Supplementary Information

Enantioconvergent Photoredox Radical−Radical Coupling Catalyzed by a Chiral-at-Rhodium Complex

Zijun Zhou,※ Xin Nie,※ Klaus Harms, Radostan Riedel, Lilu Zhang, Eric Meggers*

Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse 4, 35043 Marburg, Germany

※These authors contributed equally

*Corresponding author: meggers@chemie.uni-marburg.de

1. General Information

All reactions were carried out under an atmosphere of nitrogen with magnetic stirring unless otherwise stated. The catalytic reactions were performed by using standard Schlenk techniques. A 24 W (456 nm, Hongchangzhaoming from Chinese Taobao, https://hongchang-led.taobao.com) or 3 W blue LEDs (420 nm, constructed by the workshop of Department of Chemisty at the University of Marburg) served as light sources. The catalyst Λ-**RhS**[1] and *N*-arylglycine derivates **2b-f**[2] were synthesized according to our published procedures. *N*-phenylglycine (**2a**) and other reagents that were purchased from commercial suppliers were used without further purification. Solvents were distilled under nitrogen from calcium hydride (CH_3CN, CH_2Cl_2), sodium/benzophenone (THF, Et_2O). HPLC grade of acetone, methanol, and ethanol was used without further purification. Flash column chromatography was performed with silica gel 60 M from Macherey-Nagel (irregular shaped, 230–400 mesh, pH 6.8, pore volume: 0.81 mL × g^{-1}, mean pore size: 66 Å, specific surface: 492 $m^2 \times g^{-1}$, particle size distribution: 0.5% < 25 μm and 1.7% > 71 μm, water content: 1.6%). ^{1}H NMR, proton decoupled ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker Avance 250 (250 MHz), Bruker Avance 300 (300 MHz) or Bruker AM (500 MHz) spectrometers at ambient temperature. NMR yields were determined using 1,1,2,2-tetrachloroethane as internal standard. NMR standards were used as follows: ^{1}H NMR spectroscopy: δ = 7.26 ppm ($CDCl_3$), 5.32 ppm (CD_2Cl_2); ^{13}C NMR spectroscopy: δ = 77.0 ppm ($CDCl_3$), 53.8 ppm (CD_2Cl_2); ^{19}F NMR spectroscopy: = 0 ppm ($CFCl_3$). High-resolution mass spectra were recorded on a Bruker En Apex Ultra 7.0 TFT-MS instrument using ESI/EI technique. Optical rotations were measured on a Krüss P8000-T polarimeter with $[\alpha]_D^{22}$ values reported in degrees with concentrations reported in g/100 mL. Chiral HPLC chromatography was performed with an Agilent 1200 or Agilent 1260 HPLC system with a Daicel Chiralpak OD-H, or AD-H column (250 × 4.6 mm) using *n*-hexane/isopropanol as a mobile phase. The EPR spectrometer is from Bruker (model esp300), with a modified Varian rectangular X-band cavity and the modulation frequency was set to 100 kHz, the modulation amplitude was 0.1 mT.

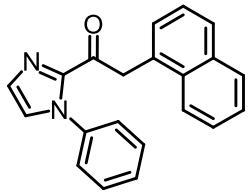
2. Synthesis of Substrates

2.1 Synthesis of 2-Acyl Imidazoles

All Weinreb amides were prepared following our published procedures.[3] 2-Acyl imidazoles were synthesized according to reported procedures.[4-7]

The data of the new compound **S1n** is shown below.

2-(Naphthalen-1-yl)-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one (S1n)



A yellow solid.

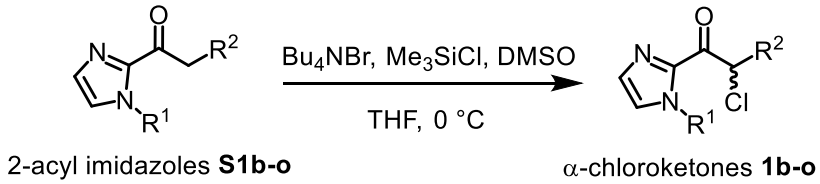
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08-8.02 (m, 1H), 7.86- 7.81 (m, 1H), 7.76 (d, J = 9.0 Hz, 1H), 7.51-7.40 (m, 4H),7.39-7.33 (m, 4H), 7.24-7.17 (m, 3H), 4.95 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 188.4, 142.8, 138.2, 133.9, 132.5, 131.2, 129.8, 128.9, 128.8, 128.61, 128.60, 127.7, 127.5, 126.2, 125.8, 125.5, 125.4, 124.4, 43.1.

HRMS (ESI, *m*/*z*) calcd. for $C_{21}H_{17}N_2O$ $[M+H]^+$: 313.1335, found: 313.1334.

2.2 Synthesis of α-Bromo- and α-Chloroketones

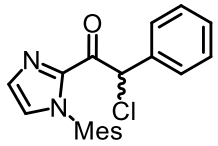
α-Bromoketones **1a** and **1p** were synthesized according to the published procedures.[8,9] α-Chloroketones **1b-o** were synthesized following the procedures shown below.[10] The analytical data of **1a**[5] and **1b**[11] are in accordance with the literature.



To a solution of tetrabutylammonium bromide (32.2 mg, 0.1 mmol) in dry THF was added trimethylchlorosilane (0.38 mL, 3.0 mmol) dropwise at room temperature. The resulting solution was stirred for 10 min at room temperature followed by addition of 2-acyl imidazoles (1.0 mmol, 1.0 equiv) and DMSO (0.21 mL, 3.0 mmol) in sequence at 0 °C. The resulting solution was allowed to warm to room temperature and stirred for 1-5 h (monitored by TLC). It was then quenched with deionized water (10 mL) and extracted with EtOAc (3 × 10 mL). The organic layer was washed

with saturated aqueous $NaHCO_3$ (1 × 30 mL) and brine (1 × 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/*n*-hexane = 1:6) to afford products **1b-o**.

2-Chloro-1-(1-mesityl-1*H*-imidazol-2-yl)-2-phenylethan-1-one (1c)



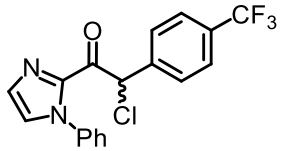
A white solid, **1c** (273 mg, 88% yield) was synthesized by following the general procedure.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56-7.51 (m, 2H), 7.39 (d, J = 3.0 Hz, 1H), 7.34-7.28 (m, 3H), 7.02 (d, J = 3.0 Hz, 1H), 6.97 (s, 1H), 6.90 (s, 1H), 6.87 (s, 1H), 2.32 (s, 3H), 1.96 (s, 3H), 1.51 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 182.2, 141.2, 138.8, 135.7, 134.4, 134.0, 133.8, 130.9, 129.1, 128.9, 128.82, 128.81, 128.6, 126.9, 60.7, 21.1, 17.4, 16.7.

HRMS (ESI, *m*/*z*) calcd. for $C_{20}H_{19}ClN_2ONa$ $[M+Na]^+$: 361.1078, found: 361.1082.

2-Chloro-1-(1-phenyl-1*H*-imidazol-2-yl)-2-(4-(trifluoromethyl)phenyl)ethan-1-one (1d)



A white solid, **1d** (278 mg, 89% yield) was synthesized by following the general procedure.

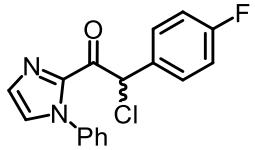
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, J = 6.0 Hz, 2H), 7.60 (d, J = 6.0 Hz, 1H), 7.49-7.43 (m, 3H), 7.33 (d, J = 3.0 Hz, 1H), 7.25-7.19 (m, 3H), 6.97 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 181.5, 140.6, 139.7, 137.5, 131.1, 130.7, 130.6, 129.3, 129.1, 128.6, 125.7, 122.0, 59.5.

^{19}F NMR (235 MHz, $CDCl_3$) δ -62.81.

HRMS (ESI, *m*/*z*) calcd. for $C_{18}H_{12}ClF_3N_2ONa$ $[M+Na]^+$: 387.0482, found: 387.0486.

2-Chloro-2-(4-fluorophenyl)-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one (1e)



A white solid, **1e** (213 mg, 67% yield) was synthesized by following the general procedure.

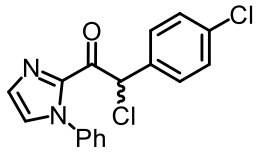
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60-7.53 (m, 2H), 7.48-7.42 (m, 3H), 7.32 (d, J = 3.0 Hz, 1H), 7.25-7.18 (m, 3H), 7.03 (t, J = 9.0 Hz, 2H), 6.91 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 182.0, 164.6, 161.3, 140.7, 137.6, 131.6, 130.8, 130.4, 129.1, 128.3, 125.7, 115.7, 59.6.

^{19}F NMR (235 MHz, $CDCl_3$) δ -112.40.

HRMS (ESI, *m*/*z*) calcd. for $C_{17}H_{12}ClFN_2ONa$ $[M+Na]^+$: 337.0514, found: 337.0517.

2-Chloro-2-(4-chlorophenyl)-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one (1f)



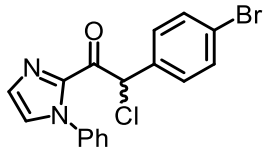
A white solid, **1f** (187 mg, 54% yield) was synthesized by following the general procedure.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55-7.50 (m, 2H), 7.48-7.43 (m, 3H), 7.34-7.29 (m, 3H), 7.24-7.19 (m, 3H), 6.90 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 181.8, 140.7, 137.6, 135.0, 134.3, 130.5, 130.3, 129.13, 129.12, 128.9, 128.4, 125.7, 59.7.

HRMS (ESI, *m*/*z*) calcd. for $C_{17}H_{12}Cl_2N_2ONa$ $[M+Na]^+$: 353.0219, found: 353.0220.

2-(4-Bromophenyl)-2-chloro-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one (1g)



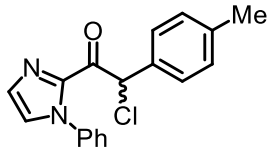
A white solid, **1g** (213 mg, 62% yield) was synthesized by following the general procedure.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.43 (m, 7H), 7.31 (d, J = 3.0 Hz, 1H), 7.24-7.20 (m, 3H), 6.88 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 181.7, 140.6, 137.6, 134.8, 131.9, 130.6, 130.5, 129.1, 128.4, 125.7, 123.2, 59.8.

HRMS (ESI, *m*/*z*) calcd. for $C_{17}H_{12}BrClN_2ONa$ $[M+Na]^+$: 396.9714, found: 396.9720.

2-Chloro-1-(1-phenyl-1*H*-imidazol-2-yl)-2-(p-tolyl)ethan-1-one (1h)



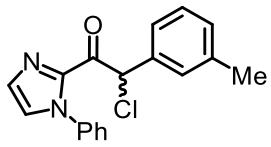
A white solid, **1h** (283 mg, 83% yield) was synthesized by following the general procedure.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.46-7.42 (m, 4H), 7.30 (d, J = 3.0 Hz, 1H), 7.23-7.19 (m, 3H), 7.15 (d, J = 9.0 Hz, 2H), 6.90 (s, 1H), 2.32 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 182.3, 140.9, 138.9, 137.7, 132.7, 130.3, 129.5, 129.1, 129.0, 128.8, 128.1, 125.7, 60.7, 21.2.

HRMS (ESI, *m*/*z*) calcd. for $C_{18}H_{15}ClN_2ONa$ $[M+Na]^+$: 333.0765, found: 333.0764.

2-Chloro-1-(1-phenyl-1*H*-imidazol-2-yl)-2-(m-tolyl)ethan-1-one (1i)



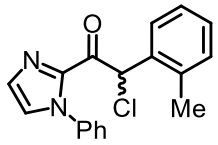
A white solid, **1i** (194 mg, 58% yield) was synthesized by following the general procedure.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.42 (m, 3H), 7.38 (d, J = 9.0 Hz, 2H), 7.31 (d, J = 3.0 Hz, 1H), 7.24-7.18 (m, 4H), 7.12 (d, J = 3.0 Hz, 1H) 6.91 (s, 1H), 2.34 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 182.3, 140.9, 138.5, 137.7, 135.6, 130.4, 129.8, 129.5, 129.1, 129.0, 128.6, 128.1, 126.0, 125.7, 60.7, 21.4.

HRMS (ESI, *m*/*z*) calcd. for $C_{18}H_{15}ClN_2ONa$ $[M+Na]^+$: 333.0765, found: 333.0766.

2-Chloro-1-(1-phenyl-1*H*-imidazol-2-yl)-2-(o-tolyl)ethan-1-one (1j)



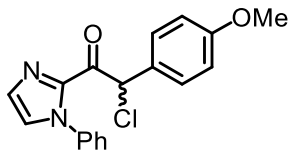
A white solid, **1j** (168 mg, 46% yield) was synthesized by following the general procedure.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52-7.45 (m, 4H), 7.31-7.26 (m, 3H), 7.25-7.19 (m, 4H), 7.16 (s, 1H), 2.66 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 182.6, 141.1, 137.7, 136.9, 134.4, 130.8, 130.3, 129.1, 129.0, 128.9, 128.5, 127.9, 126.5, 125.7, 58.1, 19.5.

HRMS (ESI, *m*/*z*) calcd. for $C_{18}H_{15}ClN_2ONa$ $[M+Na]^+$: 333.0765, found: 333.0767.

2-Chloro-2-(4-methoxyphenyl)-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one (1k)



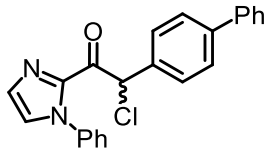
A white solid, **1k** (264 mg, 74% yield) was synthesized by following the general procedure.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (t, J = 3.0 Hz, 1H), 7.49 (t, J = 3.0 Hz, 1H), 7.47-7.42 (m, 3H), 7.30 (d, J = 3.0 Hz, 1H), 7.24-7.19 (m, 3H), 6.91 (s, 1H), 6.88 (d, J = 3.0 Hz, 1H), 6.86 (d, J = 3.0 Hz, 1H), 3.78 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 182.2, 160.1, 140.8, 137.7, 130.3, 130.1, 129.1, 129.0, 128.0, 127.6, 125.7, 114.2, 60.5, 55.3.

HRMS (ESI, *m*/*z*) calcd. for $C_{18}H_{16}ClN_2O_2$ $[M+H]^+$: 327.0895, found: 327.0898.

2-((1,1'-Biphenyl)-4-yl)-2-chloro-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one (1l)



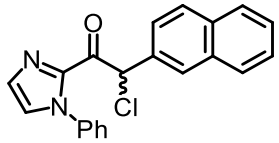
A white solid, **1l** (247 mg, 66% yield) was synthesized by following the general procedure.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, J = 8.4 Hz, 2H), 7.59-7.53 (m, 4H) 7.48-7.44 (m, 3H), 7.43 (s, 1H), 7.38 (d, J = 10.5 Hz, 1H), 7.33 (d, J = 0.9 Hz, 1H), 7.27-7.21 (m, 4H), 6.98 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 182.1, 141.9, 140.4, 134.6, 130.4, 129.3, 129.1, 129.0, 128.8, 128.2, 127.6, 127.5, 127.1, 125.7, 60.4.

HRMS (ESI, *m*/*z*) calcd. for $C_{23}H_{18}ClN_2O$ $[M+H]^+$: 373.1102, found: 373.1106.

2-Chloro-2-(naphthalen-2-yl)-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one (1m)



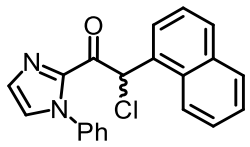
A white solid, **1m** (225 mg, 62% yield) was synthesized by following the general procedure.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, J = 1.2 Hz, 1H), 7.88-7.78 (m, 3H), 7.69 (dd, J = 4.5, 1.8 Hz, 1H), 7.51-7.42 (m, 5H), 7.32 (d, J = 1.2 Hz, 1H), 7.23-7.17 (m, 3H), 7.11 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 182.2, 140.9, 137.7, 133.4, 133.1, 133.0, 130.4, 129.1, 129.0, 128.7, 128.3, 128.2, 127.7, 126.8, 126.4, 125.9, 125.7, 61.1.

HRMS (ESI, *m*/*z*) calcd. for $C_{21}H_{16}ClN_2O$ $[M+H]^+$: 347.0946, found: 347.0949.

2-Chloro-2-(naphthalen-1-yl)-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one (1n)



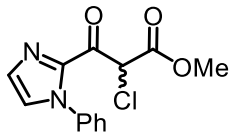
A white solid, **1n** (127 mg, 38% yield) was synthesized by following the general procedure.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (d, J = 8.4 Hz, 1H), 7.85 (t, J = 9.0 Hz, 2H), 7.77 (d, J = 8.4 Hz, 1H), 7.71 (s, 1H), 7.61 (dt, J = 1.5 Hz, 1H), 7.55-7.40 (m, 5H), 7.27 (d, J = 0.9 Hz, 1H), 7.24-7.18 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 182.5, 141.1, 137.7, 134.0, 131.5, 130.8, 130.4, 129.8, 129.1, 129.0, 128.9, 128.0, 127.8, 126.9, 126.0, 125.7, 125.4, 123.6, 58.2.

HRMS (ESI, *m*/*z*) calcd. for $C_{21}H_{16}ClN_2O$ $[M+H]^+$: 347.0946, found: 347.0950.

Methyl-2-chloro-3-oxo-3-(1-phenyl-1*H*-imidazol-2-yl)propanoate (1o)



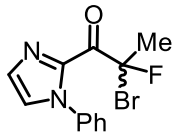
A brown solid, **1o** (80 mg, 32% yield)) was synthesized by following the general procedure.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (t, J = 3.3 Hz, 3H), 7.34 (d, J = 0.9 Hz, 1H), 7.30-7.33 (m, 2H) 7.29 (d, J = 0.9 Hz, 1H), 6.17 (s, 1H), 3.82 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 178.0, 166.1, 140.4, 137.3, 130.8, 129.2, 128.3, 125.6, 58.1, 53.6.

HRMS (ESI, *m*/*z*) calcd. for $C_{13}H_{12}ClN_2O_3$ $[M+H]^+$: 279.0531, found: 279.0530.

2-Bromo-2-fluoro-1-(1-phenyl-1*H*-imidazol-2-yl)propan-1-one (1p)



A white solid, **1p** (208 mg, 81% yield) was synthesized by following the published procedure.[9]

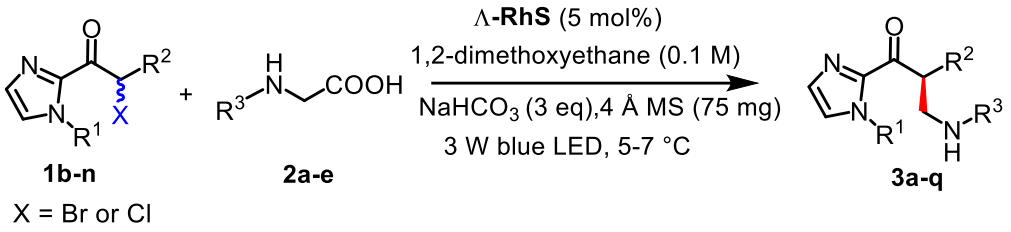
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (t, J = 3.3 Hz, 3H), 7.40 (d, J = 0.9 Hz, 1H) 7.33-7.27 (m, 2H), 7.24 (d, J = 0.9 Hz, 1H), 2.56 (d, J = 20.7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 179.1, 138.45, 138.0, 130.5, 129.2, 129.1, 127.7, 125.6, 100.5, 29.8.

^{19}F NMR (235 MHz, $CDCl_3$) δ -105.71.

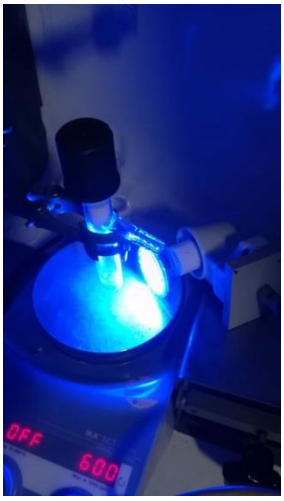
HRMS (ESI, *m*/*z*) calcd. for $C_{12}H_{11}BrFN_2O$ $[M+H]^+$: 297.0033, found: 297.0033.

3. Rhodium-Catalyzed Radical Cross-Coupling

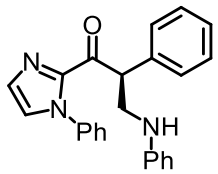


General procedure for the asymmetric photoredox catalysis: A pre-dried 10 mL Schlenk tube (using heating gun) was charged with catalyst Λ-**RhS** (6.5 mg, 5 mol%), sodium bicarbonate (37.8 mg, 0.45 mmol), 4 Å molecular sieves (50 mg/mmol), 2-acyl imidazoles **1b-n** (0.15 mmol, 1.0 equiv) and *N*-phenyl glycines **2a-e** (0.6 mmol, 4.0 equiv) under an atmosphere of nitrogen. Subsequently, 1,2-dimethoxyethane (1.5 mL) was added via syringe under nitrogen atmosphere. The resulting solution was degassed via freeze-pump-thaw for three cycles. The Schlenk tube was then sealed and placed into a cold room (air temperature 5-7 °C). The reaction tube was positioned at approximately 2.5 cm from a 3 W blue LED lamp). After stirring under nitrogen atmosphere for 65 h, the reaction solution was directly purified by flash chromatography on silica gel (*n*-hexane/EtOAc = 10:1 to 3:1) to afford the products **3a-q**. Racemic samples were obtained by carrying out the reactions with *rac*-**RhS**. The enantiomeric excess was determined by chiral HPLC analysis. The absolute configuration of the product **3e** was confirmed by single crystal X-ray structure analysis.

Reaction setup:



(*S*)-2-Phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)-3-(phenylamino)propan-1-one (3a)



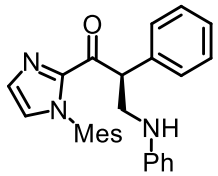
Starting from **1b** (44.5 mg, 0.15 mmol) and **2a** (90.7 mg, 0.6 mmol), **3a** was afforded as a pale yellow solid (25.0 mg, 72% yield) according to the general procedure. Enantiomeric excess was determined by HPLC analysis on a Chiralpak OD-H column, ee = 95% (OD-H, 254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1.0 mL/min, 25 °C, t_r (major) = 6.4 min, t_r (minor) = 8.0 min). $[\alpha]_D^{22}$ = -41.4° (c 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47-7.41 (m, 5H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.30-7.27 (m, 1H), 7.24 (d, *J* = 0.9 Hz, 1H), 7.20-7.17 (m, 2H), 7.16-7.13 (m, 2H), 7.12 (d, *J* = 0.9 Hz, 1H), 6.69 (t, *J* = 7.5 Hz, 1H), 6.60 (d, *J* = 7.5 Hz, 2H). 5.49 (dd, *J* = 6.6, 2.1Hz, 1H), 3.91 (dd, *J* = 8.4, 4.5 Hz, 1H), 3.49 (q, *J* = 6.6 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.8, 147.7, 142.9, 138.3, 137.0, 130.0, 129.3, 129.0, 128.9, 128.8, 127.5, 127.3, 125.7, 117.5, 113.0, 53.0, 46.5, 29.7.

HRMS (ESI, *m*/*z*) calcd. for $C_{24}H_{22}N_3O$ $[M+H]^+$: 368.1757, found: 368.1754.

(*S*)-1-(1-Mesityl-1*H*-imidazol-2-yl)-2-phenyl-3-(phenylamino)propan-1-one (3b)



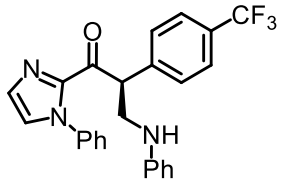
Starting from **1c** (50.8 mg, 0.15 mmol) and **2a** (90.7 mg, 0.6 mmol), **3b** was afforded as a yellow solid (43.6 mg, 71% yield) according to the general procedure. Enantiomeric excess was determined by HPLC analysis on a Chiralpak OD-H column, ee = 93% (OD-H, 254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1.0 mL/min, 25 °C, t_r (major) = 8.7 min, t_r (minor) = 9.9 min). $[\alpha]_D^{22}$ = -102.2° (c 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 6.9, 1.5 Hz, 2H), 7.32-7.26 (m, 3H), 7.25-7.22 (m, 1H), 7.14 (t, *J* = 8.1 Hz, 2H), 6.97 (s, 1H), 6.92 (d, *J* = 0.9 Hz, 1H), 6.89 (s, 1H), 6.68 (t, *J* = 7.5 Hz, 1H), 6.68 (d, *J* = 7.5 Hz, 2H), 5.46 (dd, *J* = 6.6, 1.8 Hz, 1H), 3.86 (dd, *J* = 8.4, 1.5 Hz, 1H), 3.47 (q, *J* = 6.6 Hz, 1H), 2.34 (s, 3H), 1.90 (s, 3H), 1.54 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.8, 147.7, 143.0, 138.5, 137.0, 134.4, 134.0, 130.6, 129.2, 128.9, 128.8, 128.7, 127.4, 125.9, 117.5, 113.0, 52.9, 46.2, 21.1, 17.4, 16.8.

HRMS (ESI, *m*/*z*) calcd. for $C_{27}H_{27}N_3ONa$ $[M+Na]^+$: 432.2046, found: 432.2051.

(*S*)-1-(1-Phenyl-1*H*-imidazol-2-yl)-3-(phenylamino)-2-(4-(trifluoromethyl)phenyl)propan-1-one (3c)



Starting from **1d** (54.7 mg, 0.15 mmol) and **2a** (90.7 mg, 0.6 mmol), **3c** was afforded as a white solid (48.3 mg, 74% yield) according to the general procedure. Enantiomeric excess was determined by HPLC analysis on a Chiralpak OD-H column, ee = 97% (254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1.0 mL/min, 25 °C, t_r (major) = 7.2 min, t_r (minor) = 6.2 min). $[\alpha]_D^{22}$ = +52.8° (c 1.0, CH_2Cl_2).

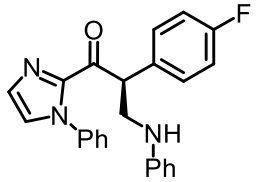
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.7, 4.2 Hz, 4H), 7.50-7.42 (m, 3H), 7.25 (d, *J* = 0.9 Hz, 1H), 7.22-7.12 (m, 5H), 6.72 (t, *J* = 7.5 Hz, 1H), 6.61 (dd, *J* = 7.5, 1.2 Hz, 2H), 5.59 (dd, *J* = 6.3, 2.1 Hz, 1H), 3.94 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.45 (q, *J* = 6.3 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.0, 147.4, 142.6, 141.2, 138.1, 130.2, 129.9, 129.5, 129.3, 129.2, 129.1, 128.9, 127.7, 125.8, 125.7, 122.3, 117.8, 113.0, 52.7, 46.5.

^{19}F NMR (235 MHz, $CDCl_3$) δ -62.56.

HRMS (ESI, *m*/*z*) calcd. for $C_{25}H_{21}F_3N_3O$ $[M+H]^+$: 436.1631, found: 436.1636.

(*S*)-2-(4-Fluorophenyl)-1-(1-phenyl-1*H*-imidazol-2-yl)-3-(phenylamino)propan-1-one (3d)



Starting from **1e** (47.2 mg, 0.15 mmol) and **2a** (90.7 mg, 0.6 mmol), **3d** was afforded as a yellow solid (37.0 mg, 64% yield) according to the general procedure. Enantiomeric excess was determined by HPLC analysis on a Chiralpak OD-H column, ee = 88% (254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1.0 mL/min, 25 °C, t_r (major) = 8.0 min, t_r (minor) = 6.5 min). $[\alpha]_D^{22}$ = +39.0° (c 1.0, CH_2Cl_2).

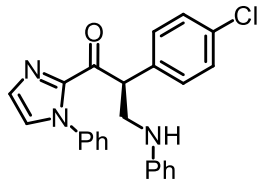
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.41 (m, 5H), 7.28 (d, *J* = 0.9 Hz, 1H), 7.23-7.15 (m, 5H), 7.06 (d, *J* = 8.7 Hz, 2H), 6.73 (t, *J* = 7.5 Hz, 1H), 6.63 (dd, *J* = 7.5, 0.9 Hz, 2H), 5.52 (dd, *J* = 6.6, 1.8 Hz, 1H), 3.92 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.49 (q, *J* = 6.6 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.7, 163.8, 160.6, 147.6, 142.7, 138.2, 132.8, 132.7, 130.4, 130.3, 130.0, 129.3, 129.03, 128.97, 128.86, 127.5, 125.9, 125.8, 117.6, 115.9, 115.6, 113.0, 52.0, 46.5.

^{19}F NMR (235 MHz, $CDCl_3$) δ -114.98.

HRMS (ESI, *m*/*z*) calcd. for $C_{24}H_{21}FN_3O$ $[M+H]^+$: 386.1663, found: 386.1664.

(*S*)-2-(4-Chlorophenyl)-1-(1-phenyl-1*H*-imidazol-2-yl)-3-(phenylamino)propan-1-one (3e)



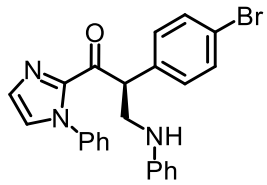
Starting from **1f** (49.6 mg, 0.15 mmol) and **2a** (90.7 mg, 0.6 mmol), **3e** was afforded as a white solid (45.2 mg, 75% yield) according to the general procedure. Enantiomeric excess was determined by HPLC analysis on a Chiralpak OD-H column, ee = 95% (254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1.0 mL/min, 25 °C, t_r (major) = 6.7 min, t_r (minor) = 8.1 min). $[\alpha]_D^{22}$ = -99.8° (c 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.42 (m, 3H), 7.34 (dd, *J* = 12.0, 8.4 Hz, 4H), 7.24 (d, *J* = 0.9 Hz, 1H), 7.20-7.12 (m, 5H), 6.70 (t, *J* = 7.5 Hz, 1H), 6.59 (d, *J* = 7.5, Hz, 2H), 5.48 (dd, *J* = 6.6, 1.8 Hz, 1H), 3.92 (dd, *J* = 8.4, 6.3 Hz, 1H), 3.49 (q, *J* = 6.6 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.4, 147.5, 142.6, 138.2, 135.6, 133.4, 130.14, 130.08, 129.3, 129.0, 128.9, 127.5, 125.8, 117.7, 113.0, 52.2, 46.4.

HRMS (ESI, *m*/*z*) calcd. for $C_{24}H_{21}ClN_3O$ $[M+H]^+$: 402.1368, found: 402.1372.

(*S*)-2-(4-Bromophenyl)-1-(1-phenyl-1*H*-imidazol-2-yl)-3-(phenylamino)propan-1-one (3f)



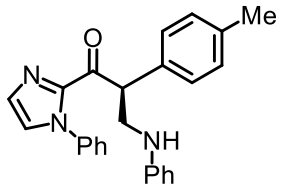
Starting from **1g** (56.3 mg, 0.15 mmol) and **2a** (90.7 mg, 0.6 mmol), **3f** was afforded as a yellow solid (46.9 mg, 70% yield) according to the general procedure. Enantiomeric excess was determined by HPLC analysis on a Chiralpak OD-H column, ee = 92% (254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1.0 mL/min, 25 °C, t_r (major) = 7.1 min, t_r (minor) = 8.6 min). $[\alpha]_D^{22}$ = -83.4° (c 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.42 (m, 5H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 0.9 Hz, 1H), 7.20-7.10 (m, 5H), 6.70 (t, *J* = 7.5 Hz, 1H), 6.59 (d, *J* = 7.5, Hz, 2H), 5.46 (dd, *J* = 6.6, 1.5 Hz, 1H), 3.88 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.45 (q, *J* = 6.6 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.3, 147.5, 142.6, 138.2, 136.1, 132.0, 130.5, 130.1, 129.3, 129.0, 128.9, 127.6, 125.8, 121.6, 117.7, 113.0, 52.3, 46.3.

HRMS (ESI, *m*/*z*) calcd. for $C_{24}H_{21}BrN_3O$ $[M+H]^+$: 446.0863, found: 446.0868.

(*S*)-1-(1-Phenyl-1*H*-imidazol-2-yl)-3-(phenylamino)-2-(p-tolyl)propan-1-one (3g)



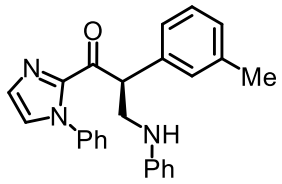
Starting from **1h** (46.6 mg, 0.15 mmol) and **2a** (90.7 mg, 0.6 mmol), **3g** was afforded as a white solid (42.3 mg, 74% yield) according to the general procedure. Enantiomeric excess was determined by HPLC analysis on a Chiralpak OD-H column, ee = 98% (254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1.0 mL/min, 25 °C, t_r (major) = 6.1 min, t_r (minor) = 7.4 min). $[\alpha]_D^{22}$ = -98.8° (c 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.41 (m, 3H), 7.32 (s, 1H), 7.30 (s, 1H), 7.23 (d, *J* = 0.9 Hz, 1H), 7.19-7.11 (m, 6H), 7.11 (d, *J* = 0.9 Hz, 1H), 6.68 (t, *J* = 7.5 Hz, 1H), 6.63 (dd, *J* = 7.8, 0.9 Hz, 2H), 5.44 (dd, *J* = 6.3, 2.1 Hz, 1H), 3.87 (dd, *J* = 8.7, 4.5 Hz, 1H), 3.45 (q, *J* = 6.6 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.9, 147.7, 142.9, 138.3, 137.1, 133.9, 130.0, 129.6, 129.2, 129.0, 128.7, 128.6, 127.2, 125.7, 117.5, 113.0, 52.5, 46.4, 21.1.

HRMS (ESI, *m*/*z*) calcd. for $C_{25}H_{24}N_3O$ $[M+H]^+$: 382.1914, found: 382.1914.

(*S*)-1-(1-Phenyl-1*H*-imidazol-2-yl)-3-(phenylamino)-2-(m-tolyl)propan-1-one (3h)



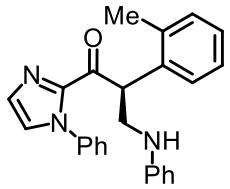
Starting from **1i** (46.6 mg, 0.15 mmol) and **2a** (90.7 mg, 0.6 mmol), **3h** was afforded as a white solid (42.3 mg, 74% yield) according to the general procedure. Enantiomeric excess was determined by HPLC analysis on a Chiralpak OD-H column, ee = 97% (254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1.0 mL/min, 25 °C, t_r (major) = 5.9 min, t_r (minor) = 7.3 min). $[\alpha]_D^{22}$ = -93.8° (c 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.44 (m, 3H), 7.29 (s, 1H), 7.26 (d, *J* = 4.8 Hz, 3H), 7.22-7.13 (m, 5H), 7.12-7.08 (m, 1H), 6.72 (t, *J* = 7.5 Hz, 1H), 6.63 (dd, *J* = 7.5, 0.9 Hz, 2H), 5.47 (dd, *J* = 6.6, 2.1 Hz, 1H), 3.91 (dd, *J* = 8.7, 4.5 Hz, 1H), 3.49 (q, *J* = 6.3 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.9, 147.7, 142.9, 138.5, 138.3, 136.9, 130.0, 129.4, 129.2, 129.0, 128.8, 128.7, 128.3, 127.2, 125.8, 125.7, 117.5, 113.0, 52.9, 46.5, 21.4.

HRMS (ESI, *m*/*z*) calcd. for $C_{25}H_{24}N_3O$ $[M+H]^+$: 382.1914, found: 382.1913.

(*S*)-1-(1-Phenyl-1*H*-imidazol-2-yl)-3-(phenylamino)-2-(o-tolyl)propan-1-one (3i)



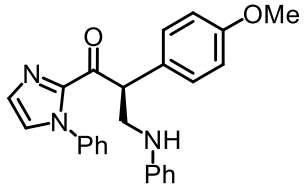
Starting from **1j** (46.6 mg, 0.15 mmol) and **2a** (90.7 mg, 0.6 mmol), **3i** was afforded as a brown oil (35.5 mg, 62% yield) according to the general procedure. Enantiomeric excess was determined by HPLC analysis on a Chiralpak OD-H column, ee = 76% (254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1.0 mL/min, 25 °C, t_r (major) = 7.5 min, t_r (minor) = 6.0 min). $[\alpha]_D^{22}$ = +96.6° (c 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57-7.51 (m, 3H), 7.34-7.28 (m, 3H), 7.27-7.20 (m, 6H), 7.17 (d, *J* = 0.9 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.68 (dd, *J* = 7.5, 1.2 Hz, 2H), 5.76 (dd, *J* = 5.7, 3.0 Hz, 1H), 3.94 (dd, *J* = 8.7, 4.8 Hz, 1H), 3.51 (q, *J* = 6.3 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.5, 147.8, 143.1, 138.3, 137.6, 135.5, 131.0, 129.9, 129.3, 129.0, 128.8, 127.3, 127.2, 127.0, 126.2, 125.7, 117.4, 112.9, 48.8, 46.2, 20.2.

HRMS (ESI, *m*/*z*) calcd. for $C_{25}H_{24}N_3O$ $[M+H]^+$: 382.1914, found: 382.1913.

(*S*)-2-(4-Methoxyphenyl)-1-(1-phenyl-1*H*-imidazol-2-yl)-3-(phenylamino)propan-1-one (3j)



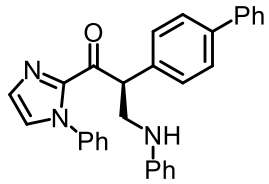
Starting from **1k** (49.0 mg, 0.15 mmol) and **2a** (90.7 mg, 0.6 mmol), **3j** was afforded as a yellow solid (38.8 mg, 65% yield) according to the general procedure. Enantiomeric excess was determined by HPLC analysis on a Chiralpak OD-H column, ee = 93% (254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1.0 mL/min, 25 °C, t_r (major) = 7.7 min, t_r (minor) = 9.6 min). $[\alpha]_D^{22}$ = -86.0° (c 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.42 (m, 3H), 7.36 (s, 1H), 7.33 (s, 1H), 7.24 (d, *J* = 0.9 Hz, 1H), 7.19-7.16 (m, 2H), 7.16-7.10 (m, 3H), 6.90-6.84 (m, 2H), 6.68 (t, *J* = 7.5 Hz, 1H), 6.60 (dd, *J* = 7.5, 0.9 Hz, 2H), 5.43 (dd, *J* = 6.6, 1.5 Hz, 1H), 3.87 (dd, *J* = 8.4, 4.5 Hz, 1H), 3.79 (s, 3H), 3.45 (q, *J* = 6.6 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.0, 159.0, 147.8, 142.9, 138.3, 129.9, 129.8, 129.2, 129.0, 128.9, 128.8, 127.2, 125.7, 117.5, 114.3, 113.0, 52.2, 52.0, 46.4.

HRMS (ESI, *m*/*z*) calcd. for $C_{25}H_{24}N_3O_2$ $[M+H]^+$: 398.1863, found: 398.1865.

(*S*)-2-((1,1'-Biphenyl)-4-yl)-1-(1-phenyl-1*H*-imidazol-2-yl)-3-(phenylamino)propan -1-one (3k)



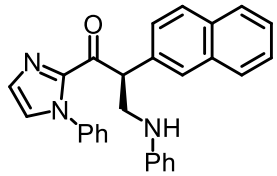
Starting from **1l** (55.9 mg, 0.15 mmol) and **2a** (90.7 mg, 0.6 mmol), **3k** was afforded as a yellow solid (40.6 mg, 61% yield) according to the general procedure. Enantiomeric excess was determined by HPLC analysis on a Chiralpak AD-H column, ee = 87% (254 nm, *n*-hexane/isopropanol = 80:20, flow rate 0.8 mL/min, 25 °C, t_r (major) = 20.6 min, t_r (minor) = 26.4 min). $[\alpha]_D^{22}$ = -139.4° (c 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.1 Hz, 4H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.48-7.40 (m, 5H), 7.37-7.32 (m, 1H), 7.27 (d, *J* = 0.9 Hz, 1H), 7.22-7.12 (m, 5H), 6.71 (t, *J* = 7.5 Hz, 1H), 6.63 (dd, *J* = 7.5, 0.9 Hz, 2H), 5.56 (dd, *J* = 6.3, 2.1 Hz, 1H), 3.96 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.54 (q, *J* = 6.6 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.7, 147.7, 142.9, 140.7, 140.4, 138.3, 136.0, 130.0, 129.3, 129.2, 129.0, 128.82, 128.78, 127.6, 127.4, 127.3, 127.0, 125.8, 117.6, 113.0, 52.6, 46.5.

HRMS (ESI, *m*/*z*) calcd. for $C_{30}H_{25}N_3O$ $[M+H]^+$: 444.2070, found: 444.2077.

(*S*)-2-(Naphthalen-2-yl)-1-(1-phenyl-1*H*-imidazol-2-yl)-3-(phenylamino)propan-1-one (3l)



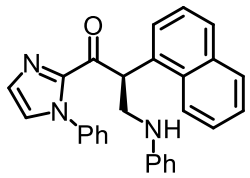
Starting from **1m** (52.0 mg, 0.15 mmol) and **2a** (90.7 mg, 0.6 mmol), **3l** was afforded as a white solid (50.1 mg, 80% yield) according to the general procedure. Enantiomeric excess was determined by HPLC analysis on a Chiralpak OD-H column, ee = 97% (254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1.0 mL/min, 25 °C, t_r (major) = 8.6 min, t_r (minor) = 10.4 min). $[\alpha]_D^{22}$ = -194.6° (c 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.84-7.77 (m, 3H), 7.57 (dd, *J* = 6.6, 1.8 Hz, 1H), 7.50-7.40 (m, 5H), 7.23 (d, *J* = 0.9 Hz, 1H), 7.19-7.12 (m, 4H), 7.10 (d, *J* = 0.9 Hz, 1H), 6.69 (t, *J* = 7.5 Hz, 1H), 6.62 (dd, *J* = 8.4, 0.9 Hz, 2H), 5.65 (dd, *J* = 6.6, 1.8 Hz, 1H), 4.00 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.58 (q, *J* = 6.6 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.7, 147.7, 142.8, 138.3, 134.5, 133.6, 132.7, 130.0, 129.3, 129.0, 128.8, 128.6, 127.9, 127.8, 127.6, 127.3, 126.7, 126.2, 126.0, 125.8, 117.6, 113.1, 53.0, 46.4.

HRMS (ESI, *m*/*z*) calcd. for $C_{28}H_{24}N_3O$ $[M+H]^+$: 418.1914, found: 418.1918.

(*S*)-2-(Naphthalen-1-yl)-1-(1-phenyl-1*H*-imidazol-2-yl)-3-(phenylamino)propan-1-one (3m)



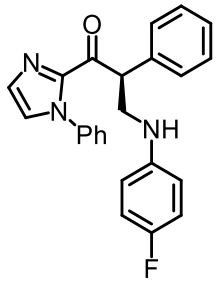
Starting from **1n** (52.0 mg, 0.15 mmol) and **2a** (90.7 mg, 0.6 mmol), **3m** was afforded as a yellow oil (35.0 mg, 56% yield) according to the general procedure. Enantiomeric excess was determined by HPLC analysis on a Chiralpak OD-H column, ee = 58% (254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1.0 mL/min, 25 °C, t_r (major) = 14.2 min, t_r (minor) = 8.3 min). $[\alpha]_D^{22}$ = -0.8° (c 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.7 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.66-7.58 (m, 1H), 7.56-7.44 (m, 6H), 7.21-7.13 (m, 5H), 7.08 (d, *J* = 0.9 Hz, 1H), 6.71 (t, *J* = 7.5 Hz, 1H), 6.62 (dd, *J* = 7.5, 0.9 Hz, 2H), 6.32 (dd, *J* = 5.4, 3.6 Hz, 1H), 4.04 (dd, *J* = 9.0, 4.2 Hz, 1H), 3.58 (dd, *J* = 7.8, 5.1 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.3, 147.7, 143.1, 138.2, 134.3, 133.5, 131.9, 130.0, 129.3, 129.0, 128.9, 128.8, 128.1, 127.2, 126.6, 125.9, 125.7, 125.5, 125.4, 123.9, 117.5, 113.0, 48.3, 46.6.

HRMS (ESI, *m*/*z*) calcd. for $C_{28}H_{23}N_3ONa$ $[M+Na]^+$: 440.1733, found: 440.1739.

(*S*)-3-((4-Fluorophenyl)amino)-2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)propan-1-one (3n)



Starting from **1b** (44.5 mg, 0.15 mmol) and **2b** (101.8 mg, 0.6 mmol), **3n** was afforded as a yellow solid (45.1 mg, 78% yield) according to the general procedure. Enantiomeric excess was determined by HPLC analysis on a Chiralpak OD-H column, ee = 88% (254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1.0 mL/min, 25 °C, t_r (major) = 6.2 min, t_r (minor) = 7.7 min). $[\alpha]_D^{22}$ = -73.2° (c 1.0, CH_2Cl_2).

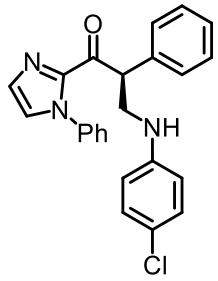
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.38 (m, 5H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.29-7.26 (m, 1H), 7.24 (d, *J* = 0.9 Hz, 1H), 7.19-7.14 (m, 2H), 7.12 (d, *J* = 0.9 Hz, 1H), 6.85 (t, *J* = 8.7 Hz, 2H), 6.53 (q, *J* = 4.5, Hz, 2H), 5.46 (dd, *J* = 6.6, 1.8 Hz, 1H), 3.86 (dd, *J* = 8.4, 4.5 Hz, 1H), 3.44 (q, *J* = 6.6 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.7, 144.0, 142.8, 138.2, 136.9, 130.0, 129.0, 128.9, 128.8, 128.7, 127.5, 127.4, 125.7, 115.8, 115.5, 114.0, 113.9, 52.8, 47.2.

^{19}F NMR (235 MHz, $CDCl_3$) δ -127.92.

HRMS (ESI, *m*/*z*) calcd. for $C_{24}H_{21}FN_3O$ $[M+H]^+$: 386.1663, found: 386.1668.

(*S*)-3-((4-Chlorophenyl)amino)-2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)propan-1-one (3o)



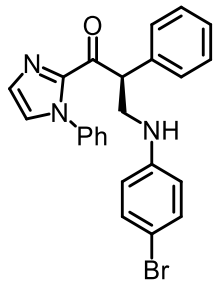
Starting from **1b** (44.5 mg, 0.15 mmol) and **2c** (111.4 mg, 0.6 mmol), **3o** was afforded as a yellow solid (41.0 mg, 68% yield) according to the general procedure. Enantiomeric excess was determined by HPLC analysis on a Chiralpak OD-H column, ee = 90% (254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1.0 mL/min, 25 °C, t_r (major) = 6.5 min, t_r (minor) = 7.7 min). $[\alpha]_D^{22}$ = -49.2° (c 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.39 (m, 5H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.30-7.26 (m, 1H), 7.24 (d, *J* = 0.9 Hz, 1H), 7.19-7.14 (m, 2H), 7.13 (d, *J* = 0.9 Hz, 1H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.52 (d, *J* = 8.7, Hz, 2H), 5.47 (dd, *J* = 6.3, 2.1 Hz, 1H), 3.88 (dd, *J* = 8.4, 4.5 Hz, 1H), 3.45 (q, *J* = 6.6 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.6, 146.3, 142.8, 138.2, 136.8, 130.0, 129.07, 129.03, 128.9, 128.8, 128.7, 127.6, 127.4, 125.7, 122.0, 114.1, 52.8, 46.5.

HRMS (ESI, *m*/*z*) calcd. for $C_{34}H_{21}ClN_3O$ $[M+H]^+$: 402.1368, found: 402.1372.

(*S*)-3-((4-Bromophenyl)amino)-2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)propan-1-one (3p)



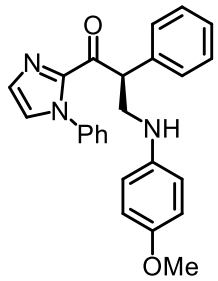
Starting from **1b** (44.5 mg, 0.15 mmol) and **2d** (138.4 mg, 0.6 mmol), **3p** was afforded as a yellow oil (44.8 mg, 67% yield) according to the general procedure. Enantiomeric excess was determined by HPLC analysis on a Chiralpak OD-H column, ee = 93% (254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1.0 mL/min, 25 °C, t_r (major) = 6.9 min, t_r (minor) = 8.2 min). $[\alpha]_D^{22}$ = -39.4° (c 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.41 (m, 4H), 7.40 (d, J = 0.9 Hz, 1H), 7.37-7.27 (m, 3H), 7.24 (d, J = 0.9 Hz, 1H), 7.23-7.19 (m, 2H), 7.18-7.14 (m, 2H), 7.13 (d, J = 0.9 Hz, 1H), 6.50-6.44 (m, 2H), 5.46 (dd, J = 6.3, 2.4 Hz, 1H), 3.87 (dd, J = 8.4, 4.8 Hz, 1H), 3.44 (q, J = 6.6 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.6, 146.6, 142.8, 138.2, 136.8, 131.9, 130.0, 129.0, 128.9, 128.8, 128.7, 127.6, 127.4, 125.7, 114.6, 109.1, 52.7, 46.4.

HRMS (ESI, *m*/*z*) calcd. for $C_{24}H_{20}BrN_3ONa$ $[M+Na]^+$: 468.0682, found: 468.0688.

(*S*)-3-((4-Methoxyphenyl)amino)-2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)propan-1-one (3q)



Starting from **1b** (44.5 mg, 0.15 mmol) and **2e** (108.7 mg, 0.6 mmol), **3q** was afforded as a yellow oil (25.0 mg, 42% yield) according to the general procedure. Enantiomeric excess was determined by HPLC analysis on a Chiralpak OD-H column, ee = 6% (254 nm, *n*-hexane/isopropanol = 80:20, flow rate 1.0 mL/min, 25 °C, t_r (major) = 10.7 min, t_r (minor) = 13.8 min). $[\alpha]_D^{22}$ = -21.2° (c 1.0, CH_2Cl_2).

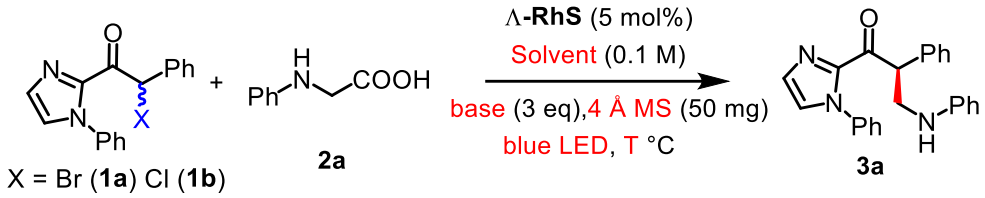
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46-7.40 (m, 5H), 7.36-7.28 (m, 3H), 7.24 (d, J = 0.9 Hz, 1H), 7.19-7.15 (m, 2H), 7.12 (d, J = 0.9 Hz, 1H), 6.78-6.72 (m, 2H), 6.59-6.54 (m, 2H), 5.47 (dd, J = 6.3, 1.8 Hz, 1H), 3.86 (dd, J = 8.4, 4.5 Hz, 1H), 3.74 (s, 3H), 3.44 (q, J = 6.6 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.9, 152.3, 142.9, 141.9, 138.3, 137.1, 129.9, 129.0, 128.8, 128.79, 128.76, 127.4, 127.3, 125.7, 114.9, 114.5, 55.8, 53.0, 47.6.

HRMS (ESI, *m*/*z*) calcd. for $C_{25}H_{24}N_3O_2$ $[M+H]^+$: 398.1863, found: 398.1868.

4. Additional Information for Conditions Screening and Substrate Scope

Table S1. Optimization of reaction conditions[a]

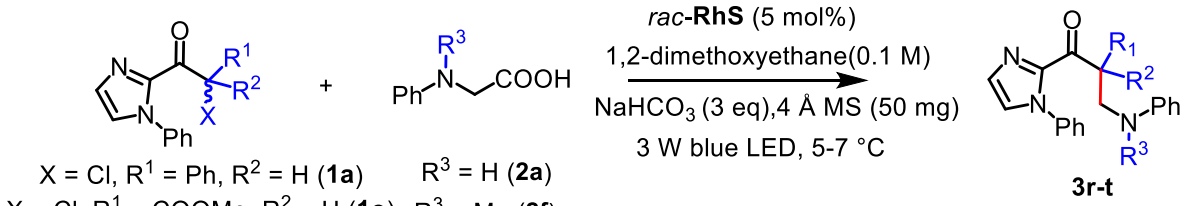


Entry	Substrate	Ratio (**1a**/**1b**:**2a**)	Base	Blue LED	Solvent (mL)	T (°C)	Yield (%)[b]	ee (%)[c]
1	**1a**	1:2	$NaHCO_3$	24 W	CH_2Cl_2	25	5	13
2	**1a**	1:2	$NaHCO_3$	24 W	$CHCl_3$	25	8	37
3	**1a**	1:2	$NaHCO_3$	24 W	Toluene	25	9	70
4	**1a**	1:2	$NaHCO_3$	24 W	Aceton	25	12	80
5	**1a**	1:2	$NaHCO_3$	24 W	Aceton	5-7	15	86
6	**1a**	1:2	$NaHCO_3$	24 W	Dioxan	5-7	10	87
7	**1a**	1:2	$NaHCO_3$	24 W	1,2-DME	5-7	20	86
8	**1a**	1:2	$NaHCO_3$	24 W	THF	5-7	20	94
9	**1a**	1:2	$NaHCO_3$	3 W	1,2-DME	5-7	26	96
10	**1a**	1:2	$NaHCO_3$	3 W	THF	5-7	12	90
11[d]	**1a**	1:2	$NaHCO_3$	3 W	1,2-DME	25	30	94
12[d]	**1a**	1:2	DIPEA	3 W	1,2-DME	25	0	-
13[d]	**1a**	1:2	2,6-Lutidine	3 W	1,2-DME	25	38	96
14[d]	**1a**	1:2	Na_2HPO_4	3 W	1,2-DME	25	24	90
15[d]	**1a**	1:2	Et_3N	3 W	1,2-DME	25	trace	-
16[d]	**1a**	1:2	Cs_2CO_3	3 W	1,2-DME	25	0	-
17[d]	**1a**	1:3	2,6-Lutidine	3 W	1,2-DME	25	52	95
18[d]	**1a**	1:4	2,6-Lutidine	3 W	1,2-DME	25	56	95
19[d]	**1a**	1:6	2,6-Lutidine	3 W	1,2-DME	25	30	94

20[d]	**1b**	1:4	2,6-Lutidine	3 W	1,2-DME	25	65[e]	85
21[d]	**1b**	1:4	DMAP	3 W	1,2-DME	25	0	84
22[d]	**1b**	1:4	K_3PO_4	3 W	1,2-DME	25	16	85
23[d]	**1b**	1:4	2,6-Lutidine	24 W	1,2-DME	25	60[e]	87
24[d]	**1b**	1:4	2,6-Lutidine	24 W	1,2-DME	5-7	64[e]	91
25[d]	**1b**	1:4	2,6-Lutidine	3 W	1,2-DME	5-7	67[e]	94
26[d]	**1b**	1:4	$NaHCO_3$	3 W	1,2-DME	5-7	72[e]	95

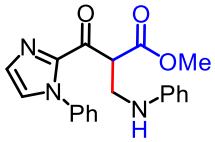
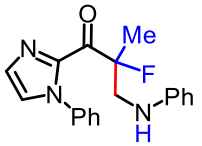
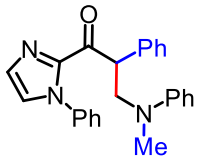
[a] Reaction conditions: **1a** or **1b** (0.1 mmol), **2a** (indicated amount) and Λ-**RhS** catalyst (5 mol%) in indicated solvent (1 mL, 0.1 M) were stirred at the indicated temperature for 14-24 h with irradiation of 24 W blue LED for 24-65 h with irradiation of 3 W blue LED under an atmosphere of nitrogen. [b] Determined by ^{1}H NMR of the crude products by using 1,1,2,2-tetrachloroethane as an internal standard. [c] Determined by HPLC analysis of crude main product on chiral stationary phase. [d] Reaction in presence of additional 4 Å MS (50 mg). [e] Isolated yield.

Table S2. Limitation of substrate scope[a]



X = Cl, R^1 = Ph, R^2 = H (**1a**) R^3 = H (**2a**)
X = Cl, R^1 = COOMe, R^2 = H (**1o**) R^3 = Me (**2f**)
X = Br, R^1 = Me, R^2 = F (**1p**)

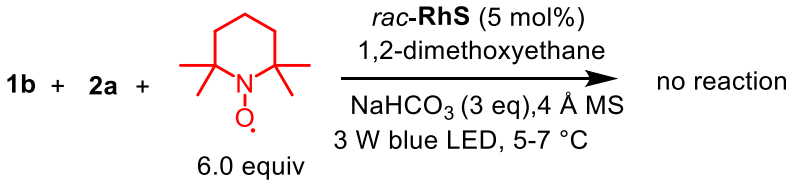
3r-t

Entry	Product	Yield (%)[b]
1	 (**3r**)	0
2	 (**3s**)	0
3	 (**3t**)[c]	38

[a] Reaction conditions: **1a**, **1o** or **1p** (0.1 mmol), **2a** or **2f** (0.4 mmol) and *rac*-**RhS** catalyst (5 mol%) in 1,2-dimethoxyethane (1 mL, 0.1 M) were stirred at 5-7 °C for 65 h with irradiation of 3 W blue LED under an atmosphere of nitrogen. [b] Isolated yield. [c] All spectroscopic data of **3t** are in agreement with our previous report.[6]

5. Mechanistic Studies

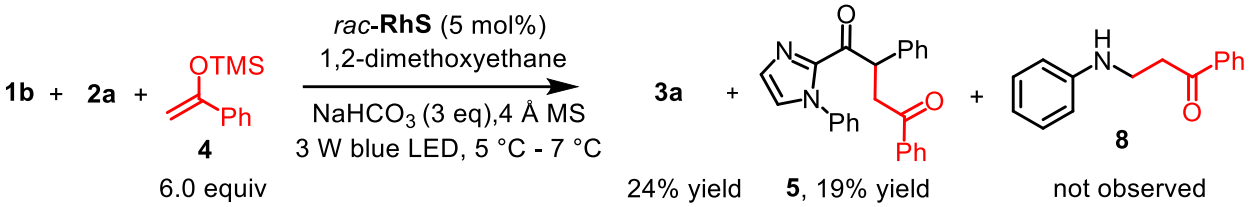
5.1 Trapping Experiment with TEMPO



Scheme S1. Trapping experiment with TEMPO.

According to the general procedure, 6.0 eq of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was added to the reaction mixture of **1b** and **2a**. The reaction mixture was stirred under an atmosphere of nitrogen for 65 h, and the reaction was totally blocked.

5.2 Trapping Experiment with Electron-Rich Alkene



Scheme S2. Trapping experiment with silyl enol ether.

According to the general procedure, 6.0 eq of trimethyl((1-phenylvinyl)oxy)silane was added to the reaction mixture of **1b** and **2a**. A mixture (22 mg) of **3a** and **5** with a ratio of 1:0.94 (see ^{1}H NMR spectra below) was isolated after stirring under an atmosphere of nitrogen under standard conditions for 65 h. Compound **8** was not detected after the reaction. The spectroscopic data of **5** are in agreement with our previous report.[7]

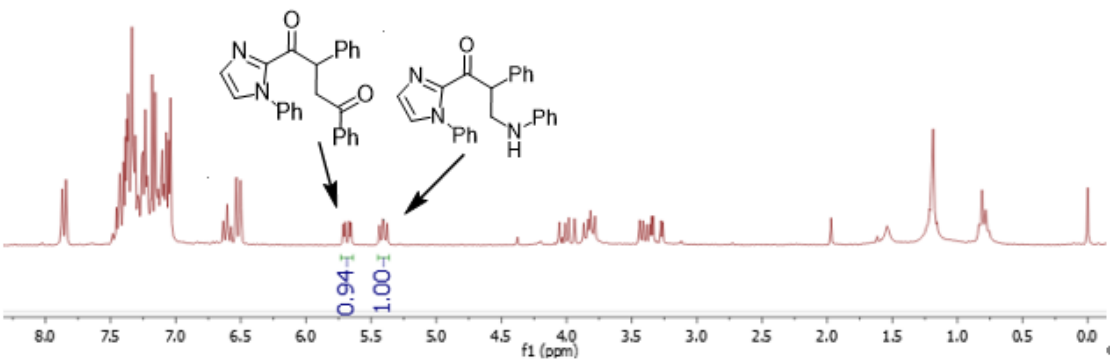
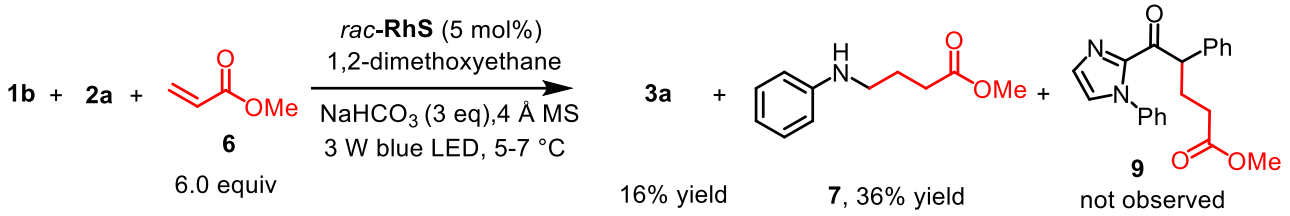


Figure S1. NMR spectra of the mixture of **3a** and **5**.

5.3 Trapping Experiment with Electron-Deficient Alkene



Scheme S3. Trapping experiment with methyl acrylate.

According to the general catalysis procedure, 6.0 eq of methyl acrylate was added to the reaction mixture of **1b** and **2a**. The product **3a** (16% yield) and compound **7** (36% yield) were isolated after stirring under an atmosphere of nitrogen under standard conditions for 65 h. Compound **9** was not observed. The spectroscopic data of **7** are in agreement with reported literature.[12]

5.4 EPR Experiments

EPR spectra were recorded at room temperature using DMPO (5,5-dimethyl-1-pyrroline *N*-oxide) as a free radical spin trapping agent. As shown in Figure S2, according to the general catalysis procedure, the reaction of **1b** and **2a** was stirred under standard conditions for 60 min. Then, a portion of the homogeneous mixture was taken out to an EPR tube and measured by EPR (9.17965 GHz; Mod. Frequency = 100 kHz; Mod. Ampl. = 0.12 mT). Two signals (signal A: g = 2.0062, A(N) = 1.46 mT, A(H) = 1.31 mT; signal B: g = 2.0062, A(N) = 1.55 mT, A(H) = 2.13 mT) were observed, which suggests that the formation of two α-carbon radicals are involved in the transformation.

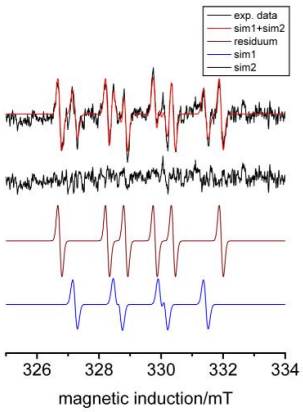


Figure S2. EPR experiments (X band, r.t.). After 60 min of irradiation, a portion of the reaction mixture was added to DMPO solution and then measured by EPR.

5.5 Quantum Yield Measurement

The quantum yield was measured following reported procedures.[13] A 455 nm LED was employed as light source. A powermeter was used as detector. The measurement was accomplished in a dark room with a 1.1 W red LEDs. The radical cross-coupling reaction was chosen as model reaction.

Step 1: The radiant power of light transmitted by the cuvette with a blank solution was measured as P_{blank} = 68.09 mW.

Step 2: The reaction mixture of **1b** (59.2 mg, 0.2 mmol), **2a** (120.96 mg, 4.0 equiv), *rac*-**RhS** (8.6 mg, 5 mol%) and $NaHCO_3$ (50.4 mg, 3.0 equiv) in 1,2-dimethoxyethane (2.0 mL, 0.1 M) was filled into a fluorescence cuvette with a stirring bar and septum and degassed by bubbling with nitrogen (15 min). Then, the cuvette was put into the setup and illuminated with the 455 nm LED. The transmitted radiant power was P_{start} = 3.72 mW was noted. The transmitted radiant power was monitored during the irradiation and P_{end} = 1.04 mW was noted. The transmitted radiant power was determined as P_{sample} = 2.38 mW.

Step 3: After illumination for 5 hours (t = 5 × 3600 s), the amount of the formed **3a** was determined as 1.21×10^{-5} mol ($n_{product}$) by ^{1}H NMR.

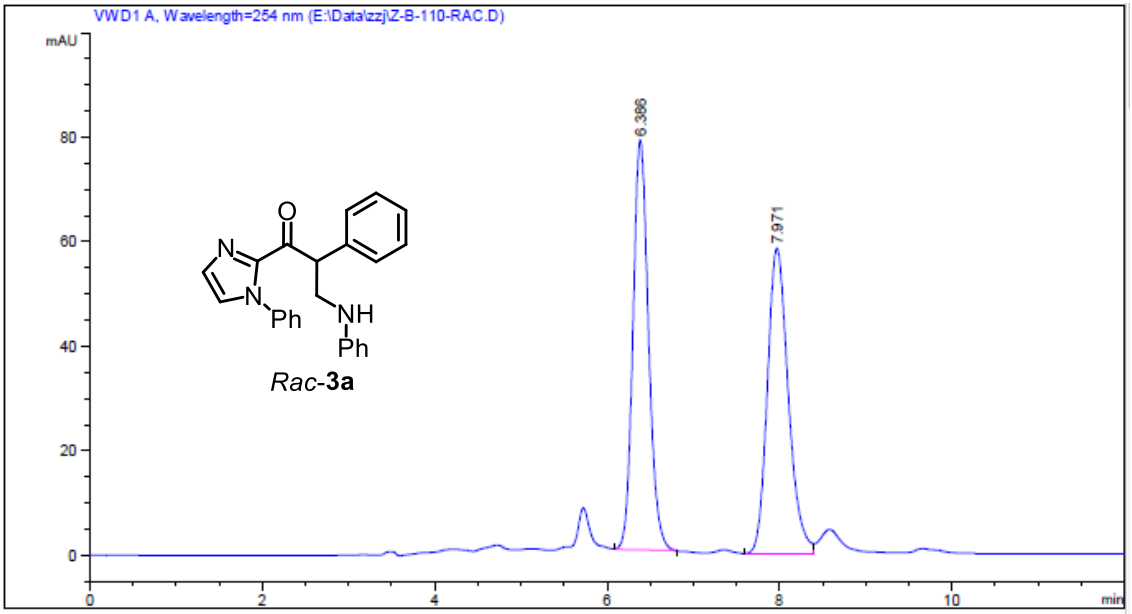
Step 4: The overall quantum yield can be calculated as following:

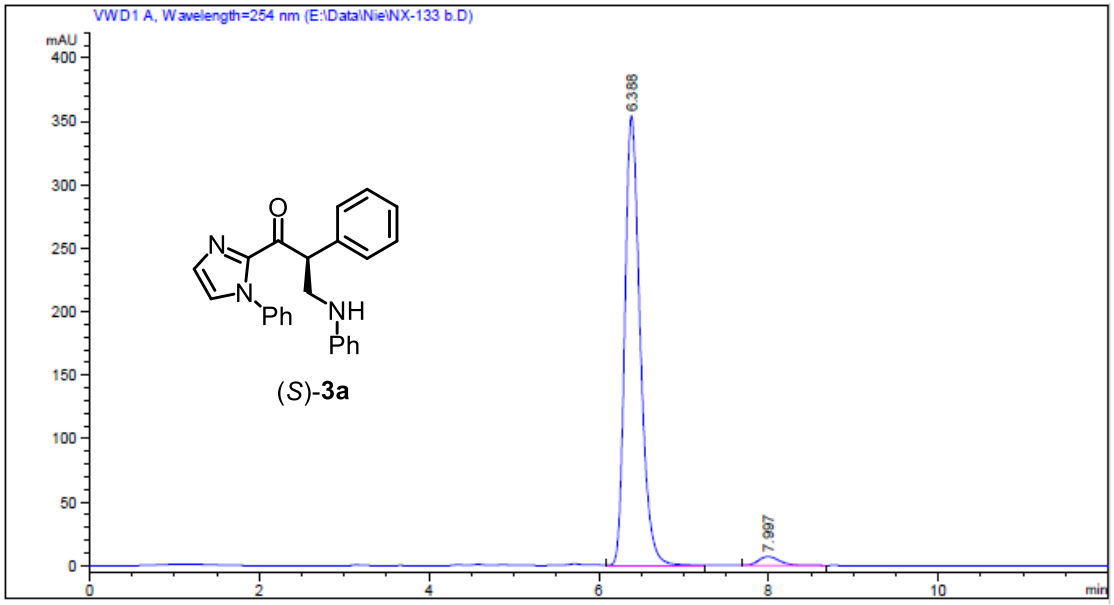
$$Quantum\ Yield = \frac{N_{product}}{N_{photo}} = \frac{N_A \times n_{product}}{\frac{P_{absorbed} \times t}{\frac{h \times c}{\lambda}}} = \frac{h \times c \times N_A \times n_{product}}{(P_{blank} - P_{sample}) \times t \times \lambda}$$

$$= \frac{6.626 \times 10^{-34} Js \times 2.998 \times 10^{8} ms^{-1} \times 6.022 \times 10^{23} mol^{-1} \times 1.21 \times 10^{-5}\ mol}{(68.09 - 2.38) \times 10^{-3} Js^{-1} \times 5 \times 3600\text{s} \times 455 \times 10^{-9} m} = 0.0027$$

where $N_{product}$ is the number of product **3a** formed; N_{photon} is the number of photons absorbed; N_A is Avogadro's constant; $n_{product}$ is the molar amount of product **3a** formed; $P_{absorbed}$ is the radiant power absorbed; t is the irradiation time; h is the Planck's constant; c is the speed of light; λ is the wavelength of light source, P_{blank} is the radiant power transmitted by the cuvette with a blank solution; P_{sample} is the radiant power transmitted by the cuvette with reaction mixture.

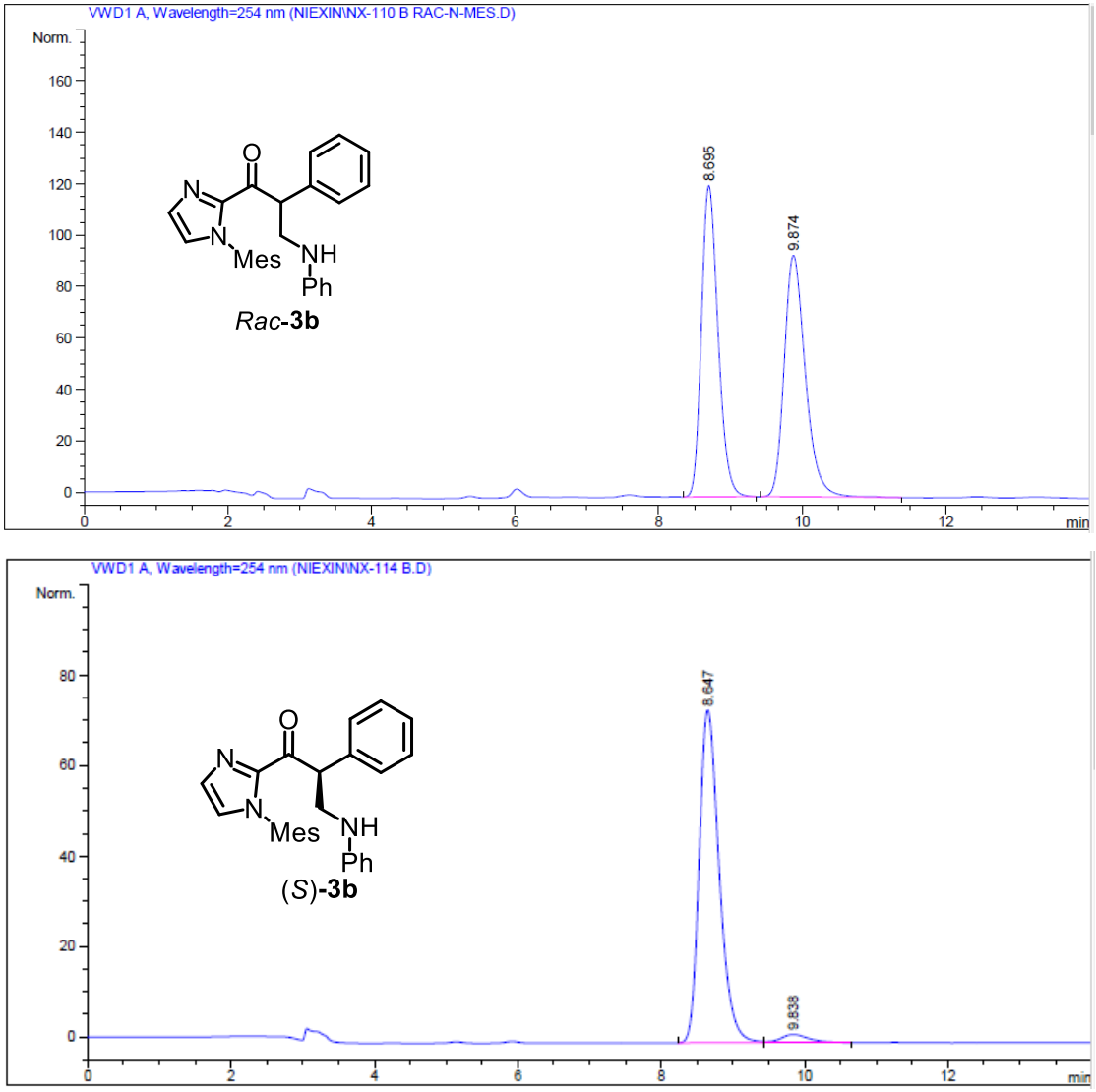
6. HPLC Traces of the Products





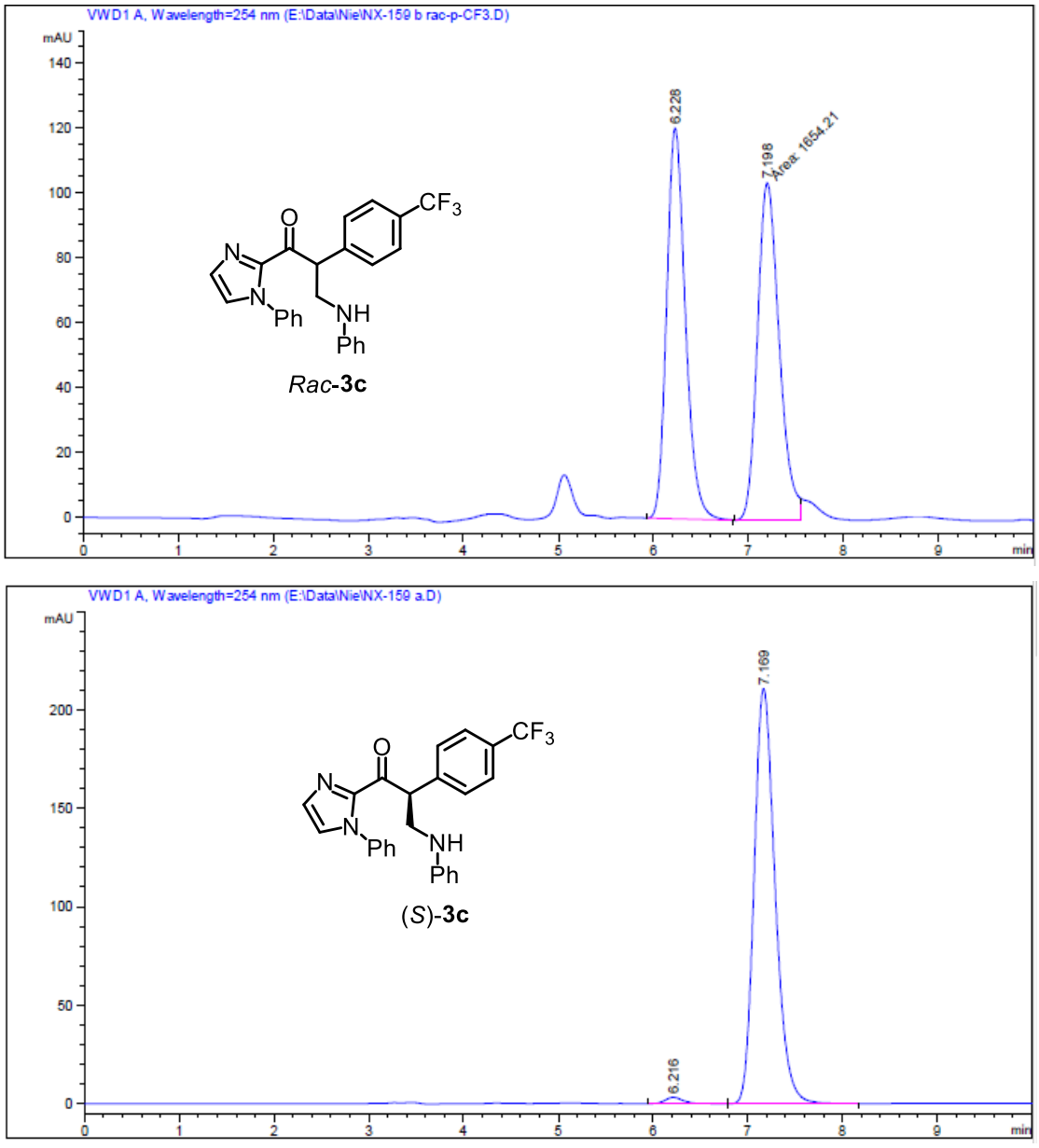
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.388	MM R	0.2092	4442.37402	353.92258	97.4178
2	7.997	BB	0.2601	117.75093	6.97075	2.5822

Figure S3. HPLC traces of *rac*-**3a** and (*S*)-**3a** (95% ee).



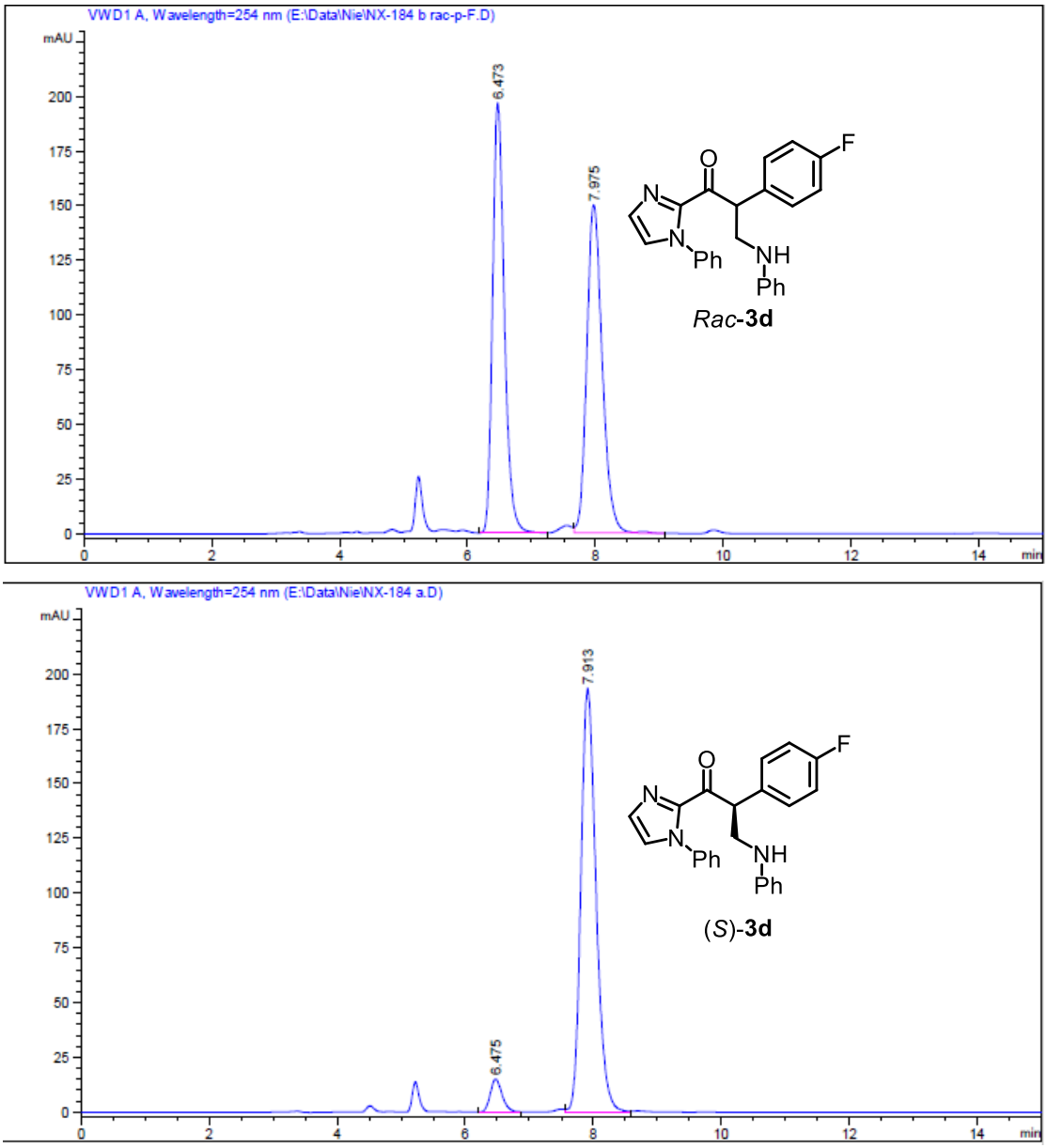
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.647	BB	0.2976	1426.27832	73.54783	96.5646
2	9.838	BB	0.4129	50.74226	1.82660	3.4354

Figure S4. HPLC traces of *rac*-**3c** and (*S*)-**3c** (93% ee).



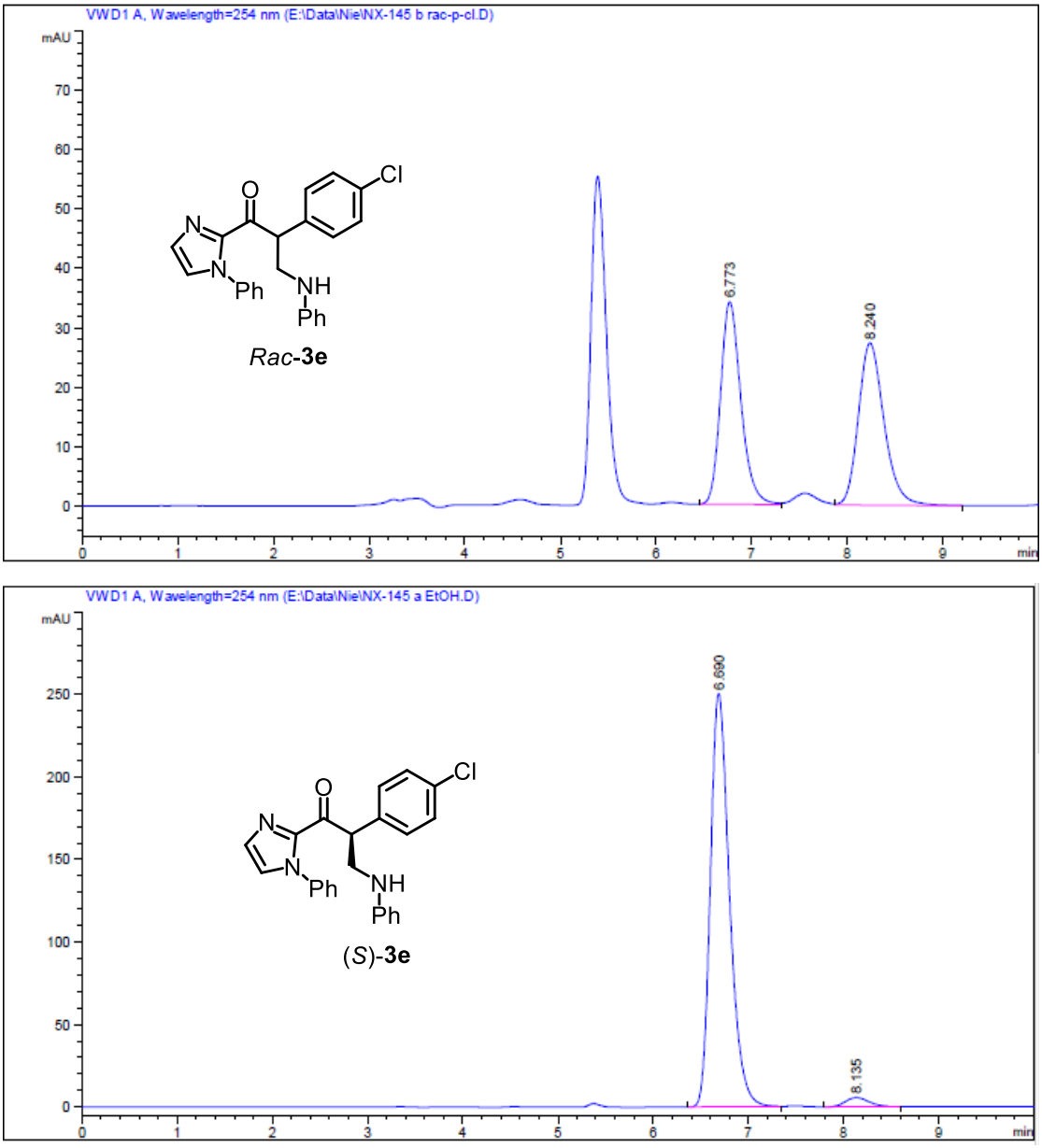
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.216	BB	0.2017	42.94460	3.21744	1.3064
2	7.169	BB	0.2377	3244.29956	210.66508	98.6936

Figure S5. HPLC traces of *rac*-**3c** and (*S*)-**3c** (97% ee).



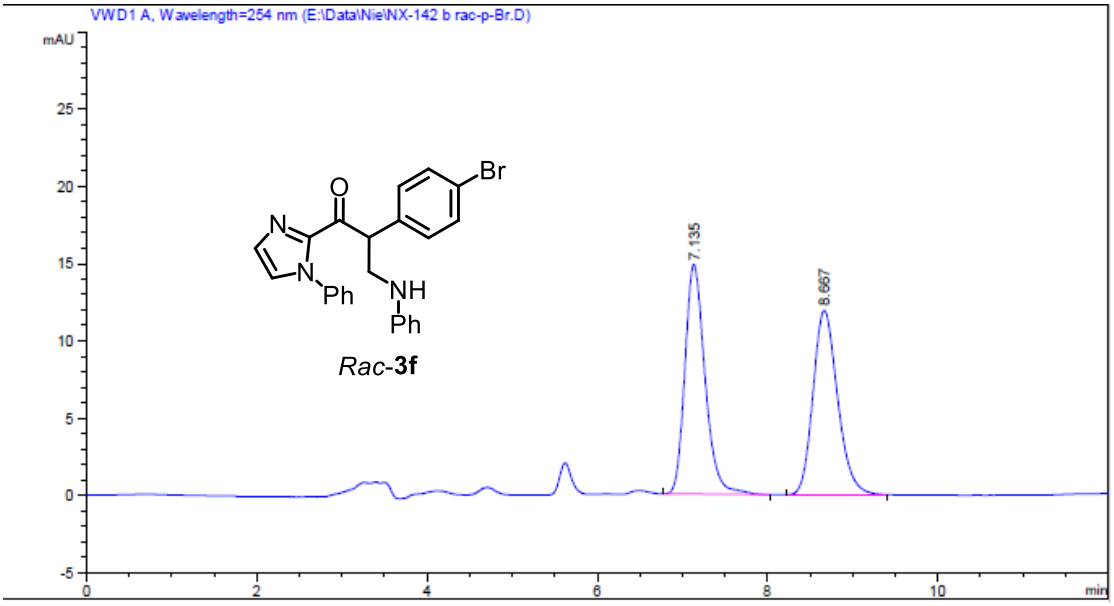
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.475	MF R	0.2169	195.74051	15.04173	5.8148
2	7.913	MF R	0.2734	3170.52637	193.31015	94.1852

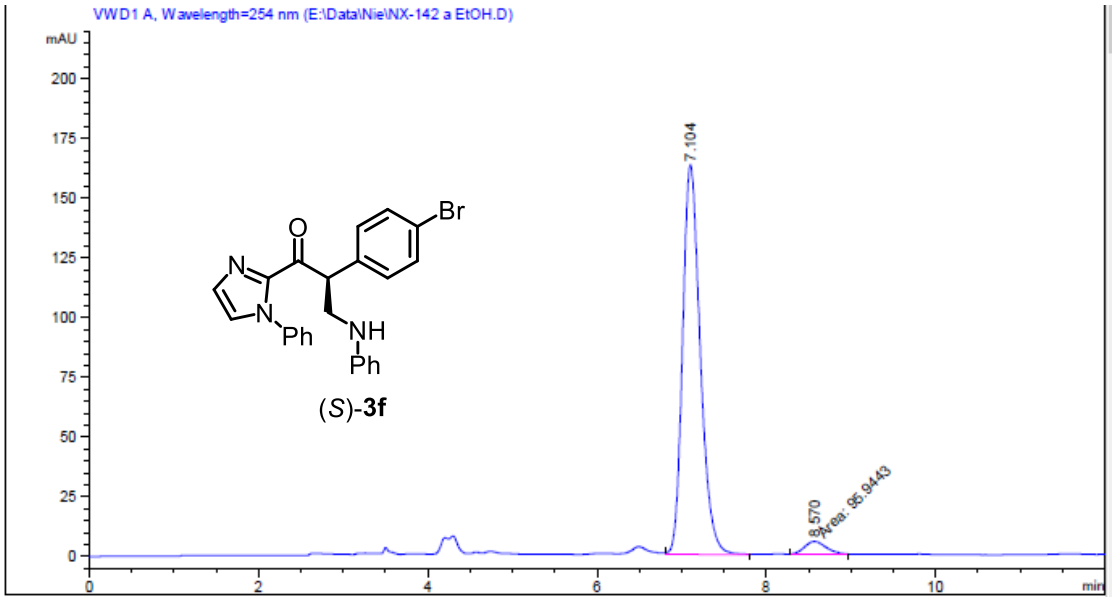
Figure S6. HPLC traces of *rac*-**3d** and (*S*)-**3d** (88% ee).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.690	BB	0.2125	3486.81934	250.36792	97.3443
2	8.135	BB	0.2634	95.12489	5.59250	2.6557

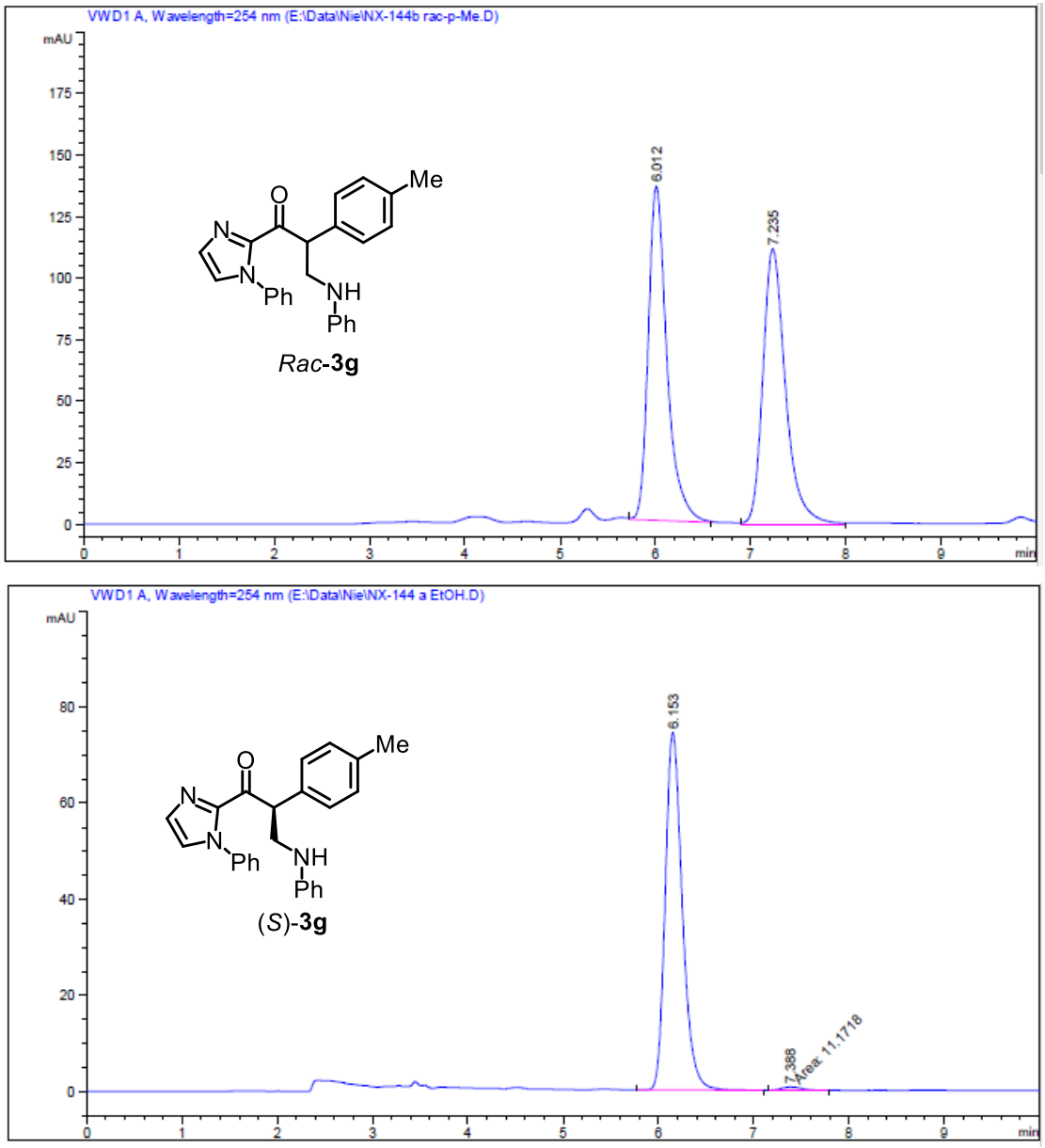
Figure S7. HPLC traces of *rac*-**3e** and (*S*)-**3e** (95% ee).





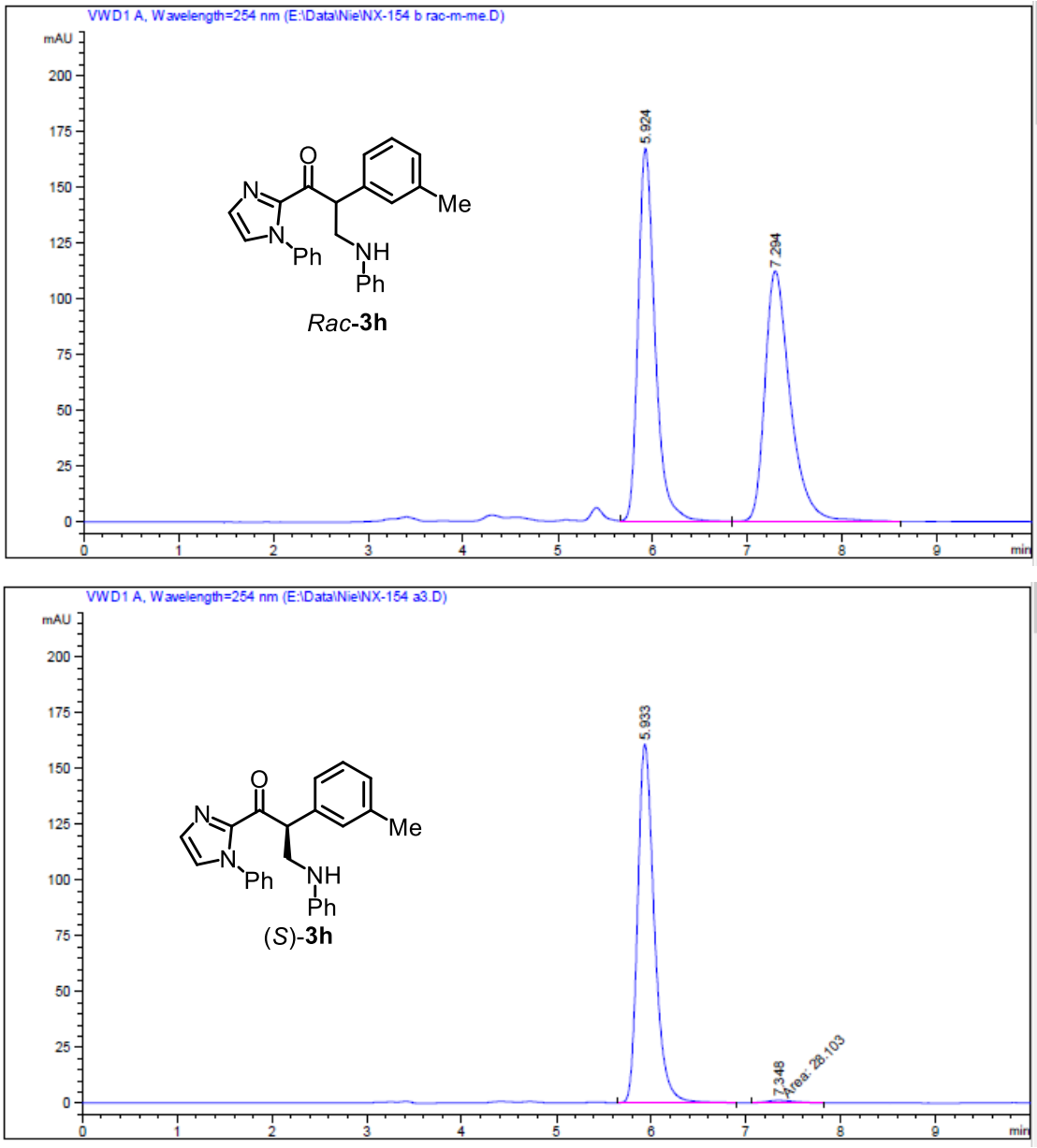
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.104	MM R	0.2409	2357.40039	163.10808	96.0892
2	8.570	MM	0.2993	95.94426	5.34317	3.9108

Figure S8. HPLC traces of *rac*-**3f** and (*S*)-**3f** (92% ee).



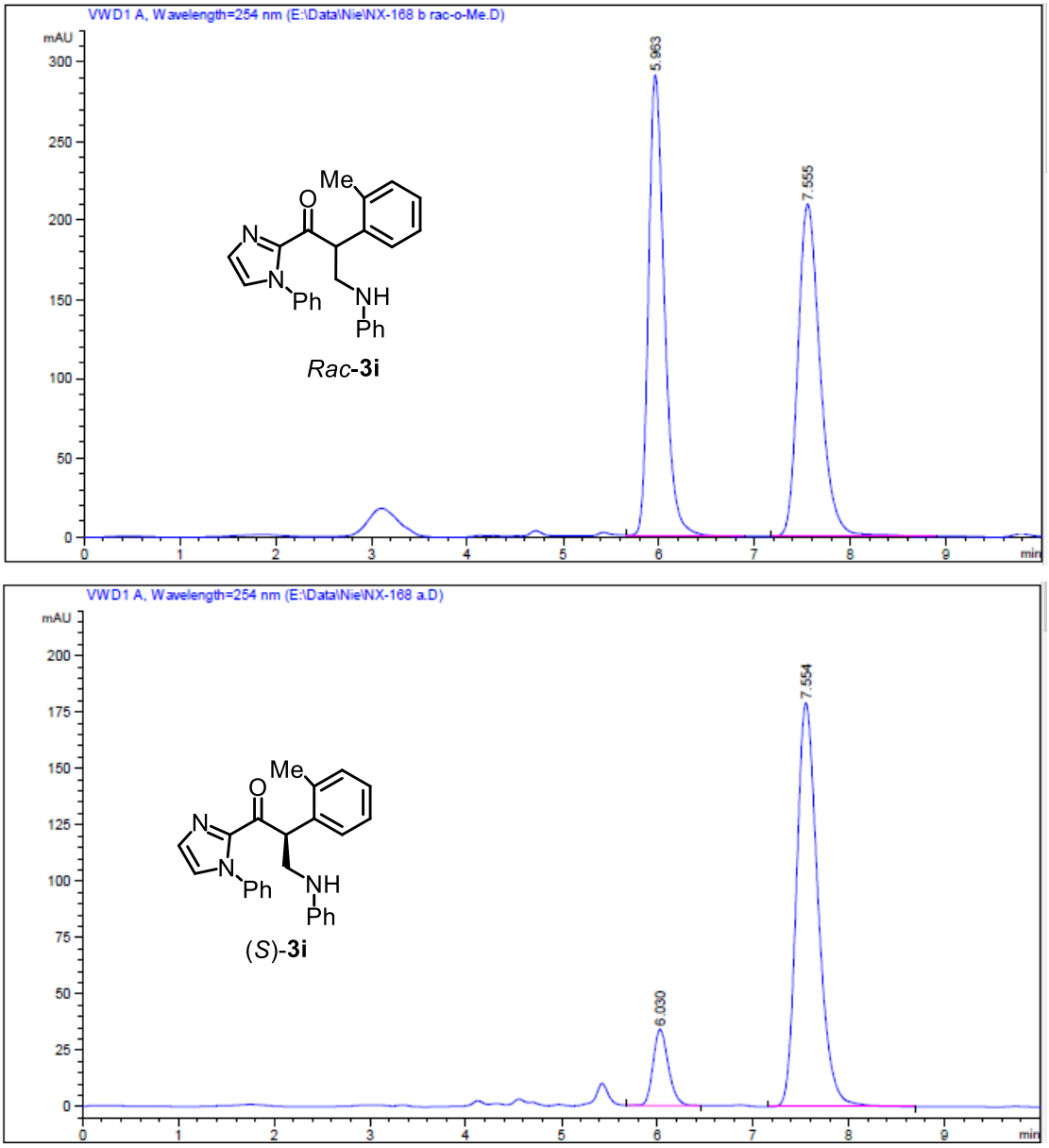
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.153	BB	0.1914	926.54187	74.34441	98.8086
2	7.388	MM	0.2569	11.17183	7.24777e-1	1.1914

Figure S9. HPLC traces of *rac*-**3g** and (*S*)-**3g** (98% ee).



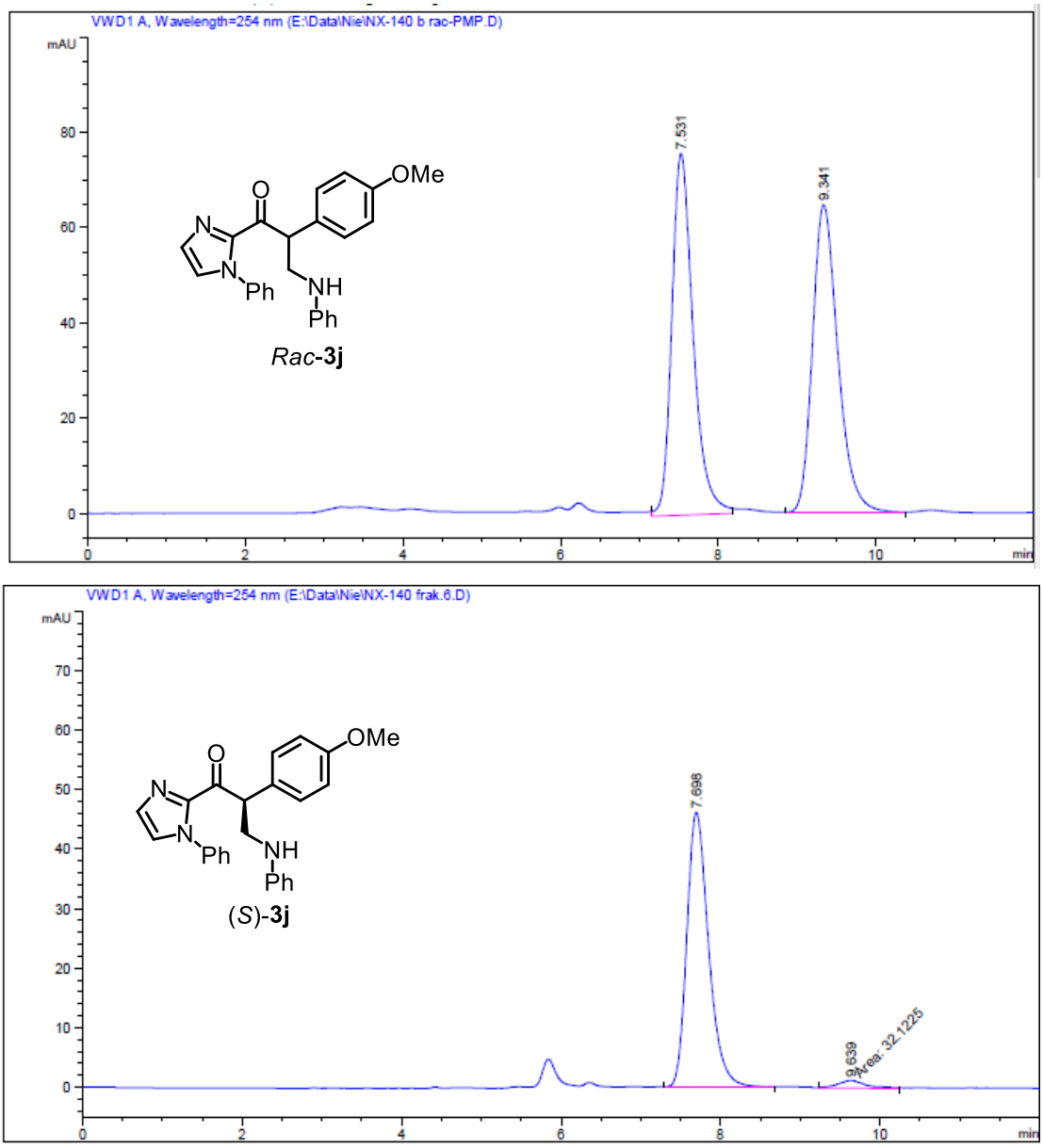
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.933	BB	0.1851	1957.80261	160.78119	98.5849
2	7.348	MM	0.3725	28.10295	1.25753	1.4151

Figure S10. HPLC traces of *rac*-**3h** and (*S*)-**3h** (97% ee).



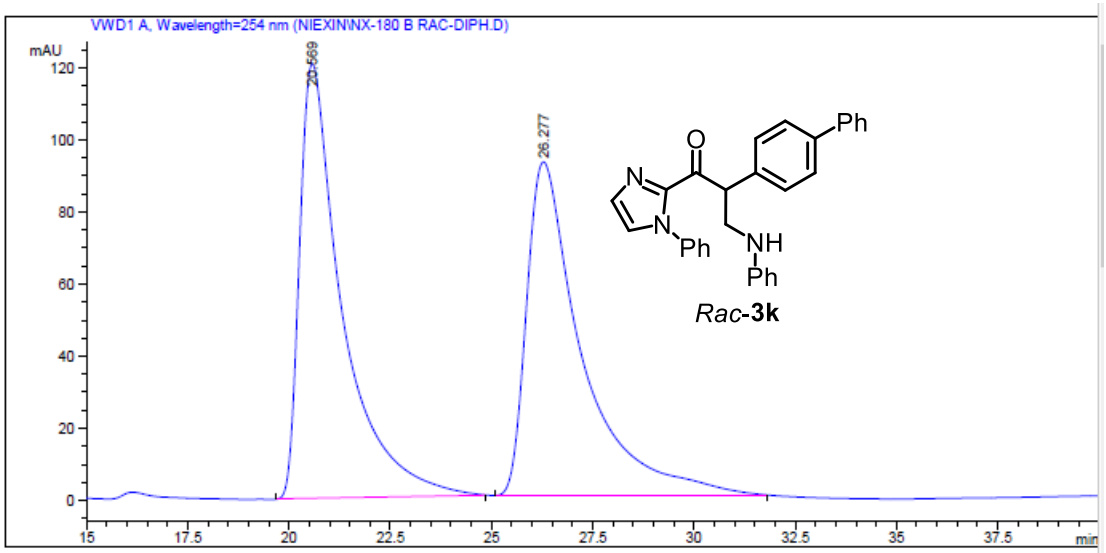
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.030	BB	0.1700	372.17117	33.65832	11.7596
2	7.554	BB	0.2389	2792.66089	179.09523	88.2404

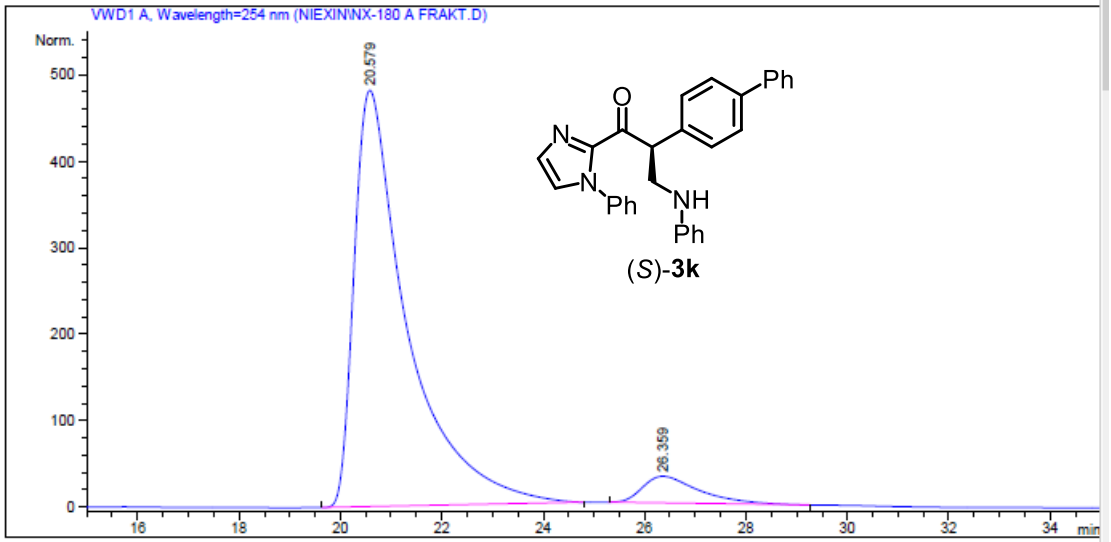
Figure S11. HPLC traces of *rac*-**3i** and (*S*)-**3i** (76% ee).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.698	BB	0.2897	871.50415	46.07123	96.4452
2	9.639	MM	0.4173	32.12254	1.28281	3.5548

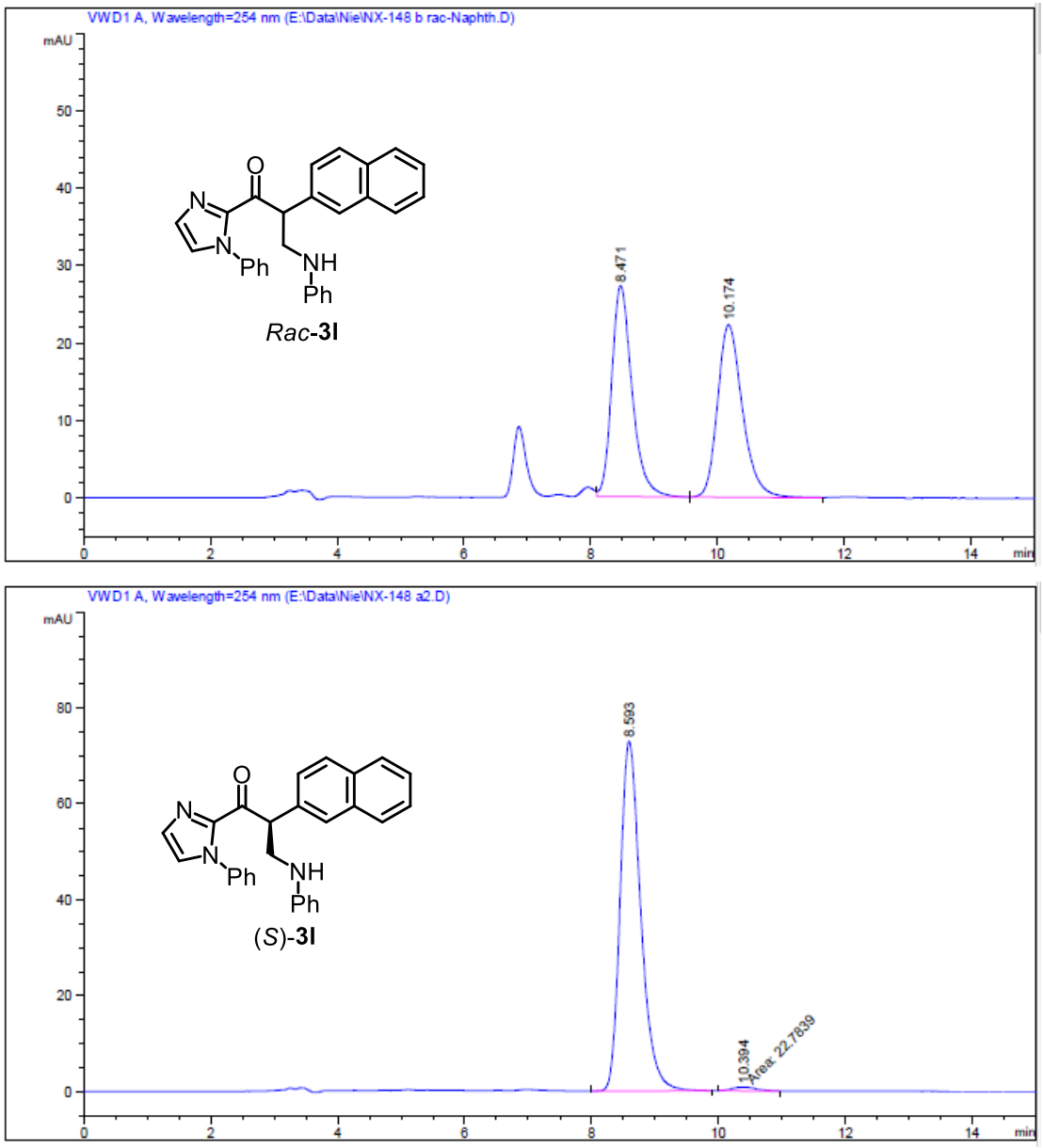
Figure S12. HPLC traces of *rac*-**3j** and (*S*)-**3j** (93% ee).





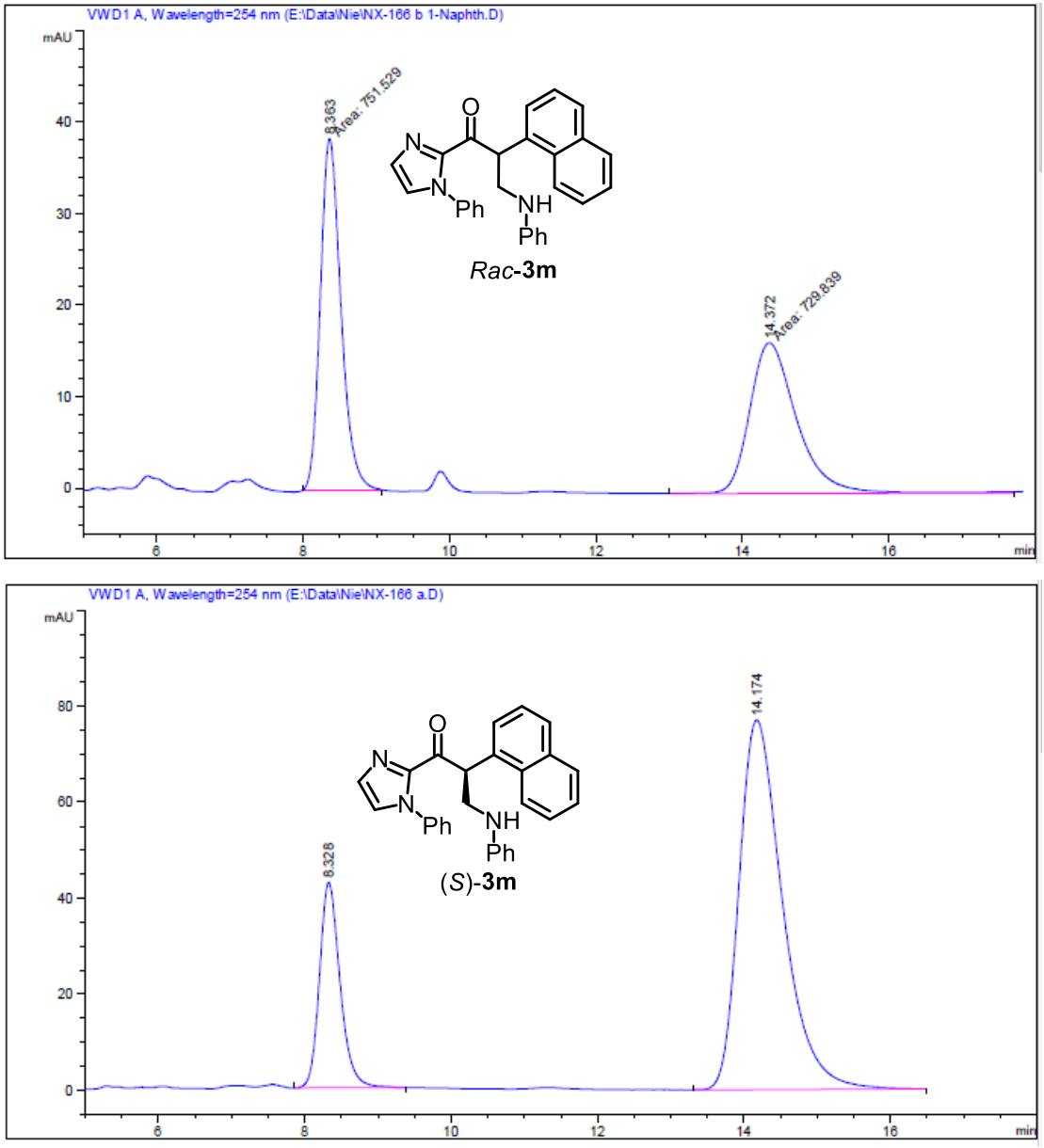
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.579	BB	1.0434	3.50008e4	481.39615	93.5818
2	26.359	BB	1.1384	2400.48047	30.83120	6.4182

Figure S13. HPLC traces of *rac*-**3k** and (*S*)-**3k** (87% ee).



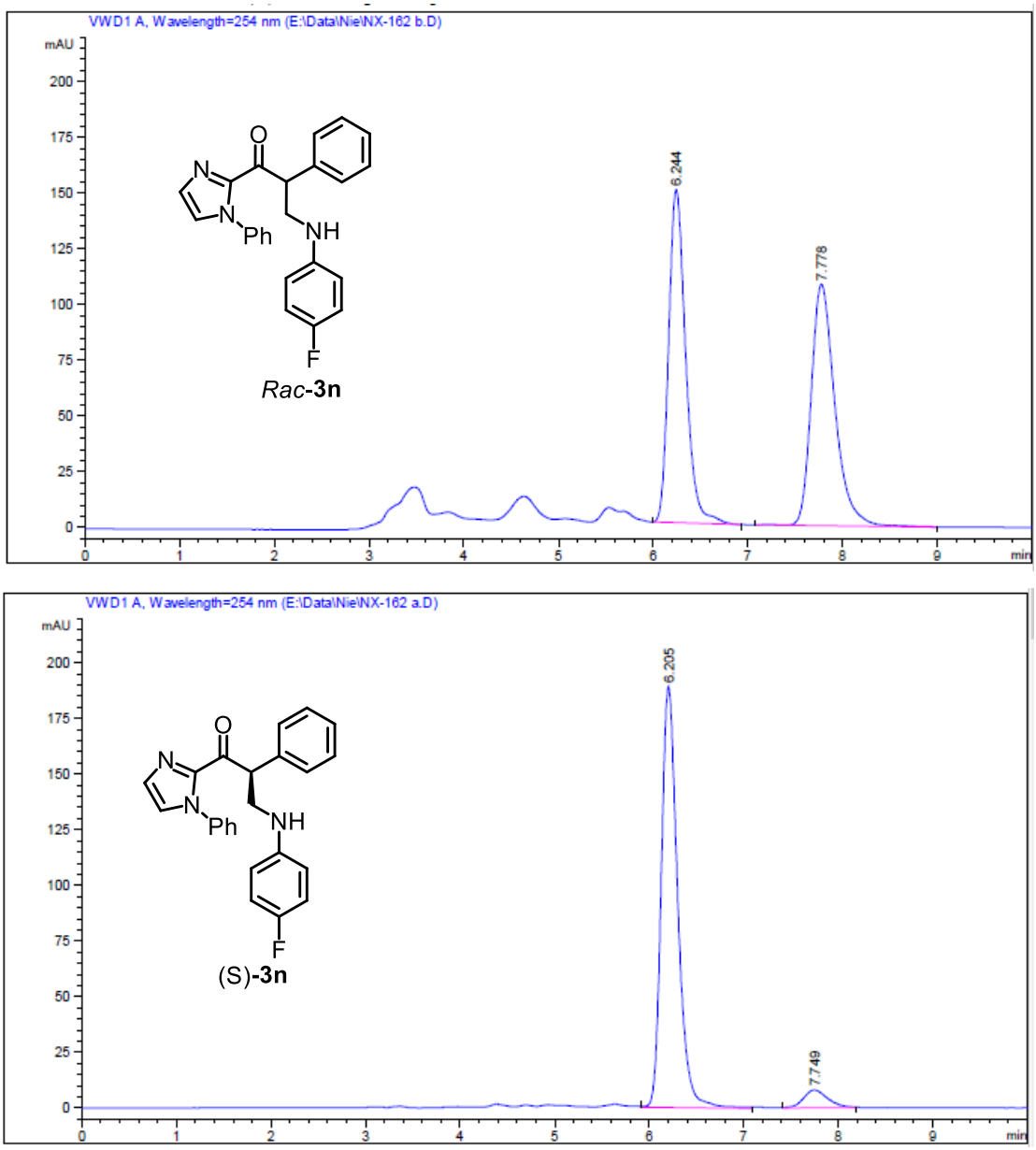
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.593	BB	0.3456	1647.15759	72.89755	98.6356
2	10.394	MM	0.4652	22.78393	8.16281e-1	1.3644

Figure S14. HPLC traces of *rac*-**3l** and (*S*)-**3l** (97% ee).



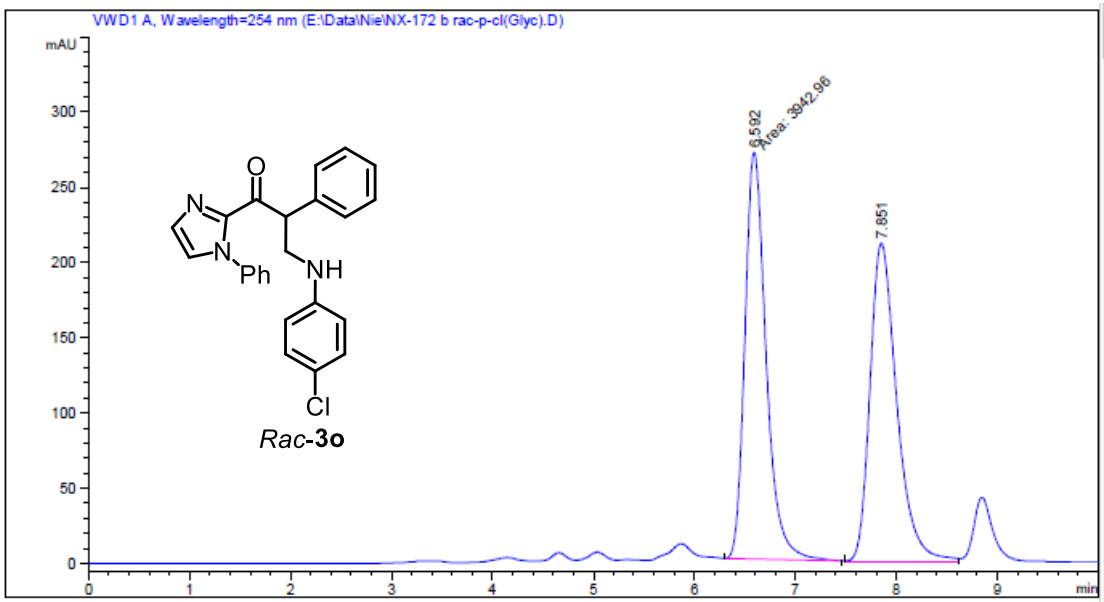
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.328	BB	0.2983	837.61029	42.79949	20.8428
2	14.174	BBA	0.6261	3181.09399	76.98032	79.1572

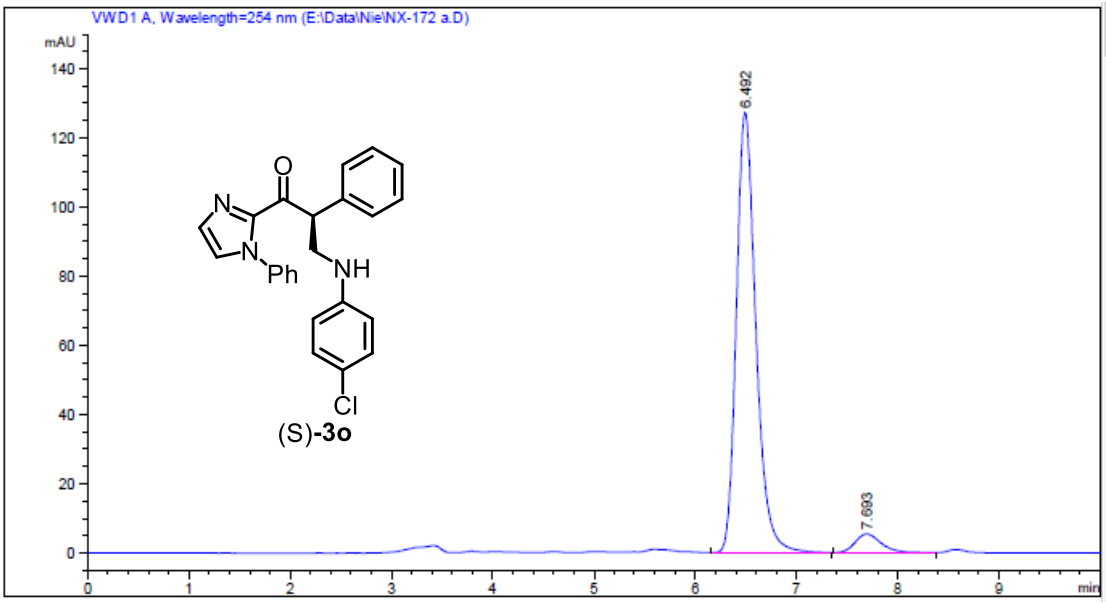
Figure S15. HPLC traces of *rac*-**3m** and (*S*)-**3m** (58% ee).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.205	MM R	0.2005	2274.92334	189.14212	94.0027
2	7.749	MM R	0.3002	145.13916	8.05854	5.9973

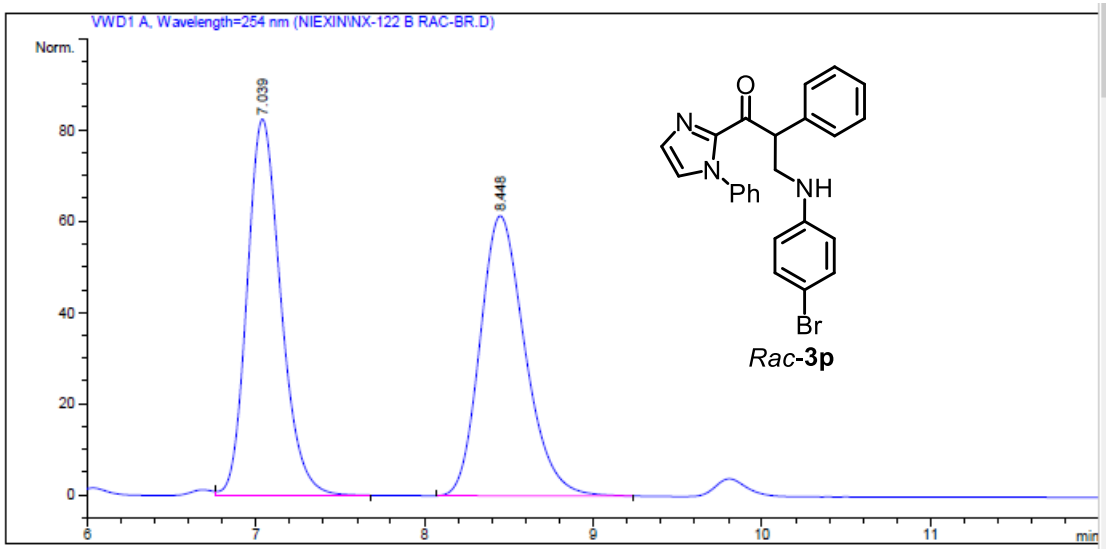
Figure S16. HPLC traces of *rac*-**3n** and (*S*)-**3n** (88% ee).

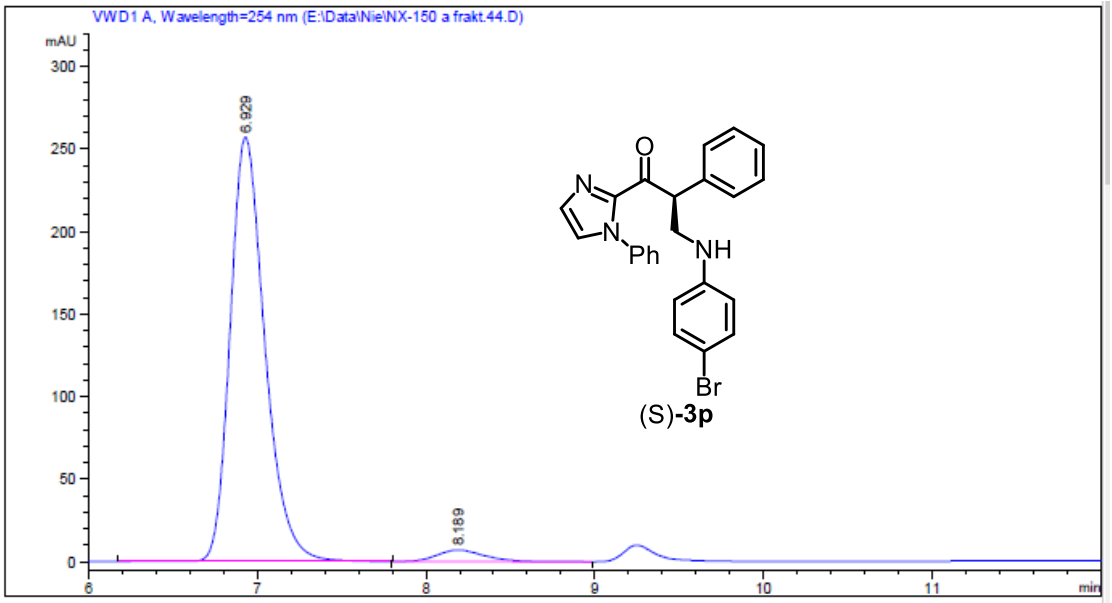




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.492	BB	0.2044	1705.70178	127.23689	94.7439
2	7.693	BB	0.2694	94.62714	5.34920	5.2561

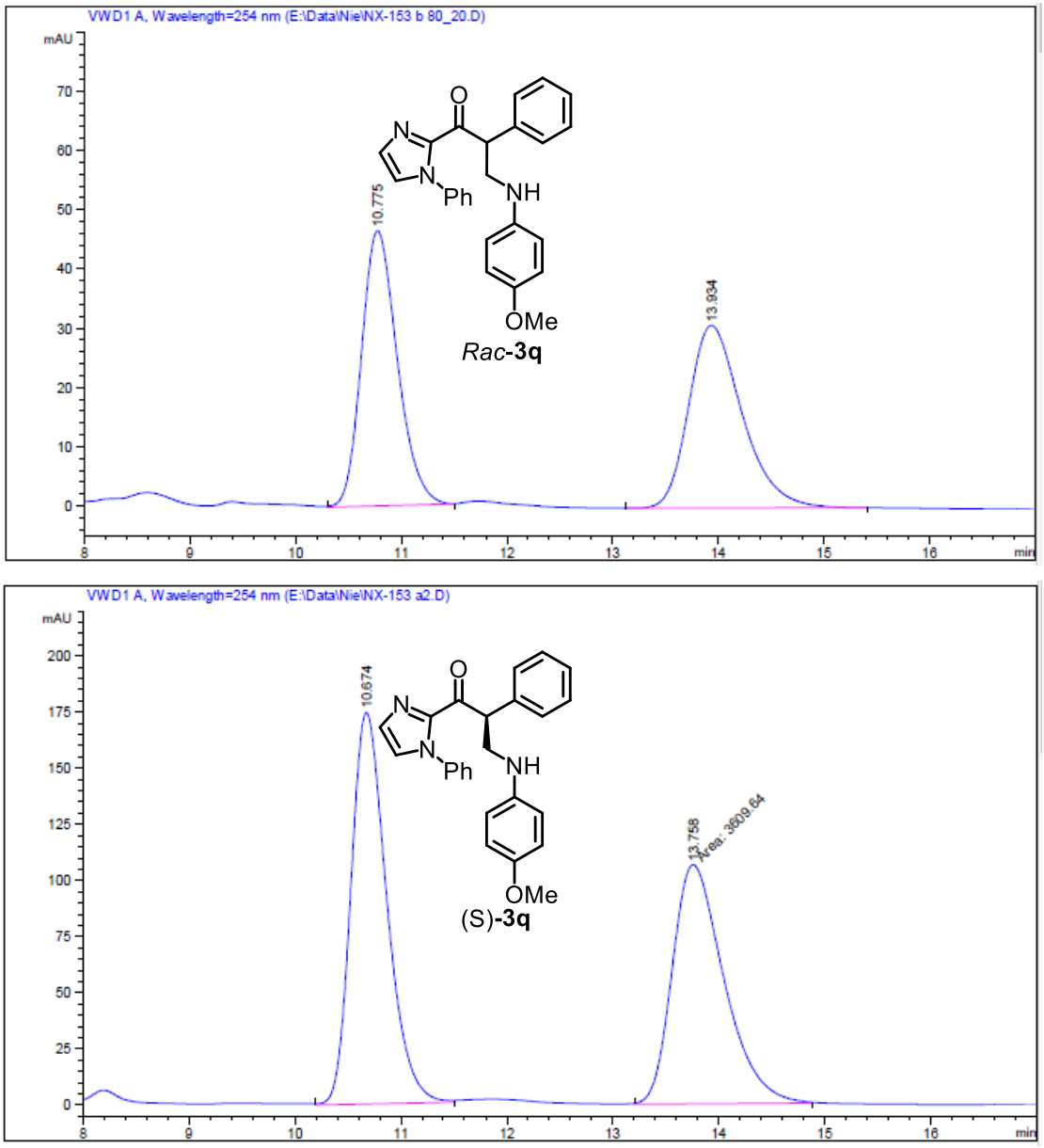
Figure S17. HPLC traces of *rac*-**3o** and (*S*)-**3o** (90% ee).





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.929	VB R	0.2188	3671.90063	256.87949	96.4917
2	8.189	BB	0.2977	133.50645	6.87009	3.5083

Figure S18. HPLC traces of *rac*-**3p** and (*S*)-**3p** (93% ee).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.674	MM R	0.3527	4084.23950	174.38588	53.0843
2	13.758	MM	0.5649	3609.64185	106.49924	46.9157

Figure S19. HPLC traces of *rac*-**3q** and (*S*)-**3q** (93% ee).

7. Single Crystal X-Ray Diffraction

Single crystals of **3e** were obtained by slow diffusion from a solution of **3e** (5 mg) in CH_2Cl_2 layered with 2-propanol at room temperature for several days.

Crystal data and details of the structure determination for **3e** are presented in Table S3. X-Ray data was collected with an STOE STADIVARI diffractometer equipped with CuK_a radiation, a graded multilayer mirror monochromator (l = 1.54186 Å) and a DECTRIS PILATUS 300K detector using an oil-coated shock-cooled crystal at 100(2) K. Absorption effects were corrected semi-empirical using multi scanned reflexions (STOE LANA, absorption correction by scaling of reflection intensities.). Cell constants were refined using 15602 of observed reflections of the data collection. The structure was solved by direct methods by using the program XT V2014/1 (Bruker AXS Inc., 2014) and refined by full-matrix least squares procedures on F^2 using SHELXL-2018/3 (Sheldrick, 2018). The non-hydrogen atoms have been refined anisotropically, carbon bonded hydrogen atoms were included at calculated positions and refined using the 'riding model' with isotropic temperature factors at 1.2 times (for CH_3 groups 1.5 times) that of the preceding carbon atom. CH_3 groups were allowed to rotate about the bond to their next atom to fit the electron density. Nitrogen bonded hydrogen atoms were located and allowed to refine isotropically. The Flack parameter was refined to 0.032(14).

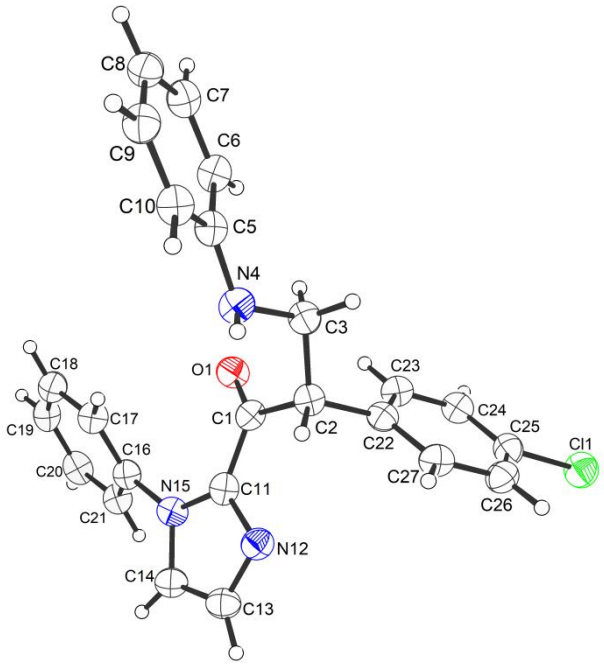


Figure S20. Crystal structure of **3e**.

Table S3. Crystal data and structure refinement for **3e**.

Crystal data		
Identification code	NX145a	
Habitus, colour	plate, colourless	
Crystal size	0.14 x 0.13 x 0.02 mm^3	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	Z = 4
Unit cell dimensions	a = 5.9802(2) Å	□= 90°.
	b = 13.6922(4) Å	□= 90°.
	c = 23.8833(9) Å	□ = 90°.
Volume	1955.61(11) $Å^3$	
Cell determination	15602 peaks with Theta 3.7 to 75.8°.	
Empirical formula	C_{24} H_{20} Cl N_3 O	
Moiety formula	C_{24} H_{20} Cl N_3 O	
Formula weight	401.88	
Density (calculated)	1.365 Mg/m^3	
Absorption coefficient	1.889 mm^{-1}	
F(000)	840	
Data collection:		
Diffractometer type	STOE STADIVARI	
Wavelength	1.54186 Å	
Temperature	100(2) K	
Theta range for data collection	3.721 to 75.756°.	
Index ranges	-7<=h<=7, -16<=k<=9, -29<=l<=27	
Data collection software	X-Area Pilatus3_SV 1.31.127.0 (STOE, 2016)[14]	
Cell refinement software	X-Area Recipe 1.33.0.0 (STOE, 2015)[15]	
Data reduction software	X-Area Integrate 1.71.0.0 (STOE, 2016)[16]	
	X-Area LANA 1.68.2.0 (STOE, 2016)[17]	
Solution and refinement:		
Reflections collected	19851	
Independent reflections	4011 [R(int) = 0.0684]	
Completeness to theta = 67.686°	99.7 %	
Observed reflections	3447[I > 2σ(I)]	
Reflections used for refinement	4011	
Absorption correction	Semi-empirical from equivalents[17]	
Max. and min. transmission	0.7635 and 0.2699	
Flack parameter (absolute struct.)	0.032(14)[18]	
Largest diff. peak and hole	0.244 and -0.289 e.$Å^{-3}$	
Solution	intrinsic phases[19]	
Refinement	Full-matrix least-squares on F^2[20]	
Treatment of hydrogen atoms	CH calculated, constr. , NH located, isotropic ref.	
Programs used	XT V2014/1 (Bruker AXS Inc., 2014)[19]	
	SHELXL-2018/3 (Sheldrick, 2018)[20]	
	DIAMOND (Crystal Impact)[21]	
	ShelXle (Hübschle, Sheldrick, Dittrich, 2011)[22]	
Data / restraints / parameters	4011 / 0 / 266	
Goodness-of-fit on F^2	1.007	

R index (all data)	wR2 = 0.1290
R index conventional [I>2sigma(I)]	R1 = 0.0497

8. NMR Spectra

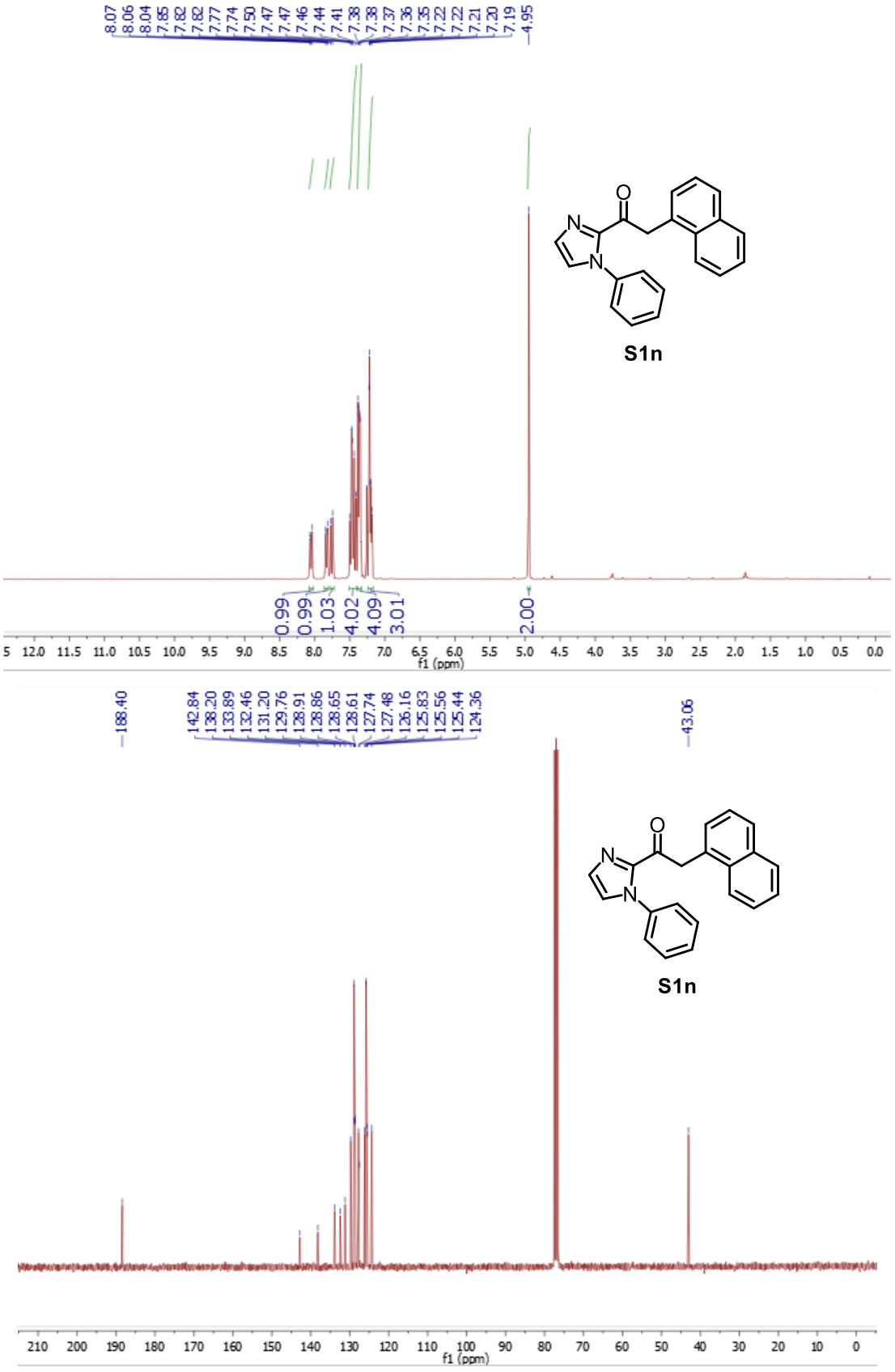


Figure S21. ^{1}H NMR and ^{13}C NMR spectra of **S1n** in $CDCl_3$.

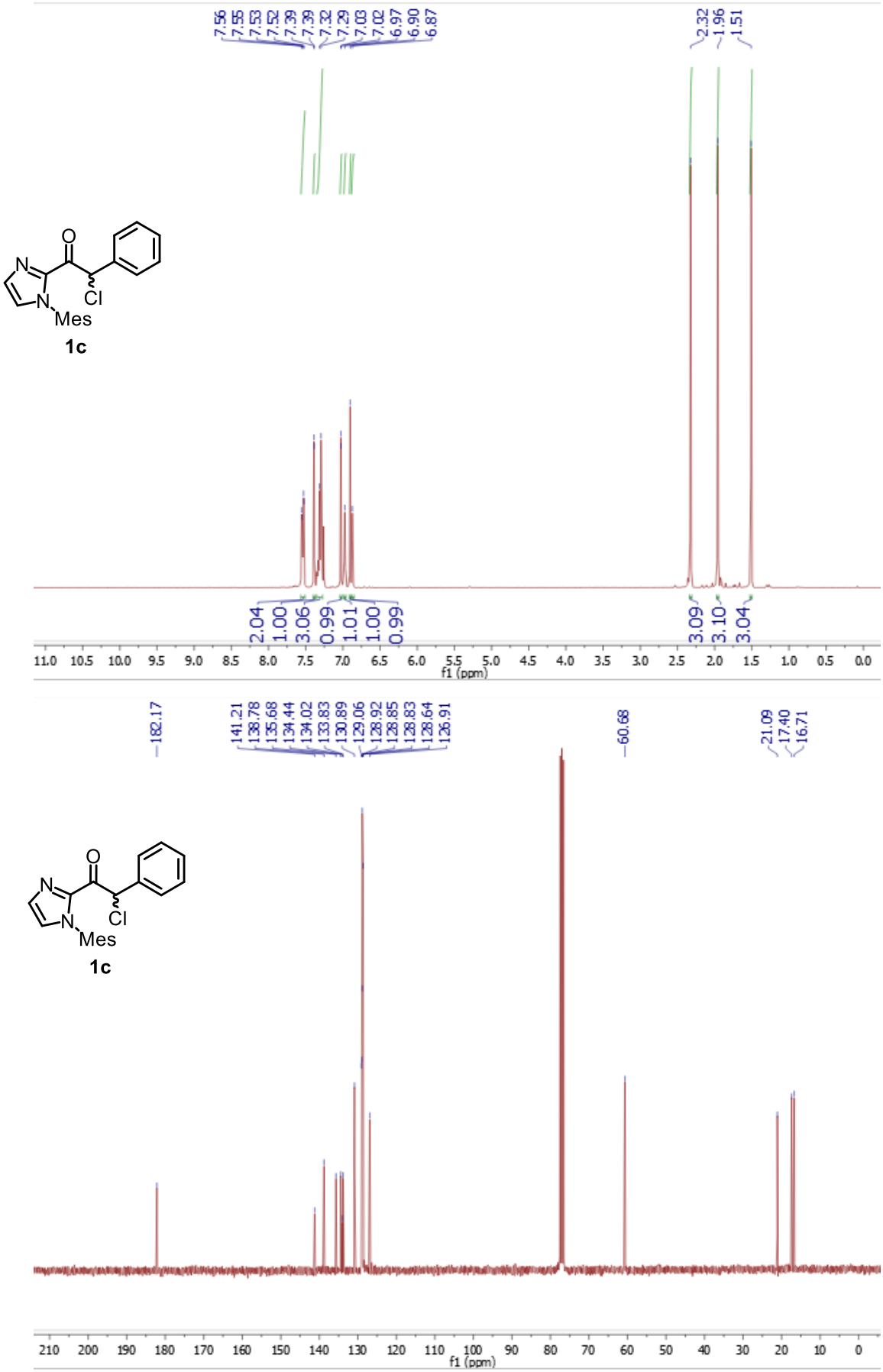
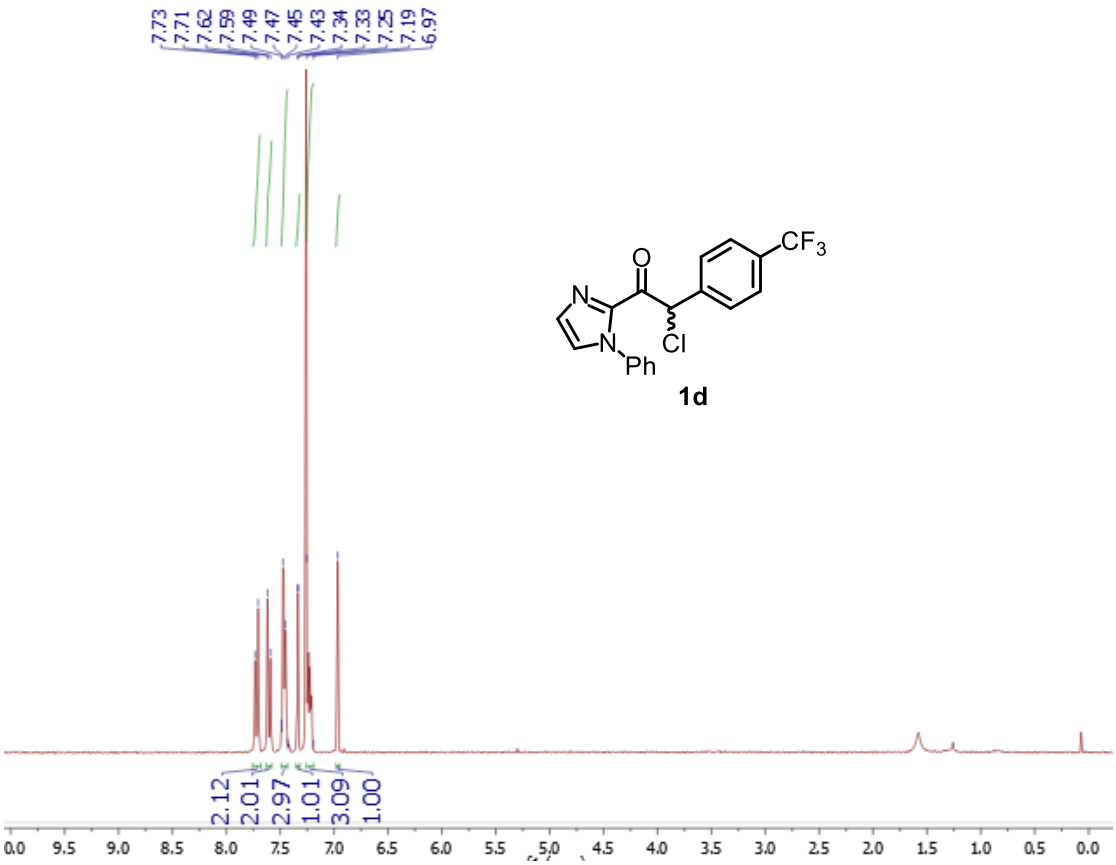
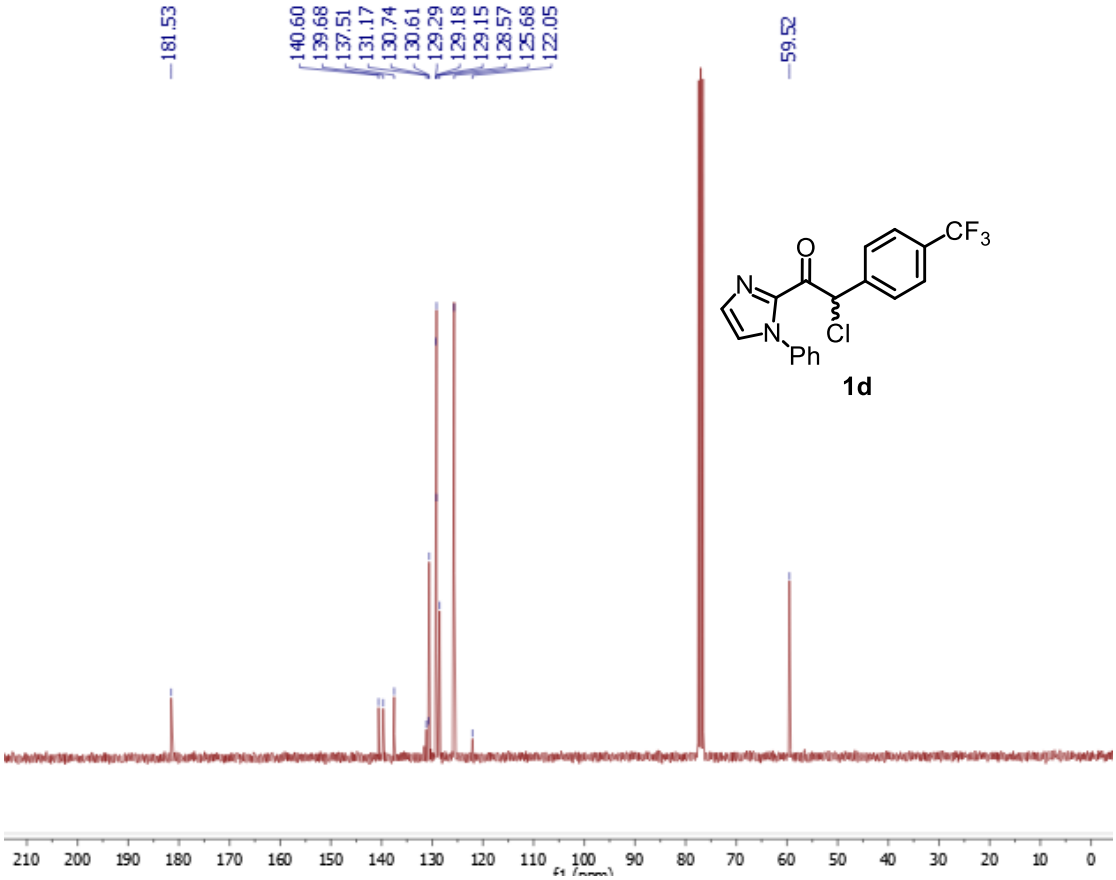


Figure S22. ^{1}H NMR and ^{13}C NMR spectra of **1c** in $CDCl_3$.


7.73
7.71
7.62
7.59
7.49
7.47
7.45
7.43
7.34
7.33
7.25
7.19
6.97
2.12
2.01
2.97
1.01
3.09
1.00
0.0 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
O
N
N
Ph
Cl
CF3

1d


181.53
140.60
139.68
137.51
131.17
130.74
130.61
129.29
129.18
129.15
128.57
125.68
122.05
59.52
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
O
N
N
Ph
Cl
CF3

1d

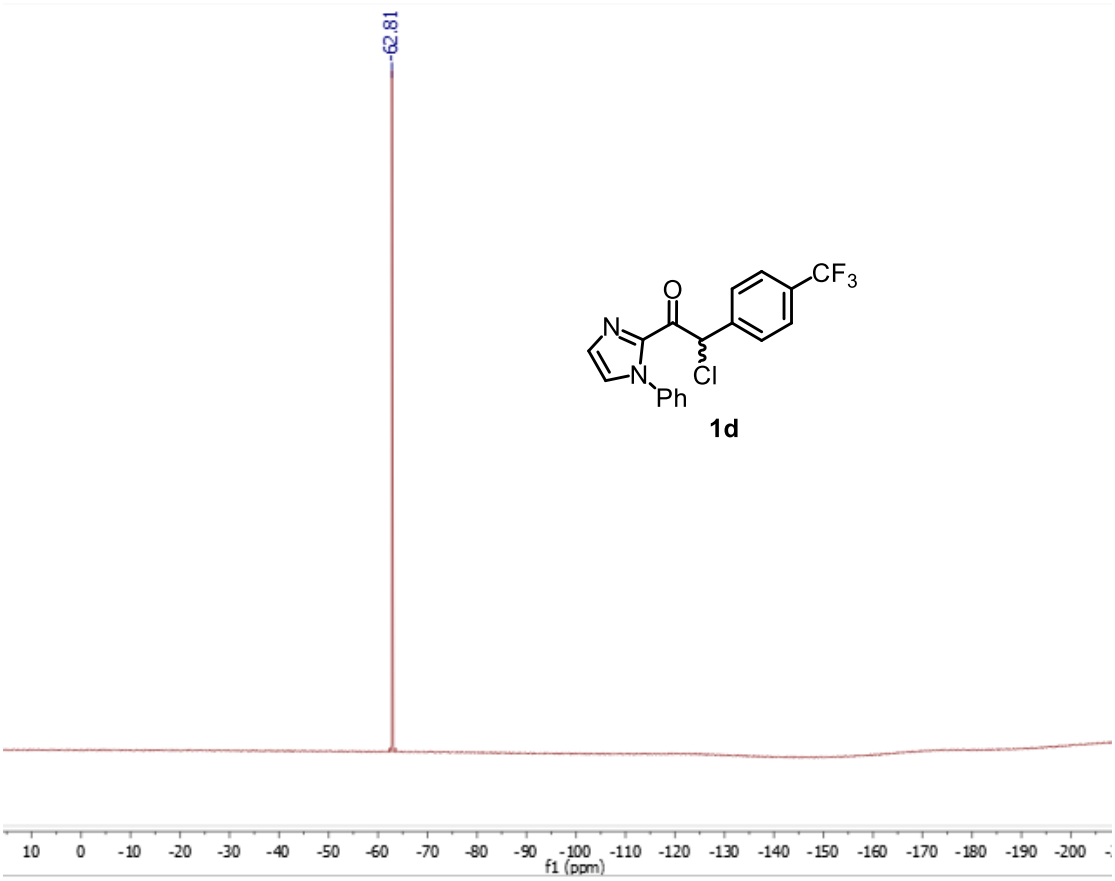
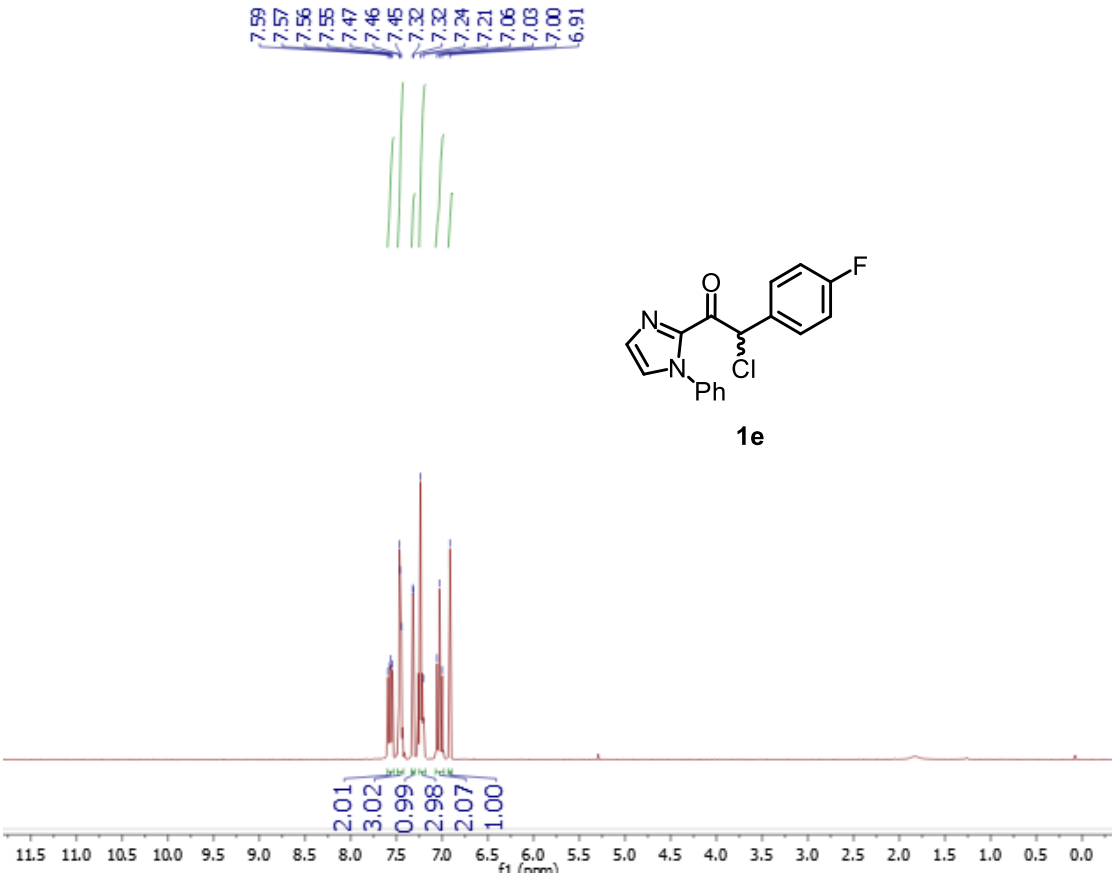
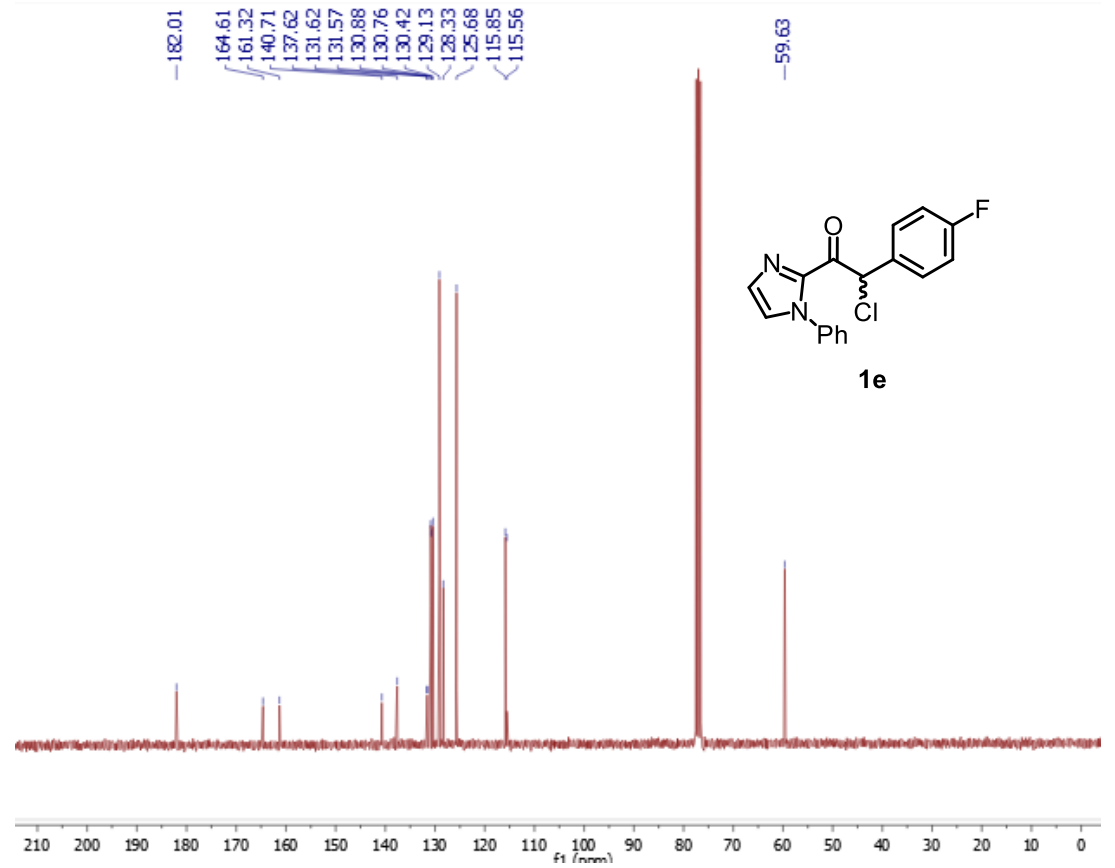


Figure S23. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **1d** in $CDCl_3$.


7.59
7.57
7.56
7.55
7.47
7.46
7.45
7.32
7.32
7.24
7.21
7.06
7.03
7.00
6.91
O
N
F
Cl
N
Ph
2.01
3.02
0.99
2.98
2.07
1.00
11.5 11.0 10.5 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)

1e


182.01
164.61
161.32
140.71
137.62
131.62
131.57
130.88
130.76
130.42
129.13
128.33
125.68
115.85
115.56
59.63
O
N
F
Cl
N
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

1e

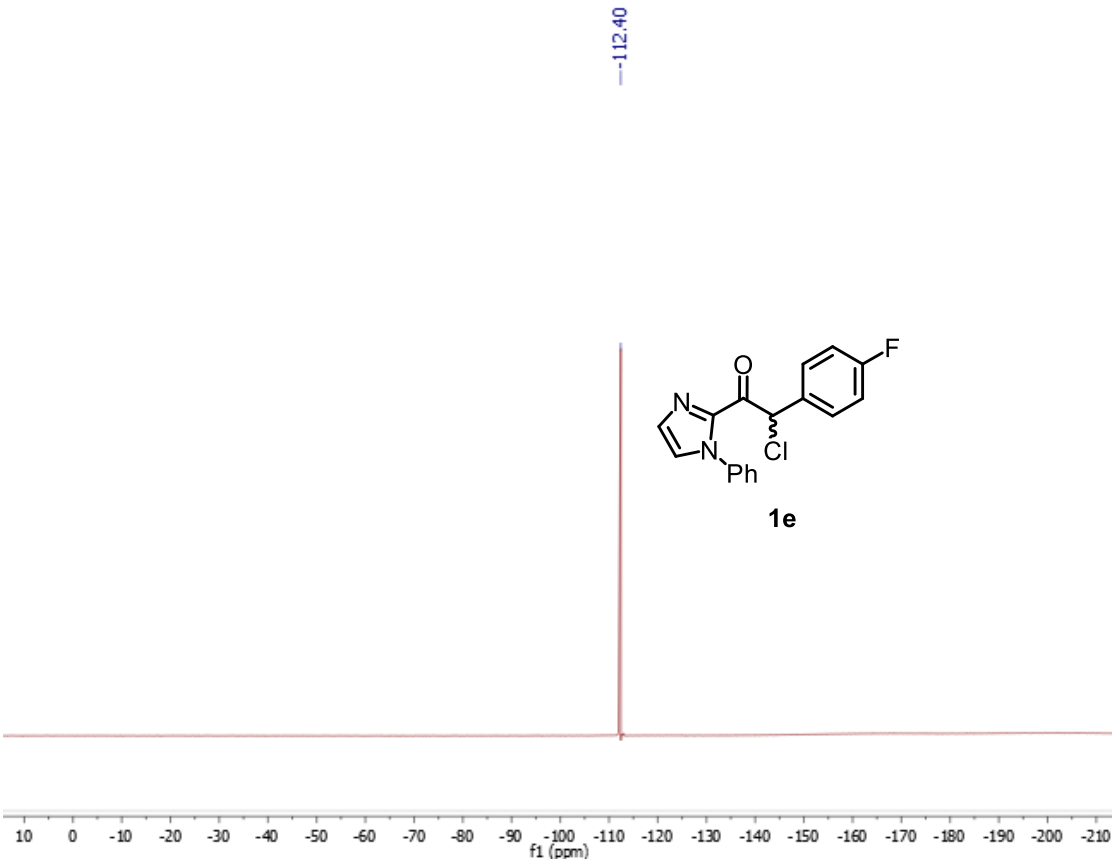


Figure S24. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **1e** in $CDCl_3$.

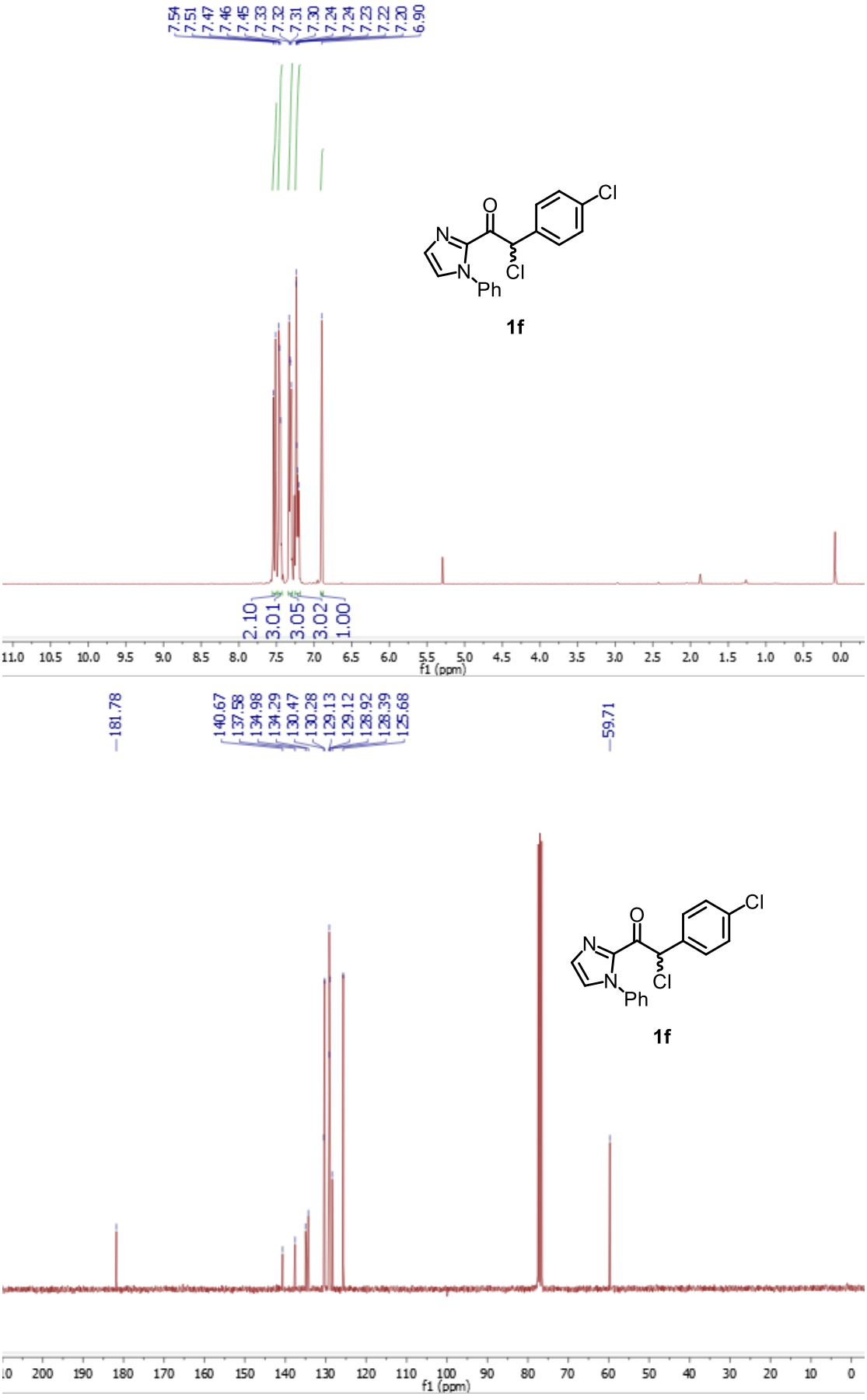


Figure S25. ^{1}H NMR and ^{13}C NMR spectra of **1f** in $CDCl_3$.

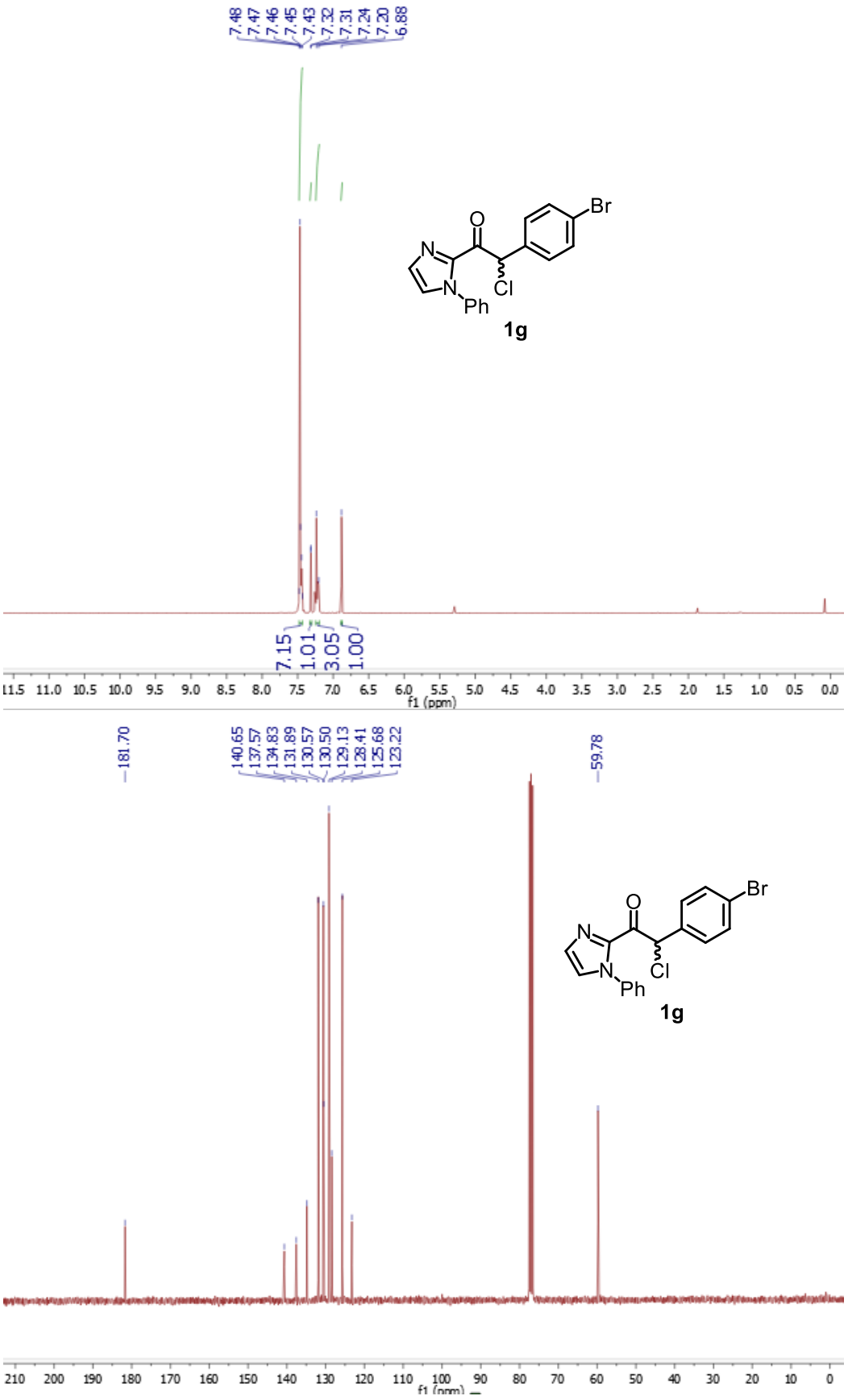


Figure S26. ^{1}H NMR and ^{13}C NMR spectra of **1g** in $CDCl_3$.

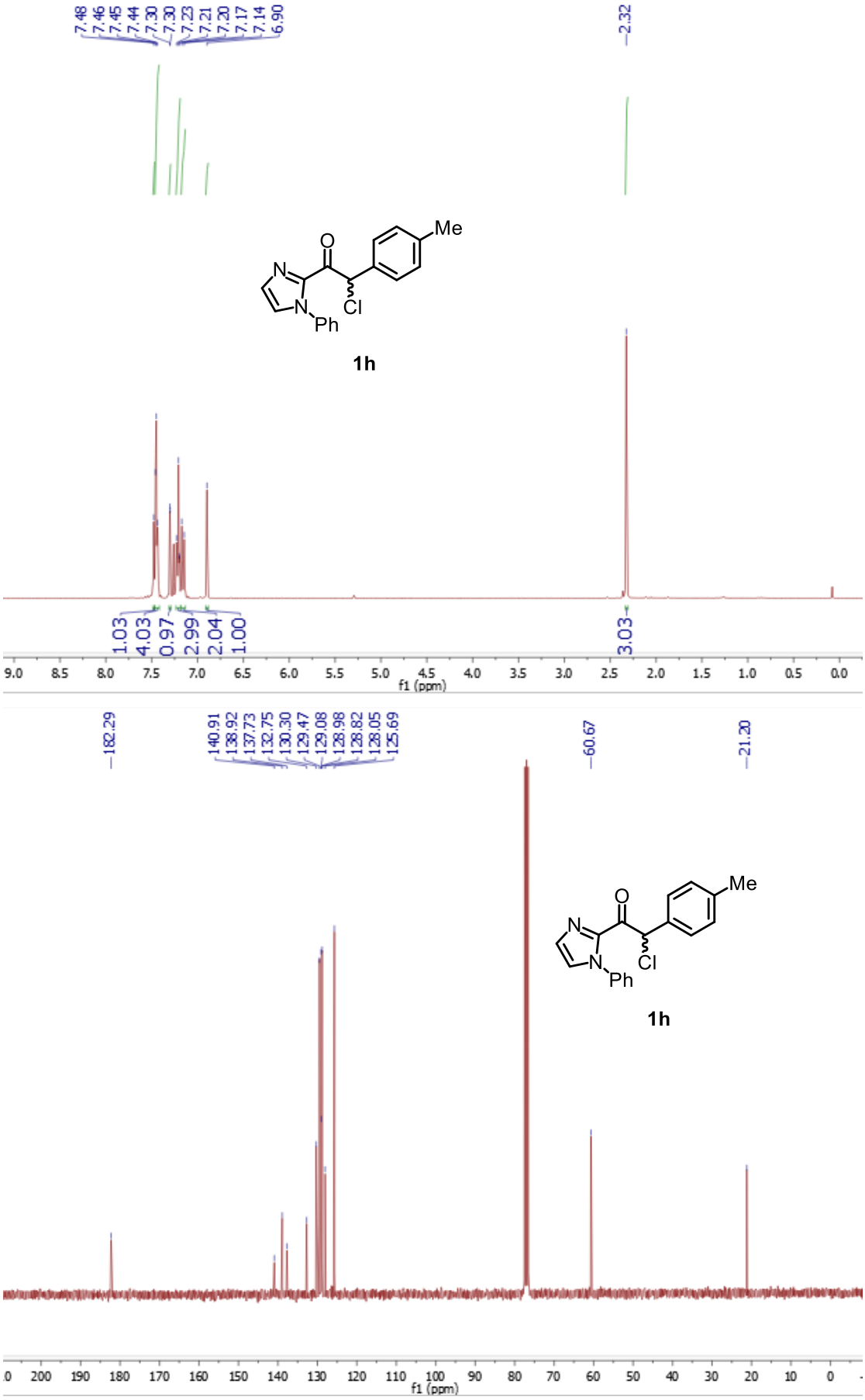


Figure S27. ^{1}H NMR and ^{13}C NMR spectra of **1h** in $CDCl_3$.

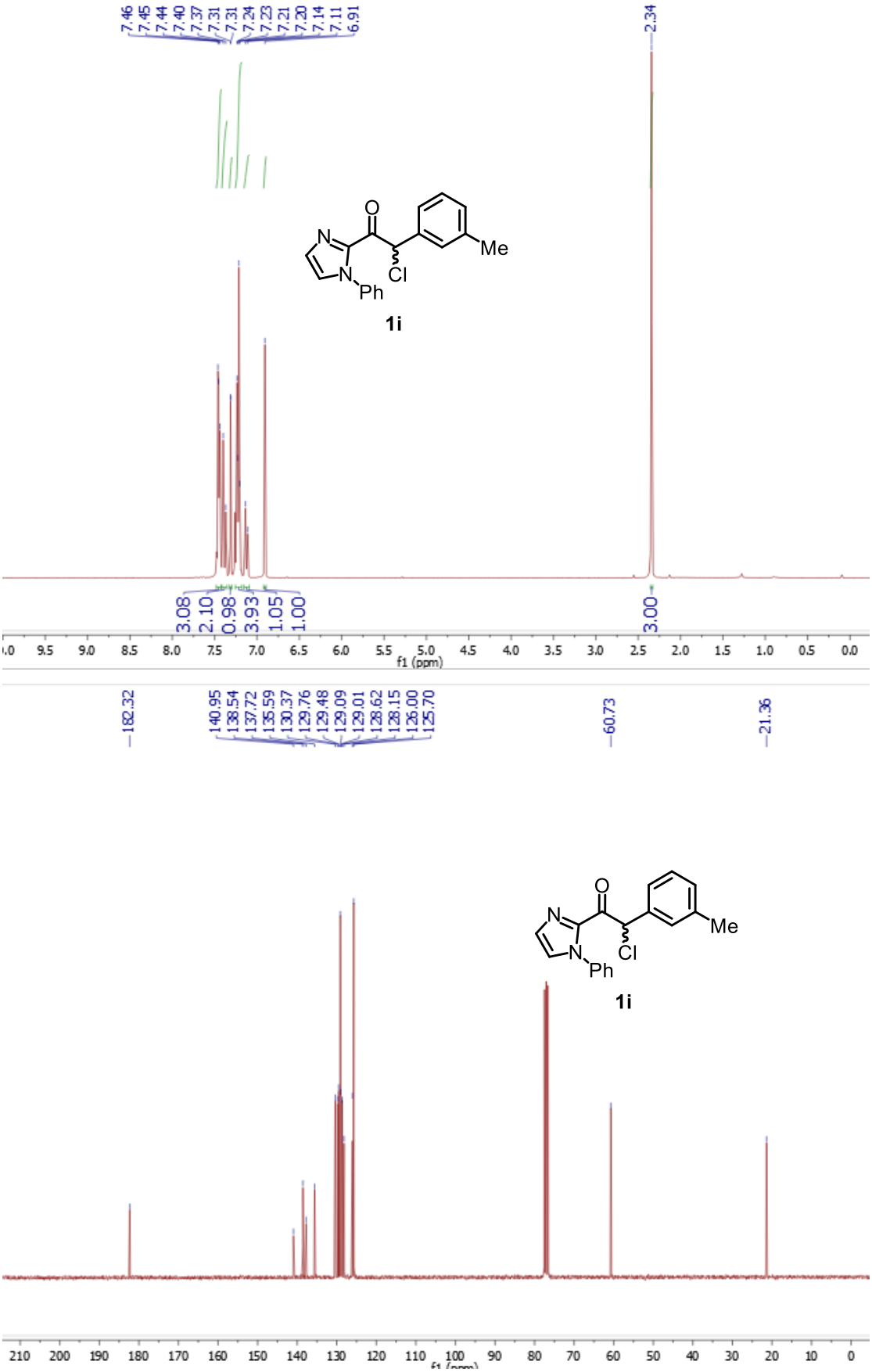


Figure S28. ^{1}H NMR and ^{13}C NMR spectra of **1i** in $CDCl_3$.

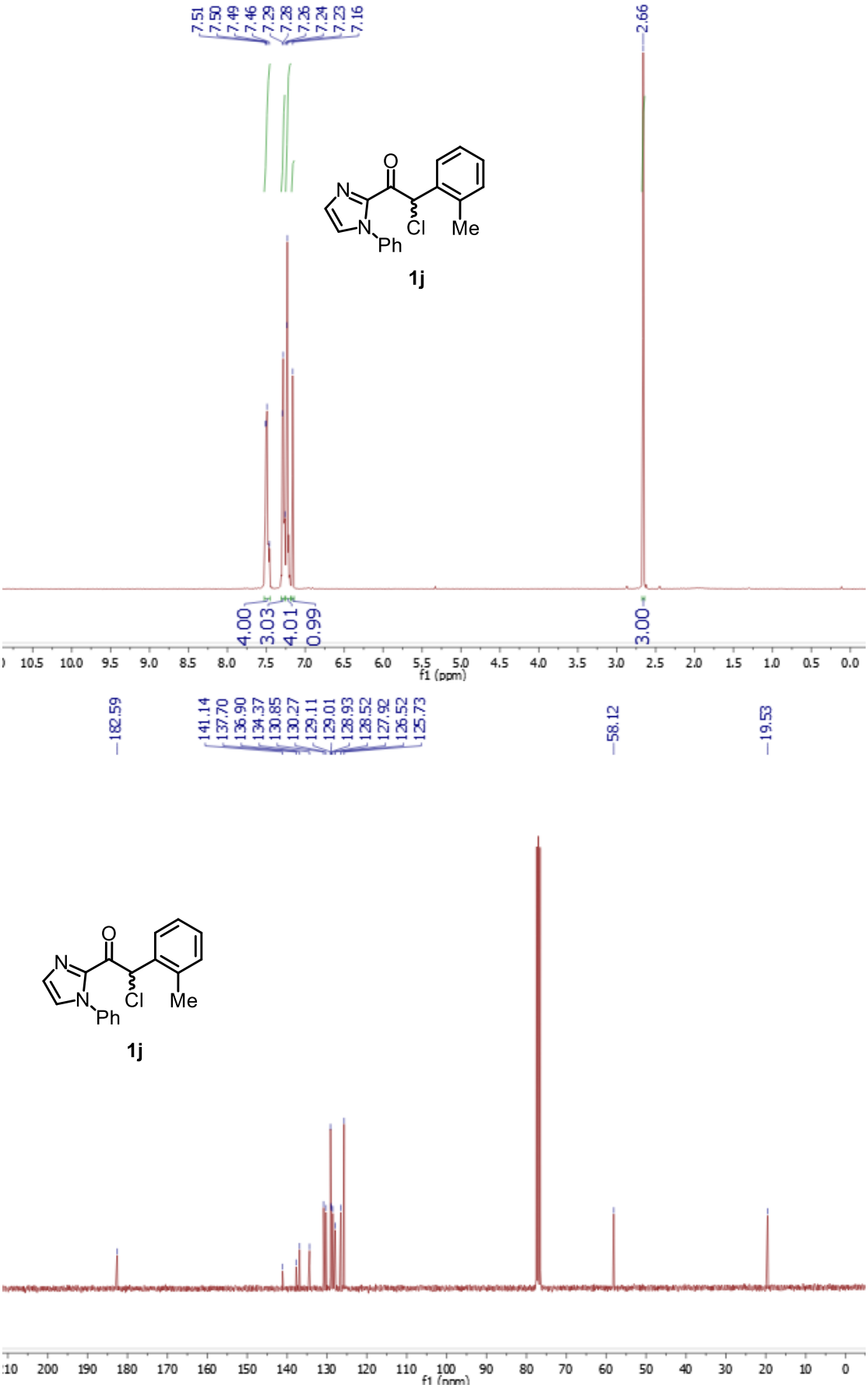


Figure S29. ^{1}H NMR and ^{13}C NMR spectra of **1j** in $CDCl_3$.

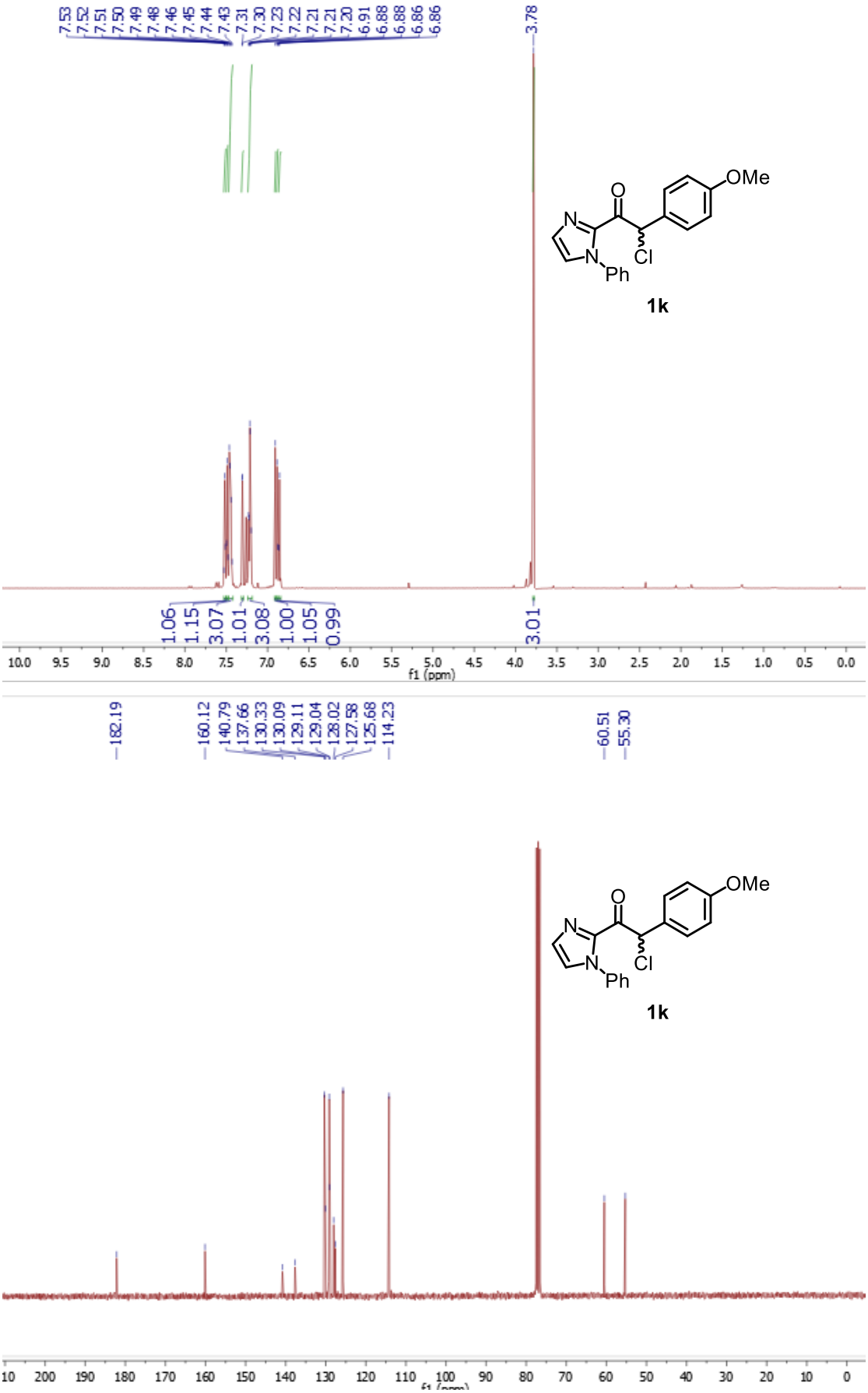


Figure S30. ^{1}H NMR and ^{13}C NMR spectra of **1k** in $CDCl_3$.

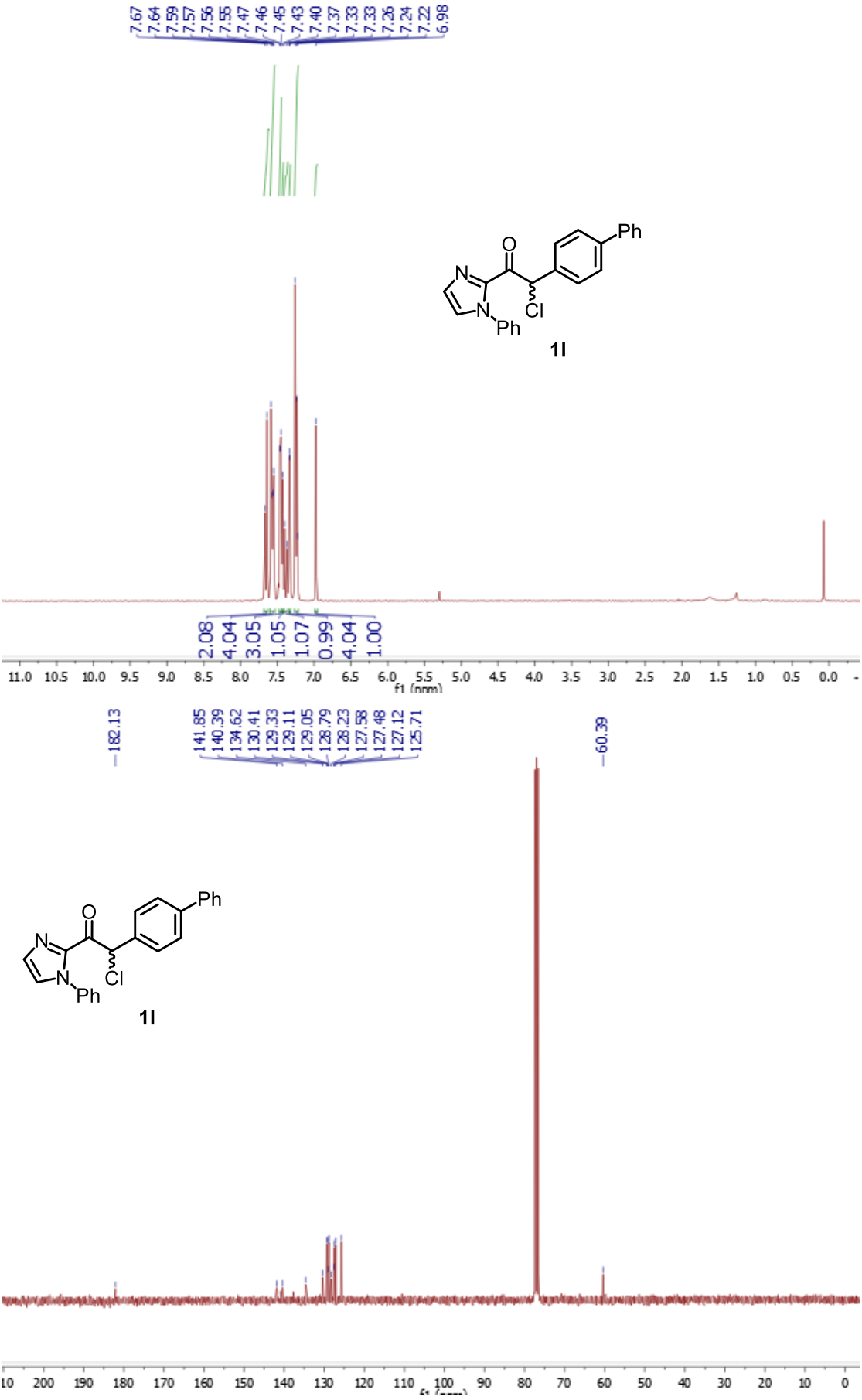


Figure S31. ^{1}H NMR and ^{13}C NMR spectra of **1l** in $CDCl_3$.

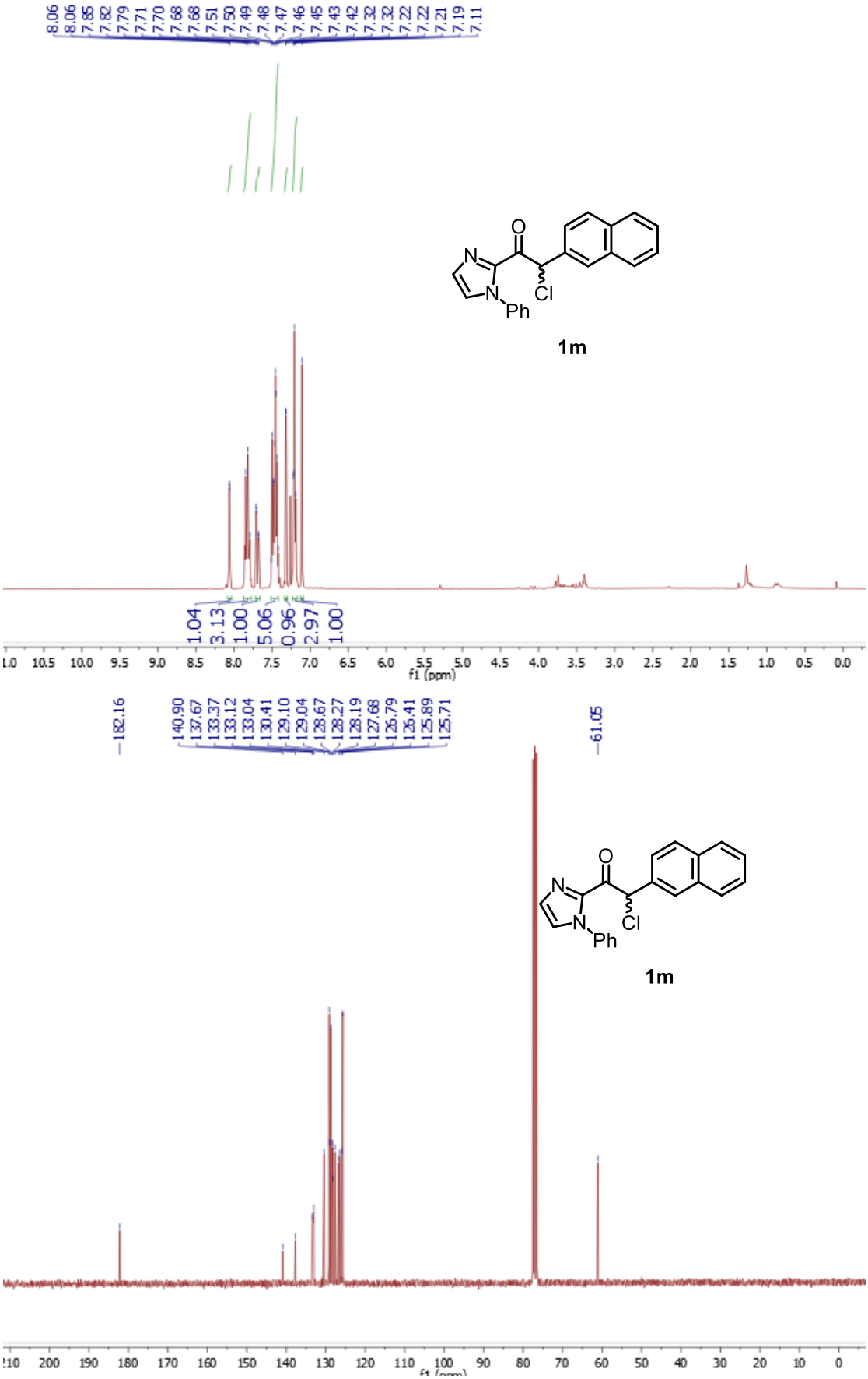


Figure S32. ^{1}H NMR and ^{13}C NMR spectra of **1m** in $CDCl_3$.

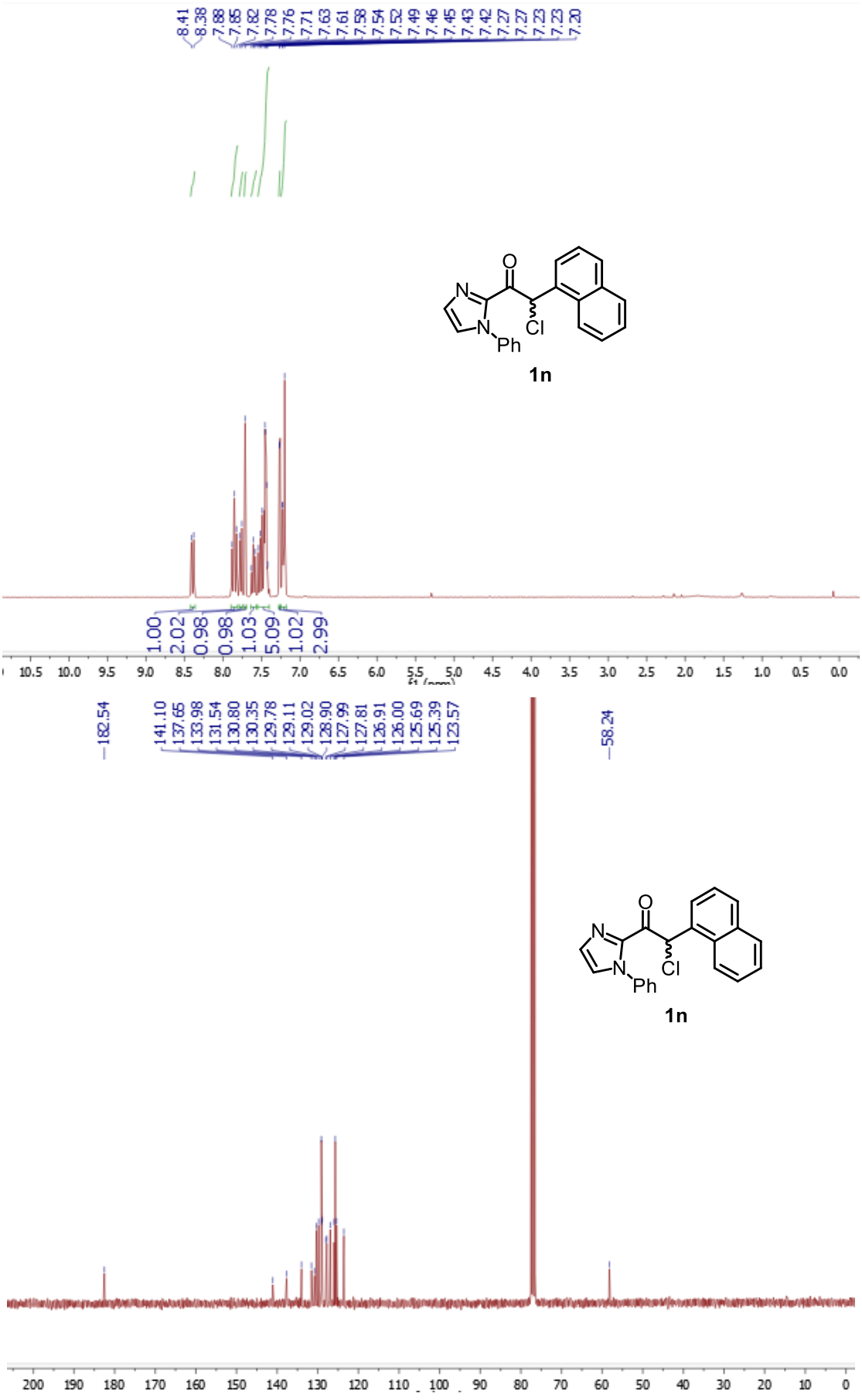


Figure S33. ^{1}H NMR and ^{13}C NMR spectra of **1n** in $CDCl_3$.

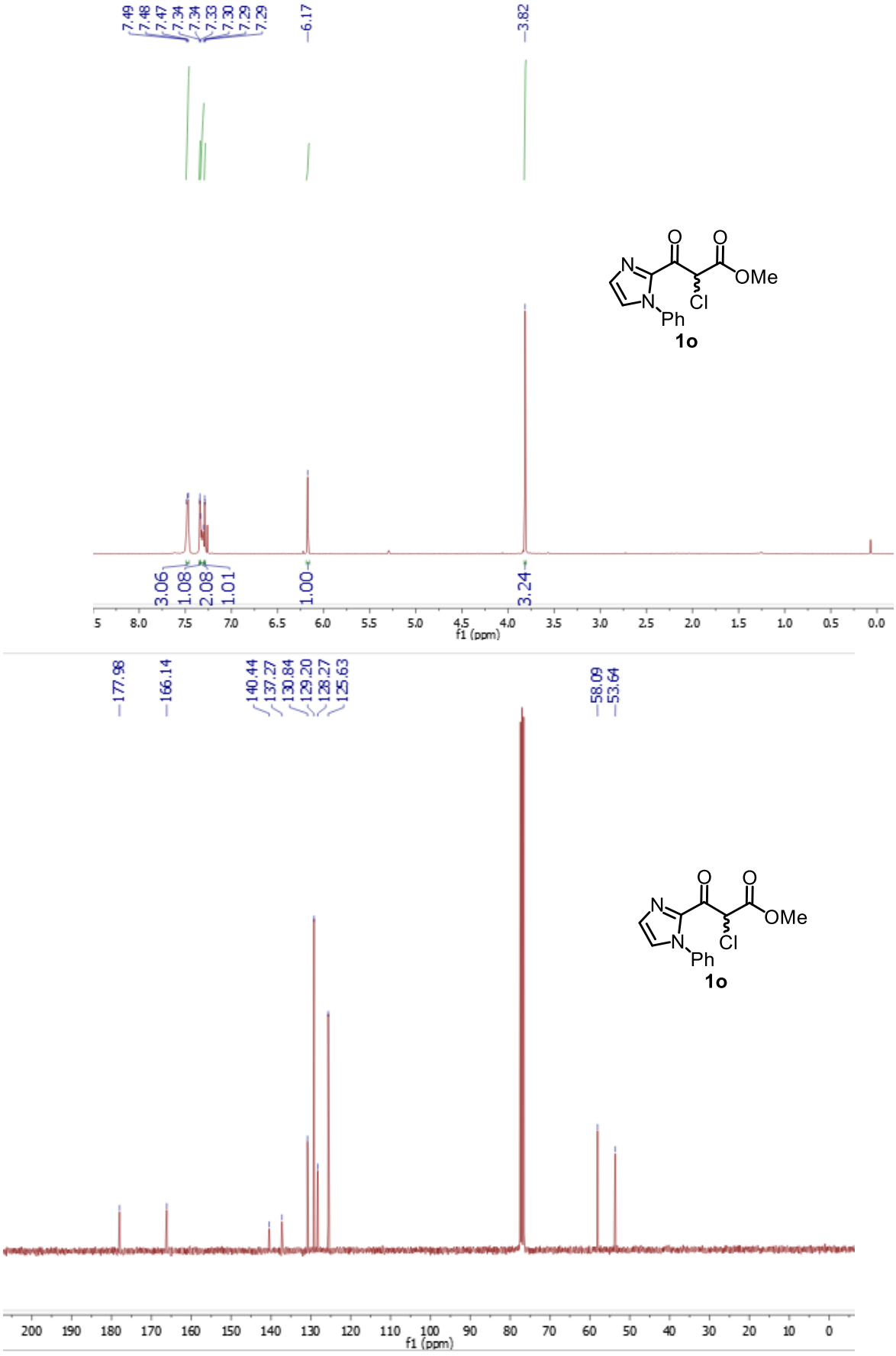
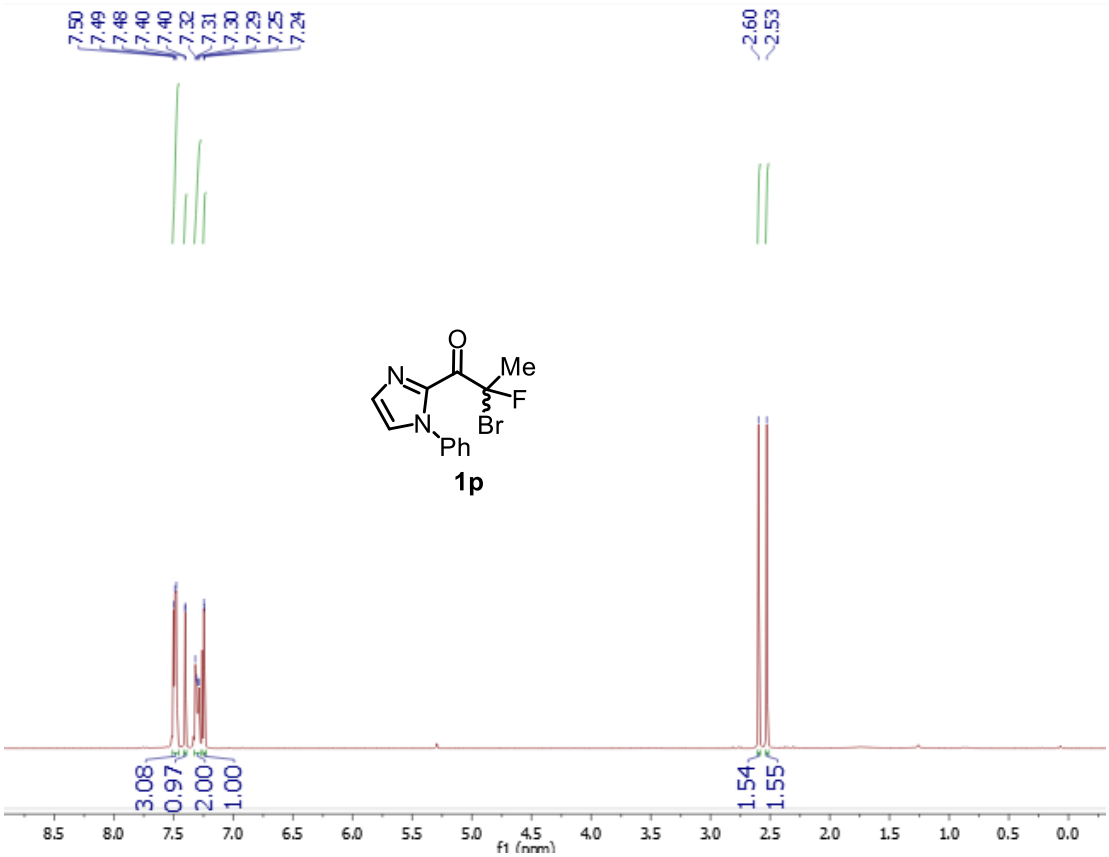
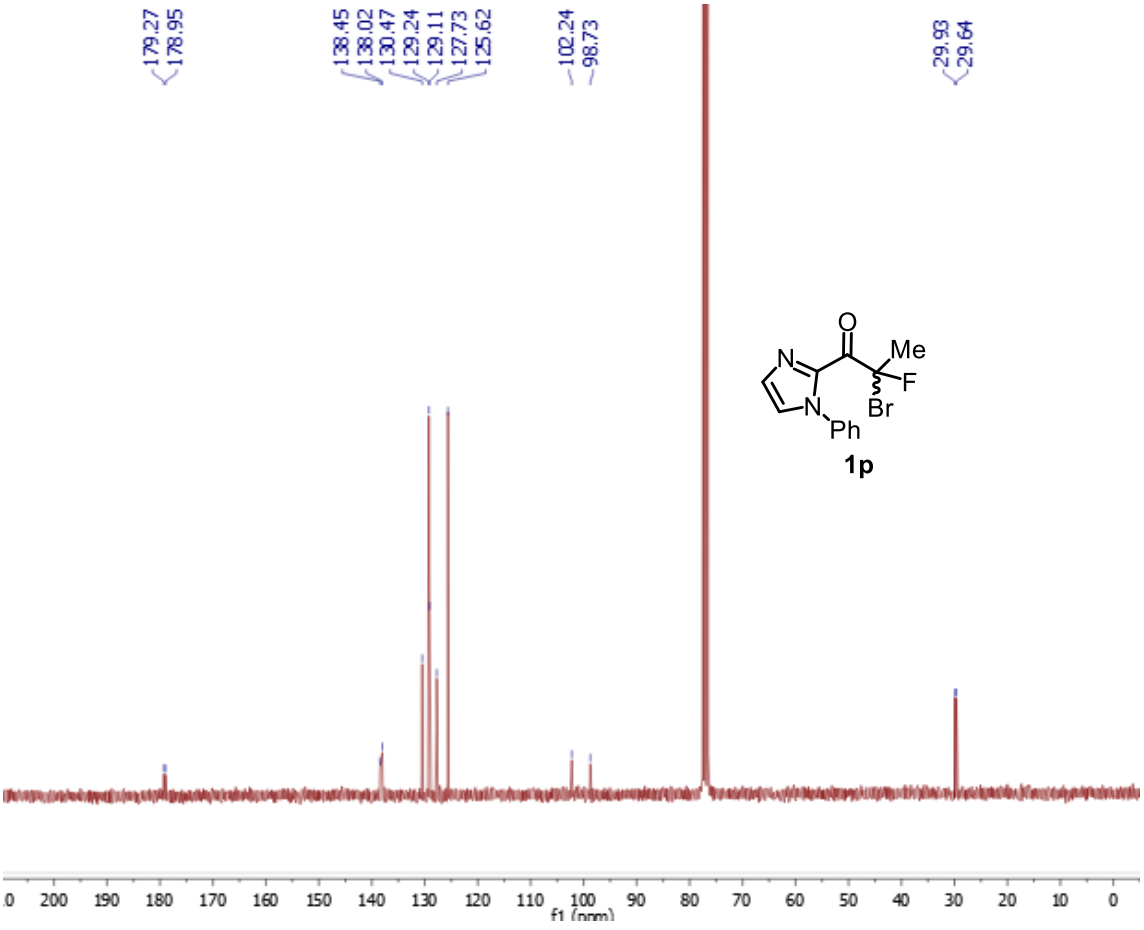


Figure S34. ^{1}H NMR and ^{13}C NMR spectra of **1o** in $CDCl_3$.


7.50
7.49
7.48
7.40
7.40
7.32
7.31
7.30
7.29
7.25
7.24
2.60
2.53
O
N
Me
F
Br
N
Ph
1p
3.08
0.97
2.00
1.00
1.54
1.55
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)


179.27
178.95
138.45
138.02
130.47
129.24
129.11
127.73
125.62
102.24
98.73
29.93
29.64
O
N
Me
F
Br
N
Ph
1p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

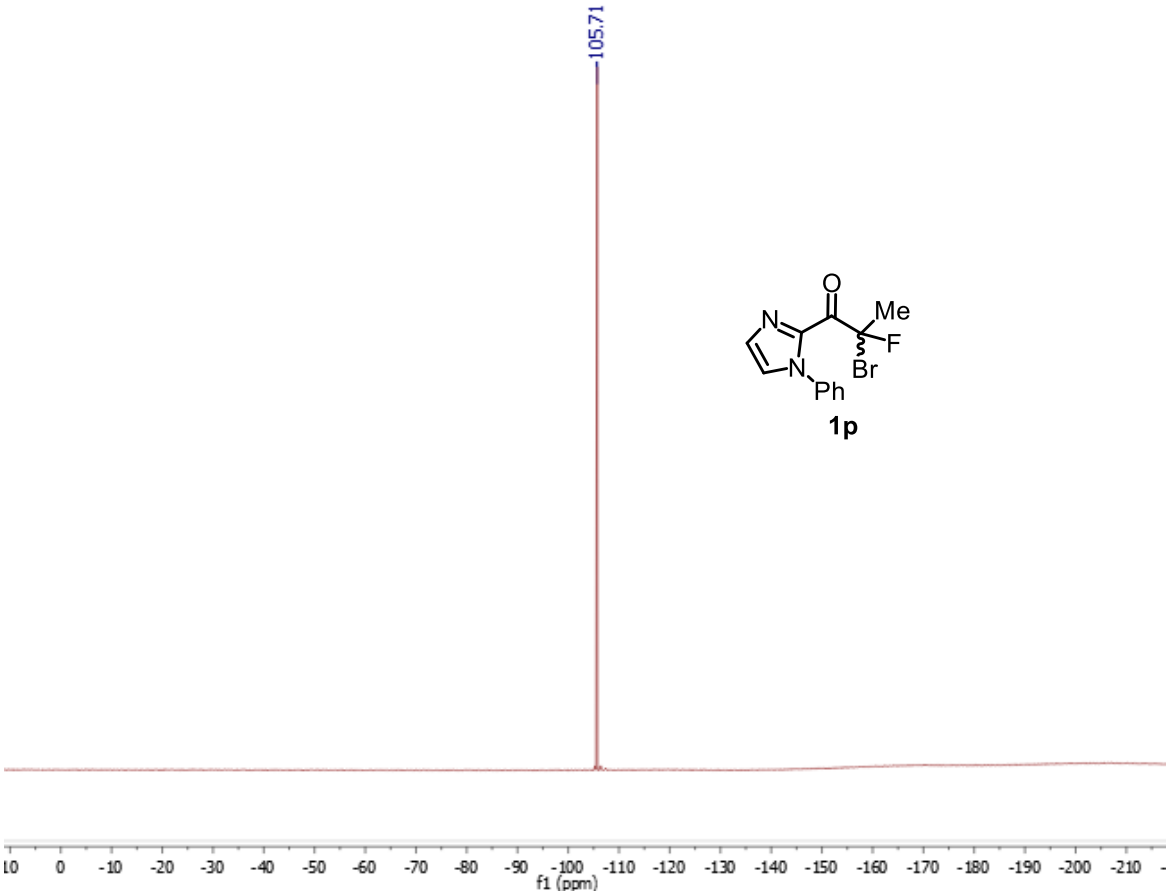


Figure S35. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **1p** in $CDCl_3$.

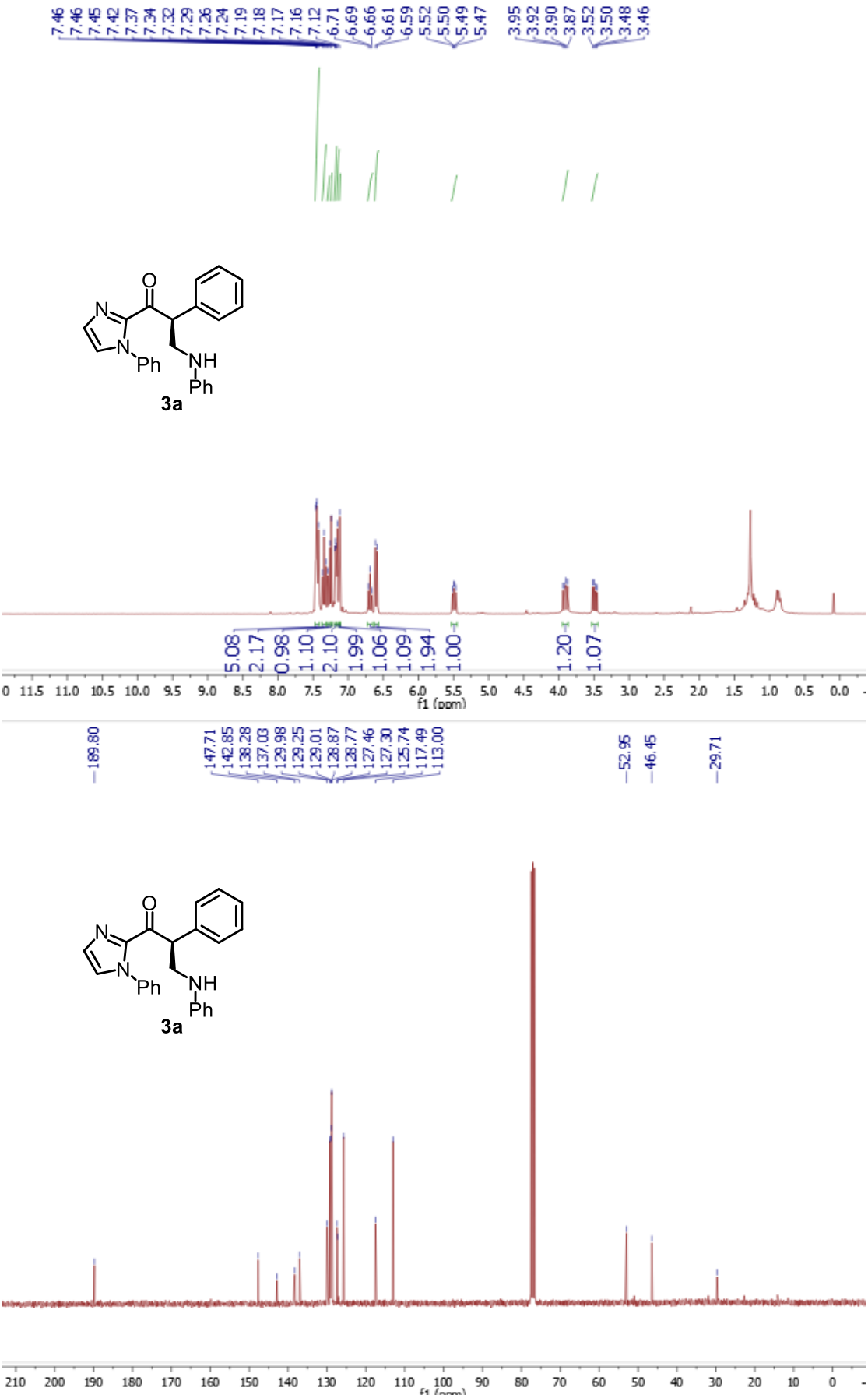
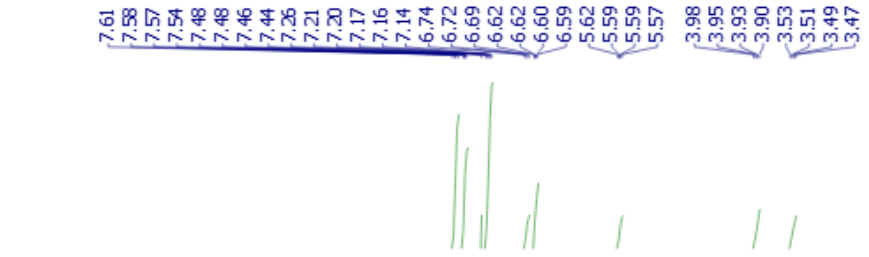


Figure S36. ^{1}H NMR and ^{13}C NMR spectra of **3a** in $CDCl_3$.

Figure S37. ^{1}H NMR and ^{13}C NMR spectra of **3b** in $CDCl_3$.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7.58
7.57
7.54
7.48
7.48
7.46
7.44
7.26
7.21
7.20
7.17
7.16
7.14
6.74
6.72
6.69
6.62
6.62
6.60
6.59
5.62
5.59
5.59
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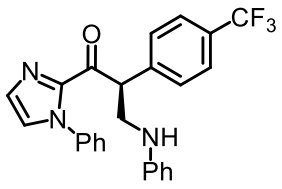
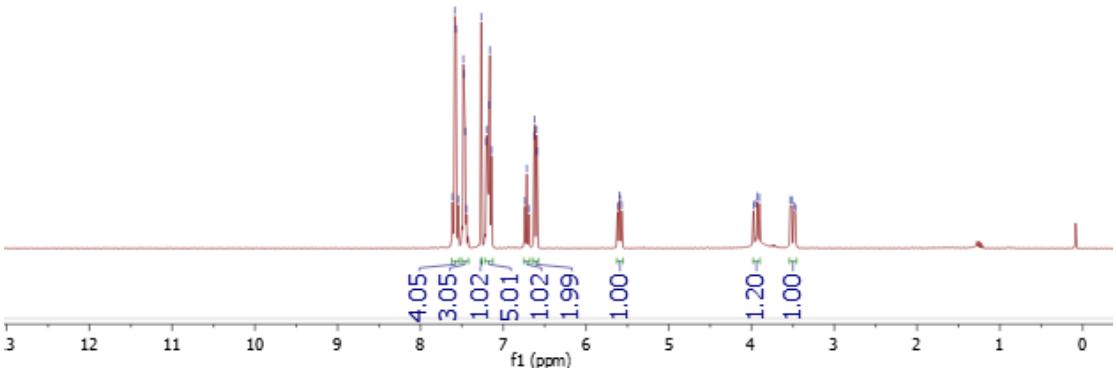
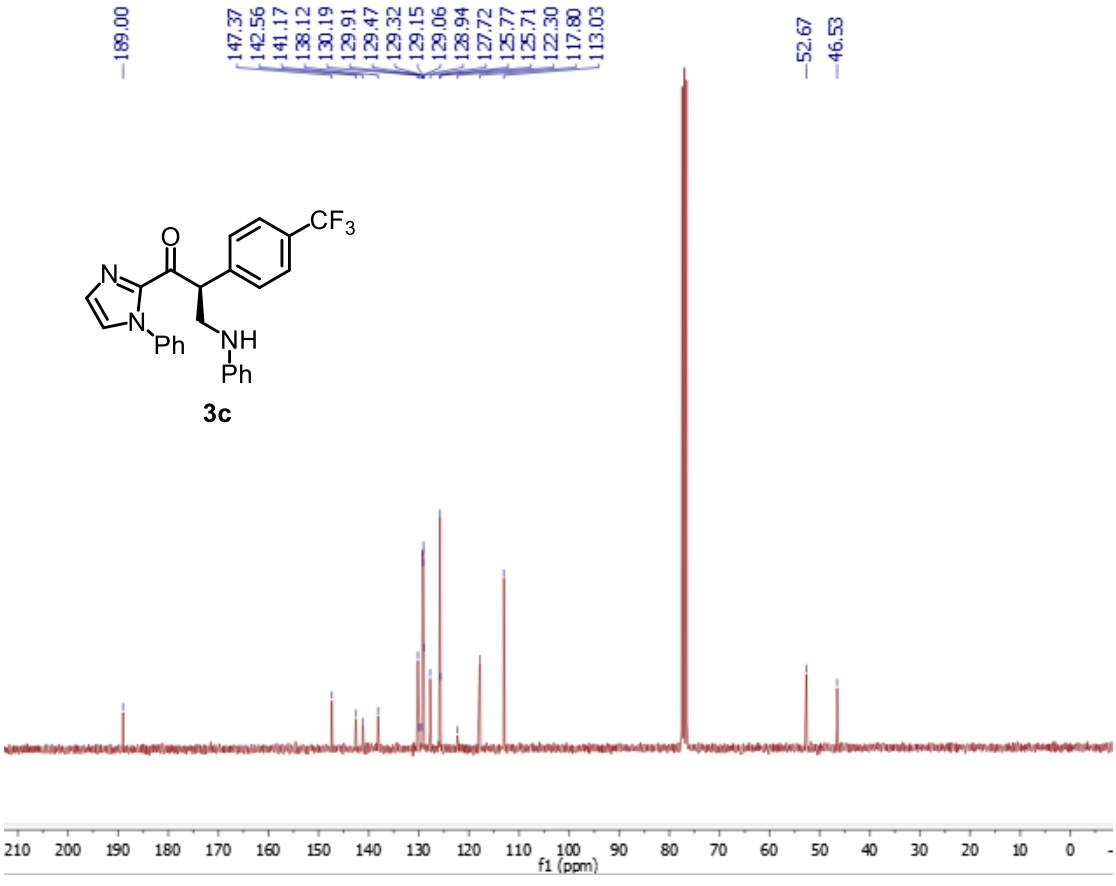
3.93
3.90
3.53
3.51
3.49
3.47


CF3
O
N
N
Ph
NH
Ph

3c


4.05
3.05
1.02
5.01
1.02
1.99
1.00
1.20
1.00
3
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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147.37
142.56
141.17
138.12
130.19
129.91
129.47
129.32
129.15
129.06
128.94
127.72
125.77
125.71
122.30
117.80
113.03
52.67
46.53
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

CF3
O
N
N
Ph
NH
Ph

3c

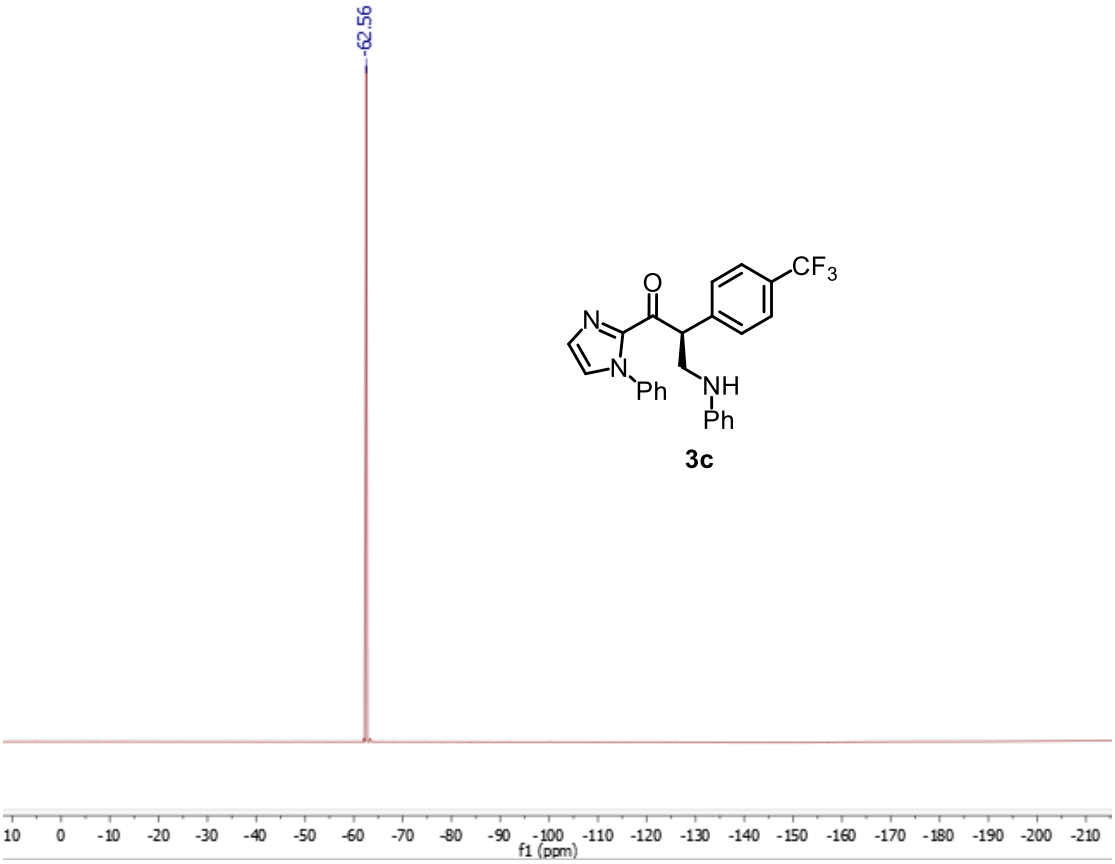
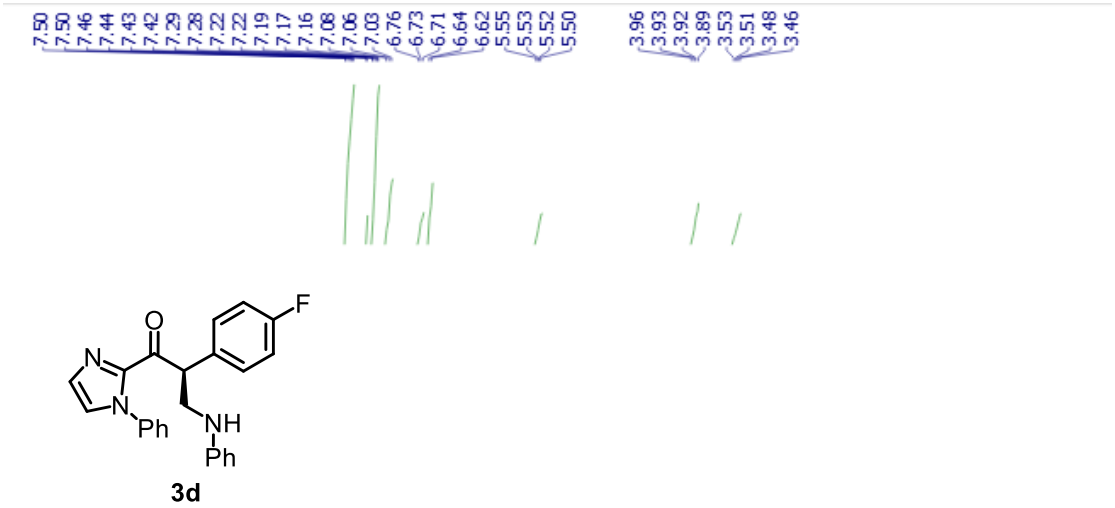
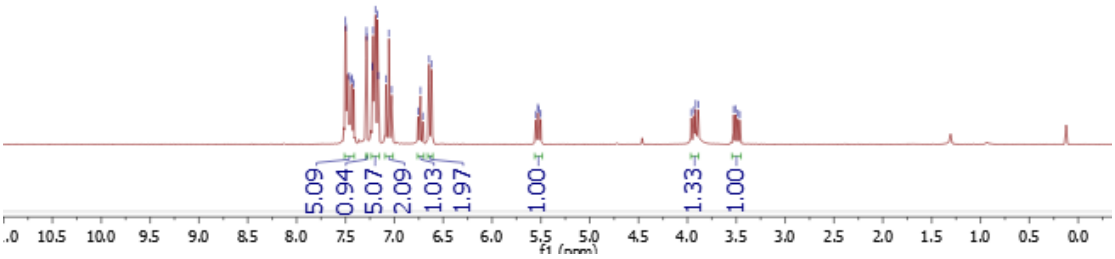
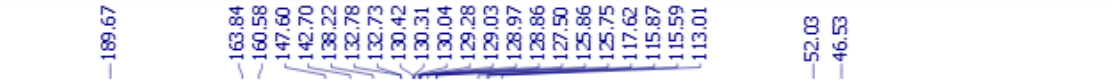


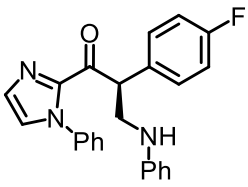
Figure S38. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **3c** in $CDCl_3$.


7.50
7.50
7.46
7.44
7.43
7.42
7.29
7.28
7.22
7.22
7.19
7.17
7.16
7.08
7.06
7.03
6.76
6.73
6.71
6.64
6.62
5.55
5.53
5.52
5.50
3.96
3.93
3.92
3.89
3.53
3.51
3.48
3.46
O
F
N
N
Ph
NH
Ph

3d


5.09
0.94
5.07
2.09
1.03
1.97
1.00
1.33
1.00


189.67
163.84
160.58
147.60
142.70
138.22
132.78
132.73
130.42
130.31
130.04
129.28
129.03
128.97
128.86
127.50
125.86
125.75
117.62
115.87
115.59
113.01
52.03
46.53


O
F
N
N
Ph
NH
Ph

3d

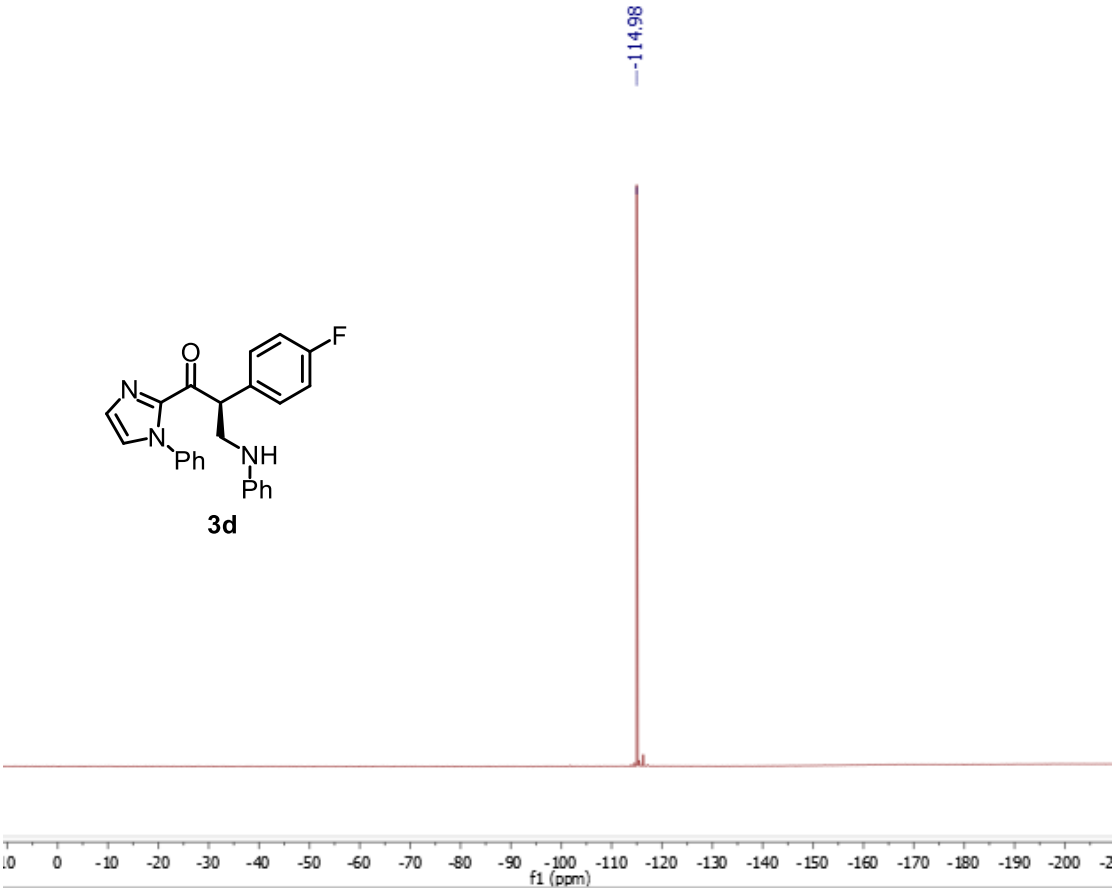


Figure S39. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **3d** in $CDCl_3$.

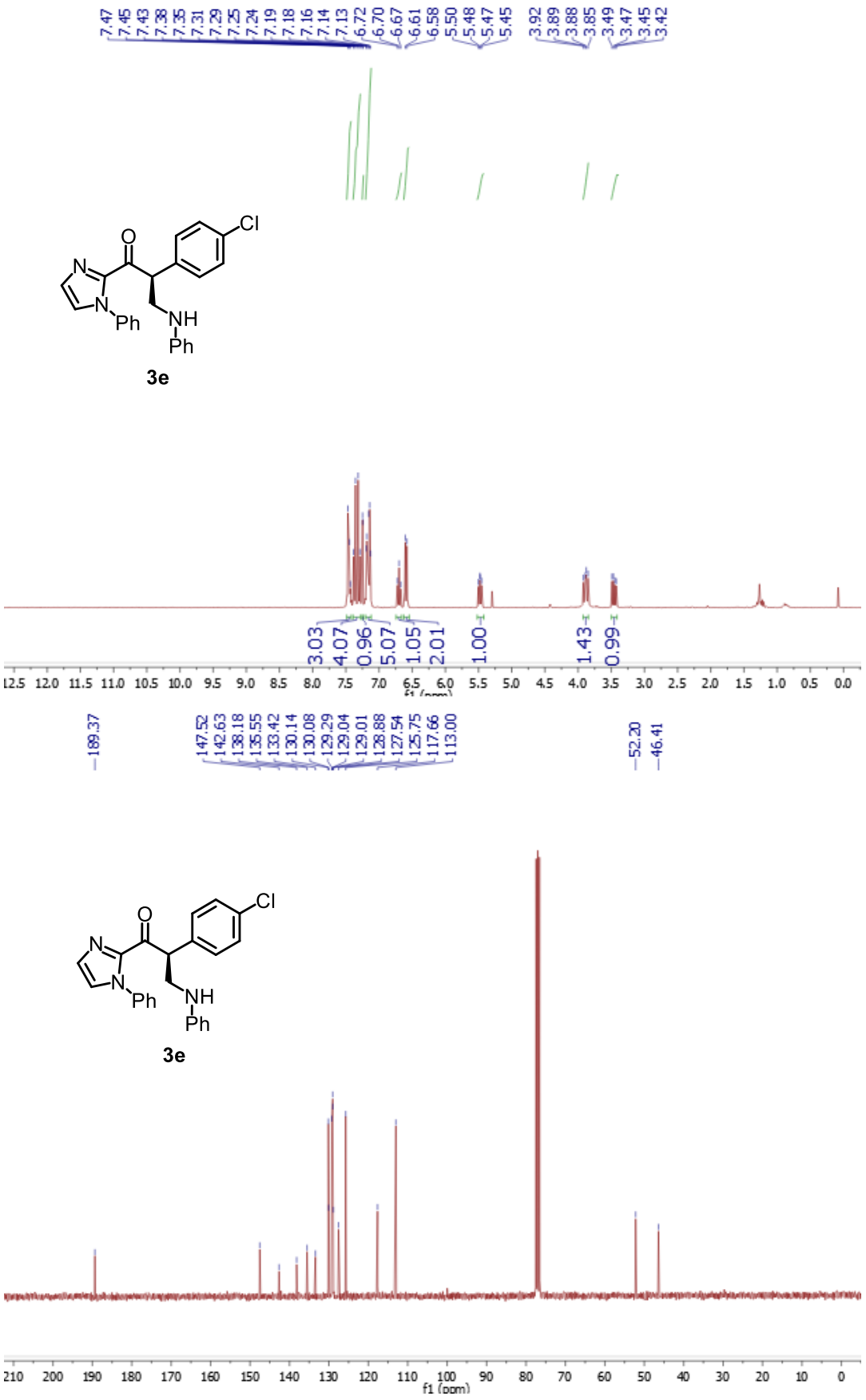


Figure S40. ^{1}H NMR and ^{13}C NMR spectra of **3e** in $CDCl_3$.

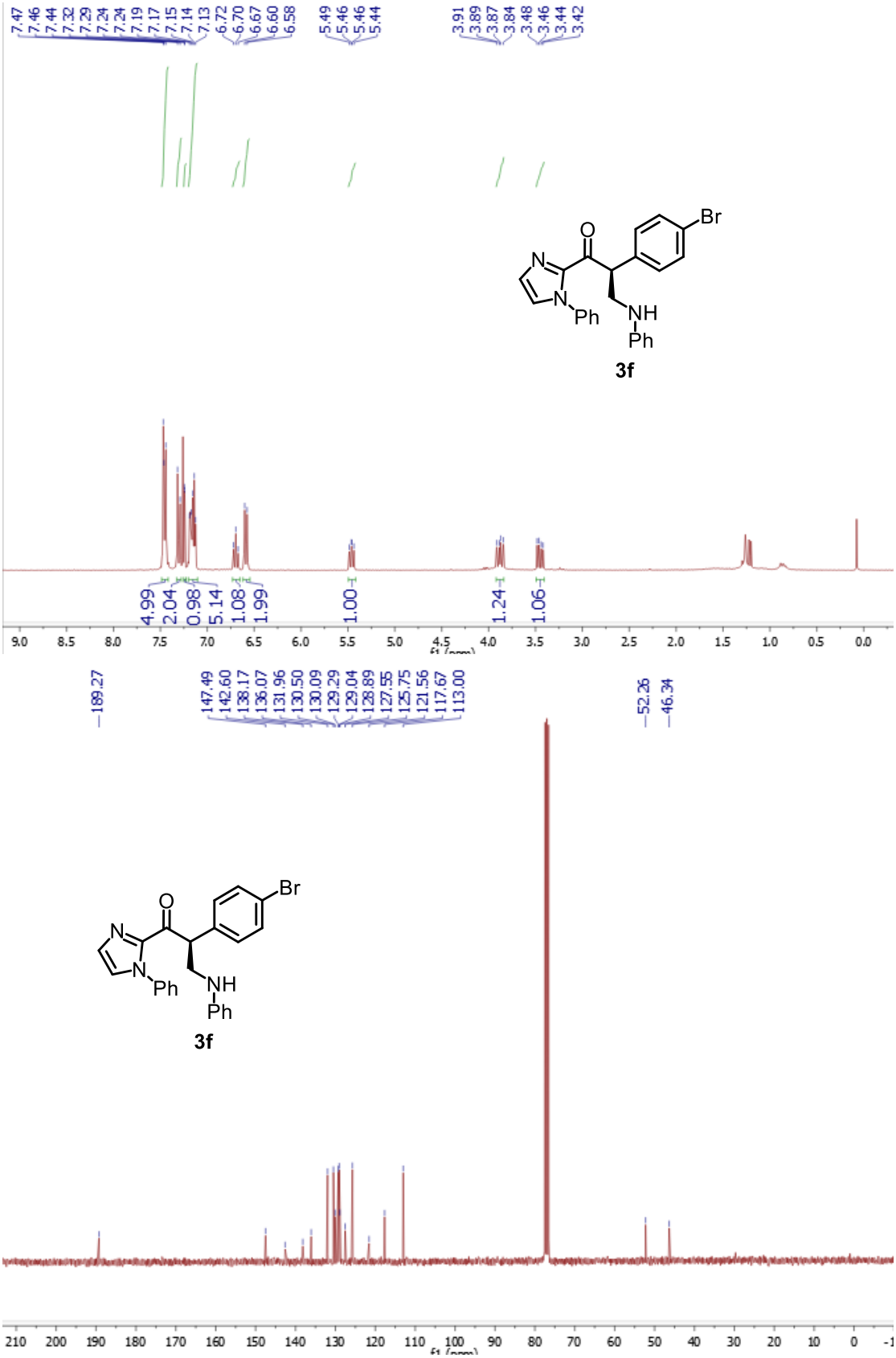


Figure S41. ^{1}H NMR and ^{13}C NMR spectra of **3f** in $CDCl_3$.

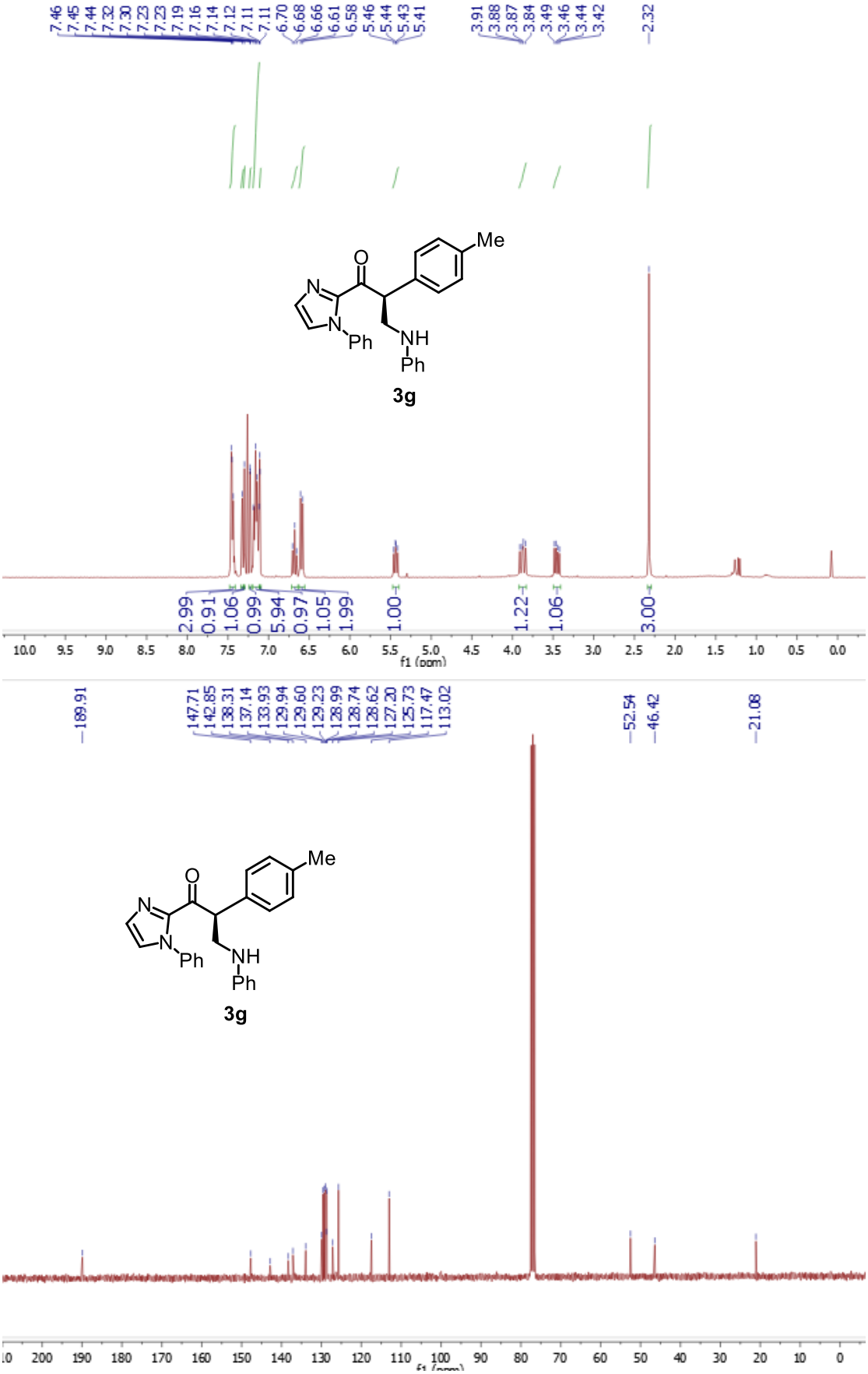


Figure S42. ^{1}H NMR and ^{13}C NMR spectra of **3g** in $CDCl_3$.

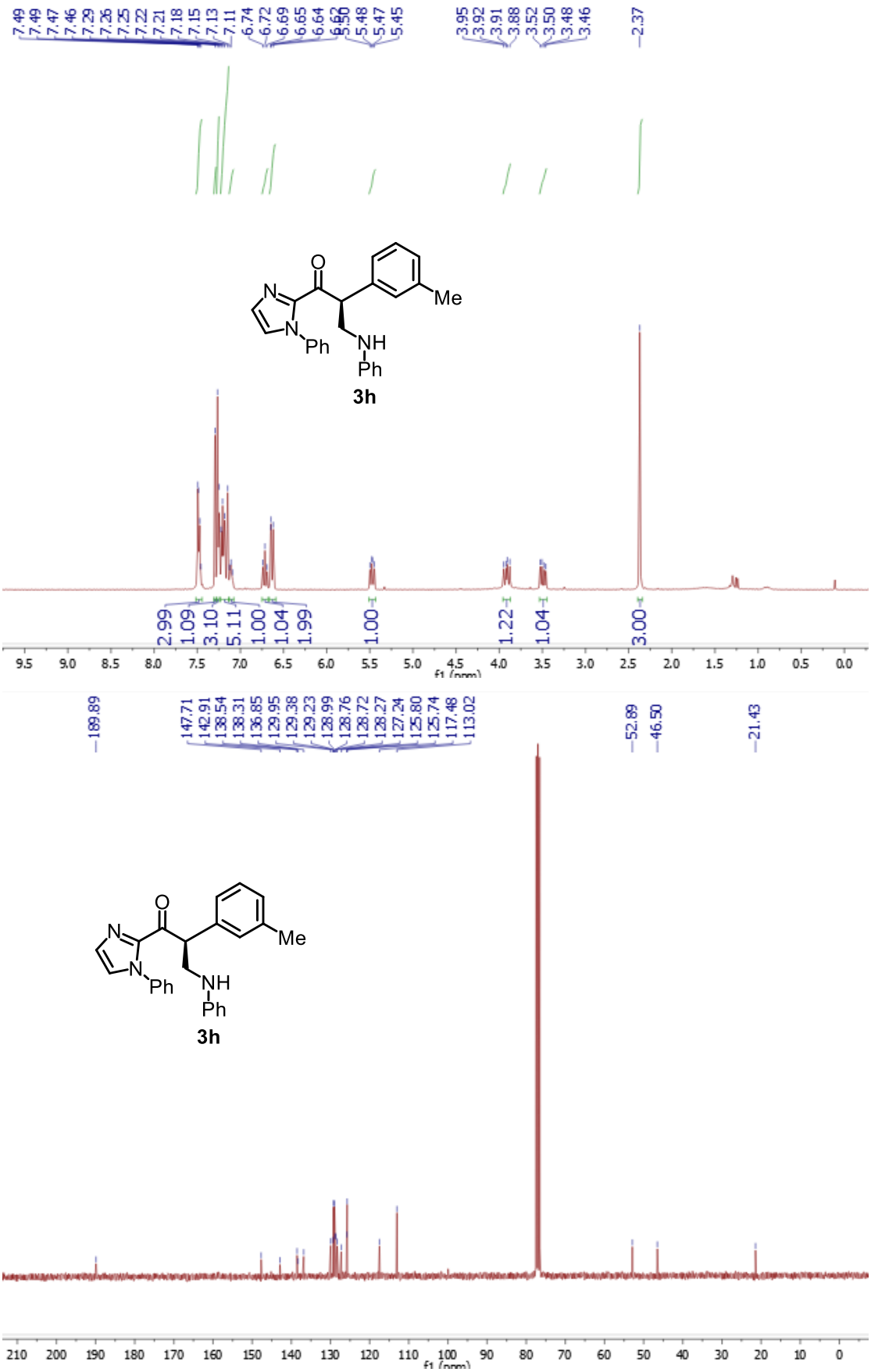


Figure S43. ^{1}H NMR and ^{13}C NMR spectra of **3h** in $CDCl_3$.

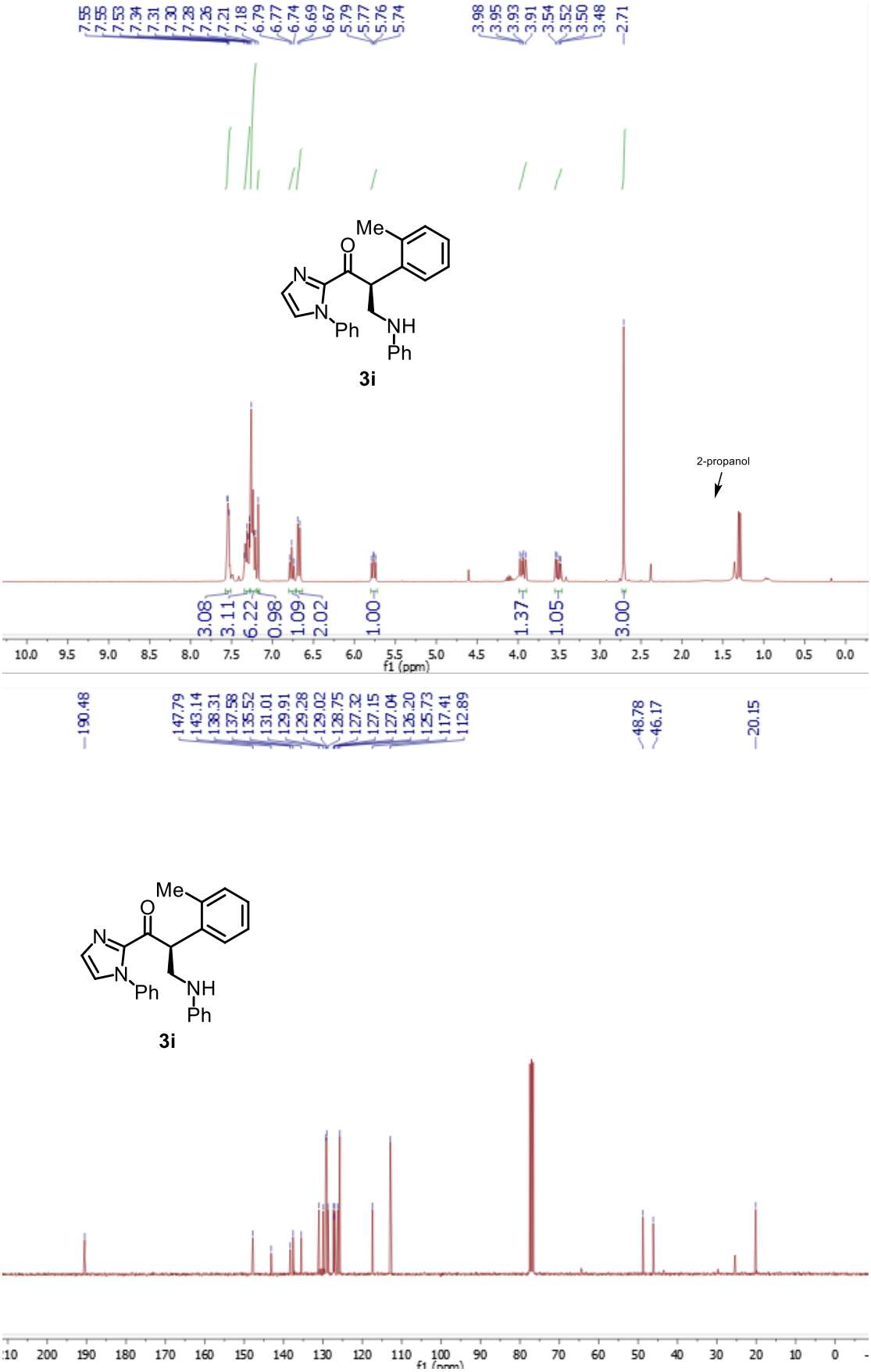


Figure S44. ^{1}H NMR and ^{13}C NMR spectra of **3i** in $CDCl_3$.

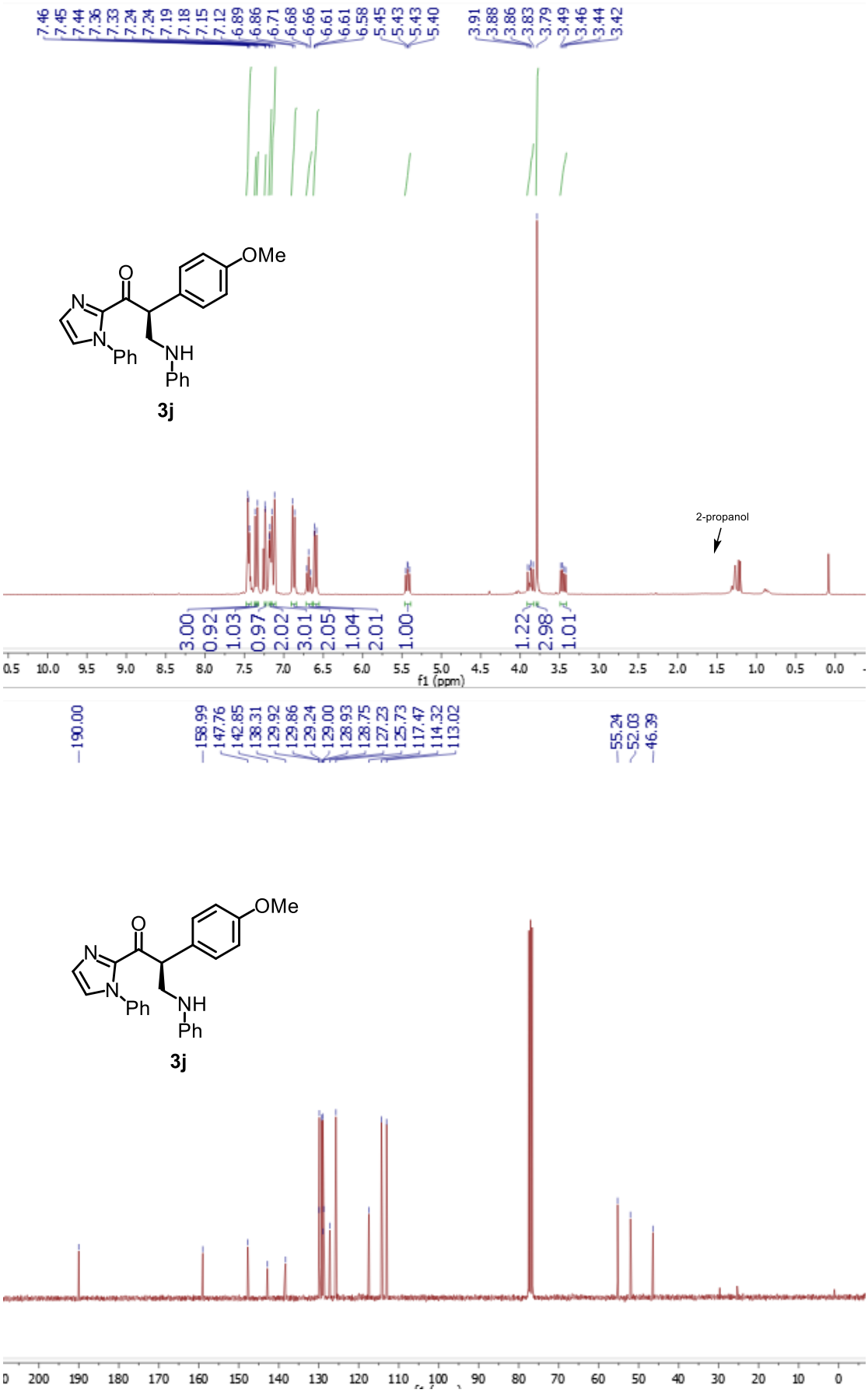


Figure S45. ^{1}H NMR and ^{13}C NMR spectra of **3j** in $CDCl_3$.

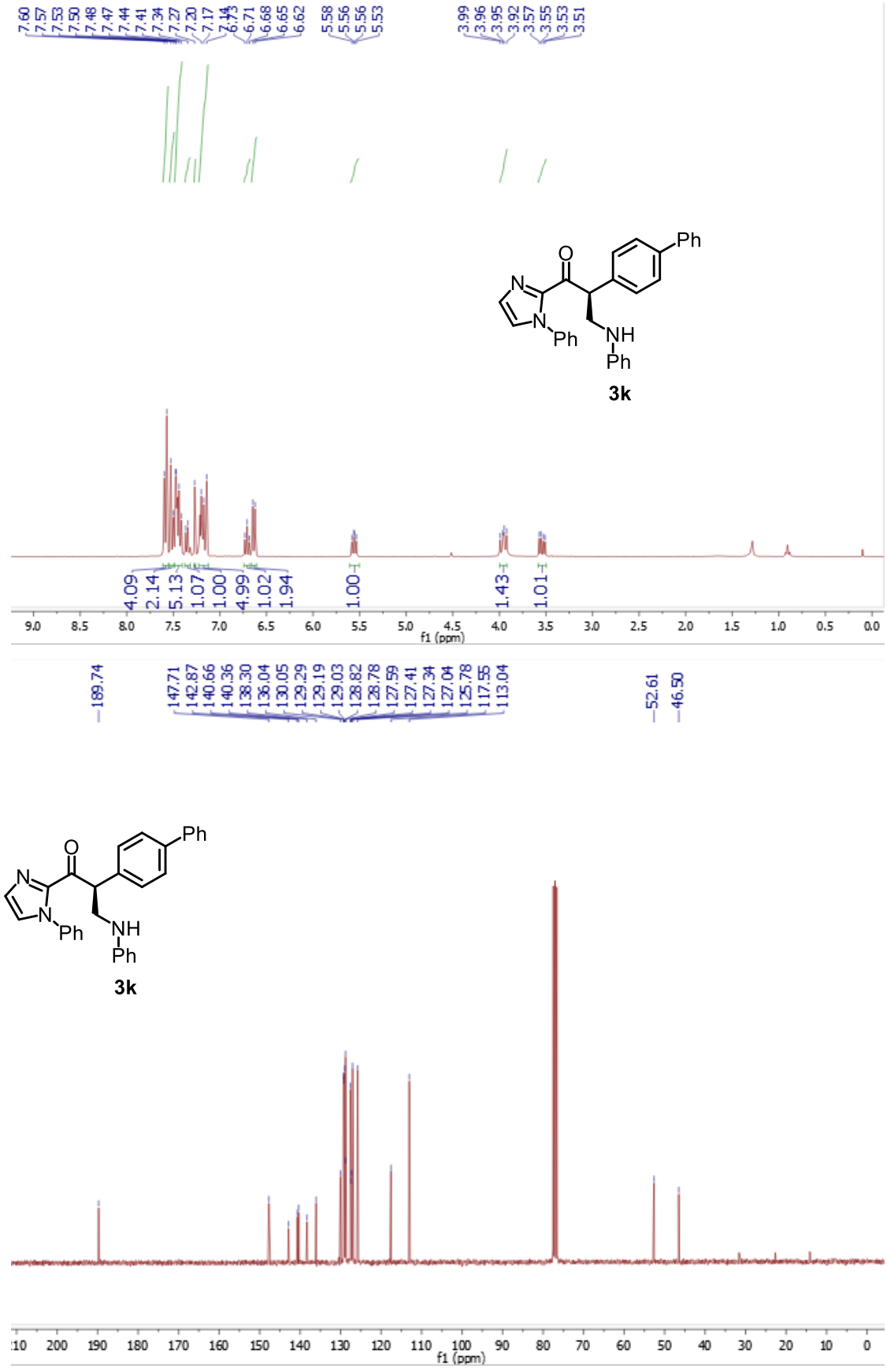


Figure S46. ^{1}H NMR and ^{13}C NMR spectra of **3k** in $CDCl_3$.

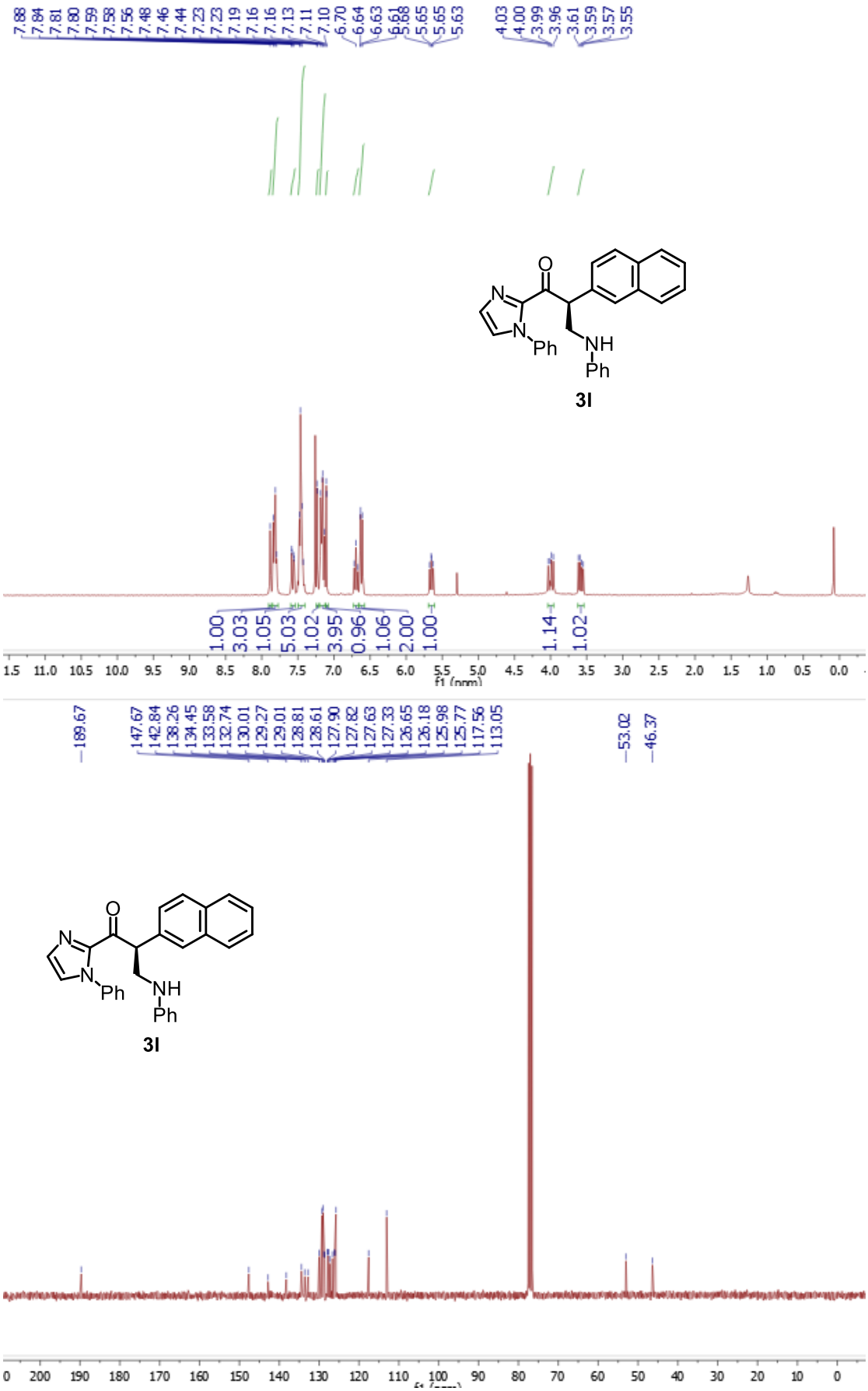


Figure S47. ^{1}H NMR and ^{13}C NMR spectra of **3l** in $CDCl_3$.

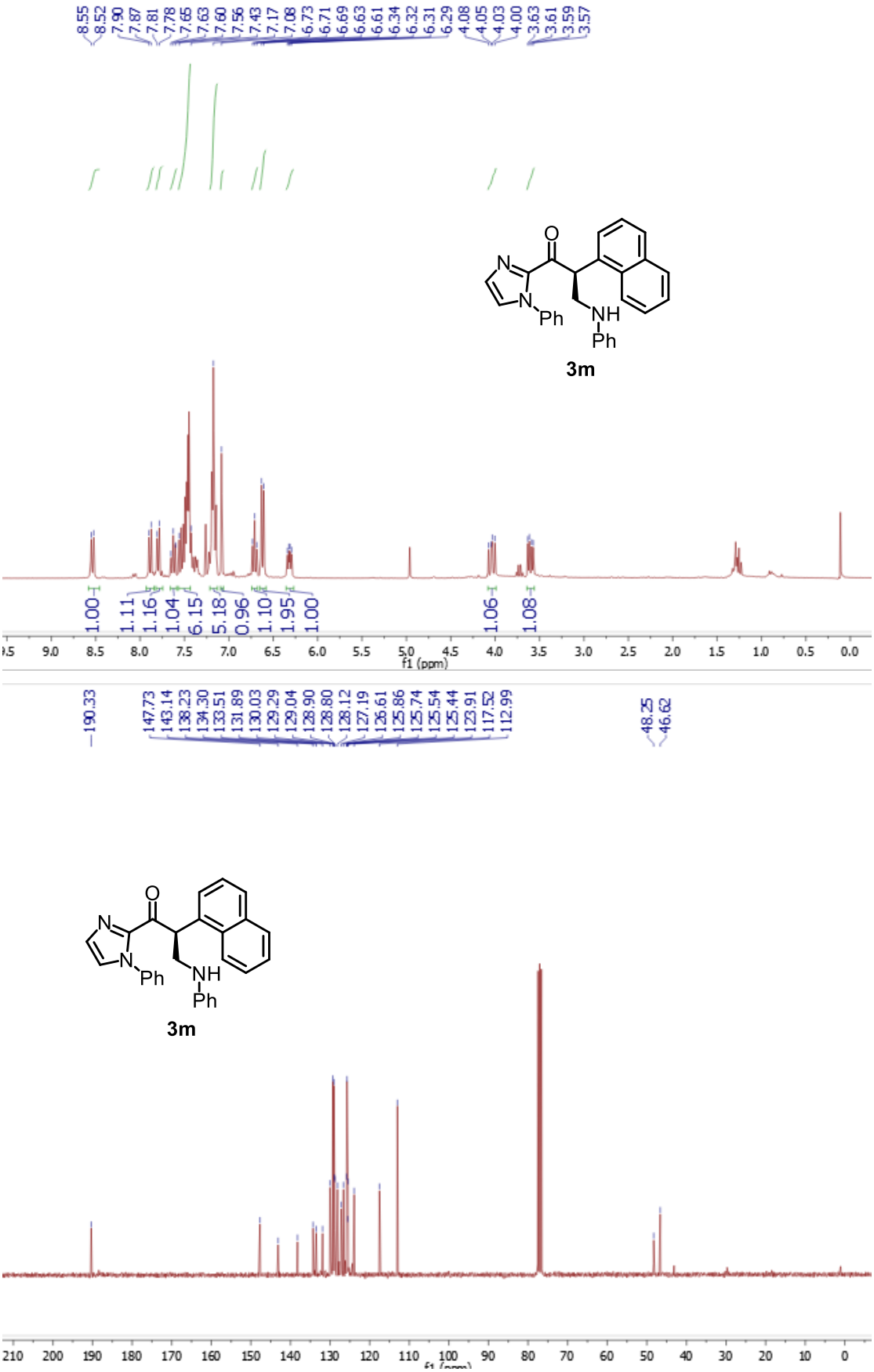
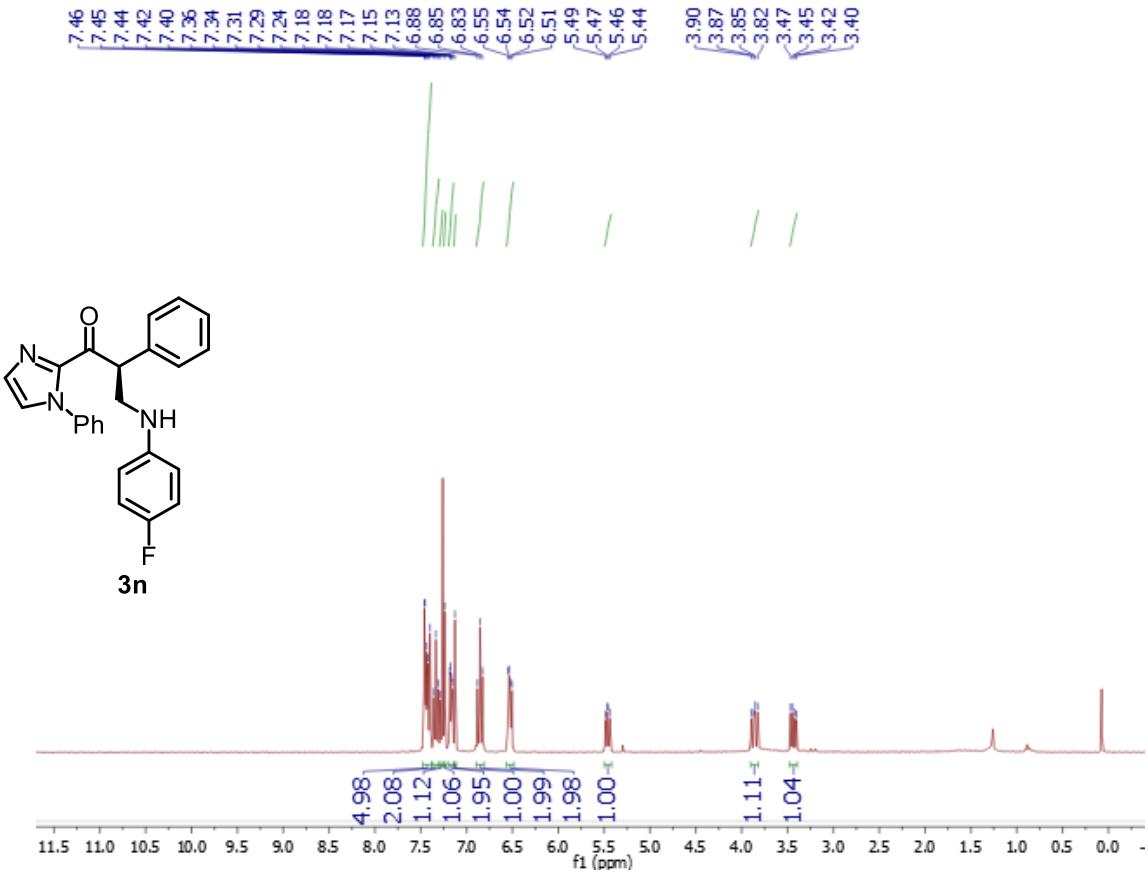
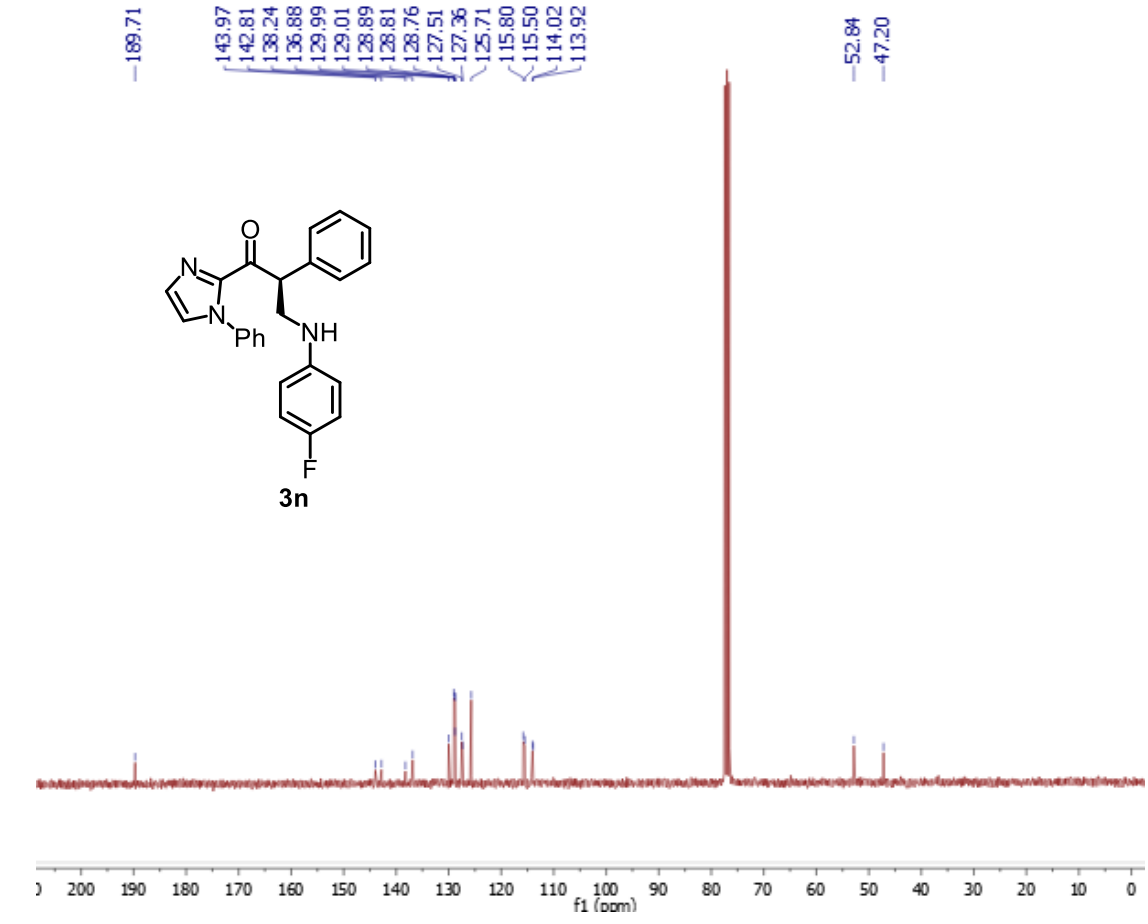


Figure S48. ^{1}H NMR and ^{13}C NMR spectra of **3m** in $CDCl_3$.


7.46
7.45
7.44
7.42
7.40
7.36
7.34
7.31
7.29
7.24
7.18
7.18
7.17
7.15
7.13
6.88
6.85
6.83
6.55
6.54
6.52
6.51
5.49
5.47
5.46
5.44
3.90
3.87
3.85
3.82
3.47
3.45
3.42
3.40
O
N
N
Ph
NH
F
3n
4.98
2.08
1.12
1.06
1.95
1.00
1.99
1.98
1.00
1.11
1.04
f1 (ppm)


189.71
143.97
142.81
138.24
136.88
129.99
129.01
128.89
128.81
128.76
127.51
127.36
125.71
115.80
115.50
114.02
113.92
52.84
47.20
O
N
N
Ph
NH
F
3n
f1 (ppm)

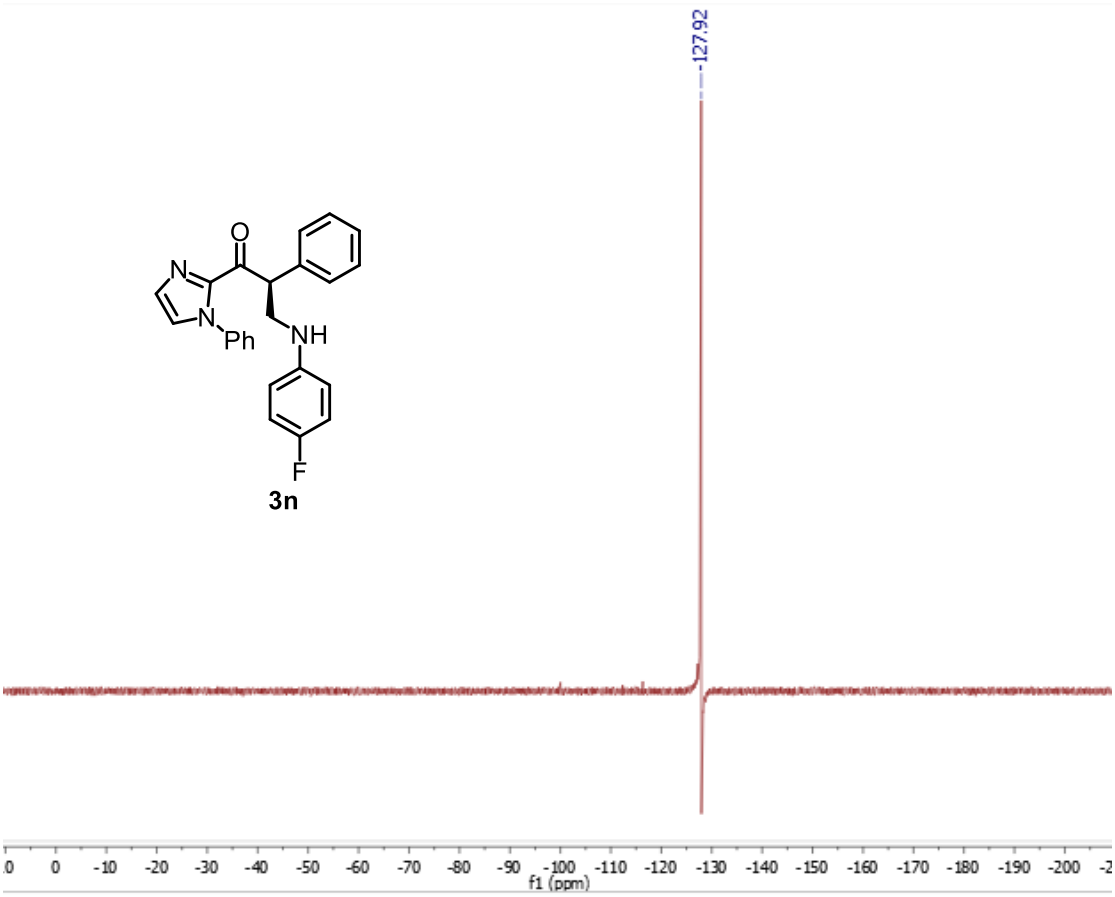


Figure S49. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **3n** in $CDCl_3$.

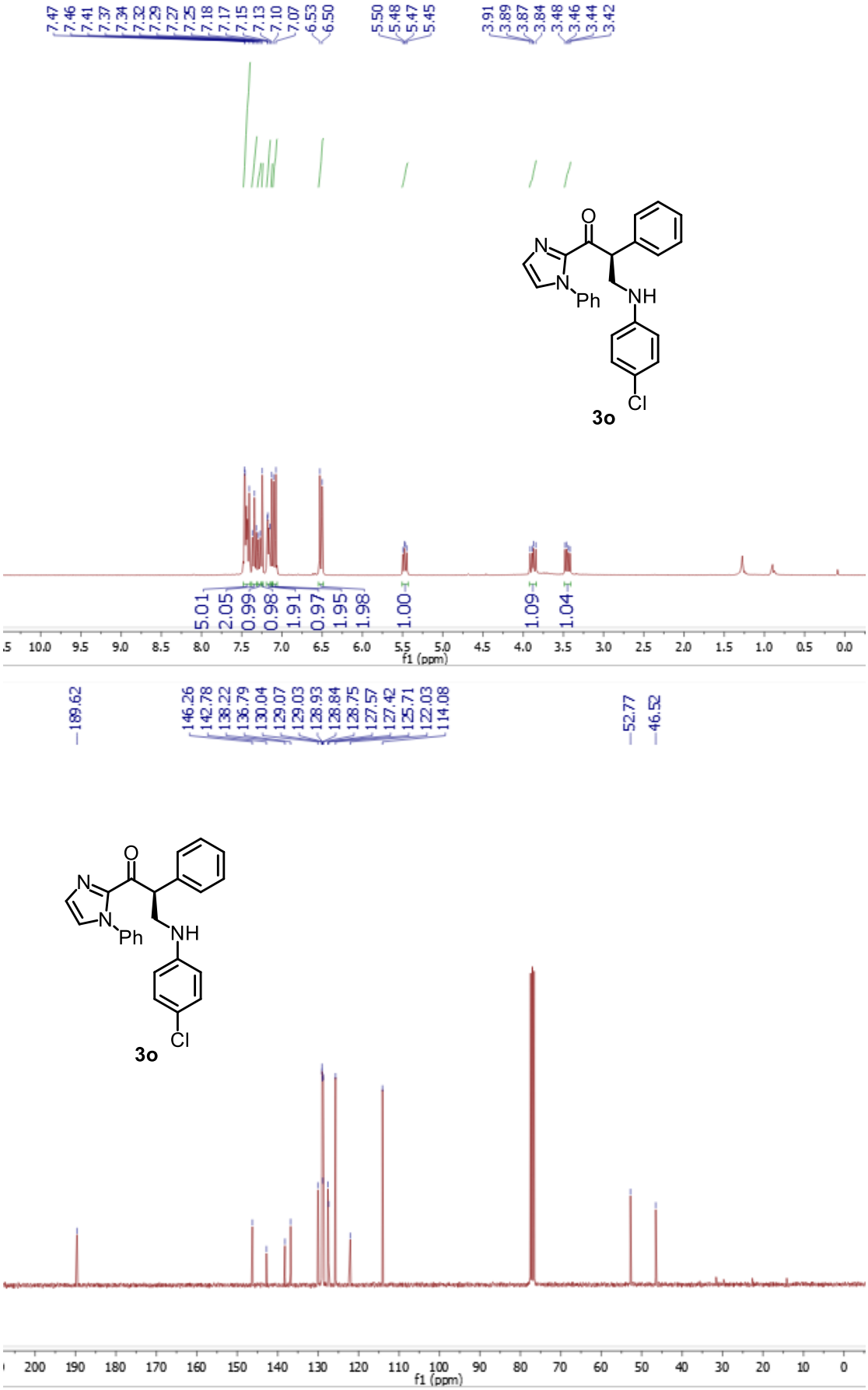


Figure S50. ^{1}H NMR and ^{13}C NMR spectra of **3o** in $CDCl_3$.

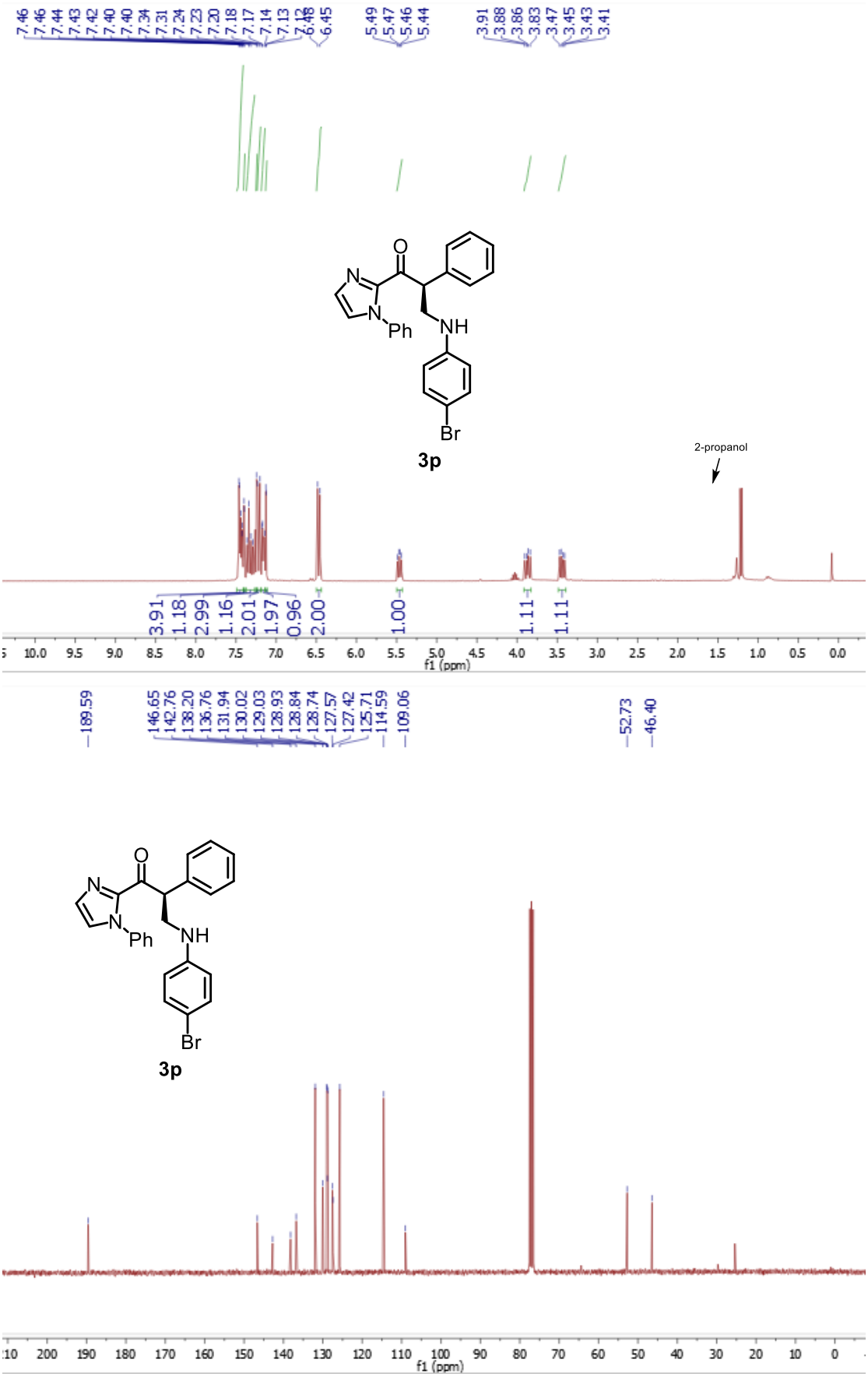


Figure S51. ^{1}H NMR and ^{13}C NMR spectra of **3p** in $CDCl_3$.

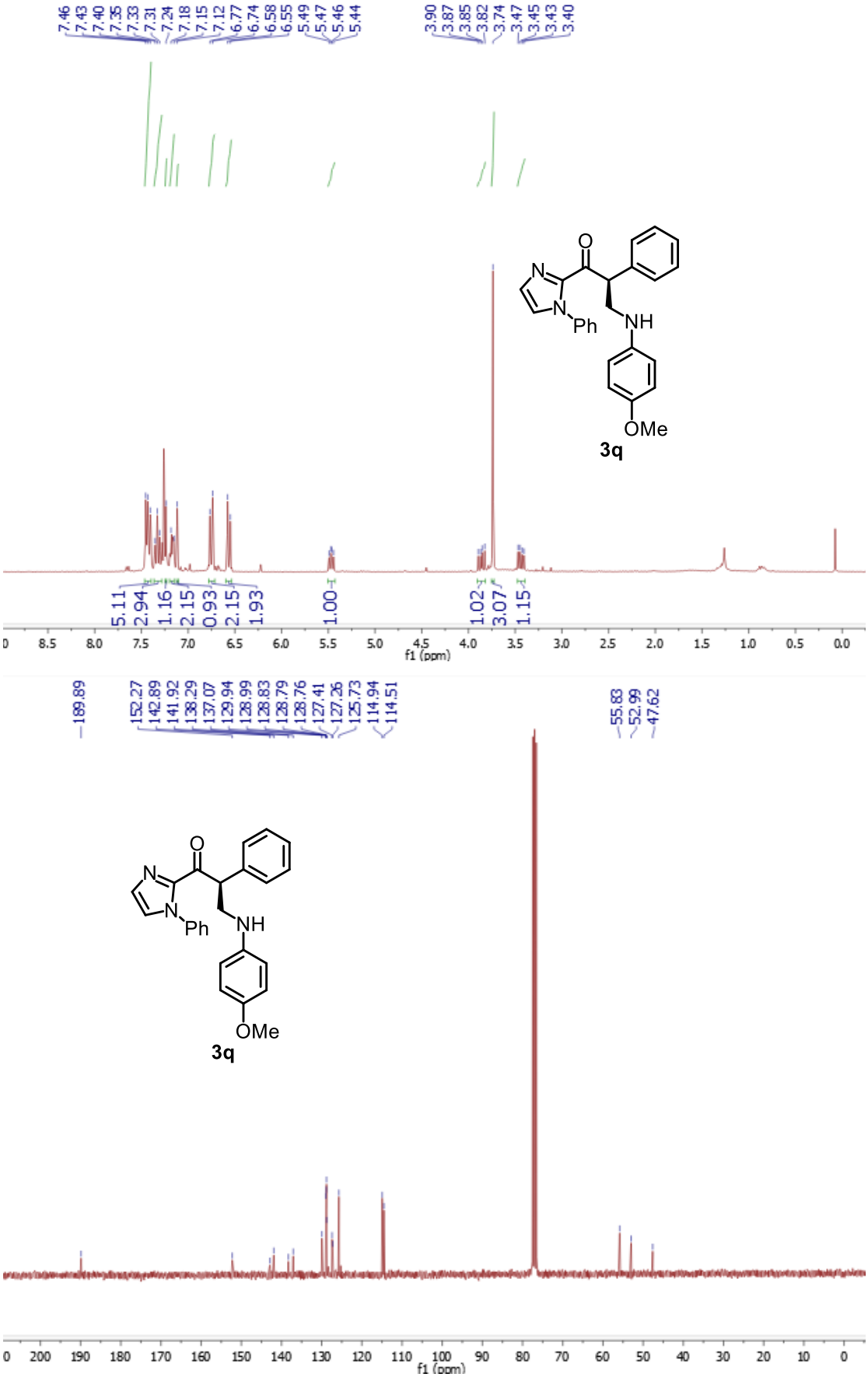


Figure S52. ^{1}H NMR and ^{13}C NMR spectra of **3q** in $CDCl_3$.

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