Supplementary Information

N-Heterocyclic Carbene-Catalyzed Atroposelective Synthesis of Axially Chiral 5-Aryl 2-Pyrones from Enals

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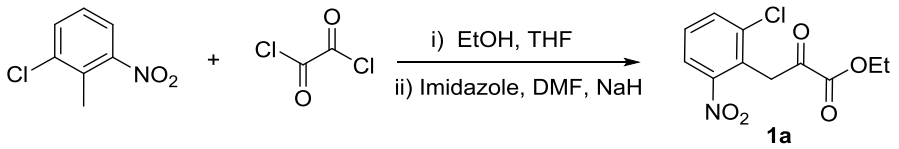
I: General Information

Chemicals were purchased as reagent grade and used without further purification. Solvents (THF, toluene) were distilled from appropriate drying agents prior to use. In addition, more solvents were purchased from commercial suppliers and dried over molecular sieves. Thin-layer chromatography (TLC) was performed using silica gel pre-coated glass plates (0.20 mm), which were visualized with a UV lamp (254 or 366 nm). Column chromatography (CC) was carried out using Tsingdao silica gel (60 Å, 200−300 mesh, particle size 0.040−0.063 mm). All reported yields, unless otherwise specified, refer to spectroscopically and chromatographically pure compounds. ^{1}H, ^{13}C, ^{19}F nuclear magnetic resonance (NMR) spectra were recorded on a Bruker spectrometer (400 MHz) in a suitable deuterated solvent. The solvent employed and respective measuring frequency is indicated for each experiment. Chemical shifts are reported with tetramethylsilane (TMS) serving as a universal reference of all nuclides. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and bs (broad singlet). All spectra were recorded at 298 K unless otherwise noted. The residual deuterated solvent signal relative to tetramethylsilane was used as the internal reference in ^{1}H NMR spectra ($CDCl_3$ δ 7.26), and are reported as follows: chemical shift in ppm (multiplicity, coupling constant *J* in Hz, number of protons). ^{13}C NMR spectra reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ δ 77.2). High resolution mass spectrometry (HRMS) was performed on a Waters Q-TOF Permier Spectrometer. Optical rotations were determined with Jasco P-1030 polarimeter. Data are reported as follows: $[\alpha]_D^{rt}$, concentration (c; g/100 mL), and solvents. Enantiomeric excesses (ee) were determined on a Shimadzu LC-20AD HPLC system employing a chiral stationary phase column specified in the individual experiment, by comparing the samples with the appropriate racemic mixtures.

II. General procedure

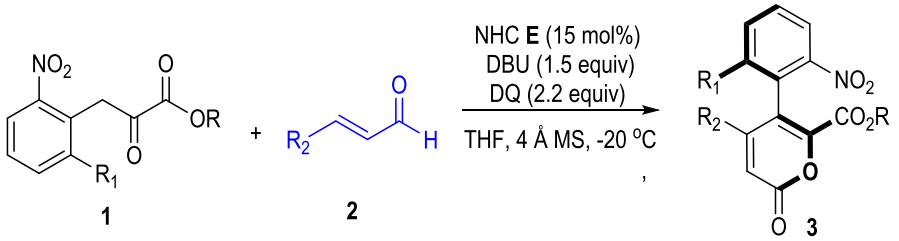
a) Preparation of substrates 1.



1a

(Synthe of **1a** as an example) To a solution of oxalyl chloride (5.0 mmol) in THF at 0 ^{o}C, was added ethanol (5.0 mmol, 1.0 equiv). After 1 h at 0 ^{o}C, a solution of imidazole (15.0 mmol, 3.0 equiv) in THF (20 mL) was added dropwise over 10 min. The mixture ws then stirred 30 min at 0 ^{o}C, filtered and concentrated under reduced pressure to give ethyl-2-oxoacetate as yellow oil, which was used directed without purification. To a solution of the obtained ethyl-2-oxoacetate above in DMF (30 mL) was added 1-chloro-2-methyl-3-nitrobenzene (5.0 mmol, 1.0 equiv). The mixture was cooled to 0 ^{o}C and added NaH (7.5 mmol, 1.5 equiv) slowly. After stirring at 0 ^{o}C for 30 min, the reaction mixture was warmed to r.t. and stirred for another 1 h, at which time the solution turned to wine red. Poured into aqueous NH_4Cl solution, and diluted with EtOAc, the organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel using EtOAc/PE = 1:10 as eluent to afford the desired product **1a** as a yellow oil (86% yield). **1b**-**1p** was synthesized according to the method described above.

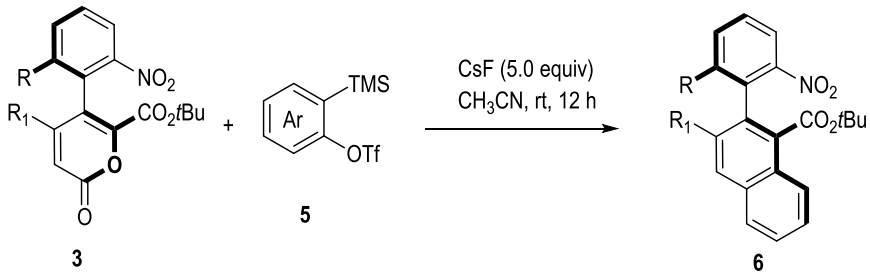
b) General Procedure for Asymmetric Synthesis of Axial Chiral 2-Pyrones 3.



1 2 3

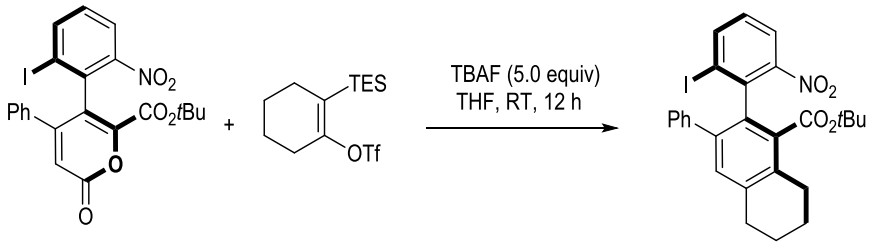
To an oven-dried screw-capped test tube equipped with a magnetic stir bar, the 2-oxoacetate **1** (0.1 mmol, 1.0 equiv)**,** triazolium salt NHC **E** (7.5 mg, 15 mol%), DQ (89.8 mg, 2.2 equiv), 4Å MS (100 mg) were added. To this mixture was added anhydrous THF (1.0 mL, 0.1 M) and then enal **2** (0.18 mmol, 1.8 equiv). As cooled to 0 ^{o}C, the resultant reaction mixture was added DBU (0.15 mmol, 1.5 equiv). When completed after stirring at -20 ^{o}C for 24 h, the reaction was purified by flash column chromatography on silica gel using EtOAc/PE (1:8) as eluent to afford the desired axially chiral 2-pyrones **3**.

c) General Procedure for Synthesis of Axially Chiral Biaryls 6 from 3.



3 5 6

Synthesis of axially chiral biaryls **6** is realized by Diels-Alder/Retro-Diels-Alder reaction between 2-pyrones **3** and arynes **5**. To an oven-dried screw-capped test tube equipped with a magnetic stir bar, the axially chiral 2-pyrones **3** (0.1 mmol, 1.0 equiv) and CsF (0.5 mmol, 5.0 eqquiv) were added. To this mixture was added anhydrous CH_3CN (1.0 mL, 0.1 M) and aryne (0.2 mmol, 2.0 equiv). When completed after stirring at r.t. for 12 h (monitored by TLC), the reaction was purified by flash column chromatography on silica gel using EtOAc/PE (1:10) as eluent to afford the desired chiral biaryls **6**. **6a-6i** was synthesized according to the method described above.

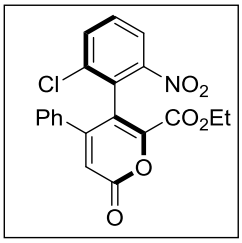


3i **6j**

To an oven-dried screw-capped test tube equipped with a magnetic stir bar, the axially chiral 2-pyrones **3i** (0.1 mmol, 1.0 equiv) and TBAF (0.5 mmol, 5.0 eqquiv) were added. To this mixture was added anhydrous THF (1.0 mL, 0.1 M) and alkyne 2-(triethylsilyl)cyclohex-1-en-1-yl trifluoromethanesulfonate (0.2 mmol, 2.0 equiv). When completed after stirring at r.t. for 12 h (monitored by TLC), the reaction was purified by flash column chromatography on silica gel using EtOAc/PE (1:10) as eluent to afford the desired chiral biaryls **6j**.

d) Studies of the Configurational Stability of Axially Chiral Products.

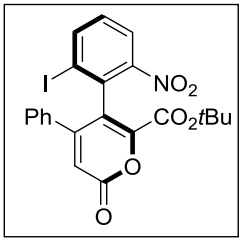
Table S1. Studies of the configurational stability of **3a**



entry[a]	Solvent	T (^{o}C)	Time	er
1	mesitylene	60	6 h	94.5:5.5
2	mesitylene	80	6 h	94.5:5.5
3	mesitylene	100	6 h	94.5:5.5
4	mesitylene	110	6 h	94.5:5.5
5	mesitylene	130	6 h	94.5:5.5

The configurational stability of the product **3a** was studied by heating a solution of 10 mg **3a** in 1 mL mesitylene for 6 h. The enantiomeric ratio (er) was determined by HPLC.

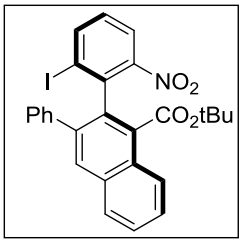
Table S2. Studies of the configurational stability of **3i**



entry[a]	Solvent	T (^{o}C)	Time	Ee (%)
1	mesitylene	60	6 h	99:1
2	mesitylene	80	6 h	99:1
3	mesitylene	100	6 h	99:1
4	mesitylene	110	6 h	99:1
5	mesitylene	130	6 h	decomposed partially

The configurational stability of the product **3i** was studied by heating a solution of 10 mg **3i** in 1 mL mesitylene for 6 h. The enantiomeric ratio (er) was determined by HPLC.

Table S3. Studies of the configurational stability of **6c**

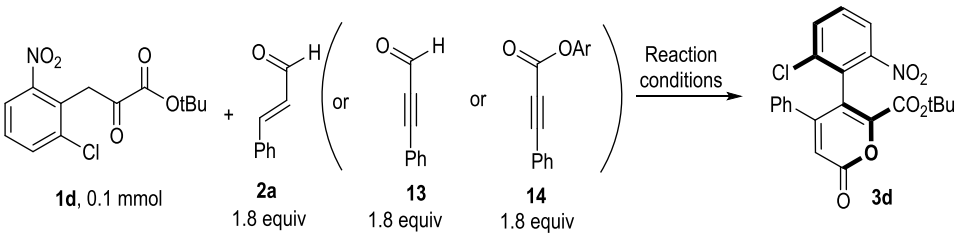


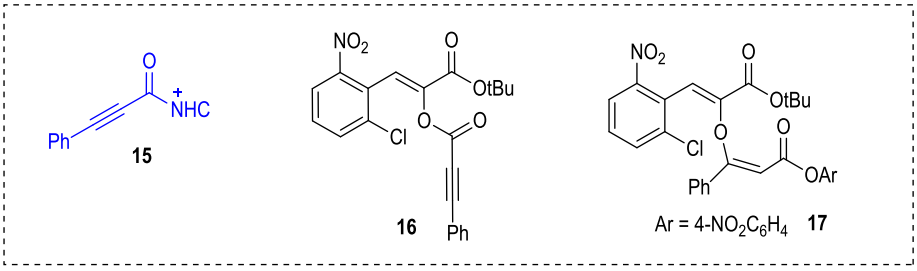
entry[a]	Solvent	T (^{o}C)	Time	Ee (%)
1	mesitylene	60	6 h	99:1
2	mesitylene	80	6 h	99:1
3	mesitylene	100	6 h	99:1
4	mesitylene	110	6 h	99:1
5	mesitylene	130	6 h	99:1

The configurational stability of the product **6c** was studied by heating a solution of 10 mg **6c** in 1 mL mesitylene for 6 h. The enantiomeric ratio (er) was determined by HPLC.

e) Comparison of enals reactions with ynal and alkyne ester.

Table S4. Comparison of enals reactions with ynal and alkyne ester





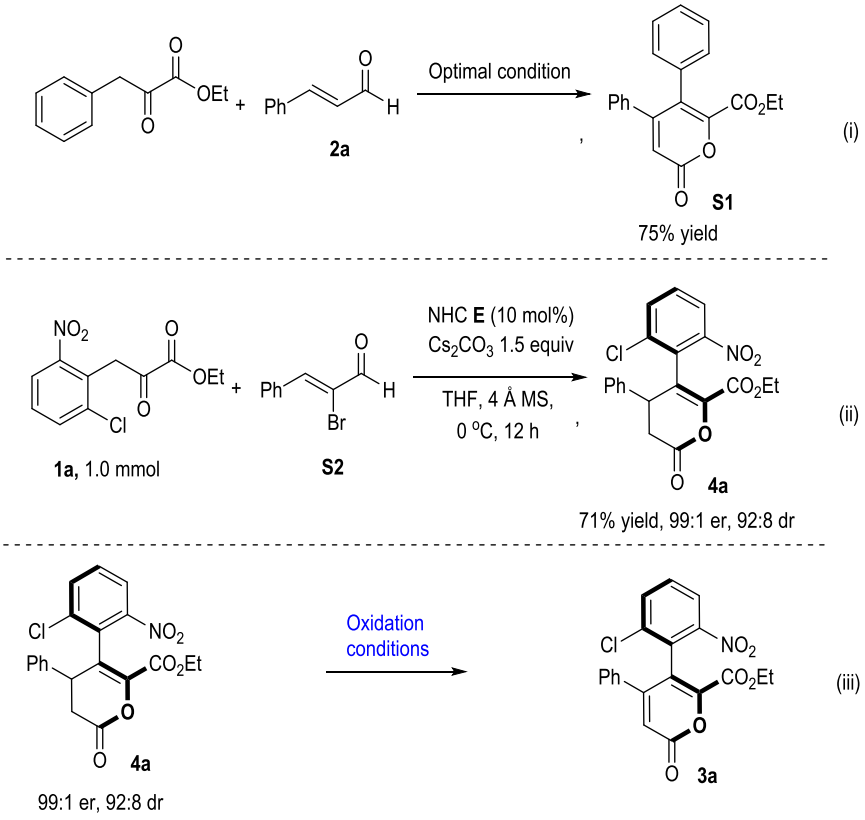
entry	Reaction	Conditions	Yield **3d**	er **3d**	**16**	**17**
1	enal **2a**	as Table 1, entry 22	90	97.5:2.5	n.d.	n.d.
2	ynal **5**	as Table 1, entry 22	n.d.	/	n.d.	n.d.
3	ynal **5**	N_2 other conditions as Table 1, entry 22	n.d.	/	n.d.	n.d.
4	alkyne ester **6**	except not adding DQ , other conditions as Table 1, entry 22	n.d.	/	< 10	n.d.
5	enal **2a**	NHC **E** (15 mol%), DQ (2.2 equiv), Cs_2CO_3 (1.5 equiv) , RT	63	83:17	n.d.	n.d.
6	ynal **5**	as entry 5 above	n.d.	/	43	n.d.
7	ynal **5**	as entry 5 above, except using Et_3N as base	n.d.	/	35	n.d.
8	ynal **5**	as entry 5 above, except using NaOAc as base	n.d.	/	<10	n.d.
9	alkyne ester **6**	NHC **E** (15 mol%), Cs_2CO_3 (1.5 equiv) , RT	n.d.	/	34	45
10	alkyne ester **6**	as entry 7 above, except using Et_3N as base	n.d.	/	35	<10
11	alkyne ester **6**	as entry 7 above, except using NaOAc as base	n.d.	/	31	<10

NHC-catalyzes ynals under oxidative conditions or directly catalyzes alkynyl esters to obtain acetylenic acylazolium intermediates, which have been demonstrated as powerful tools to heteroarene formation. We hypothesize that the 2-oxoacetate **1** can also undergo a asymmetric annulation reaction with this acetylenic acylazolium intermediates to obtain axially chiral 2-pyrones **3**. We conducted some control

experiments and the results are summarized as follows. Under the optimal conditions reported in the text (Table 1, entry 22), the cinnamaldehyde **2a** could react with *tert*-butyl-2-oxoacetate **1d** to obtain the desired axially chiral 2-pyrones **3d** with excellent result (90% yield, 97.5:1.5 er). But when using ynal **13** to react with *tert*-butyl 2-oxoacetate **1d** in an air atmosphere or even in a N_2 atmosphere, no product formation was detected (entries 2 & 3); Using alkyne ester **14**, under the conditions of excluding oxidant, reacted with substrate **1d**, only a trace amount of esterification product **16** was detected (entry 4). Taking into account the nucleophilicity of DBU, it might be unfriendly to the highly acetylenic acylazolium intermediate when using as base. Next, we screened the reaction conditions by using different bases. Using Cs_2CO_3 as the base , cinnamaldehyde could react with **1d** to obtain the desired axially chiral 2-pyrones **3d** with moderate yield and er values (entry 5, 63% yield, 83:17 er). However, when Cs_2CO_3, Et_3N or NaOAc was used as the base, the reaction of ynal **13** and **1d** does not yield the target product, and **16** is a by-product that can be monitored (entries 6-8). It is worth noting that when alkyne ester **14** was used to react with **1d** by using Cs_2CO_3 as base, the esterification product **16** and the product **17** which features an O-attack manner of **1d** to the β carbon of acetylenic acylazolium intermediates were produced as by-products in comparable yield (entry 9). Et_3N and NaOAc produced **16** as main by-product accompanied by trace amounts of **17** (entries 10 &11)**.**

f) Mechanism Study.

Table S5. Studies of the aromatization condition of **4**



entry[a]	Oxidation conditions	yield **3a**	er **3a**
1	NHC **E** (10 mol%), DBU (1.5 equiv), DQ (1.2 equiv)	70	88:12
2	DBU (1.5 equiv), DQ (1.2 equiv)	65	88.5:11.5
3	DQ (1.2 equiv)	n.d.	/
4	DBU (1.5 equiv)	n.d.	/
5	Cs_2CO_3 (1.5 equiv), DQ (1.2 equiv)	39	90:10
6	DBU (1.5 equiv), MnO_2	30	83:17

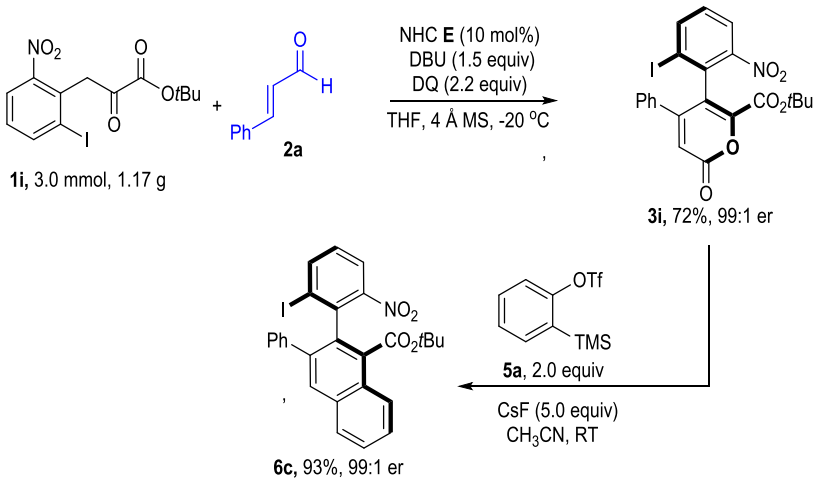
[a] Reaction conditions: **4a** (32.0 mg, 0.08 mmol), THF (0.8 mL, 0.1 M), RT, 6 h.

In order to determine the aromatization condition, we conducted some control experiments. First, by using ethyl 2-oxo-3-phenylpropanoate to react with cinnamaldehyde **2a**, under our optimal reaction conditions, the aromatized product **S1** can be obtained smoothly (Table S5i), which shows that the nitro group in the enol substrate structure is not a necessary condition for aromatization. Next, using 2-bromoenal **S2** instead of cinnamaldehyde **2a**, we prepared the unaromatized product **4a** in 71% yield with excellent dr and er values (Table S5ii, 92:8 dr, 99:1 er). This unaromatized product can continue to be oxidized under the reaction conditions, and the target product **3a** can be obtained in 70% yield with 88:12 er (entry 1). Excluding the NHC catalyst from the reaction system has little effect on the oxidation results (entry 2). However, when DQ or DBU was investigated separately, the oxidation step couldn't take place (entries 3&4). While adding DQ, but using Cs_2CO_3 as the base, the reaction yield was reduced with a slightly increased er value (entry 5). Furthermore, when DBU was added as a base but MnO_2 was used as an oxidant, the yield and er value of the reaction were both reduced (entry 6). According to these experimental results described above, it can be clearly seen that the suse of DBU as a base in combination with DQ as an oxidant is a key factor to ensure the effective progress of the oxidation step.

Preparation of product **4a:**

To an oven-dried screw-capped test tube equipped with a magnetic stir bar, the Ethyl-2-oxoacetate **1a** (27.2 mg, 0.1 mmol)**,** (*Z*)-2-bromo-3-phenylacrylaldehyde **S2** (25.3 mg, 1.2 equiv)**,** triazolium salt NHC **E** (4.9 mg, 10 mol%), DQ (49.0 mg, 1.2 equiv), Cs_2CO_3 (48.9 mg, 1.5 equiv) and 4Å MS (100 mg) were added. To this mixture was added anhydrous THF (1.0 mL, 0.1 M) and then cooled to 0 ^oC. When completed after stirring at 0 ^oC for 12 h, the reaction was purified by flash column chromatography on silica gel using EtOAc/PE/DCM (1:10:1) as eluent to afford the desired product **4a** as yellow oil (71% yield, 99:1 er, 92:8 dr) .

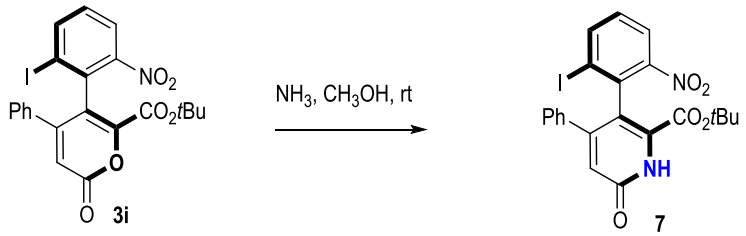
g) Gram scale synthesis of 3i and 6d.



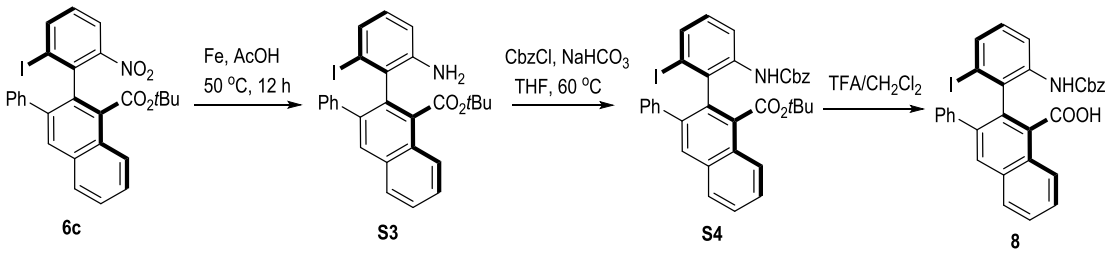
To an oven-dried 50 ml round-bottomed flask equipped with a magnetic stir bar, the *tert*-butyl-2-oxoacetate **1i** (1.17 g, 3.0 mmol)**,** triazolium salt NHC **E** (0.15 g, 10 mol%), DQ (2.69 g, 2.2 equiv), 4Å MS (1.0 g) were added. To this mixture was added anhydrous THF (30 mL, 0.15 M) and then cinnamaldehyde **2a** (0.68 mL, 5.4 mmol). As cooled to 0 ^{o}C, the resultant reaction mixture was added DBU (0.69 g, 1.5 equiv). When completed after stirring at -20 ^{o}C for 24 h, the reaction was purified by flash column chromatography on silica gel using EtOAc/PE (1:8) as eluent to afford the desired axially chiral 2-pyrones **3i** (1.12 g, 72% yield, 99:1 er).

To an oven-dried 50 ml round-bottomed flask equipped with a magnetic stir bar, the obtained axially chiral 2-pyrones **3i** (1.12 g, 2.16 mmol) and CsF (1.64 g, 10.8 mmol) were added. To this mixture was added anhydrous CH_3CN (15 mL, 0.15 M) and then aryne **5a** (1.29, 4.32 mmol). When completed after stirring at r.t. for 12 h (monitored by TLC), the reaction was purified by flash column chromatography on silica gel using EtOAc/PE (1:10) as eluent to afford the desired chiral biaryls **6c** (1.10 g, 93% yield, 99:1 er).

h) Synthetic transformations



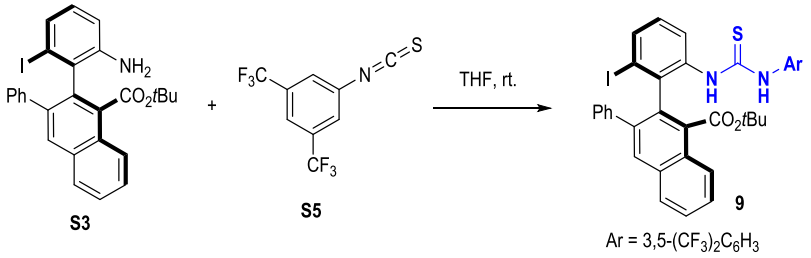
To an oven-dried screw-capped test tube equipped with a magnetic stir bar, the axially chiral 2-pyrones **3i** (0.1 mmol, 1.0 equiv) were added. To this mixture was added anhydrous CH_3OH (0.5 mL, 0.2 M) and then NH_3 (NH_3 in CH_3OH, 10.0 equiv, 2.0 M). When completed after stirring at r.t. for 6 h, the reaction was purified by flash column chromatography on silica gel using EtOAc/PE (1:8) as eluent to afford the desired axially chiral 2-pyridone 7 (73% yield, 97.5:2.5 er).



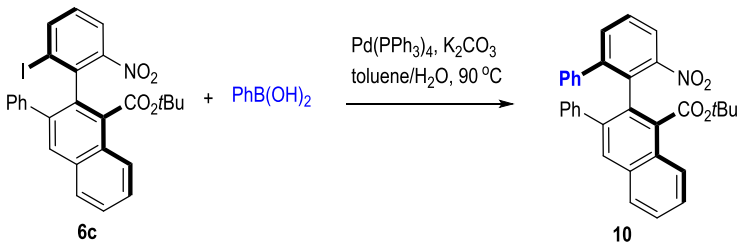
To an oven-dried screw-capped test tube equipped with a magnetic stir bar, **6c** (55.1 mg, 0.1 mmol) and Fe powder (28.0 mg, 0.5 mmol) were added. To this mixture was added AcOH (1.0 mL, 0.1 M). When completed after stirring at 50 °C for 20 h, the reaction was diluted with CH_2Cl_2 and filtered was filtered through celite. The residue obtained after the *in vacuo* removal of solvent was further purified by flash column chromatography on silica gel using EtOAc/PE (1:10) as eluent to afford the desired product **S3** (91% yield, 99:1 er).

To an oven-dried screw-capped test tube equipped with a magnetic stir bar, **S3** (52.1 mg, 0.1 mmol) and $NaHCO_3$ (42.0 mg, 5.0 equiv) were added. To this mixture was added anhydrous THF (1.0 mL, 0.1 M) and then benzyl chloroformate (51.2 mg, 3.0 equiv). When completed after stirring at 60 °C for 24 h, the reaction was diluted with CH_2Cl_2 and filtered through celite. The residue obtained after the *in vacuo* removal of solvent was further purified by flash column chromatography on silica gel using EtOAc/PE (1:10) as eluent to afford the desired product **S4** (89% yield, 99:1 er).

To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added **S4** (52.5 mg, 0.08 mmol) and then TFA/CH_2Cl_2 (v/v = 1:4, 1.0 mL). When completed after stirring at r.t. for 6 h, the reaction was diluted with CH_2Cl_2 and filtered was filtered through celite. The residue obtained after the *in vacuo* removal of solvent was further purified by flash column chromatography on silica gel using CH_2Cl_2/CH_3OH (30:1) as eluent to afford the desired axial chiral amino acids **8** (92% yield, 99:1 er).

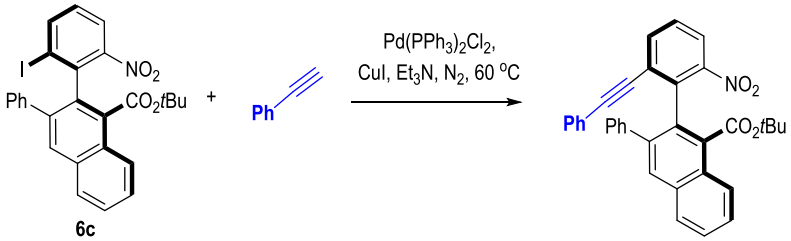


To an oven-dried screw-capped test tube equipped with a magnetic stir bar, **S3** (52.1 mg, 0.1 mmol) was added. To this tube was added anhydrous THF (1.0 mL, 0.1 M) and then 1-isothiocyanato-3,5-bis(trifluoromethyl)benzene **S5** (29.8 mg, 1.1 equiv). When completed after stirring at r.t. for 24 h, the reaction was purified by flash column chromatography on silica gel using EtOAc/PE (1:8) as eluent to afford the desired axially chiral thiourea **9** (89% yield, 99:1 er).



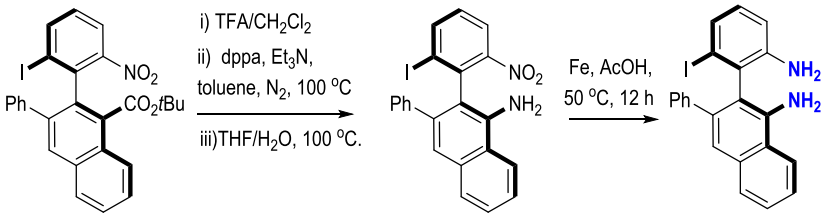
6c 10

To an oven-dried screw-capped test tube equipped with a magnetic stir bar, **6c** (55.1 mg, 0.1 mmol)**,** $PhB(OH)_2$ (18.3 mg, 1.5 equiv), K_2CO_3 (27.6 mg, 2.0 equiv) and $Pd(PPh_3)_4$ (11.6 mg, 0.1 mmol) were added. To this mixture was added toluene/H_2O (v/v = 4:1, 1 mL). After having been stirred at 90 °C for 12 h, the reaction was diluted with EtOAc (10 mL) and filtered through celite. The residue obtained after the *in vacuo* removal of solvent was further purified by flash column chromatography on silica gel using EtOAc/PE/CH_2Cl_2 (1:8:1) as eluent to afford the desired axially chiral product **10** (93% yield, 99:1 er).



6c 11

To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added **6c** (55.1 mg, 0.1 mmol), ethynylbenzene (12.3 mg, 0.12 mmol), $Pd(PPh_3)_2Cl_2$ (7.0 mg, 10 mol%), CuI (1.0 mg, 5 mol%) and Et_3N (1 mL) under N_2 atmosphere. After having been stirred at 60 ℃ for 12 h. the reaction was evaporated to give a residue, which was purified by column chromatography EtOAc/PE (1:8) to obtained product **11** as a white solid (92% yield, 96:4 er).

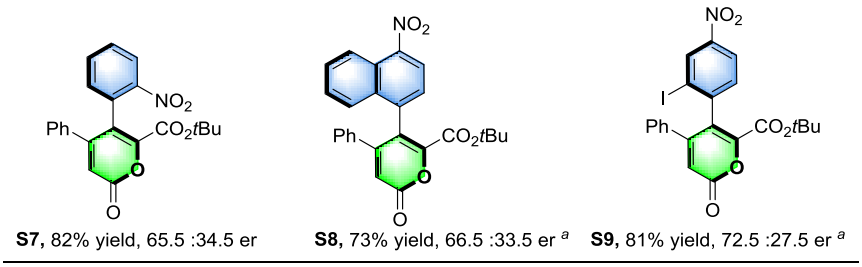


6c S6 12

To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added **6c** (55.1 mg, 0.1 mmol) and then TFA/CH_2Cl_2 (v/v = 1:4, 1.0 mL). When completed after stirring at r.t. for 6 h, the solvent was removed *in vacuo*. The acid obtained was dissolved in toluene, Et_3N (50.6 mg, 0.5 mmol) and diphenylphosphoryl azide (55.0 mg, 0.2 mmol) was sequentially added under N_2 atmosphere. After stirring for 30 minutes at r.t, the reaction was heated to 90 ℃ for another 10 hours. The toluene was removed under reduced pressure and replaced with THF and H_2O (v/v = 1:1, 1.0 mL). The solution was stirred for 6 hours at 90 ℃ and then THF was removed *in vacuo*. To the residue was added K_2CO_3 (aq) and EtOAc. The two phases were

separated and the aqueous layer was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel using EtOAc/PE (1:6) as eluent to afford the resulting product **S6** (81% yield for two steps, 99:1 er). Following the produce described above, reduction of **S6** affording the desired BINAM analogue **12** (86% yield, 99:1 er).

i) Expanded substrate scope examination.

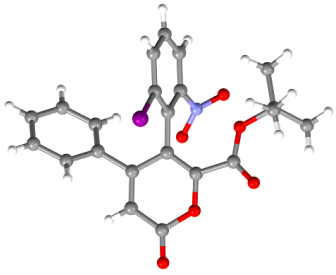


S7, 82% yield, 65.5 :34.5 er **S8**, 73% yield, 66.5 :33.5 er [a] **S9**, 81% yield, 72.5 :27.5 er [a]

Standard condition as Table 1, entry 22; (a) Reaction was performed at 0 °C.

We expanded the substrate scope examination. When substrates **1** only bearing one nitro group at ortho-position, the reaction can proceed smoothly with high yield but decreased er value. Similar result were observed when substrates **1** bearing a para -NO_2 group instead of ortho-nitro group. Substrates**1** bearing a meta-NO_2 group can not be prepared using our method at this time.

j) X-Ray Crystallographic Data of 3i and 6d.



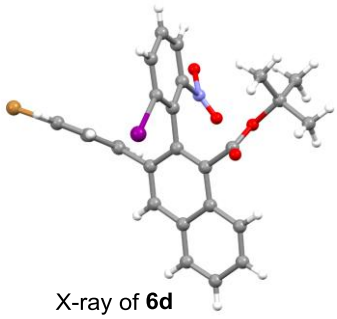
X-ray of **3i**

Product **3i** was crystallized as a colorless crystal via vaporization of a hexane/ethyl acetate solution, and its absolute configuration was determined by X-ray structure analaysis. CCDC 2096844 contains the supplementary crystallographic data that can be obtained free of charge from The Cambridge Crystallographic Data Centrevia www.ccdc.cam.ac.uk/data request/cif.

Table S6. Crystal data and structure refinement for **3i**.

Identification code	2573
Empirical formula	$C_{22}H_{18}INO_6$
Formula weight	519.27
Temperature/K	149.99(10)
Crystal system	monoclinic

Space group	$P2_1$
Unit cell dimensions	A = 7.9117(3) Å α = 90 ° B = 10.5206(4) Å β = 99.285(4) ° C = 13.0453(6) γ = 90 °
Volume/Å^3	1071.61(8)
Z	2
ρ_{calc}g/cm^3	1.609
μ/mm^{-1}	1.532
F(000)	516.0
Crystal size/mm^3	0.13 ×0.11 ×0.09
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5 to 58.868
Index ranges	-10 ≤ h ≤ 10, -13 ≤ k ≤ 14, -17 ≤ l ≤ 11
Reflections collected	8958
Independent reflections	4824 [R_{int} = 0.0297, R_{sigma} = 0.0535]
Data/restraints/parameters	4824/1/274
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0323, wR_2 = 0.0564
Final R indexes [all data]	R_1 = 0.0351, wR_2 = 0.0586
Largest diff. peak/hole / e Å^{-3}	0.56/-0.51
Flack parameter	-0.011(12)



X-ray of **6d**

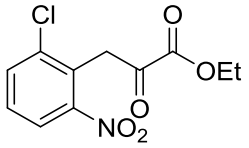
Product **6d** was crystallized as a colorless crystal via vaporization of a hexane/ethyl acetate solution, and its absolute configuration was determined by X-ray structure analaysis. CCDC 2096843 contains the supplementary crystallographic data that can be obtained free of charge from The Cambridge Crystallographic Data Centrevia www.ccdc.cam.ac.uk/data request/cif.

Table S7. Crystal data and structure refinement for **6d**.

Identification code	046-ar
Empirical formula	$C_{27}H_{21}BrINO_4$
Formula weight	630.26
Temperature/K	150.00(10)
Crystal system	monoclinic

Space group	$P2_1$	
Unit cell dimensions	a = 18.1954(12) Å	α = 90 °
	b = 7.7720(4) Å	β = 111.631(8) °
	c = 18.4933(14) Å	γ = 90 °
Volume/Å^3	2431.1(3)	
Z	4	
ρ_{calc}g/cm^3	1.722	
μ/mm^{-1}	2.995	
F(000)	1240.0	
Crystal size/mm^3	0.12 × 0.11 × 0.09	
Radiation	Mo Kα (λ = 0.71073)	
2Θ range for data collection/°	3.952 to 59.058	
Index ranges	$-24 \leq h \leq 24$, $-10 \leq k \leq 7$, $-15 \leq l \leq 24$	
Reflections collected	13229	
Independent reflections	8828 [R_{int} = 0.0372, R_{sigma} = 0.0762]	
Data/restraints/parameters	8828/53/630	
Goodness-of-fit on F^2	1.057	
Final R indexes [I>=2σ (I)]	R_1 = 0.0585, wR_2 = 0.1356	
Final R indexes [all data]	R_1 = 0.0763, wR_2 = 0.1492	
Largest diff. peak/hole / e Å^{-3}	1.28/-1.20	
Flack parameter	-0.011(19)	

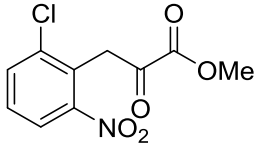
k) Full Characterization of Substrates and Products.



1a

Ethyl 3-(2-chloro-6-nitrophenyl)-2-oxopropanoate (1a)

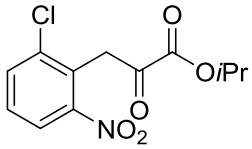
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 4.69 (s, 2H), 4.38 (q, *J* = 6.8 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 188.26, 160.13, 150.38, 137.54, 134.63, 129.20, 127.62, 123.86, 63.18, 40.84, 14.08; **HRMS** (ESI) Calcd for $C_{11}H_{11}ClNO_5^+$ $[M+H]^+$ 272.0320; Found: 272.0323.



1b

Methyl 3-(2-chloro-6-nitrophenyl)-2-oxopropanoate (1b)

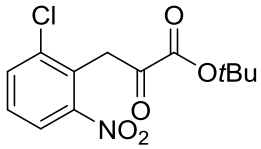
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.4 Hz, 1H), 4.68 (s, 2H), 3.93 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 187.92, 160.52, 150.36, 137.52, 134.66, 129.26, 127.47, 123.88, 53.57, 40.89. **HRMS** (ESI) Calcd for $C_{10}H_9ClNO_5^+$ $[M+H]^+$ 258.0164; Found: 258.0167.



1c

Isopropyl 3-(2-chloro-6-nitrophenyl)-2-oxopropanoate (1c)

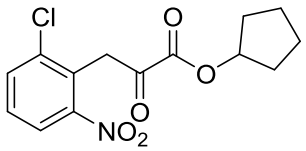
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 8.4 Hz, 1H), 5.14-5.20 (m, 1H), 4.64 (s, 2H), 1.35 (d, *J* = 6.4 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 188.59, 159.72, 150.36, 137.51, 134.61, 129.17, 127.72, 123.83, 71.53, 40.76, 21.65. **HRMS** (ESI) Calcd for $C_{12}H_{13}ClNO_5^+$ $[M+H]^+$ 286.0477; Found: 286.0480.



1d

Tert-butyl 3-(2-chloro-6-nitrophenyl)-2-oxopropanoate (1d)

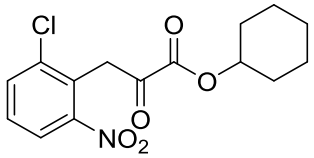
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 4.62 (s, 2H), 1.57 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 189.24, 159.40, 150.39, 137.58, 134.58, 129.04, 128.01, 123.81, 84.86, 40.60, 27.86. **HRMS** (ESI) Calcd for $C_{13}H_{15}ClNO_5^+$ $[M+H]^+$ 300.0633; Found: 300.0629.



1e

Cyclopentyl 3-(2-chloro-6-nitrophenyl)-2-oxopropanoate (1e)

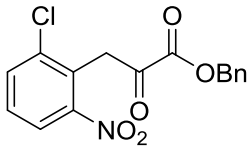
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 5.30-5.34 (m, 1H), 4.63 (s, 2H), 1.87-1.97 (m, 2H), 1.71-1.85 (m, 4H), 1.58-1.65 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 188.54, 160.03, 150.34, 137.50, 134.60, 129.17, 127.72, 123.82, 80.45, 40.76, 32.66, 23.80. **HRMS** (ESI) Calcd for $C_{14}H_{14}ClNNaO_5^+$ $[M+Na]^+$ 334.0453; Found: 334.0448.



1f

Cyclohexyl 3-(2-chloro-6-nitrophenyl)-2-oxopropanoate (1f)

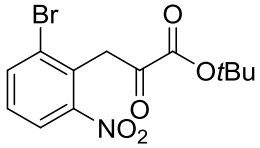
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 4.93-5.00 (m, 1H), 4.68 (s, 2H), 1.93-1.97 (m, 2H), 1.75-1.82 (m, 2H), 1.53-1.63 (m, 3H), 1.24-1.46 (m, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 188.61, 159.62, 150.38, 137.58, 134.61, 129.12, 127.81, 123.85, 76.24, 40.84, 31.33, 25.23, 23.71; **HRMS** (ESI) Calcd for $C_{15}H_{17}ClNO_5^+$ $[M+H]^+$ 326.0790; Found: 326.0793.



1g

Benzyl 3-(2-chloro-6-nitrophenyl)-2-oxopropanoate (1g)

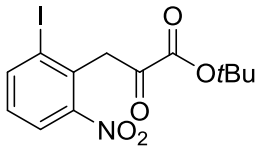
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.36-7.44 (m, 6H), 5.36 (s, 2H), 4.70 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 187.92, 159.95, 150.35, 137.57, 134.66, 134.37, 129.22, 128.99, 128.94, 128.87, 128.78, 127.56, 123.90, 68.60, 40.93; **HRMS** (ESI) Calcd for $C_{16}H_{13}ClNO_5^+$ $[M+H]^+$ 334.0477; Found: 334.0471.



1h

***Tert*-butyl 3-(2-bromo-6-nitrophenyl)-2-oxopropanoate (1h)**

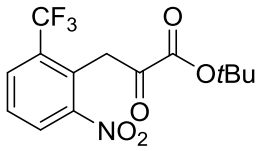
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 4.66 (s, 2H), 1.58 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 189.16, 159.41, 150.45, 137.88, 129.61, 129.43, 128.26, 124.43, 84.86, 43.51, 27.88; **HRMS** (ESI) Calcd for $C_{13}H_{15}BrNO_5^+$ $[M+H]^+$ 344.0128; Found: 344.0120.



1i

***Tert*-butyl 3-(2-iodo-6-nitrophenyl)-2-oxopropanoate (1i)**

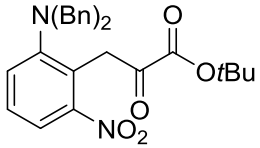
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 4.67 (s, 2H), 1.59 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 189.15, 159.46, 149.74, 144.54, 132.62, 129.91, 125.28, 105.02, 84.86, 48.69, 27.89. **HRMS** (ESI) Calcd for $C_{13}H_{15}INO_5^+$ $[M+H]^+$ 391.9989; Found: 391.9982.



1j

***Tert*-butyl 3-(2-nitro-6-(trifluoromethyl)phenyl)-2-oxopropanoate (1j)**

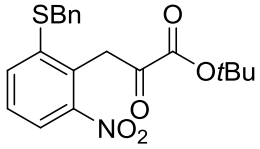
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 4.61 (s, 2H), 1.58 (s, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -59.2; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 188.87, 159.13, 150.66, 132.28 (q, *J* = 30.3 Hz) 130.99 (q, *J* = 5.7 Hz), 128.97, 128.73, 128.50, 123.16 (q, *J* = 273.0 Hz), 84.97, 39.23, 27.82. **HRMS** (ESI) Calcd for $C_{14}H_{15}F_3NO_5^+$ $[M+H]^+$ 334.0897; Found: 334.0898.



1k

***Tert*-butyl 3-(2-(dibenzylamino)-6-nitrophenyl)-2-oxopropanoate (1k)**

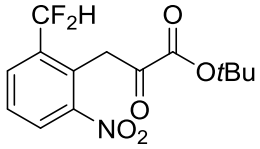
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.23-7.33 (m, 8H), 7.14-7.16 (m, 4H), 4.80 (s, 2H), 4.05 (s, 4H), 1.559 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 191.68, 160.06, 152.36, 149.62, 136.68, 130.17, 129.16, 128.51, 127.98, 127.92, 127.61, 121.57, 84.37, 58.23, 38.41, 27.91. **HRMS** (ESI) Calcd for $C_{27}H_{28}N_2NaO_5^+$ $[M+Na]^+$ 483.1890; Found: 483.1891.



1l

***Tert*-butyl 3-(2-(benzylthio)-6-nitrophenyl)-2-oxopropanoate (1l)**

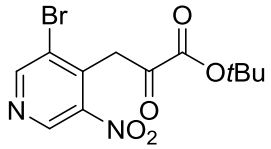
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.23-7.28 (m, 3H), 7.16-7.18 (m, 2H), 4.62 (s, 2H), 4.02 (s, 2H), 1.57 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 190.33, 159.59, 149.94, 139.88, 137.71, 136.26, 131.43, 129.08, 128.75, 128.25, 127.75, 124.16, 84.57, 40.93, 40.70, 27.90. **HRMS** (ESI) Calcd for $C_{20}H_{21}NNaO_5S^+$ $[M+Na]^+$ 410.1033; Found: 410.1027.



1m

***Tert*-butyl 3-(2-(difluoromethyl)-6-nitrophenyl)-2-oxopropanoate (1m)**

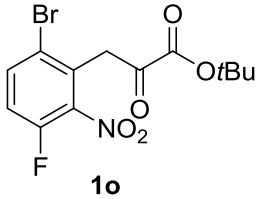
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 6.76 (t, *J* = 54.8 Hz, 1H), 4.56 (s, 2H), 1.58 (s, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.43 (d, *J* = 56.02); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 189.51, 159.35, 150.10, 135.76 (t, *J* = 21.0 Hz), 131.55 (t, *J* = 7.9 Hz), 128.95, 128.22 (t, *J* = 3.4 Hz), 127.50, 113.55 (t, *J* = 239.4 Hz), 85.00, 38.35, 27.85. **HRMS** (ESI) Calcd for $C_{14}H_{16}F_2NO_5^+$ $[M+H]^+$ 316.0991; Found: 316.0998.



1n

***Tert*-butyl 3-(3-bromo-5-nitropyridin-4-yl)-2-oxopropanoate (1n)**

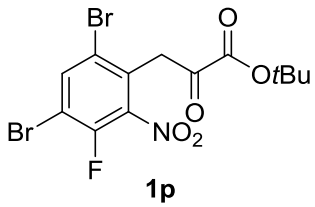
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.98 (s, 1H), 4.73 (s, 2H), 1.58 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 187.76, 158.87, 155.95, 146.05, 144.83, 138.52, 125.76, 85.40, 43.02, 27.84. **HRMS** (ESI) Calcd for $C_{12}H_{14}BrN_2O_5^+$ $[M+H]^+$ 345.0081; Found: 345.0077.



1o

***Tert*-butyl 3-(6-bromo-3-fluoro-2-nitrophenyl)-2-oxopropanoate (1o)**

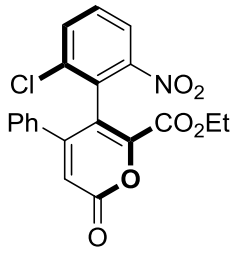
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.74 (m, 1H), 7.14 (t, *J* = 9.2 Hz, 1H), 4.36 (s, 2H), 1.53 (s, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -121.98; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 188.26, 158.94, 153.45 (d, *J* = 258.8 Hz), 136.48 (d, *J* = 7.8 Hz), 129.57, 121.18 (d, *J* = 3.9 Hz), 118.04 (d, *J* = 20.5 Hz), 85.16, 42.71, 27.76. **HRMS** (ESI) Calcd for $C_{13}H_{13}BrFNNaO_5^+$ $[M+Na]^+$ 383.9853; Found: 383.9855.



1p

***Tert*-butyl 3-(4,6-dibromo-3-fluoro-2-nitrophenyl)-2-oxopropanoate (1p)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 6.4 Hz, 1H), 4.35 (s, 2H), 1.57 (s, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.57; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 187.79, 158.88, 150.82 (d, *J* = 258.0 Hz), 138.89, 128.78, 121.45 (d, *J* = 4.8 Hz), 110.80 (d, *J* = 20.9Hz), 85.39, 42.59, 27.84; **HRMS** (ESI) Calcd for $C_{13}H_{12}Br_2FNNaO_5^+$ $[M+Na]^+$ 461.8958; Found: 461.8956.

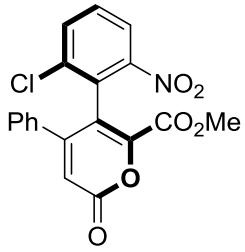


3a

Ethyl 5-(2-chloro-6-nitrophenyl)-2-oxo-4-phenyl-2*H*-pyran-6-carboxylate (3a): 82% yield, 94.5:5.5 er. $[\alpha]_D^{25}$ (c 1.0, $CHCl_3$) = +29.33

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 90/10, 1.0 mL/min, t_R (major) = 15.9 min, t_R (minor) = 14.5 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.23-7.27 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.08-7.10 (m, 2H), 6.59 (s, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 1.18 (t, *J* = 8.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.30, 159.23, 157.38, 149.40, 145.02, 136.11, 134.96, 134.47, 130.15, 129.63, 129.10, 128.36, 127.58, 123.29, 120.56, 119.16, 62.79, 13.85. **HRMS** (ESI) Calcd for $C_{20}H_{15}ClNO_6^+$ $[M+H]^+$ 400.0582; Found: 400.0584.

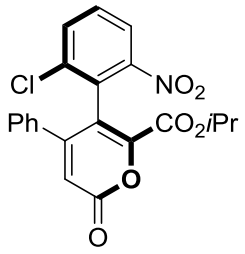


3b

Methyl 5-(2-chloro-6-nitrophenyl)-2-oxo-4-phenyl-2*H*-pyran-6-carboxylate (3b): 80% yield, 94:6 er. $[\alpha]_D^{25}$ (c 1.0, $CHCl_3$) = +26.89

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 30.4 min, t_R (minor) = 26.6 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.24-7.28 (m, 1H), 7.16-7.20 (m, 2H), 7.08-7.11 (m, 2H), 6.61 (s, 1H), 3.77 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.87, 159.07, 157.34, 149.34, 144.58, 136.08, 134.90, 134.52, 130.17, 129.66, 128.92, 128.38, 127.58, 123.34, 120.99, 119.36, 53.34; **HRMS** (ESI) Calcd for $C_{19}H_{13}ClNO_6^+$ $[M+H]^+$ 386.0426; Found: 386.0427.

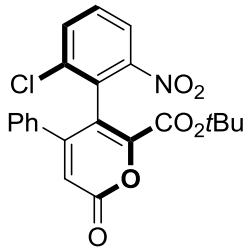


3c

Isopropyl 5-(2-chloro-6-nitrophenyl)-2-oxo-4-phenyl-2*H*-pyran-6-carboxylate (3c): 85% yield, 95.5:4.5 er. $[\alpha]_D^{25}$ (c 1.0, $CHCl_3$) = +50.44

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 26.0 min, t_R (minor) = 22.5 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.23-7.26 (m, 1H), 7.15-7.18 (m, 2H), 7.07-7.09 (m, 2H), 6.57 (s, 1H), 4.94-5.00 (m, 1H), 1.12 (d, *J* = 6.4 Hz, 3H), 1.09 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.34, 158.71, 157.37, 149.52, 145.51, 136.22, 135.03, 134.36, 130.07, 129.57, 129.34, 128.34, 127.58, 123.22, 120.04, 119.00, 70.93, 21.42, 21.35. **HRMS** (ESI) Calcd for $C_{21}H_{17}ClNO_6^+$ $[M+H]^+$ 414.0739; Found: 414.0740.

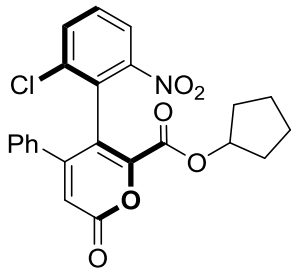


3d

***Tert*-butyl 5-(2-chloro-6-nitrophenyl)-2-oxo-4-phenyl-2*H*-pyran-6-carboxylate (3d):** 90% yield, 97.5:2.5 er. $[\alpha]_D^{25}$ (c 1.0, $CHCl_3$) = +99.73

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 22.4 min, t_R (minor) = 20.6 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 8.0 Hz, 2H), 7.04-7.06 (m, 2H), 6.53 (s, 1H), 1.27 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.46, 158.06, 157.42, 149.42, 146.54, 136.31, 135.12, 134.30, 130.03, 129.53, 129.49, 128.30, 127.54, 123.29, 118.83, 118.57, 84.46, 27.59. **HRMS** (ESI) Calcd for $C_{22}H_{19}ClNO_6^+$ $[M+H]^+$ 428.0895; Found: 428.0901.



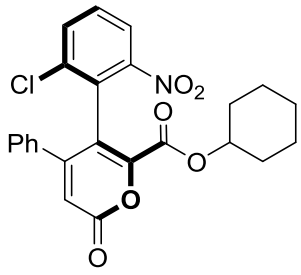
3e

Cyclopentyl 5-(2-chloro-6-nitrophenyl)-2-oxo-4-phenyl-2*H*-pyran-6-carboxylate (3e): 73% yield, 96:4 er. $[\alpha]_D^{25}$ (c 0.5, $CHCl_3$) = +26.4

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 29.5 min, t_R (minor) = 25.5 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.23-7.27 (m, 1H), 7.15-7.19 (m, 2H), 7.06-7.08 (m, 2H),

6.57 (s, 1H), 5.13-5.16 (m, 1H), 1.74-1.81 (m, 2H), 1.46-1.56 (m, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.34, 159.08, 157.34, 149.37, 145.54, 136.24, 135.01, 134.38, 130.09, 129.56, 129.33, 128.34, 127.54, 123.26, 119.91, 119.02, 80.22, 32.44, 23.72. **HRMS** (ESI) Calcd for $C_{23}H_{19}ClNO_6^+$ $[M+H]^+$ 440.0895; Found: 440.0896.

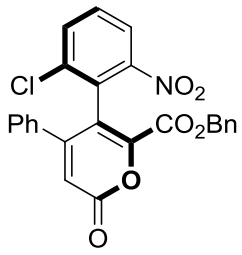


3f

Cyclohexyl 5-(2-chloro-6-nitrophenyl)-2-oxo-4-phenyl-2*H*-pyran-6-carboxylate (3f): 81% yield, 97:3 er. $[\alpha]_D^{25}$ (c 0.3, $CHCl_3$) = +43.33

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 29.1 min, t_R (minor) = 23.5 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 1.2, 8.4 Hz, 1H), 7.59 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.22-7.26 (m, 1H), 7.14-7.18 (m, 2H), 7.06-7.09 (m, 2H), 6.57 (s, 1H), 1.47-1.77 (m, 5H), 1.11-1.32 (m, 5H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.37, 158.73, 157.36, 149.47, 145.59, 136.22, 135.04, 134.37, 130.07, 129.56, 129.35, 128.33, 127.57, 123.25, 120.00, 118.99, 75.97, 31.22, 31.16, 25.12, 23.82. **HRMS** (ESI) Calcd for $C_{24}H_{21}ClNO_6^+$ $[M+H]^+$ 454.1052; Found: 454.1053.

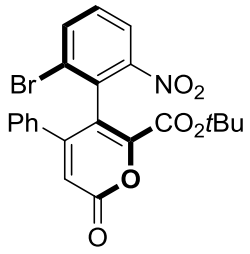


3g

Benzyl 5-(2-chloro-6-nitrophenyl)-2-oxo-4-phenyl-2*H*-pyran-6-carboxylate (3g): 70% yield, 93:7 er. $[\alpha]_D^{25}$ (c 0.3, $CHCl_3$) = +13.78

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 17.9 min, t_R (minor) = 16.6 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.29-7.30 (m, 3H), 7.13-7.23 (m, 6H), 7.05-7.06 (m, 2H), 6.57 (s, 1H), 5.08 (q, *J* = 14.8 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.15, 159.09, 157.34, 149.16, 144.93, 135.96, 134.91, 134.37, 134.05, 130.16, 129.64, 128.85, 128.78, 128.72, 128.37, 127.55, 123.22, 120.79, 119.27, 68.37. **HRMS** (ESI) Calcd for $C_{25}H_{17}ClNO_6^+$ $[M+H]^+$ 462.0739; Found: 462.0740.

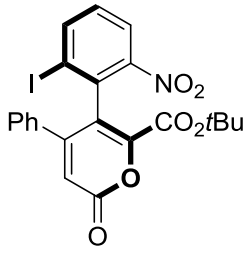


3h

***Tert*-butyl 5-(2-bromo-6-nitrophenyl)-2-oxo-4-phenyl-2*H*-pyran-6-carboxylate (3h):** 87% yield, 99:1 er. $[\alpha]_D^{25}$ (c 0.3, $CHCl_3$) = +11.78

HPLC condition: Chiralpak ODH (Hex/*i*PrOH = 90/10, 1.0 mL/min, t_R (major) = 20.2 min, t_R (minor) = 18.1 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.22-7.26 (m, 1H), 7.14-7.18 (m, 2H), 7.07-7.09 (m, 2H), 6.55 (s, 1H), 1.28 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.47, 158.00, 157.30, 149.49, 146.49, 137.56, 135.07, 131.22, 130.32, 129.50, 128.28, 127.71, 126.91, 123.89, 120.86, 118.66, 84.44, 27.58. **HRMS** (ESI) Calcd for $C_{22}H_{19}BrNO_6^+$ $[M+H]^+$ 472.0390; Found: 472.0390.

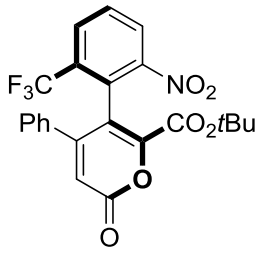


3i

***Tert*-butyl 5-(2-iodo-6-nitrophenyl)-2-oxo-4-phenyl-2*H*-pyran-6-carboxylate (3i):** 86% yield, 99:1 er. $[\alpha]_D^{25}$ (c 1.0, $CHCl_3$) = -30.53

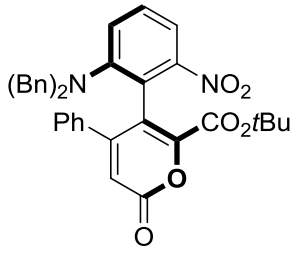
HPLC condition: Chiralpak IA (Hex/*i*PrOH = 97/3, 1.0 mL/min, t_R (major) = 36.9 min, t_R (minor) = 34.4 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.21-7.26 (m, 1H), 7.13-7.17 (m, 3H), 7.07-7.09 (m, 2H), 6.55 (s, 1H), 1.26 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.45, 157.89, 157.06, 148.98, 146.47, 143.98, 134.98, 134.53, 130.56, 129.50, 128.23, 128.03, 124.65, 124.37, 118.93, 103.95, 84.42, 27.62. **HRMS** (ESI) Calcd for $C_{22}H_{19}INO_6^+$ $[M+H]^+$ 520.0252; Found: 520.0252.



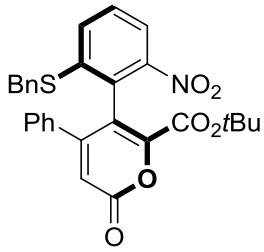
3j

***Tert*-butyl**
5-(2-nitro-6-(trifluoromethyl)phenyl)-2-oxo-4-phenyl-2*H*-pyran-6-carboxylate (3j): 51% yield, 93:7 er. $[\alpha]_D^{25}$ (c 0.5, $CHCl_3$) = +39.40
HPLC condition: Chiralpak IA (Hex/*i*PrOH = 97/3, 1.0 mL/min, t_R (major) = 23.5 min, t_R (minor) = 25.1 min).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.21-7.26 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.96-6.98 (m, 2H), 6.52 (s, 1H), 1.27 (s, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.9; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.32, 158.01, 157.55, 149.39, 145.98, 134.93, 131.37 (q, *J* = 5.1 Hz), 130.90 (q, *J* = 30.0 Hz), 130.01, 129.52, 129.20, 128.42, 128.23, 127.91, 122.81 (q, *J* = 273.5 Hz), 118.37, 117.46, 84.57, 27.56. **HRMS** (ESI) Calcd for $C_{23}H_{19}F_3NO_6^+$ $[M+H]^+$ 462.1159; Found: 462.1159.



3k

***Tert*-butyl**
5-(2-(dibenzylamino)-6-nitrophenyl)-2-oxo-4-phenyl-2*H*-pyran-6-carboxylate (3k): 42% yield, 96:4 er. $[\alpha]_D^{25}$ (c 0.3, $CHCl_3$) = +96.33
HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 20.7 min, t_R (minor) = 14.1 min).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.21-7.30 (m, 7H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.05-7.07 (m, 2H), 6.94-6.98 (m, 2H), 6.85-6.88 (m, 4H), 6.73 (s, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 3.83 (d, *J* = 14.4 Hz, 2H), 3.38 (d, *J* = 14.4 Hz, 2H), 1.41 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 160.12, 159.26, 158.66, 151.16, 150.76, 145.64, 135.44, 134.96, 130.10, 129.35, 129.21, 128.84, 128.33, 127.92, 127.85, 127.58, 126.33, 120.51, 120.24, 118.64, 84.79, 54.04, 27.84. **HRMS** (ESI) Calcd for $C_{36}H_{33}N_2O_6^+$ $[M+H]^+$ 589.2333; Found: 589.2334.

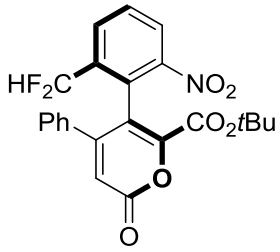


3l

***Tert*-butyl**
5-(2-(benzylthio)-6-nitrophenyl)-2-oxo-4-phenyl-2*H*-pyran-6-carboxylate (3l): 78% yield, 92:8 er. $[\alpha]_D^{25}$ (c 1.0, $CHCl_3$) = +90.00
HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 36.5

min, t_R (minor) = 30.6 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 2.4, 6.8 Hz, 1H), 7.21-7.36 (m, 8H), 7.06-7.13 (m, 4H), 6.53 (s, 1H), 3.98-4.08 (m, 2H), 1.25 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.69, 158.17, 157.80, 149.00, 146.57, 141.41, 135.31, 135.16, 130.46, 129.49, 129.38, 128.97, 128.86, 128.07, 128.00, 127.90, 127.86, 121.16, 118.96, 118.68, 84.17, 37.62, 27.59. **HRMS** (ESI) Calcd for $C_{29}H_{26}NO_6S^+$ $[M+H]^+$ 516.1475; Found: 516.1473.

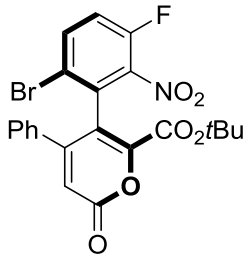


3m

***Tert*-butyl**
5-(2-(difluoromethyl)-6-nitrophenyl)-2-oxo-4-phenyl-2*H*-pyran-6-carboxylate (3m): 83% yield, 95:5 er. $[\alpha]_D^{25}$ (c 0.5, $CHCl_3$) = -6.80

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 14.2 min, t_R (minor) = 45.7 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.14-7.26 (m, 3H), 6.96-6.98 (m, 2H), 6.56 (s, 1H), 6.52 (t, *J* = 54.4 Hz, 1H), 1.24 (s, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -108.81 (dd, *J* = 56.4, 307.94 Hz), -112.71 (dd, *J* = 56.00, 307.94 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.14, 157.94, 157.09, 148.74, 146.62, 134.82 (t, *J* = 22.6 Hz), 134.75, 130.92 (t, *J* = 5.7 Hz), 130.20, 129.70, 128.56, 127.74, 127.01, 118.57, 116.72, 111.92 (t, *J* = 239.3 Hz), 84.89, 27.54. **HRMS** (ESI) Calcd for $C_{23}H_{20}F_2NO_6^+$ $[M+H]^+$ 444.1253; Found: 444.1253.



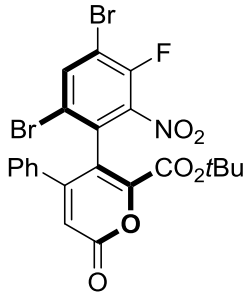
3n

***Tert*-butyl**
5-(6-bromo-3-fluoro-2-nitrophenyl)-2-oxo-4-phenyl-2*H*-pyran-6-carboxylate (3n): 81% yield, >99:1 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = +29.20

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 19.6 min).

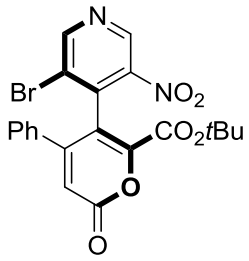
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 4.8, 9.2 Hz, 1H), 7.29-7.33 (m, 1H), 7.20-7.24 (m, 4H), 7.13 (t, *J* = 8.8 Hz, 1H), 6.52 (s, 1H), 1.36 (s, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -121.61; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.98, 157.53, 157.04,

153.41 (d, *J* = 260.0 Hz), 147.96, 136.06 (d, *J* = 8.0 Hz), 134.74, 131.44, 129.79, 128.35, 128.04, 120.34 (d, *J* = 3.7 Hz), 118.78 (d, *J* = 20.7 Hz), 118.80, 117.94, 84.95, 27.61. **HRMS** (ESI) Calcd for $C_{22}H_{18}BrFNO_6^+$ $[M+H]^+$ 490.0296; Found: 490.0298.



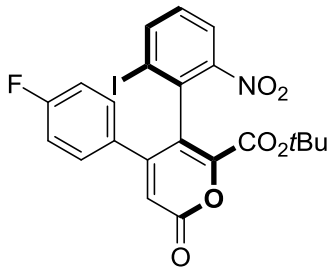
3o

***Tert*-butyl**
5-(4,6-dibromo-3-fluoro-2-nitrophenyl)-2-oxo-4-phenyl-2*H*-pyran-6-carboxylate (3o): 85% yield, >99:1 er. $[\alpha]_D^{25}$ (c 0.3 $CHCl_3$) = +33.30
HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 12.0 min).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 6.0 Hz, 1H), 7.33-7.37 (m, 1H), 7.25-7.29 (m, 2H), 7.20-7.22 (m, 2H), 6.52 (s, 1H), 1.40 (s, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.47; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.80, 157.54, 156.74, 150.74 (d, *J* = 258.6 Hz), 148.19, 138.56, 134.59, 130.48, 129.99, 128.53, 128.01, 120.57, 118.89, 117.39, 111.70 (d, *J* = 21.1 Hz), 85.29, 27.67. **HRMS** (ESI) Calcd for $C_{22}H_{17}Br_2FNO_6^+$ $[M+H]^+$ 567.9401; Found: 567.9402.



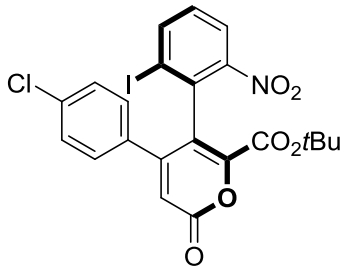
3p

***Tert*-butyl**
5-(3-bromo-5-nitropyridin-4-yl)-2-oxo-4-phenyl-2*H*-pyran-6-carboxylate (3p): 75% yield, 96:4 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = -4.60
HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 14.5 min, t_R (minor) = 13.3 min).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.85 (s, 1H), 7.25-7.29 (m, 1H), 7.16-7.20 (m, 2H), 7.02-7.04 (m, 2H), 6.55 (s, 1H), 1.33 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.90, 157.75, 156.01, 155.74, 146.40, 144.77, 144.34, 139.91, 134.36, 129.95, 128.61, 127.46, 124.23, 119.04, 118.86, 85.35, 27.63. **HRMS** (ESI) Calcd for $C_{21}H_{18}BrN_2O_6^+$ $[M+H]^+$ 473.0343; Found: 473.0343.



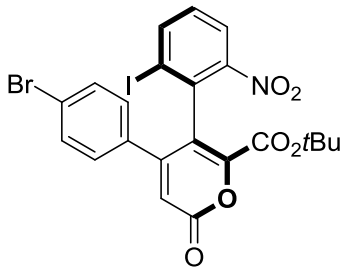
3q

***Tert*-butyl**
4-(4-fluorophenyl)-5-(2-iodo-6-nitrophenyl)-2-oxo-2*H*-pyran-6-carboxylate (3q):
85% yield, 98:2 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = -11.37
HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 31.8 min, t_R (minor) = 35.5 min).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.09-7.13 (m, 2H), 6.84-6.89 (m, 2H), 6.55 (s, 1H), 1.27 (s, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.56; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.24 (d, *J* = 249.5 Hz), 159.25, 157.81, 156.11, 149.13, 146.54, 144.04, 134.28, 131.03 (d, *J* = 3.3 Hz), 130.72, 130.21, 130.12, 124.68, 124.11, 119.05, 115.60, 115.39, 103.80, 84.56, 27.61. **HRMS** (ESI) Calcd for $C_{22}H_{18}FINO_6^+$ $[M+H]^+$ 538.0157; Found: 538.0158.



3r

***Tert*-butyl**
4-(4-chlorophenyl)-5-(2-iodo-6-nitrophenyl)-2-oxo-2*H*-pyran-6-carboxylate (3r):
82% yield, 98.5:1.5 er. $[\alpha]_D^{25}$ (c 0.5 $CHCl_3$) = -12.53
HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 33.8 min, t_R (minor) = 37.7 min).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.14-7.17 (m, 2H), 7.06-7.08 (m, 2H), 6.55 (s, 1H), 1.28 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.15, 157.77, 155.99, 149.15, 146.58, 144.07, 135.87, 134.14, 133.45, 130.80, 129.47, 128.59, 124.72, 123.93, 119.08, 103.75, 84.61, 27.61; **HRMS** (ESI) Calcd for $C_{22}H_{18}ClINO_6^+$ $[M+H]^+$ 553.9862; Found: 553.9861.

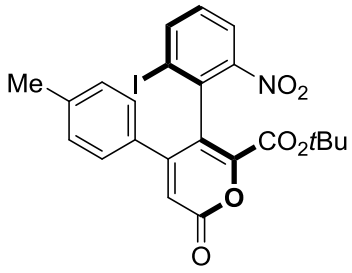


3s

***Tert*-butyl 4-(4-bromophenyl)-5-(2-iodo-6-nitrophenyl)-2-oxo-2*H*-pyran-6-carboxylate (3s):** 83% yield, >99:1 er. $[\alpha]_D^{25}$ (c 0.5 $CHCl_3$) = -22.70

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 36.1 min, t_R (minor) = 39.9 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-8.07 (m, 1H), 7.96-7.99 (m, 1H), 7.26-7.31 (m, 2H), 7.20 (t, *J* = 8.0 Hz, 1H), 6.98-7.01 (m, 2H), 6.52 (s, 1H), 1.23 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.11, 157.73, 156.06, 149.15, 146.56, 144.12, 134.03, 133.91, 131.53, 130.91, 129.70, 124.75, 124.19, 123.85, 119.01, 103.74, 84.61, 27.59. **HRMS** (ESI) Calcd for $C_{22}H_{18}BrINO_6^+$ $[M+H]^+$ 597.9357; Found: 597.9363.

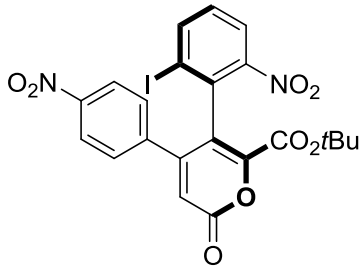


3t

***Tert*-butyl 5-(2-iodo-6-nitrophenyl)-2-oxo-4-(*p*-tolyl)-2*H*-pyran-6-carboxylate (3t):** 77% yield, 98:2 er. $[\alpha]_D^{25}$ (c 0.3 $CHCl_3$) = -47.33

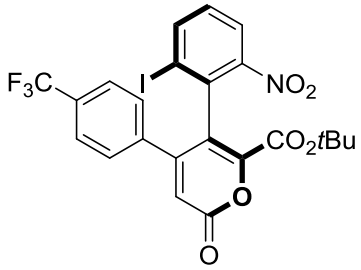
HPLC condition: Chiralpak ODH (Hex/*i*PrOH = 90/10, 1.0 mL/min, t_R (major) = 16.7 min, t_R (minor) = 14.1 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 1H), 6.95 (s, 4H), 6.53 (s, 1H), 2.23 (s, 3H), 1.27 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.58, 157.96, 157.17, 149.05, 146.40, 143.97, 139.69, 134.63, 132.13, 130.52, 128.95, 128.00, 124.64, 118.67, 103.97, 84.36, 27.62, 21.32. **HRMS** (ESI) Calcd for $C_{23}H_{21}INO_6^+$ $[M+H]^+$ 534.0408; Found: 534.0409.



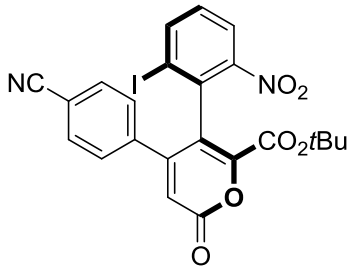
3u

***Tert*-butyl**
5-(2-iodo-6-nitrophenyl)-4-(4-nitrophenyl)-2-oxo-2*H*-pyran-6-carboxylate (3u): 90% yield, 99:1 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = +31.00
HPLC condition: Chiralpak ODH (Hex/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 36.9 min, t_R (minor) = 27.9 min).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-8.06 (m, 4H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 1H), 6.58 (s, 1H), 1.23 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.61, 157.52, 155.02, 149.22, 148.28, 146.82, 144.21, 141.23, 133.51, 131.23, 129.38, 124.83, 123.43, 123.27, 119.55, 103.55, 84.90, 27.56; **HRMS** (ESI) Calcd for $C_{22}H_{18}IN_2O_8^+$ $[M+H]^+$ 565.0102; Found: 565.0098.



3v

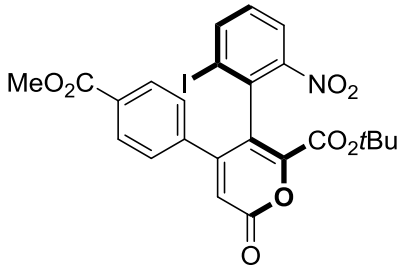
***Tert*-butyl**
5-(2-iodo-6-nitrophenyl)-2-oxo-4-(4-(trifluoromethyl)phenyl)-2*H*-pyran-6-carboxylate (3v): 90% yield, 98:2 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = +9.33
HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 29.0 min, t_R (minor) = 32.0 min).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 8.4 Hz, 2H), 7.20 (t, *J* = 8.0 Hz, 1H), 6.57 (s, 1H), 1.27 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.93, 157.67, 155.78, 149.12, 146.70, 144.13, 138.57, 133.86, 131.50 (q, *J* = 33.00 Hz), 130.99, 128.56, 125.25 (q, *J* = 3.8 Hz), 124.97, 124.77, 123.69, 123.61 (q, *J* = 270.9 Hz), 122.26, 119.44, 103.68, 84.72, 27.58. **HRMS** (ESI) Calcd for $C_{23}H_{18}F_3INO_6^+$ $[M+H]^+$ 588.0125; Found: 588.0126.



3w

***Tert*-butyl**
4-(4-cyanophenyl)-5-(2-iodo-6-nitrophenyl)-2-oxo-2*H*-pyran-6-carboxylate (3w): 89% yield, 99:1 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = +15.60
HPLC condition: Chiralpak ODH (Hex/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 33.8 min, t_R (minor) = 29.1 min).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 1H), 6.56 (s,

1H), 1.27 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.71, 157.56, 155.25, 149.18, 146.83, 144.14, 139.44, 133.64, 132.02, 131.08, 128.92, 124.78, 123.34, 119.43, 117.93, 113.54, 103.59, 84.86, 27.59; **HRMS** (ESI) Calcd for $C_{23}H_{18}IN_2O_6^+$ $[M+H]^+$ 545.0204; Found: 545.0206.

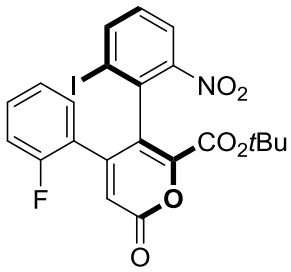


3x

***Tert*-butyl 5-(2-iodo-6-nitrophenyl)-4-(4-(methoxycarbonyl)phenyl)-2-oxo-2*H*-pyran-6-carboxylate (3x):** 75% yield, 99:1 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = +14.07

HPLC condition: Chiralpak ODH (Hex/*i*PrOH = 90/10, 1.0 mL/min, t_R (major) = 34.6 min, t_R (minor) = 28.4 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.80-7.83 (m, 2H), 7.15-7.19 (m, 3H), 6.56 (s, 1H), 3.84 (s, 3H), 1.23 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.23, 159.02, 157.69, 156.18, 149.05, 146.59, 144.08, 139.31, 133.99, 131.01, 130.89, 129.40, 128.20, 124.72, 123.83, 119.16, 103.71, 84.61, 52.46, 27.57; **HRMS** (ESI) Calcd for $C^{24}H_{21}INO_8^+$ $[M+H]^+$ 578.0306; Found: 578.0308.

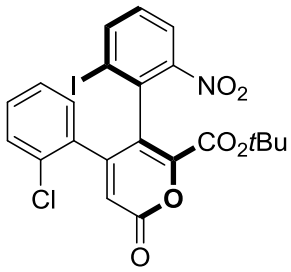


3y

***Tert*-butyl 4-(2-fluorophenyl)-5-(2-iodo-6-nitrophenyl)-2-oxo-2*H*-pyran-6-carboxylate (3y):** 70% yield, 97:3 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = -2.33

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 30.6 min, t_R (minor) = 29.0 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.8 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.21-7.26 (m, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.90-6.95 (m, 2H), 6.61 (s, 1H), 1.27 (s, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.90; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.99, 158.79 (d, *J* = 246.2 Hz), 157.79, 151.01, 148.67, 147.37, 144.05, 133.92, 131.76 (d, *J* = 8.2 Hz), 130.57, 130.12, 124.63, 124.21, 123.96, 123.92, 122.28 (d, *J* = 14.0 Hz), 120.92, 116.16, 115.94, 104.02, 84.41, 27.61. **HRMS** (ESI) Calcd for $C_{22}H_{18}FINO_6^+$ $[M+H]^+$ 538.0157; Found: 538.0159.

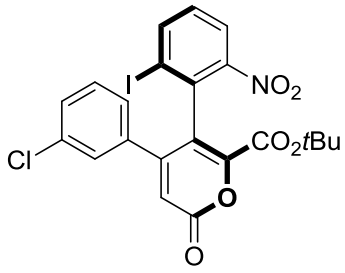


3z

***Tert*-butyl**
4-(2-chlorophenyl)-5-(2-iodo-6-nitrophenyl)-2-oxo-2*H*-pyran-6-carboxylate (3z): 83% yield, 95:5 er. $[\alpha]_D^{25}$ (c 0.5 $CHCl_3$) = -164.47

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 32.1 min, t_R (minor) = 29.2 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-8.11 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 8.0 Hz, 2H), 6.96-7.01 (m, 2H), 6.61 (s, 1H), 1.27 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.05, 157.74, 144.10, 132.59, 130.68, 130.60, 130.52, 129.57, 126.29, 125.05, 124.37, 121.46, 84.38, 27.61. **HRMS** (ESI) Calcd for $C_{22}H_{18}ClINO_6^+$ $[M+H]^+$ 553.9862; Found: 553.9863.

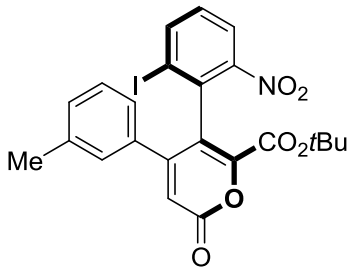


3aa

***Tert*-butyl**
4-(3-chlorophenyl)-5-(2-iodo-6-nitrophenyl)-2-oxo-2*H*-pyran-6-carboxylate (3aa): 83% yield, 99:1 er. $[\alpha]_D^{25}$ (c 0.5 $CHCl_3$) = -6.93

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 29.2 min, t_R (minor) = 26.8 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.17-7.23 (m, 2H), 7.08-7.13 (m, 2H), 7.00-7.02 (m, 1H), 76.56 (s, 1H), 1.27 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.07, 157.72, 155.59, 149.13, 146.61, 144.04, 136.58, 134.23, 134.05, 130.81, 129.69, 129.58, 128.24, 126.24, 124.68, 123.84, 119.20, 103.70, 84.63, 27.61; **HRMS** (ESI) Calcd for $C_{22}H_{18}ClINO_6^+$ $[M+H]^+$ 553.9862; Found: 553.9863.

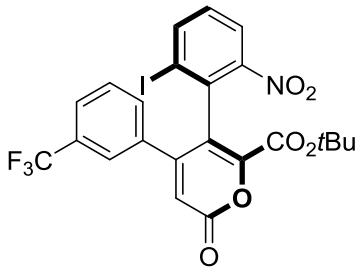


3ab

***Tert*-butyl 5-(2-iodo-6-nitrophenyl)-2-oxo-4-(*m*-tolyl)-2*H*-pyran-6-carboxylate (3ab):** 81% yield, 98:2 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = +29.63

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 24.4 min, t_R (minor) = 22.7 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.00-7.05 (m, 2H), 6.90 (s, 1H), 6.84-6.86 (m, 1H), 6.55 (s, 1H), 2.19 (s, 3H), 1.27 (s, 9H), 5.09 (d, *J* = 15.6 Hz, 1H), 4.75 (d, *J* = 15.6 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.51, 157.92, 157.18, 148.95, 146.48, 143.92, 138.07, 134.89, 134.65, 130.50, 130.21, 128.82, 128.04, 124.94, 124.59, 124.42, 118.72, 104.02, 84.36, 27.62, 21.31. **HRMS** (ESI) Calcd for $C_{23}H_{21}INO_6^+$ $[M+H]^+$ 534.0408; Found: 534.0410.

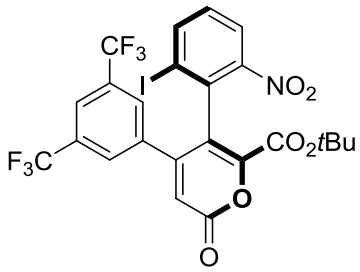


3ac

***Tert*-butyl 5-(2-iodo-6-nitrophenyl)-2-oxo-4-(3-(trifluoromethyl)phenyl)-2*H*-pyran-6-carboxylate (3ac):** 88% yield, 97.5:2.5 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = +29.63

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 21.9 min, t_R (minor) = 19.4 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.33-7.41 (m, 3H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.60 (s, 1H), 1.27 s, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.90; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.95, 157.65, 155.49, 149.20, 146.75, 144.03, 135.65, 133.85, 131.66, 130.87, 130.56 (q, *J* = 32.6 Hz), 129.04, 126.24 (q, *J* = 3.9 Hz), 125.01 (q, *J* = 4.0 Hz), 124.62, 123.46 (q, *J* = 271.3 Hz), 123.66, 119.29, 103.64, 84.72, 27.58. **HRMS** (ESI) Calcd for $C_{23}H_{17}F_3INNaO_6^+$ $[M+Na]^+$ 609.9945; Found: 609.9949.

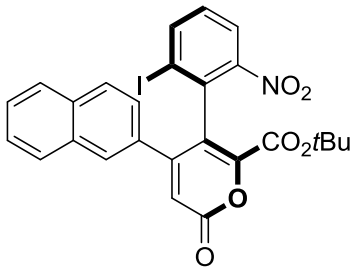


3ad

***Tert*-butyl 4-(3,5-bis(trifluoromethyl)phenyl)-5-(2-iodo-6-nitrophenyl)-2-oxo-2*H*-pyran-6-carboxylate (3ad):** 80% yield, 98.5:1.5 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = +19.67

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 10.3 min, t_R (minor) = 8.3 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.76 (s, 1H), 7.66 (s, 2H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.65 (s, 1H), 1.27 (s, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.04; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.42, 157.42, 153.92, 149.53, 147.10, 144.02, 136.85, 133.18, 131.74 (q, *J* = 33.8 Hz), 131.15, 128.64, 124.57, 123.25, 122.83, 122.68 (q, *J* = 271.70 Hz), 119.69, 103.32, 85.05, 27.57. **HRMS** (ESI) Calcd for $C_{24}H_{17}F_6INO_6^+$ $[M+H]^+$ 655.9999; Found: 656.0004.

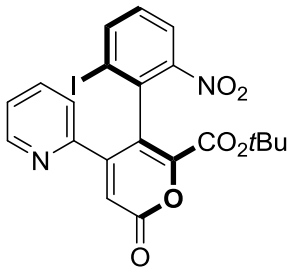


3ae

***Tert*-butyl 5-(2-iodo-6-nitrophenyl)-4-(naphthalen-2-yl)-2-oxo-2*H*-pyran-6-carboxylate (3ae):** 54% yield, 99:1 er. $[\alpha]_D^{25}$ (c 0.3 $CHCl_3$) = +4.78

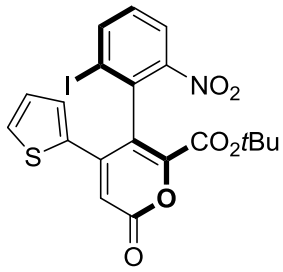
HPLC condition: Chiralpak ASH (Hex/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 70.5 min, t_R (minor) = 46.7 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.68-7.74 (m, 2H), 7.59-7.63 (m, 2H), 7.45-7.50 (m, 2H), 7.15-7.18 (m, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.65 (s, 1H), 1.28 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.45, 157.93, 157.14, 149.10, 146.56, 143.98, 134.50, 133.18, 132.48, 130.60, 128.49, 128.33, 128.00, 127.69, 127.40, 126.89, 124.84, 124.65, 124.37, 119.21, 103.95, 84.48, 27.64; **HRMS** (ESI) Calcd for $C_{26}H_{21}INO_6^+$ $[M+H]^+$ 570.0408; Found: 570.0408.



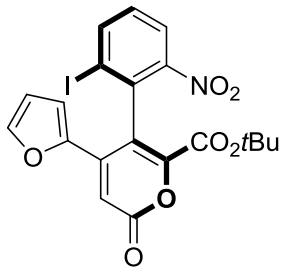
3af

***Tert*-butyl**
5-(2-iodo-6-nitrophenyl)-2-oxo-4-(pyridin-2-yl)-2*H*-pyran-6-carboxylate (3af): 83% yield, 99:1 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = -190.73
HPLC condition: Chiralpak ODH (Hex/*i*PrOH = 90/10, 1.0 mL/min, t_R (major) = 26.7 min, t_R (minor) = 31.7 min).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 6.4 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.61-7.65 (m, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.11-7.17 (m, 2H), 6.74 (s, 1H), 1.27 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.62, 157.87, 154.22, 153.19, 149.63, 148.75, 147.53, 143.39, 136.90, 134.80, 130.06, 124.06, 123.89, 123.53, 118.69, 103.57, 84.28, 27.63. **HRMS** (ESI) Calcd for $C_{21}H_{18}IN_2O_6^+$ $[M+H]^+$ 521.0204; Found: 521.0206.



3ag

***Tert*-butyl**
5-(2-iodo-6-nitrophenyl)-2-oxo-4-(thiophen-2-yl)-2*H*-pyran-6-carboxylate (3ag): 81% yield, 98.5:1.5 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = +19.50
HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 42.1 min, t_R (minor) = 37.3 min).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.6 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.30-7.34 (m, 2H), 6.88-6.93 (m, 2H), 6.77 (s, 1H), 1.27 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.37, 157.92, 150.08, 149.45, 146.75, 143.99, 135.74, 133.98, 131.31, 130.31, 129.95, 127.71, 124.68, 122.98, 116.38, 104.21, 84.63, 27.62; **HRMS** (ESI) Calcd for $C_{20}H_{17}INO_6S^+$ $[M+H]^+$ 525.9816; Found: 525.9817.

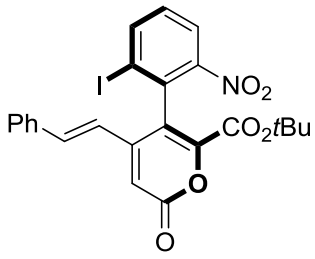


3ah

***Tert*-butyl 4-(furan-2-yl)-5-(2-iodo-6-nitrophenyl)-2-oxo-2*H*-pyran-6-carboxylate (3ah):** 83% yield, 97.5:2.5 er. $[\alpha]_D^{25}$ (c 0.5 $CHCl_3$) = +43.27

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 44.6 min, t_R (minor) = 38.6 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 1.6 Hz, 1H), 7.41 (t *J* = 8.0 Hz, 1H), 7.02 (s, 1H), 6.26 (dd, *J* = 1.6, 3.6 Hz, 1H), 5.37 (d, *J* = 3.6 Hz, 1H), 1.29 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.82, 157.96, 149.62, 147.17, 145.63, 144.05, 143.12, 134.40, 131.26, 124.74, 120.72, 114.44, 112.88, 112.19, 103.56, 84.58, 27.63. **HRMS** (ESI) Calcd for $C_{20}H_{17}INO_7^+$ $[M+H]^+$ 510.0044; Found: 510.0047.

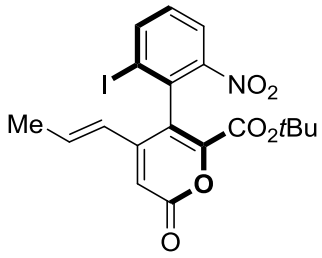


3ai

Tert-butyl (*E*)-5-(2-iodo-6-nitrophenyl)-2-oxo-4-styryl-2*H*-pyran-6-carboxylate (3ai): 77% yield, 96:4 er. $[\alpha]_D^{25}$ (c 0.5 $CHCl_3$) = +180.89

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 43.4 min, t_R (minor) = 37.6 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.29-7.31 (m, 3H), 7.20-7.25 (m, 3H), 6.81 (s, 1H), 6.12 (d, *J* = 16.4 Hz, 1H), 1.27 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.95, 157.85, 152.57, 149.53, 146.08, 143.99, 138.37, 135.24, 133.87, 130.99, 129.88, 128.99, 127.67, 124.58, 123.78, 120.73, 112.65, 102.87, 84.39, 27.63. **HRMS** (ESI) Calcd for $C_{24}H_{21}INO_6^+$ $[M+H]^+$ 546.0408; Found: 546.0408.

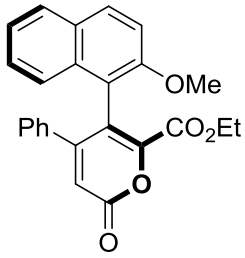


3aj

***Tert*-butyl (*E*)-5-(2-iodo-6-nitrophenyl)-2-oxo-4-(prop-1-en-1-yl)-2*H*-pyran-6-carboxylate (3aj):** 48% yield, 93:7 er. $[\alpha]_D^{25}$ (c 0.5 $CHCl_3$) = +119.00

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 90/10, 1.0 mL/min, t_R (major) = 15.3 min, t_R (minor) = 14.0 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 1.2, 8.0 Hz, 1H), 8.09 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 6.62 (s, 1H), 6.41-6.50 (m, 1H), 5.45-5.51 (m, 1H), 1.73 (dd, *J* = 1.6, 6.8 Hz, 3H), 1.25 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 160.08, 157.87, 152.87, 149.39, 145.96, 143.95, 137.41, 133.96, 130.85, 124.55, 124.22, 123.67, 112.52, 102.84, 84.26, 27.61, 19.17; **HRMS** (ESI) Calcd for $C_{19}H_{19}INO_6^+$ $[M+H]^+$ 484.0252; Found: 484.0248.

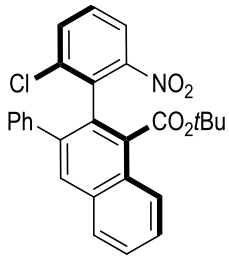


3ak

Ethyl 5-(2-methoxynaphthalen-1-yl)-2-oxo-4-phenyl-2H-pyran-6-carboxylate (3ak): 43% yield, 60.5:39.5 er. $[\alpha]_D^{25}$ (c 0.5 $CHCl_3$) = +72.66

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 90/10, 1.0 mL/min, t_R (major) = 12.2 min, t_R (minor) = 13.2 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.41-7.45 (m, 1H), 7.30-7.34 (m, 1H), 7.09-7.13 (m, 1H), 7.04 (d, *J* = 8.8 Hz, 1H), 6.97-7.01 (m, 2H), 6.87-6.09 (m, 2H), 6.62 (s, 1H), 3.90 (q, *J* = 8.1 Hz, 2H), 3.58 (s, 3H), 0.75 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 160.33, 159.92, 159.79, 153.85, 147.59, 136.11, 133.44, 130.66, 128.99, 128.56, 128.45, 127.63, 127.44, 127.38, 123.75, 123.33, 119.36, 118.21, 115.98, 112.36, 61.91, 56.03, 13.37. **HRMS** (ESI) Calcd for $C_{25}H_{21}O_5^+$ $[M+H]^+$ 401.1384; Found: 401.1377.

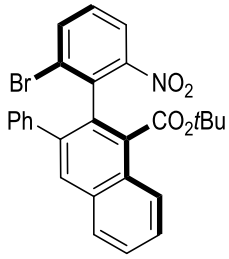


6a

***Tert*-butyl (*R*)-2-(2-chloro-6-nitrophenyl)-3-phenyl-1-naphthoate (6a):** 96% yield, 97:3 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = +2.33

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 11.2 min, t_R (minor) = 9.6 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-8.02 (m, 4H), 7.57-7.61 (m, 3H), 7.32-7.39 (m, 3H), 7.18-7.22 (m, 3H), 1.30 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.24, 150.33, 140.20, 138.91, 137.33, 134.17, 134.14, 133.39, 131.47, 130.60, 130.33, 129.37, 129.18, 129.08, 128.45, 127.85, 127.46, 127.27, 125.34, 123.08, 82.72, 27.73. **HRMS** (ESI) Calcd for $C_{27}H_{22}ClNNaO_4^+$ $[M+H]^+$ 482.1130; Found: 482.1133.

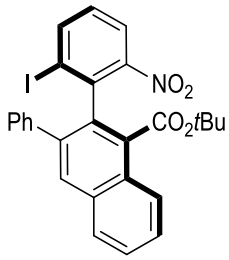


6b

***Tert*-butyl (*R*)-2-(2-bromo-6-nitrophenyl)-3-phenyl-1-naphthoate (6b):** 93% yield, 98.5:1.5 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = -13.33

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 14.0 min, t_R (minor) = 9.9 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-8.04 (m, 4H), 7.78 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.57-7.61 (m, 2H), 7.35-7.37 (m, 2H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.18-7.23 (m, 3H), 1.31 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.19, 150.42, 140.16, 138.70, 137.44, 135.88, 133.39, 132.24, 131.25, 130.74, 129.65, 129.36, 129.09, 128.46, 127.82, 127.47, 127.45, 127.27, 125.40, 123.69, 82.74, 27.75. **HRMS** (ESI) Calcd for $C_{27}H_{22}BrNNaO_4^+$ $[M+Na]^+$ 526.0624; Found: 526.0625.

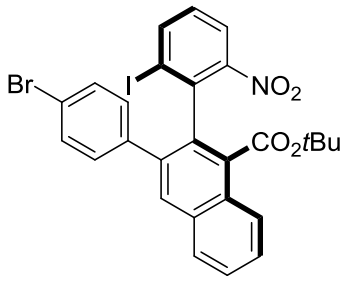


6c

***Tert*-butyl (*R*)-2-(2-iodo-6-nitrophenyl)-3-phenyl-1-naphthoate (6c):** 95% yield, 99:1 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = -12.13

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 23.5 min, t_R (minor) = 11.1 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-8.09 (m, 2H), 7.93-8.00 (m, 3H), 7.57-7.61 (m, 2H), 7.36-7.38 (m, 2H), 7.18-7.22 (m, 3H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.30 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.11, 149.84, 143.91, 140.00, 139.24, 138.32, 135.52, 133.41, 131.02, 129.88, 129.69, 129.14, 128.46, 127.76, 127.46, 127.41, 127.25, 125.46, 124.44, 104.78, 82.78, 27.77; **HRMS** (ESI) Calcd for $C_{27}H_{22}INNaO_4^+$ $[M+Na]^+$ 574.0486; Found: 574.0491.

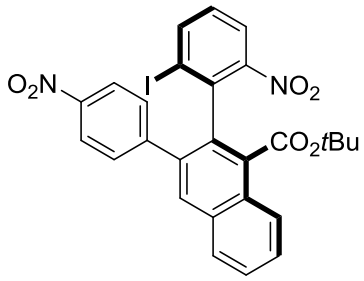


6d

***Tert*-butyl 4-(4-bromophenyl)-5-(2-iodo-6-nitrophenyl)-2-oxo-2*H*-pyran-6-carboxylate (6d):** 93% yield, 98.5:1.5 er. $[\alpha]_D^{25}$ (c 0.5 $CHCl_3$) = -6.53

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 43.4 min, t_R (minor) = 20.3 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-8.10 (m, 2H), 7.93-7.96 (m, 3H), 7.57-7.61 (m, 2H), 7.32-7.34 (m, 2H), 7.25-7.27 (m, 2H), 7.18 (t, *J* = 8.0 Hz, 1H), 1.29 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.98, 149.93, 144.02, 139.02, 138.77, 137.19, 135.05, 133.33, 131.36, 131.23, 130.96, 130.89, 130.13, 129.20, 128.44, 127.69, 127.43, 125.47, 124.51, 121.88, 104.67, 82.96, 27.76. **HRMS** (ESI) Calcd for $C_{27}H_{22}BrINO_4^+$ $[M+H]^+$ 629.9771; Found: 629.9773.

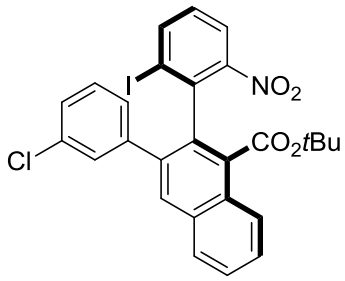


6e

***Tert*-butyl (*R*)-2-(2-iodo-6-nitrophenyl)-3-(4-nitrophenyl)-1-naphthoate (6e):** 92% yield, 97.5:2.5 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = -11.20

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 80/20, 1.0 mL/min, t_R (major) = 74.9 min, t_R (minor) = 16.3 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-8.10 (m, 4H), 7.95-7.98 (m, 3H), 7.58-7.65 (m, 4H), 7.20 (t, *J* = 8.0 Hz, 1H), 1.30 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.77, 150.11, 147.17, 146.89, 144.08, 138.15, 136.23, 134.44, 133.20, 131.64, 131.03, 130.71, 130.48, 129.51, 128.59, 128.24, 127.77, 125.52, 124.60, 123.03, 104.49, 83.26, 27.75. **HRMS** (ESI) Calcd for $C_{27}H_{21}IN_2NaO_6^+$ $[M+Na]^+$ 619.0337; Found: 619.0335.

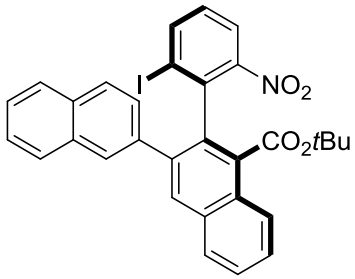


6f

***Tert*-butyl (*R*)-3-(3-chlorophenyl)-2-(2-iodo-6-nitrophenyl)-1-naphthoate (6f):** 93% yield, 98.5:1.5 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = +5.50

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 43.0 min, t_R (minor) = 11.4 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.10 (m, 2H), 7.93-7.98 (m, 3H), 7.58-7.62 (m, 2H), 7.42-7.43 (m, 1H), 7.26-7.28 (m, 1H), 7.15-7.21 (m, 2H), 7.12 (t, *J* = 8.0 Hz, 1H), 1.30 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.96, 149.99, 143.98, 141.79, 138.67, 136.94, 135.03, 133.60, 133.32, 131.25, 130.99, 130.17, 129.95, 129.27, 129.01, 128.51, 127.83, 127.79, 127.62, 127.48, 125.48, 124.49, 104.57, 82.99, 27.77; **HRMS** (ESI) Calcd for $C_{27}H_{22}ClINO_4^+$ $[M+H]^+$ 586.0277; Found: 586.0275**.**

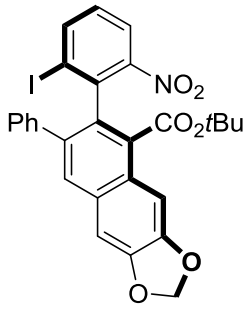


6g

***Tert*-butyl (*R*)-3-(2-iodo-6-nitrophenyl)-[2,2'-binaphthalene]-4-carboxylate (6g):** 96% yield, 99:1 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = +0.83

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 47.7 min, t_R (minor) = 20.6 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-8.07 (m, 5H), 7.88 (s, 1H), 7.72-7.79 (m, 2H), 7.66 (t, *J* = 8.8 Hz, 1H), 7.59-7.63 (m, 2H), 7.52 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.43-7.47 (m, 2H), 7.07 (t, *J* = 8.0 Hz, 1H), 1.32 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.14, 149.91, 143.96, 139.14, 138.31, 137.59, 135.58, 133.45, 132.95, 132.48, 131.36, 131.13, 129.95, 129.19, 129.04, 128.50, 128.31, 127.62, 127.55, 127.33, 127.27, 126.20, 126.17, 125.50, 124.45, 104.82, 82.86, 27.79, 27.73. **HRMS** (ESI) Calcd for $C_{31}H_{24}INNaO_4^+$ $[M+Na]^+$ 624.0642; Found: 624.0643.

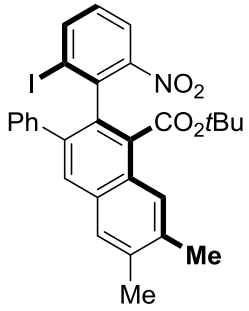


6h

***Tert*-butyl (*R*)-6-(2-iodo-6-nitrophenyl)-7-phenylnaphtho[2,3-d][1,3]dioxole-5-carboxylate (6h):** 96% yield, 98.5:1.5 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = -43.27

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 90/10, 1.0 mL/min, t_R (major) = 35.4 min, t_R (minor) = 14.5 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (t, *J* = 8.0 Hz, 1H), 7.77 (s, 1H), 7.29-7.33 (m, 3H), 7.16-7.19 (m, 4H), 7.12 (t, *J* = 8.0 Hz, 1H), 1.27 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.31, 149.87, 149.07, 148.60, 143.80, 140.08, 139.47, 136.84, 134.03, 131.00, 130.19, 130.17, 129.77, 129.62, 127.73, 127.26, 126.35, 124.42, 105.17, 104.32, 101.95, 101.57, 82.69, 27.75; **HRMS** (ESI) Calcd for $C_{28}H_{22}INNaO_6^+$ $[M+Na]^+$ 618.0384; Found: 618.0386.

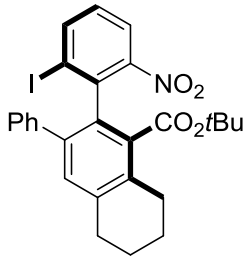


6i

***Tert*-butyl (*R*)-2-(2-iodo-6-nitrophenyl)-6,7-dimethyl-3-phenyl-1-naphthoate (6i):** 90% yield, 99:1 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = -47.63

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 90/10, 1.0 mL/min, t_R (major) = 29.5 min, t_R (minor) = 12.2 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-8.07 (m, 2H), 7.86 (s, 1H), 7.74 (s, 1H), 7.69 (s, 1H), 7.35-7.37 (m, 2H), 7.18-7.20 (m, 3H), 7.12 (t, *J* = 8.0 Hz, 1H), 2.46 (s, 6H), 1.31 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.35, 149.87, 143.81, 140.31, 139.53, 137.46, 137.36, 137.24, 134.65, 132.44, 130.10, 130.04, 129.76, 129.72, 127.98, 127.92, 127.72, 127.24, 124.90, 124.41, 105.11, 82.54, 27.80, 20.84, 20.32. **HRMS** (ESI) Calcd for $C_{29}H_{26}INNaO_4^+$ $[M+H]^+$ 602.0799; Found: 602.0795.

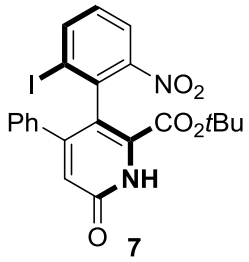


6j

***Tert*-butyl (*R*)-2-(2-iodo-6-nitrophenyl)-3-phenyl-5,6,7,8-tetrahydronaphthalene-1-carboxylate (6i):** 86% yield, 99:1 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = -38.75

HPLC condition: Chiralpak IC (Hex/*i*PrOH = 99/1, 0.4 mL/min, t_R (major) = 34.6 min, t_R (minor) = 38.0 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (t, *J* = 8.4 Hz, 2H), 7.25-7.27 (m, 2H), 7.14-7.18 (m, 4H), 7.08 (t, *J* = 8.0 Hz, 1H), 2.75-2.89 (m, 4H) 1.86 (s, 4H), 1.22 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.75, 150.08, 143.71, 140.28, 139.18, 138.50, 137.87, 133.53, 133.39, 133.17, 132.00, 129.59, 129.36, 127.69, 127.05, 124.34, 105.32, 82.03, 29.83, 27.69, 26.57, 22.95, 22.64. **HRMS** (ESI) Calcd for $C_{27}H_{27}INO_4^+$ $[M+H]^+$ 556.0979; Found: 556.0983.

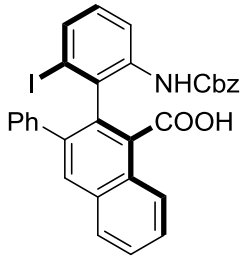


7

***Tert*-butyl 3-(2-iodo-6-nitrophenyl)-6-oxo-4-phenyl-1,6-dihydropyridine-2-carboxylate (7):** 73% yield, 97.5:2.5 er. $[\alpha]_D^{25}$ (c 0.5 $CHCl_3$) = -66.47

HPLC condition: Chiralpak IC (Hex/*i*PrOH = 80/20, 1.0 mL/min, t_R (major) = 19.6 min, t_R (minor) = 16.3 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (brs, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.04-7.21 (m, 6H), 6.80 (s, 1H), 1.19 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.27, 159.44, 154.49, 149.23, 143.47, 136.62, 131.78, 129.98, 128.61, 128.10, 127.98, 126.55, 124.33, 123.00, 105.10, 85.00, 27.49; **HRMS** (ESI) Calcd for $C_{22}H_{20}IN_2O_5^+$ $[M+H]^+$ 519.0411; Found: 519.0413.

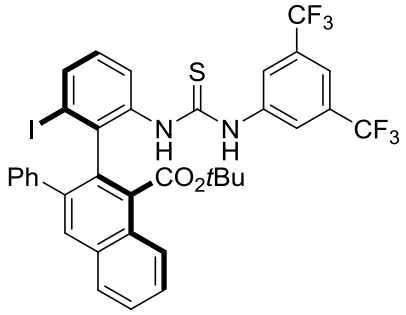


8

(*R*)-2-(2-(((benzyloxy)carbonyl)amino)-6-iodophenyl)-3-phenyl-1-naphthoic acid (8): 75% yield, 99:1 er. $[\alpha]_D^{25}$ (c 0.5 $CHCl_3$) = +14.07

HPLC condition: Chiralpak ADH (Hex/*i*PrOH = 90/10, 1.0 mL/min, t_R (major) = 43.4 min, t_R (minor) = 33.0 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.91 (m, 3H), 7.09-7.46 (m, 15H), 6.92 (brs, 1H), 6.65-6.68 (m, 1H), 4.98 (d, *J* = 12.0 Hz, 1H), 4.81 (d, *J* = 12.0 Hz, 1H)；**^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.30, 139.88, 139.05, 137.11, 135.85, 134.70, 133.46, 130.42, 129.88, 129.35, 128.52, 128.35, 128.26, 128.15, 127.64, 127.28, 127.22, 126.26, 122.16，101.91, 67.26. **HRMS** (ESI) Calcd for $C_{31}H_{22}INNaO_4^+$ $[M+Na]^+$ 622.0486; Found: 622.0487.

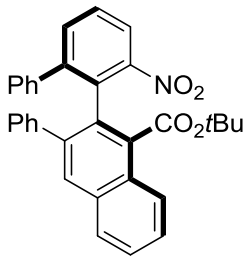


9

***Tert*-butyl (*R*)-2-(2-(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)-6-iodophenyl)-3-phenyl-1-naphthoate (9):** 89% yield, 99:1 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = -30.47

HPLC condition: Chiralpak AD (Hex/*i*PrOH = 98/2, 0.8 mL/min, t_R (major) = 12.5 min, t_R (minor) = 8.9 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (brs, 1H), 8.02 (s, 1H), 7.94-7.98 (m, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.77 (s, 2H), 7.59-7.63 (m, 2H), 7.51 (s, 1H), 7.42-7.45 (m, 2H), 7.28-7.32 (m, 4H), 7.12 (s, 1H), 7.08 (t, *J* = 8.0 Hz, 1H), 1.49 (s, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.79; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 179.48, 168.84, 141.97, 140.05, 139.80, 138.70, 138.16, 136.07, 135.66, 133.58, 132.67, 131.90, 131.61 (q, *J* = 33.3 Hz), 130.65, 129.70, 129.60, 128.88, 128.79, 128.45, 127.96, 127.79, 127.64, 127.25, 126.91, 124.81, 123.55, 123.08 (q, *J* = 271.6 Hz), 118.46, 102.80, 84.49, 27.90; **HRMS** (ESI) Calcd for $C_{36}H_{28}F_6IN_2O_2S^+$ $[M+H]^+$ 793.0815; Found: 793.0822.



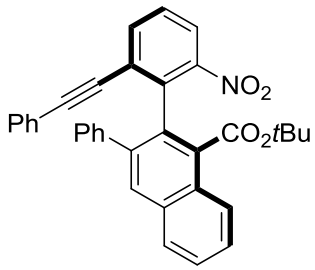
10

***Tert*-butyl (*S*)-2-(3-nitro-[1,1'-biphenyl]-2-yl)-3-phenyl-1-naphthoate (10):** 93% yield, 99:1 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = -109.03

HPLC condition: Chiralpak ID (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 9.5

min, t_R (minor) = 17.4 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.67 (s, 1H), 7.50-7.59 (m, 3H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.09-7.17 (m, 2H), 7.04 (t, *J* = 8.0 Hz, 2H), 6.95 (t, *J* = 8.0 Hz, 2H), 6.69-6.75 (m, 4H), 1.39 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.13, 151.18, 144.52, 140.02, 138.69, 138.58, 135.07, 133.12, 133.07, 132.50, 130.54, 130.37, 129.61, 129.43, 128.83, 128.71, 128.42, 127.52, 127.50, 127.24, 127.22, 126.94, 126.85, 125.05, 123.67, 83.28, 27.80; **HRMS** (ESI) Calcd for $C_{33}H_{27}NNaO_4^+$ $[M+H]^+$ 524.1832; Found: 524.1834.

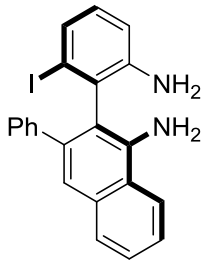


11

***Tert*-butyl (*S*)-2-(2-nitro-6-(phenylethynyl)phenyl)-3-phenyl-1-naphthoate (11):** 92% yield, 99:1 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = -199.63

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 97/3, 1.0 mL/min, t_R (major) = 8.2 min, t_R (minor) = 10.9 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.11 (m, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.94-7.96 (m, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.58-7.62 (m, 2H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.30-7.32 (m, 2H), 7.16-7.22 (m, 4H), 7.11 (t, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 7.6 Hz, 2H), 1.29 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.28, 149.12, 140.44, 139.32, 137.72, 135.90, 133.13, 132.55, 131.66, 131.59, 130.31, 129.41, 129.24, 128.76, 128.50, 128.33, 128.28, 127.93, 127.74, 127.25, 126.96, 125.47, 124.00, 122.32, 96.04, 86.90, 82.37, 27.75; **HRMS** (ESI) Calcd for $C_{35}H_{27}NO_4^+$ $[M+H]^+$ 526.2013; Found: 526.2024.



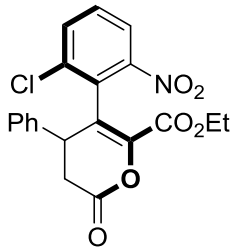
12

(*R*)-2-(2-amino-6-iodophenyl)-3-phenylnaphthalen-1-amine (12): 70% yield, 99:1 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = -201.11

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 80/20, 1.0 mL/min, t_R (major) = 34.5 min, t_R (minor) = 17.2 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (t, *J* = 8.0 Hz, 2H), 7.49-7.56 (m, 2H), 7.39-7.42 (m, 3H), 7.20-7.26 (m, 4H), 6.77 (t, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 3.81 (brs, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 146.19, 141.33, 140.50, 139.89, 134.20,

130.47, 129.24, 129.08, 128.86, 127.46, 127.16, 126.88, 126.75, 125.22, 122.83, 121.44, 120.26, 119.76, 114.89, 103.84; **HRMS** (ESI) Calcd for $C_{22}H_{18}IN_2^+$ $[M+H]^+$ 437.0509; Found: 437.0509.

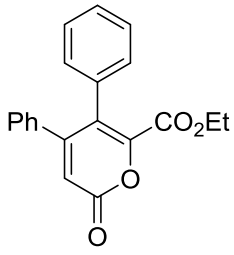


4

Ethyl 5-(2-chloro-6-nitrophenyl)-2-oxo-4-phenyl-3,4-dihydro-2*H*-pyran-6-carboxylate (4): 71% yield, 99:1 er, 92:8 dr. $[\alpha]_D^{25}$ (c 0.3 $CHCl_3$) = -136.11

HPLC condition: Chiralpak IB (Hex/*i*PrOH = 90/10, 1.0 mL/min, t_R (major) = 22.5 min, t_R (minor) = 19.2 min; t_R (major) = 16.0 min, t_R (minor) = 14.6 min;).

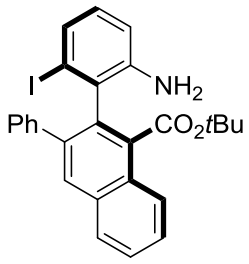
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.11-7.15 (m, 3H), 7.01-7.04 (m, 2H), 4.18 (dd, *J* = 6.4, 9.6 Hz, 1H), 4.03-4.12 (m, 2H), 3.25-3.31 (m, 1H), 3.13-3.18 (m, 1H), 1.07 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.22, 159.93, 148.30, 139.24, 136.09, 134.39, 134.31, 131.39, 129.36, 128.95, 128.37, 127.72, 126.40, 123.15, 62.04, 42.48, 34.28, 13.81. **HRMS** (ESI) Calcd for $C_{20}H_{17}ClNO_6^+$ $[M+H]^+$ 402.0739; Found: 402.0740.



S1

Ethyl 2-oxo-4,5-diphenyl-2*H*-pyran-6-carboxylate (S1): 75 % yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.26 (m, 6H), 6.94-6.99 (m, 4H), 6.50 (s, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 1.04 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 160.44, 159.78, 158.10, 147.38, 135.75, 132.92, 129.96, 129.24, 128.49, 128.27, 128.23, 128.15, 123.50, 117.65, 62.33, 13.70; **HRMS** (ESI) Calcd for $C_{20}H_{17}O_4^+$ $[M+H]^+$ 321.1121; Found: 321.1123.

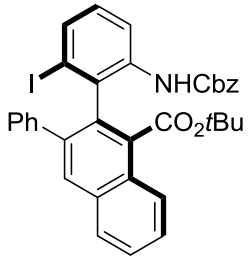


S3

***Tert*-butyl (*R*)-2-(2-amino-6-iodophenyl)-3-phenyl-1-naphthoate (S3):** 71% yield, 99:1 er. $[\alpha]_D^{25}$ (c 0.3 $CHCl_3$) = -102.03

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 90/10, 1.0 mL/min, t_R (major) = 13.6 min, t_R (minor) = 15.0 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.93-7.96 (m, 2H), 7.58-7.60 (m, 2H), 7.47-7.50 (m, 2H), 7.23-7.26 (m, 3H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.74 (t, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 3.79 (s, 2H), 1.35 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.97, 146.67, 140.16, 140.06, 134.58, 133.88, 133.43, 131.01, 130.25, 129.55, 129.15, 128.64, 128.39, 127.56, 127.25, 127.13, 125.16, 114.94, 102.63, 82.69, 27.80; **HRMS** (ESI) Calcd for $C_{27}H_{25}INO_2^+$ $[M+H]^+$ 522.0924; Found: 522.0923.

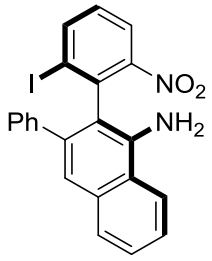


S4

***Tert*-butyl (*R*)-2-(2-(((benzyloxy)carbonyl)amino)-6-iodophenyl)-3-phenyl-1-naphthoate (S4):** 71% yield, 99:1 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = -8.87

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 90/10, 1.0 mL/min, t_R (major) = 12.4 min, t_R (minor) = 7.0 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-8.02 (m, 4H), 7.61-7.66 (m, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.31-7.35 (m, 5H), 7.14-7.23 (m, 5H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.62 (s, 1H), 5.10 (q, *J* = 12.0 Hz, 2H), 1.29 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.35, 153.31, 139.46, 139.29, 137.63, 136.02, 134.04, 133.90, 133.63, 131.21, 130.17, 129.29, 129.04, 128.64, 128.53, 128.49, 128.43, 127.73, 127.62, 127.55, 127.47, 125.36, 101.82, 83.05, 67.17, 27.68; **HRMS** (ESI) Calcd for $C_{35}H_{30}INNaO_4^+$ $[M+Na]^+$ 678.1112; Found: 678.1119.



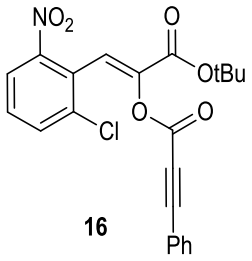
S6

(*R*)-2-(2-iodo-6-nitrophenyl)-3-phenylnaphthalen-1-amine (S6): 71% yield, 99:1 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = -84.05

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 90/10, 1.0 mL/min, t_R (major) = 37.4 min, t_R (minor) = 30.4 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.13 (m, 1H), 7.85-7.91 (m, 2H), 7.76-7.79 (m, 1H), 7.50-7.57 (m, 2H), 7.36 (s, 1H), 7.17-7.23 (m, 5H), 7.08-7.13 (m, 1H), 4.09 (s,

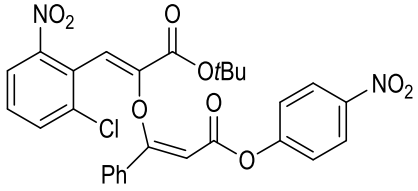
2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 151.13, 143.80, 140.82, 139.47, 138.81, 137.46, 134.21, 130.10, 129.29, 128.94, 127.69, 127.05, 125.49, 124.35, 122.75, 121.37, 121.34, 120.18, 120.14, 106.25; **HRMS** (ESI) Calcd for $C_{22}H_{16}IN_2O_2^+$ $[M+H]^+$ 467.0251; Found: 427.0251.



16

***Tert*-butyl (*Z*)-3-(2-chloro-6-nitrophenyl)-2-((3-phenylpropioloyl)oxy)acrylate (16)**

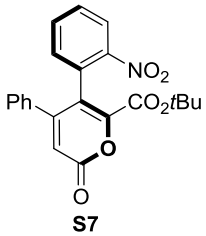
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.55-7.57 (m, 2H), 7.44-7.49 (m, 3H), 7.34-7.40 (m, 2H), 1.55 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.55, 150.28, 149.85, 140.65, 135.78, 134.34, 133.47, 131.34, 130.00, 128.79, 128.73, 126.07, 123.24, 120.58, 119.02, 89.64, 83.85, 79.22, 28.00; **HRMS** (ESI) Calcd for $C_{22}H_{18}ClNNaO_6^+$ $[M+Na]^+$ 450.0715; Found: 450.0714.



17

***Tert*-butyl (*Z*)-3-(2-chloro-6-nitrophenyl)-2-(((*Z*)-3-(4-nitrophenoxy)-3-oxo-1-phenylprop-1-en-1-yl)oxy)acrylate (17)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-8.07 (m, 2H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.57-7.62 (m, 3H), 7.36-7.46 (m, 4H), 7.34 (s, 1H), 6.92-6.96 (m, 2H), 6.26 (s, 1H), 1.48 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.45, 161.81, 160.05, 159.86, 150.13, 142.77, 141.28, 135.82, 133.94, 132.42, 132.04, 129.66, 129.30, 127.09, 126.09, 125.91, 122.91, 119.26, 116.32, 104.34, 83.43, 27.97; **HRMS** (ESI) Calcd for $C_{28}H_{23}ClN_2NaO_9^+$ $[M+Na]^+$ 589.0984; Found: 589.0983.

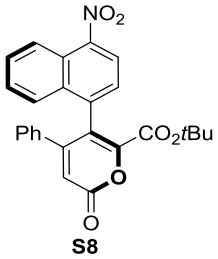


S7

***Tert*-butyl 5-(2-nitrophenyl)-2-oxo-4-phenyl-2H-pyran-6-carboxylate (S7):** 82% yield, 65.5:34.5er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = +27.80

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 30.3 min, t_R (minor) = 21.7 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-8.01 (m, 1H), 7.53-7.57 (m, 1H), 7.44-7.48 (m, 1H), 7.20-7.25 (m, 2H), 7.13-7.17 (m, 2H), 6.95-6.98 (m, 2H), 6.52 (s, 1H), 1.24 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.59, 158.59, 157.52, 148.15, 146.25, 135.34, 133.24, 132.57, 130.04, 129.63, 129.29, 128.34, 127.99, 124.90, 121.21, 117.95, 84.42, 27.58. **HRMS** (ESI) Calcd for $C_{22}H_{20}NO_6^+$ $[M+H]^+$ 394.1285; Found: 394.1287.

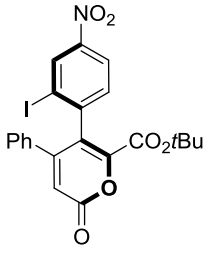


S8

***Tert*-butyl 5-(4-nitronaphthalen-1-yl)-2-oxo-4-phenyl-2H-pyran-6-carboxylate (S8):** 73% yield, 66.5:33.5 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = +38.31

HPLC condition: Chiralpak ODH (Hex/*i*PrOH = 90/10, 1.0 mL/min, t_R (major) = 34.5 min, t_R (minor) = 46.2 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.67-7.71 (m, 1H), 7.58-7.62 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.11-7.14 (m, 1H), 7.00-7.04 (m, 2H), 6.83-6.85 (m, 2H), 6.59 (s, 1H), 0.89 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.49, 158.44, 157.98, 149.31, 146.71, 138.51, 135.30, 133.63, 129.62, 129.59, 128.38, 128.27, 127.54, 126.61, 125.75, 124.95, 123.64, 122.80, 119.38, 117.93, 84.45, 27.15. **HRMS** (ESI) Calcd for $C_{26}H_{22}NO_6^+$ $[M+H]^+$ 444.1442; Found: 444.1447.



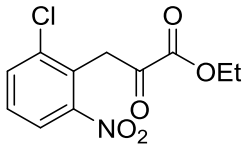
S9

***Tert*-butyl 5-(2-iodo-4-nitrophenyl)-2-oxo-4-phenyl-2H-pyran-6-carboxylate (S9):** 81% yield, 72.5:27.5 er. $[\alpha]_D^{25}$ (c 1.0 $CHCl_3$) = +33.55

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 22.1 min, t_R (minor) = 18.4 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 2.4 Hz, 1H), 8.09 (dd, *J* = 2.0, 8.4 Hz, 1H), 7.25-7.29 (m, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.18-7.21 (m, 2H), 7.00-7.02 (m, 2H), 6.54 (s, 1H), 1.31 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.22, 158.03, 156.84, 148.07, 147.18, 146.40, 134.86, 133.73, 131.25, 129.68, 128.46, 128.22, 124.45, 122.73, 118.54, 100.98, 84.84, 27.69. **HRMS** (ESI) Calcd for $C_{22}H_{19}INO_6^+$ $[M+H]^+$ 520.0252; Found: 520.0263.

III Copies of NMR Spectra and HPLC Chromatographs



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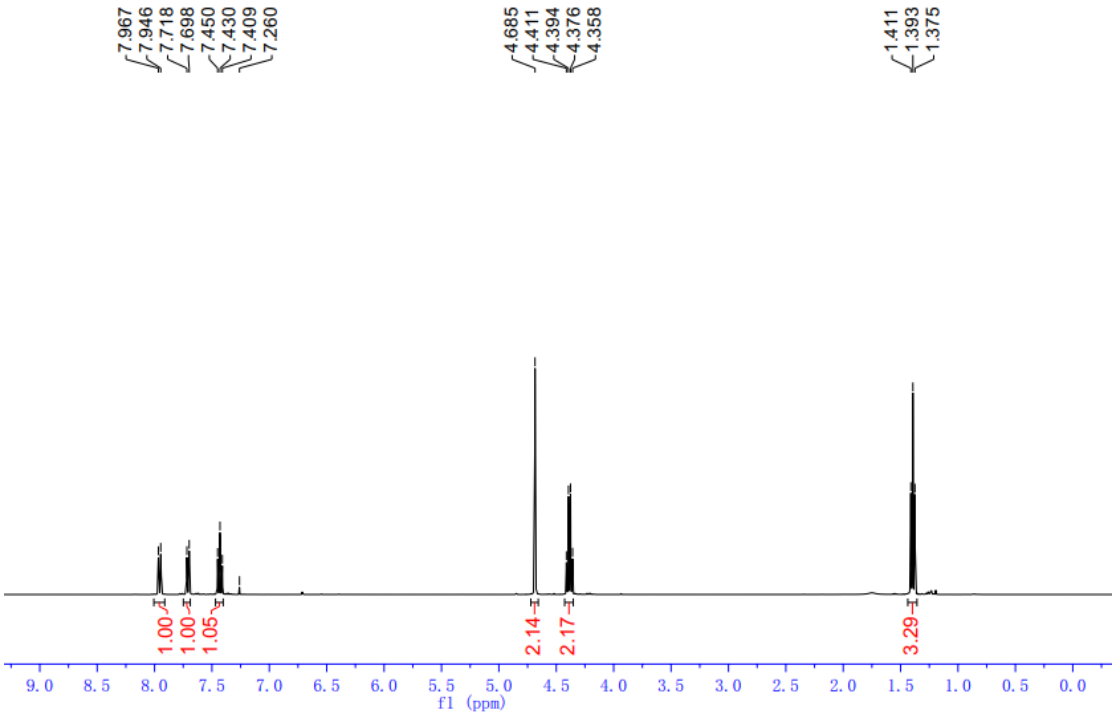

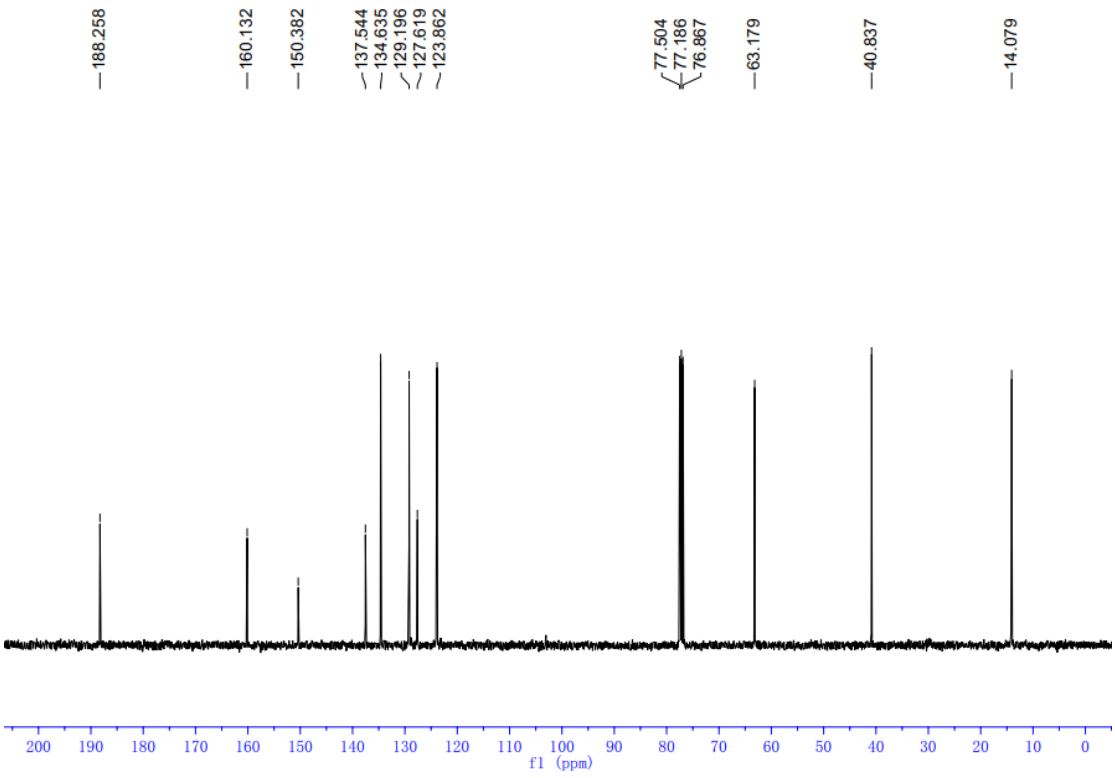

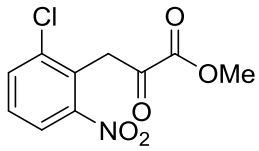
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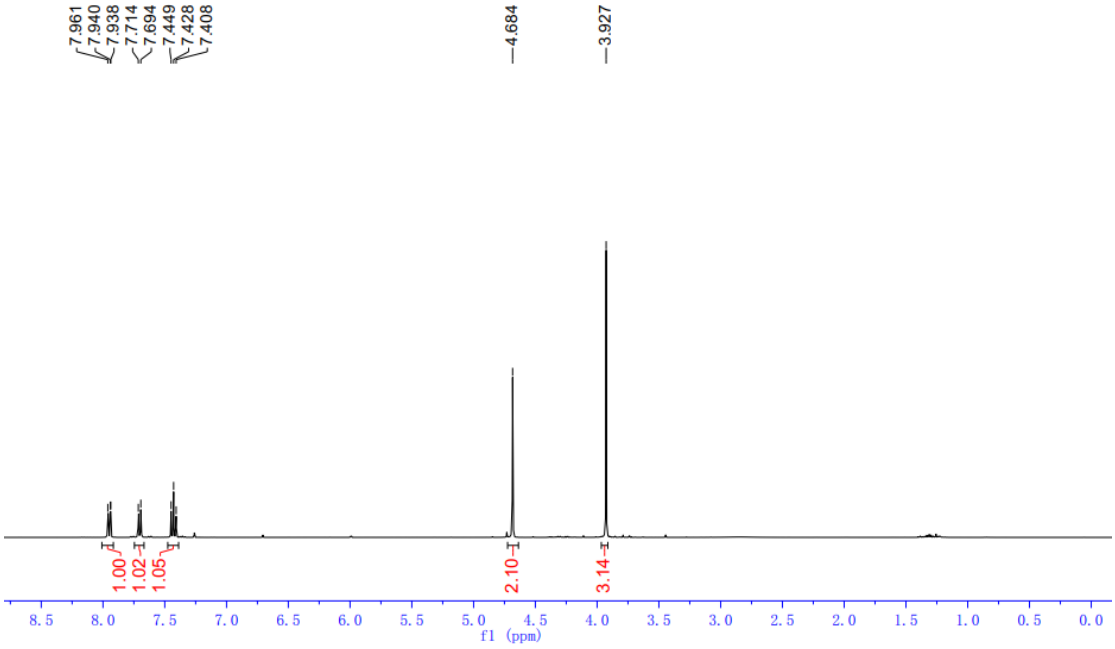
OMe
O
NO2

1b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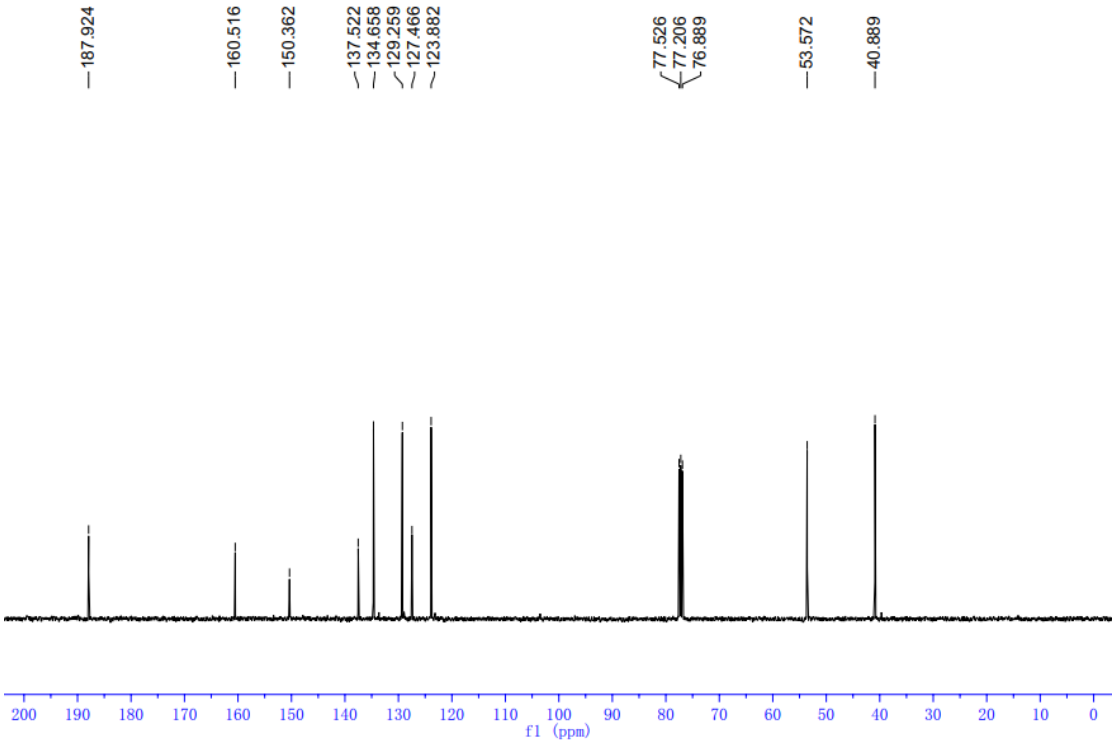
1.00
1.02
1.05
2.10
3.14
f1 (ppm)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77.206
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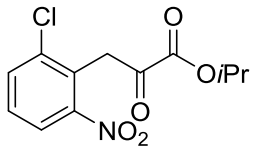
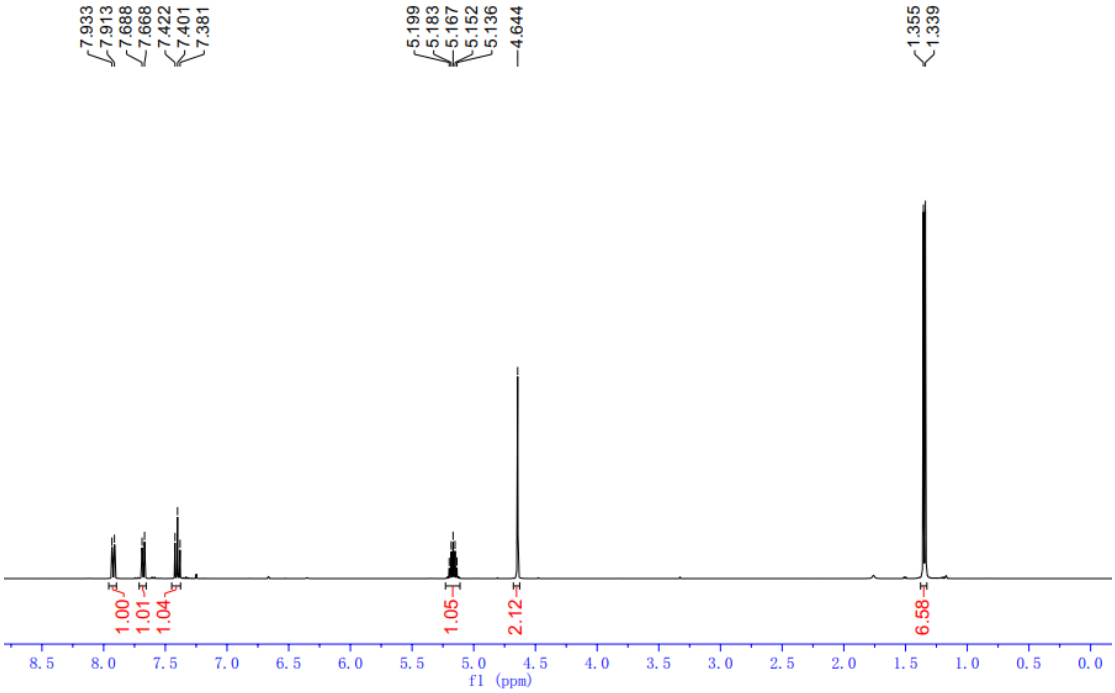
40.889
f1 (ppm)


Cl
O
OiPr
O
NO2

1c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5.167
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1.01
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1.05
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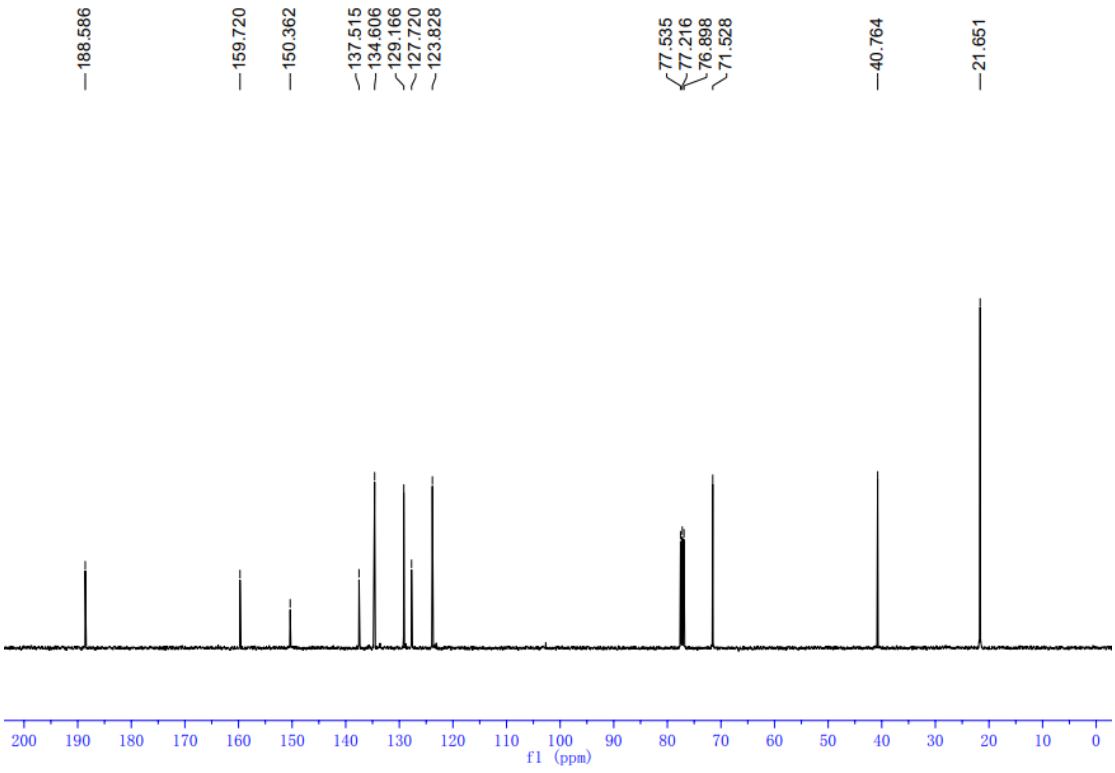
6.58
f1 (ppm)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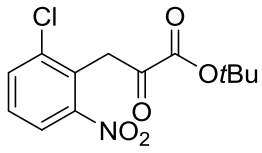
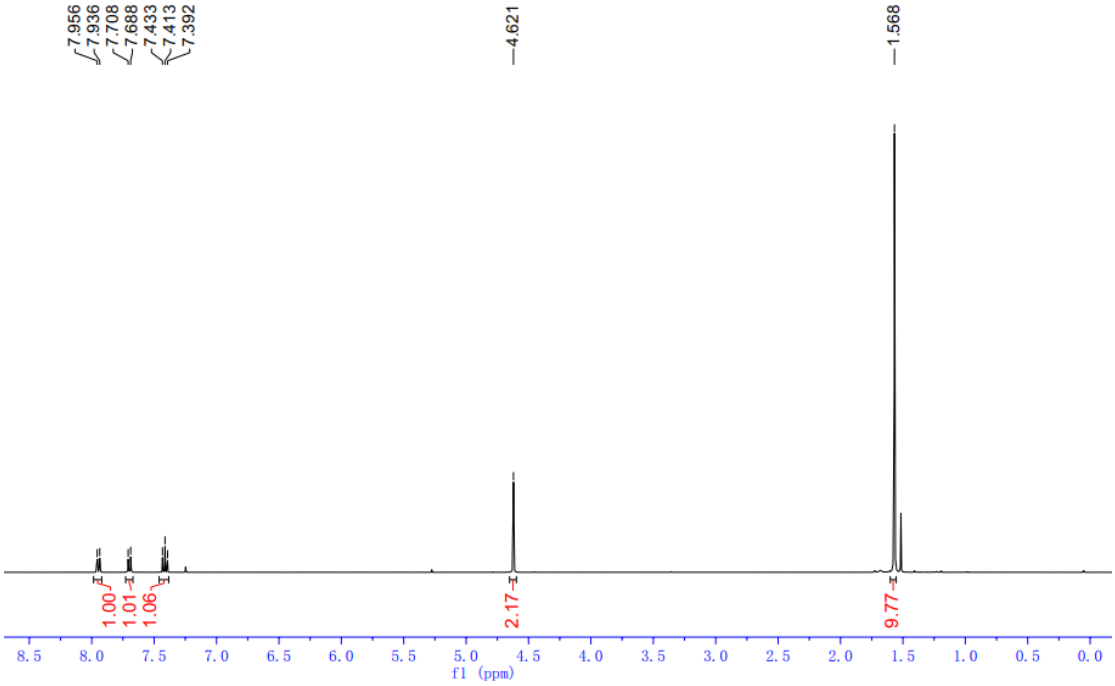
21.651
f1 (ppm)


Cl
O
OtBu
O
NO2

1d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4.621
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1.01
1.06
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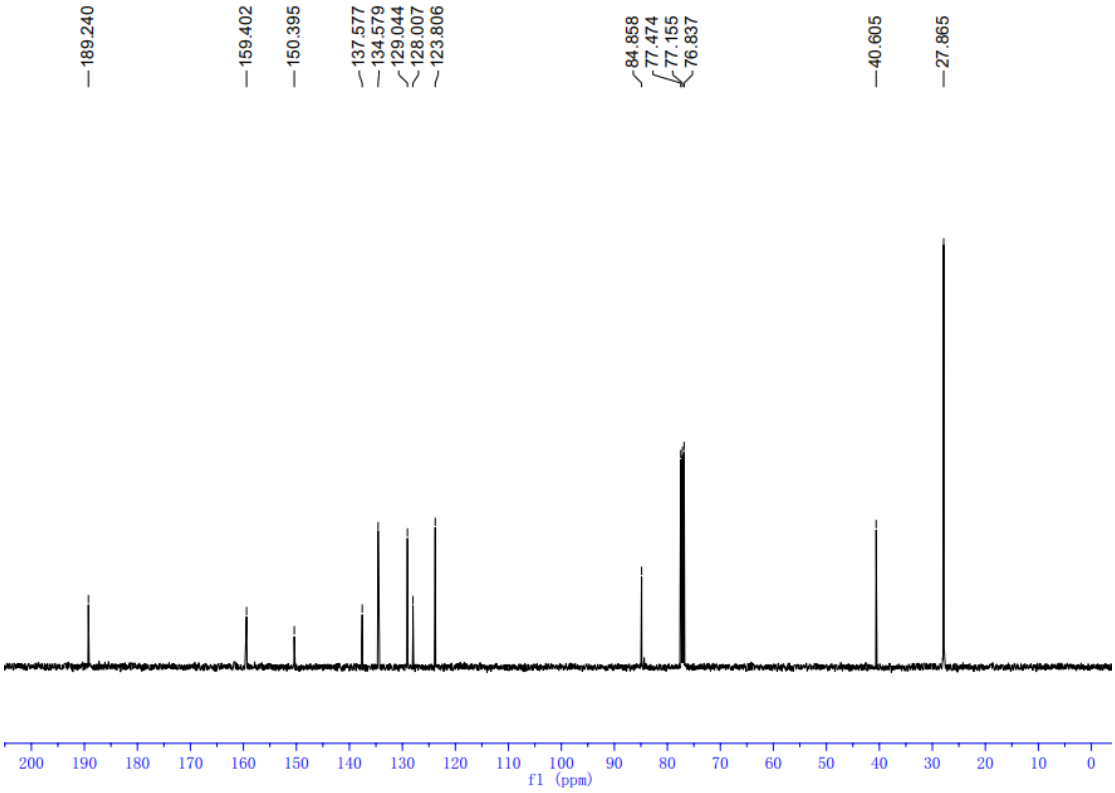
9.77
f1 (ppm)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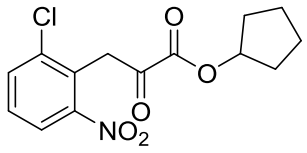
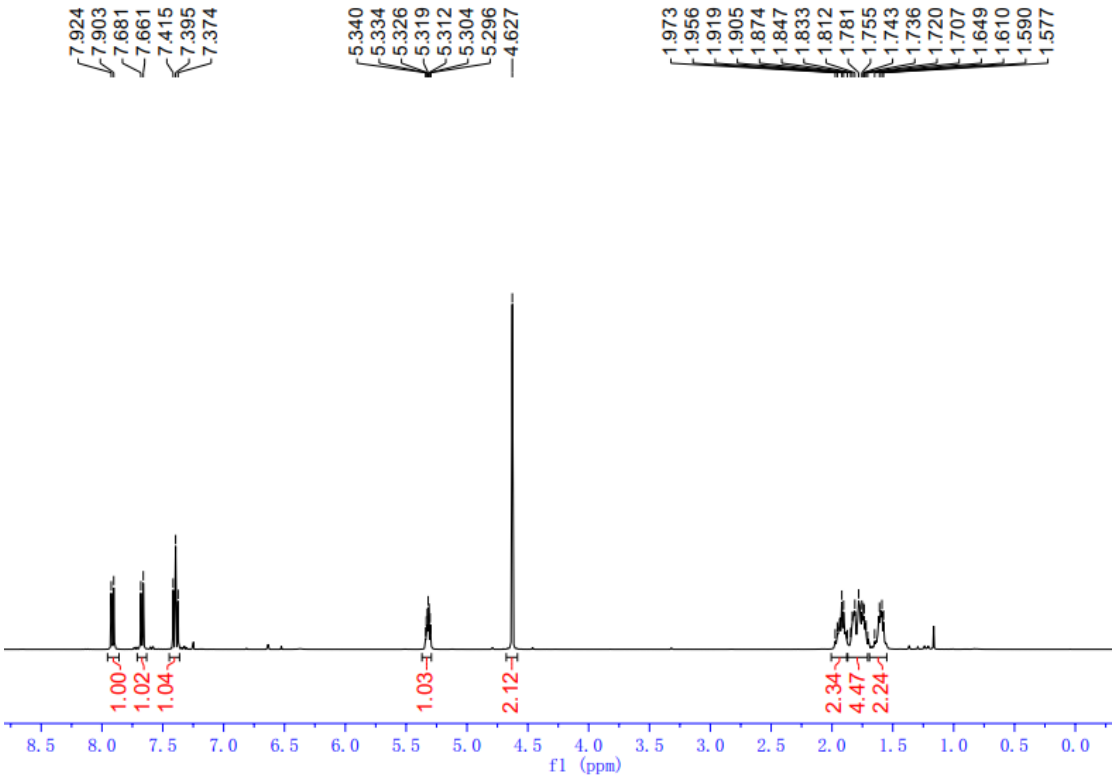
27.865
f1 (ppm)


Cl
O
O
O
NO2

1e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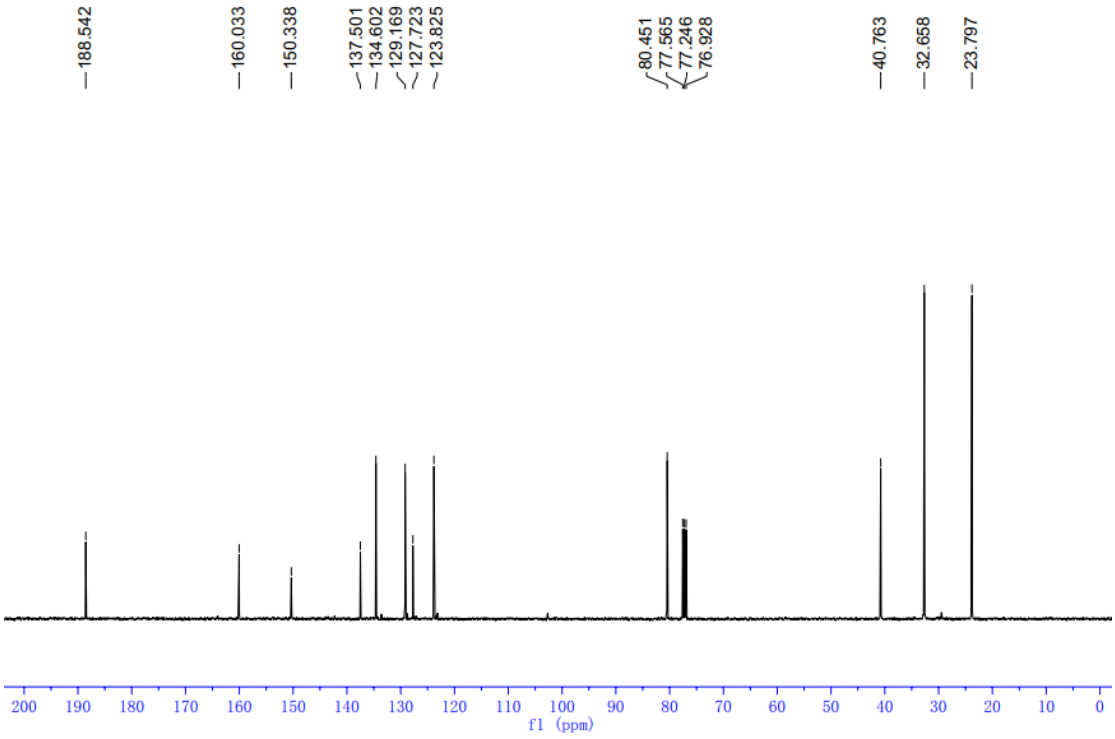
5.319
5.312
5.304
5.296
4.627
1.973
1.956
1.919
1.905
1.874
1.847
1.833
1.812
1.781
1.755
1.743
1.736
1.720
1.707
1.649
1.610
1.590
1.577
1.00
1.02
1.04
1.03
2.12
2.34
4.47
2.24
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.169
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123.825
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77.246
76.928
40.763
32.658
23.797
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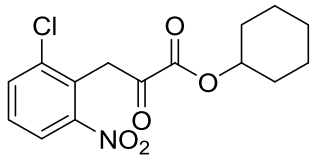
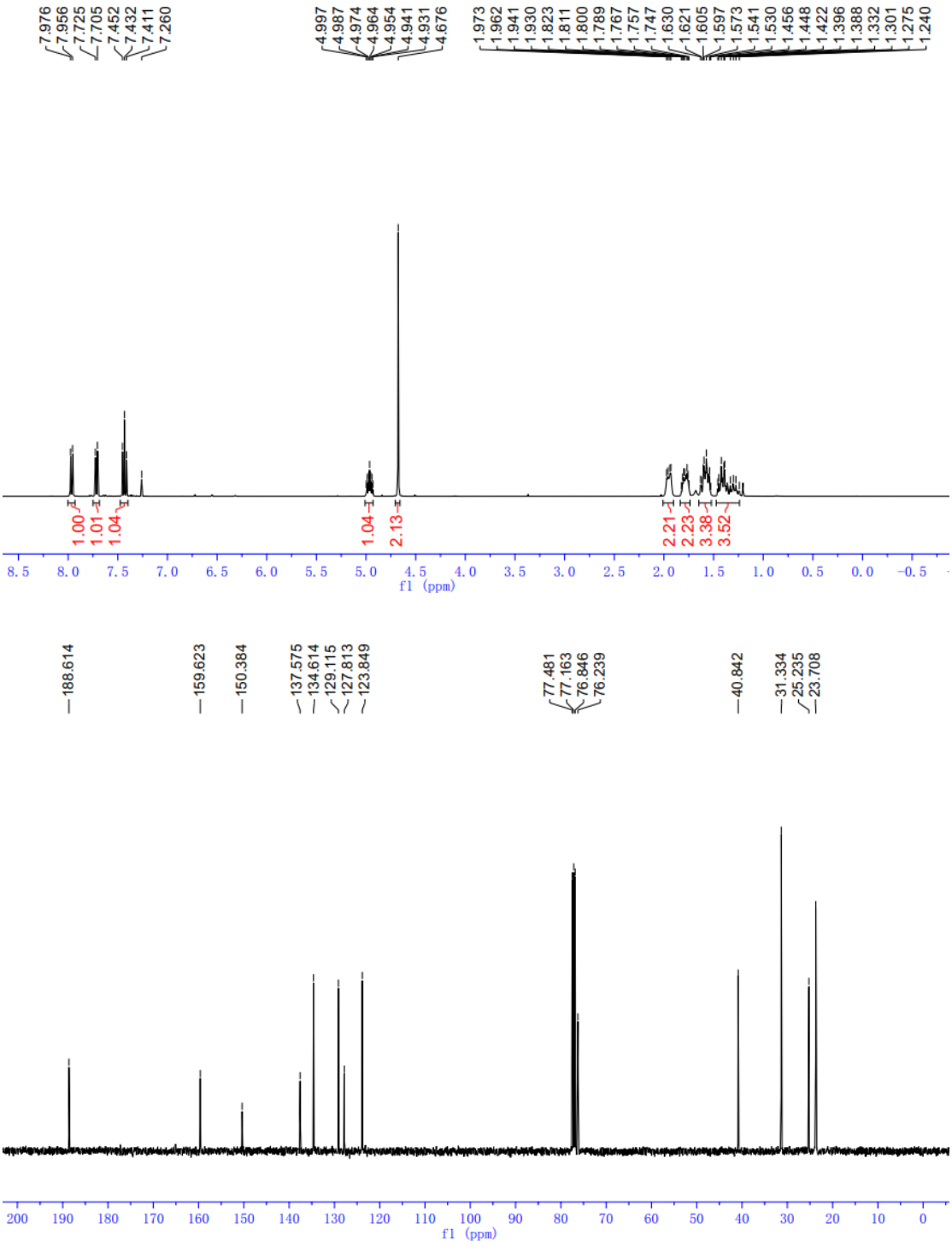
f1 (ppm)


Cl
O
O
O
NO2

1f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4.941
4.931
4.676
1.973
1.962
1.941
1.930
1.823
1.811
1.800
1.789
1.767
1.757
1.747
1.630
1.621
1.605
1.597
1.573
1.541
1.530
1.456
1.448
1.422
1.396
1.388
1.332
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1.240
1.00
1.01
1.04
1.04
2.13
2.21
2.23
3.38
3.52
f1 (ppm)
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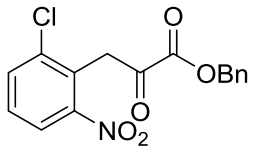
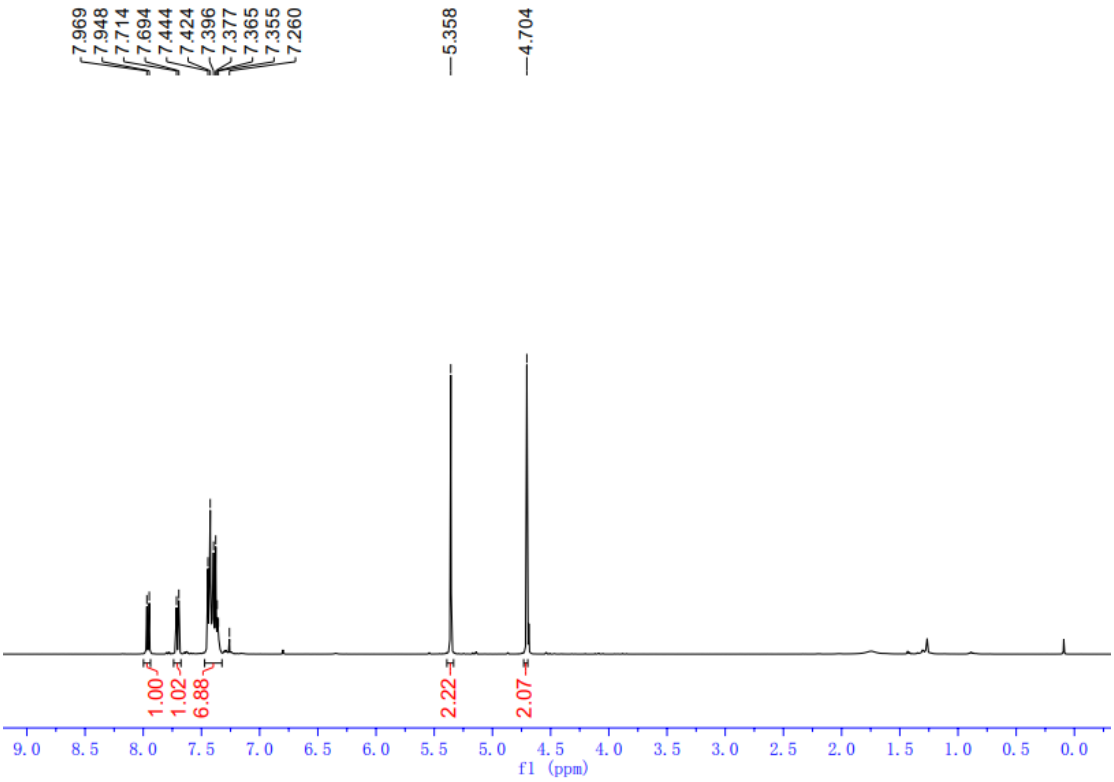
f1 (ppm)


Cl
O
OBn
O
NO2

1g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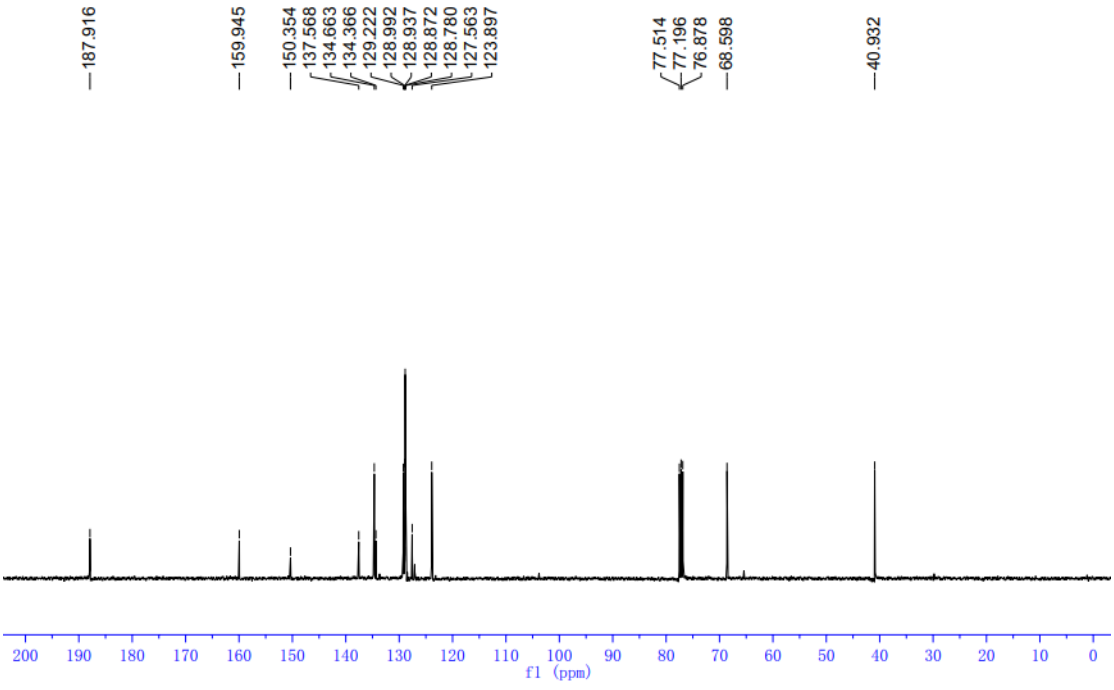
7.377
7.365
7.355
7.260
5.358
4.704
1.00
1.02
6.88
2.22
2.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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127.563
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77.196
76.878
68.598
40.932
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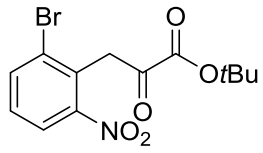
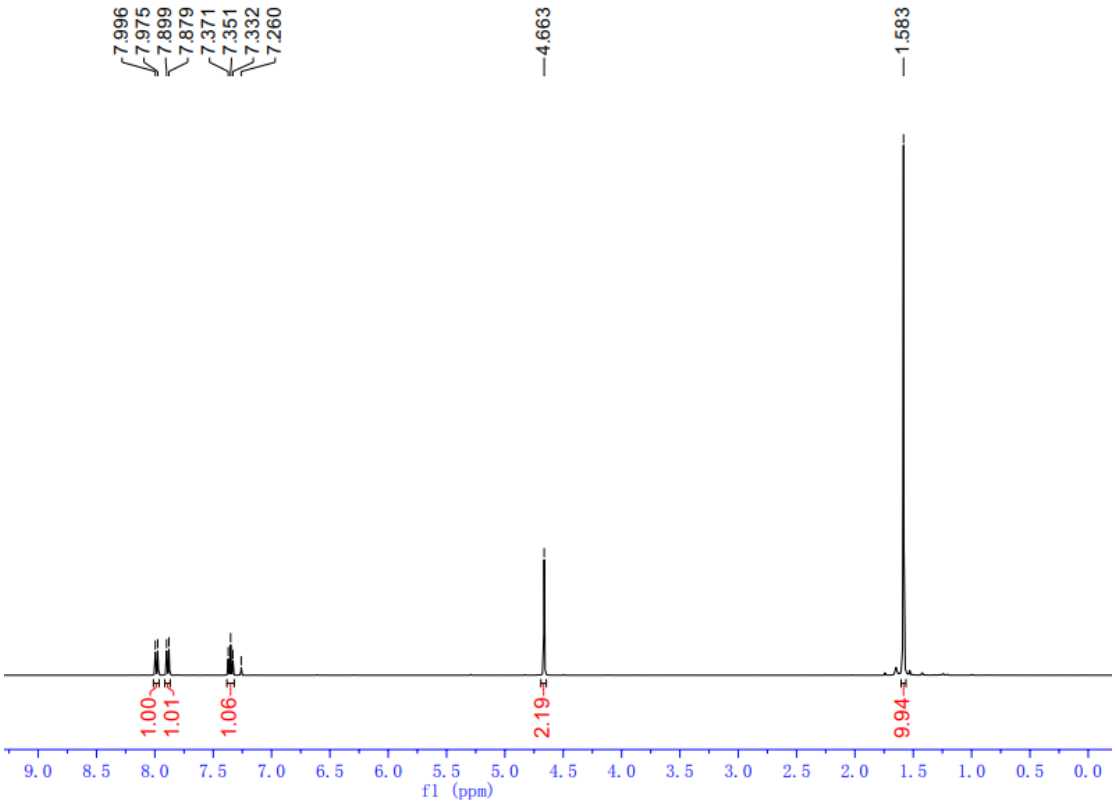
f1 (ppm)


Br
O
OtBu
O
NO2

1h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7.351
7.332
7.260
4.663
1.583
1.00
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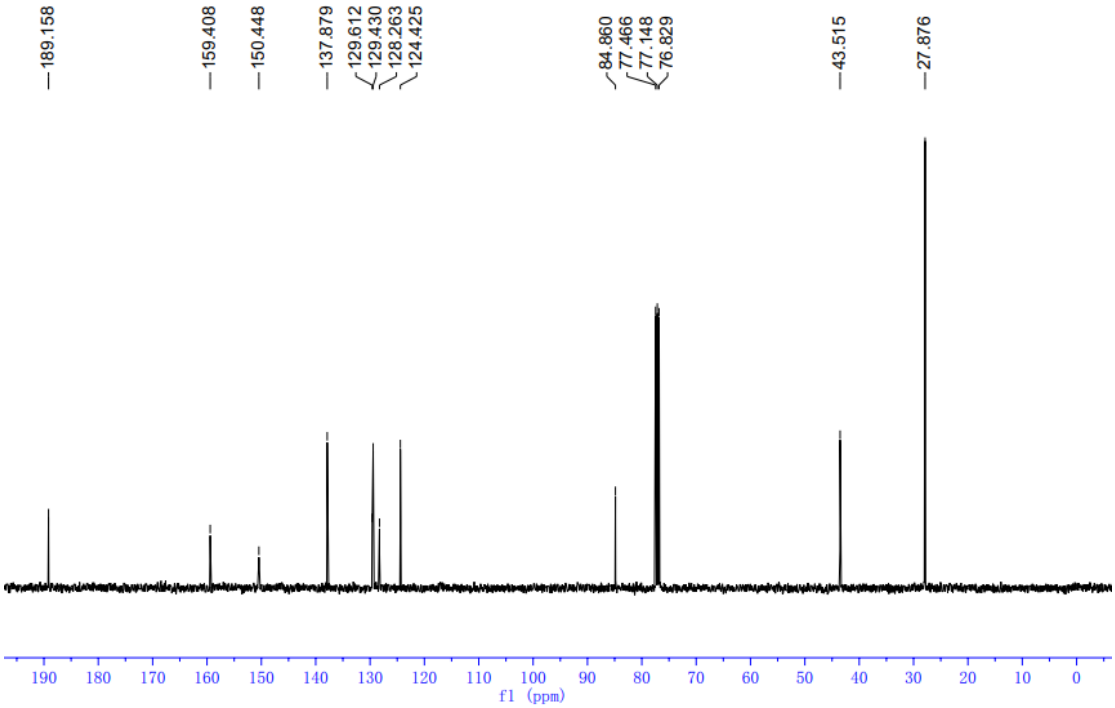
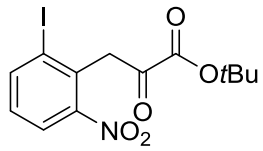
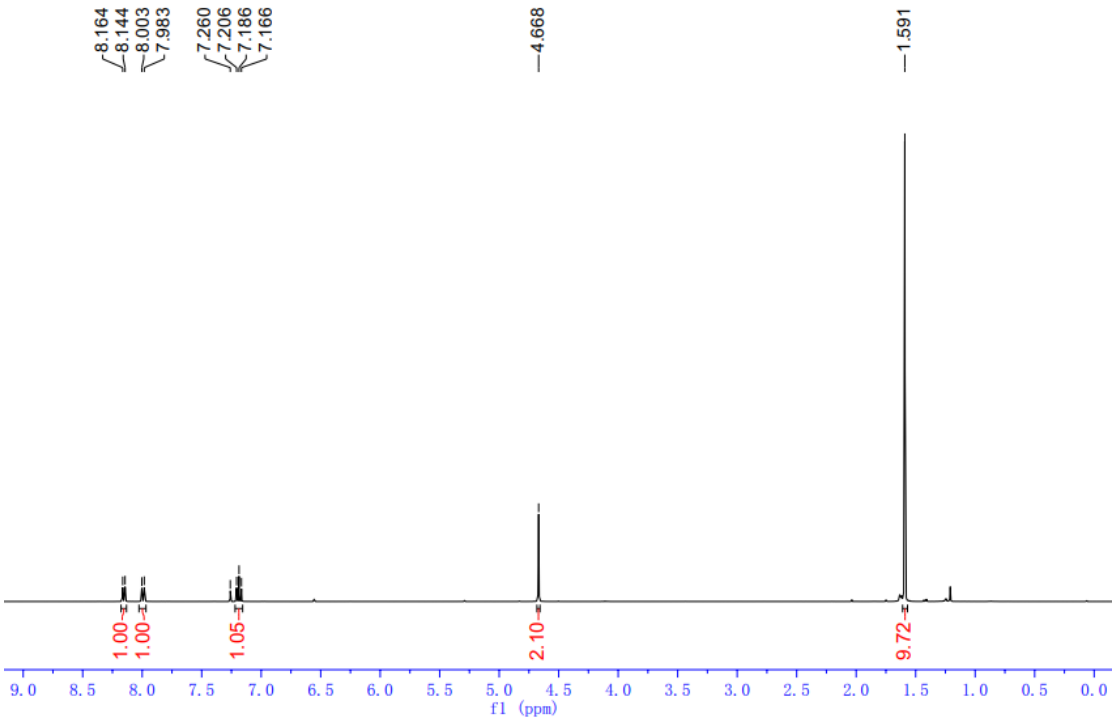
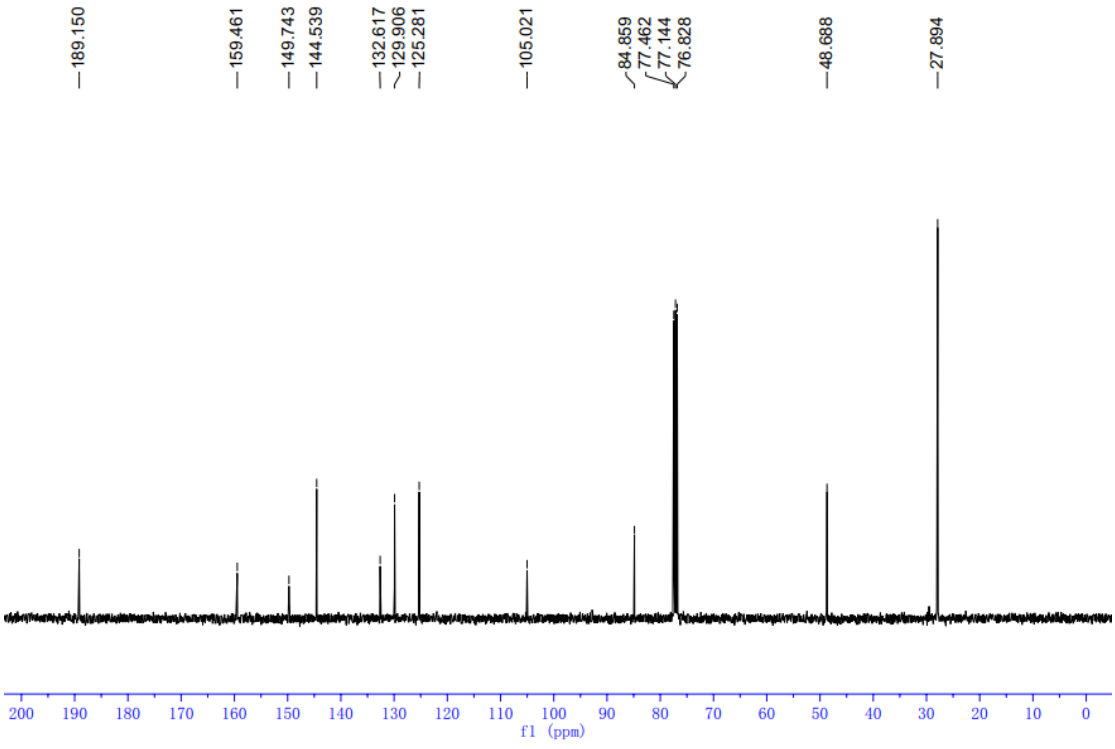
1.06
2.19
9.94
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

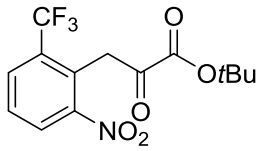

189.158
159.408
150.448
137.879
129.612
129.430
128.263
124.425
84.860
77.466
77.148
76.829
43.515
27.876
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


I
O
OtBu
O
NO2

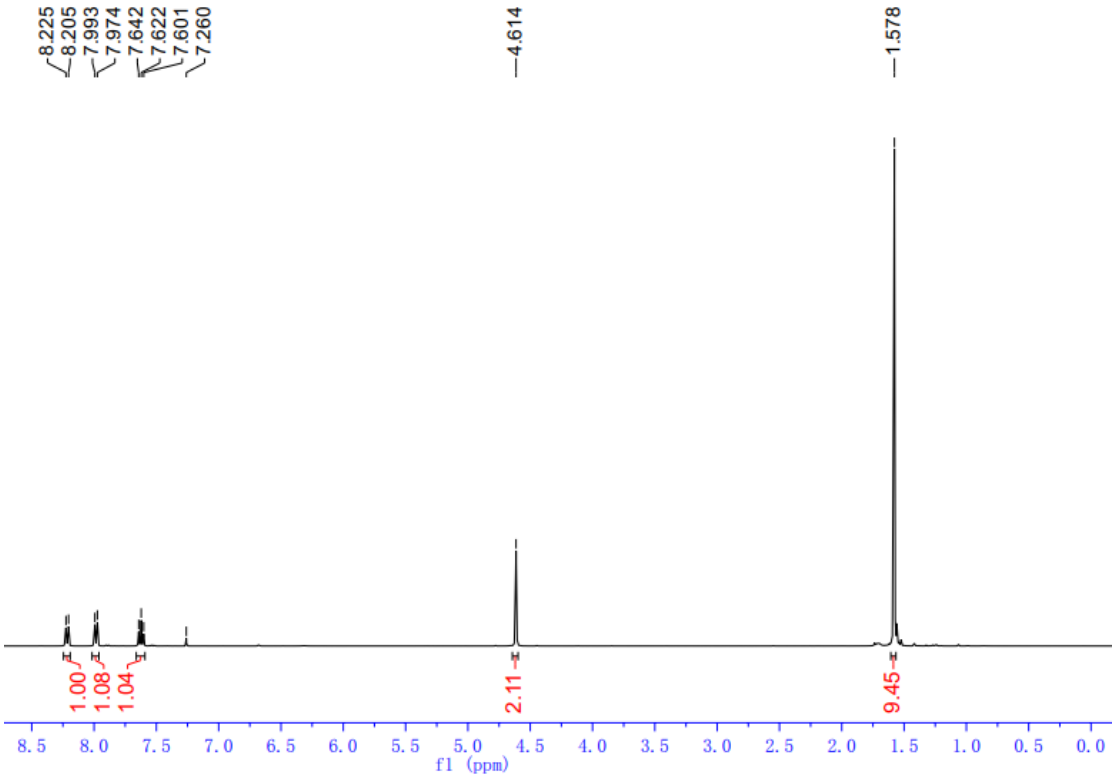
1i

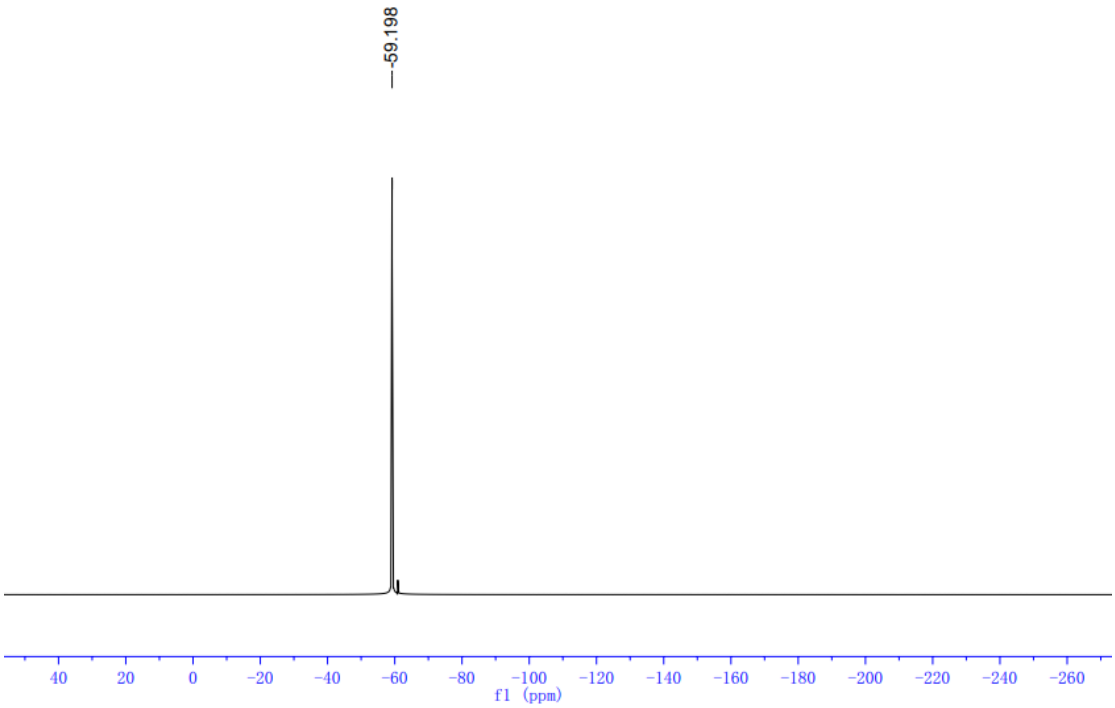

8.164
8.144
8.003
7.983
7.260
7.206
7.186
7.166
4.668
1.591
1.00
1.00
1.05
2.10
9.72
f1 (ppm)

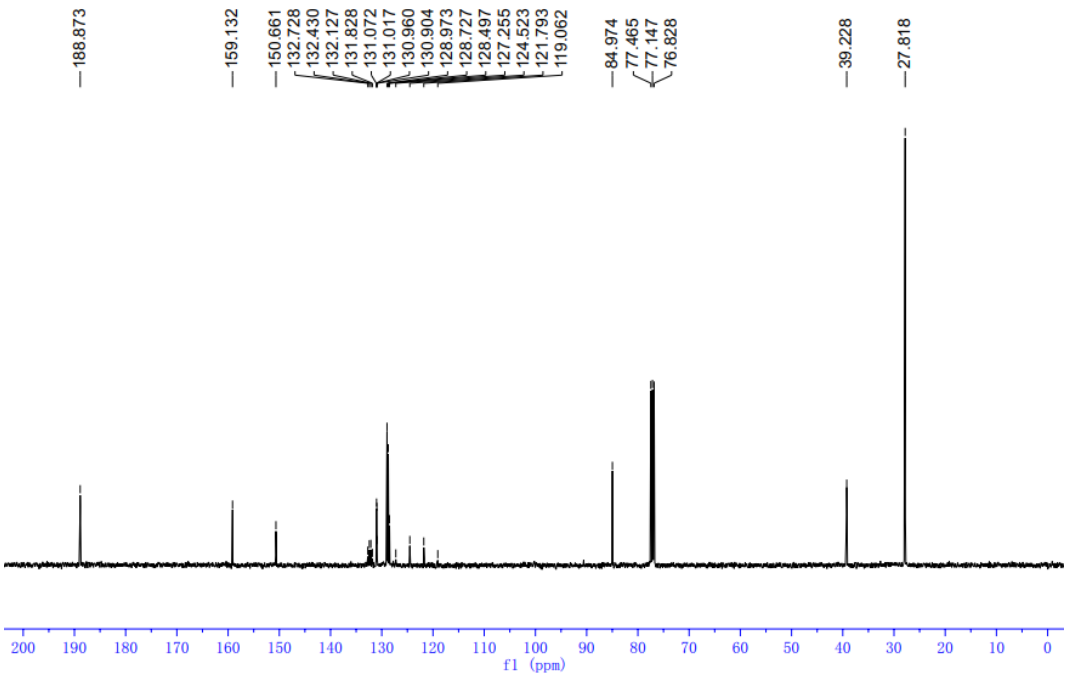

189.150
159.461
149.743
144.539
132.617
129.906
125.281
105.021
84.859
77.462
77.144
76.828
48.688
27.894
f1 (ppm)

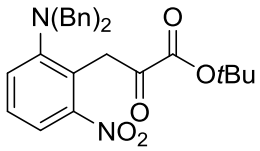

CF3
O
OtBu
O
NO2

1j

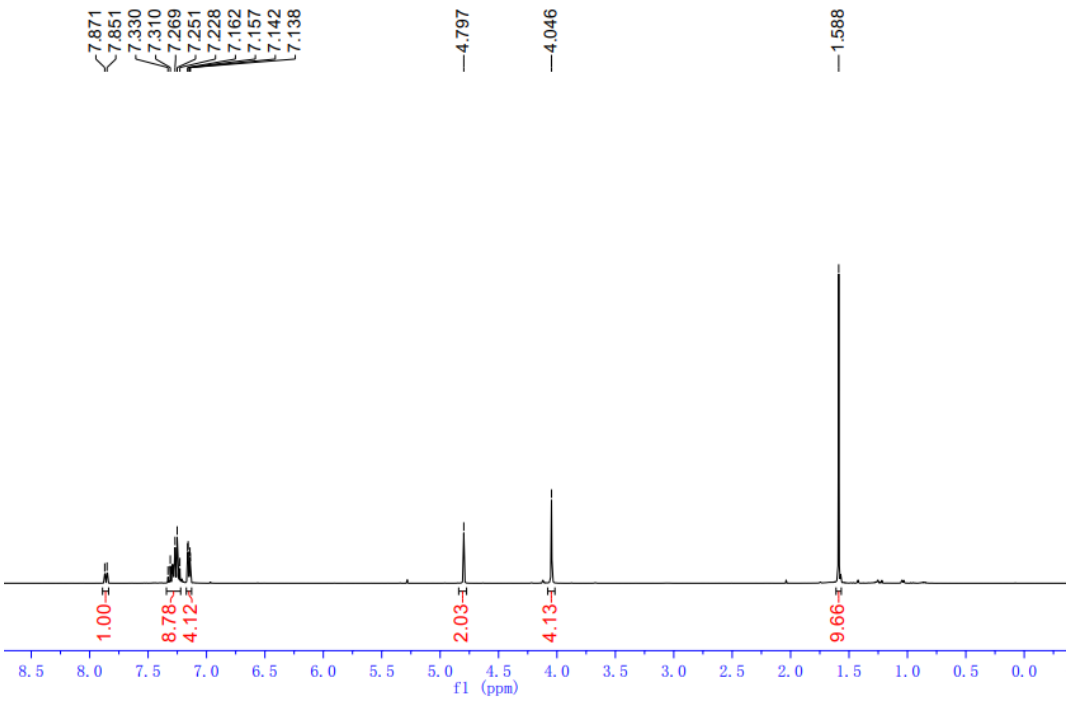

8.225
8.205
7.993
7.974
7.642
7.622
7.601
7.260
4.614
1.578
1.00
1.08
1.04
2.11
9.45
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

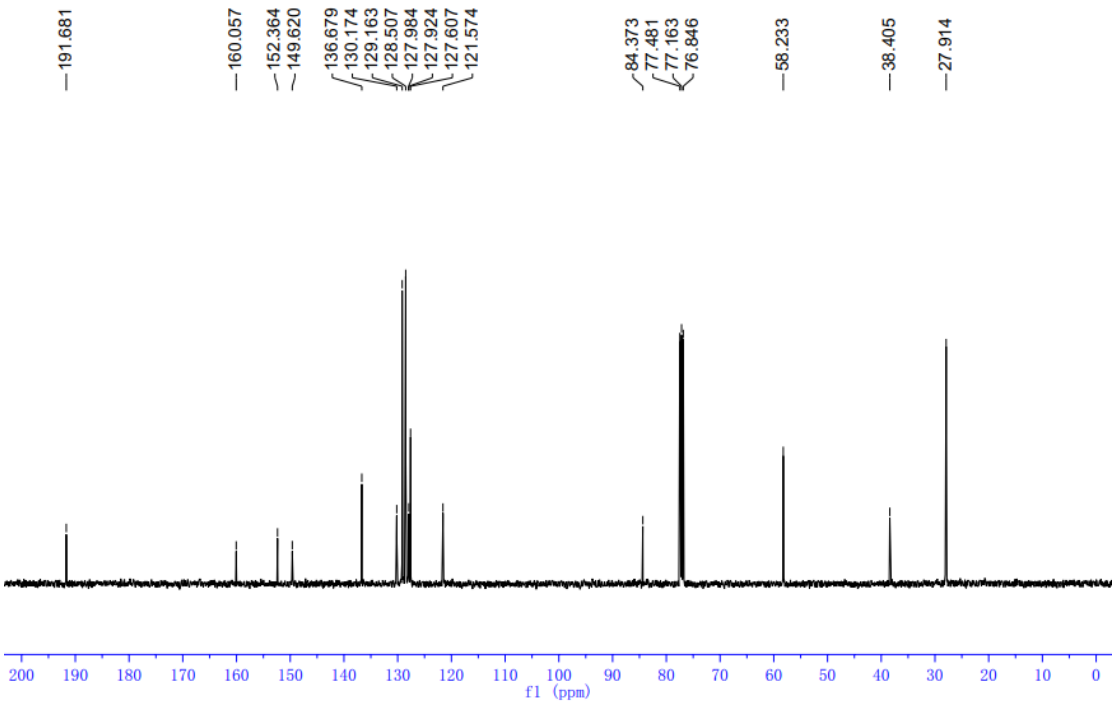

-59.198
40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)

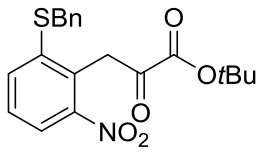

188.873
159.132
150.661
132.728
132.430
132.127
131.828
131.072
131.017
130.960
130.904
128.973
128.727
128.497
127.255
124.523
121.793
119.062
84.974
77.465
77.147
76.828
39.228
27.818
f1 (ppm)


N(Bn)2
O
OtBu
O
NO2

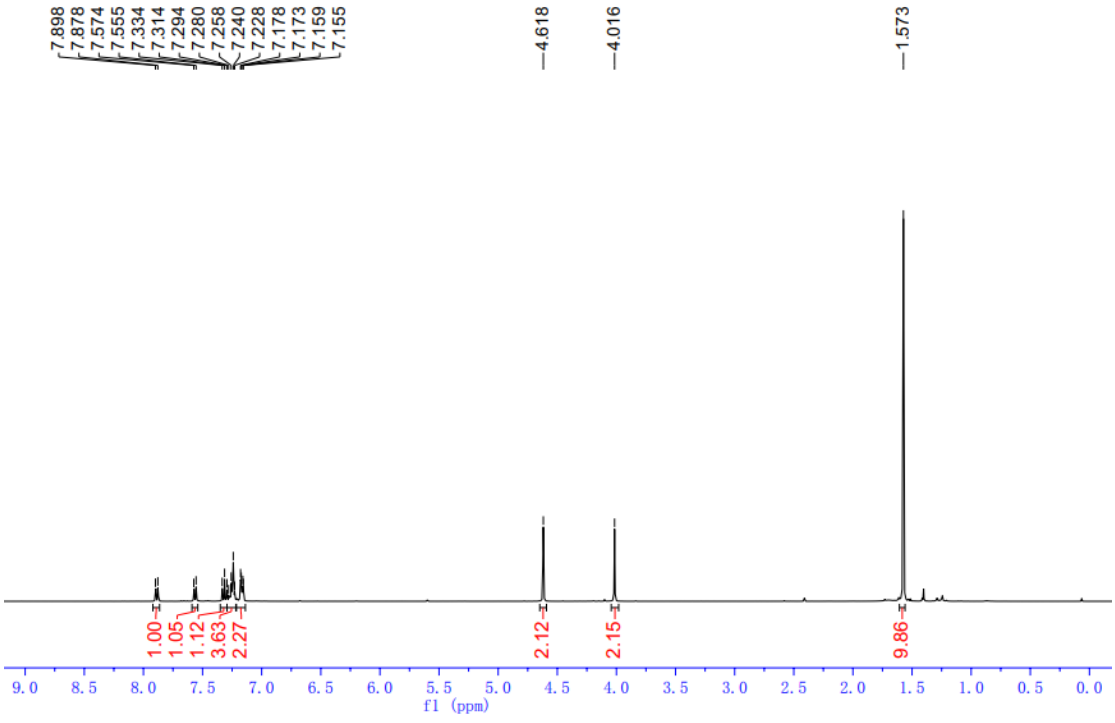
1k

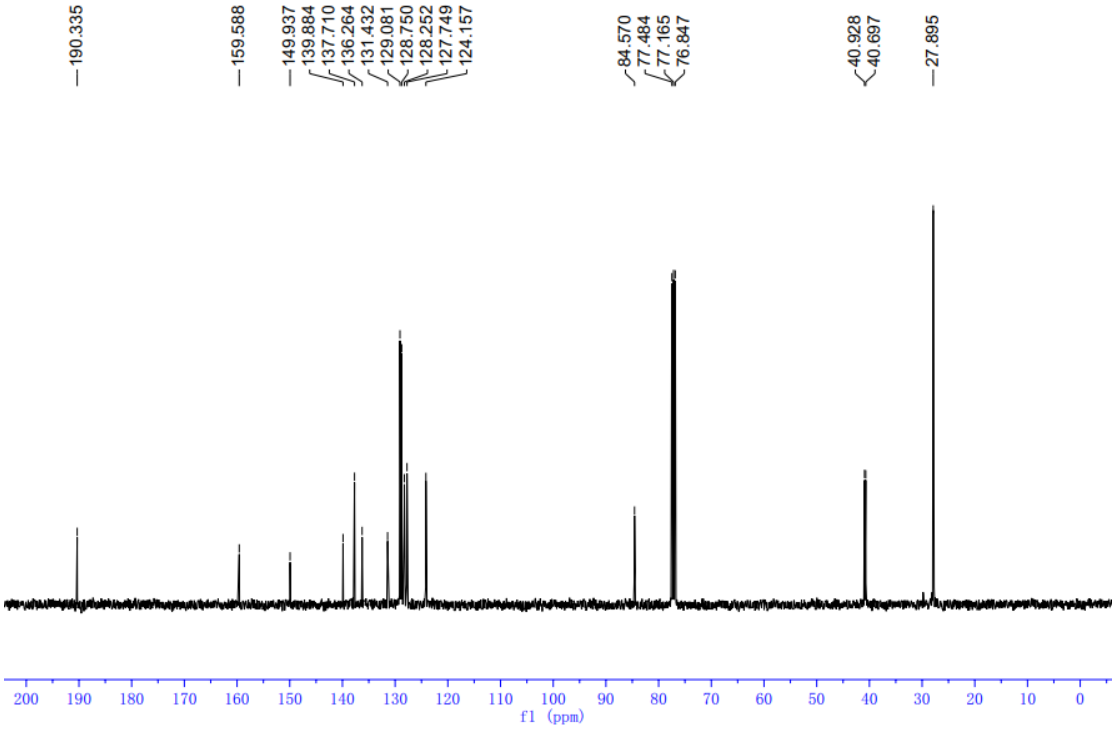

7.871
7.851
7.330
7.310
7.269
7.251
7.228
7.162
7.157
7.142
7.138
4.797
4.046
1.588
1.00
8.78
4.12
2.03
4.13
9.66
f1 (ppm)


191.681
160.057
152.364
149.620
136.679
130.174
129.163
128.507
127.984
127.924
127.607
121.574
84.373
77.481
77.163
76.846
58.233
38.405
27.914
f1 (ppm)


SBn
O
OtBu
O
NO2

1l


7.898
7.878
7.574
7.555
7.334
7.314
7.294
7.280
7.258
7.240
7.228
7.178
7.173
7.159
7.155
4.618
4.016
1.573
1.00
1.05
1.12
3.63
2.27
2.12
2.15
9.86
f1 (ppm)


190.335
159.588
149.937
139.884
137.710
136.264
131.432
129.081
128.750
128.252
127.749
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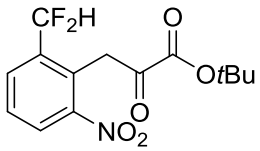
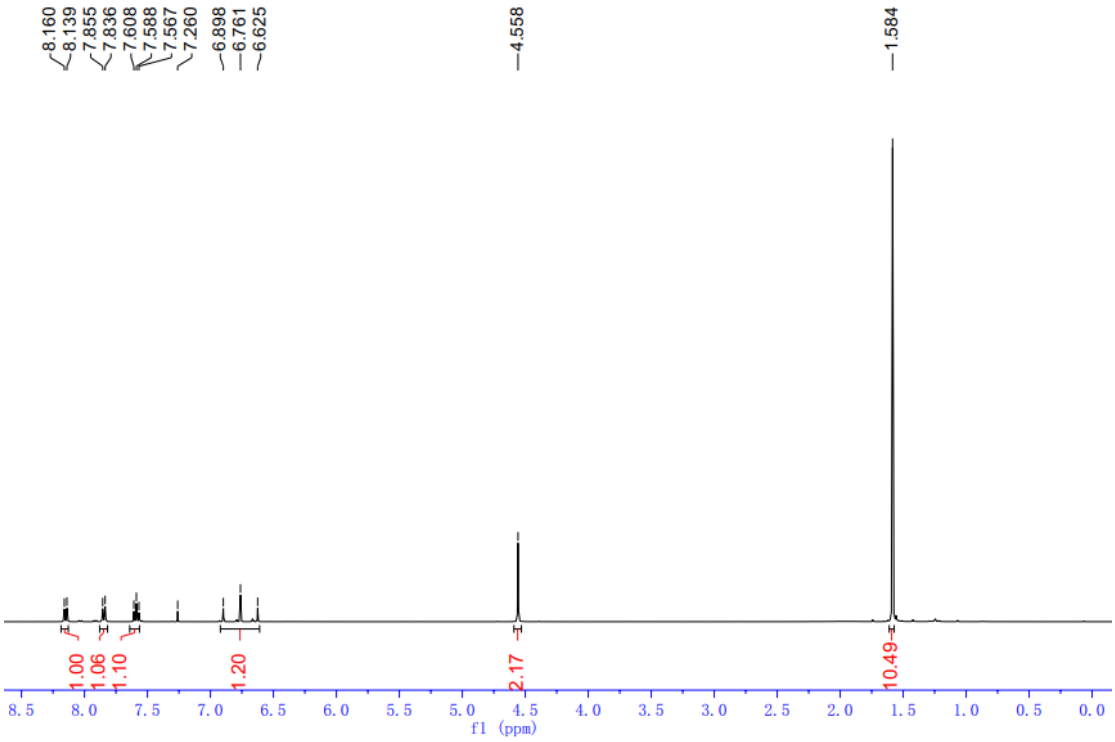
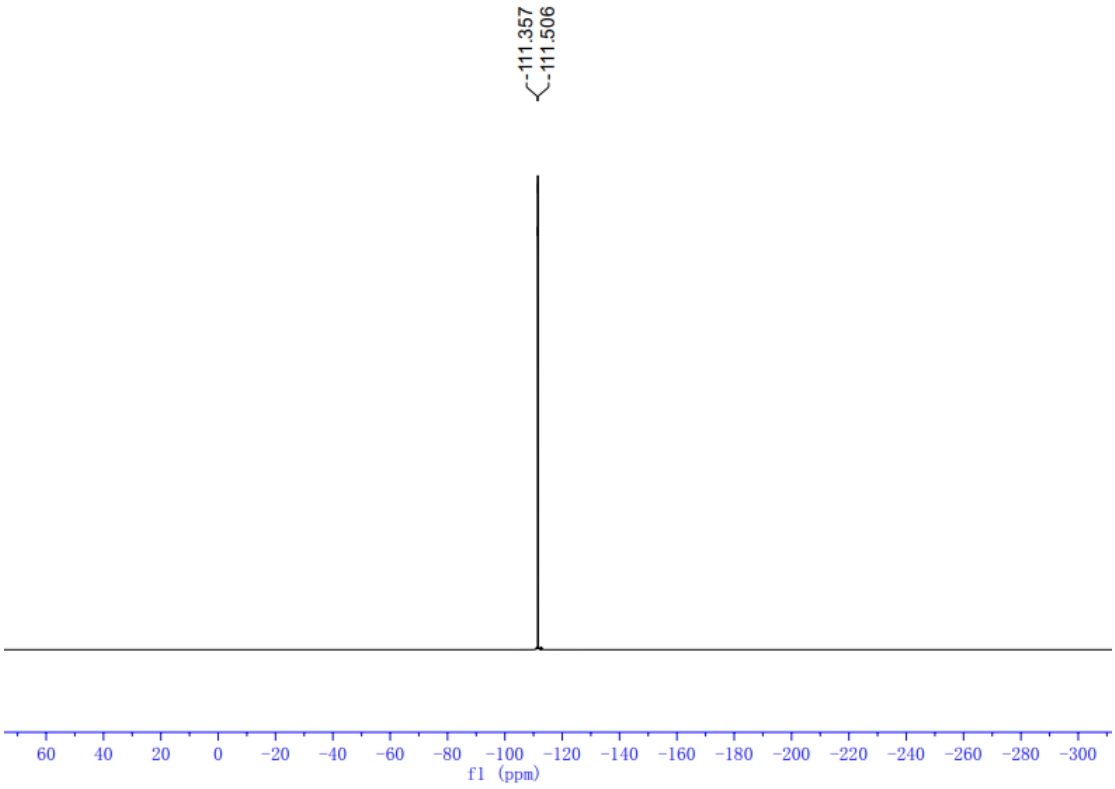
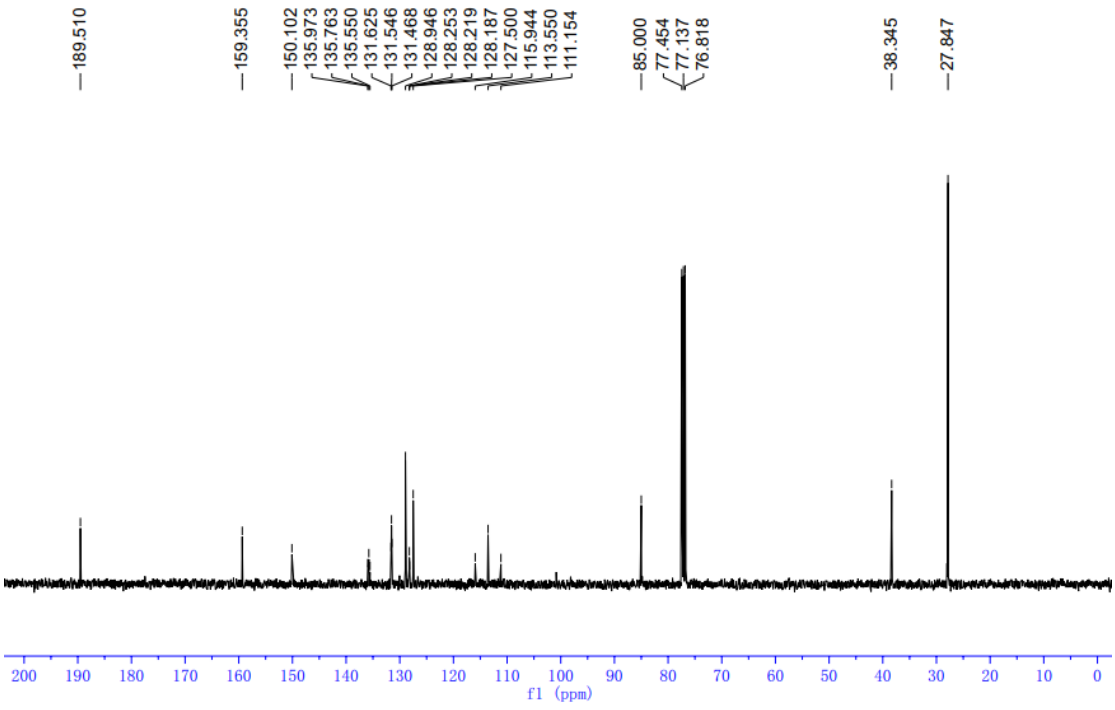
84.570
77.484
77.165
76.847
40.928
40.697
27.895
f1 (ppm)

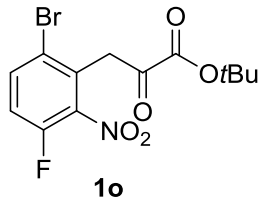

CF2H
O
OtBu
O
NO2

1m

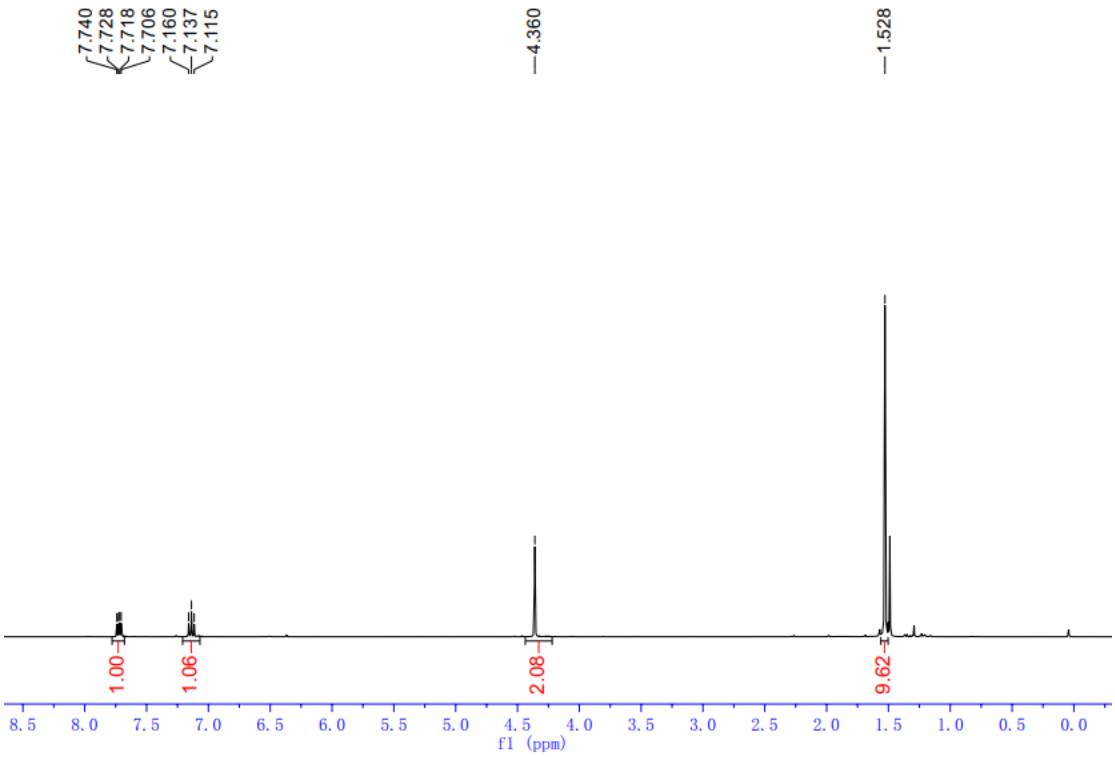

8.160
8.139
7.855
7.836
7.608
7.588
7.567
7.260
6.898
6.761
6.625
4.558
1.584
1.00
1.06
1.10
1.20
2.17
10.49
f1 (ppm)

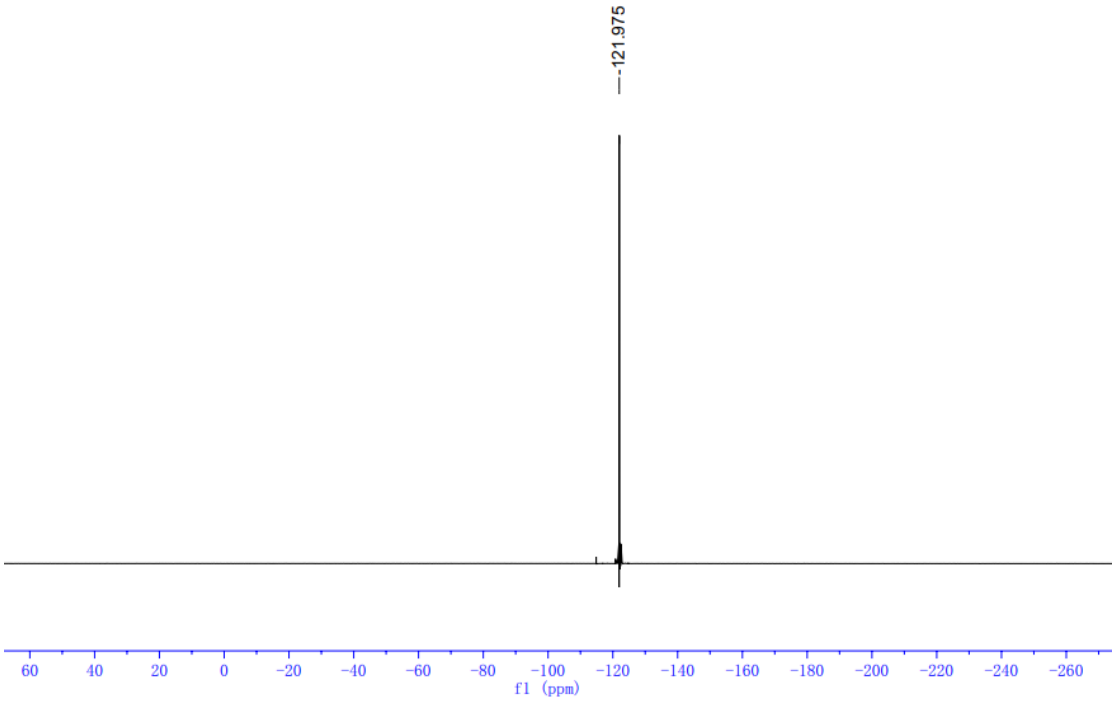

-111.357
-111.506
60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

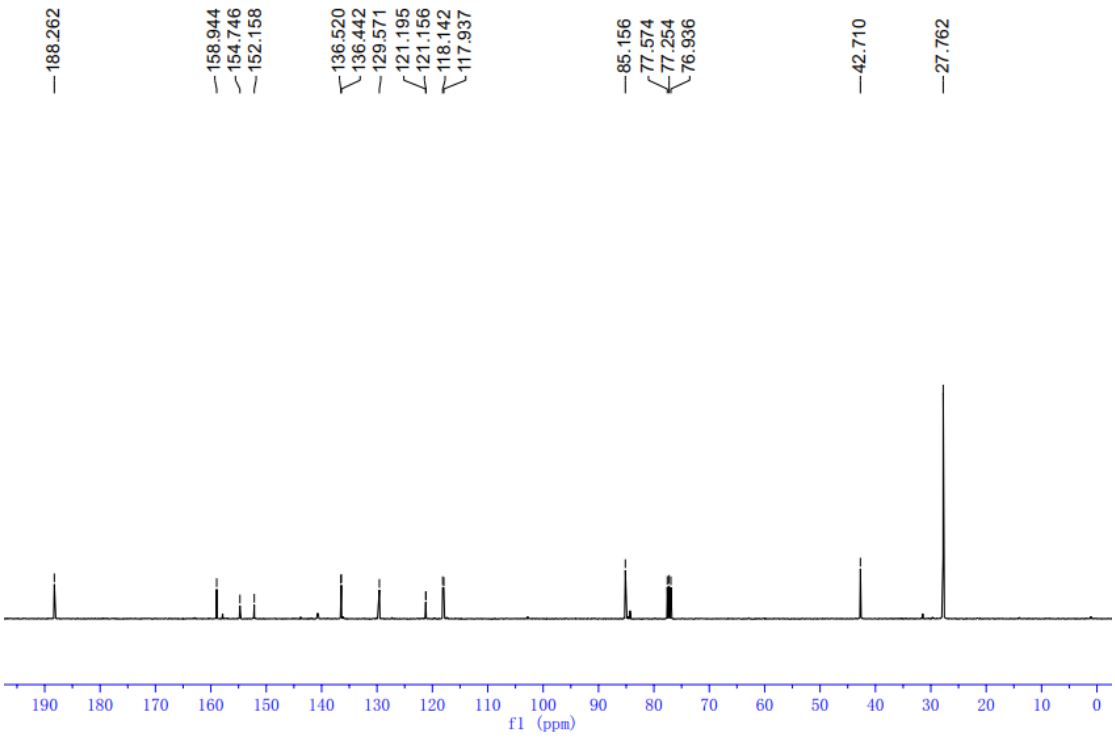

189.510
159.355
150.102
135.973
135.763
135.550
131.625
131.546
131.468
128.946
128.253
128.219
128.187
127.500
115.944
113.550
111.154
85.000
77.454
77.137
76.818
38.345
27.847
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

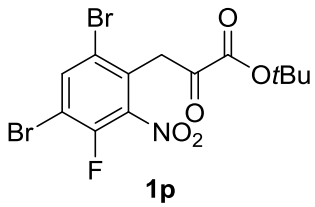

Br
O
OtBu
O
NO2
F

1o

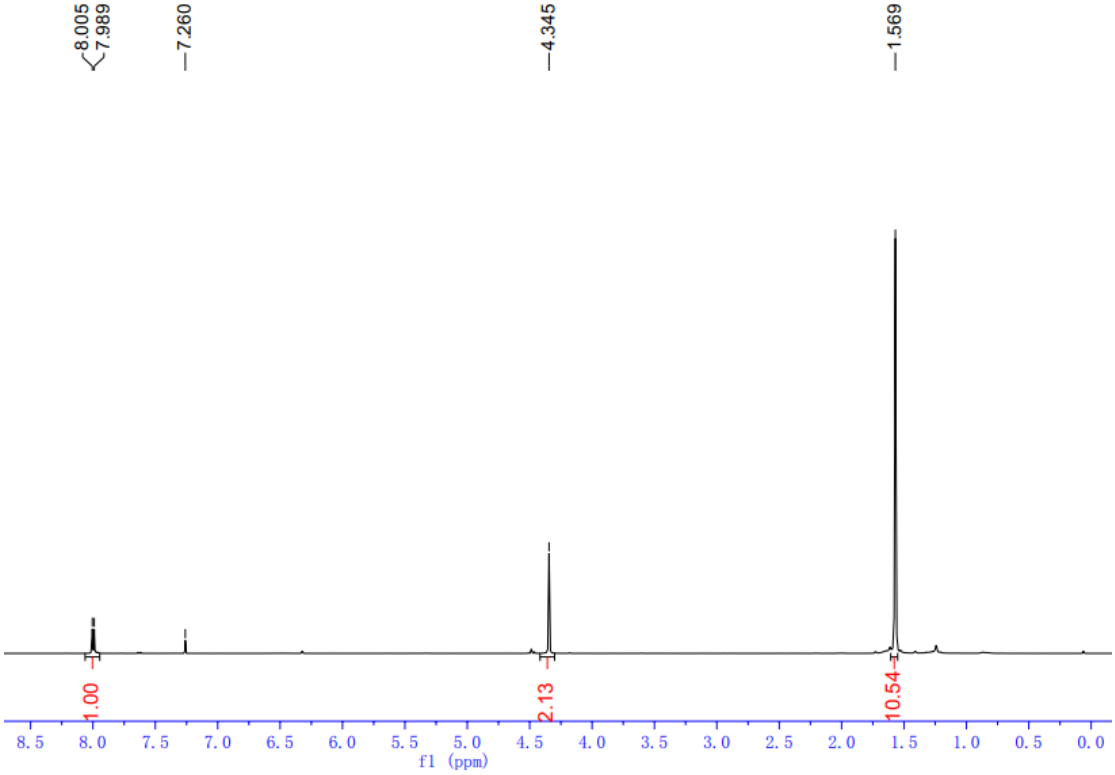

7.740
7.728
7.718
7.706
7.160
7.137
7.115
4.360
1.528
1.00
1.06
2.08
9.62
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

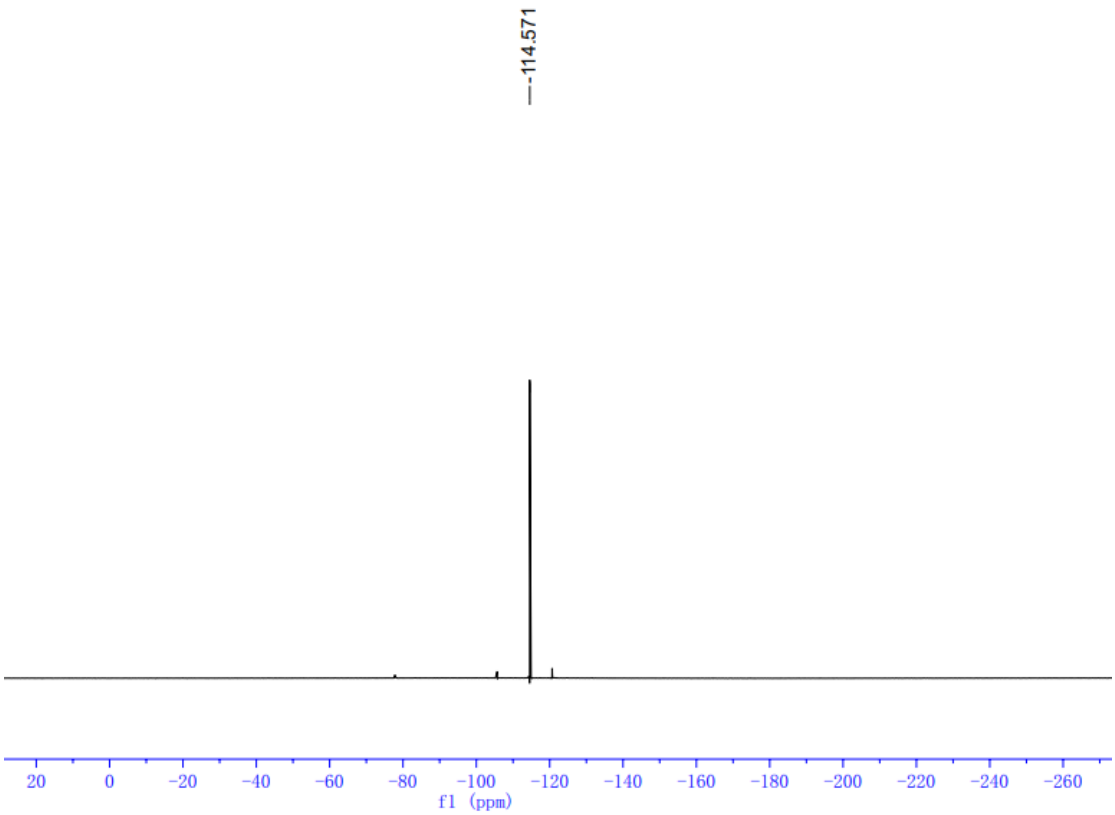

-121.975
60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)

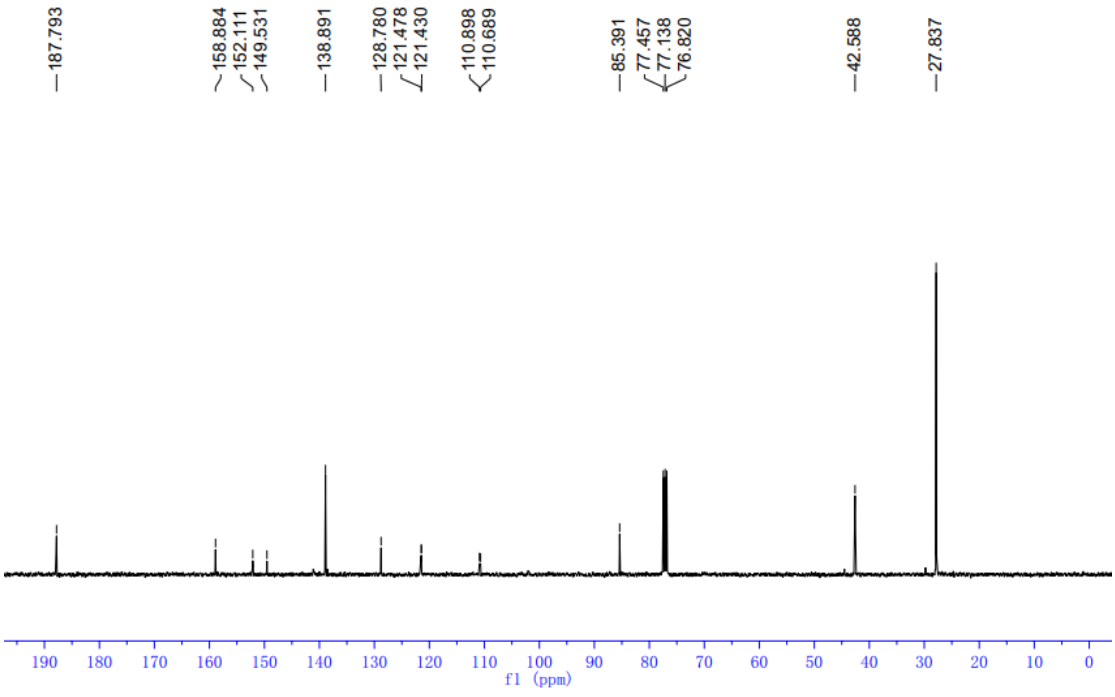

188.262
158.944
154.746
152.158
136.520
136.442
129.571
121.195
121.156
118.142
117.937
85.156
77.574
77.254
76.936
42.710
27.762
f1 (ppm)

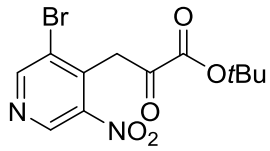

Br
O
OtBu
O
Br
NO2
F

1p

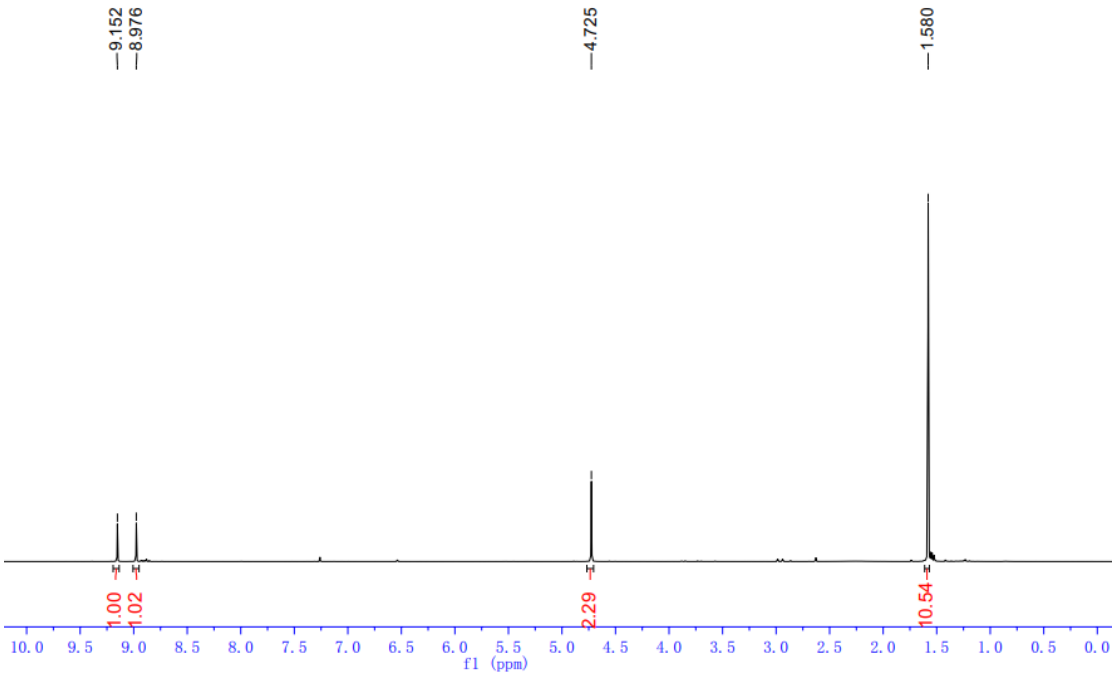

8.005
7.989
7.260
4.345
1.569
1.00
2.13
10.54
f1 (ppm)

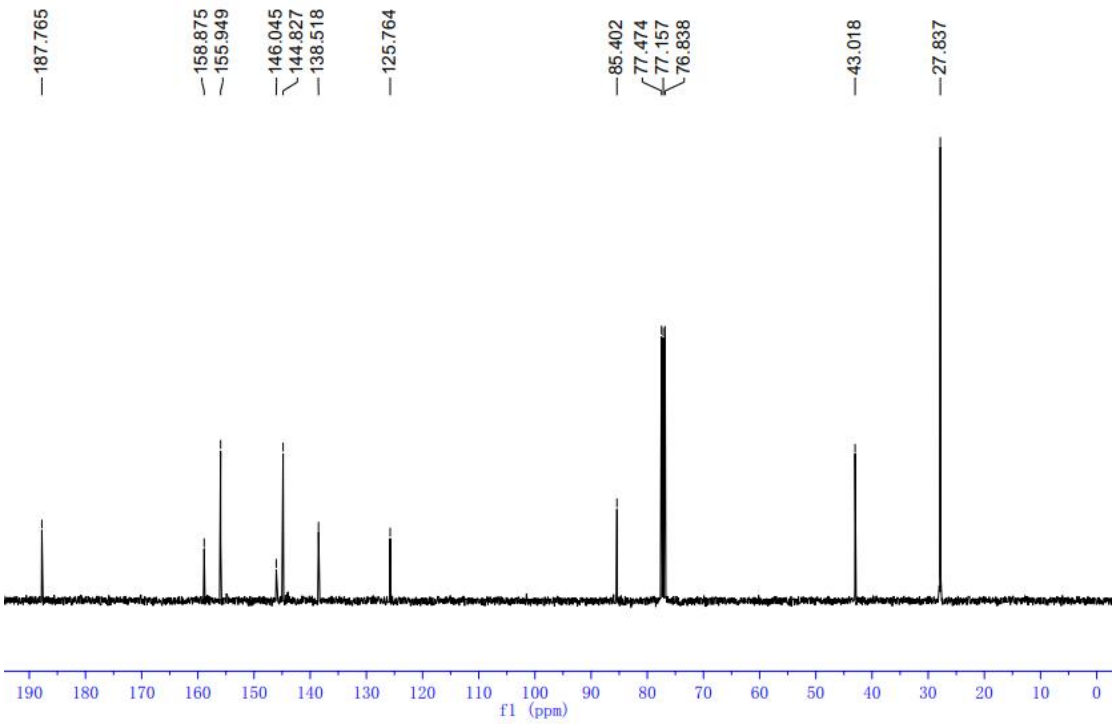

-114.571
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
f1 (ppm)

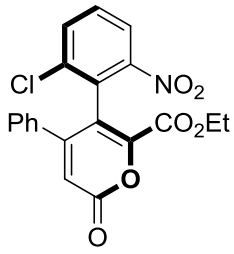

187.793
158.884
152.111
149.531
138.891
128.780
121.478
121.430
110.898
110.689
85.391
77.457
77.138
76.820
42.588
27.837
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Br
O
OtBu
N
O
NO2

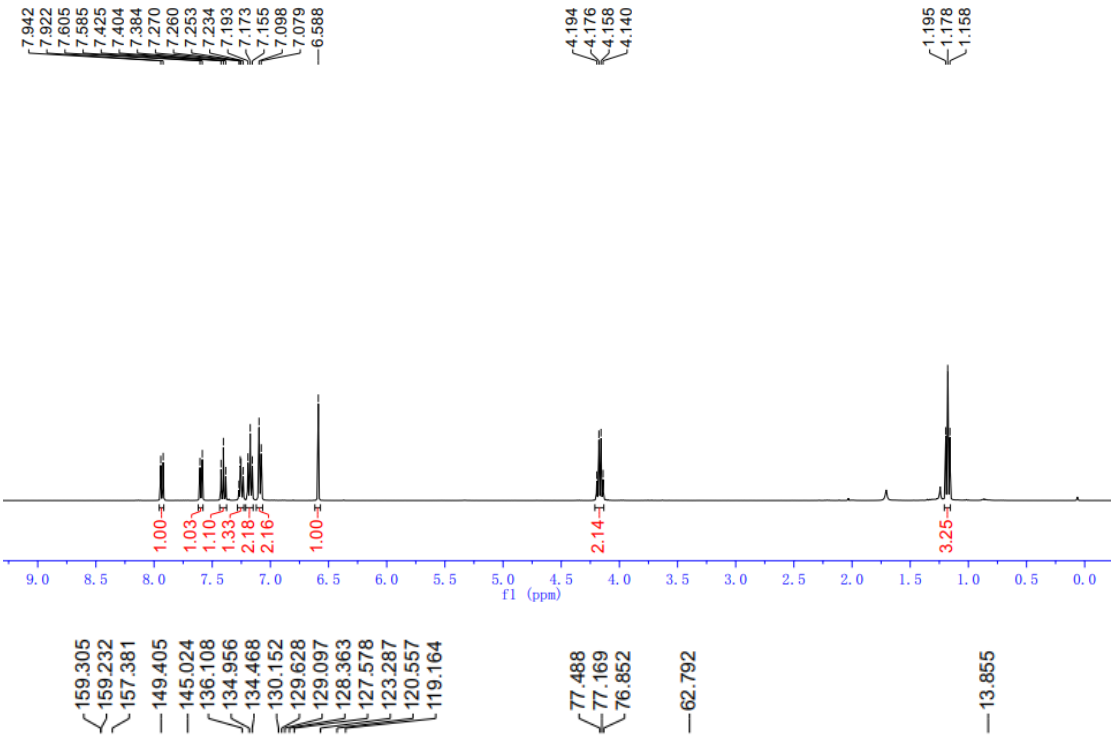
1n

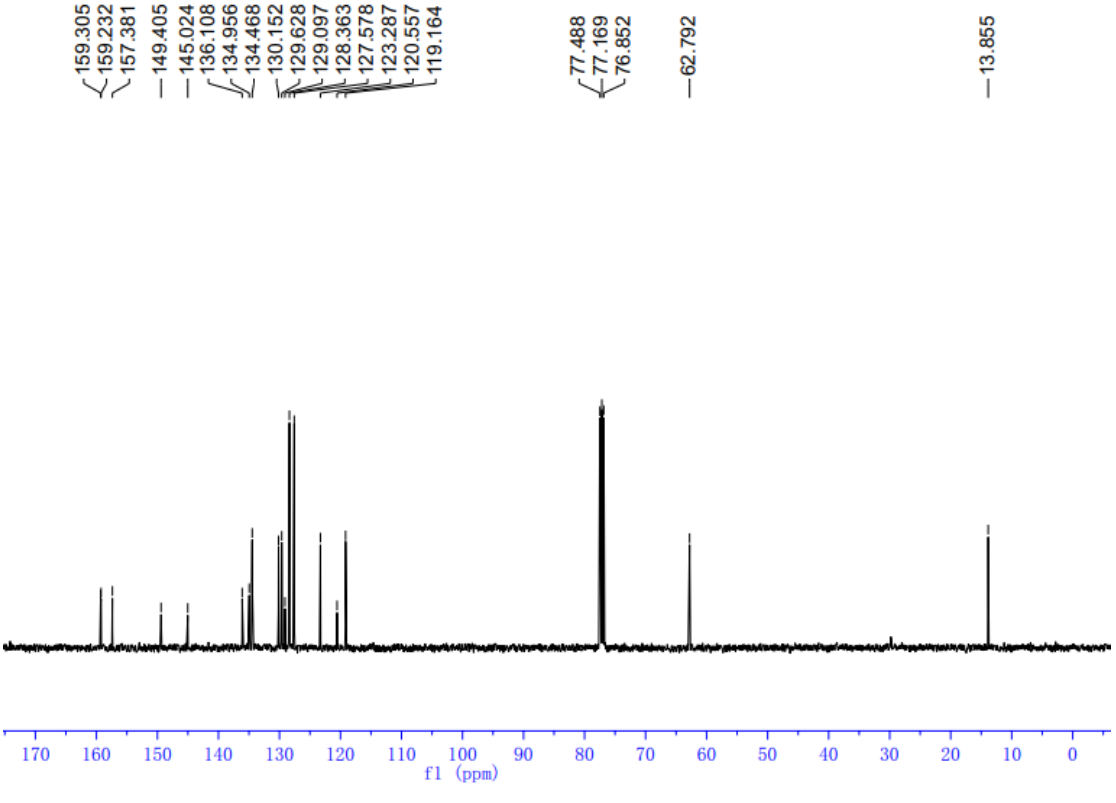

9.152
8.976
4.725
1.580
1.00
1.02
2.29
10.54
f1 (ppm)

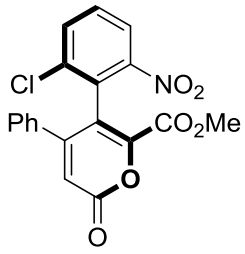

187.765
158.875
155.949
146.045
144.827
138.518
125.764
85.402
77.474
77.157
76.838
43.018
27.837
f1 (ppm)


Cl
NO2
Ph
CO2Et
O
O

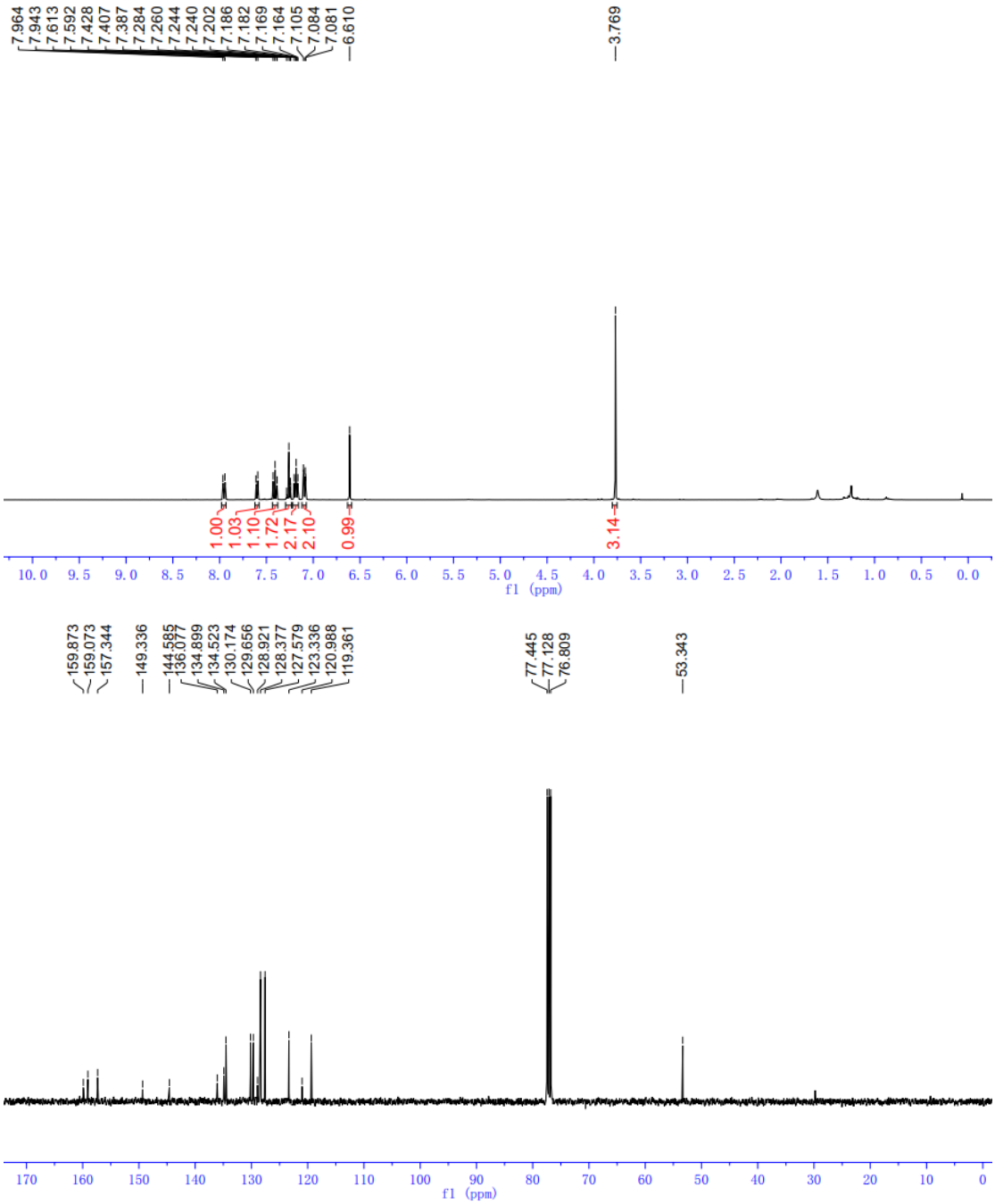
3a

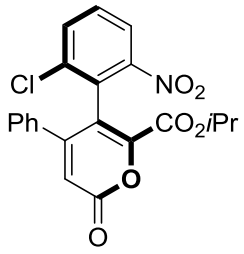

7.942
7.922
7.605
7.585
7.425
7.404
7.384
7.270
7.260
7.253
7.234
7.193
7.173
7.155
7.098
7.079
6.588
4.194
4.176
4.158
4.140
1.195
1.178
1.158
1.00
1.03
1.10
1.33
2.18
2.16
1.00
2.14
3.25
f1 (ppm)


159.305
159.232
157.381
149.405
145.024
136.108
134.956
134.468
130.152
129.628
129.097
128.363
127.578
123.287
120.557
119.164
77.488
77.169
76.852
62.792
13.855
f1 (ppm)

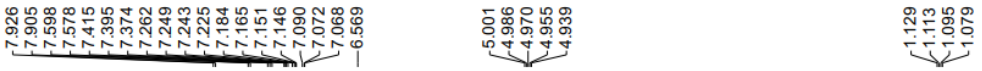

Cl
NO2
Ph
CO2Me
O
O

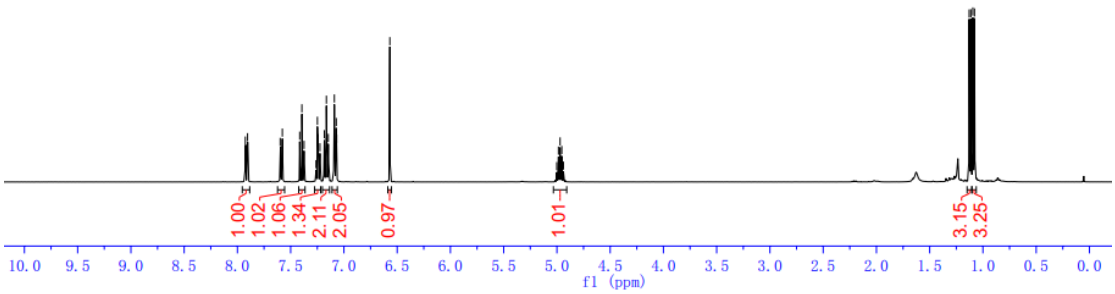
3b

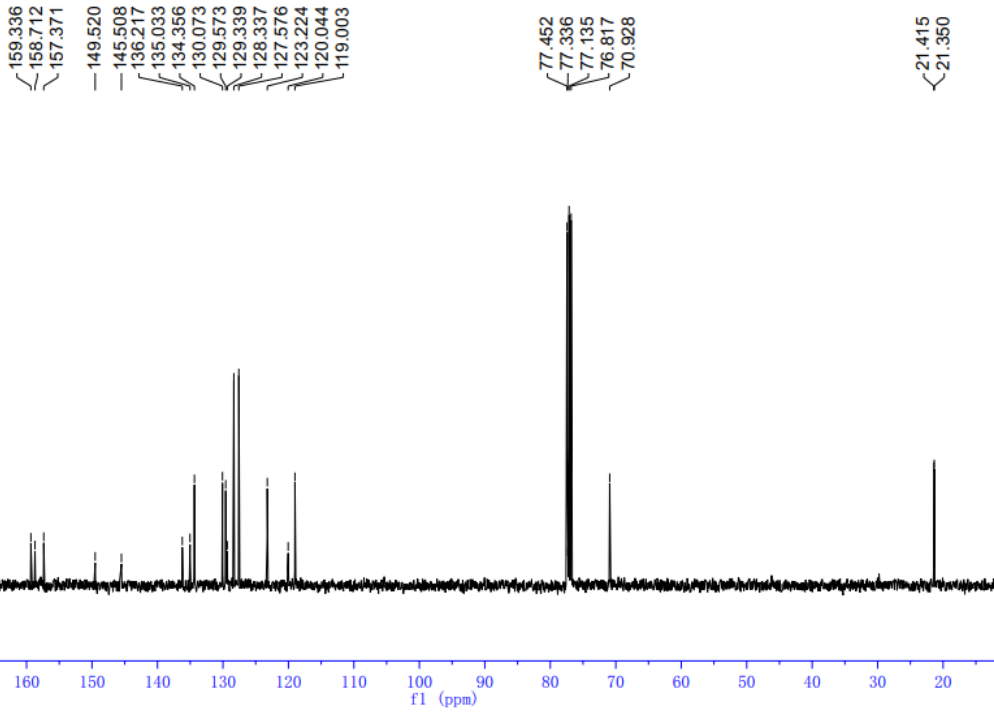

7.964
7.943
7.613
7.592
7.428
7.407
7.387
7.284
7.260
7.244
7.240
7.202
7.186
7.182
7.169
7.164
7.105
7.084
7.081
6.610
3.769
1.00
1.03
1.10
1.72
2.17
2.10
0.99
3.14
f1 (ppm)
159.873
159.073
157.344
149.336
144.585
136.077
134.899
134.523
130.174
129.656
128.921
128.377
127.579
123.336
120.988
119.361
77.445
77.128
76.809
53.343
f1 (ppm)

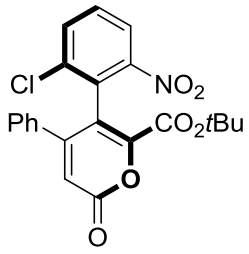

Cl
NO2
Ph
CO2iPr
O
O

3c


7.926
7.905
7.598
7.578
7.415
7.395
7.374
7.262
7.249
7.243
7.225
7.184
7.165
7.151
7.146
7.090
7.072
7.068
6.569
5.001
4.986
4.970
4.955
4.939
1.129
1.113
1.095
1.079


1.00
1.02
1.06
1.34
2.11
2.05
0.97
1.01
3.15
3.25
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)


159.336
158.712
157.371
149.520
145.508
136.217
135.033
134.356
130.073
129.573
129.339
128.337
127.576
123.224
120.044
119.003
77.452
77.336
77.135
76.817
70.928
21.415
21.350
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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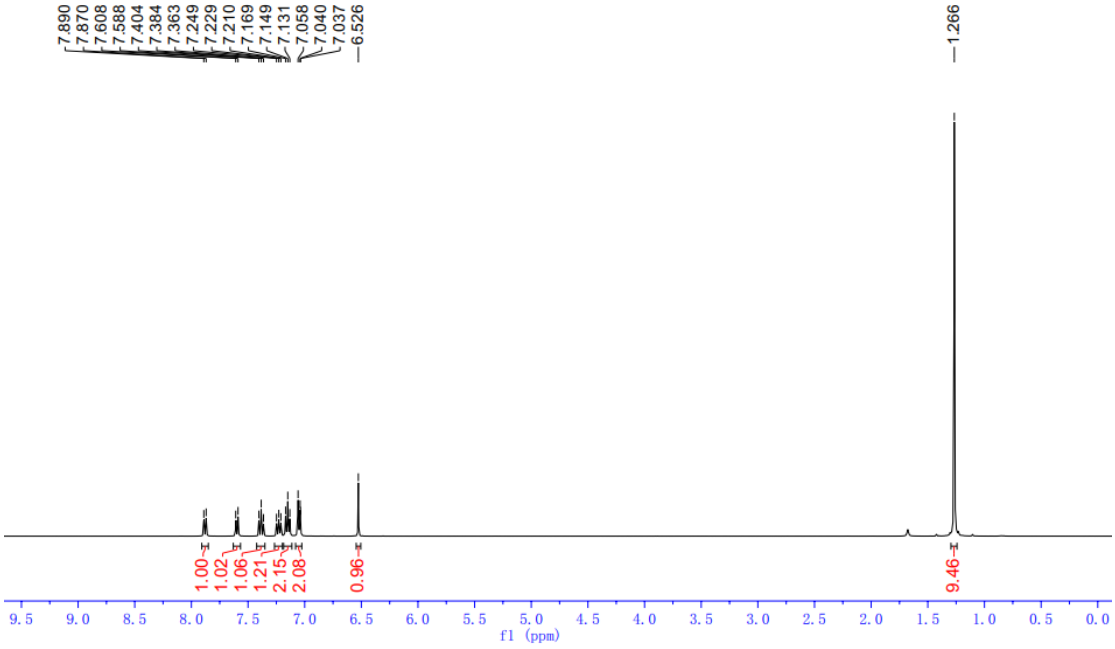
NO2
Ph
CO2tBu
O
O

3d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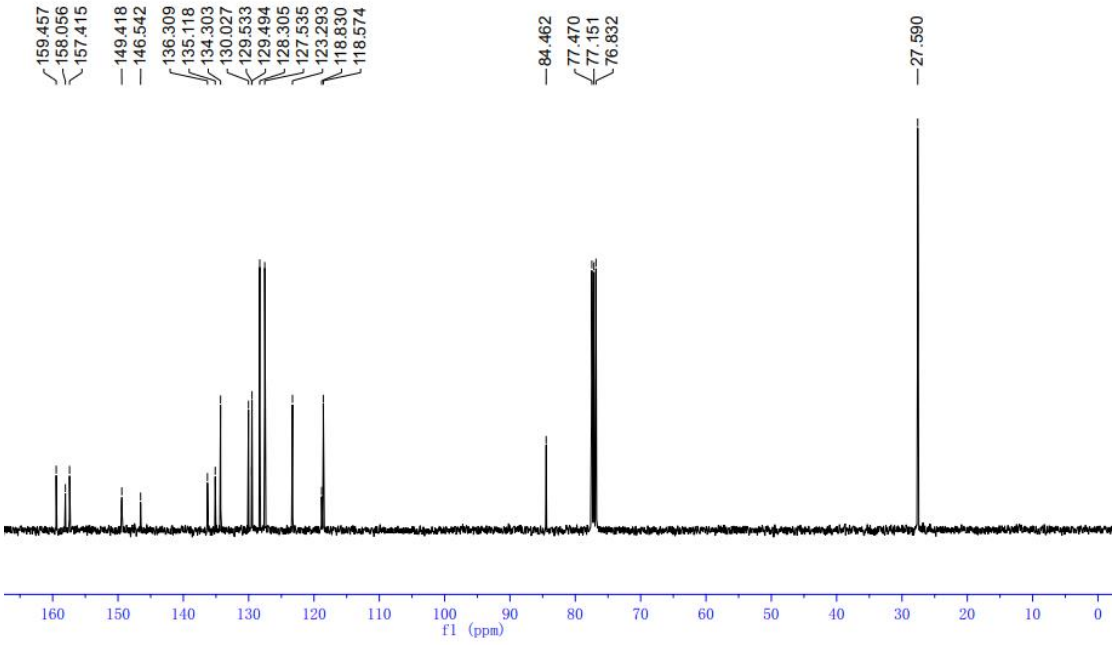
7.384
7.363
7.249
7.229
7.210
7.169
7.149
7.131
7.058
7.040
7.037
6.526
1.266
1.00
1.02
1.06
1.21
2.15
2.08
0.96
9.46
f1 (ppm)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146.542
136.309
135.118
134.303
130.027
129.533
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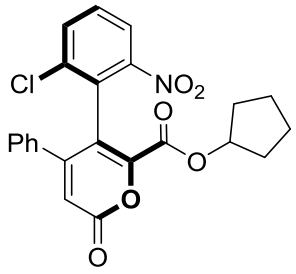
128.305
127.535
123.293
118.830
118.574
84.462
77.470
77.151
76.832
27.590
f1 (ppm)


Cl
NO2
Ph
O
O
O
O

3e


7.932
7.911
7.615
7.595
7.421
7.401
7.381
7.268
7.260
7.250
7.231
7.190
7.170
7.152
7.082
7.063
7.060
6.573
5.155
5.141
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1.806
1.785
1.776
1.753
1.738
1.555
1.537
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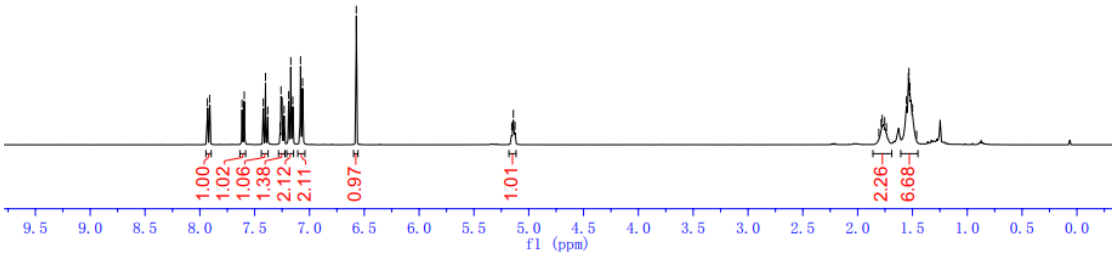
1.523
1.499
1.462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2.11
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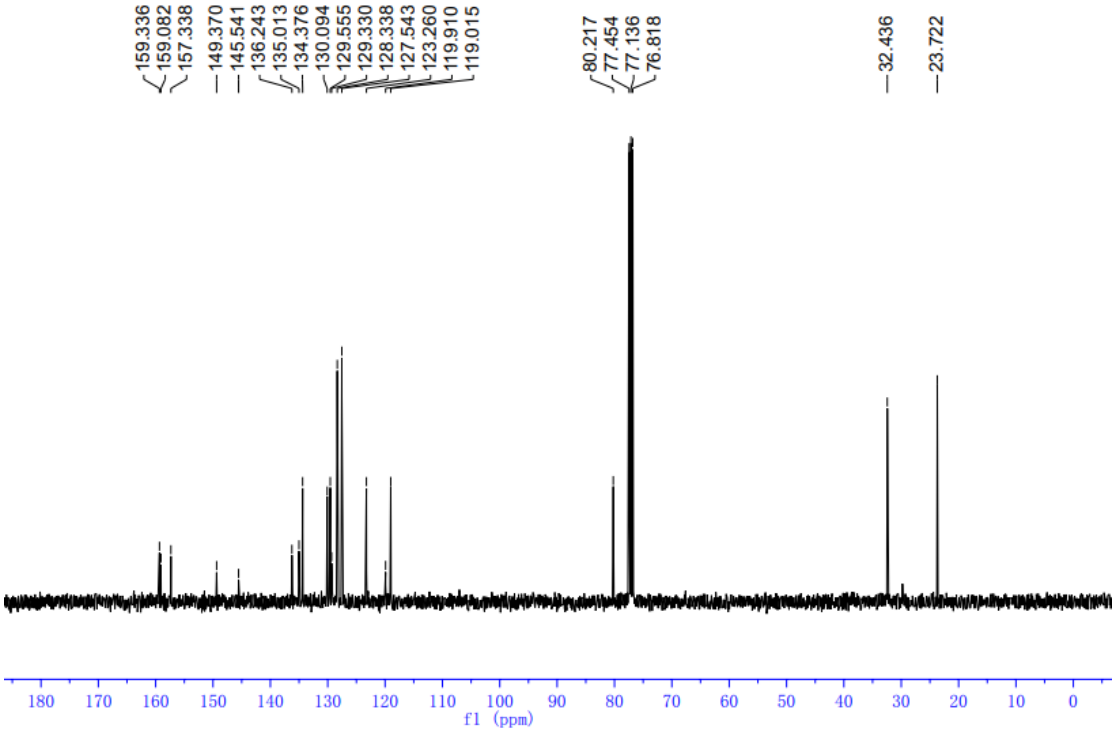
1.01
2.26
6.68
f1 (ppm)


159.336
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157.338
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136.243
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134.376
130.094
129.555
129.330
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127.543
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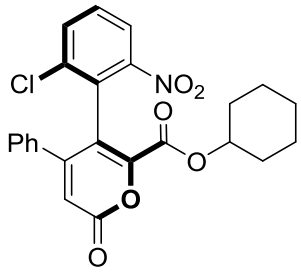
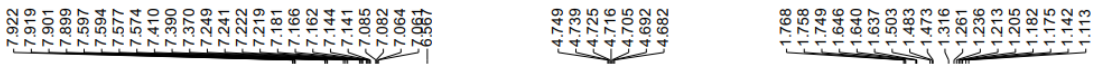
119.910
119.015
80.217
77.454
77.136
76.818
32.436
23.722
f1 (ppm)


Cl
NO2
O
Ph
O
O
O

3f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7.919
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7.899
7.597
7.594
7.577
7.574
7.410
7.390
7.370
7.249
7.241
7.222
7.219
7.181
7.166
7.162
7.144
7.141
7.085
7.082
7.064
7.061
6.587
4.749
4.739
4.725
4.716
4.705
4.692
4.682
1.768
1.758
1.749
1.646
1.640
1.637
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1.473
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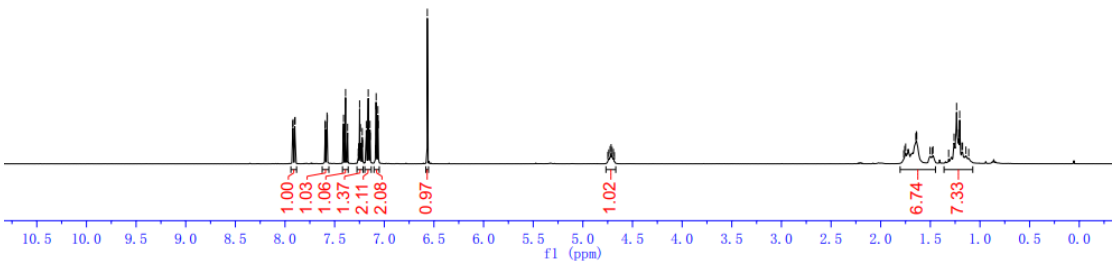
1.236
1.213
1.205
1.182
1.175
1.142
1.113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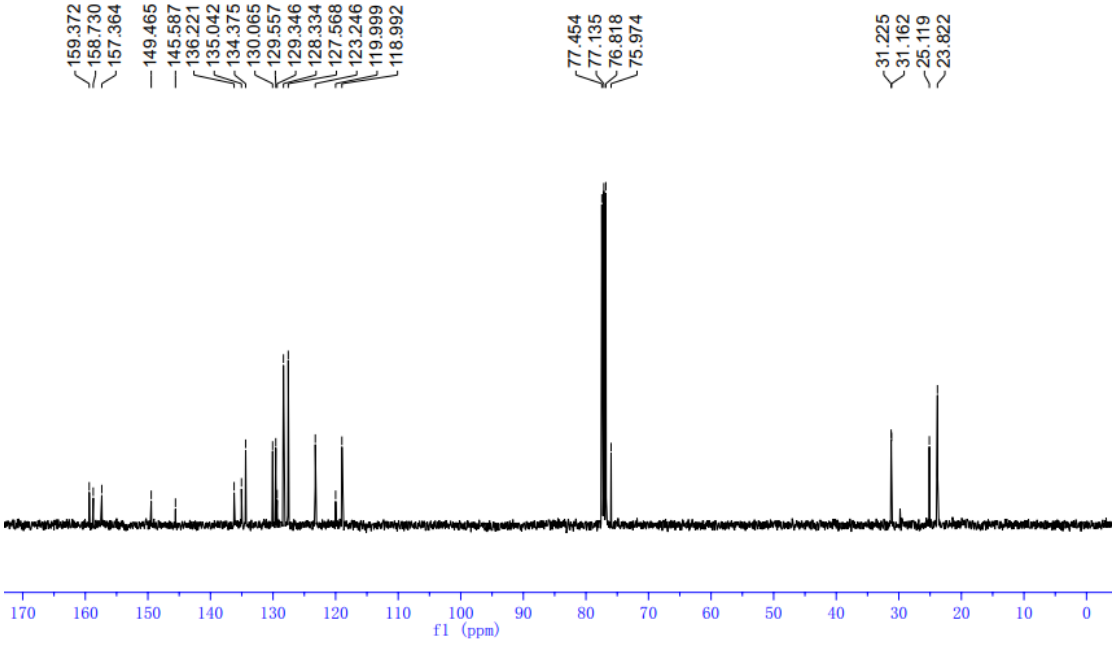
1.03
1.06
1.37
2.11
2.08
0.97
1.02
6.74
7.33
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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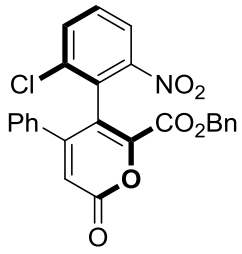
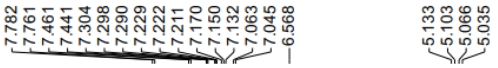
157.364
149.465
145.587
136.221
135.042
134.375
130.065
129.557
129.346
128.334
127.568
123.246
119.999
118.992
77.454
77.135
76.818
75.974
31.225
31.162
25.119
23.822
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Cl
NO2
Ph
CO2Bn
O
O

3g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7.441
7.304
7.298
7.290
7.229
7.222
7.211
7.170
7.150
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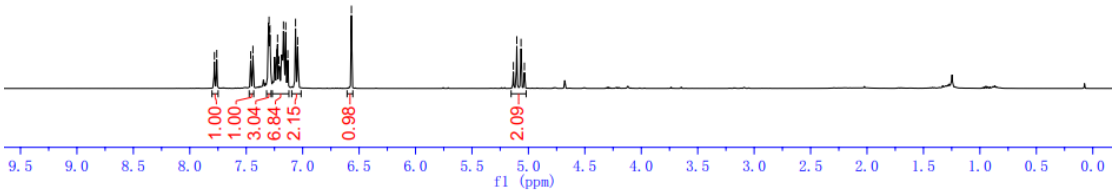
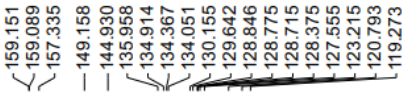
7.045
6.568
5.133
5.103
5.066
5.035


1.00
1.00
3.04
6.84
2.15
0.98
2.09
f1 (ppm)


159.151
159.089
157.335
149.158
144.930
135.958
134.914
134.367
134.051
130.155
129.642
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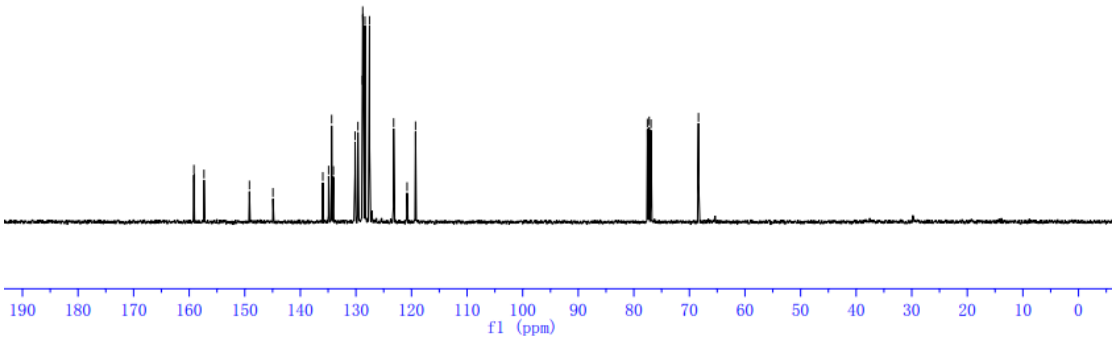
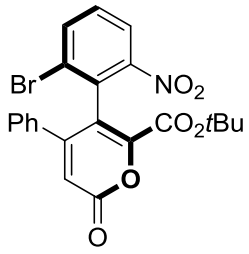
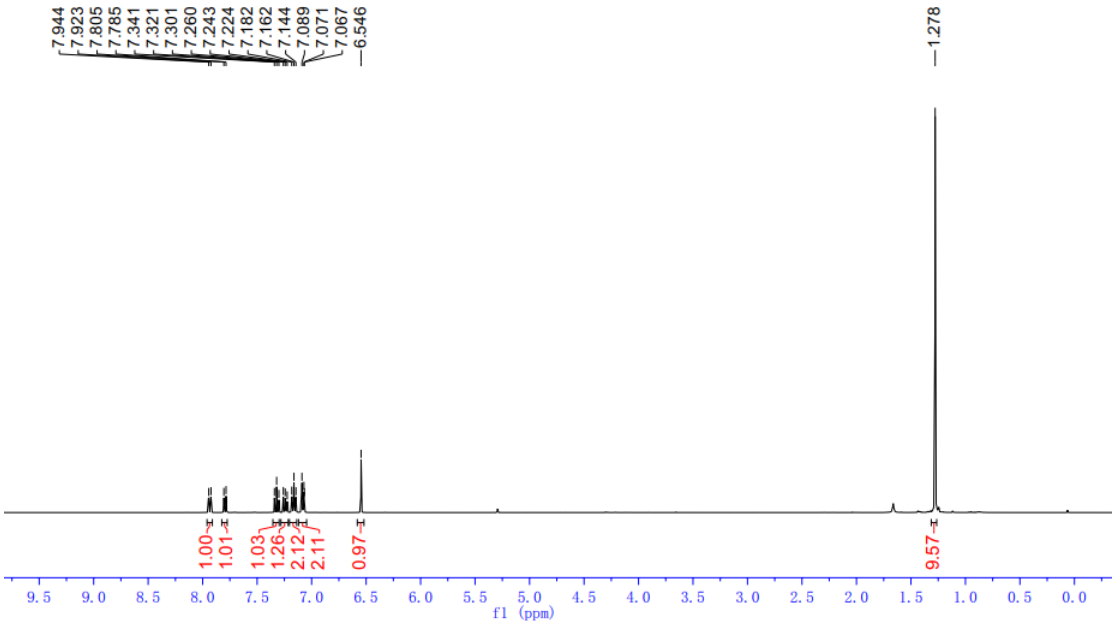
128.775
128.715
128.375
127.555
123.215
120.793
119.273
77.553
77.235
76.916
68.367


f1 (ppm)


Br
NO2
Ph
CO2tBu
O
O

3h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7.785
7.341
7.321
7.301
7.260
7.243
7.224
7.182
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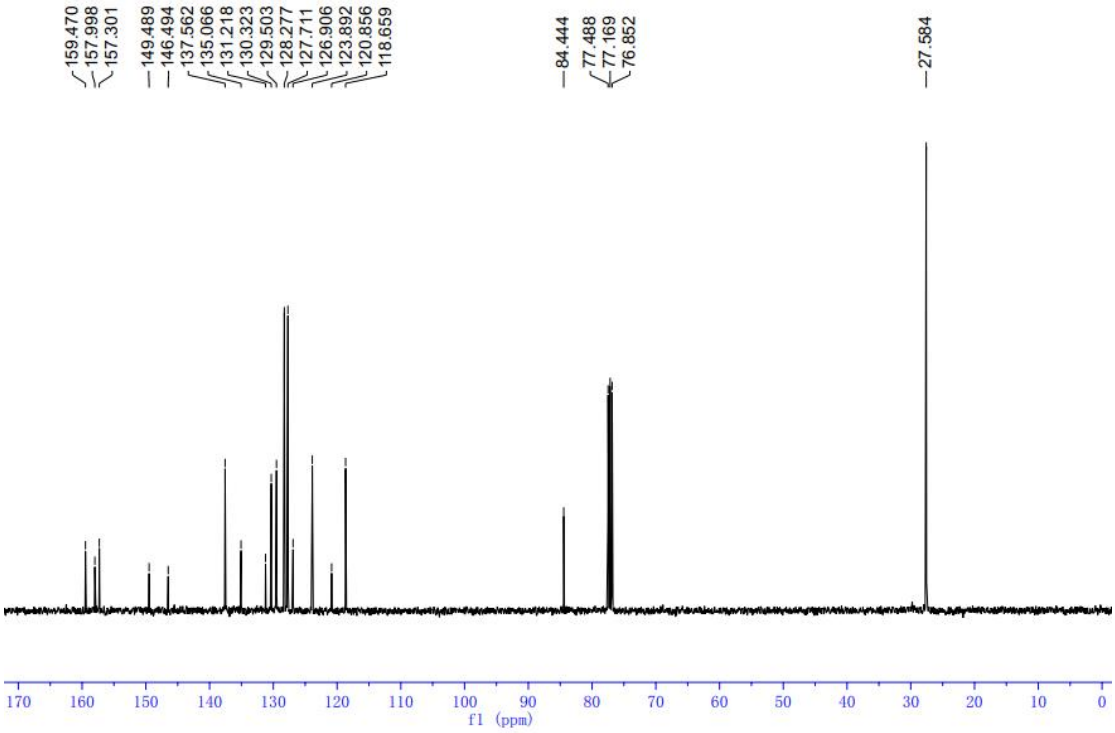
7.144
7.089
7.071
7.067
6.546
1.278
1.00
1.01
1.03
1.26
2.12
2.11
0.97
9.57
f1 (ppm)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157.301
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146.494
137.562
135.066
131.218
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129.503
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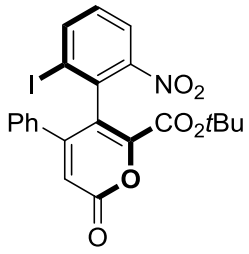
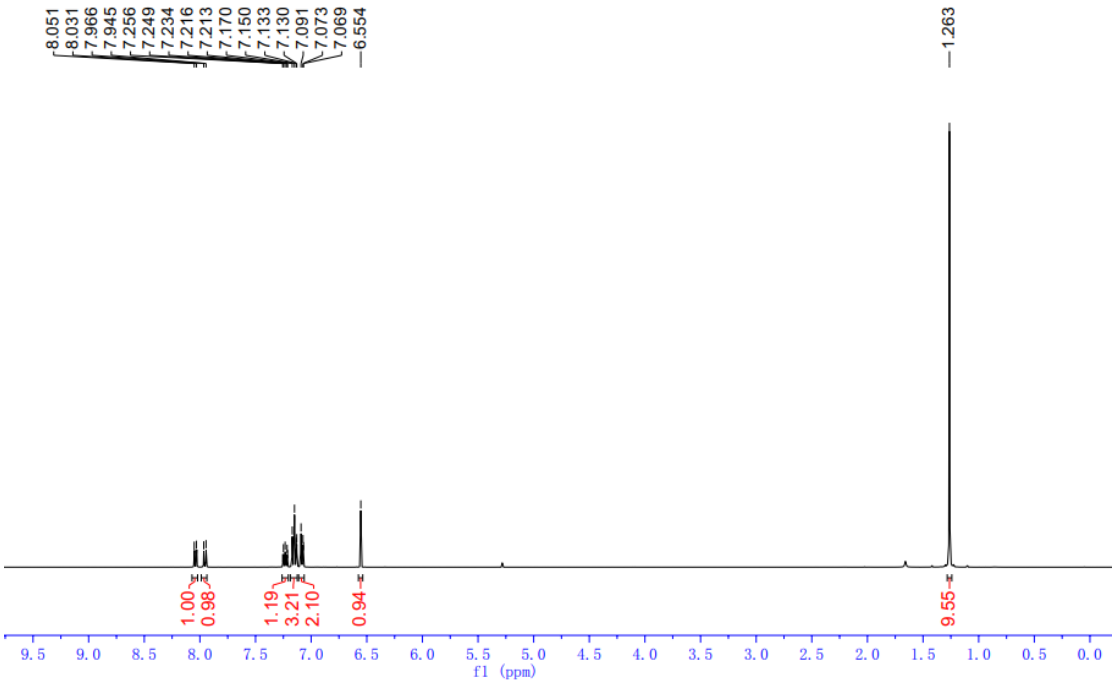
84.444
77.488
77.169
76.852
27.584
f1 (ppm)


I
NO2
Ph
CO2tBu
O
O

3i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8.031
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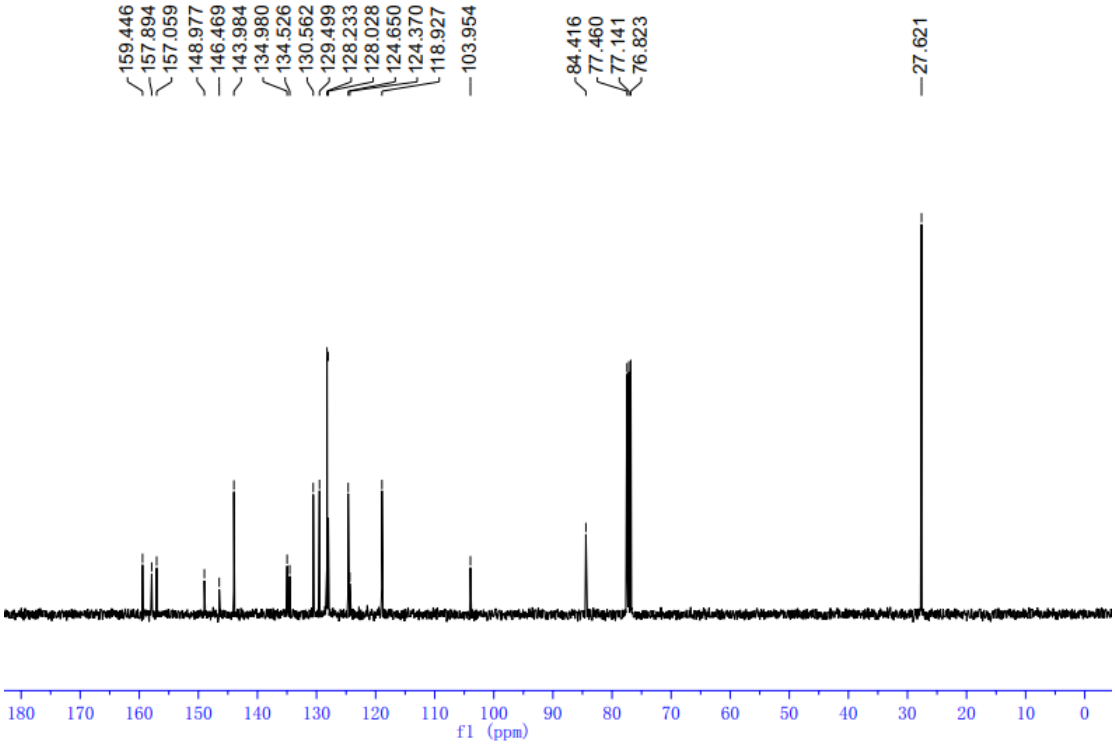
7.256
7.249
7.234
7.216
7.213
7.170
7.150
7.133
7.130
7.091
7.073
7.069
6.554
1.263
1.00
0.98
1.19
3.21
2.10
0.94
9.55
f1 (ppm)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134.526
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129.499
128.233
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124.370
118.927
103.954
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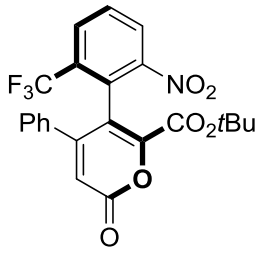
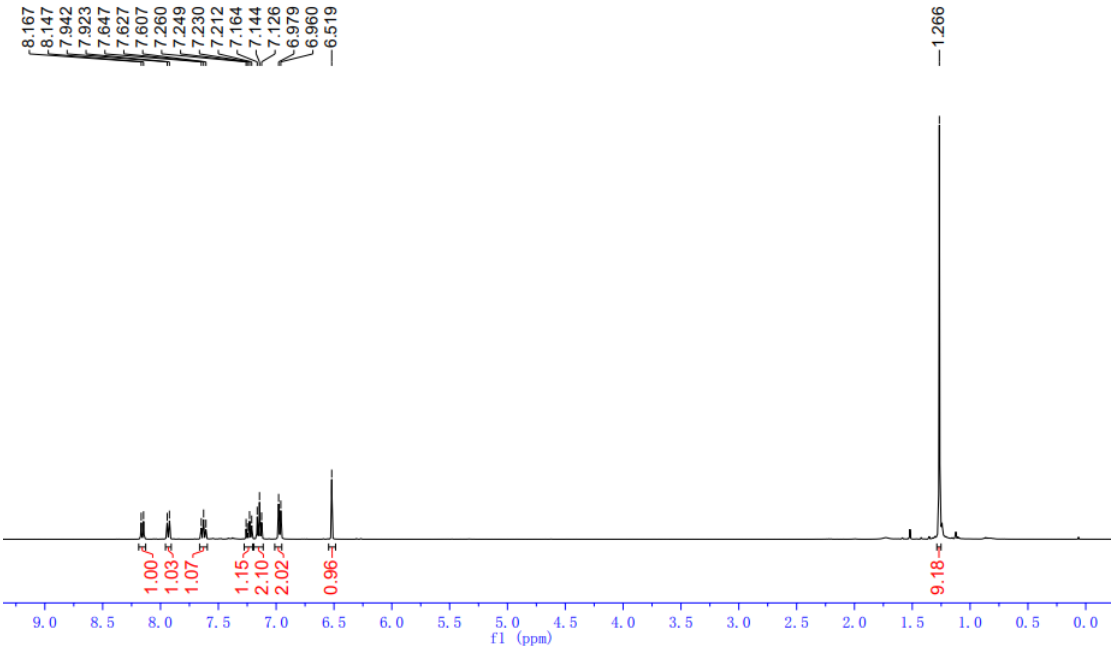
77.141
76.823
27.621
f1 (ppm)


F3C
NO2
Ph
CO2tBu
O
O

3j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7.647
7.627
7.607
7.260
7.249
7.230
7.212
7.164
7.144
7.126
6.979
6.960
6.519
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1.00
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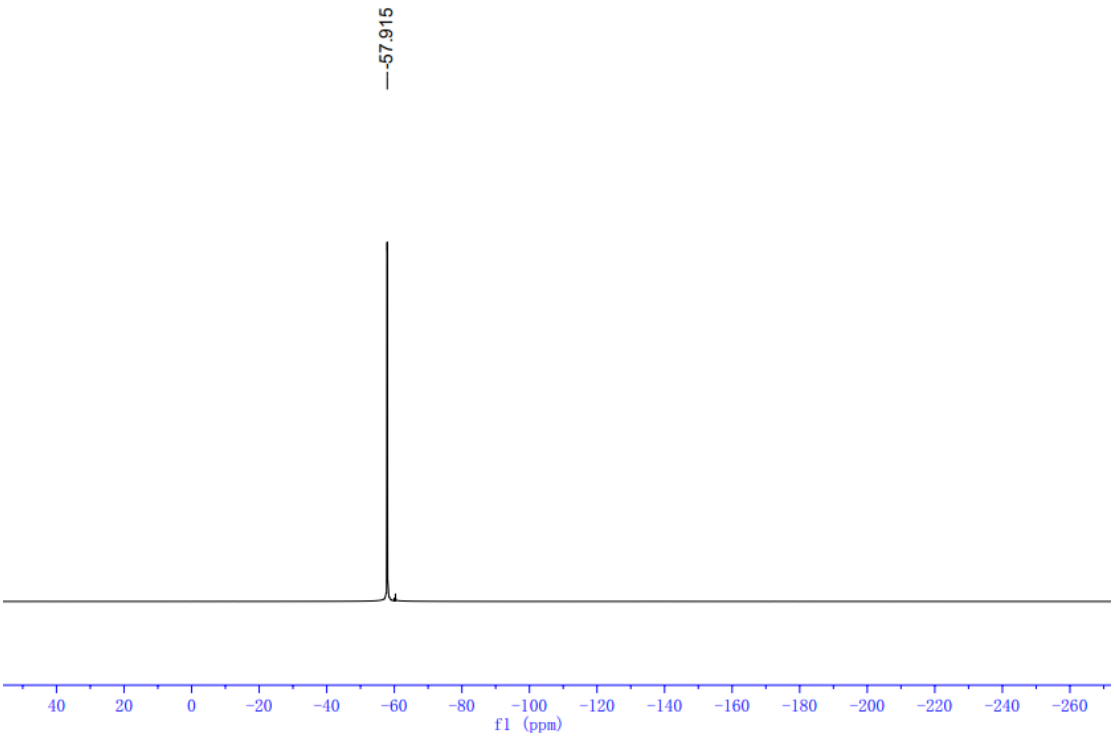
1.07
1.15
2.10
2.02
0.96
9.18
f1 (ppm)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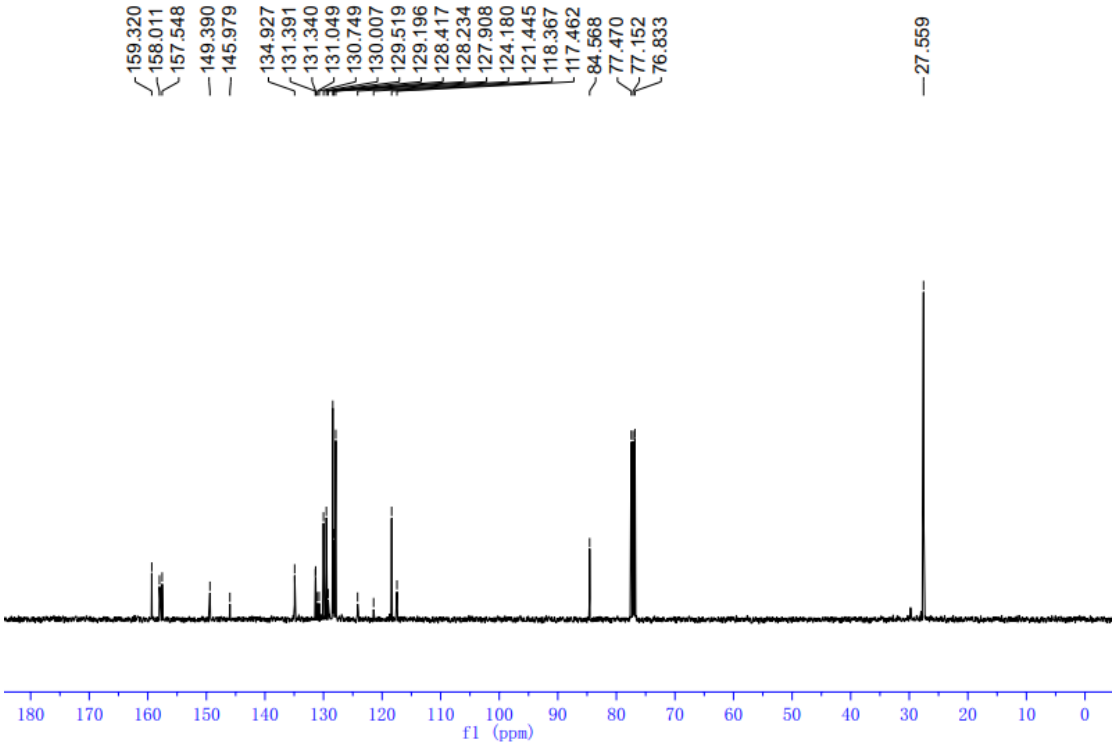
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130.007
129.519
129.196
128.417
128.234
127.908
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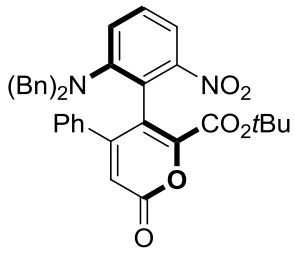
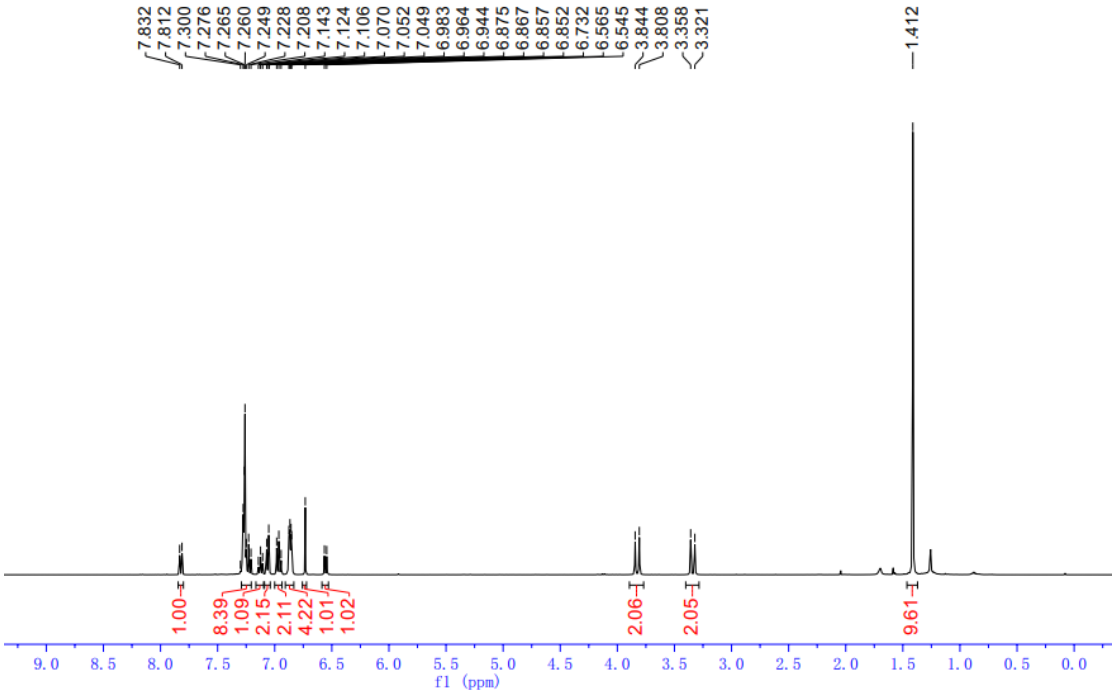
121.445
118.367
117.462
84.568
77.470
77.152
76.833
27.559
f1 (ppm)


(Bn)2N
NO2
Ph
CO2tBu
O
O

3k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7.260
7.249
7.228
7.208
7.143
7.124
7.106
7.070
7.052
7.049
6.983
6.964
6.944
6.875
6.867
6.857
6.852
6.732
6.565
6.545
3.844
3.808
3.358
3.321
1.412
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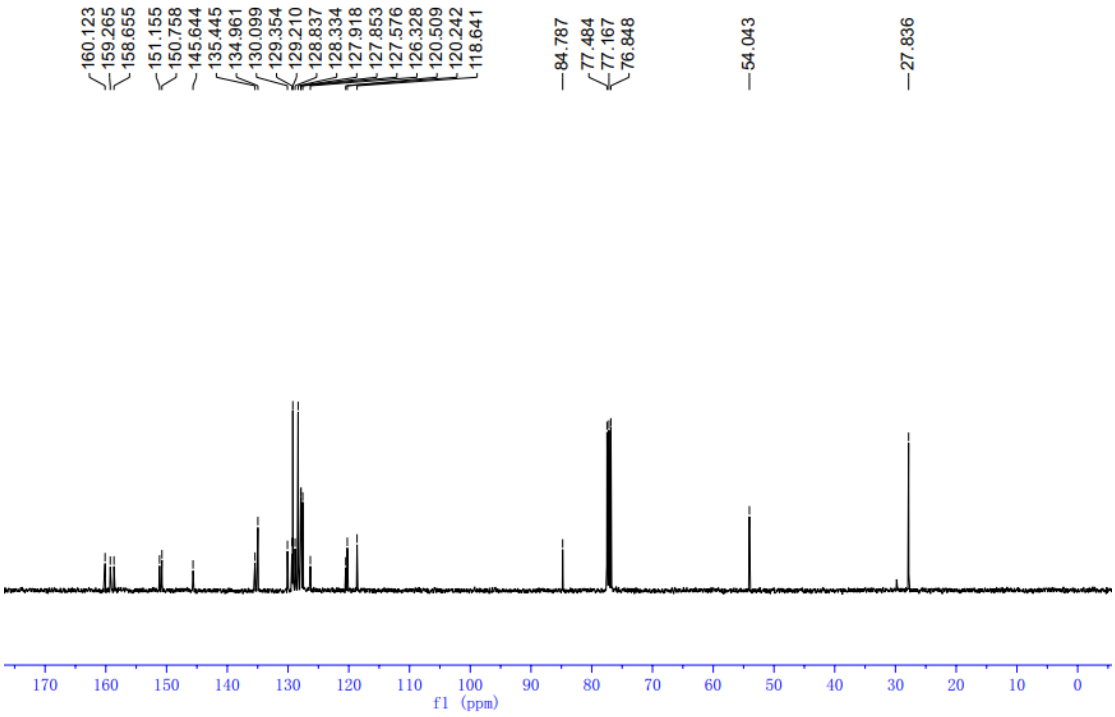
2.15
2.11
4.22
1.01
1.02
2.06
2.05
9.61
f1 (ppm)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135.445
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129.354
129.210
128.837
128.334
127.918
127.853
127.576
126.328
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120.242
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77.484
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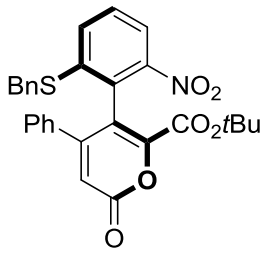
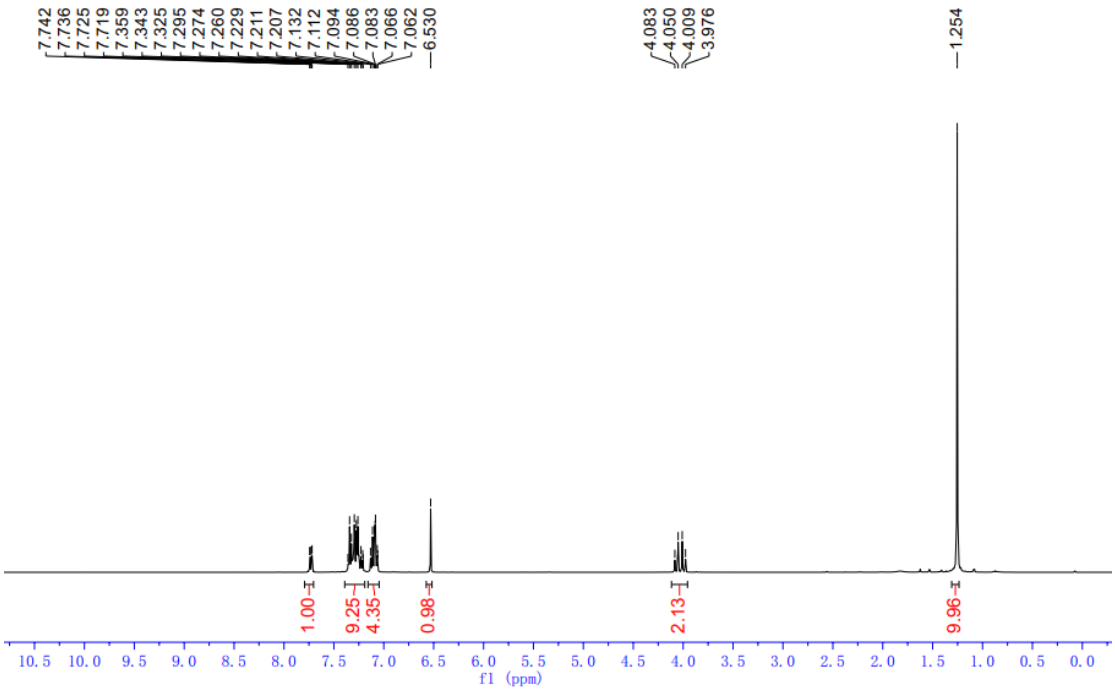
76.848
54.043
27.836
f1 (ppm)


BnS
NO2
Ph
CO2tBu
O
O

3l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7.725
7.719
7.359
7.343
7.325
7.295
7.274
7.260
7.229
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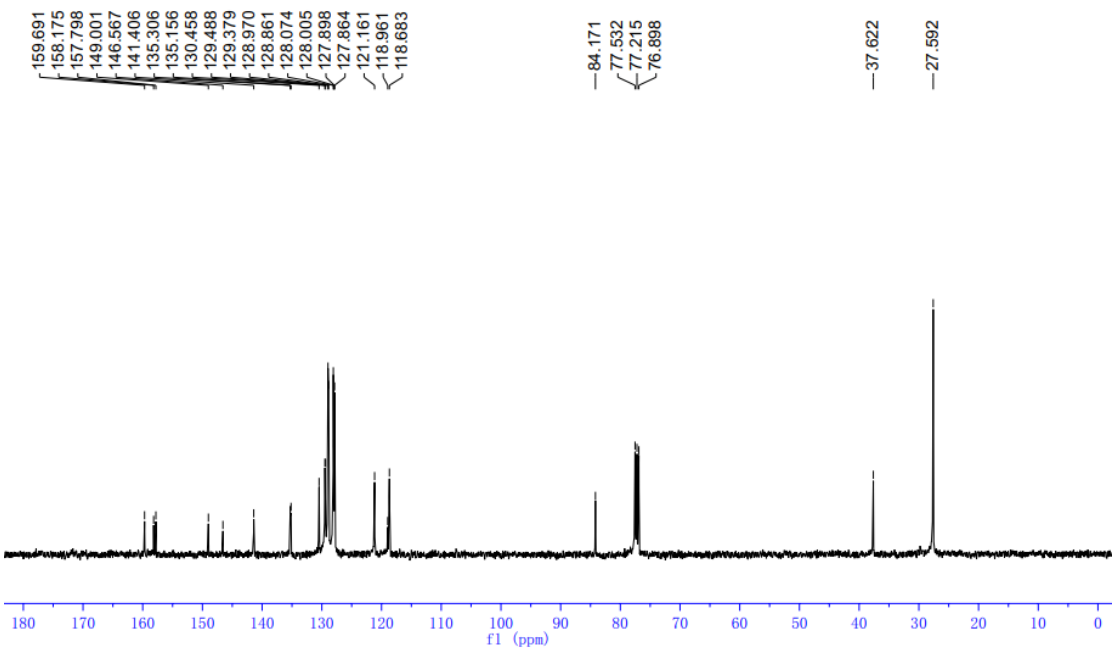
7.207
7.132
7.112
7.094
7.086
7.083
7.066
7.062
6.530
4.083
4.050
4.009
3.976
1.254
1.00
9.25
4.35
0.98
2.13
9.96
f1 (ppm)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135.156
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129.488
129.379
128.970
128.861
128.074
128.005
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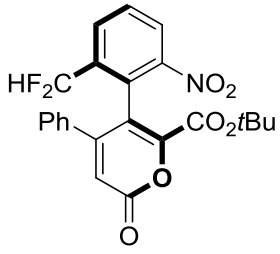
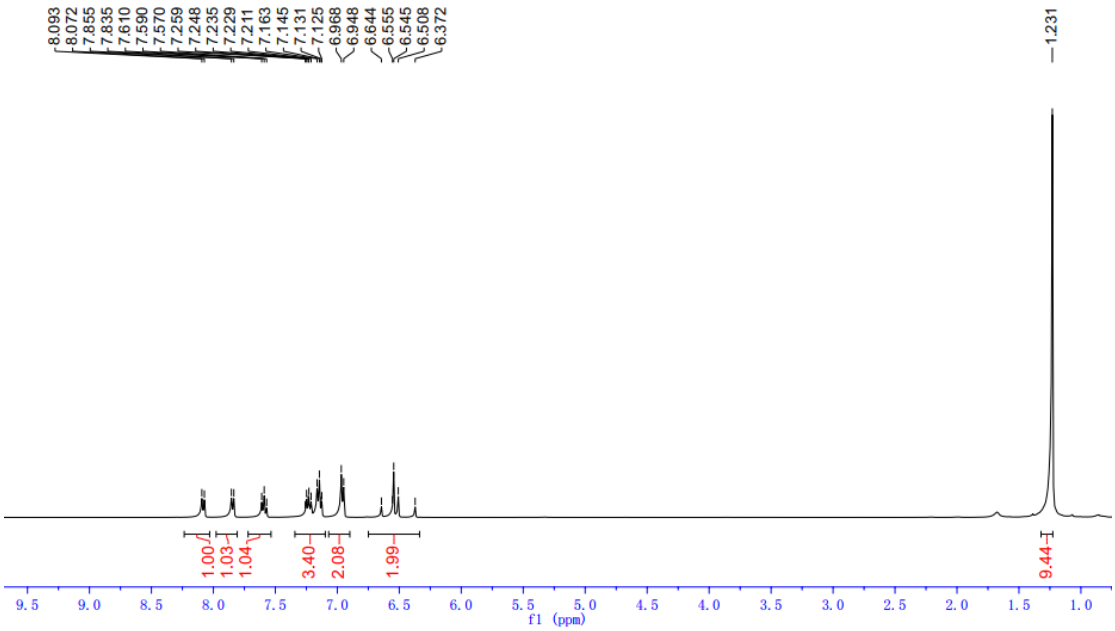
77.532
77.215
76.898
37.622
27.592
f1 (ppm)


HF2C
NO2
Ph
CO2tBu
O
O

3m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8.072
7.855
7.835
7.610
7.590
7.570
7.259
7.248
7.235
7.229
7.211
7.163
7.145
7.131
7.125
6.968
6.948
6.644
6.555
6.545
6.508
6.372
1.231
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1.03
1.04
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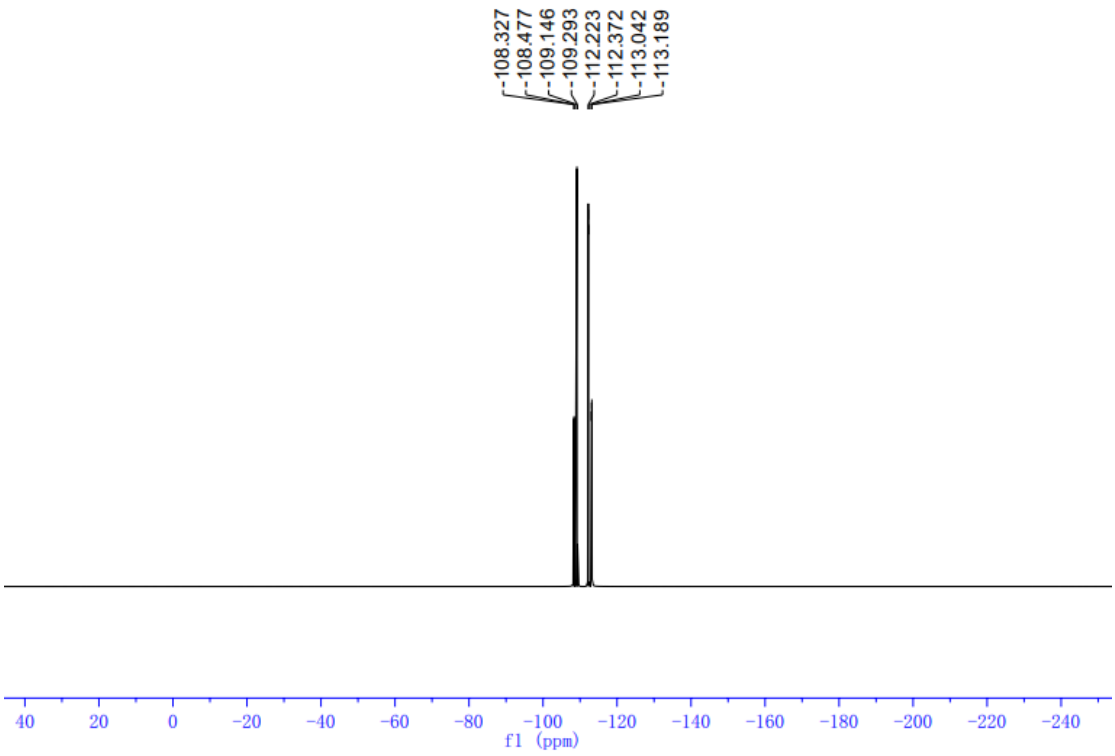
2.08
1.99
9.44
f1 (ppm)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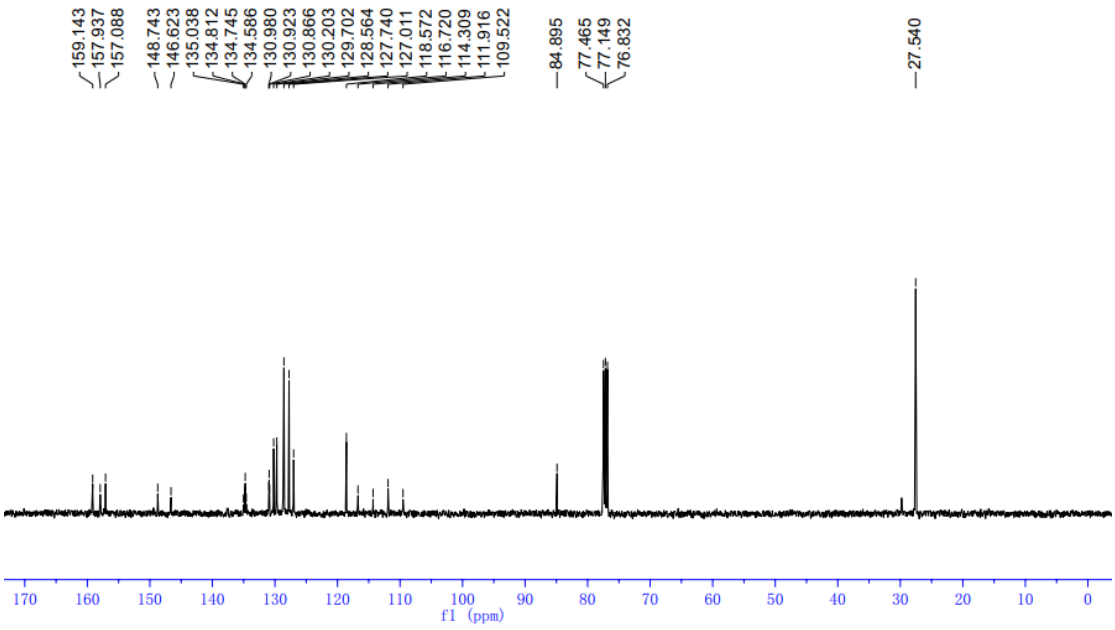
109.293
112.223
112.372
113.042
113.189
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)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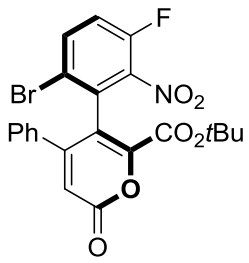
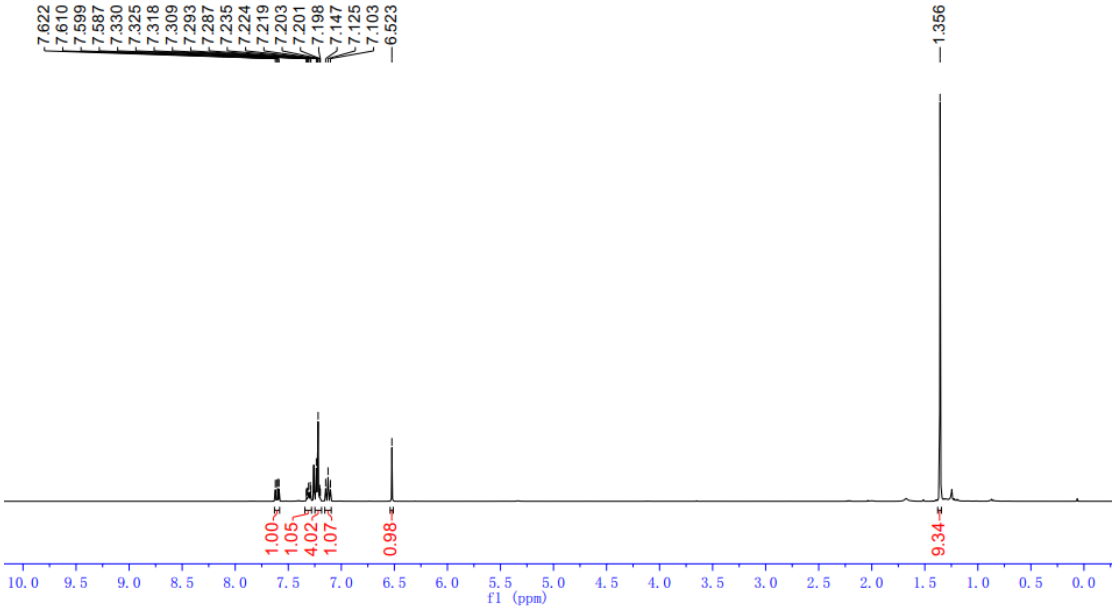
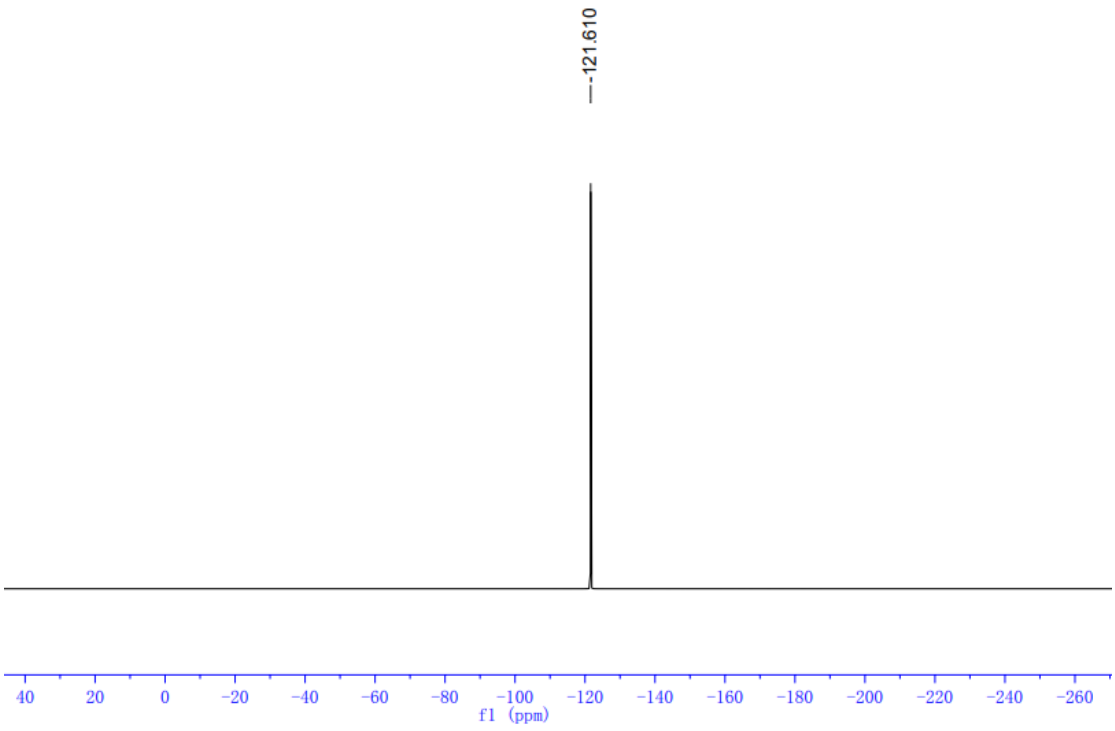
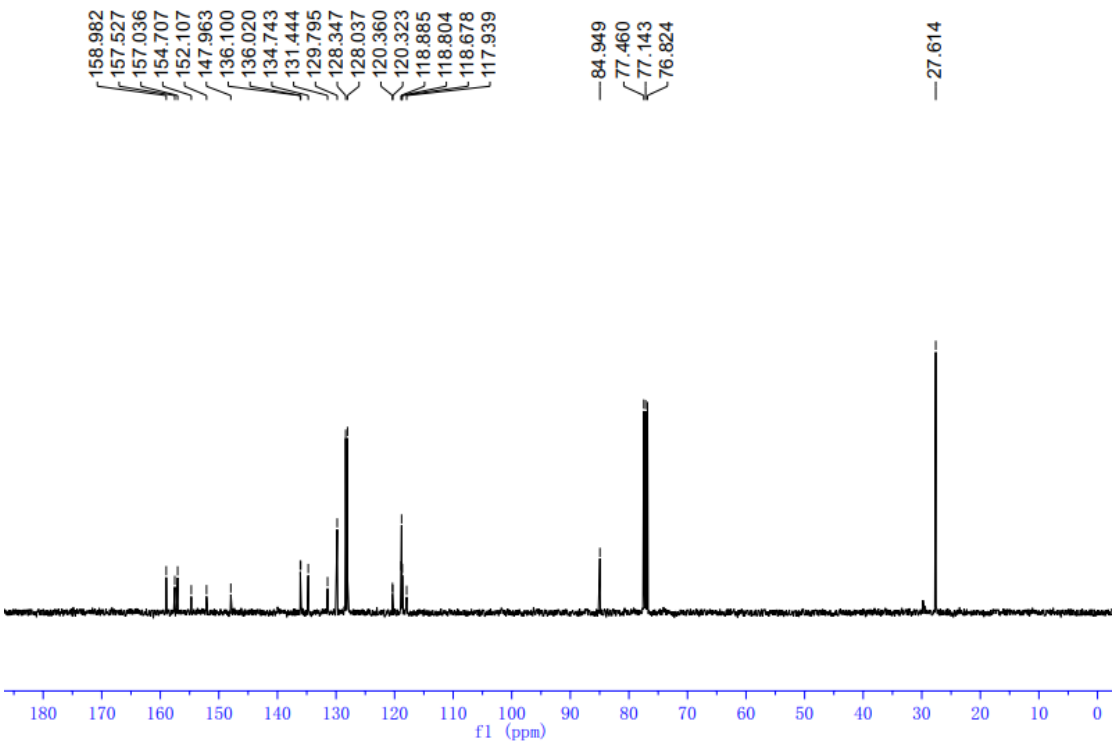
146.623
135.038
134.812
134.745
134.586
130.980
130.923
130.866
130.203
129.702
128.564
127.740
127.011
118.572
116.720
114.309
111.916
109.522
84.895
77.465
77.149
76.832
27.540
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

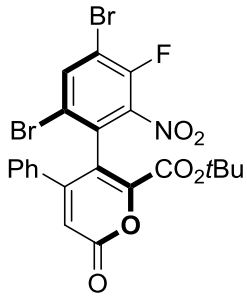

F
Br
NO2
Ph
CO2tBu
O
O

3n

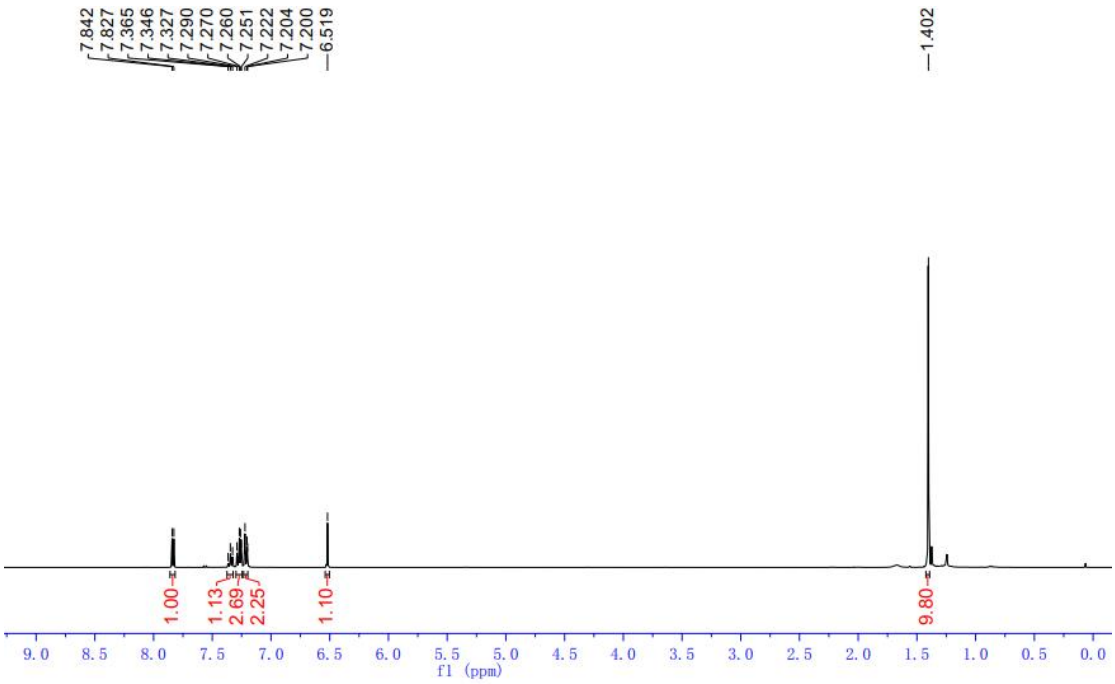

7.622
7.610
7.599
7.587
7.330
7.325
7.318
7.309
7.293
7.287
7.235
7.224
7.219
7.203
7.201
7.198
7.147
7.125
7.103
6.523
1.356
1.00
1.05
4.02
1.07
0.98
9.34
f1 (ppm)

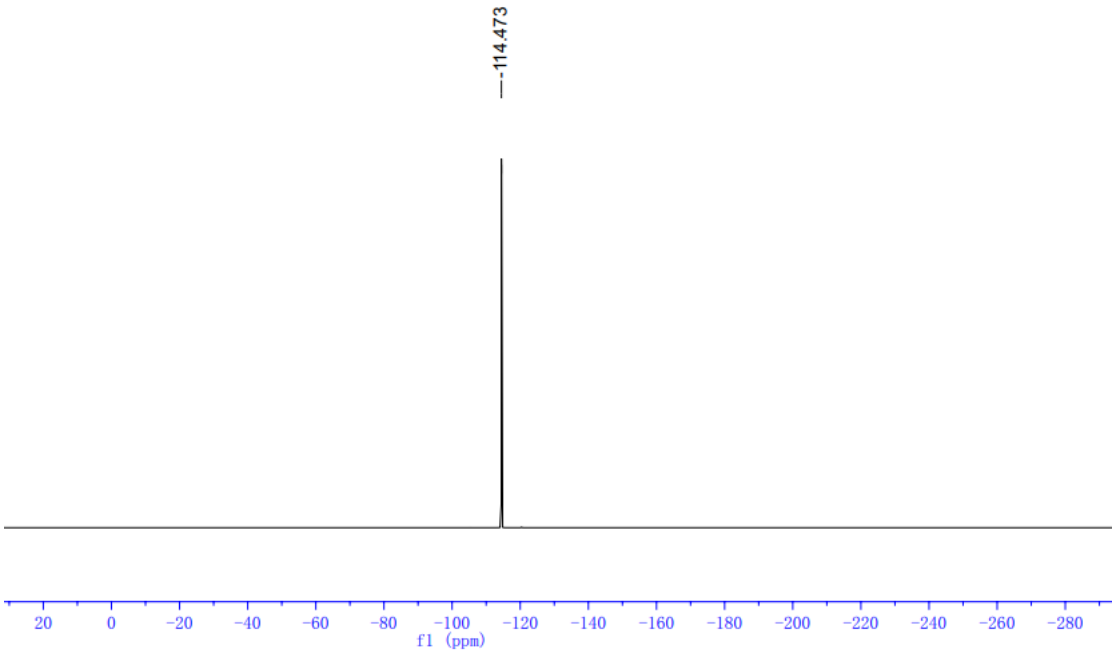

-121.610
f1 (ppm)

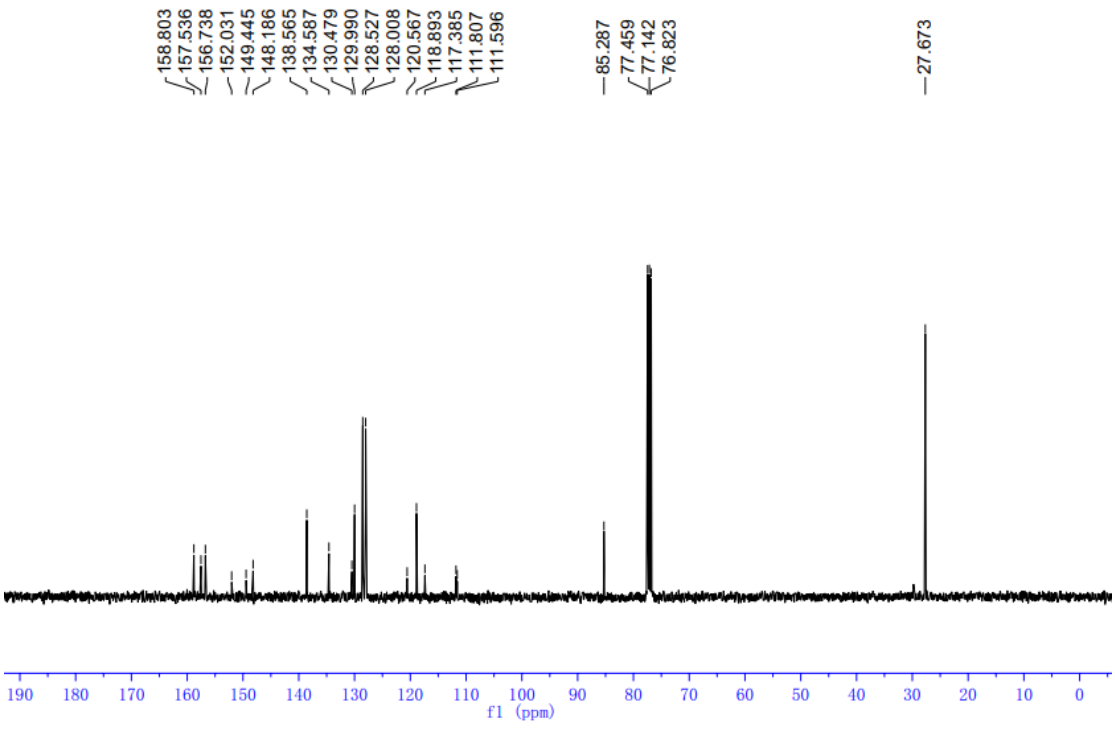

158.982
157.527
157.036
154.707
152.107
147.963
136.100
136.020
134.743
131.444
129.795
128.347
128.037
120.360
120.323
118.885
118.804
118.678
117.939
84.949
77.460
77.143
76.824
27.614
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

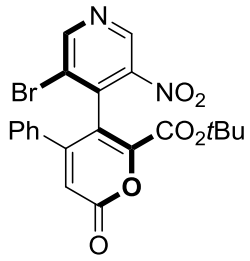

Br
F
Br
NO2
Ph
CO2tBu
O
O

3o

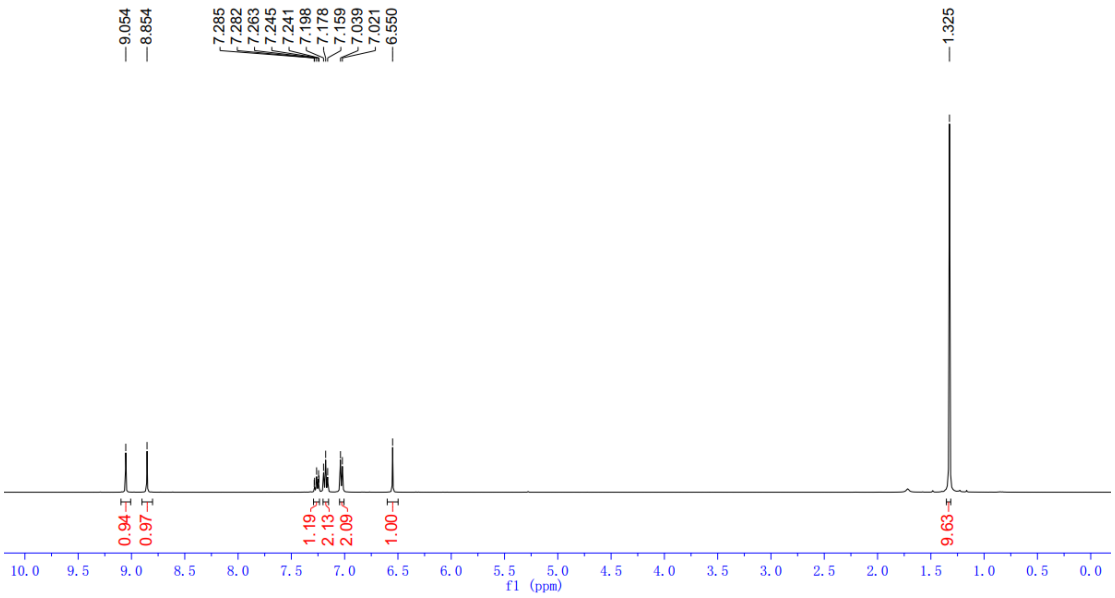

7.842
7.827
7.365
7.346
7.327
7.290
7.270
7.260
7.251
7.222
7.204
7.200
6.519
1.402
1.00
1.13
2.69
2.25
1.10
9.80
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

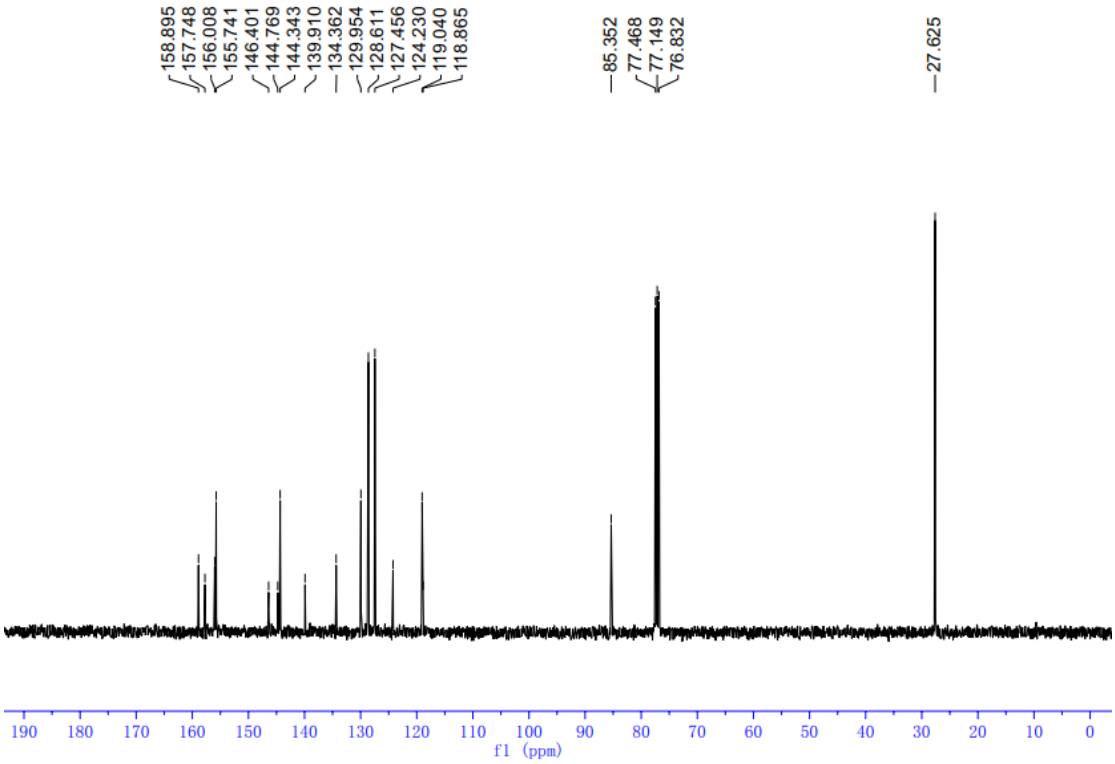

-114.473
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
f1 (ppm)

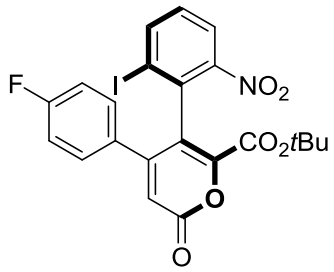

158.803
157.536
156.738
152.031
149.445
148.186
138.565
134.587
130.479
129.990
128.527
128.008
120.567
118.893
117.385
111.807
111.596
85.287
77.459
77.142
76.823
27.673
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
Br
NO2
Ph
CO2tBu
O
O

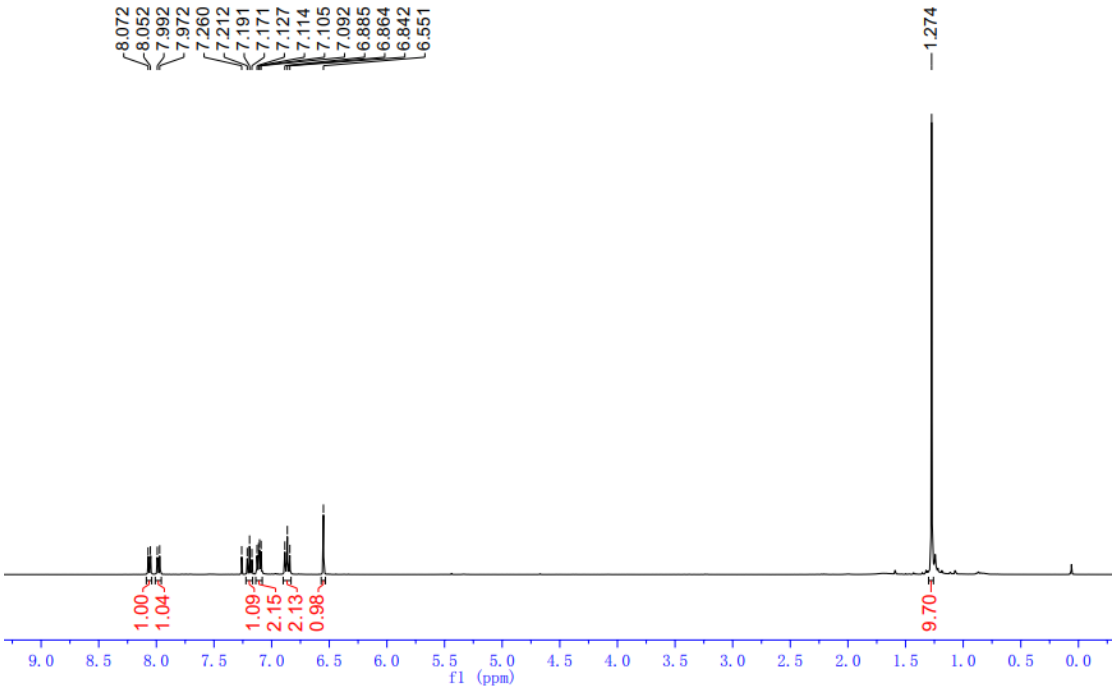
3p

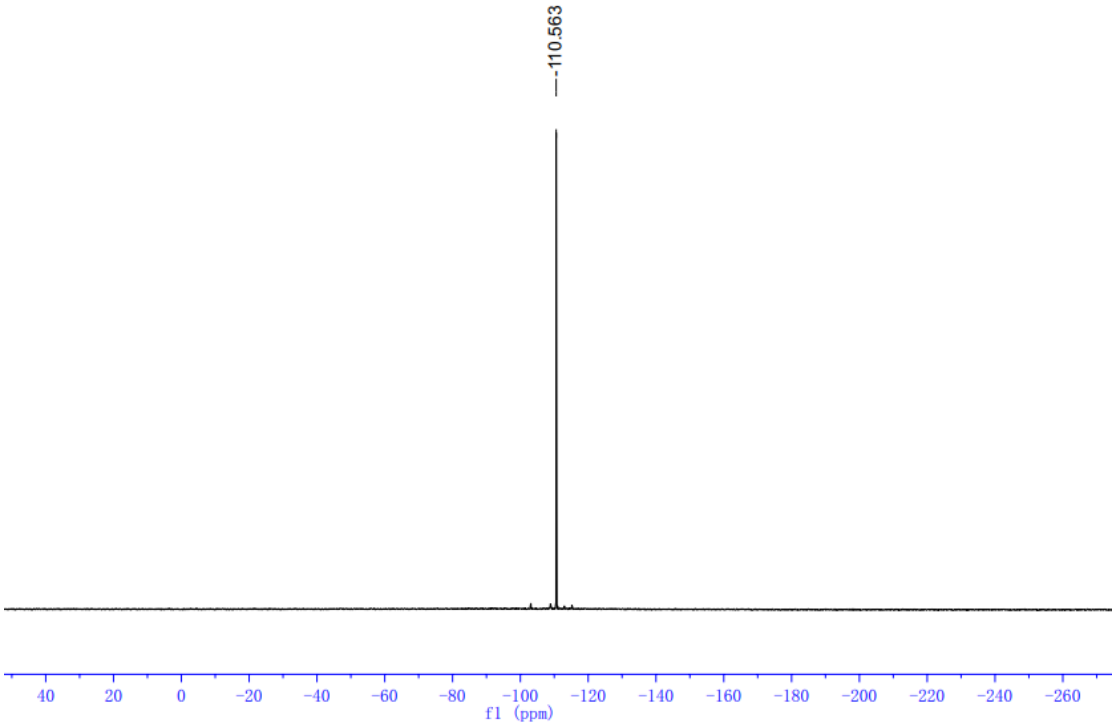

9.054
8.854
7.285
7.282
7.263
7.245
7.241
7.198
7.178
7.159
7.039
7.021
6.550
1.325
0.94
0.97
1.19
2.13
2.09
1.00
9.63
f1 (ppm)

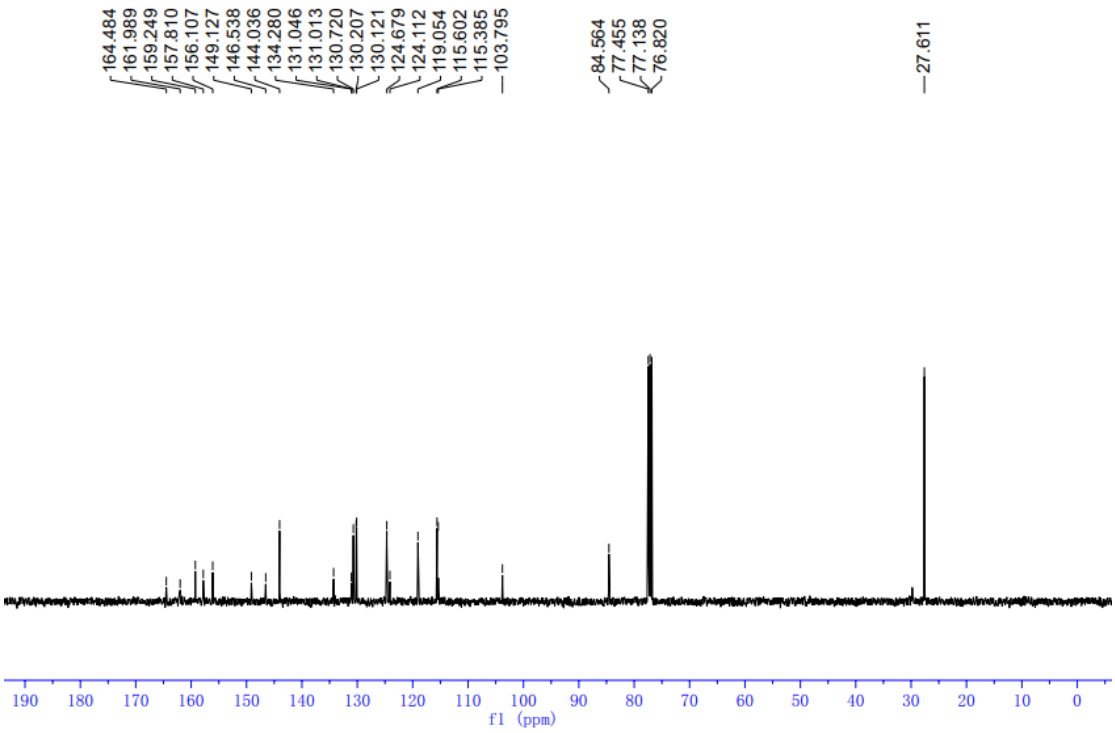

158.895
157.748
156.008
155.741
146.401
144.769
144.343
139.910
134.362
129.954
128.611
127.456
124.230
119.040
118.865
85.352
77.468
77.149
76.832
27.625
f1 (ppm)

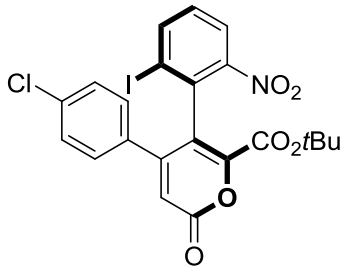

F
I
NO2
CO2tBu
O
O

3q

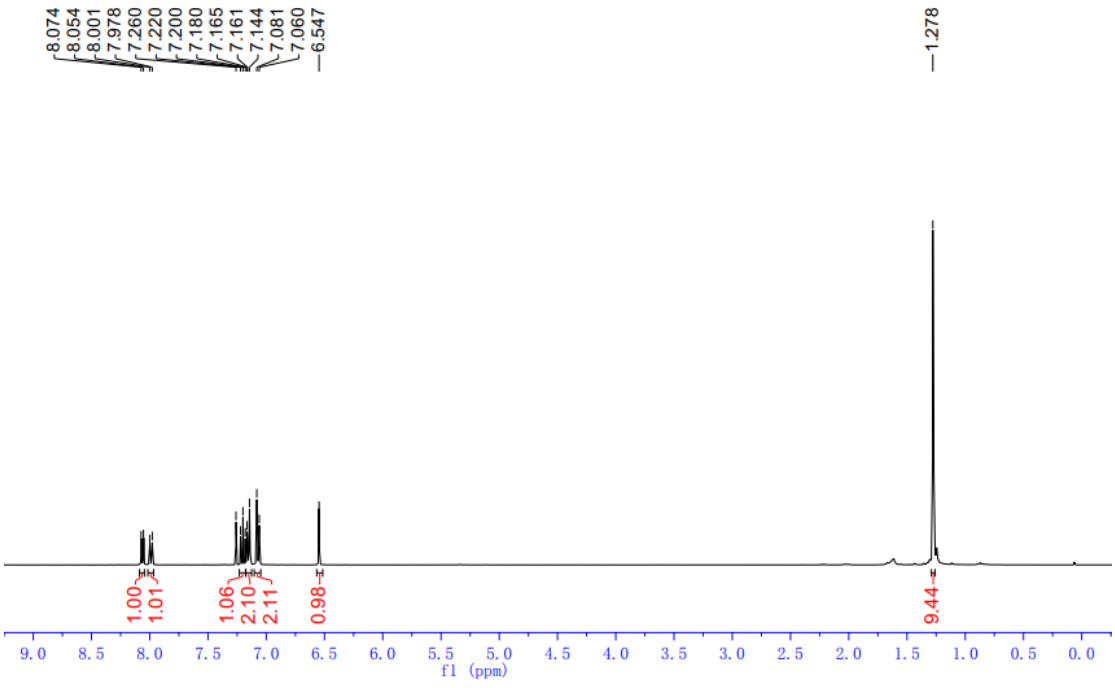

8.072
8.052
7.992
7.972
7.260
7.212
7.191
7.171
7.127
7.114
7.105
7.092
6.885
6.864
6.842
6.551
1.274
1.00
1.04
1.09
2.15
2.13
0.98
9.70
f1 (ppm)

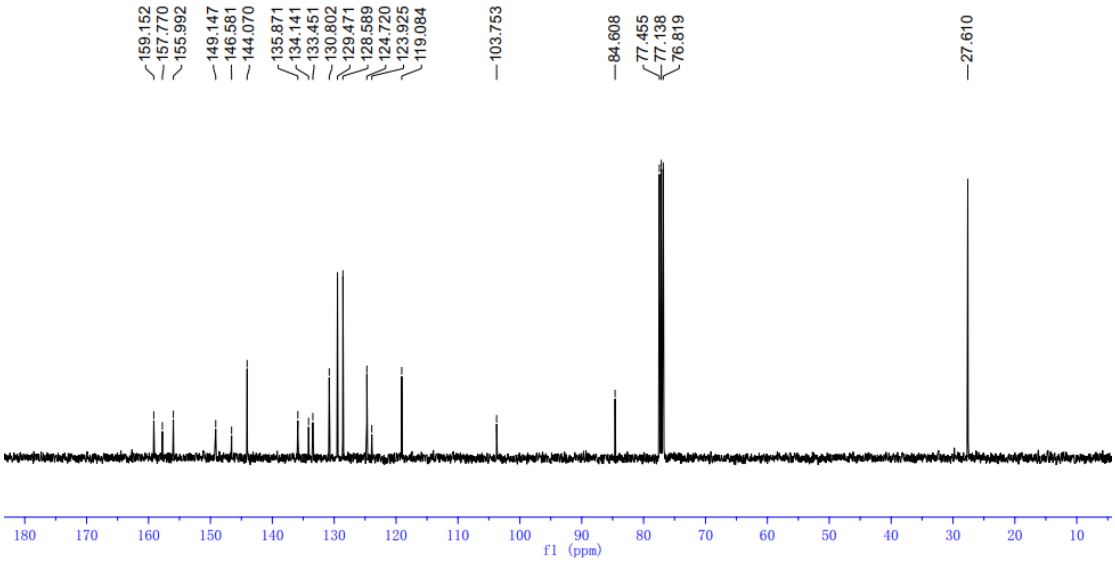

-110.563
f1 (ppm)

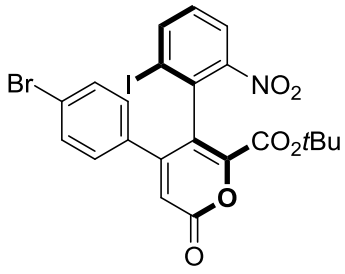

164.484
161.989
159.249
157.810
156.107
149.127
146.538
144.036
134.280
131.046
131.013
130.720
130.207
130.121
124.679
124.112
119.054
115.602
115.385
103.795
84.564
77.455
77.138
76.820
27.611
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Cl
I
NO2
CO2tBu
O
O

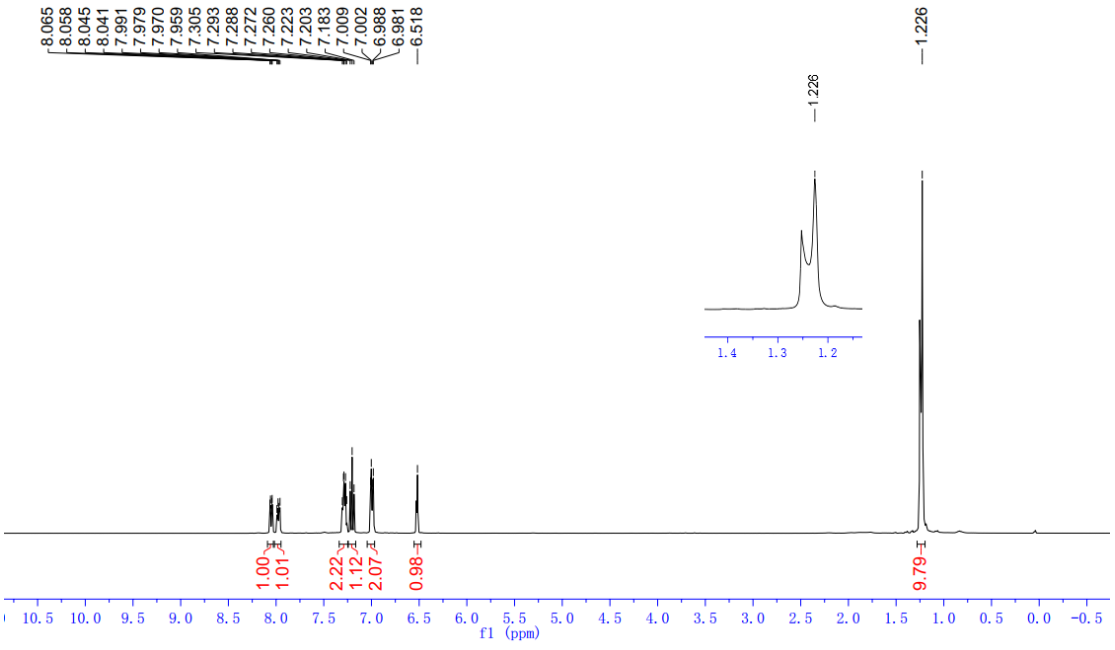
3r

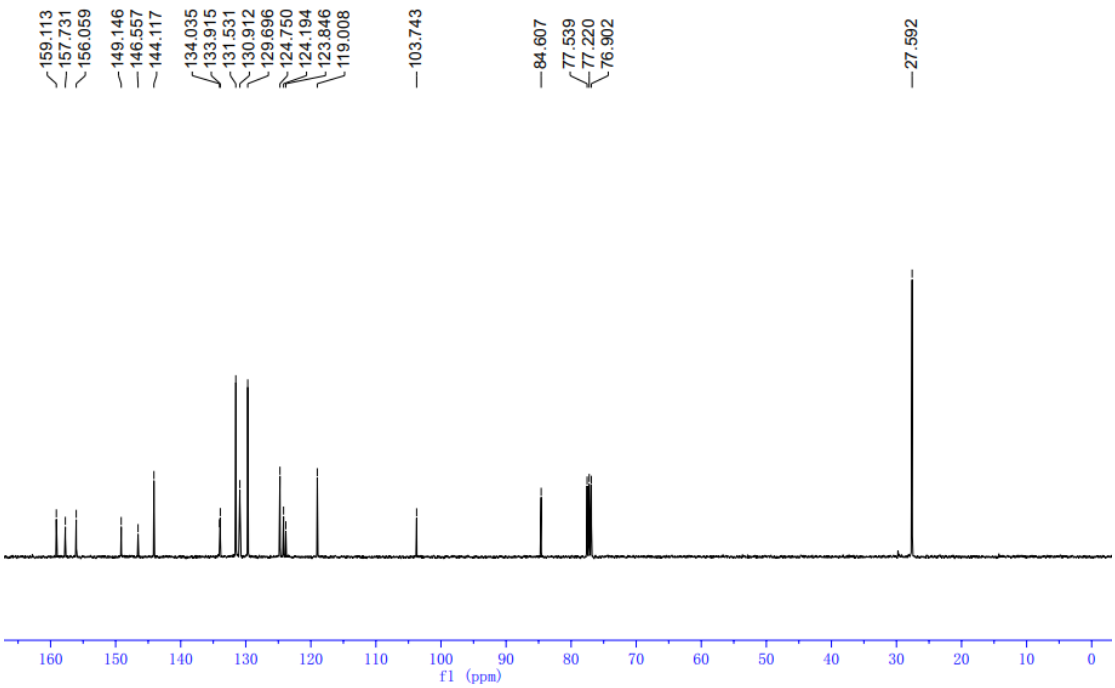

8.074
8.054
8.001
7.978
7.260
7.220
7.200
7.180
7.165
7.161
7.144
7.081
7.060
6.547
1.278
1.00
1.01
1.06
2.10
2.11
0.98
9.44
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

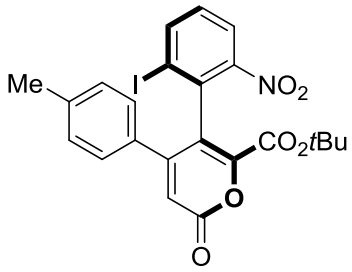

159.152
157.770
155.992
149.147
146.581
144.070
135.871
134.141
133.451
130.802
129.471
128.589
124.720
123.925
119.084
103.753
84.608
77.455
77.138
76.819
27.610
f1 (ppm)


Br
I
NO2
CO2tBu
O
O

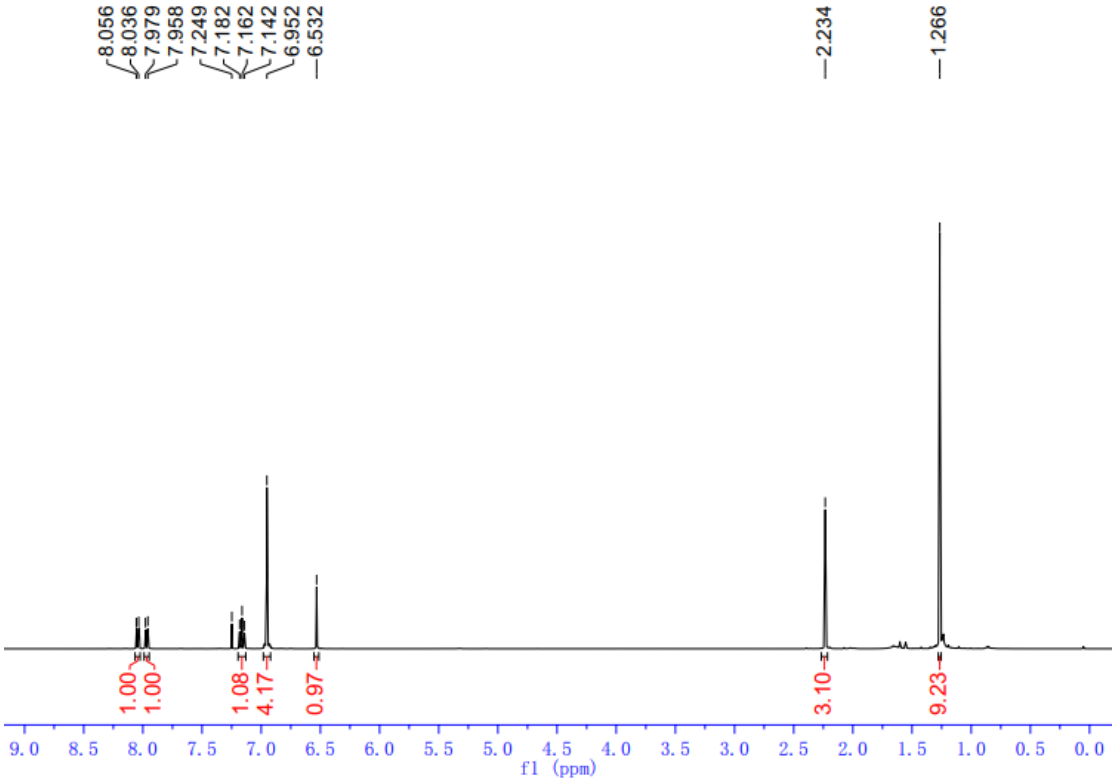
3s

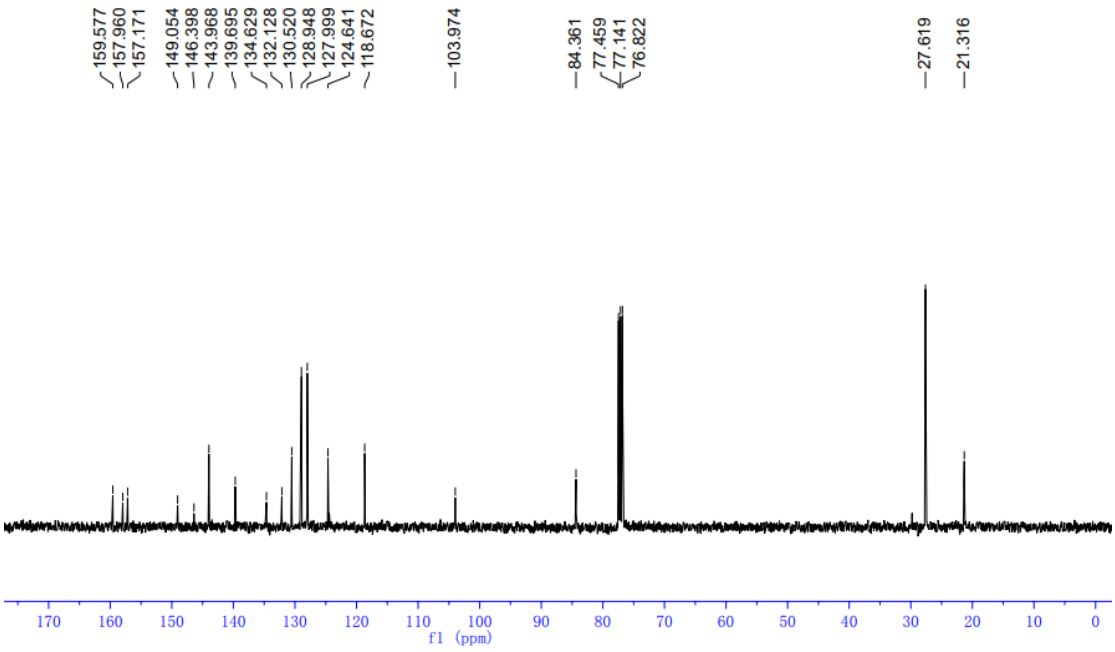

8.065
8.058
8.045
8.041
7.991
7.979
7.970
7.959
7.305
7.293
7.288
7.272
7.260
7.223
7.203
7.183
7.009
7.002
6.988
6.981
6.518
1.226
1.226
1.00
1.01
2.22
1.12
2.07
0.98
9.79
f1 (ppm)

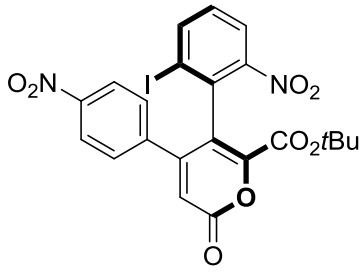

159.113
157.731
156.059
149.146
146.557
144.117
134.035
133.915
131.531
130.912
129.696
124.750
124.194
123.846
119.008
103.743
84.607
77.539
77.220
76.902
27.592
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
I
NO2
CO2tBu
O
O

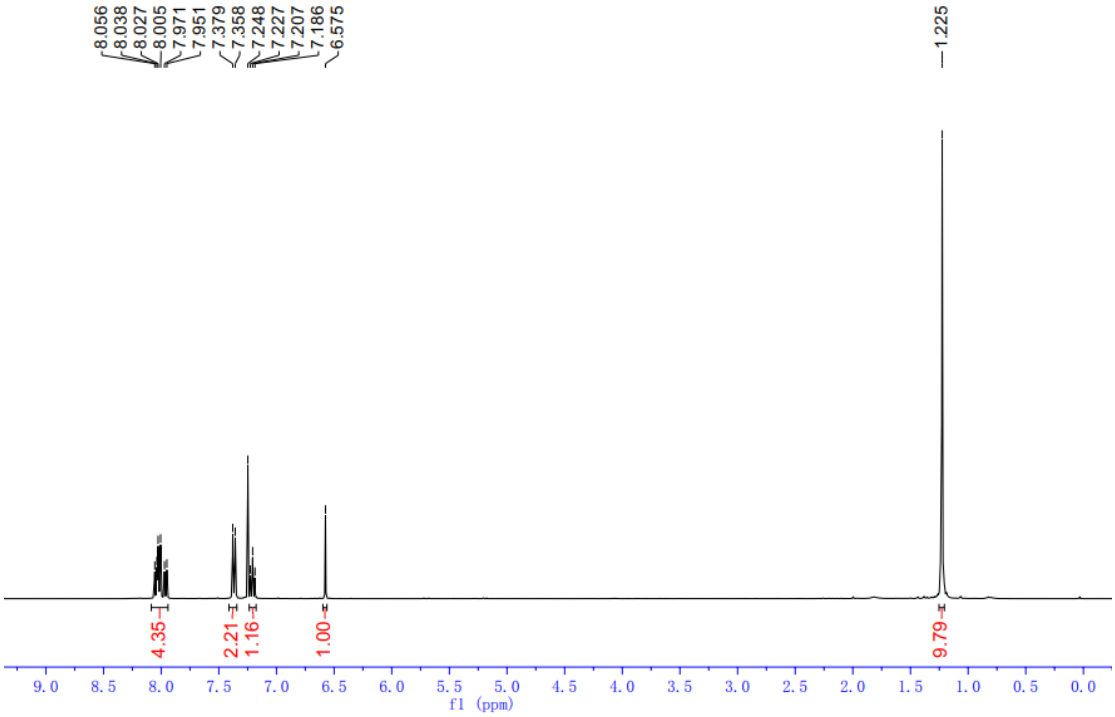
3t


8.056
8.036
7.979
7.958
7.249
7.182
7.162
7.142
6.952
6.532
2.234
1.266
1.00
1.00
1.08
4.17
0.97
3.10
9.23
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)


159.577
157.960
157.171
149.054
146.398
143.968
139.695
134.629
132.128
130.520
128.948
127.999
124.641
118.672
103.974
84.361
77.459
77.141
76.822
27.619
21.316
f1 (ppm)


O2N
I
NO2
CO2tBu
O
O

3u


8.056
8.038
8.027
8.005
7.971
7.951
7.379
7.358
7.248
7.227
7.207
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6.575
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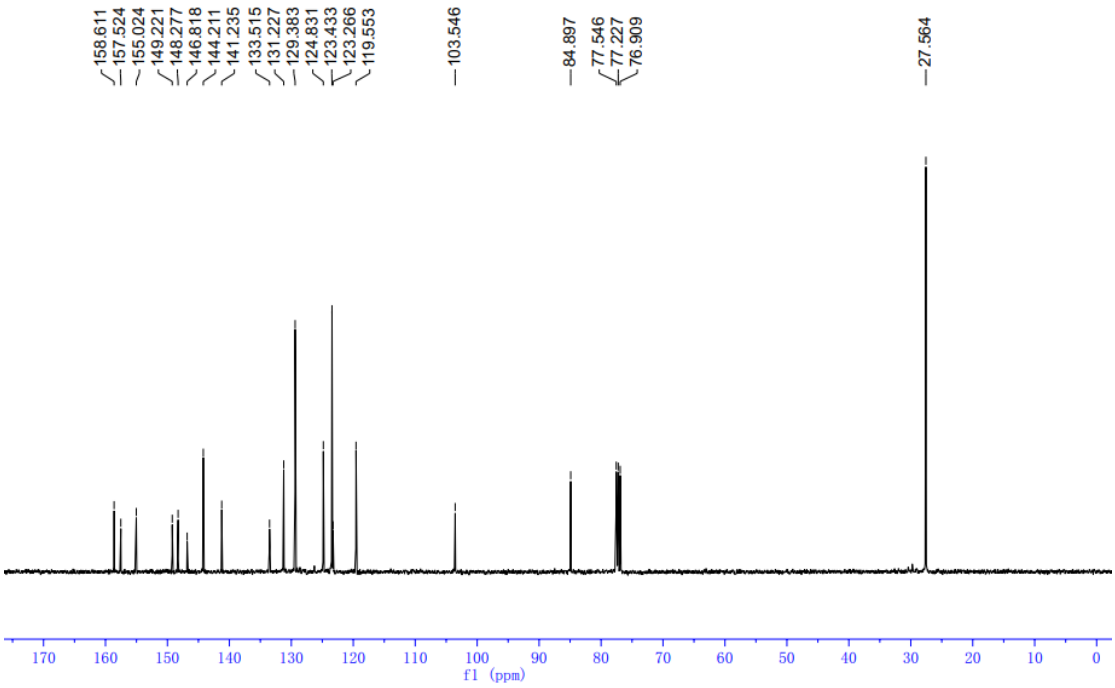
4.35
2.21
1.16
1.00
9.79
f1 (ppm)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155.024
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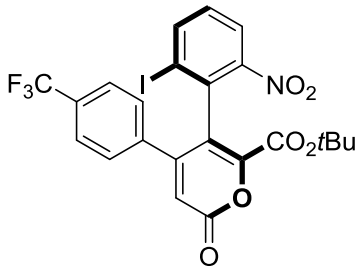
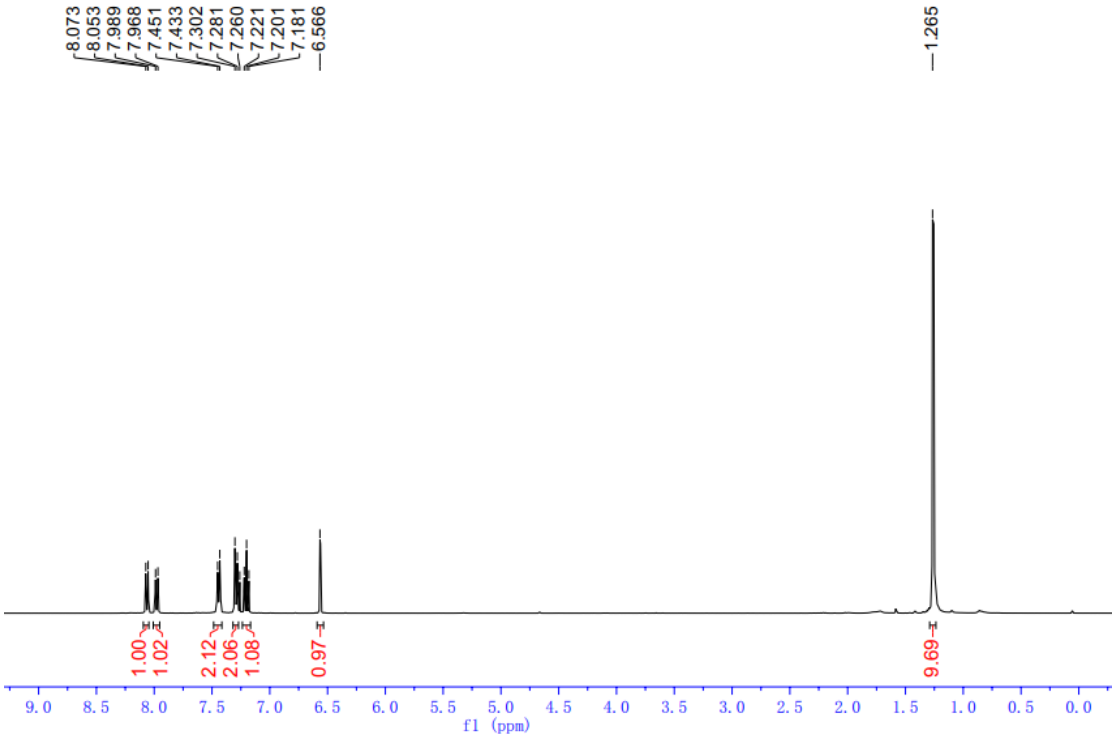
148.277
146.818
144.211
141.235
133.515
131.227
129.383
124.831
123.433
123.266
119.553
103.546
84.897
77.546
77.227
76.909
27.564
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


F3C
I
NO2
CO2tBu
O
O

3v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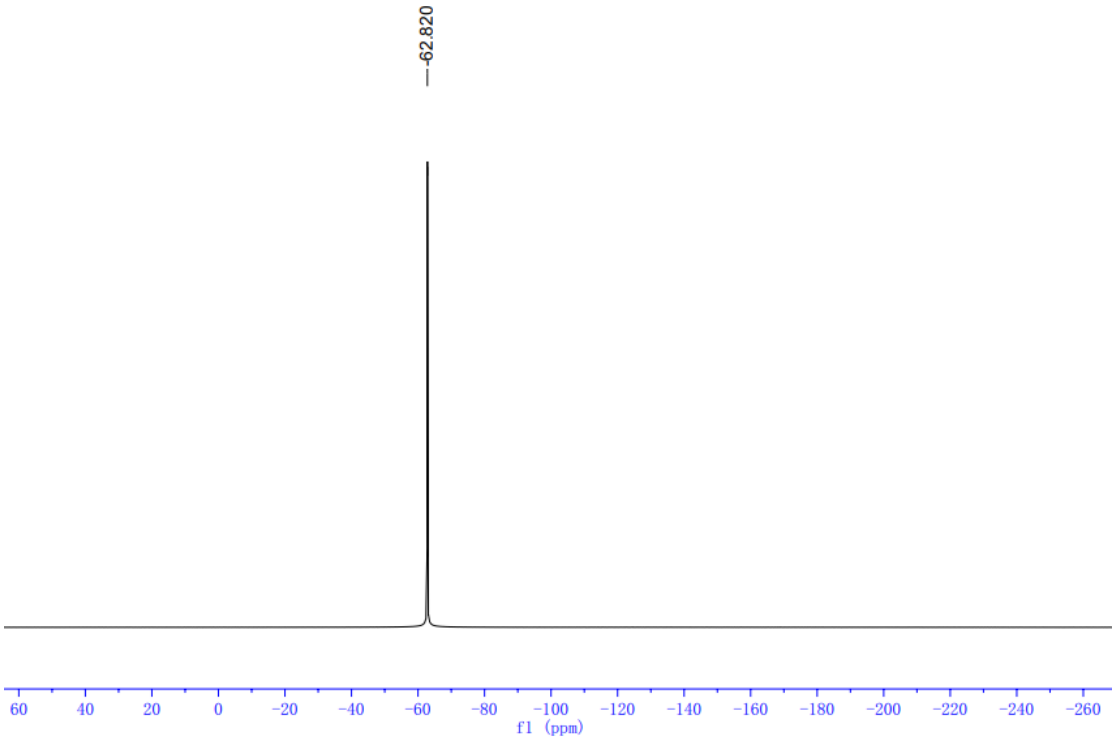
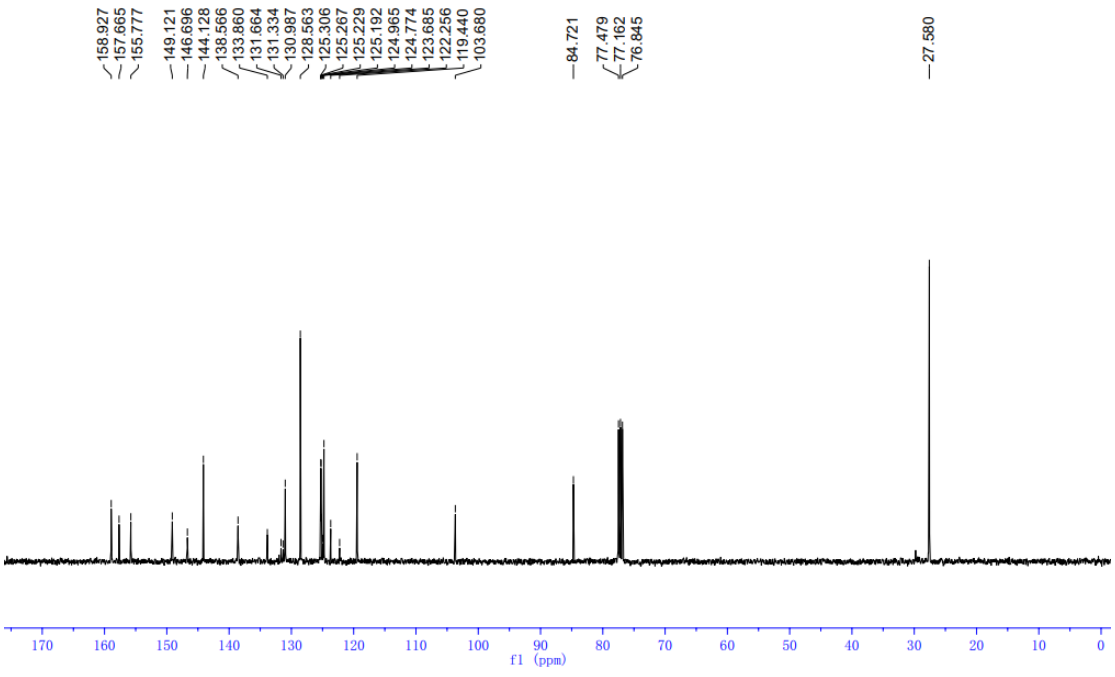
8.053
7.989
7.968
7.451
7.433
7.302
7.281
7.260
7.221
7.201
7.181
6.566
1.265
1.00
1.02
2.12
2.06
1.08
0.97
9.69
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


-62.820
60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)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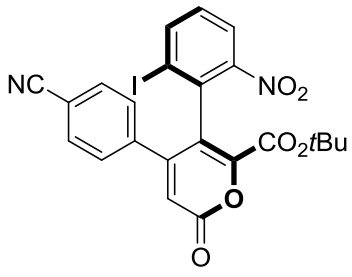
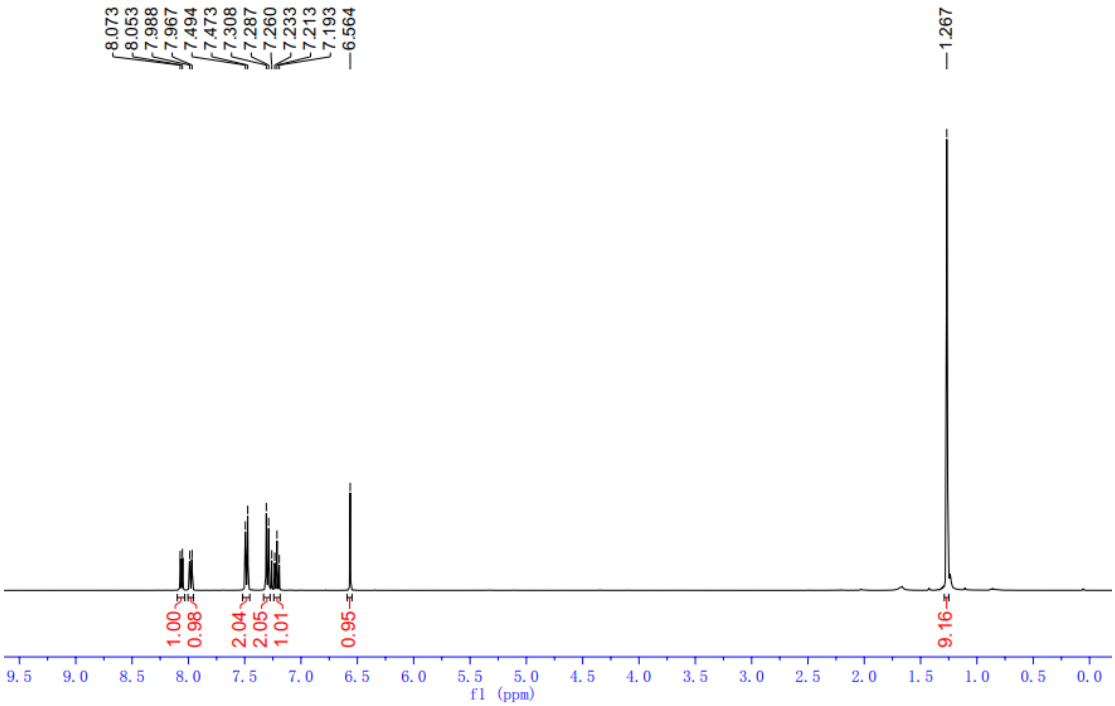
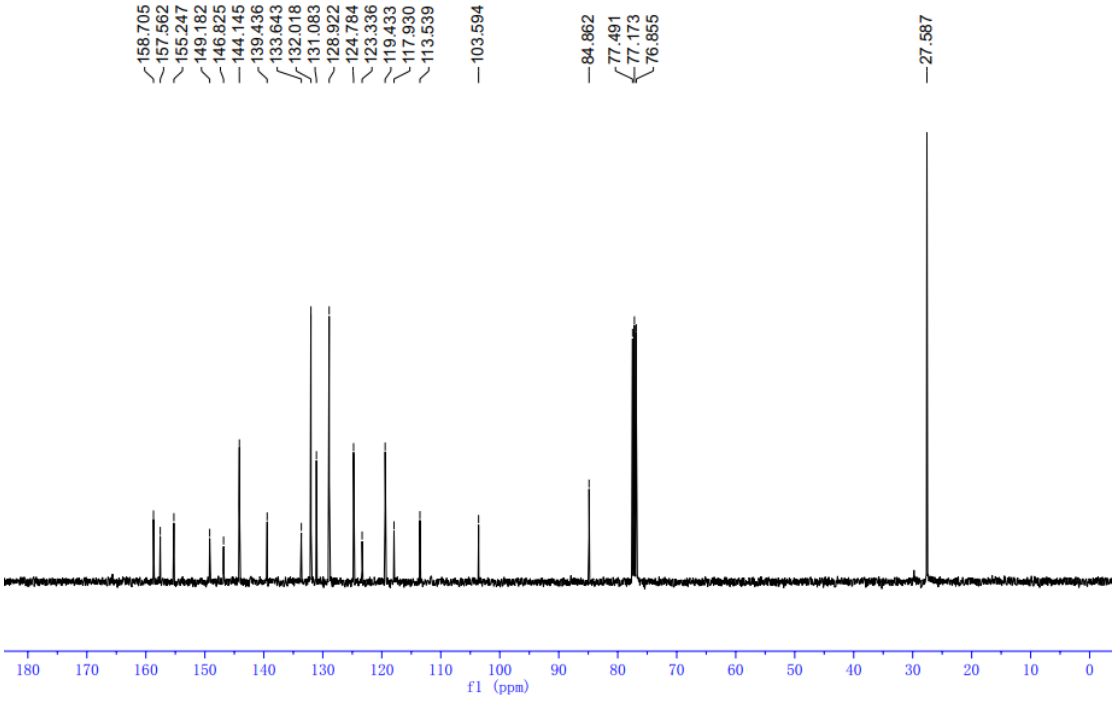
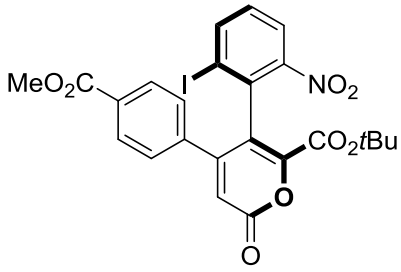
155.777
149.121
146.696
144.128
138.566
133.860
131.664
131.334
130.987
128.563
125.306
125.267
125.229
125.192
124.965
124.774
123.685
122.256
119.440
103.680
84.721
77.479
77.162
76.845
27.580
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


NC
I
NO2
CO2tBu
O
O

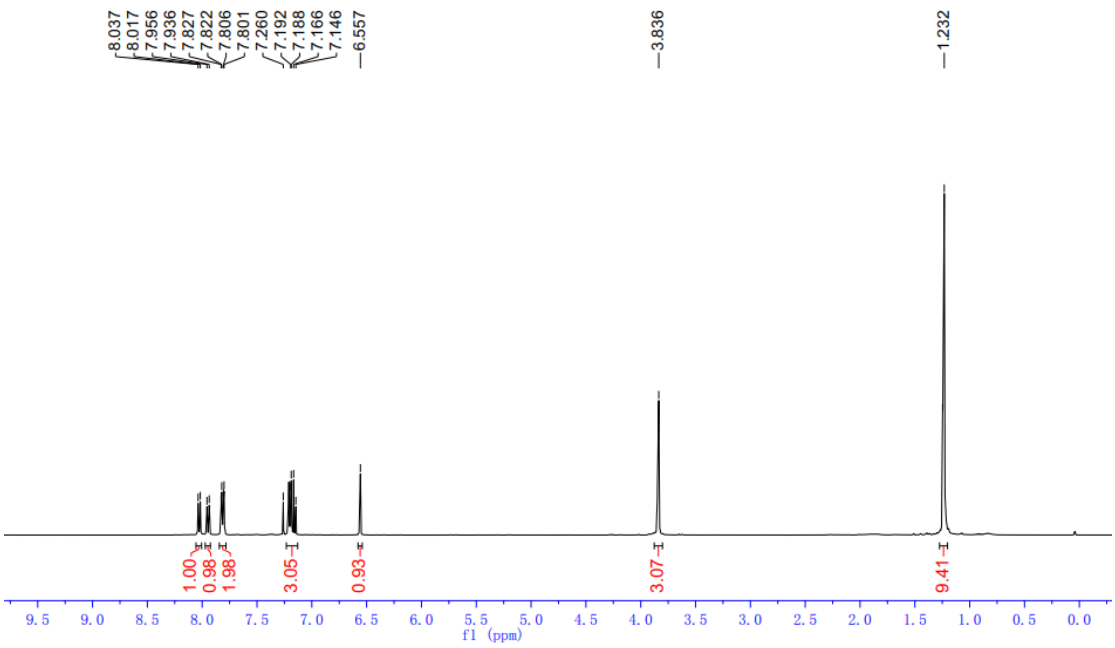
3w


8.073
8.053
7.988
7.967
7.494
7.473
7.308
7.287
7.260
7.233
7.213
7.193
6.564
1.267
1.00
0.98
2.04
2.05
1.01
0.95
9.16
f1 (ppm)


158.705
157.562
155.247
149.182
146.825
144.145
139.436
133.643
132.018
131.083
128.922
124.784
123.336
119.433
117.930
113.539
103.594
84.862
77.491
77.173
76.855
27.587
f1 (ppm)


MeO2C
I
NO2
CO2tBu
O
O

3x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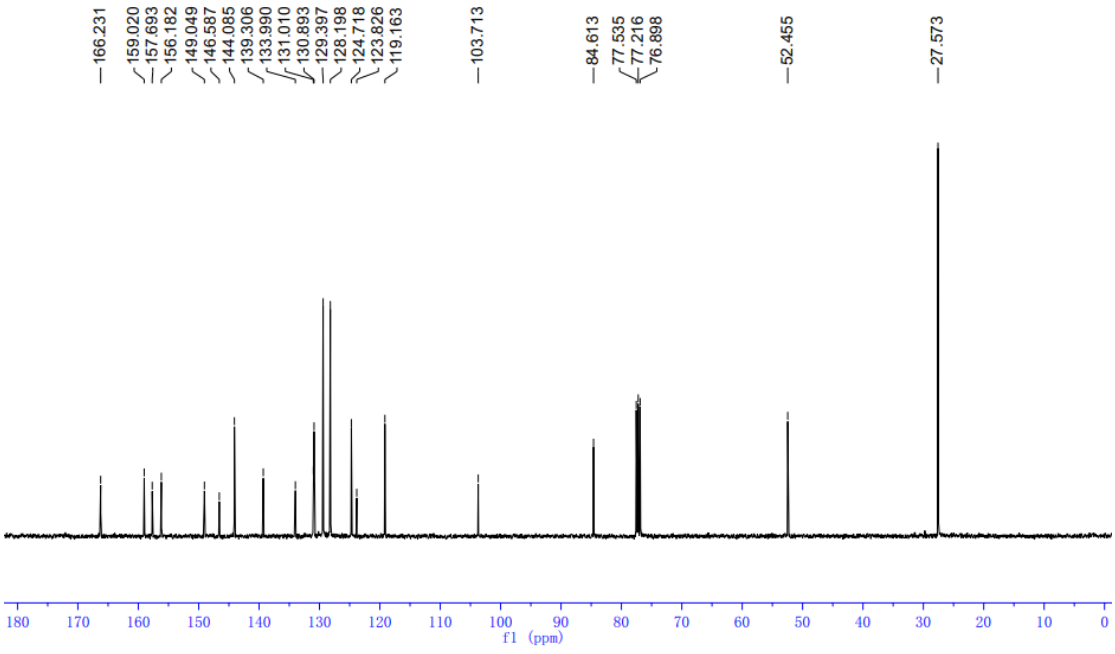
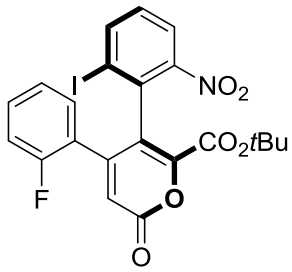
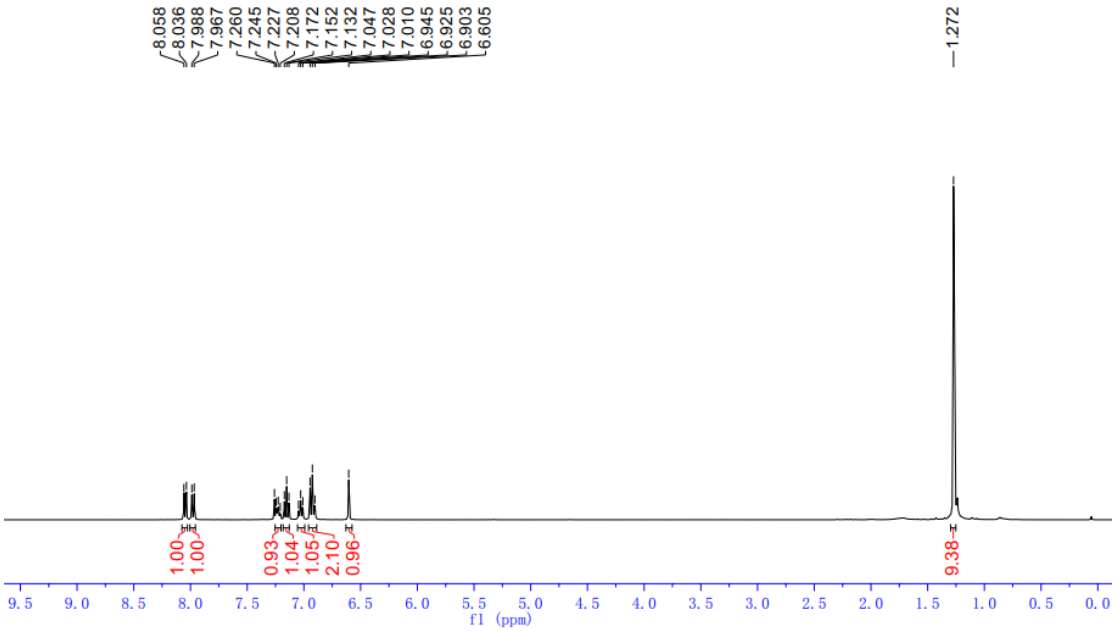
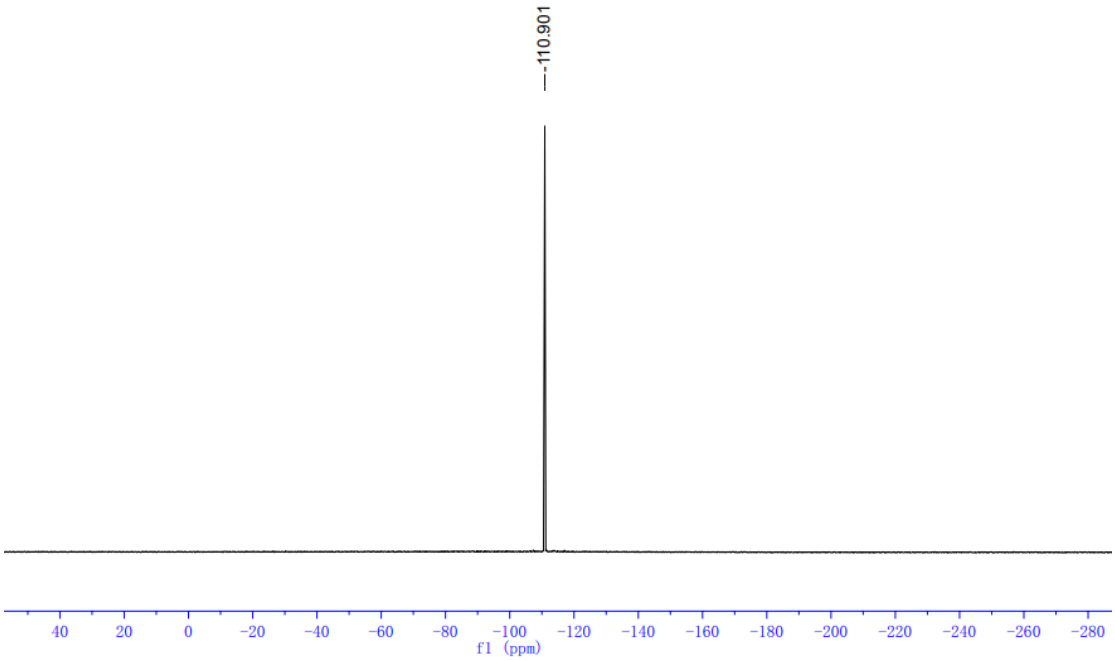
8.017
7.956
7.936
7.827
7.822
7.806
7.801
7.260
7.192
7.188
7.166
7.146
6.557
3.836
1.232
1.00
0.98
1.98
3.05
0.93
3.07
9.41
f1 (ppm)

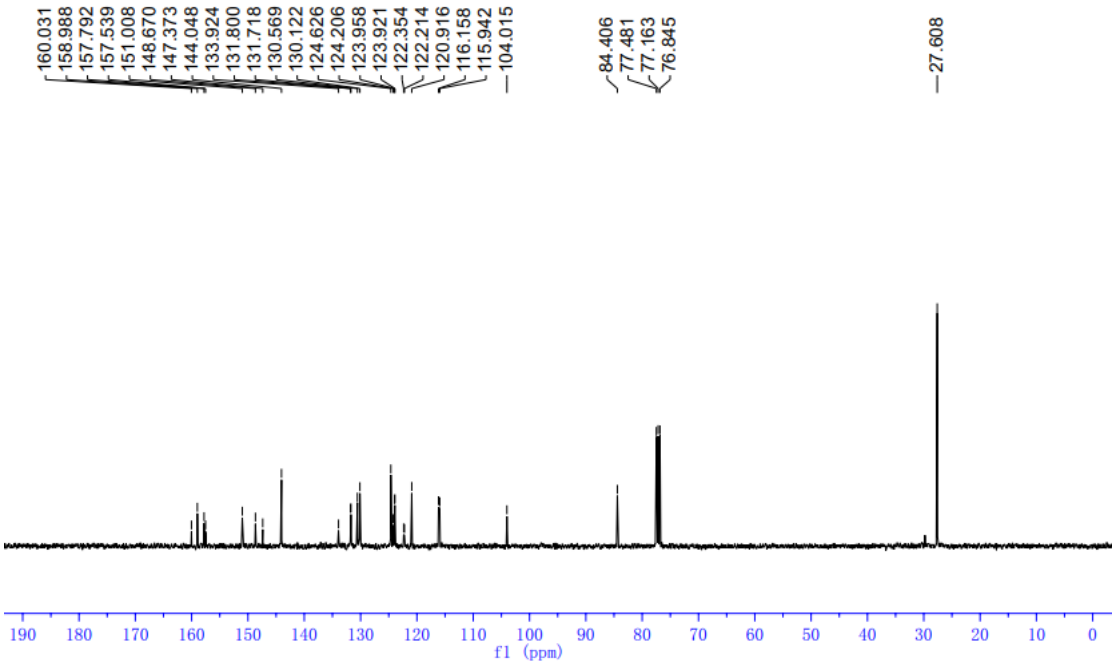

166.231
159.020
157.693
156.182
149.049
146.587
144.085
139.306
133.990
131.010
130.893
129.397
128.198
124.718
123.826
119.163
103.713
84.613
77.535
77.216
76.898
52.455
27.573
f1 (ppm)

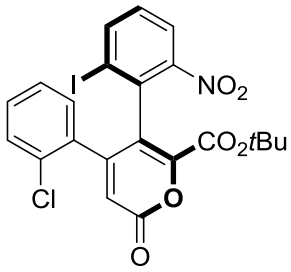

I
NO2
CO2tBu
F
O
O

3y

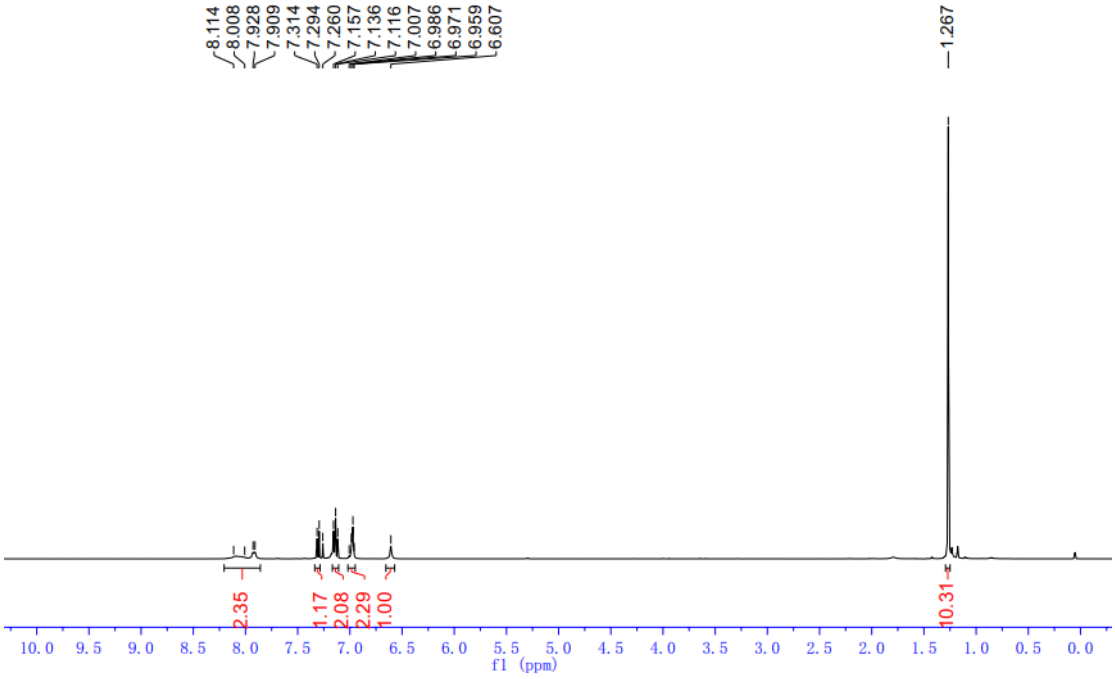

8.058
8.036
7.988
7.967
7.260
7.245
7.227
7.208
7.172
7.152
7.132
7.047
7.028
7.010
6.945
6.925
6.903
6.605
1.272
1.00
1.00
0.93
1.04
1.05
2.10
0.96
9.38
f1 (ppm)

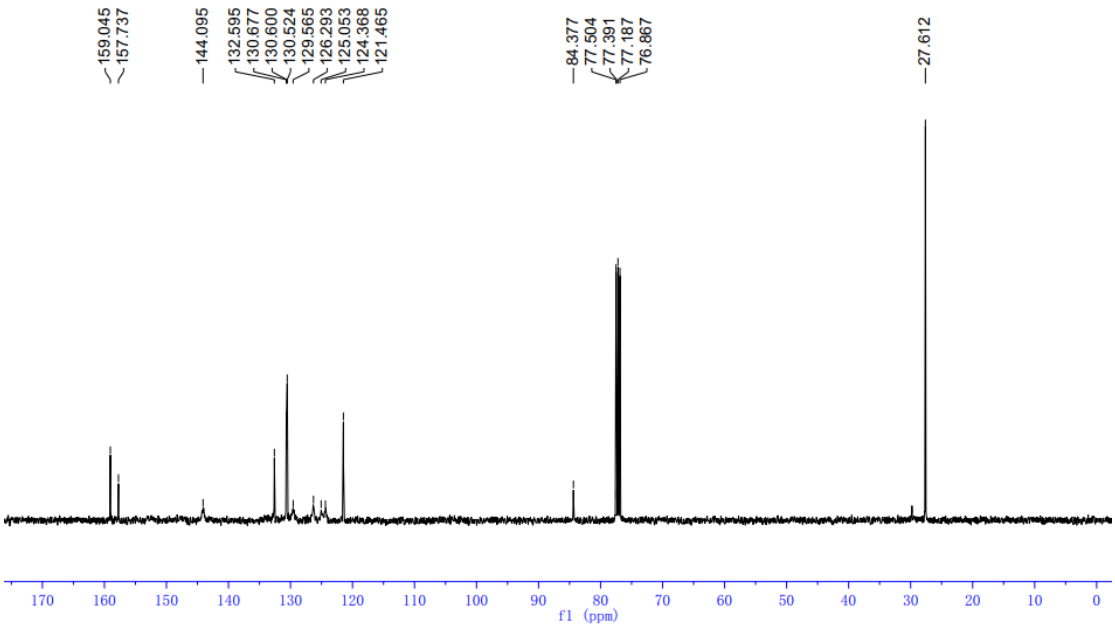

-110.901
f1 (ppm)


160.031
158.988
157.792
157.539
151.008
148.670
147.373
144.048
133.924
131.800
131.718
130.569
130.122
124.626
124.206
123.958
123.921
122.354
122.214
120.916
116.158
115.942
104.015
84.406
77.481
77.163
76.845
27.608
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


I
NO2
CO2tBu
Cl
O
O

3z


8.114
8.008
7.928
7.909
7.314
7.294
7.260
7.157
7.136
7.116
7.007
6.986
6.971
6.959
6.607
1.267
2.35
1.17
2.08
2.29
1.00
10.31
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)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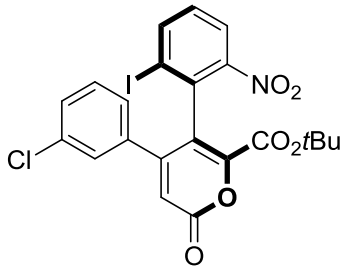
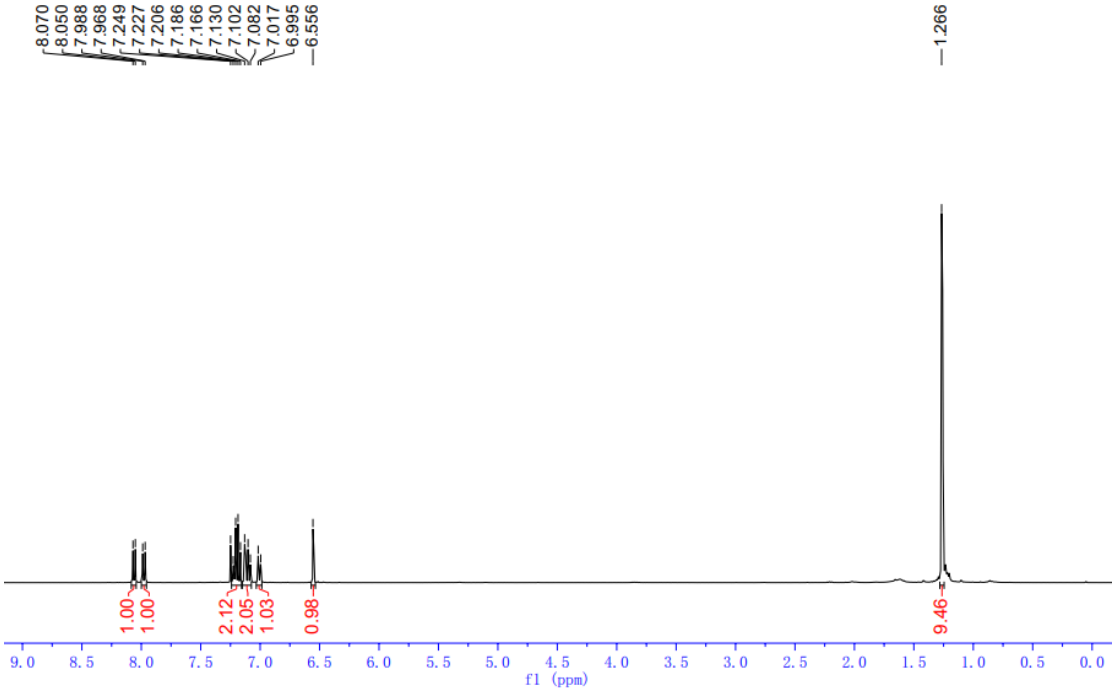
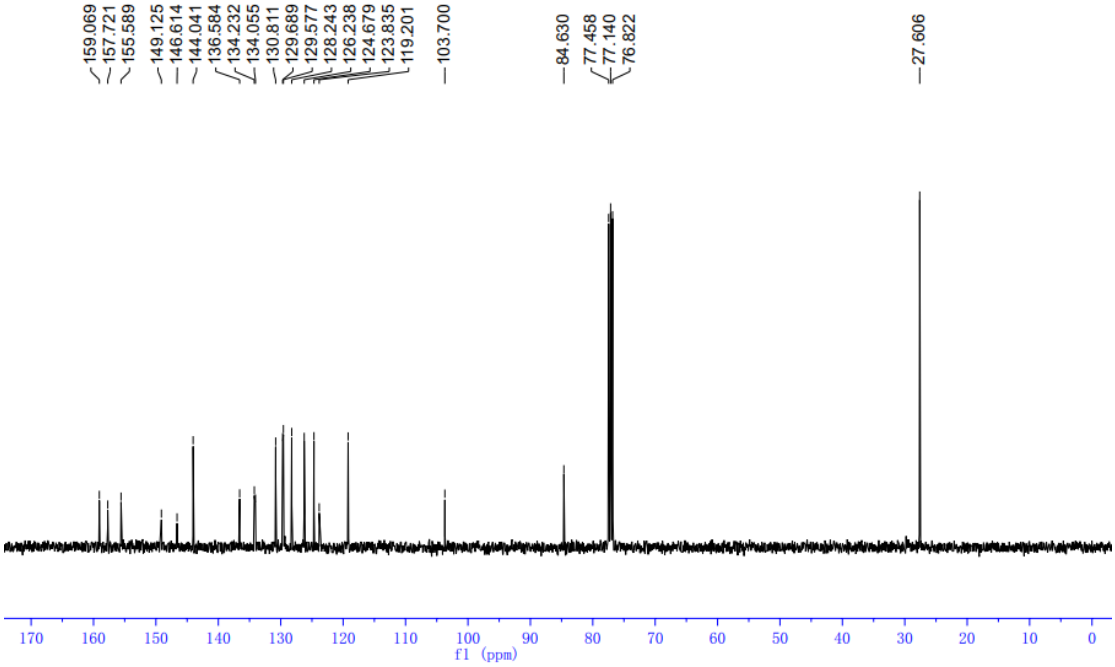
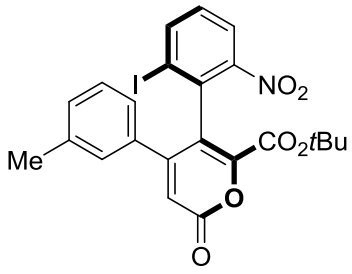
157.737
144.095
132.595
130.677
130.600
130.524
129.565
126.293
125.053
124.368
121.465
84.377
77.504
77.391
77.187
76.867
27.612
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


I
NO2
Cl
CO2tBu
O
O

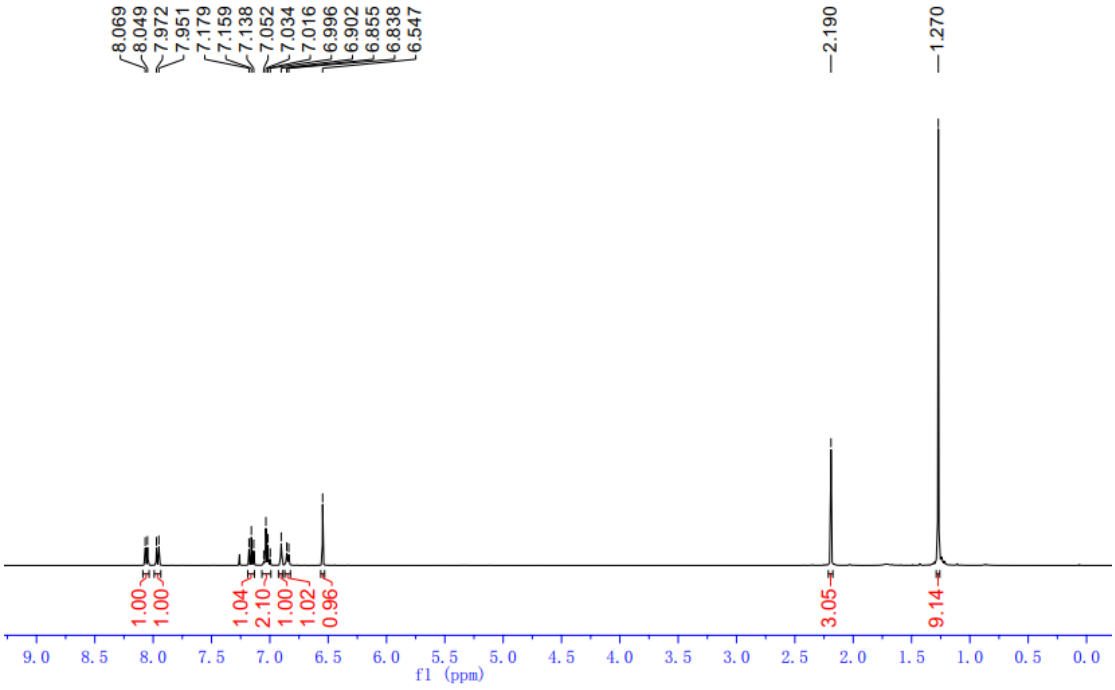
3aa

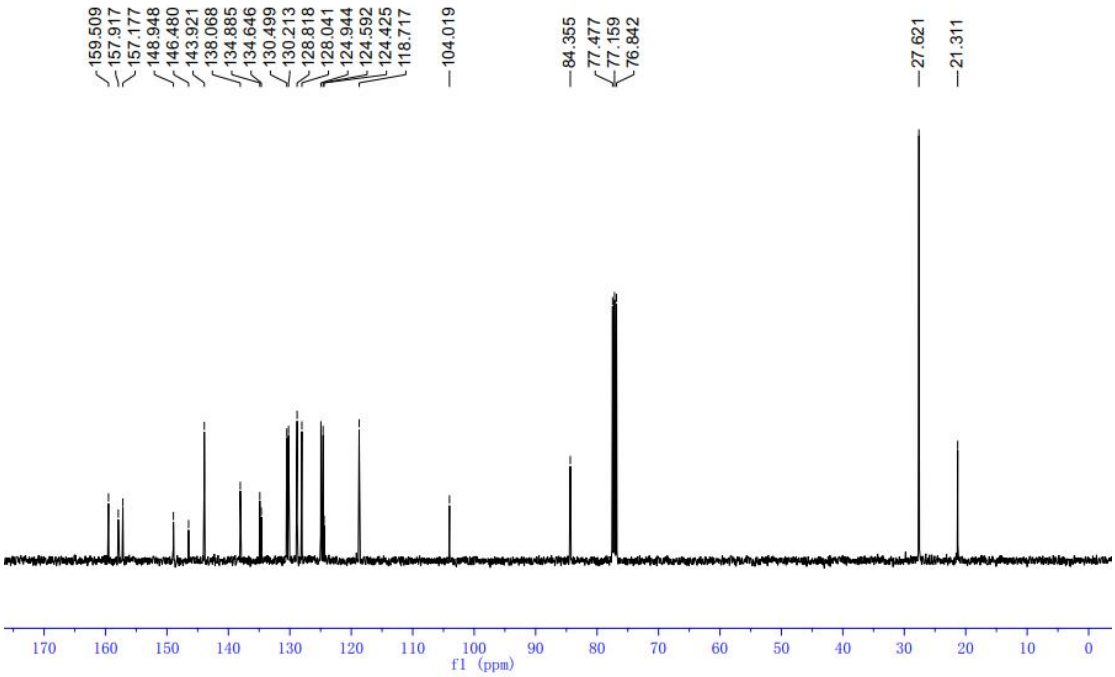

8.070
8.050
7.988
7.968
7.249
7.227
7.206
7.186
7.166
7.130
7.102
7.082
7.017
6.995
6.556
1.266
1.00
1.00
2.12
2.05
1.03
0.98
9.46
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

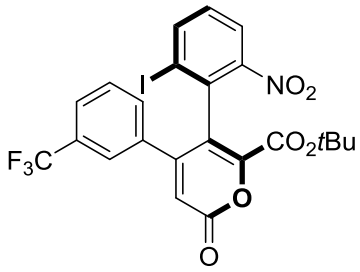

159.069
157.721
155.589
149.125
146.614
144.041
136.584
134.232
134.055
130.811
129.689
129.577
128.243
126.238
124.679
123.835
119.201
103.700
84.630
77.458
77.140
76.822
27.606
f1 (ppm)


I
NO2
CO2tBu
Me
O
O

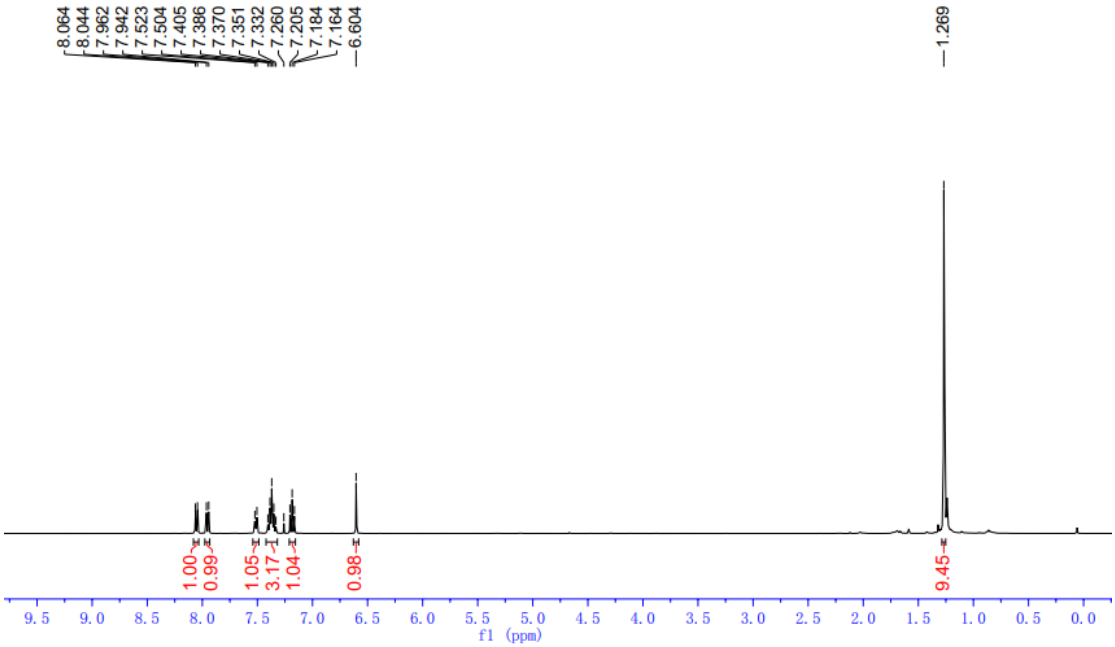
3ab

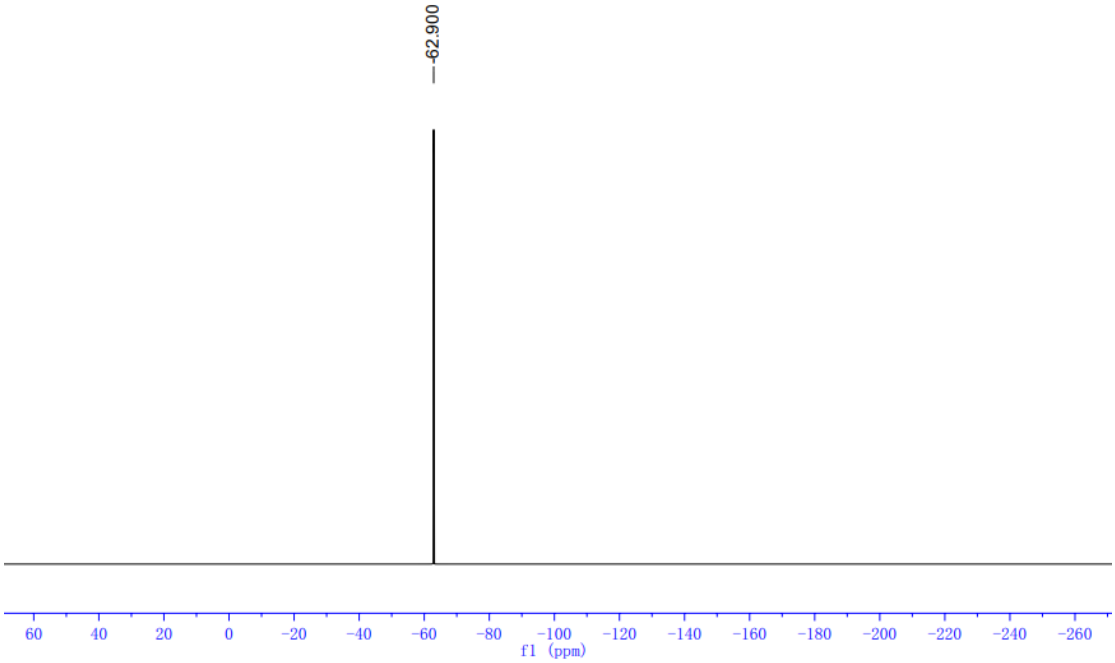

8.069
8.049
7.972
7.951
7.179
7.159
7.138
7.052
7.034
7.016
6.996
6.902
6.855
6.838
6.547
2.190
1.270
1.00
1.00
1.04
2.10
1.00
1.02
0.96
3.05
9.14
f1 (ppm)

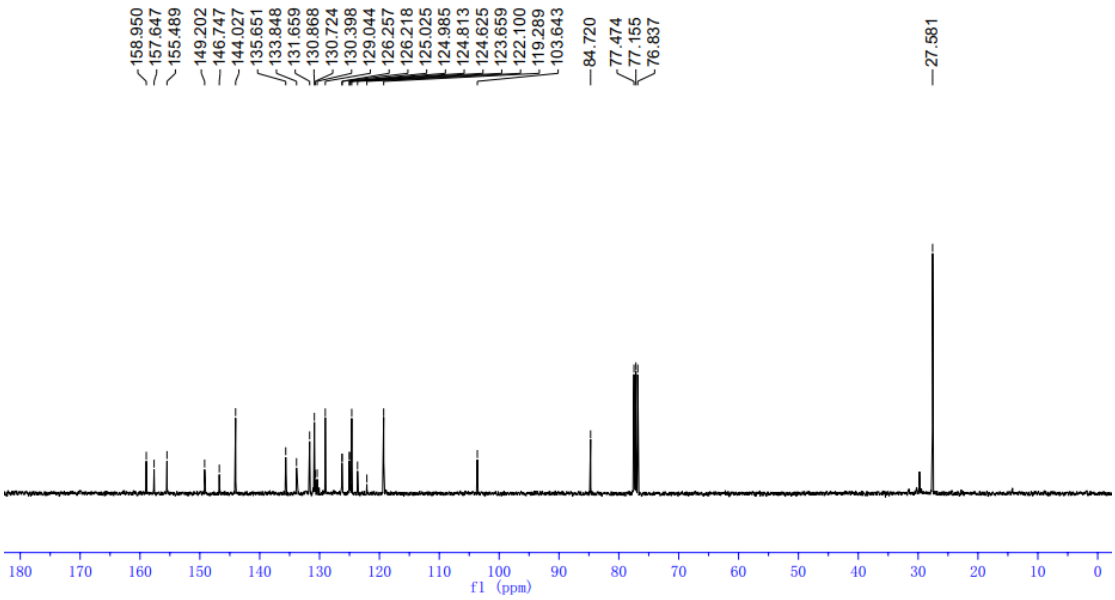

159.509
157.917
157.177
148.948
146.480
143.921
138.068
134.885
134.646
130.499
130.213
128.818
128.041
124.944
124.592
124.425
118.717
104.019
84.355
77.477
77.159
76.842
27.621
21.311
f1 (ppm)

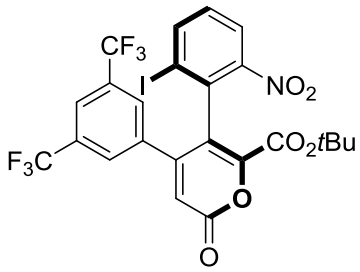

I
NO2
CO2tBu
F3C
O
O

3ac

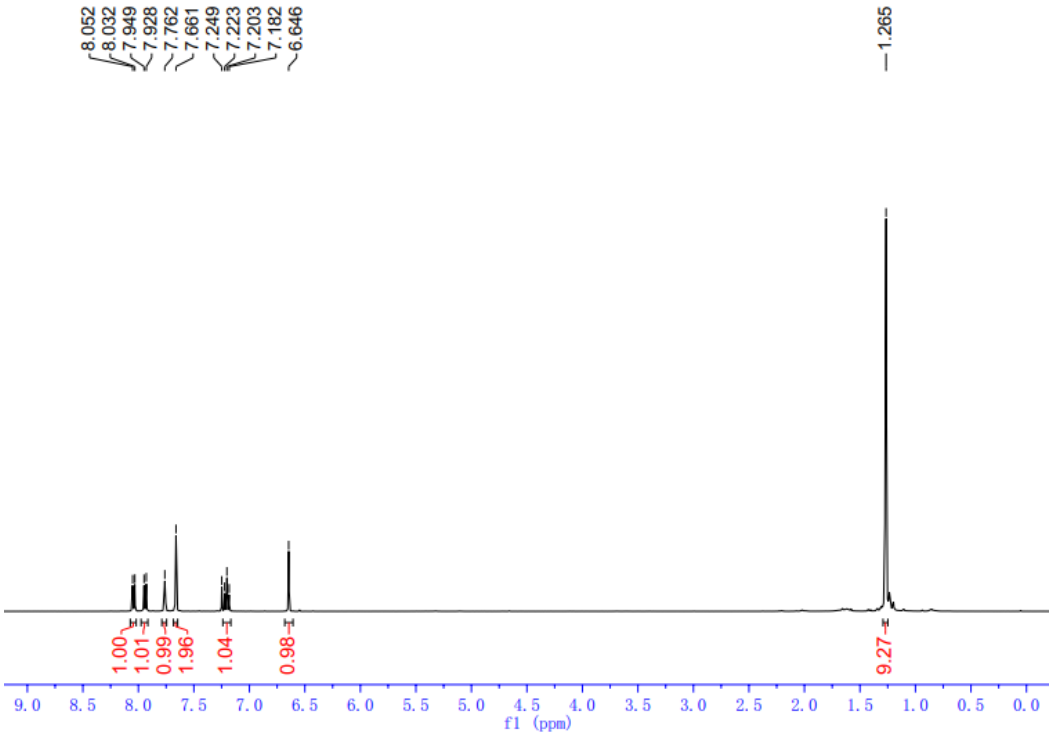

8.064
8.044
7.962
7.942
7.523
7.504
7.405
7.386
7.370
7.351
7.332
7.260
7.205
7.184
7.164
6.604
1.269
1.00
0.99
1.05
3.17
1.04
0.98
9.45
f1 (ppm)

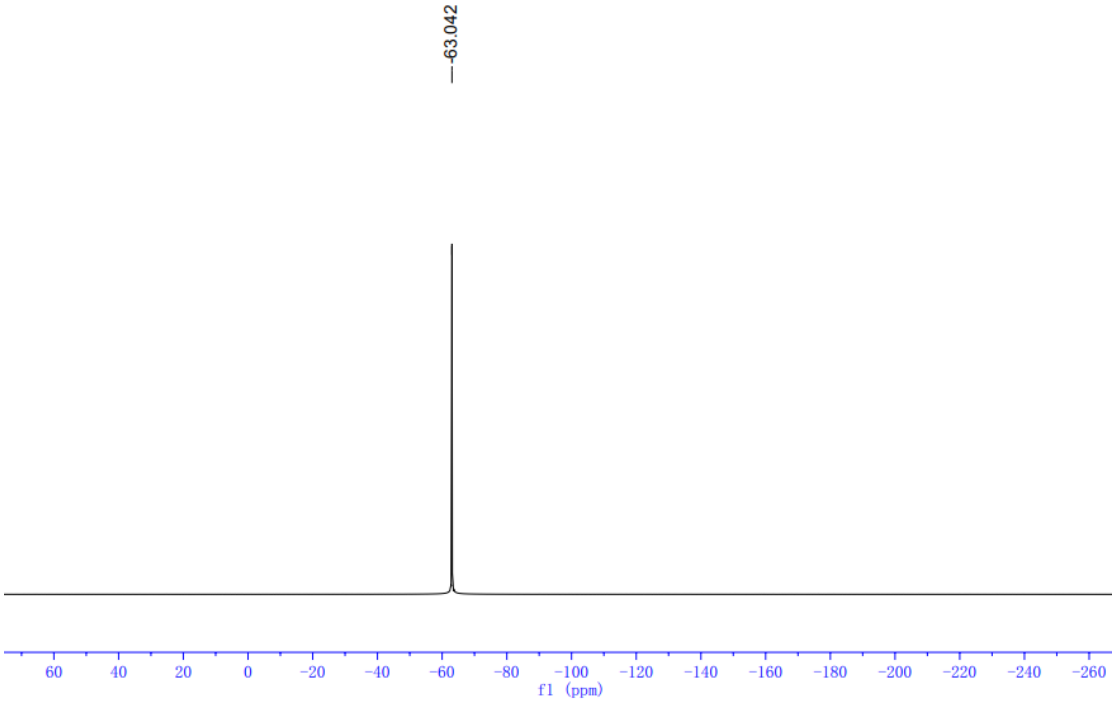

-62.900
60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)

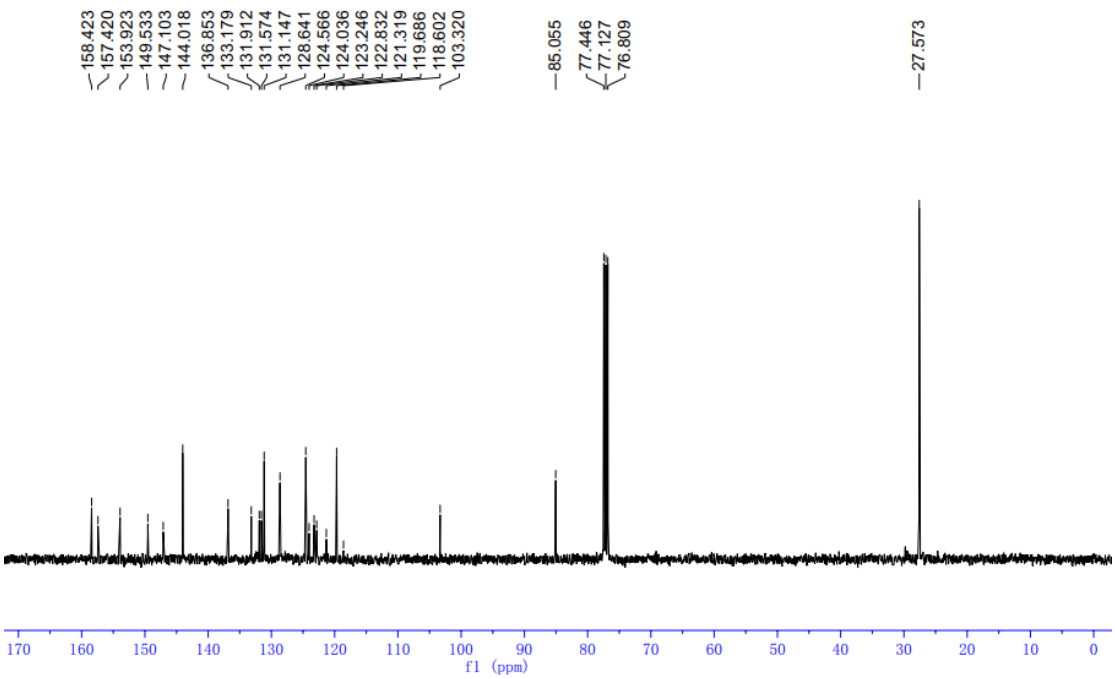

158.950
157.647
155.489
149.202
146.747
144.027
135.651
133.848
131.659
130.868
130.724
130.398
129.044
126.257
126.218
125.025
124.985
124.813
124.625
123.659
122.100
119.289
103.643
84.720
77.474
77.155
76.837
27.581
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CF3
I
NO2
CO2tBu
F3C
O
O

3ad


8.052
8.032
7.949
7.928
7.762
7.661
7.249
7.223
7.203
7.182
6.646
1.265
1.00
1.01
0.99
1.96
1.04
0.98
9.27
f1 (ppm)


-63.042
f1 (ppm)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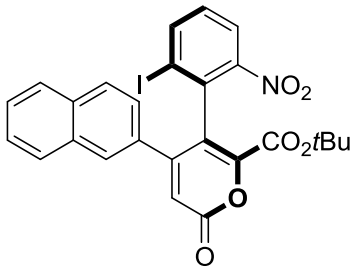
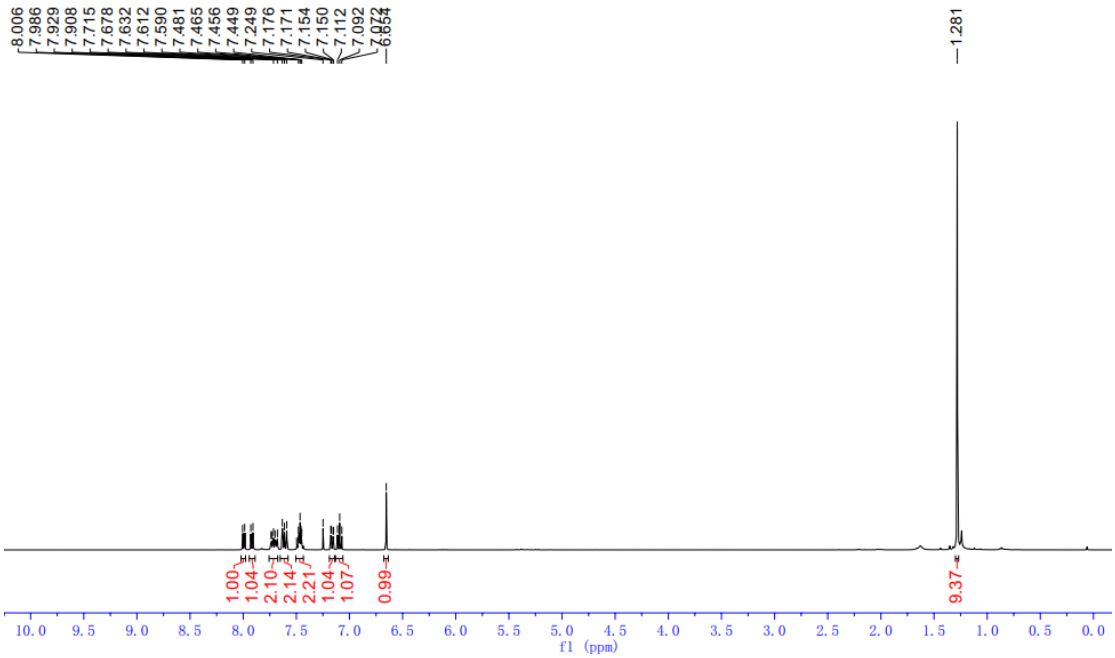
157.420
153.923
149.533
147.103
144.018
136.853
133.179
131.912
131.574
131.147
128.641
124.566
124.036
123.246
122.832
121.319
119.686
118.602
103.320
85.055
77.446
77.127
76.809
27.573
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


I
NO2
CO2tBu
O
O

3ae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7.986
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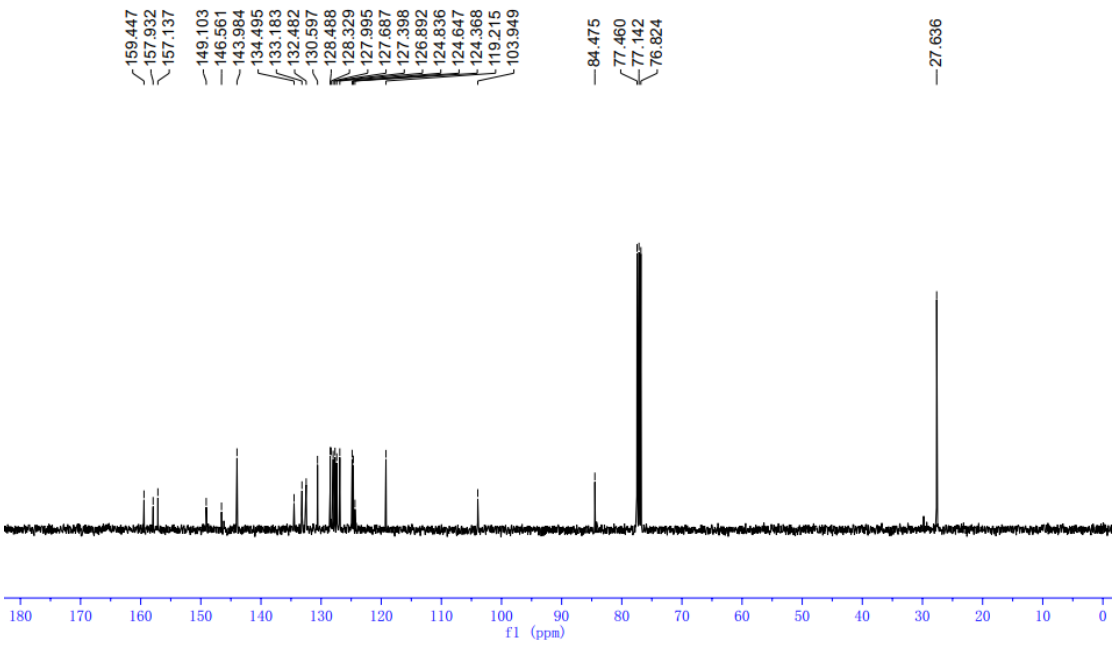
7.908
7.715
7.678
7.632
7.612
7.590
7.481
7.465
7.456
7.449
7.249
7.176
7.171
7.154
7.150
7.112
7.092
7.072
6.654
1.281
1.00
1.04
2.10
2.14
2.21
1.04
1.07
0.99
9.37
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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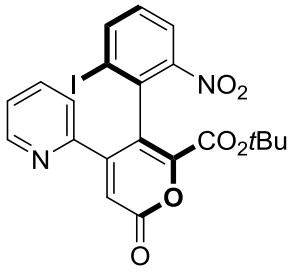
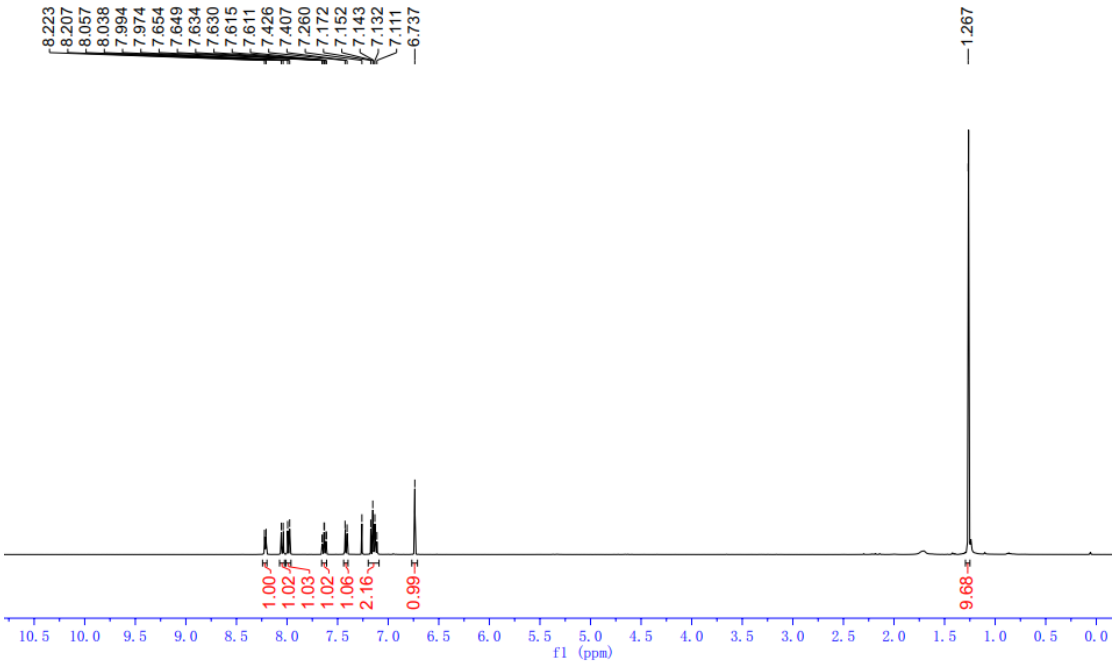
157.137
149.103
146.561
143.984
134.495
133.183
132.482
130.597
128.488
128.329
127.995
127.687
127.398
126.892
124.836
124.647
124.368
119.215
103.949
84.475
77.460
77.142
76.824
27.636
f1 (ppm)


I
NO2
CO2tBu
N
O
O

3af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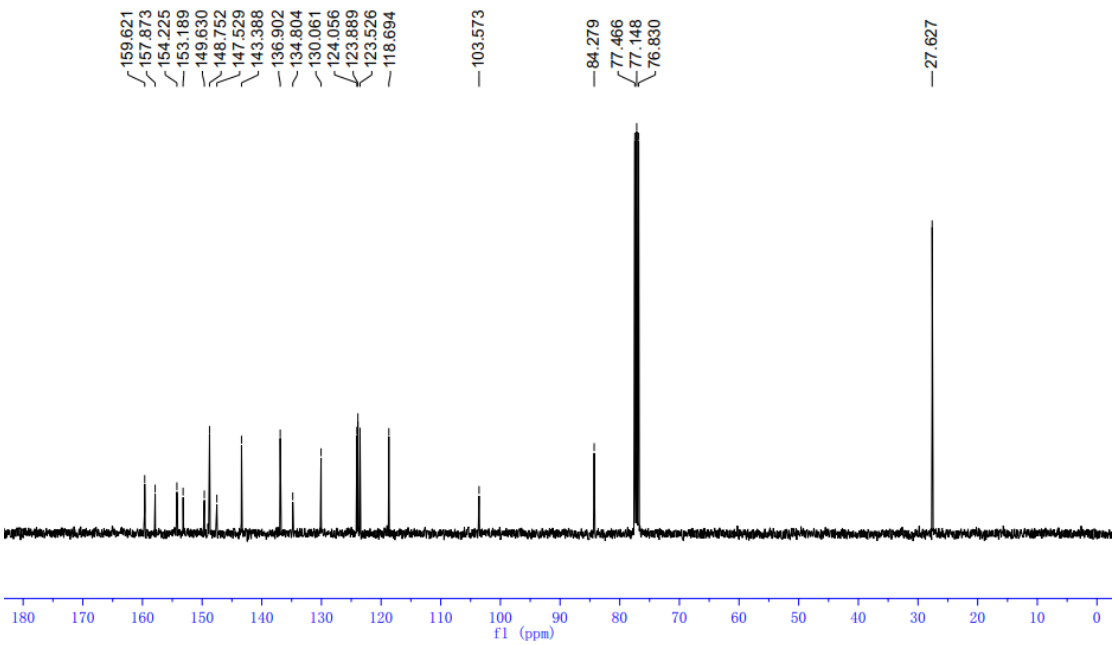
8.207
8.057
8.038
7.994
7.974
7.654
7.649
7.634
7.630
7.615
7.611
7.426
7.407
7.260
7.172
7.152
7.143
7.132
7.111
6.737
1.267
1.00
1.02
1.03
1.02
1.06
2.16
0.99
9.68
f1 (ppm)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153.189
149.630
148.752
147.529
143.388
136.902
134.804
130.061
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123.526
118.694
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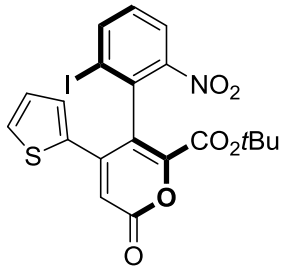
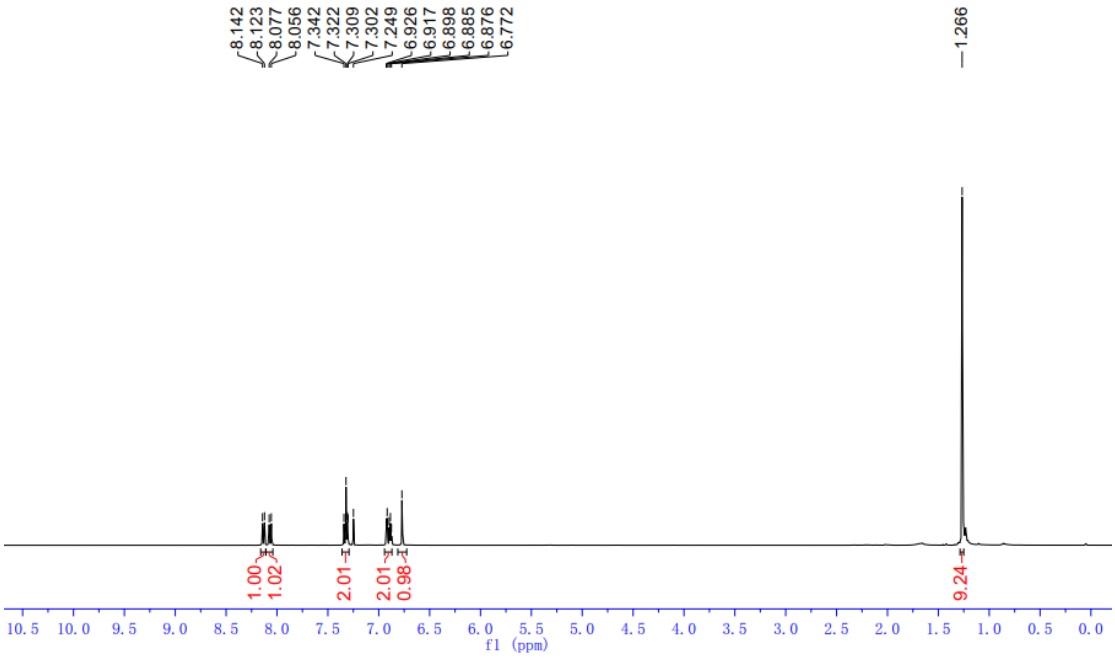
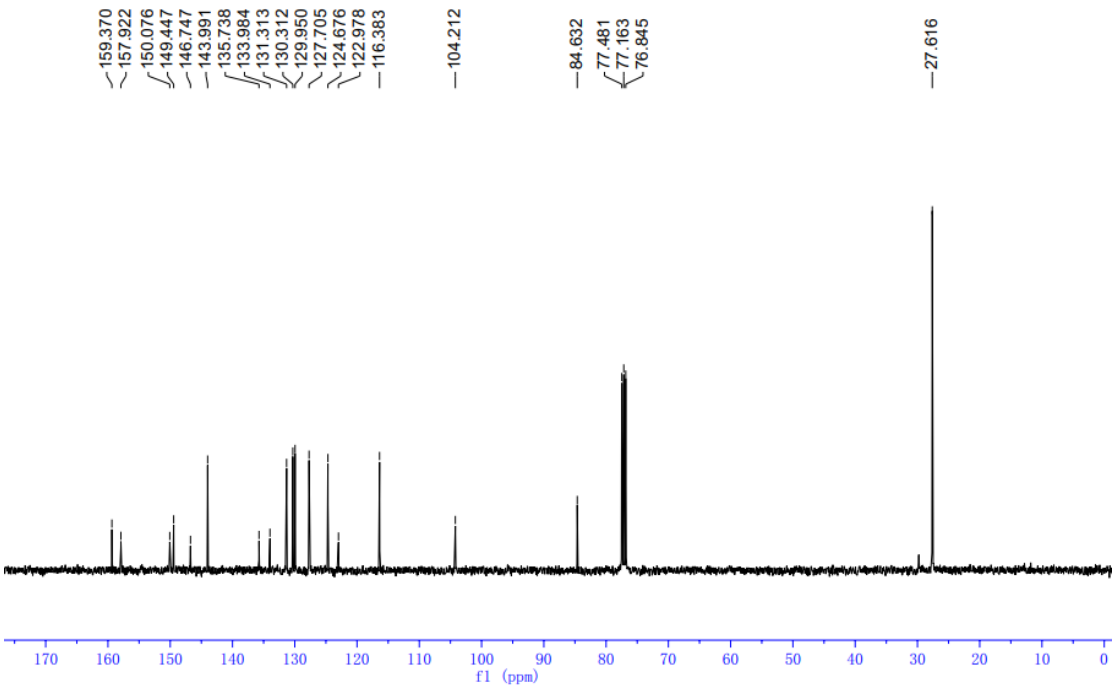
77.466
77.148
76.830
27.627
f1 (ppm)


I
NO2
CO2tBu
S
O
O

3ag


8.142
8.123
8.077
8.056
7.342
7.322
7.309
7.302
7.249
6.926
6.917
6.898
6.885
6.876
6.772
1.266
1.00
1.02
2.01
2.01
0.98
9.24
f1 (ppm)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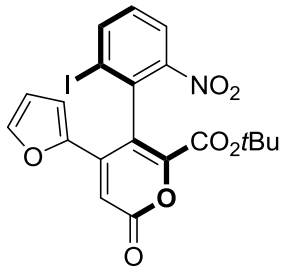
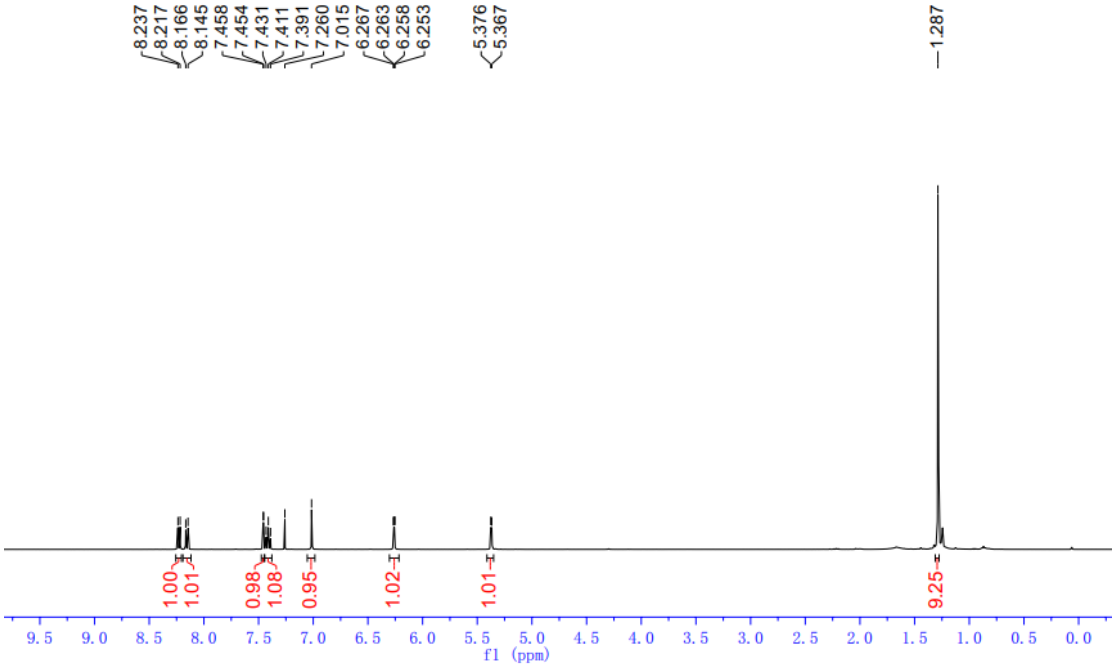
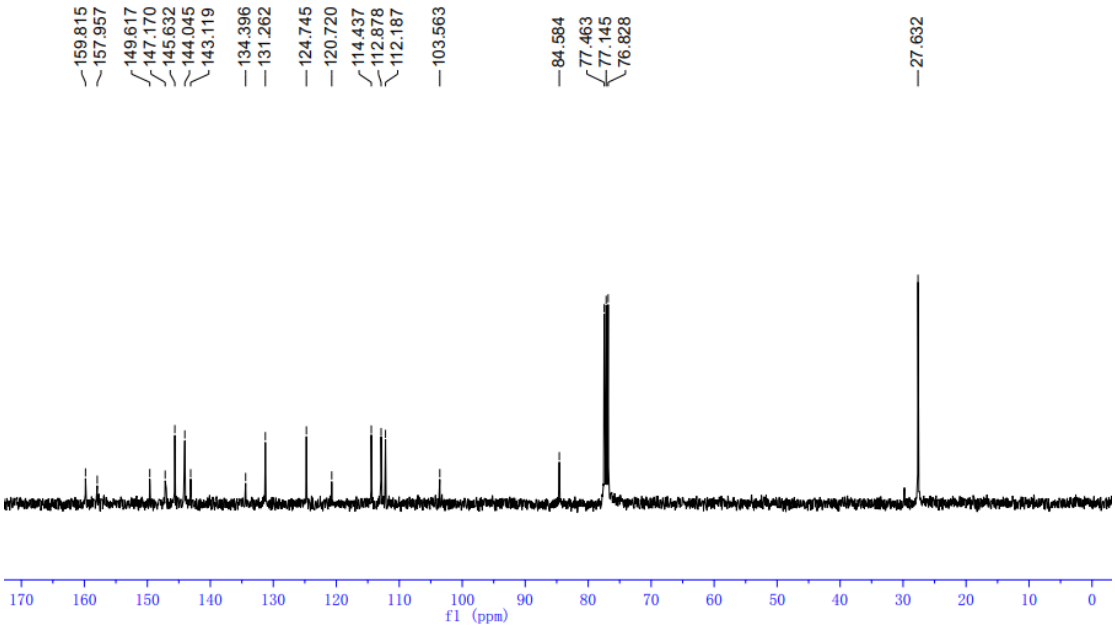
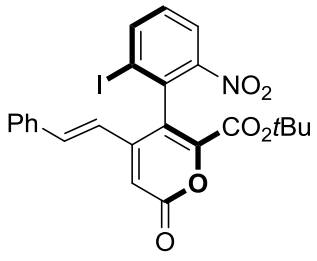
149.447
146.747
143.991
135.738
133.984
131.313
130.312
129.950
127.705
124.676
122.978
116.383
104.212
84.632
77.481
77.163
76.845
27.616
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


I
NO2
CO2tBu
O
O
O

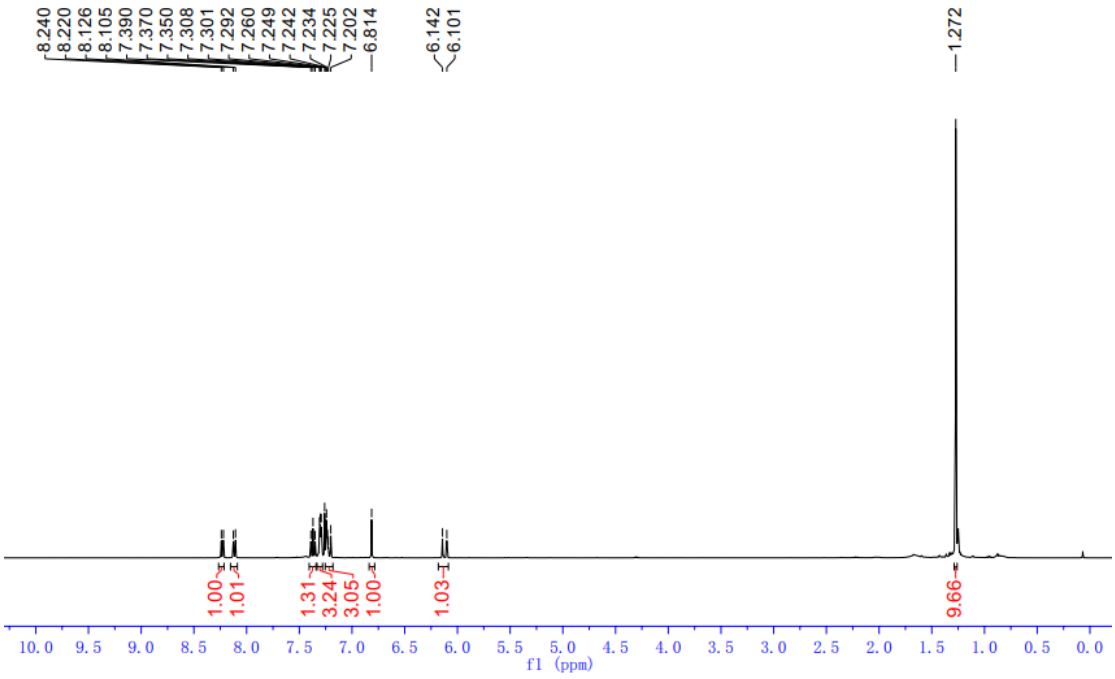
3ah


8.237
8.217
8.166
8.145
7.458
7.454
7.431
7.411
7.391
7.260
7.015
6.267
6.263
6.258
6.253
5.376
5.367
1.287
1.00
1.01
0.98
1.08
0.95
1.02
1.01
9.25
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)


159.815
157.957
149.617
147.170
145.632
144.045
143.119
134.396
131.262
124.745
120.720
114.437
112.878
112.187
103.563
84.584
77.463
77.145
76.828
27.632
f1 (ppm)


I
NO2
Ph
CO2tBu
O
O

3ai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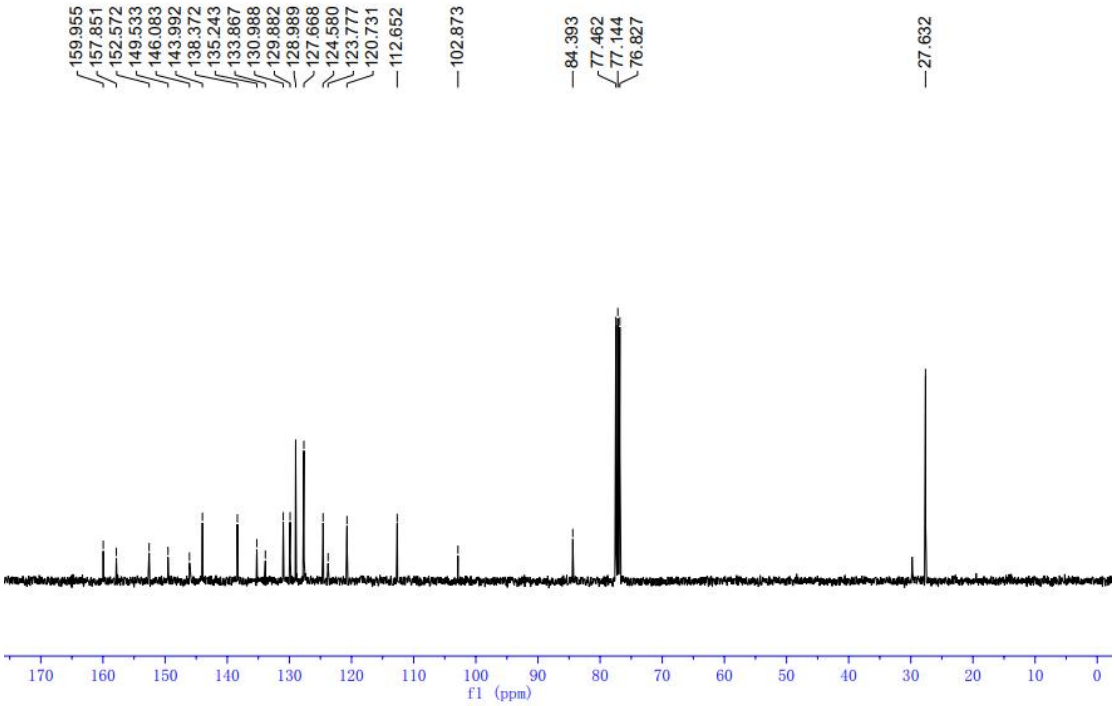
8.105
7.390
7.370
7.350
7.308
7.301
7.292
7.260
7.249
7.242
7.234
7.225
7.202
6.814
6.142
6.101
1.272
1.00
1.01
1.31
3.24
3.05
1.00
1.03
9.66
f1 (ppm)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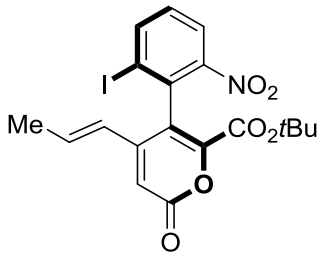
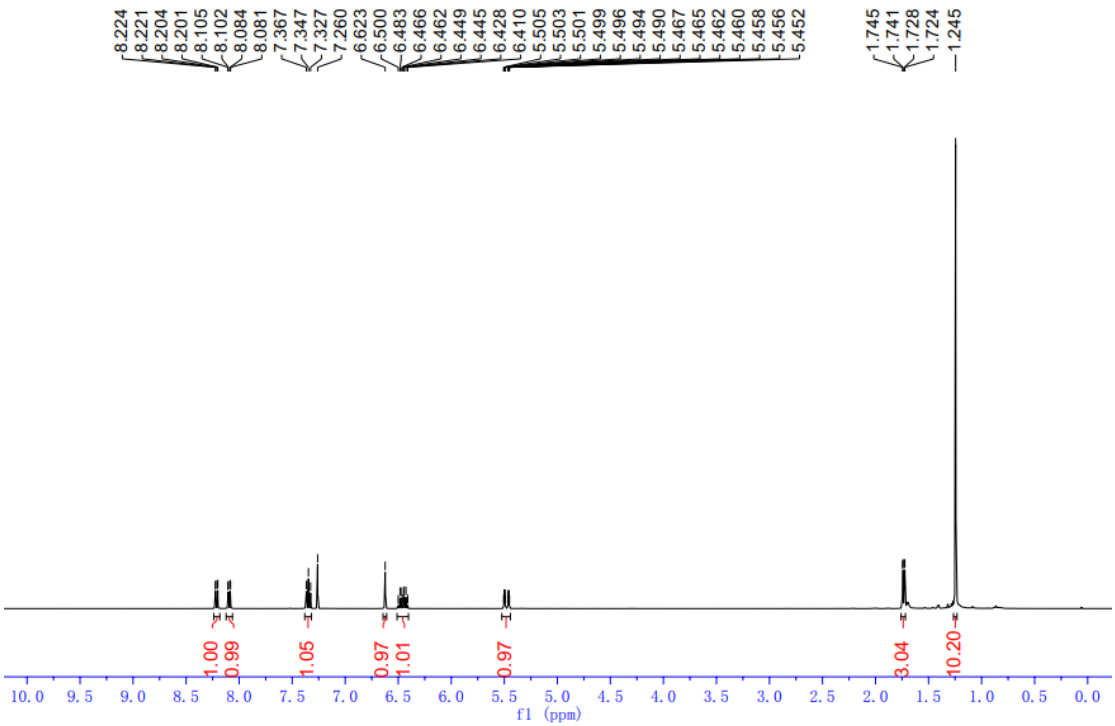
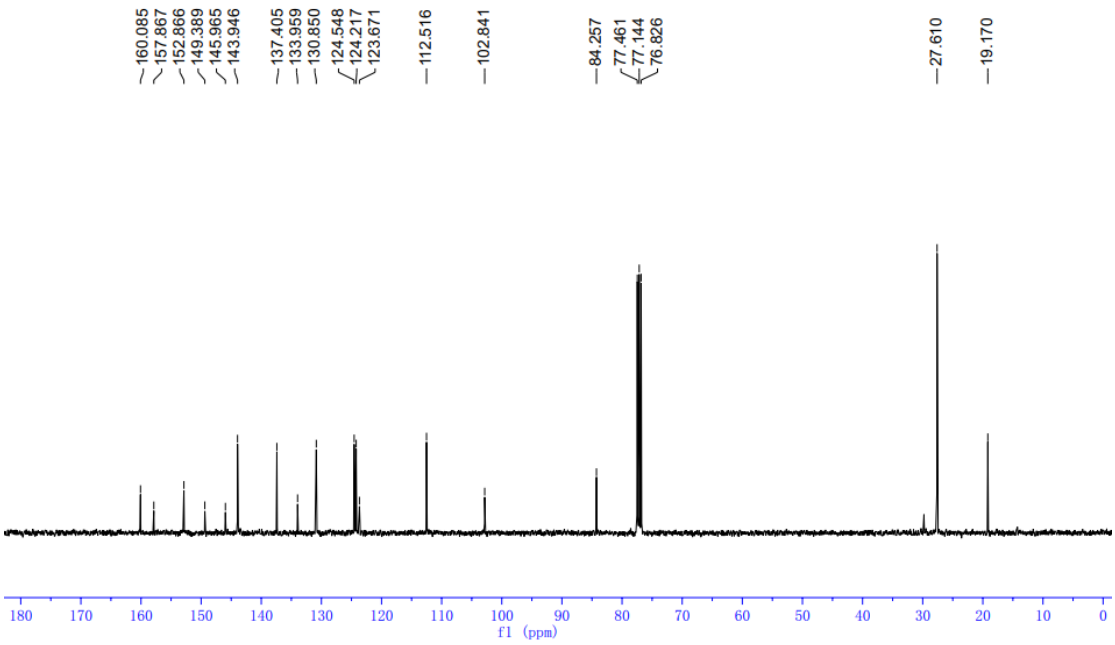
157.851
152.572
149.533
146.083
143.992
138.372
135.243
133.867
130.988
129.882
128.989
127.668
124.580
123.777
120.731
112.652
102.873
84.393
77.462
77.144
76.827
27.632
f1 (ppm)


I
NO2
Me
CO2tBu
O
O

3aj


8.224
8.221
8.204
8.201
8.105
8.102
8.084
8.081
7.367
7.347
7.327
7.260
6.623
6.500
6.483
6.466
6.462
6.449
6.445
6.428
6.410
5.505
5.503
5.501
5.499
5.496
5.494
5.490
5.467
5.465
5.462
5.460
5.458
5.456
5.452
1.745
1.741
1.728
1.724
1.245
1.00
0.99
1.05
0.97
1.01
0.97
3.04
10.20
f1 (ppm)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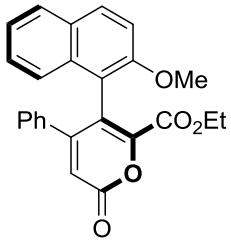
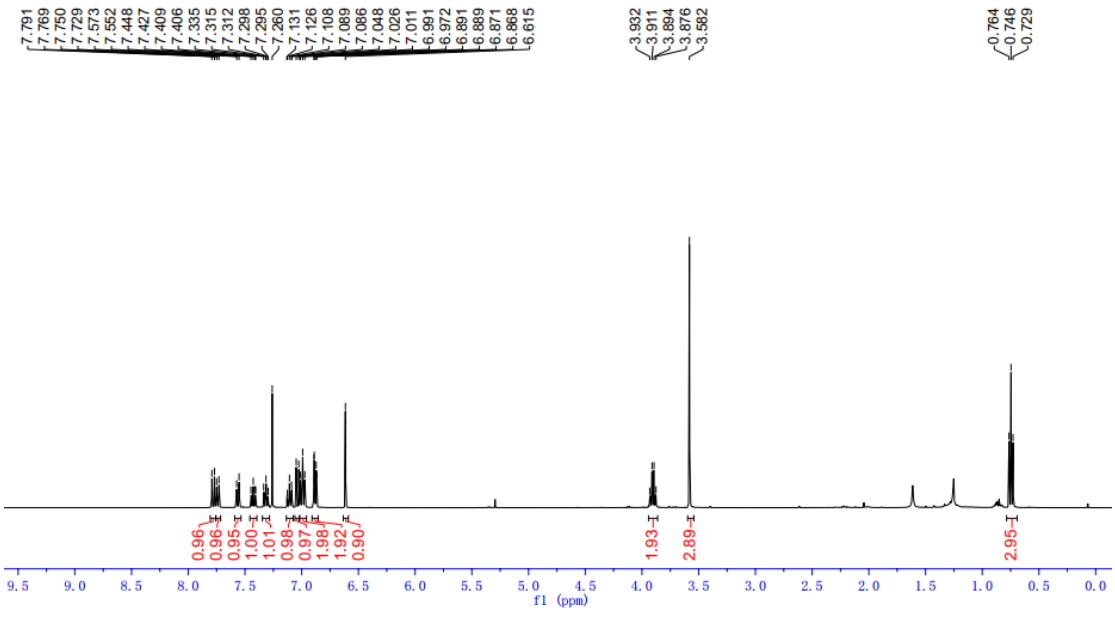
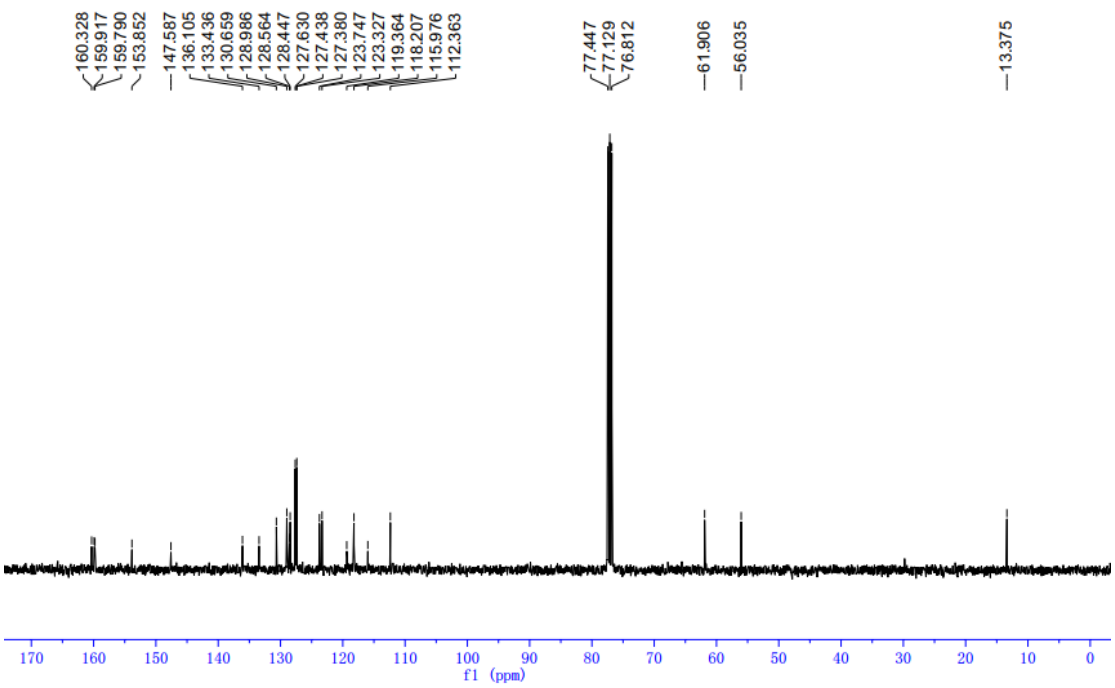
157.867
152.866
149.389
145.965
143.946
137.405
133.959
130.850
124.548
124.217
123.671
112.516
102.841
84.257
77.461
77.144
76.826
27.610
19.170
f1 (ppm)


OMe
Ph
CO2Et
O
O

3ak


7.791
7.769
7.750
7.729
7.573
7.552
7.448
7.427
7.409
7.406
7.335
7.315
7.312
7.298
7.295
7.260
7.131
7.126
7.108
7.089
7.086
7.048
7.026
7.011
6.991
6.972
6.891
6.889
6.871
6.868
6.615
3.932
3.911
3.894
3.876
3.582
0.764
0.746
0.729
0.96
0.96
0.95
1.00
1.01
0.98
0.97
1.98
1.92
0.90
1.93
2.89
2.95
f1 (ppm)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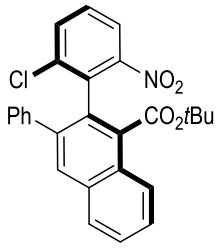
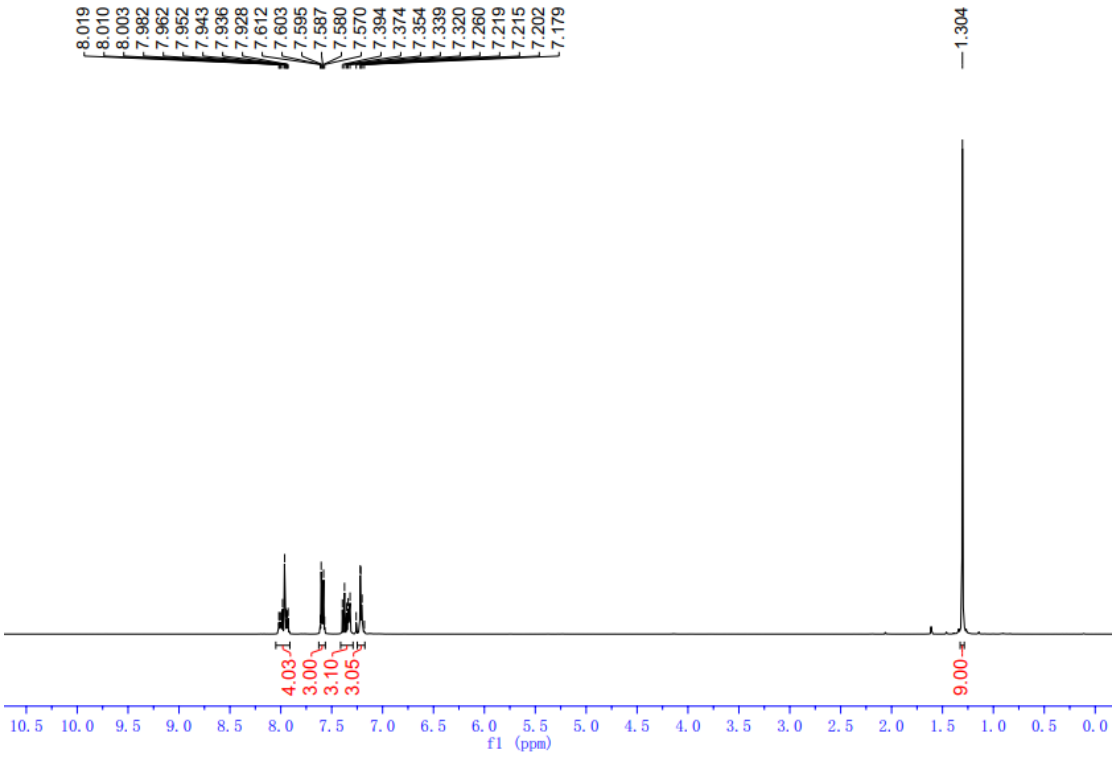
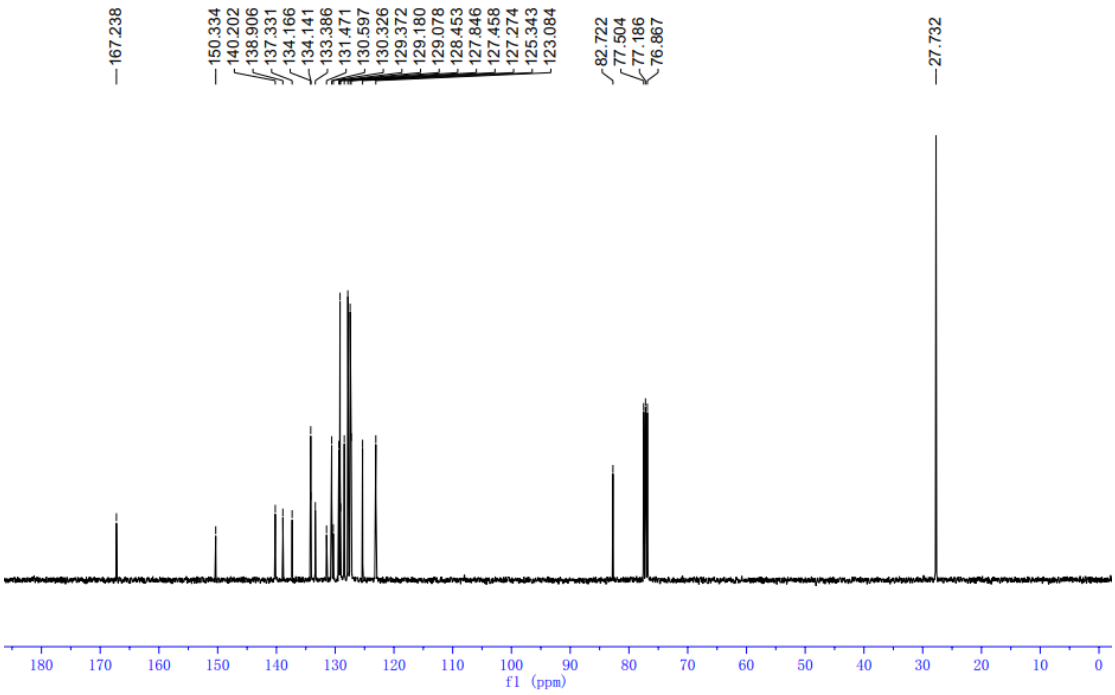
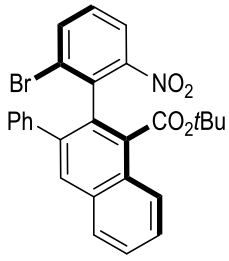
159.790
153.852
147.587
136.105
133.436
130.659
128.986
128.564
128.447
127.630
127.438
127.380
123.747
123.327
119.364
118.207
115.976
112.363
77.447
77.129
76.812
61.906
56.035
13.375
f1 (ppm)


Cl
NO2
Ph
CO2tBu

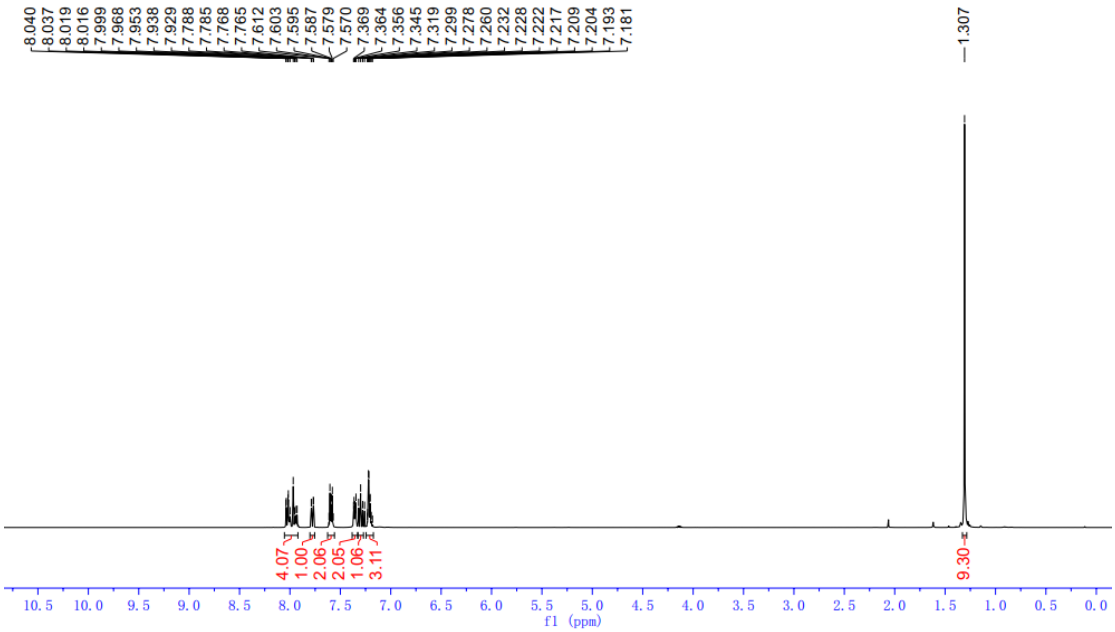
6a

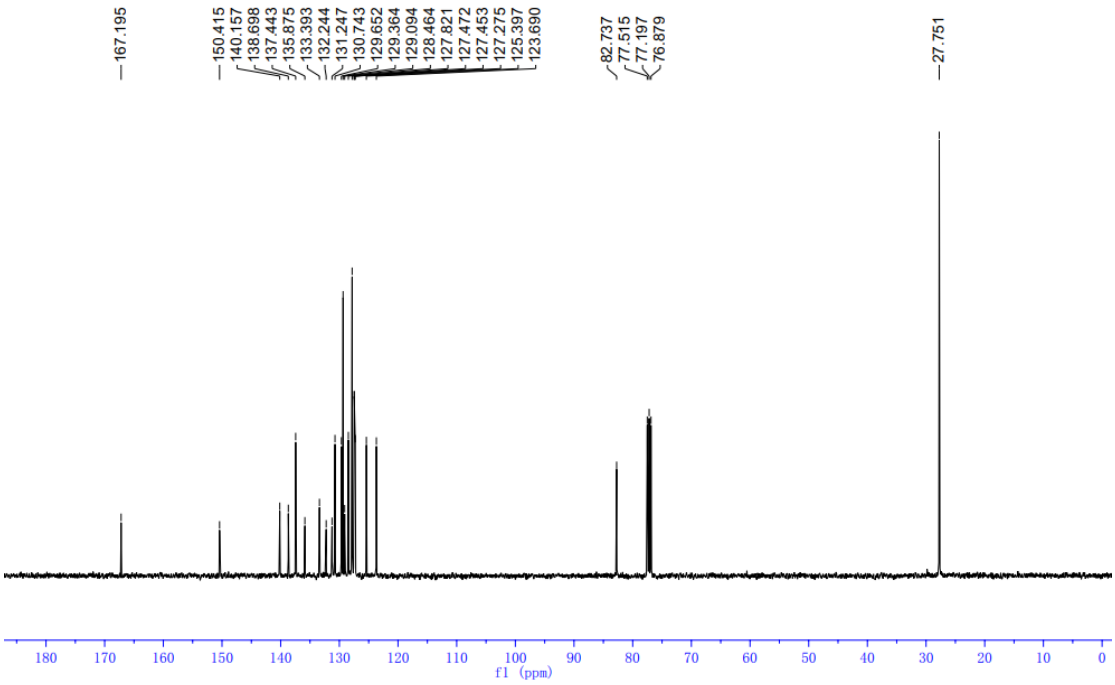

8.019
8.010
8.003
7.982
7.962
7.952
7.943
7.936
7.928
7.612
7.603
7.595
7.587
7.580
7.570
7.394
7.374
7.354
7.339
7.320
7.260
7.219
7.215
7.202
7.179
1.304
4.03
3.00
3.10
3.05
9.00
f1 (ppm)


167.238
150.334
140.202
138.906
137.331
134.166
134.141
133.386
131.471
130.597
130.326
129.372
129.180
129.078
128.453
127.846
127.458
127.274
125.343
123.084
82.722
77.504
77.186
76.867
27.732
f1 (ppm)


Br
NO2
Ph
CO2tBu

6b


8.040
8.037
8.019
8.016
7.999
7.968
7.953
7.938
7.929
7.788
7.785
7.768
7.765
7.612
7.603
7.595
7.587
7.579
7.570
7.369
7.364
7.356
7.345
7.319
7.299
7.278
7.260
7.232
7.228
7.222
7.217
7.209
7.204
7.193
7.181
1.307
4.07
1.00
2.06
2.05
1.06
3.11
9.30
f1 (ppm)


167.195
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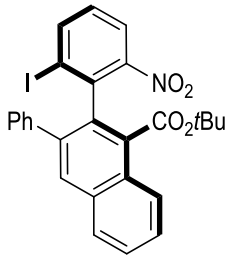
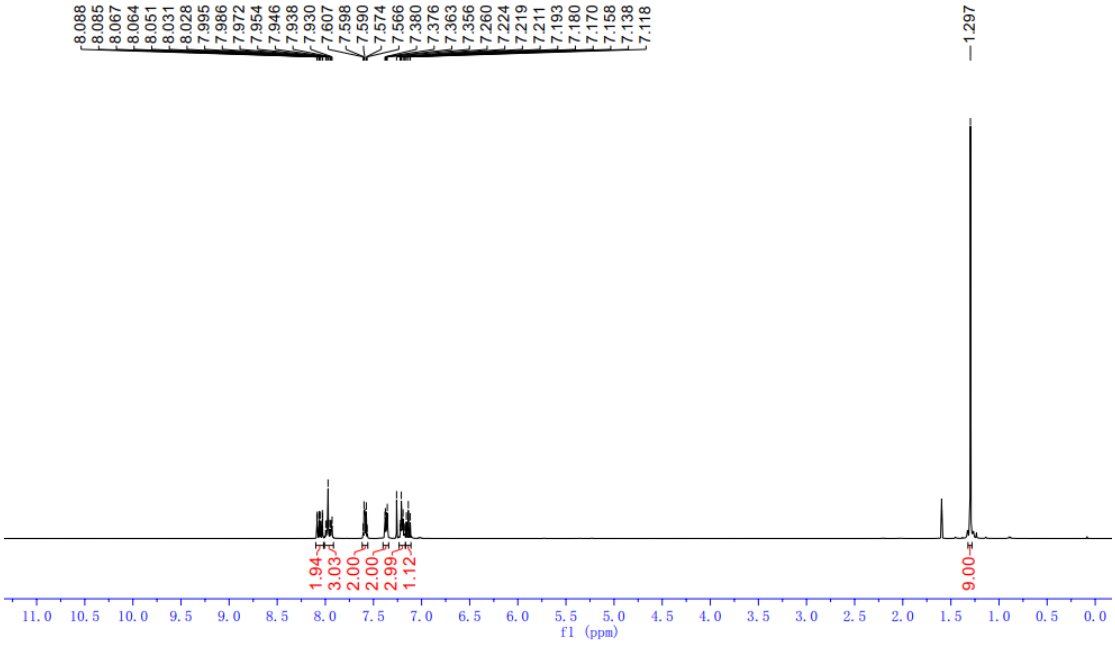
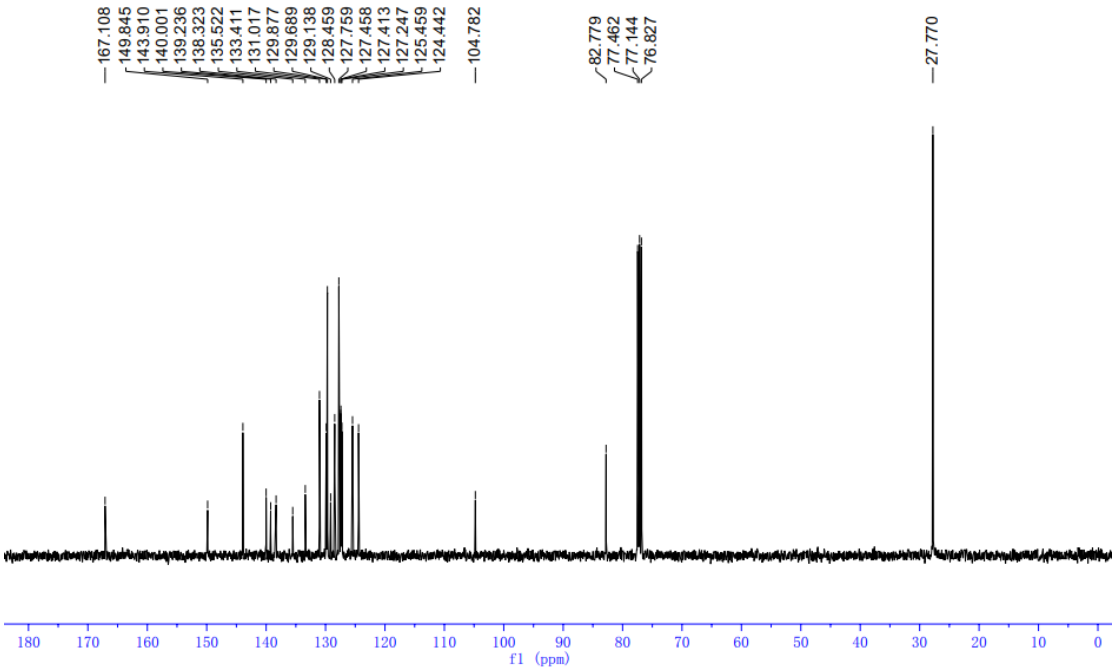
140.157
138.698
137.443
135.875
133.393
132.244
131.247
130.743
129.652
129.364
129.094
128.464
127.821
127.472
127.453
127.275
125.397
123.690
82.737
77.515
77.197
76.879
27.751
f1 (ppm)


I
NO2
Ph
CO2tBu

6c


8.088
8.085
8.067
8.064
8.051
8.031
8.028
7.995
7.986
7.972
7.954
7.946
7.938
7.930
7.607
7.598
7.590
7.574
7.566
7.380
7.376
7.363
7.356
7.260
7.224
7.219
7.211
7.193
7.180
7.170
7.158
7.138
7.118
1.297
1.94
3.03
2.00
2.00
2.99
1.12
9.00
f1 (ppm)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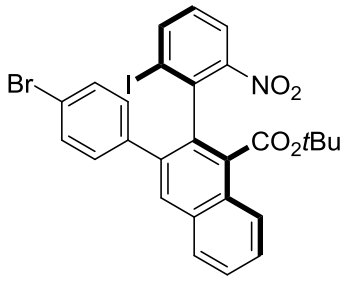
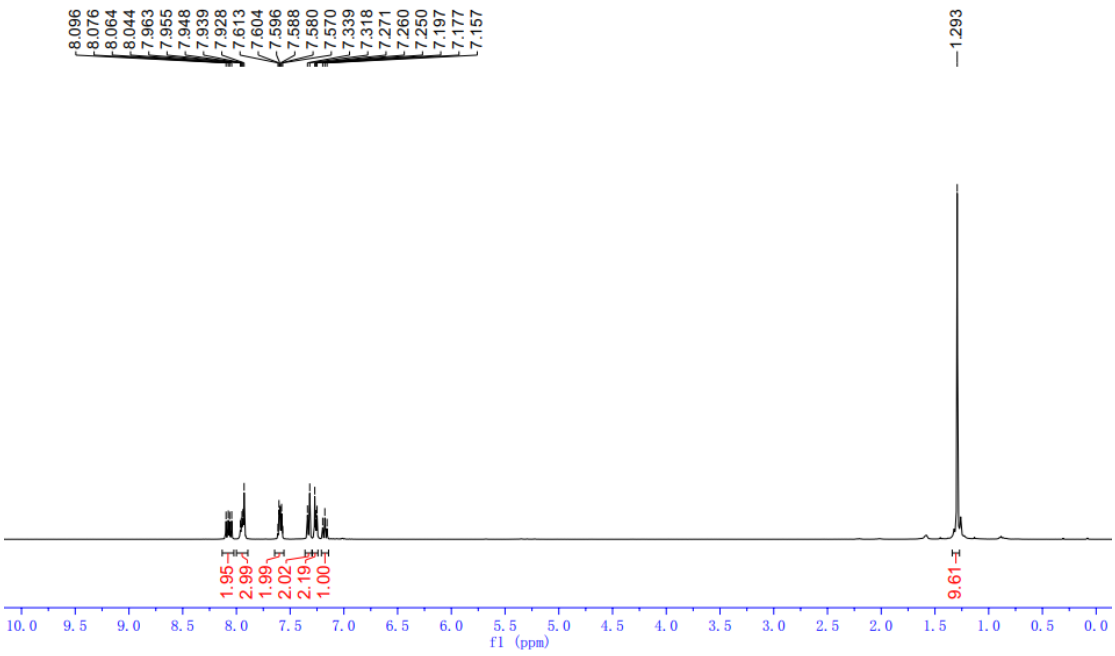
149.845
143.910
140.001
139.236
138.323
135.522
133.411
131.017
129.877
129.689
129.138
128.459
127.759
127.458
127.413
127.247
125.459
124.442
104.782
82.779
77.462
77.144
76.827
27.770
f1 (ppm)


Br
I
NO2
CO2tBu

6d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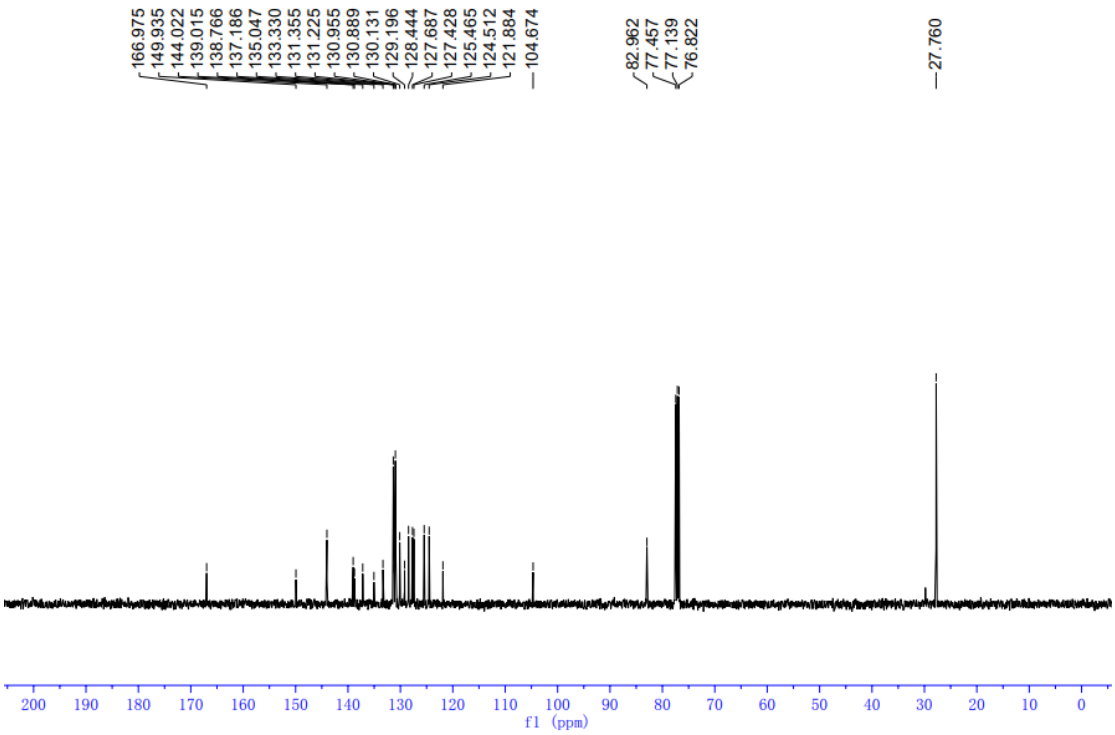
8.076
8.064
8.044
7.963
7.955
7.948
7.939
7.928
7.613
7.604
7.596
7.588
7.580
7.570
7.339
7.318
7.271
7.260
7.250
7.197
7.177
7.157
1.293
1.95
2.99
1.99
2.02
2.19
1.00
9.61
f1 (ppm)


166.975
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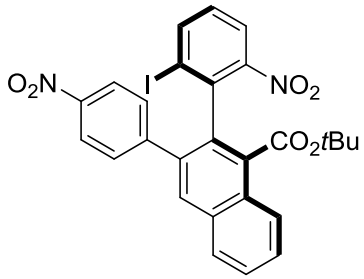
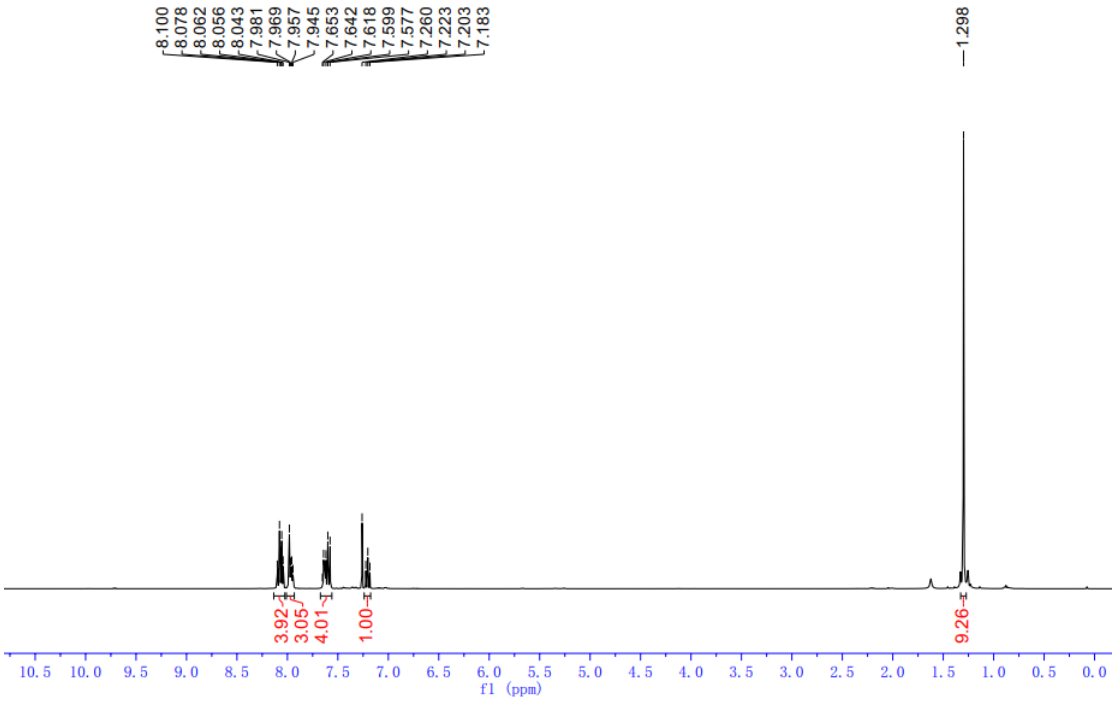
139.015
138.766
137.186
135.047
133.330
131.355
131.225
130.955
130.889
130.131
129.196
128.444
127.687
127.428
125.465
124.512
121.884
104.674
82.962
77.457
77.139
76.822
27.760
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O2N
I
NO2
CO2tBu

6e


8.100
8.078
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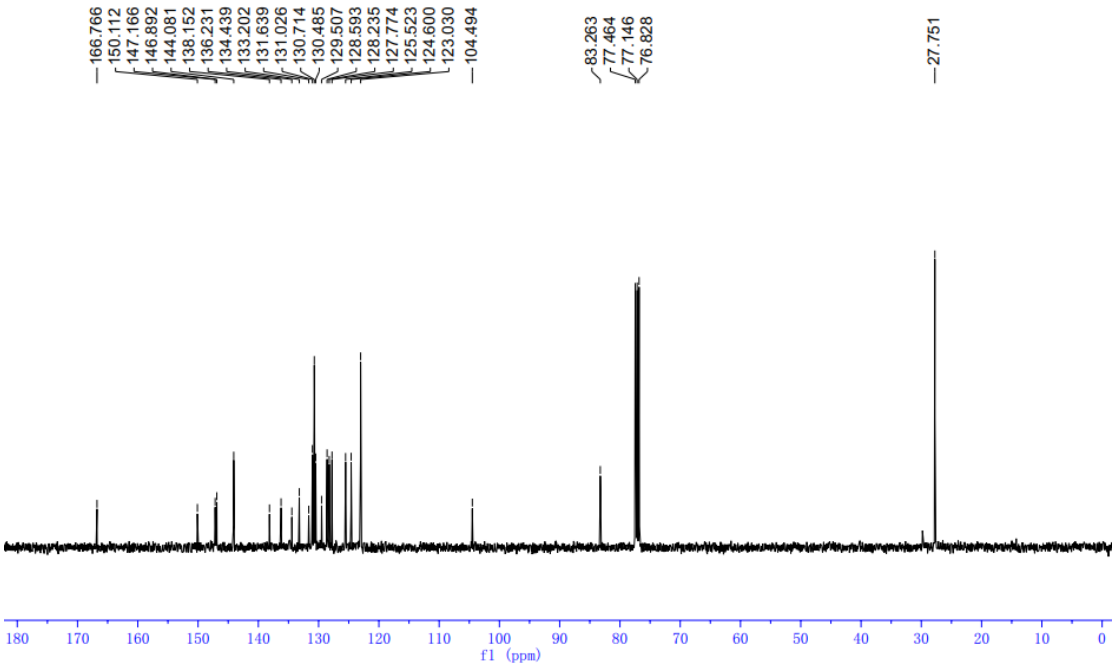
8.056
8.043
7.981
7.969
7.957
7.945
7.653
7.642
7.618
7.599
7.577
7.260
7.223
7.203
7.183
1.298
3.92
3.05
4.01
1.00
9.26
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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144.081
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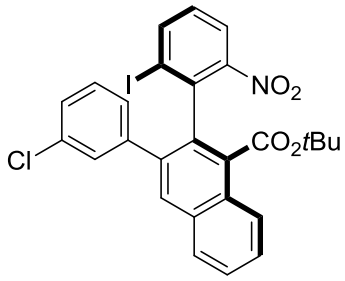
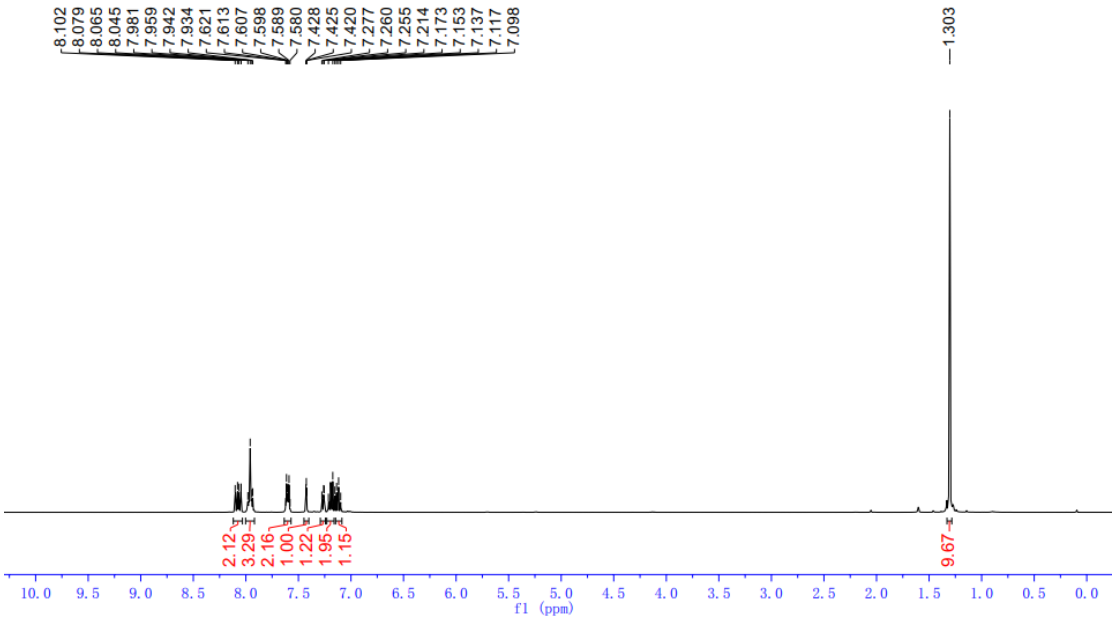
136.231
134.439
133.202
131.639
131.026
130.714
130.485
129.507
128.593
128.235
127.774
125.523
124.600
123.030
104.494
83.263
77.464
77.146
76.828
27.751
f1 (ppm)


I
NO2
Cl
CO2tBu

6f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7.959
7.942
7.934
7.621
7.613
7.607
7.598
7.589
7.580
7.428
7.425
7.420
7.277
7.260
7.255
7.214
7.173
7.153
7.137
7.117
7.098
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2.12
3.29
2.16
1.00
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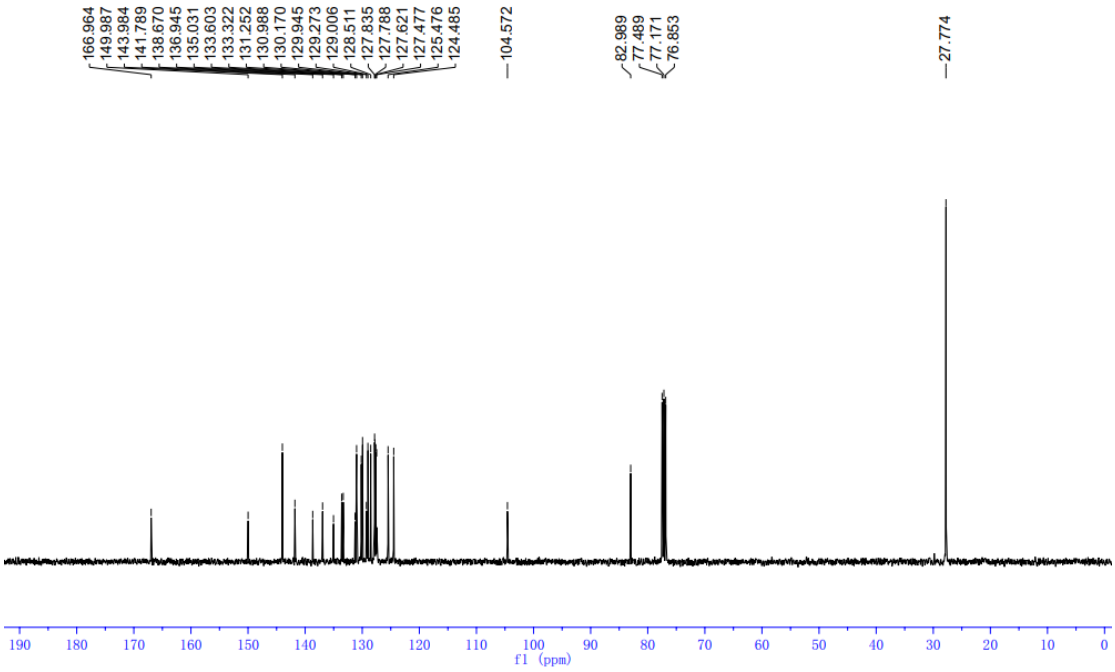
1.95
1.15
9.67
f1 (ppm)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133.322
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128.511
127.835
127.788
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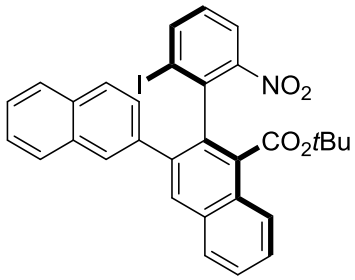
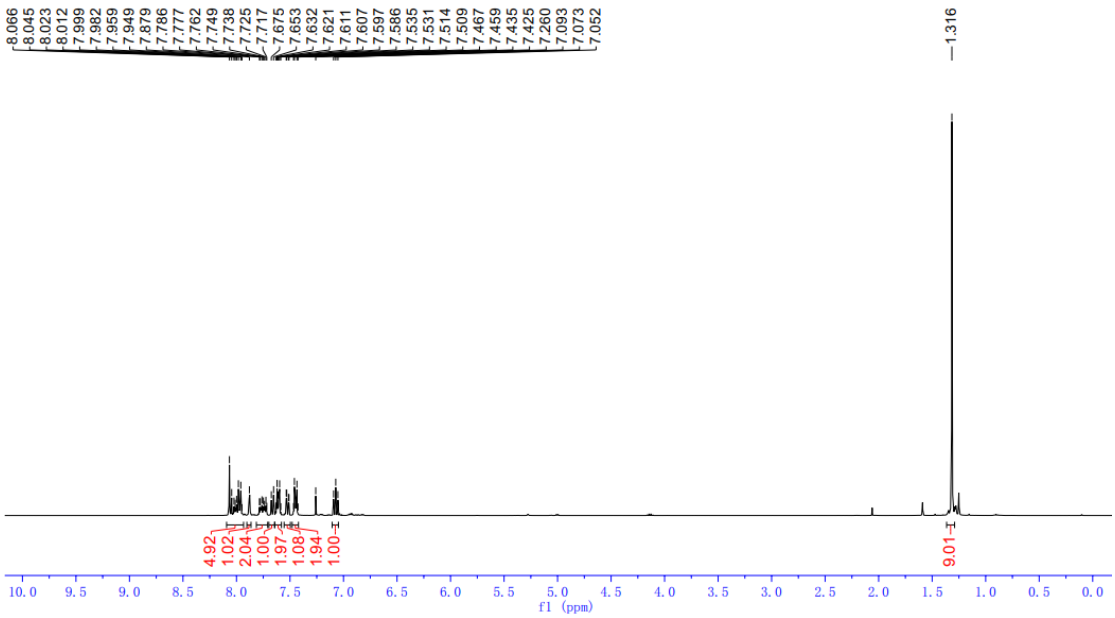
104.572
82.989
77.489
77.171
76.853
27.774
f1 (ppm)


NO2
CO2tBu

6g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8.012
7.999
7.982
7.959
7.949
7.879
7.786
7.777
7.762
7.749
7.738
7.725
7.717
7.675
7.653
7.632
7.621
7.611
7.607
7.597
7.586
7.535
7.531
7.514
7.509
7.467
7.459
7.435
7.425
7.260
7.093
7.073
7.052
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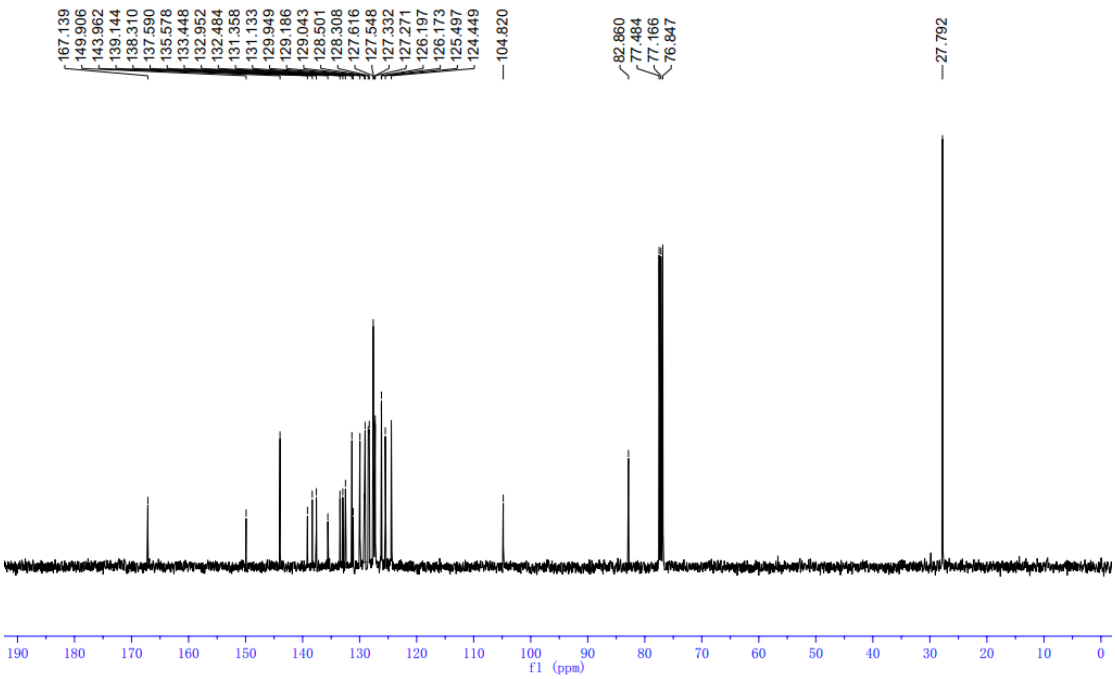
1.02
2.04
1.00
1.97
1.08
1.94
1.00
9.01
f1 (ppm)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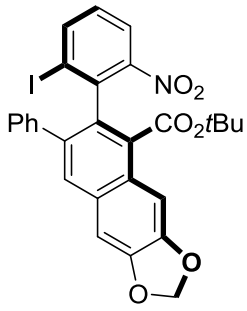
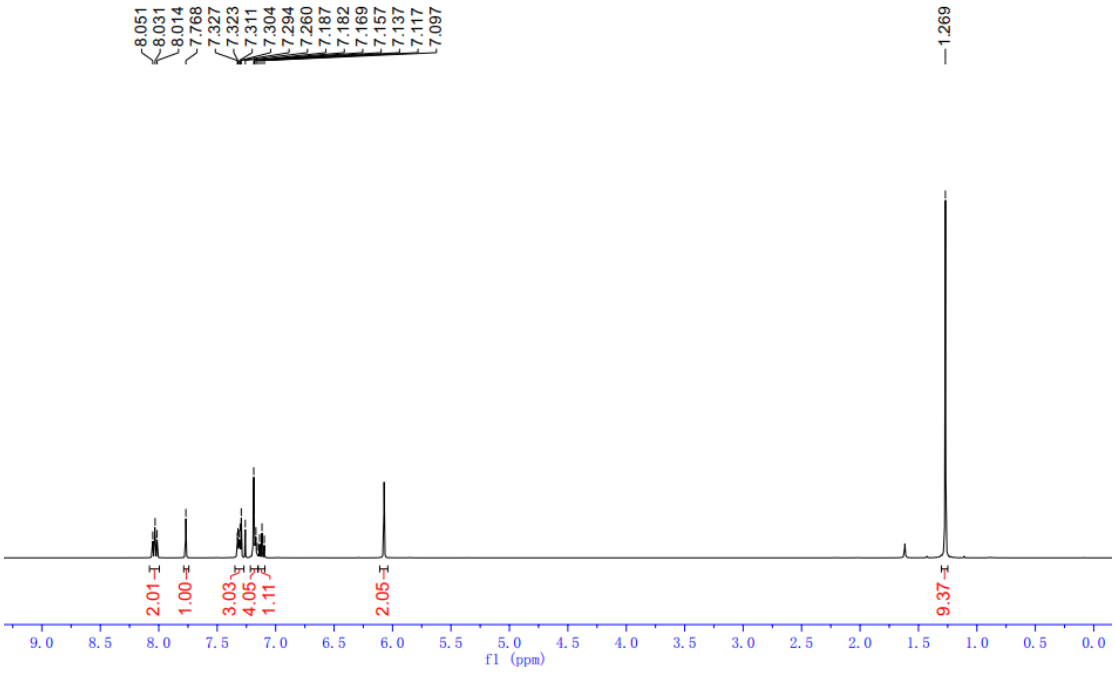
137.590
135.578
133.448
132.952
132.484
131.358
131.133
129.949
129.186
129.043
128.501
128.308
127.616
127.548
127.332
127.271
126.197
126.173
125.497
124.449
104.820
82.860
77.484
77.166
76.847
27.792
f1 (ppm)


I
NO2
Ph
CO2tBu
O
O

6h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8.031
8.014
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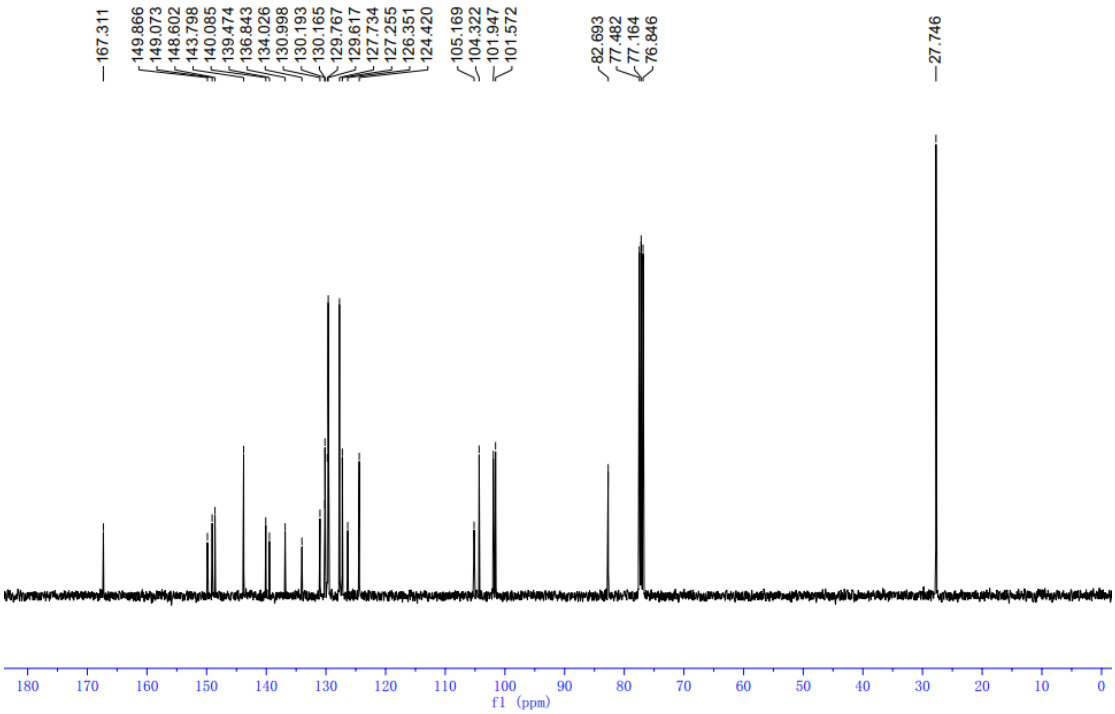
7.327
7.323
7.311
7.304
7.294
7.260
7.187
7.182
7.169
7.157
7.137
7.117
7.097
1.269
2.01
1.00
3.03
4.05
1.11
2.05
9.37
f1 (ppm)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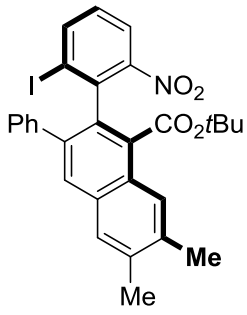
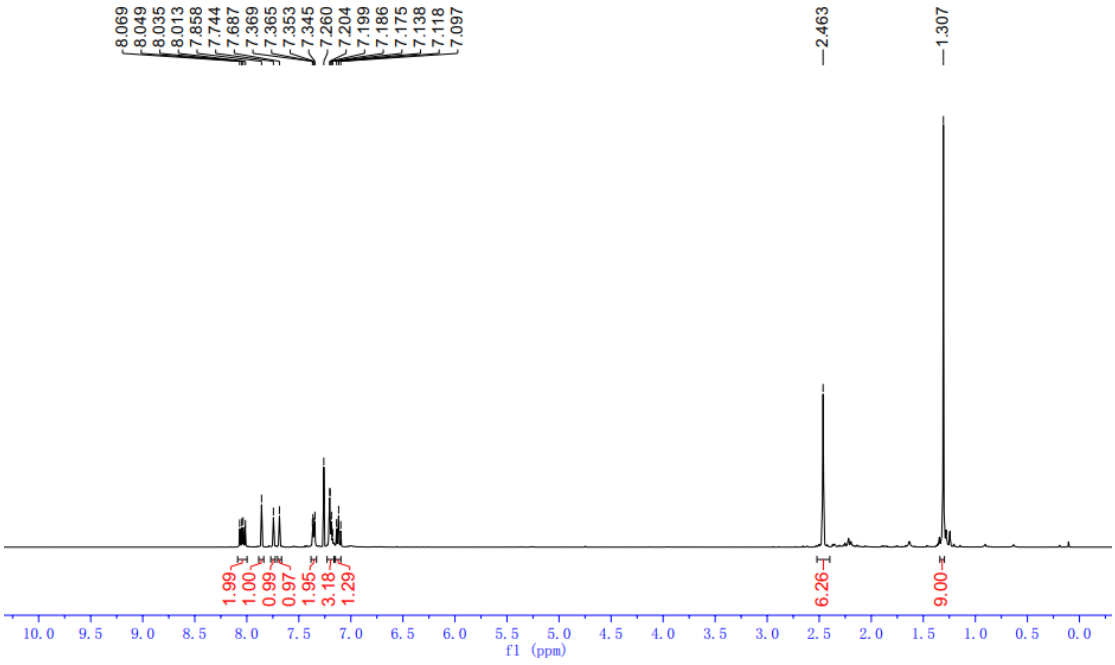
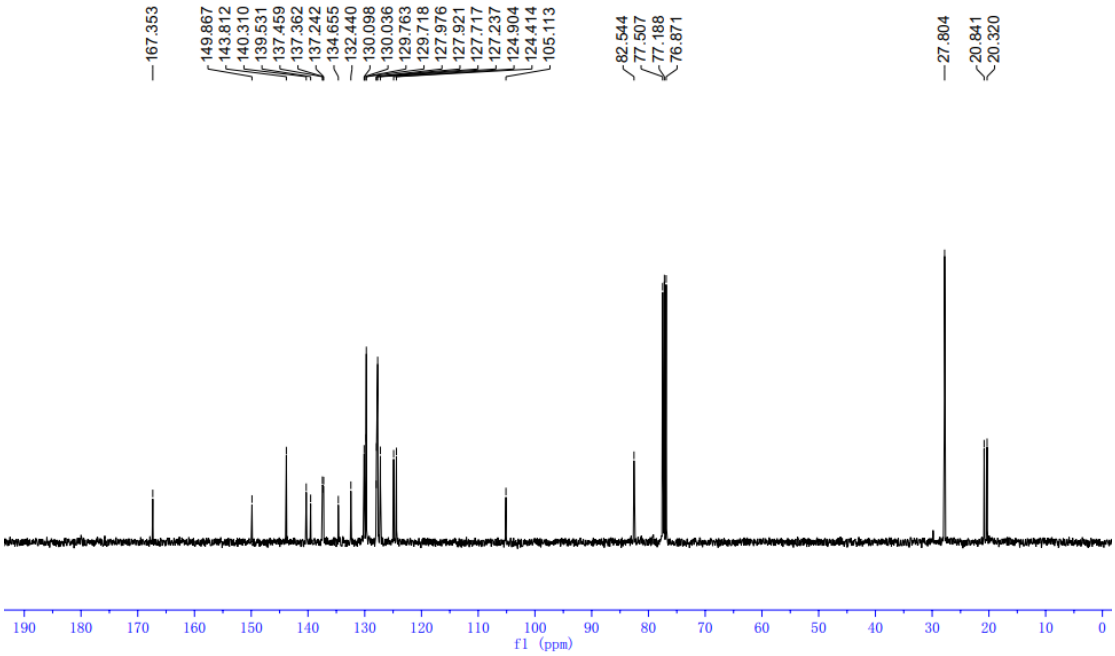
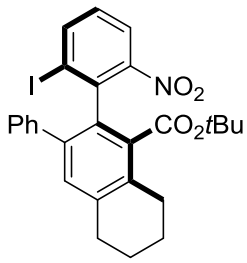
130.193
130.165
129.767
129.617
127.734
127.255
126.351
124.420
105.169
104.322
101.947
101.572
82.693
77.482
77.164
76.846
27.746
f1 (ppm)


I
NO2
Ph
CO2tBu
Me
Me

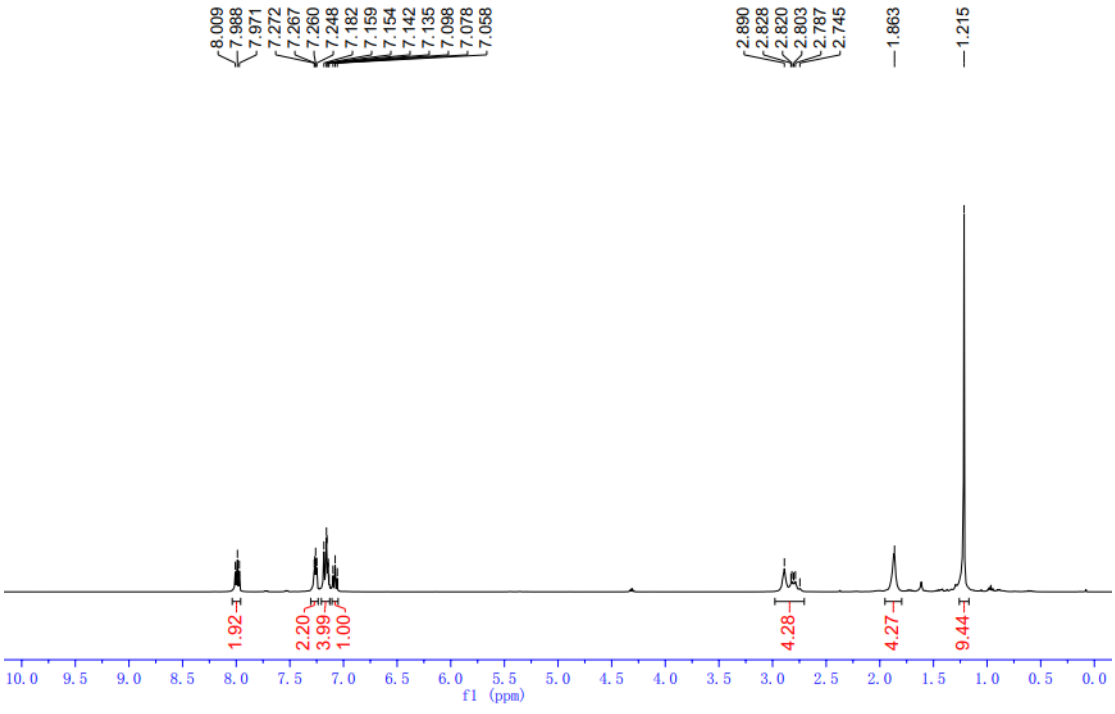
6i

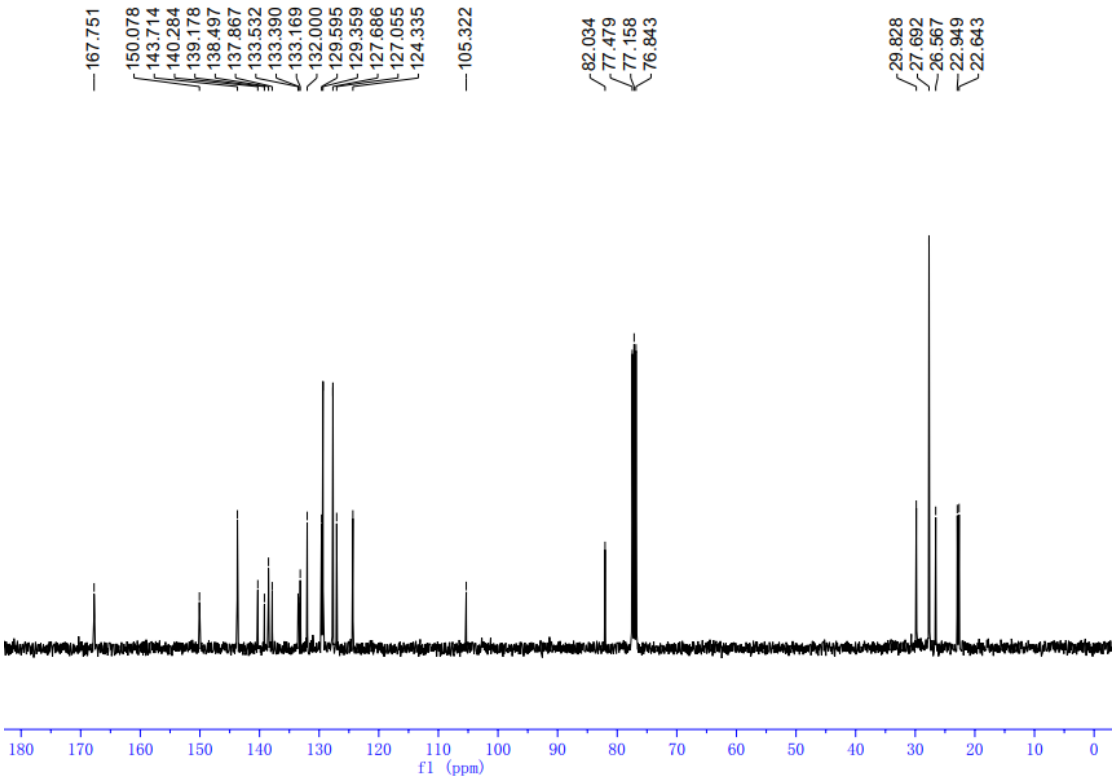

8.069
8.049
8.035
8.013
7.858
7.744
7.687
7.369
7.365
7.353
7.345
7.260
7.204
7.199
7.186
7.175
7.138
7.118
7.097
2.463
1.307
1.99
1.00
0.99
0.97
1.95
3.18
1.29
6.26
9.00
f1 (ppm)

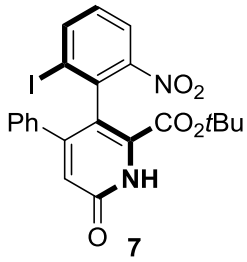

167.353
149.867
143.812
140.310
139.531
137.459
137.362
137.242
134.655
132.440
130.098
130.036
129.763
129.718
127.976
127.921
127.717
127.237
124.904
124.414
105.113
82.544
77.507
77.188
76.871
27.804
20.841
20.320
f1 (ppm)


I
NO2
Ph
CO2tBu

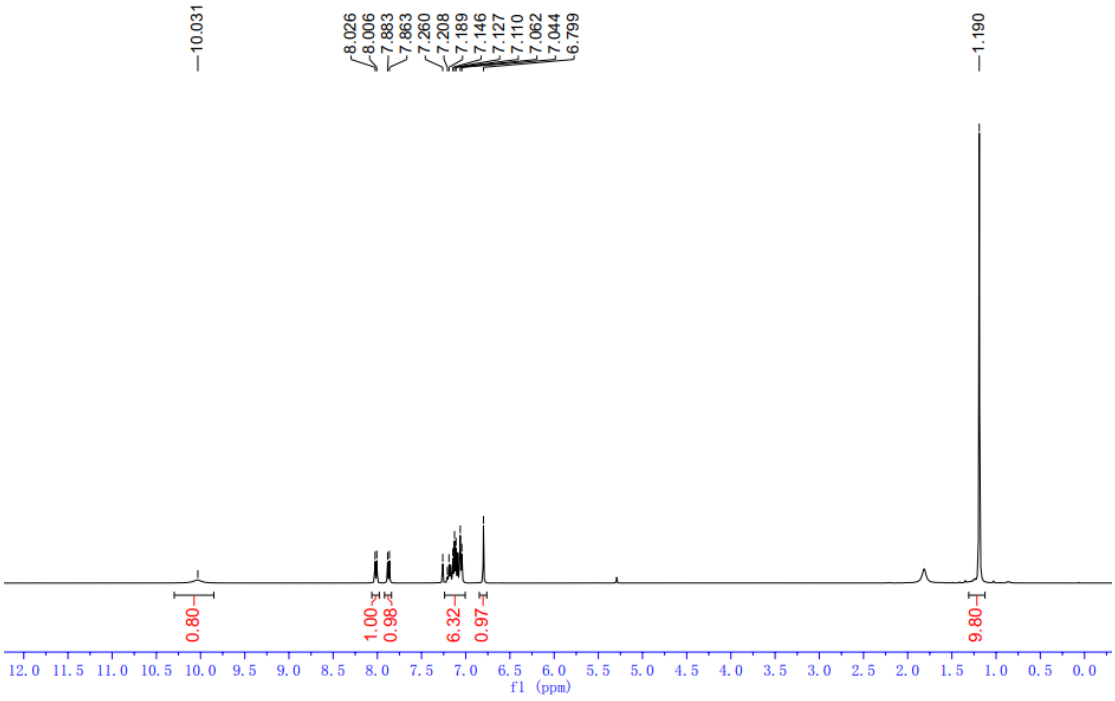
6j

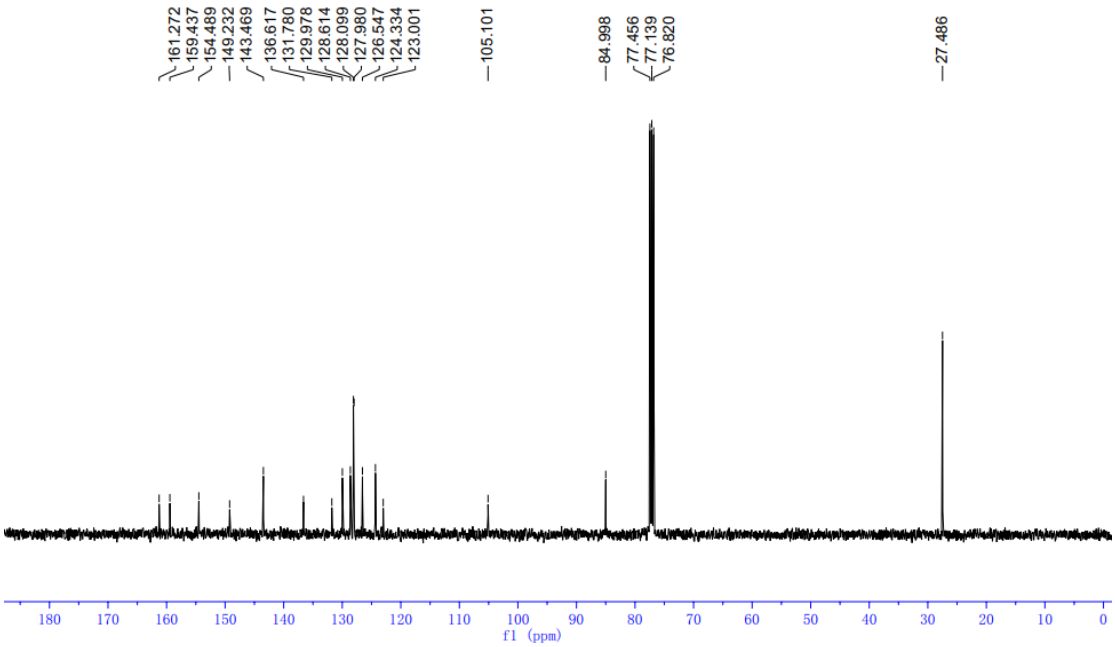

8.009
7.988
7.971
7.272
7.267
7.260
7.248
7.182
7.159
7.154
7.142
7.135
7.098
7.078
7.058
2.890
2.828
2.820
2.803
2.787
2.745
1.863
1.215
1.92
2.20
3.99
1.00
4.28
4.27
9.44
f1 (ppm)

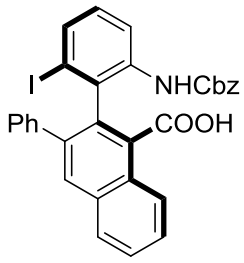

167.751
150.078
143.714
140.284
139.178
138.497
137.867
133.532
133.390
133.169
132.000
129.595
129.359
127.686
127.055
124.335
105.322
82.034
77.479
77.158
76.843
29.828
27.692
26.567
22.949
22.643
f1 (ppm)


I
NO2
Ph
CO2tBu
NH
O

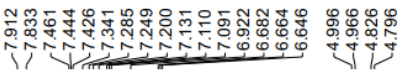
7

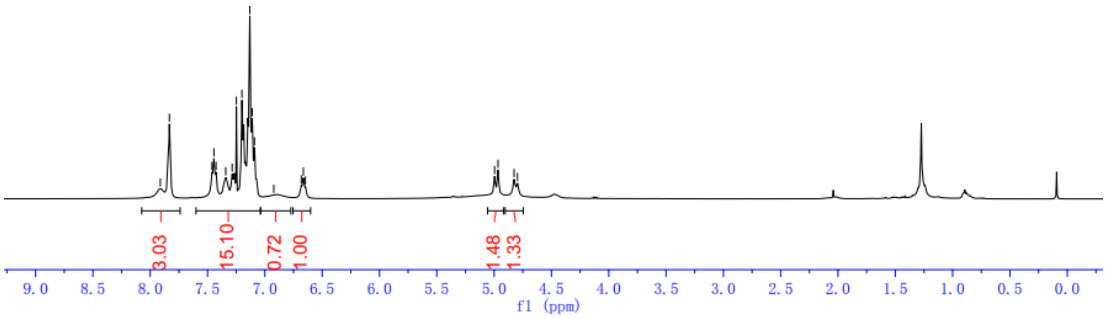

10.031
8.026
8.006
7.883
7.863
7.260
7.208
7.189
7.146
7.127
7.110
7.062
7.044
6.799
1.190
0.80
1.00
0.98
6.32
0.97
9.80
f1 (ppm)

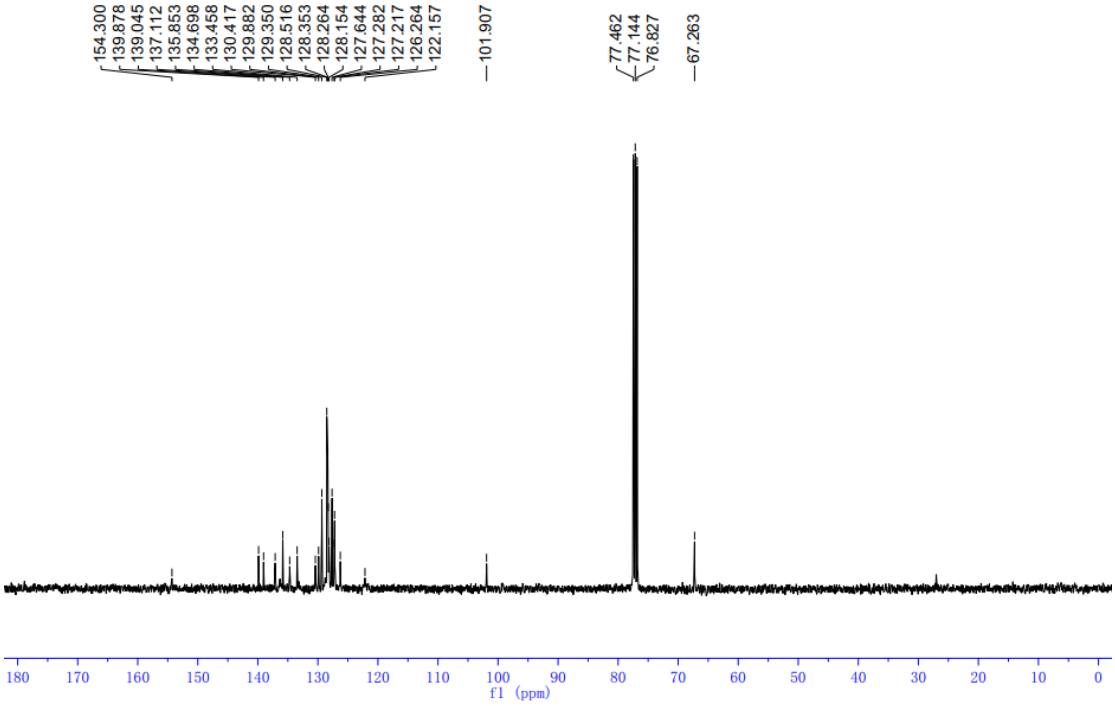

161.272
159.437
154.489
149.232
143.469
136.617
131.780
129.978
128.614
128.099
127.980
126.547
124.334
123.001
105.101
84.998
77.456
77.139
76.820
27.486
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

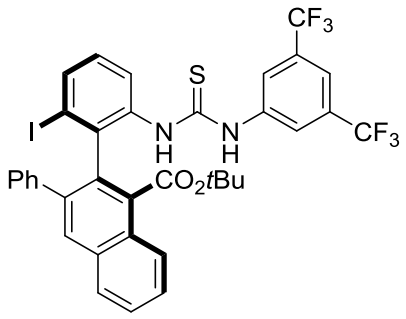

I
NHCbz
Ph
COOH

8

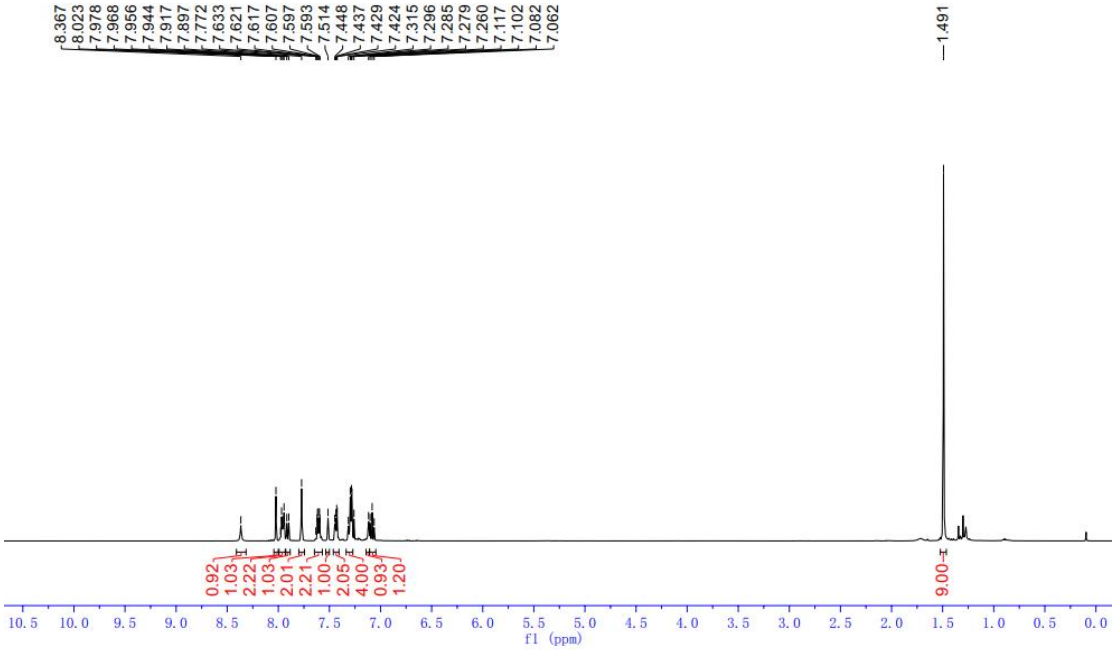

7.912
7.833
7.461
7.444
7.426
7.341
7.285
7.249
7.200
7.131
7.110
7.091
6.922
6.682
6.664
6.646
4.996
4.966
4.826
4.796

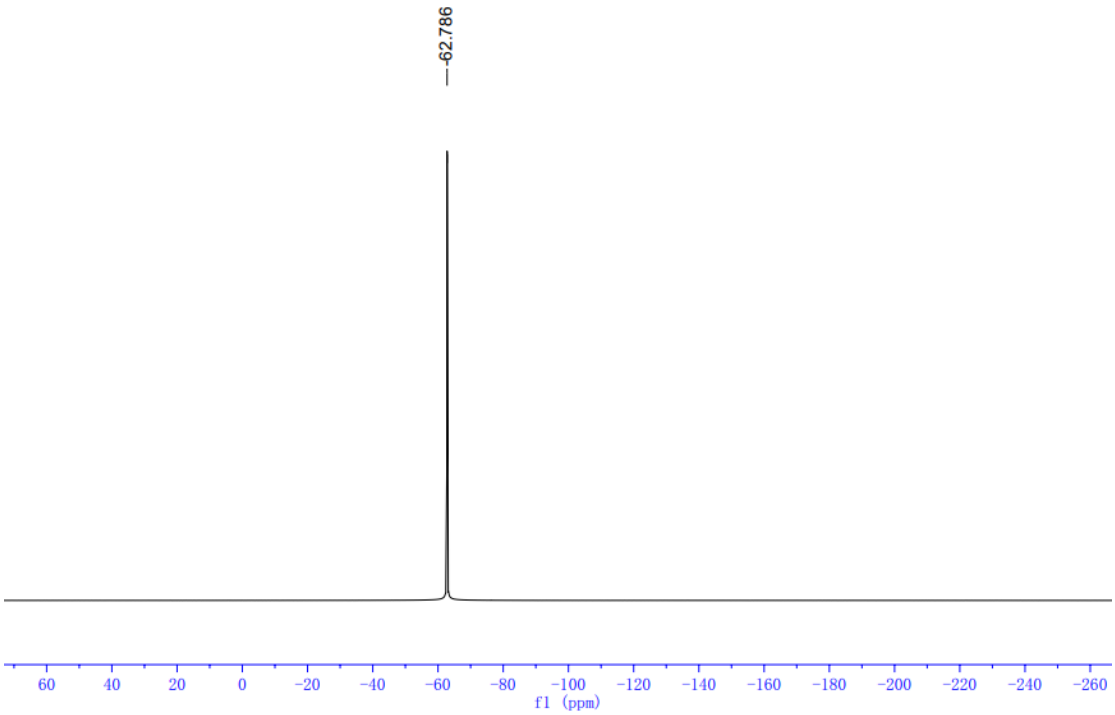

3.03
15.10
0.72
1.00
1.48
1.33
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

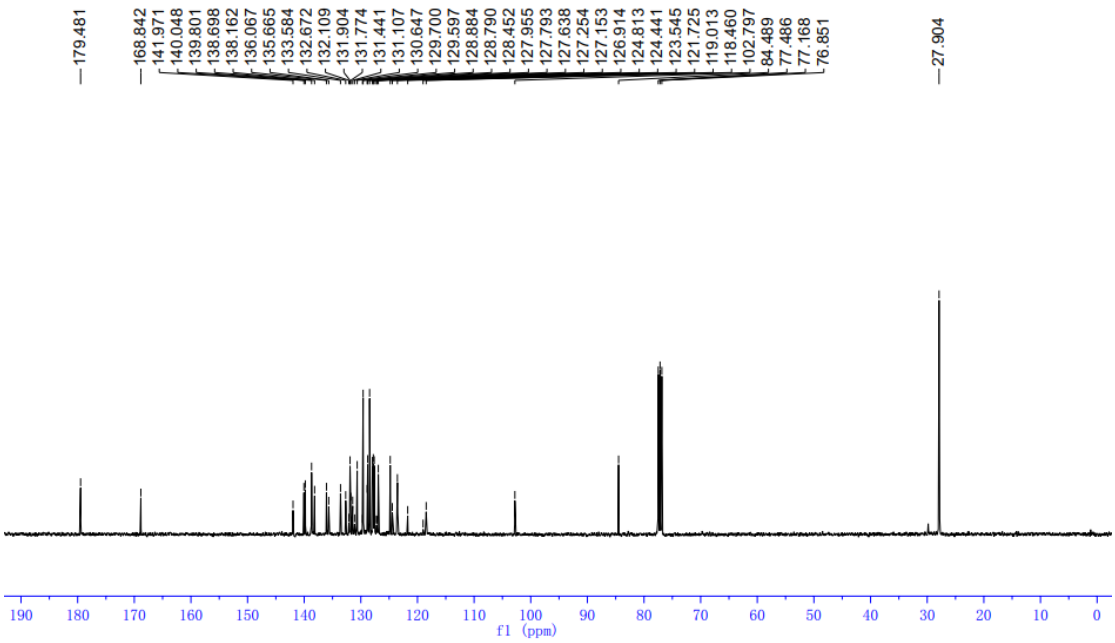

154.300
139.878
139.045
137.112
135.853
134.698
133.458
130.417
129.882
129.350
128.516
128.353
128.264
128.154
127.644
127.282
127.217
126.264
122.157
101.907
77.462
77.144
76.827
67.263
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

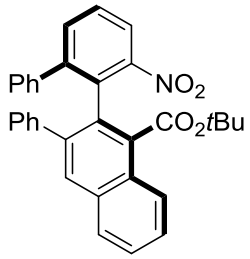

CF3
S
N
H
N
H
CF3
I
Ph
CO2tBu

9

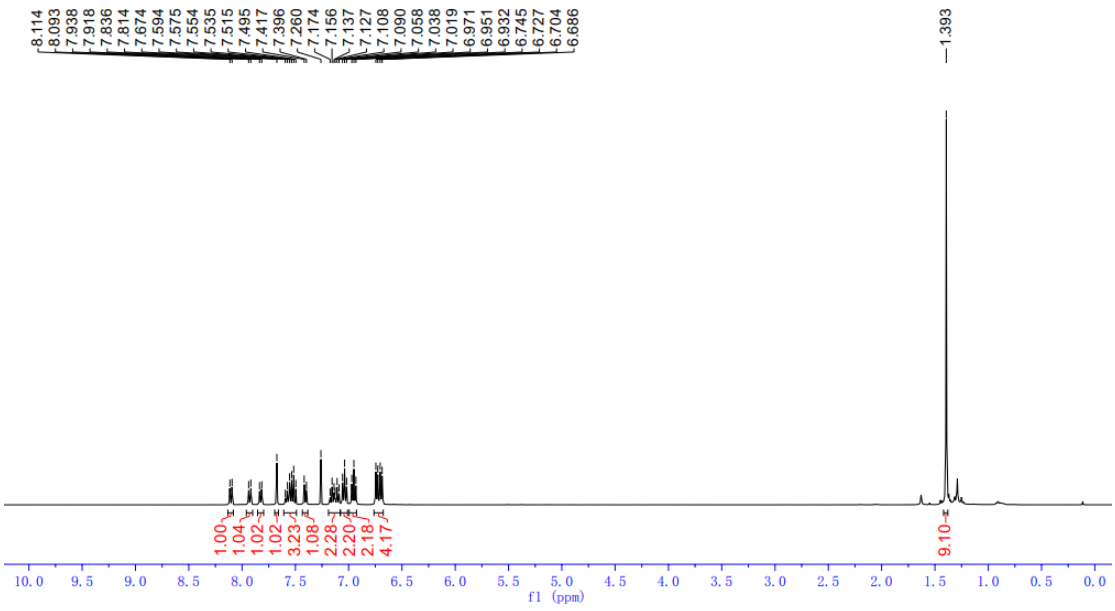

8.367
8.023
7.978
7.968
7.956
7.944
7.917
7.897
7.772
7.633
7.621
7.617
7.607
7.597
7.593
7.514
7.448
7.437
7.429
7.424
7.315
7.296
7.285
7.279
7.260
7.117
7.102
7.082
7.062
1.491
0.92
1.03
2.22
1.03
2.01
2.21
1.00
2.05
4.00
0.93
1.20
9.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

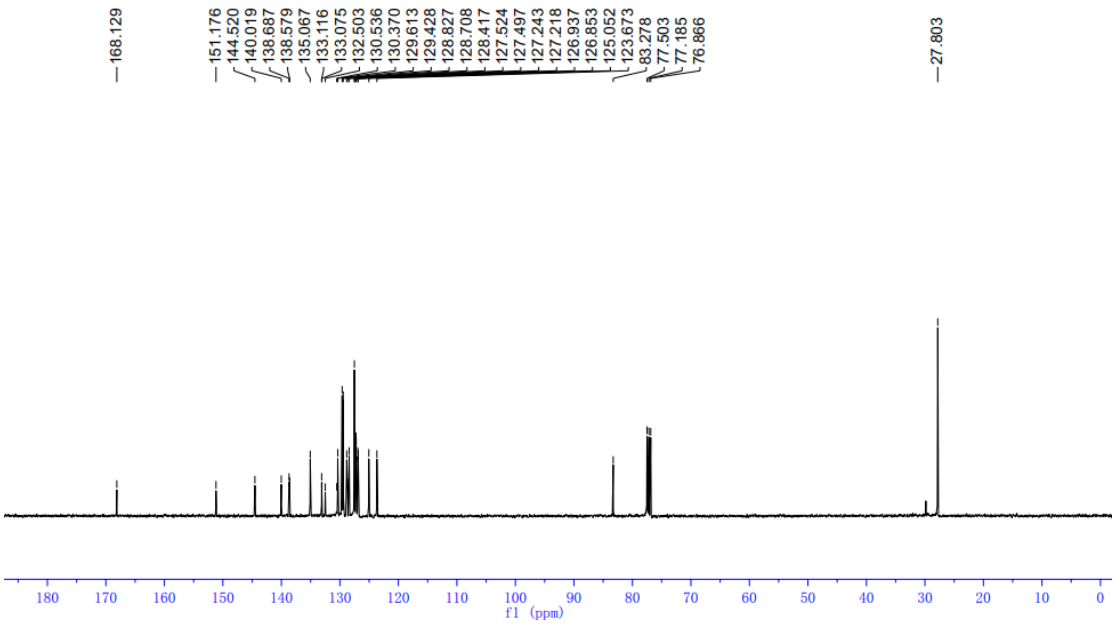

-62.786
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
f1 (ppm)

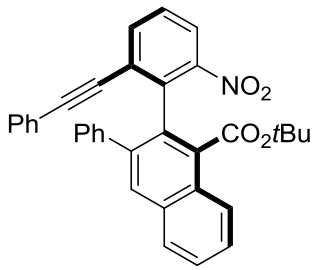

179.481
168.842
141.971
140.048
139.801
138.698
138.162
136.067
135.665
133.584
132.672
132.109
131.904
131.774
131.441
131.107
130.647
129.700
129.597
128.884
128.790
128.452
127.955
127.793
127.638
127.254
127.153
126.914
124.813
124.441
123.545
121.725
119.013
118.460
102.797
84.489
77.486
77.168
76.851
27.904
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
NO2
Ph
CO2tBu

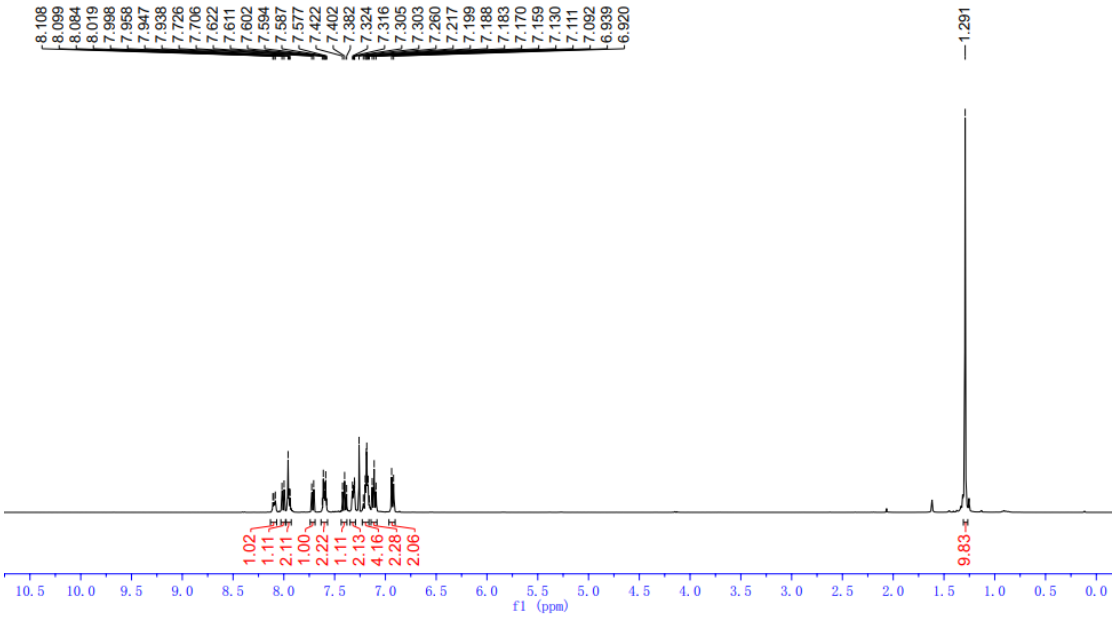
10

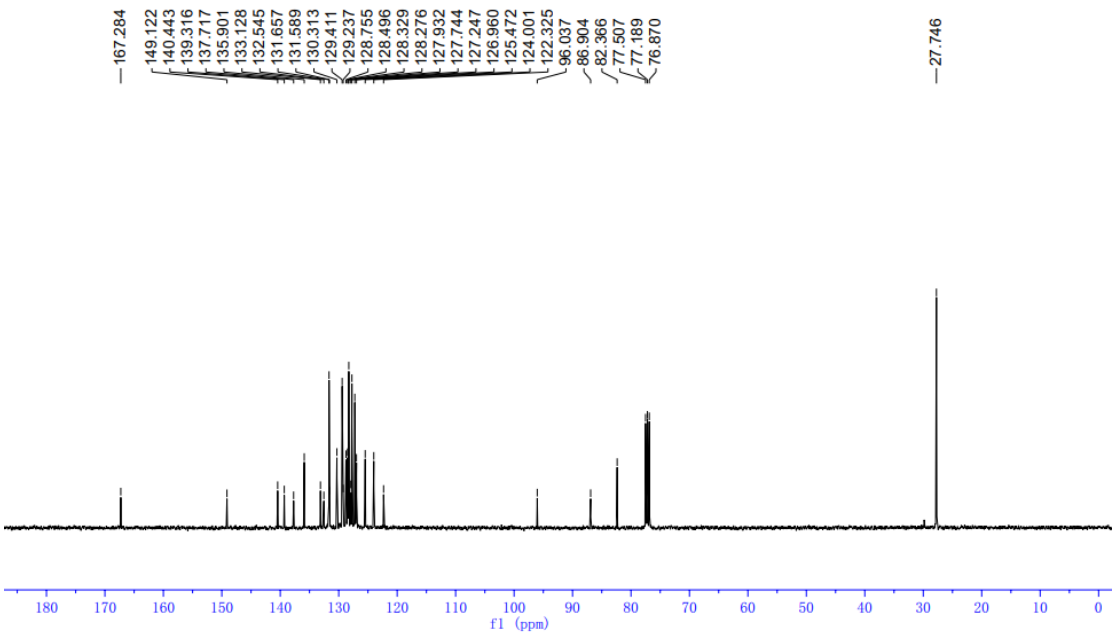

8.114
8.093
7.938
7.918
7.836
7.814
7.674
7.594
7.575
7.554
7.535
7.515
7.495
7.417
7.396
7.260
7.174
7.156
7.137
7.127
7.108
7.090
7.058
7.038
7.019
6.971
6.951
6.932
6.745
6.727
6.704
6.686
1.393
1.00
1.04
1.02
1.02
3.23
1.08
2.28
2.20
2.18
4.17
9.10
f1 (ppm)

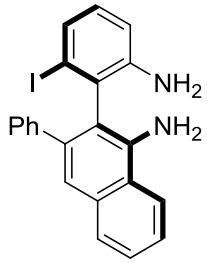

168.129
151.176
144.520
140.019
138.687
138.579
135.067
133.116
133.075
132.503
130.536
130.370
129.613
129.428
128.827
128.708
128.417
127.524
127.497
127.243
127.218
126.937
126.853
125.052
123.673
83.278
77.503
77.185
76.866
27.803
f1 (ppm)


NO2
Ph
Ph
CO2tBu

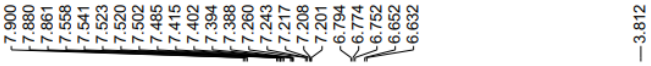
11

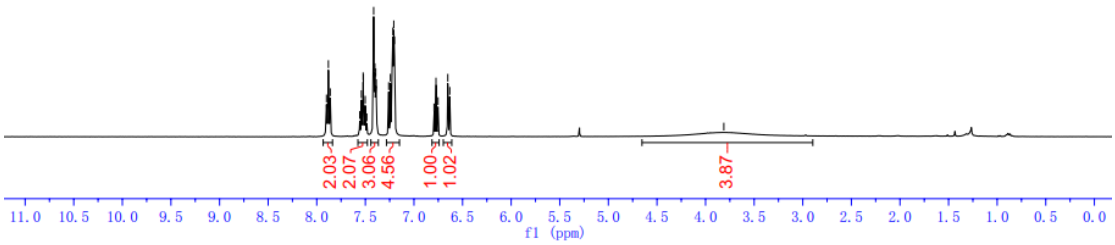

8.108
8.099
8.084
8.019
7.998
7.958
7.947
7.938
7.726
7.706
7.622
7.611
7.602
7.594
7.587
7.577
7.422
7.402
7.382
7.324
7.316
7.305
7.303
7.260
7.217
7.199
7.188
7.183
7.170
7.159
7.130
7.111
7.092
6.939
6.920
1.291
1.02
1.11
2.11
1.00
2.22
1.11
2.13
4.16
2.28
2.06
9.83
f1 (ppm)

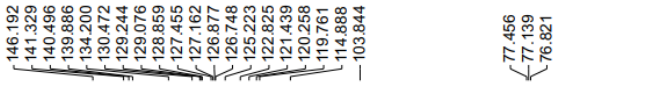

167.284
149.122
140.443
139.316
137.717
135.901
133.128
132.545
131.657
131.589
130.313
129.411
129.237
128.755
128.496
128.329
128.276
127.932
127.744
127.247
126.960
125.472
124.001
122.325
96.037
86.904
82.366
77.507
77.189
76.870
27.746
f1 (ppm)

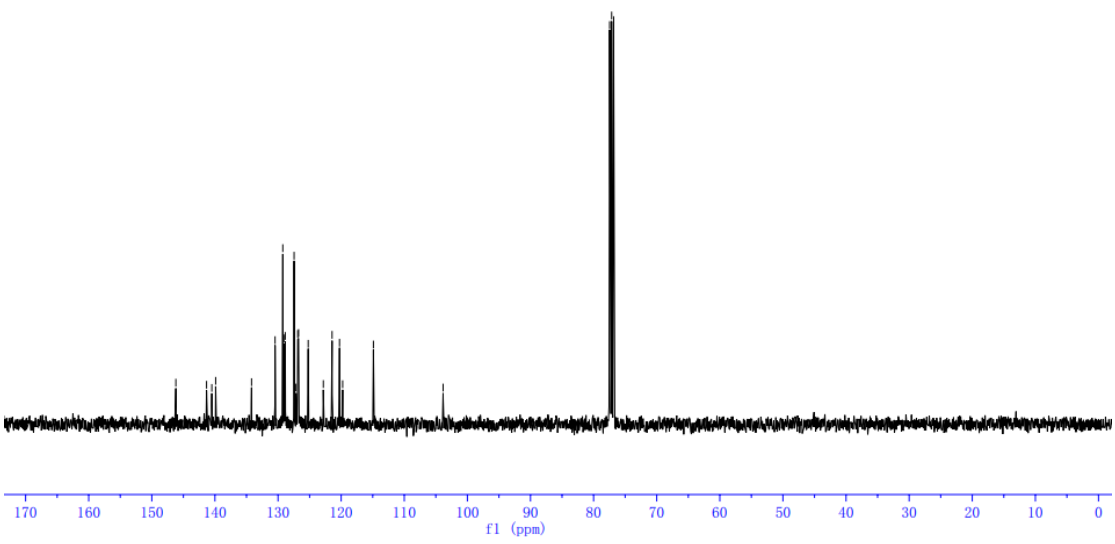

I
NH2
Ph
NH2

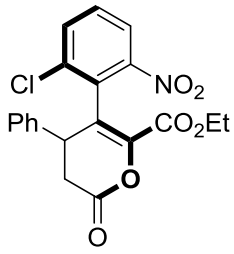
12


7.900
7.880
7.861
7.558
7.541
7.523
7.520
7.502
7.485
7.415
7.402
7.394
7.388
7.260
7.243
7.217
7.208
7.201
6.794
6.774
6.752
6.652
6.632
3.812

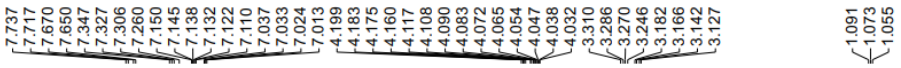

2.03
2.07
3.06
4.56
1.00
1.02
3.87
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

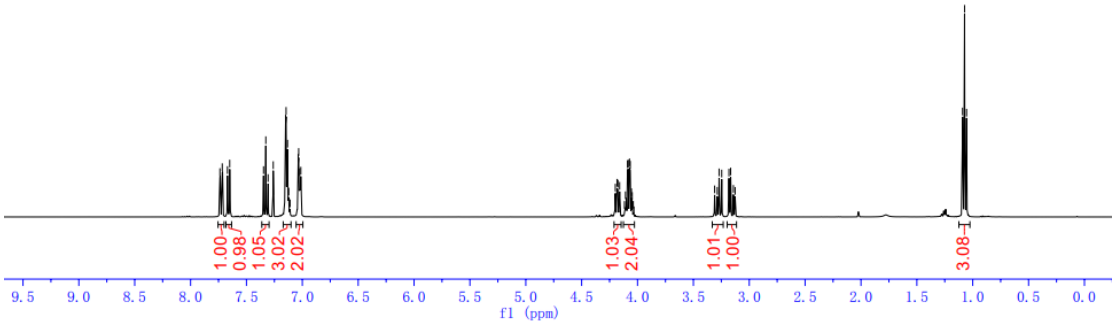

146.192
141.329
140.496
139.886
134.200
130.472
129.244
129.076
128.859
127.455
127.162
126.877
126.748
125.223
122.825
121.439
120.258
119.761
114.888
103.844
77.456
77.139
76.821


170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

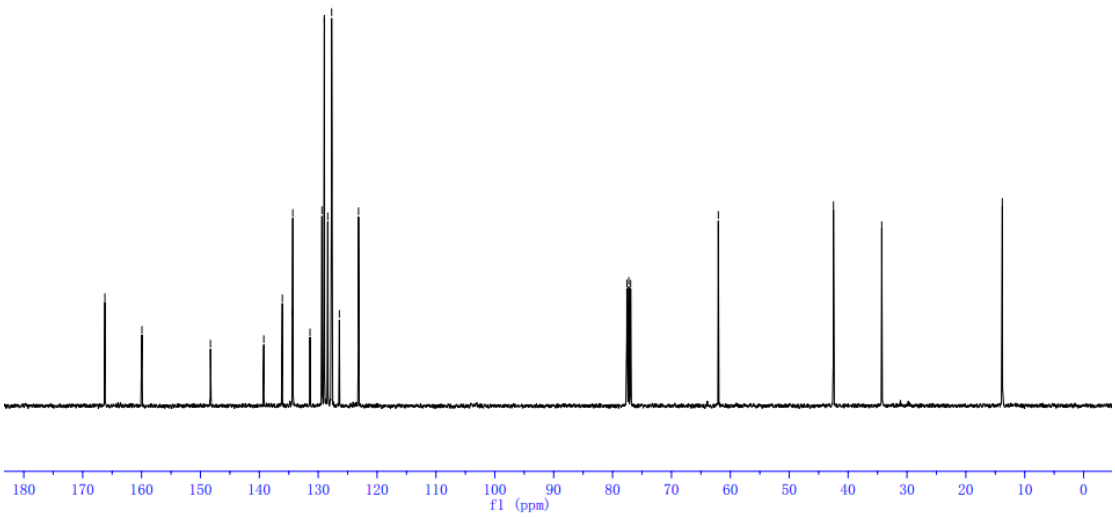

Cl
NO2
Ph
CO2Et
O
O

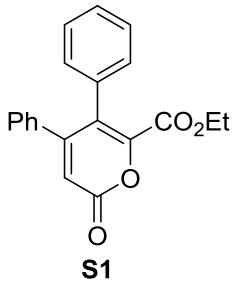
4


7.737
7.717
7.670
7.650
7.347
7.327
7.306
7.260
7.150
7.145
7.138
7.132
7.122
7.110
7.037
7.033
7.024
7.013
4.199
4.183
4.175
4.160
4.117
4.108
4.090
4.083
4.072
4.065
4.054
4.047
4.038
4.032
3.310
3.286
3.270
3.246
3.182
3.166
3.142
3.127
1.091
1.073
1.055


1.00
0.98
1.05
3.02
2.02
1.03
2.04
1.01
1.00
3.08
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)

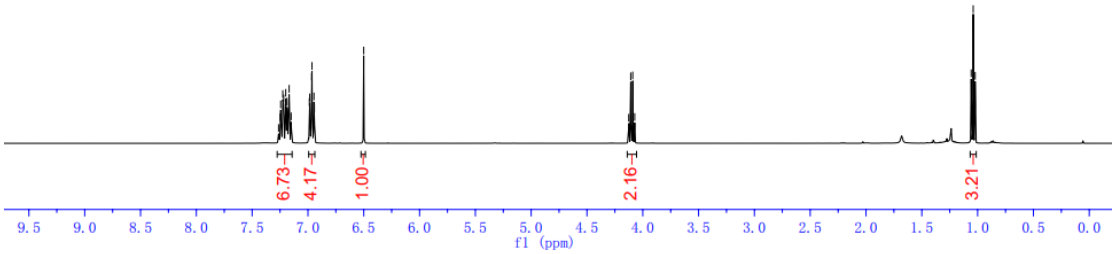

166.223
159.932
148.299
139.240
136.089
134.391
134.313
131.388
129.364
128.953
128.371
127.716
126.403
123.149
77.571
77.253
76.934
62.043
42.485
34.284
13.808

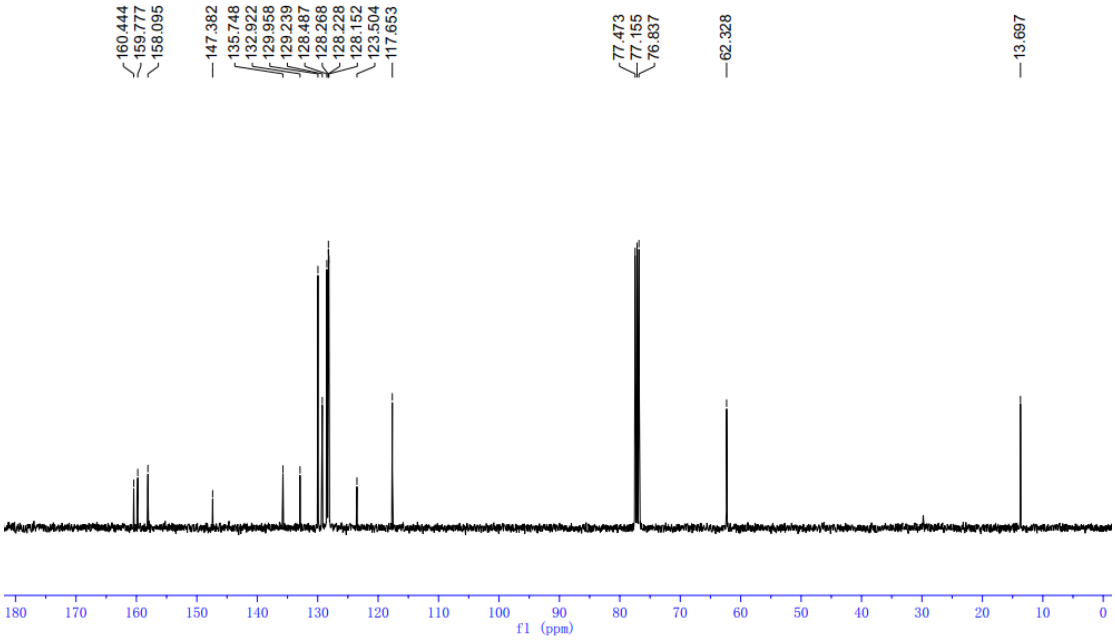

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

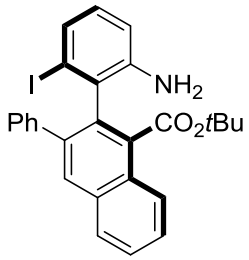

Ph
CO2Et
O
O

S1

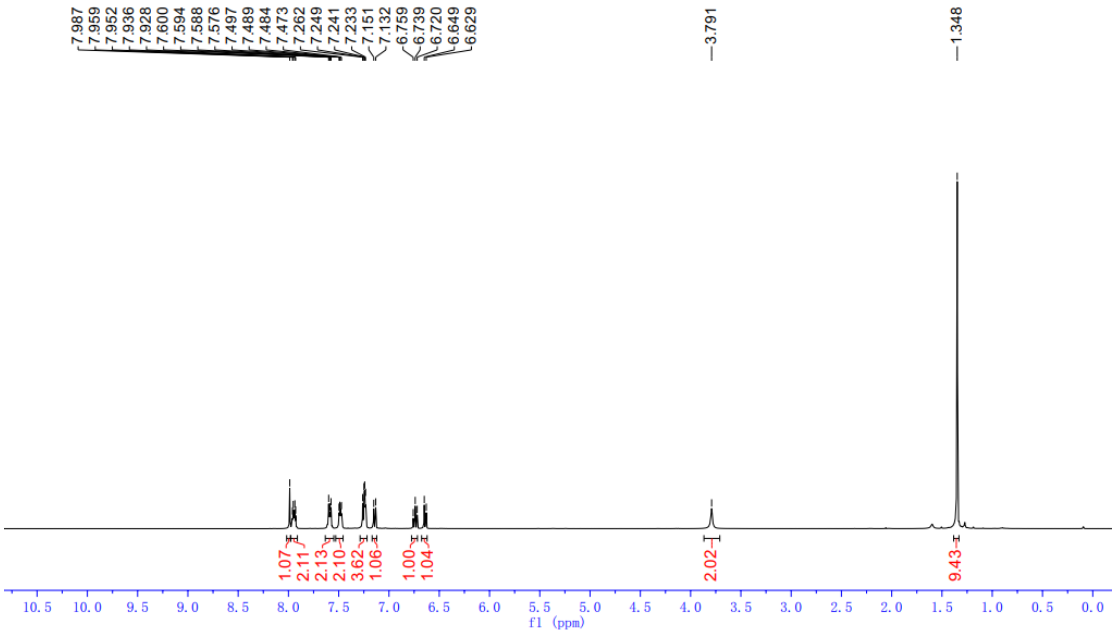

7.263
7.249
7.244
7.225
7.218
7.203
7.199
7.188
7.184
7.172
7.169
7.155
7.151
6.987
6.984
6.967
6.964
6.946
6.942
6.500
4.126
4.108
4.090
4.072
1.058
1.040
1.022

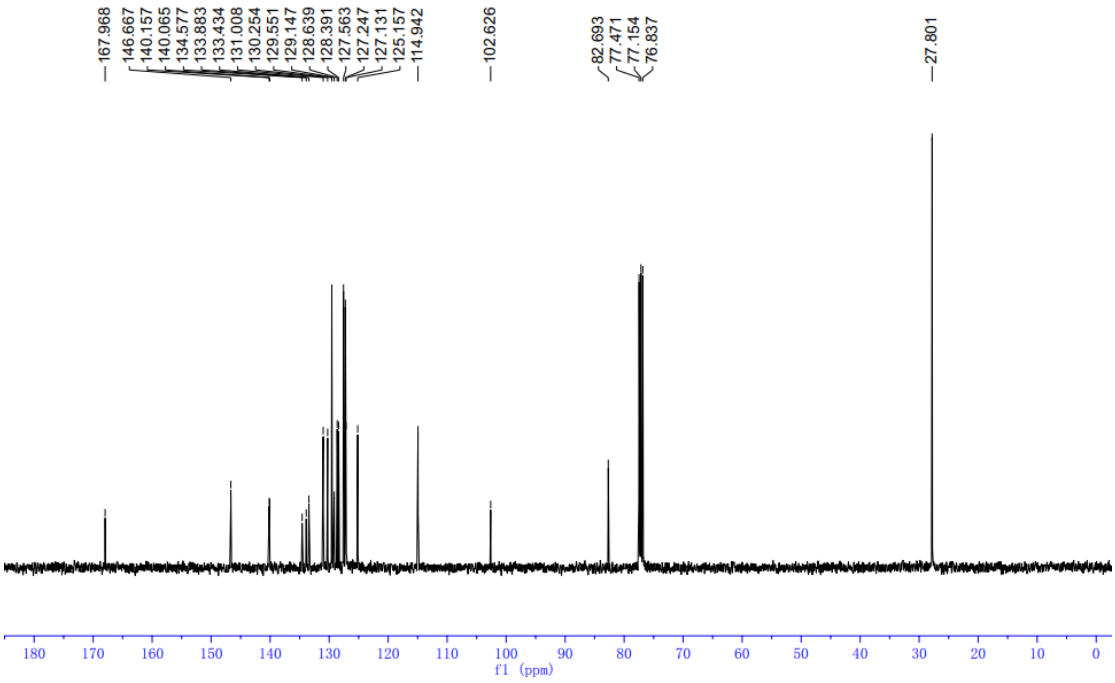

6.73
4.17
1.00
2.16
3.21
f1 (ppm)

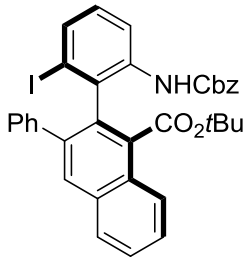

160.444
159.777
158.095
147.382
135.748
132.922
129.958
129.239
128.487
128.268
128.228
128.152
123.504
117.653
77.473
77.155
76.837
62.328
13.697
f1 (ppm)


I
NH2
Ph
CO2tBu

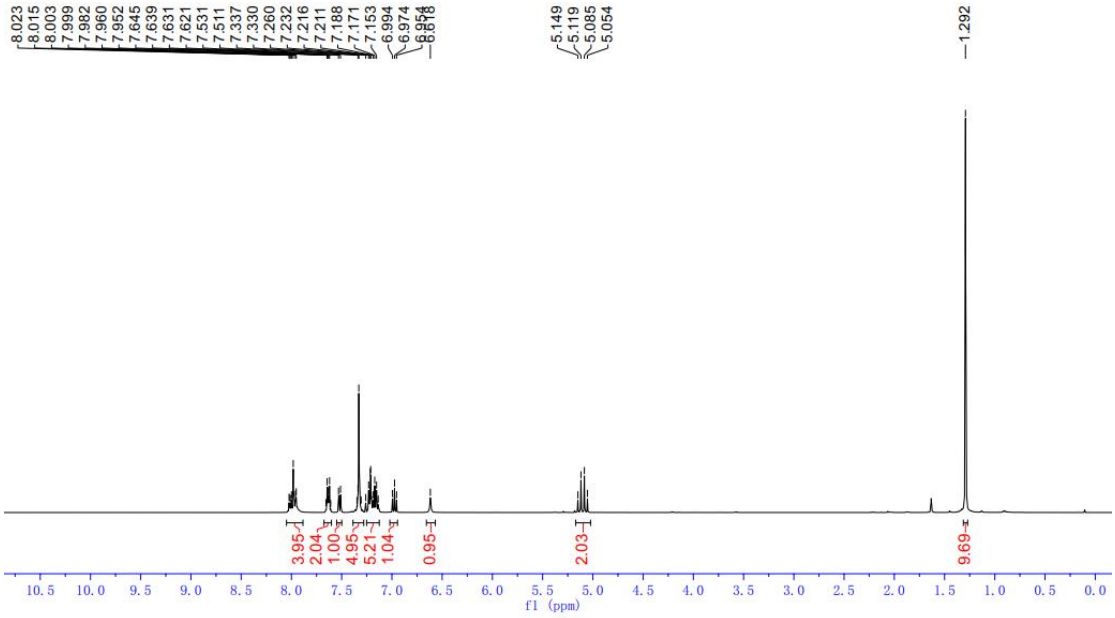
S3

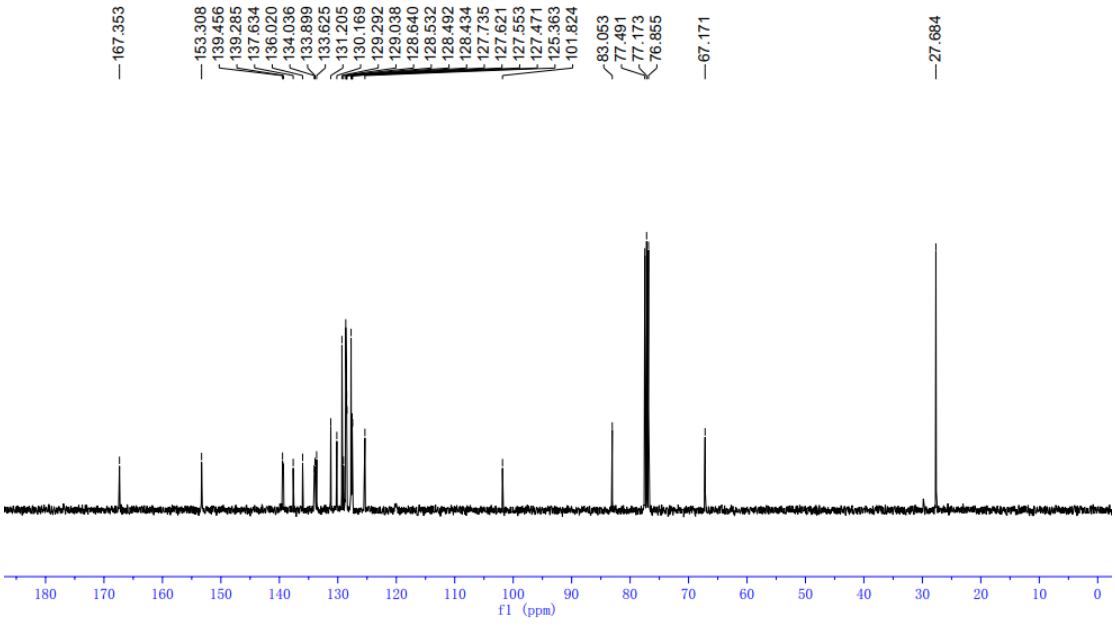

7.987
7.959
7.952
7.936
7.928
7.600
7.594
7.588
7.576
7.497
7.489
7.484
7.473
7.262
7.249
7.241
7.233
7.151
7.132
6.759
6.739
6.720
6.649
6.629
3.791
1.348
1.07
2.11
2.13
2.10
3.62
1.06
1.00
1.04
2.02
9.43
f1 (ppm)

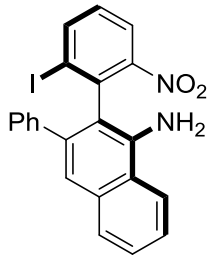

167.968
146.667
140.157
140.065
134.577
133.883
133.434
131.008
130.254
129.551
129.147
128.639
128.391
127.563
127.247
127.131
125.157
114.942
102.626
82.693
77.471
77.154
76.837
27.801
f1 (ppm)


I
NHCbz
Ph
CO2tBu

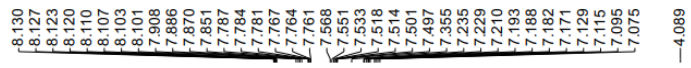
S4

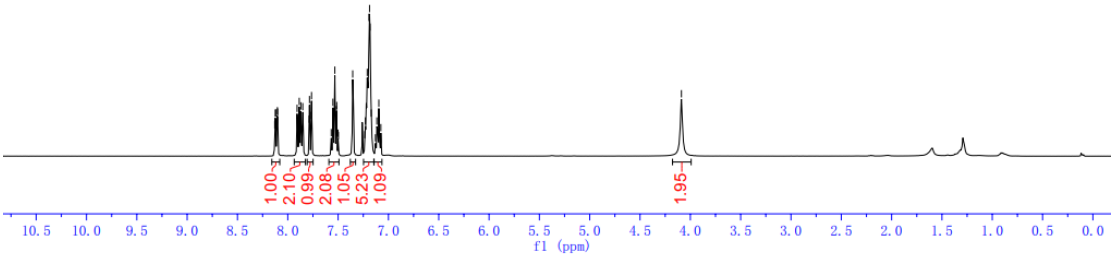

8.023
8.015
8.003
7.999
7.982
7.960
7.952
7.645
7.639
7.631
7.621
7.531
7.511
7.337
7.330
7.260
7.232
7.216
7.211
7.188
7.171
7.153
6.994
6.974
6.954
6.918
5.149
5.119
5.085
5.054
1.292
3.95
2.04
1.00
4.95
5.21
1.04
0.95
2.03
9.69
f1 (ppm)

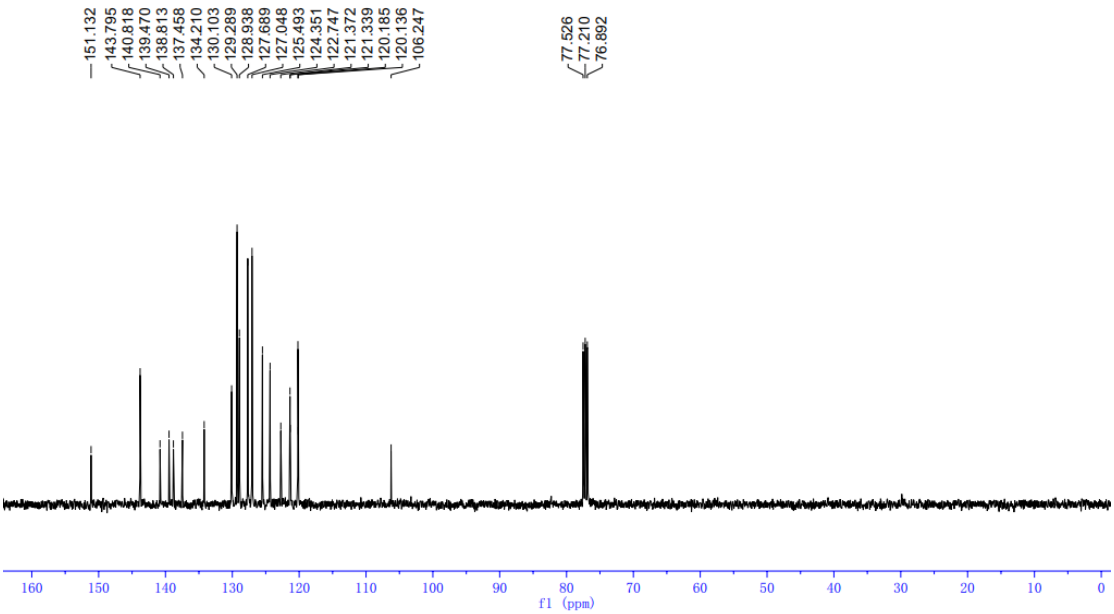

167.353
153.308
139.456
139.285
137.634
136.020
134.036
133.899
133.625
131.205
130.169
129.292
129.038
128.640
128.532
128.492
128.434
127.735
127.621
127.553
127.471
125.363
101.824
83.053
77.491
77.173
76.855
67.171
27.684
f1 (ppm)

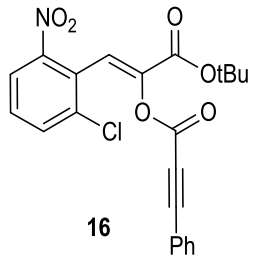

I
NO2
Ph
NH2

S6

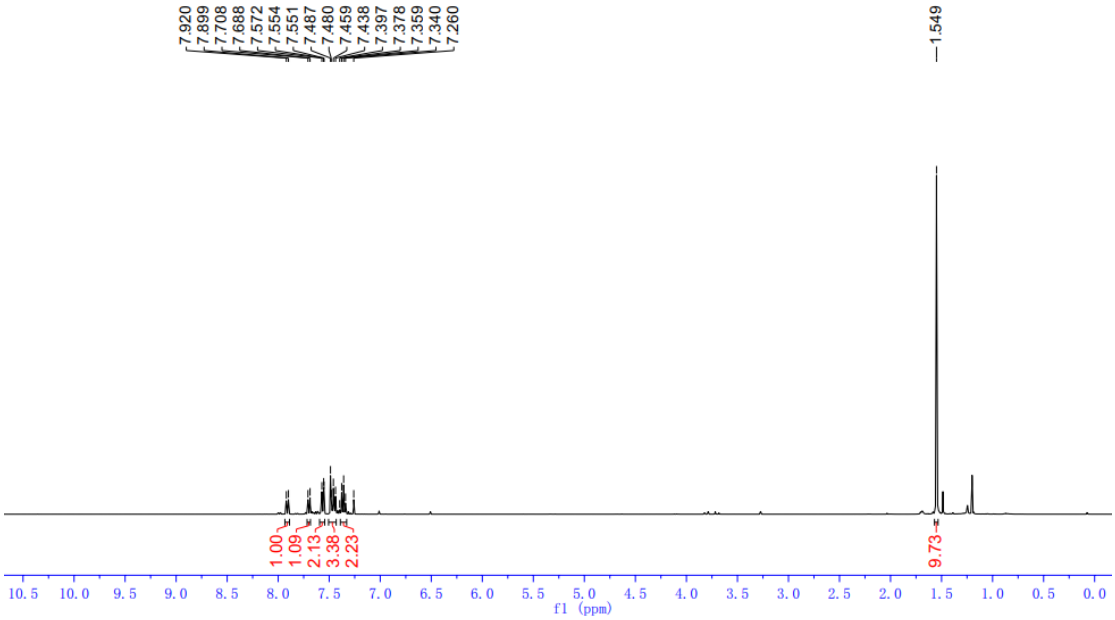

8.130
8.127
8.123
8.120
8.110
8.107
8.103
8.101
7.908
7.886
7.870
7.851
7.787
7.784
7.781
7.767
7.764
7.761
7.568
7.551
7.533
7.518
7.514
7.501
7.497
7.355
7.235
7.229
7.210
7.193
7.188
7.182
7.171
7.129
7.115
7.095
7.075
4.089

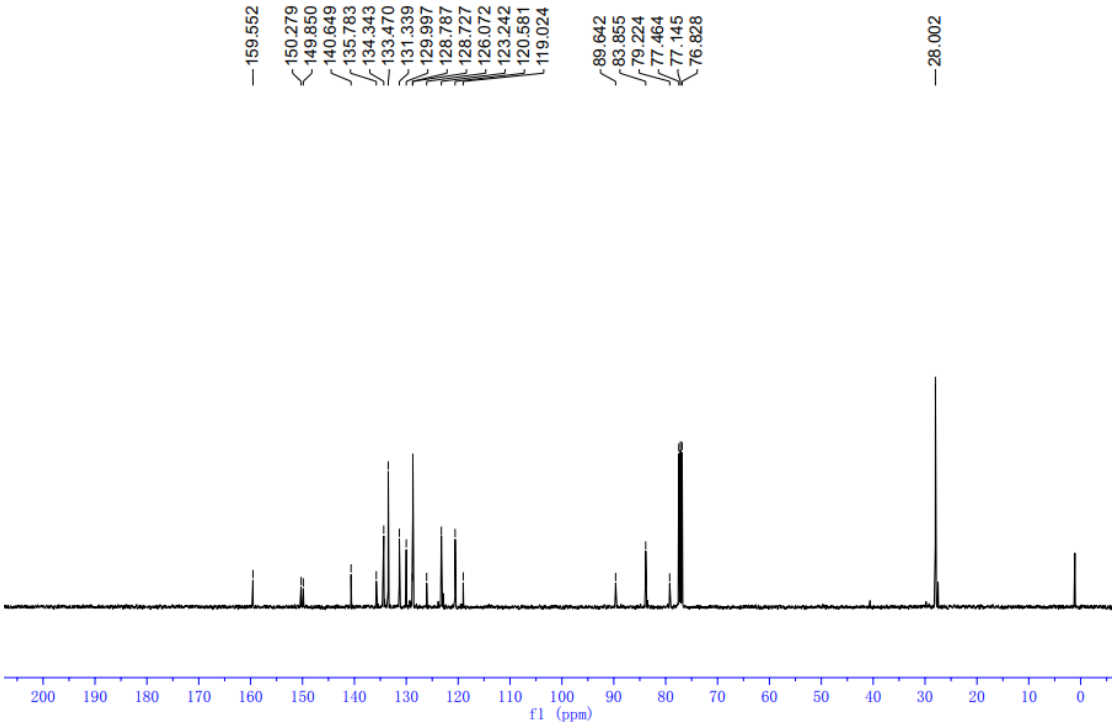

1.00
2.10
0.99
2.08
1.05
5.23
1.09
1.95
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

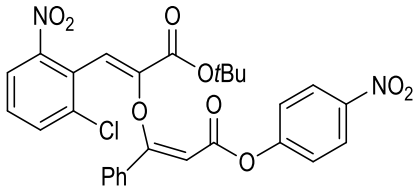

151.132
143.795
140.818
139.470
138.813
137.458
134.210
130.103
129.289
128.938
127.689
127.048
125.493
124.351
122.747
121.372
121.339
120.185
120.136
106.247
77.526
77.210
76.892
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


NO2
O
OtBu
O
O
Cl
Ph

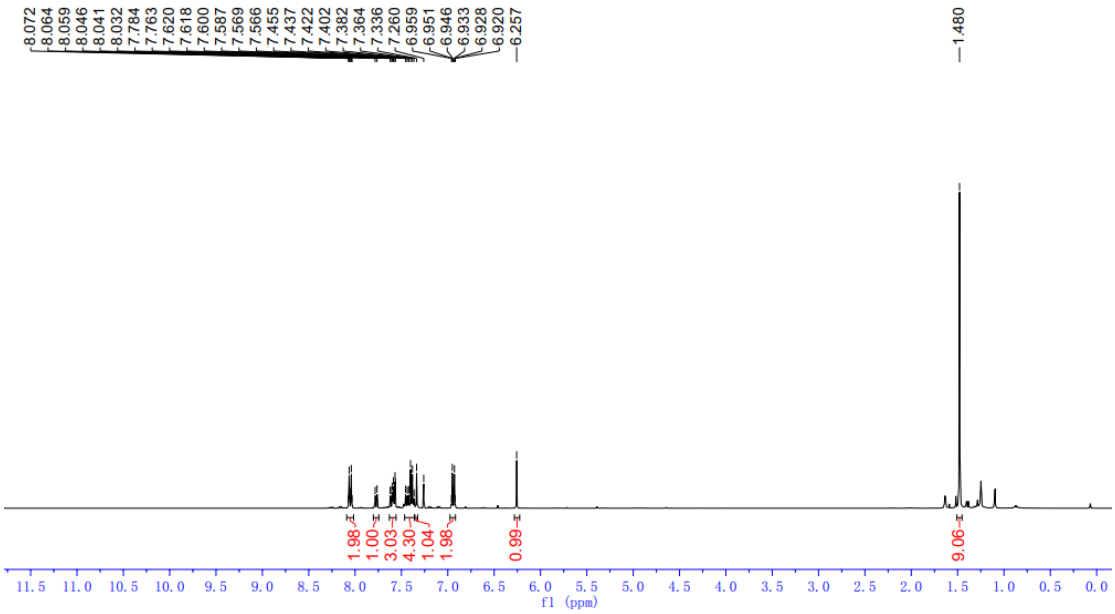
16

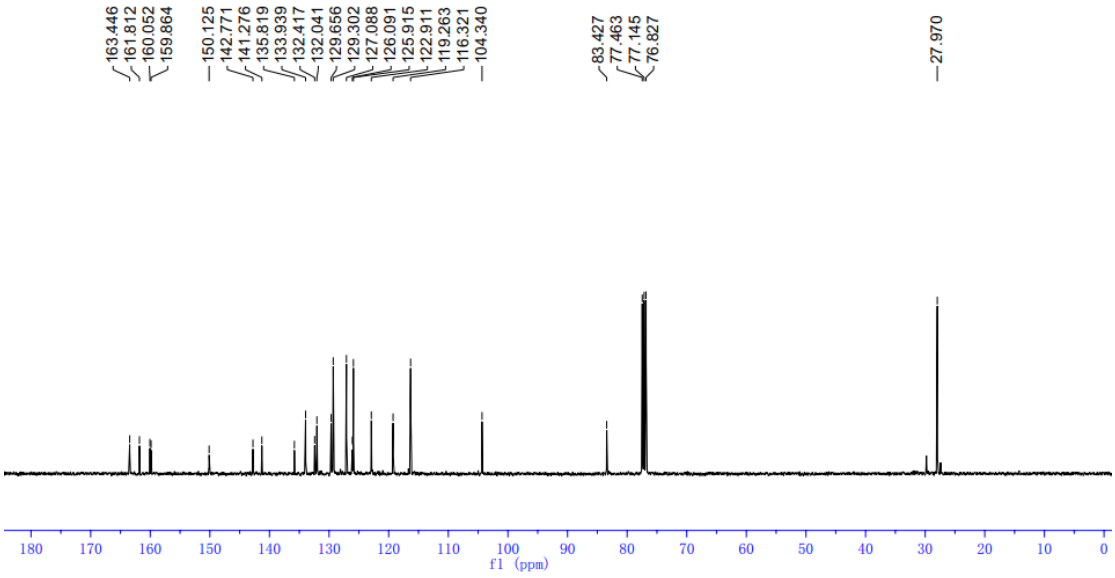

7.920
7.899
7.708
7.688
7.572
7.554
7.551
7.487
7.480
7.459
7.438
7.397
7.378
7.359
7.340
7.260
1.549
1.00
1.09
2.13
3.38
2.23
9.73
f1 (ppm)

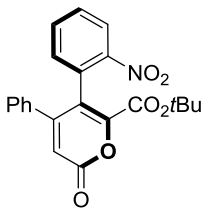

159.552
150.279
149.850
140.649
135.783
134.343
133.470
131.339
129.997
128.787
128.727
126.072
123.242
120.581
119.024
89.642
83.855
79.224
77.464
77.145
76.828
28.002
f1 (ppm)


NO2
O
OtBu
NO2
Cl
O
O
Ph
O

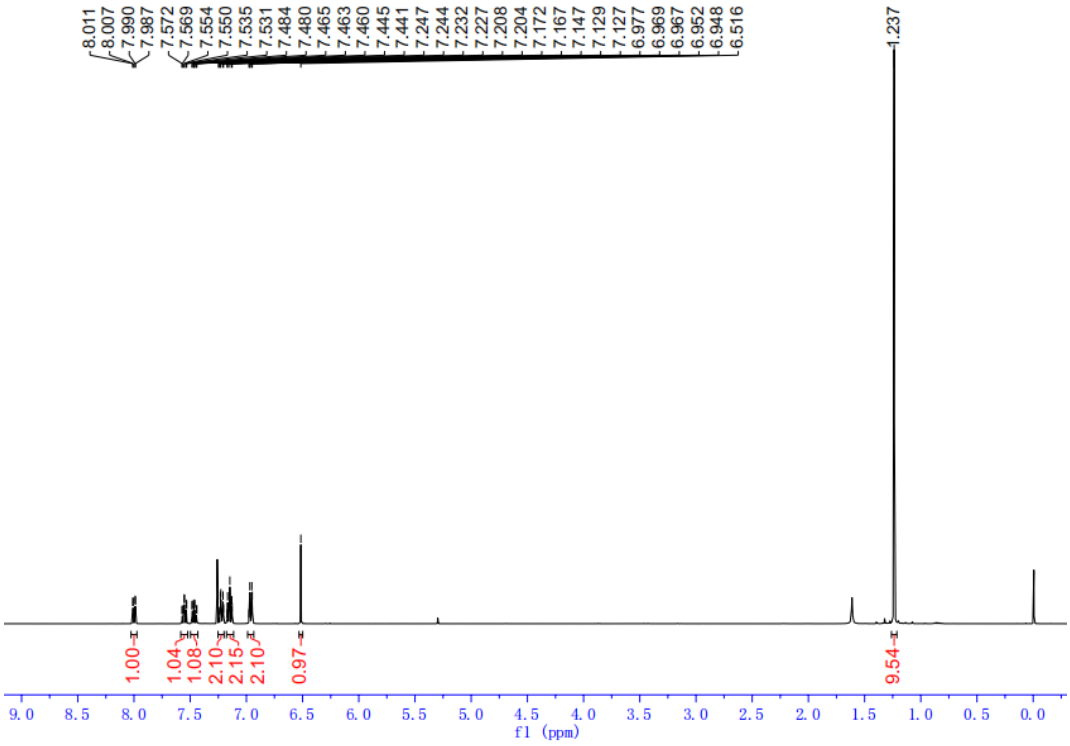
17

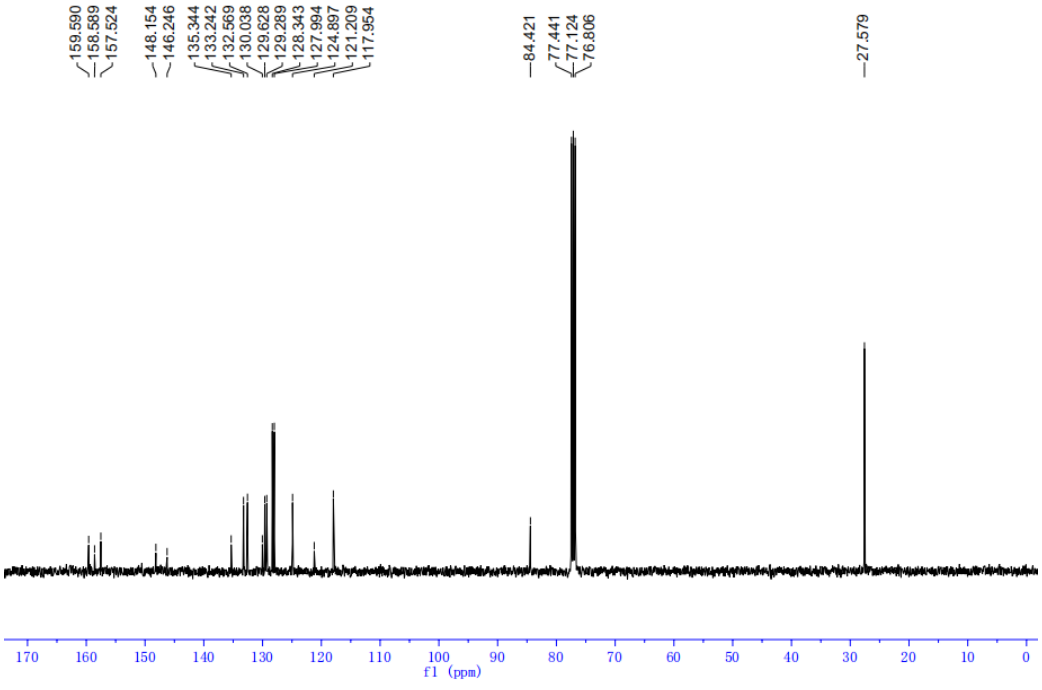

8.072
8.064
8.059
8.046
8.041
8.032
7.784
7.763
7.620
7.618
7.600
7.587
7.569
7.566
7.455
7.437
7.422
7.402
7.382
7.364
7.336
7.260
6.959
6.951
6.946
6.933
6.928
6.920
6.257
1.480
1.98
1.00
3.03
4.30
1.04
1.98
0.99
9.06
f1 (ppm)

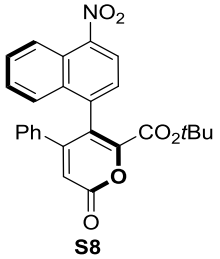

163.446
161.812
160.052
159.864
150.125
142.771
141.276
135.819
133.939
132.417
132.041
129.656
129.302
127.088
126.091
125.915
122.911
119.263
116.321
104.340
83.427
77.463
77.145
76.827
27.970
f1 (ppm)


NO2
Ph
CO2tBu
O
O

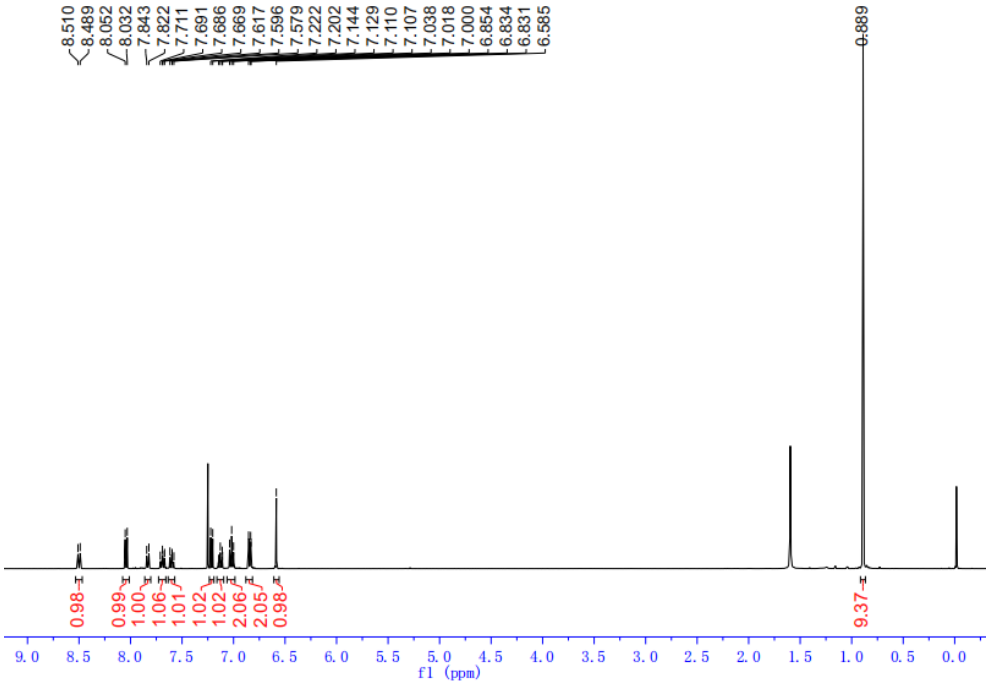
S7

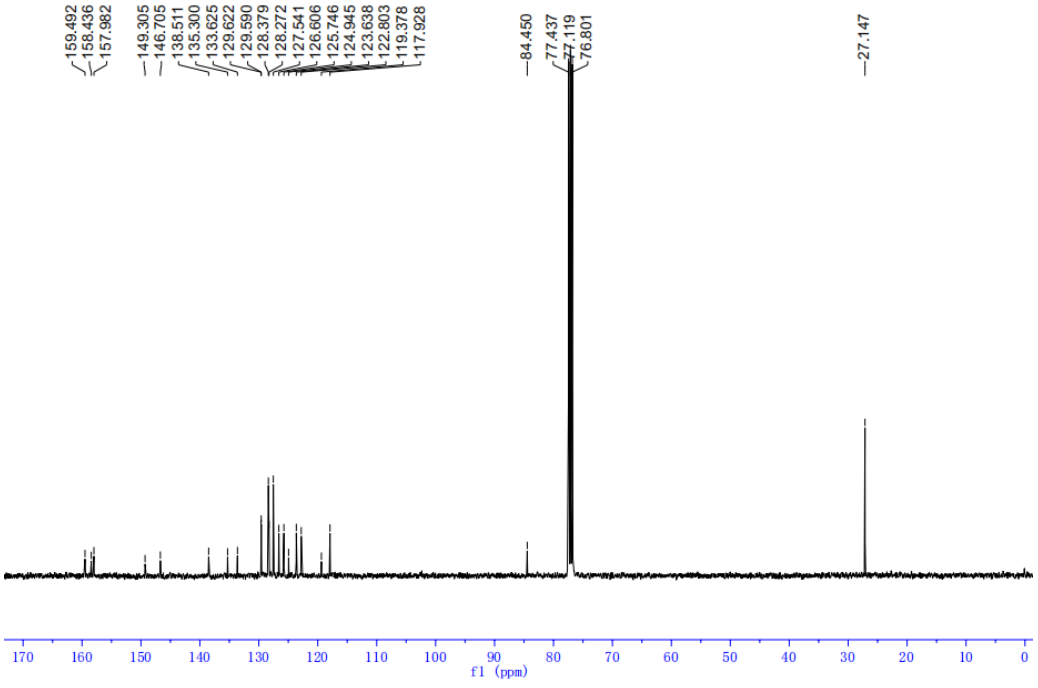

8.011
8.007
7.990
7.987
7.572
7.569
7.554
7.550
7.535
7.531
7.484
7.480
7.465
7.463
7.460
7.445
7.441
7.247
7.244
7.232
7.227
7.208
7.204
7.172
7.167
7.147
7.129
7.127
6.977
6.969
6.967
6.952
6.948
6.516
1.237
1.00
1.04
1.08
2.10
2.15
2.10
0.97
9.54
f1 (ppm)

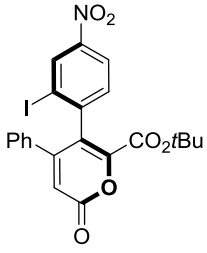

159.590
158.589
157.524
148.154
146.246
135.344
133.242
132.569
130.038
129.628
129.289
128.343
127.994
124.897
121.209
117.954
84.421
77.441
77.124
76.806
27.579
f1 (ppm)


NO2
Ph
CO2tBu
O
O

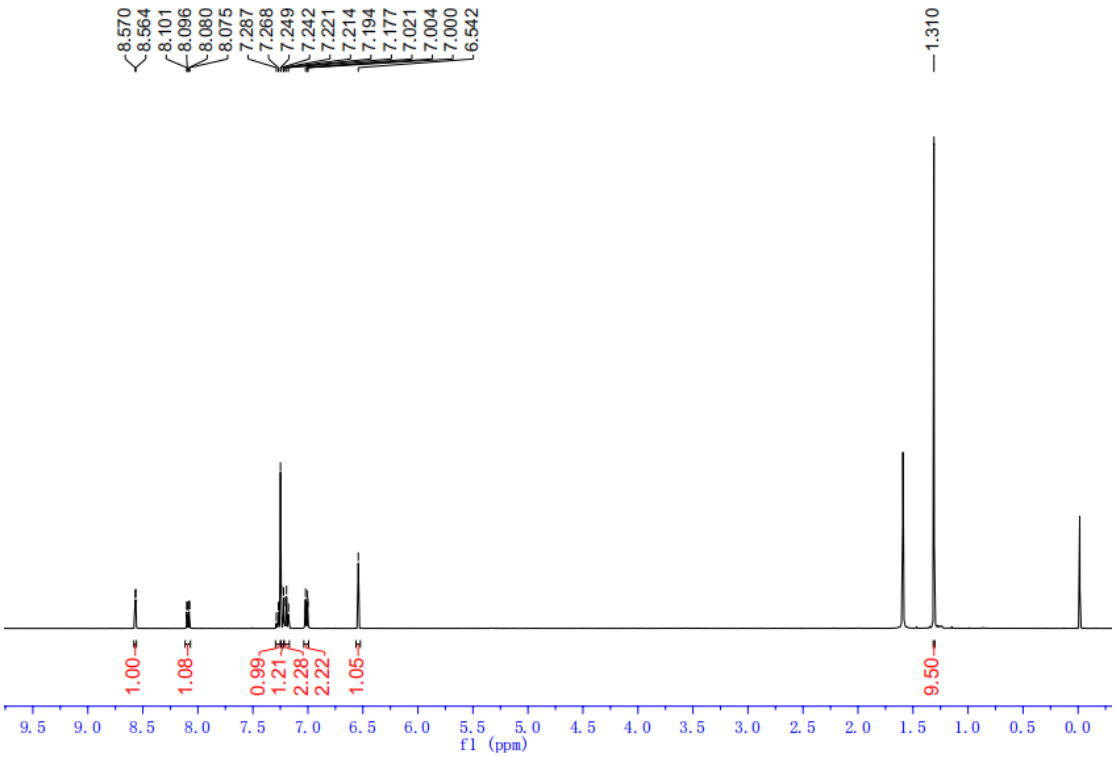
S8

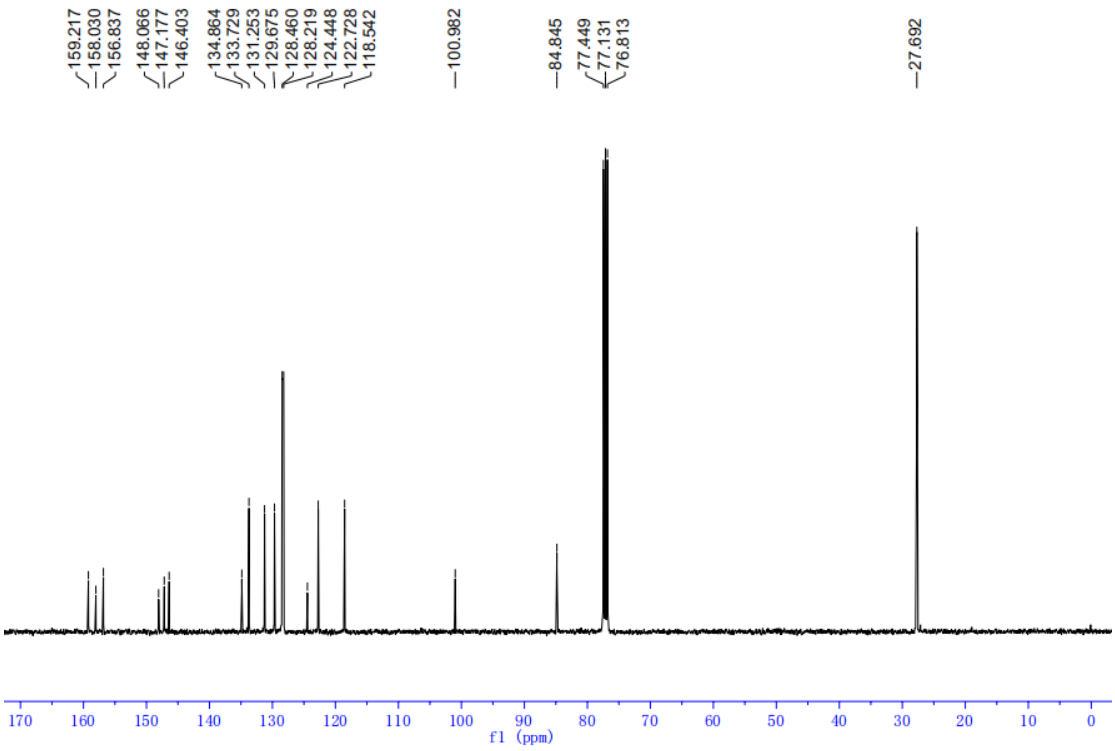

8.510
8.489
8.052
8.032
7.843
7.822
7.711
7.691
7.686
7.669
7.617
7.596
7.579
7.222
7.202
7.144
7.129
7.110
7.107
7.038
7.018
7.000
6.854
6.834
6.831
6.585
0.889
0.98
0.99
1.00
1.06
1.01
1.02
1.02
2.06
2.05
0.98
9.37
f1 (ppm)

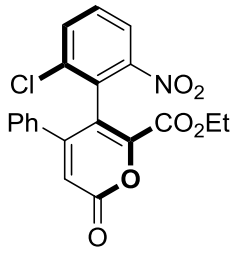

159.492
158.436
157.982
149.305
146.705
138.511
135.300
133.625
129.622
129.590
128.379
128.272
127.541
126.606
125.746
124.945
123.638
122.803
119.378
117.928
84.450
77.437
77.119
76.801
27.147
f1 (ppm)


NO2
I
Ph
CO2tBu
O
O

S9


8.570
8.564
8.101
8.096
8.080
8.075
7.287
7.268
7.249
7.242
7.221
7.214
7.194
7.177
7.021
7.004
7.000
6.542
1.310
1.00
1.08
0.99
1.21
2.28
2.22
1.05
9.50
f1 (ppm)


159.217
158.030
156.837
148.066
147.177
146.403
134.864
133.729
131.253
129.675
128.460
128.219
124.448
122.728
118.542
100.982
84.845
77.449
77.131
76.813
27.692
f1 (ppm)



3a

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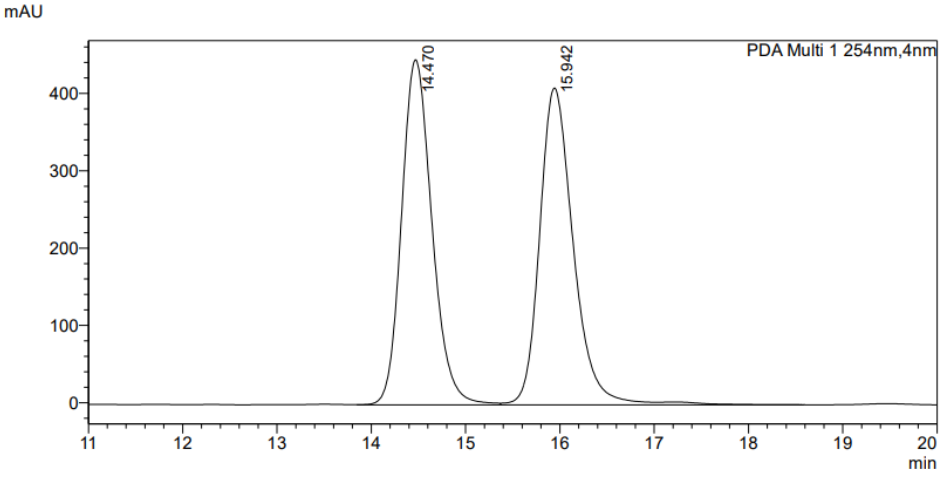
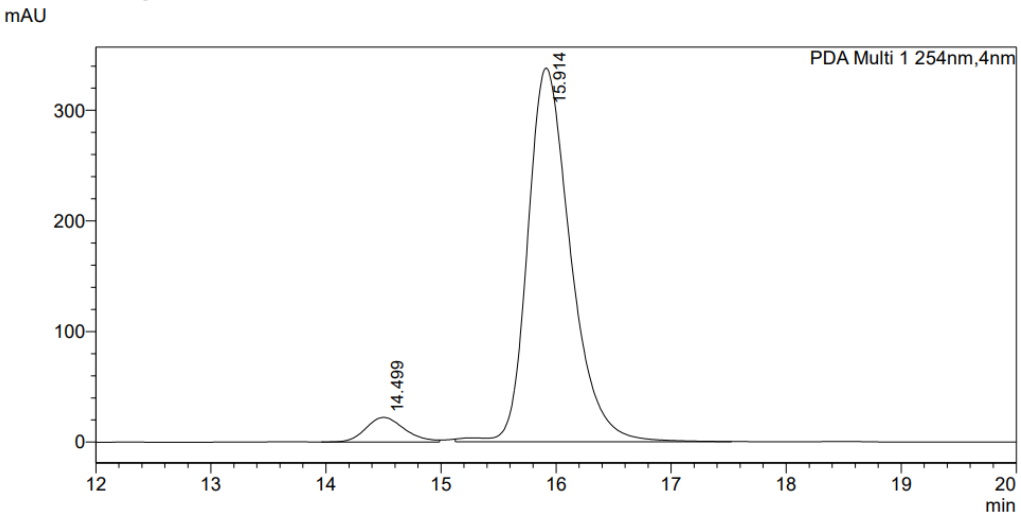


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	14.470	9989578	49.484	445664
2	15.942	10198036	50.516	409220
Total		20187614	100.000	854884

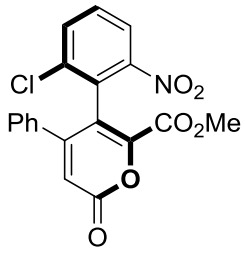
<Chromatogram>



<Peak Table>

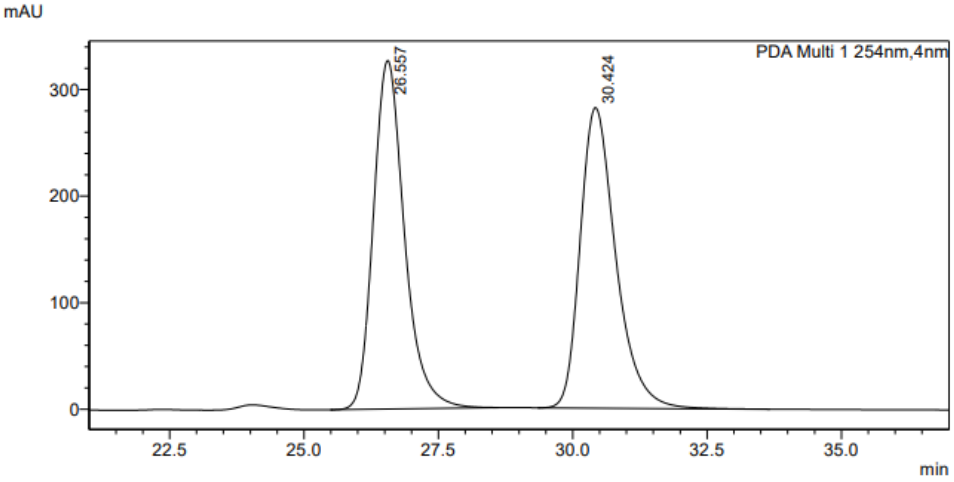
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	14.499	521047	5.619	22230
2	15.914	8751365	94.381	337919
Total		9272412	100.000	360149



3b

<Chromatogram>

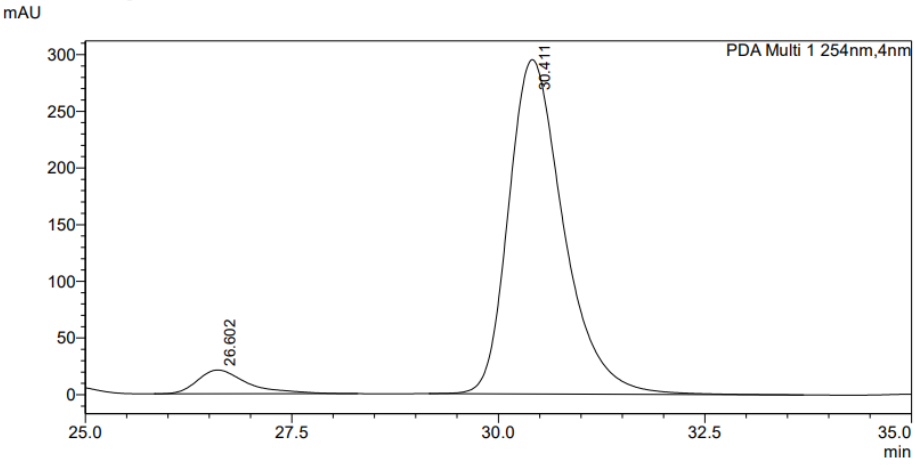


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	26.557	13170219	50.296	327076
2	30.424	13015364	49.704	282107
Total		26185582	100.000	609183

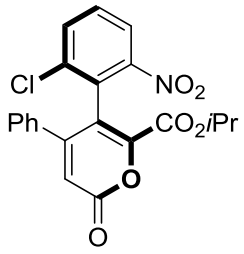
<Chromatogram>



<Peak Table>

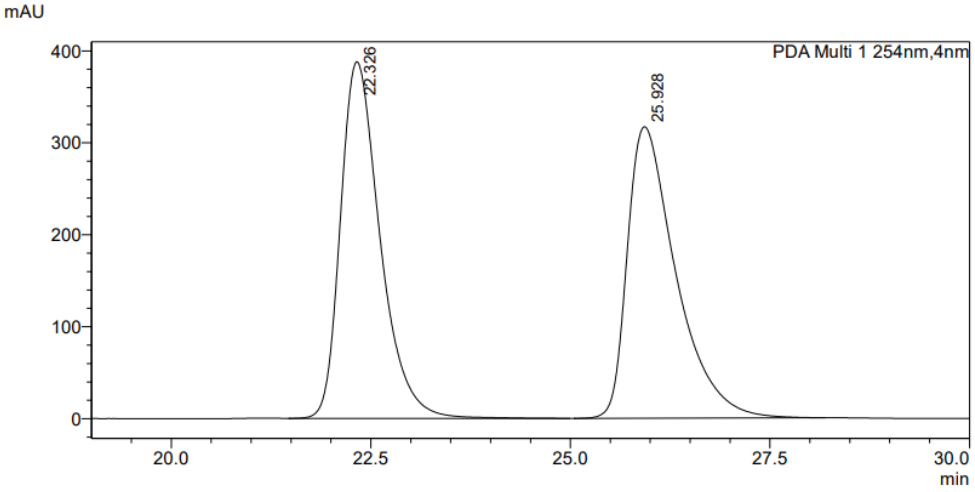
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	26.602	883175	6.073	20954
2	30.411	13660285	93.927	294898
Total		14543460	100.000	315852



3c

<Chromatogram>

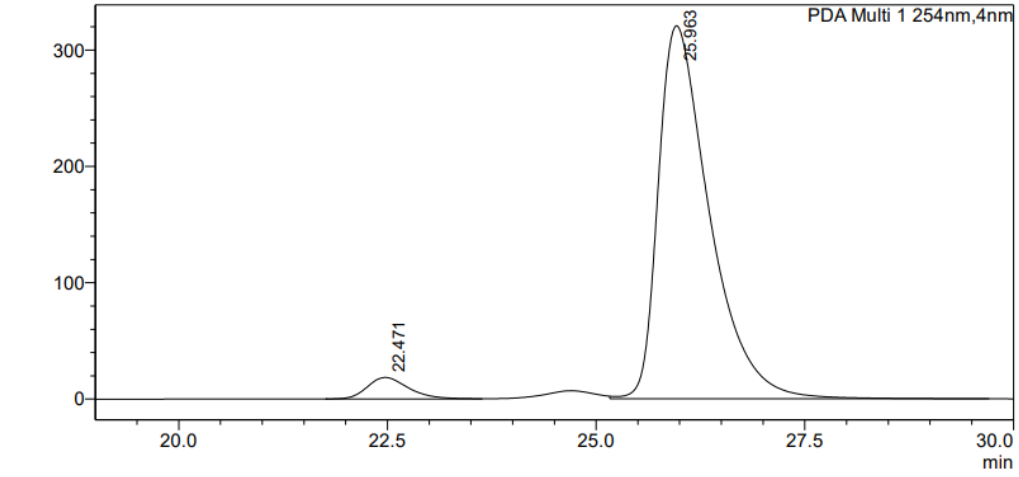


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	22.326	13410046	49.965	387964
2	25.928	13429062	50.035	316957
Total		26839107	100.000	704921

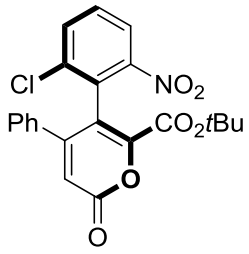
<Chromatogram>



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	22.471	634428	4.435	18452
2	25.963	13671733	95.565	320521
Total		14306161	100.000	338973



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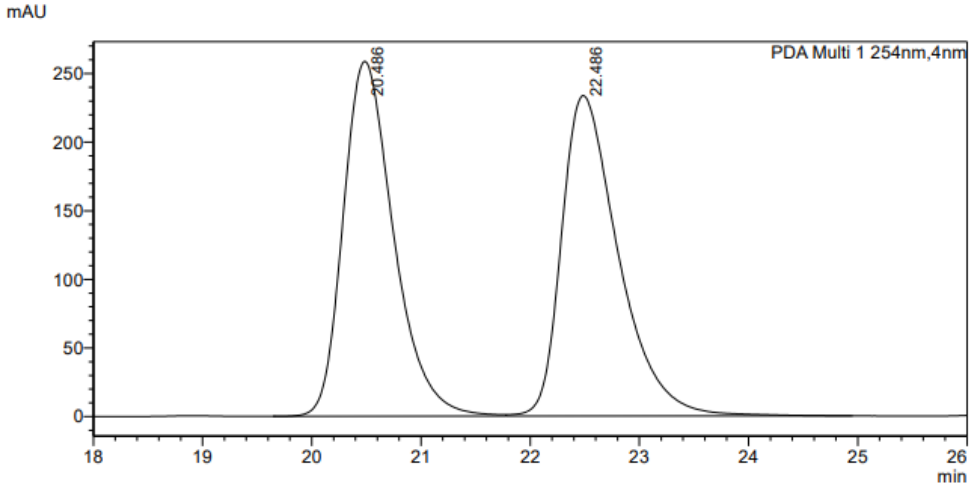
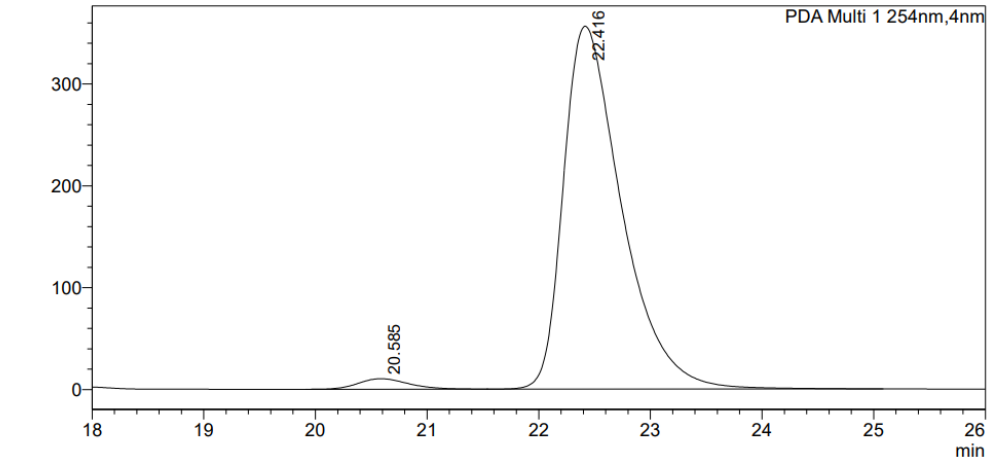


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	20.486	8328177	49.538	258578
2	22.486	8483653	50.462	233631
Total		16811829	100.000	492209

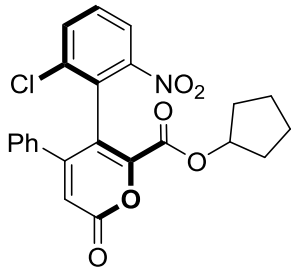
<Chromatogram>



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	20.585	326780	2.465	10390
2	22.416	12928090	97.535	356207
Total		13254870	100.000	366597



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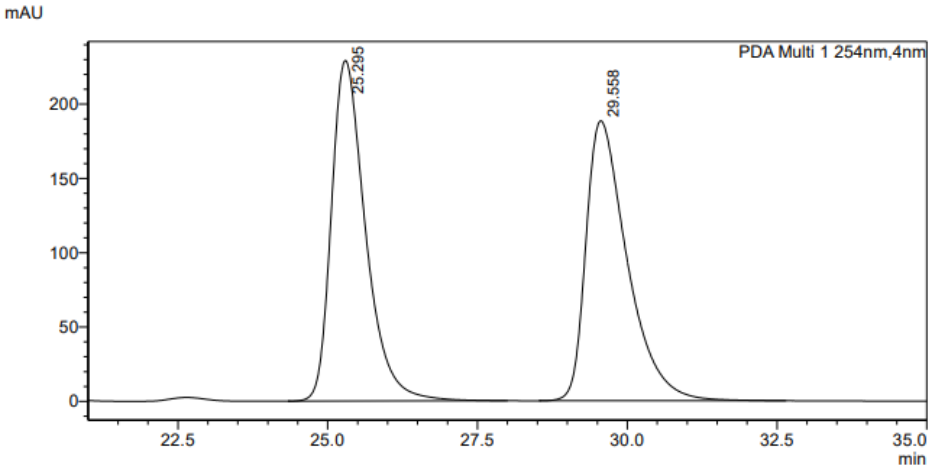

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	25.295	9119140	50.211	229180
2	29.558	9042454	49.789	188405
Total		18161594	100.000	417585

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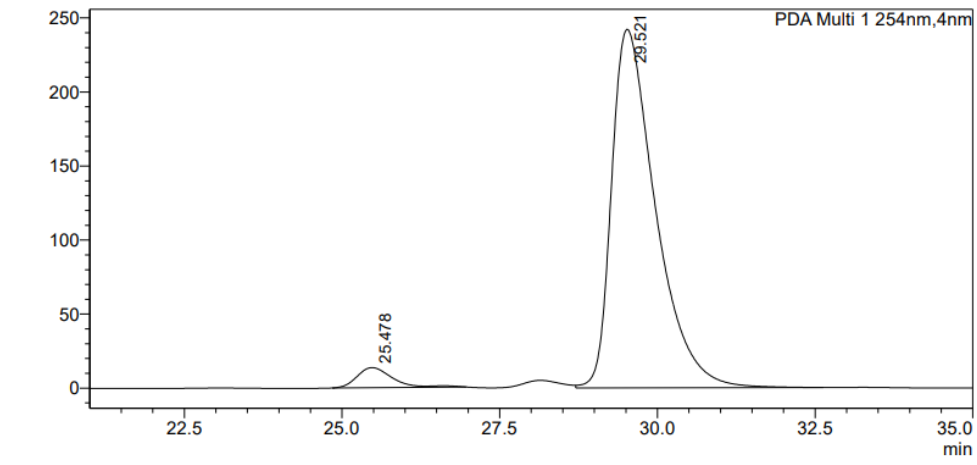
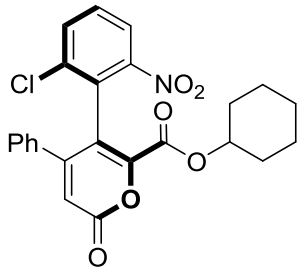


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	25.478	528264	4.307	13532
2	29.521	11737563	95.693	242041
Total		12265826	100.000	255573



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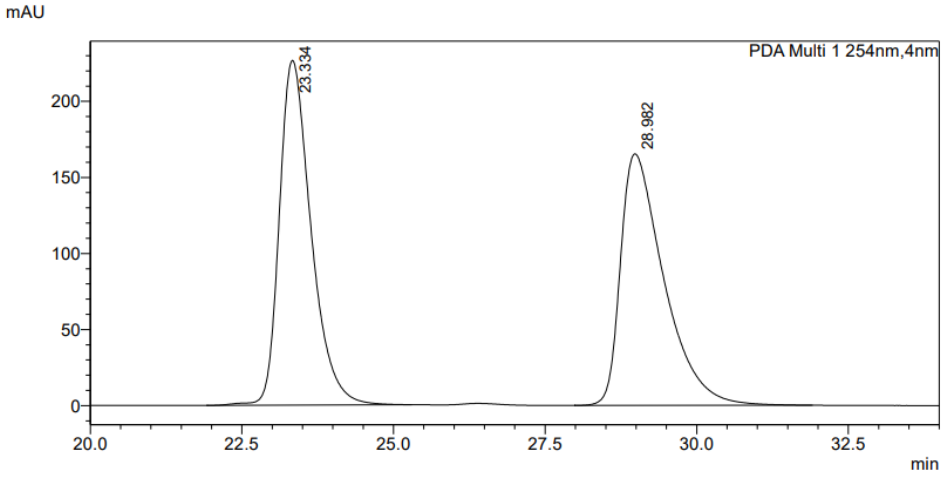

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	23.334	8257460	50.061	226553
2	28.982	8237304	49.939	165383
Total		16494764	100.000	391936

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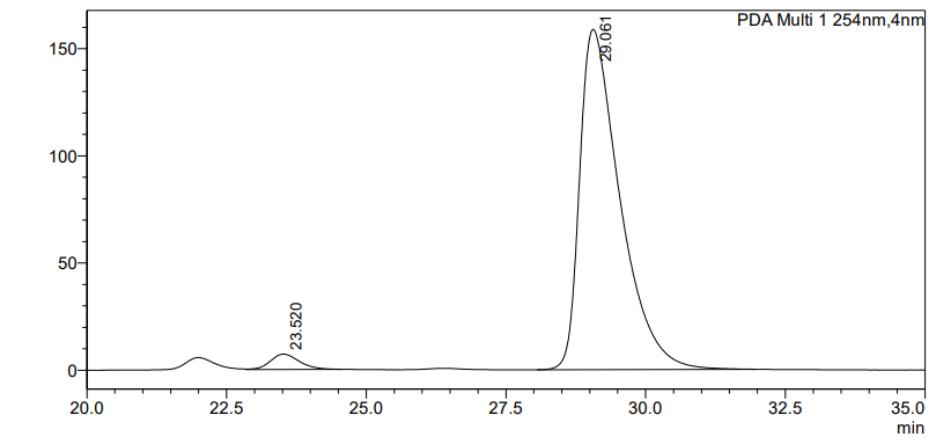
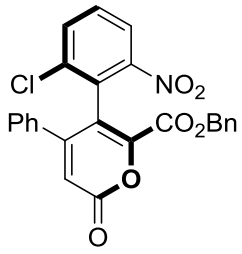


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	23.520	257985	3.134	7151
2	29.061	7974804	96.866	158712
Total		8232789	100.000	165863



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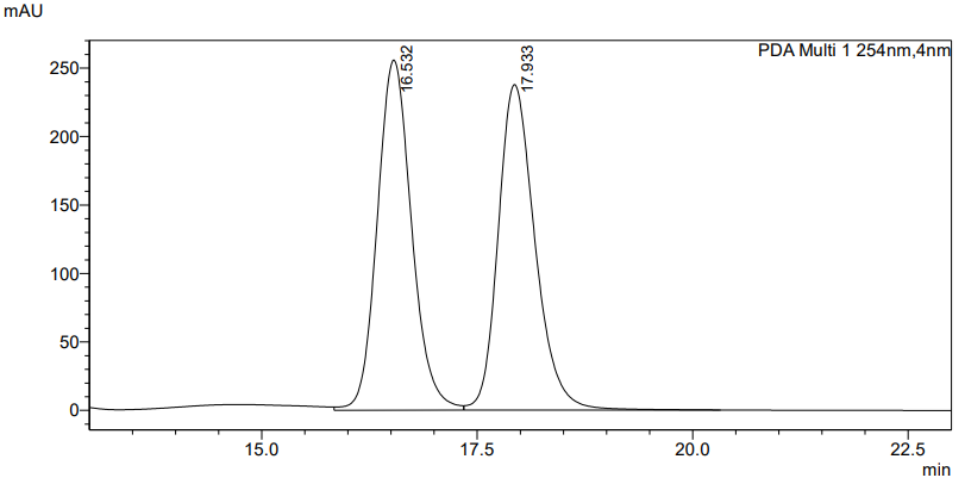

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	16.532	7089179	50.081	255732
2	17.933	7066319	49.919	237868
Total		14155497	100.000	493599

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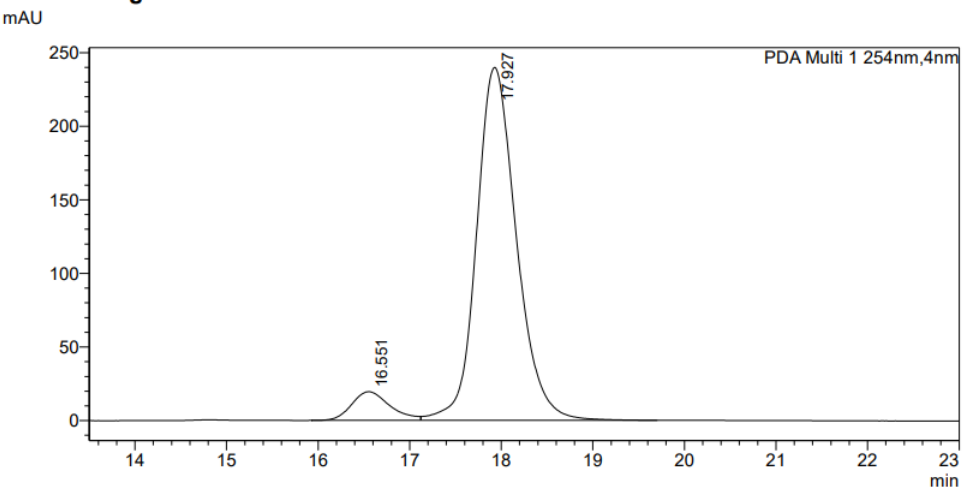
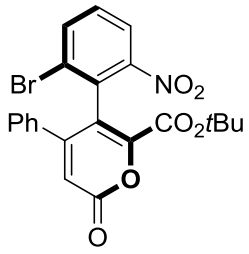


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	16.551	567826	7.251	19513
2	17.927	7263374	92.749	239802
Total		7831200	100.000	259316



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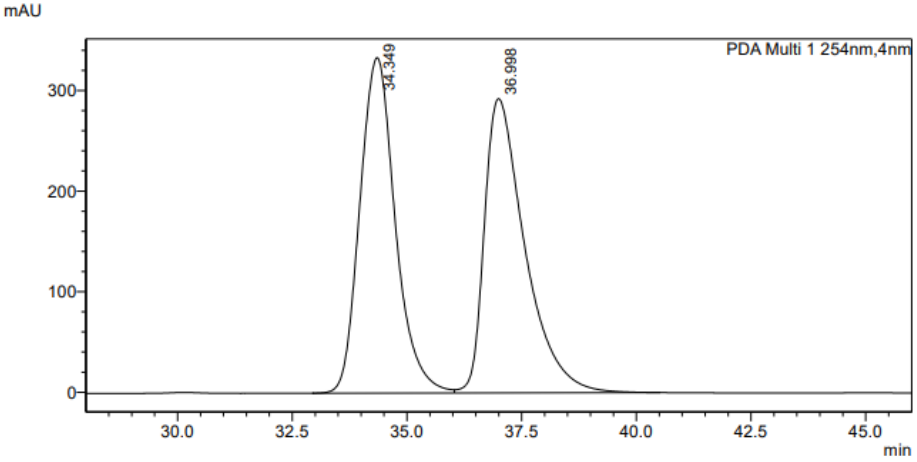

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	34.349	17920865	49.898	333477
2	36.998	17993952	50.102	292487
Total		35914817	100.000	625964

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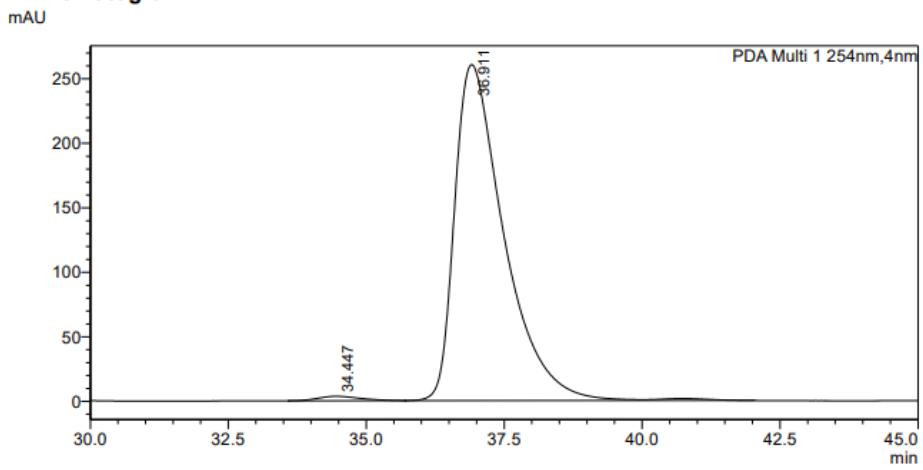
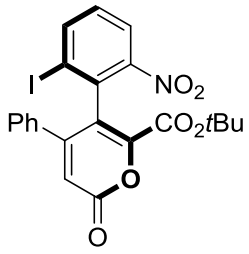


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	34.447	184877	1.124	3447
2	36.911	16264596	98.876	260542
Total		16449473	100.000	263989



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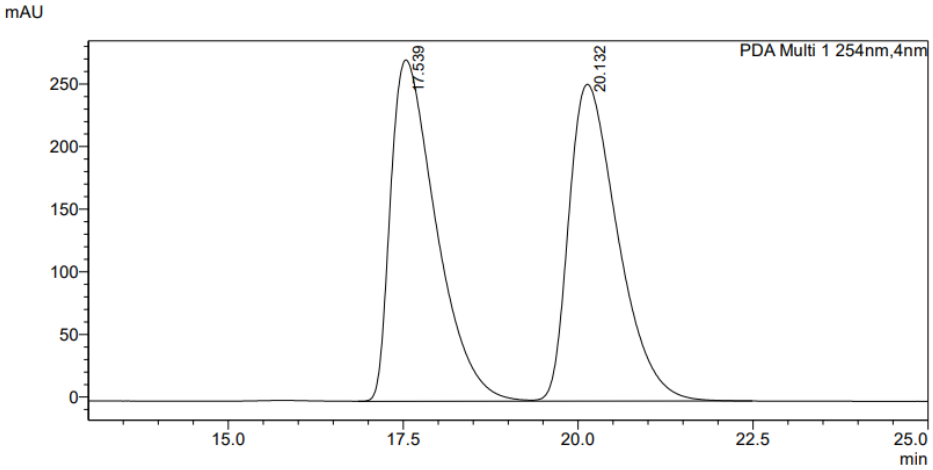

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	17.539	12307640	49.989	272497
2	20.132	12313030	50.011	252979
Total		24620670	100.000	525476

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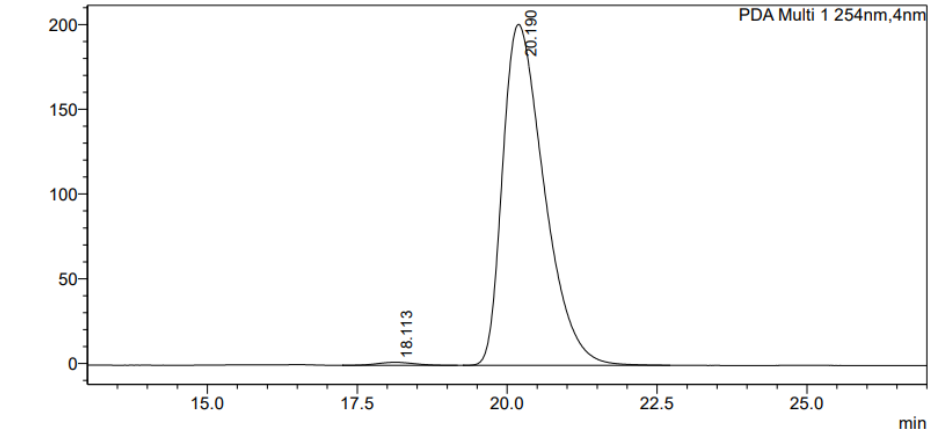
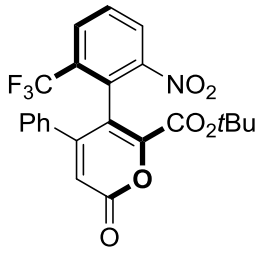


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	18.113	79391	0.813	1812
2	20.190	9690145	99.187	201281
Total		9769535	100.000	203094



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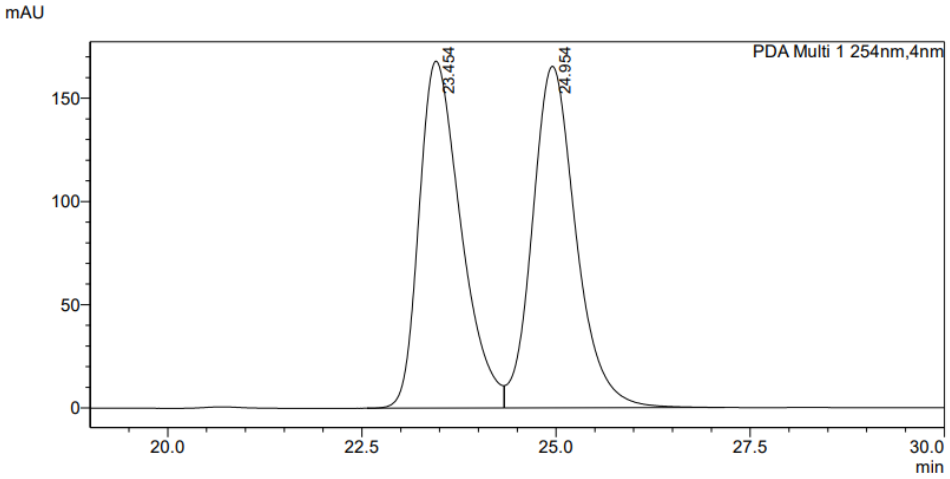

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	23.454	6291032	49.344	168013
2	24.954	6458423	50.656	165398
Total		12749455	100.000	333411

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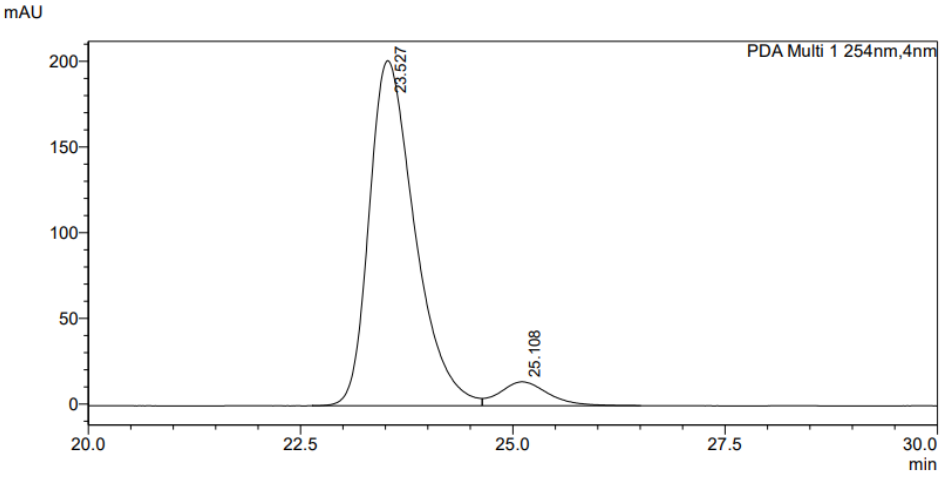
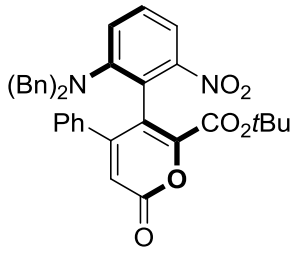


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	23.527	7526259	93.195	201411
2	25.108	549578	6.805	13924
Total		8075837	100.000	215335



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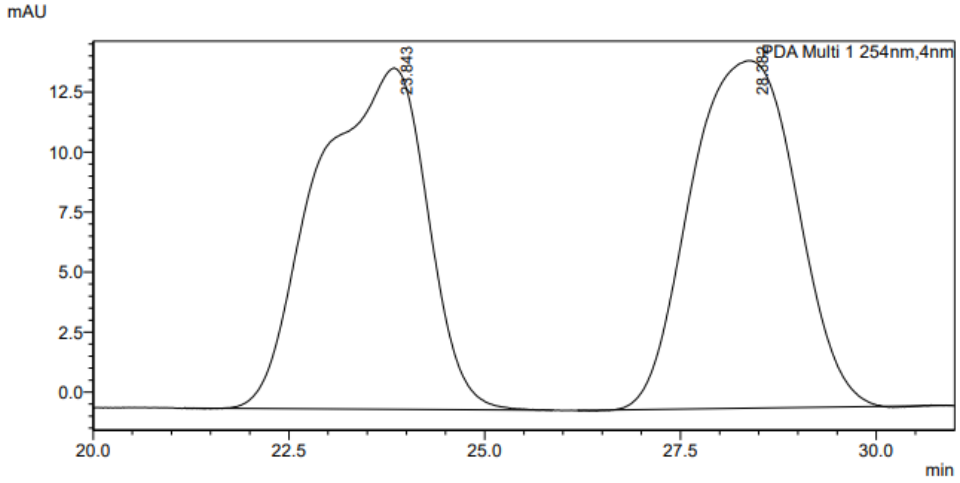

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	23.843	1391923	50.494	14217
2	28.382	1364714	49.506	14472
Total		2756637	100.000	28688

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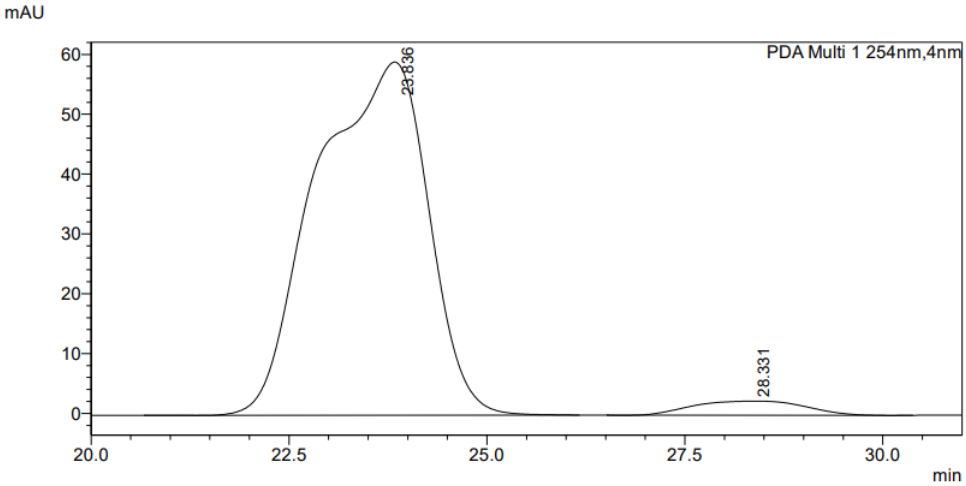
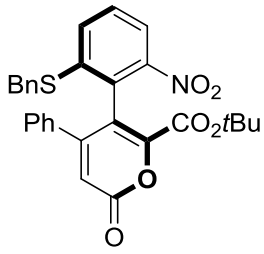


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	23.836	5788972	96.142	59034
2	28.331	232295	3.858	2371
Total		6021267	100.000	61405



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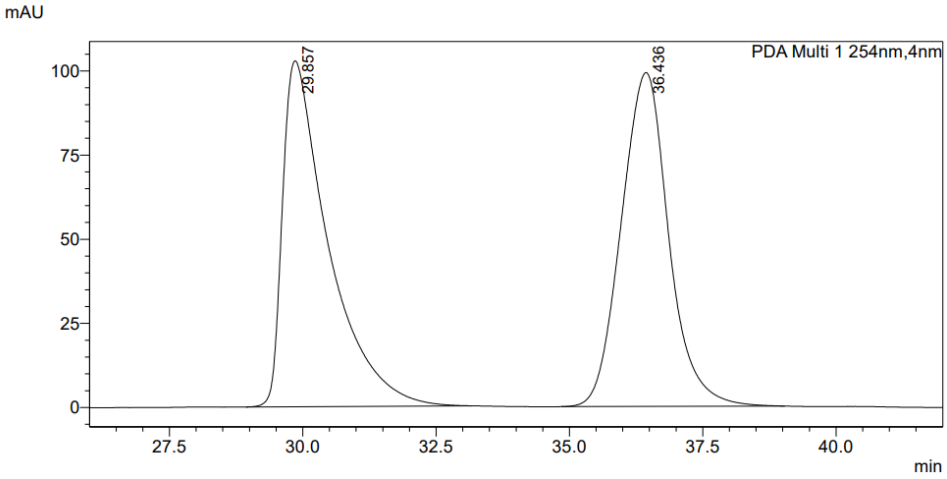

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	29.857	6130906	49.964	102770
2	36.436	6139738	50.036	99191
Total		12270644	100.000	201961

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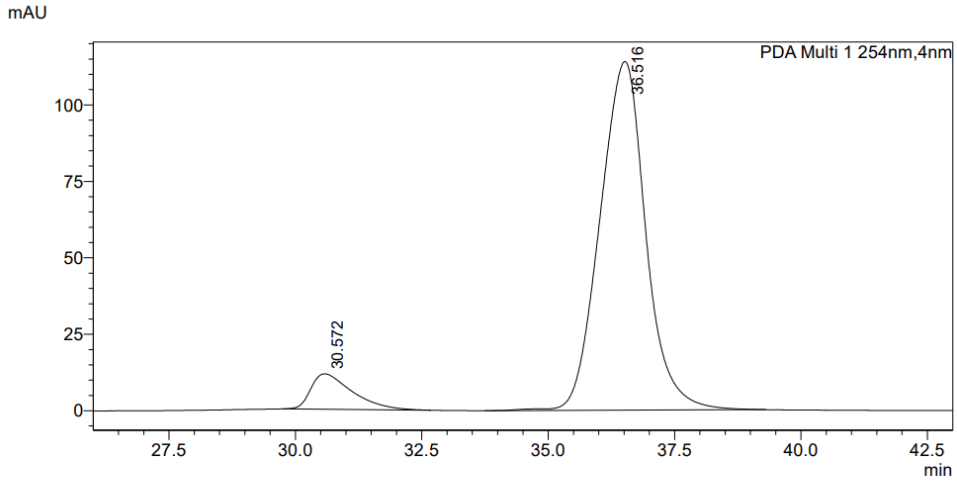
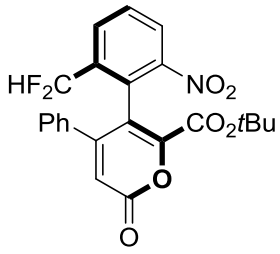


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	30.572	656498	8.364	11567
2	36.516	7192820	91.636	113993
Total		7849318	100.000	125560



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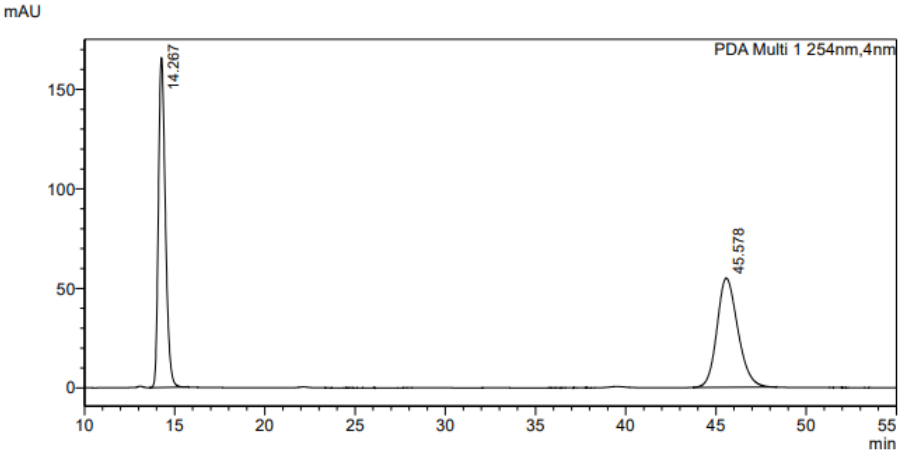

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	14.267	4442474	50.193	165686
2	45.578	4408245	49.807	54847
Total		8850719	100.000	220533

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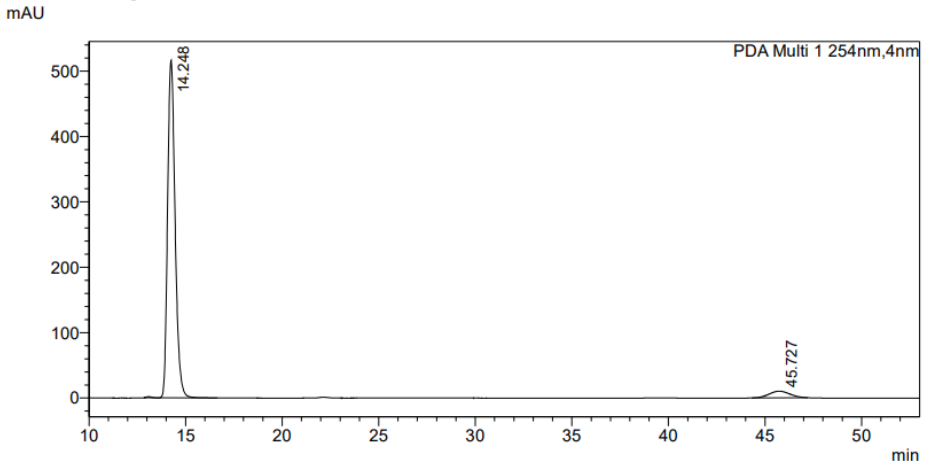
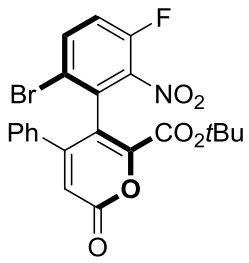


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	14.248	13962221	94.891	516085
2	45.727	751674	5.109	10123
Total		14713896	100.000	526208



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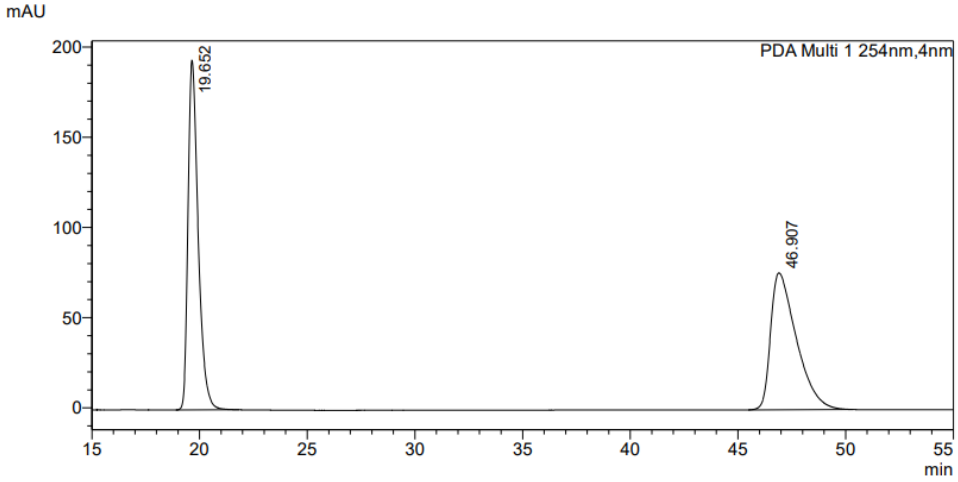

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	19.652	6368198	50.226	193678
2	46.907	6310958	49.774	75823
Total		12679156	100.000	269500

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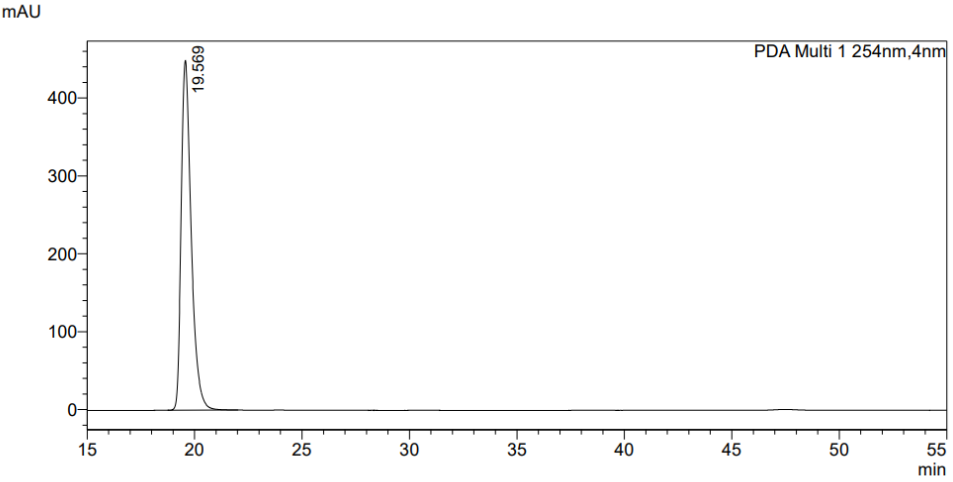
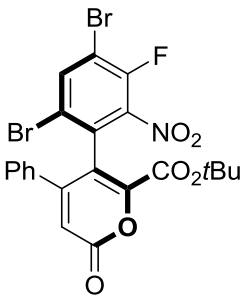


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	19.569	14596304	100.000	448770
Total		14596304	100.000	448770



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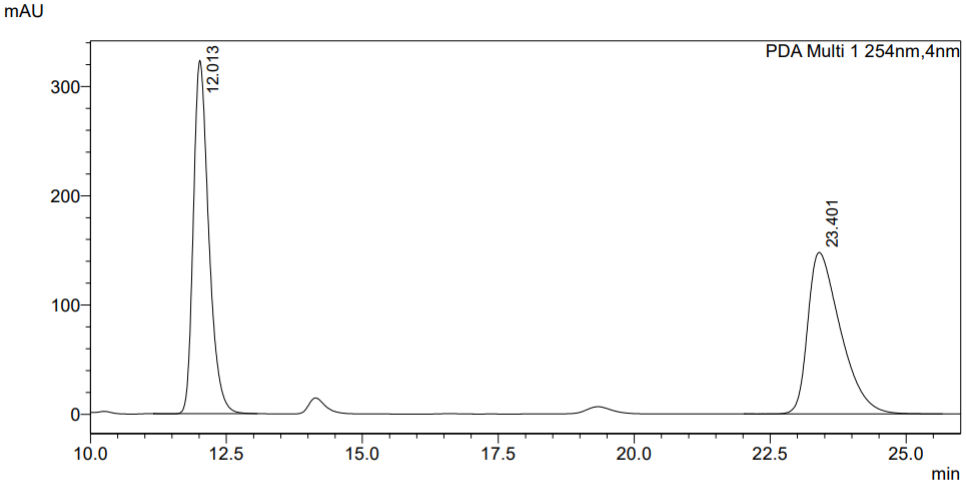

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	12.013	6375167	50.763	323175
2	23.401	6183554	49.237	147832
Total		12558721	100.000	471007

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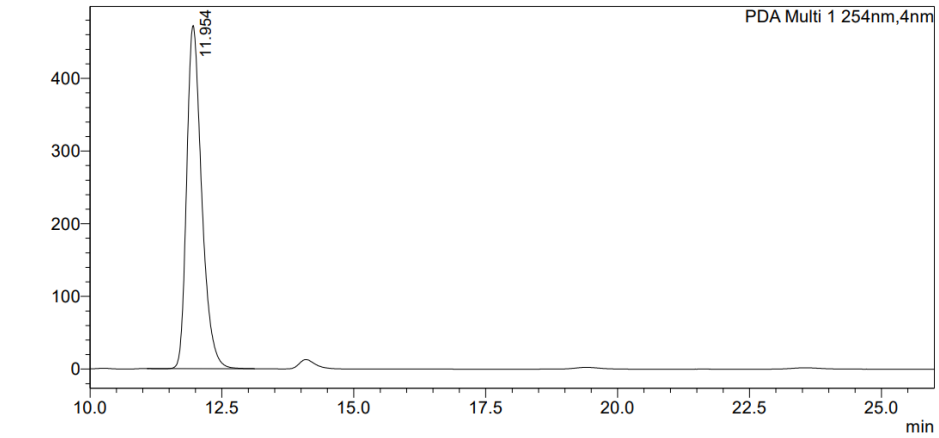
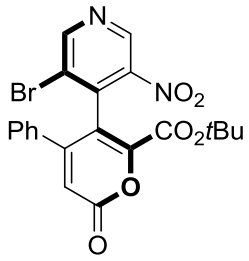


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	11.954	9328917	100.000	471956
Total		9328917	100.000	471956



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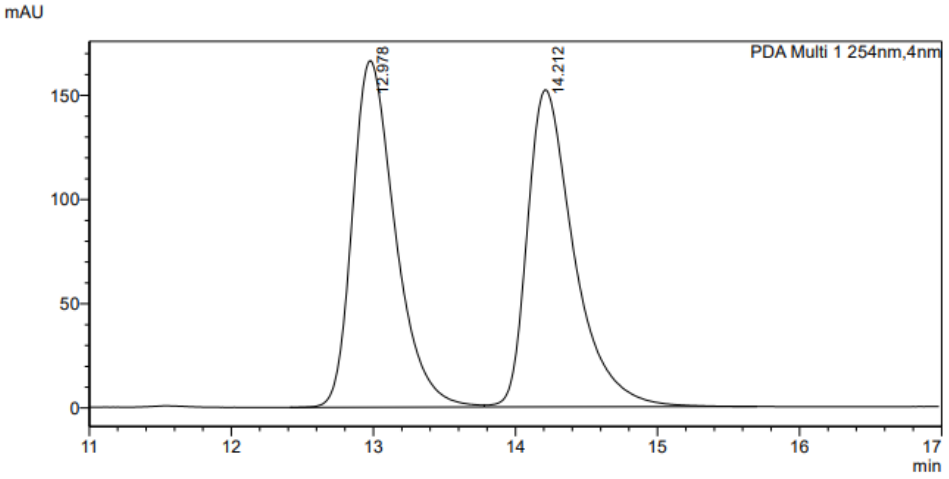

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	12.978	3484629	50.036	166263
2	14.212	3479632	49.964	152123
Total		6964261	100.000	318386

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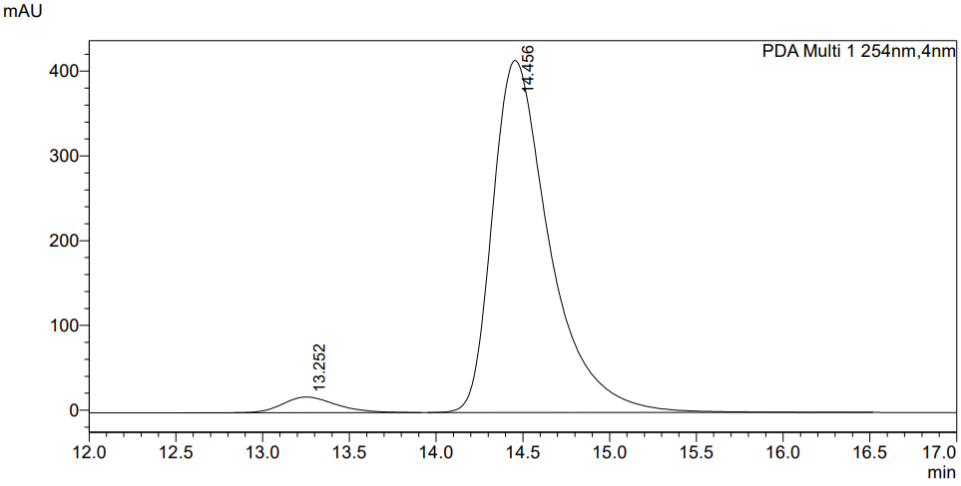
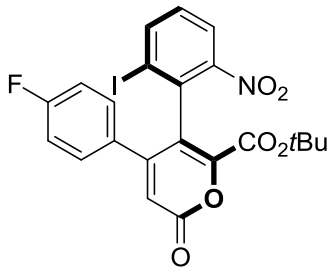


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	13.252	392883	3.963	18412
2	14.456	9520419	96.037	415519
Total		9913302	100.000	433930



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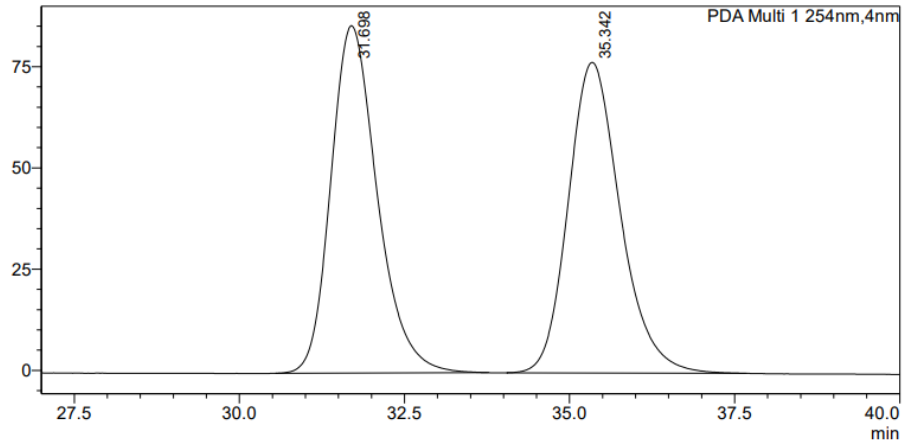
mAU



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	31.698	4201094	49.951	85780
2	35.342	4209363	50.049	76717
Total		8410457	100.000	162497

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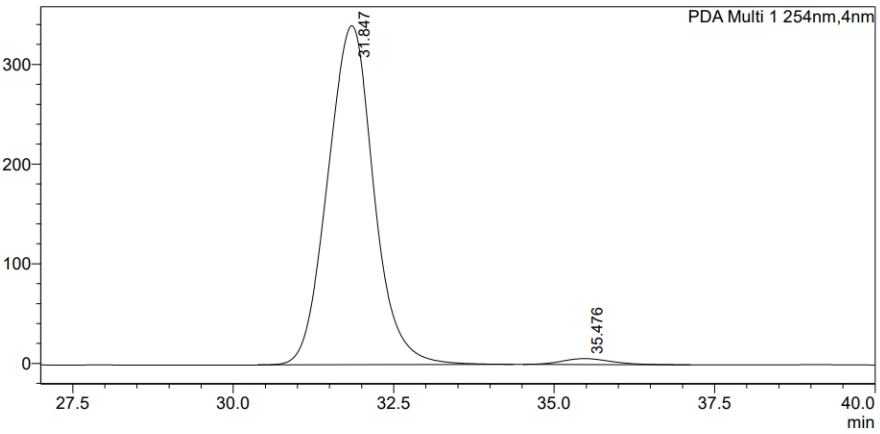
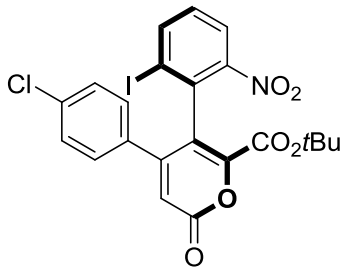
mAU



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	31.847	16992236	98.186	340087
2	35.476	313971	1.814	5925
Total		17306207	100.000	346011



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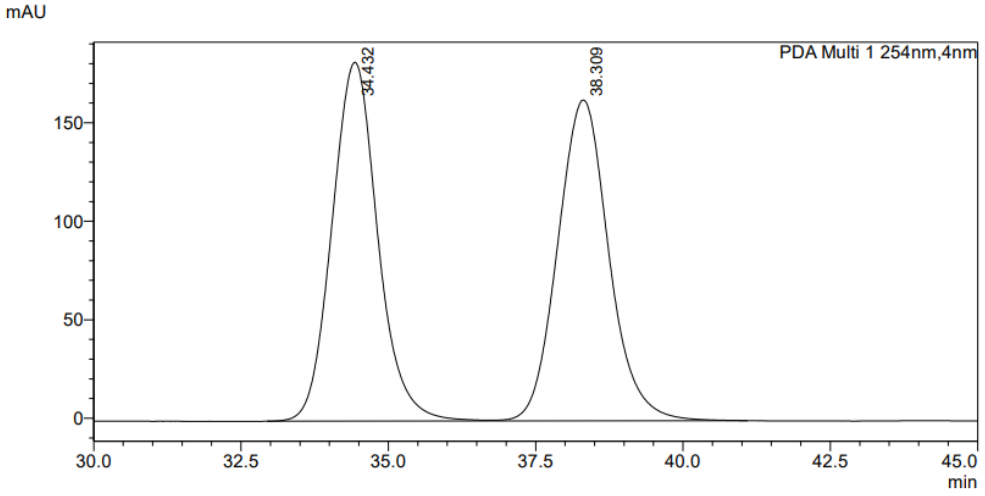

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	34.432	9859917	50.030	182196
2	38.309	9848218	49.970	162929
Total		19708135	100.000	345125

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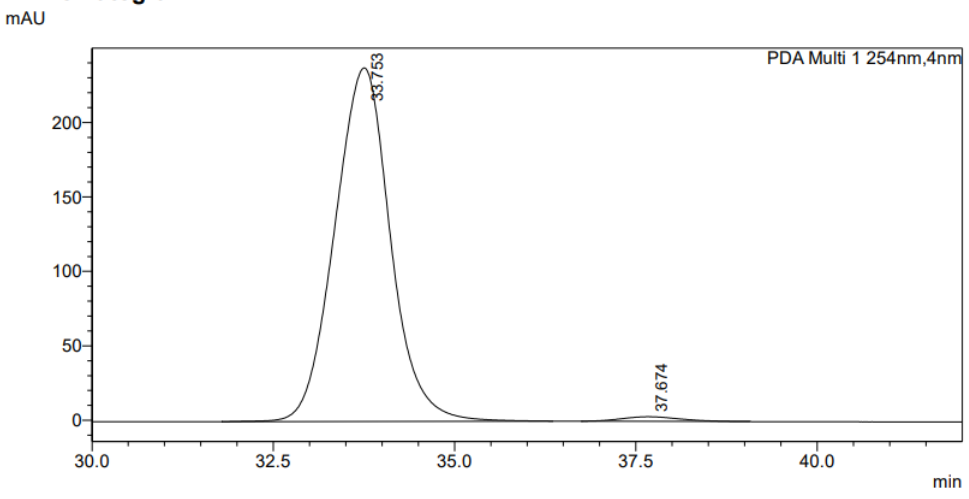
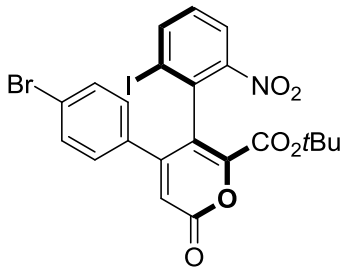


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	33.753	12685201	98.664	237398
2	37.674	171709	1.336	3081
Total		12856910	100.000	240479



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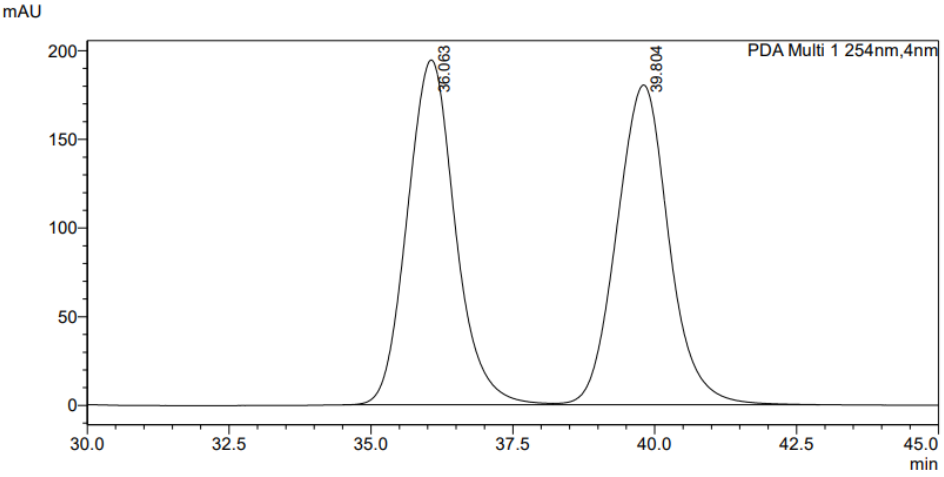

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	36.063	11455072	49.822	194469
2	39.804	11536839	50.178	180291
Total		22991912	100.000	374760

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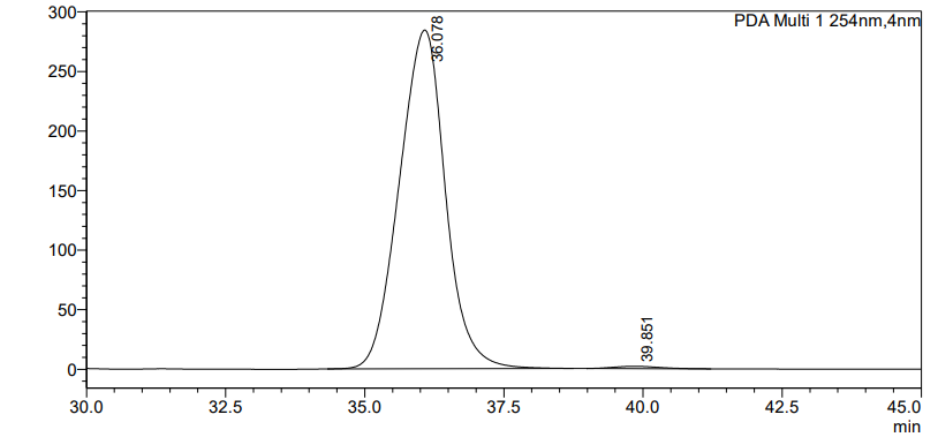
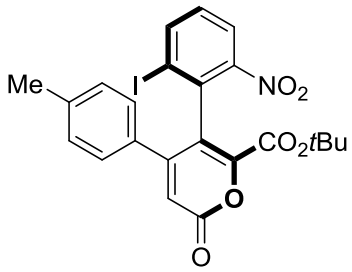


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	36.078	16388820	99.336	284220
2	39.851	109609	0.664	1942
Total		16498428	100.000	286162



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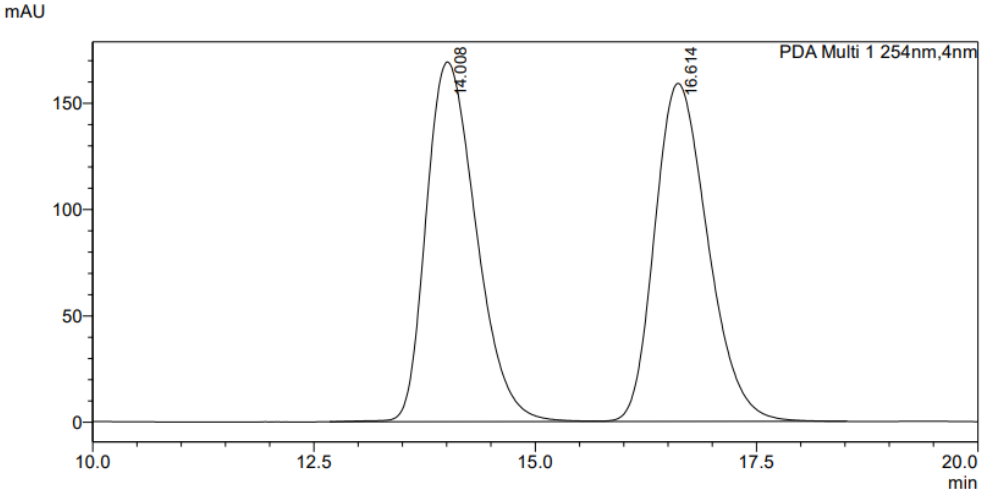

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	14.008	6632367	50.021	169085
2	16.614	6626834	49.979	158909
Total		13259200	100.000	327994

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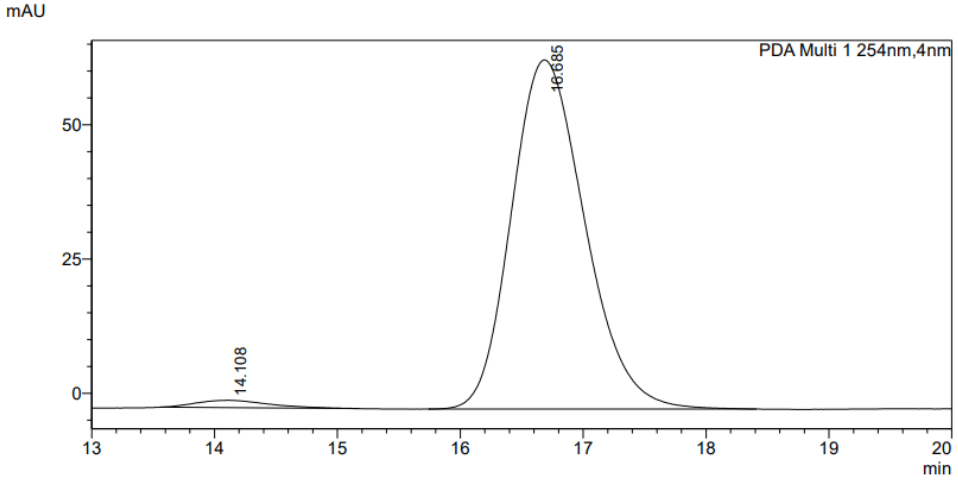
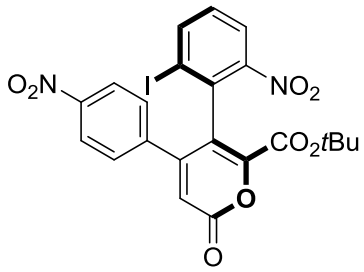


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	14.108	56426	2.047	1366
2	16.685	2700617	97.953	65030
Total		2757043	100.000	66396



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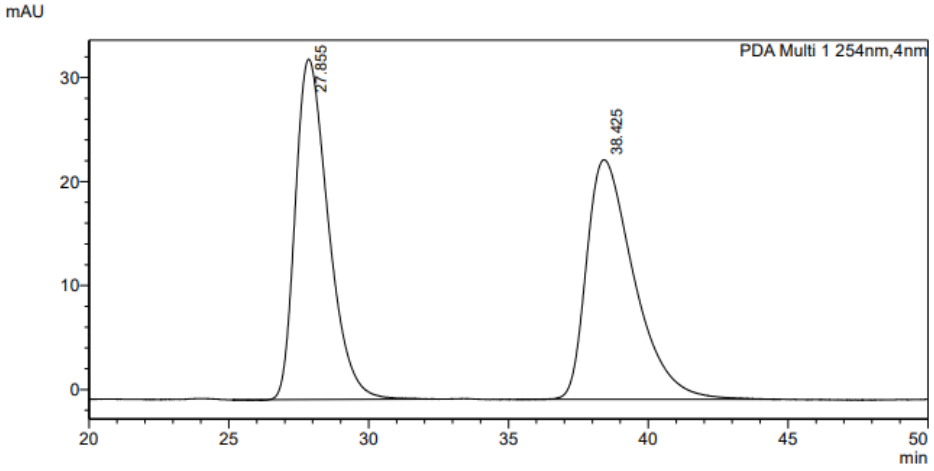

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	27.855	2687149	49.629	32726
2	38.425	2727312	50.371	23048
Total		5414461	100.000	55773

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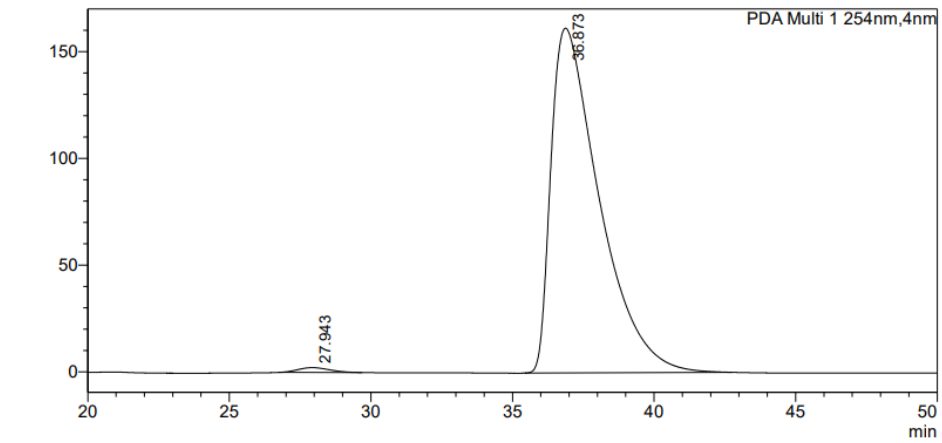
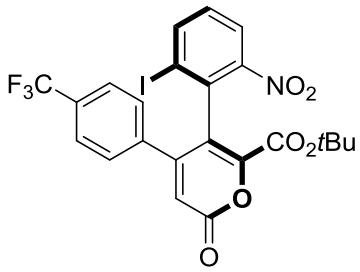


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	27.943	175367	0.906	2260
2	36.873	19176381	99.094	161509
Total		19351747	100.000	163769



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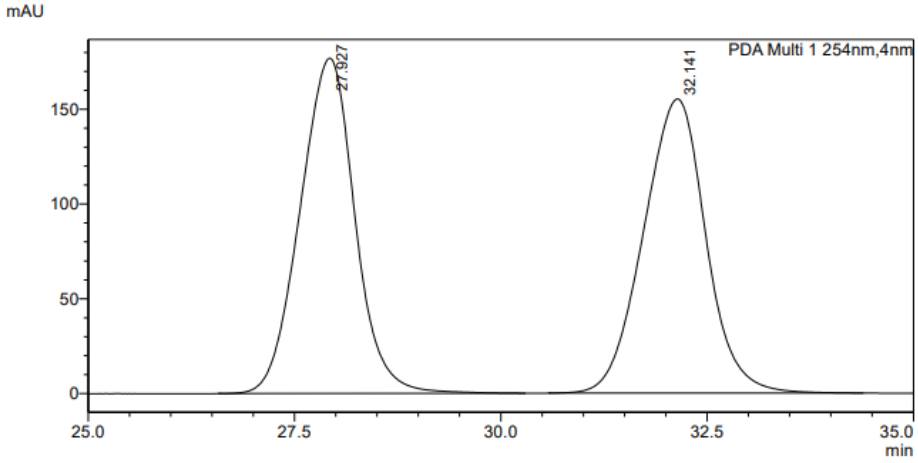

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	27.927	8191280	50.048	176903
2	32.141	8175454	49.952	155224
Total		16366734	100.000	332127

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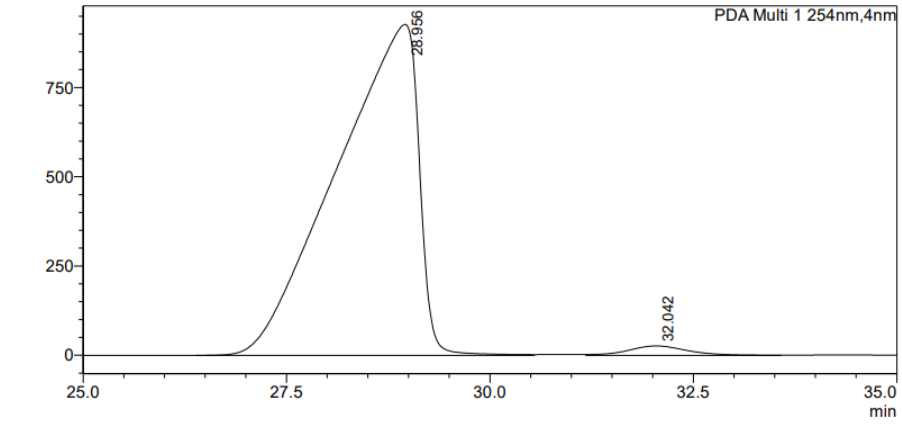
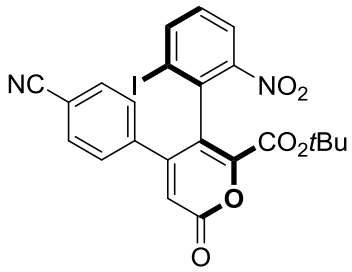


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	28.956	65184512	97.982	927123
2	32.042	1342713	2.018	26307
Total		66527225	100.000	953430



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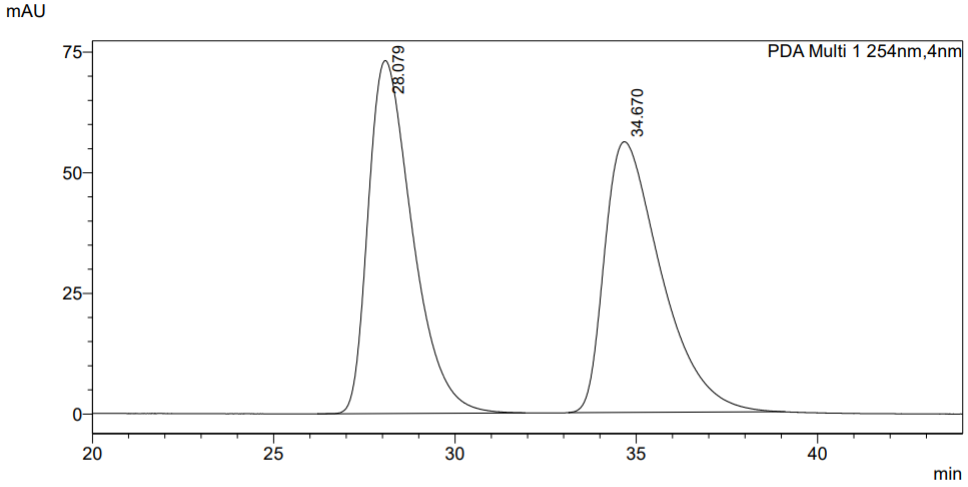

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	28.079	6189494	50.300	73151
2	34.670	6115684	49.700	56096
Total		12305178	100.000	129248

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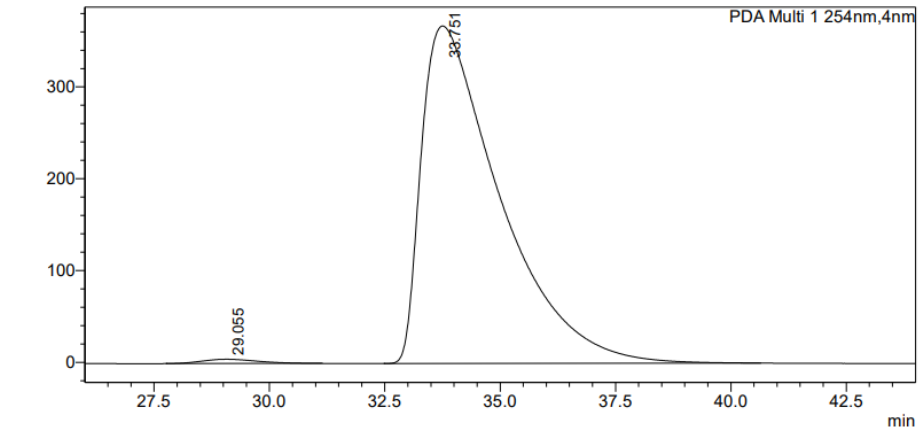
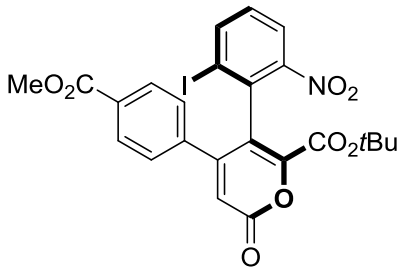


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	29.055	390220	0.889	4659
2	33.751	43514498	99.111	367653
Total		43904718	100.000	372313



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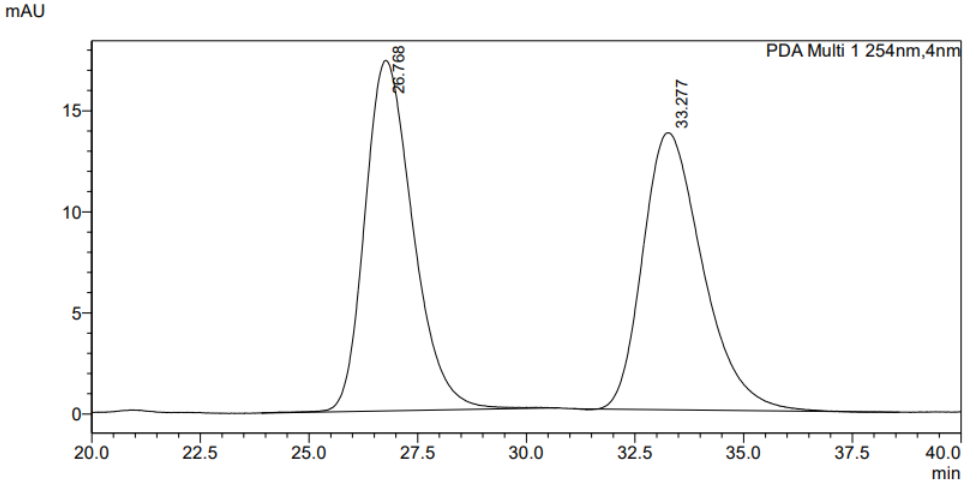

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	26.768	1332884	50.385	17330
2	33.277	1312501	49.615	13697
Total		2645384	100.000	31027

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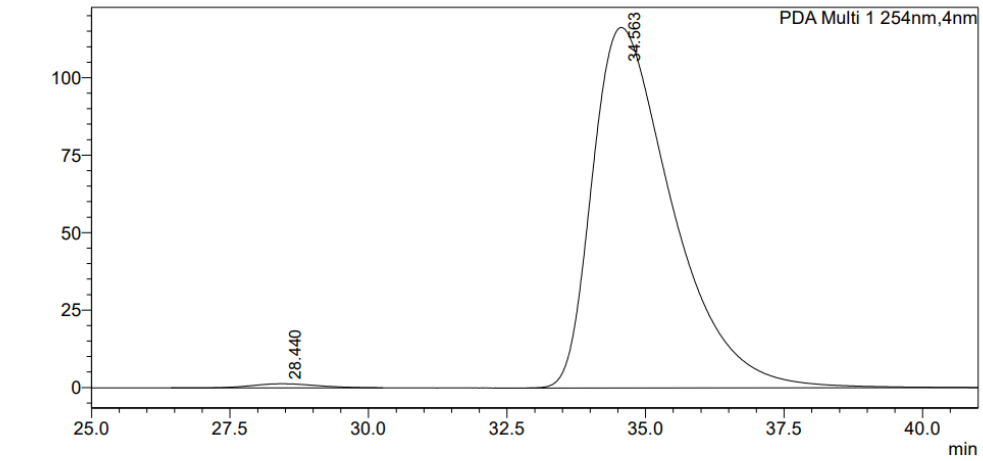
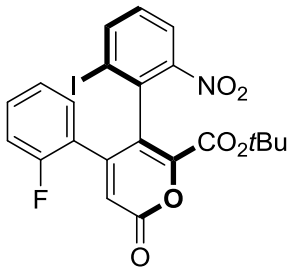


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	28.440	107385	0.910	1319
2	34.563	11696029	99.090	116308
Total		11803414	100.000	117627



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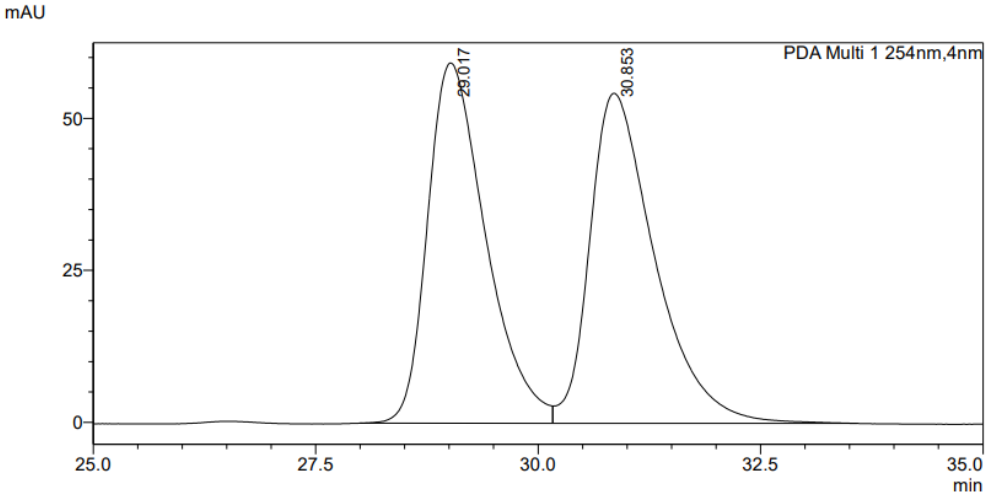

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	29.017	2694352	49.353	59238
2	30.853	2764989	50.647	54267
Total		5459341	100.000	113505

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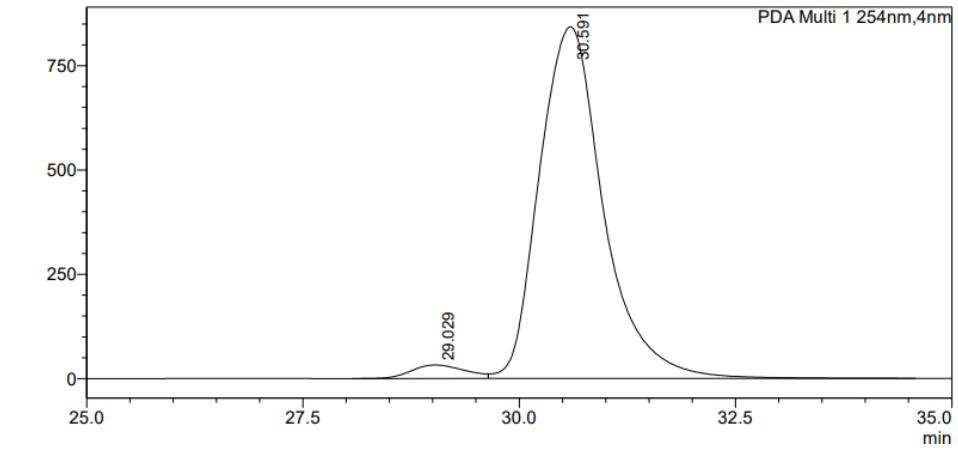
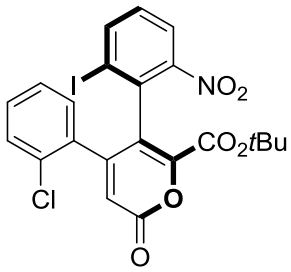


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	29.029	1410763	3.147	32498
2	30.591	43418130	96.853	842902
Total		44828894	100.000	875400



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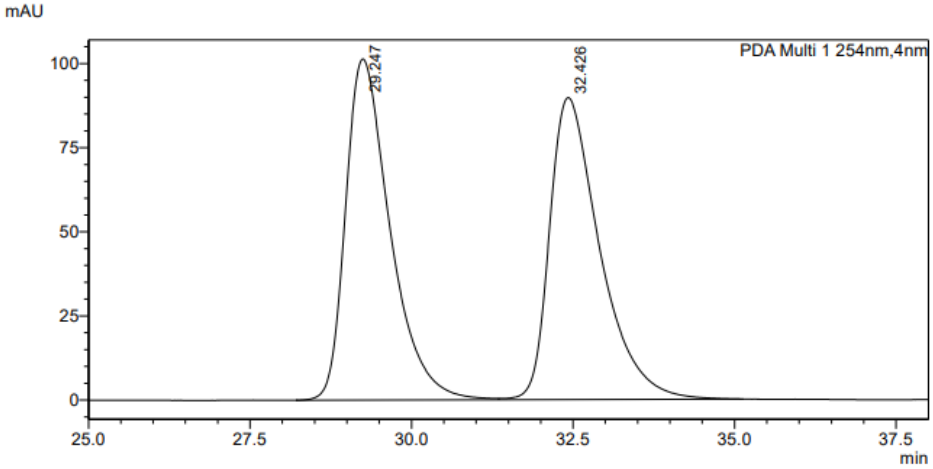

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	29.247	4860126	50.056	101369
2	32.426	4849235	49.944	89725
Total		9709362	100.000	191093

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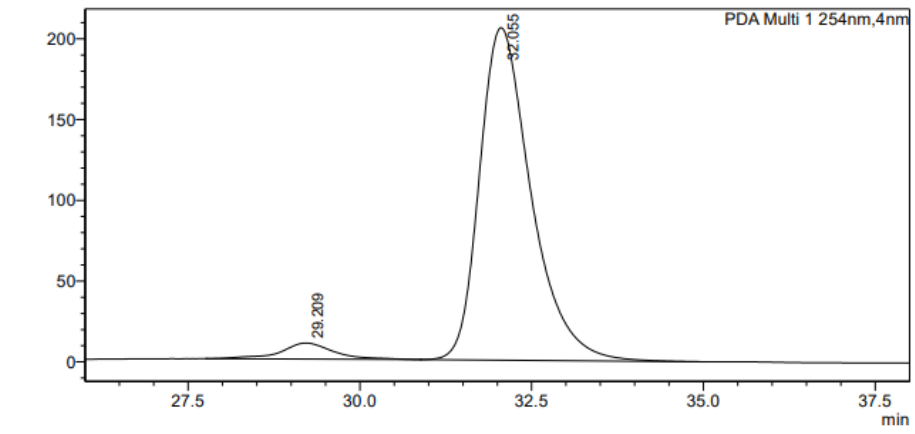
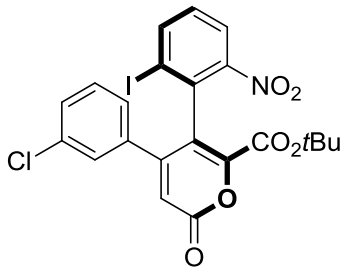


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	29.209	535816	4.747	9932
2	32.055	10752238	95.253	205789
Total		11288054	100.000	215721



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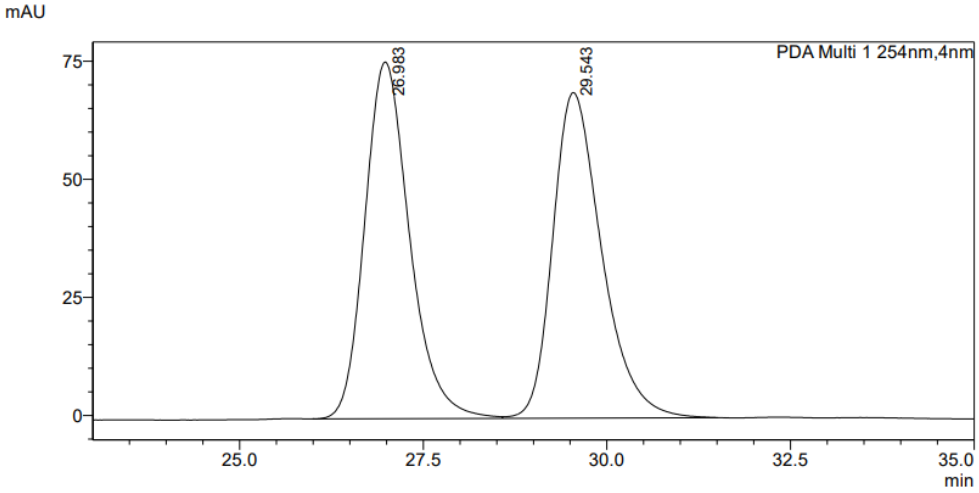

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	26.983	3210010	50.087	75508
2	29.543	3198875	49.913	68899
Total		6408885	100.000	144407

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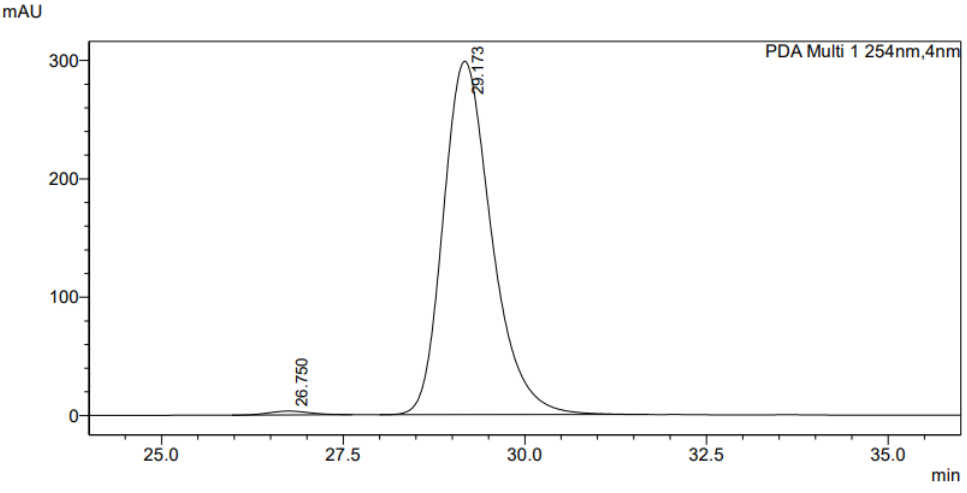
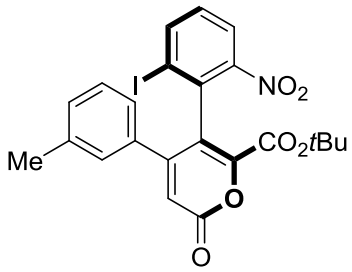


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	26.750	126239	0.902	3225
2	29.173	13862847	99.098	298702
Total		13989086	100.000	301926



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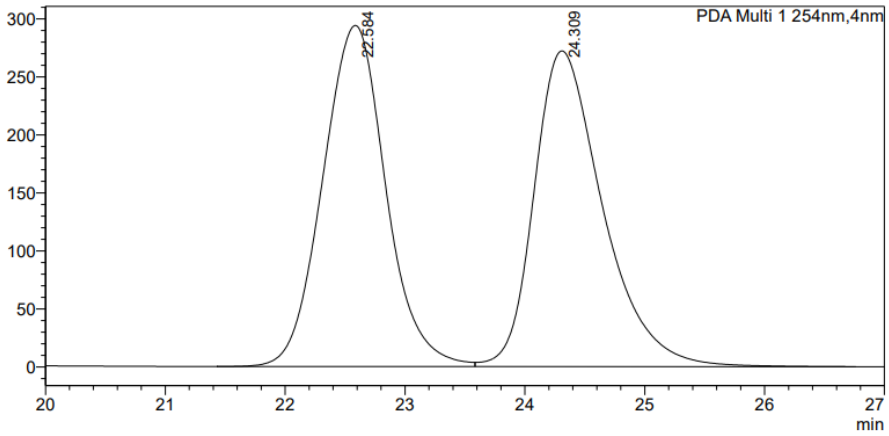

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	22.584	10765452	49.826	294133
2	24.309	10840668	50.174	272283
Total		21606120	100.000	566416

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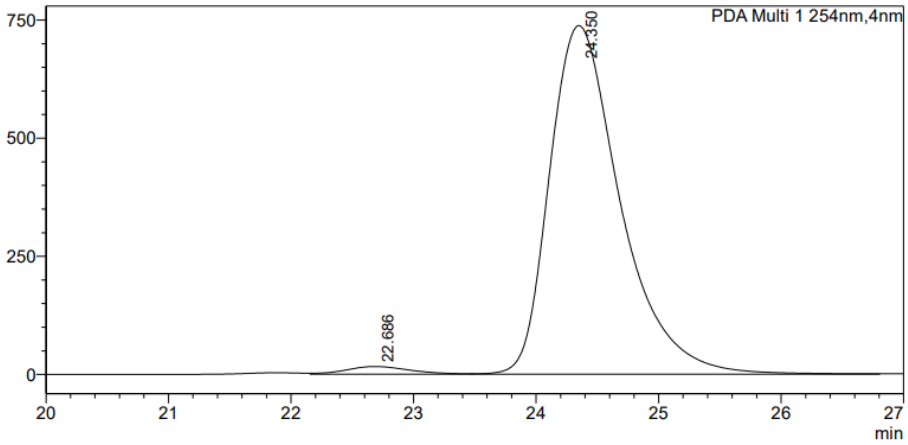
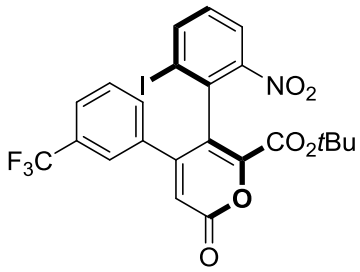


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	22.686	604536	1.998	16399
2	24.350	29649886	98.002	737726
Total		30254422	100.000	754124



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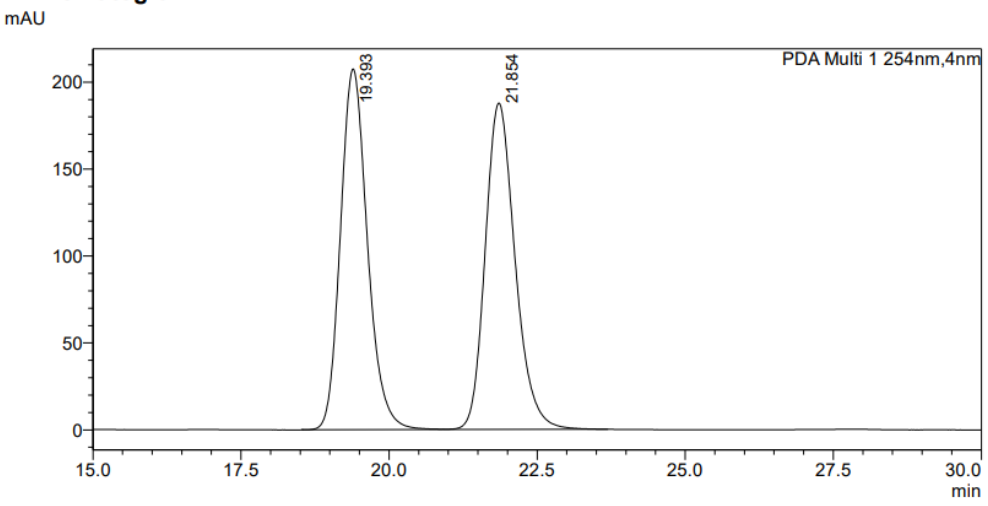

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	19.393	6579000	49.951	207476
2	21.854	6591909	50.049	187727
Total		13170909	100.000	395203

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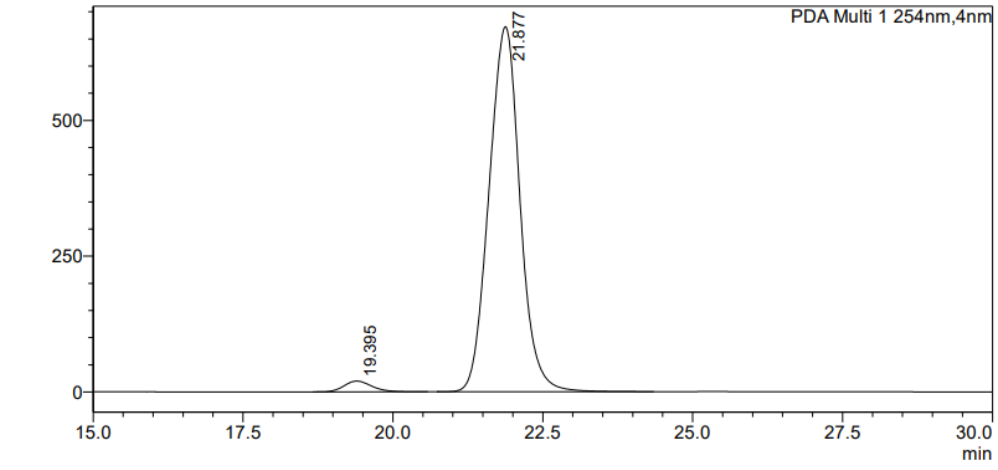
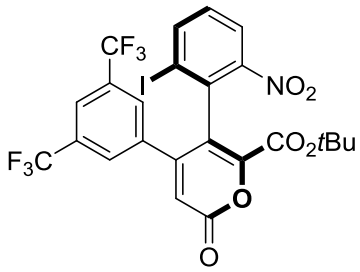


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	19.395	643845	2.593	19844
2	21.877	24186172	97.407	672245
Total		24830017	100.000	692089



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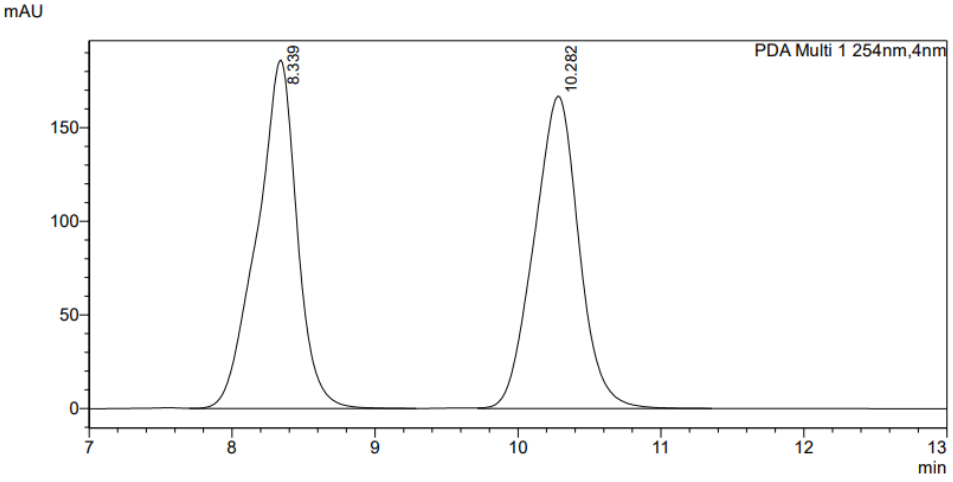

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	8.339	3629294	49.882	186046
2	10.282	3646463	50.118	166766
Total		7275757	100.000	352812

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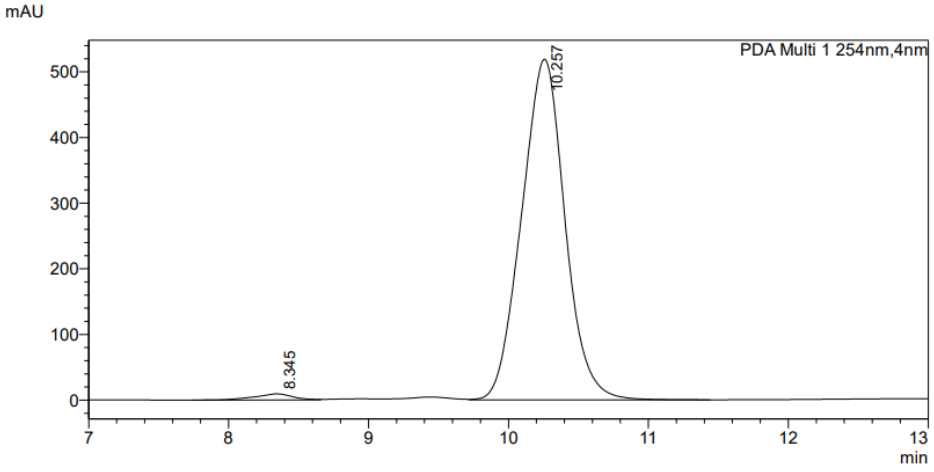
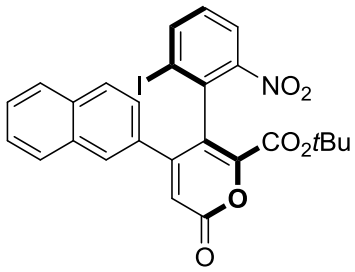


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	8.345	180046	1.586	9287
2	10.257	11170418	98.414	518768
Total		11350464	100.000	528055



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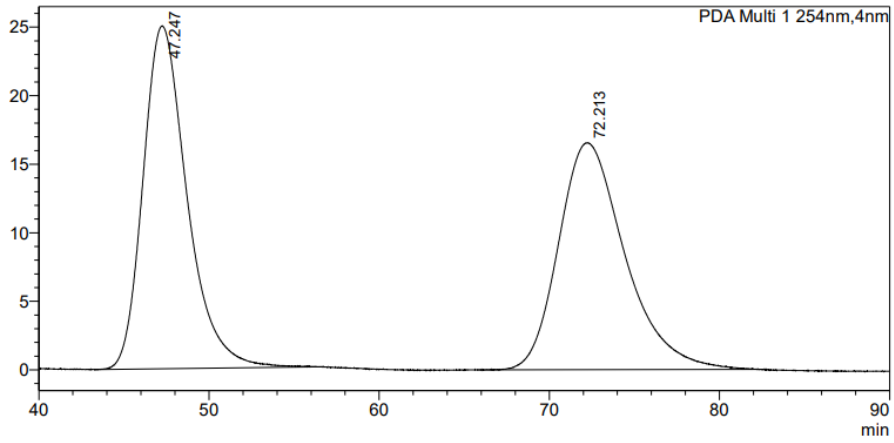

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	47.247	4496732	50.055	25006
2	72.213	4486860	49.945	16546
Total		8983591	100.000	41552

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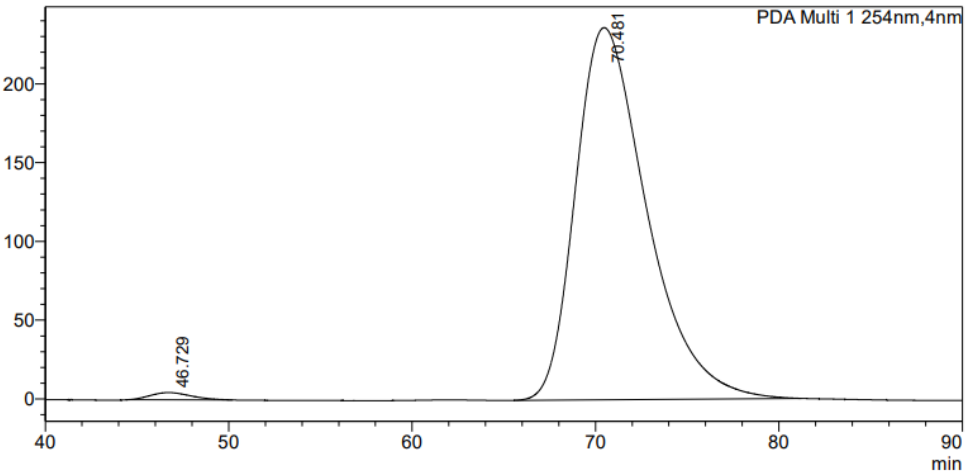
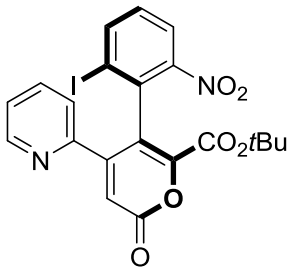
mAU



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	46.729	721528	1.117	4639
2	70.481	63896832	98.883	236135
Total		64618360	100.000	240774



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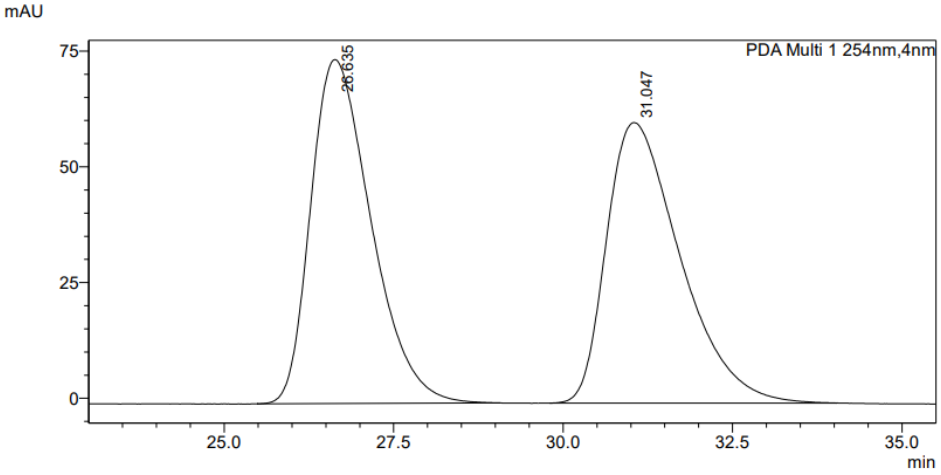
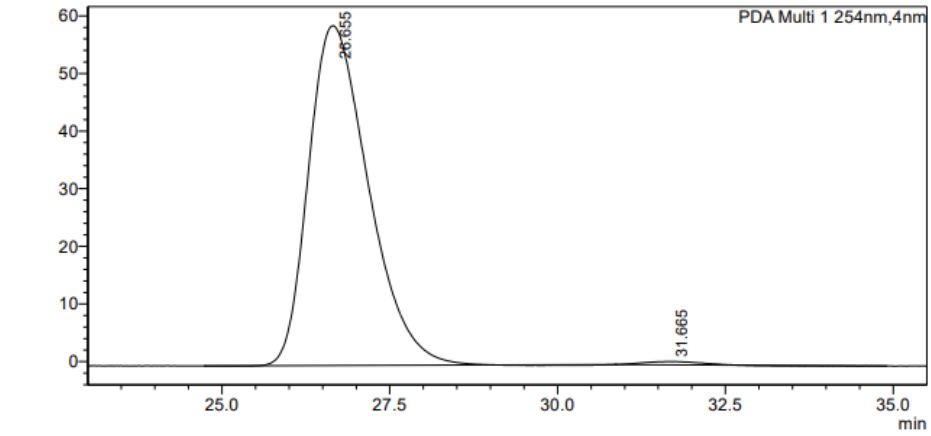


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	26.635	4607763	50.160	74292
2	31.047	4578309	49.840	60574
Total		9186072	100.000	134866

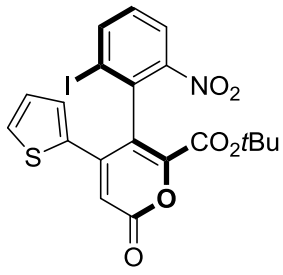
<Chromatogram>



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	26.655	3657733	99.228	58978
2	31.665	28465	0.772	580
Total		3686198	100.000	59558



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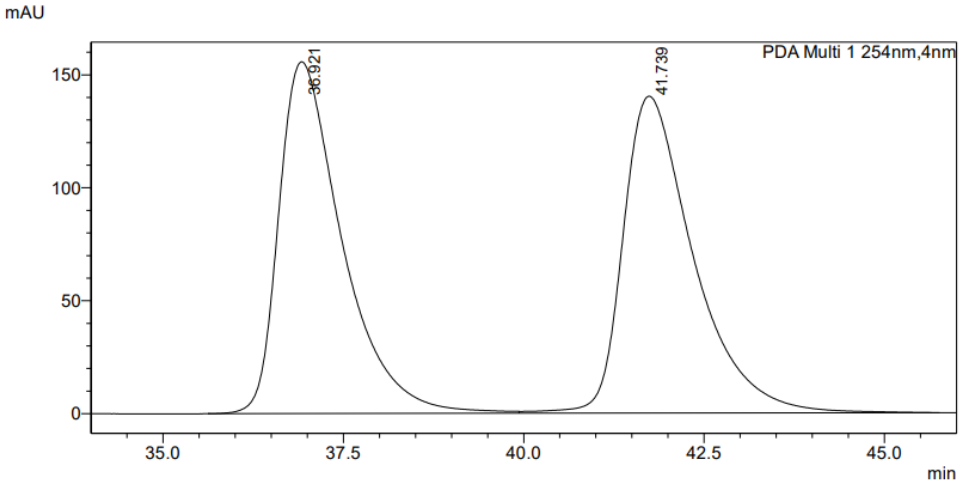

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	36.921	9506946	49.857	155733
2	41.739	9561463	50.143	140313
Total		19068408	100.000	296046

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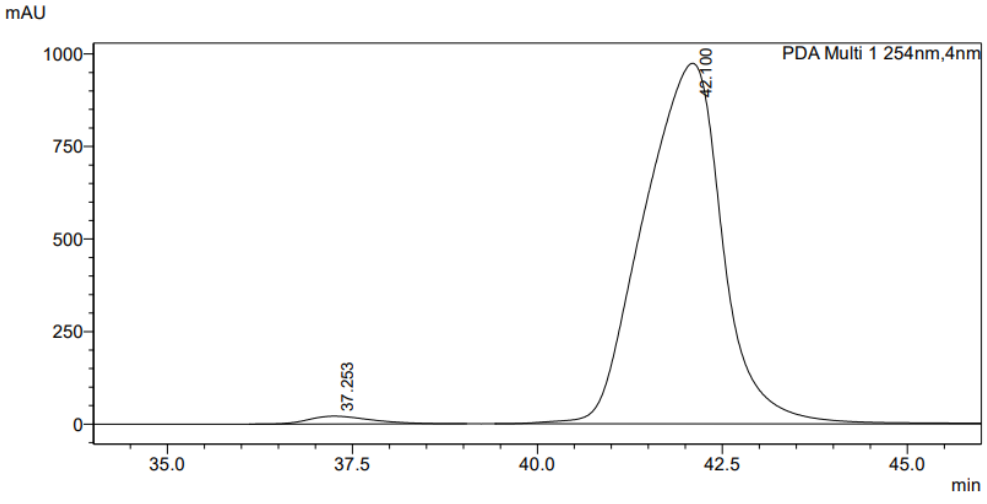
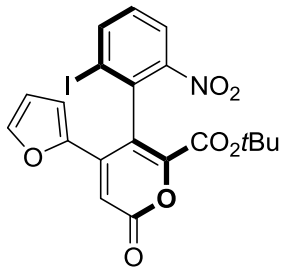


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	37.253	1243617	1.690	21099
2	42.100	72325298	98.310	973962
Total		73568915	100.000	995061



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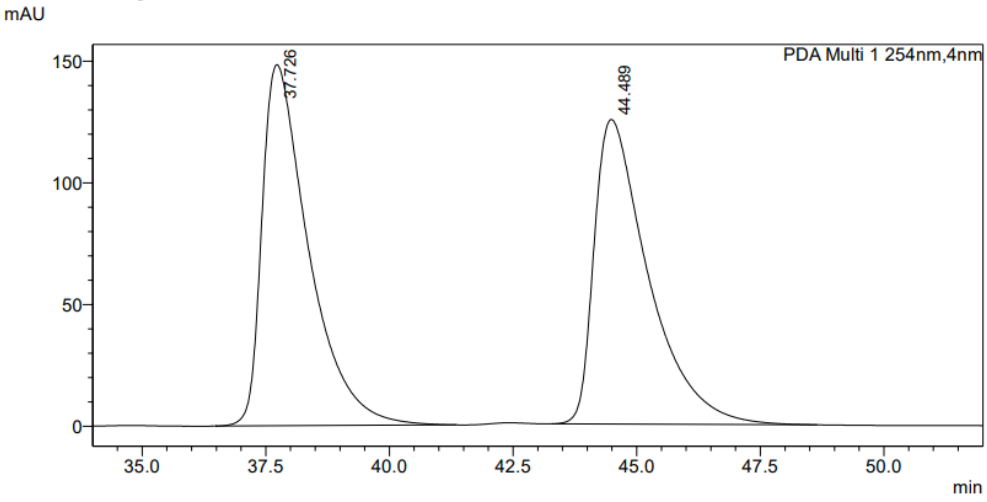

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	37.726	9749635	50.476	148435
2	44.489	9565820	49.524	125234
Total		19315455	100.000	273669

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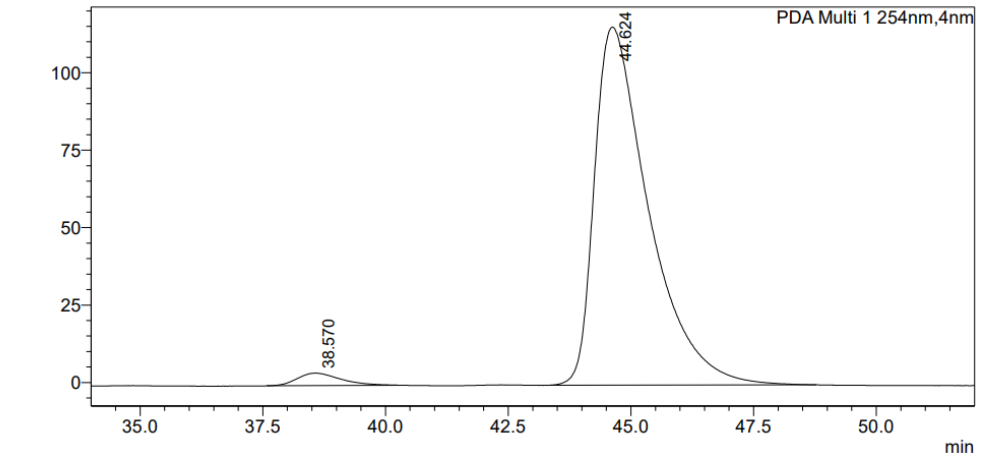
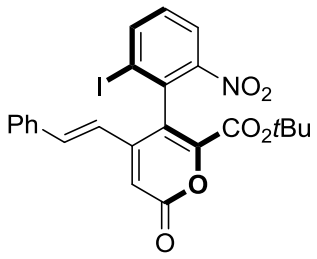


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	38.570	246692	2.700	4032
2	44.624	8889654	97.300	115623
Total		9136346	100.000	119655



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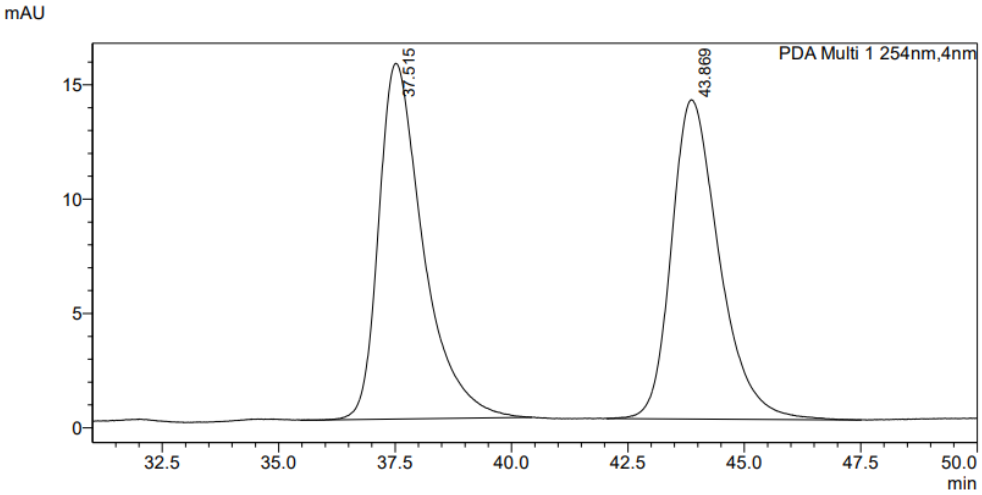
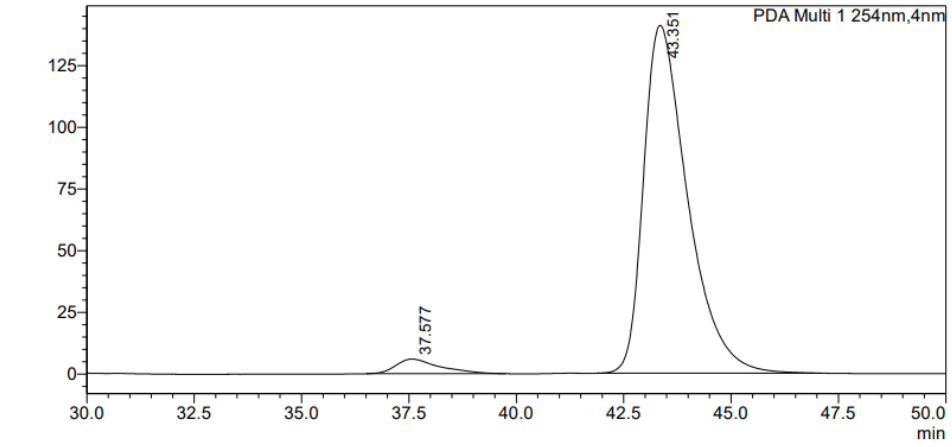


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	37.515	1035301	50.934	15556
2	43.869	997333	49.066	13958
Total		2032634	100.000	29514

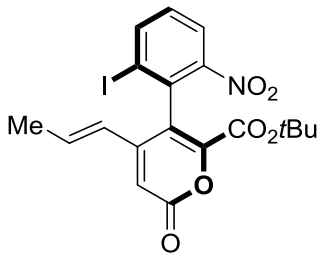
<Chromatogram>



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	37.577	420079	4.005	5933
2	43.351	10069637	95.995	140983
Total		10489716	100.000	146916



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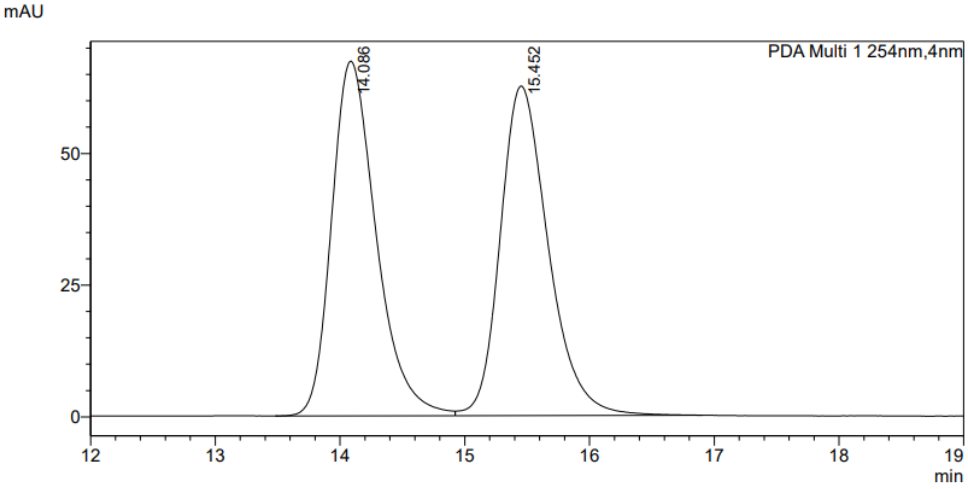

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	14.086	1674466	50.014	67333
2	15.452	1673523	49.986	62568
Total		3347989	100.000	129900

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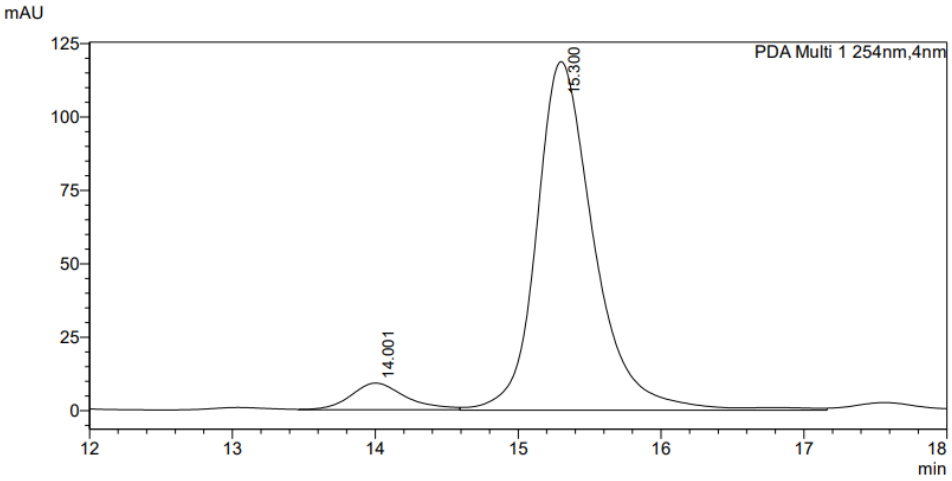
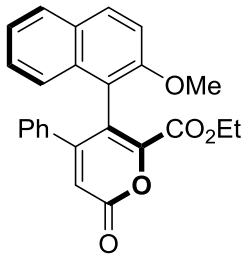


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	14.001	243734	6.831	9098
2	15.300	3324075	93.169	118683
Total		3567808	100.000	127781



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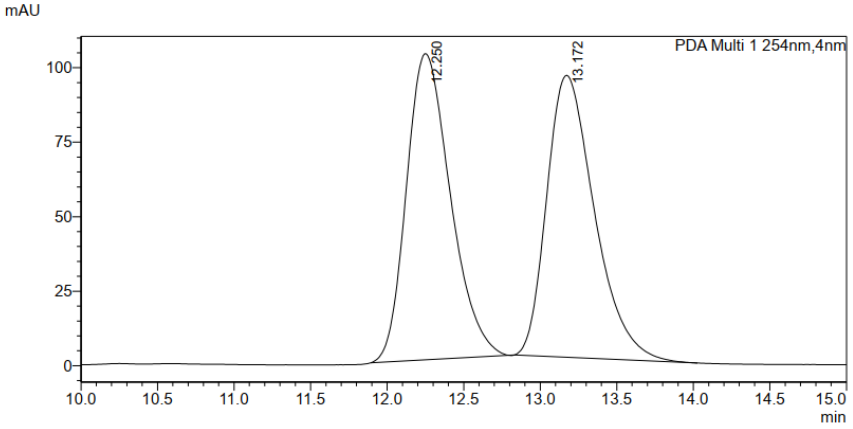

<Peak Table>

PDA Ch1 254nm

Ret. Time	Area	Area%	Height
12.250	2052268	50.035	102695
13.172	2049369	49.965	94622
	4101637	100.000	197317

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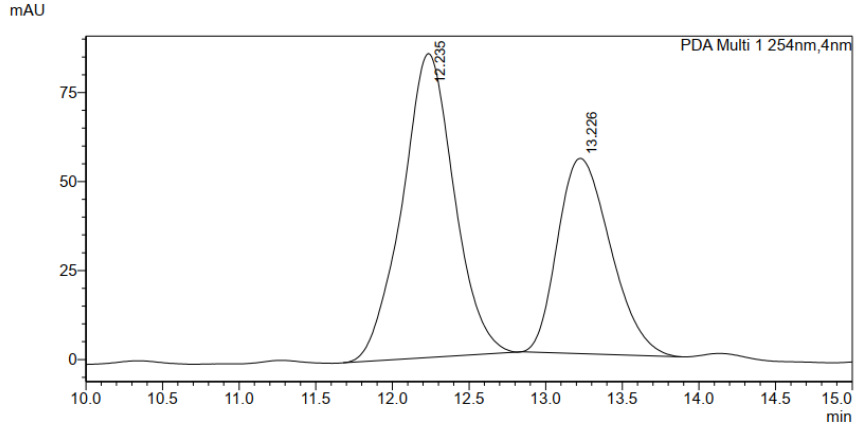
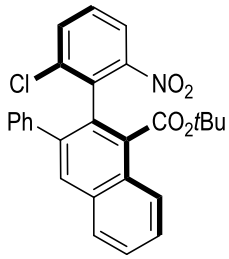


<Peak Table>

PDA Ch1 254nm

Ret. Time	Area	Area%	Height
12.235	2016559	60.460	85436
13.226	1318825	39.540	54880
	3335384	100.000	140316



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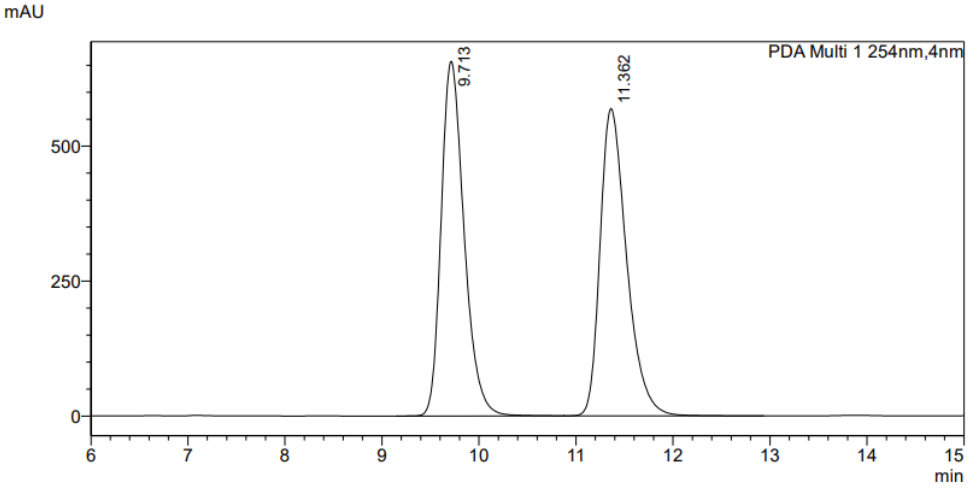

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	9.713	10824295	49.962	656453
2	11.362	10840572	50.038	569147
Total		21664867	100.000	1225601

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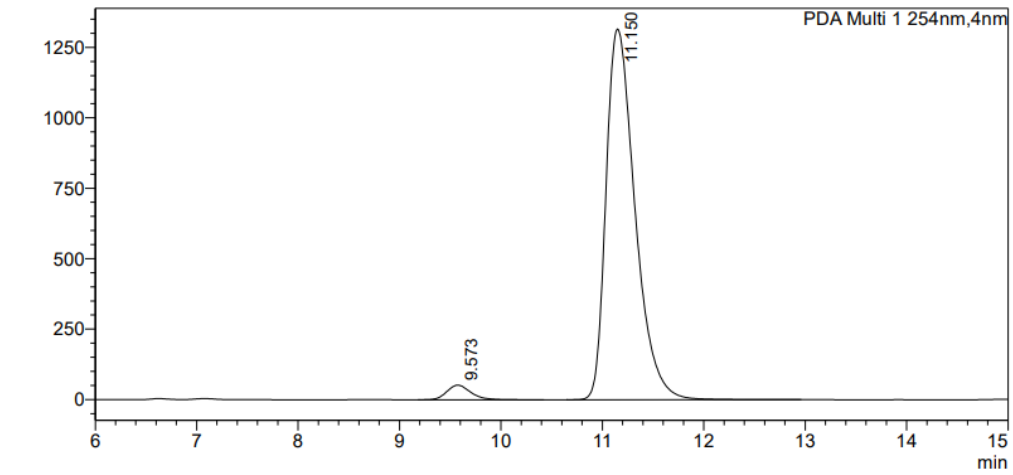
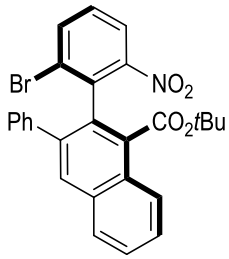


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	9.573	848590	3.146	51764
2	11.150	26128497	96.854	1315759
Total		26977087	100.000	1367523



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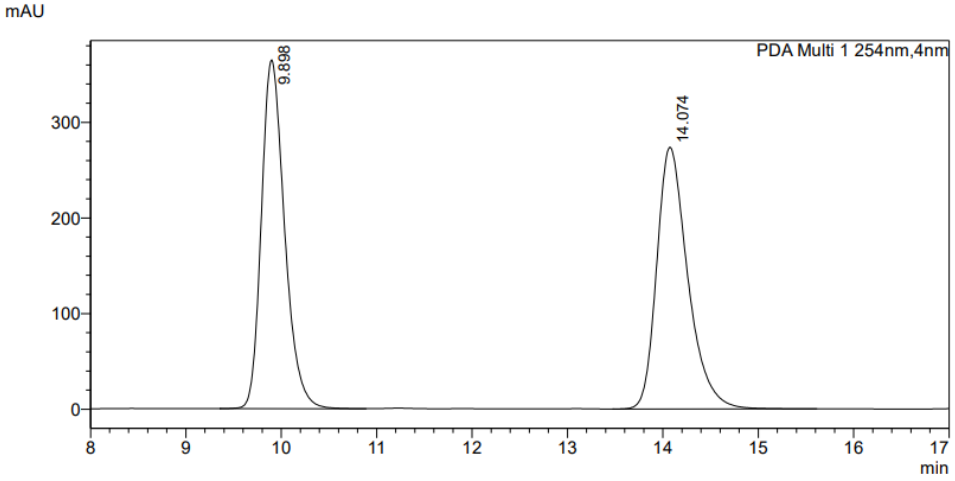

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	9.898	6170890	49.896	364514
2	14.074	6196651	50.104	273571
Total		12367541	100.000	638085

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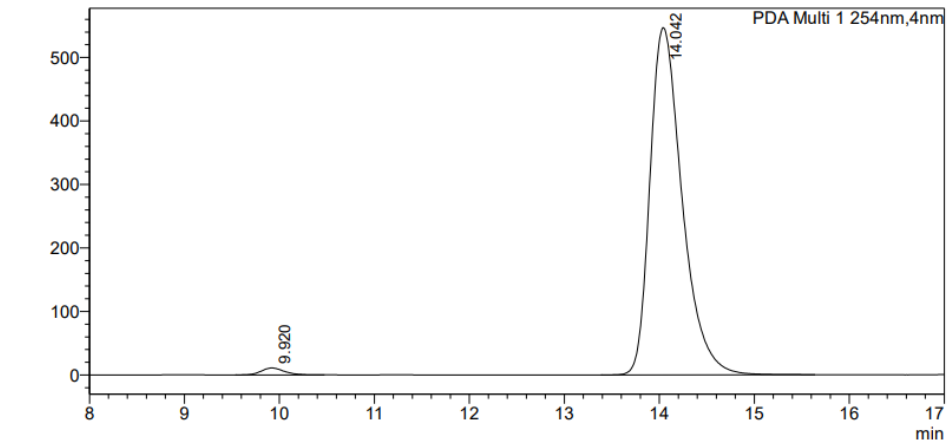
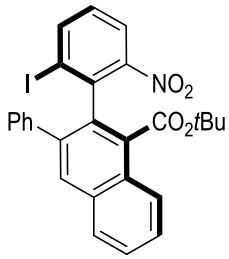


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	9.920	184345	1.411	10951
2	14.042	12882181	98.589	546686
Total		13066526	100.000	557637



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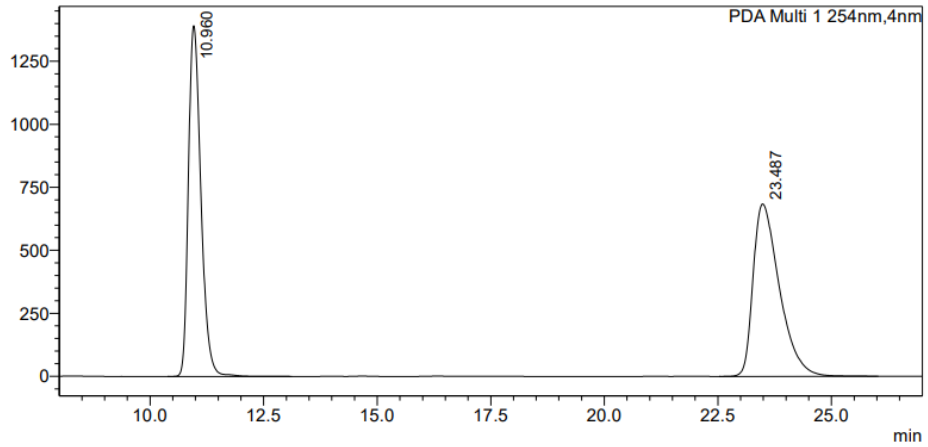
mAU



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	10.960	26668628	49.136	1390929
2	23.487	27606668	50.864	684234
Total		54275296	100.000	2075163

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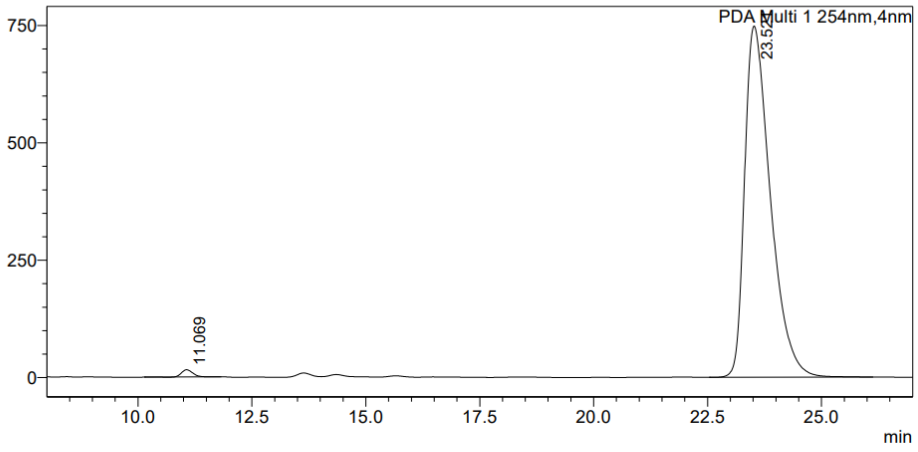
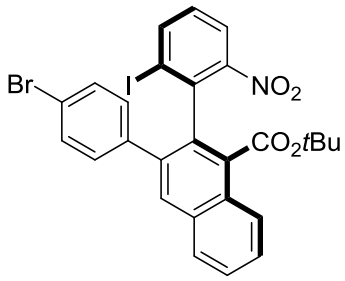
mAU



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	11.069	253541	0.854	15310
2	23.521	29443843	99.146	748349
Total		29697384	100.000	763659



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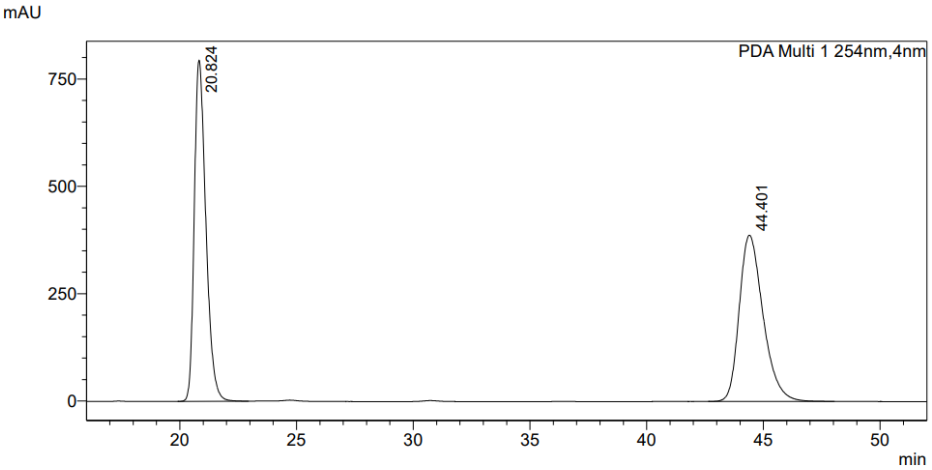

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	20.824	27503765	49.980	794333
2	44.401	27525582	50.020	387200
Total		55029347	100.000	1181533

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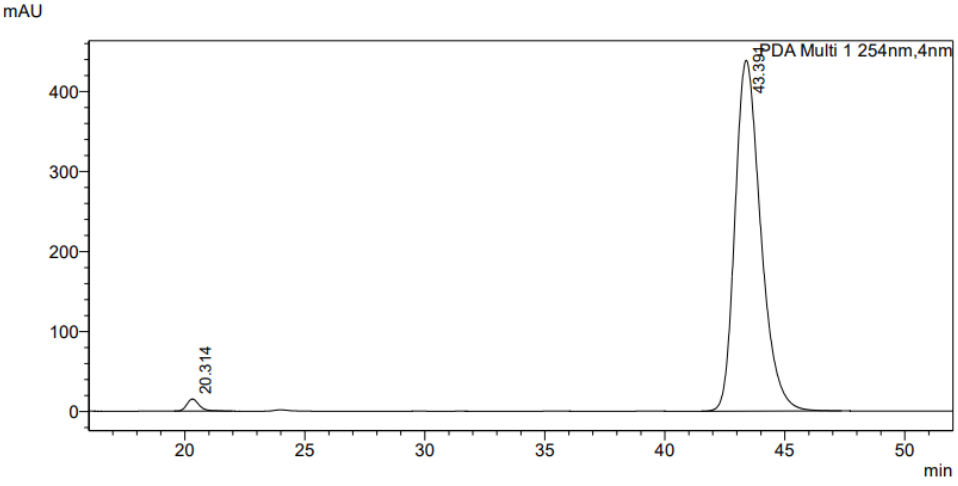
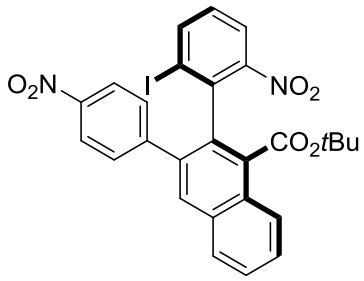


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	20.314	551128	1.659	15169
2	43.391	32662023	98.341	438418
Total		33213151	100.000	453588



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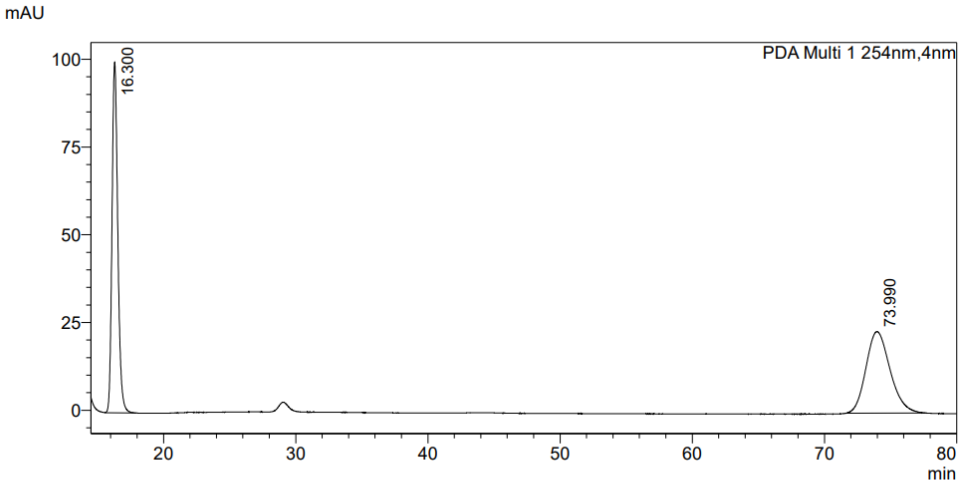

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	16.300	3036599	50.711	99919
2	73.990	2951469	49.289	23241
Total		5988068	100.000	123160

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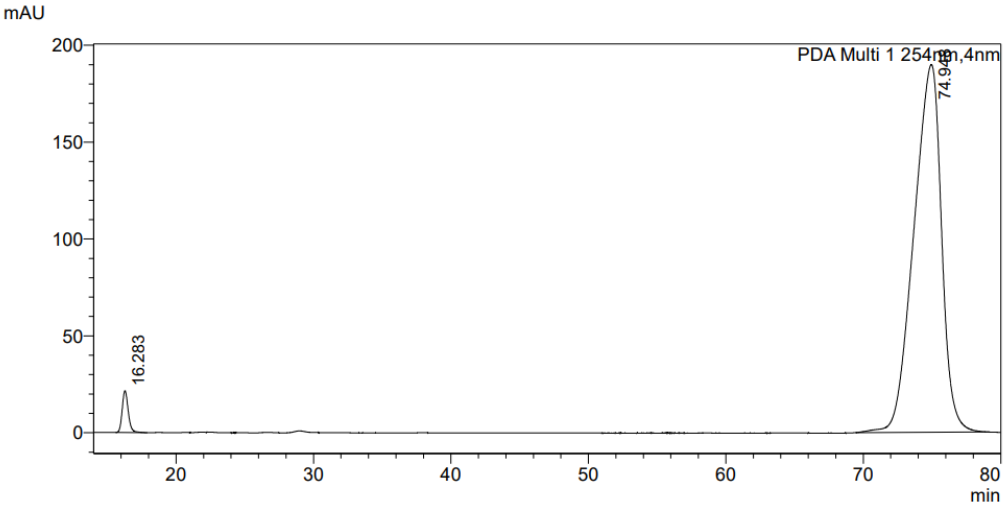
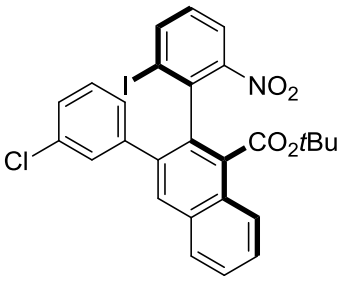


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	16.283	660699	2.429	21563
2	74.948	26540717	97.571	189815
Total		27201417	100.000	211378



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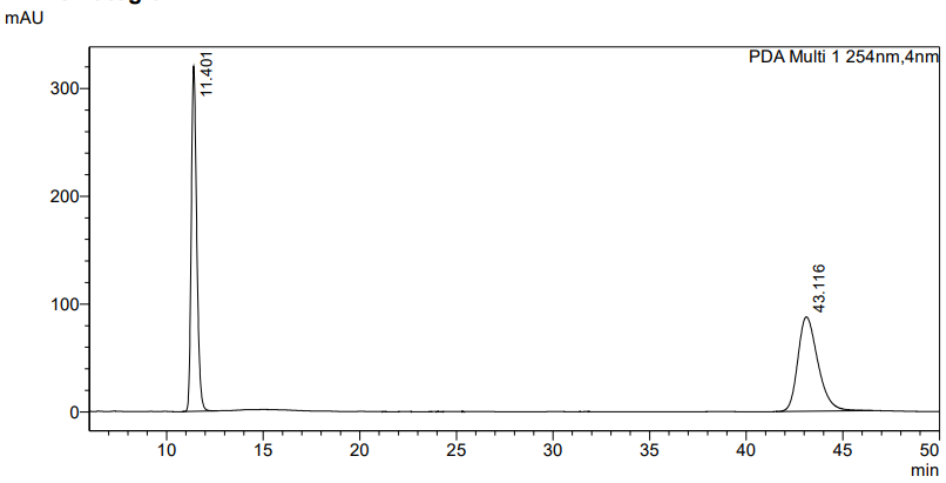

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	11.401	6289340	49.896	320127
2	43.116	6315673	50.104	87542
Total		12605012	100.000	407669

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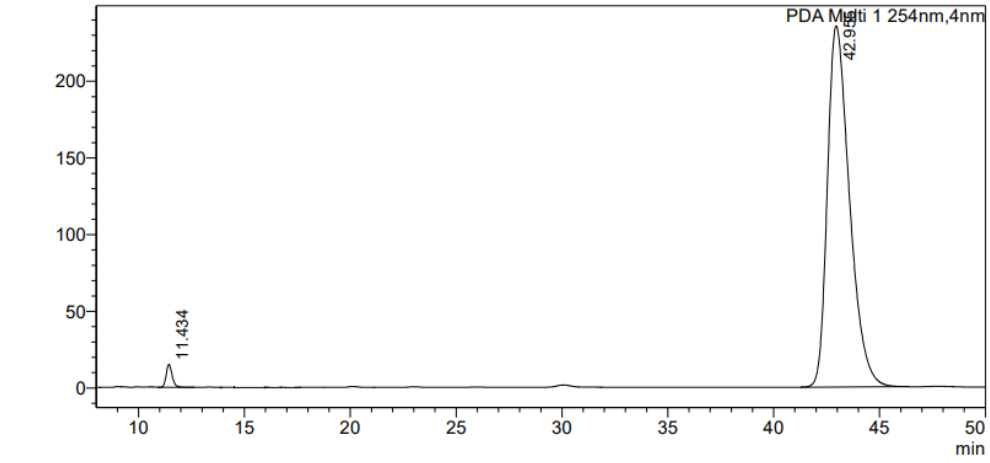
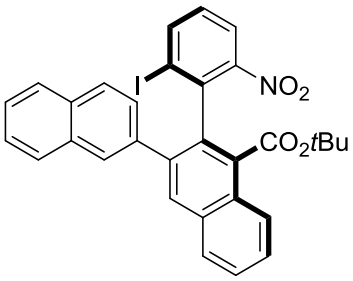


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	11.434	294071	1.689	14927
2	42.955	17114512	98.311	235498
Total		17408583	100.000	250425



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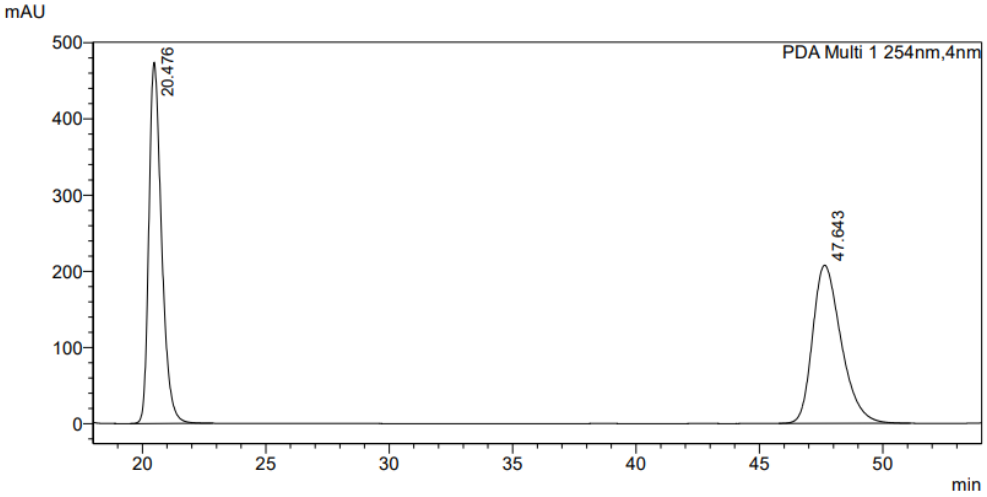

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	20.476	16935062	50.337	473926
2	47.643	16708541	49.663	207568
Total		33643603	100.000	681493

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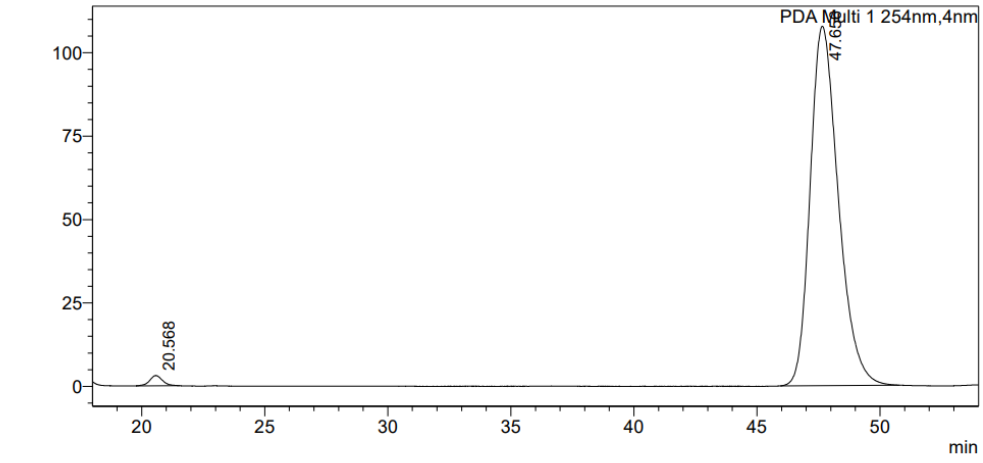
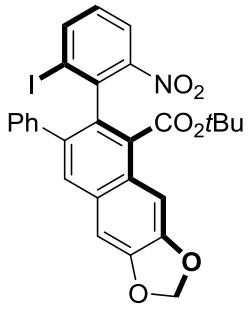


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	20.568	109660	1.261	3072
2	47.656	8584565	98.739	107706
Total		8694225	100.000	110778



6h

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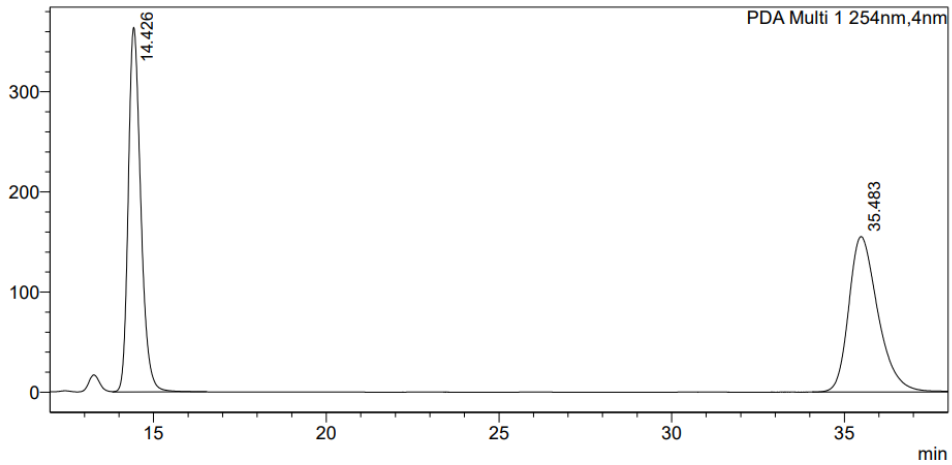

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	14.426	9146756	50.047	363881
2	35.483	9129527	49.953	155298
Total		18276283	100.000	519178

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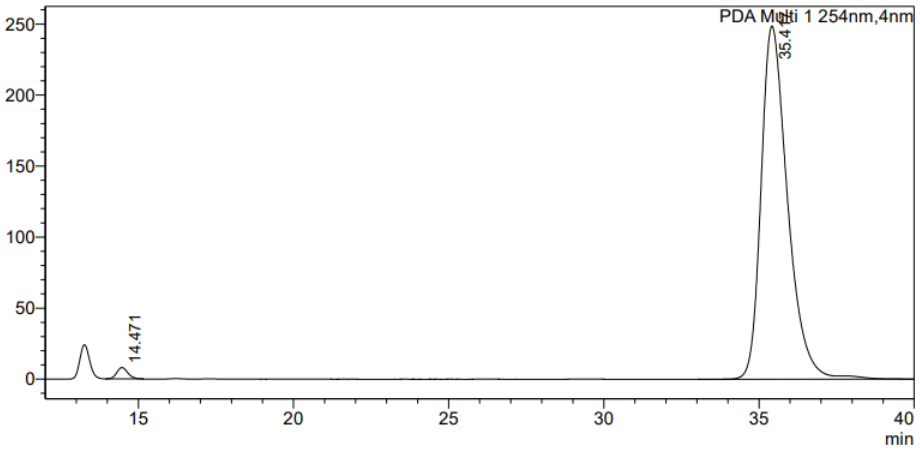
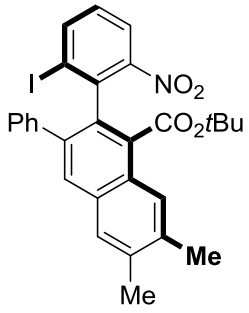
mAU



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	14.471	198417	1.323	7977
2	35.417	14794296	98.677	248592
Total		14992713	100.000	256570



6i

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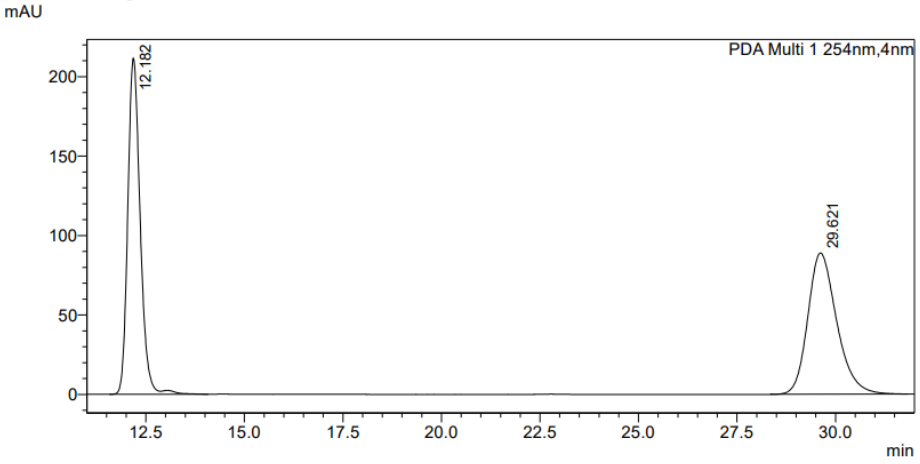

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	12.182	4630896	50.503	211510
2	29.621	4538712	49.497	88910
Total		9169608	100.000	300419

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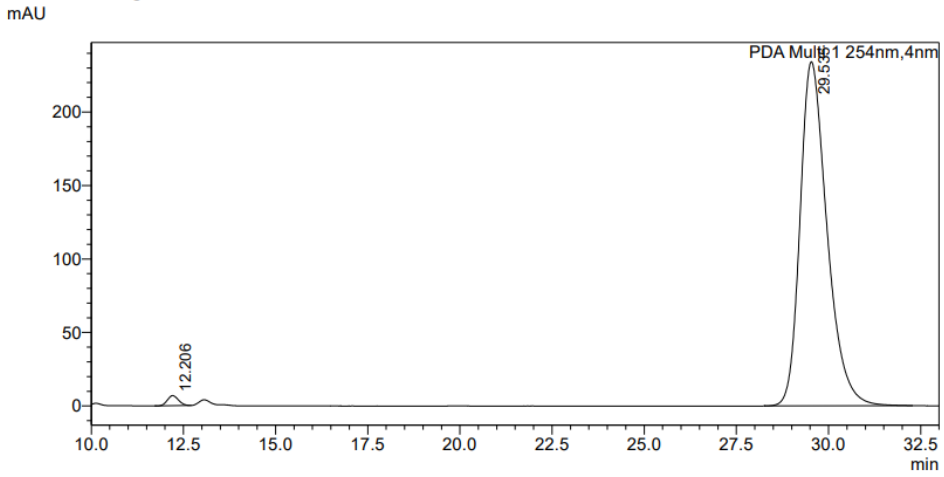
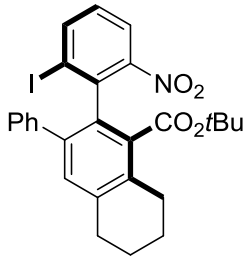


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	12.206	144450	1.196	6888
2	29.535	11928944	98.804	234153
Total		12073394	100.000	241041



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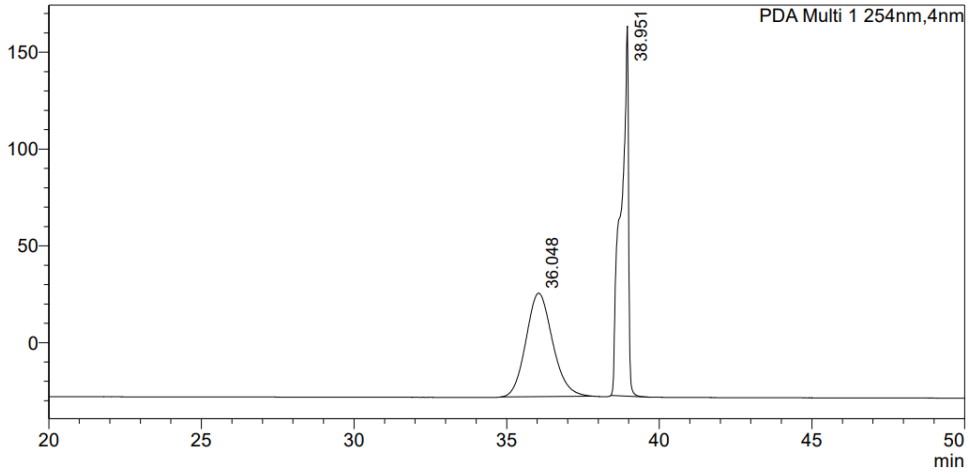

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	36.048	3241859	49.677	53486
2	38.951	3284052	50.323	191248
Total		6525911	100.000	244734

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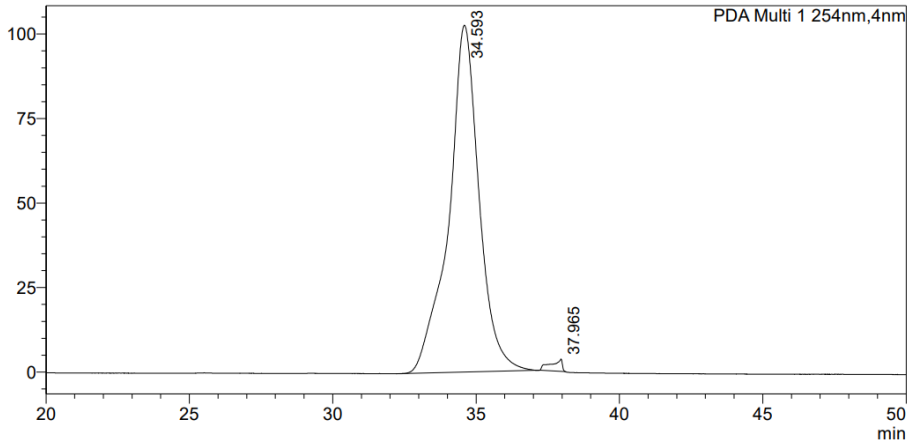
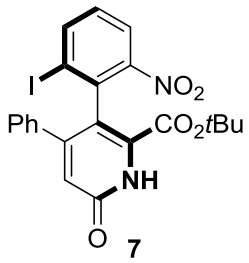
mAU



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	34.593	7539982	98.699	102613
2	37.965	99422	1.301	3678
Total		7639404	100.000	106291



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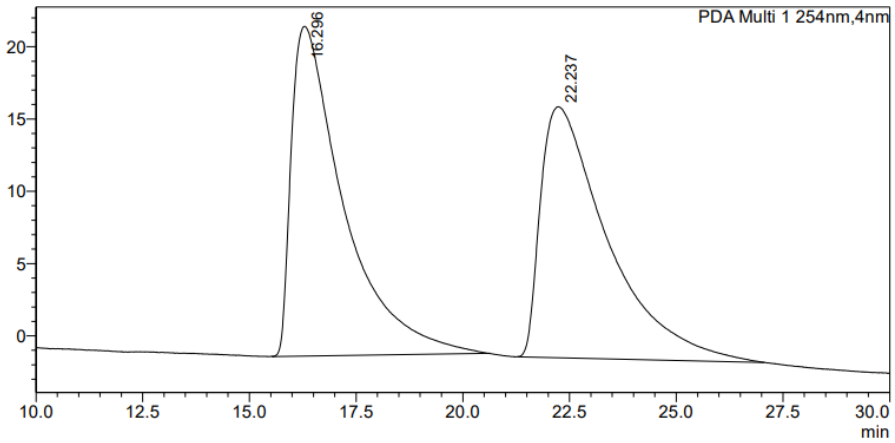

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	16.296	1943140	50.640	22800
2	22.237	1894002	49.360	17352
Total		3837141	100.000	40152

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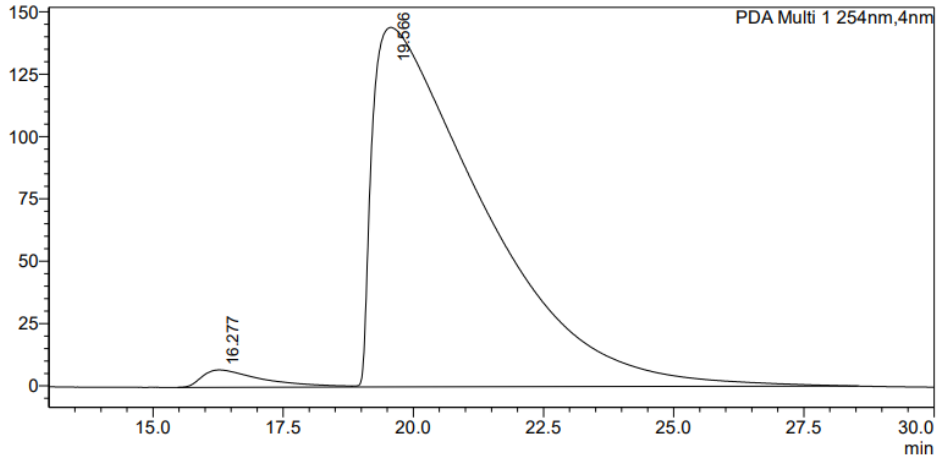
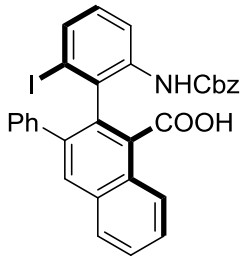
mAU



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	16.277	561121	2.552	6973
2	19.566	21424928	97.448	144165
Total		21986049	100.000	151138



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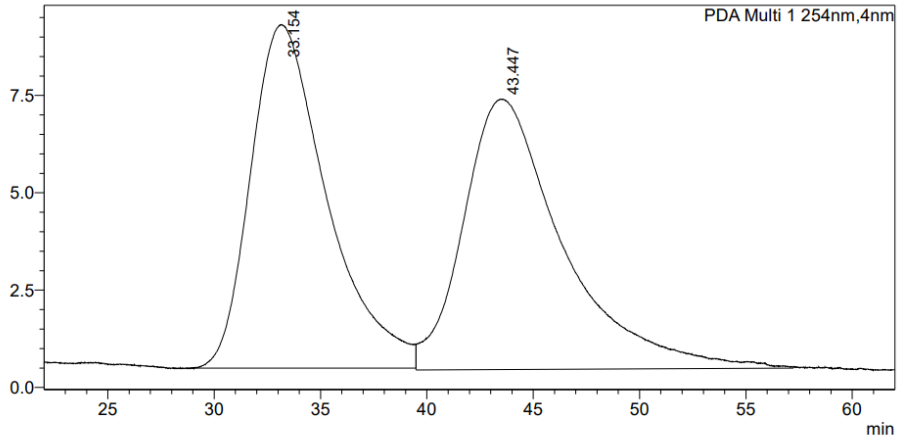

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	33.154	2196003	49.260	8821
2	43.447	2262000	50.740	6947
Total		4458004	100.000	15768

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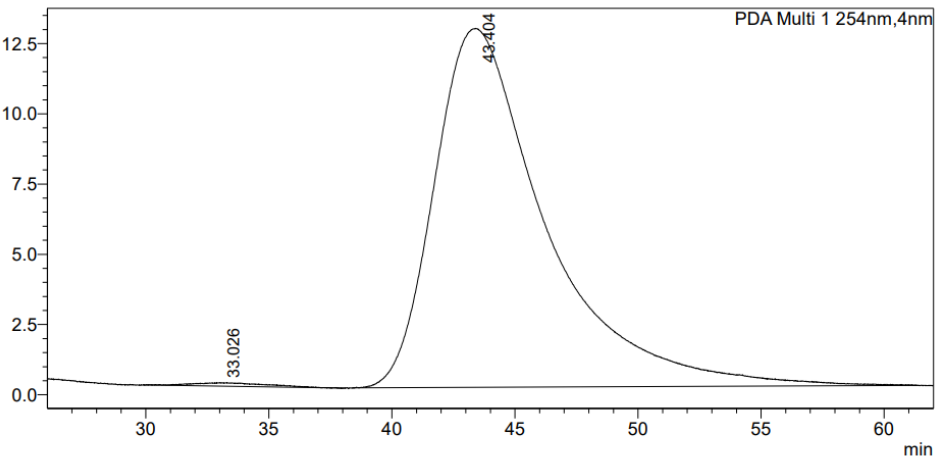
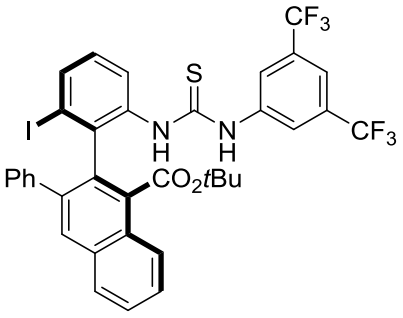
mAU



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	33.026	25197	0.621	122
2	43.404	4030966	99.379	12776
Total		4056162	100.000	12898



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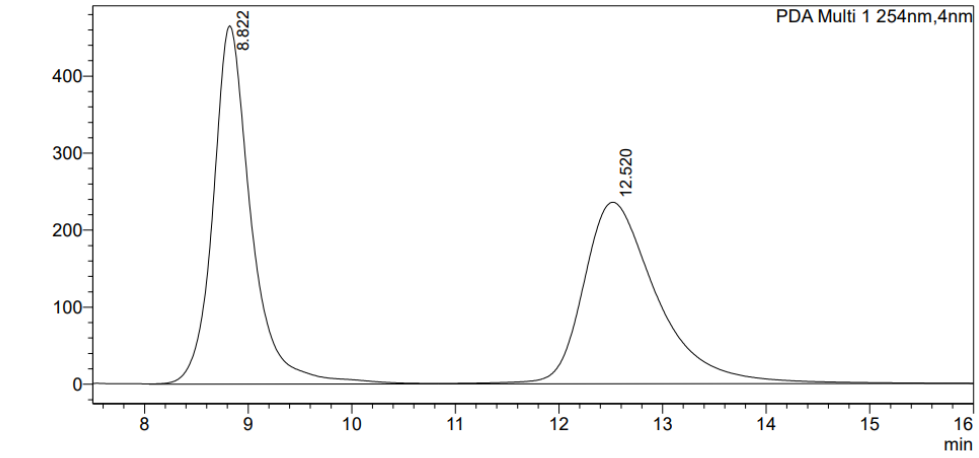

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	8.822	11874366	50.409	465023
2	12.520	11681637	49.591	235704
Total		23556003	100.000	700727

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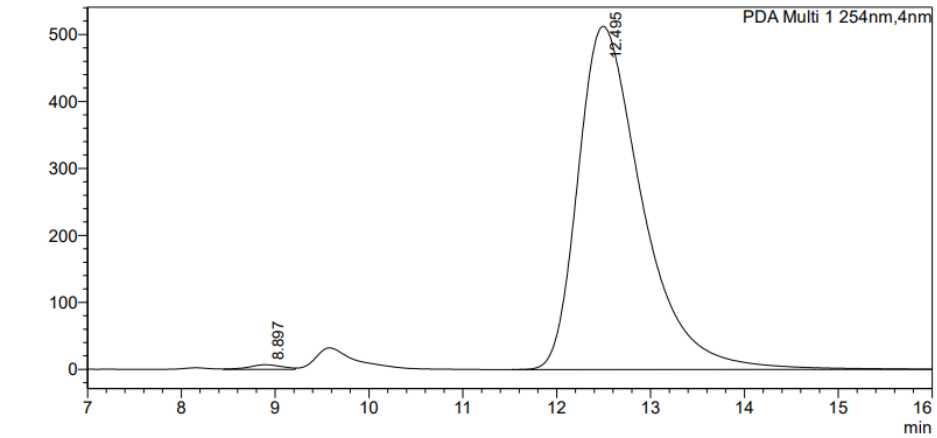
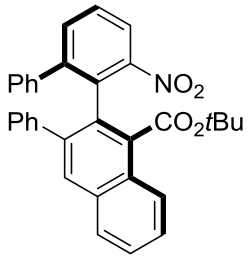


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	8.897	176248	0.719	7065
2	12.495	24349588	99.281	512299
Total		24525836	100.000	519364



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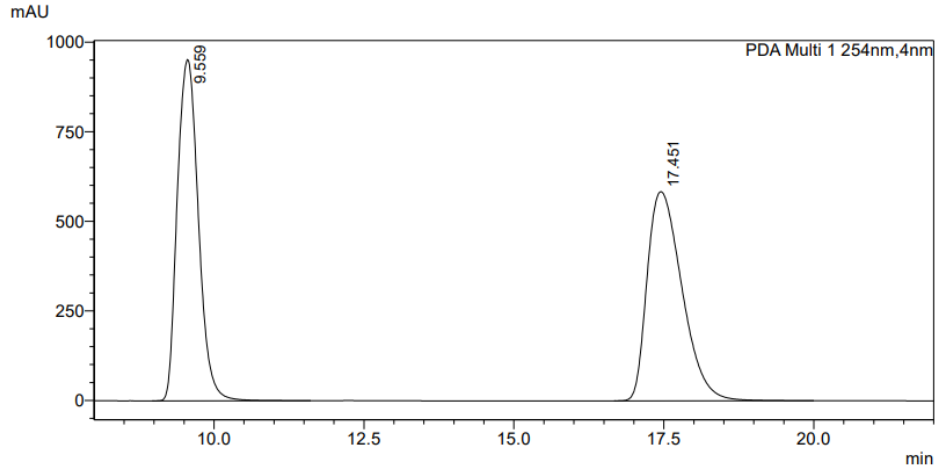

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	9.559	23318916	49.706	952198
2	17.451	23595098	50.294	583881
Total		46914015	100.000	1536079

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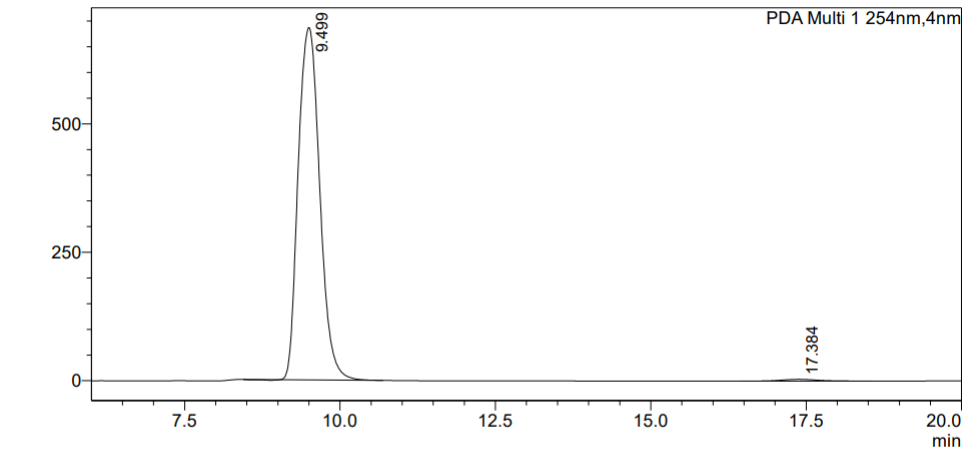
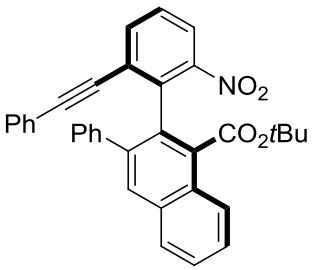


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	9.499	16535947	99.227	685758
2	17.384	128862	0.773	3378
Total		16664808	100.000	689136



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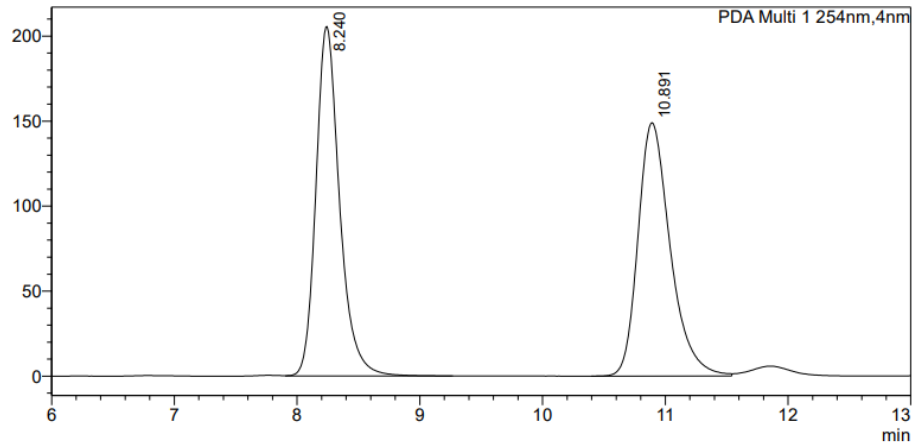
mAU



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	8.240	2760825	50.347	205454
2	10.891	2722723	49.653	149062
Total		5483548	100.000	354515

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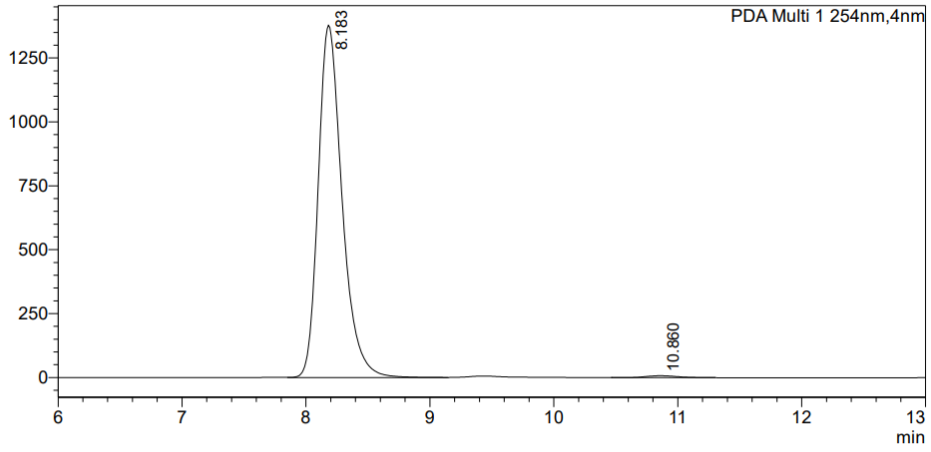
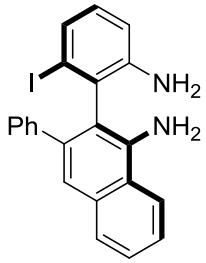


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	8.183	18536195	99.267	1378564
2	10.860	136873	0.733	7739
Total		18673068	100.000	1386303



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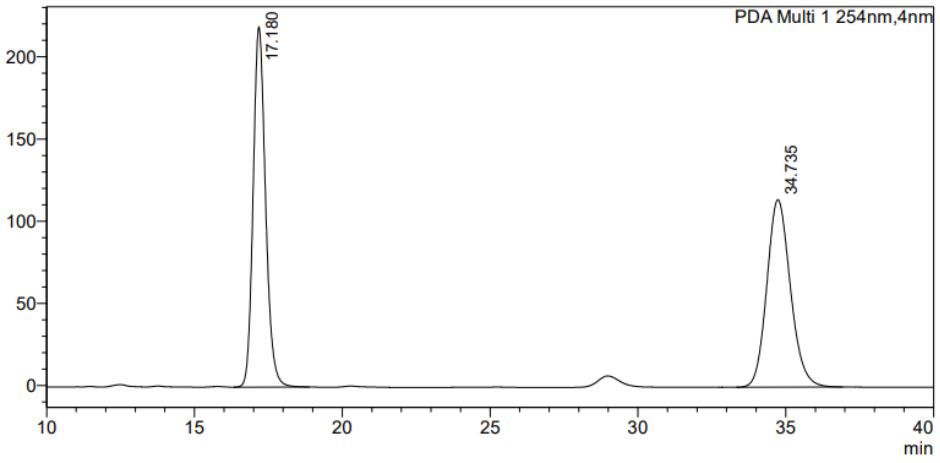

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	17.180	6407915	50.299	219153
2	34.735	6331785	49.701	114056
Total		12739699	100.000	333210

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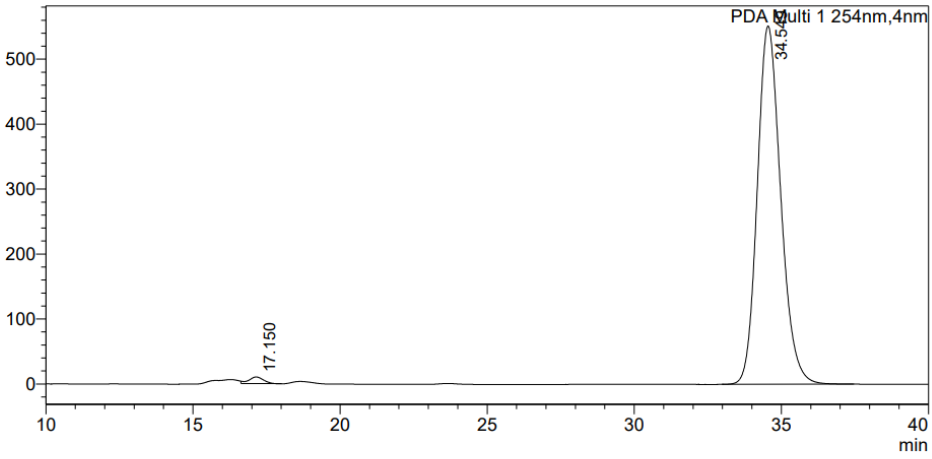
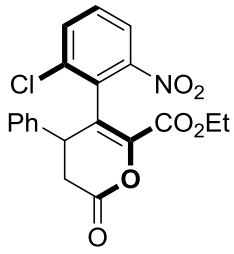


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	17.150	343193	1.112	10162
2	34.549	30525680	98.888	551684
Total		30868873	100.000	561846



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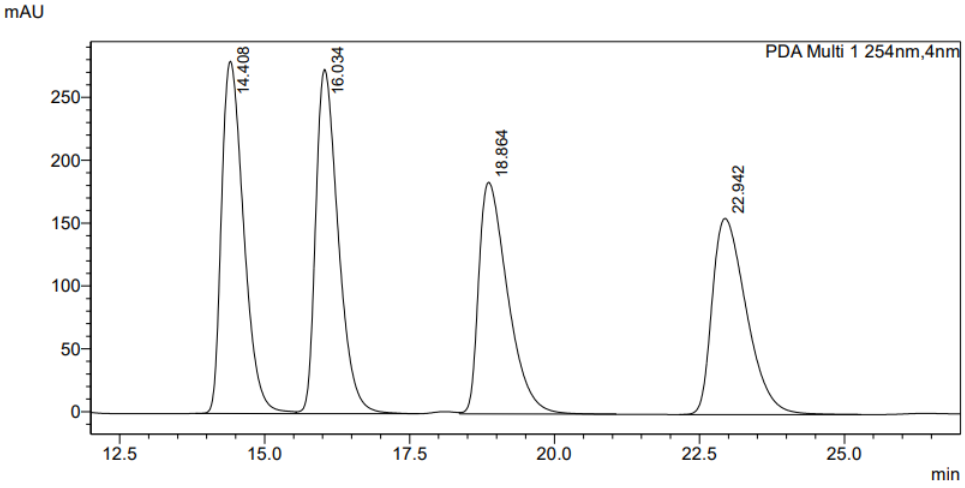

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	14.408	7448748	26.937	280148
2	16.034	7400143	26.761	273756
3	18.864	6399612	23.143	184184
4	22.942	6403885	23.159	155992
Total		27652388	100.000	894080

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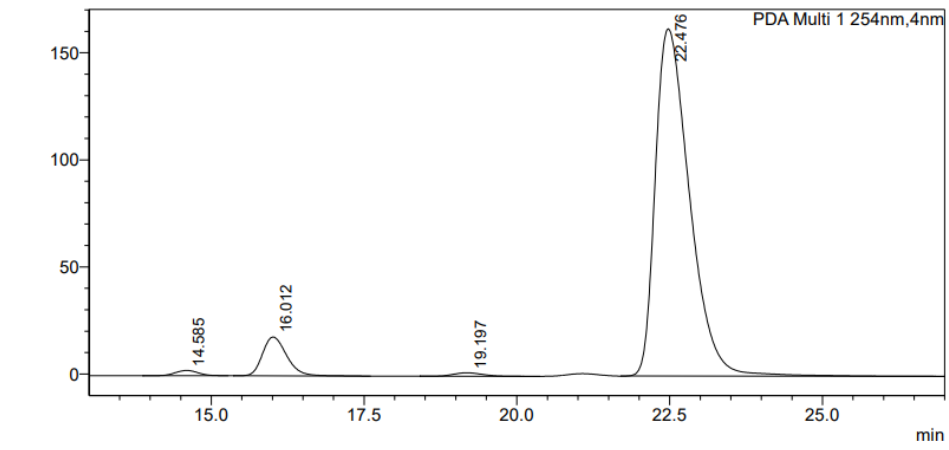
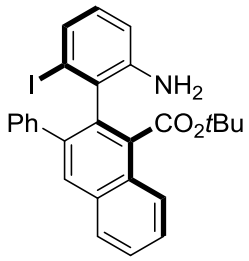


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	14.585	62186	0.896	2414
2	16.012	497707	7.172	18104
3	19.197	51890	0.748	1597
4	22.476	6327953	91.184	162124
Total		6939736	100.000	184240



S3

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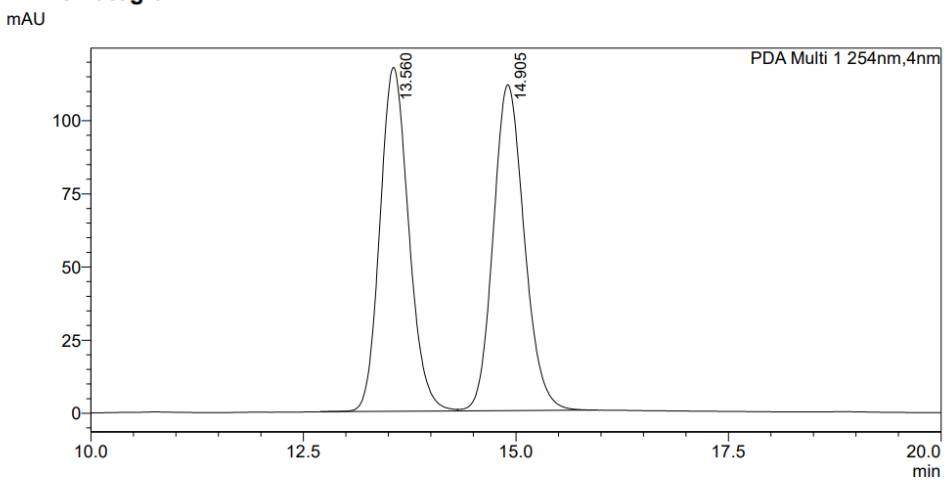

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	13.560	2764780	49.391	117542
2	14.905	2832976	50.609	111400
Total		5597756	100.000	228942

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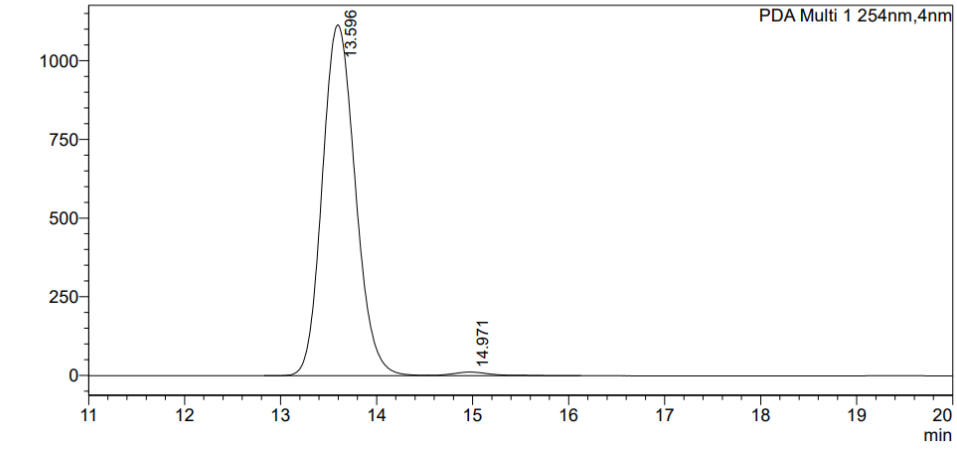
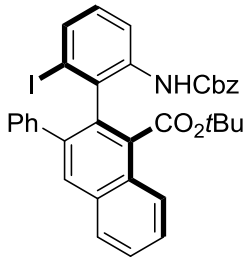


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	13.596	26626792	98.741	1113798
2	14.971	339580	1.259	11613
Total		26966372	100.000	1125411



S4

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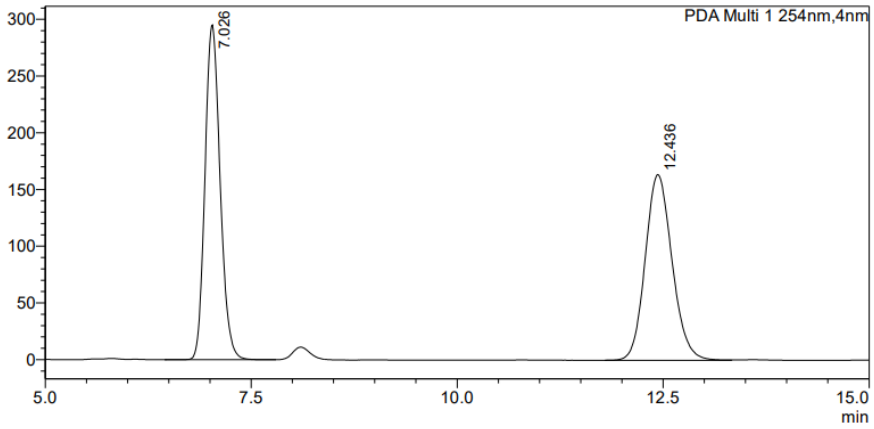

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	7.026	3775890	50.464	294991
2	12.436	3706440	49.536	163621
Total		7482330	100.000	458612

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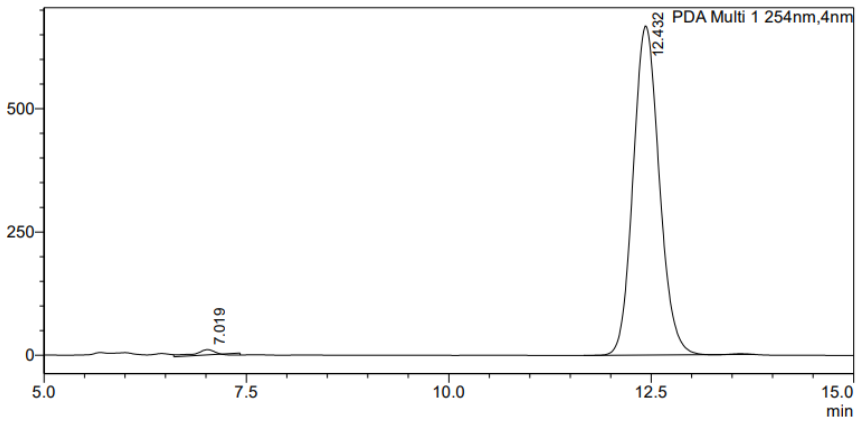
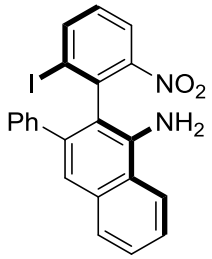


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	7.019	141500	0.935	10663
2	12.432	14999616	99.065	667382
Total		15141116	100.000	678045



S6

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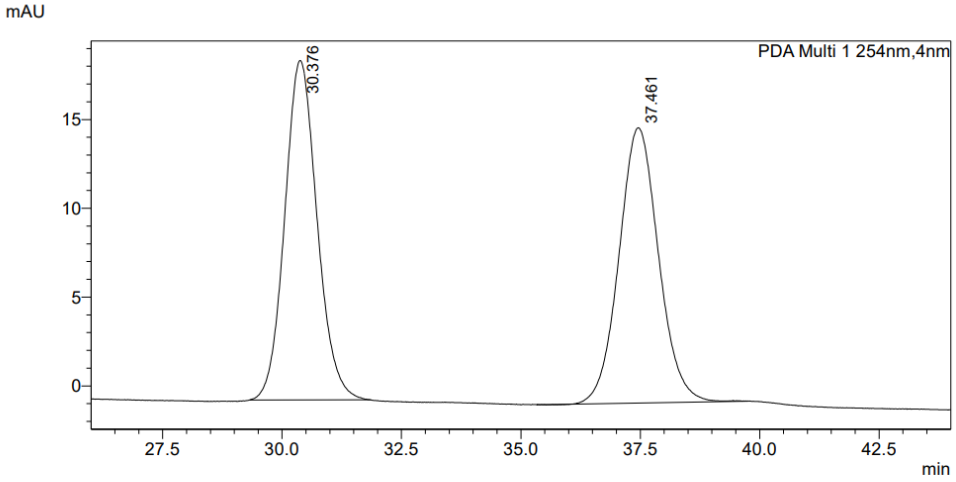

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	30.376	900997	50.240	19114
2	37.461	892399	49.760	15499
Total		1793396	100.000	34613

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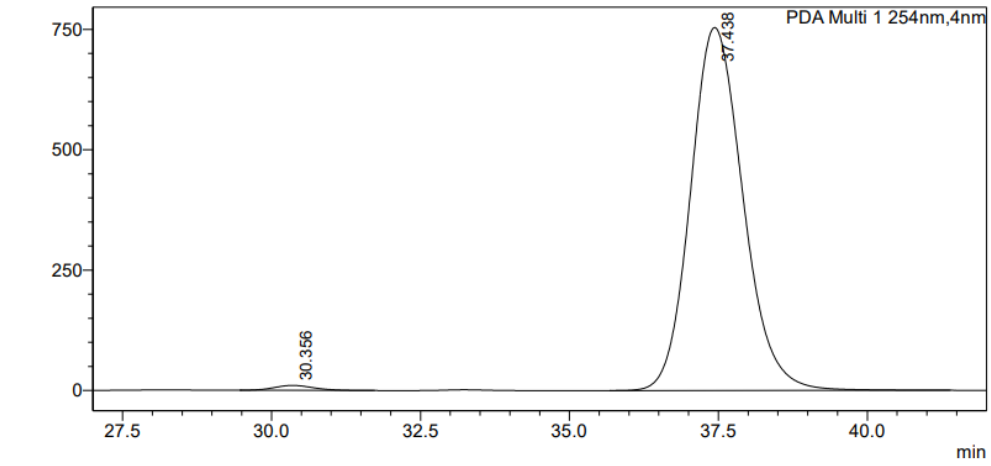
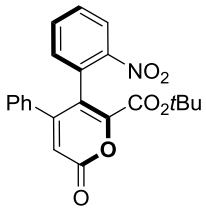


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	30.356	471017	1.009	10219
2	37.438	46231390	98.991	753932
Total		46702407	100.000	764151



S7

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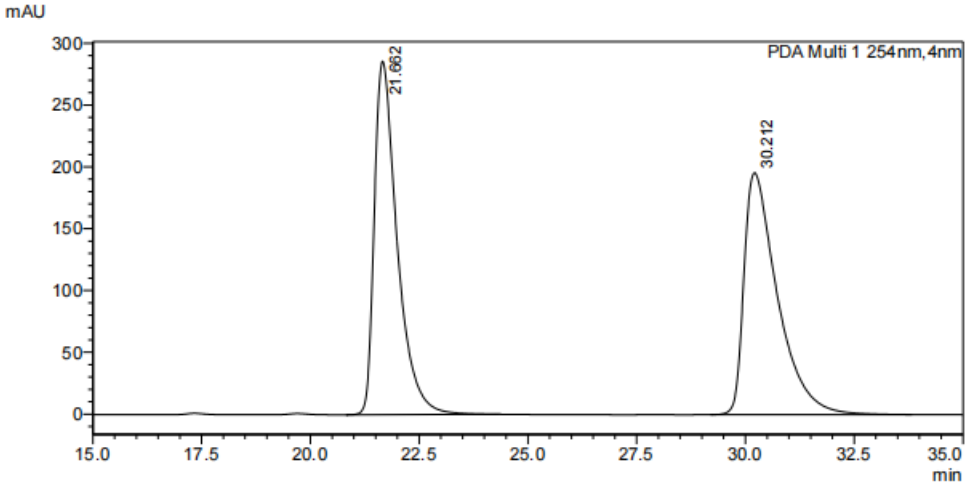

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	21.662	10460158	49.957	285819
2	30.212	10478322	50.043	195660
Total		20938479	100.000	481478

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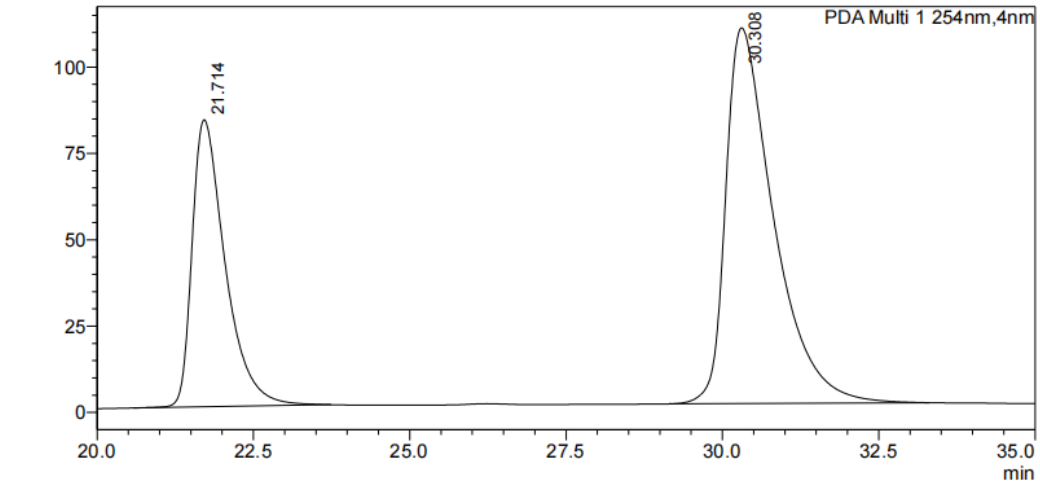
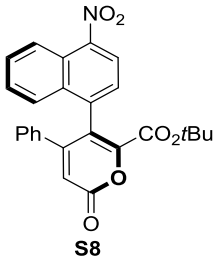


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	21.714	3063419	34.551	83103
2	30.308	5802885	65.449	108781
Total		8866304	100.000	191883



S8

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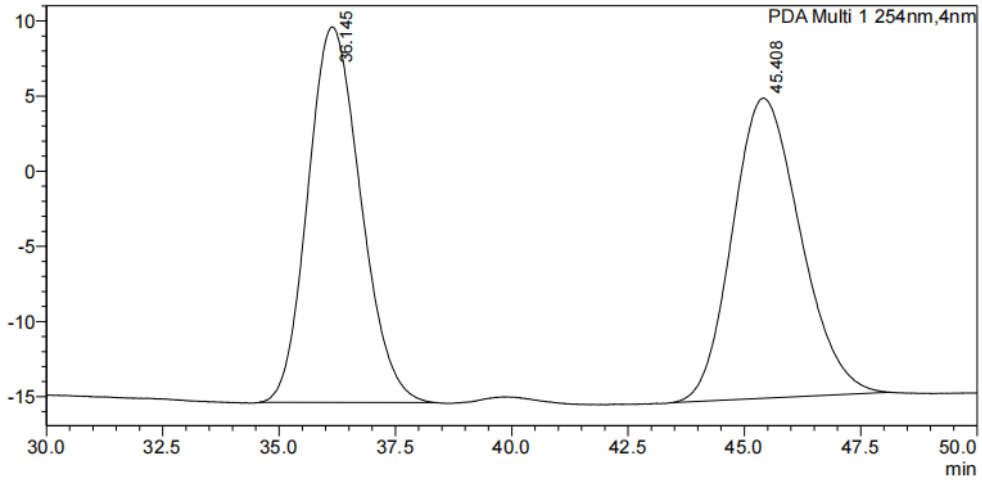
mAU



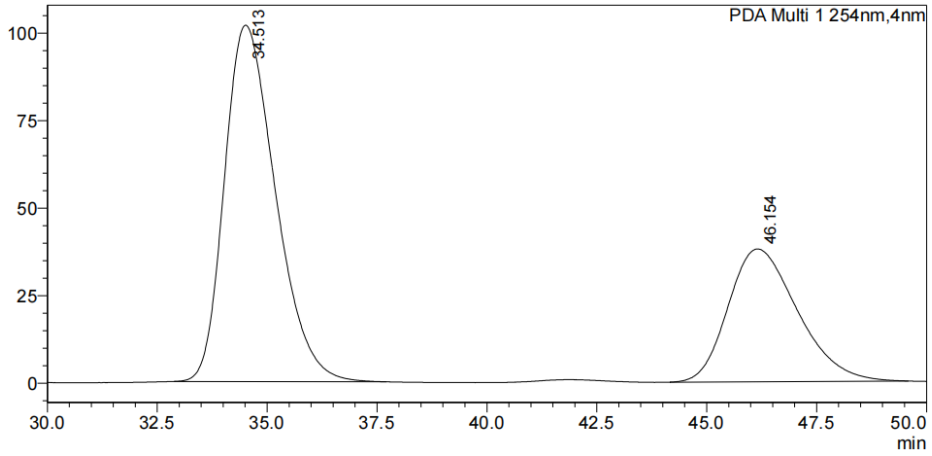
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	36.145	1974423	49.343	24993
2	45.408	2027018	50.657	19979
Total		4001441	100.000	44972

<Chromatogram>

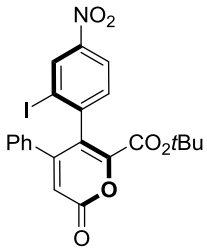
mAU



<Peak Table>

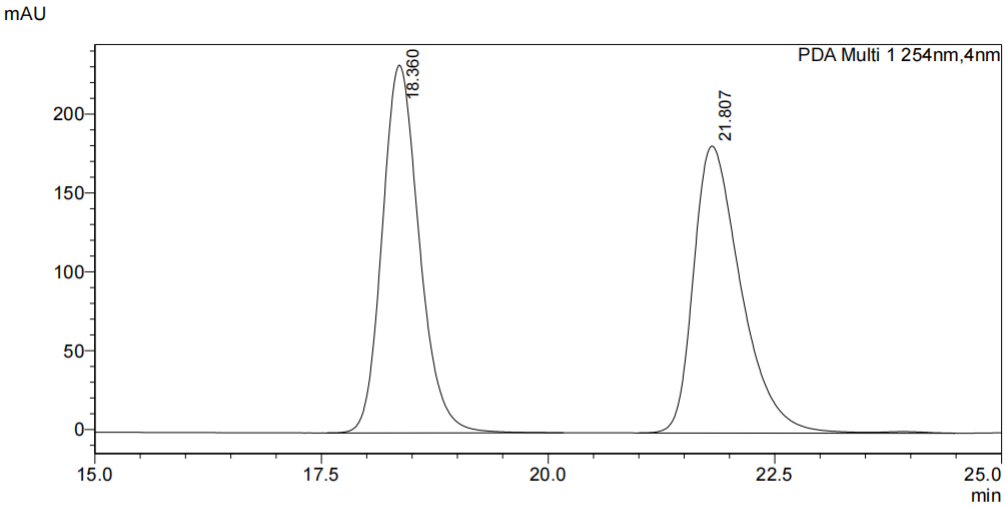
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	34.513	8224637	66.411	101782
2	46.154	4159887	33.589	37924
Total		12384524	100.000	139705



S9

<Chromatogram>

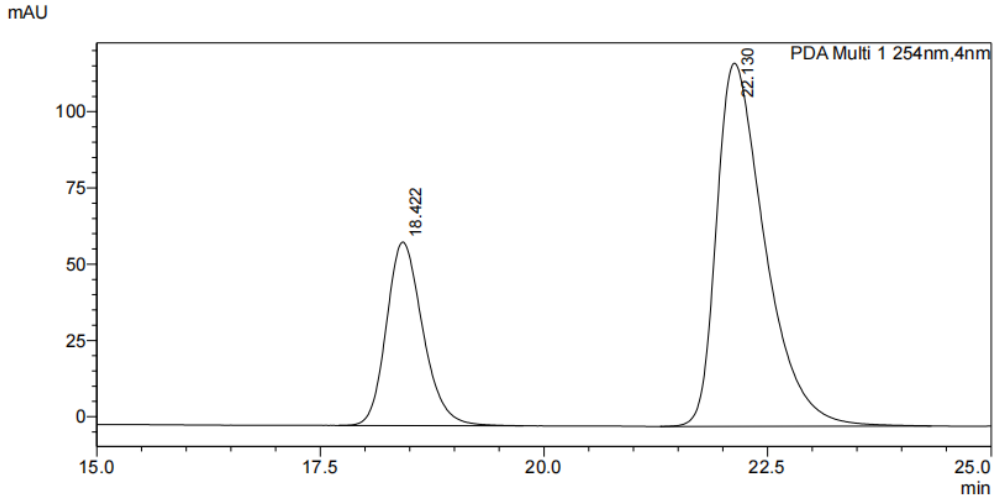


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	18.360	6632198	49.991	233171
2	21.807	6634666	50.009	181890
Total		13266864	100.000	415061

<Chromatogram>



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	18.422	1703675	27.564	60169
2	22.130	4477022	72.436	119039
Total		6180697	100.000	179208