

Supporting Information

Distal Iodine Migration of Arylalkynes via Cyclic Monoaryliodonium Salts

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The general information for the synthetic experiments

Synthesis details for key compounds are described here. All solvents were commercially available and were used without a further purification unless stated. The chemicals used were either purchased from commercial sources or prepared according to literature procedures. The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance spectrometer 400 at 400 MHz and 100 MHz respectively. Chemical shifts are given in ppm (δ) referenced to CDCl_3 with 7.26 for ^1H and 77.10 for ^{13}C , and to d_6 -DMSO with 2.50 for ^1H and 39.5 for ^{13}C . In the case of multiplet, the signals are reported as intervals. Signals are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants are expressed in hertz. High-resolution mass spectra (HRMS) were recorded on Thermo Fisher spectrometer, Orbitrap QExactive GC/MS (EI mode) and Orbitrap QExactive LC/MS (ESI mode) or BRUKER VPXII spectrometer (ESI mode). The progress of the reactions was monitored by thin-layer chromatography on a glass plate coated with silica gel with fluorescent indicator (GF254). Column chromatography was performed on silica gel (200-300 mesh).

Cell Lines.

The human lung cancer cell line A549, DLD1, and PANC1 were obtained from ATCC. All cells were cultured in RPMI-1640 (Gibco, Carlsbad, CA), supplemented with 10% fetal bovine serum (FBS, Biological Industries) at 37 °C and 5% CO_2 . All cells used in the study had been tested for mycoplasma contamination every three weeks.

Cell Viability Assay.

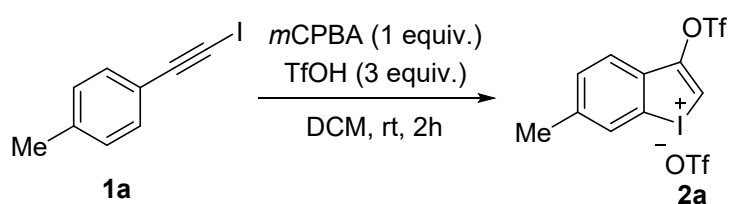
Cell viability was determined by the MTS assay.

MTS [3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2H-tetrazolium, inner salt] can be reduced by dehydrogenase enzymes in metabolically active cells into a colored formazan product that is soluble in the medium and is directly detected by visible light absorption at 490 nm with a 96-well plate reader. A549 (3000 cells/well in 100 μL of medium), DLD1 (2000 cells/well in 100 μL of medium), and PANC1 (3000 cells/well in 100 μL of medium) cells were seeded in 96-well plates for 24 h. Then, they were exposed to gradient concentrations of compound **2** for 3 days. After the indicated incubation time, 20 μL of MTS was added to each well and cells were incubated for an additional 4 h at 37 °C supplied with 5% carbon dioxide. Then, the optical density (OD) was determined at a wavelength of 490 nm with a BioTek Gen5 microplate reader (BioTek Instruments, Winooski, VT).

compound	IC50 (μM)		
	A549	DLD 1	PANC 1
2a	3.54	2.76	1.22
2b	5.37	3.85	0.71
2c	3.13	2.07	0.55
2d	2.20	1.45	0.30
2e	1.15	0.51	0.62
2f	3.34	1.55	0.30
2g	2.26	1.30	0.30
2h	2.14	1.47	0.65

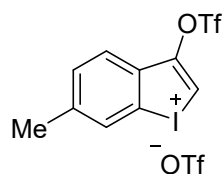
Table S1. Anticancer potency of cyclic monoaryliodonium salts against A549, DLD1, PANC1.

General procedure for the synthesis of cyclic monoaryliodonium salts (**2**):



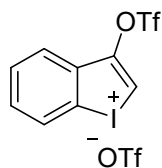
To a stirred solution of **1a** (48 mg, 0.2 mmol) in DCM (2 mL) was added TfOH (52.5 μL , 0.6 mmol) at rt, then a solution of *m*-CPBA (85%, 40.7 mg, 0.2 mmol) in DCM (2 mL) was added dropwise, rt. The solution was stirred for 2h at r.t. before DCM was removed by rotary evaporation. The residue was purified by column chromatography on a silica gel (PE/EtOAc = 10/1-3/1, DCM/EtOAc = 3/1-1/1) to provide product **2a** (79 mg, 74% yield) as a light yellow solid.

6-methyl-3-(((trifluoromethyl)sulfonyl)oxy)benzo[b]iodol-1-ium trifluoromethanesulfonate (**2a**):



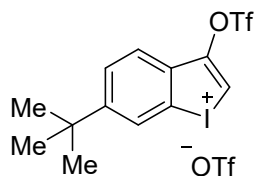
¹H NMR (400 MHz, DMSO) δ 8.71 (s, 1H), 8.14 (s, 1H), 7.80 – 7.74 (m, 2H), 2.52 (s, 3H) ppm. ¹³C NMR (100 MHz, DMSO) δ 149.8, 143.2, 132.0, 130.3, 126.2, 120.7 (q, J = 257 Hz), 120.1, 108.0, 21.4 ppm. ¹⁹F NMR (376 MHz, DMSO) δ -72.4, -77.8 ppm. HRMS (ESI) for C₁₀H₇F₃IO₃S [M-TfO]⁺ Calculated: 390.91072, found: 390.91074.

3-(((trifluoromethyl)sulfonyl)oxy)benzo[b]iodol-1-ium trifluoromethanesulfonate (2b):



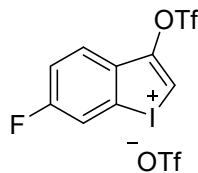
2b (64 mg, 60% yield, white solid) was synthesized according to the procedure for **2a**. ^1H NMR (400 MHz, DMSO) δ 8.88 – 8.78 (m, 1H), 8.41 (s, 1H), 7.94 (t, J = 7.5 Hz, 1H), 7.82 (dd, J = 7.2, 5.9 Hz, 2H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 149.4, 134.5, 131.3, 130.8, 130.3, 125.9, 121.5, 120.9 (q, J = 310 Hz), 113.6 ppm. ^{19}F NMR (376 MHz, DMSO) δ -72.0, -72.7 ppm. HRMS (ESI) for $\text{C}_9\text{H}_5\text{F}_3\text{IO}_3\text{S}$ $[\text{M-TfO}]^+$ Calculated: 376.89507, found: 376.89511.

6-(tert-butyl)-3-(((trifluoromethyl)sulfonyl)oxy)benzo[b]iodol-1-ium trifluoromethanesulfonate (2c):



2c (78 mg, 67% yield, gray solid) was synthesized according to the procedure for **2a**. ^1H NMR (400 MHz, DMSO) δ 8.74 (s, 1H), 8.36 (d, J = 1.4 Hz, 1H), 8.03 (dd, J = 8.4, 1.5 Hz, 1H), 7.80 (d, J = 8.3 Hz, 1H), 1.37 (s, 9H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 155.7, 149.7, 132.1, 128.6, 126.8, 126.2, 122.0, 120.7 (q, J = 257 Hz), 120.6, 119.4, 119.4, 116.8, 108.5, 35.7, 30.8 ppm. ^{19}F NMR (471 MHz, DMSO) δ -72.5, -77.8 ppm. HRMS (ESI) for : $\text{C}_{13}\text{H}_{13}\text{F}_3\text{IO}_3\text{S}$ $[\text{M-TfO}]^+$ Calculated: 432.95767, found: 432.95786.

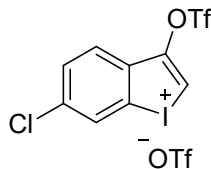
6-fluoro-3-(((trifluoromethyl)sulfonyl)oxy)benzo[b]iodol-1-ium trifluoromethanesulfonate (2d):



2d (62 mg, 57% yield, yellow solid) was synthesized according to the procedure for **2a**. ^1H NMR (400 MHz, DMSO) δ 8.77 (s, 1H), 8.16 (dd, J = 7.7, 2.4 Hz, 1H), 7.91 (dd, J = 8.8, 4.9 Hz, 1H), 7.86 (td, J = 8.6, 2.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 162.8 (d, J = 254 Hz), 148.8, 131.3 (d, J = 3 Hz), 128.4 (d, J = 10 Hz), 121.2 (d, J = 10 Hz), 119.7, 119.5, 119.4 (d, J = 60 Hz), 119.3, 118.2, 117.9, 116.5, 109.7 (d, J = 3 Hz) ppm. ^{19}F NMR (471 MHz, DMSO) δ -72.4, -77.8, -105.3, -105.3, -105.3, -

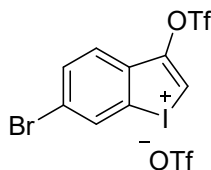
105.3, -105.3, -105.3 ppm. HRMS (ESI) for $C_9H_4F_4IO_3S$ [M-TfO]⁺ Calculated: 394.88565, found: 394.88586.

6-chloro-3-(((trifluoromethyl)sulfonyl)oxy)benzo[b]iodol-1-ium trifluoromethanesulfonate (2e):



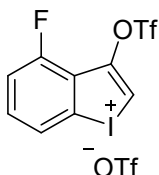
2e (60 mg, 54% yield, light yellow solid) was synthesized according to the procedure for **2a**. ¹H NMR (400 MHz, DMSO) δ 8.85 (s, 1H), 8.34 (s, 1H), 8.03 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 1H) ppm. ¹³C NMR (100 MHz, DMSO) δ 149.0, 136.3, 133.6, 131.4, 129.9, 127.7, 121.3, 118.1 (q, *J* = 256 Hz), 110.6 ppm. ¹⁹F NMR (471 MHz, DMSO) δ -72.4, -77.8 ppm. HRMS (ESI) for $C_9H_4ClF_3IO_3S$ [M-TfO]⁺ Calculated: 410.85610, found: 410.85635.

6-bromo-3-(((trifluoromethyl)sulfonyl)oxy)benzo[b]iodol-1-ium trifluoromethanesulfonate (2f):



2f (47 mg, 39% yield, brown solid) was synthesized according to the procedure for **2a**. ¹H NMR (400 MHz, DMSO) δ 8.84 (s, 1H), 8.47 (d, *J* = 1.7 Hz, 1H), 8.16 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H) ppm. ¹³C NMR (100 MHz, DMSO) δ 149.2, 134.2, 133.9, 132.6, 127.9, 124.8, 121.5, 120.7 (q, *J* = 262 Hz), 110.6 ppm. ¹⁹F NMR (376 MHz, DMSO) δ -71.8, -72.4, -77.8 ppm. HRMS (ESI) for: $C_9H_4BrF_3IO_3S$ [M-TfO]⁺ Calculated: 454.80558, found: 454.80585.

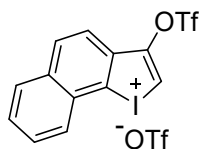
4-fluoro-3-(((trifluoromethyl)sulfonyl)oxy)benzo[b]iodol-1-ium trifluoromethanesulfonate (2g):



2g (57 mg, 52% yield, light yellow solid) was synthesized according to the procedure for **2a**. ¹H NMR (400 MHz, DMSO) δ 8.90 (s, 1H), 8.28 – 8.19 (m, 1H), 7.89 – 7.77 (m, 2H) ppm. ¹³C NMR (100 MHz, DMSO) δ 159.5 (d, *J* = 258 Hz), 147.8, 133.1 (d, *J* = 8.8 Hz), 127.0 (d, *J* = 2.5 Hz), 123.2 (d, *J* = 12.6 Hz), 122.0, 121.5, 118.1 (q, *J* = 320 Hz), 111.4 ppm. ¹⁹F NMR (376 MHz, DMSO) δ -72.8, -72.8, -77.8, -115.2, -115.2, -115.3 ppm. HRMS (ESI) for : $C_9H_4F_4IO_3S$ [M-TfO]⁺ Calculated: 394.88565, found:

394.88541.

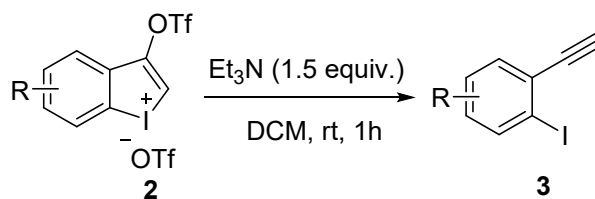
3-(((trifluoromethyl)sulfonyl)oxy)naphtho[1,2-b]iodol-1-ium trifluoromethanesulfonate (2h):



2h (83 mg, 72% yield, brown solid) was synthesized according to the procedure for **2a**. ¹H NMR (400 MHz, DMSO) δ 9.16 (s, 1H), 8.60 – 8.54 (m, 1H), 8.49 (d, J = 8.6 Hz, 1H), 8.27 (dd, J = 6.6, 2.6 Hz, 1H), 7.91 (ddd, J = 6.6, 5.4, 3.5 Hz, 2H), 7.84 (d, J = 8.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, DMSO) δ 150.5, 134.3, 133.7, 132.1, 130.6, 129.9, 129.7, 129.3, 126.6, 125.0, 122.3, 122.0, 120.7 (q, J = 256 Hz), 119.4, 116.9, 109.6 ppm. ¹⁹F NMR (376 MHz, DMSO) δ -72.3, -77.7 ppm. HRMS (ESI) for: C₁₃H₇F₃IO₃S [M-TfO]⁺ Calculated:426.91072, found: 426.91104.

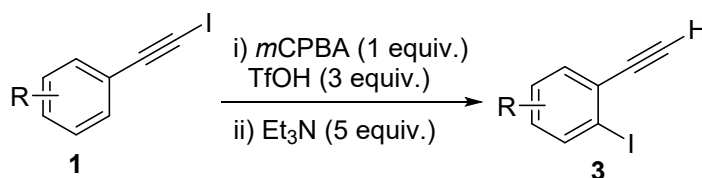
General one-pot procedure for the synthesis of *ortho*-iodo aromatic acetylenes

GP 1: General procedure for the synthesis of *ortho*-iodo aromatic acetylenes 3a-3c from cyclic monoaryliodonium salts 2a-2c:



To a stirred solution of **2a** (54 mg, 0.1 mmol) in DCM (2 mL) was added Et₃N (20.8 μ L, 0.15 mmol) and the solution was stirred for 2h at r.t. before DCM was removed by rotary evaporation. The residue was purified by column chromatography on a silica gel (PE) to provide product **3a** (22.7 mg, 94% yield) as a light yellow oil.

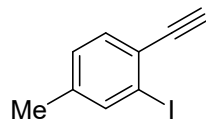
GP 2: General procedure for the synthesis of *ortho*-iodo aromatic acetylenes 3 from iodoethynylarenes 1:



To a stirred solution of **1a** (48 mg, 0.2 mmol) in DCM (2 mL) was added TfOH (52.5 μ L, 0.6 mmol) at rt, then a solution of *m*-CPBA (85%, 40.7 mg, 0.2 mmol) in DCM (2 mL) was added dropwise, rt. The solution was stirred for 2h at r.t. before DCM was removed by rotary evaporation. Next, to the residue

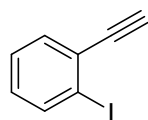
was added DCM (2 mL) and Et₃N (139.3 μL, 1 mmol), the solution was stirred for 2h at r.t. before DCM was removed by rotary evaporation. The residue was purified by column chromatography on a silica gel (PE) to provide product **3a** (33 mg, 68% yield) as a light yellow oil.

1-ethynyl-2-iodo-4-methylbenzene (3a):



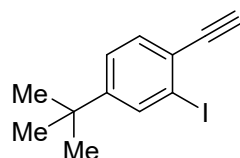
¹H NMR (400 MHz, CDCl₃) δ 7.69 (s, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 3.33 (s, 1H), 2.31 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 140.7, 139.5, 133.2, 128.9, 125.9, 100.5, 85.4, 80.3, 21.1 ppm. HRMS (EI) for C₉H₇I [M]⁺ Calculated: 241.9587, found: 241.9586.

1-ethynyl-2-iodobenzene (3b):



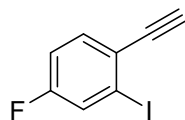
3b (21.3 mg, 93% yield, colorless oil) was synthesized according to **GP 1** and **3b** (24 mg, 53% yield, colorless oil) was synthesized according to **GP 2**. ¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.82 (m, 1H), 7.51 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.04 (td, *J* = 7.8, 1.6 Hz, 1H), 3.39 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 138.9, 133.6, 130.1, 128.8, 127.9, 100.6, 85.3, 77.5, 77.2, 76.8 ppm. HRMS (EI) for C₈H₅I [M]⁺ Calculated: 227.9430, found: 227.9424.

4-(tert-butyl)-1-ethynyl-2-iodobenzene (3c):



3c (27.6 mg, 97% yield, light yellow oil) was synthesized according to **GP 1** and **3c** (34 mg, 60% yield, light yellow oil) was synthesized according to **GP 2**. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 1.9 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.32 (dd, *J* = 8.2, 1.9 Hz, 1H), 3.33 (s, 1H), 1.29 (s, 9H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 153.9, 136.0, 133.1, 125.9, 125.3, 100.8, 85.4, 80.3, 34.9, 31.1 ppm. HRMS (EI) for C₁₂H₁₃I [M]⁺ Calculated: 284.0056, found: 284.0050.

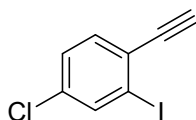
1-ethynyl-4-fluoro-2-iodobenzene (3d):



3d (24.7 mg, 50% yield, light yellow crystal) was synthesized according to **GP 2**. ¹H NMR (400 MHz,

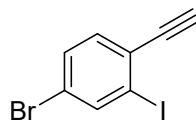
CDCl₃) δ 7.57 (dd, J = 8.0, 2.6 Hz, 1H), 7.47 (dd, J = 8.6, 5.8 Hz, 1H), 7.08 – 6.98 (m, 1H), 3.35 (d, J = 0.5 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 161.8 (d, J = 256 Hz), 134.5 (d, J = 8.8 Hz), 126.2 (d, J = 24 Hz), 125.3 (d, J = 3.8 Hz), 115.6 (d, J = 21.4 Hz), 100.5 (d, J = 7.6 Hz), 84.3, 80.9 ppm. ¹⁹F NMR (376 MHz, CDCl₃) δ -108.7 ppm. HRMS (EI) for C₈H₄FI [M]⁺ Calculated: 245.9336, found: 245.9329.

4-chloro-1-ethynyl-2-iodobenzene (3e):



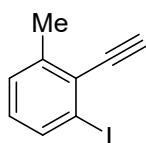
3e (25 mg, 48% yield, yellow solid) was synthesized according to **GP 2**. ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, J = 1.8 Hz, 1H), 7.41 (d, J = 8.3 Hz, 1H), 7.29 (dd, J = 8.3, 1.9 Hz, 1H), 3.42 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 138.5, 135.2, 133.9, 128.4, 127.5, 100.7, 84.4, 82.1, 82.1 ppm. HRMS (EI) for C₈H₄ClI [M]⁺ Calculated: 261.9041, found: 261.9034.

4-bromo-1-ethynyl-2-iodobenzene (3f):



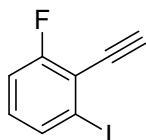
3f (19 mg, 31% yield, yellow solid) was synthesized according to **GP 2**. ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, J = 1.5 Hz, 1H), 7.44 (dd, J = 8.3, 1.5 Hz, 1H), 7.34 (d, J = 8.3 Hz, 1H), 3.43 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 141.1, 134.2, 131.3, 127.9, 123.2, 101.1, 84.4, 82.2 ppm. HRMS (EI) for C₈H₄BrI [M]⁺ Calculated: 305.8536, found: 305.8531.

2-ethynyl-1-iodo-3-methylbenzene (3g):



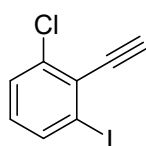
3g (29 mg, 59% yield, yellow oil) was synthesized according to **GP 2**. ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 8.0 Hz, 1H), 7.18 (d, J = 7.6 Hz, 1H), 6.93 (t, J = 7.8 Hz, 1H), 3.62 (s, 1H), 2.50 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 143.0, 137.3, 136.3, 130.5, 130.4, 129.8, 129.1, 128.5, 101.3, 85.4, 84.3, 22.3 ppm. HRMS (EI) for C₉H₇I [M]⁺ Calculated: 241.9587, found: 241.9581.

2-ethynyl-1-fluoro-3-iodobenzene (3h):



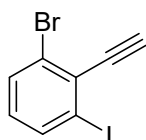
3h (22 mg, 45% yield, yellow solid) was synthesized according to **GP 2**. ^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, $J = 7.7$ Hz, 1H), 7.13 – 7.00 (m, 2H), 3.64 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 163.3 (d, $J = 322$ Hz), 134.6 (d, $J = 3.8$ Hz), 131.1 (q, $J = 5$ Hz), 118.1 (d, $J = 21.4$ Hz), 115.3 (d, $J = 26.5$ Hz), 101.3, 86.7 (d, $J = 5$ Hz), 86.6 (d, $J = 6$ Hz), 79.0 (d, $J = 3.8$ Hz) ppm. ^{19}F NMR (376 MHz, CDCl_3) δ -103.6 ppm. HRMS (EI) for $\text{C}_8\text{H}_4\text{FI}$ $[\text{M}]^+$ Calculated: 245.9336, found: 245.9333.

1-chloro-2-ethynyl-3-iodobenzene (3i):



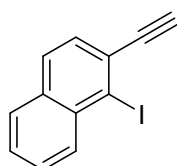
3i (27 mg, 51% yield, yellow solid) was synthesized according to **GP 2**. ^1H NMR (400 MHz, CDCl_3) δ 7.77 (dd, $J = 8.0, 1.0$ Hz, 1H), 7.40 (dd, $J = 8.1, 1.1$ Hz, 1H), 6.96 (t, $J = 8.0$ Hz, 1H), 3.69 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 137.3, 136.8, 130.5, 129.1, 128.3, 101.6, 86.5, 82.6 ppm. HRMS (EI) for $\text{C}_8\text{H}_4\text{ClI}$ $[\text{M}]^+$ Calculated: 261.9041, found: 261.9037.

1-bromo-2-ethynyl-3-iodobenzene (3j):



3j (21 mg, 34% yield, yellow solid) was synthesized according to **GP 2**. ^1H NMR (400 MHz, CDCl_3) δ 7.81 (dd, $J = 8.0, 1.1$ Hz, 1H), 7.58 (dd, $J = 8.1, 1.1$ Hz, 1H), 6.87 (t, $J = 8.0$ Hz, 1H), 3.68 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 137.9, 132.3, 130.7, 130.1, 125.7, 101.4, 85.9, 84.4 ppm. HRMS (EI) for $\text{C}_8\text{H}_4\text{BrI}$ $[\text{M}]^+$ Calculated: 305.8536, found: 305.8535.

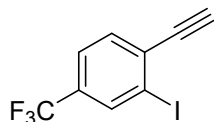
2-ethynyl-1-iodonaphthalene (3k):



3k (36 mg, 65% yield, yellow oil) was synthesized according to **GP 2**. ^1H NMR (400 MHz, CDCl_3) δ 8.20 (d, $J = 8.5$ Hz, 1H), 7.79 – 7.73 (m, 2H), 7.59 (t, $J = 7.2$ Hz, 1H), 7.53 (dd, $J = 7.9, 4.5$ Hz, 2H),

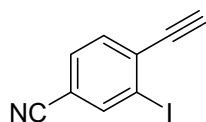
3.54 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 133.6, 129.3, 128.8, 128.5, 128.5, 127.5, 82.0 ppm.
HRMS (EI) for $\text{C}_{12}\text{H}_7\text{I}$ $[\text{M}]^+$ Calculated: 277.9587, found: 277.9586.

1-ethynyl-2-iodo-4-(trifluoromethyl)benzene (3l):



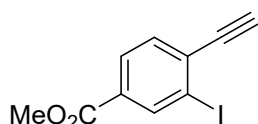
3l (27 mg, 45% yield, yellow solid) was synthesized according to **GP 2**. ^1H NMR (400 MHz, CDCl_3) δ 8.10 (s, 1H), 7.58 (q, $J = 8.3$ Hz, 2H), 3.52 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 135.7 (q, $J = 3.8$ Hz), 133.6, 132.7, 131.7 (q, $J = 32.8$ Hz), 124.8 (d, $J = 3.8$ Hz), 122.7 (q, $J = 273$ Hz), 100.4, 84.2, 83.7 ppm. ^{19}F NMR (376 MHz, CDCl_3) δ -63.0 ppm. HRMS (EI) for $\text{C}_9\text{H}_4\text{F}_3\text{I}$ $[\text{M}]^+$ Calculated: 295.9304, found: 295.9303.

4-ethynyl-3-iodobenzonitrile (3m):



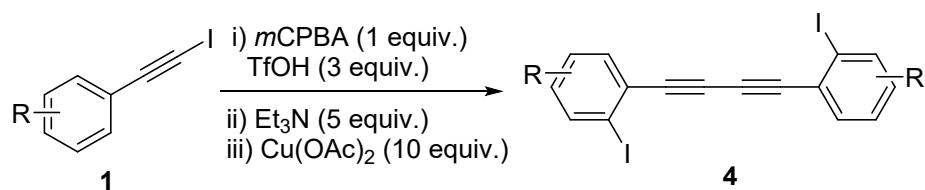
3m (21 mg, 42% yield, yellow oil) was synthesized according to **GP 2**. ^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, $J = 1.2$ Hz, 1H), 7.63 – 7.53 (m, 2H), 3.63 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 141.9, 141.9, 133.7, 133.5, 131.2, 116.7, 113.5, 100.4, 85.6, 85.5, 84.1, 84.0 ppm. HRMS (EI) for $\text{C}_9\text{H}_4\text{IN}$ $[\text{M}]^+$ Calculated: 252.9383, found: 252.9380.

methyl 4-ethynyl-3-iodobenzoate (3n):



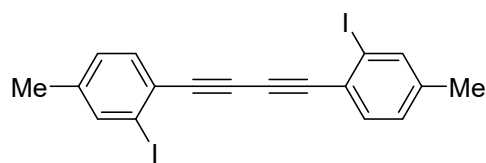
3n (28 mg, 49% yield, yellow solid) was synthesized according to **GP 2**. ^1H NMR (400 MHz, CDCl_3) δ 8.50 (d, $J = 1.6$ Hz, 1H), 7.96 (dd, $J = 8.1, 1.6$ Hz, 1H), 7.55 (d, $J = 8.1$ Hz, 1H), 3.92 (s, 3H), 3.55 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 165.1, 139.8, 133.3, 133.2, 131.3, 128.8, 100.1, 84.7, 84.0, 52.7 ppm. HRMS (EI) for $\text{C}_{10}\text{H}_7\text{IO}_2$ $[\text{M}]^+$ Calculated: 285.9485, found: 285.9484.

GP 3: General procedure for the synthesis of 1, 3-diynes 4 from iodoethynylarenes 1:



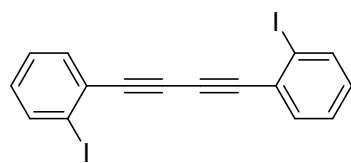
To a stirred solution of **1a** (48 mg, 0.2 mmol) in DCM (2 mL) was added TfOH (52.5 μL , 0.6 mmol) at rt, then a solution of *m*-CPBA (85%, 40.7 mg, 0.2 mmol) in DCM (2 mL) was added dropwise, rt. The solution was stirred for 2h at r.t. before DCM was removed by rotary evaporation. Next, to the residue was added DCM (2 mL) and Et₃N (139.3 μL , 1 mmol), the solution was stirred for 2h at r.t. before DCM was removed by rotary evaporation. Then, to residue was added Cu(OAc)₂ (181.6 mg, 1 mmol), MeOH (2 mL), pyridine (2 mL), the solution was stirred for 24h at r.t. before the reaction mixture was concentrated by rotary evaporation. The residue was purified by column chromatography on a silica gel (PE) to provide product **4a** (25 mg, 52% yield) as a light yellow solid.

1,4-bis(2-iodo-4-methylphenyl)buta-1,3-diyne (4a):



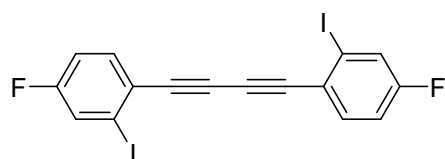
¹H NMR (400 MHz, CDCl₃) δ 7.70 (s, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 2.32 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 141.2, 139.6, 133.8, 129.0, 125.7, 101.0, 84.3, 76.8, 21.2 ppm. HRMS (EI) for C₁₈H₁₂I₂ [M]⁺ Calculated: 481.9023, found: 481.9029.

1,4-bis(2-iodophenyl)buta-1,3-diyne (4b):



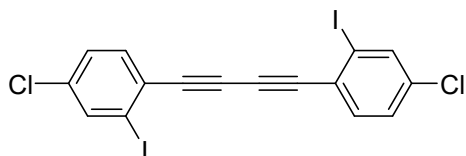
4b (22 mg, 47% yield, yellow oil) was synthesized according to **GP 3**. ¹H NMR (400 MHz, CDCl₃) δ 7.87 (dd, *J* = 8.0, 0.9 Hz, 2H), 7.56 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.33 (td, *J* = 7.6, 1.1 Hz, 2H), 7.06 (td, *J* = 7.8, 1.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 139.0, 134.1, 130.5, 128.7, 128.0, 101.0, 84.5 ppm. HRMS (EI) for C₁₆H₈I₂ [M]⁺ Calculated: 453.8710, found: 453.8712.

1,4-bis(4-fluoro-2-iodophenyl)buta-1,3-diyne (4c):



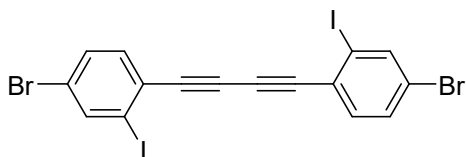
4c (23.4 mg, 48% yield, yellow solid) was synthesized according to **GP 3**. ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, $J = 2.5$ Hz, 1H), 7.58 (d, $J = 2.5$ Hz, 1H), 7.52 (dd, $J = 8.7, 5.7$ Hz, 2H), 7.10 – 7.03 (m, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 162.0 (d, $J = 257$ Hz), 135.2 (d, $J = 8.8$ Hz), 126.5 (d, $J = 23.9$ Hz), 125.0, 115.8 (d, $J = 21.4$ Hz), 101.2, 83.4 ppm. ^{19}F NMR (376 MHz, CDCl_3) δ -107.1 ppm. HRMS (EI) for $\text{C}_{16}\text{H}_6\text{F}_2\text{I}_2$ $[\text{M}]^+$ Calculated: 489.8521, found: 489.8525.

1,4-bis(4-chloro-2-iodophenyl)buta-1,3-diyne (4d):



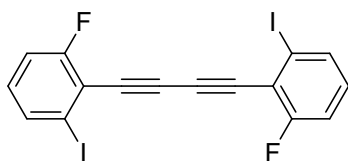
4d (22.7 mg, 43% yield, yellow solid) was synthesized according to **GP 3**. ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, $J = 2.0$ Hz, 2H), 7.46 (d, $J = 8.4$ Hz, 2H), 7.32 (dd, $J = 8.4, 2.0$ Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 138.6, 135.8, 134.5, 128.6, 127.1, 101.1, 84.0, 78.0 ppm. HRMS (ESI) for $\text{C}_{16}\text{H}_7\text{Cl}_2\text{I}_2$ $[\text{M}+\text{H}]^+$ Calculated: 522.80087, found: 522.80933.

1,4-bis(4-bromo-2-iodophenyl)buta-1,3-diyne (4e):



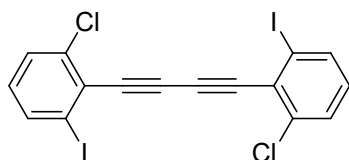
4e (15.2 mg, 25% yield, yellow solid) was synthesized according to **GP 3**. ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, $J = 1.8$ Hz, 2H), 7.47 (dd, $J = 8.3, 1.9$ Hz, 2H), 7.39 (d, $J = 8.3$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.3, 134.7, 131.4, 127.5, 124.0, 101.4, 84.1, 78.1 ppm.

1,4-bis(2-fluoro-6-iodophenyl)buta-1,3-diyne (4f):



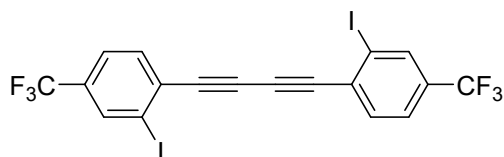
4f (19.5 mg, 40% yield, yellow solid) was synthesized according to **GP 3**. ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, $J = 2.5$ Hz, 1H), 7.58 (d, $J = 2.5$ Hz, 1H), 7.52 (dd, $J = 8.7, 5.7$ Hz, 2H), 7.10 – 7.03 (m, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 162.0 (d, $J = 257$ Hz), 135.2 (d, $J = 8.8$ Hz), 126.4 (d, $J = 23.9$ Hz), 125.1 (d, $J = 3.8$ Hz), 115.8 (d, $J = 21.4$ Hz), 101.1 (d, $J = 8.8$ Hz), 83.4 ppm. ^{19}F NMR (376 MHz, CDCl_3) δ -107.1, -107.1, -107.1, -107.2 ppm. HRMS (EI) for $\text{C}_{16}\text{H}_6\text{F}_2\text{I}_2$ $[\text{M}]^+$ Calculated: 489.8521, found: 489.8523.

1,4-bis(2-chloro-6-iodophenyl)buta-1,3-diyne (4g):



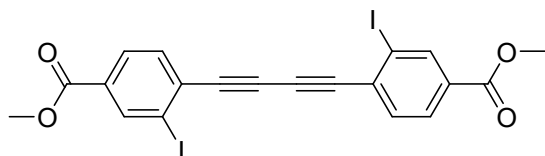
4g (24.4 mg, 47% yield, yellow solid) was synthesized according to **GP 3**. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.77 (dd, $J = 8.0, 0.9$ Hz, 2H), 7.42 (dd, $J = 8.1, 1.0$ Hz, 2H), 6.98 (t, $J = 8.0$ Hz, 2H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 137.7, 137.4, 130.8, 129.2, 128.2, 102.0, 83.2 ppm. HRMS (EI) for $\text{C}_{16}\text{H}_6\text{Cl}_2\text{I}_2$ $[\text{M}]^+$ Calculated: 521.7930, found: 521.7930.

1,4-bis(2-iodo-4-(trifluoromethyl)phenyl)buta-1,3-diyne (4h):



4h (24 mg, 41% yield, yellow solid) was synthesized according to **GP 3**. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.11 (s, 2H), 7.62 (dd, $J = 20.0, 8.2$ Hz, 4H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 135.8 (q, $J = 3.8$ Hz), 134.1, 132.1, 125.0 (q, $J = 3.8$ Hz), 122.6 (q, $J = 273$ Hz), 100.8, 84.3, 79.0 ppm. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -63.1 ppm. HRMS (EI) for $\text{C}_{18}\text{H}_6\text{F}_6\text{I}_2$ $[\text{M}]^+$ Calculated: 589.8458, found: 589.8473.

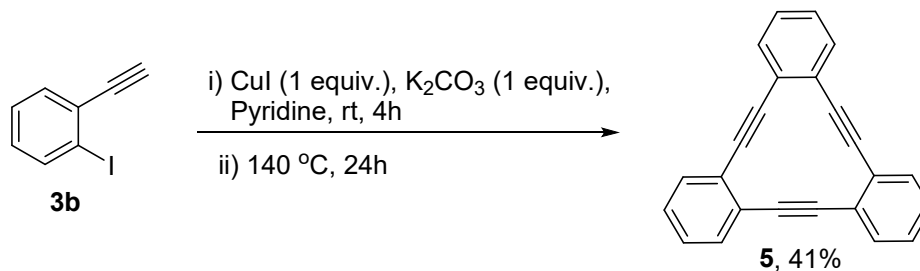
dimethyl 4,4'-(buta-1,3-diyne-1,4-diyl)bis(3-iodobenzoate) (4i):



4i (24.5 mg, 43% yield, yellow solid) was synthesized according to **GP 3**. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.52 (s, 2H), 8.06 – 7.92 (m, 2H), 7.61 (d, $J = 8.1$ Hz, 2H), 3.93 (s, 6H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 165.0, 139.9, 133.8, 132.7, 131.6, 128.9, 100.5, 85.1, 79.6, 52.8 ppm.

Synthetic applications

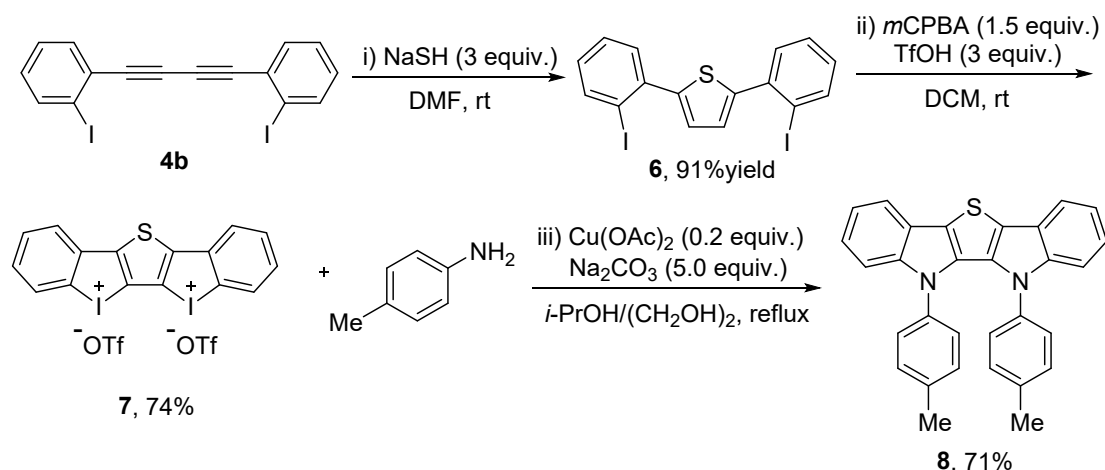
Synthesis of tribenzohexadehydro[12]annulene 5 from 3b:



To a stirred solution of **3b** (90 mg, 0.39 mmol) in pyridine (3 mL) was added CuI (75.2 mg, 0.39 mmol), K_2CO_3 (54.6 mg, 0.39 mmol), the solution was stirred for 4h at r.t. Then, the solution was

stirred for 24h at 140 °C in a sealed tube before the reaction mixture was concentrated by rotary evaporation. The residue was purified by column chromatography on a silica gel (PE) to provide product **5** (16 mg, 41% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.34 (dd, *J* = 5.6, 3.4 Hz, 6H), 7.18 (dd, *J* = 5.7, 3.4 Hz, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 132.1, 128.7, 126.8, 93.0 ppm. Data are identical with reported work. ^[1]

Synthesis of ladder-type π -conjugated PAH **8** from **4b**



i) synthesis of 2,5-bis(2-iodophenyl)thiophene (**6**):

To **4b** (455 mg, 1 mol) in a flask was added NaSH (168.5 mg, 3 mol), DMF (5 mL). The reaction mixture was stirred at rt for 24h. The remained mixture was extracted with EtOAc, the combined organic layers were washed with H₂O and brine and dried over anhydrous Na₂SO₄, evaporated in vacuum. The residue was purified by column chromatography on a silica gel (PE/EtOAc = 100/1-50/1) to provide products **6** (445 mg, 91% yield) as a yellow oil.

ii) synthesis of bis-iodonium salt (**7**):

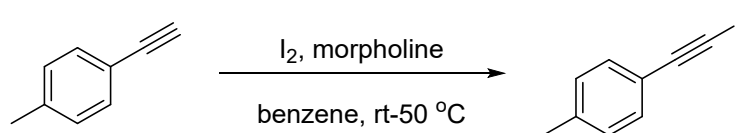
To a stirred solution of **6** (440 mg, 0.9 mmol) in DCM (10 mL) was added *m*-CPBA (85%, 275 mg, 1.35 mmol), TfOH (0.24 mL, 2.7 mmol) at 0 °C, and 30 mins later, the solution was stirred for 1h at r.t. before DCM was removed by rotary evaporation. tert-butyl methyl ether (10 mL) was added to the remained solid. The mixture was stirred for 30 min, and then filtered. The obtained solid was washed

with tert-butyl methyl ether three times, dried in high vacuo to provide **7** (523 mg, 94% yield) as a brown solid. ¹H NMR (400 MHz, DMSO) δ 8.45 – 8.28 (m, 4H), 7.93 (t, *J* = 7.5 Hz, 2H), 7.77 – 7.71 (m, 2H) ppm. ¹³C NMR (100 MHz, DMSO) δ 148.2, 136.0, 131.4, 131.1, 130.9, 126.7, 126.2, 111.1 ppm. ¹⁹F NMR (376 MHz, DMSO) δ -77.7 ppm. HRMS (ESI) for: C₁₇H₈F₃I₂O₃S₂ [M-TfO]⁺ Calculated: 634.79508, found: 634.79492. Data are identical with reported work. [2]

iii) synthesis of 5,6-di-p-tolyl-5,6-dihydrothieno[3,2-b:4,5-b']diindole (**8**):

Performed according to reported work [3]: to **7** (157 mg, 0.2 mmol) in a flask was added Na₂CO₃ (106 mg, 5 equiv.), Cu(OAc)₂ (7.3 mg, 0.2 equiv.), p-toluidine (150 mg, 1.4 mmol). The reaction flask was degassed and recharged with Ar three times, and then a solution of *i*-PrOH (3.6 mL) and ethylene glycol (0.4 mL) was added via a syringe. The reaction mixture was stirred at reflux heated by an oil bath under Ar atmosphere for 16h. The remained mixture was extracted with EtOAc, the combined organic layers were washed with H₂O and brine and dried over anhydrous Na₂SO₄, evaporated in vacuum. The residue was purified by column chromatography on a silica gel (PE/EtOAc = 50/1-10/1) to provide products **8** (63 mg, 71% yield) as a white crystal. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 7.5 Hz, 2H), 7.35 – 7.19 (m, 6H), 7.05 (d, *J* = 7.9 Hz, 4H), 6.90 (d, *J* = 7.9 Hz, 4H), 2.38 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 142.5, 136.8, 136.5, 130.5, 129.6, 126.8, 123.3, 122.9, 121.3, 120.6, 118.3, 111.5, 21.3 ppm. HRMS (ESI) for C₃₀H₂₃N₂S [M+H]⁺ Calculated: 443.15765, found: 443.15793.

Synthesis of (iodoethynyl)benzene Derivatives **1**



Performed according to reported work [4]: Iodine (7.21 g, 28.41 mmol) and morpholine (6.75 g, 6.78 mL, 77.48 mmol) were dissolved in benzene (30 ml) and the solution was stirred at room temperature for 30 min. 1-Ethynyl-4-methylbenzene (3 g, 25.83 mmol) in benzene (30 ml) was added dropwise and the mixture was stirred at 50 °C for 24 h. The suspension was filtered and the residue was washed with Et₂O (2 x 30 mL). The combined organic layers were washed with saturated aqueous solutions of NH₄Cl (2 x 30 mL) and NaHCO₃ (2 x 30 mL) and H₂O (2 x 30 mL). The organic layer was dried over MgSO₄ and filtered. The solvent was removed under reduced pressure and the crude product was purified by silica column chromatography (petroleum ether as eluent) to afford 1-(iodoethynyl)-4-methylbenzene **1a** (5.89 g, 94%) as light yellow oil.

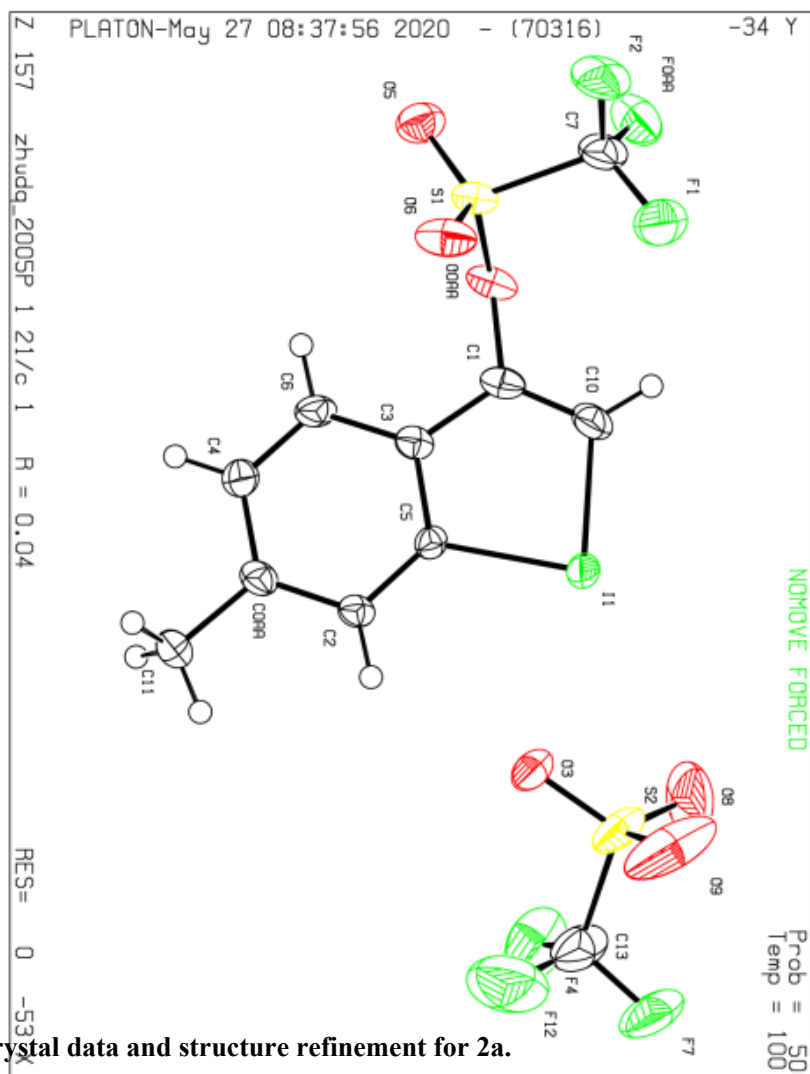


Table S2 Crystal data and structure refinement for 2a.

Identification code	2a
Empirical formula	C ₁₁ H ₇ F ₆ IO ₆ S ₂
Formula weight	540.19
Temperature/K	100.01(14)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	14.7333(2)
b/Å	5.45270(10)
c/Å	21.8703(3)
α/°	90
β/°	109.658(2)
γ/°	90
Volume/Å ³	1654.58(5)
Z	4
ρ _{calc} /cm ³	2.169
μ/mm ⁻¹	18.481
F(000)	1040.0

Crystal size/mm ³	0.2 × 0.05 × 0.05
Radiation	CuK α (λ = 1.54184)
2 Θ range for data collection/ $^{\circ}$	6.37 to 153.108
Index ranges	-17 \leq h \leq 18, -6 \leq k \leq 6, -27 \leq l \leq 24
Reflections collected	31465
Independent reflections	3396 [R_{int} = 0.0559, R_{sigma} = 0.0215]
Data/restraints/parameters	3396/0/236
Goodness-of-fit on F ²	1.116
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0448, wR_2 = 0.1188
Final R indexes [all data]	R_1 = 0.0452, wR_2 = 0.1191
Largest diff. peak/hole / e \AA^{-3}	2.12/-2.00

Table S3 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 2a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U_{eq}
I1	6253.1(2)	2883.7(6)	4779.0(2)	34.41(14)
S1	9675.9(8)	6681(2)	5918.9(6)	28.9(3)
S2	3786.1(11)	1535(3)	3942.2(7)	45.6(4)
F1	9111(3)	3969(10)	6700.3(17)	60.1(11)
F2	10363(3)	6178(9)	7156.5(16)	54.7(10)
O0AA	9180(2)	4707(7)	5381.7(16)	31.3(8)
F0AA	10479(3)	2922(7)	6638.0(19)	51.6(9)
O5	10578(3)	7207(8)	5858(2)	39.6(9)
O6	9022(3)	8521(8)	5943(2)	43.6(10)
O3	4411(3)	3385(8)	3854(2)	44.2(10)
F7	2272(3)	-648(11)	3163.7(19)	77.0(16)
F4	3315(4)	375(10)	2720(2)	81.4(16)
C5	6685(3)	5642(8)	4274(2)	20.5(8)
C1	8165(3)	4533(10)	5107(2)	27.3(10)
C2	6087(3)	6936(9)	3749(2)	22.0(9)
C3	7670(3)	6065(9)	4554(2)	22.5(9)
C4	7492(4)	9196(11)	3755(2)	32.6(11)
C0AA	6500(3)	8755(10)	3484(2)	26.5(10)
C6	8070(3)	7899(10)	4278(2)	29.6(11)
C7	9922(4)	4774(12)	6654(2)	38.2(12)
O8	4268(6)	-814(11)	4112(3)	93(2)
O9	3271(5)	1925(16)	4351(3)	108(3)
C10	7698(4)	2889(10)	5329(3)	39.2(13)
C11	5880(4)	10279(10)	2922(2)	34.0(11)

F12	2459(4)	3101(14)	2922(4)	114(2)
C13	2931(5)	973(18)	3152(3)	60(2)

Table S4 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 2a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	38.3(2)	35.7(2)	21.03(19)	4.42(11)	-0.81(13)	-19.18(13)
S1	20.9(5)	36.4(6)	25.5(6)	-5.5(5)	2.7(4)	1.9(4)
S2	45.7(8)	60.1(9)	41.0(7)	-21.3(7)	27.9(6)	-30.1(7)
F1	48(2)	100(3)	33.1(17)	2(2)	15.3(15)	-24(2)
F2	54(2)	76(3)	24.0(15)	-13.2(17)	0.0(14)	-10(2)
O0AA	24.1(16)	41(2)	23.2(16)	-7.0(15)	0.1(13)	9.6(15)
F0AA	54(2)	51(2)	43(2)	8.1(16)	6.1(17)	9.7(17)
O5	30.3(19)	52(2)	37(2)	-3.3(18)	11.8(16)	-6.1(17)
O6	29.7(18)	44(2)	48(2)	-16.4(19)	0.2(17)	7.3(17)
O3	31.6(19)	38(2)	58(3)	10.0(19)	9.3(18)	-11.2(17)
F7	70(3)	114(4)	47(2)	-26(2)	19(2)	-63(3)
F4	121(4)	96(4)	46(2)	-29(2)	54(3)	-42(3)
C5	21.2(19)	24(2)	18.6(19)	-1.0(16)	9.1(16)	-3.1(16)
C1	23(2)	31(3)	23(2)	-6.4(19)	0.8(17)	2.2(18)
C2	21(2)	29(2)	16(2)	-2.6(17)	6.5(16)	-0.4(17)
C3	21(2)	31(2)	17.2(19)	-3.2(18)	7.6(16)	1.7(18)
C4	31(2)	45(3)	22(2)	4(2)	8.6(19)	-10(2)
C0AA	27(2)	34(3)	17(2)	0.0(19)	4.6(17)	-1(2)
C6	18(2)	50(3)	22(2)	0(2)	7.5(18)	-6(2)
C7	31(2)	57(4)	22(2)	-4(2)	2.8(19)	-5(2)
O8	131(6)	42(3)	86(4)	25(3)	11(4)	-17(3)
O9	95(4)	180(8)	77(4)	-89(5)	66(4)	-92(5)
C10	43(3)	30(3)	28(3)	5(2)	-10(2)	-8(2)
C11	35(3)	33(3)	27(2)	8(2)	1(2)	-3(2)
F12	64(3)	112(5)	133(6)	19(4)	-12(4)	13(3)
C13	51(4)	93(6)	38(3)	-13(4)	21(3)	-32(4)

Table S5 Bond Lengths for 2a.

Atom	Atom	Length/ \AA	Atom	Atom	Length/ \AA
I1	C5	2.089(4)	F0AA	C7	1.310(7)
I1	C10	2.063(6)	F7	C13	1.320(8)
S1	O0AA	1.579(4)	F4	C13	1.295(8)
S1	O5	1.409(4)	C5	C2	1.382(6)
S1	O6	1.405(4)	C5	C3	1.391(6)

S1	C7	1.845(6)	C1	C3	1.449(7)
S2	O3	1.422(4)	C1	C10	1.318(8)
S2	O8	1.451(7)	C2	C0AA	1.388(7)
S2	O9	1.369(5)	C3	C6	1.396(7)
S2	C13	1.790(7)	C4	C0AA	1.400(7)
F1	C7	1.308(7)	C4	C6	1.371(7)
F2	C7	1.318(7)	C0AA	C11	1.510(7)
O0AAC1		1.414(6)	F12	C13	1.359(11)

Table S6 Bond Angles for 2a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	I1	C5	82.5(2)	C5	C3	C1	115.5(4)
O0AAS1		C7	99.8(2)	C5	C3	C6	117.3(4)
O5	S1	O0AA	106.5(2)	C6	C3	C1	127.3(4)
O5	S1	C7	106.4(3)	C6	C4	C0AA	122.1(5)
O6	S1	O0AA	111.3(2)	C2	C0AA	C4	119.2(4)
O6	S1	O5	122.6(3)	C2	C0AA	C11	120.2(4)
O6	S1	C7	107.8(3)	C4	C0AA	C11	120.6(5)
O3	S2	O8	112.2(4)	C4	C6	C3	119.7(4)
O3	S2	C13	105.5(3)	F1	C7	S1	109.9(4)
O8	S2	C13	102.8(4)	F1	C7	F2	109.7(5)
O9	S2	O3	120.3(4)	F1	C7	F0AA	109.9(6)
O9	S2	O8	107.5(5)	F2	C7	S1	107.3(4)
O9	S2	C13	107.0(4)	F0AAC7		S1	110.6(4)
C1	O0AAS1		121.3(3)	F0AAC7		F2	109.4(5)
C2	C5	I1	125.7(3)	C1	C10	I1	110.5(4)
C2	C5	C3	124.1(4)	F7	C13	S2	112.3(5)
C3	C5	I1	110.2(3)	F7	C13	F12	106.9(7)
O0AAC1		C3	118.6(4)	F4	C13	S2	114.2(5)
C10	C1	O0AA	119.8(5)	F4	C13	F7	110.5(7)
C10	C1	C3	121.4(4)	F4	C13	F12	103.8(7)
C5	C2	C0AA	117.7(4)	F12	C13	S2	108.5(6)

Table S7 Torsion Angles for 2a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
I1	C5	C2	C0AA	178.4(3)	O3	S2	C13	F12	-59.3(6)
I1	C5	C3	C1	0.9(5)	C5	C2	C0AA	C4	0.1(7)
I1	C5	C3	C6	-178.8(4)	C5	C2	C0AA	C11	-178.3(4)
S1	O0AAC1		C3	86.7(5)	C5	C3	C6	C4	0.3(7)

S1	O0AAC1	C10	-97.7(5)	C1	C3 C6	C4	-179.4(5)	
O0AAS1	C7	F1	-62.0(5)	C2	C5 C3	C1	179.1(4)	
O0AAS1	C7	F2	178.8(4)	C2	C5 C3	C6	-0.7(7)	
O0AAS1	C7	F0AA	59.5(4)	C3	C5 C2	C0AA	0.5(7)	
O0AAC1	C3	C5	174.5(4)	C3	C1 C10	I1	0.6(7)	
O0AAC1	C3	C6	-5.8(7)	C0AA	C4 C6	C3	0.3(8)	
O0AAC1	C10	I1	-174.9(3)	C6	C4 C0AA	C2	-0.5(8)	
O5	S1	O0AAC1	-151.8(4)	C6	C4 C0AA	C11	177.9(5)	
O5	S1	C7	F1	-172.6(4)	C7	S1 O0AAC1	97.7(4)	
O5	S1	C7	F2	68.2(4)	O8	S2 C13	F7	65.2(7)
O5	S1	C7	F0AA	-51.0(5)	O8	S2 C13	F4	-61.7(7)
O6	S1	O0AAC1	-15.8(5)	O8	S2 C13	F12	-176.9(6)	
O6	S1	C7	F1	54.2(5)	O9	S2 C13	F7	-48.0(8)
O6	S1	C7	F2	-65.0(4)	O9	S2 C13	F4	-174.8(7)
O6	S1	C7	F0AA	175.8(4)	O9	S2 C13	F12	70.0(7)
O3	S2	C13	F7	-177.2(6)	C10	C1 C3	C5	-1.1(7)
O3	S2	C13	F4	56.0(8)	C10	C1 C3	C6	178.6(5)

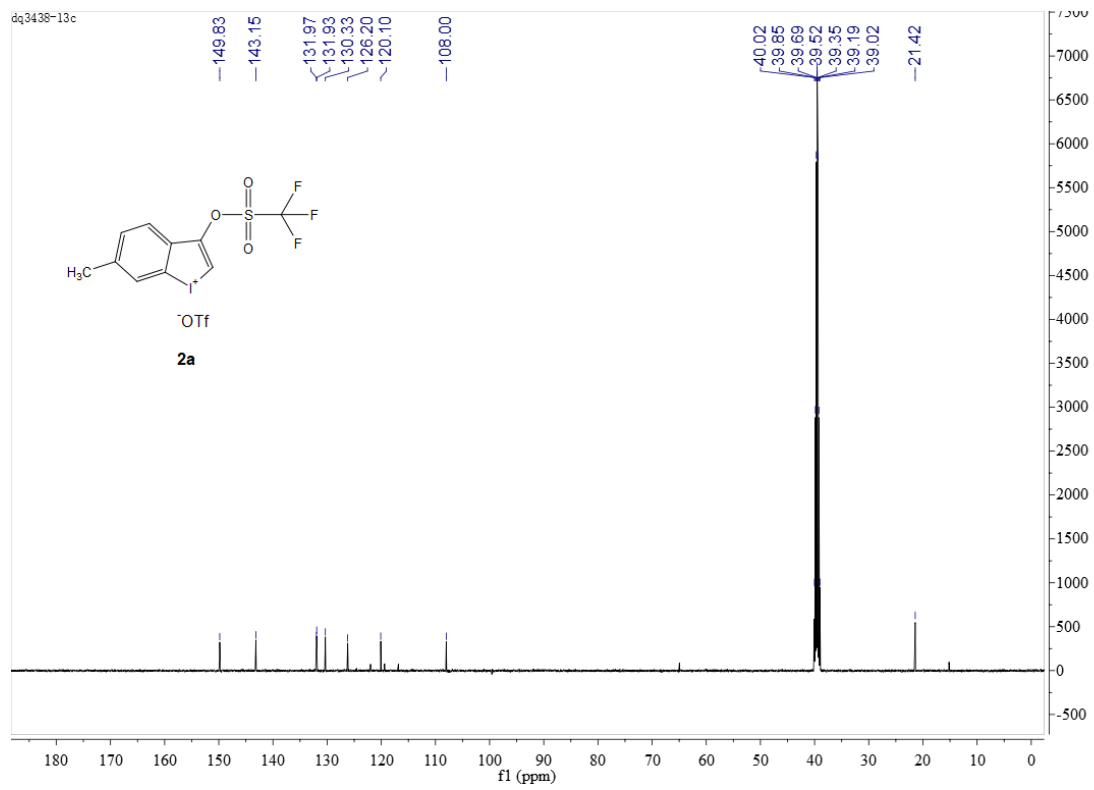
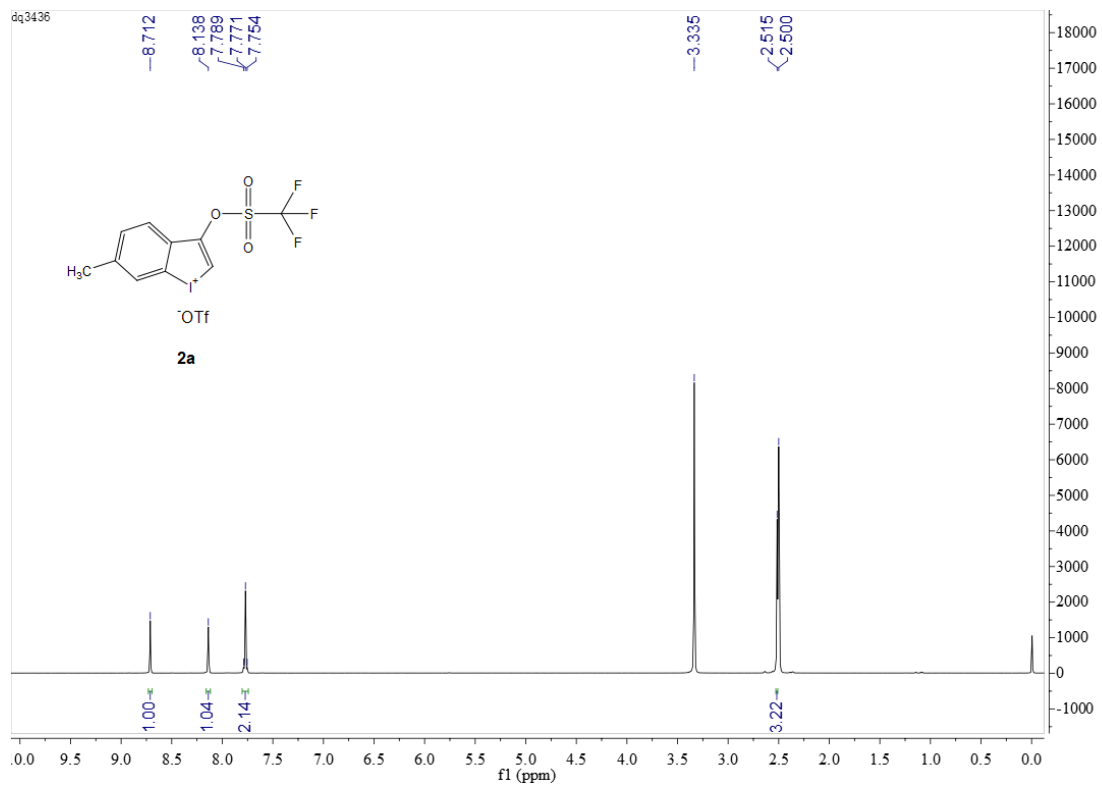
Table S8 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 2a.

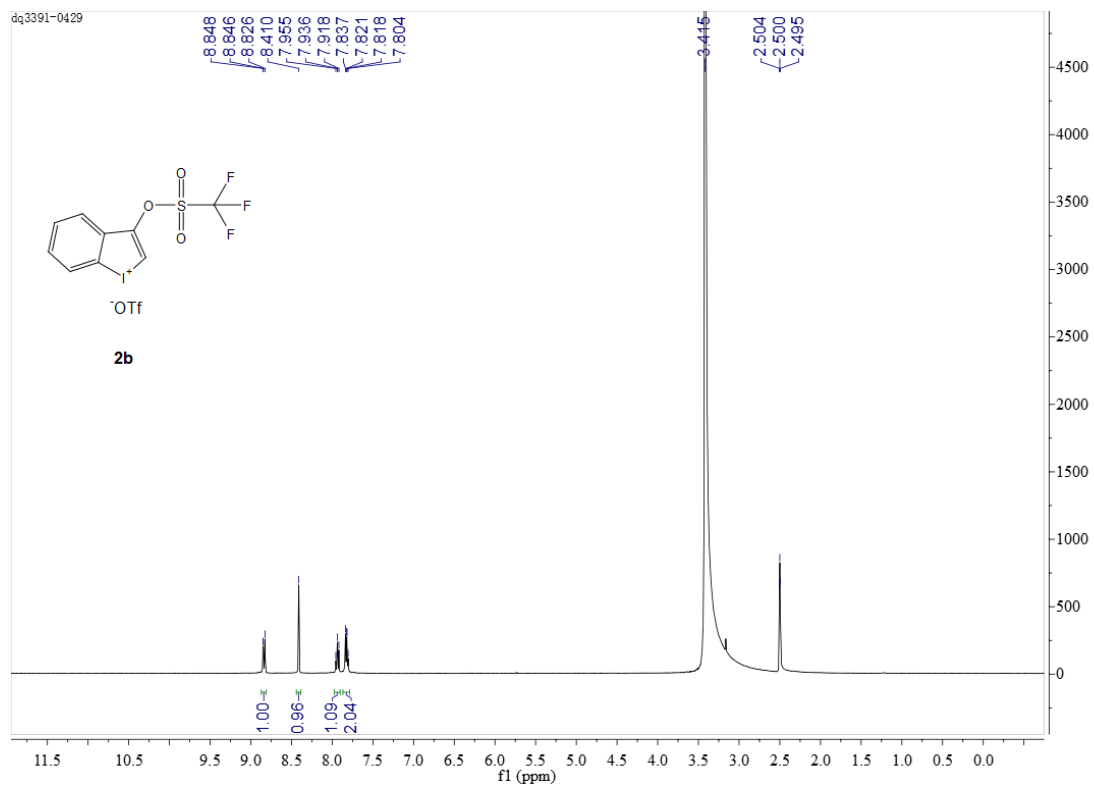
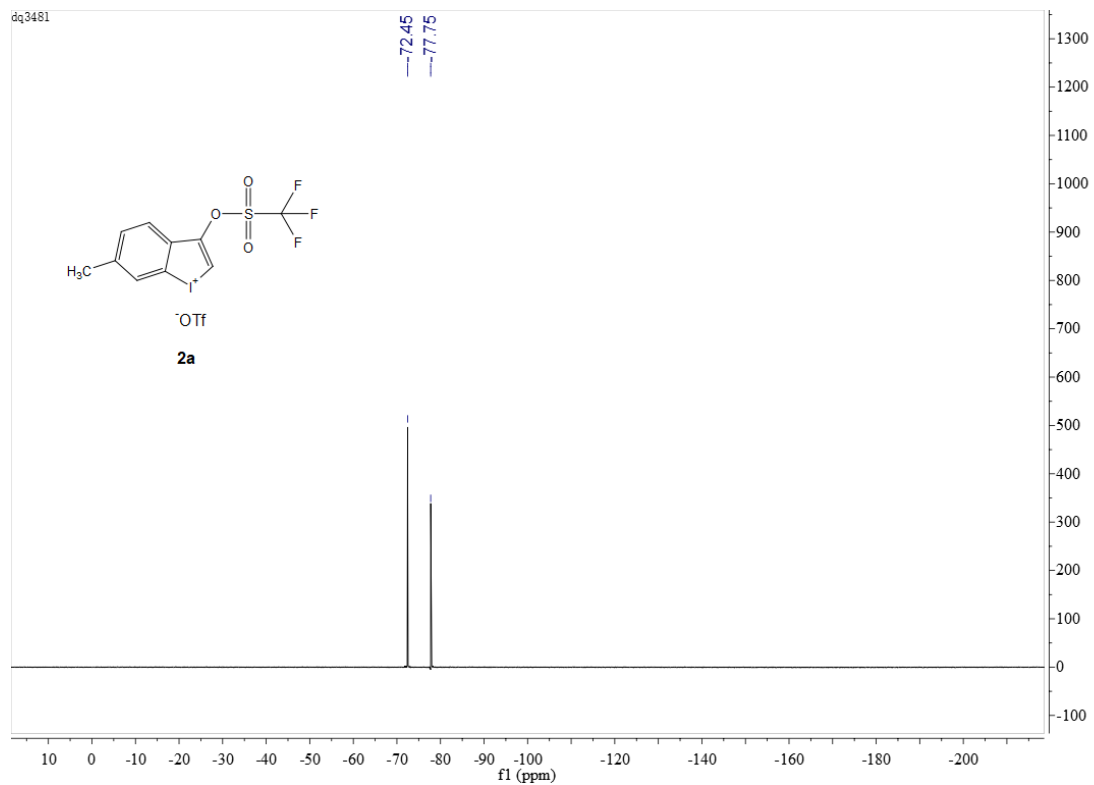
Atom	x	y	z	U(eq)
H2	5431.14	6598.75	3579.35	26
H4	7766.81	10408.14	3574.12	39
H6	8726.04	8238.32	4449.01	36
H10	7980.37	1874.08	5684.2	47
H11A	6057.63	9960.44	2545.98	51
H11B	5973.51	11986.81	3032.61	51
H11C	5214.75	9859.65	2831.67	51

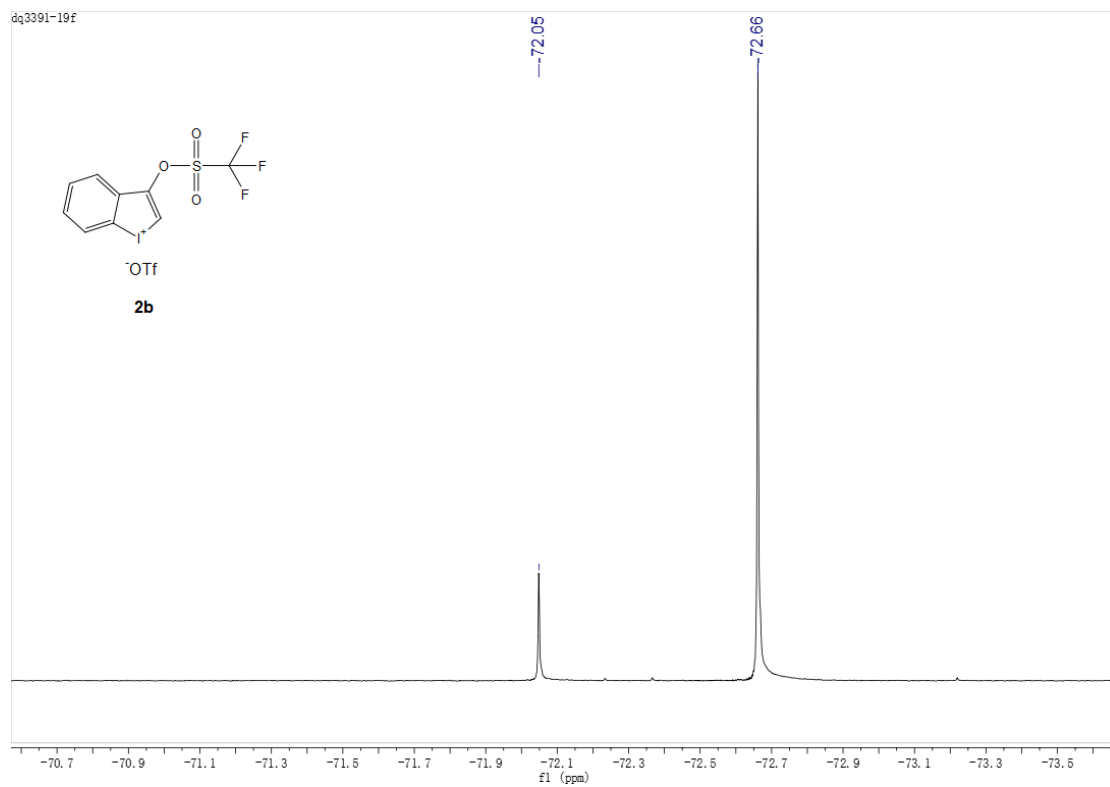
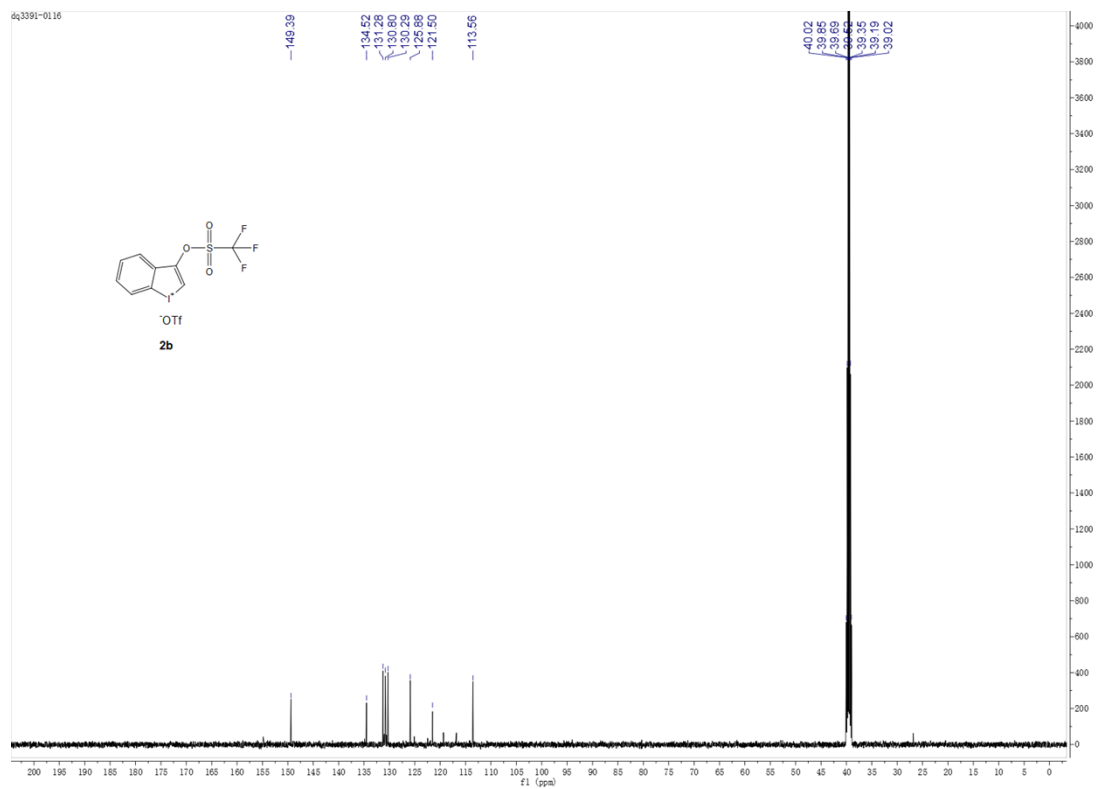
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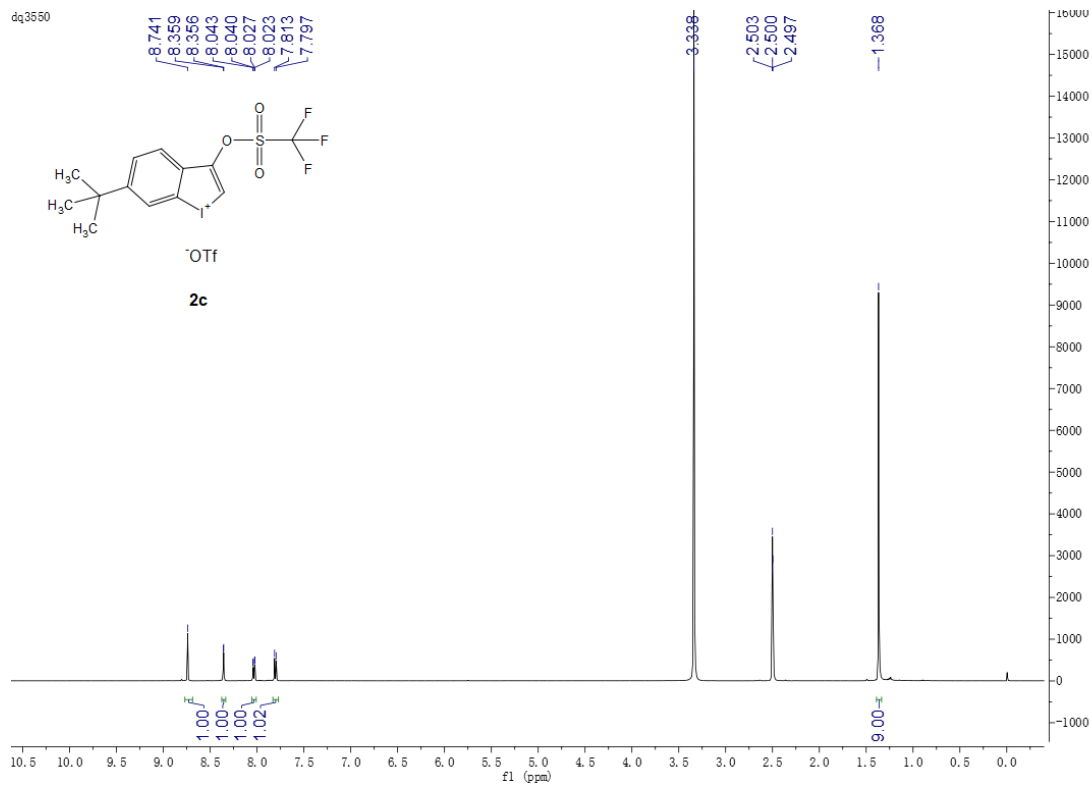
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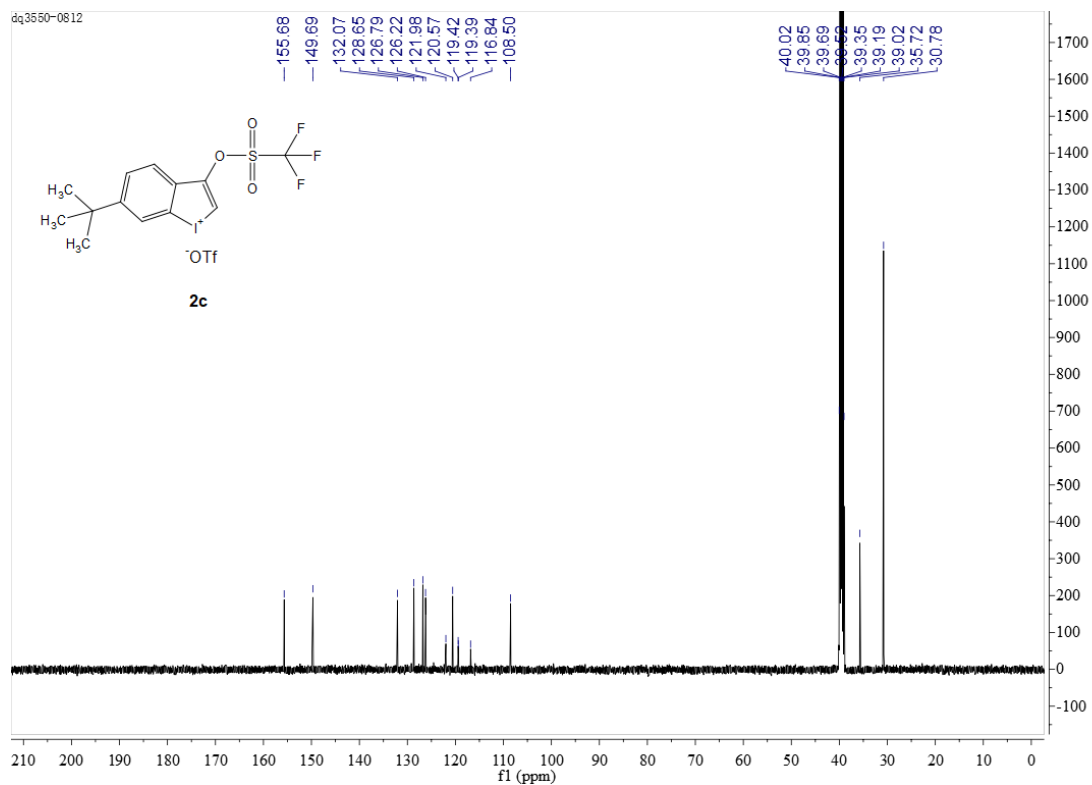


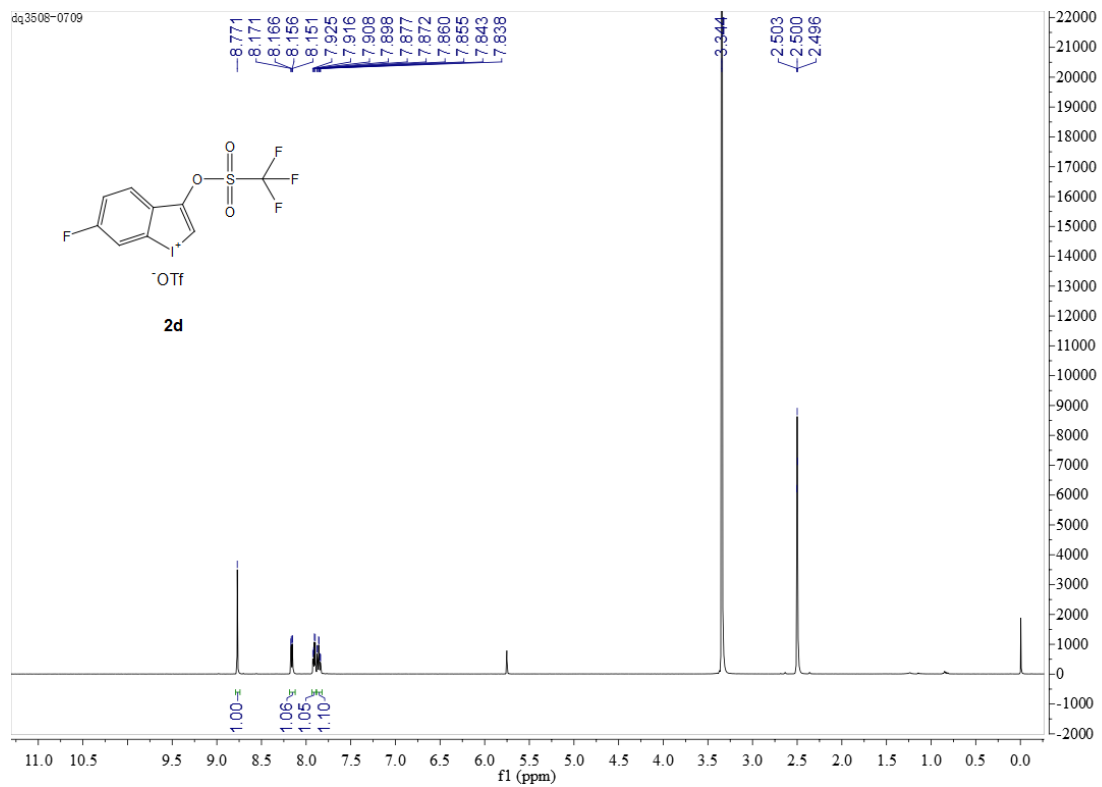
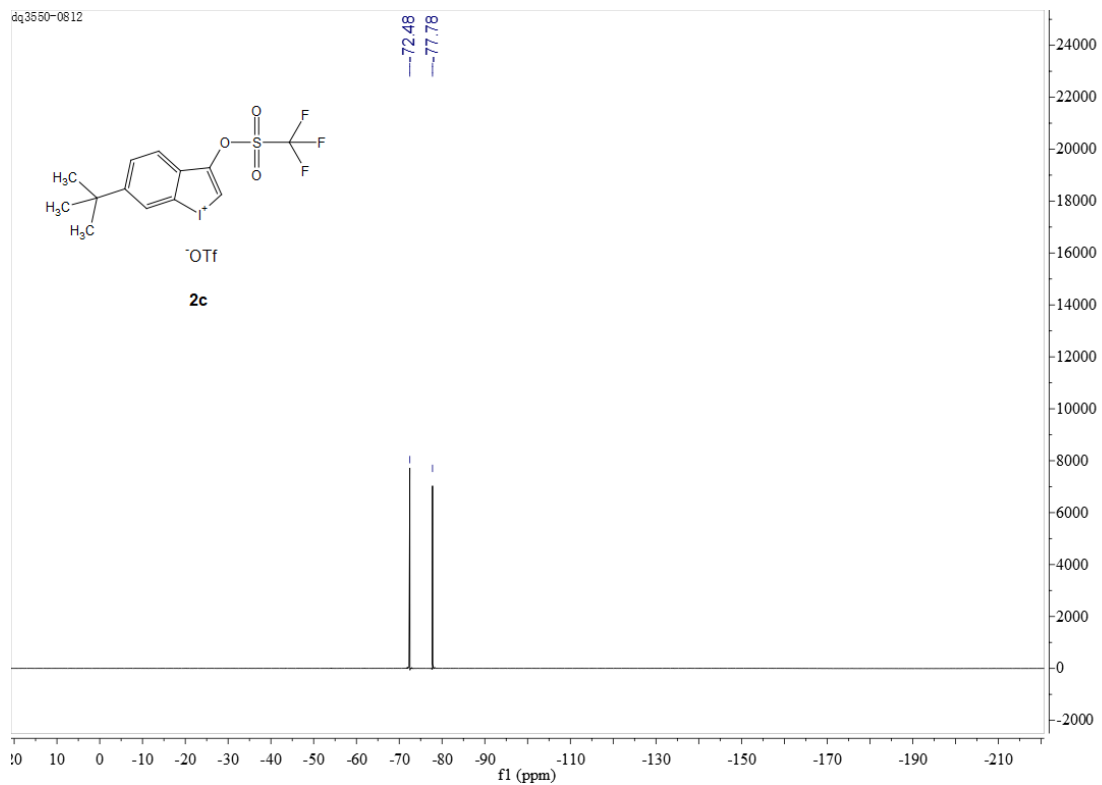


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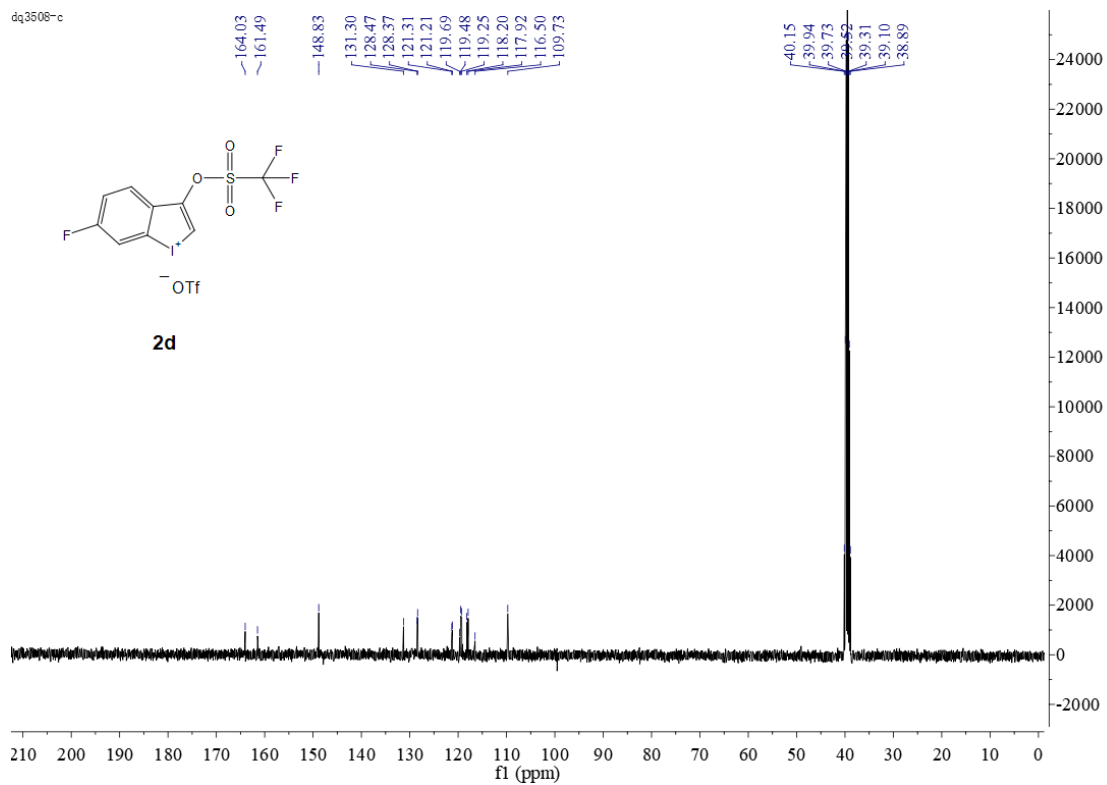


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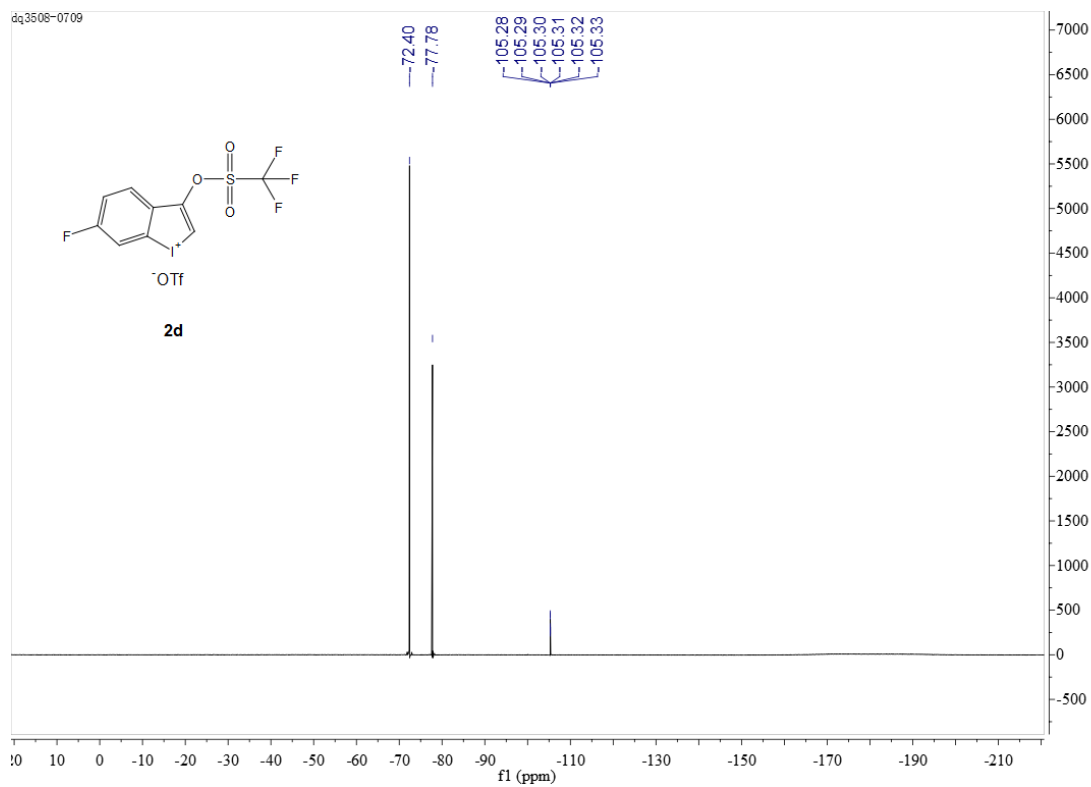


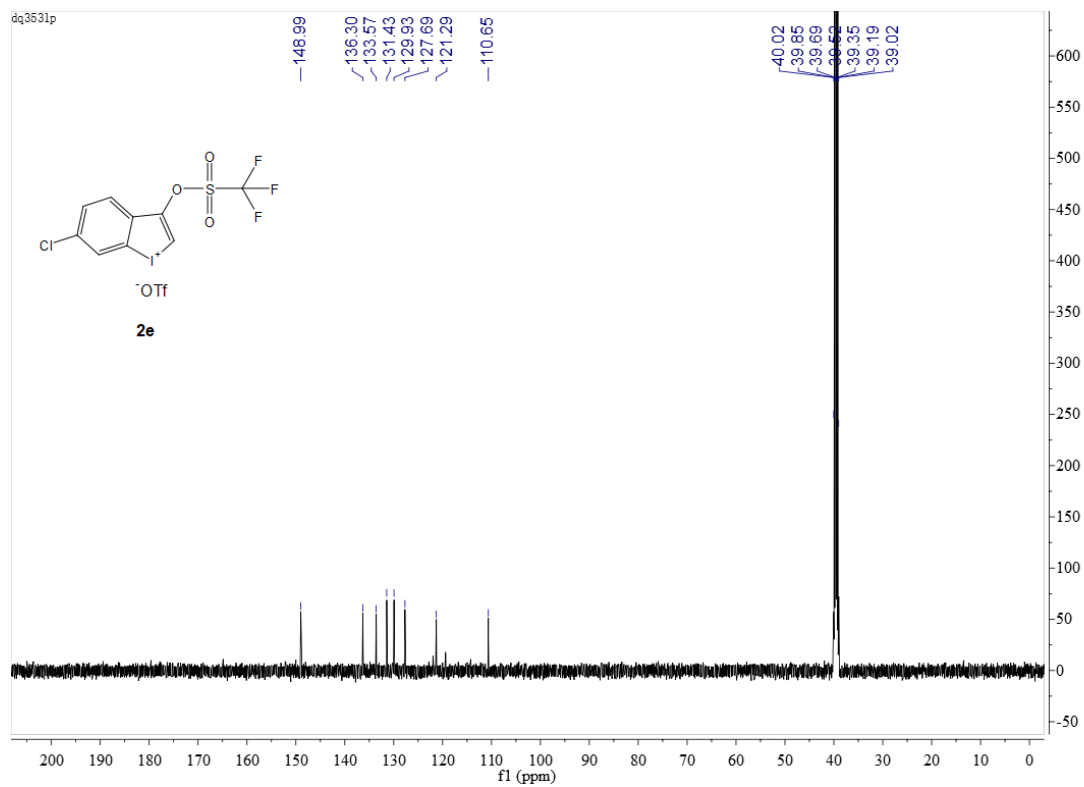
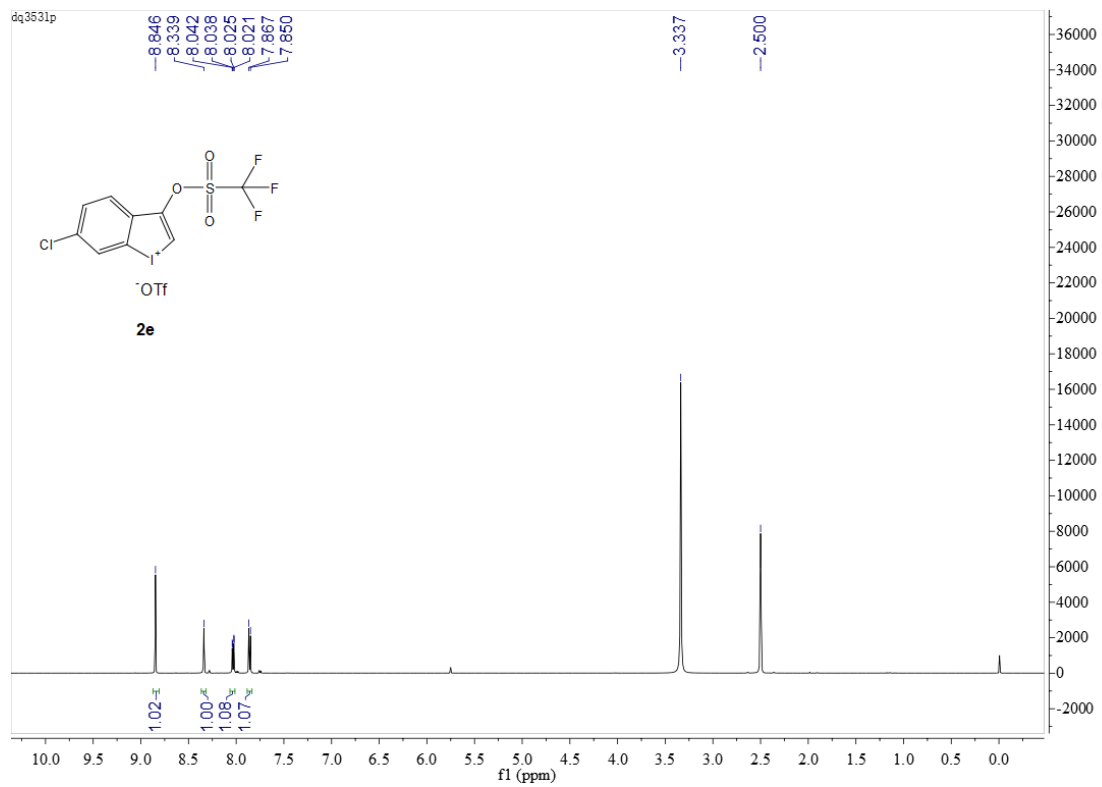


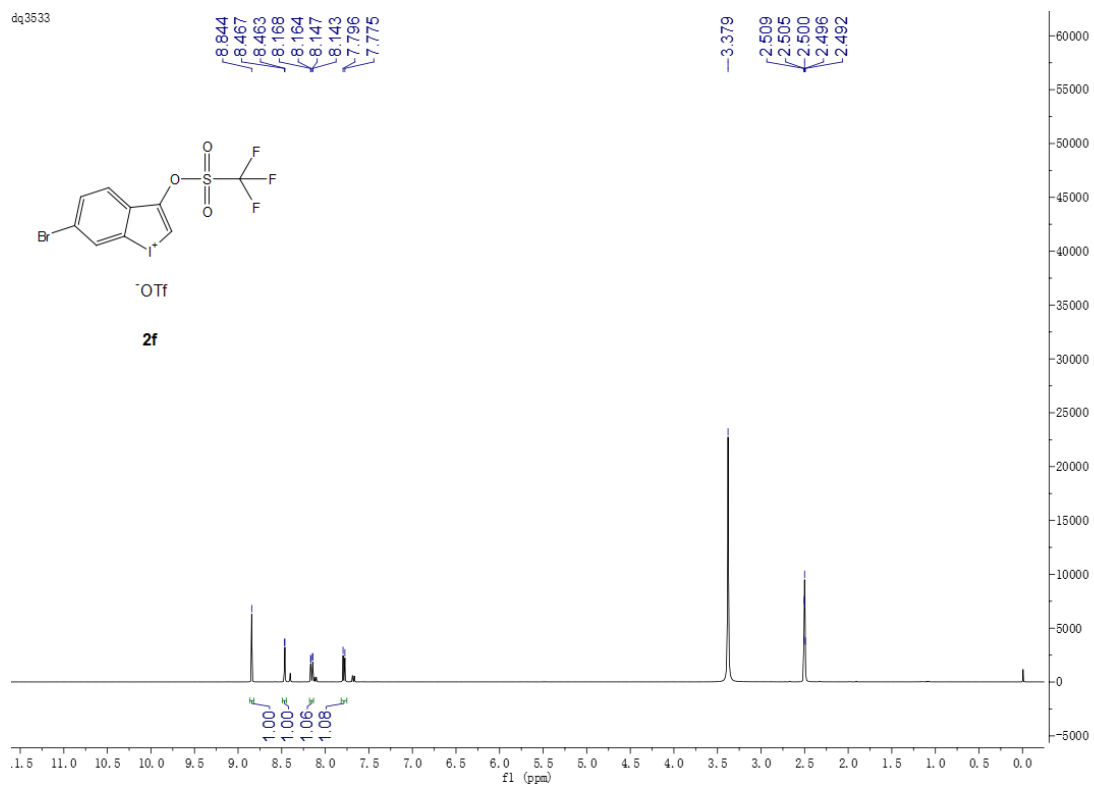
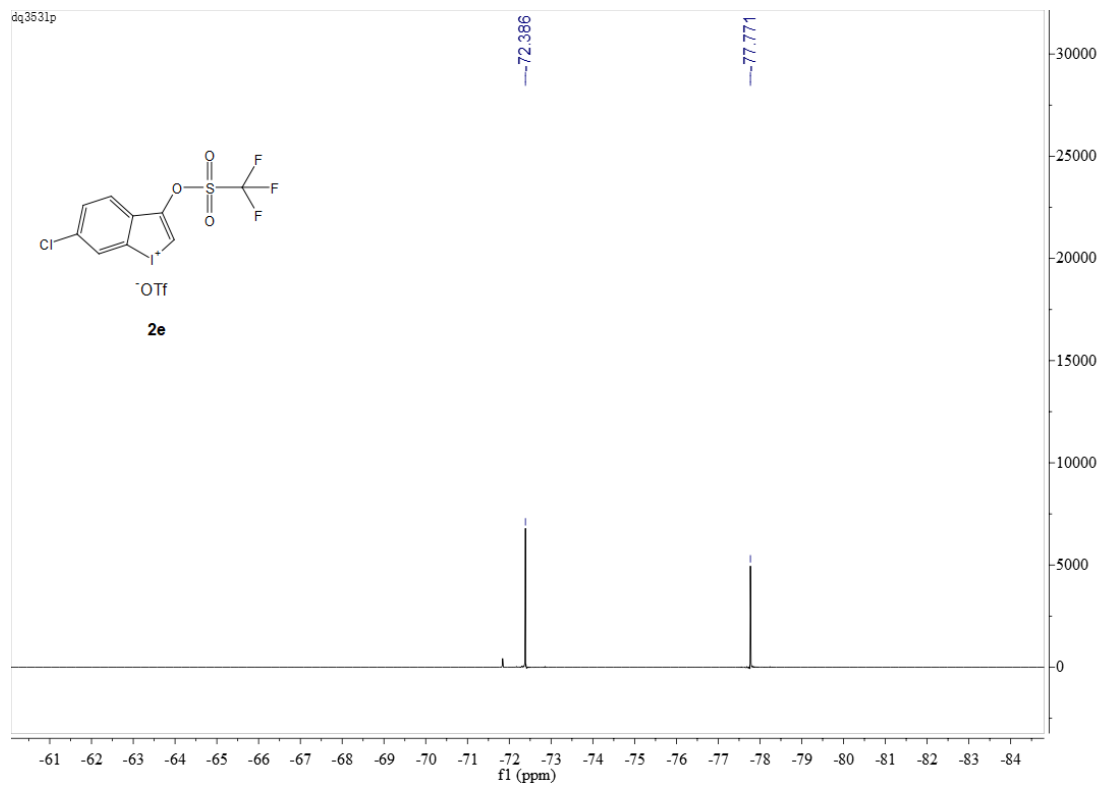
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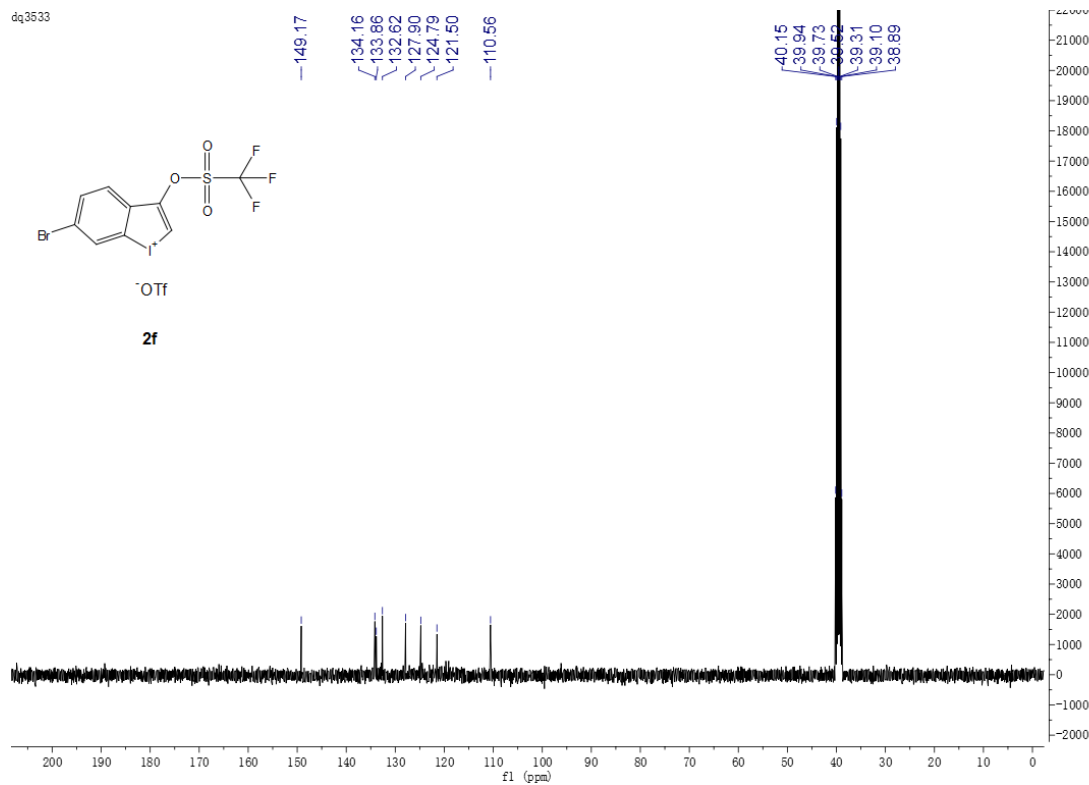
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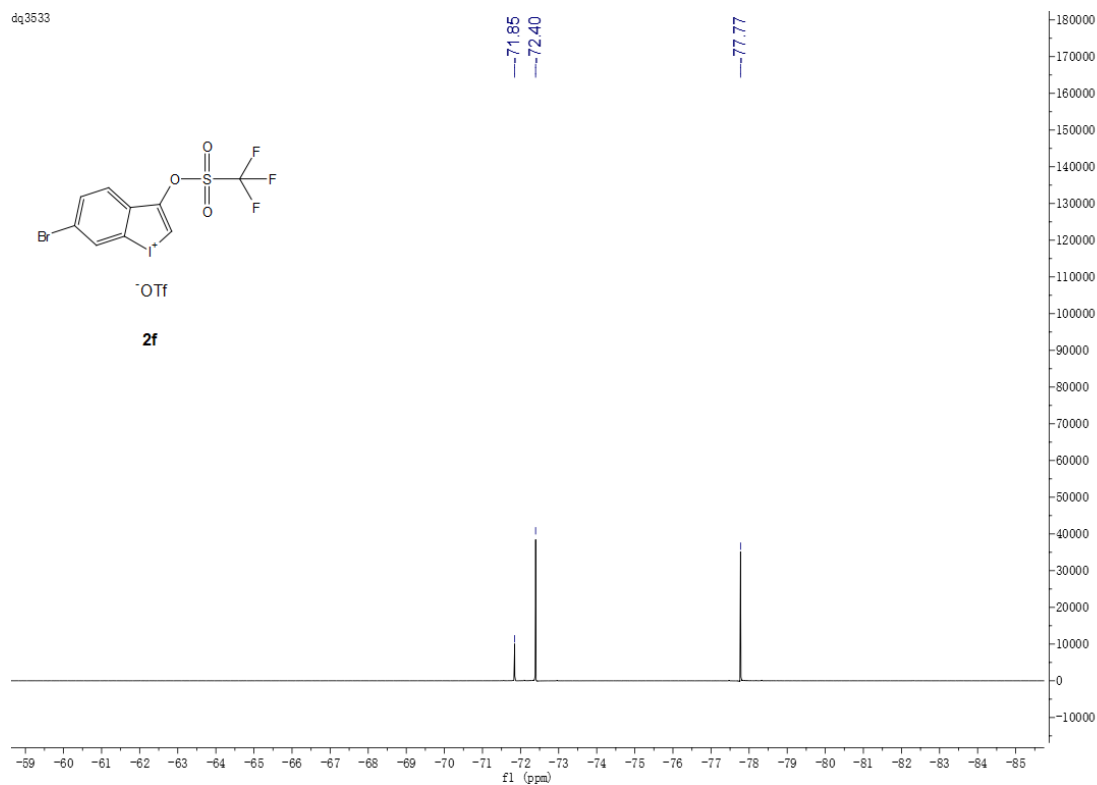


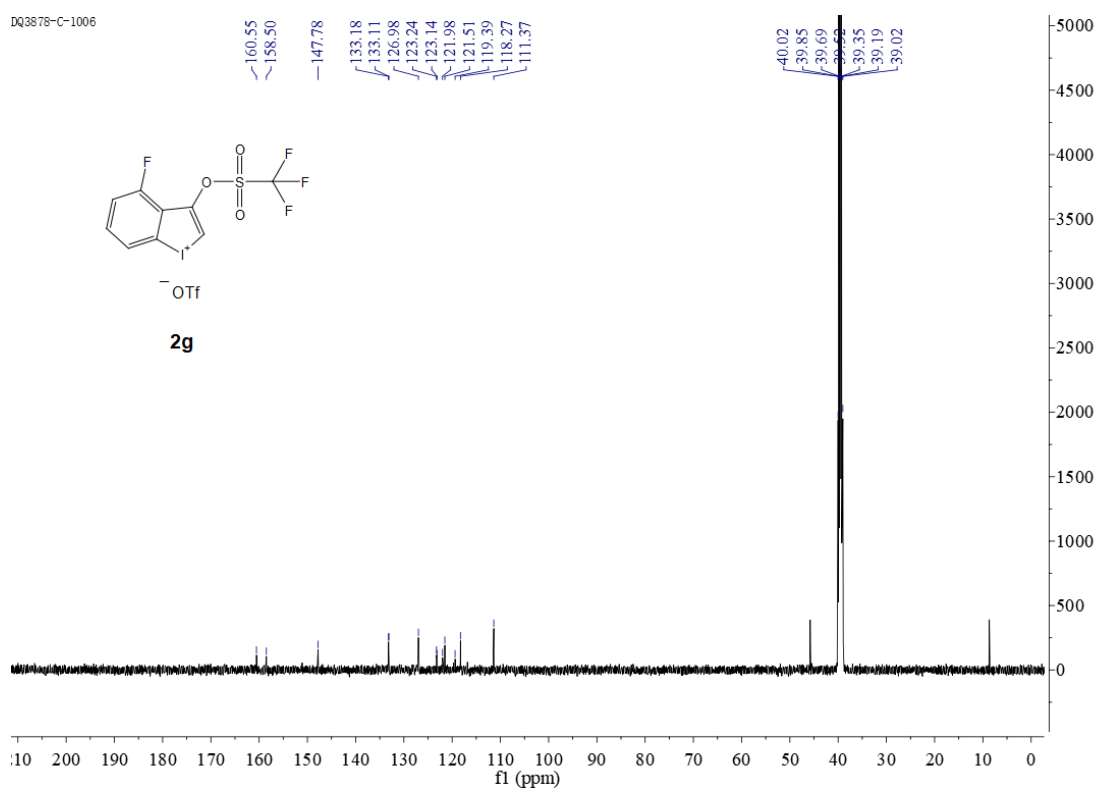
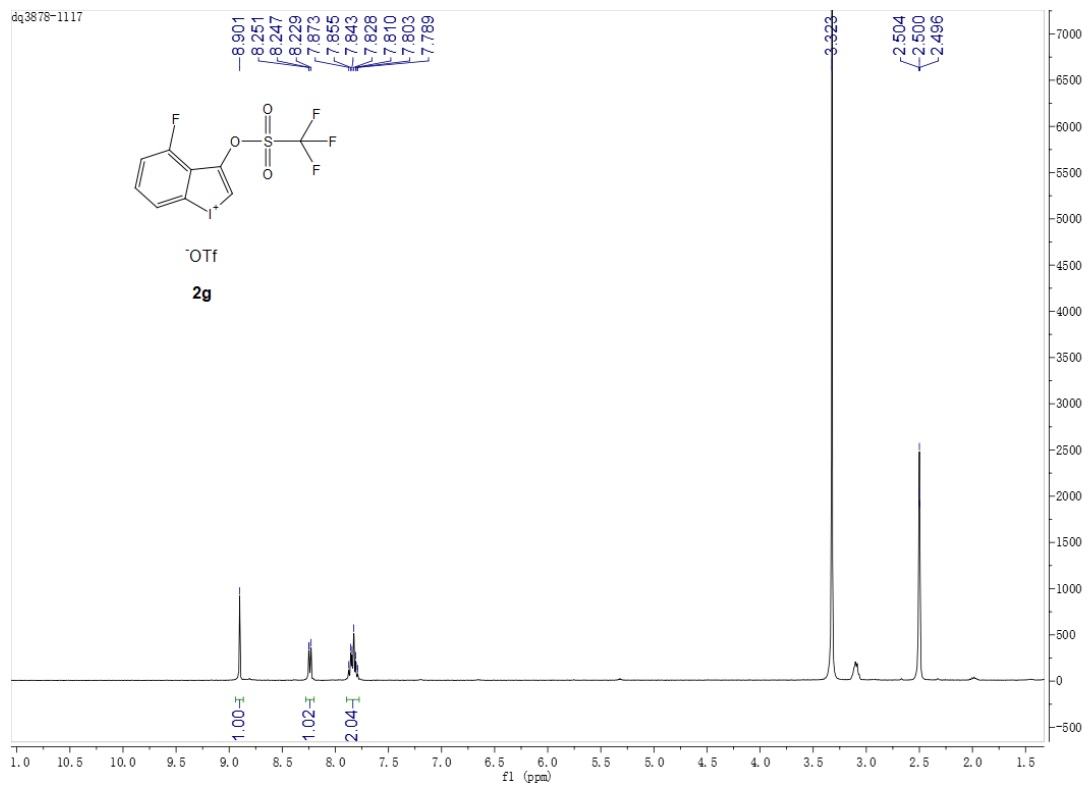


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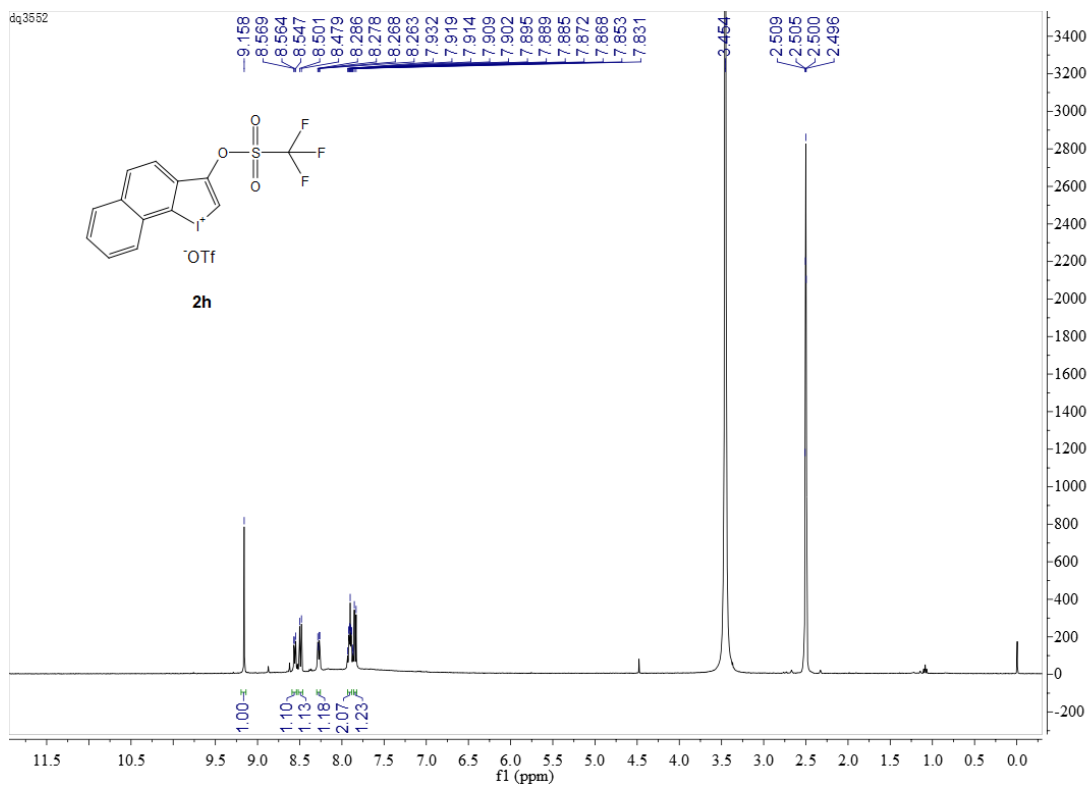
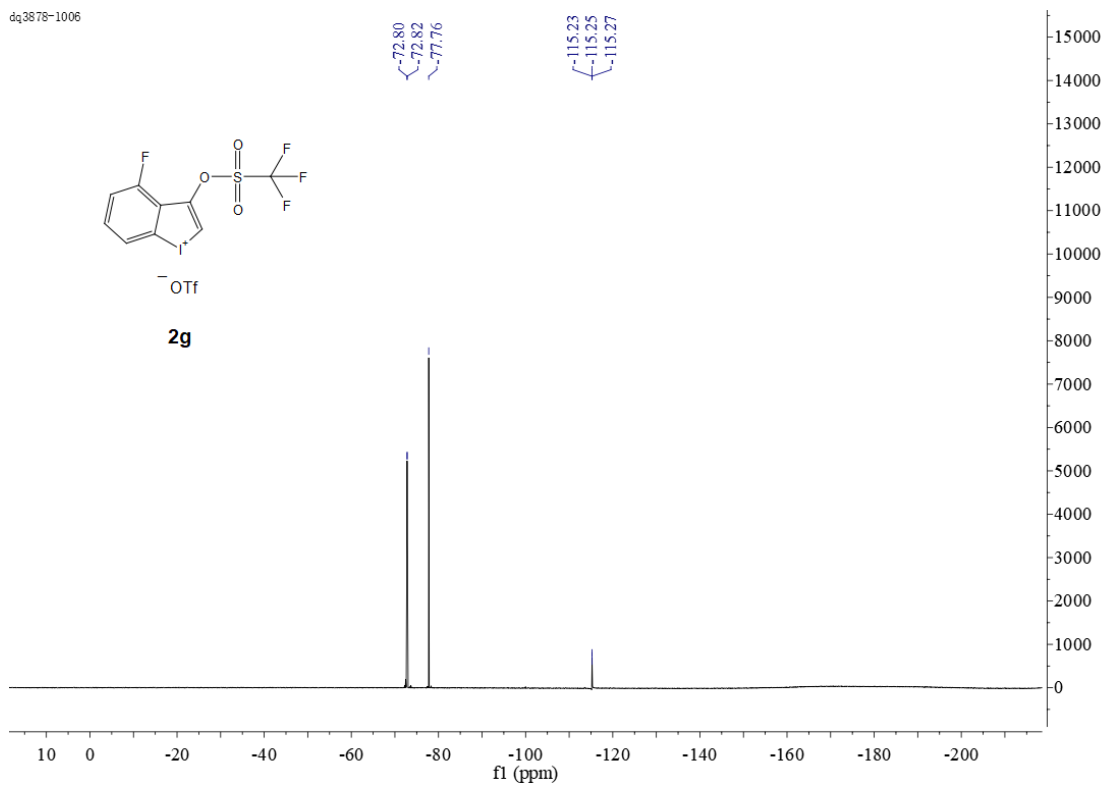


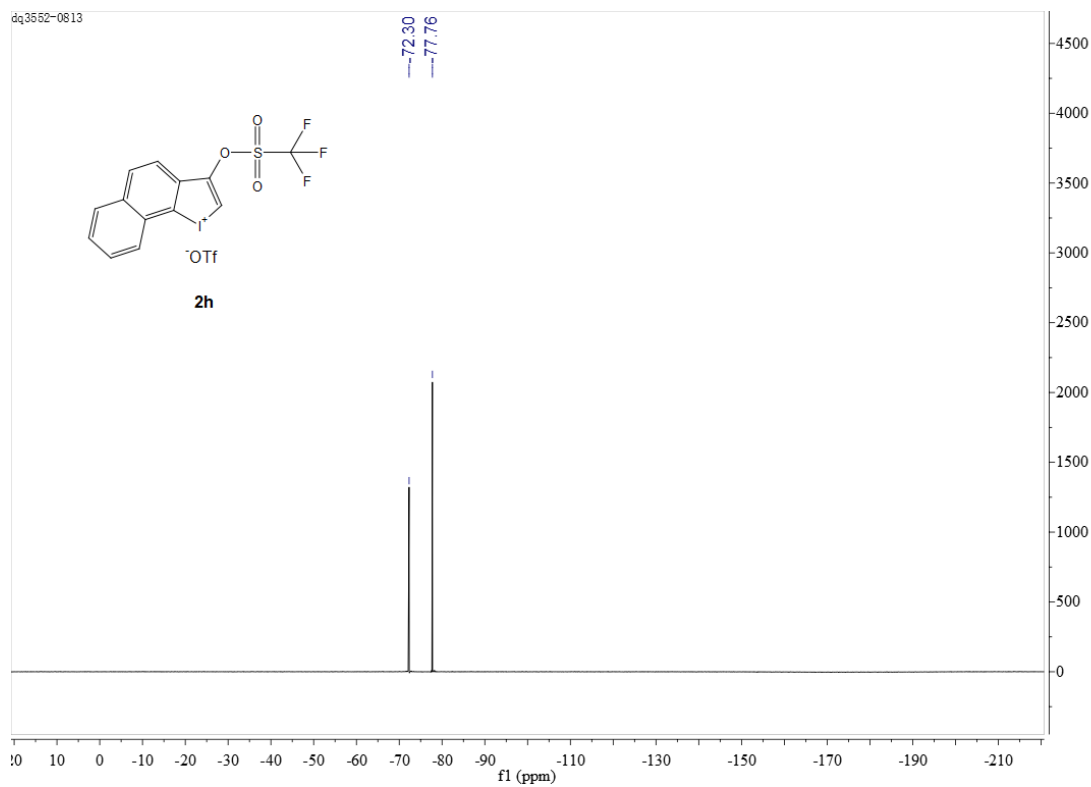
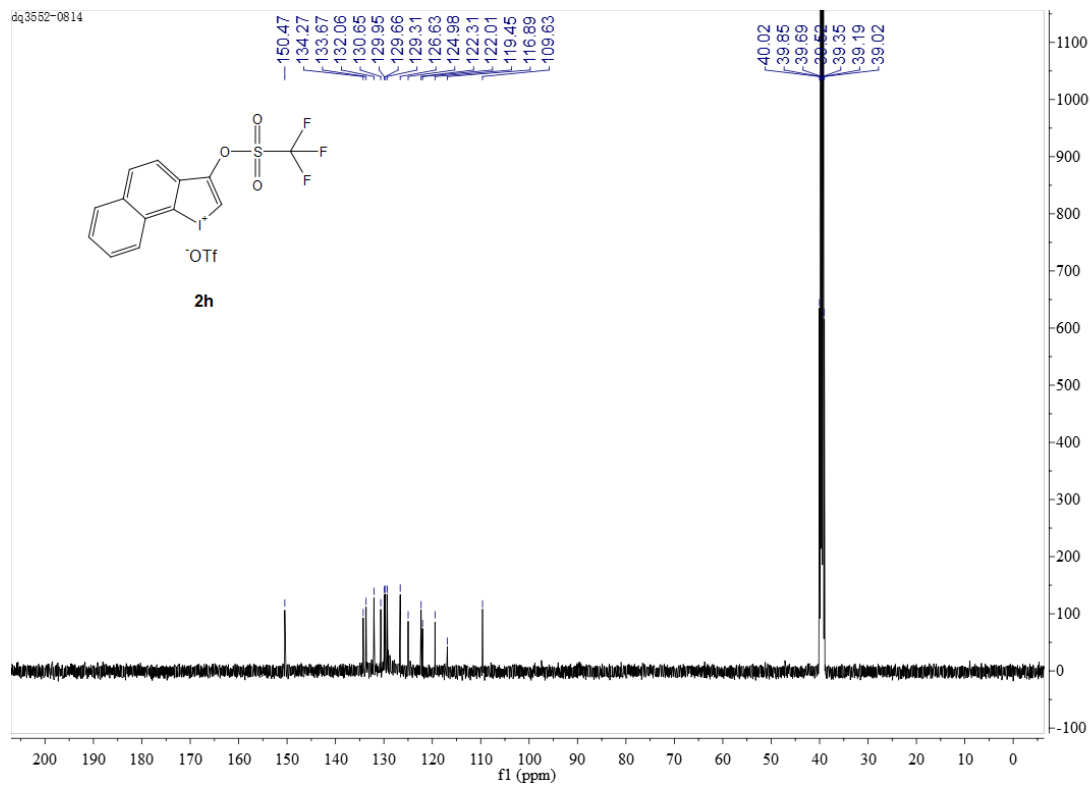
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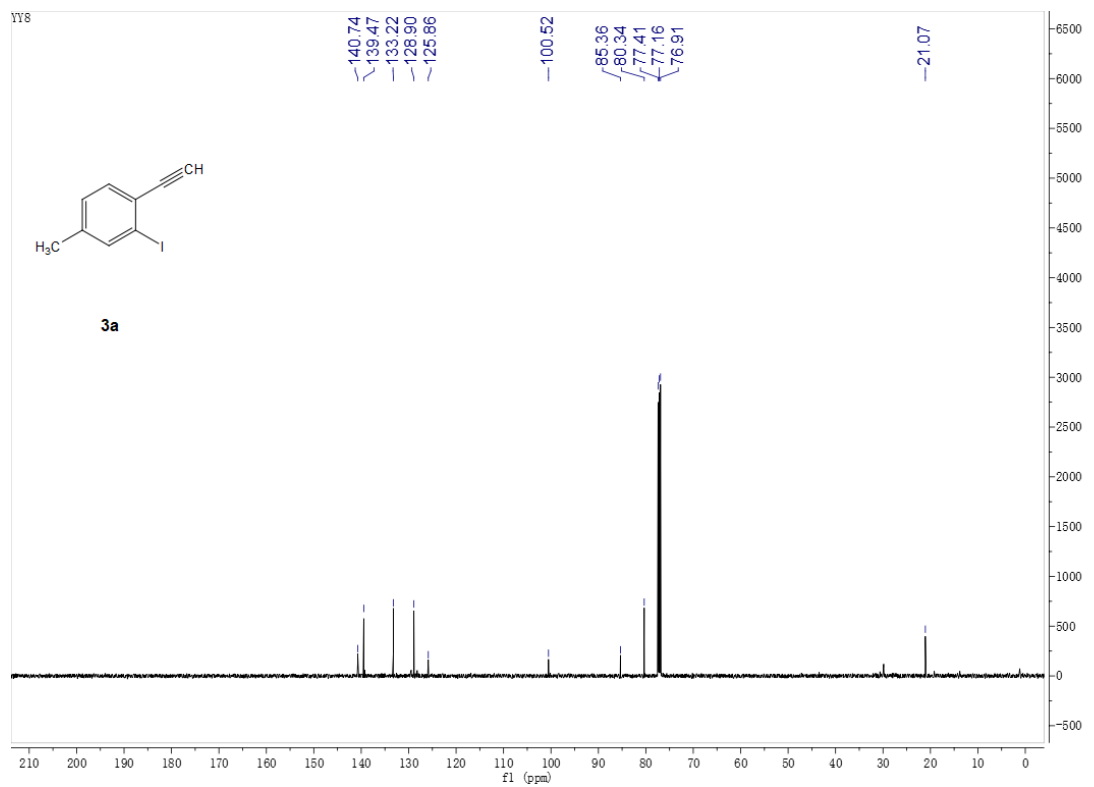
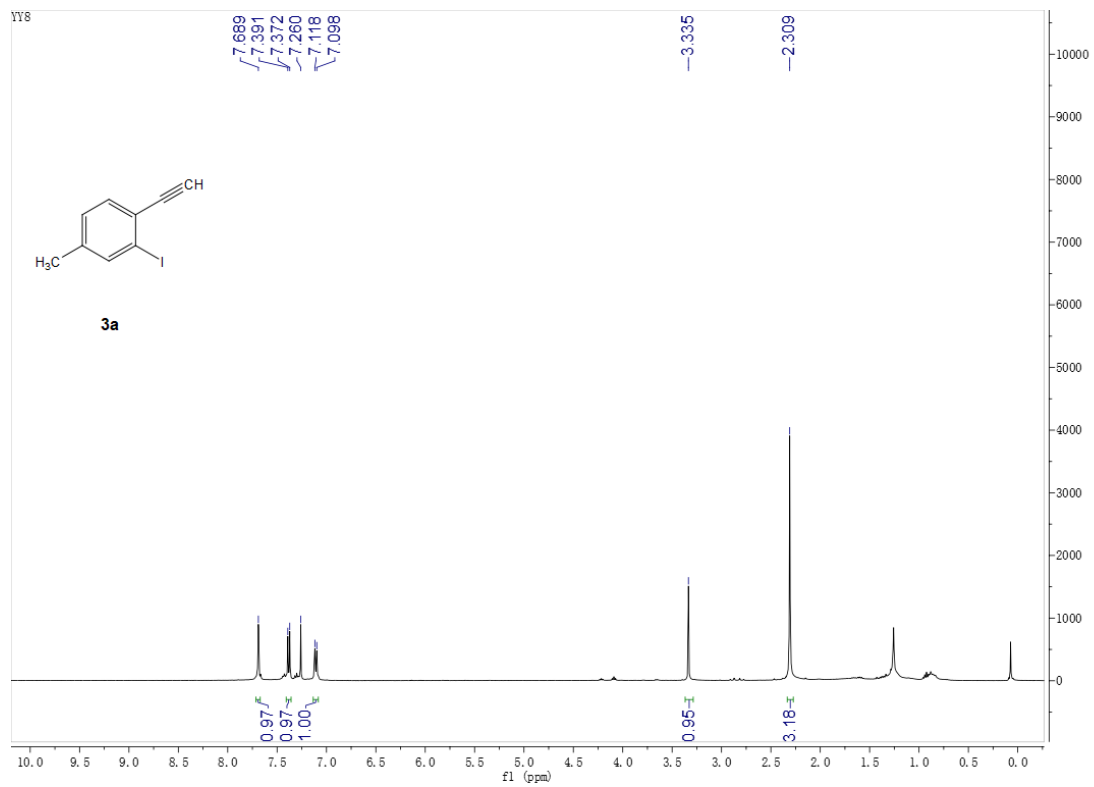




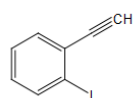
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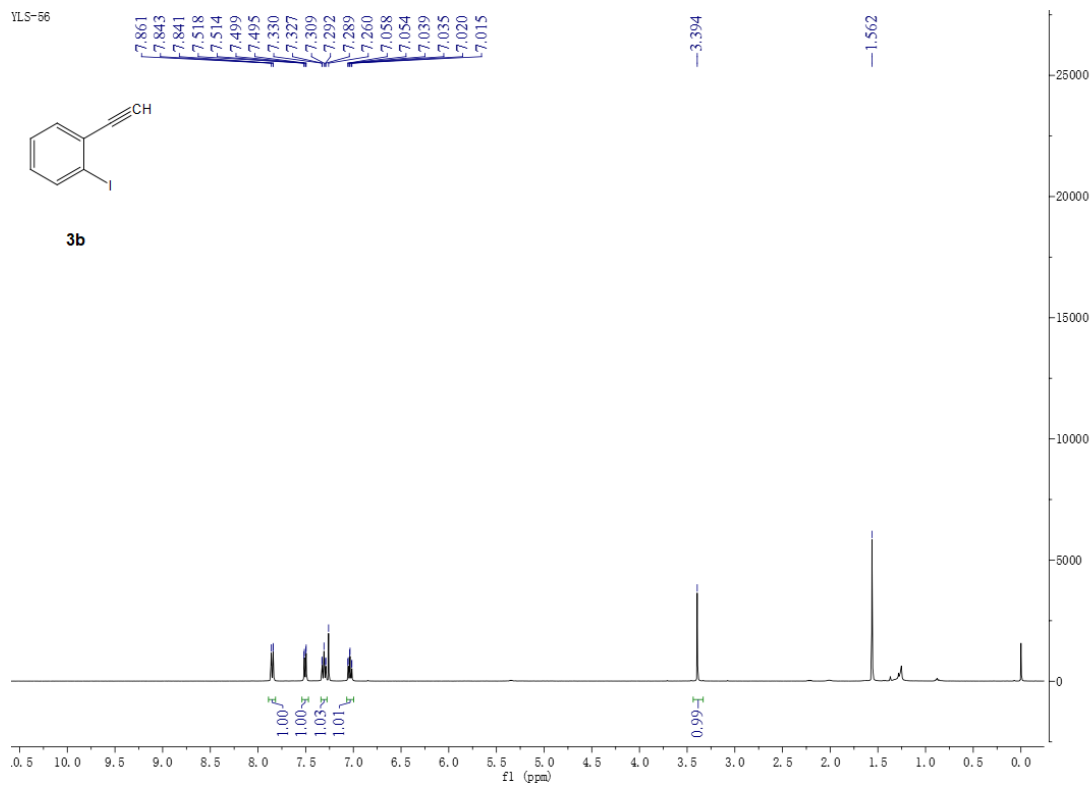




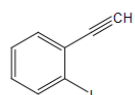
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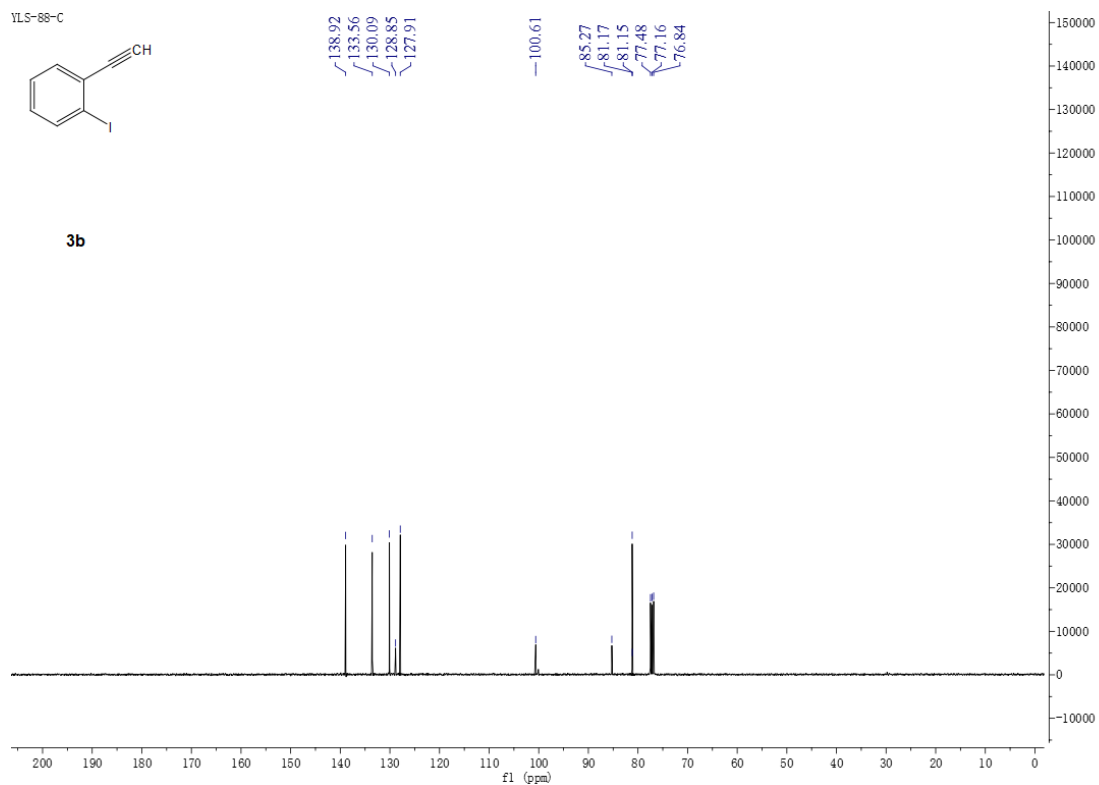
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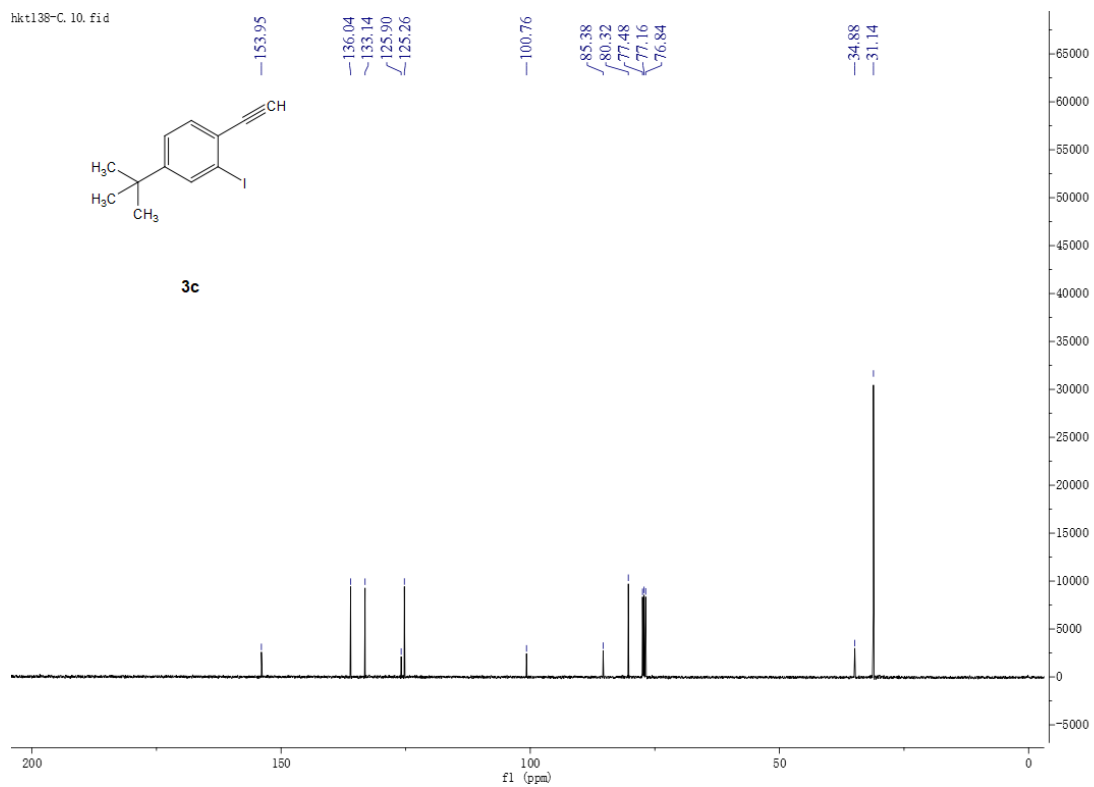
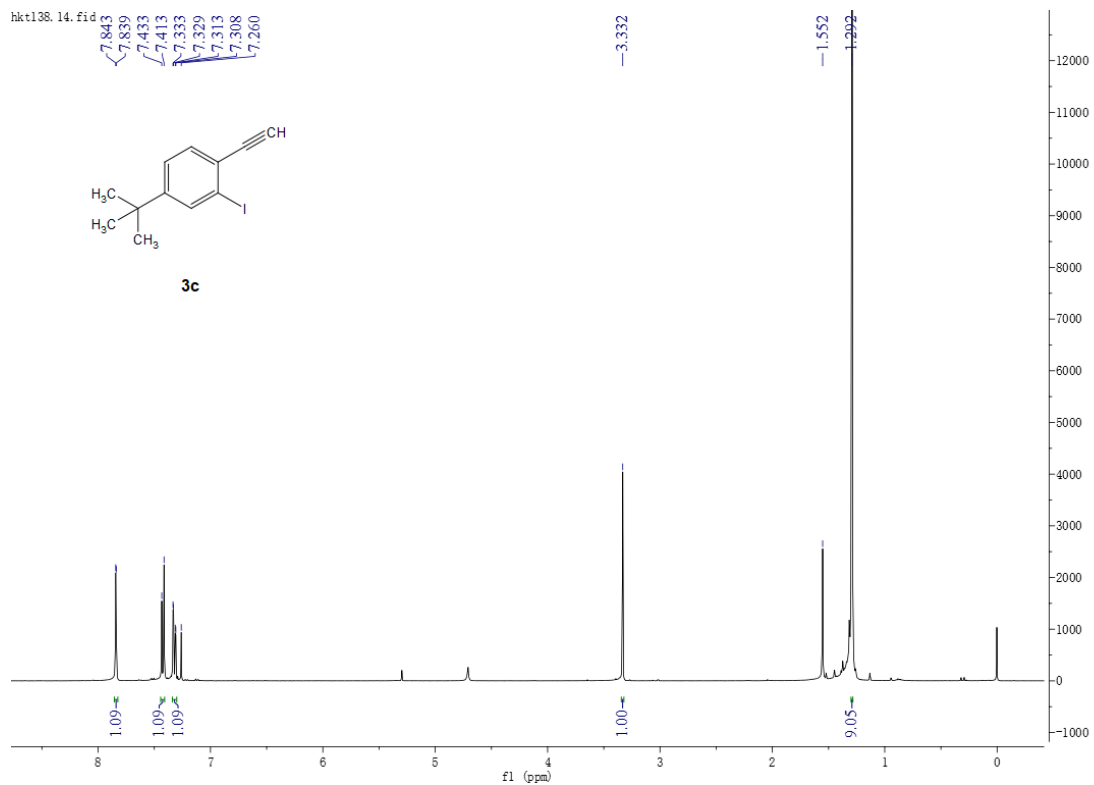


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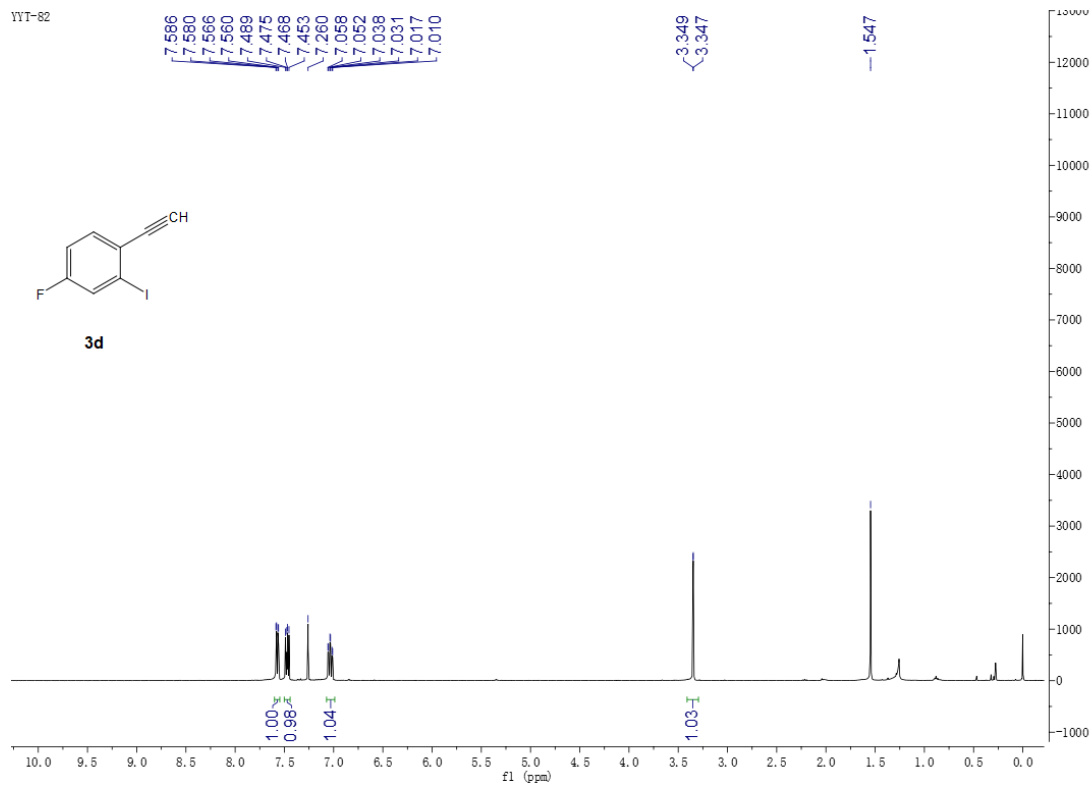


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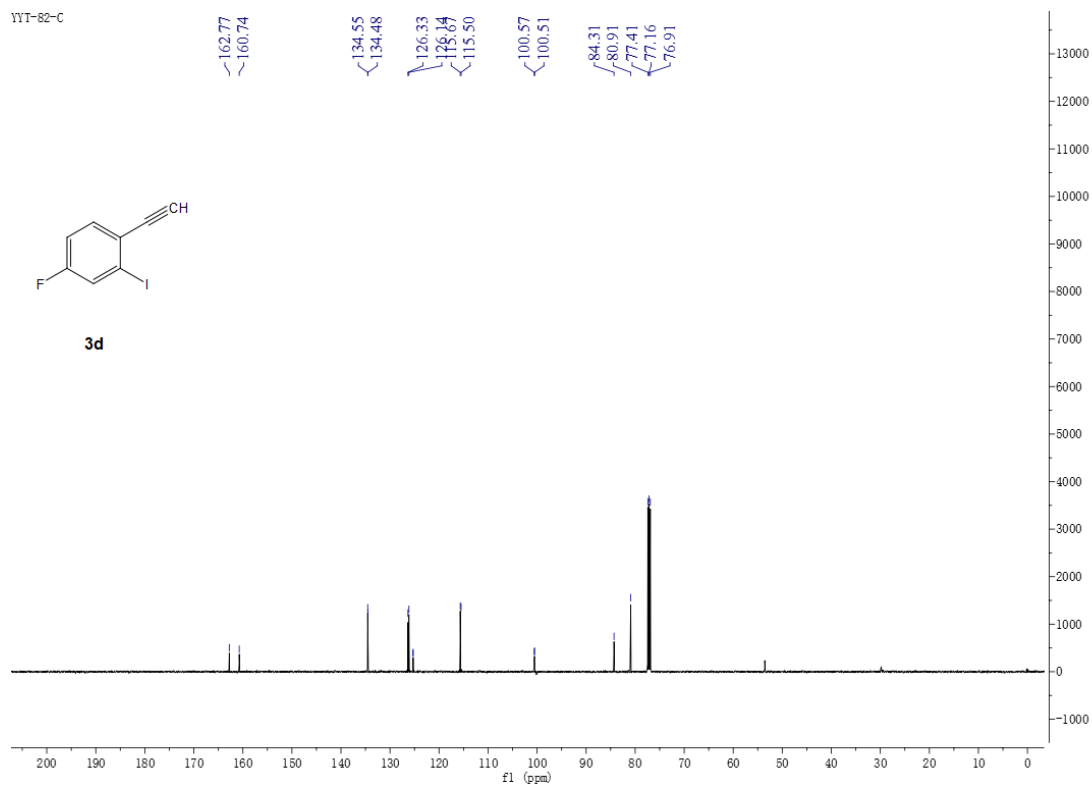




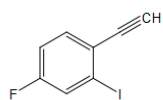
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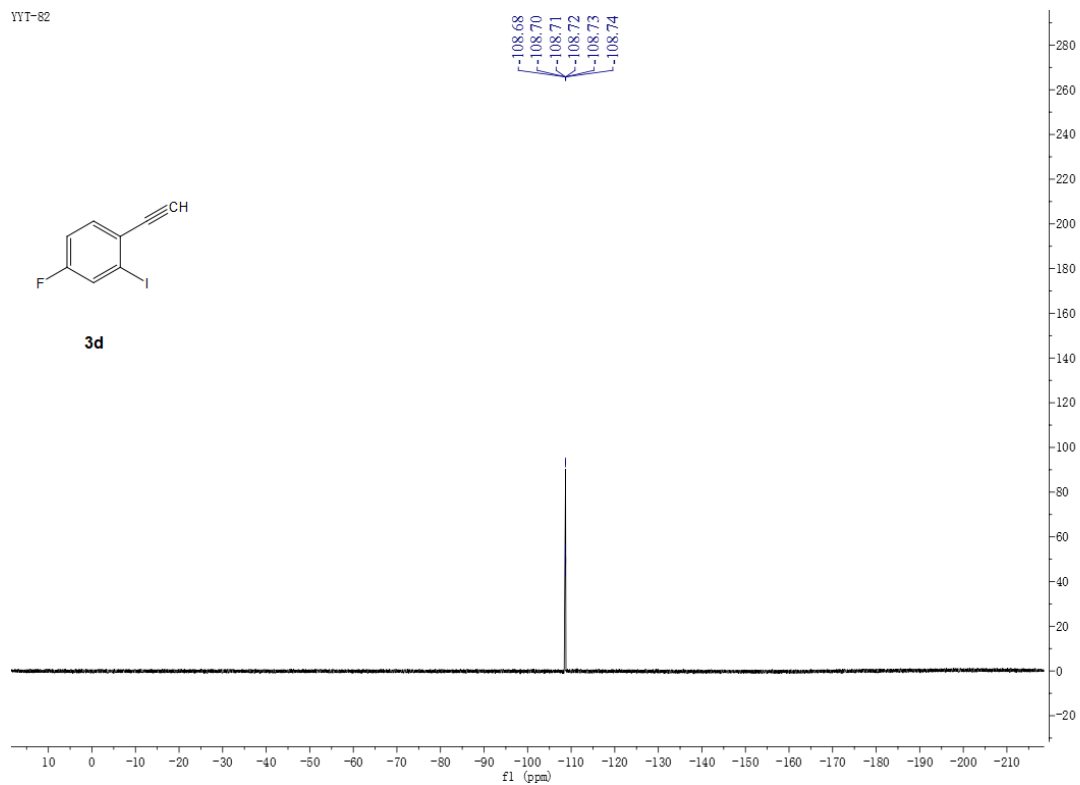
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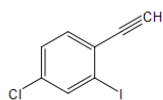
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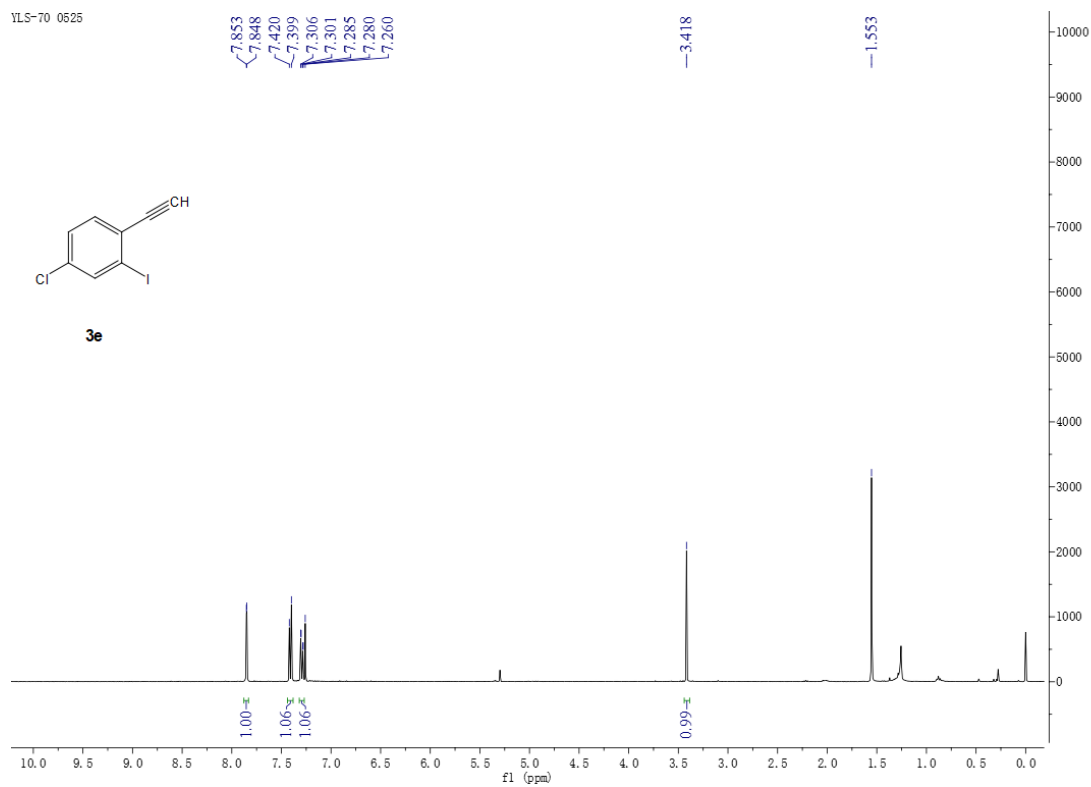
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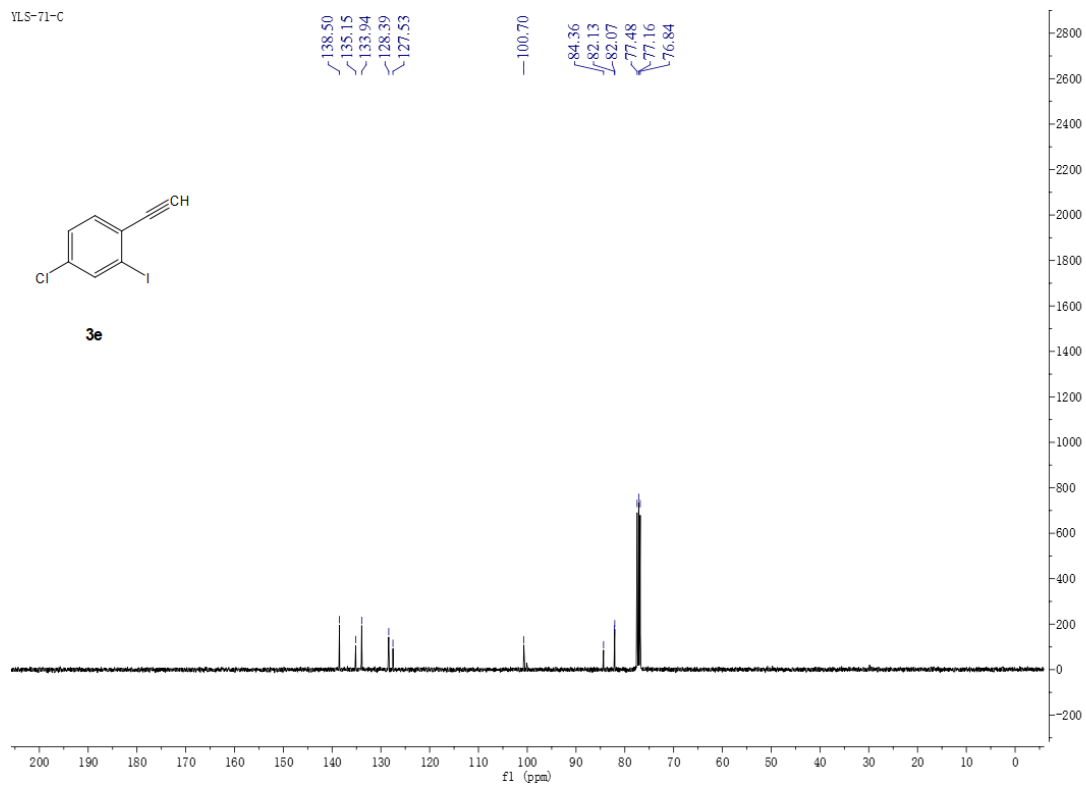
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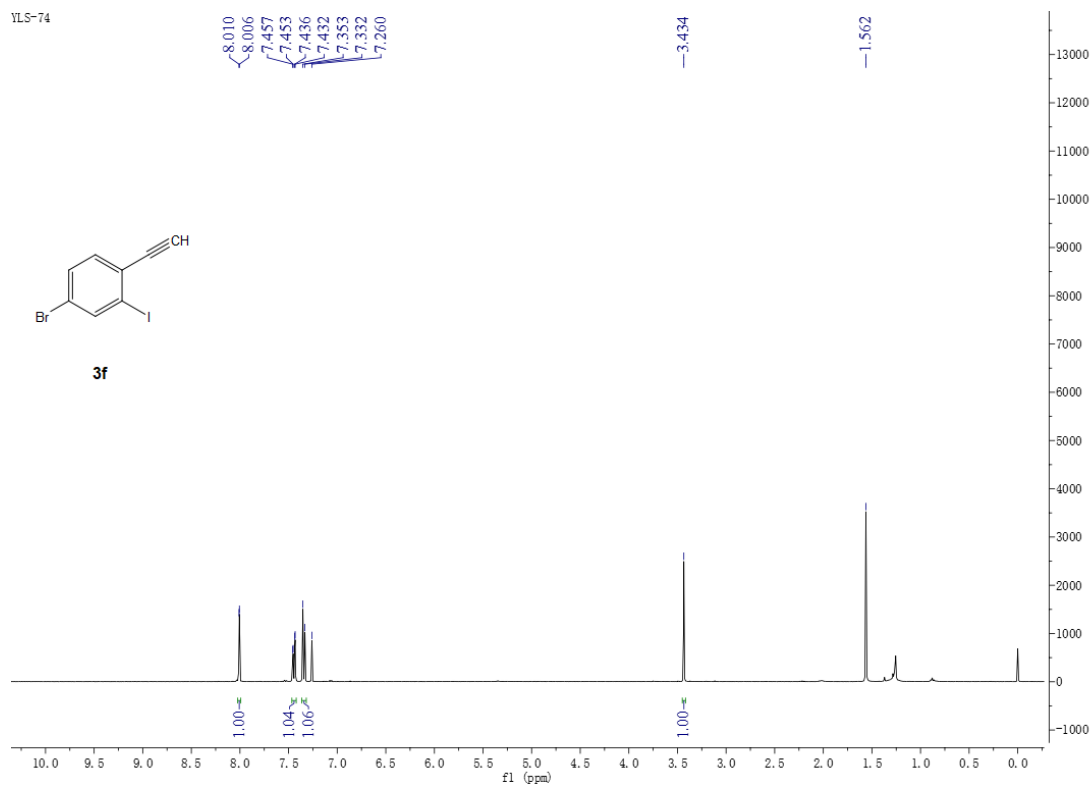
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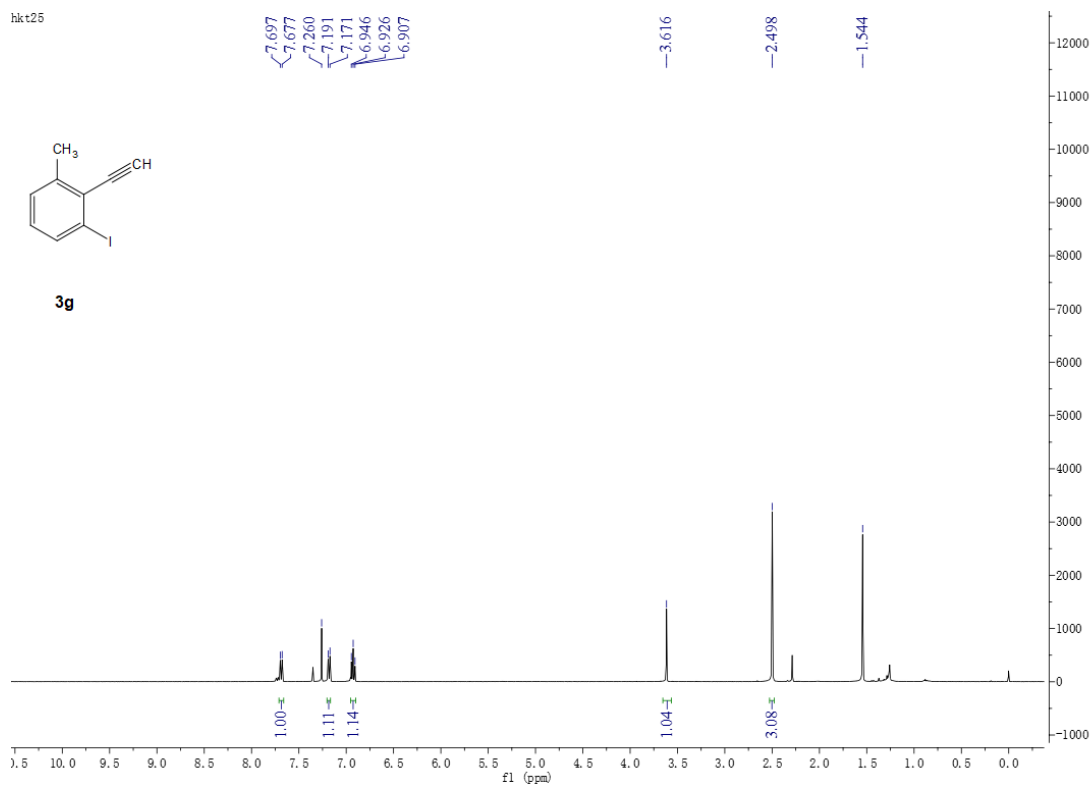
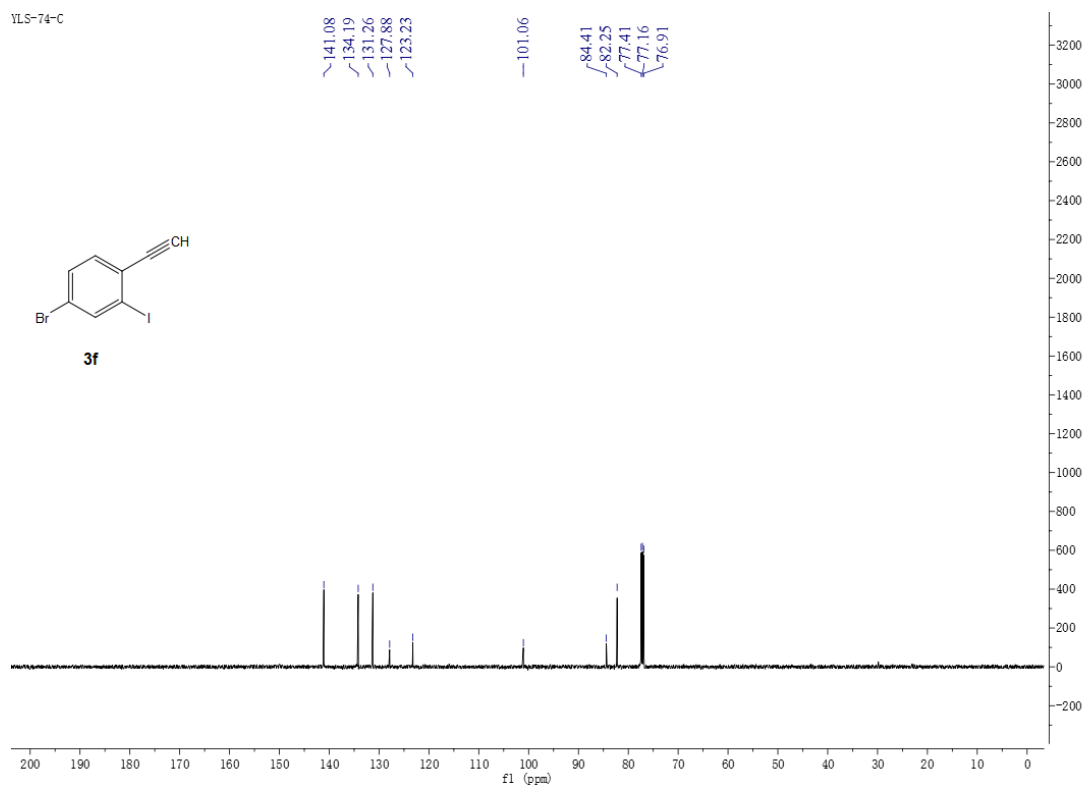
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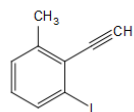
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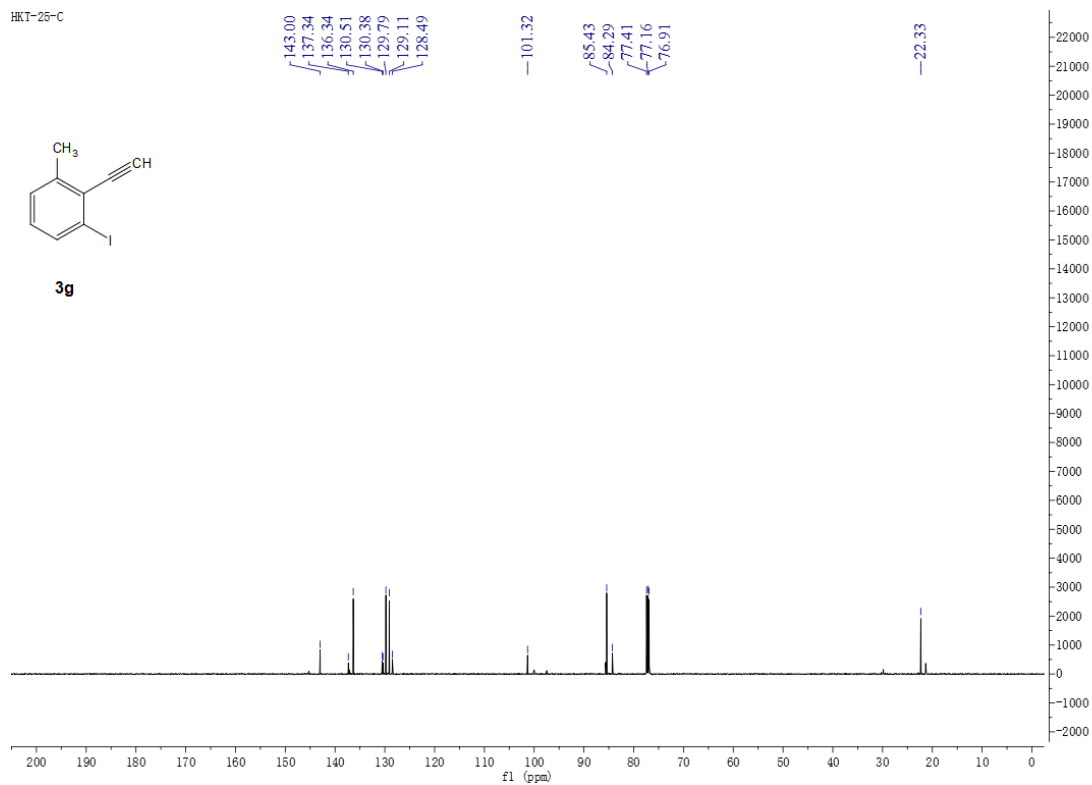
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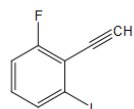
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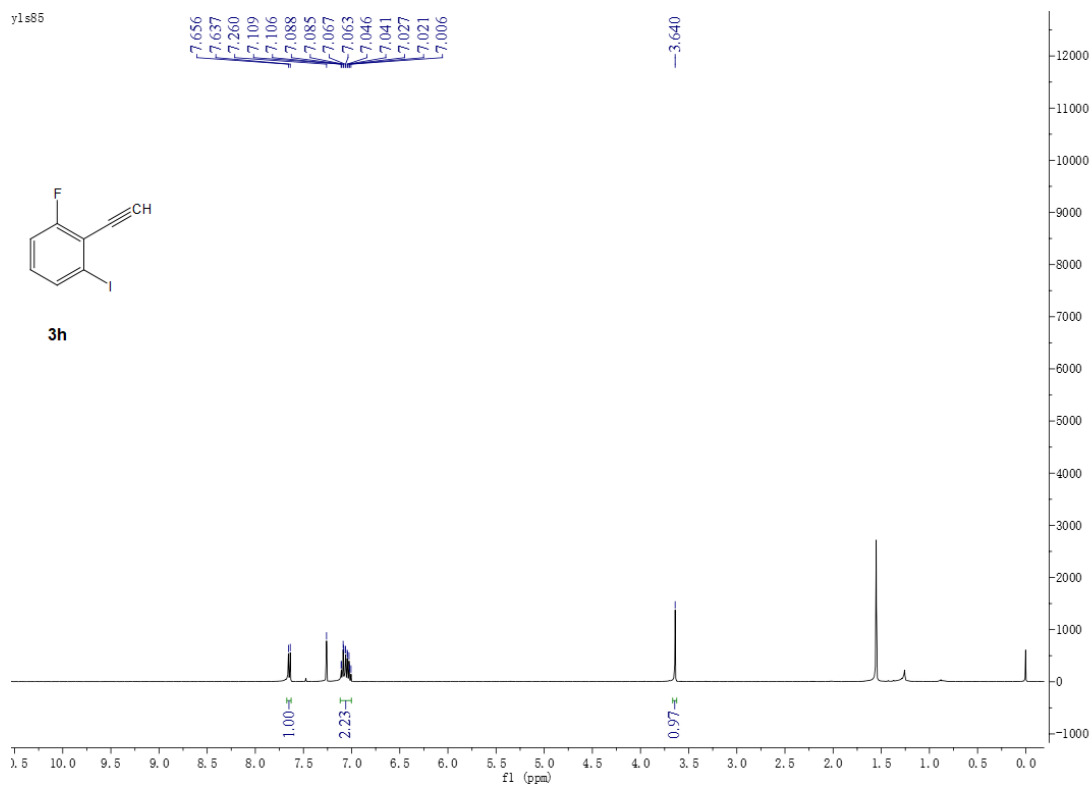
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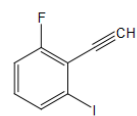
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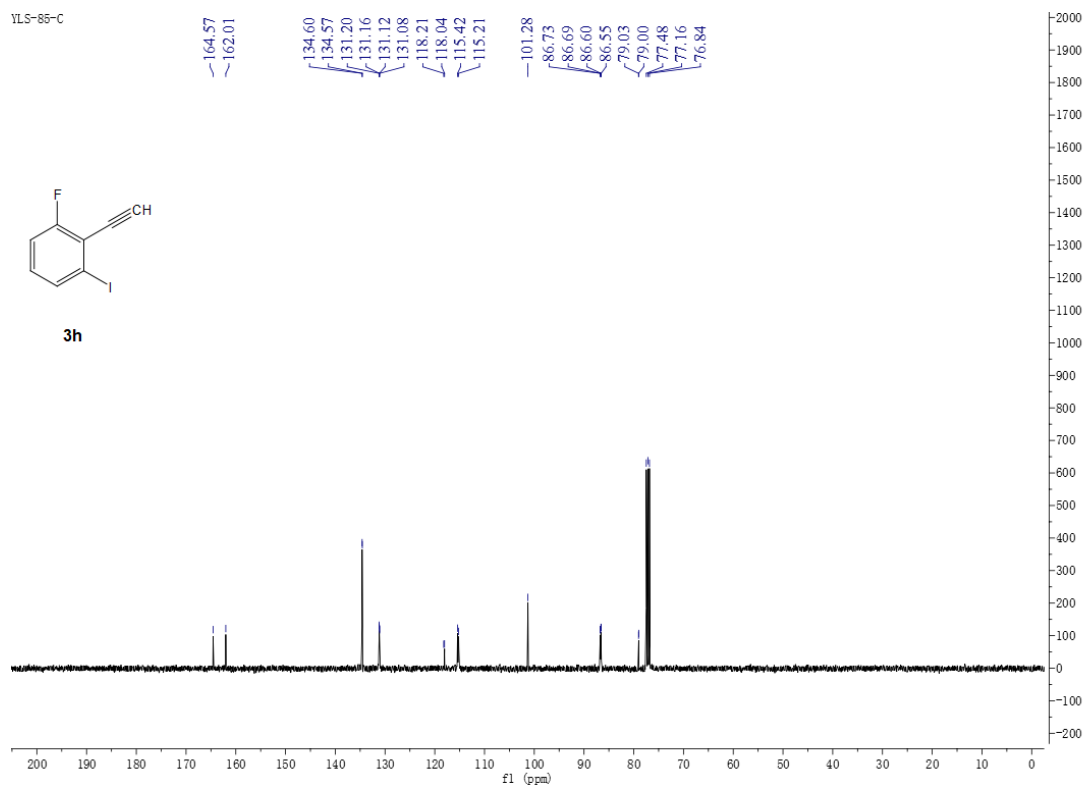
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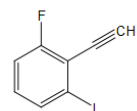
YLS-85-C



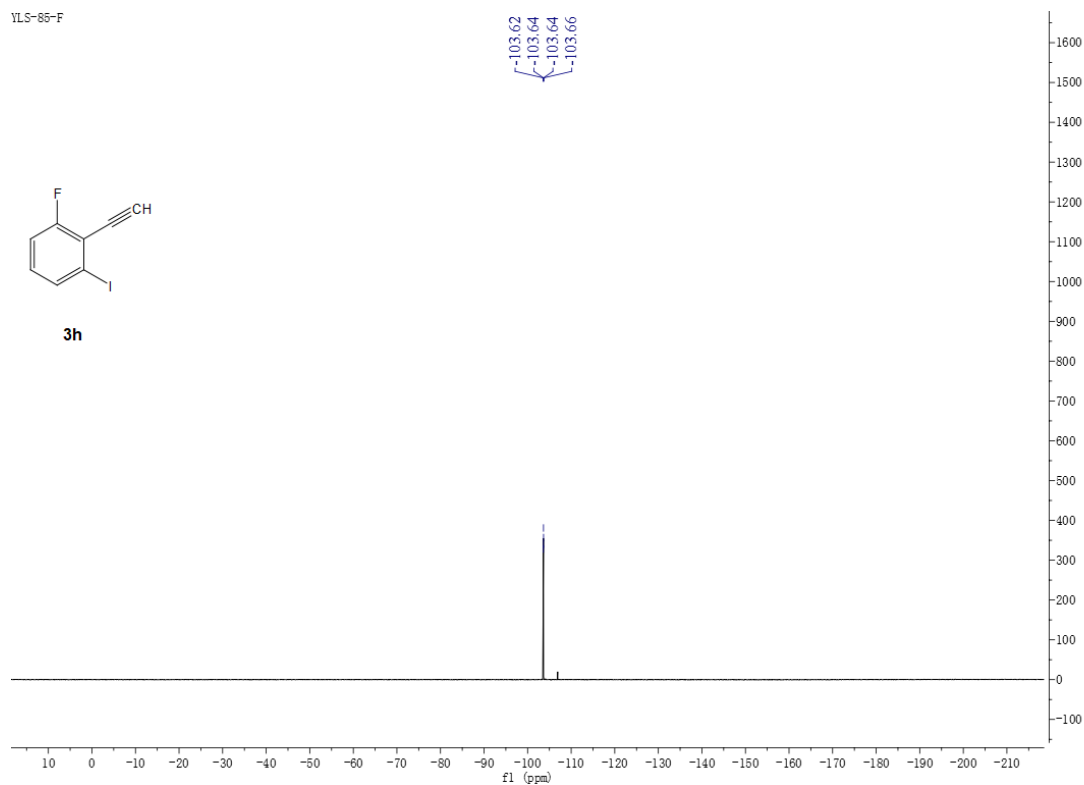
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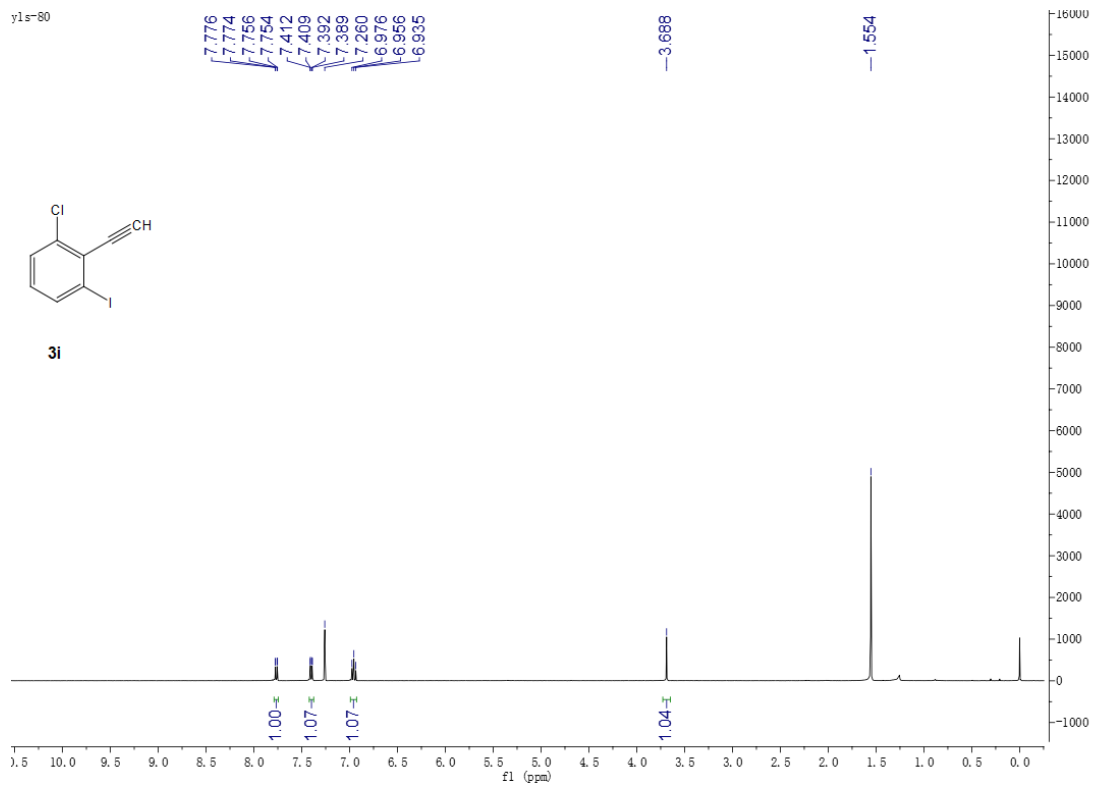
YLS-85-F



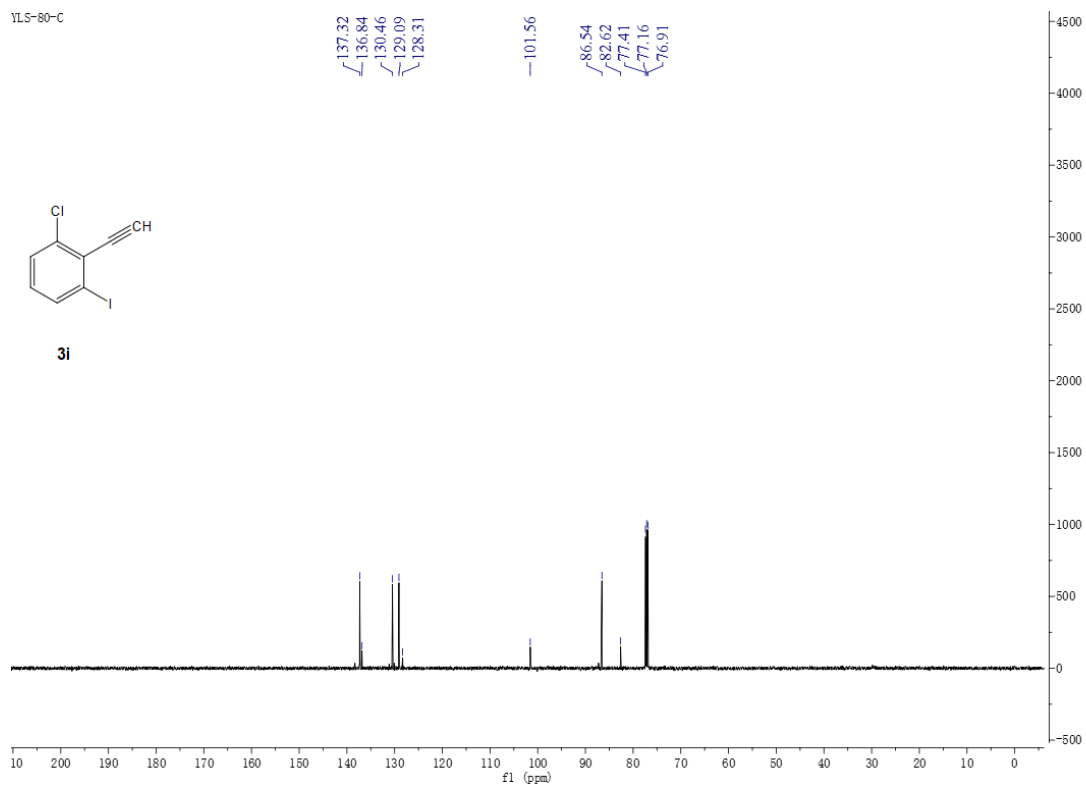
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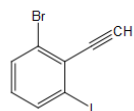
yls-80



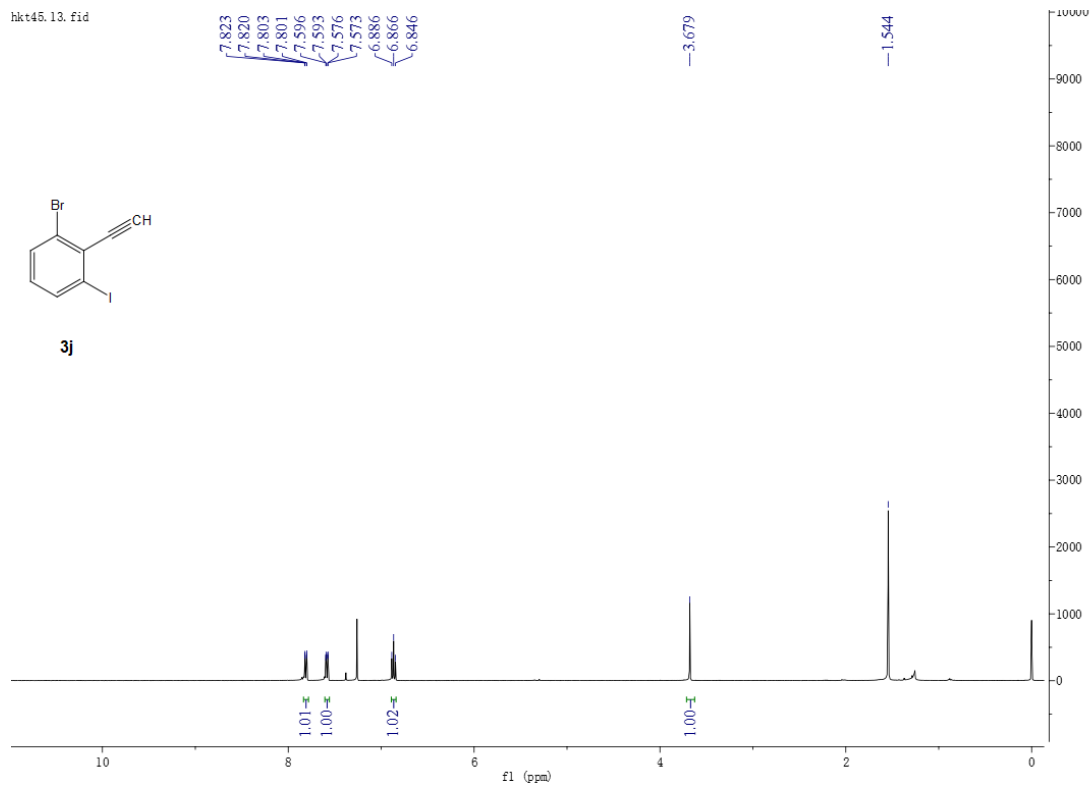
YLS-80-C



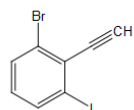
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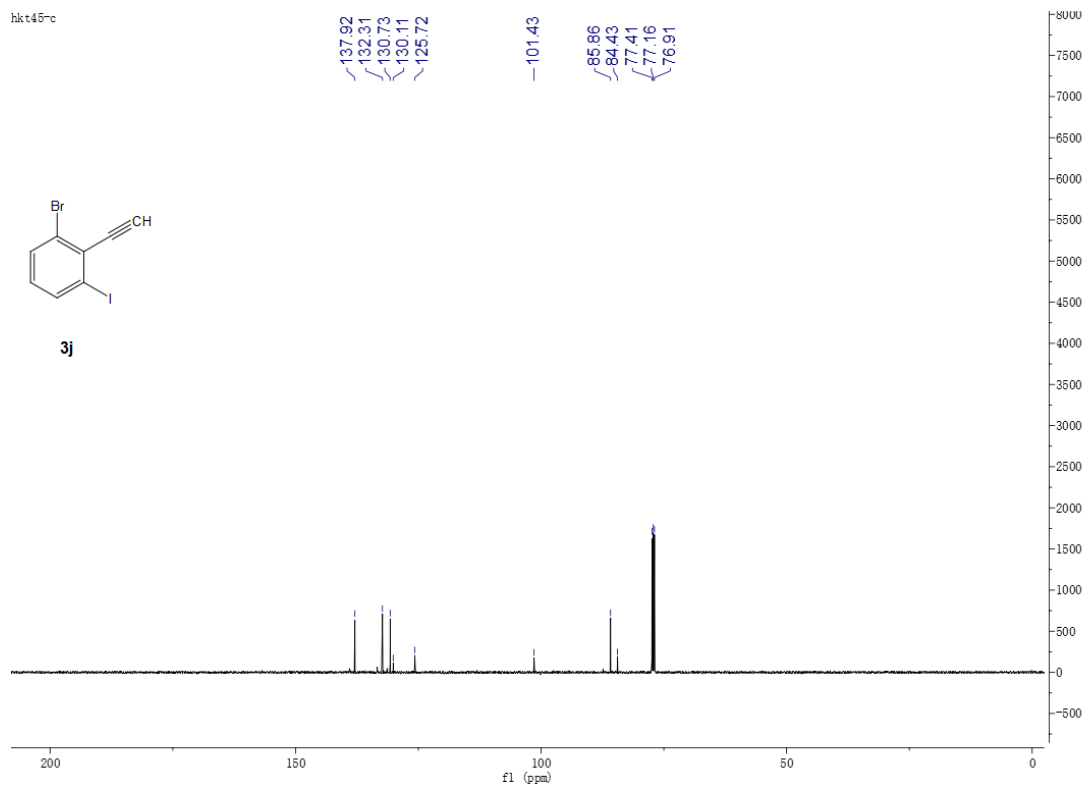
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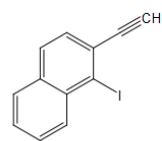
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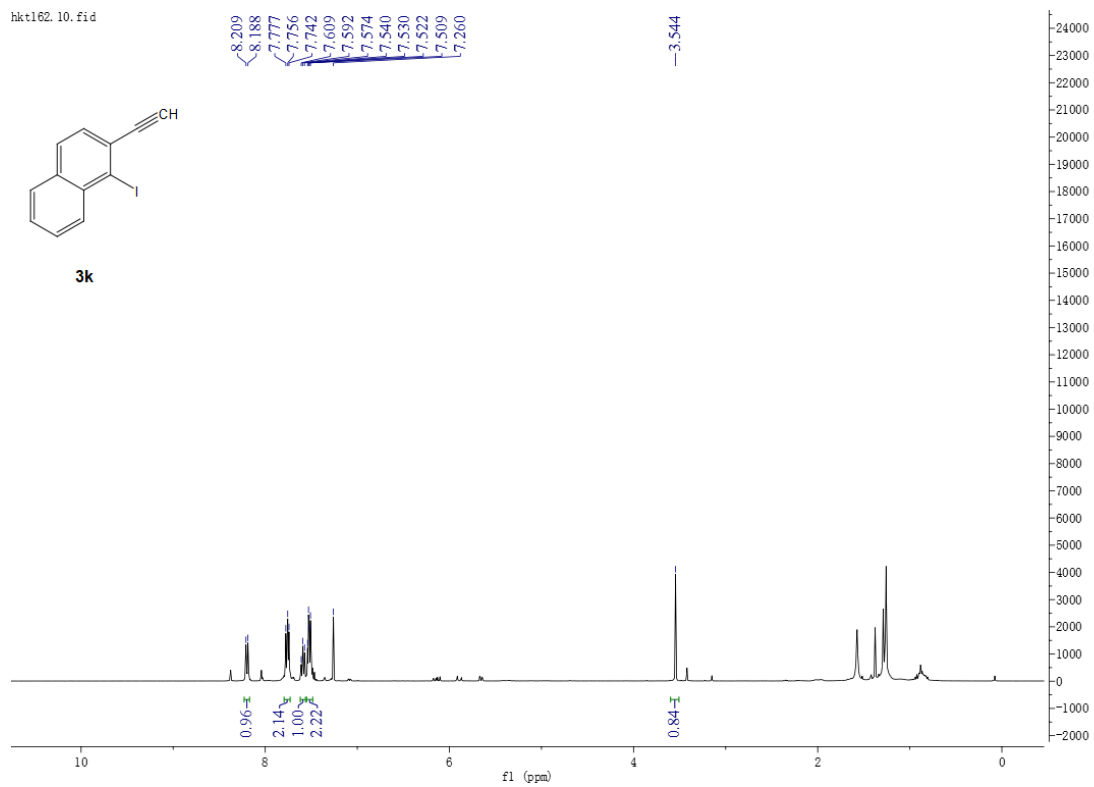
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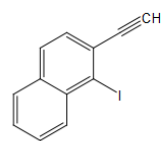
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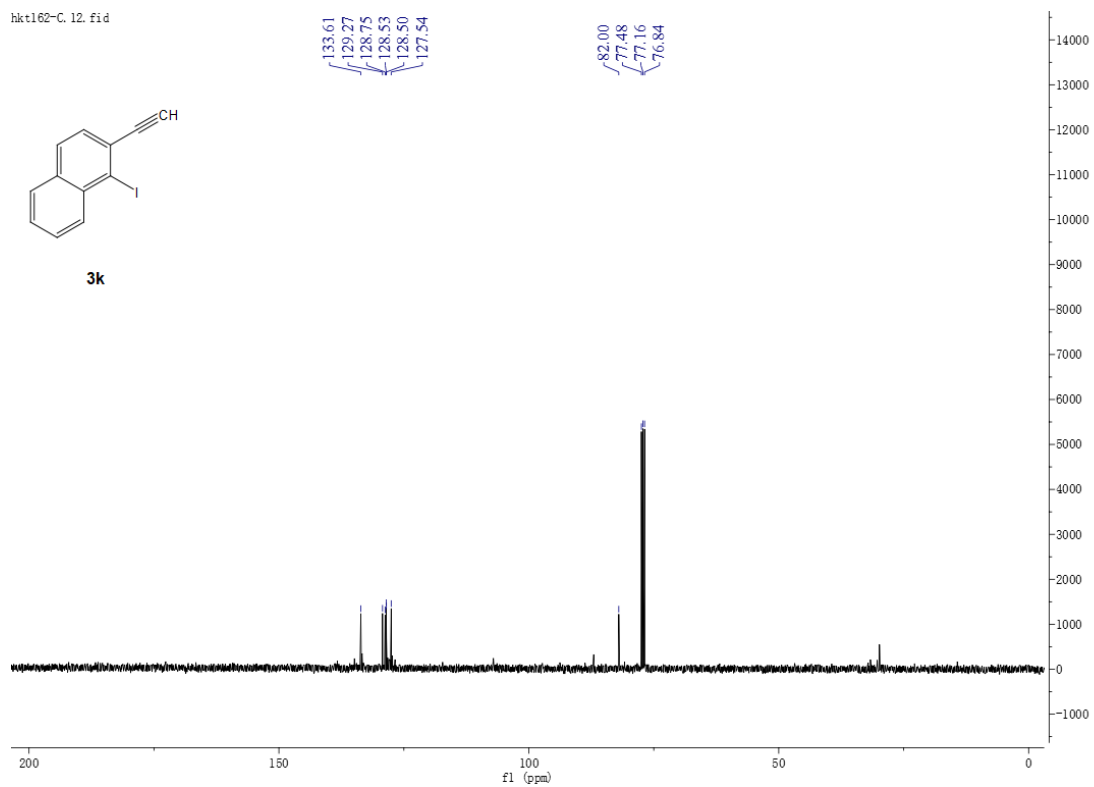
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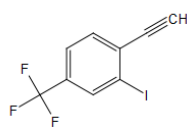
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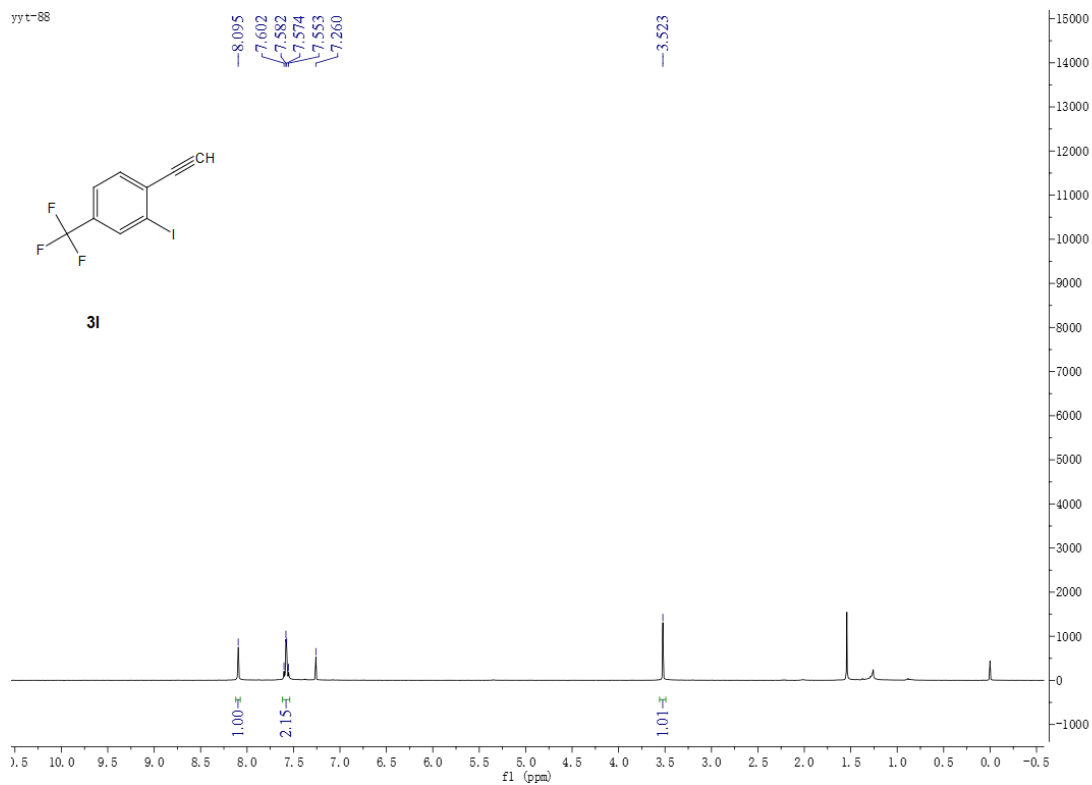
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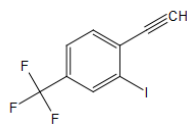
yyt-88



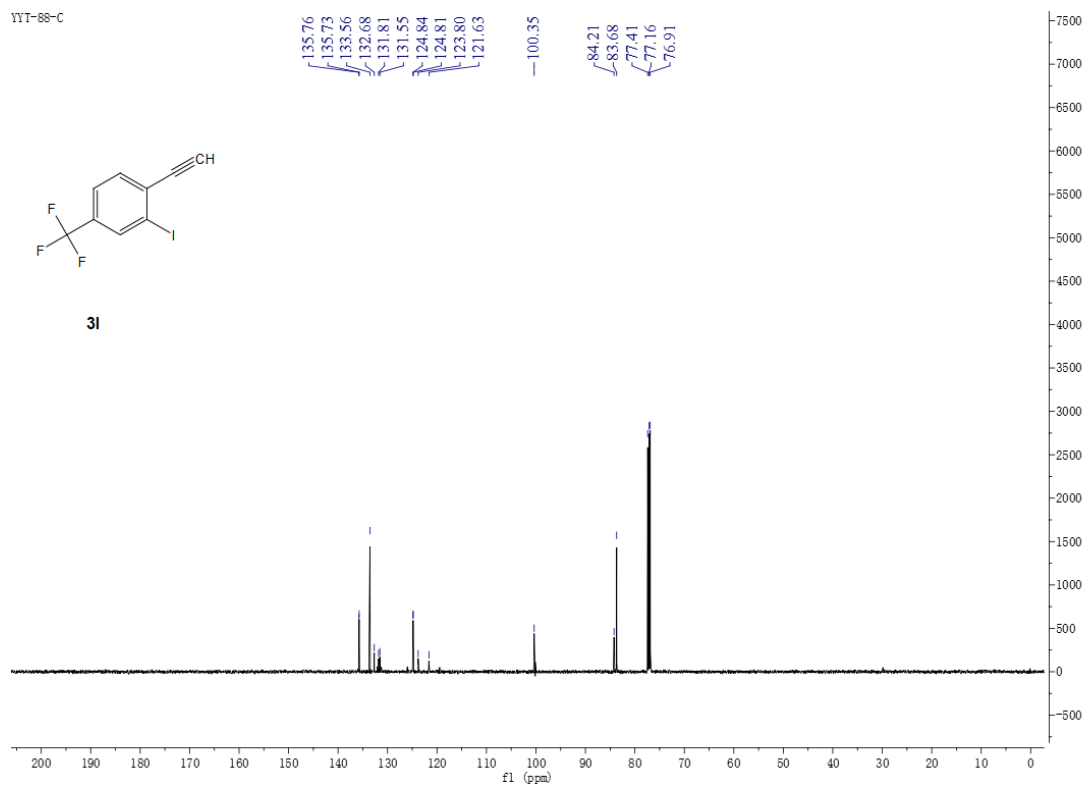
31



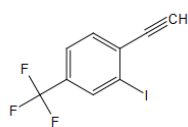
YYT-88-C



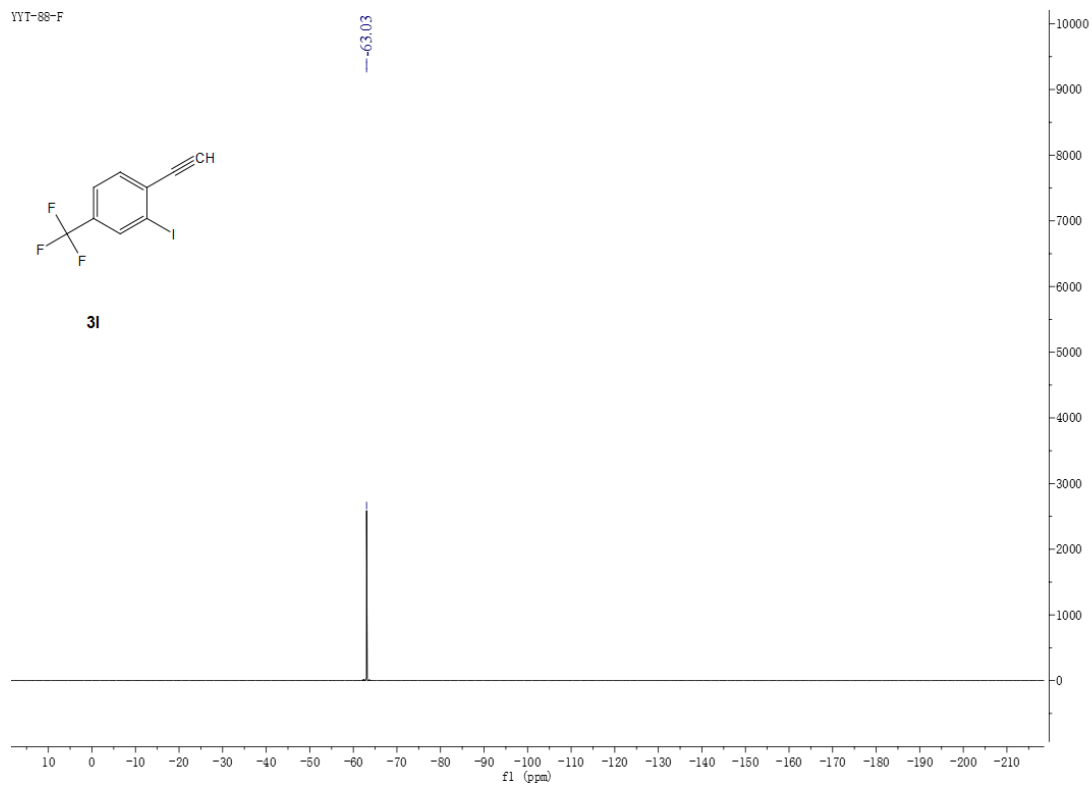
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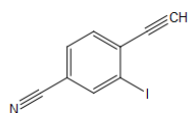
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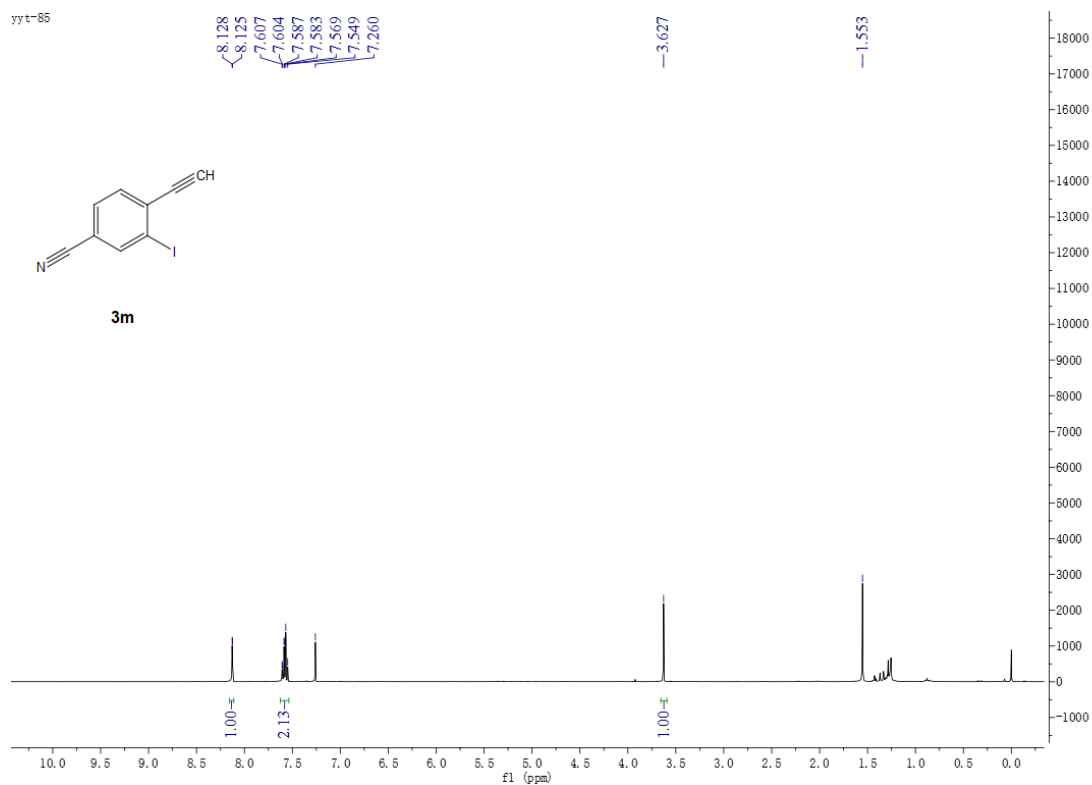
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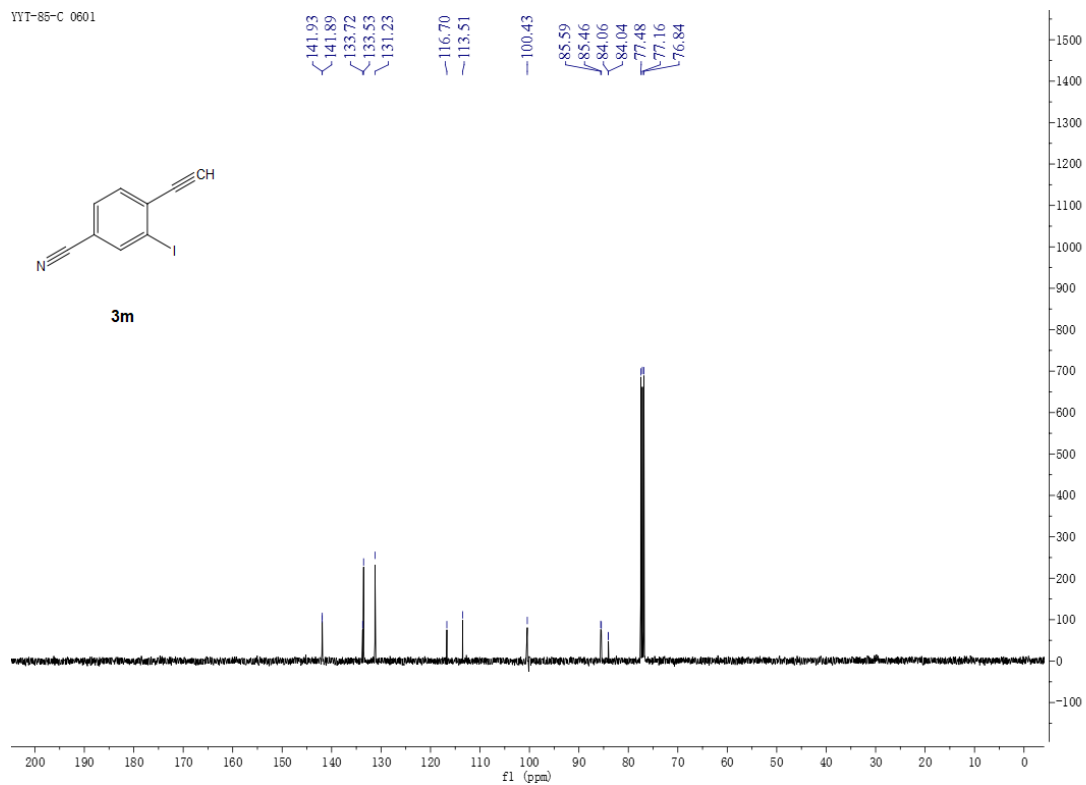
yyt-85



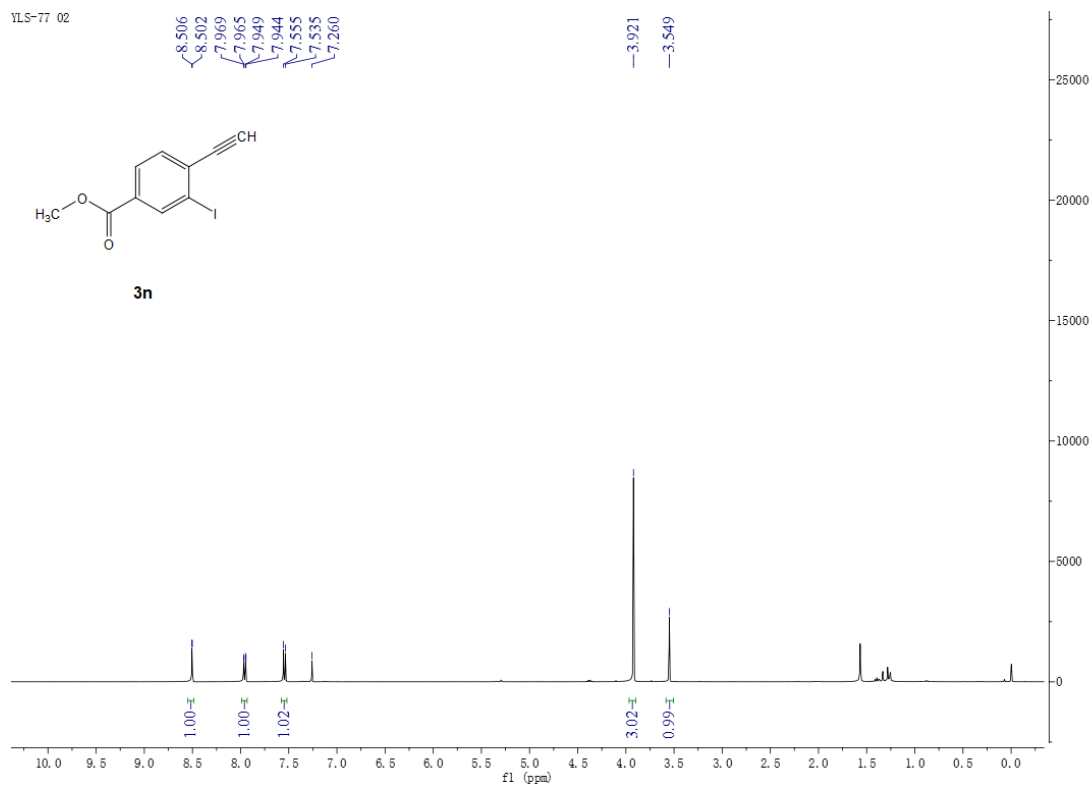
3m



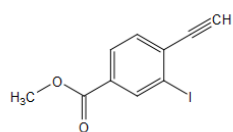
YYT-85-C 0601



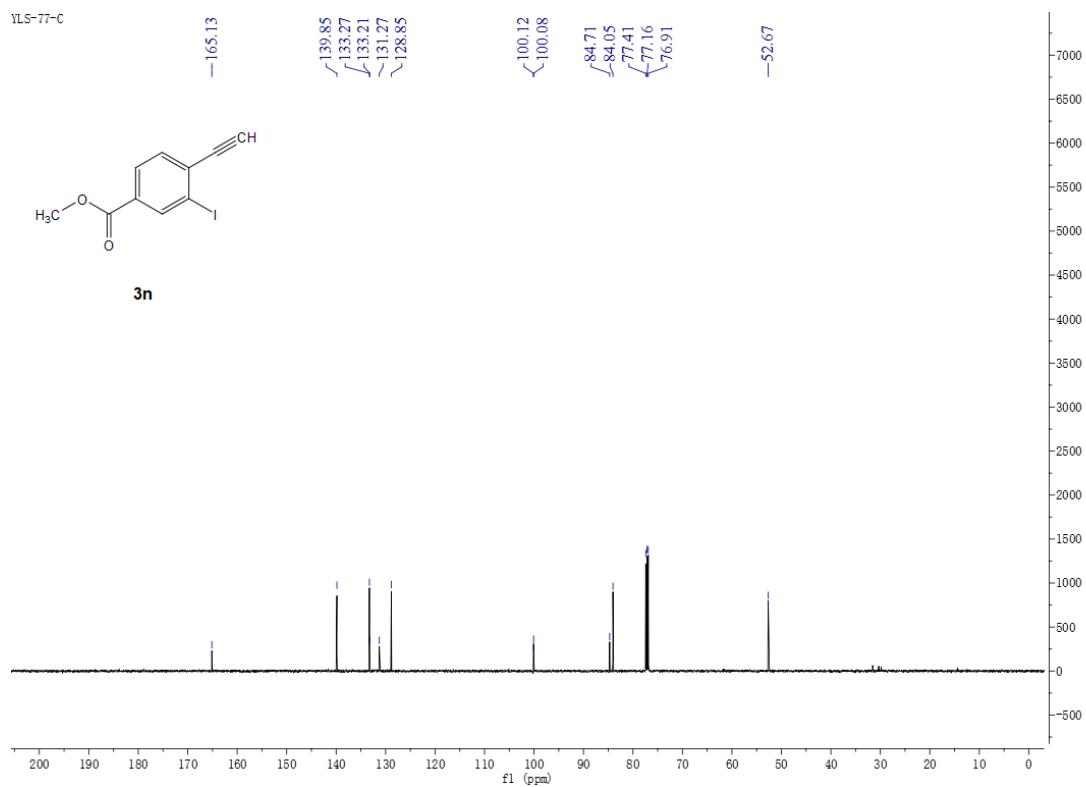
YLS-77 02



YLS-77-C



3n

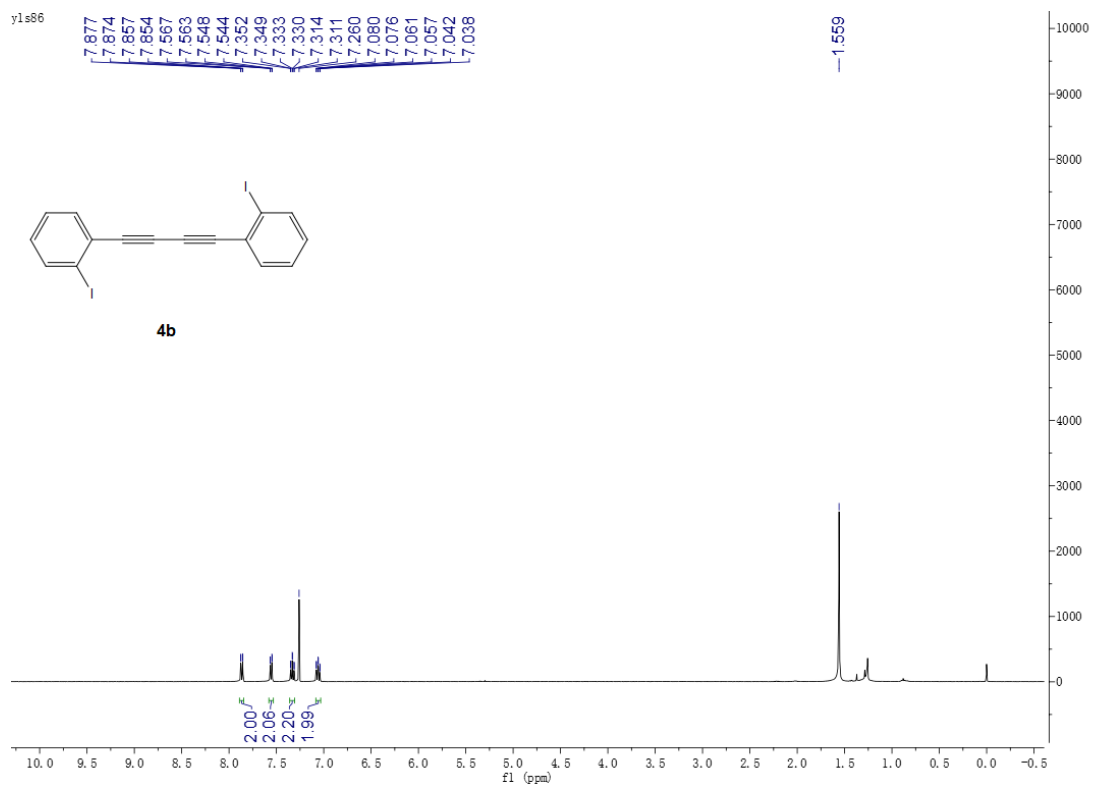
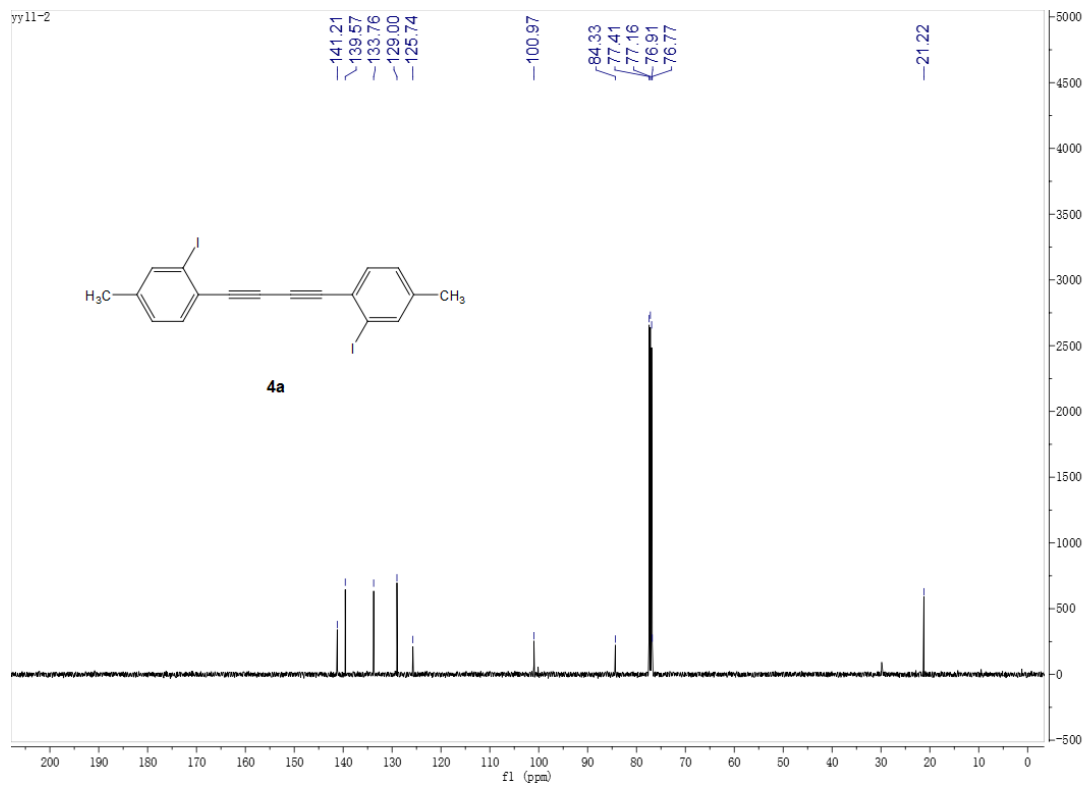


YY11-2

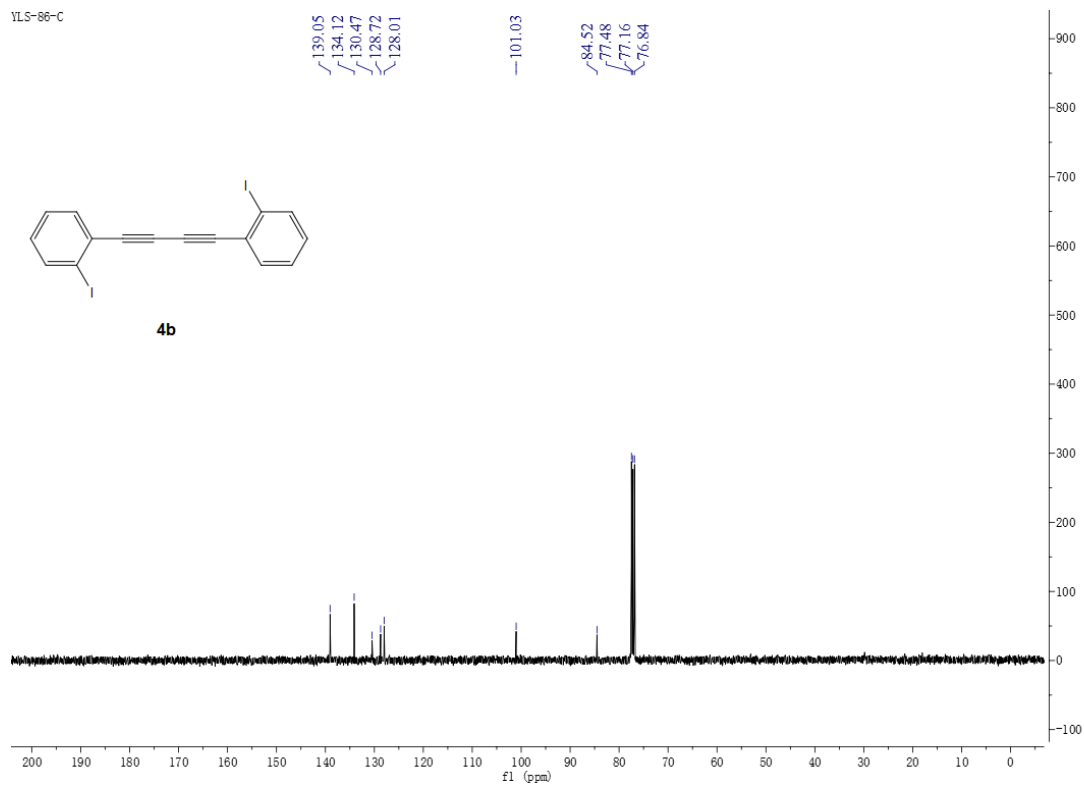


4a

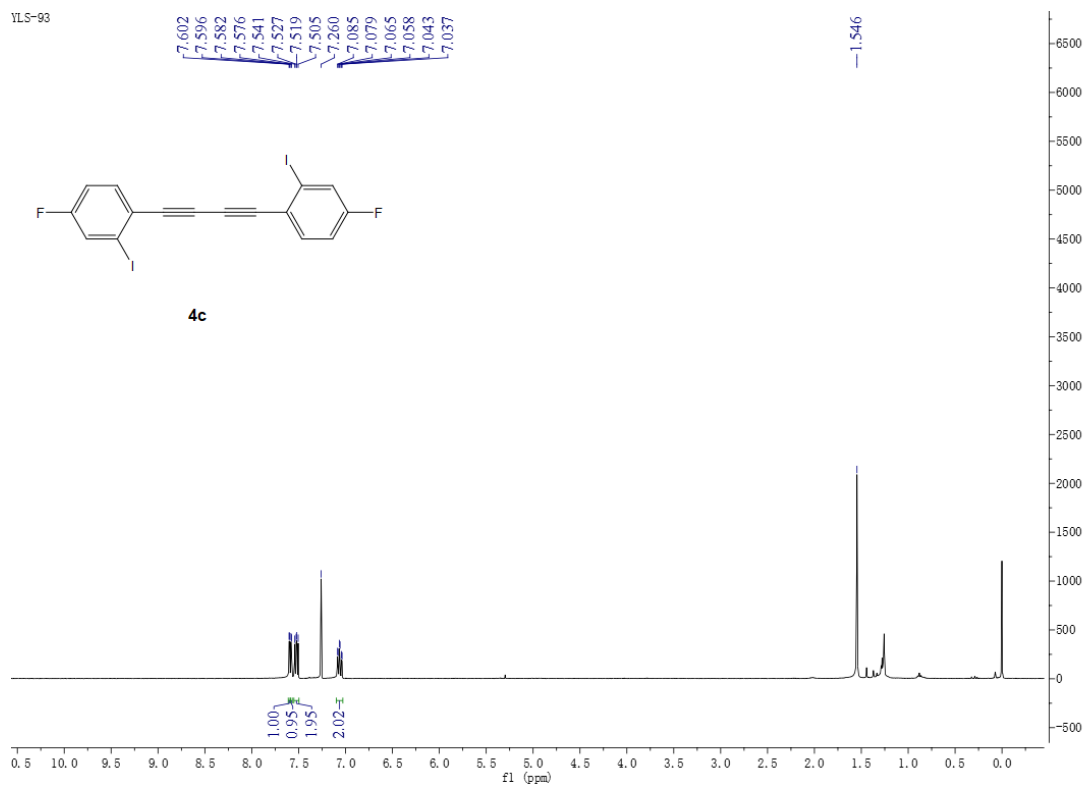




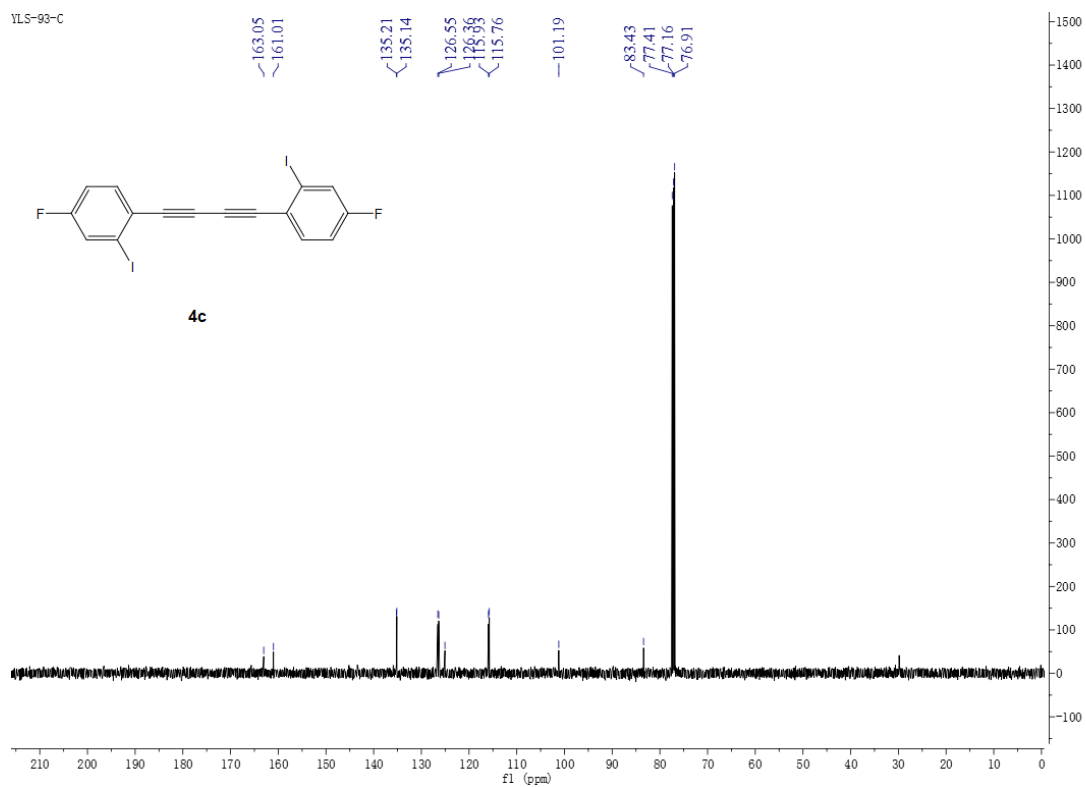
YLS-86-C



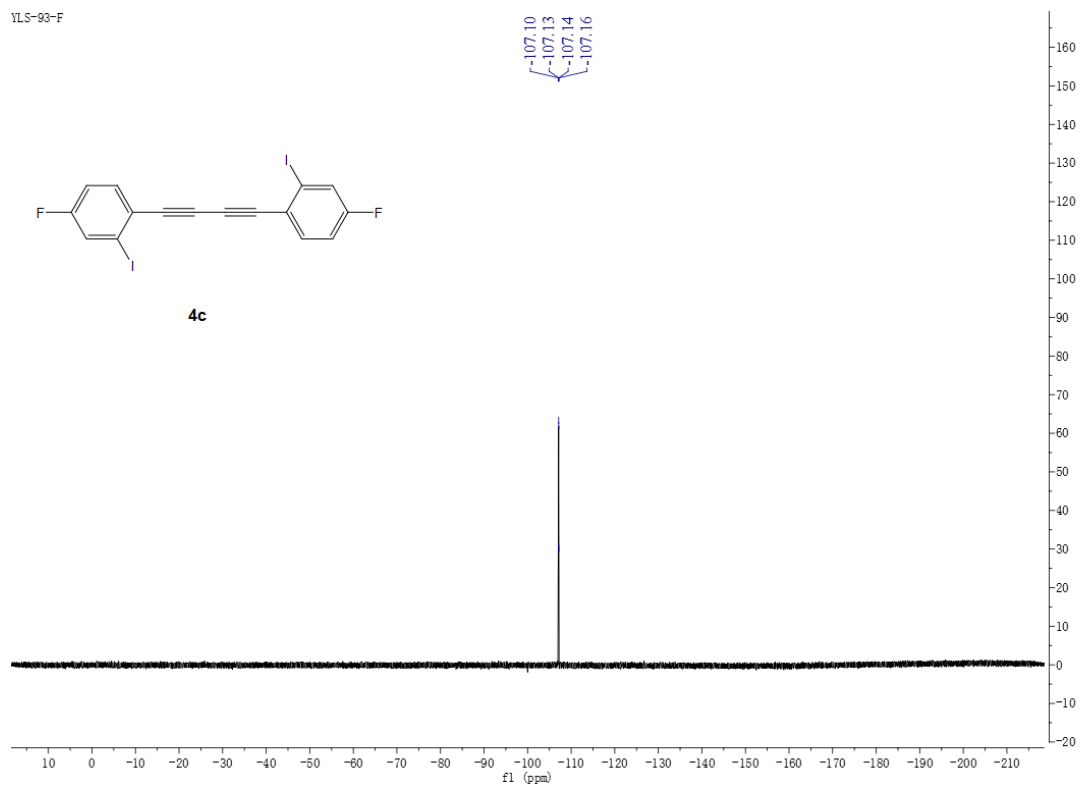
YLS-93



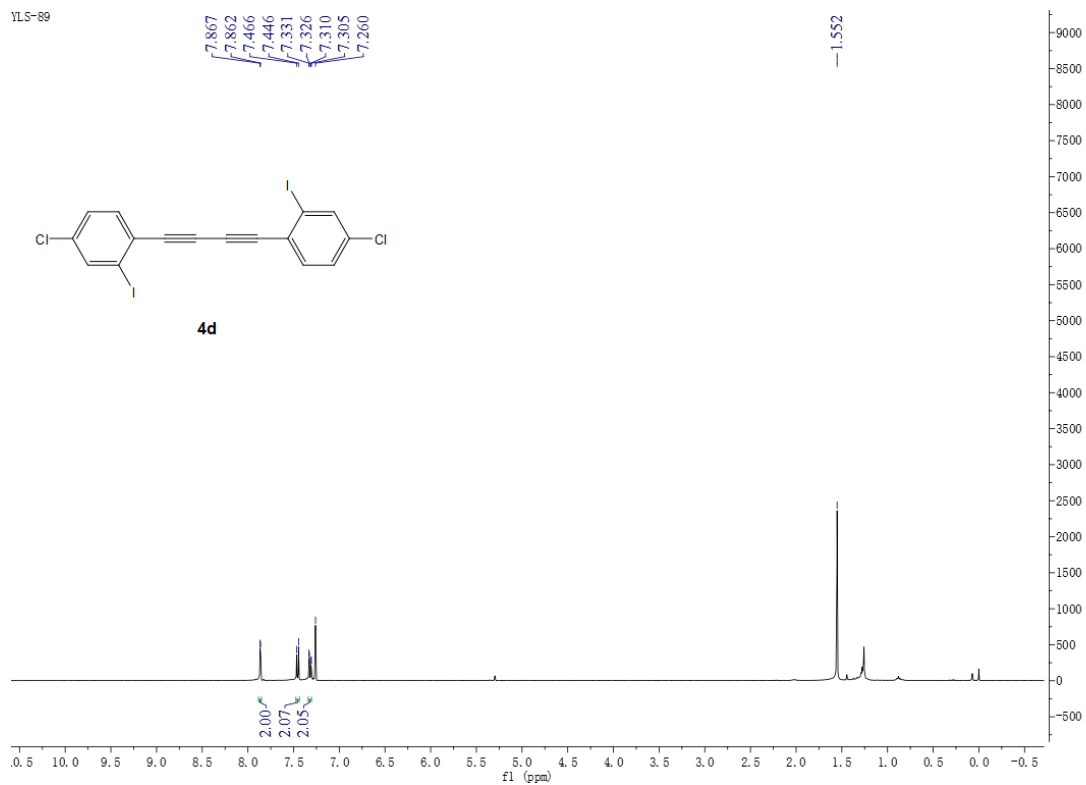
YLS-93-C



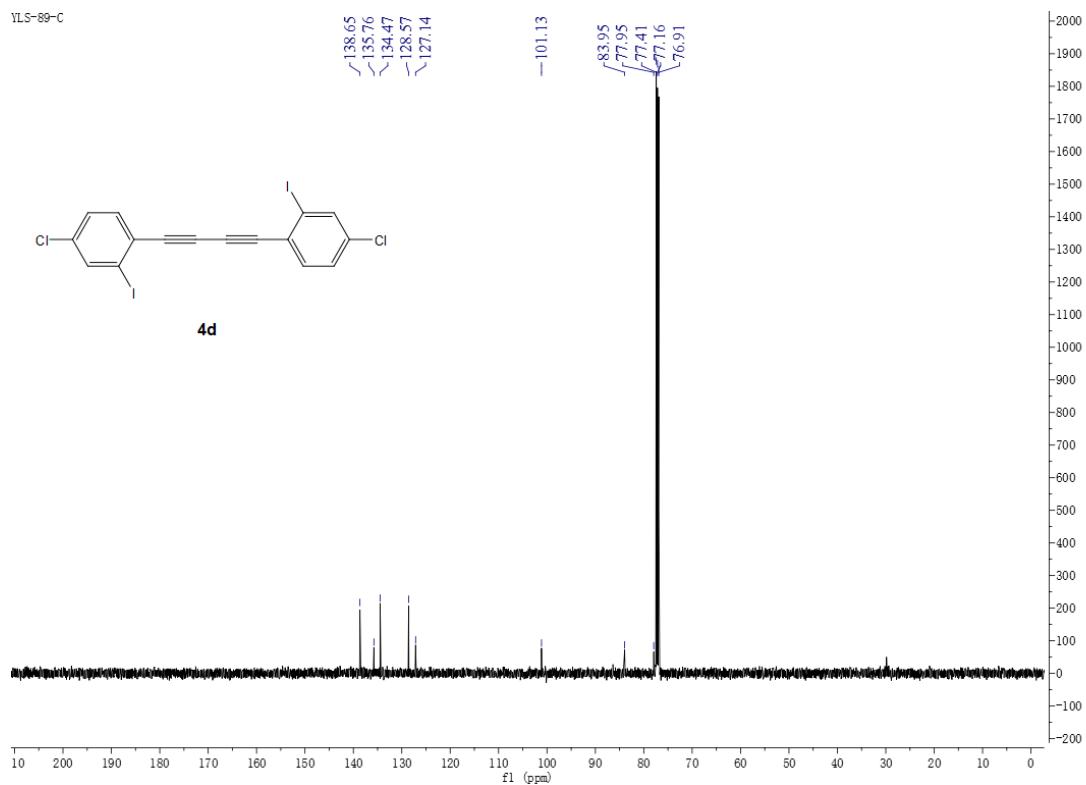
YLS-93-F



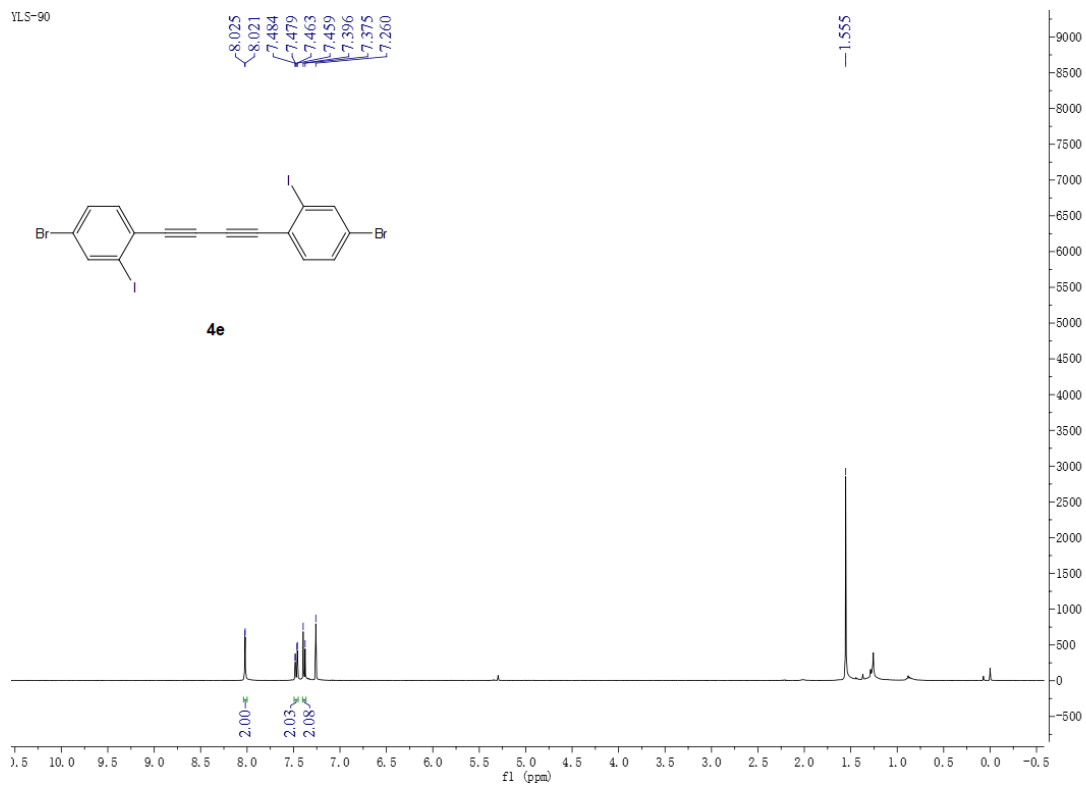
YLS-89



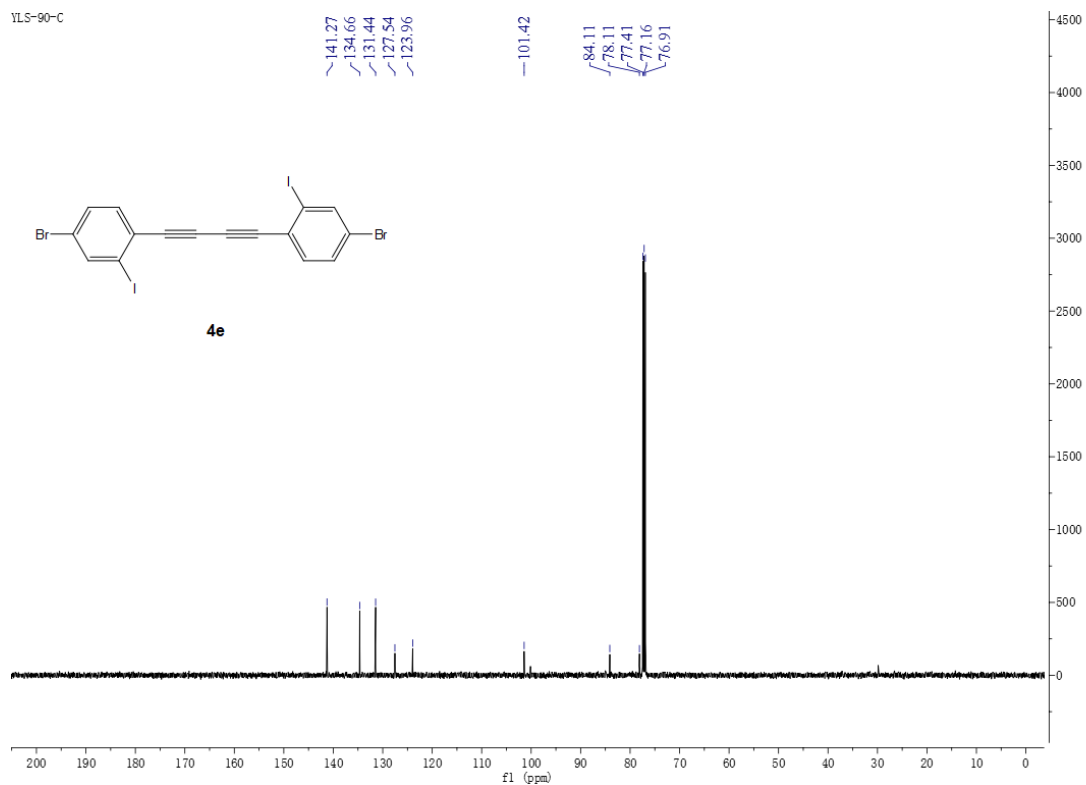
YLS-89-C



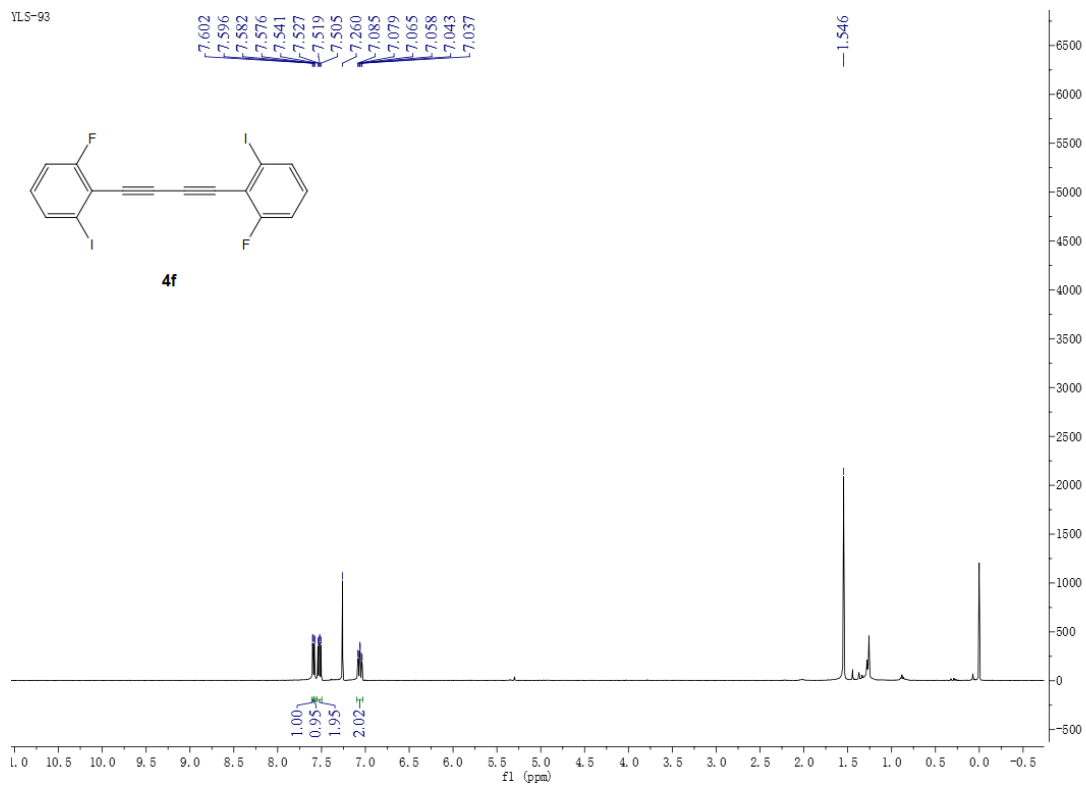
YLS-90



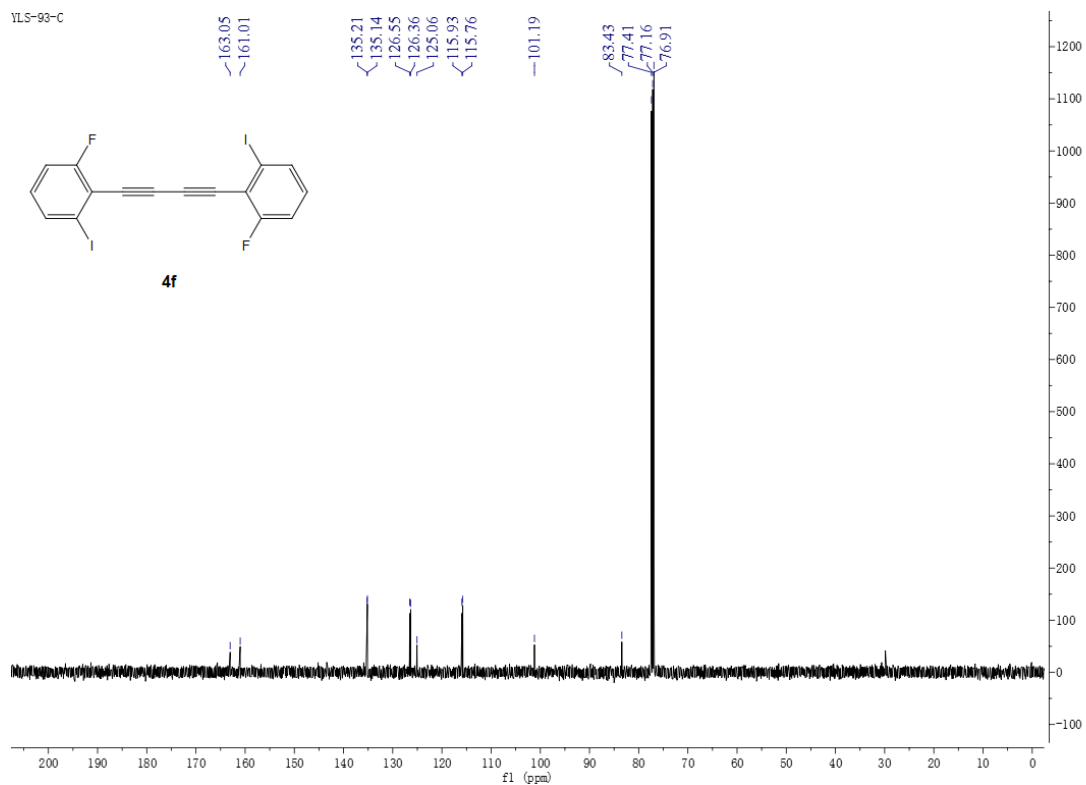
YLS-90-C



YLS-93



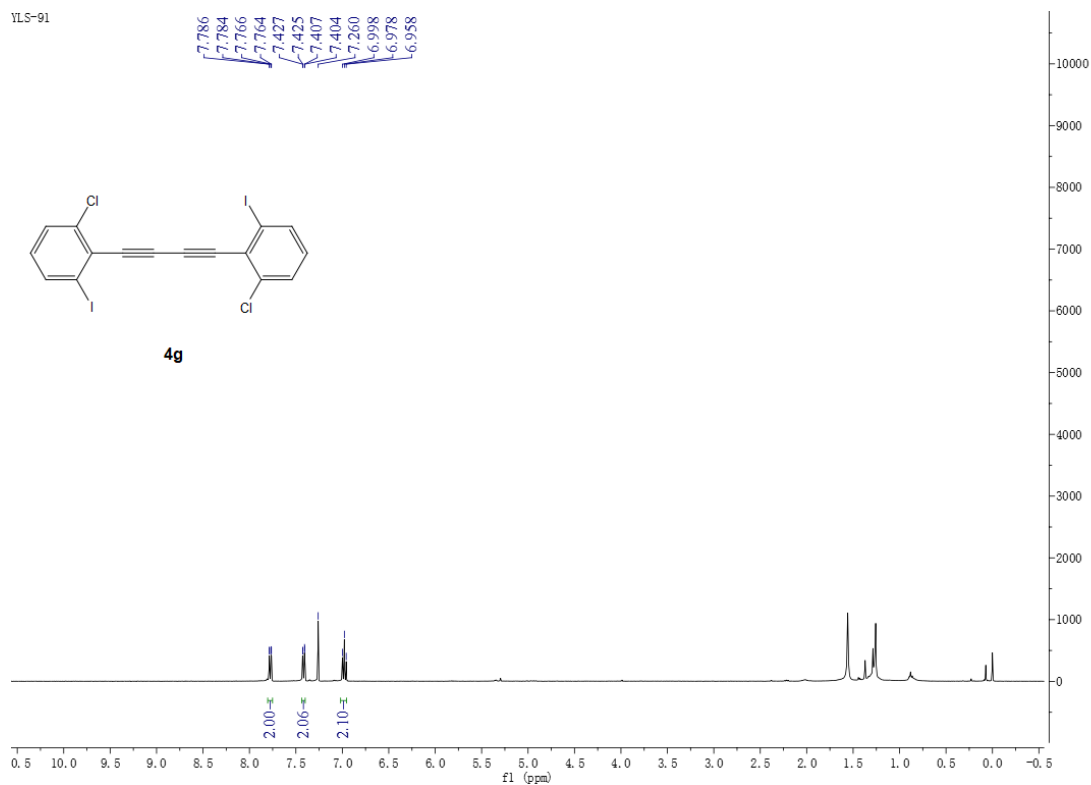
YLS-93-C



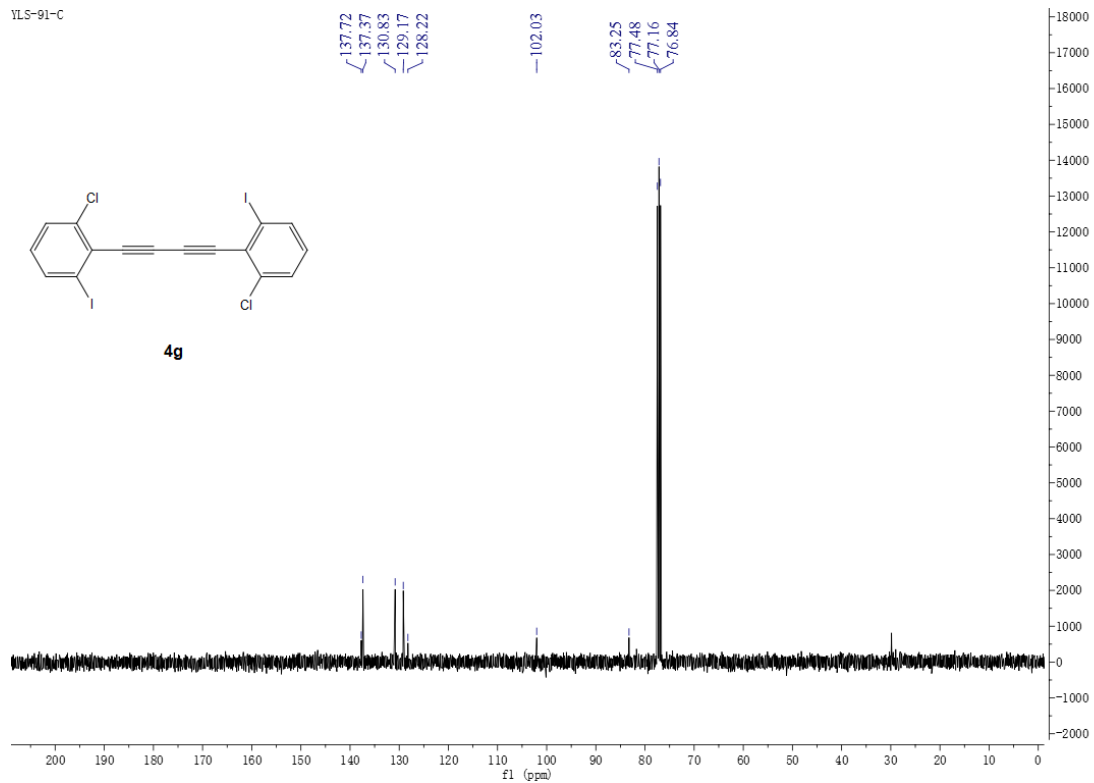
YLS-93-F



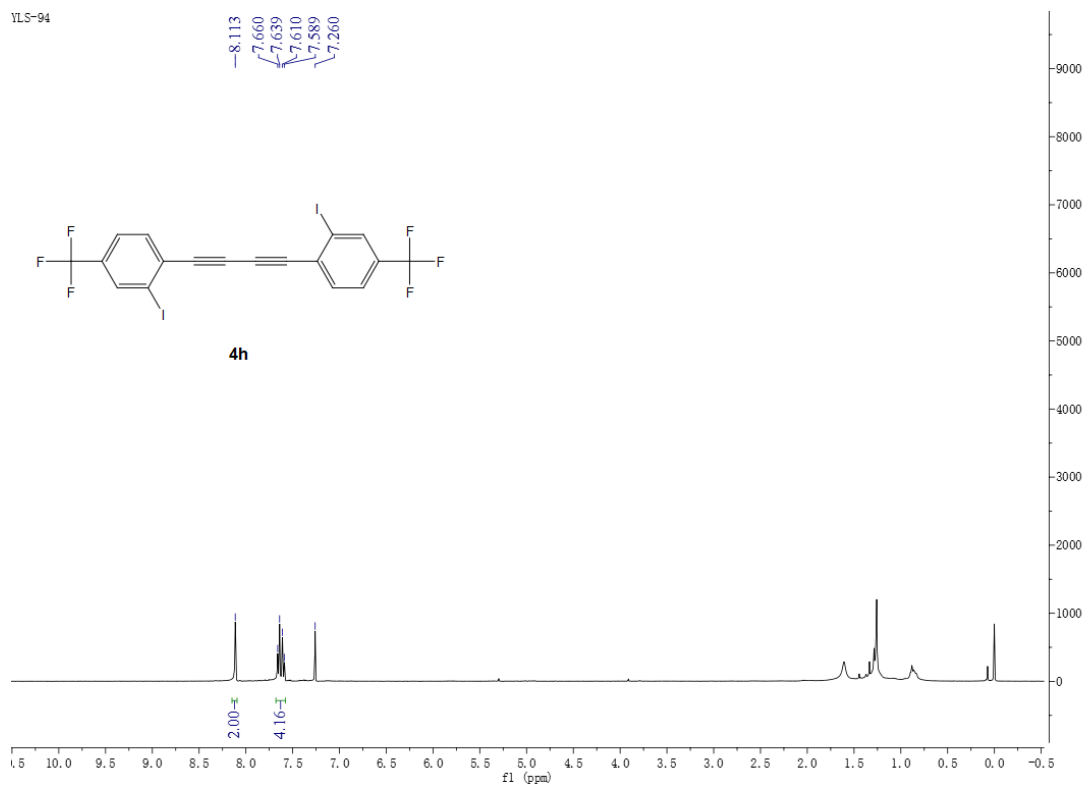
YLS-91



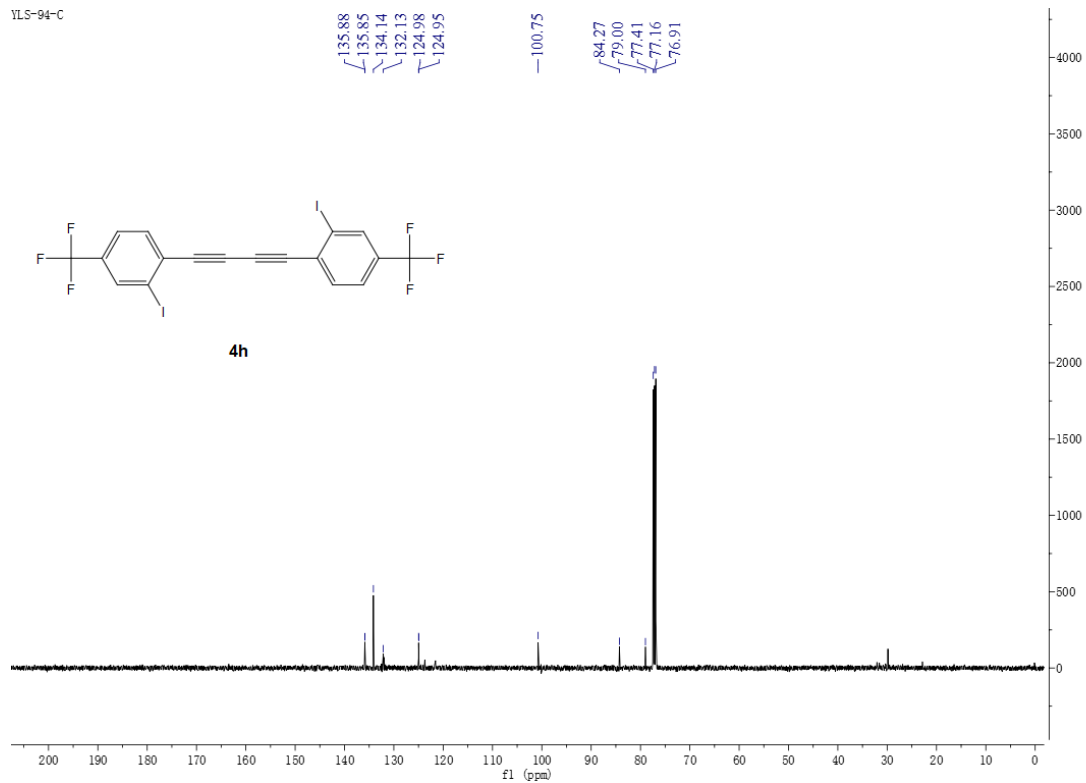
YLS-91-C



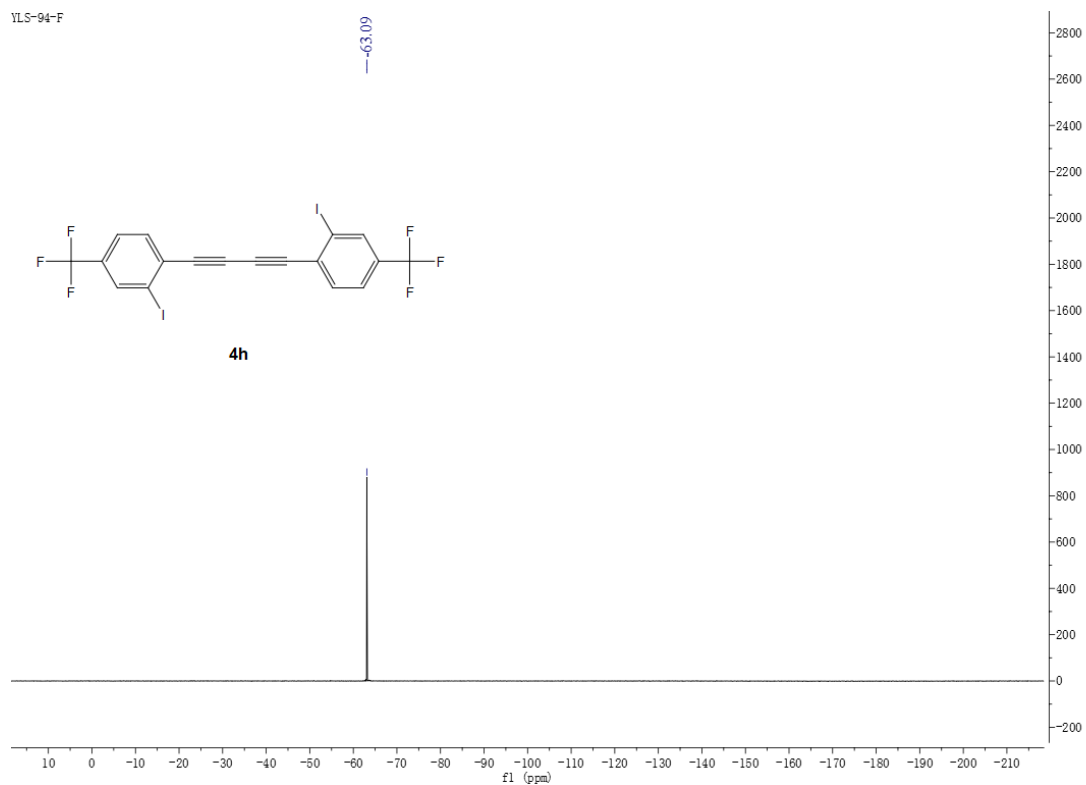
YLS-94



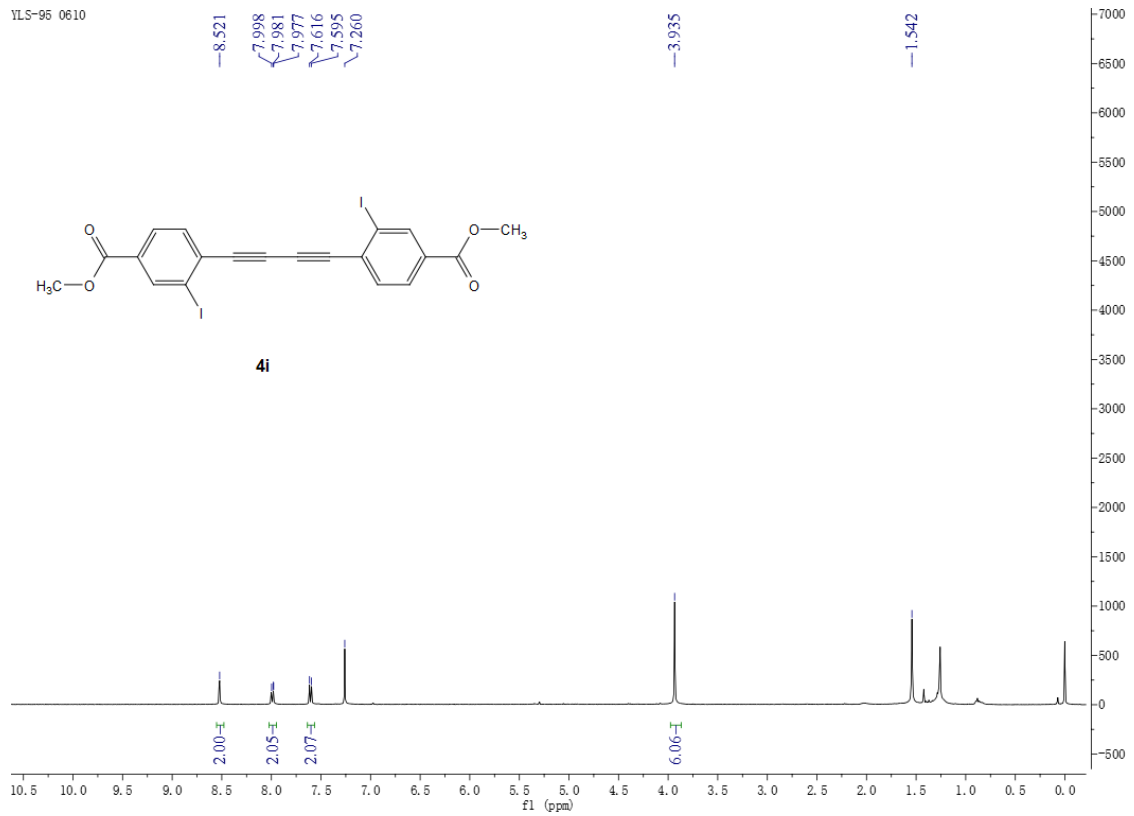
YLS-94-C



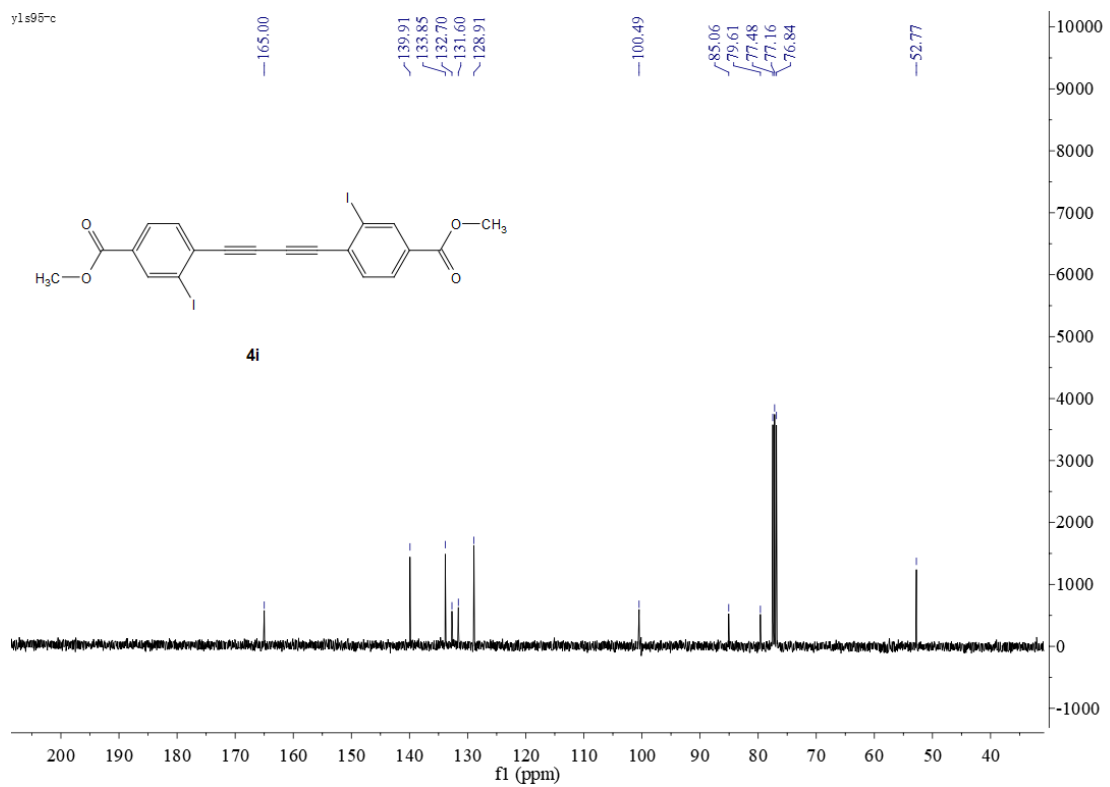
YLS-94-F



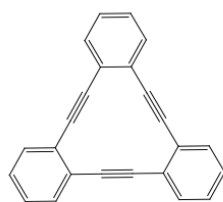
YLS-95 0610



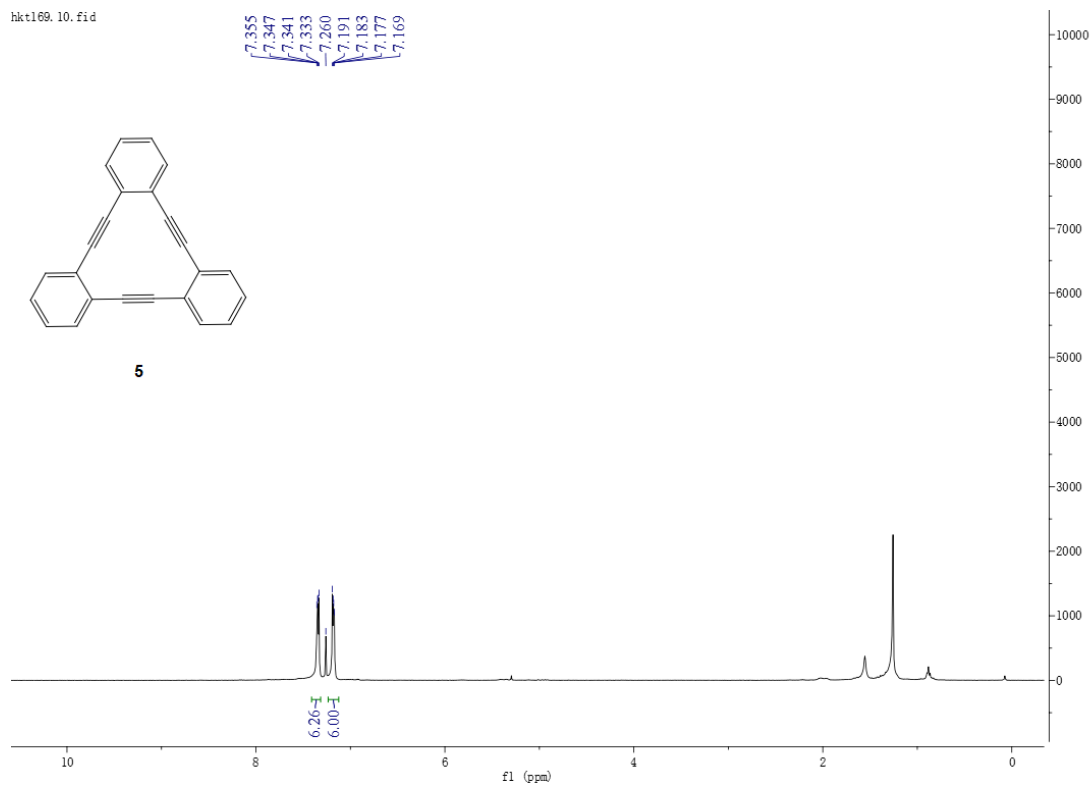
yls95-c



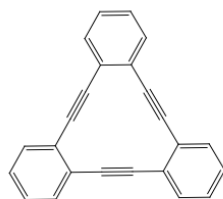
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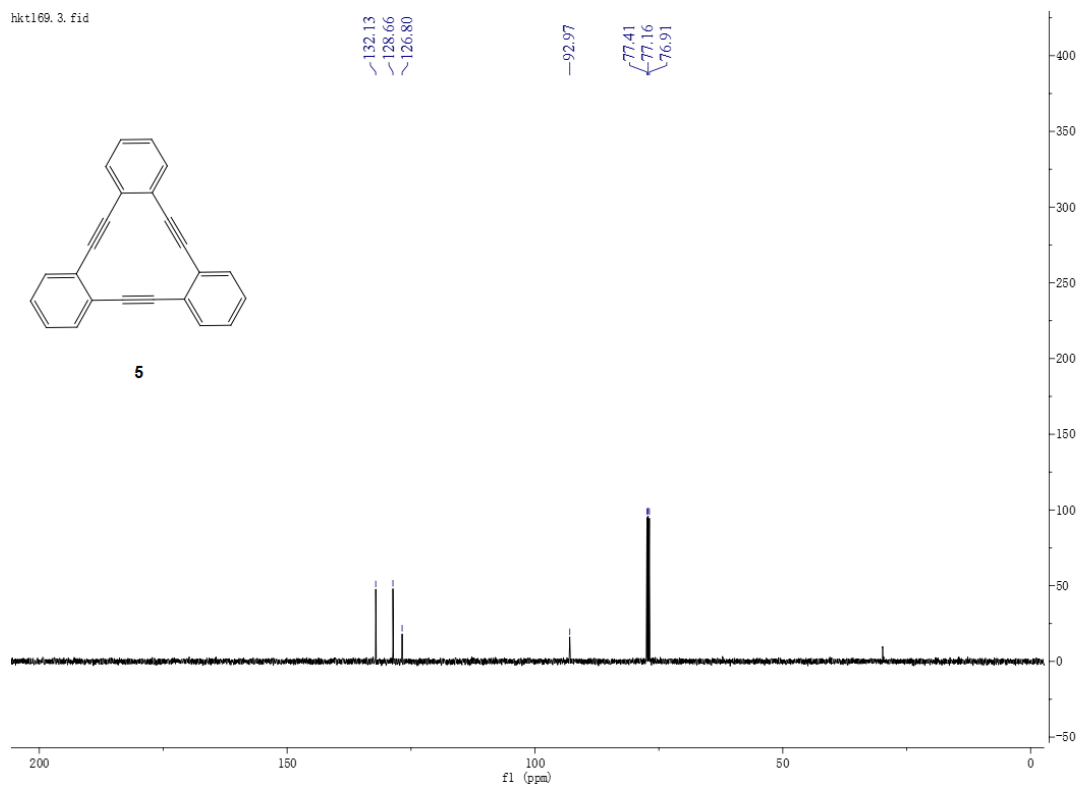
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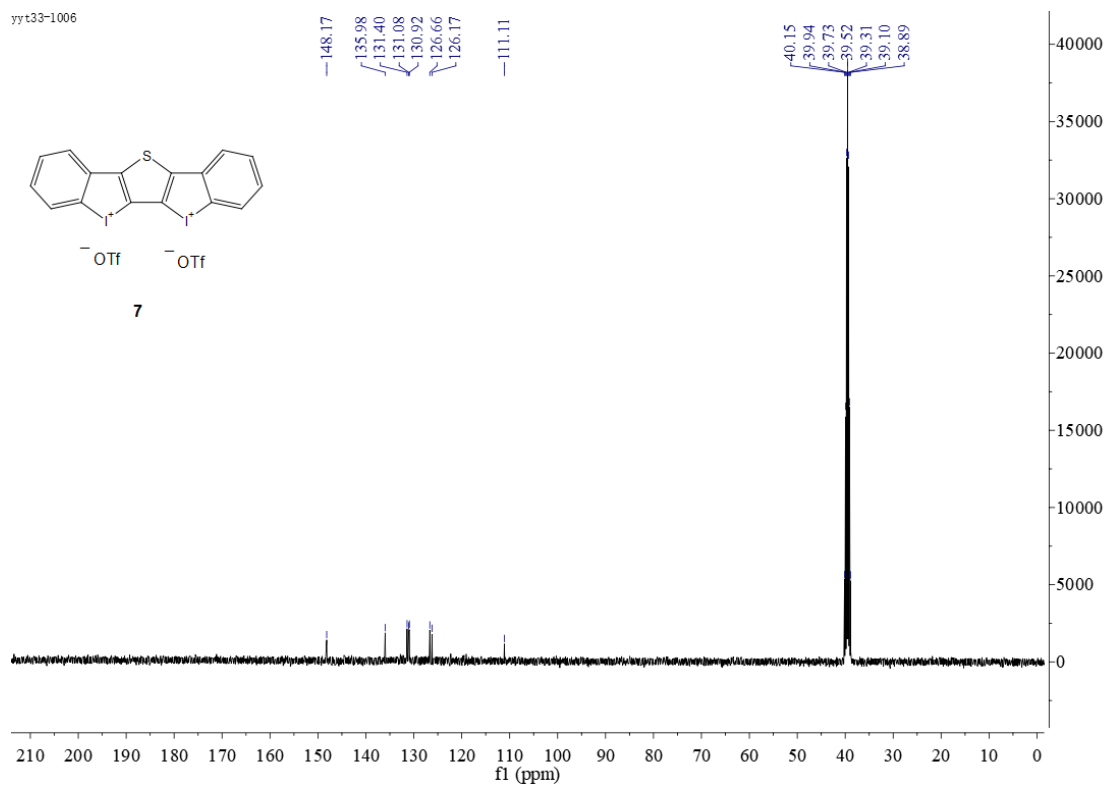
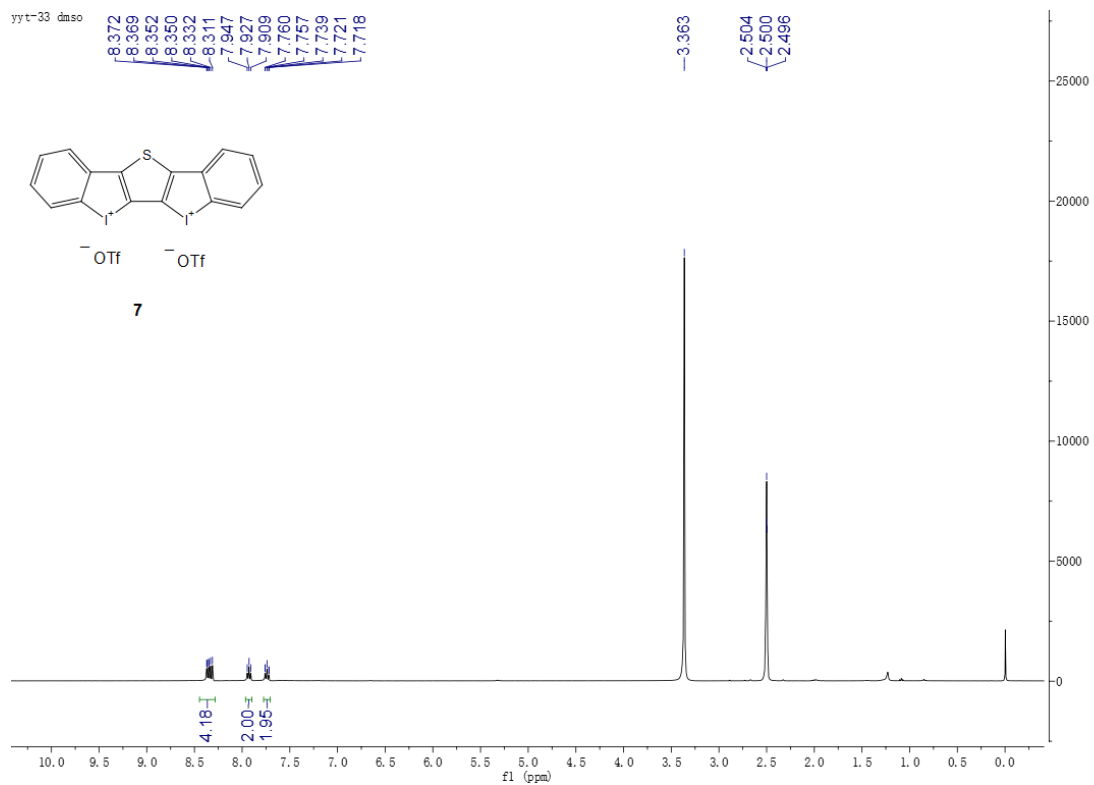


hkt169.3.fid



5





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