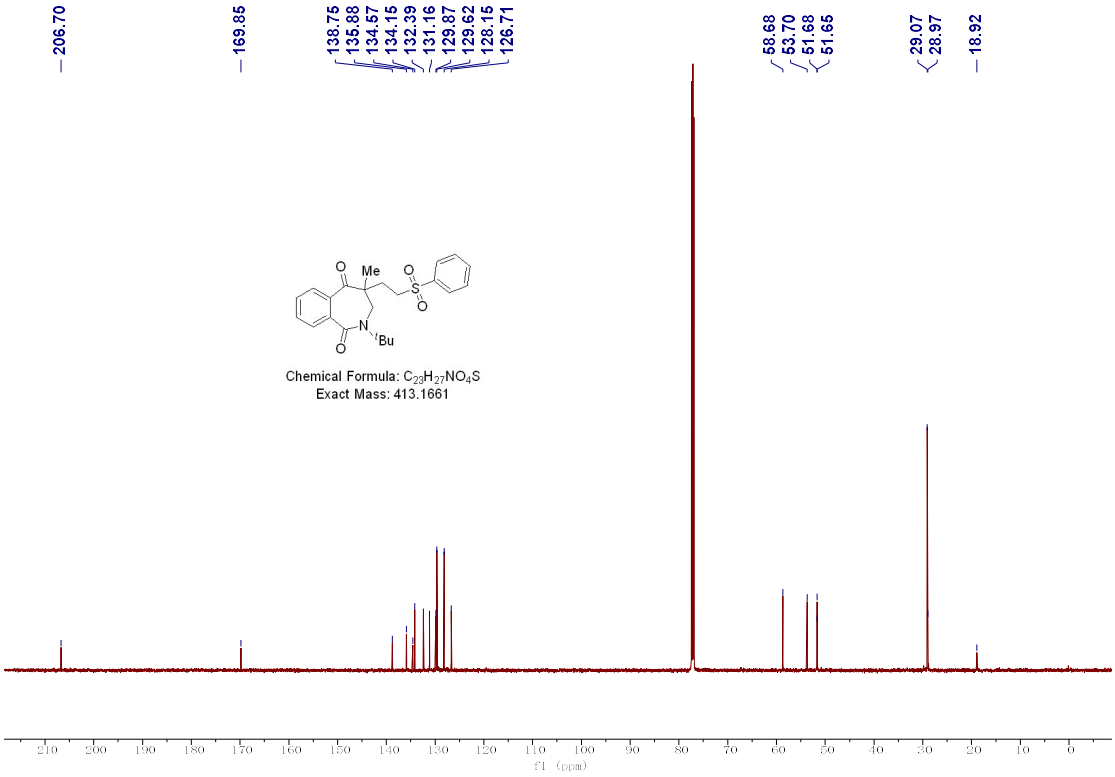

207.59
172.01
169.88
142.64
135.82
135.52
131.81
130.95
129.59
126.82
58.43
54.32
51.43
33.10
29.84
29.01
19.26
Me
O
O
N
Ph
Ph
N
tBu
O
Chemical Formula: C30H32N2O3
Exact Mass: 468.2413
f1 (ppm)

6dj

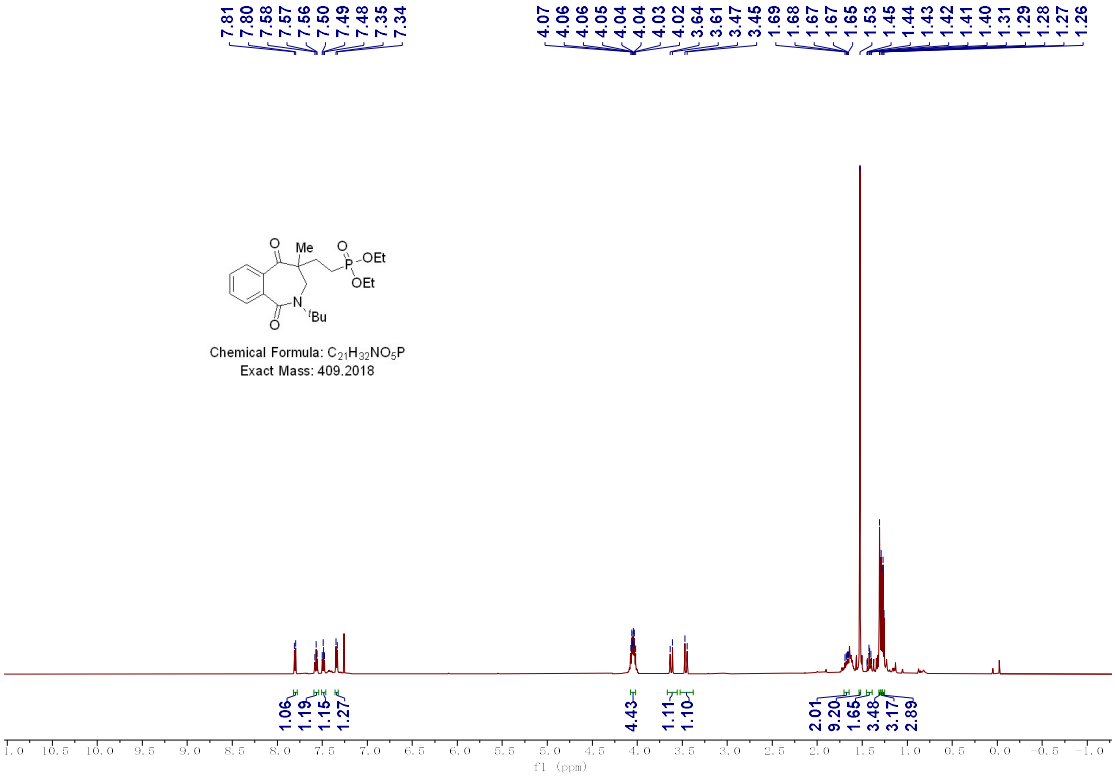

7.87 7.81 7.81 7.79 7.79 7.57 7.57 7.56 7.55 7.54 7.53 7.47 7.47 7.46 7.46 7.45 7.44 7.44 7.35 7.35 7.33 7.33 7.29 7.27 7.25 7.09 7.07 7.05 3.67 3.63 3.51 3.47 2.42 2.41 2.40 2.38 2.37 2.37 2.36 2.35 2.35 2.33 2.31 2.31 2.29 1.83 1.83 1.81 1.80 1.79 1.78 1.77 1.76 1.74 1.74 1.54 1.33
Me
tBu
Chemical Formula: C24H28N2O3
Exact Mass: 392.2100
1.00 1.01 1.10 3.00 0.94 1.98 0.83 1.02 1.02 1.94 1.84 8.92 2.92
f1 (ppm)
206.95 169.43 169.02 136.96 134.92 134.29 131.08 130.08 128.69 128.07 125.69 123.37 118.90 57.58 53.61 50.83 31.07 30.75 28.05 17.88
Me
tBu
Chemical Formula: C24H28N2O3
Exact Mass: 392.2100
f1 (ppm)

6dk


7.88 7.88 7.87 7.87 7.86 7.86 7.85 7.80 7.80 7.78 7.78 7.70 7.68 7.67 7.66 7.59 7.59 7.58 7.58 7.58 7.57 7.57 7.57 7.56 7.56 7.55 7.55 7.54 7.45 7.45 7.43 7.43 7.41 7.41 7.13 7.13 7.11 7.11 3.61 3.57 3.49 3.45 3.15 3.14 3.14 3.13 3.13 3.11 1.79 1.78 1.77 1.76 1.76 1.75 1.74 1.50 1.25
Me
Bu
Chemical Formula: C23H27NO4S
Exact Mass: 413.1661
2.01 0.97 1.03 3.07 1.00 0.93 1.06 1.02 2.01 1.94 9.00 2.97
f1 (ppm)


206.70 169.85 138.75 135.88 134.57 134.15 132.39 131.16 129.87 129.62 128.15 126.71 58.68 53.70 51.68 51.65 29.07 28.97 18.92
Me
Bu
Chemical Formula: C23H27NO4S
Exact Mass: 413.1661
f1 (ppm)

6dl


7.81
7.80
7.58
7.57
7.56
7.50
7.49
7.48
7.35
7.34
4.07
4.06
4.06
4.05
4.04
4.04
4.03
4.02
3.64
3.61
3.47
3.45
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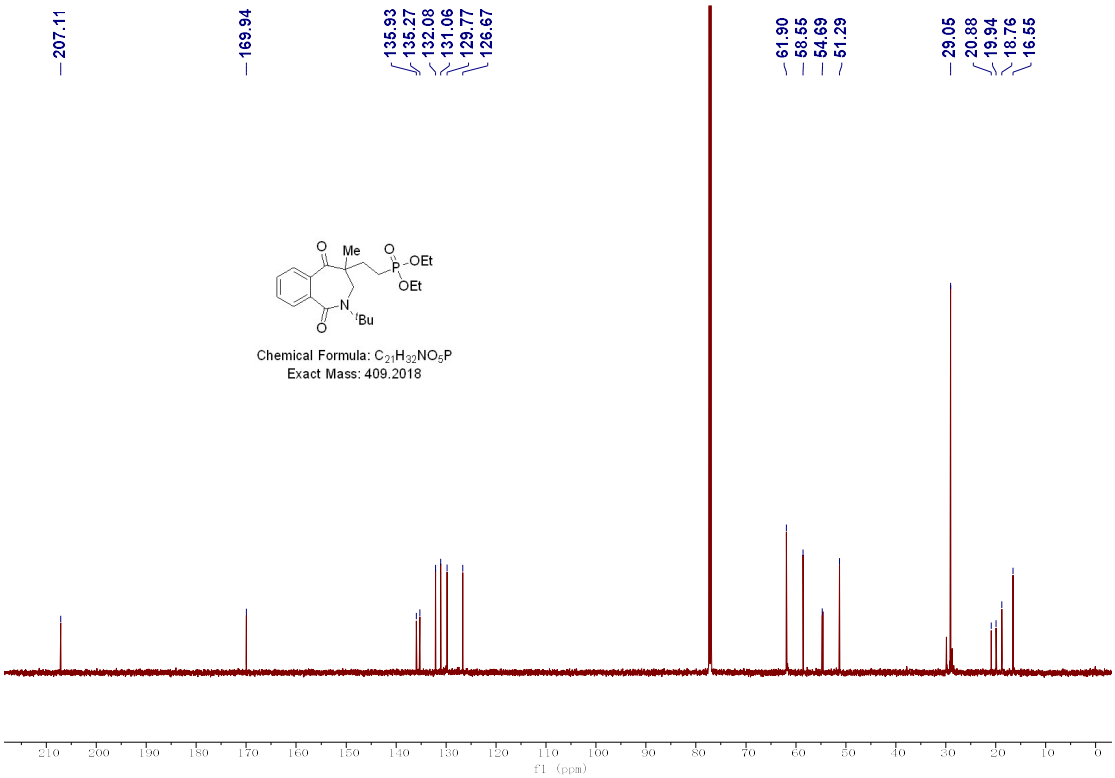
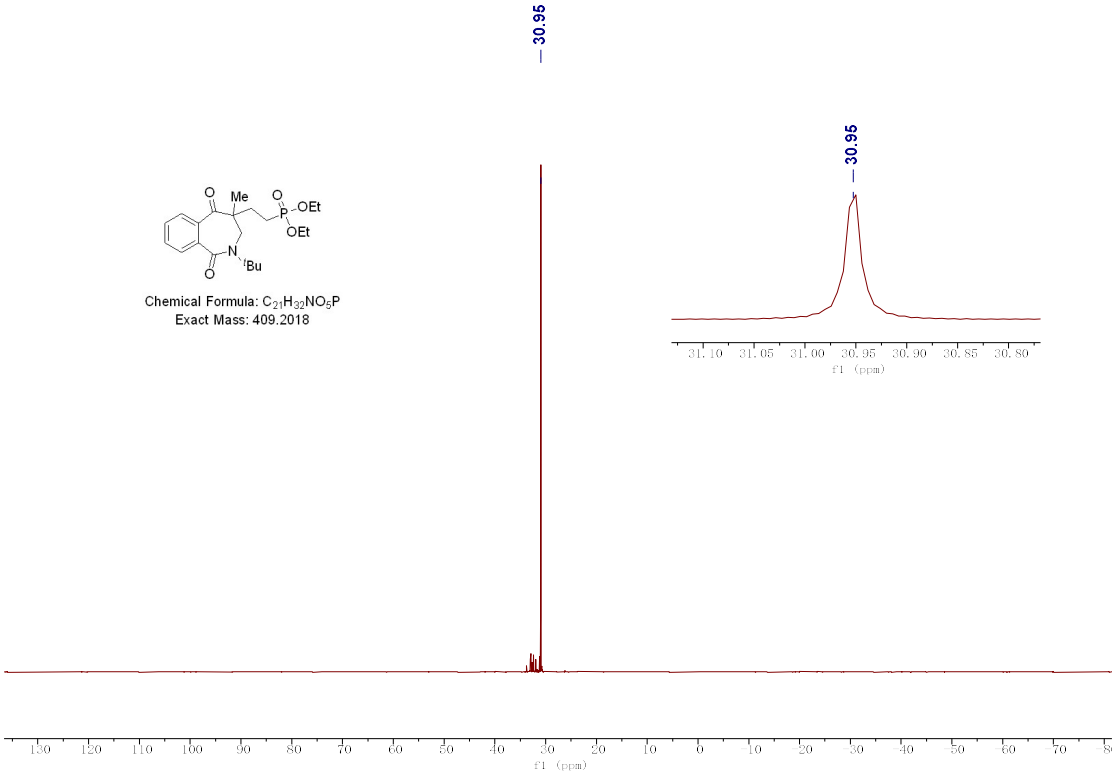
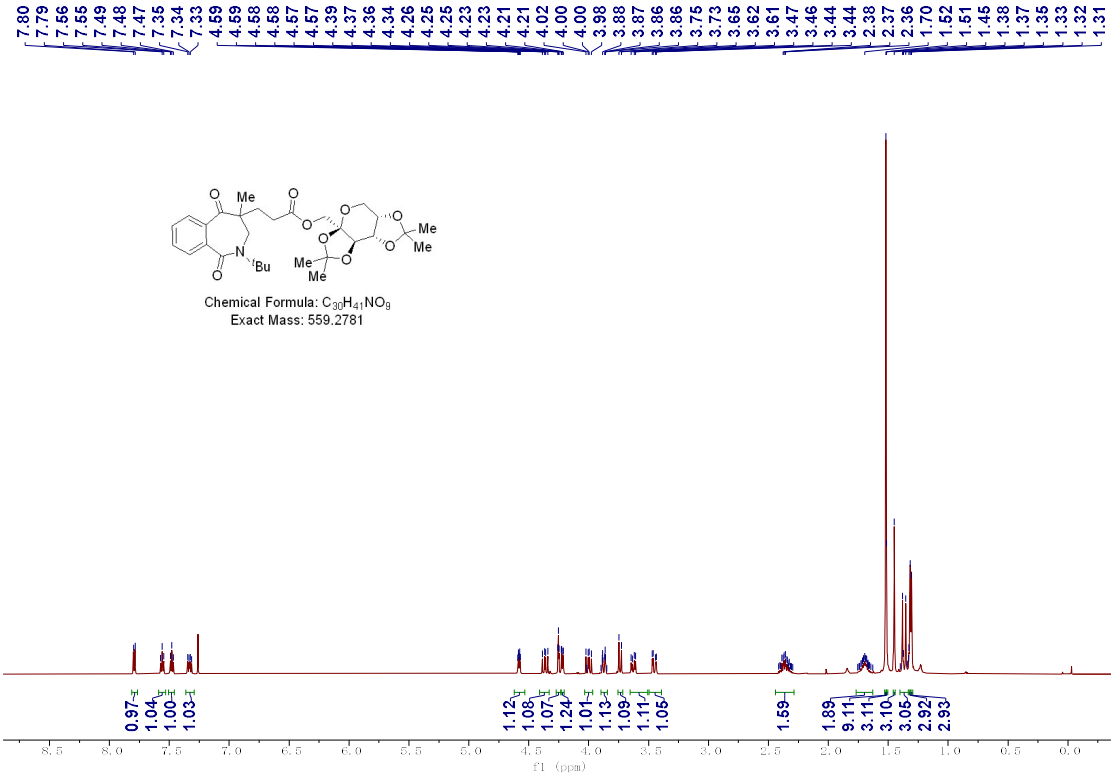
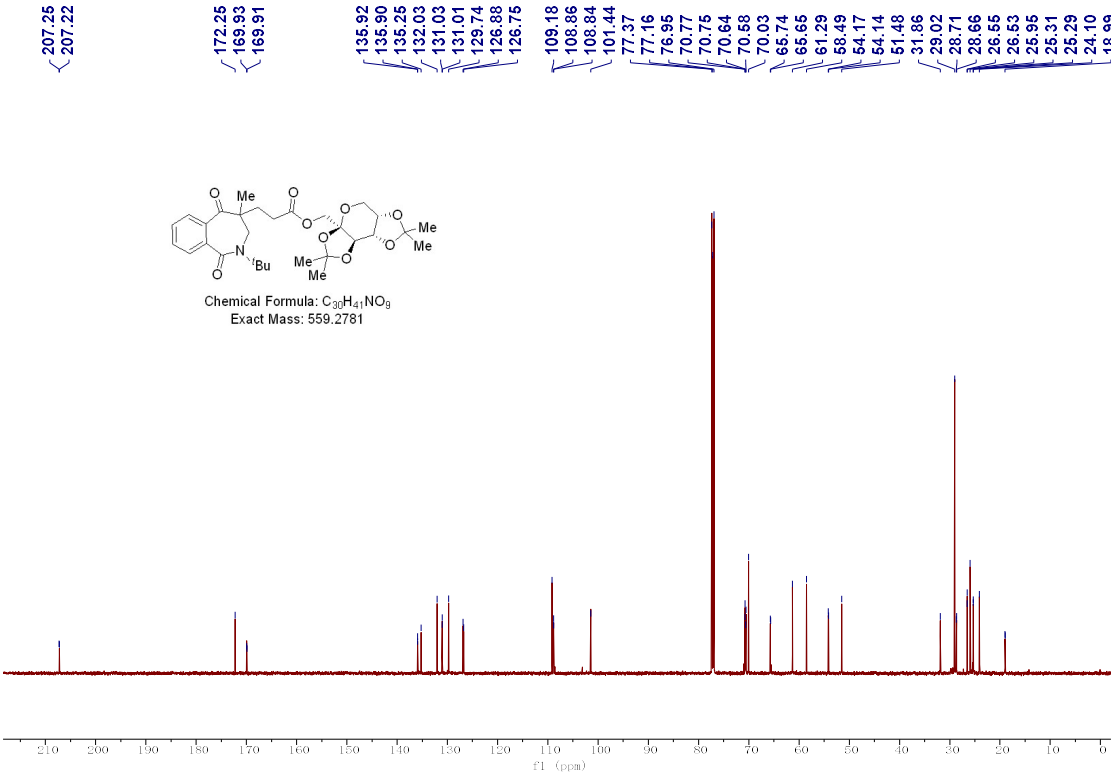
1.67
1.65
1.53
1.45
1.44
1.43
1.42
1.41
1.40
1.31
1.29
1.28
1.27
1.26
Me
OEt
OEt
tBu
Chemical Formula: C21H32NO5P
Exact Mass: 409.2018
1.06
1.19
1.15
1.27
4.43
1.11
1.10
2.01
9.20
1.65
3.48
3.17
2.89
f1 (ppm)


207.11
169.94
135.93
135.27
132.08
131.06
129.77
126.67
61.90
58.55
54.69
51.29
29.05
20.88
19.94
18.76
16.55
Me
OEt
OEt
tBu
Chemical Formula: C21H32NO5P
Exact Mass: 409.2018
f1 (ppm)

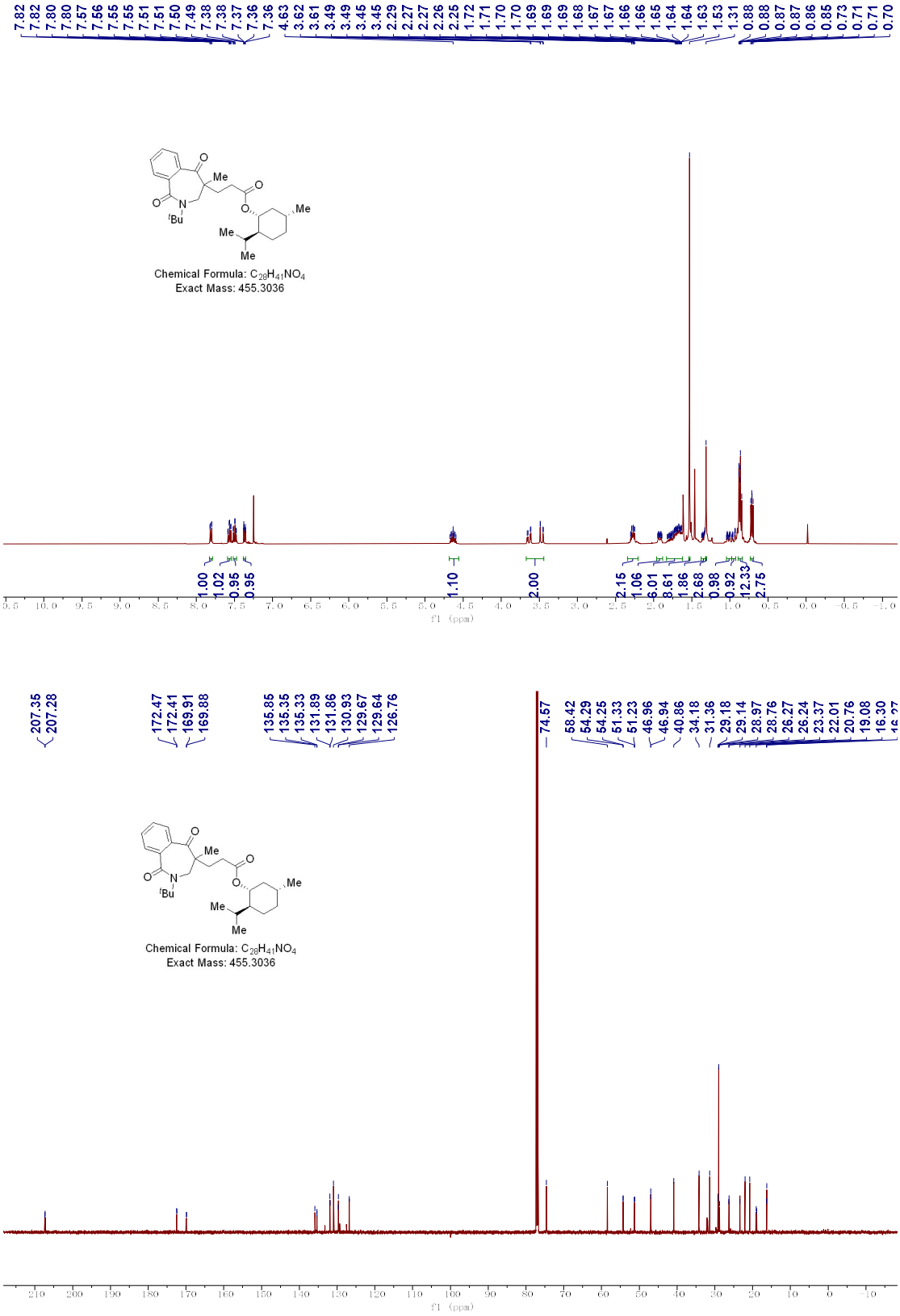

30.95
Me
OEt
OEt
tBu
Chemical Formula: C21H32NO5P
Exact Mass: 409.2018
30.95
31.10 31.05 31.00 30.95 30.90 30.85 30.80
f1 (ppm)
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)

6dm

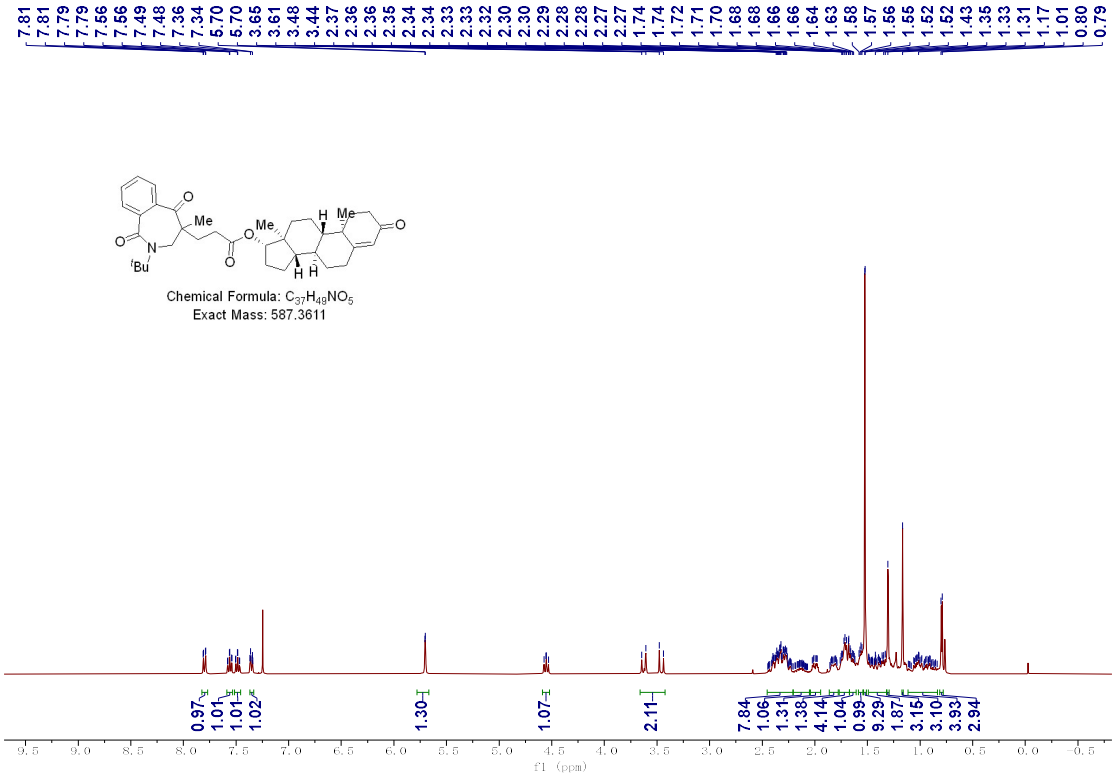

7.80 7.79 7.56 7.55 7.49 7.48 7.47 7.35 7.34 7.33 4.59 4.59 4.58 4.58 4.57 4.57 4.39 4.37 4.36 4.34 4.26 4.25 4.25 4.23 4.23 4.21 4.21 4.02 4.00 4.00 3.98 3.88 3.87 3.86 3.86 3.75 3.73 3.65 3.62 3.61 3.47 3.46 3.44 3.44 2.38 2.37 2.36 1.70 1.52 1.51 1.45 1.38 1.37 1.35 1.33 1.32 1.31
Me
O
O
N
Bu
Me
Me
Me
Me
Chemical Formula: C30H41NO9
Exact Mass: 559.2781
0.97 1.04 1.00 1.03 1.12 1.08 1.07 1.24 1.01 1.13 1.09 1.11 1.05 1.59 1.89 9.11 3.11 3.10 3.05 2.92 2.93
f1 (ppm)

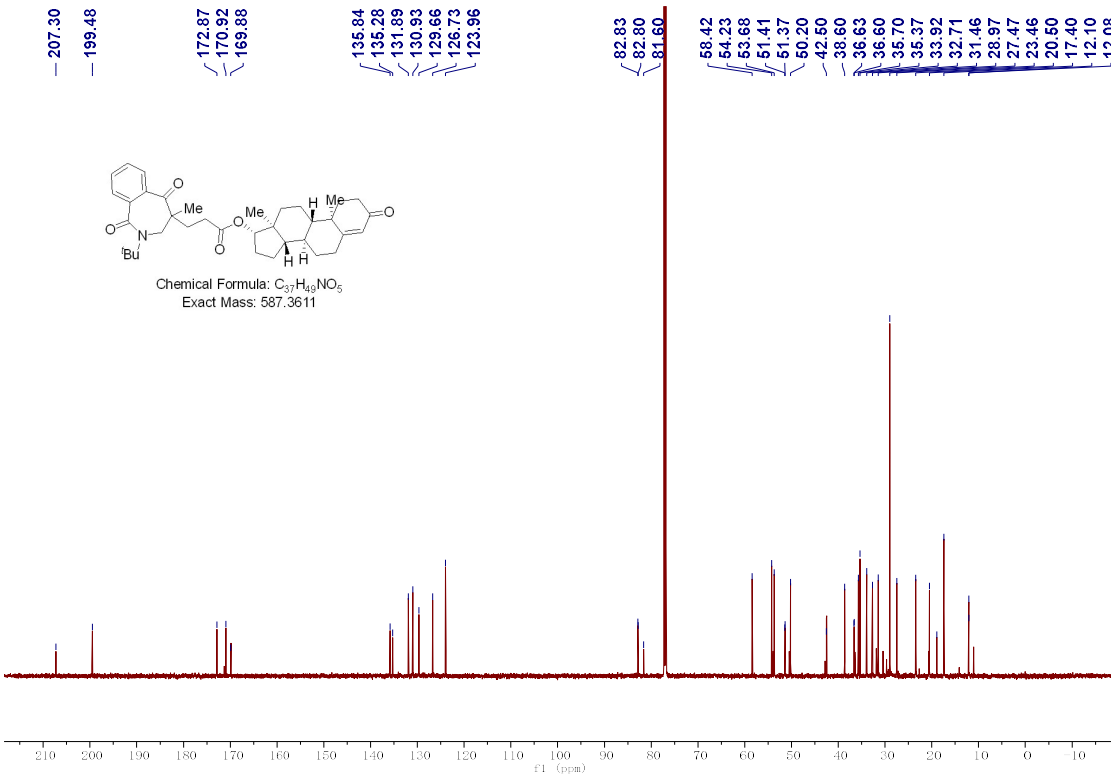

207.25 207.22 172.25 169.93 169.91 135.92 135.90 135.25 132.03 131.03 131.01 129.74 126.88 126.75 109.18 108.86 108.84 101.44 77.37 77.16 76.95 70.77 70.75 70.64 70.58 70.03 65.74 65.65 61.29 58.49 54.17 54.14 51.48 31.86 29.02 28.71 28.66 26.55 26.53 25.95 25.31 25.29 24.10
Me
O
O
N
Bu
Me
Me
Me
Me
Chemical Formula: C30H41NO9
Exact Mass: 559.2781
f1 (ppm)

6dn

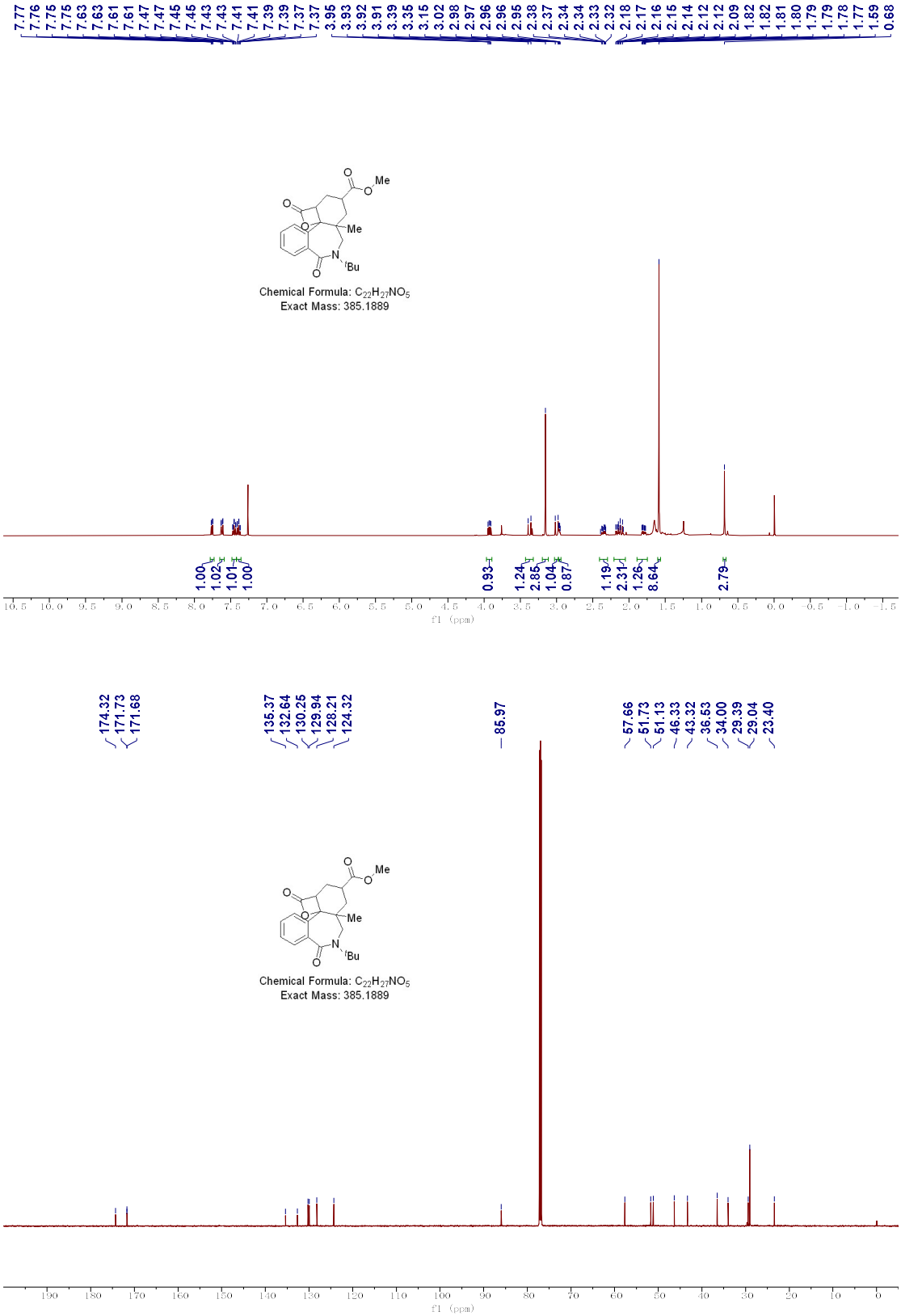

7.82 7.82 7.80 7.80 7.57 7.56 7.55 7.55 7.51 7.51 7.50 7.49 7.38 7.37 7.36 7.36 4.63 3.62 3.61 3.49 3.49 3.45 3.45 2.29 2.27 2.27 2.26 2.25 1.72 1.71 1.70 1.70 1.69 1.69 1.69 1.68 1.67 1.67 1.66 1.66 1.65 1.64 1.64 1.63 1.53 1.31 0.88 0.88 0.87 0.87 0.86 0.85 0.73 0.71 0.71 0.70
Chemical Formula: C28H41NO4
Exact Mass: 455.3036
1.00 1.02 0.95 0.95 1.10 2.00 2.15 1.06 6.01 8.61 1.86 2.68 0.98 0.92 12.33 2.75
f1 (ppm)
207.35 207.28 172.47 172.41 169.91 169.88 135.85 135.35 135.33 131.89 131.86 130.93 129.67 129.64 126.76 74.57 58.42 54.29 54.25 51.33 51.23 46.96 46.94 40.86 34.18 31.36 29.18 29.14 28.97 28.76 26.27 26.24 23.37 22.01 20.76 19.08 16.30
Chemical Formula: C28H41NO4
Exact Mass: 455.3036
f1 (ppm)

6do

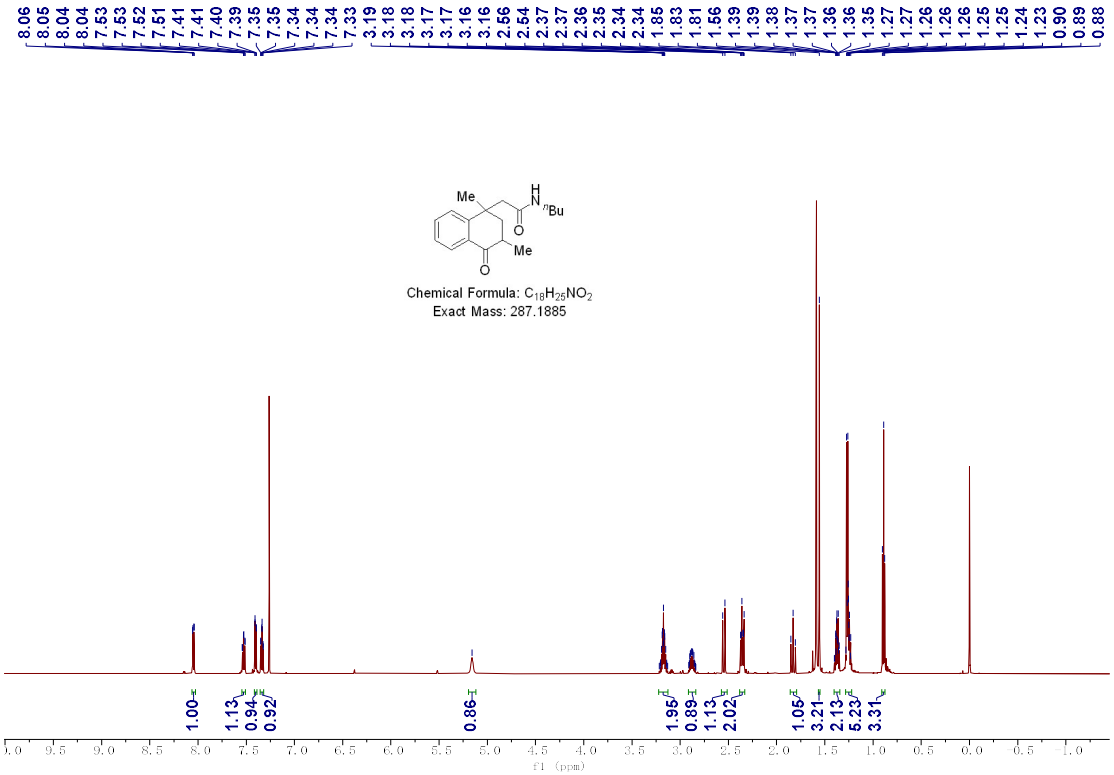

Chemical Formula: C37H49NO5
Exact Mass: 587.3611
0.97
1.01
1.01
1.02
1.30
1.07
2.11
7.84
1.06
1.31
1.38
4.14
1.04
0.99
9.29
1.87
3.15
3.10
3.93
2.94
f1 (ppm)

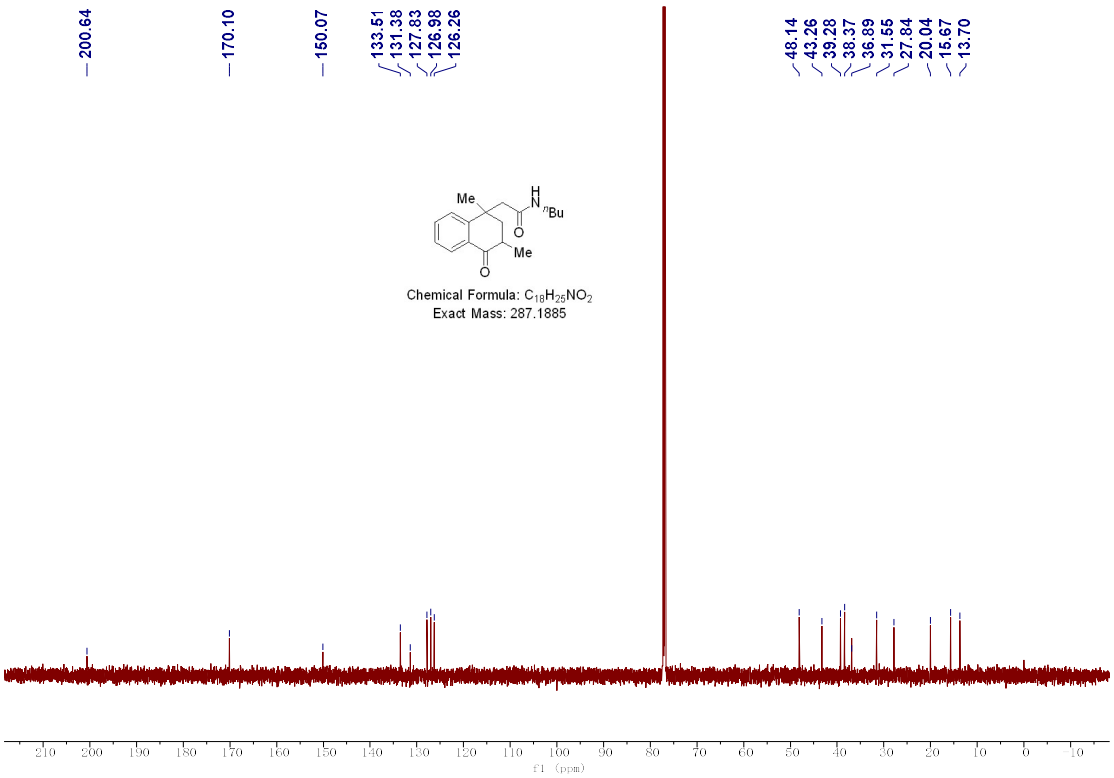

207.30
199.48
172.87
170.92
169.88
135.84
135.28
131.89
130.93
129.66
126.73
123.96
82.83
82.80
81.60
58.42
54.23
53.68
51.41
51.37
50.20
42.50
38.60
36.83
36.60
35.70
35.37
33.92
32.71
31.46
28.97
27.47
23.46
20.50
17.40
12.10
Chemical Formula: C37H49NO5
Exact Mass: 587.3611
f1 (ppm)

7

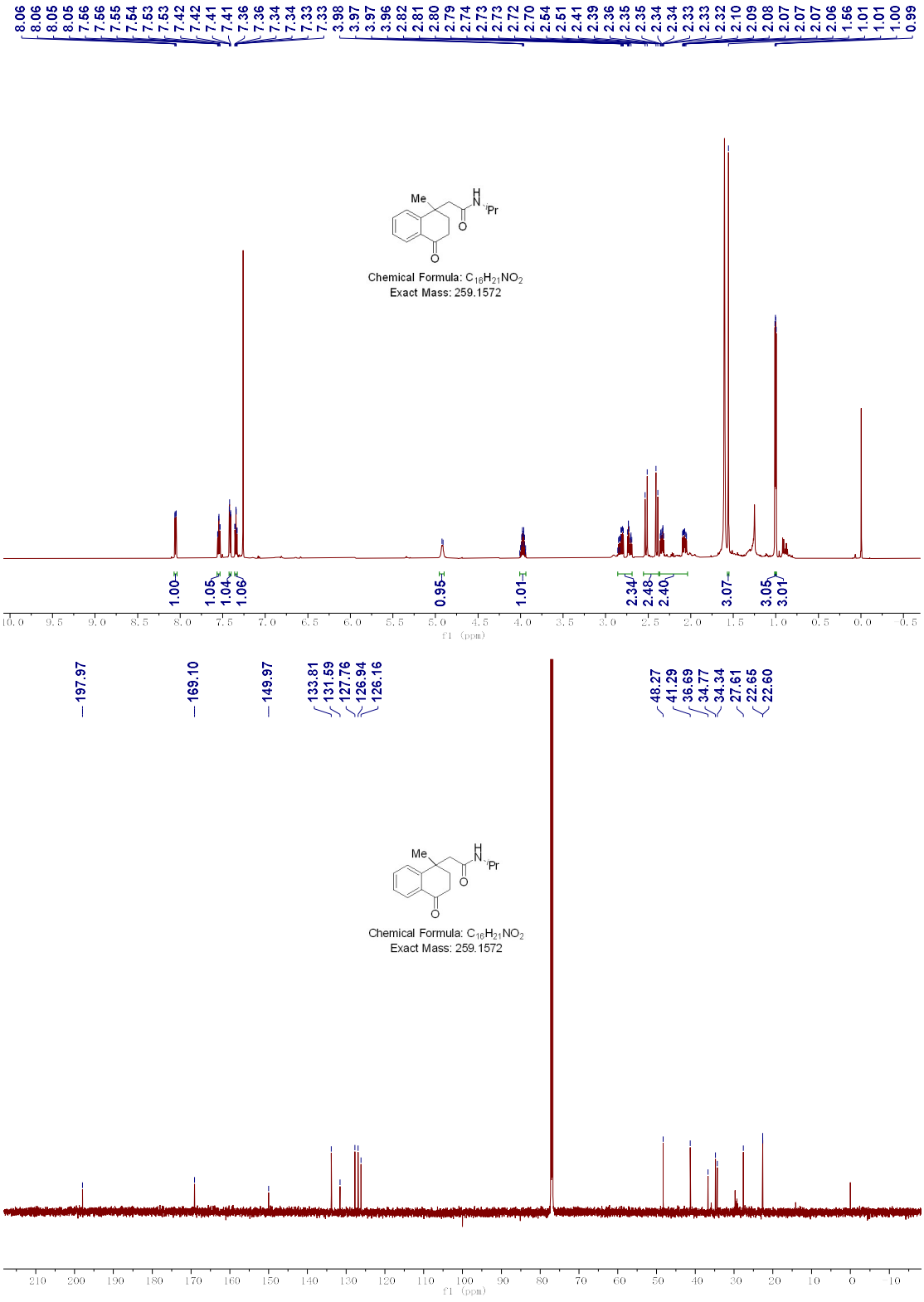

7.77 7.76 7.75 7.75 7.63 7.63 7.61 7.61 7.47 7.47 7.45 7.45 7.43 7.43 7.41 7.41 7.39 7.39 7.37 7.37 3.95 3.93 3.92 3.91 3.39 3.35 3.15 3.02 2.98 2.97 2.96 2.96 2.95 2.38 2.37 2.34 2.34 2.33 2.32 2.18 2.17 2.16 2.15 2.14 2.12 2.12 2.09 1.82 1.82 1.81 1.80 1.79 1.79 1.78 1.77 1.59 0.68
Me
Me
tBu
Chemical Formula: C22H27NO5
Exact Mass: 385.1889
1.00 1.02 1.01 1.00 0.93 1.24 2.85 1.04 0.87 1.19 2.31 1.26 8.64 2.79
f1 (ppm)
174.32 171.73 171.68 135.37 132.64 130.25 129.94 128.21 124.32 85.97 57.66 51.73 51.13 46.33 43.32 36.53 34.00 29.39 29.04 23.40
Me
Me
tBu
Chemical Formula: C22H27NO5
Exact Mass: 385.1889
f1 (ppm)

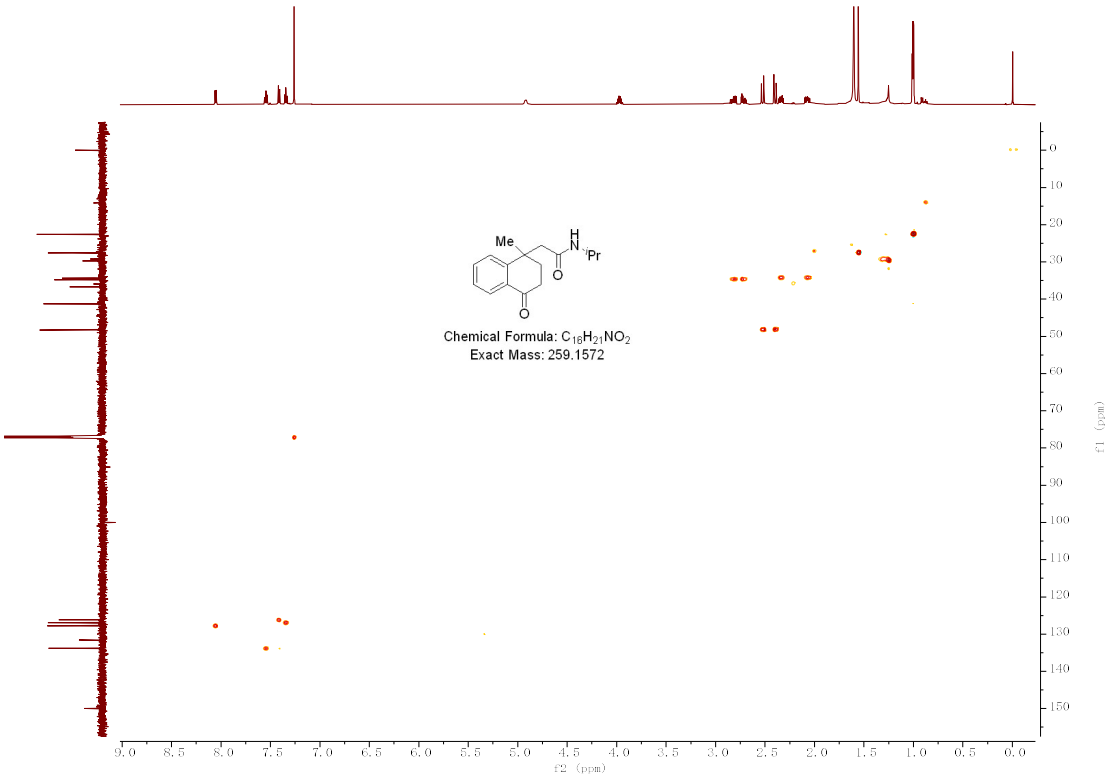
9

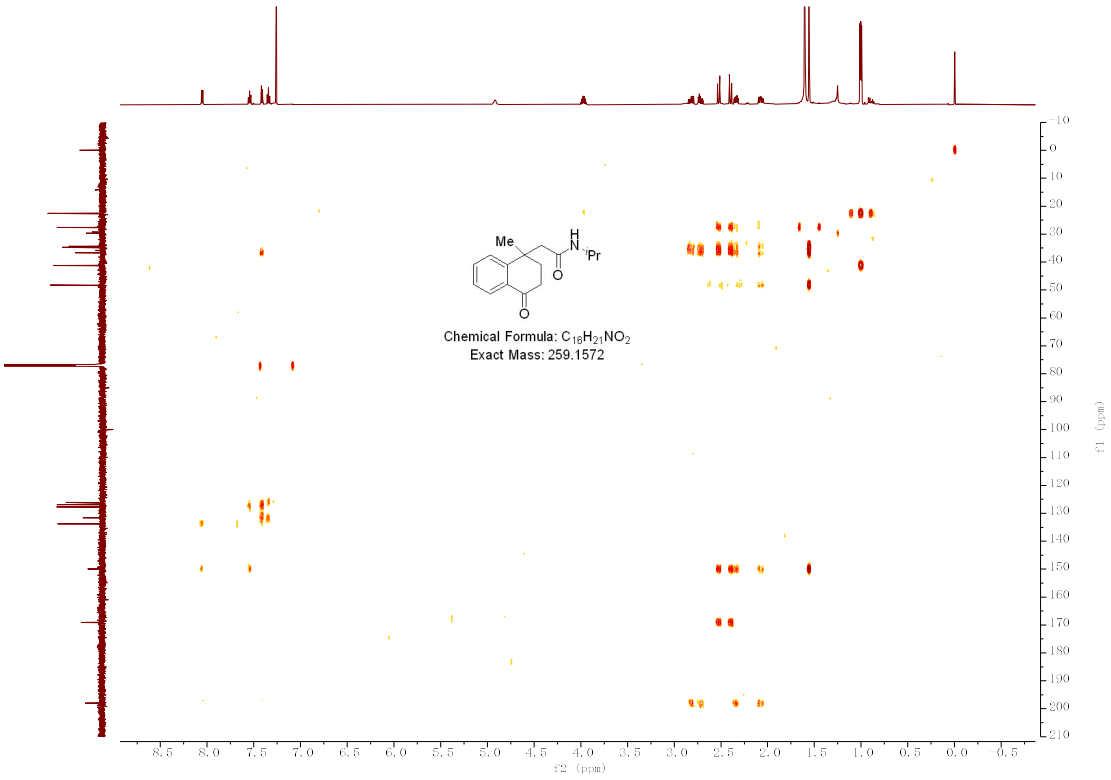

8.06 8.05 8.04 8.04 7.53 7.53 7.52 7.51 7.41 7.41 7.40 7.39 7.35 7.35 7.34 7.34 7.34 7.33
3.19 3.18 3.18 3.17 3.17 3.16 3.16 2.56 2.54 2.37 2.37 2.36 2.35 2.34 2.34 1.85 1.83 1.81 1.56 1.39 1.39 1.38 1.37 1.37 1.36 1.36 1.35 1.27 1.27 1.26 1.26 1.26 1.25 1.25 1.24 1.23 0.90 0.89 0.88
Me
H
N
nBu
O
Me
O
Chemical Formula: C18H25NO2
Exact Mass: 287.1885
1.00 1.13 0.94 0.92 0.86 1.95 0.89 1.13 2.02 1.05 3.21 2.13 5.23 3.31
f1 (ppm)


200.64 170.10 150.07 133.51 131.38 127.83 126.98 126.26 48.14 43.26 39.28 38.37 36.89 31.55 27.84 20.04 15.67 13.70
Me
H
N
nBu
O
Me
O
Chemical Formula: C18H25NO2
Exact Mass: 287.1885
f1 (ppm)

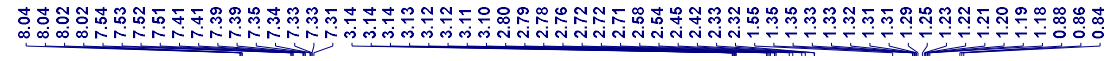
10

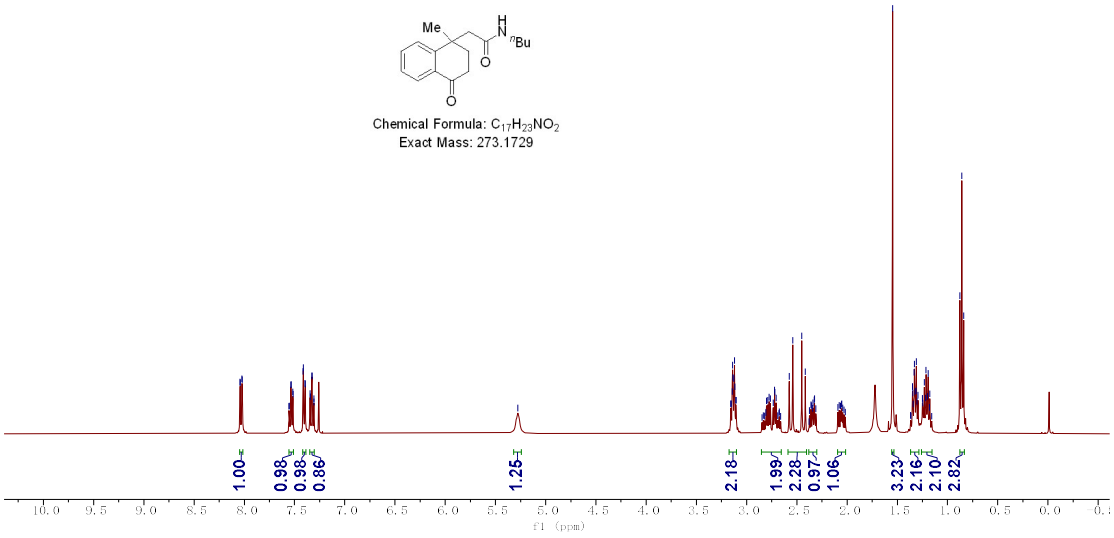

8.06 8.06 8.05 8.05 7.56 7.56 7.55 7.54 7.53 7.53 7.42 7.42 7.41 7.41 7.36 7.36 7.34 7.34 7.33 7.33 3.98 3.97 3.97 3.96 2.82 2.81 2.80 2.79 2.74 2.73 2.73 2.72 2.70 2.54 2.51 2.41 2.39 2.36 2.35 2.35 2.34 2.34 2.33 2.33 2.32 2.10 2.09 2.08 2.07 2.07 2.07 2.06 1.56 1.01 1.01 1.00 0.99
Me
H
N
iPr
O
O
Chemical Formula: C16H21NO2
Exact Mass: 259.1572
1.00
1.05
1.04
1.06
0.95
1.01
2.34
2.48
2.40
3.07
3.05
3.01
f1 (ppm)
197.97
169.10
149.97
133.81
131.59
127.76
126.94
126.16
48.27
41.29
36.69
34.77
34.34
27.61
22.65
22.60
Me
H
N
iPr
O
O
Chemical Formula: C16H21NO2
Exact Mass: 259.1572
f1 (ppm)


Me
H
N
iPr
O
O
Chemical Formula: C18H21NO2
Exact Mass: 259.1572
f2 (ppm)
f1 (ppm)

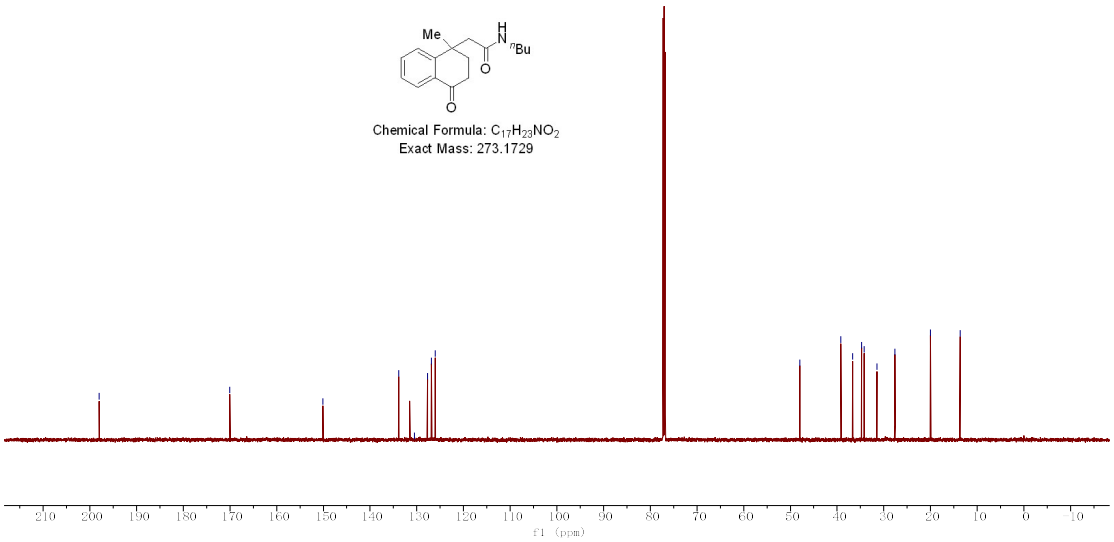

Me
H
N
iPr
O
O
Chemical Formula: C18H21NO2
Exact Mass: 259.1572
f2 (ppm)
f1 (ppm)

11

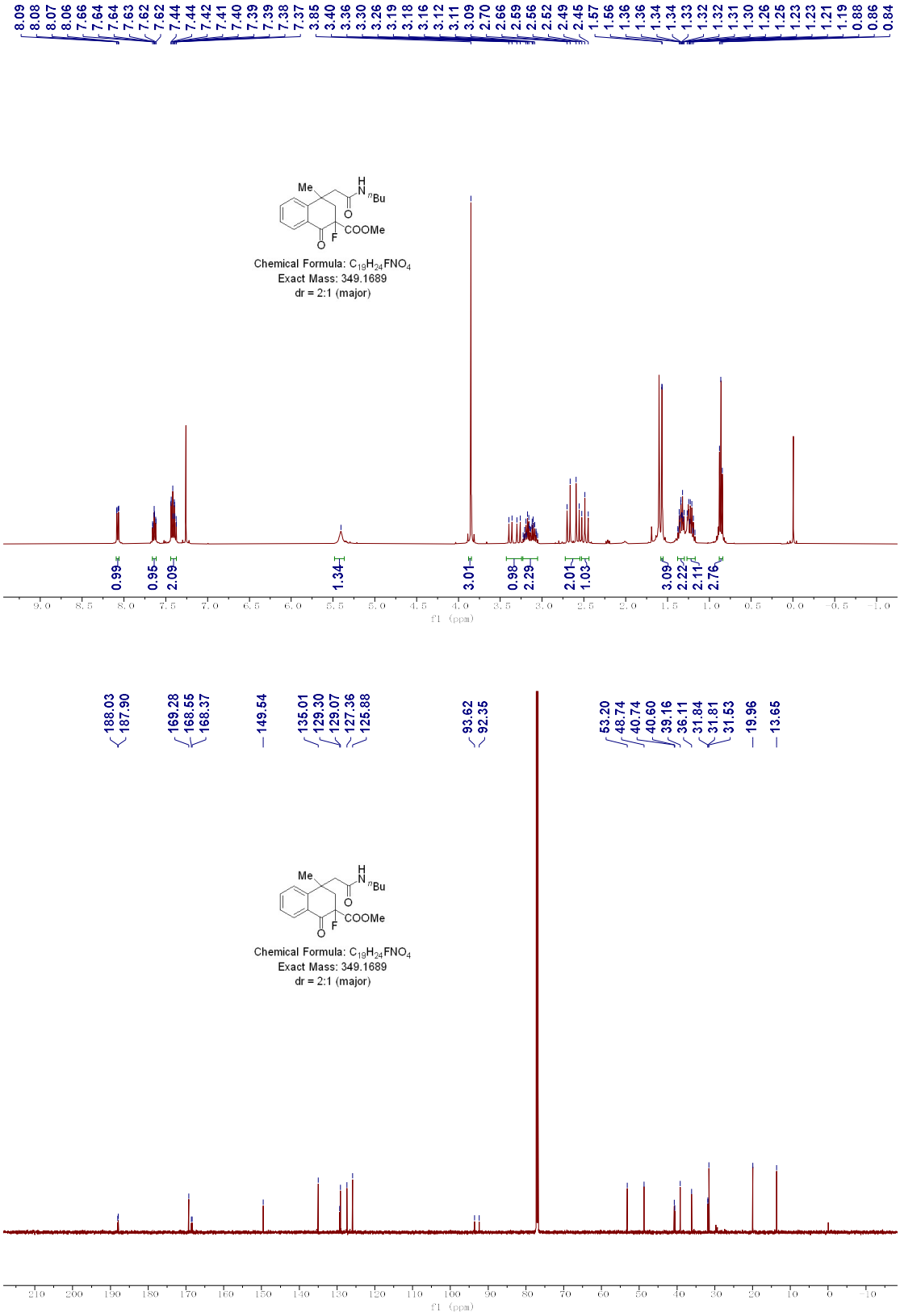

8.04
8.04
8.02
8.02
7.54
7.53
7.52
7.51
7.41
7.41
7.39
7.39
7.35
7.34
7.33
7.33
7.31
3.14
3.14
3.14
3.13
3.12
3.12
3.11
3.10
2.80
2.79
2.78
2.76
2.72
2.72
2.71
2.58
2.54
2.45
2.42
2.33
2.32
1.55
1.35
1.35
1.33
1.33
1.32
1.31
1.31
1.29
1.25
1.23
1.22
1.21
1.20
1.19
1.18
0.88
0.86
0.84

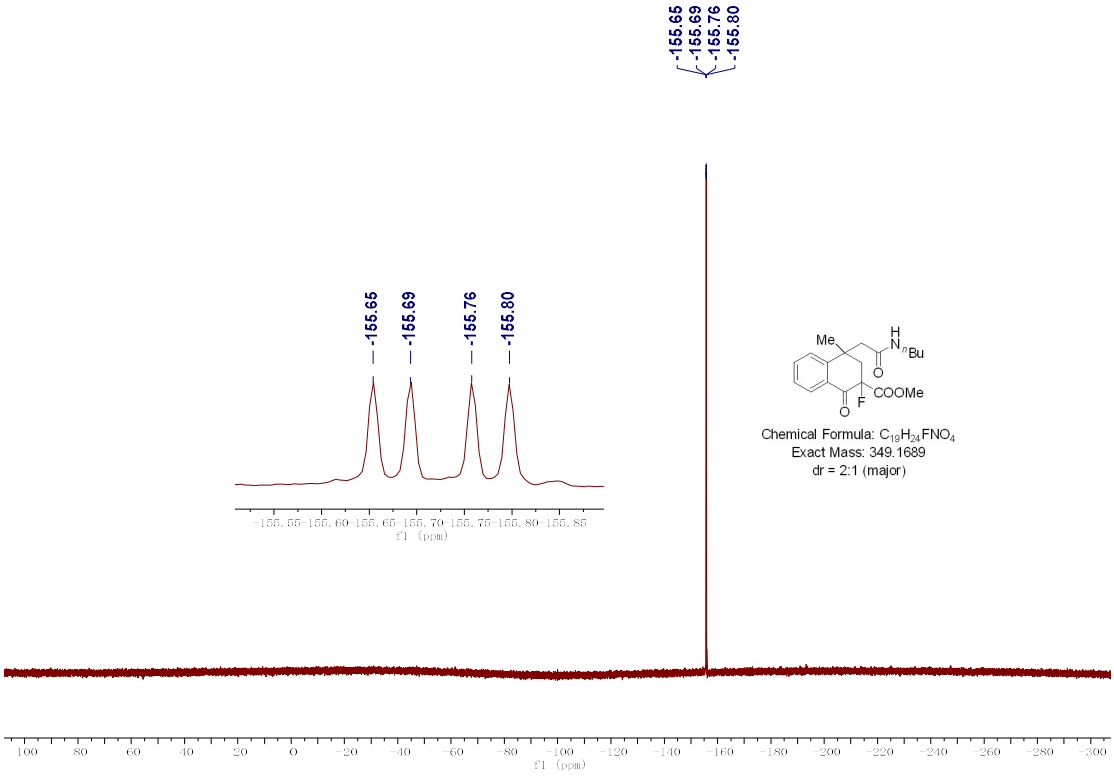

Me
H
N
nBu
O
O
Chemical Formula: C17H23NO2
Exact Mass: 273.1729
1.00
0.98
0.98
0.86
1.25
2.18
1.99
2.28
0.97
1.06
3.23
2.16
2.10
2.82
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


198.01
170.02
150.12
133.84
130.51
127.72
126.90
126.07
47.98
39.20
36.65
34.77
34.20
31.49
27.62
20.00
13.68

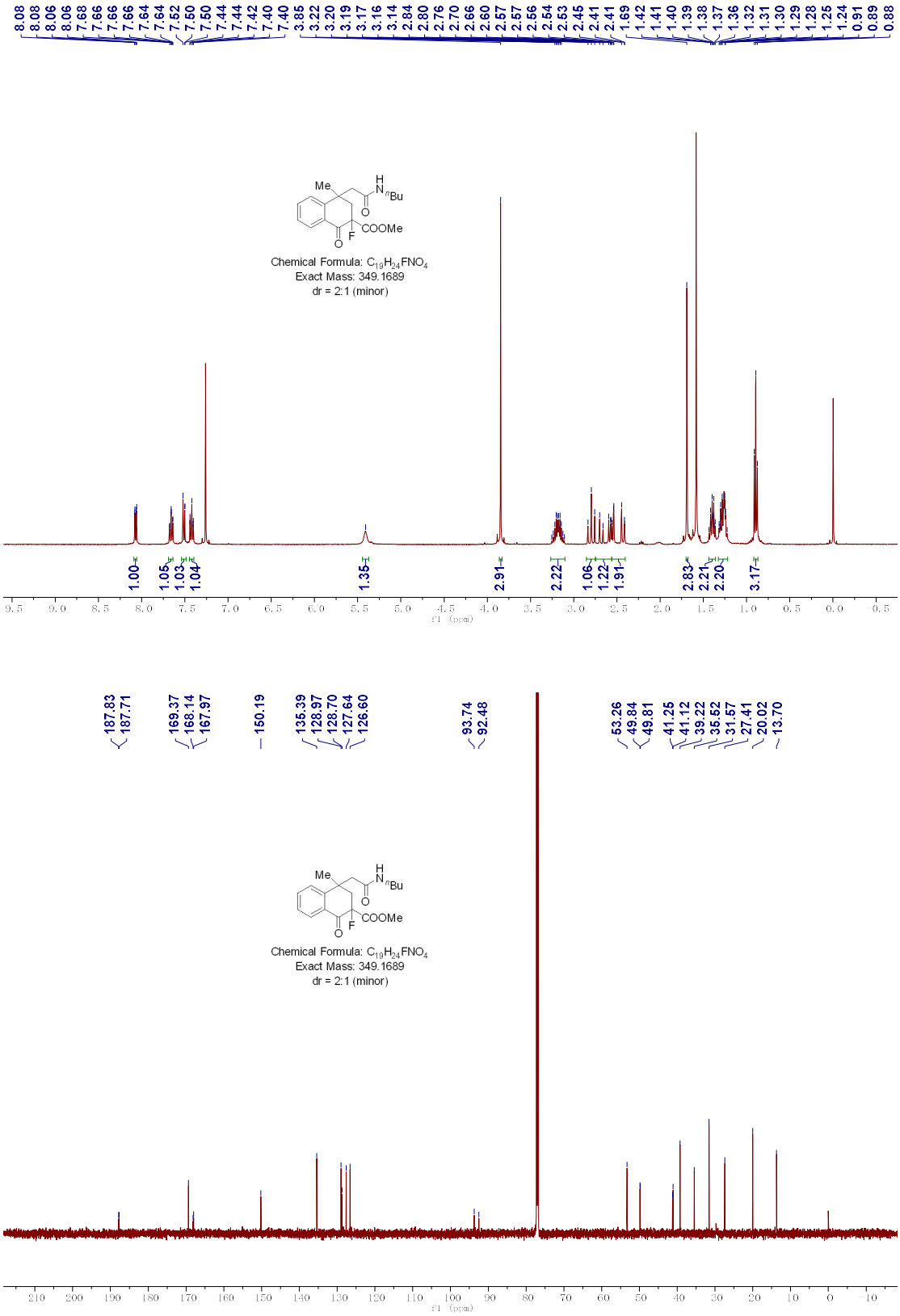

Me
H
N
nBu
O
O
Chemical Formula: C17H23NO2
Exact Mass: 273.1729
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

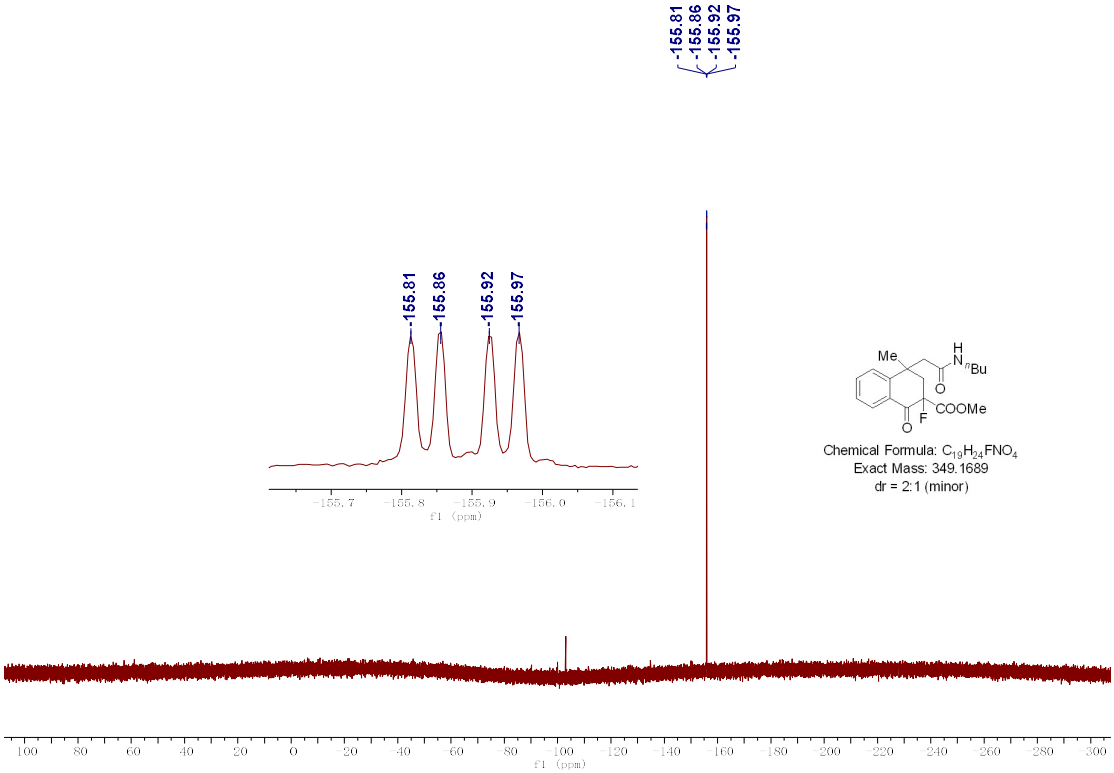
12 (major)


8.09 8.08 8.07 8.06 7.66 7.64 7.64 7.63 7.62 7.62 7.44 7.44 7.42 7.41 7.40 7.39 7.39 7.38 7.37 3.85 3.40 3.36 3.30 3.26 3.19 3.18 3.16 3.12 3.11 3.09 2.70 2.66 2.59 2.56 2.52 2.49 2.45 1.57 1.56 1.36 1.36 1.34 1.34 1.33 1.32 1.32 1.31 1.30 1.26 1.25 1.23 1.23 1.21 1.19 0.88 0.86 0.84
Me
H
N
nBu
O
COOMe
F
O
Chemical Formula: C19H24FNO4
Exact Mass: 349.1689
dr = 2:1 (major)
0.99 0.95 2.09 1.34 3.01 0.98 2.29 2.01 1.03 3.09 2.22 2.11 2.76
f1 (ppm)
188.03 187.90 169.28 168.55 168.37 149.54 135.01 129.30 129.07 127.36 125.88 93.62 92.35 53.20 48.74 40.74 40.60 39.16 36.11 31.84 31.81 31.53 19.96 13.65
f1 (ppm)

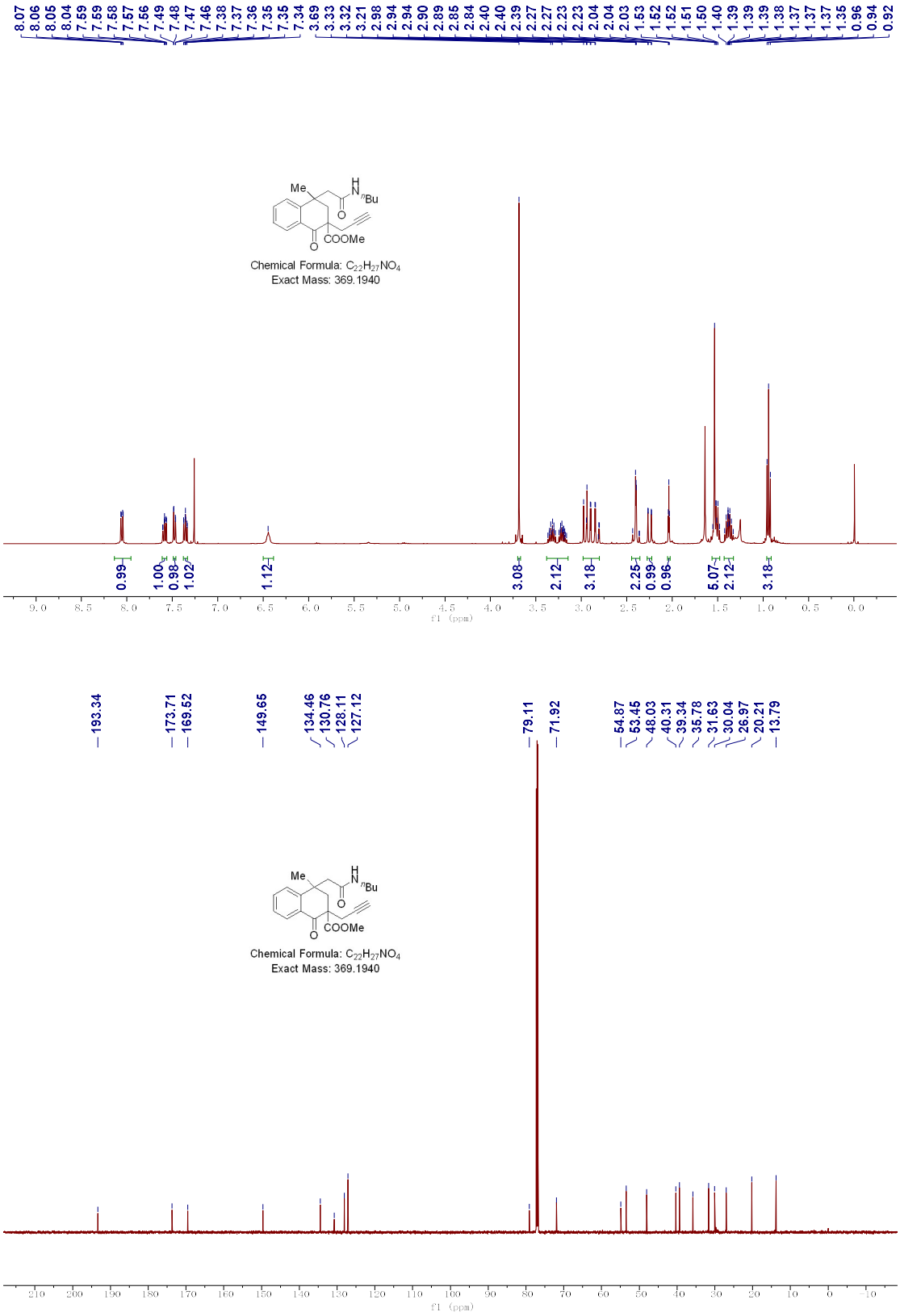

-155.65
-155.69
-155.76
-155.80
-155.65
-155.69
-155.76
-155.80
-155.55 -155.60 -155.65 -155.70 -155.75 -155.80 -155.85
f1 (ppm)
Me
H
N
nBu
O
COOMe
F
O
Chemical Formula: C19H24FNO4
Exact Mass: 349.1689
dr = 2:1 (major)
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

12 (minor)

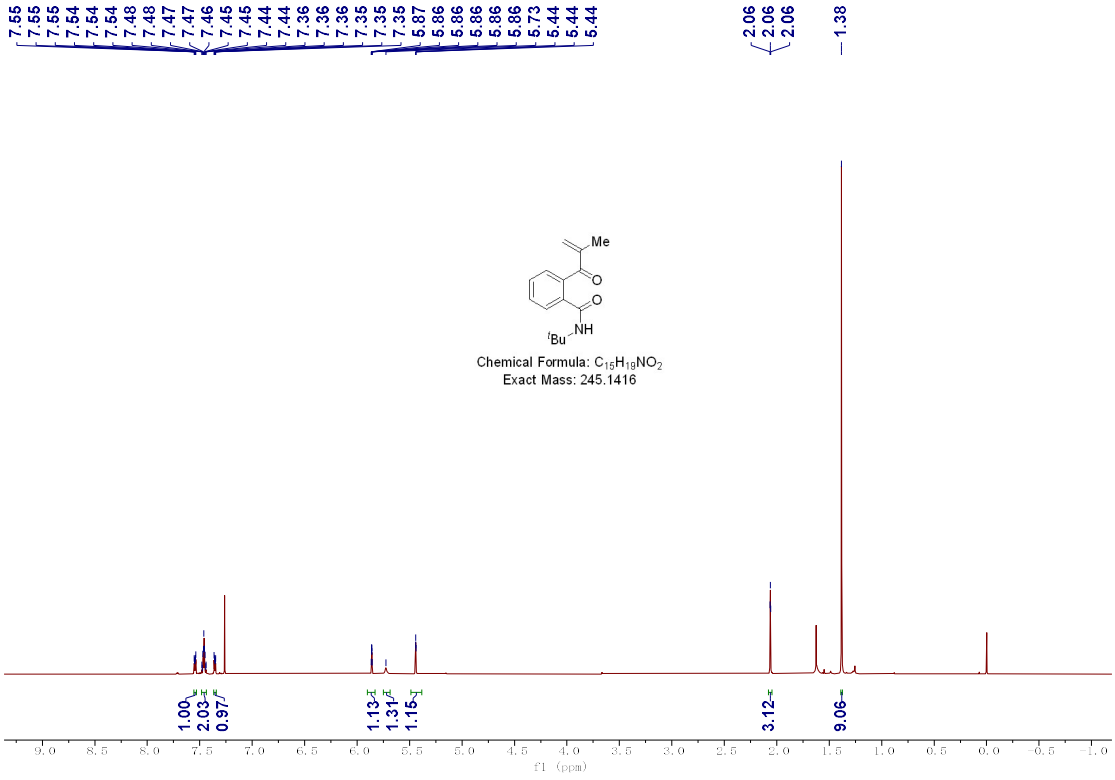

8.08 8.08 8.06 8.06 7.68 7.66 7.66 7.66 7.64 7.64 7.52 7.50 7.50 7.44 7.44 7.42 7.40 7.40 3.85 3.22 3.20 3.19 3.17 3.16 3.14 2.84 2.80 2.76 2.70 2.66 2.60 2.57 2.57 2.56 2.54 2.53 2.45 2.41 2.41 1.69 1.42 1.41 1.40 1.39 1.38 1.37 1.36 1.32 1.31 1.30 1.29 1.28 1.25 1.24 0.91 0.89 0.88
Me
H
N
nBu
O
F
COOMe
O
Chemical Formula: C19H24FNO4
Exact Mass: 349.1689
dr = 2:1 (minor)
1.00 1.05 1.03 1.04 1.35 2.91 2.22 1.06 1.22 1.91 2.83 2.21 2.20 3.17
f1 (ppm)
187.83 187.71 169.37 168.14 167.97 150.19 135.39 128.97 128.70 127.64 126.60 93.74 92.48 53.26 49.84 49.81 41.25 41.12 39.22 35.52 31.57 27.41 20.02 13.70
f1 (ppm)

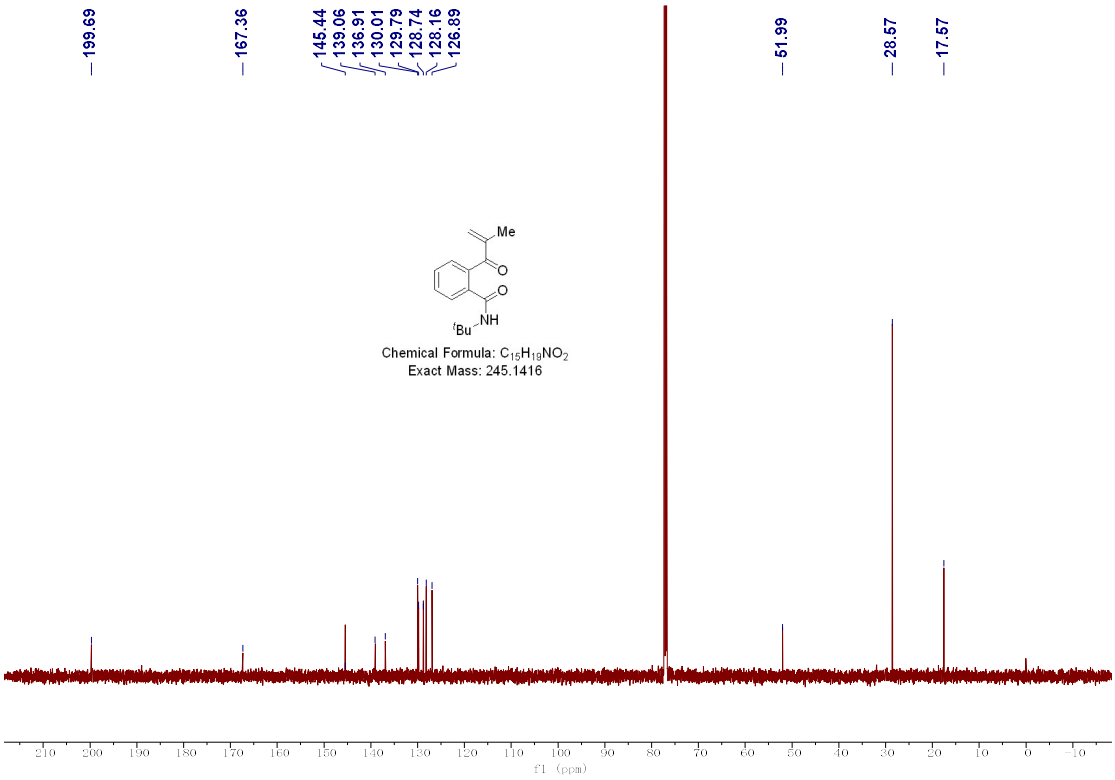

-155.81
-155.86
-155.92
-155.97
-155.81
-155.86
-155.92
-155.97
-155.7
-155.8
-155.9
-156.0
-156.1
f1 (ppm)
Me
H
N
nBu
O
COOMe
F
O
Chemical Formula: C19H24FNO4
Exact Mass: 349.1689
dr = 2:1 (minor)
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-300
f1 (ppm)

13


8.07 8.06 8.05 8.04 7.59 7.59 7.58 7.57 7.56 7.49 7.48 7.47 7.46 7.38 7.37 7.36 7.35 7.35 7.34 3.69 3.33 3.32 3.21 2.98 2.94 2.94 2.90 2.89 2.85 2.84 2.40 2.40 2.39 2.27 2.27 2.23 2.23 2.04 2.04 2.03 1.53 1.52 1.52 1.51 1.50 1.40 1.39 1.39 1.39 1.38 1.37 1.37 1.37 1.35 0.96 0.94 0.92
Me
H
N
nBu
O
O
COOMe
O
Chemical Formula: C22H27NO4
Exact Mass: 369.1940
0.99 1.00 0.98 1.02 1.12 3.08 2.12 3.18 2.25 0.99 0.96 5.07 2.12 3.18
f1 (ppm)
193.34 173.71 169.62 149.65 134.46 130.76 128.11 127.12 79.11 71.92 54.87 53.45 48.03 40.31 39.34 36.78 31.63 30.04 26.97 20.21 13.79
Me
H
N
nBu
O
O
COOMe
O
Chemical Formula: C22H27NO4
Exact Mass: 369.1940
f1 (ppm)

19


7.55
7.55
7.55
7.54
7.54
7.54
7.48
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.44
7.36
7.36
7.36
7.35
7.35
7.35
5.87
5.86
5.86
5.86
5.86
5.73
5.44
5.44
5.44
2.06
2.06
2.06
1.38
Me
O
O
NH
tBu
Chemical Formula: C15H19NO2
Exact Mass: 245.1416
1.00
2.03
0.97
1.13
1.31
1.15
3.12
9.06
f1 (ppm)


199.69
167.36
145.44
139.06
136.91
130.01
129.79
128.74
128.16
126.89
51.99
28.57
17.57
Me
O
O
NH
tBu
Chemical Formula: C15H19NO2
Exact Mass: 245.1416
f1 (ppm)

10. Supplementary References

1. Ping, Y.; Pan, Q.; Guo, Y.; Liu, Y.; Li, X.; Wang, M.; Kong, W. Switchable 1,2-Rearrangement Enables Expedient Synthesis of Structurally Diverse Fluorine-Containing Scaffolds. *J. Am. Chem. Soc.* **2022**, *144*, 11626-11637.

2. Wang, T.; Phillips, E. M.; Dalby, S. M.; Sirota, E.; Axnanda, S.; Shultz, C. S.; Patel, P.; Waldman, J. H.; Alwedi, E.; Wang, X.; Zawatzky, K.; Chow, M.; Padivitage, N.; Weisel, M.; Whittington, M.; Duan, J.; Lu, T. Manufacturing Process Development for Belzutifan, Part 5: A Streamlined Fluorination–Dynamic Kinetic Resolution Process. *Org. Process Res. Dev.* **2022**, *26*, 543-550.

3. Mugnaini, C.; Brizzi, A.; Ligresti, A.; Allarà, M.; Lamponi, S.; Vacondio, F.; Silva, C.; Mor, M.; Di Marzo, V.; Corelli, F. Investigations on the 4-Quinolone-3-carboxylic Acid Motif. 7. Synthesis and Pharmacological Evaluation of 4-Quinolone-3-carboxamides and 4-hydroxy-2-quinolone-3-carboxamides as High Affinity Cannabinoid Receptor 2 (CB2R) Ligands with Improved Aqueous Solubility. *J. Med. Chem.* **2016**, *59*, 1052-1067.