

Supporting Information

Efficient synthesis of 1-iodoalkynes via Al₂O₃ mediated reaction of terminal alkynes and *N*-iodosuccinimide

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General Information

All reagents and solvents were purchased from commercial suppliers and used as delivered. NMR (^1H and ^{13}C) spectra were recorded on a Bruker Avance 400 FTNMR spectrometer using CDCl_3 and DMSO-d_6 as solvents. Chemical shifts are reported in parts per million (ppm) and coupling constants in Hertz (Hz). Tetramethylsilane (TMS) ($\delta = 0.00$ ppm) or residual solvent peak in CDCl_3 ($\delta = 7.26$ ppm) and DMSO-d_6 ($\delta = 2.50$ ppm) served as internal standard for recording. TLC analyses were performed on precoated GF254 silica gel plates and were visualized under UV254 nm light or by I_2 staining. Column chromatography was carried out using 200-300 mesh silica gel. Substrate **2at** was synthesized according to the literature method.^[17]

Experimental Section

1. General procedure (A) for the direct iodination of alkynes

Terminal alkynes (**1aa-1be**) (2.0 mmol, 1.0 equiv), Al_2O_3 (2.6 mmol, 1.3 equiv), 4 Å MS (200 mg) and CH_3CN (10 mL) were added in a 25 mL round-bottomed flask. *N*-iodosuccinimide (2.2 mmol, 1.1 equiv) was added and the resulting mixture was heated to 80 °C and stirred for 1 h at this temperature. After completion of the reaction, the mixture was quenched with saturated aqueous sodium thiosulfate and extracted with ethyl acetate (10×3 mL). The combined organic layers were washed with aqueous sodium chloride and dried over anhydrous sodium sulfate, filtered and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (petroleum ether and ethyl acetate).

2. General procedure (B) for the direct iodination of alkynes

Terminal alkynes (**1aa, 1ab, 1af, 1al, 1an, 1ar**) (2.0 mmol, 1.0 equiv), *N*-iodosuccinimide (2.2 mmol, 1.1 equiv) CH_3CN (2 mL) and Al_2O_3 (2.6 mmol, 1.3 equiv) were mixed in a 15 mL thick wall pressure flask. The resulting mixture was heated to 80 °C and stirred for 1 h at this temperature. After completion of the reaction,

the mixture was cooled to room temperature, added ethyl acetate (30 mL), washed with saturated aqueous sodium thiosulfate and aqueous sodium chloride, dried over anhydrous sodium sulfate, filtered and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (petroleum ether and ethyl acetate).

3. General procedure for the scale-up synthesis of 1-iodoalkynes (3aa, 3af, 3ak, 3ap, 3bc)

Terminal alkynes (10.0 mmol, 1.0 equiv), Al₂O₃ (13.0 mmol, 1.3 equiv), 4 Å MS (1.0 g) and CH₃CN (50 mL) were added in a 100 mL round-bottomed flask. *N*-iodosuccinimide (11.0 mmol, 1.1 equiv) was added and the resulting mixture was heated to 80 °C and stirred for 1 h at this temperature. After completion of the reaction, the mixture was quenched with saturated aqueous sodium thiosulfate and extracted with ethyl acetate (30×3 mL). The combined organic layers were washed with aqueous sodium chloride and dried over anhydrous sodium sulfate, filtered and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (petroleum ether and ethyl acetate).

4. General procedure for the synthesis of tri-iodination of alkynes (C)

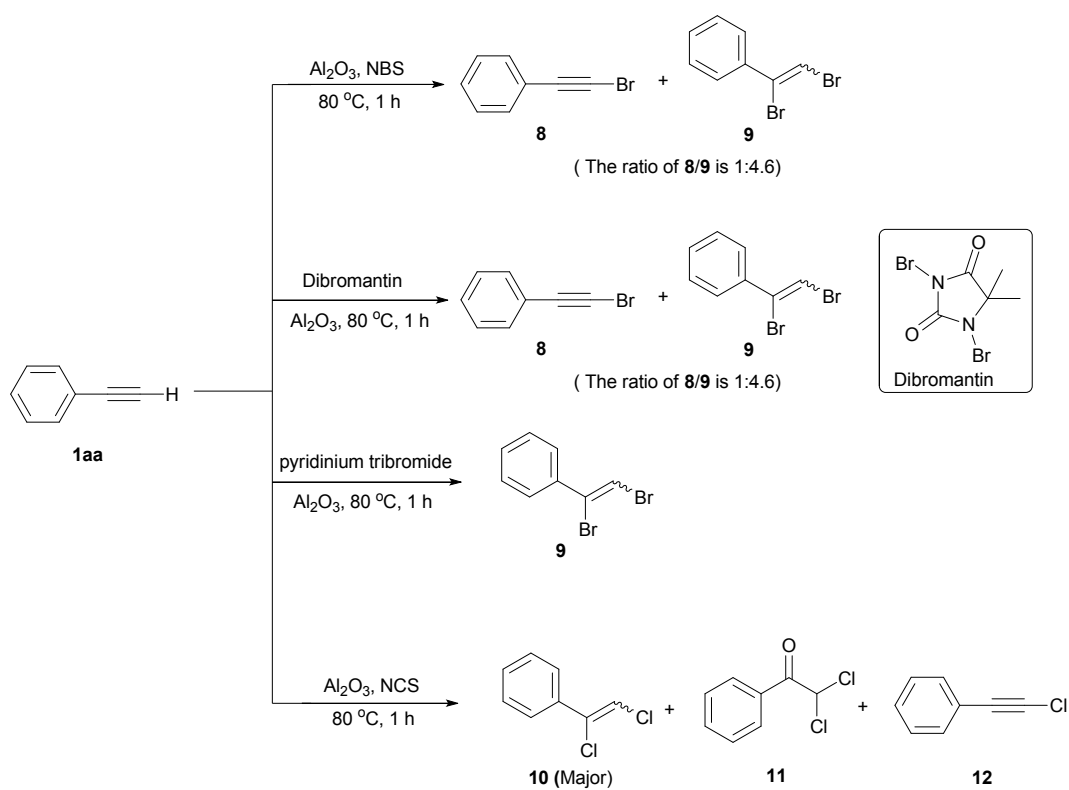
Phenyl acetylene **1aa** (2.0 mmol, 1.0 equiv), Al₂O₃ (2.6 mmol, 1.3 equiv), 4 Å MS (200 mg) and CH₃CN (10 mL) were added in a 25 mL round-bottomed flask. *N*-iodosuccinimide (2.2 mmol, 1.1 equiv) was added and the resulting mixture was heated to 80 °C and stirred for 1 h at this temperature. Then I₂ (3.0 mmol, 1.5 equiv) was added to the reaction mixture. The reaction was stirred at 80 °C for 3 h. After completion of the reaction (determined by HPLC), the mixture was quenched with saturated aqueous sodium thiosulfate and extracted with ethyl acetate (10×3 mL). The combined organic layers were washed with aqueous sodium chloride and dried over anhydrous sodium sulfate, filtered and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (petroleum ether and ethyl acetate).

5. General procedure for the recovery of the Al₂O₃ and 4 Å MS

Terminal alkynes (10.0 mmol, 1.0 equiv), Al₂O₃ (13.0 mmol, 1.3 equiv), 4 Å MS (1.0 g) and CH₃CN (50 mL) were added in a 100 mL round-bottomed flask. *N*-iodosuccinimide (11.0 mmol, 1.1 equiv) was added and the resulting mixture was heated to 80 °C and stirred for 1 h at this temperature. After completion of the reaction, the mixture was quenched with saturated aqueous sodium thiosulfate and filtered. The filter cake was washed with water (10×3 mL) and ethyl acetate (10×3 mL). All filtrate was extracted with ethyl acetate (30×2 mL). The combined organic layers were washed with aqueous sodium chloride and dried over anhydrous sodium sulfate, filtered and concentrated under vacuum. The filter cake was dried in a vacuum drying box at 60 °C for 8 h, activated at 600 °C for 8 h in a muffle furnace and transferred to desiccators when cooled to 100 °C.

Table S1 Optimization of the reaction conditions

Entry	CH ₃ CN (mL)	alkynes	2a (equiv.)	T(°C)	4 Å MS	Al ₂ O ₃ (equiv.)	Yield
1	—	1aa (2 mmol)	1.1	80	—	1.3	3aa , 89%
2	2	1aa (2 mmol)	1.1	80	—	1.3	3aa , 95%
3	10	1aa (2 mmol)	1.1	80	200 mg	1.3	3aa , 98%
4	—	1aa (10 mmol)	1.1	80	—	1.3	3aa , 93%
5	4	1aa (10 mmol)	1.1	80	—	1.3	3aa , 98%
6	50	1aa (10 mmol)	1.1	80	1.0 g	1.3	3aa , 96%
7	2	1ab (2 mmol)	1.1	80	—	1.3	3ab , 93%
8	2	1af (2 mmol)	1.1	80	—	1.3	3af , 95%
9	2	1al (2 mmol)	1.1	80	—	1.3	3al , 99%
10	2	1an (2 mmol)	1.1	80	—	1.3	3an , 98%
11	2	1ar (2 mmol)	1.1	80	—	1.3	3ar , 96%



Scheme S1 Bromination and chlorination of phenyl acetylene mediated by Al_2O_3

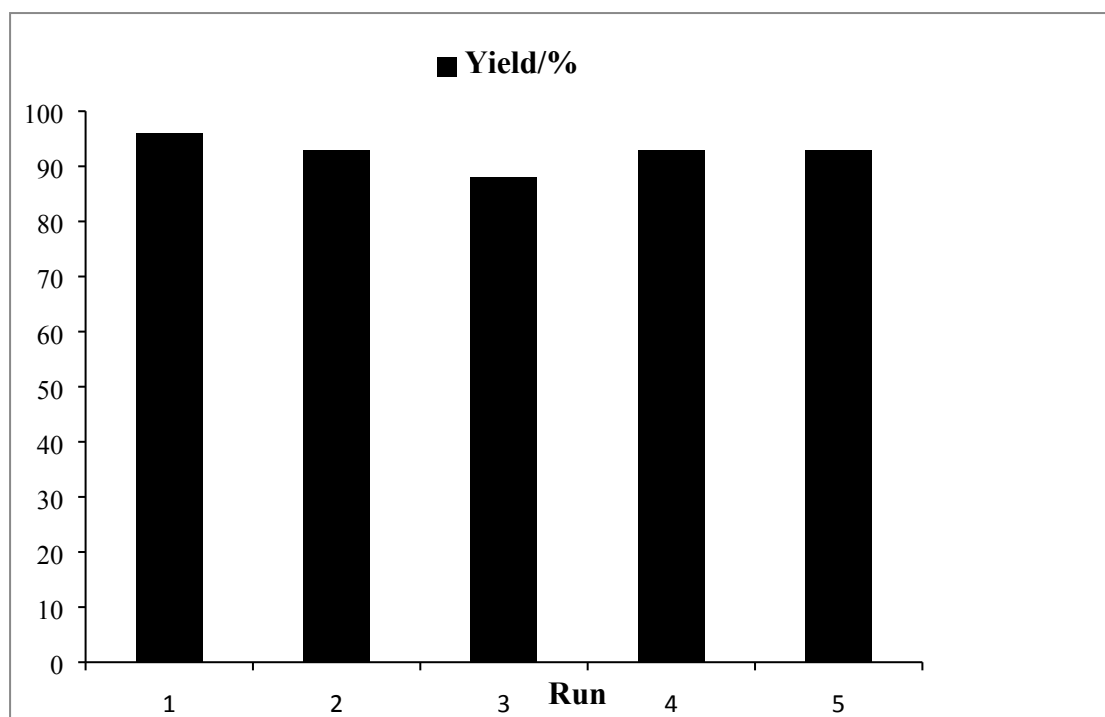
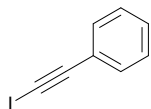


Figure S1 Recycling test of Al_2O_3 and 4 Å MS

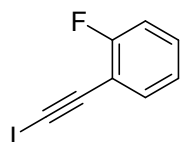
The yield of the first, second, third, fourth and fifth run was 96%, 93%, 88%, 93% and 93%, respectively. The increase of the yield of the reaction during the fourth and

fifth run was due to the addition of 20% and 40% (Based on the weight of the solid catalyst used) recycled solid catalyst (Al_2O_3 and 4 Å MS).

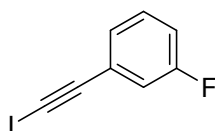
Characterizations of Products



(iodoethynyl)benzene (3aa): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether afforded the title compound as pale yellow oil; yield 446.9 mg, 98%. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 7.47-7.44 (m, 2H), 7.34-7.32 (m, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 101 MHz): δ (ppm) 132.43, 128.91, 128.35, 123.47, 94.26, 6.44; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[1]

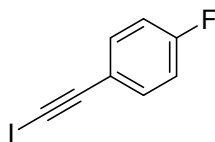


1-fluoro-2-(iodoethynyl)benzene (3ab): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether afforded the title compound as pale yellow oil; yield 452.7 mg, 92%. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 7.45-7.41 (m, 1H), 7.33-7.28 (m, 1H), 7.11-7.04 (m, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 101 MHz): δ (ppm) 163.83 (d, $J = 253$ Hz), 134.31 (d, $J = 1.3$ Hz), 130.62 (d, $J = 8.0$ Hz), 123.99 (d, $J = 3.7$ Hz), 115.61 (d, $J = 20.8$ Hz), 112.01 (d, $J = 15.8$ Hz), 87.48, 12.01 (d, $J = 3.2$ Hz); the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[2]

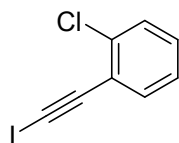


1-fluoro-3-(iodoethynyl)benzene (3ac): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether afforded the title compound as pale yellow oil; yield 433.0 mg, 88%. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 7.30-7.20 (m, 2H), 7.14-7.11 (m, 1H), 7.04-7.01 (m, 1H); $^{13}\text{C NMR}$ (CDCl_3 ,

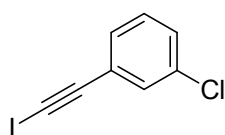
101 MHz): δ (ppm) 162.30 (d, $J = 248$ Hz), 129.94 (d, $J = 8.7$ Hz), 128.35 (d, $J = 3.1$ Hz), 125.19 (d, $J = 9.5$ Hz), 119.26 (d, $J = 23$ Hz), 116.40 (d, $J = 21.3$ Hz), 92.99 (d, $J = 3.4$ Hz), 8.40; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[1]



1-fluoro-4-(iodoethynyl)benzene (3ad): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether afforded the title compound as pale brown oil; yield 428.2 mg, 87%. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 7.44-7.40 (m, 2H), 7.03-6.98 (m, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 101 MHz): δ (ppm) 162.80 (d, $J = 251.4$ Hz), 134.35 (d, $J = 8.6$ Hz), 119.52 (d, $J = 3.5$ Hz), 115.65 (d, $J = 22.3$ Hz), 93.14, 6.44; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[1]

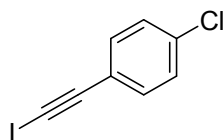


1-chloro-2-(iodoethynyl)benzene (3ae): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether afforded the title compound as pale yellow oil; yield 489.2 mg, 93%. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 7.47 (dd, $J = 7.6, 2.0$ Hz, 1H), 7.39 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.28-7.19 (m, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 101 MHz): δ (ppm) 136.77, 134.26, 129.87, 129.31, 126.47, 123.29, 90.99, 12.50; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[1]

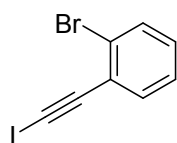


1-chloro-3-(iodoethynyl)benzene (3af): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether afforded the title compound as pale brown oil; yield 493.2 mg, 94%. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 7.42-7.41 (m, 1H), 7.33-7.29 (m, 2H), 7.26-7.22 (m, 1H); $^{13}\text{C NMR}$ (CDCl_3 ,

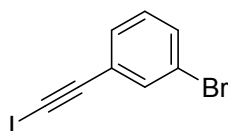
101 MHz): δ (ppm) 134.12, 132.28, 130.52, 129.54, 129.21, 125.02, 92.81, 8.88; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[1]



1-chloro-4-(iodoethynyl)benzene (3ag): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether afforded the title compound as pale yellow solid, Mp. 84-85 °C, (literature^[13]: 83-84 °C); yield 473.0 mg, 90%. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.36 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H); ¹³C NMR(CDCl₃, 101 MHz): δ (ppm) 135.04, 133.66, 128.73, 121.96, 93.10, 7.86; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[3]

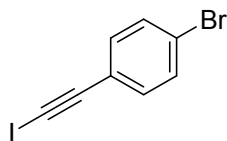


1-bromo-2-(iodoethynyl)benzene (3ah): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether afforded the title compound as yellow oil; yield 577.0 mg, 94%. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.57 (dd, J = 8.0, 1.2 Hz, 1H), 7.46 (dd, J = 7.8, 2.0 Hz, 1H), 7.26 (dt, J = 7.6, 1.6 Hz, 1H), 7.17 (dt, J = 7.8, 1.6 Hz, 1H); ¹³C NMR(CDCl₃, 101 MHz): δ (ppm) 134.32, 132.39, 129.98, 127.01, 126.10, 125.46, 92.74, 12.33; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[1]

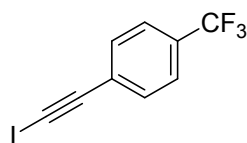


1-bromo-3-(iodoethynyl)benzene (3ai): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether afforded the title compound as pale yellow oil; yield 607.7 mg, 99%; ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.58-7.57 (m, 1H), 7.47-7.44 (m, 1H), 7.37-7.34 (m, 1H), 7.18 (t, J = 8.0 Hz, 1H); ¹³C NMR(CDCl₃, 101 MHz): δ (ppm) 135.21, 132.13, 130.98, 129.78, 125.36,

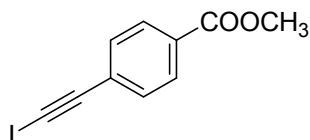
122.12, 92.68, 8.81; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[1]



1-bromo-4-(iodoethynyl)benzene (3aj): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether afforded the title compound as pale yellow solid, Mp. 92-93 °C, (literature^[14]: 93-95 °C); yield 558.6 mg, 91%; ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.44 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.8 Hz, 2H); ¹³C NMR(CDCl₃, 101 MHz): δ (ppm) 133.86, 131.66, 123.29, 122.42, 93.16, 8.08; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[2]

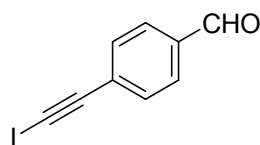


1-(iodoethynyl)-4-(trifluoromethyl)benzene (3ak): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether afforded the title compound as white solid, Mp. 63-66 °C, (literature^[15]: 54-59 °C); yield 556.5 mg, 94%. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.59-7.52 (m, 4H); ¹³C NMR(CDCl₃, 101 MHz): δ (ppm) 132.75, 130.62 (q, *J* = 32.8 Hz), 127.18, 125.34 (q, *J* = 3.8 Hz), 123.94 (q, *J* = 273.3 Hz), 92.96, 10.31; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[1]

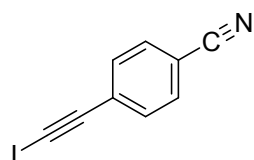


methyl 4-(iodoethynyl)benzoate (3al): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether and ethyl acetate (petroleum ether/ethyl acetate = 15:1) afforded the title compound as white solid; yield 566.4 mg, 99%. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.98 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H); ¹³C NMR(CDCl₃, 101 MHz): δ (ppm) 166.52,

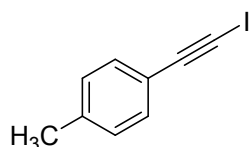
132.41, 130.15, 129.54, 128.02, 93.58, 52.43, 10.60; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[1]



4-(iodoethynyl)benzaldehyde (3am): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether and ethyl acetate (petroleum ether/ethyl acetate = 20:1) afforded the title compound as pale yellow oil; yield 419.9 mg, 82%. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 10.0 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H); ¹³C NMR(CDCl₃, 101 MHz): δ (ppm) 191.44, 135.91, 133.04, 129.57, 129.52, 93.47, 12.27; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[5]

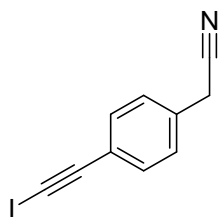


4-(iodoethynyl)benzotrile (3ar): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether and ethyl acetate (petroleum ether/ethyl acetate = 10:1) afforded the title compound as white solid, Mp. 171-172 °C, (literature^[13]: 169-170 °C); yield 495.4 mg, 98%. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.60 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H); ¹³C NMR(CDCl₃, 101 MHz): δ (ppm) 132.99, 132.07, 128.18, 118.38, 112.24, 92.67, 13.20; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[1]

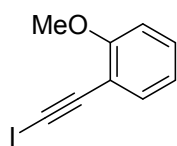


1-(iodoethynyl)-4-methylbenzene (3ao): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether afforded the title compound as pale yellow oil; yield 469.6 mg, 97%. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.33 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H); ¹³C NMR(CDCl₃, 101 MHz): δ (ppm) 139.12, 132.31, 129.10, 120.46, 94.36, 21.66, 5.14;

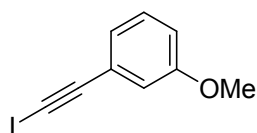
the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[1]



2-(4-(iodoethynyl)phenyl)acetonitrile (3ap): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether and ethyl acetate (petroleum ether/ethyl acetate = 10:1) afforded the title compound as yellow solid, Mp. 79-80 °C; yield 532.0 mg, 99%. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.44 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 3.75 (s, 2H); ¹³C NMR(CDCl₃, 101 MHz): δ (ppm) 133.09, 130.56, 127.95, 123.41, 117.43, 93.31, 23.66, 7.98. HRMS (EI): *m/z* (%): 266.9545, calcd for C₁₀H₆NI⁺: 266.9548.

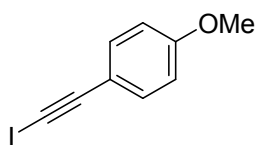


1-(iodoethynyl)-2-methoxybenzene (3aq): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether and ethyl acetate (petroleum ether/ethyl acetate = 10:1) afforded the title compound as pale yellow oil; yield 500.6 mg, 97%. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.40 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.31-7.27 (m, 1H), 6.92-6.86 (m, 2H), 3.88 (s, 3H); ¹³C NMR(CDCl₃, 101 MHz): δ (ppm) 160.97, 134.40, 130.29, 120.35, 112.50, 110.61, 90.41, 55.84, 9.60; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[3]

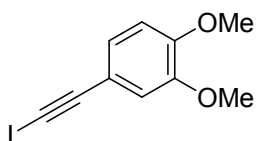


1-(iodoethynyl)-3-methoxybenzene (3ar): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether afforded the title compound as colorless oil; yield 505.8 mg, 98%. ¹H NMR (CDCl₃, 400

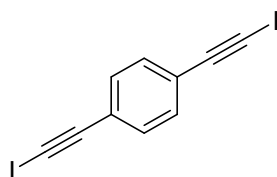
MHz): δ (ppm) 7.24-7.20 (m, 1H), 7.05-7.02 (m, 1H), 6.97-6.96 (m, 1H), 6.90-6.87 (m, 1H), 3.79 (s, 3H); ^{13}C NMR(CDCl_3 , 101 MHz): δ (ppm) 159.26, 129.41, 124.96, 124.40, 117.15, 115.68, 94.16, 55.39, 6.39; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[6]



1-(iodoethynyl)-4-methoxybenzene (3as): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether afforded the title compound as pale yellow oil; yield 474.8 mg, 92%. ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) 7.37 (d, $J = 8.8$ Hz, 2H), 6.83 (d, $J = 8.8$ Hz, 2H), 3.81 (s, 3H); ^{13}C NMR(CDCl_3 , 101 MHz): δ (ppm) 160.02, 133.87, 115.62, 113.93, 94.08, 55.40, 4.11; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[1]

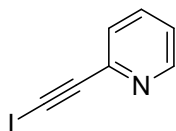


4-(iodoethynyl)-1,2-dimethoxybenzene (3at): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether and ethyl acetate (petroleum ether/ethyl acetate = 10:1) afforded the title compound as pale yellow oil; yield 570.3 mg, 99%. ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) 7.04 (dd, $J = 8.0, 2.0$ Hz, 1H), 6.93 (d, $J = 2.0$ Hz, 1H), 6.78 (d, $J = 8.0$ Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H); ^{13}C NMR(CDCl_3 , 101 MHz): δ (ppm) 150.03, 148.53, 125.83, 115.69, 114.92, 110.85, 94.21, 56.00, 4.05; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[7]

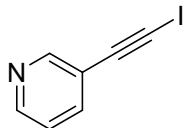


1,4-bis(iodoethynyl)benzene (3au): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether afforded the title

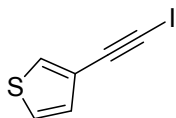
compound as brown yellow solid; yield 748.3 mg, 99%. $^1\text{H NMR}$ (DMSO- d_6 , 400 MHz): δ (ppm) 7.40 (s, 4H); $^{13}\text{C NMR}$ (DMSO- d_6 , 101 MHz): δ (ppm) 132.09, 123.22, 92.09, 21.10; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[1]



2-(iodoethynyl)pyridine (3av): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether and ethyl acetate (petroleum ether/ethyl acetate = 10:1) afforded the title compound as white solid; yield 403.1 mg, 88%. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 8.57-8.55 (m, 1H), 7.65 (dt, $J = 7.7, 2.0$ Hz, 1H), 7.42-7.39 (m, 1H), 7.25-7.22 (m, 1H); $^{13}\text{C NMR}$ (CDCl_3 , 101 MHz): δ (ppm) 149.91, 143.11, 136.24, 127.67, 123.42, 93.81, 10.98; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[2]

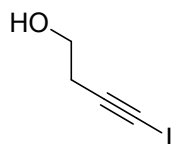


3-(iodoethynyl)pyridine (3aw): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether and ethyl acetate (petroleum ether/ethyl acetate = 10:1) afforded the title compound as pale yellow solid; yield 425.9 mg, 93%. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 8.67 (dd, $J = 2.0, 1.2$ Hz, 1H), 8.53 (dd, $J = 4.8, 1.6$ Hz, 1H), 7.71 (dt, $J = 8.0, 2.0$ Hz, 1H), 7.27-7.23 (m, 1H); $^{13}\text{C NMR}$ (CDCl_3 , 101 MHz): δ (ppm) 153.06, 148.96, 139.35, 123.05, 120.72, 90.76, 11.93; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[1]

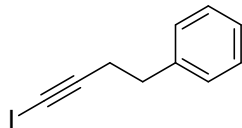


3-(iodoethynyl)thiophene (3ax): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether afforded the title

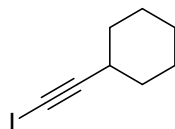
compound as pale yellow oil; yield 426.5 mg, 91%. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 7.48 (dd, $J = 2.8, 1.2$ Hz, 1H), 7.26 (dd, $J = 5.0, 2.8$ Hz, 1H), 7.11 (dd, $J = 5.0, 1.2$ Hz, 1H); $^{13}\text{C NMR}$ (CDCl_3 , 101 MHz): δ (ppm) 130.44, 130.11, 125.30, 122.60, 89.29, 6.05; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[1]



4-iodobut-3-yn-1-ol (3ay): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether and ethyl acetate (petroleum ether/ethyl acetate = 5:1) afforded the title compound as yellow oil; yield 301.8 mg, 77%. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 3.74-3.69 (m, 2H), 2.62 (t, $J = 6.2$ Hz, 2H), 2.09 (brs, 1H); $^{13}\text{C NMR}$ (CDCl_3 , 101 MHz): δ (ppm) 91.38, 60.94, 25.05, -4.07; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[8]

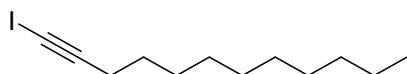


(4-iodobut-3-yn-1-yl)benzene (3az): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether afforded the title compound as pale yellow oil; yield 450.7 mg, 88%. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 7.31-7.27 (m, 2H), 7.23-7.18 (m, 3H), 2.83 (t, $J = 7.6$ Hz, 2H), 2.63 (t, $J = 7.4$ Hz, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 101 MHz): δ (ppm) 140.31, 128.53, 128.49, 126.49, 93.98, 35.00, 23.12, -5.72; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[1]

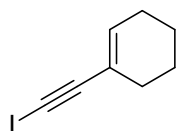


(iodoethynyl)cyclohexane (3ba): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether afforded the title compound as pale yellow oil; yield 328.2 mg, 70%. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ

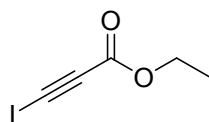
(ppm) 2.56-2.50 (m, 1H), 1.80-1.66 (m, 4H), 1.52-1.43 (m, 3H), 1.32-1.20 (m, 3H); ^{13}C NMR(CDCl_3 , 101 MHz): δ (ppm) 99.17, 32.60, 31.37, 25.89, 24.90, -7.17; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[9]



1-iodododec-1-yne (3bb): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether afforded the title compound as pale yellow oil; yield 520.1 mg, 89%. ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) 2.35 (t, $J = 7.0$ Hz, 2H), 1.54-1.47 (m, 2H), 1.28-1.26 (m, 14H), 0.90-0.86 (m, 3H); ^{13}C NMR(CDCl_3 , 101 MHz): δ (ppm) 94.99, 32.05, 29.71, 29.64, 29.46, 29.22, 28.93, 28.64, 22.84, 20.97, 14.27, -7.51; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[10]

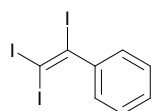


1-(iodoethynyl)cyclohex-1-ene (3bc): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether afforded the title compound as pale yellow oil; yield 371.2 mg, 80%. ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) 6.13-6.11 (m, 1H), 2.11-2.07 (m, 4H), 1.65-1.53 (m, 4H); ^{13}C NMR(CDCl_3 , 101 MHz): δ (ppm) 137.23, 121.41, 96.31, 29.10, 25.66, 22.31, 21.49, 2.09; the overall spectroscopic data are in agreement with assigned structures and consistent with literature.^[11]



ethyl 3-iodopropiolate (3bd): Following general procedure A and purified by silica gel column chromatography, eluting with petroleum ether and ethyl acetate (petroleum ether/ethyl acetate = 15:1) afforded the title compound as white solid Mp. 73-75 °C (literature^[16]: 74.5 °C); yield 416.6 mg, 93%. ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) 4.23 (q, $J = 7.2$ Hz, 2H), 1.31 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR(CDCl_3 , 101 MHz): δ (ppm) 152.43, 87.21, 62.58, 14.10, 13.43; the overall spectroscopic data are

in agreement with assigned structures and consistent with literature.^[12]



(1,2,2-triiodovinyl)benzene (7): Following general procedure C and purified by silica gel column chromatography, eluting with petroleum ether afforded the title compound as pale yellow solid Mp. 106-107 °C (literature^[18]: 107-110 °C); yield 857.6 mg, 89%. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.39-7.33 (m, 3H), 7.27-7.25 (m, 2H); ¹³C NMR(CDCl₃, 101 MHz): δ (ppm) 147.81, 128.86, 128.73, 127.52, 112.58, 22.65.

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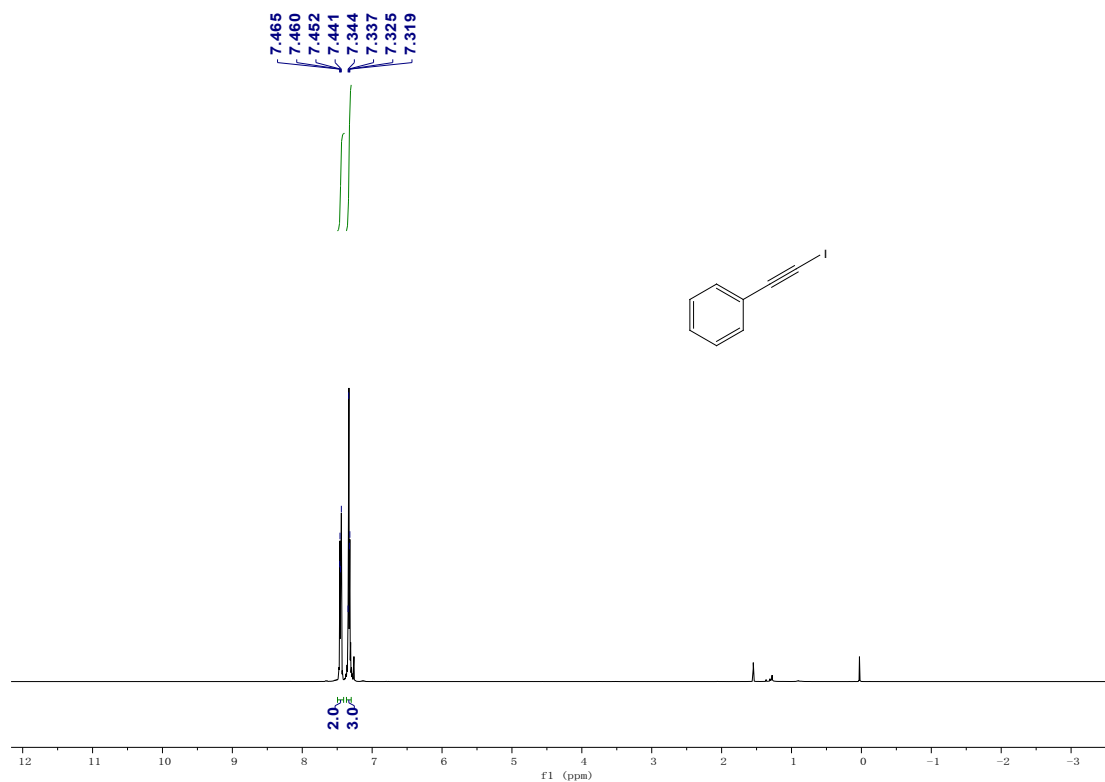
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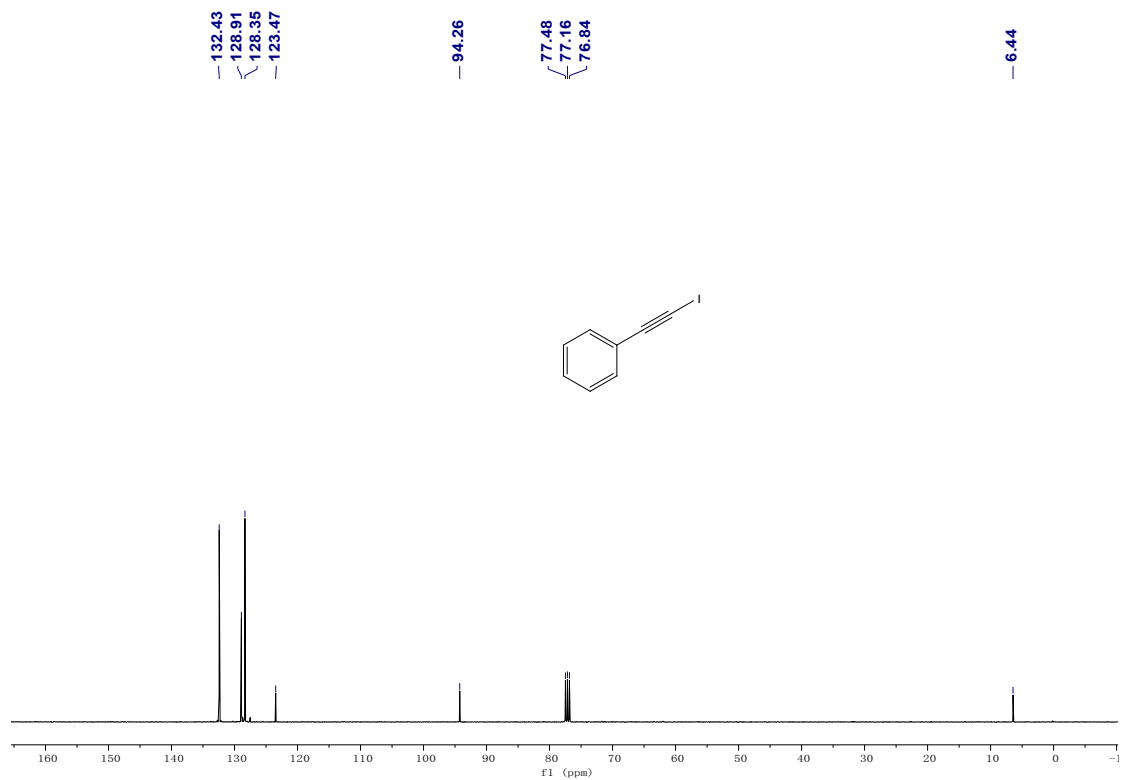
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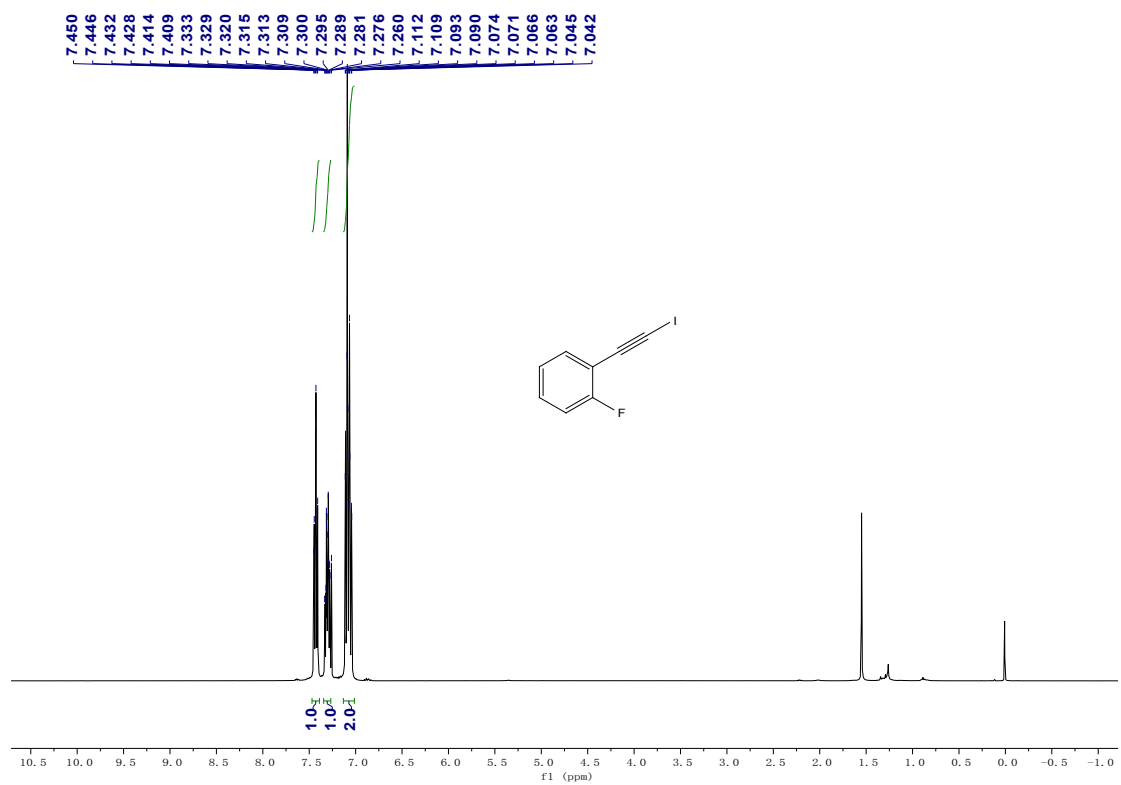
NMR spectra



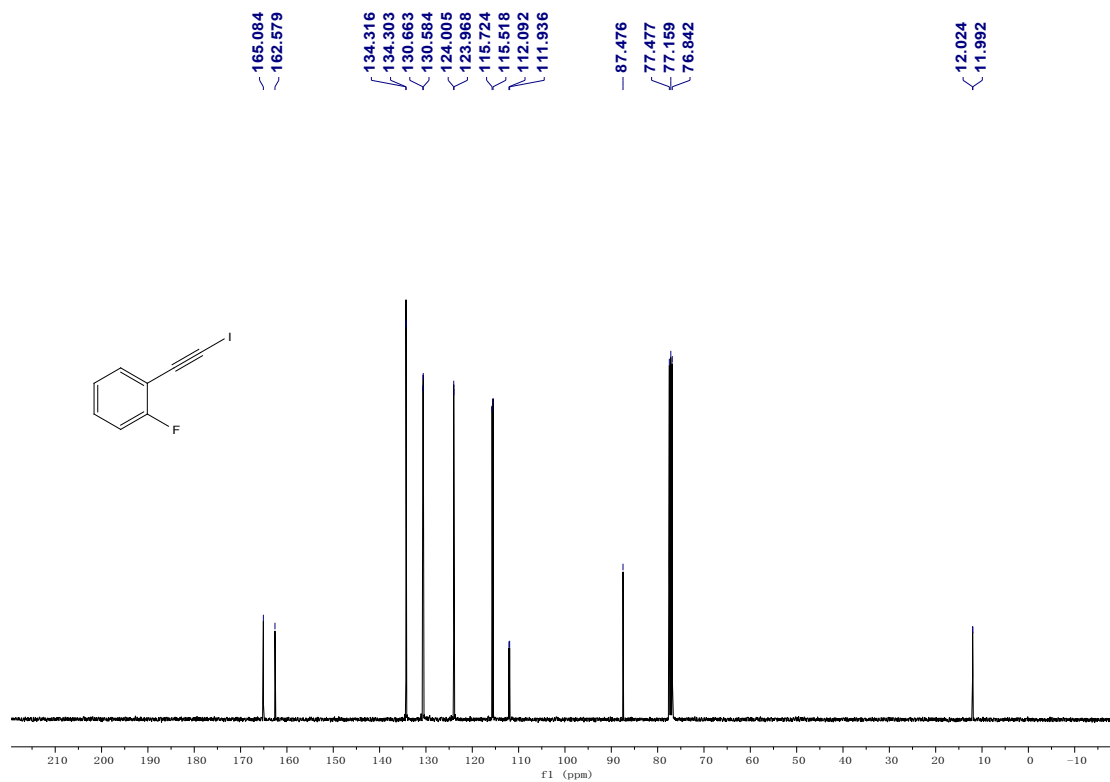
¹H NMR (CDCl₃, 400 MHz) spectra of compound **3aa**



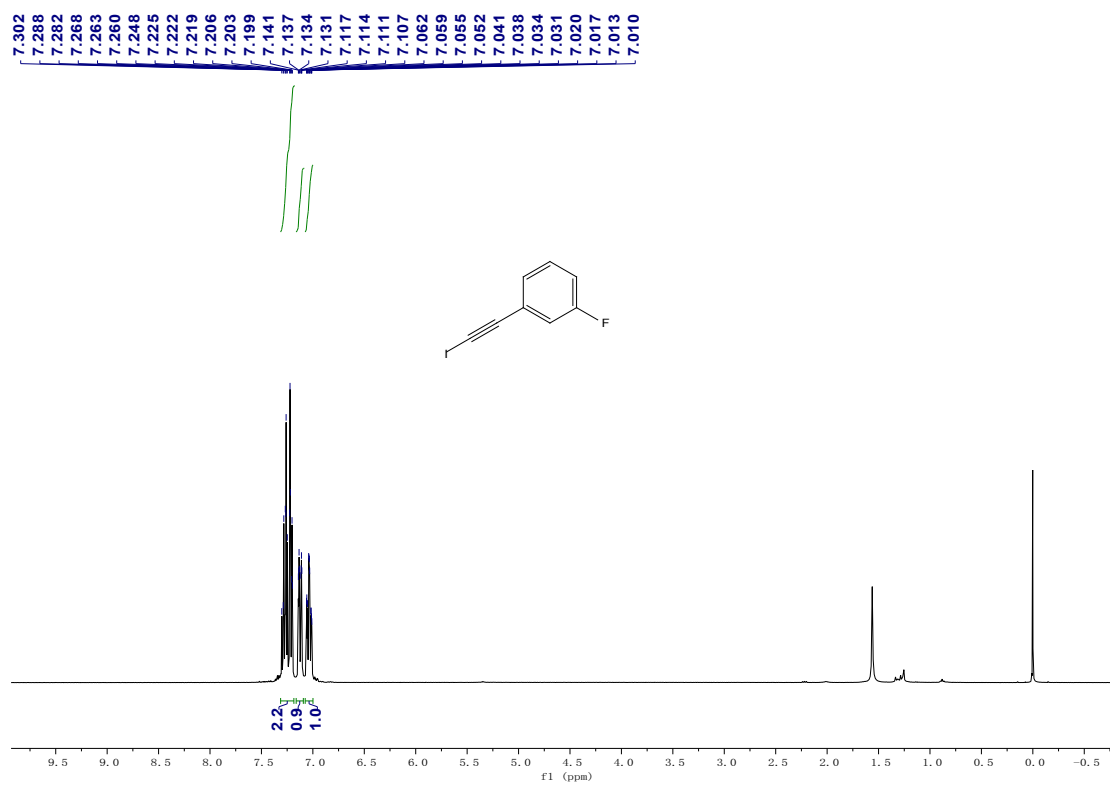
¹³C NMR(CDCl₃, 101 MHz) spectra of compound **3aa**



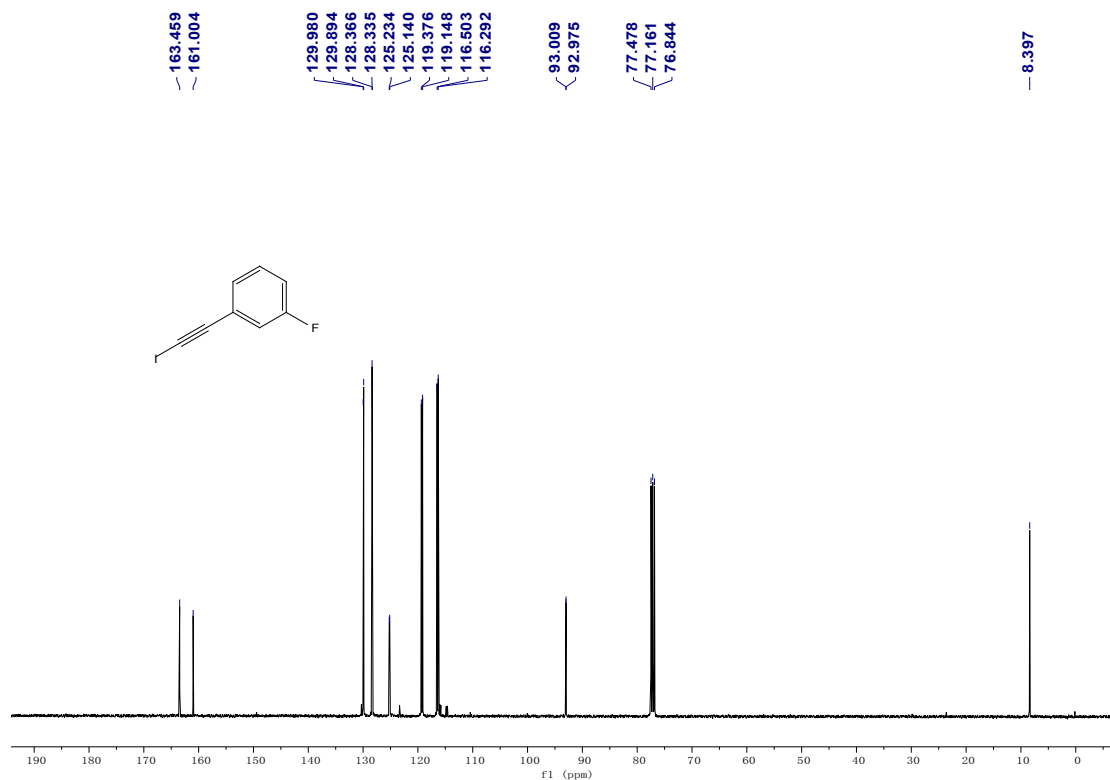
¹H NMR (CDCl₃, 400 MHz) spectra of compound **3ab**



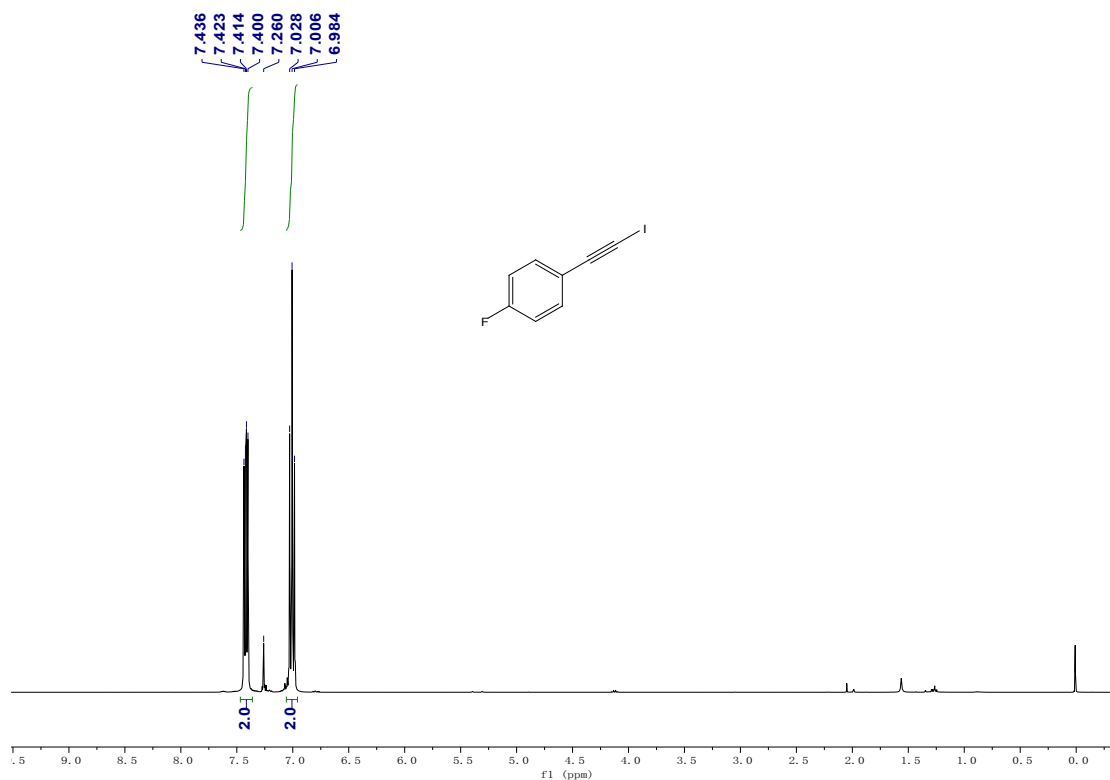
^{13}C NMR (CDCl₃, 101 MHz) spectra of compound **3ab**



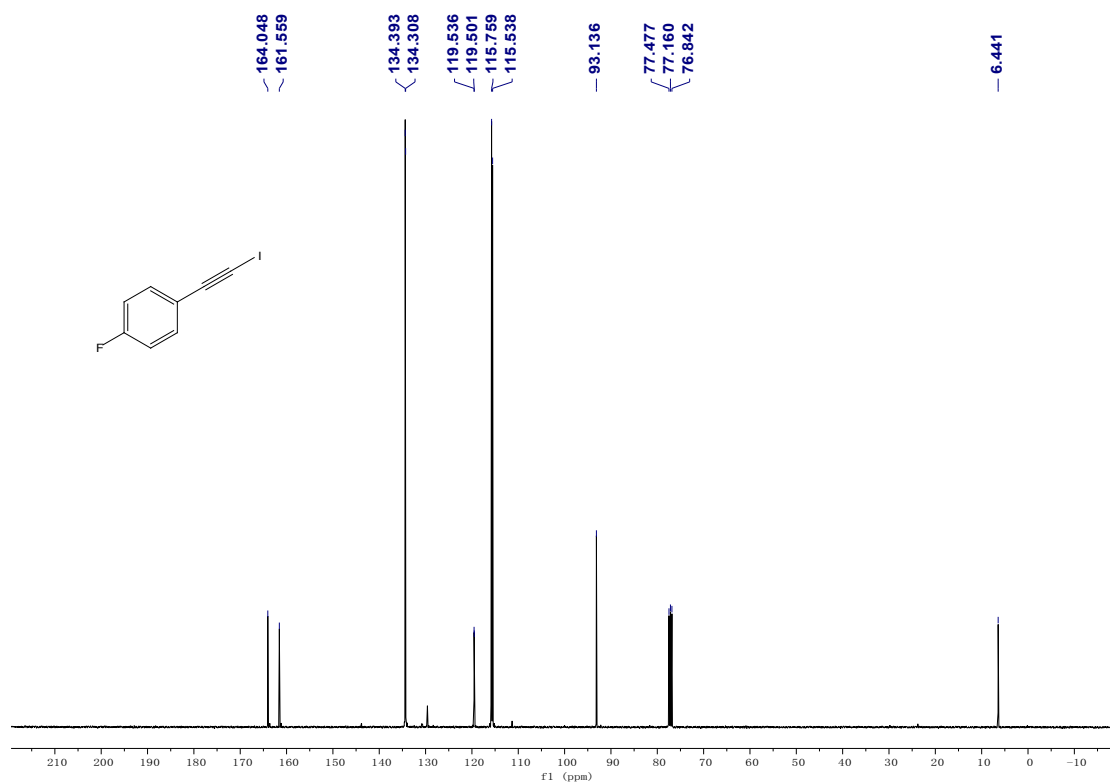
^1H NMR (CDCl₃, 400 MHz) spectra of compound **3ac**



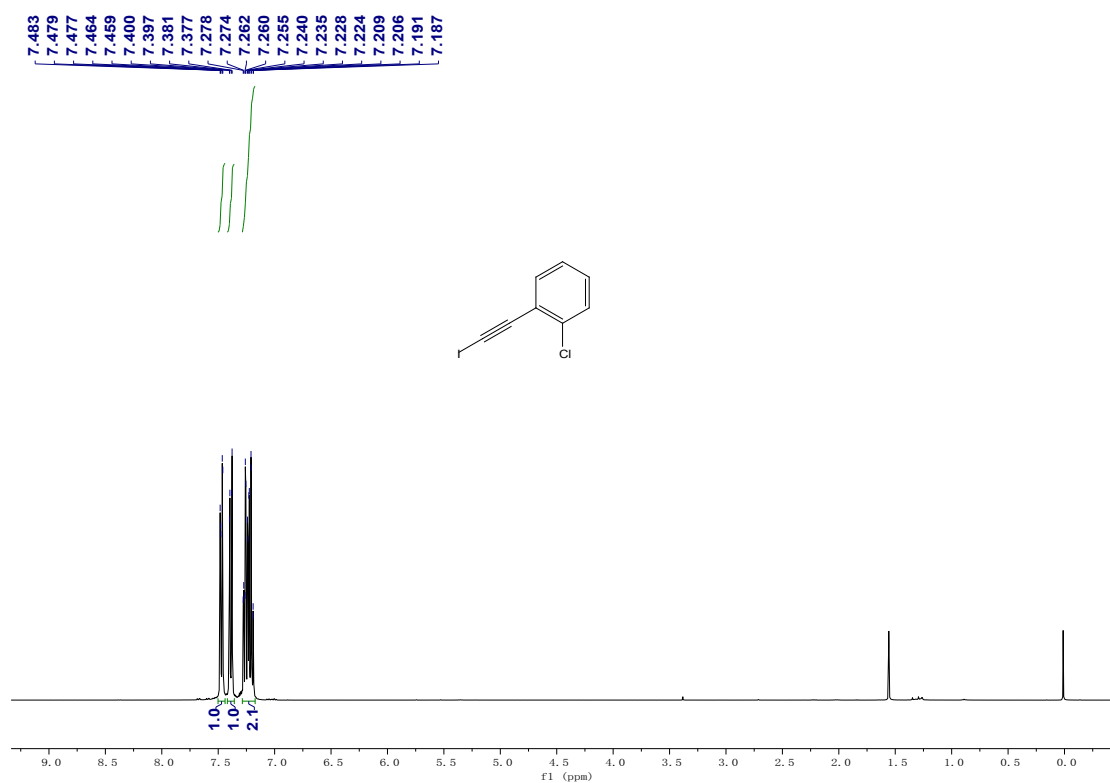
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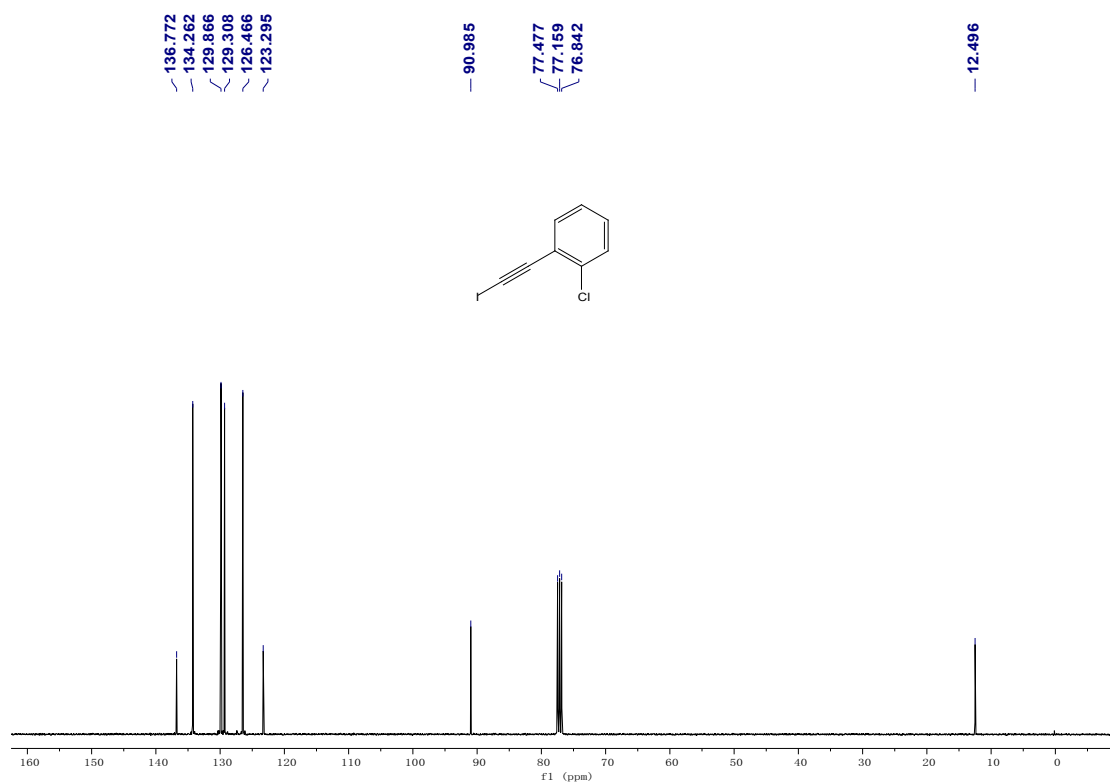
¹H NMR (CDCl₃, 400 MHz) spectra of compound **3ad**



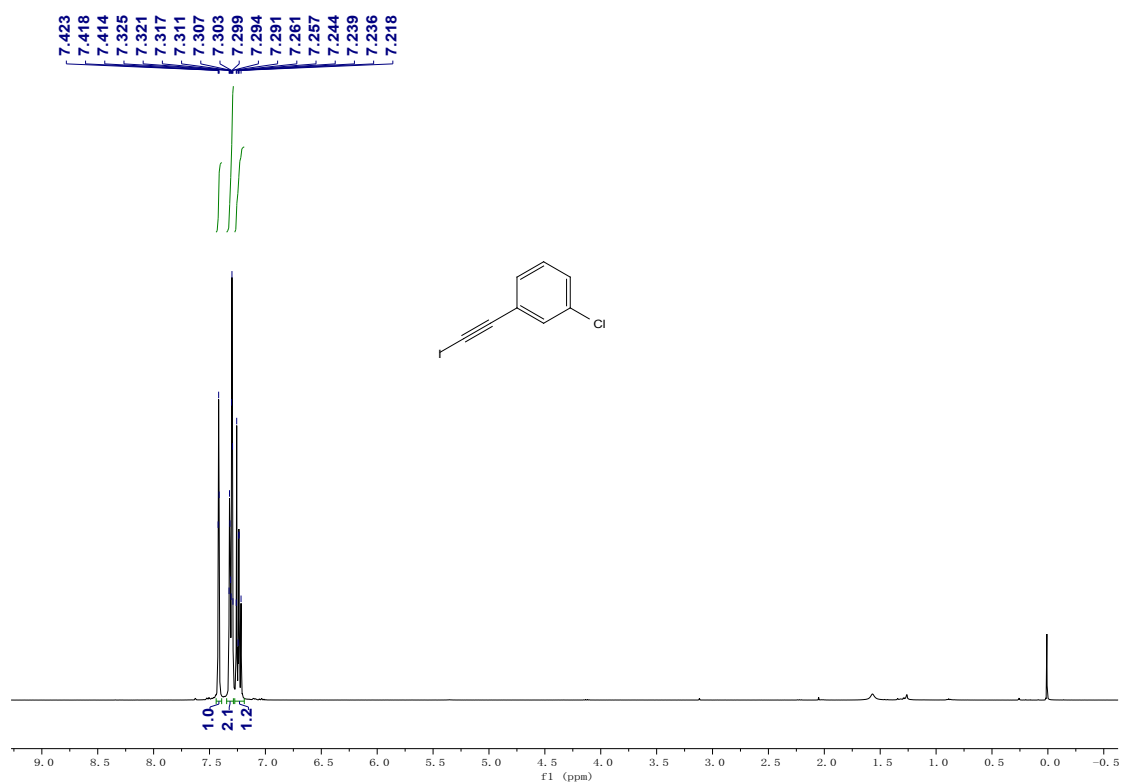
^{13}C NMR(CDCl_3 , 101 MHz) spectra of compound **3ad**



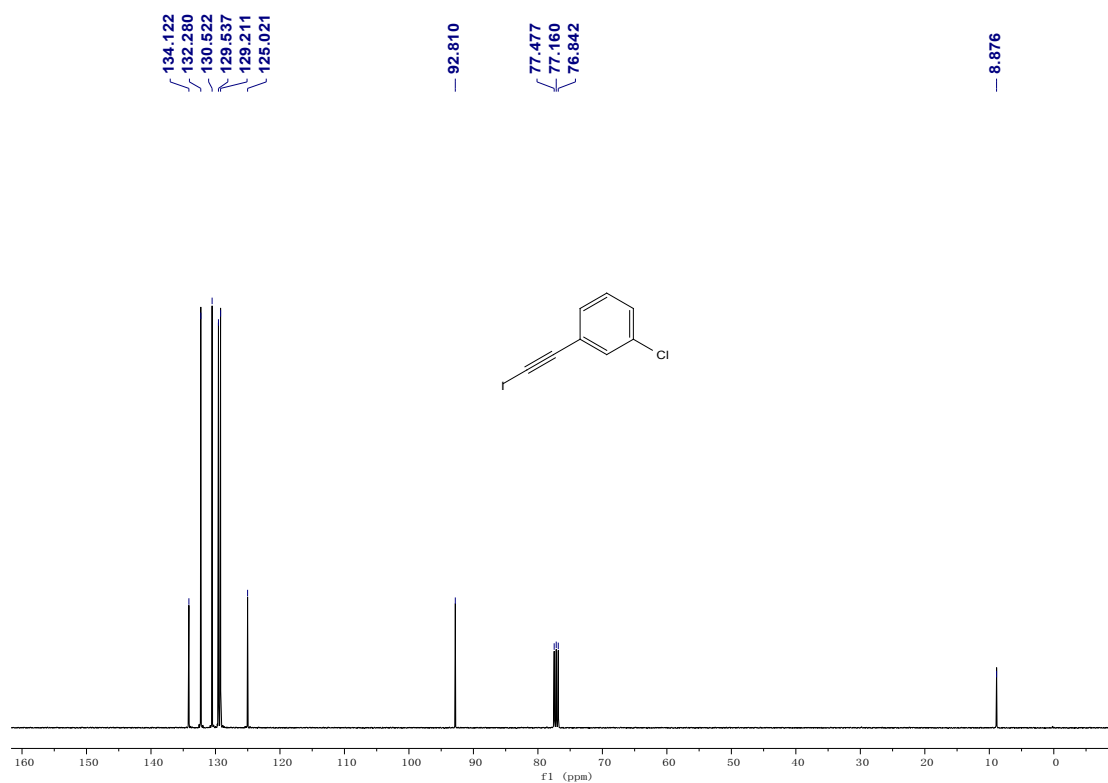
^1H NMR (CDCl_3 , 400 MHz) spectra of compound **3ae**



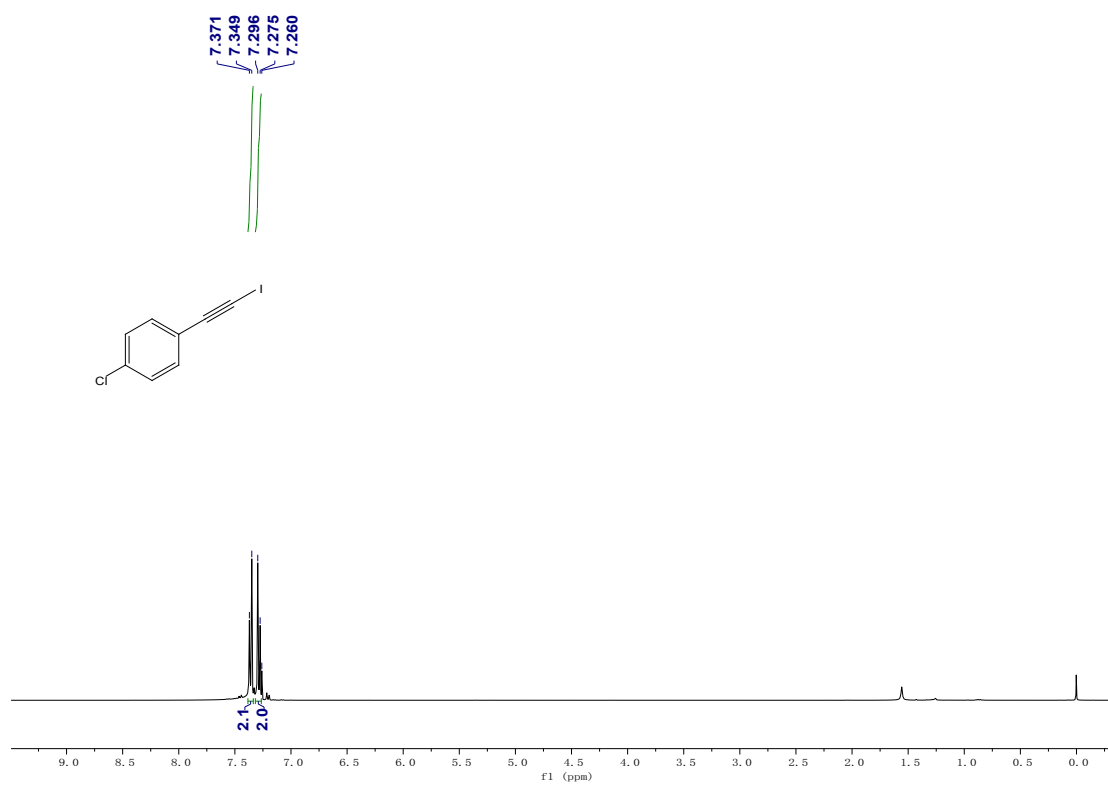
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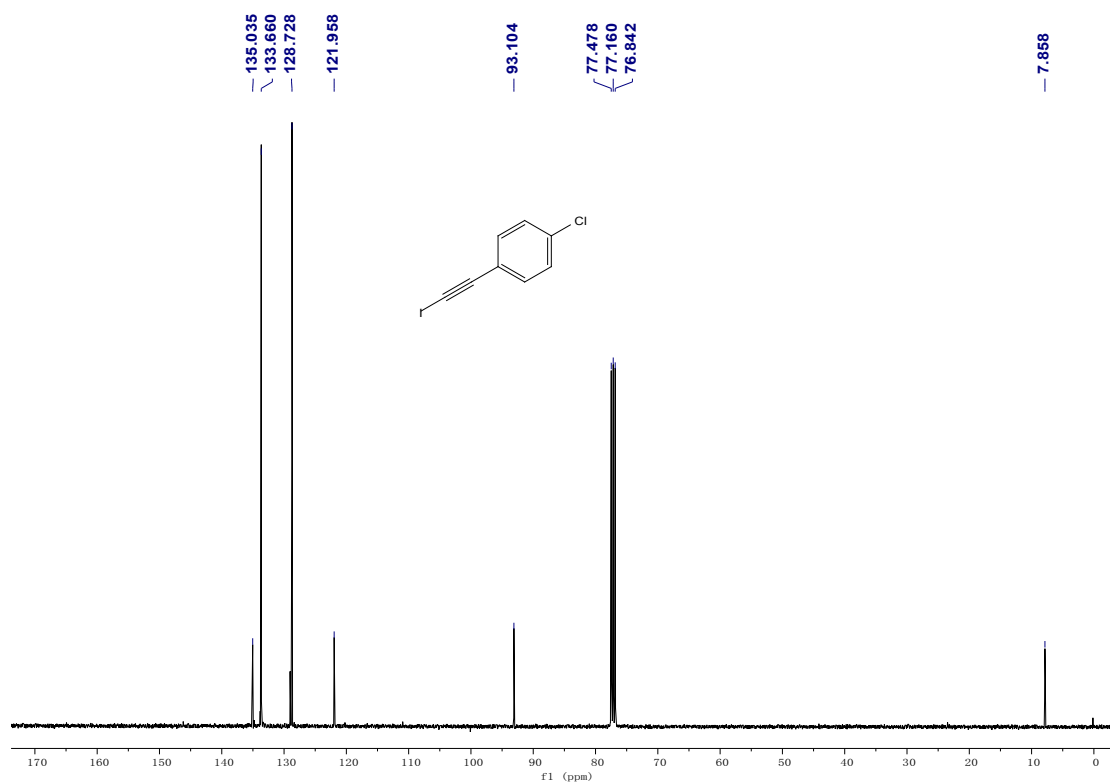
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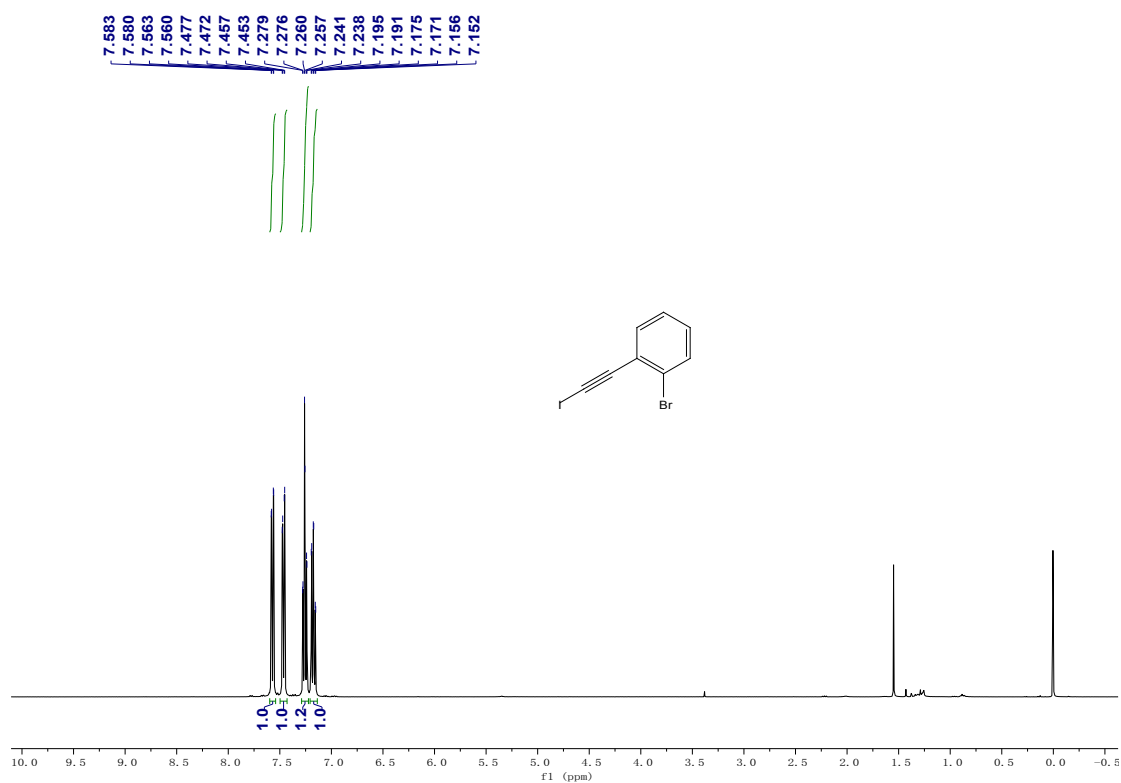
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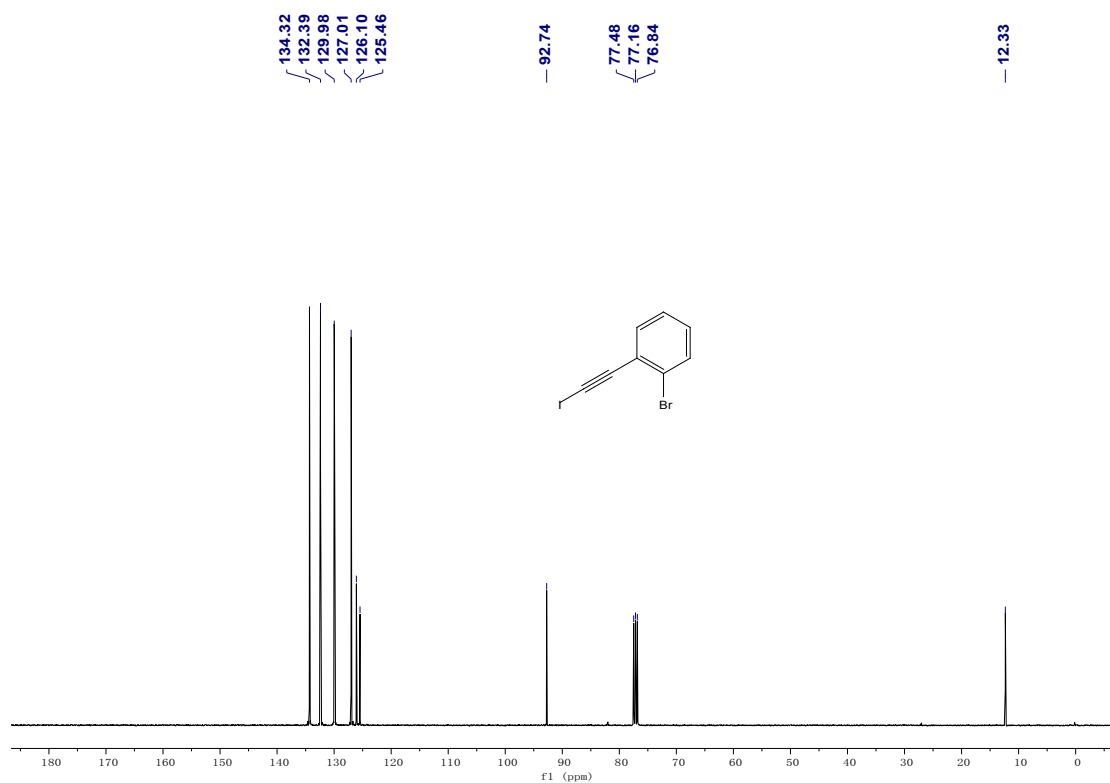
^1H NMR (CDCl_3 , 400 MHz) spectra of compound **3ag**



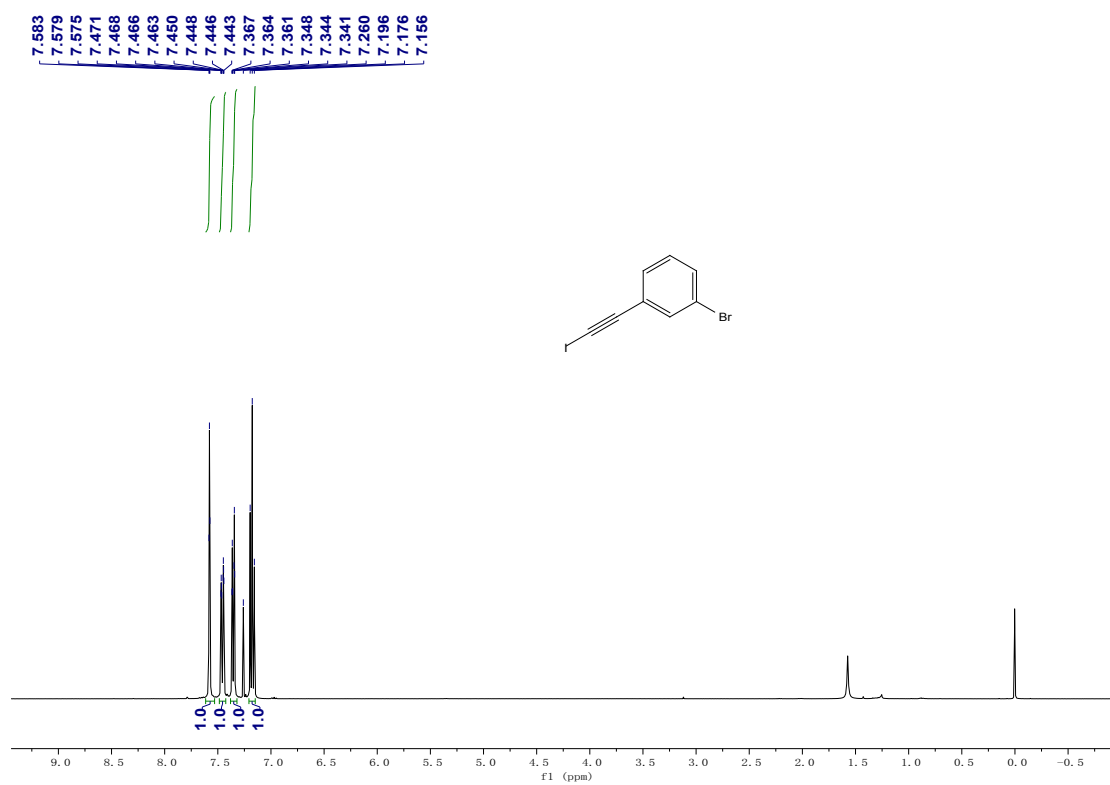
^{13}C NMR(CDCl_3 , 101 MHz) spectra of compound **3ag**



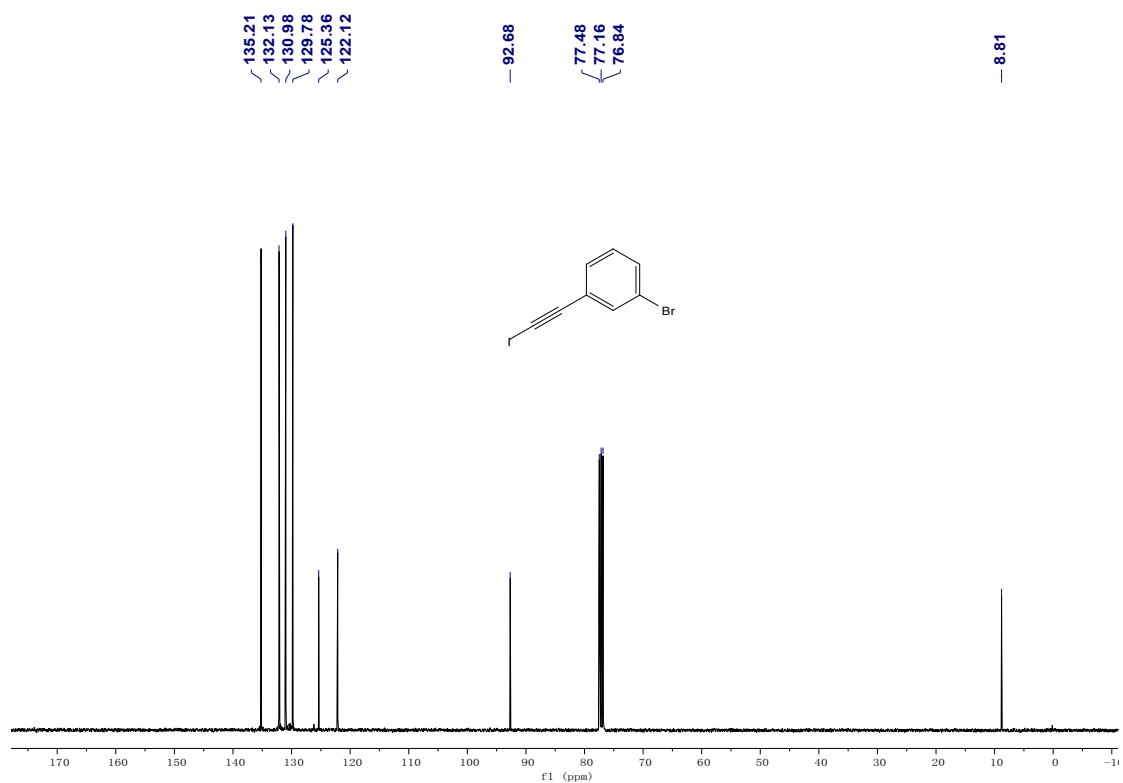
^1H NMR (CDCl_3 , 400 MHz) spectra of compound **3ah**



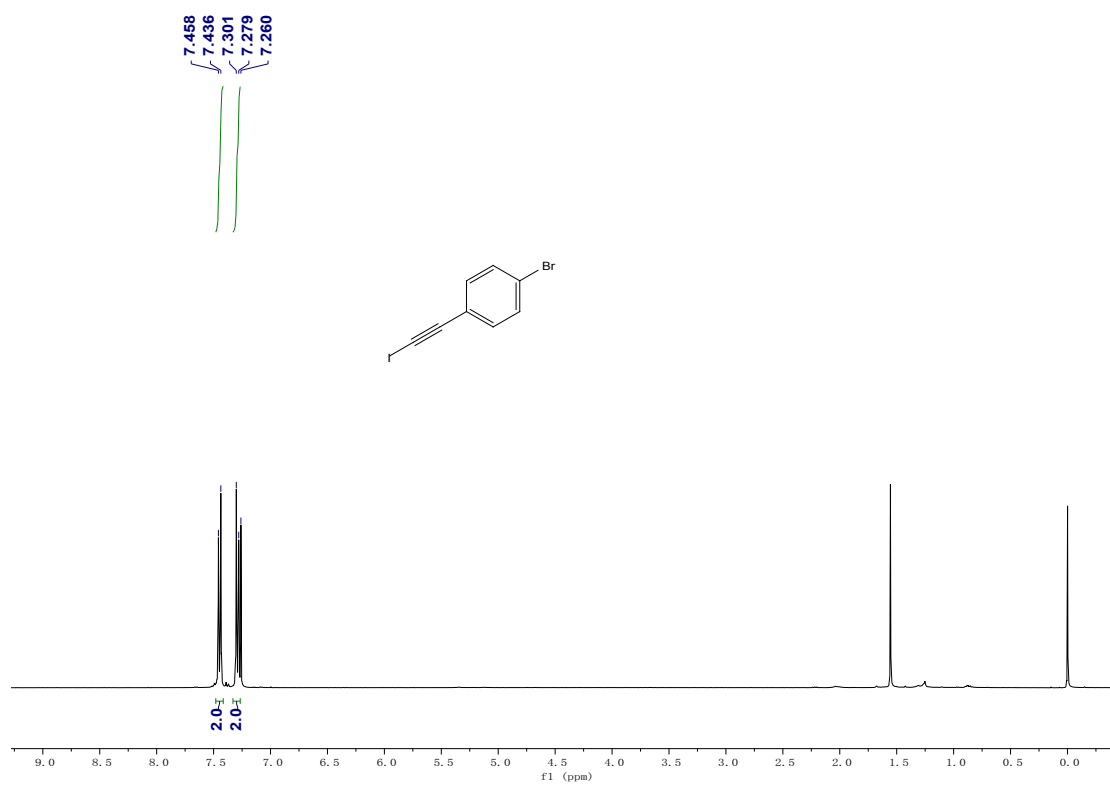
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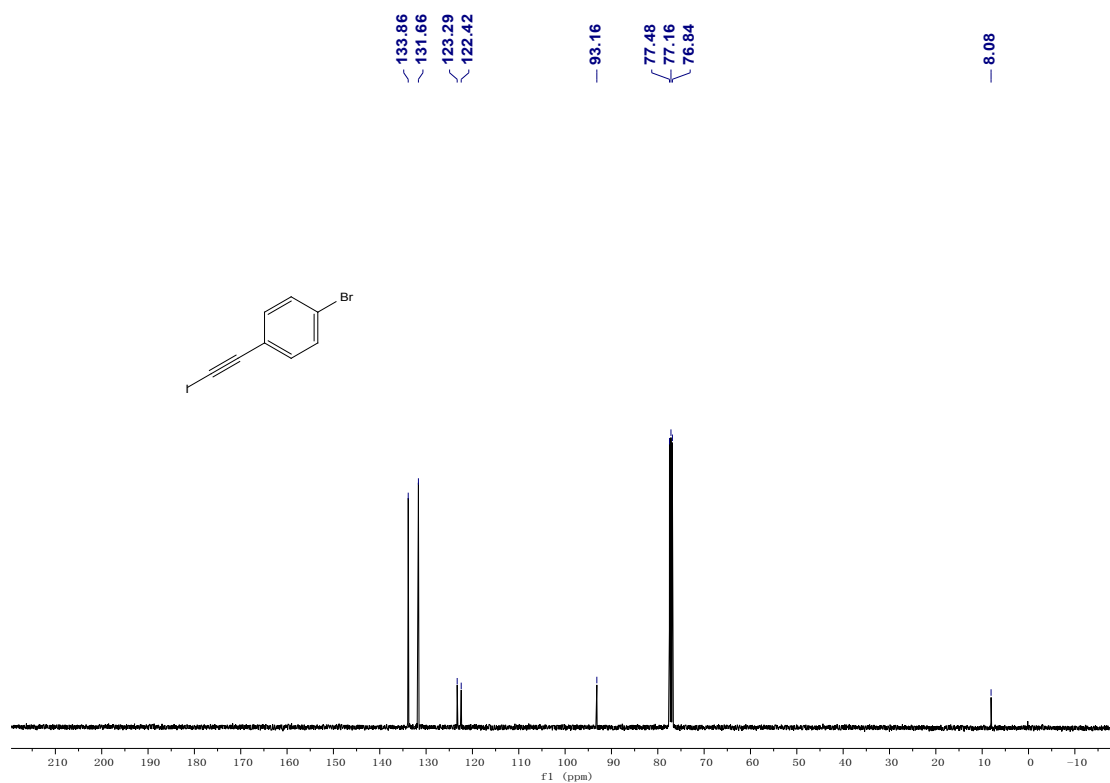
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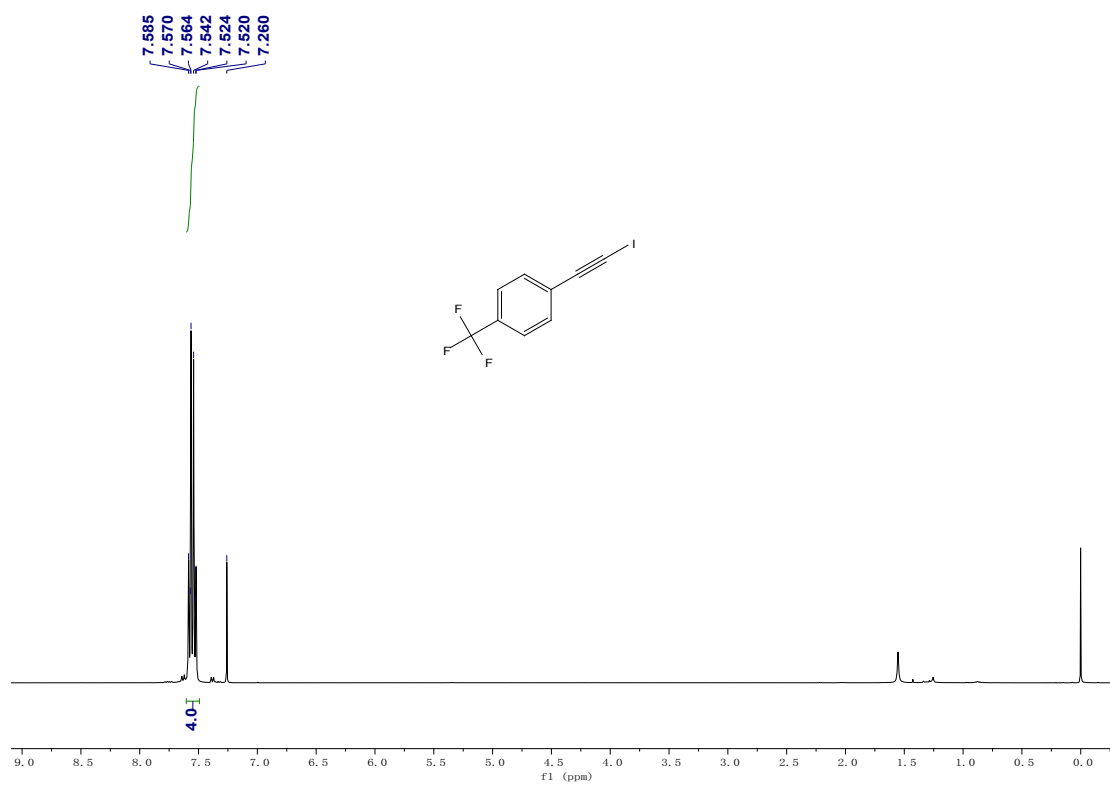
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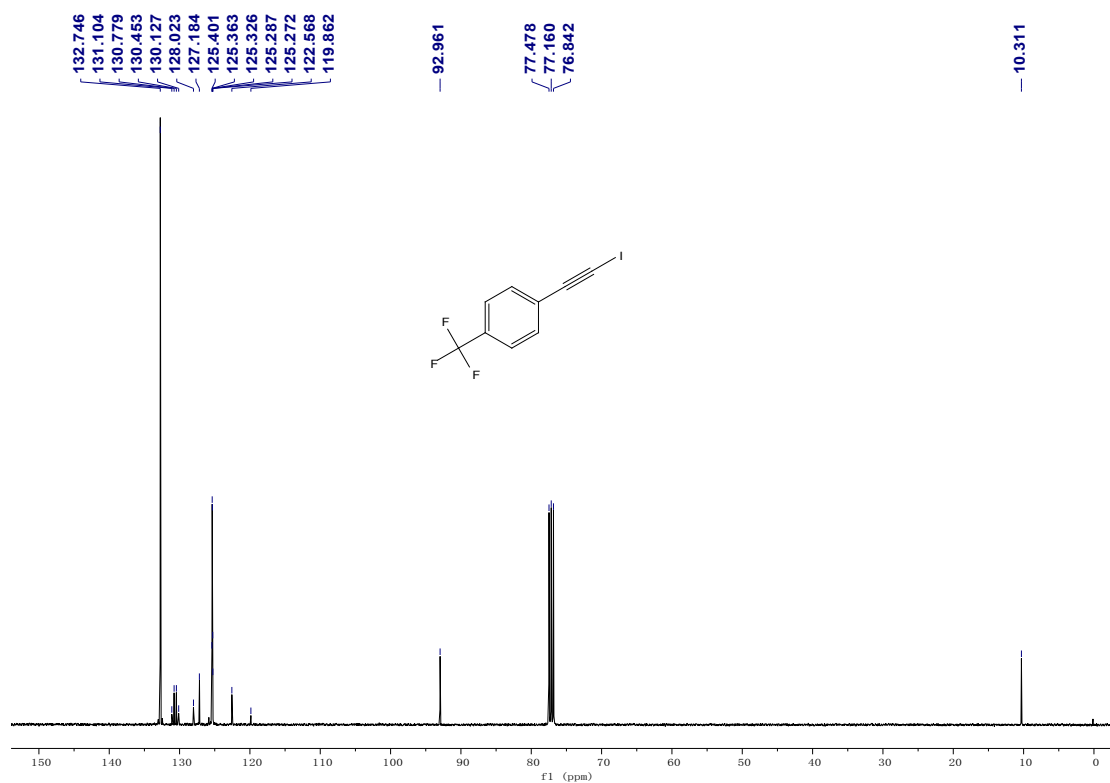
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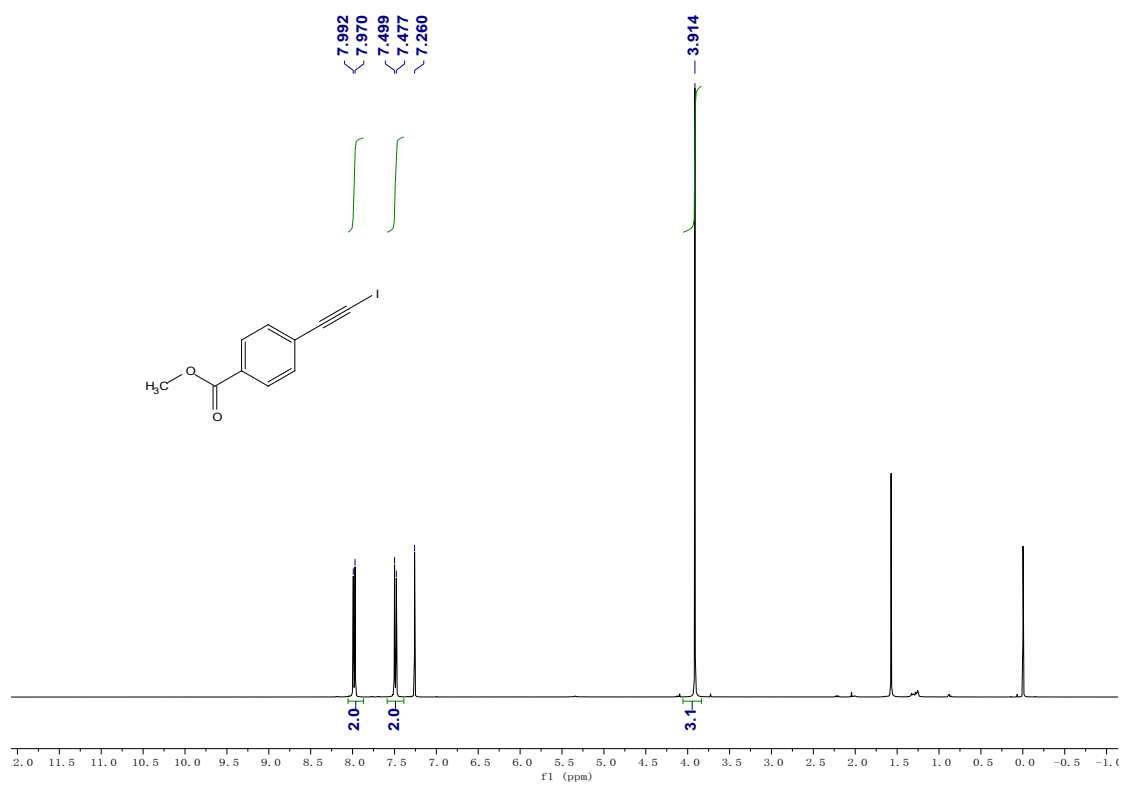
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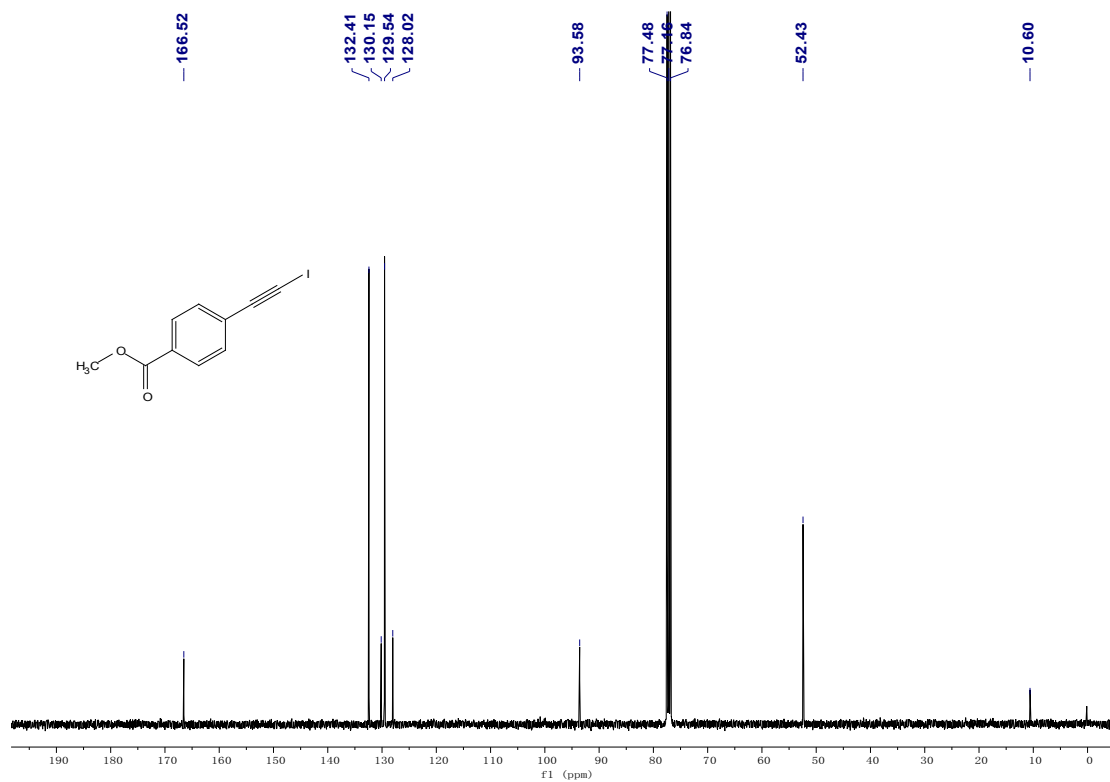
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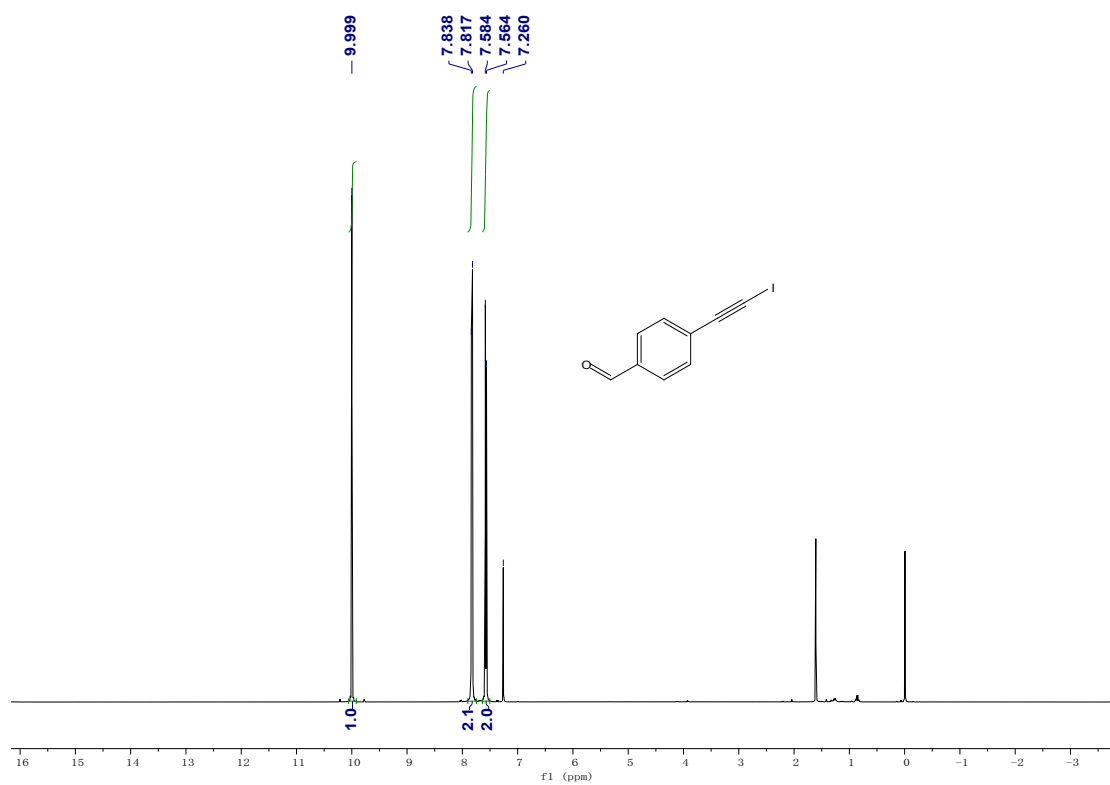
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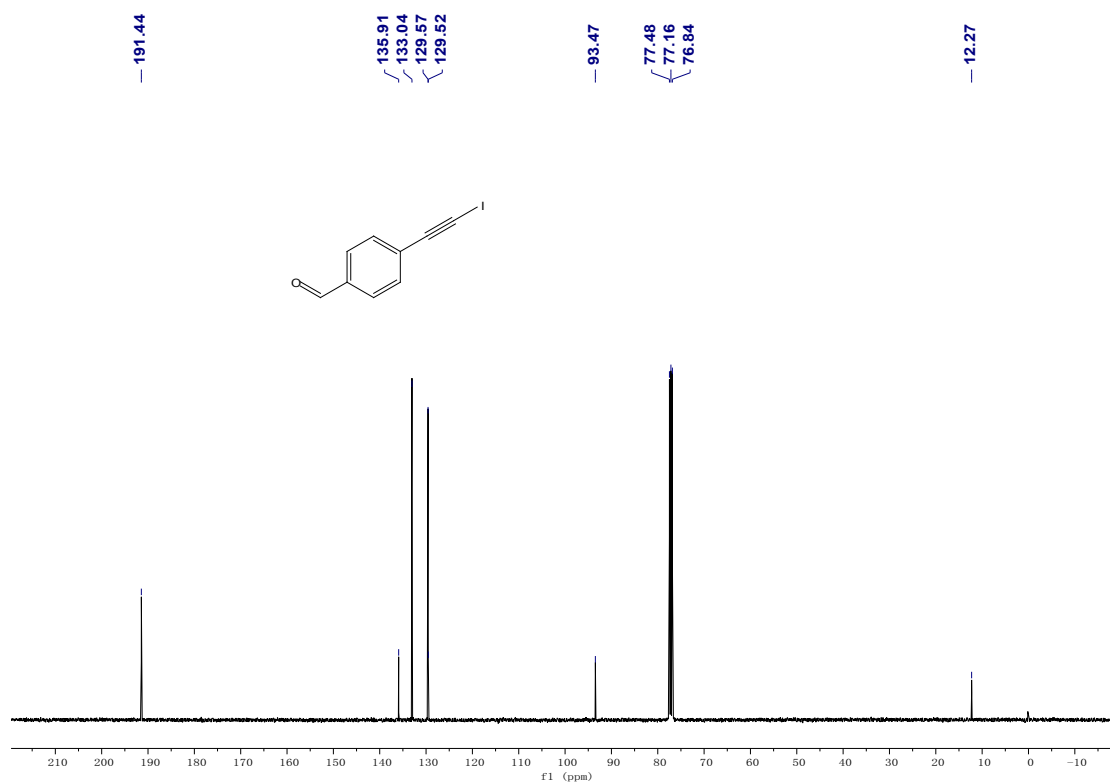
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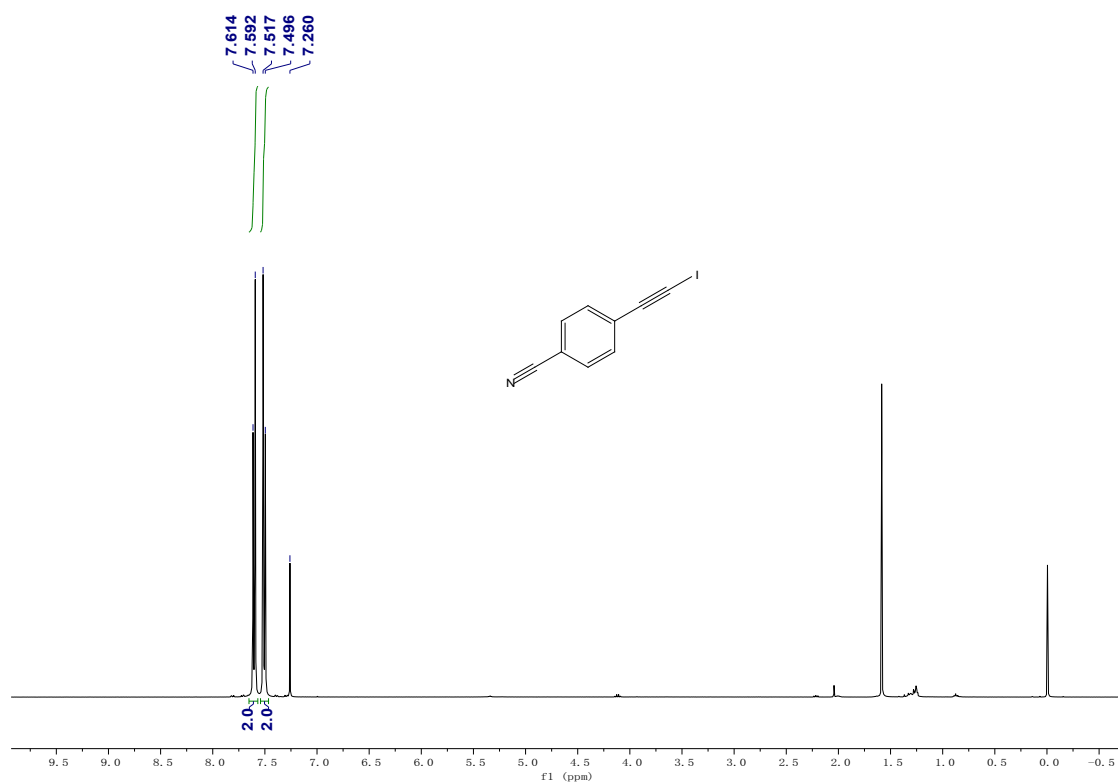
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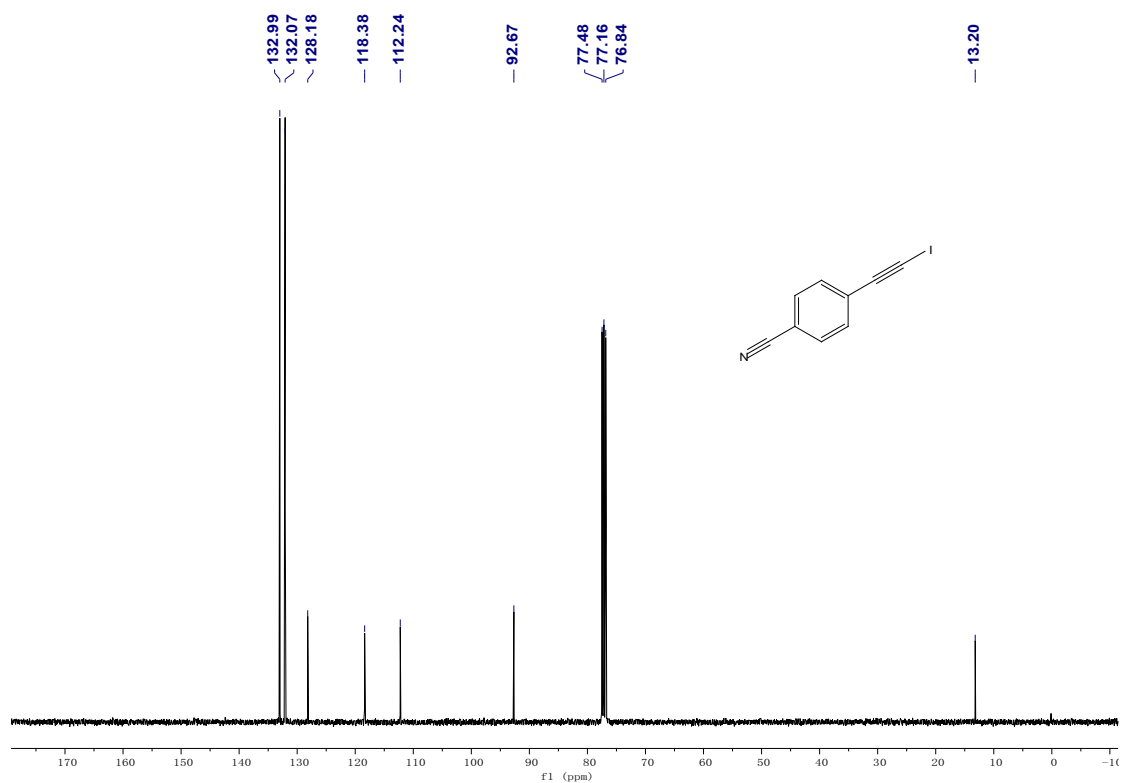
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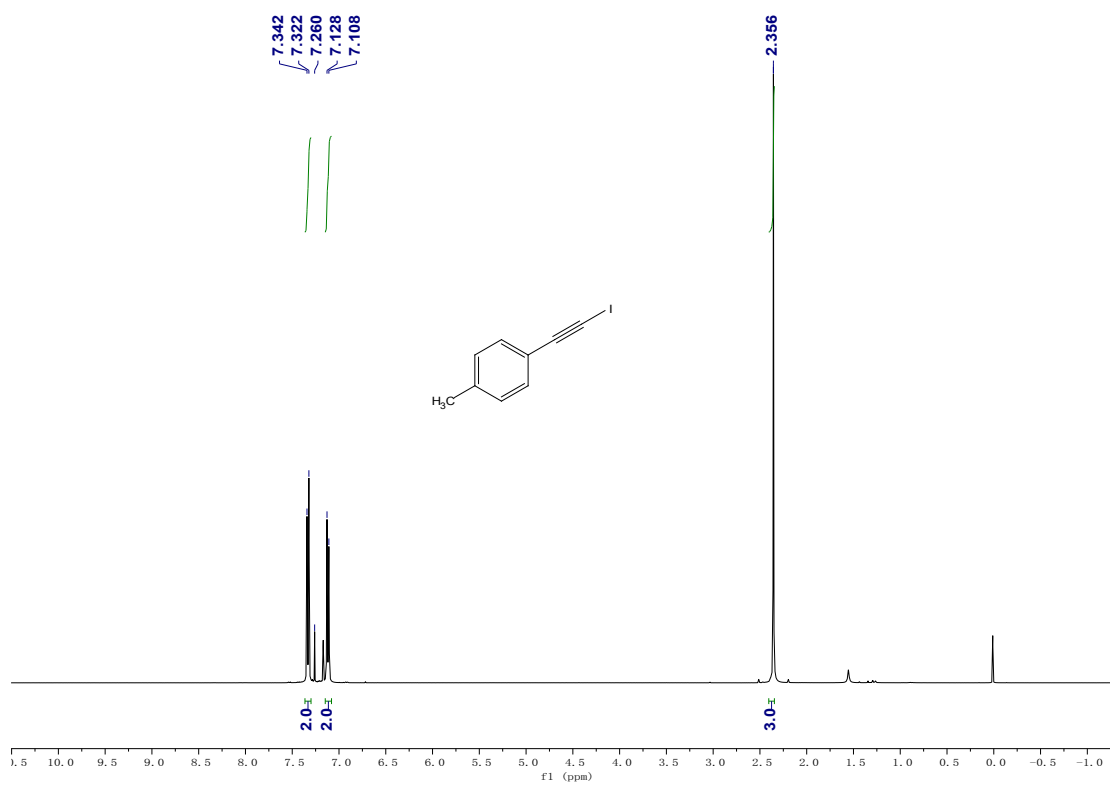
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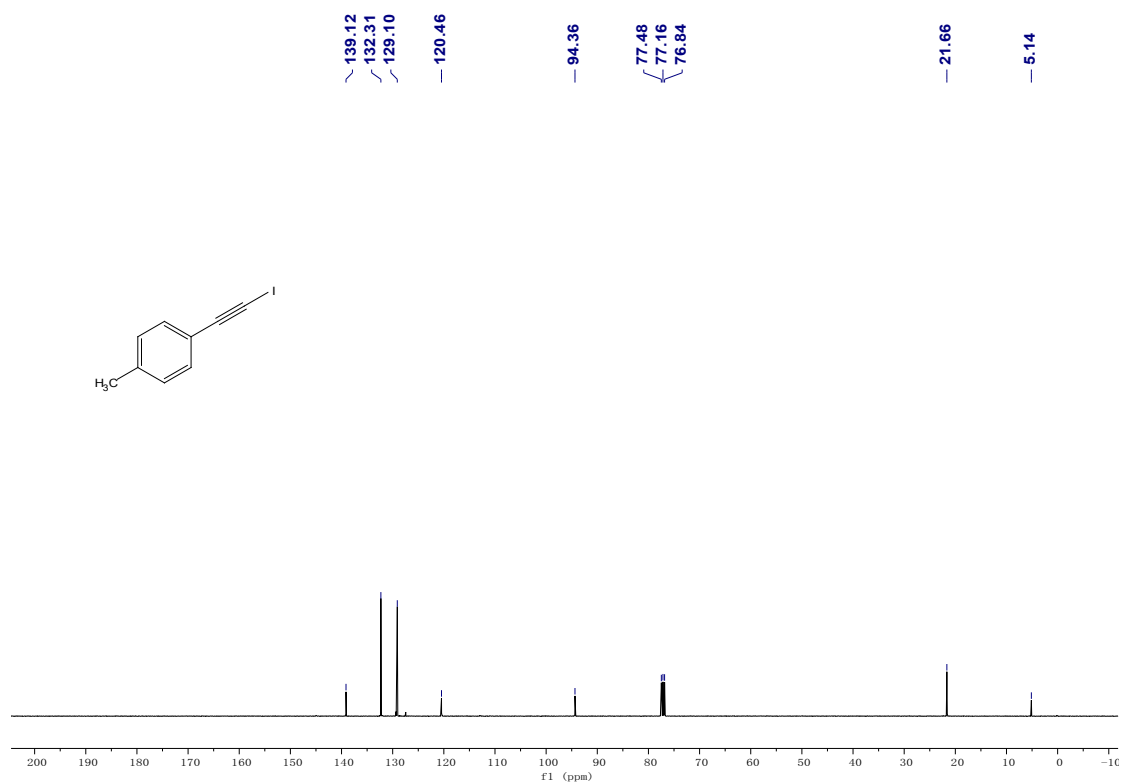
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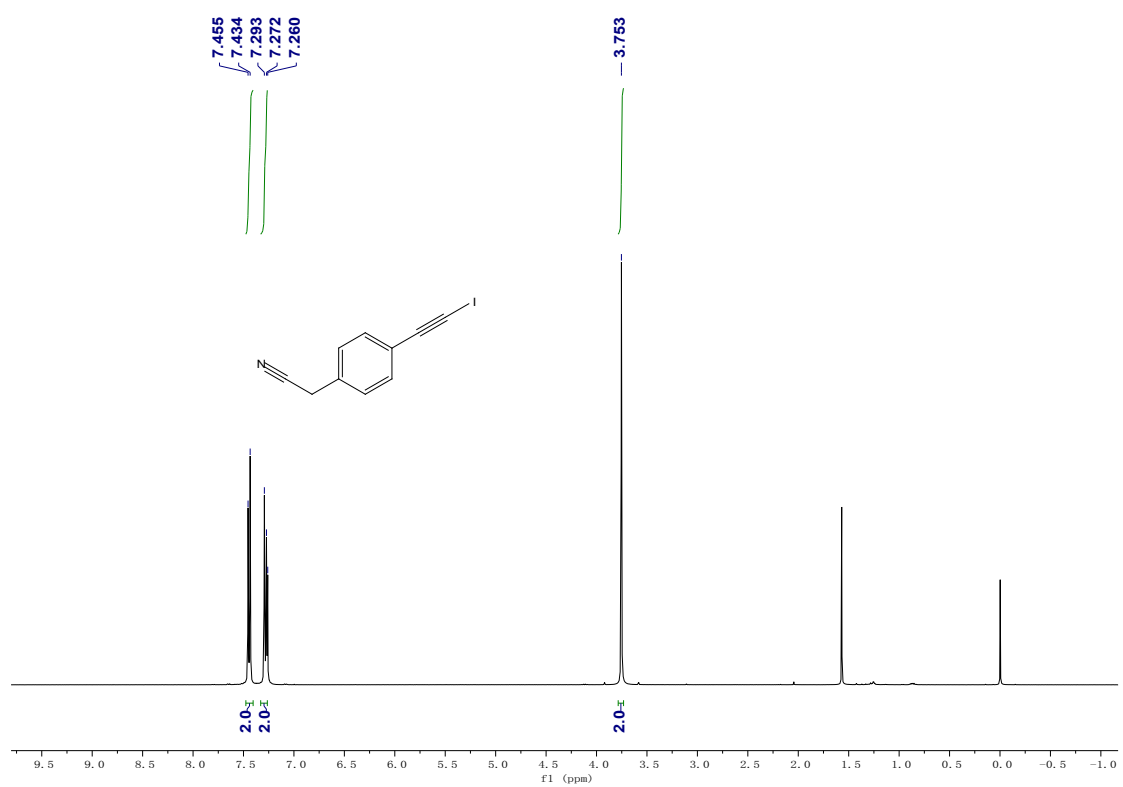
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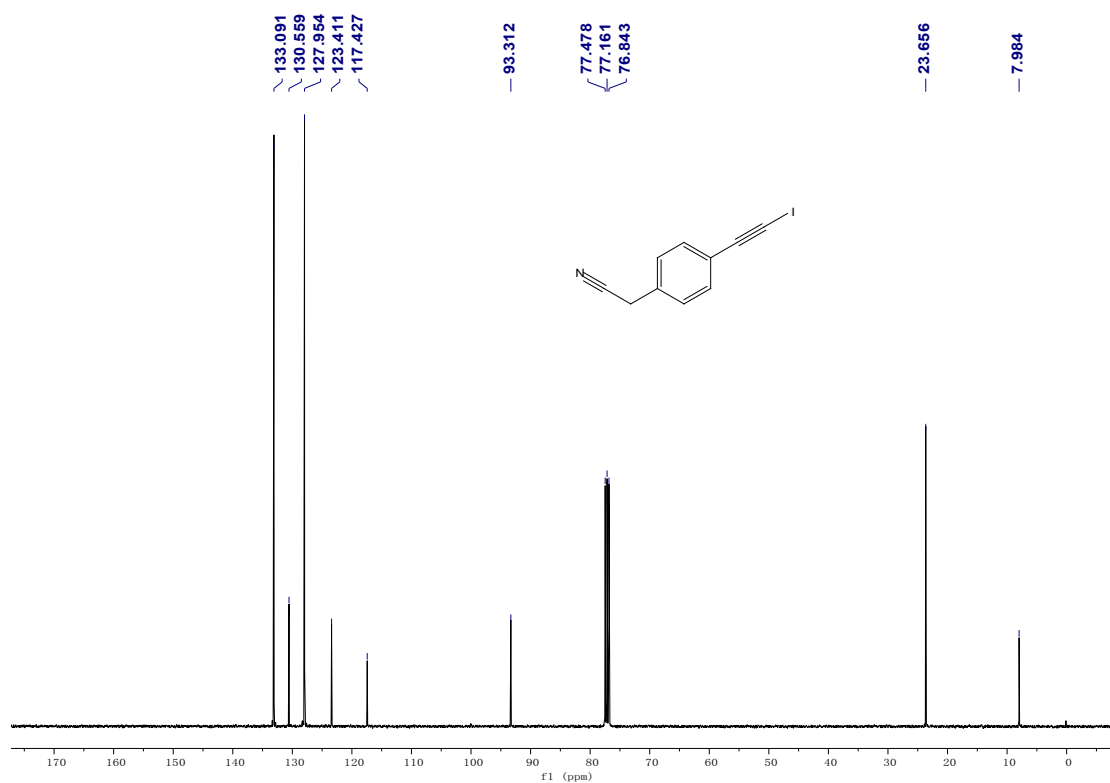
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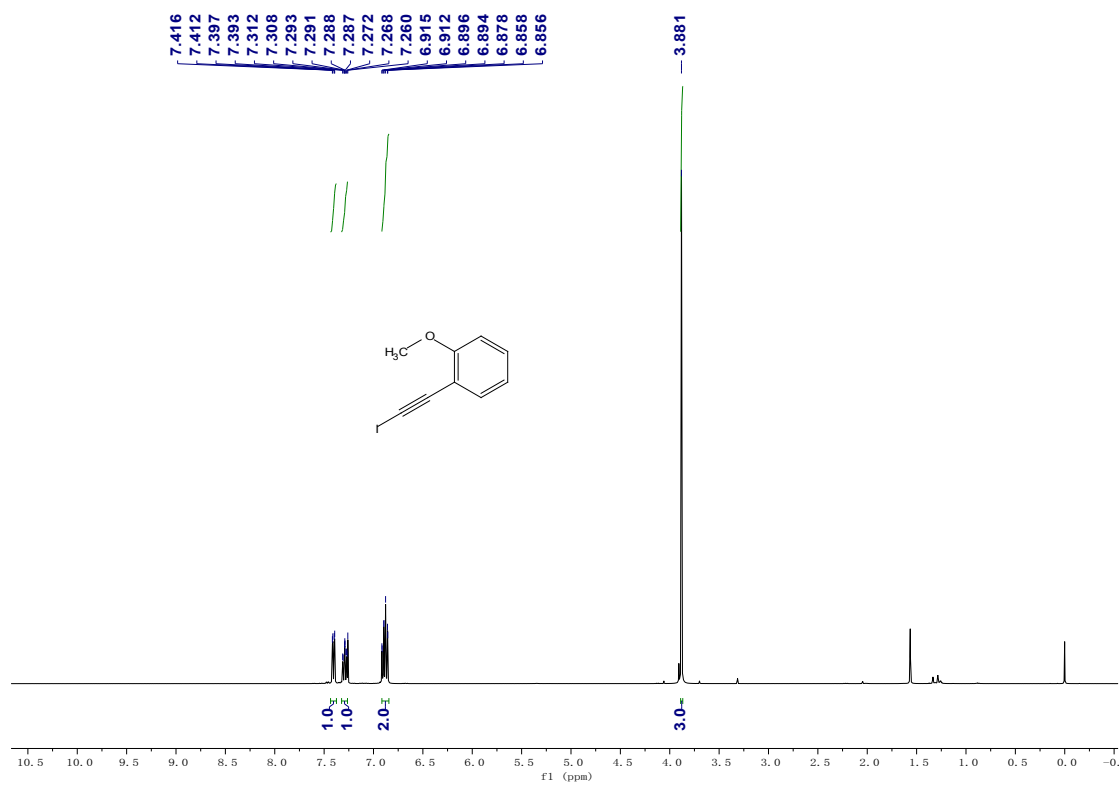
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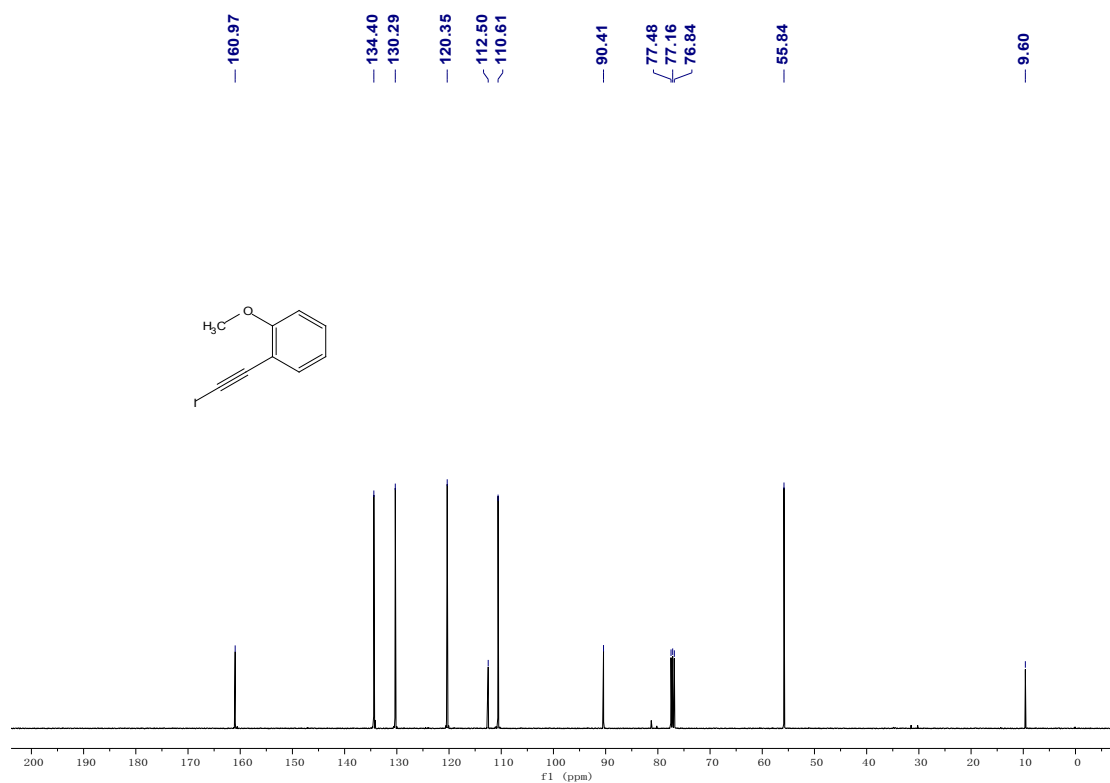
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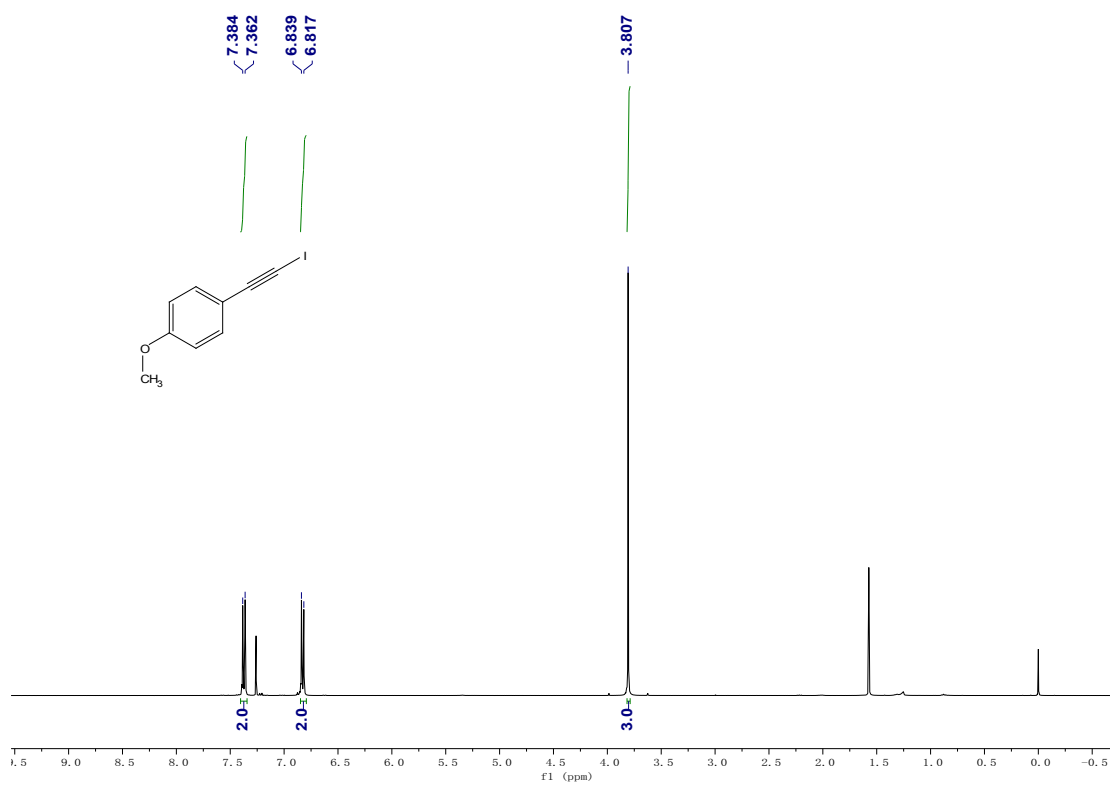
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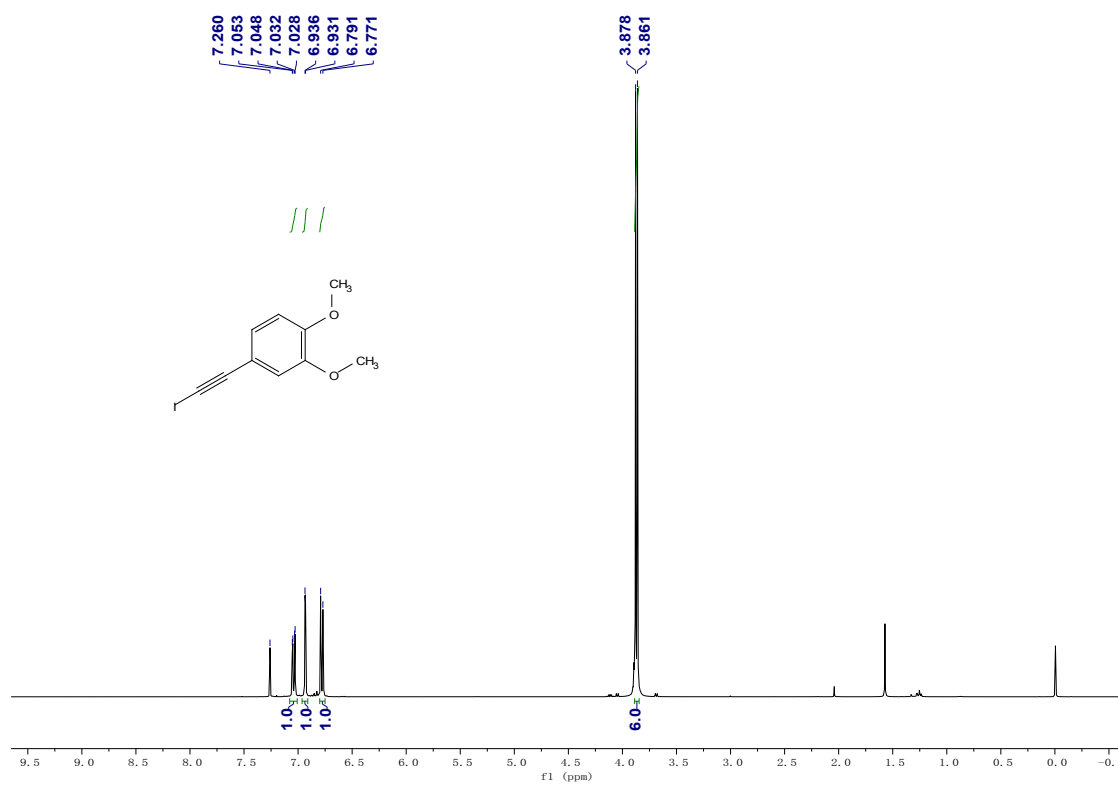
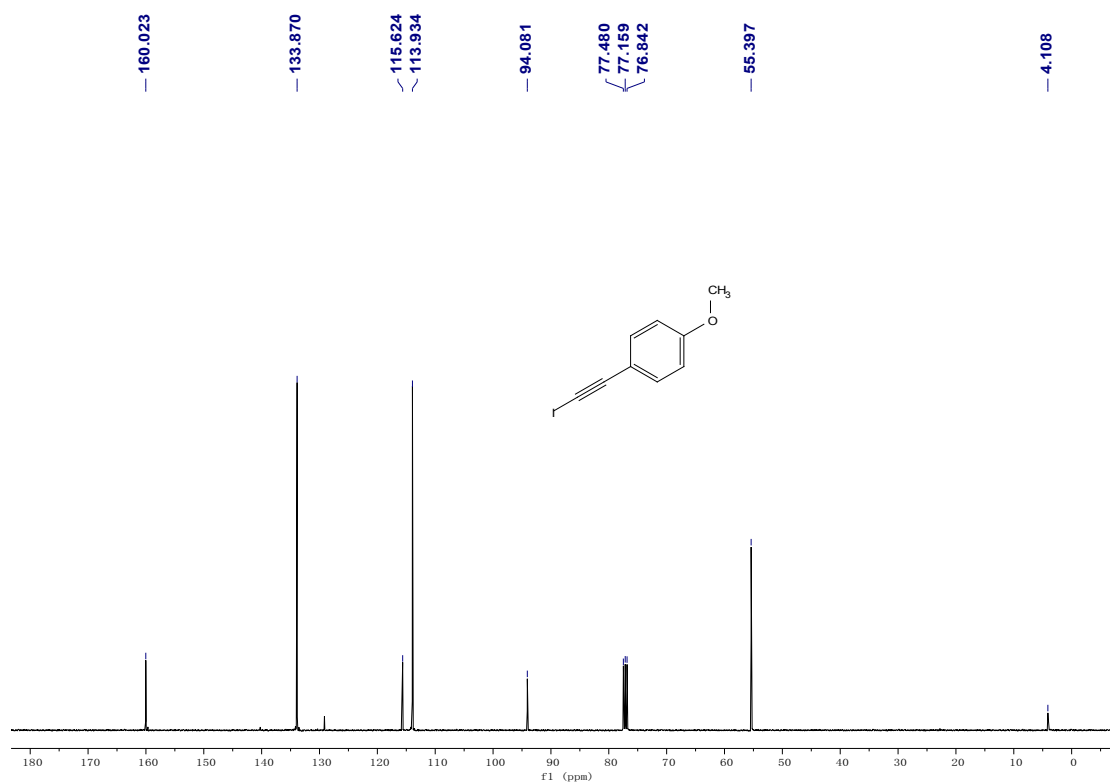
^1H NMR (CDCl_3 , 400 MHz) spectra of compound **3aq**

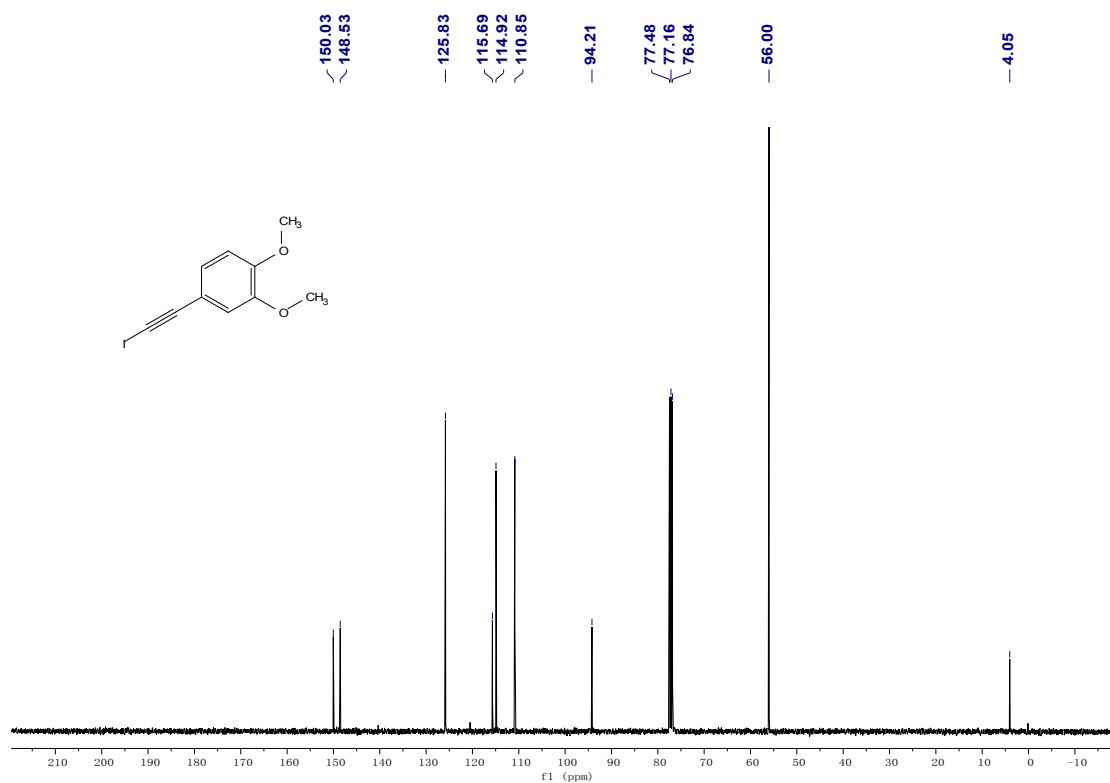


^{13}C NMR(CDCl₃, 101 MHz) spectra of compound **3aq**

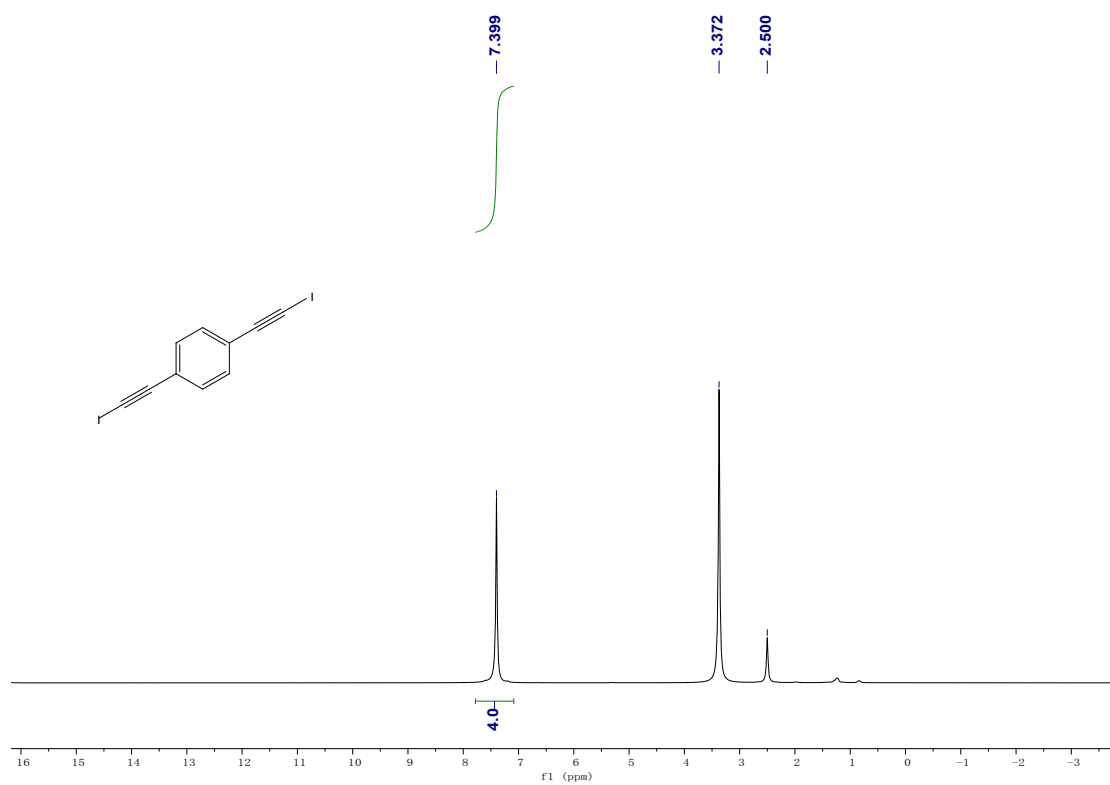


^1H NMR (CDCl₃, 400 MHz) spectra of compound **3as**

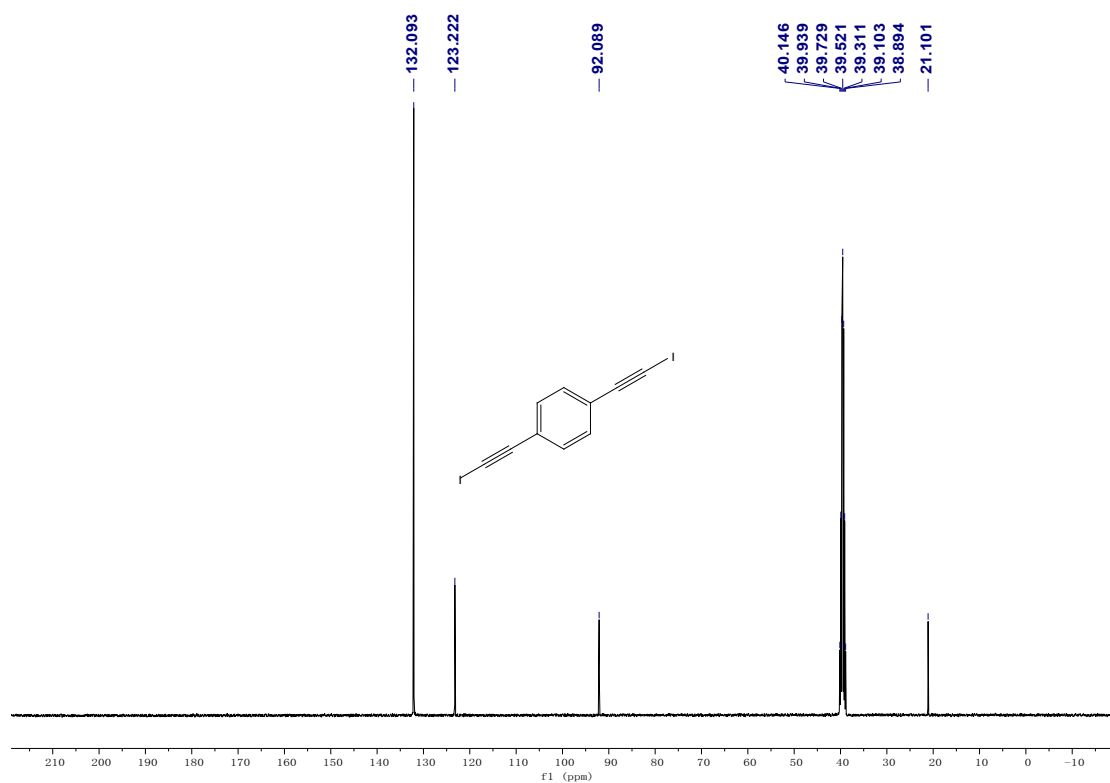




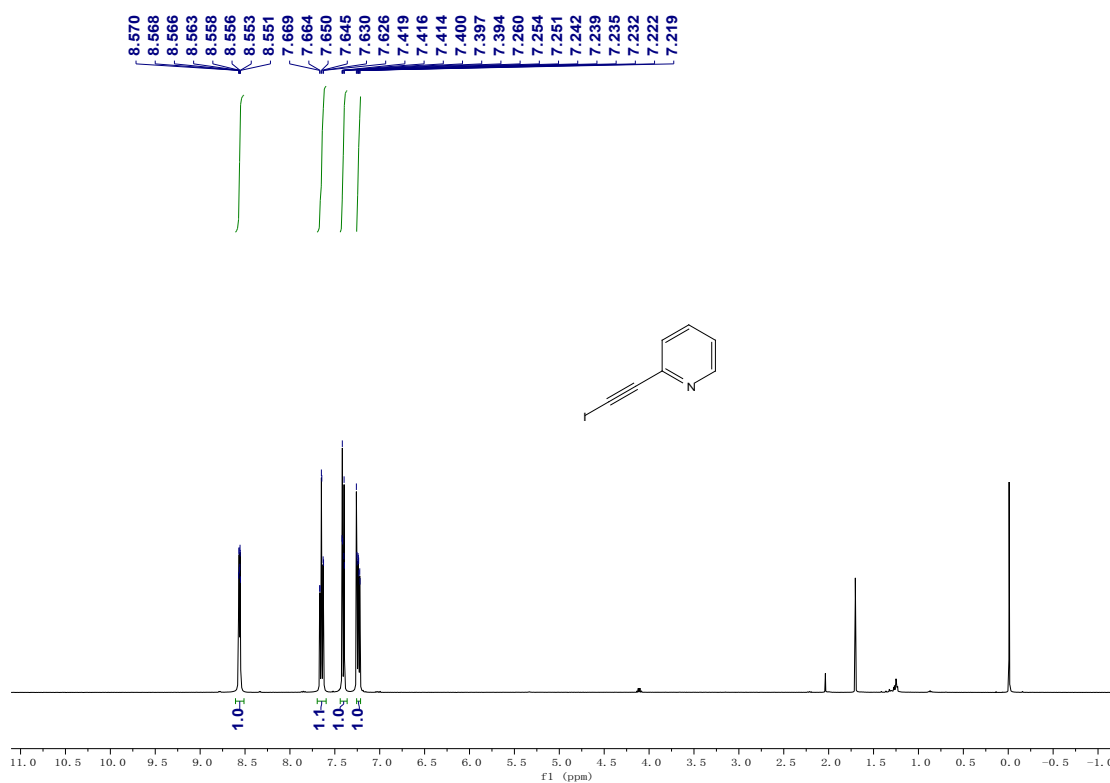
^{13}C NMR(CDCl₃, 101 MHz) spectra of compound **3at**



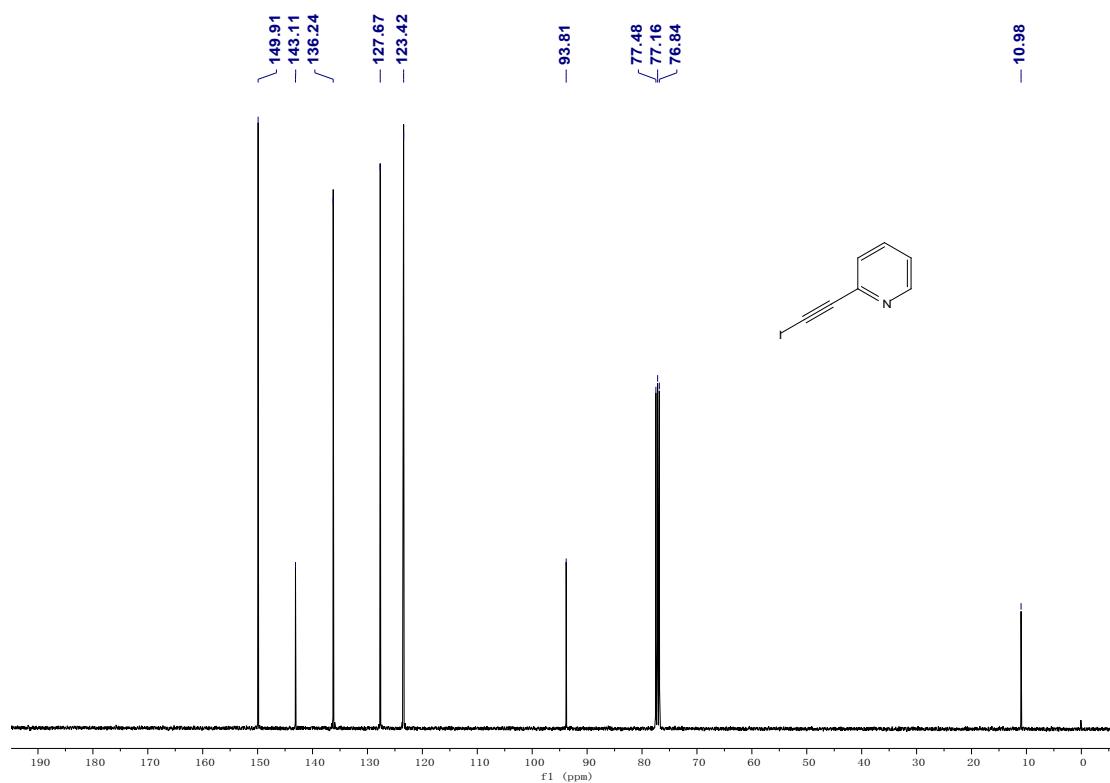
^1H NMR (CDCl₃, 400 MHz) spectra of compound **3au**



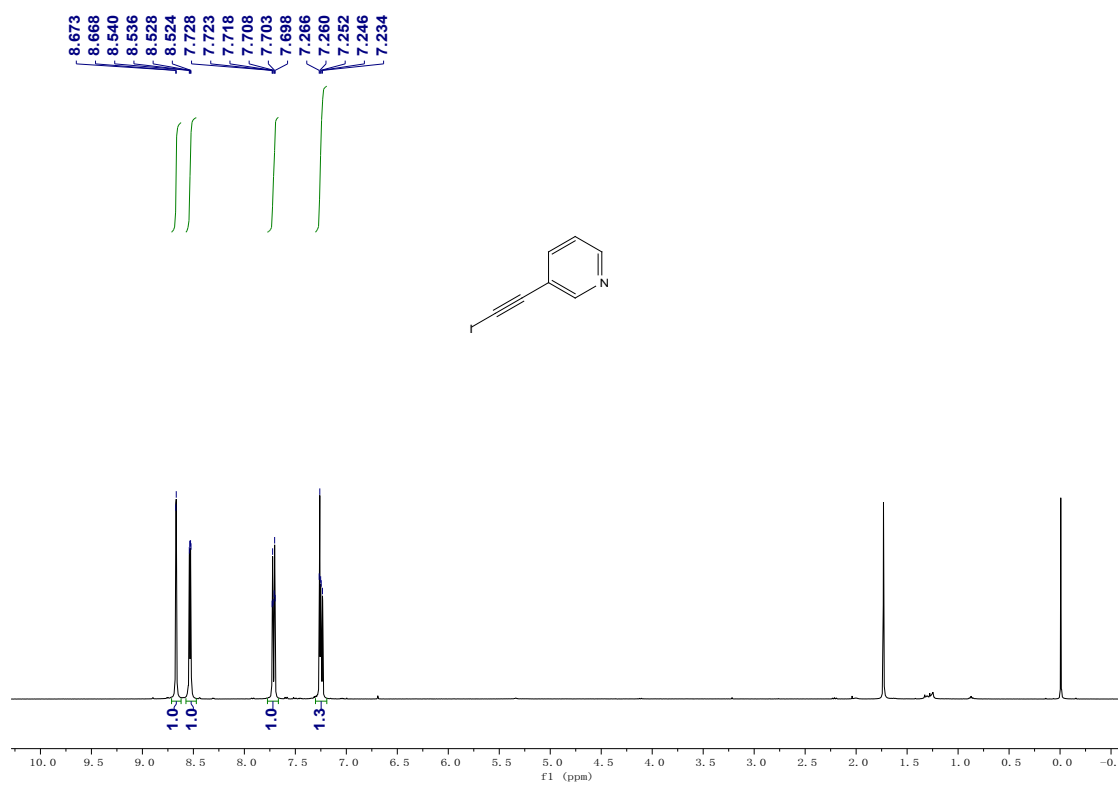
^{13}C NMR(CDCl_3 , 101 MHz) spectra of compound **3au**



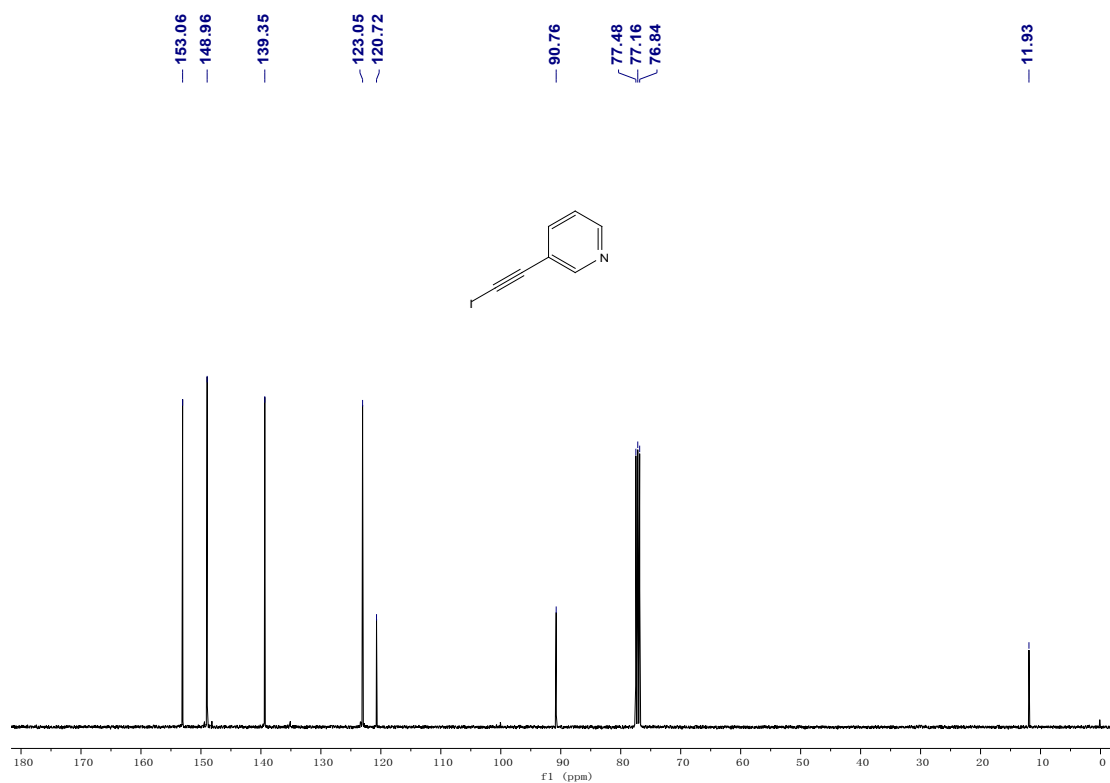
^1H NMR (CDCl_3 , 400 MHz) spectra of compound **3av**



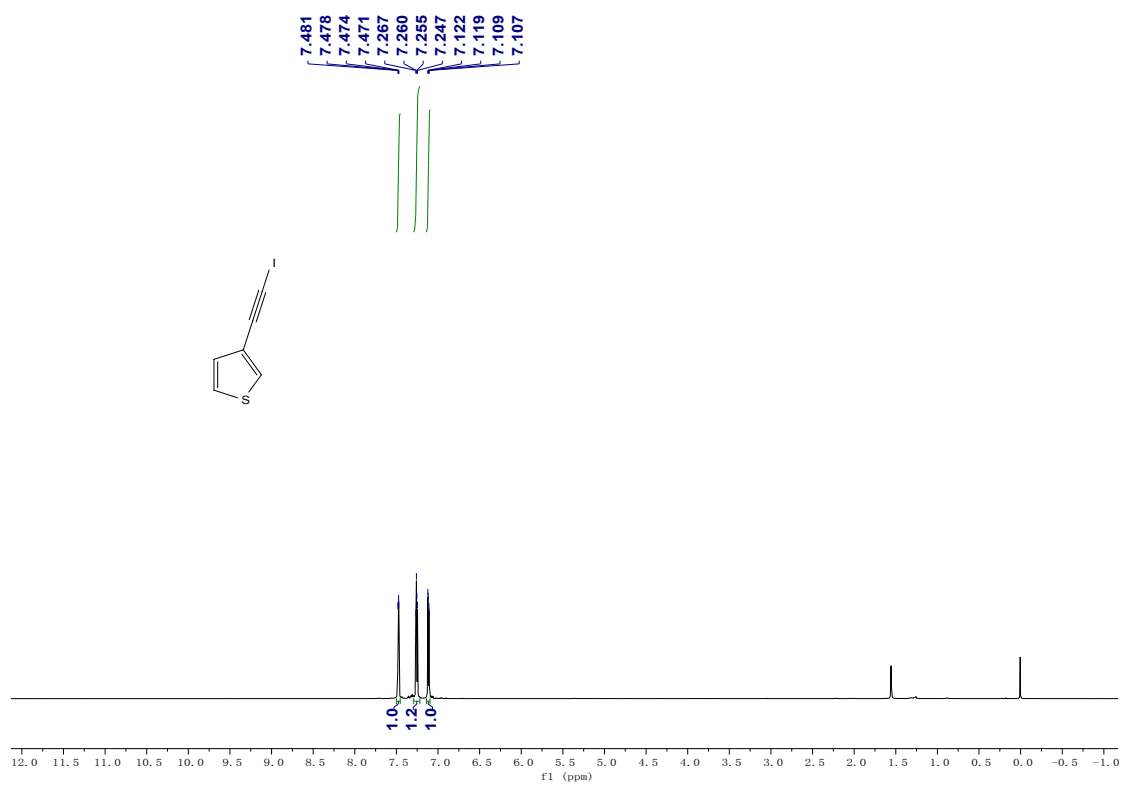
^{13}C NMR(CDCl₃, 101 MHz) spectra of compound **3av**



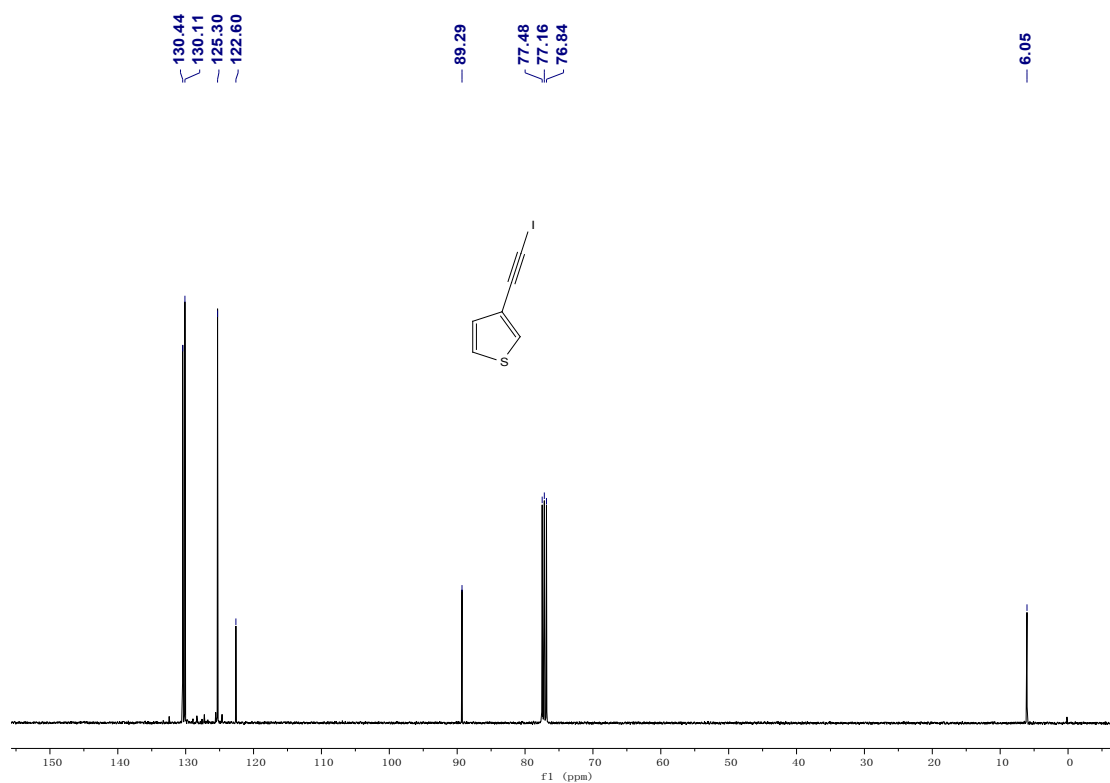
^1H NMR (CDCl₃, 400 MHz) spectra of compound **3av**



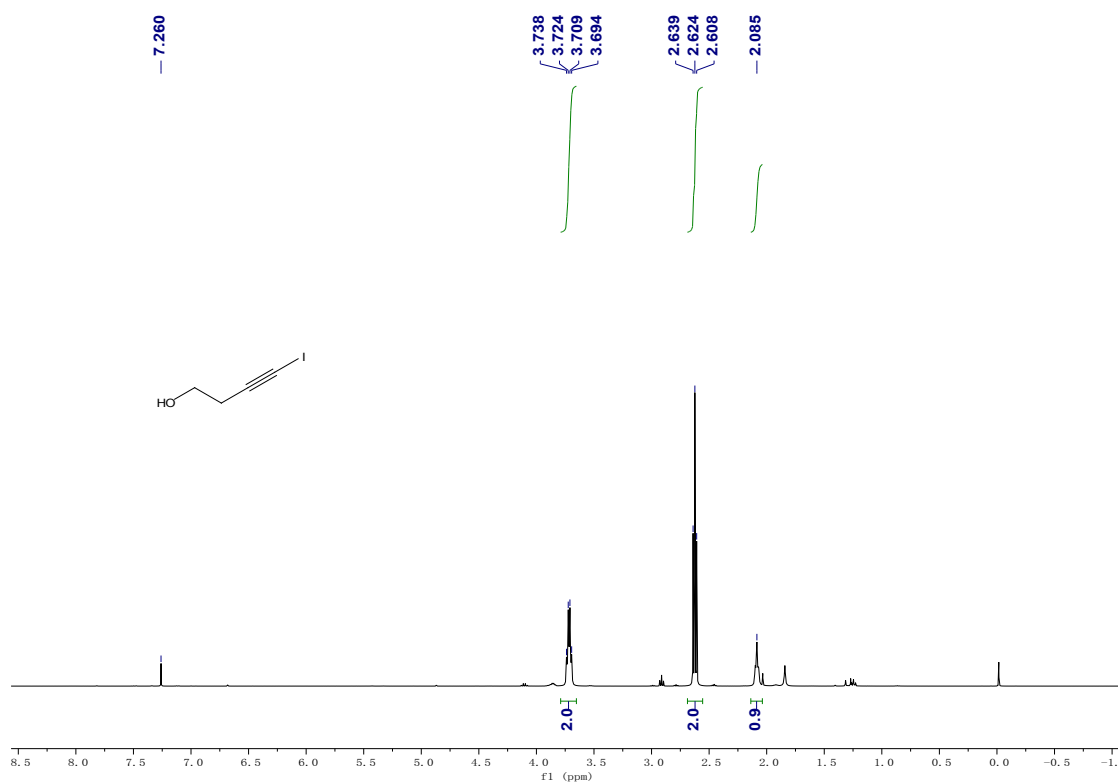
^{13}C NMR(CDCl_3 , 101 MHz) spectra of compound **3aw**



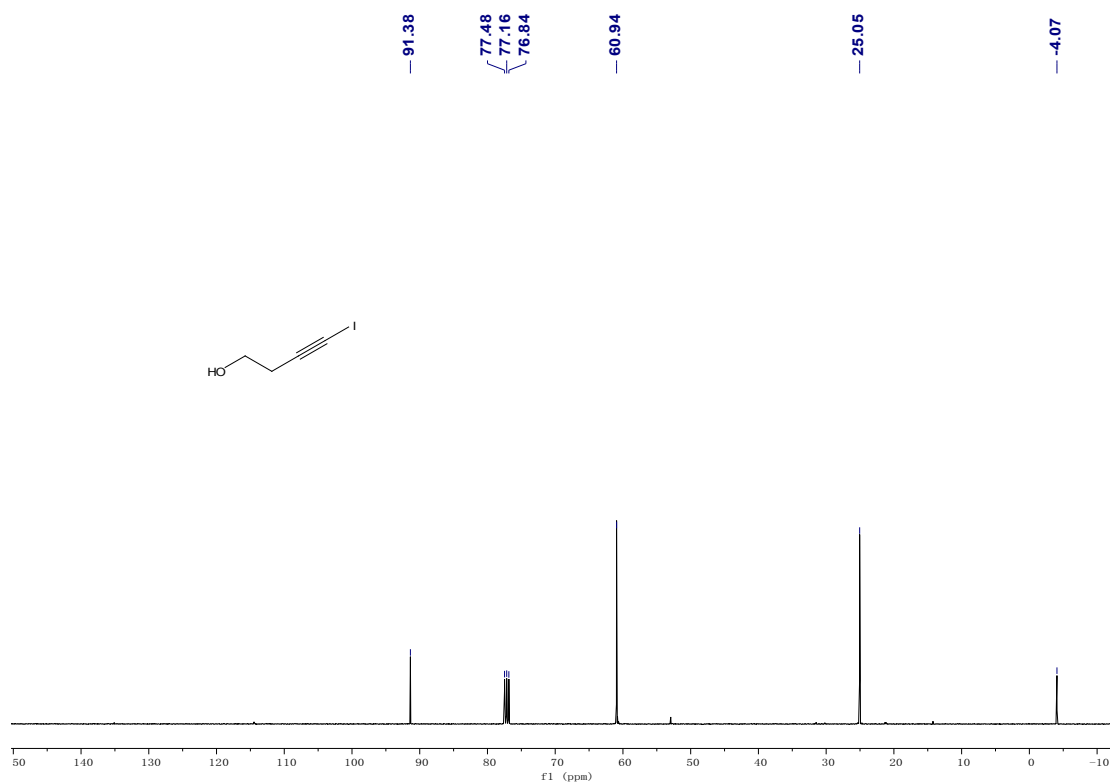
^1H NMR (CDCl_3 , 400 MHz) spectra of compound **3ax**



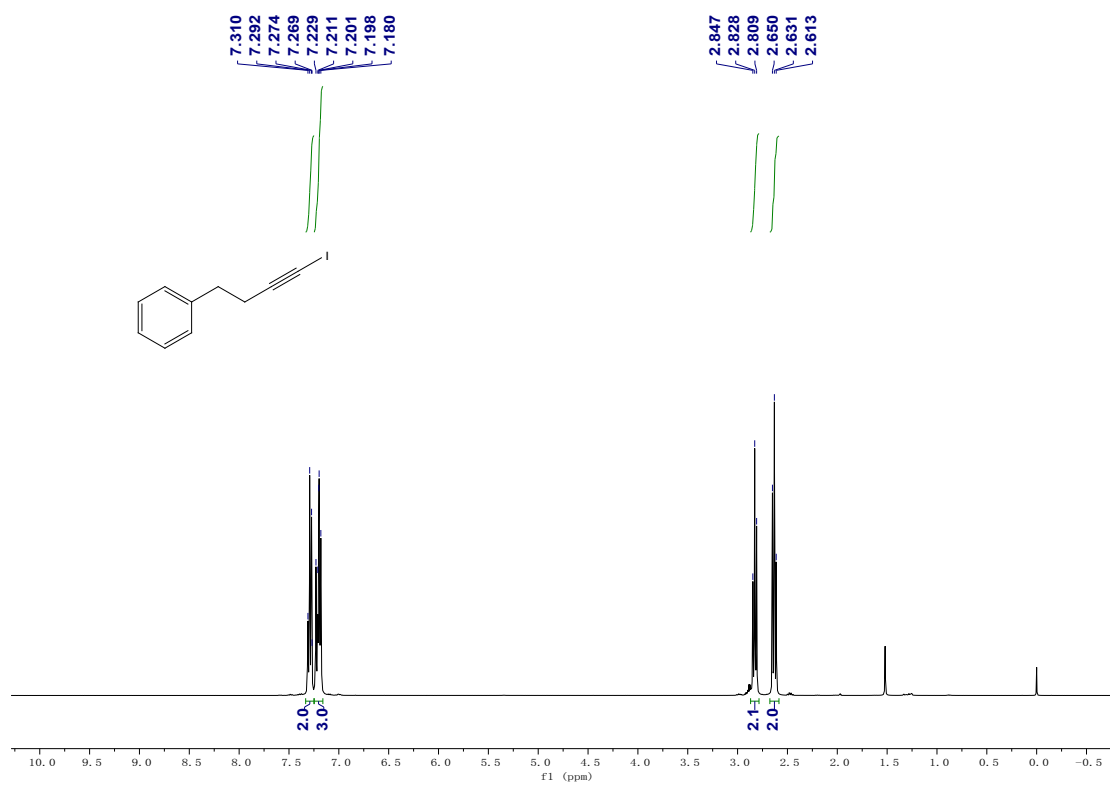
^{13}C NMR(CDCl_3 , 101 MHz) spectra of compound **3ax**



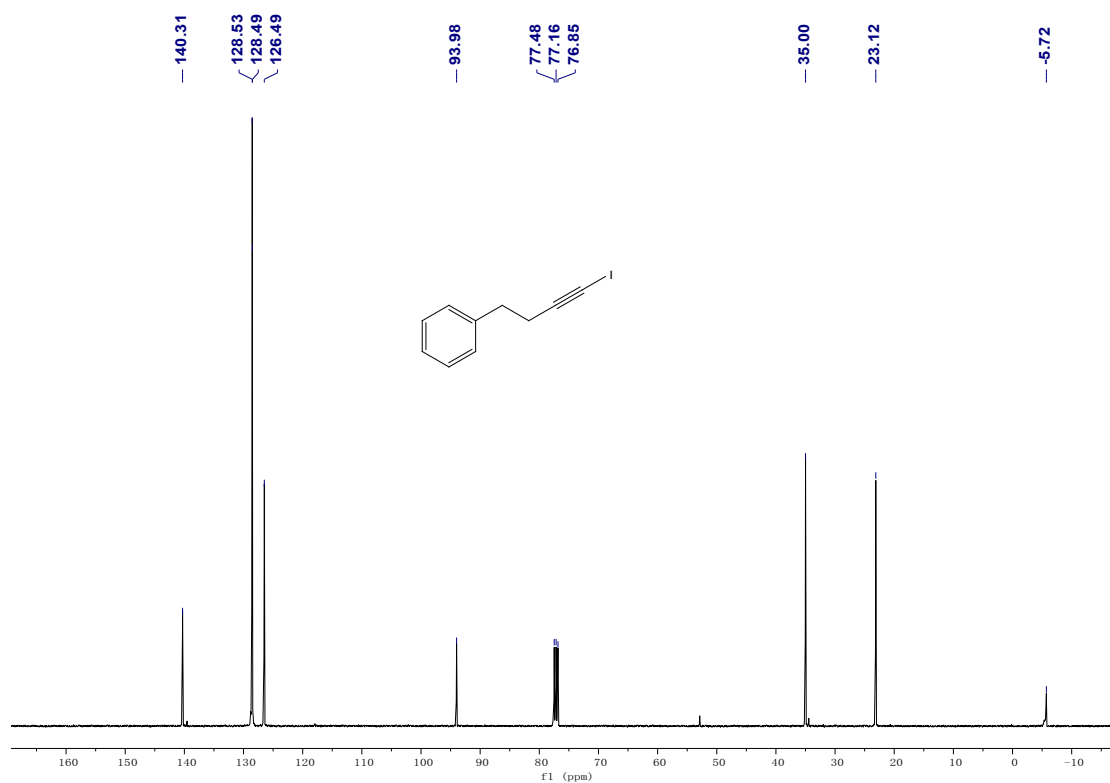
^1H NMR (CDCl_3 , 400 MHz) spectra of compound **3ay**



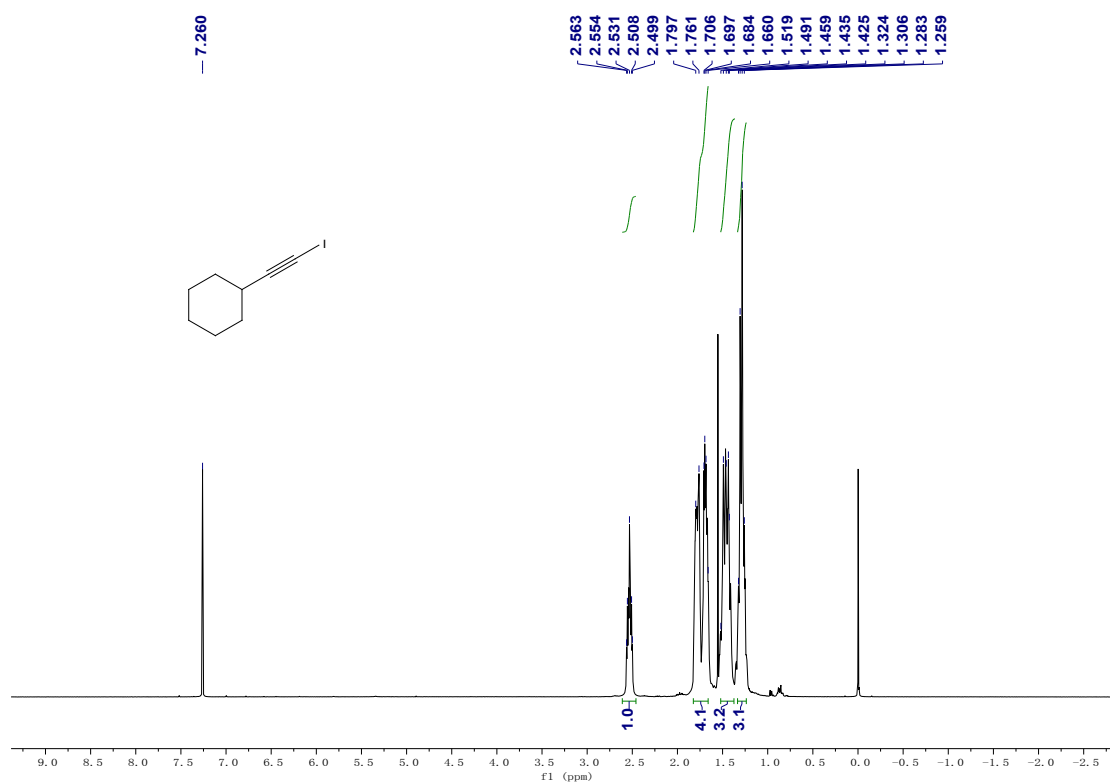
^{13}C NMR(CDCl₃, 101 MHz) spectra of compound **3ay**



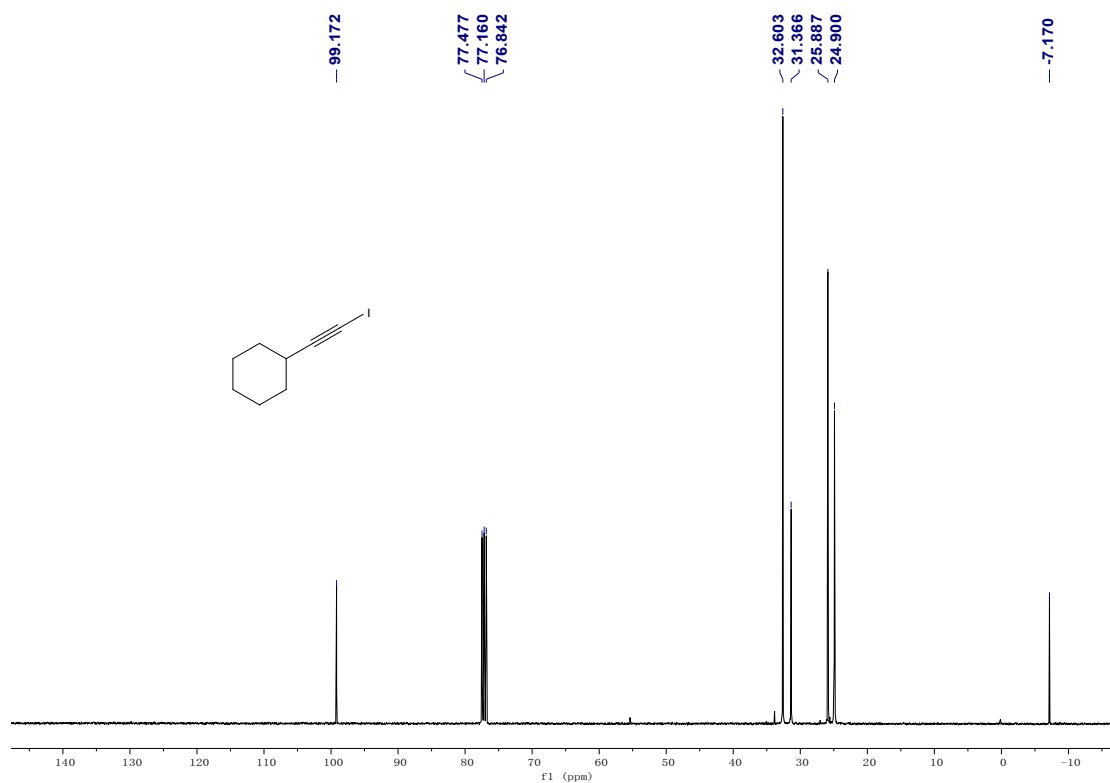
^1H NMR (CDCl₃, 400 MHz) spectra of compound **3az**



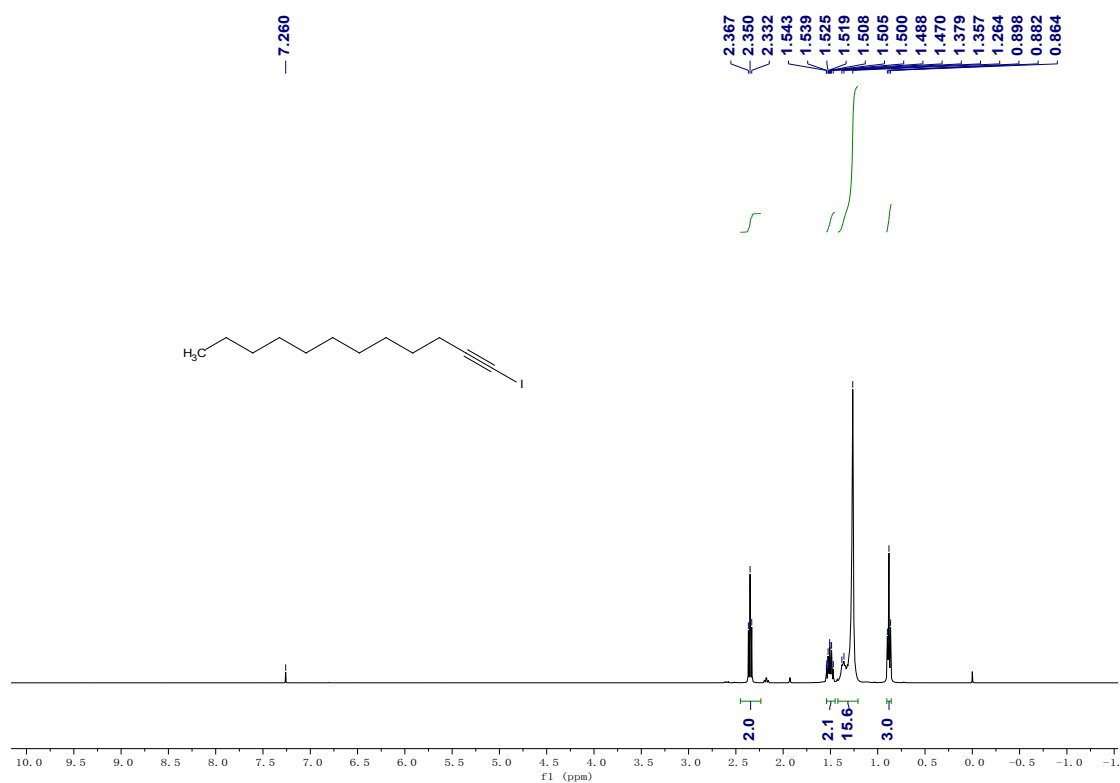
^{13}C NMR(CDCl₃, 101 MHz) spectra of compound **3az**



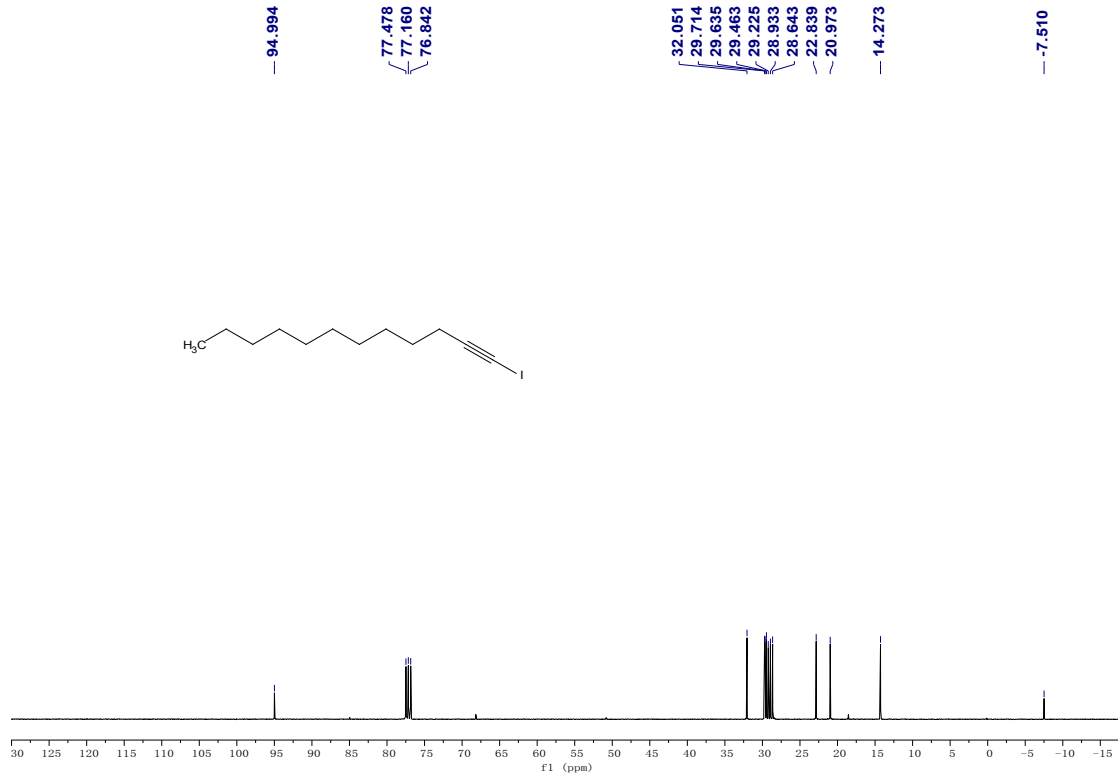
^1H NMR (CDCl₃, 400 MHz) spectra of compound **3ba**



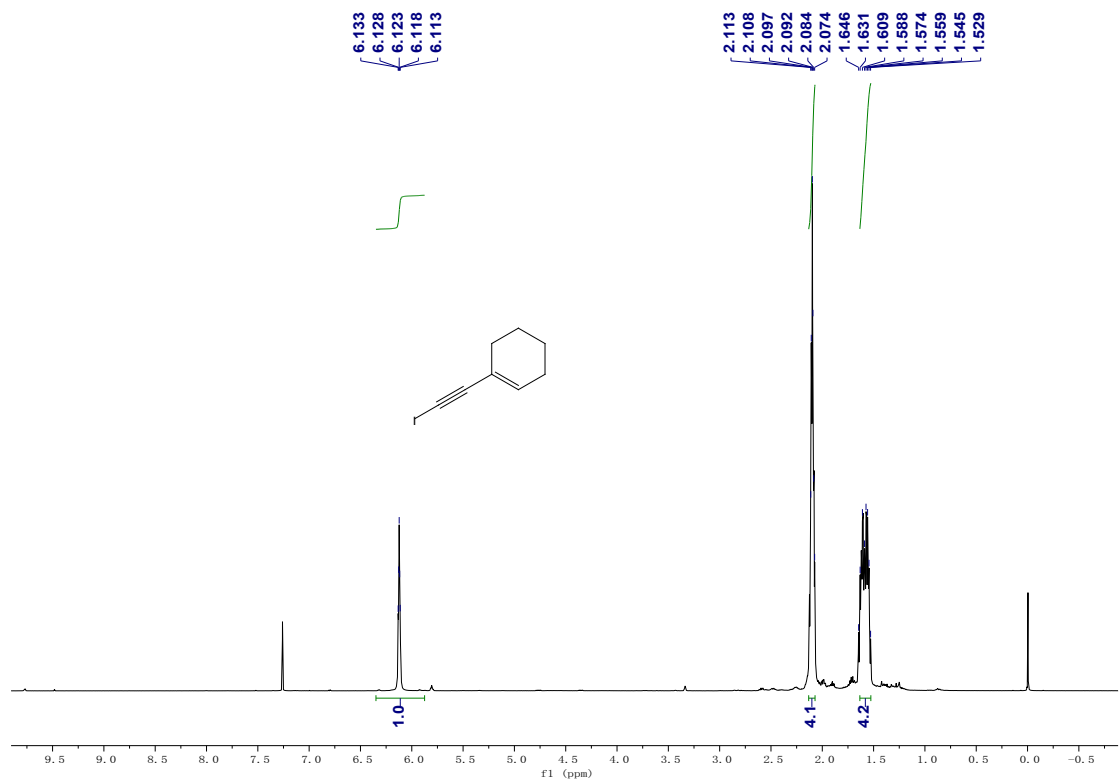
¹³C NMR(CDCl₃, 101 MHz) spectra of compound **3ba**



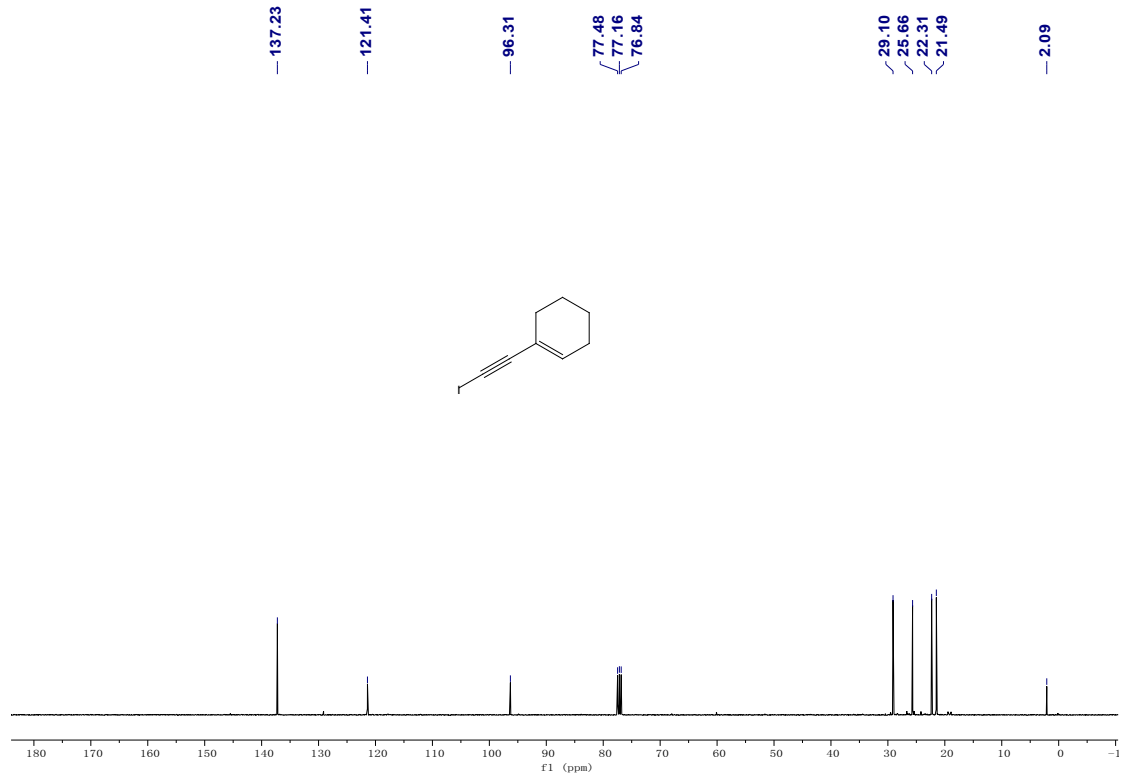
¹H NMR (CDCl₃, 400 MHz) spectra of compound **3bb**



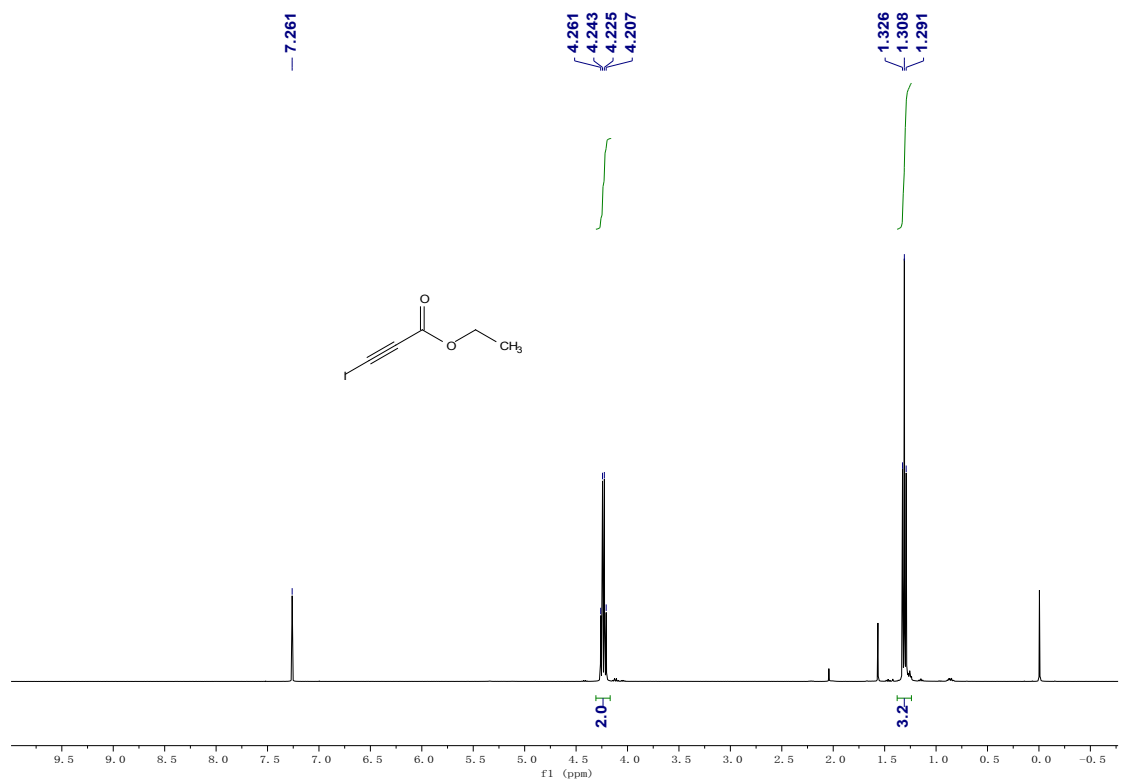
^{13}C NMR(CDCl₃, 101 MHz) spectra of compound **3bb**



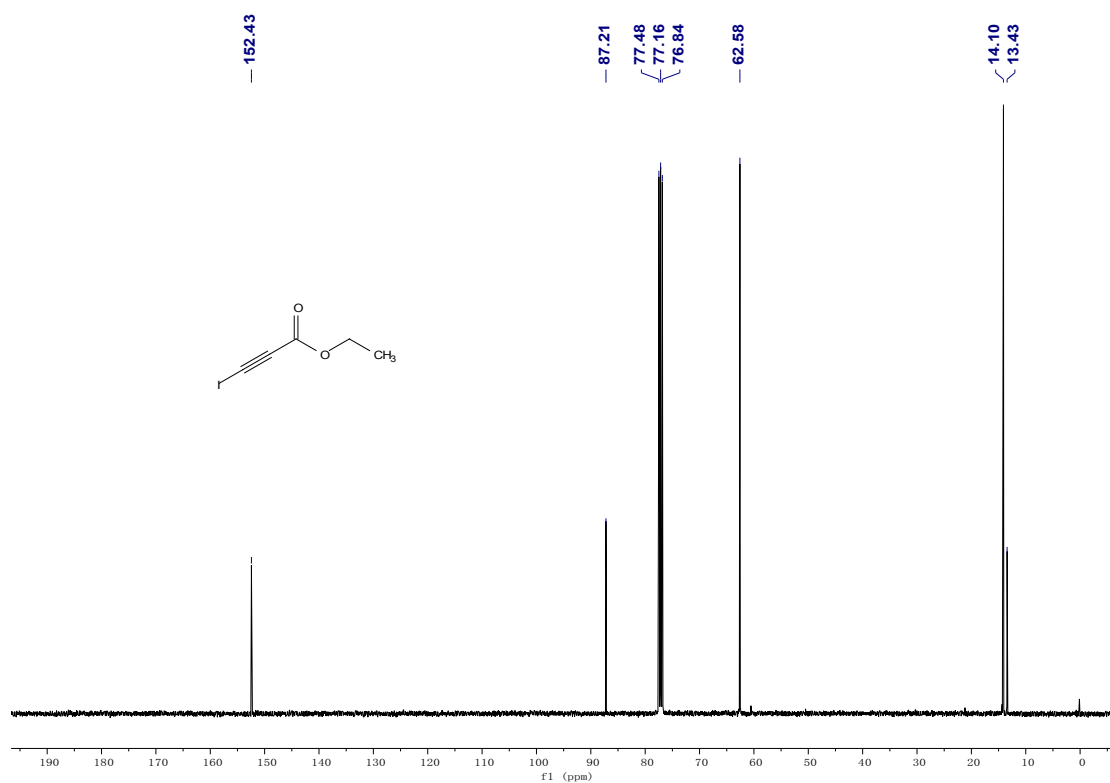
^1H NMR (CDCl₃, 400 MHz) spectra of compound **3bc**



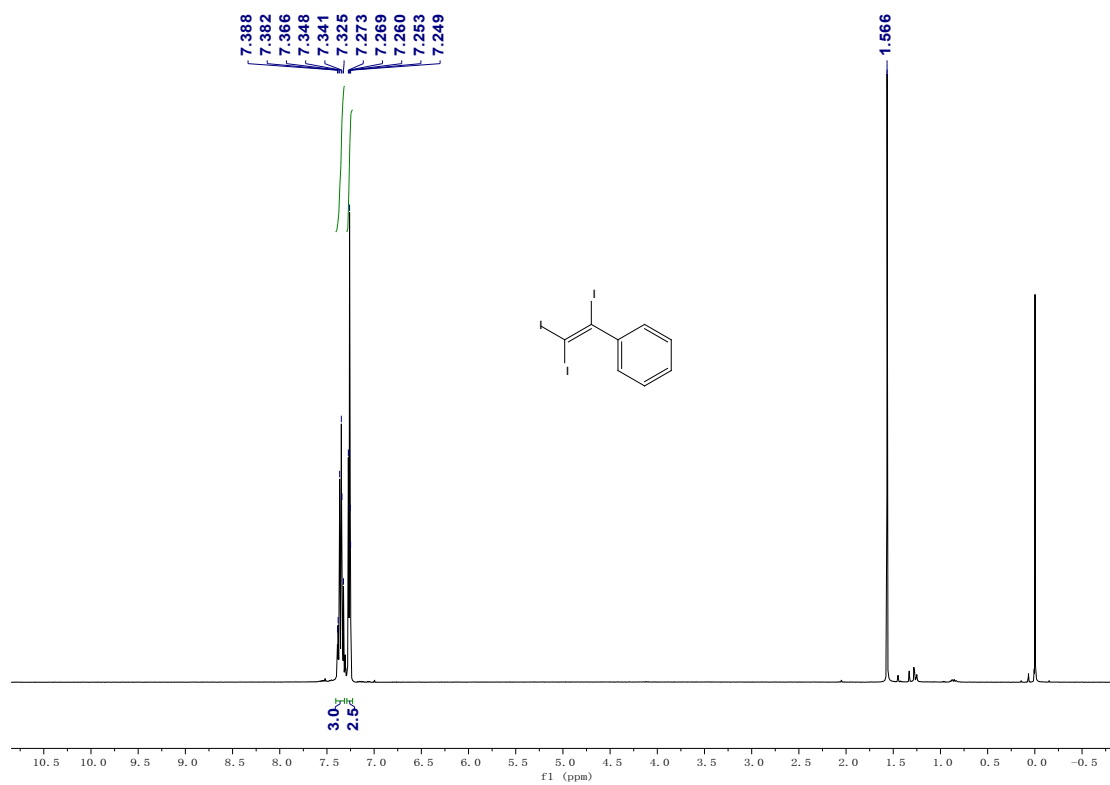
^{13}C NMR(CDCl₃, 101 MHz) spectra of compound **3bc**



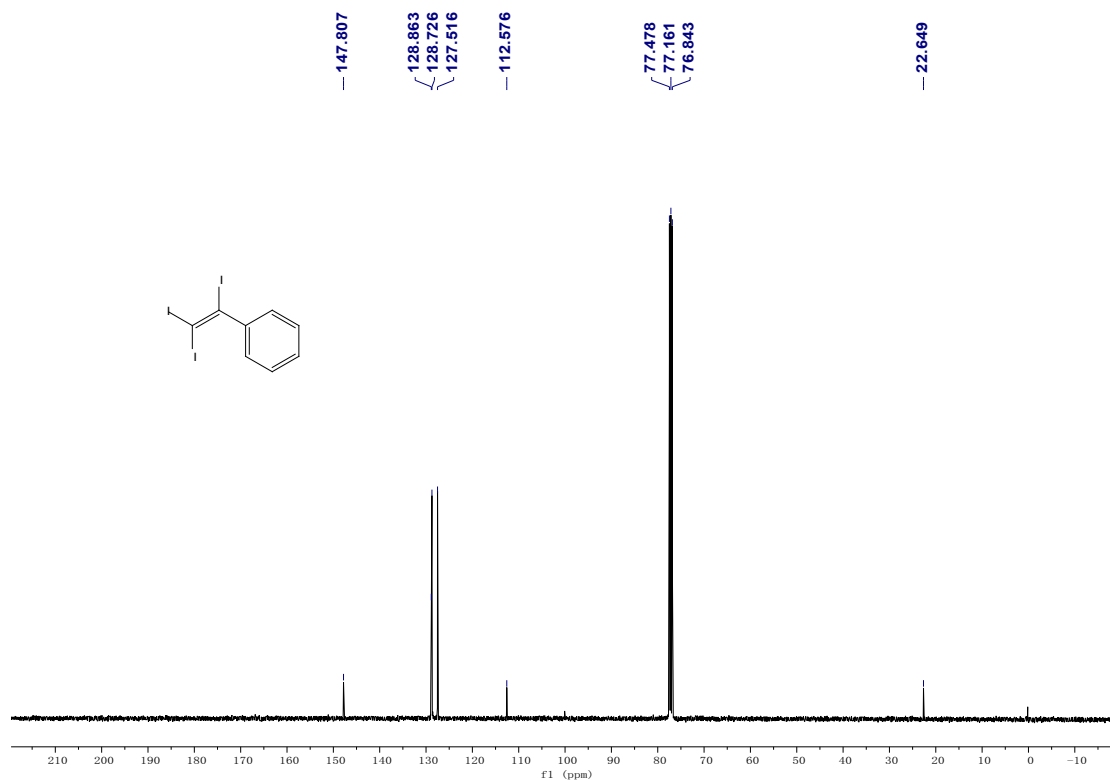
^1H NMR (CDCl₃, 400 MHz) spectra of compound **3bd**



¹³C NMR(CDCl₃, 101 MHz) spectra of compound **3bd**



¹H NMR (CDCl₃, 400 MHz) spectra of compound **7**



^{13}C NMR(CDCl₃, 101 MHz) spectra of compound 7