Supporting Information

A gold-catalyzed cycloisomerization/aerobic oxidation cascade strategy for 2-aryl indenones from 1,5-enynes

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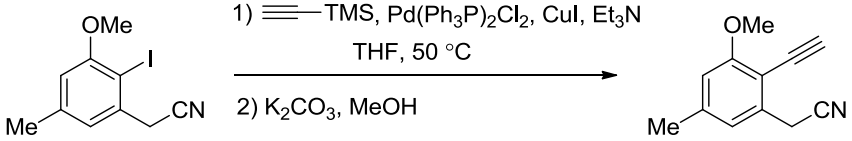
Content

1. General Information

Unless otherwise noted, reagents were obtained commercially and used without further purification. THF was distilled from sodium-benzophenone under a nitrogen atmosphere. TLC analysis of reaction mixtures was performed on Dynamicadsorbents silica gel F-254 TLC plates. Flash chromatography was carried out on Zeoprep 60 ECO silica gel. ^{1}H and ^{13}C NMR spectra were recorded with Bruker Avance-III 600 spectrometers and referenced to $CDCl_3$. HR-ESI-MS was recorded on a Bruker micro-TOFQ-Q instrument. IR spectra were recorded on a Thermo Nicolet Avatar 370 FT-IR spectrometer. Melting points were tested on Thomas Hoover capillary melting point apparatus. Compounds were detected by monitoring UV absorbance at 254 nm.

2. Preparation of 7 and Characterization Data

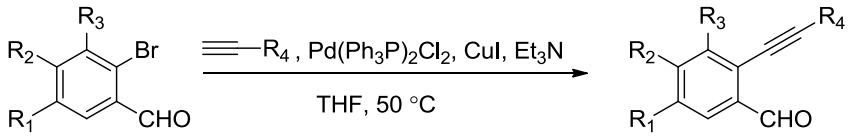


9 **7**

To a solution of compound **9**[2] (1 mmol, 287 mg), $(PPh_3)_2PdCl_2$ (0.05 mmol, 35.1 mg), CuI (0.1 mmol, 19.1 mg) and Et_3N (5 mmol, 0.7 mL) in dry THF was added trimethylsilylacetylene (1.2 mmol, 0.17 mL). The resulting mixture was stirred at room temperature and the reaction progress was monitored by TLC. When all of compound **9** had been consumed, the reaction mixture was quenched by saturated aq. NH_4Cl (10 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*.

The crude product obtained above was dissolved in MeOH (10 mL) and K_2CO_3 (3 mmol, 0.41 g) was added. The reaction mixture was stirred at room temperature for 2 h and quenched by saturated aq. NH_4Cl (10 mL). The resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by a flash column chromatography (petroleum ether:ethyl acetate, 20:1, v/v) on silica gel to afford the desired product **7** as a yellowish oil (139 mg) with a yield of 75%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 6.94 (s, 1H), 6.69 (s, 1H), 3.90 (s, 3H), 3.87 (s, 2H), 3.59 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 161.3, 141.3, 134.1, 121.1, 117.6, 111.3, 107.9, 87.0, 77.3, 56.2, 22.7, 22.1; HRMS (ESI): *m/z*: Calcd for $C_{12}H_{12}ON$ $[M+H]^+$ 186.0913, Found 186.0916; IR (thin film, cm^{-1}): 3445, 3254, 2924, 1608, 1575, 1303, 1147, 1079, 832.

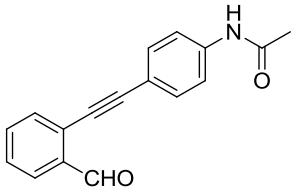
3. General Preparation of 6-6s and Characterization Data



8-8s **6-6s**

To a solution of the corresponding 2-bromobenzaldehyde **8-8s** (1 mmol), $(PPh_3)_2PdCl_2$ (0.05 mmol, 35.1 mg), CuI (0.1 mmol, 19.1 mg) and Et_3N (5 mmol, 0.7 mL) in dry THF was added the appropriate acetylene (1.2 mmol). The resulting mixture was heated at 50 ℃ for 12 h. After the reaction was completed, the reaction mixture was quenched with distilled water and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the desired products **6-6s**.

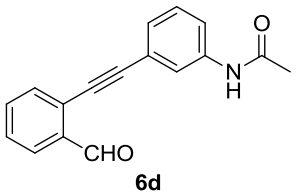
Spectral data were consistent with those reported in the literature.[1]



6c

***N*-(4-((2-Formylphenyl)ethynyl)phenyl)acetamide(6c)**

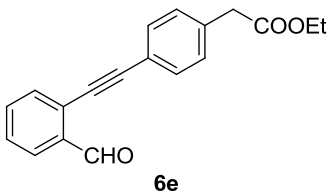
TLC (petroleum ether:ethyl acetate, 3:1, v/v): R_f=0.3; yellowish solid, Mp 202–203 ℃; 76%; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.50 (s, 1H), 10.18 (s, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.73 – 7.72 (m, 2H), 7.67 (d, J = 8.6 Hz, 2H), 7.59 – 7.57 (m, 3H), 2.07 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 191.37, 168.67, 140.34, 135.29, 134.36, 133.17, 132.43, 128.98, 127.61, 125.58, 118.81, 115.65, 96.16, 84.46, 24.15; HRMS (ESI): *m/z*: Calcd for $C_{17}H_{14}NO_2$ 264.1019 $[M+H]^+$, Found 264.1021; IR (thin film, cm^{-1}): 3321, 2212, 1685, 1590, 1526, 1307, 835, 767.



6d

***N*-(3-((2-Formylphenyl)ethynyl)phenyl)acetamide(6d)**

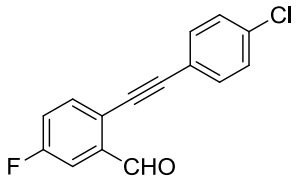
TLC (petroleum ether:ethyl acetate, 3:1, v/v): R_f=0.3; yellowish solid, Mp 168–169 ℃; 85%; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.48 (s, 1H), 10.10 (s, 1H), 7.92 (s, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.78 – 7.71 (m, 2H), 7.63 – 7.57 (m, 2H), 7.38 (t, J = 7.9 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 191.19, 168.62, 139.63, 135.51, 134.35, 133.38, 129.33, 127.86, 126.26, 124.98, 121.89, 121.57, 120.00, 95.67, 85.02, 24.06; HRMS (ESI): *m/z*: Calcd for $C_{17}H_{14}NO_2$ $[M+H]^+$ 264.1019, Found 264.1014; IR (thin film, cm^{-1}): 3425, 3255, 3080, 2208, 1699, 1591, 1425, 1264, 883, 757.



6e

Ethyl 2-(4-((2-formylphenyl)ethynyl)phenyl)acetate(6e)

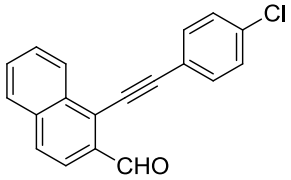
TLC (petroleum ether:ethyl acetate, 20:1, v/v): R_f=0.3; yellowish oil, 80%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.64 (d, *J* = 0.6 Hz, 1H), 7.95 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.67 – 7.62 (m, 1H), 7.59 (td, *J* = 7.6, 1.4 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.89, 171.19, 135.96, 135.41, 133.95, 133.37, 131.99, 129.67, 128.77, 127.41, 127.02, 121.25, 96.24, 85.14, 77.37, 77.16, 76.95, 61.22, 41.48, 14.31; HRMS (ESI): *m/z*: Calcd for $C_{18}H_{15}O_3$ $[M+H]^+$ 279.1016, Found 279.1023; IR (thin film, cm^{-1}): 3425, 2923, 1732, 1631, 1387, 1008, 832, 760, 703.



6m

2-((4-Chlorophenyl)ethynyl)-5-fluorobenzaldehyde (6m)

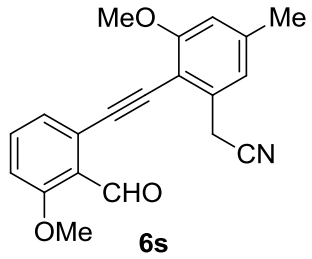
TLC (petroleum ether:ethyl acetate, 100:1, v/v): R_f=0.3; yellowish solid, Mp 130–131 ℃; 85%; ^{1}H NMR (600 MHz, $CDCl_3$) *δ* = 10.50 (s, 1H), 7.95 (dd, *J* = 8.7 Hz, 5.9 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.28 (dd, *J* = 8.9 Hz, 2.5 Hz, 1H), 7.19 – 7.06 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) *δ* = 189.8 (d, *J* = 8.1 Hz), 165.7 (d, *J* = 257.0 Hz), 135.7, 133.1, 133.1, 132.7 (d, *J* = 2.6 Hz), 130.4 (d, *J* = 10.2 Hz), 129.1, 129.1, 128.9 (d, *J* = 11.0 Hz), 120.4, 119.8 (d, *J* = 23.6 Hz), 116.8 (d, *J* = 22.1 Hz), 96.2, 84.8 (d, *J* = 2.9 Hz); HRMS (ESI): *m/z*: Calcd for $C_{15}H_9OClF$ $[M+H]^+$ 259.0320, Found 259.0315; IR (thin film, cm^{-1}): 3422, 3038, 2922, 2210, 1694, 1602, 1568, 1491, 1401, 1207, 869, 820, 649.



6r

1-((4-Chlorophenyl)ethynyl)-2-naphthaldehyde (6r)

TLC (petroleum ether:ethyl acetate, 100:1, v/v): R_f=0.3; yellowish solid, Mp 141–143 ℃; 83%; ^{1}H NMR (600 MHz, $CDCl_3$) *δ* = 10.83 (s, 1H), 8.58 – 8.51 (m, 1H), 7.97 (d, *J* = 8.6 Hz, 1H), 7.92 – 7.84 (m, 2H), 7.70 – 7.65 (m, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) *δ* = 192.0, 135.9, 135.6, 134.4, 133.1, 133.1, 133.1, 129.6, 129.3, 129.2, 129.2, 128.7, 127.9, 127.2, 127.1, 122.2, 120.9, 101.2, 84.0; HRMS (ESI): *m/z*: Calcd for $C_{19}H_{11}OClNa$ $[M+Na]^+$ 313.0391, Found 313.0398; IR (thin film, cm^{-1}): 3423, 3052, 2841, 1695, 1491, 1094, 824, 817, 745.

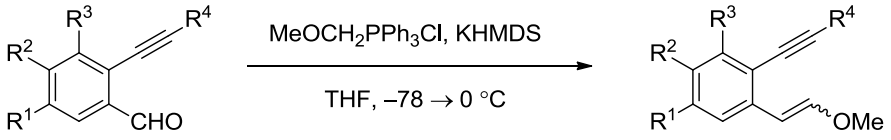


6s

2-(2-((2-Formyl-3-methoxyphenyl)ethynyl)-3-methoxy-5-methylphenyl)acetonitrile (6s)

TLC (petroleum ether:ethyl acetate, 5:1, v/v): R_f=0.3; yellowish oil, 75%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 10.56 (s, 1H), 7.39 (t, J = 8.1 Hz, 1H), 7.18 (d, J = 6.7 Hz, 1H), 6.88 (d, J = 6.1 Hz, 2H), 6.61 (s, 1H), 4.07 (s, 2H), 3.85 (s, 3H), 3.83 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 189.8, 161.7, 161.1, 141.4, 134.5, 134.2, 126.6, 125.3, 124.7, 121.2, 118.2, 111.7, 111.2, 109.0, 97.1, 88.8, 56.2, 56.1, 22.7, 22.2. HRMS (ESI): *m/z*: Calcd for $C_{20}H_{18}O_3N$ $[M+H]^+$ 320.1281, Found 320.1280; IR (thin film, cm^{-1}): 3395, 2922, 2851, 2195, 1687, 1566, 1465, 1258, 1065, 793, 542.

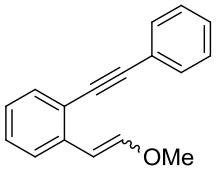
4. General Preparation of 1-1s and Characterization Data



6-6s **1-1s**

To a suspension of (methoxymethyl)triphenylphosphonium chloride (2 mmol, 685.6 mg) in anhydrous THF was added 1 M solution of KHMDS in anhydrous THF (1.8 mmol, 1.8 mL) at –78 ℃. The mixture was stirred at –78 ℃ for 0.5 h, then a solution of 2-phenylethynyl benzaldehyde **6-6s** (1 mmol) in anhydrous THF was added. The reaction was allowed to warm up to 0 ℃ over 3 h, and then hexane was added. The resulting mixture was filtered through Celite and thoroughly washed with hexane. The filtrate was concentrated *in vacuo* and the residue was diluted with hexane. The resulting mixture was filtered through Celite again to remove the remaining triphenylphosphine oxide. After evaporation to dryness, the crude vinyl ether was purified by silica gel chromatography eluting with petroleum ether/ethyl acetate to yield the products **1-1s**.

Spectral data were consistent with those reported in the literature.[3]

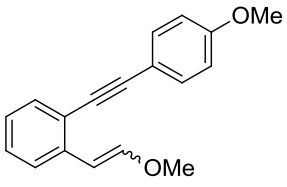


1

1-(2-Methoxyvinyl)-2-(phenylethynyl)benzene (1)

TLC (petroleum ether:ethyl acetate, 100:1, v/v): R_f=0.3; yellowish oil, (1:0.38 *E*/*Z*), 75%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.09 (d, J = 8.0 Hz, 1H, *Z*), 7.52 – 7.46 (m, 2H,

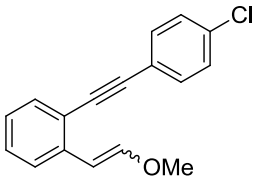
Z + 2H, *E*), 7.45 (d, *J* = 7.9 Hz, 1H, *E*), 7.32 – 7.20 (m, 5H, *Z* + 4H, *E*), 7.15 (t, *J* = 7.6 Hz, 1H, *E*), 7.12 (d, *J* = 13.0 Hz, 1H, *E*), 7.05 (q, *J* = 7.2 Hz, 1H, *Z* + 1H, *E*), 6.32 (d, *J* = 13.0 Hz, 1H, *E*), 6.18 (d, *J* = 7.2 Hz, 1H, *Z*), 5.87 (d, *J* = 7.2 Hz, 1H, *Z*), 3.68 (s, 1H, *Z*), 3.65 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 150.3 (*E*), 149.2 (*Z*), 138.2 (*E*), 137.4 (*Z*), 132.6 (*E*), 132.2 (*Z*), 131. 6 (*Z*), 131.6 (*Z*), 131.5 (*E*), 131.5 (*E*), 128.7 (*Z*), 128.6 (*E*), 128.5 (*E*), 128.5 (*E*), 128.4 (*E*), 128.3 (*Z*), 128.3 (*Z*), 128.3 (*Z*), 128.2 (*Z*), 125.5 (*Z*), 125.5 (*E*), 123.7 (*E*), 123.6 (*Z*), 123.6 (*E*), 120.9 (*Z*), 120.6 (*E*), 103.7 (*E*), 103.3 (*Z*), 93.8 (*E*), 93. 6 (*Z*), 88.7 (*Z*), 88.5 (*E*), 60.8 (*Z*), 56.5 (*E*); HRMS (ESI): *m/z*: Calcd for $C_{17}H_{15}O$ $[M+H]^+$ 235.1117, Found 235.1125; IR (thin film, cm^{-1}): 3430, 2850, 1697, 1493, 1446, 1124, 757, 690.



1a

1-((4-Methoxyphenyl)ethynyl)-2-(2-methoxyvinyl)benzene (1a)

TLC (petroleum ether:ethyl acetate, 30:1, v/v): R_f=0.25; yellowish oil (1:0.56 *E*/*Z*), 72%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.17 (d, *J* = 8.0 Hz, 1H, *Z*), 7.57 – 7.47 (m, 3H, *Z* + 3H, *E*), 7.39 (t, *J* = 8.0 Hz, 1H, *E*), 7.31 (t, *J* = 7.6 Hz, 1H, *Z*), 7.25 (s, 1H, *E*), 7.22 (d, *J* = 13.1 Hz, 1H, *E*), 7.15 (dt, *J* = 11.1 Hz, 5.5 Hz, 1H, *Z* + 1H, *E*), 6.94 – 6.88 (m, 2H, *Z* + 2H, *E*), 6.41 (d, *J* = 13.0 Hz, 1H, *E*), 6.29 (d, *J* = 7.2 Hz, 1H, *Z*), 5.96 (d, *J* = 7.2 Hz, 1H, *Z*), 3.83 (s, 3H, *E*), 3.83 (s, 3H, *Z*), 3.81 (s, 3H, *Z*), 3.77 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.7 (*E*), 159.6 (*Z*), 150.2 (*E*), 149.1 (*Z*), 137.9 (*E*), 137.14 (*Z*), 133.0 (*Z*), 133.0 (*Z*), 132.9 (*E*), 132.9 (*E*), 132.4 (*E*), 132.0 (*Z*), 128.6 (*Z*), 128.3 (*E*), 128.0 (*Z*), 125.5 (*Z*), 125.5 (*E*), 123.7 (*E*), 121.3 (*Z*), 121.0 (*E*), 115.8 (*Z*), 115.7 (*E*), 114.1 (*E*), 114.1 (*E*), 114.1 (*Z*), 114.1 (*Z*), 103.8 (*E*), 103.4 (*Z*), 93.8 (*E*), 93.6 (*Z*), 87.3 (*Z*), 87.2 (*E*), 60.9 (*Z*), 56.6 (*E*), 55.3 (*E* + *Z*); HRMS (ESI): *m/z*: Calcd for $C_{18}H_{17}O_2$ $[M+H]^+$ 265.1223, Found 265.1249; IR (thin film, cm^{-1}): 3426, 2934, 1638, 1606, 1249, 832, 755.

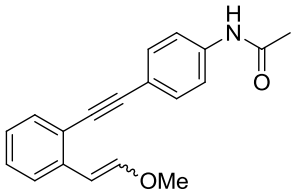


1b

1-((4-Chlorophenyl)ethynyl)-2-(2-methoxyvinyl)benzene (1b)

TLC (petroleum ether:ethyl acetate, 10:1, v/v): R_f=0.3; yellowish oil (1:0.60 *E*/*Z*), 72%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 8.0 Hz, 1H, *Z*), 7.36 (t, *J* = 7.3 Hz, 1H, *Z* + 1H, *E*), 7.32 (dd, *J* = 8.4 Hz, 3.6 Hz, 2H, *Z* + 2H, *E*), 7.23 (d, *J* = 7.9 Hz, 1H, *E*), 7.20 – 7.14 (m, 2H, *E* + 3H, *Z*), 7.10 (t, *J* = 7.5 Hz, 1H, *E*), 7.03 (d, *J* = 13.0 Hz, 1H, *E*), 6.99 (dt, *J* = 11.7 Hz, 5.9 Hz, 1H, *Z* + 1H, *E*), 6.20 (d, *J* = 13.0 Hz, 1H, *E*), 6.12 (d, *J* = 7.2 Hz, 1H, *Z*), 5.74 (d, *J* = 7.2 Hz, 1H, *Z*), 3.64 (s, 3H, *Z*), 3.59 (s, 3H, *E*); ^{13}C NMR

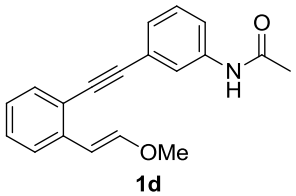
(150 MHz, $CDCl_3$) δ = 150.4 (*E*), 149.3 (*Z*), 138.3 (*E*), 137.4 (*Z*), 134.3 (*E*), 134.2 (*Z*), 132.8 (*Z*), 132.8 (*Z*), 132.7 (*E*), 132.7 (*E*), 132.6 (*E*), 132.2 (*Z*), 128.8 (*E*), 128.8 (*E*), 128.8 (*E*), 128.7 (*Z*), 128.7 (*Z*), 128.7 (*Z*), 128.6, (*Z*) 125.6 (*Z*), 125.5 (*E*), 123.8 (*E*), 122.2 (*Z*), 122.1 (*E*), 120.6 (*Z*), 120.3 (*E*), 103.6 (*E*), 103.2 (*Z*), 92.6 (*E*), 92.4 (*Z*), 89.6 (*Z*), 89.5 (*E*), 60.9 (*Z*), 56.7 (*E*); HRMS (ESI): *m/z*: Calcd for $C_{17}H_{14}ClO$ $[M+H]^+$ 269.0728, Found 269.0742; IR (thin film, cm^{-1}): 3434, 2932, 1727, 1638, 1492, 1091, 828, 758.



1c

***N*-(4-((2-(2-Methoxyvinyl)phenyl)ethynyl)phenyl)acetamide (1c)**

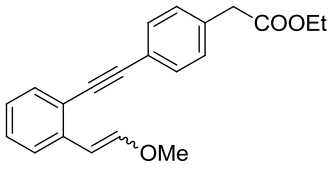
TLC (petroleum ether:ethyl acetate, 2:1, v/v): R_f=0.3; yellowish solid, Mp 137–138 ℃; (1/0.3 *E/Z*), 76%; ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 10.14 (s, 1H, *E* + 1H, *Z*), 8.02 (d, *J* = 7.8 Hz, 1H, *Z*), 7.66 – 7.64 (m, 1H, *E* + 1H, *Z*), 7.55 (d, *J* = 7.9 Hz, 1H, *Z*), 7.50 – 7.47 (m, 2H, *E* + 2H, *Z*), 7.46 – 7.43 (m, 1H, *E*), 7.41 (d, *J* = 12.9 Hz, 1H, *E*), 7.33 – 7.29 (m, 1H, *Z*), 7.29 – 7.25 (m, 1H, *E*), 7.16 – 7.13 (m, 1H, *E* + 1H, *Z*), 6.48 (d, *J* = 7.2 Hz, 1H, *Z*), 6.25 (d, *J* = 12.9 Hz, 1H, *E*), 5.75 (d, *J* = 7.2 Hz, 1H, *Z*), 3.79 (s, 2H, *Z*), 3.71 (s, 2H, *E*), 2.07 (s, 3H, *E* + 3H, *Z*); ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ 168.57 (*E*), 151.08 (*E*), 150.42 (*Z*), 139.73 (*E*), 137.61 (*E*), 136.88 (*Z*), 131.98 (*Z*), 131.94 (*E*), 131.90 (*E*), 131.78 (*Z*), 128.67 (*E*), 128.38 (*Z*), 128.14 (*Z*), 125.53 (*Z*), 125.50 (*E*), 123.51 (*E*), 119.90 (*Z*), 119.53 (*E*), 118.91 (*E*), 118.84 (*Z*), 116.55 (*E*), 102.66 (*E*), 101.67 (*Z*), 93.80 (*E*), 93.62 (*Z*), 87.34 (*Z*), 87.30 (*E*), 60.89 (*Z*), 56.62 (*E*), 24.12 (*E*); HRMS (ESI): *m/z*: Calcd for $C_{19}H_{18}NO_2$ $[M+H]^+$ 292.1332, Found 292.1335; IR (thin film, cm^{-1}): 3424, 3247, 1665, 1596, 1367, 1239, 1129, 836, 753.



1d

(*E*)-*N*-(3-((2-(2-Methoxyvinyl)phenyl)ethynyl)phenyl)acetamide (1d)

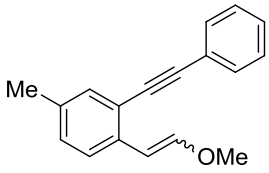
TLC (petroleum ether:ethyl acetate, 2:1, v/v): R_f=0.3; yellowish solid, Mp 129–130 ℃; 75%; ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 10.08 (s, 1H), 7.90 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.54 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.49 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.44 (d, *J* = 12.9 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.32 – 7.29 (m, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.17 (td, *J* = 7.6, 1.0 Hz, 1H), 6.26 (d, *J* = 12.9 Hz, 1H), 3.73 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ 168.61, 151.24, 139.66, 137.87, 132.11, 129.31, 129.00, 125.75, 125.55, 123.55, 122.67, 121.20, 119.28, 119.12, 102.57, 93.62, 87.90, 56.67, 24.09; HRMS (ESI): *m/z*: Calcd for $C_{19}H_{18}NO_2$ $[M+H]^+$ 292.1332, Found 292.1331; IR (thin film, cm^{-1}): 3293, 3137, 2930, 1668, 1637, 1427, 1235, 1154, 751.



1e

Ethyl 2-(4-((2-(2-methoxyvinyl)phenyl)ethynyl)phenyl)acetate (1e)

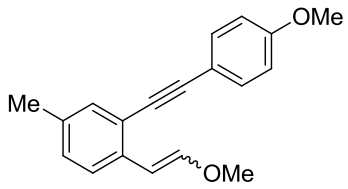
TLC (petroleum ether:ethyl acetate, 20:1, v/v): R_f=0.3; yellowish oil, (1/0.8 *E/Z*) 91%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.5 Hz, 1H, *Z*), 7.51 – 7.48 (m, 3H, *E* + 3H, *Z*), 7.37 (d, *J* = 7.9 Hz, 1H, *Z*), 7.30 – 7.26 (m, 2H, *E* + 3H, *Z*), 7.23 (d, *J* = 0.9 Hz, 1H, *E*), 7.18 (d, *J* = 13.0 Hz, 1H, *E*), 7.12 (td, *J* = 7.6, 3.8 Hz, 1H, *E* + 1H, *Z*), 6.34 (d, *J* = 13.0 Hz, 1H, *E*), 6.27 (d, *J* = 7.2 Hz, 1H, *Z*), 5.88 (d, *J* = 7.2 Hz, 1H, *Z*), 4.16 (q, *J* = 7.1, 2H, *E* + 2H, *Z*), 3.81 (s, 3H, *Z*), 3.75 (s, 3H, *E*), 3.63 (s, 2H, *E* + 2H, *Z*), 1.29 – 1.24 (m, 3H, *E* + 3H, *Z*); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.24 (*E*), 171.23 (*Z*), 150.21 (*E*), 149.10 (*Z*), 138.11 (Z), 137.24 (*E*), 134.31 (*E*), 134.22 (*Z*), 132.53 (*E*), 132.10 (*Z*), 131.68 (*Z*), 131.63 (*E*), 129.39 (*E*), 129.31 (*Z*), 128.57 (*E*), 128.30 (*Z*), 125.47 (*Z*), 125.46 (*E*), 123.62 (*E*), 122.38 (*Z*), 122.30 (*E*), 120.81 (*Z*), 120.52 (*E*), 103.53 (*E*), 103.19 (*Z*), 93.45 (*E*), 93.21 (*Z*), 88.61 (*Z*), 88.48 (*E*), 61.04 (*E*), 61.02 (*Z*), 60.88 (*Z*), 56.54 (*E*), 41.36 (*Z*), 41.34 (*E*), 14.20 (*E*); HRMS (ESI): *m/z*: Calcd for $C_{20}H_{19}O_3$ $[M+H]^+$ 307.1329, Found 307.1327; IR (thin film, cm^{-1}): 3438, 2981, 2935, 1732, 1639, 1237, 1031, 937, 755.



1f

1-(2-Methoxyvinyl)-4-methyl-2-(phenylethynyl)benzene (1f)

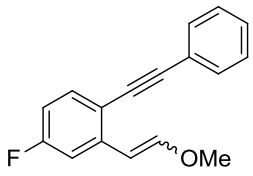
TLC (petroleum ether:ethyl acetate, 100:1, v/v): R_f=0.2; yellowish oil (1:0.3 *E*/*Z*), 72%; ^{1}H NMR (600 MHz, $CDCl_3$) *δ* = 8.14 (d, *J* = 8.1 Hz, 1H, *Z*), 7.67 – 7.61 (m, 2H, *Z* + 2H, *E*), 7.46 – 7.38 (m, 4H, *Z* + 4H, *E*), 7.35 (d, *J* = 8.1 Hz, 1H, *E*), 7.24 (d, *J* = 13.0 Hz, 1H, *E*), 7.20 (dd, *J* = 8.2 Hz, 1.3 Hz, 1H, *Z*), 7.12 (dd, *J* = 8.1 Hz, 1.2 Hz, 1H, *E*), 6.45 (d, *J* = 13.0 Hz, 1H, *E*), 6.29 (d, *J* = 7.2 Hz, 1H, *Z*), 6.00 (d, *J* = 7.2 Hz, 1H, *Z*), 3.82 (s, 3H, *Z*), 3.80 (s, 3H, *E*), 2.40 (s, 3H, *Z*), 2.38 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) *δ* = 149.6 (*E*), 148.5 (*Z*), 135.3 (*E*), 135.1 (*Z*), 135.1 (*E*), 134.6 (*Z*), 132.9 (*E*), 132.5 (*Z*), 131.5 (*Z*), 131.5 (*Z*), 131.5 (*Z*), 131.5 (*E*), 131.5 (*E*), 129.7 (*E*), 129.4 (*Z*), 128.6 (*Z*), 128.4 (*E*), 128.4 (*E*), 128.4 (*E*), 128.2 (*E*), 128.2 (*E*), 128.1 (*Z*), 123.7 (*Z*), 123.6 (*E*), 120.7 (*Z*), 120.4 (*E*), 103.5 (*E*), 103.2 (*Z*), 93.4 (*E*), 93.2 (*Z*), 88.8 (*Z*), 88.7 (*E*), 60.7 (*Z*), 56.4 (*E*), 21.0 (*Z*), 20.8 (*E*); HRMS (ESI): *m/z*: Calcd for $C_{18}H_{17}O$ $[M+H]^+$ 249.1274, Found 249.1277; IR (thin film, cm^{-1}): 3427, 2931, 1638, 1237, 1103, 756, 690.



1g

2-((4-Methoxyphenyl)ethynyl)-1-(2-methoxyvinyl)-4-methylbenzene (1g)

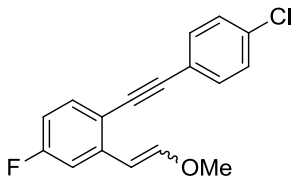
TLC (petroleum ether:ethyl acetate, 30:1, v/v): R_f=0.25; yellowish oil (1:0.46 *E*/*Z*), 72%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.01 (d, *J* = 8.1 Hz, 1H, *Z*), 7.48 (dd, *J* = 8.9 Hz, 2.5 Hz, 2H, *Z* + 2H, *E*), 7.32 (s, 1H, *E*), 7.27 (d, *J* = 8.1 Hz, 1H, *E*), 7.15 (d, *J* = 13.0 Hz, 1H, *E*), 7.10 (d, *J* = 8.1 Hz, 1H, *Z*), 7.04 (d, *J* = 8.0 Hz, 1H, *E*), 6.94 – 6.82 (m, 3H, *Z* + 2H, *E*), 6.34 (d, *J* = 13.0 Hz, 1H, *E*), 6.22 (d, *J* = 7.2 Hz, 1H, *Z*), 5.88 (d, *J* = 7.1 Hz, 1H, *Z*), 3.83 (s, 3H, *E*), 3.82 (s, 3H, *Z*), 3.79 (s, 3H, *Z*), 3.74 (s, 3H, *E*), 2.32 (s, 3H, *Z*), 2.31 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.7 (*E*), 159.6 (*Z*), 149.6 (*E*), 148.4 (*Z*), 135.2 (*Z*), 135.1 (*E*), 135.1 (*E*), 134.4 (*Z*), 133.0 (*Z*), 133.0 (*Z*), 133.0 (*E*), 133.0 (*E*), 132.8 (*E*), 132.4 (*Z*), 129.4 (*E*), 129.1 (*Z*), 128.6 (*Z*), 123.7 (*E*), 121.2 (*Z*), 120.8 (*E*), 115.9 (*Z*), 115.8 (*E*), 114.1 (*E*), 114.1 (*E*), 114.1 (*Z*), 114.1 (*Z*), 103.7 (*E*), 103.3 (*Z*), 93.4 (*E*), 93.2 (*Z*), 87.4 (*Z*), 87.3 (*E*), 68.1 (*Z*), 60.8 (*Z*), 56.6 (*E*), 55.4 (*E*), 21.1 (*Z*), 20.9 (*E*); HRMS (ESI): *m/z*: Calcd for $C_{19}H_{19}O_2$ $[M+H]^+$ 279.1380, Found 279.1371; IR (thin film, cm^{-1}): 3441, 2921, 2851, 1637, 1512, 1384, 1249, 1161, 830, 619.



1l

4-Fluoro-2-(2-methoxyvinyl)-1-(phenylethynyl)benzene (1l)

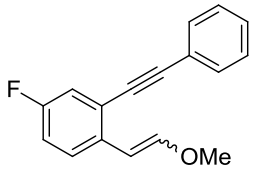
TLC (petroleum ether:ethyl acetate, 100:1, v/v): R_f=0.3; yellowish oil (1:0.5 *E*/*Z*), 75%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.19 (dd, *J* = 8.8 Hz, 6.0 Hz, 1H, *Z*), 7.61 (m, 6H, *Z*), 7.41 (m, 5H, *E*), 7.34 (dd, *J* = 8.7 Hz, 5.6 Hz, 1H, *E*), 7.30 – 7.24 (m, 1H, *E*), 7.15 (d, *J* = 13.0 Hz, 1H, *E*), 7.07 (td, *J* = 8.6 Hz, 2.7 Hz, 1H, *Z*), 7.00 (td, *J* = 8.5 Hz, 2.7 Hz, 1H, *E*), 6.37 (d, *J* = 13.0 Hz, 1H, *E*), 6.28 (d, *J* = 7.2 Hz, 1H, *Z*), 5.93 (d, *J* = 7.2 Hz, 1H, *Z*), 3.81 (s, 3H, *Z*), 3.77 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 160.6 (d, *J* = 254 Hz, *E*), 159.9 (d, *J* = 254 Hz, *Z*), 150.0 (d, *J* = 1.4 Hz, *E*), 148.7 (d, *J* = 2.0 Hz, *Z*), 134.5 (d, *J* = 3.2 Hz), 133.8 (d, *J* = 3.2 Hz), 131.6 (*Z*), 131.6 (*Z*), 131.6 (*E*), 131.6 (*E*), 131.5 (d, *J* = 9.5 Hz), 130.3 (d, *J* = 8.1 Hz), 128.6 (*E*), 128.5 (*Z*), 128.5 (*E*), 128.5 (*E*), 128.5 (*Z*), 128.4 (*Z*), 128.4 (*Z*), 125.3 (d, *J* = 8.2 Hz), 123.1 (*Z*), 123.08 (*E*), 122.5 (d, *J* = 9.2 Hz, *Z*), 121.9 (d, *J* = 9.2 Hz, *E*), 118.6 (d, *J* = 22.7 Hz, *E*), 118.3 (d, *J* = 22.8 Hz, *Z*), 116.1 (d, *J* = 21.7 Hz, *E*), 115.7 (d, *J* = 21.0 Hz, *Z*), 102.8 (*E*), 102.3 (*Z*), 94.6 (*E*), 94.4 (*Z*), 87.5 (d, *J* = 3.2 Hz, *Z*), 87.4 (d, *J* = 3.2 Hz, *E*), 60.8 (*Z*), 56.5 (*E*); HRMS (ESI): *m/z*: Calcd for $C_{17}H_{14}FO$ $[M+H]^+$ 253.1023, Found 253.1036; IR (thin film, cm^{-1}): 3447, 2938, 1696, 1604, 1573, 1497, 1217, 757, 690.



1m

1-((4-Chlorophenyl)ethynyl)-4-fluoro-2-(2-methoxyvinyl)benzene (1m)

TLC (petroleum ether:ethyl acetate, 100:1, v/v): R_f=0.3; yellowish oil (0.6:1 *E*/*Z*), 74%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.18 (dd, *J* = 8.8 Hz, 6.0 Hz, 1H, *Z*), 7.52 – 7.46 (m, 2H, *Z* + 2H, *E*), 7.38 – 7.34 (m, 2H, *Z* + 2H, *E*), 7.32 (dd, *J* = 8.7 Hz, 5.6 Hz, 1H, *E*), 7.24 (m, 1H, *Z* + 1H, *E*), 7.12 (d, *J* = 13.0 Hz, 1H, *E*), 7.06 (td, *J* = 8.6 Hz, 2.7 Hz, 1H, *Z*), 6.99 (td, *J* = 8.5 Hz, 2.7 Hz, 1H, *E*), 6.31 (d, *J* = 13.0 Hz, 1H, *E*), 6.28 (d, *J* = 7.1 Hz, 1H, *Z*), 5.87 (d, *J* = 7.1 Hz, 1H, *Z*), 3.81 (s, 3H, *Z*), 3.76 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 160.5 (d, *J* = 243.0 Hz, *E*), 159.9 (d, *J* = 243.0 Hz, *Z*), 150.1 (d, *J* = 1.3 Hz, *E*), 148.8 (d, *J* = 1.9 Hz, *Z*), 137.3 (d, *J* = 11.2 Hz, *Z*), 134.58 (*E*), 134.5 (d, *J* = 3.2 Hz, *E*), 134.49 (*Z*), 133.8 (*E*), 133.8 (d, *J* = 3.2 Hz, *Z*), 133.7 (*E*), 132.77 (*Z*), 132.72 (*E*), 130.4 (d, *J* = 8.1 Hz, *Z*), 128.80 (*E*), 128.74 (*Z*), 128.5 (d, *J* = 6.8 Hz, *E*), 125.3 (d, *J* = 8.2 Hz, *E*), 122.1 (d, *J* = 9.1 Hz, *Z*), 121.58 (*Z*), 121.54 (*E*), 121.52 (*Z*), 118.59 (d, *J* = 22.7 Hz, *E*), 118.3 (d, *J* = 22.7 Hz, *Z*), 116.3 (d, *J* = 21.7 Hz, *E*), 115.9 (d, *J* = 21.7 Hz, *Z*), 102.72 (*E*), 102.21 (*Z*), 93.33 (*E*), 93.13 (*Z*), 88.5 (d, *J* = 3.1 Hz, *Z*), 88.4 (d, *J* = 3.1 Hz, *E*), 60.78 (*Z*), 56.56 (*E*); HRMS (ESI): *m/z*: Calcd for $C_{17}H_{13}OClF$ $[M+H]^+$ 287.0633, Found 287.0666; IR (thin film, cm^{-1}): 3677, 2962, 1640, 1491, 1240, 1089, 930, 824, 694.

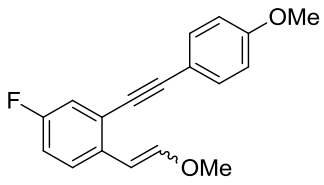


1n

4-Fluoro-1-(2-methoxyvinyl)-2-(phenylethynyl)benzene (1n)

TLC (petroleum ether:ethyl acetate, 100:1, v/v): R_f=0.2; yellowish oil (1:0.44 *E*/*Z*), 72%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.13 (dd, *J* = 8.9 Hz, 6.0 Hz, 1H, *Z*), 7.59 – 7.55 (m, 2H, *Z* + 2H, *E*), 7.40 – 7.35 (m, 4H, *Z* + 3H, *E*), 7.32 (dd, *J* = 8.7 Hz, 5.6 Hz, 1H, *E*), 7.22 (dd, *J* = 9.2 Hz, 2.8 Hz, 1H, *E*), 7.12 (d, *J* = 13.0 Hz, 1H, *E*), 7.02 (td, *J* = 8.6 Hz, 2.8 Hz, 1H, *Z*), 6.98 (td, *J* = 8.5 Hz, 2.8 Hz, 1H, *E*), 6.32 (d, *J* = 13.0 Hz, 1H, *E*), 6.26 (d, *J* = 7.2 Hz, 1H, *Z*), 5.87 (d, *J* = 7.2 Hz, 1H, *Z*), 3.81 (s, 3H, *Z*), 3.75 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 160.7 (d, *J* = 254 Hz, *E*), 160.0 (d, *J* = 254 Hz, *Z*), 150.05 (d, *J* = 1.5 Hz, *E*), 148.7 (d, *J* = 2.1 Hz, *Z*), 134.5 (d, *J* = 3.2 Hz, *E*), 133.9 (*E*), 133.8 (*E*), 133.75 (d, *J* = 3.2 Hz), 131.7 (*Z*), 131.7 (*Z*), 131.6 (*E*), 131.6 (*E*), 130.3 (*E*), 128.8 (*Z*), 128.7 (*Z*), 128.7 (*Z*), 128.6 (*Z*), 128.6 (*E*), 128.6 (*E*), 128.6 (*E*), 128.5 (*E*), 125.3 (d, *J* = 8.2 Hz, *E*), 123.2 (*Z*), 123.1 (*E*), 122.5 (d, *J* = 9.3 Hz, *Z*), 122.0 (d, *J* = 9.3 Hz, *E*), 118.7 (d, *J* = 22.7 Hz, *E*), 118.3 (d, *J* = 22.8 Hz, *Z*), 116.2 (d, *J* = 21.7 Hz, *E*), 115.7 (d, *J* = 21.1 Hz, *Z*), 102.9 (*E*), 102.4 (*Z*), 94.6 (*E*), 94.3 (*Z*), 87.5 (d, *J* = 3.3 Hz, *Z*), 87.4 (d, *J* = 3.2 Hz, *E*), 60.9 (*Z*), 56.6 (*E*); HRMS (ESI): *m/z*: Calcd for $C_{17}H_{14}FO$

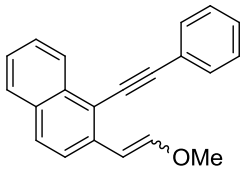
$[M+H]^+$ 253.1023, Found 253.1036; IR (thin film, cm^{-1}): 3429, 2932, 1639, 1602, 1493, 1238, 1098, 756, 690.



1o

4-Fluoro-2-((4-methoxyphenyl)ethynyl)-1-(2-methoxyvinyl)benzene (1o)

TLC (petroleum ether:ethyl acetate, 100:1, v/v): R_f=0.25; yellowish oil (1:0.57 *E*/*Z*), 74%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.13 (dd, *J* = 8.8 Hz, 6.1 Hz, 1H, *Z*), 7.54 – 7.46 (m, 2H, *Z* + 2H, *E*), 7.30 (dd, *J* = 8.7 Hz, 5.6 Hz, 1H, *E*), 7.24 – 7.17 (m, 1H, *Z* + 1H, *E*), 7.11 (d, *J* = 13.0 Hz, 1H, *E*), 7.01 (td, *J* = 8.6 Hz, 2.7 Hz, 1H, *Z*), 6.95 (td, *J* = 8.5 Hz, 2.6 Hz, 1H, *E*), 6.91 (dd, *J* = 8.6 Hz, 3.5 Hz, 2H, *Z* + 2H, *E*), 6.86 (d, *J* = 8.6 Hz, 1H, *E*), 6.32 (d, *J* = 13.0 Hz, 1H, *E*), 6.25 (d, *J* = 7.2 Hz, 1H, *Z*), 5.88 (d, *J* = 7.1 Hz, 1H, *Z*), 3.82 (s, 3H, *E*), 3.80 (s, 3H, *Z*), 3.79 (s, 3H, *Z*), 3.74 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 160.5 (d, *J* = 238.5 Hz, *E*), 160.3 (*E*), 160.1 (d, *J* = 238.5 Hz, *Z*), 159.9 (*E*), 159.9 (*Z*), 149.9 (d, *J* = 1.2 Hz), 148.6 (d, *J* = 1.9 Hz), 134.2 (d, *J* = 3.2 Hz, *E*), 134.1 (*E*), 133.5 (d, *J* = 3.1 Hz, *Z*), 133.1 (*Z*), 133.1 (*Z*), 133.0 (*E*), 133.0 (*E*), 130.3 (d, *J* = 8.1 Hz, *Z*), 125.2 (d, *J* = 8.3 Hz, *E*), 122.9 (d, *J* = 9.3 Hz, *Z*), 122.3 (d, *J* = 9.3 Hz, *E*), 118.4 (d, *J* = 22.7 Hz, *E*), 118.1 (d, *J* = 22.3 Hz, *Z*), 115.7 (d, *J* = 21.7 Hz, *E*), 115.4 (*Z*), 115.2 (d, *J* = 4.2 Hz, *Z*), 115.1 (*Z*), 114.2 (*Z*), 114.2 (*Z*), 114.2 (*E*), 114.2 (*E*), 114.1 (*E*), 113.9 (*Z*), 102.9 (*E*), 102.4 (*Z*), 94.7 (*E*), 94.5 (*Z*), 86.2 (d, *J* = 3.1 Hz, *Z*), 86.1 (d, *J* = 3.1 Hz, *E*), 60.8 (*Z*), 56.5 (*E*), 55.3 (*Z* + *E*); HRMS (ESI): *m/z*: Calcd for $C_{18}H_{16}FO_2$ $[M+H]^+$ 283.1129, Found 283.1129; IR (thin film, cm^{-1}): 3431, 2935, 1639, 1601, 1512, 1250, 830, 535.

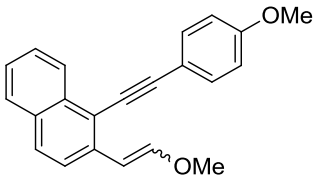


1p

2-(2-Methoxyvinyl)-1-(phenylethynyl)naphthalene (1p)

TLC (petroleum ether:ethyl acetate, 50:1, v/v): R_f=0.2; yellowish oil (1:0.7 *E*/*Z*), 71%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.46 – 8.40 (m, 1H, *Z* + 1H, *E*), 8.30 (d, *J* = 8.8 Hz, 1H, *Z*), 7.79 (t, *J* = 8.2 Hz, 1H, *Z* + 1H, *E*), 7.76 (d, *J* = 8.8 Hz, 1H, *Z*), 7.72 (d, *J* = 8.7 Hz, 1H, *E*), 7.67 (m, 5H, *Z*), 7.59 – 7.56 (m, 1H, *E*), 7.56 – 7.51 (m, 3H, *Z*), 7.46 (d, *J* = 6.8 Hz, 2H, *E*), 7.42 (m, 5H, *E*), 7.34 (d, *J* = 13.0 Hz, 1H, *E*), 6.68 (d, *J* = 13.0 Hz, 1H, *E*), 6.35 (d, *J* = 7.2 Hz, 1H, *Z*), 6.16 (d, *J* = 7.2 Hz, 1H, *Z*), 3.86 (s, 3H, *Z*), 3.82 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 151.1 (*E*), 149.7 (*Z*), 136.9 (*E*), 136.7 (*Z*), 134.0 (*E*), 133.7 (*Z*), 131.7 (*Z*), 131.7 (*Z*), 131.7 (*Z*), 131.6 (*E*), 131.6 (*E*), 131.6 (*E*), 128.7 (*E*), 128.6 (*E*), 128.6 (*E*), 128.6 (*Z*), 128.6 (*Z*), 128.4 (*E*), 128.4 (*Z*), 128.2 (*E*), 128.1 (*Z*), 128.1 (*Z*), 127.2 (*E*), 126.8 (*Z*), 126.7 (*Z*), 126.6 (*Z*), 126.3 (*E*), 125.8 (*Z*), 125.6 (*E*), 123.9 (*Z*), 123.9 (*E*), 121.9 (*E*), 117.2 (*Z*), 116.5 (*E*), 104.7 (*E*), 104.3 (*Z*),

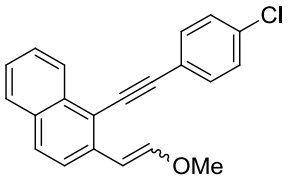
99.6 (*E*), 99.5 (*Z*), 86.8 (*Z*), 86.5 (*E*), 61.1 (*Z*), 56.8 (*E*); HRMS (ESI): *m/z*: Calcd for $C_{21}H_{17}O$ $[M+H]^+$ 285.1274, Found 285.1276; IR (thin film, cm^{-1}): 3432, 2931, 1634, 1490, 1201, 753, 689.



1q

1-((4-Methoxyphenyl)ethynyl)-2-(2-methoxyvinyl)naphthalene (1q)

TLC (petroleum ether:ethyl acetate, 15:1, v/v): R_f=0.3; yellowish oil (1:0.5 *E*/*Z*), 65%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.44 (s, 1H, *Z*), 8.41 (d, *J* = 8.4 Hz, 1H, *E*), 8.29 (d, *J* = 8.7 Hz, 1H, *Z*), 7.78 (t, *J* = 8.3 Hz, 1H, *Z* + 1H, *E*), 7.74 (d, *J* = 8.8 Hz, 1H, *Z*), 7.70 (d, *J* = 8.7 Hz, 1H, *E*), 7.60 (dd, *J* = 8.4 Hz, 3.5 Hz, 2H, *Z* + 2H, *E*), 7.57 – 7.51 (m, 2H, *Z* + 2H, *E*), 7.49 – 7.42 (m, 2H, *Z* + 2H, *E*), 7.32 (d, *J* = 13.0 Hz, 1H, *E*), 6.94 (d, *J* = 8.6 Hz, 2H, *Z* + 2H, *E*), 6.86 (d, *J* = 8.7 Hz, 1H, *E*), 6.67 (d, *J* = 13.0 Hz, 1H, *E*), 6.34 (d, *J* = 7.2 Hz, 1H, *Z*), 6.15 (d, *J* = 7.2 Hz, 1H, *Z*), 3.86 (s, 3H, *E*), 3.85 (s, 3H, *Z*), 3.81 (s, 3H, *Z* + 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 160.4(*Z*), 159.8 (*E*), 151.0 (*E*), 149.6 (*Z*), 136.5 (*E*), 136.4 (*Z*), 134.2 (*E*), 134.0 (*Z*), 133.7 (*Z*), 133.1 (*Z*), 133.1 (*Z*), 133.1 (*E*), 133.1 (*E*), 131.7 (*E*), 131.6 (*Z*), 128.4 (*E*), 128.1 (*E*), 128.1 (*Z*), 127.8 (*Z*), 127.1 (*E*), 126.7 (*Z*), 126.7 (*E*), 126.4 (*E*), 125.7 (*Z*), 125.6 (*E*), 121.9 (*E*), 117.6 (*Z*), 116.9 (*E*), 116.0 (*Z*), 116.0 (*E*), 114.3 (*E*), 114.3 (*E*), 114.2 (*Z*), 114.2 (*Z*), 114.1 (*Z*), 104.8 (*E*), 104.4 (*Z*), 99.6 (*E*), 99.5 (*Z*), 85.4 (*Z*), 85.2 (*E*), 61.1 (*Z*), 56.8 (*E*), 55.5 (*E*), 55.5 (*Z*); HRMS (ESI): *m/z*: Calcd for $C_{22}H_{19}O_2$ $[M+H]^+$ 315.1380, Found 315.1370; IR (thin film, cm^{-1}): 3429, 2932, 1634, 1603, 1509, 1248, 829.

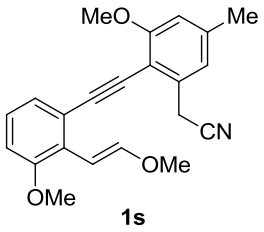


1r

1-((4-Chlorophenyl)ethynyl)-2-(2-methoxyvinyl)naphthalene (1r)

TLC (petroleum ether:ethyl acetate, 20:1, v/v): R_f=0.25; yellowish oil (1:0.7 *E*/*Z*); 63%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.41 (d, *J* = 8.5 Hz, 1H, *Z*), 8.39 (d, *J* = 8.4 Hz, 1H, *E*), 8.32 (d, *J* = 8.8 Hz, 1H, *Z*), 7.81 (d, *J* = 8.2 Hz, 1H, *Z*), 7.78 (m, 4H, *Z*), 7.72 (d, *J* = 8.7 Hz, 1H, *E*), 7.59 (d, *J* = 6.7 Hz, 2H, *E*), 7.57 (d, *J* = 6.7 Hz, 2H, *E*), 7.53 (d, *J* = 8.7 Hz, 1H, *E*), 7.47 (q, *J* = 7.4 Hz, 3H, *Z*), 7.39 (dd, *J* = 8.4 Hz, 2.7 Hz, 3H, *E*), 7.32 (d, *J* = 13.0 Hz, 1H, *E*), 6.65 (d, *J* = 13.0 Hz, 1H, *E*), 6.36 (d, *J* = 7.2 Hz, 1H, *Z*), 6.13 (d, *J* = 7.2 Hz, 1H, *Z*), 3.85 (s, 3H, *Z*), 3.82 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 151.1 (*E*), 149.7 (*Z*), 136.9 (*E*), 136.7 (*Z*), 134.0 (*E*), 133.7 (*Z*), 131.7 (*Z*), 131.7 (*Z*), 131.6 (*E*), 131.6 (*E*), 128.7 (*E*), 128.6 (*E*), 128.6 (*E*), 128.6 (*Z*), 128.6 (*Z*), 128.4 (*E*), 128.4 (*Z*), 128.2 (*E*), 128.1 (*Z*), 128.1 (*Z*), 127.2 (*E*), 126.8 (*Z*), 126.7 (*Z*), 126.6 (*Z*), 126.3 (*E*), 125.8 (*Z*), 125.6 (*E*), 123.9 (*Z*), 123.9 (*E*), 121.9 (*E*), 117.2 (*Z*), 116.5 (*Z*), 104.7 (*E*), 104.3 (*Z*), 99.6 (*E*), 99.5 (*Z*), 86.8 (*Z*), 86.5 (*E*), 61.1 (*Z*), 56.8 (*E*); HRMS

(ESI): *m/z*: Calcd for $C_{21}H_{16}OCl$ $[M+H]^+$ 319.0884, Found 319.0901; IR (thin film, cm^{-1}) 3419, 2921, 1634, 1488, 1204, 1089, 826.

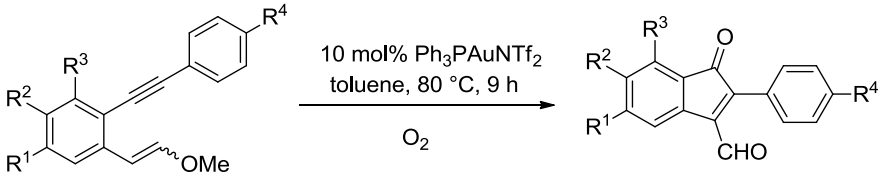


1s

(*E*)-2-(3-Methoxy-2-((3-methoxy-2-(2-methoxyvinyl)phenyl)ethynyl)-5-methylphenyl)acetonitrile (1s)

TLC (petroleum ether:ethyl acetate, 8:1, v/v): R_f=0.25; yellowish oil (*E*); 73%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.76 (d, *J* = 12.8 Hz, 1H), 7.18 (dd, *J* = 7.7 Hz, 1.0 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.96 (s, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.71 (s, 1H), 6.37 (d, *J* = 12.8 Hz, 1H), 3.96 (s, 2H), 3.91 (s, 3H), 3.88 (s, 3H), 3.76 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 160.7, 156.7, 153.7, 140.5, 132.9, 126.8, 125.6, 125.5, 121.8, 121.1, 117.8, 111.3, 111.1, 109.7, 100.5, 99.1, 87.0, 56.3, 56.0, 55.6, 22.8, 22.1; HRMS (ESI): *m/z*: Calcd for $C_{22}H_{22}O_3N$ $[M+H]^+$ 348.1594, Found 348.1593; IR (thin film, cm^{-1}) 3442, 2960, 2925, 1639, 1460, 1384, 1260, 1088, 1033, 802.

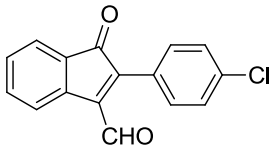
5. General Preparation of 3-3s and Characterization Data



1-1s **3-3s**

The 1,5-enyne substrates **1-1s** (1 mmol) and the $Ph_3PAuNTf_2$ (0.1 mmol, 73.8 mg) in toluene (2 mL) were placed in a screw-cap vial containing a stirring bar. The reaction vial was fitted with a cap, evacuated, filled with oxygen, bubbled over all the time, and heated with stirring at 80 ℃ for 10-20 h. The reaction mixture was cooled, filtered through a plug of silica gel. The filtrate was concentrated and the obtained residue was purified by flash column chromatography to afford the indenones **3-3s**.

Spectral data were consistent with those reported in the literature. [4]

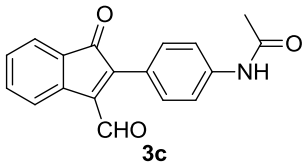


3b

2-(4-Chlorophenyl)-1-oxo-1H-indene-3-carbaldehyde (3b)

TLC (petroleum ether:ethyl acetate, 100:1, v/v): R_f=0.2; red solid, Mp 143–145 ℃; 75%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 10.30 (s, 1H), 7.98 (d, *J* = 7.4 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.52 – 7.45 (m, 5H), 7.34 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 196.7, 190.5, 144.0, 143.7, 142.3, 137.2, 135.0, 132.0, 132.0, 129.7, 129.6, 129.3, 129.3, 126.7, 124.5, 124.5; HRMS (ESI): *m/z*: Calcd for $C_{16}H_{10}O_2Cl$ $[M+H]^+$

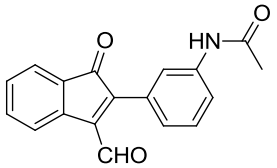
269.0364, Found 269.0388; IR (thin film, cm^{-1}): 3392, 2922, 1706, 1673, 1591, 1462, 1090, 1003, 755, 512.



3c

***N*-(4-(3-Formyl-1-oxo-1*H*-inden-2-yl)phenyl)acetamide (3c)**

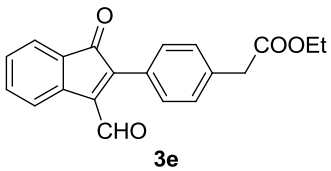
TLC (petroleum ether:ethyl acetate, 1:1, v/v): R_f=0.3; red solid, Mp 223–225 ℃; 57%; ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 10.25 (s, 1H), 10.19 (s, 1H), 7.90 (d, *J* = 7.4 Hz, 1H), 7.75 (d, *J* = 8.6 Hz, 2H), 7.63 – 7.59 (m, 3H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 7.3 Hz, 1H), 2.10 (s, 3H); ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ 196.88, 191.11, 168.81, 143.46, 142.44, 141.59, 141.45, 134.87, 131.71, 129.20, 129.17, 123.92, 123.43, 122.47, 118.60, 24.18; HRMS (ESI): *m/z*: Calcd for $C_{18}H_{14}NO_3$ $[M+H]^+$ 292.0968, Found 292.0970; IR (thin film, cm^{-1}): 3381, 2922, 1701, 1664, 1370, 1184, 826, 746.



3d

***N*-(3-(3-Formyl-1-oxo-1*H*-inden-2-yl)phenyl)acetamide (3d)**

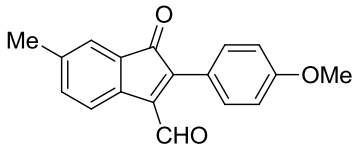
TLC (petroleum ether:ethyl acetate, 1:1, v/v): R_f=0.3; red solid, Mp 188–189 ℃; 46%; ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 10.20 (s, 1H), 10.15 (s, 1H), 7.89 (d, *J* = 7.3 Hz, 1H), 7.77 (d, *J* = 6.7 Hz, 2H), 7.63 (d, *J* = 7.1 Hz, 1H), 7.59 (td, *J* = 7.6, 1.0 Hz, 1H), 7.46 (t, *J* = 8.2 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 2.07 (s, 3H); ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ 196.38, 191.22, 168.61, 143.62, 143.13, 142.03, 139.41, 134.84, 129.66, 129.51, 129.22, 128.97, 128.32, 125.47, 123.99, 123.60, 120.97, 120.79, 24.05; HRMS (ESI): *m/z*: Calcd for $C_{18}H_{14}NO_3$ $[M+H]^+$ 292.0968, Found 292.0968; IR (thin film, cm^{-1}): 3394, 3246, 2922, 1677, 1660, 1385, 1014, 758.



3e

Ethyl 2-(4-(3-formyl-1-oxo-1*H*-inden-2-yl)phenyl)acetate (3e)

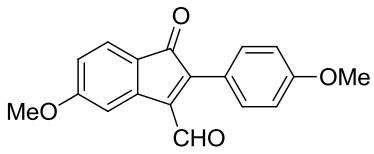
TLC (petroleum ether:ethyl acetate, 15:1, v/v): R_f=0.3; red oil, 61%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.31 (s, 1H), 7.98 (d, *J* = 7.4 Hz, 1H), 7.62 (d, *J* = 7.1 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.48 (td, *J* = 7.6, 1.1 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.30 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.92, 190.99, 170.96, 144.59, 143.54, 142.31, 136.86, 134.72, 130.86, 129.74, 129.50, 129.31, 126.94, 124.26, 124.18, 61.16, 41.28, 14.19; HRMS (ESI): *m/z*: Calcd for $C_{19}H_{15}O_4$ $[M+H]^+$ 307.0965, Found 307.0970; IR (thin film, cm^{-1}): 3425, 2981, 2932, 1732, 16373, 1460, 1369, 1156, 1029, 758.



3f

2-(4-Methoxyphenyl)-6-methyl-1-oxo-1H-indene-3-carbaldehyde (3f)

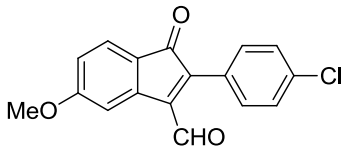
TLC (petroleum ether:ethyl acetate, 50:1, v/v): R_f=0.2; red solid, Mp 166–167 ℃; 82%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 10.27 (s, 1H), 7.82 (d, J = 7.5 Hz, 1H), 7.52 (d, J = 8.6 Hz, 2H), 7.42 (s, 1H), 7.25 (d, J = 7.5 Hz, 1H), 7.02 (d, J = 8.6 Hz, 2H), 3.88 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 197.9, 191.2, 161.8, 144.3, 142.5, 140.1, 139.4, 134.9, 132.5, 123.0, 125.2, 123.8, 121.0, 114.5, 55.6, 21.5; HRMS (ESI): *m/z*: Calcd for $C_{18}H_{15}O_3$ $[M+H]^+$ 279.1016, Found 279.1016; IR (thin film, cm^{-1}): 3442, 2924, 1716, 1667, 1608, 1507, 1458, 1383, 1256, 1115, 825.



3i

5-Methoxy-2-(4-methoxyphenyl)-1-oxo-1H-indene-3-carbaldehyde (3i)

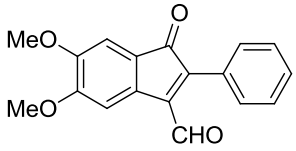
TLC (petroleum ether:ethyl acetate, 5:1, v/v): R_f=0.3; red solid, Mp 178–180 ℃; 82%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 10.25 (s, 1H), 7.57 (m, 2H), 7.55 (d, J = 8.7 Hz, 2H), 7.03 (d, J = 8.7 Hz, 2H), 6.70 (dd, J = 8.2 Hz, 2.2 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 195.6, 191.0, 165.4, 162.0, 146.8, 145.8, 140.3, 132.7, 132.7, 126.4, 122.3, 121.1, 114.5, 114.5, 112.4, 111.6, 56.1, 55.6; HRMS (ESI): *m/z*: Calcd for $C_{18}H_{14}O_4Na$ $[M+Na]^+$ 317.0784, Found 317.0777; IR (thin film, cm^{-1}): 3422, 2924, 1666, 1601, 1475, 1290, 1262, 1181, 1025, 831.



3j

2-(4-Chlorophenyl)-5-methoxy-1-oxo-1H-indene-3-carbaldehyde (3j)

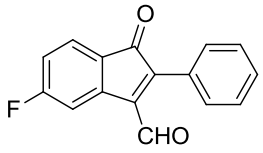
TLC (petroleum ether:ethyl acetate, 15:1, v/v): R_f=0.2; red solid, Mp 152–154 ℃; 79%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 10.25 (s, 1H), 7.58 (d, J = 8.2 Hz, 1H), 7.57 (d, J = 2.0 Hz, 1H), 7.49 (s, 4H), 6.73 (dd, J = 8.1 Hz, 2.1 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 194.9, 190.4, 165.4, 145.7, 145.1, 142.1, 137.2, 132.1, 132.1, 129.2, 129.2, 126.9, 126.6, 122.2, 112.8, 112.2, 56.1; HRMS (ESI): *m/z*: Calcd for $C_{17}H_{10}ClO_3$ $[M-H]^-$ 297.0324, Found 297.0360; IR (thin film, cm^{-1}): 3421, 2923, 1700, 1676, 1599, 1470, 1221, 1183, 890, 793, 526.



3k

5,6-Dimethoxy-1-oxo-2-phenyl-1H-indene-3-carbaldehyde (3k)

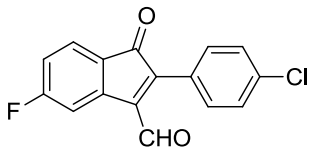
TLC (petroleum ether:ethyl acetate, 50:1, v/v): R_f=0.25; red solid, Mp 179–181 ℃; 77%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 10.24 (s, 1H), 7.60 (s, 1H), 7.51 (m, 5H), 7.19 (s, 1H), 4.02 (s, 3H), 3.92 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 196.0, 191.2, 153.9, 149.5, 145.4, 142.5, 137.8, 130.7, 130.7, 130.5, 128.8, 128.8, 128.5, 121.9, 108.3, 108.1, 56.7, 56.5; HRMS (ESI): *m/z*: Calcd for $C_{18}H_{15}O_4$ $[M+H]^+$ 295.0965, Found 295.0970; IR (thin film, cm^{-1}): 3424, 2923, 1702, 1664, 1466, 1366, 1124, 1022, 692.



3l

5-Fluoro-1-oxo-2-phenyl-1H-indene-3-carbaldehyde (3l)

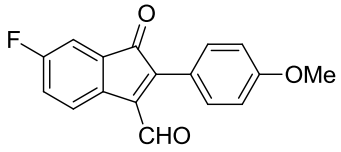
TLC (petroleum ether:ethyl acetate, 100:1, v/v): R_f=0.3; red solid, Mp 130–132 ℃; 70%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 10.29 (s, 1H), 7.97 (dd, *J* = 8.1 Hz, 4.7 Hz, 1H), 7.55 – 7.50 (m, 5H), 7.32 (dd, *J* = 7.0 Hz, 2.3 Hz, 1H), 7.14 (td, *J* = 8.5 Hz, 2.3 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 195.76, 190.96, 163.8 (d, *J* = 251.5 Hz), 145.16 (d, *J* = 4.7 Hz), 143.52 (d, *J* = 1.8 Hz), 138.0 (d, *J* = 3.3 Hz), 131.9 (d, *J* = 7.2 Hz), 130.8, 130.7, 130.7, 128.9, 128.9, 128.0, 125.7 (d, *J* = 7.7 Hz), 120.3 (d, *J* = 22.5 Hz), 112.5 (d, *J* = 24.6 Hz); HRMS (ESI): *m/z*: Calcd for $C_{16}H_{10}O_2F$ $[M+H]^+$ 253.0659, Found 253.0680; IR (thin film, cm^{-1}): 3418, 2923, 1724, 1672, 1469, 1260, 1013, 803, 692.



3m

2-(4-Chlorophenyl)-5-fluoro-1-oxo-1H-indene-3-carbaldehyde (3m)

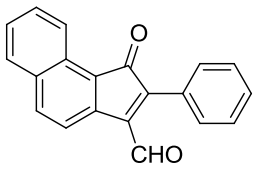
TLC (petroleum ether:ethyl acetate, 100:1, v/v): R_f=0.2; red solid, Mp 153–155 ℃; 72%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 10.28 (s, 1H), 7.97 (dd, *J* = 8.2 Hz, 4.7 Hz, 1H), 7.52 – 7.46 (m, 5H), 7.33 (dd, *J* = 7.0 Hz, 2.4 Hz, 1H), 7.15 (td, *J* = 8.6 Hz, 2.5 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 195.4, 190.4, 163.9 (d, *J* = 251.9 Hz), 143.7, 137.8 (d, *J* = 3.3 Hz), 137.3, 132.1, 131.9, 131.9, 129.4, 129.4, 129.4, 126.4, 125.8 (d, *J* = 7.7 Hz), 120.5 (d, *J* = 22.5 Hz), 112.7 (d, *J* = 24.6 Hz); HRMS (ESI): *m/z*: Calcd for $C_{16}H_9ClFO_2$ $[M+H]^+$ 287.0270, Found 287.0302; IR (thin film, cm^{-1}): 3417, 2923, 1724, 1672, 1590, 1474, 1224, 1007, 833, 795.



3n

6-Fluoro-2-(4-methoxyphenyl)-1-oxo-1*H*-indene-3-carbaldehyde (3n)

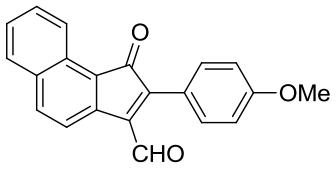
TLC (petroleum ether:ethyl acetate, 50:1, v/v): R_f=0.3; red solid, Mp 168–170 ℃; 75%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 10.28 (s, 1H), 7.95 (dd, *J* = 8.1 Hz, 4.7 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.30 (dd, *J* = 7.0 Hz, 2.4 Hz, 1H), 7.13 (td, *J* = 8.6 Hz, 2.4 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 196.2, 190.8, 163.3 (d, *J* = 250.9 Hz), 161.8, 144.6 (d, *J* = 4.7 Hz), 141.6, 138.2 (d, *J* = 3.3 Hz), 132.3, 132.3, 131.6 (d, *J* = 7.1 Hz), 125.1 (d, *J* = 7.7 Hz), 120.3, 120.2 (d, *J* = 22.5 Hz), 114.4, 114.4, 112.2 (d, *J* = 24.5 Hz), 55.4; HRMS (ESI): *m/z*: Calcd for $C_{17}H_{12}O_3F$ $[M+H]^+$ 283.0700, Found 283.0692; IR (thin film, cm^{-1}): 3420, 2924, 1723, 1671, 1607, 1468, 1253, 1176, 1020, 797.



3p

1-Oxo-2-phenyl-1H-cyclopenta[a]naphthalene-3-carbaldehyde (3p)

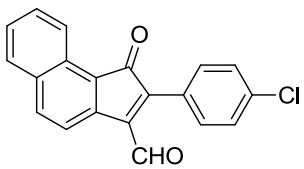
TLC (petroleum ether:ethyl acetate, 100:1, v/v): R_f=0.2; red solid, Mp 153–154 ℃; 56%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 10.33 (s, 1H), 8.76 (d, *J* = 8.5 Hz, 1H), 8.20 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.61 – 7.57 (m, 3H), 7.54 (dd, *J* = 5.2 Hz, 1.8 Hz, 3H), 7.45 – 7.40 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 198.4, 191.0, 145.2, 142.7, 135.8, 134.7, 130.9, 130.9, 130.7, 130.0, 129.8, 128.9, 128.9, 128.8, 128.3, 126.6, 123.8, 121.8, 121.8; HRMS (ESI): *m/z*: Calcd for $C_{20}H_{13}O_2$ $[M+H]^+$ 285.0910, Found 285.0946; IR (thin film, cm^{-1}): 3395, 22924, 2853, 1702, 1670, 1464, 1443, 1384, 825, 694.



3q

2-(4-Methoxyphenyl)-1-oxo-1H-cyclopenta[a]naphthalene-3-carbaldehyde (3q)

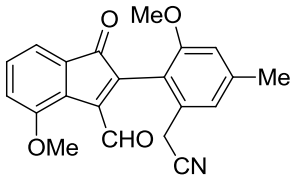
TLC (petroleum ether:ethyl acetate, 50:1, v/v): R_f=0.3; brown solid, Mp 163–166 ℃; 59%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 10.31 (s, 1H), 8.76 (d, *J* = 8.5 Hz, 1H), 8.20 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.58 – 7.56 (m, 1H), 7.41 (m, 1H), 7.05 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 198.9, 190.9, 162.1, 145.8, 144.9, 140.9, 135.8, 134.5, 132.8, 132.8, 129.9, 129.8, 128.8, 126.4, 123.8, 121.8, 121.6, 120.9, 114.6, 114.6, 55.7, 53.6; HRMS (ESI): *m/z*: Calcd for $C_{21}H_{15}O_3$ $[M+H]^+$ 315.1016, Found 315.1029; IR (thin film, cm^{-1}): 3405, 2925, 1700, 1670, 1459, 1384, 1255, 832.



3r

2-(4-Chlorophenyl)-1-oxo-1H-cyclopenta[a]naphthalene-3-carbaldehyde (3r)

TLC (petroleum ether:ethyl acetate, 100:1, v/v): R_f=0.2; brown solid, Mp 101–102 ℃; 52%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 10.31 (s, 1H), 8.74 (d, *J* = 8.5 Hz, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 198.0, 190.4, 145.0, 143.7, 142.9, 137.2, 135.9, 134.8, 132.1, 132.1, 130.1, 129.8, 129.3, 129.3, 128.8, 126.7, 126.7, 123.8, 121.9, 121.7; HRMS (ESI): *m/z*: Calcd for $C_{20}H_{12}O_2Cl$ $[M+H]^+$ 319.0520, Found 319.0561; IR (thin film, cm^{-1}): 3395, 2956, 2924, 1709, 1672, 1465, 1383, 1090, 1078, 828, 739.

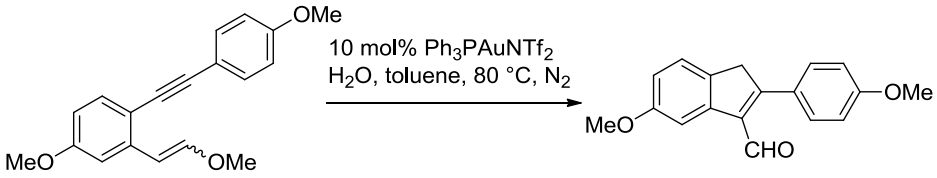


3s

2-(2-(3-Formyl-4-methoxy-1-oxo-1H-inden-2-yl)-3-methoxy-5-methylphenyl)acetonitrile (3s)

TLC (petroleum ether:ethyl acetate, 3:1, v/v): R_f=0.25; red solid, Mp 188–191 ℃; 61%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 10.39 (s, 1H), 7.33 (dd, *J* = 8.4, 7.1 Hz, 1H), 7.25 (s, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 6.97 (s, 1H), 6.71 (s, 1H), 3.95 (s, 3H), 3.70 (s, 3H), 3.68 (d, *J* = 18.7 Hz, 1H), 3.62 (d, *J* = 18.6 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 195.5, 190.8, 157.9, 153.7, 149.9, 141.4, 133.6, 132.0, 131.9, 131.5, 128.7, 121.7, 119.1, 118.0, 117.7, 115.6, 111.6, 56.0, 56.00, 22.5, 22.0; HRMS (ESI): *m/z*: Calcd for $C_{21}H_{18}O_4N$ $[M+H]^+$ 348.1158, Found 348.1177; IR (thin film, cm^{-1}): 3398, 2922, 2855, 2195, 1687, 1601, 1568, 1465, 1260, 1065, 793.

6. Preparation of 4i and Characterization Data

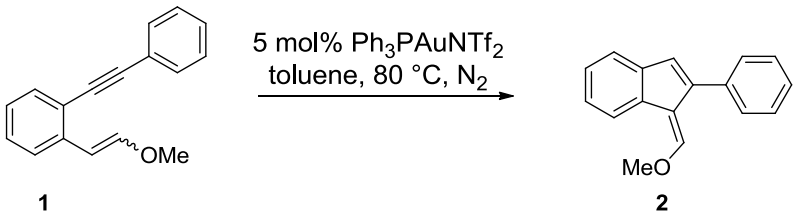


1i **4i**

To a solution of 4-methoxy-1-((4-methoxyphenyl)ethynyl)-2-(2-methoxyvinyl)-benzene **1i** (1 mmol, 294.3 mg) and $Ph_3PAuNTf_2$ (0.1 mmol, 73.8 mg) in toluene was added three drops of water. The resulting mixture was stirred at 80 ℃ for 9 h under a nitrogen atmosphere. After the reaction was completed, the reaction mixture was quenched with distilled water and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography (petroleum ether:ethyl acetate, 20:1, v/v) on silica gel to afford the desired product **4i** (230 mg) as a yellowish solid with a yield of 82%; Mp 151–152 ℃; 82%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 10.15 (s, 1H), 7.85 (d, *J* = 2.2 Hz, 1H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.26 (s, 1H), 7.01 (d, *J* = 8.6 Hz, 2H), 6.85 (dd, *J* = 8.2 Hz, 2.3 Hz, 1H), 3.92 (s,

2H), 3.88 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 189.8, 164.5, 161.2, 159.5, 142.8, 136.0, 132.9, 131.0, 131.0, 127.1, 124.0, 114.5, 114.5, 113.4, 107.5, 55.8, 55.6, 42.4; HRMS (ESI): *m/z*: Calcd for $C_{18}H_{16}O_3Na$ $[M+Na]^+$ 303.0992, Found 303.0993; IR (thin film, cm^{-1}): 3441, 2924, 2852, 1656, 1600, 1474, 1262, 1105, 1022, 803.

7. Preparation of 2 and Characterization Data



1 **2**

To a solution of 1-(2-methoxyvinyl)-2-(phenylethynyl)benzene **1** (1 mmol, 234.3 mg) in toluene was added $Ph_3PAuNTf_2$ (0.1 mmol, 73.8 mg). The resulting mixture was stirred at 80 ℃ for 1 h under a nitrogen atmosphere. After the reaction was completed, the reaction mixture was quenched with distilled water and extracted with CH_2Cl_2 (3 ×10 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography (petroleum ether:ethyl acetate, 100:1, v/v) on silica gel to afford the desired product **2** (223 mg) as a yellowish oil with a yield of 95%; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.87 (d, *J* = 7.4 Hz, 1H), 7.49 (dd, *J* = 8.1 Hz, 1.1 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 7.3 Hz, 2H), 7.24 (s, 1H), 7.19 (td, *J* = 7.4 Hz, 1.2 Hz, 1H), 7.15 (td, *J* = 7.4 Hz, 1.2 Hz, 1H), 6.74 (s, 1H), 4.04 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 155.6, 141.4, 140.2, 135.7, 134.2, 128.8, 128.8, 128.6, 128.6, 127.2, 125.9, 124.2, 123.9, 123.4, 120.3, 117.8, 62.4; HRMS (ESI): *m/z*: Calcd for $C_{17}H_{15}O$ $[M+H]^+$ 235.1117, Found 235.1125; IR (thin film, cm^{-1}): 3329, 2852, 1695, 1493, 1449, 1126, 757, 690.

8. X-Ray Structure of 3o

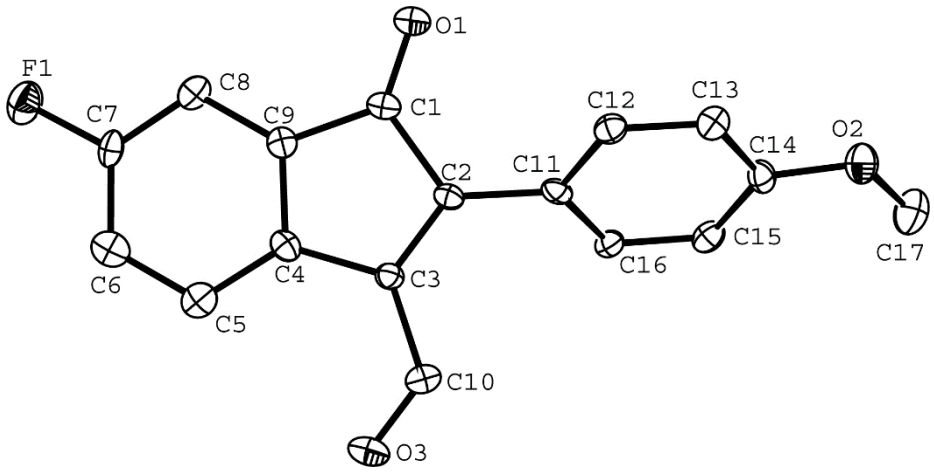


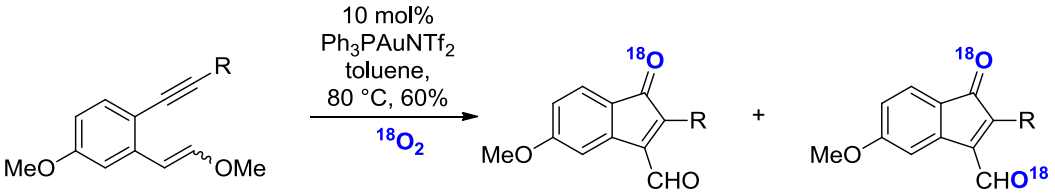
Figure S1. Single crystal structure of **3o**.

Table 1 Crystal data and structure refinement for exp_5652.

Identification code	exp_5652
Empirical formula	$C_{17}H_{11}FO_3$
Formula weight	282.26
Temperature/K	180.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	14.778(3)
b/Å	5.9149(9)
c/Å	29.159(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2548.8(8)
Z	8
ρ_{calc}g/cm^3	1.471
μ/mm^{-1}	0.110
F(000)	1168.0
Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.182 to 52.022
Index ranges	$-18 \leq h \leq 14$, $-6 \leq k \leq 7$, $-35 \leq l \leq 26$
Reflections collected	7133
Independent reflections	2496 [R_{int} = 0.1222, R_{sigma} = 0.1853]
Data/restraints/parameters	2496/0/191
Goodness-of-fit on F^2	1.087
Final R indexes [I>=2σ (I)]	R_1 = 0.0801, wR_2 = 0.1415
Final R indexes [all data]	R_1 = 0.2018, wR_2 = 0.2043

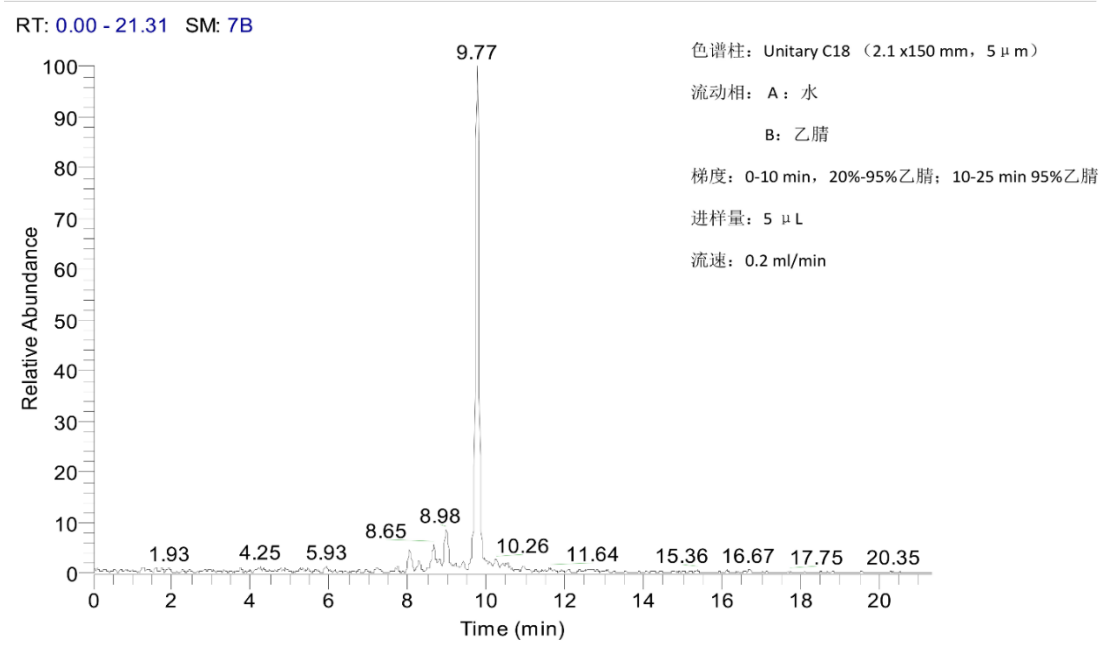
Largest diff. peak/hole / e Å^{-3} 0.49/-0.34

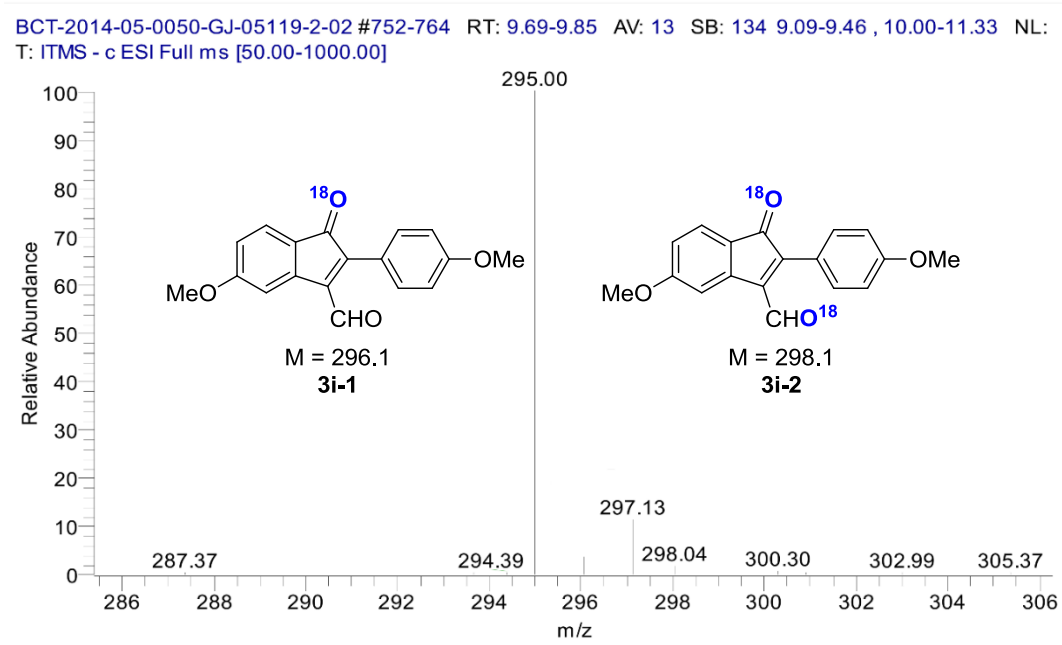
9. Detailed Information on Control Experiments under $^{18}O_2$ Atmosphere

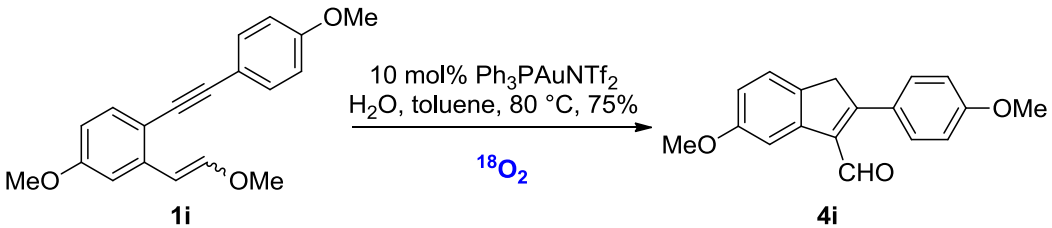


1i R=*p*-OMeC$_6$H$_4$ **3i-1** R=*p*-OMeC$_6$H$_4$ **3i-2** R=*p*-OMeC$_6$H$_4$

1i (1 mmol) and the $Ph_3PAuNTf_2$ (0.1 mmol, 73.8 mg) in toluene (2 mL) were placed in a screw-cap vial containing a stirring bar. The reaction vial was fitted with a cap, filled with $^{18}O_2$ and heated with stirring at 80 ℃ for 10 h. The reaction mixture was cooled, filtered through a plug of silica gel. The filtrate was concentrated and the obtained residue was purified by flash column chromatography to afford the indenones **3i-1** and **3i-2** with a yield of 60%.

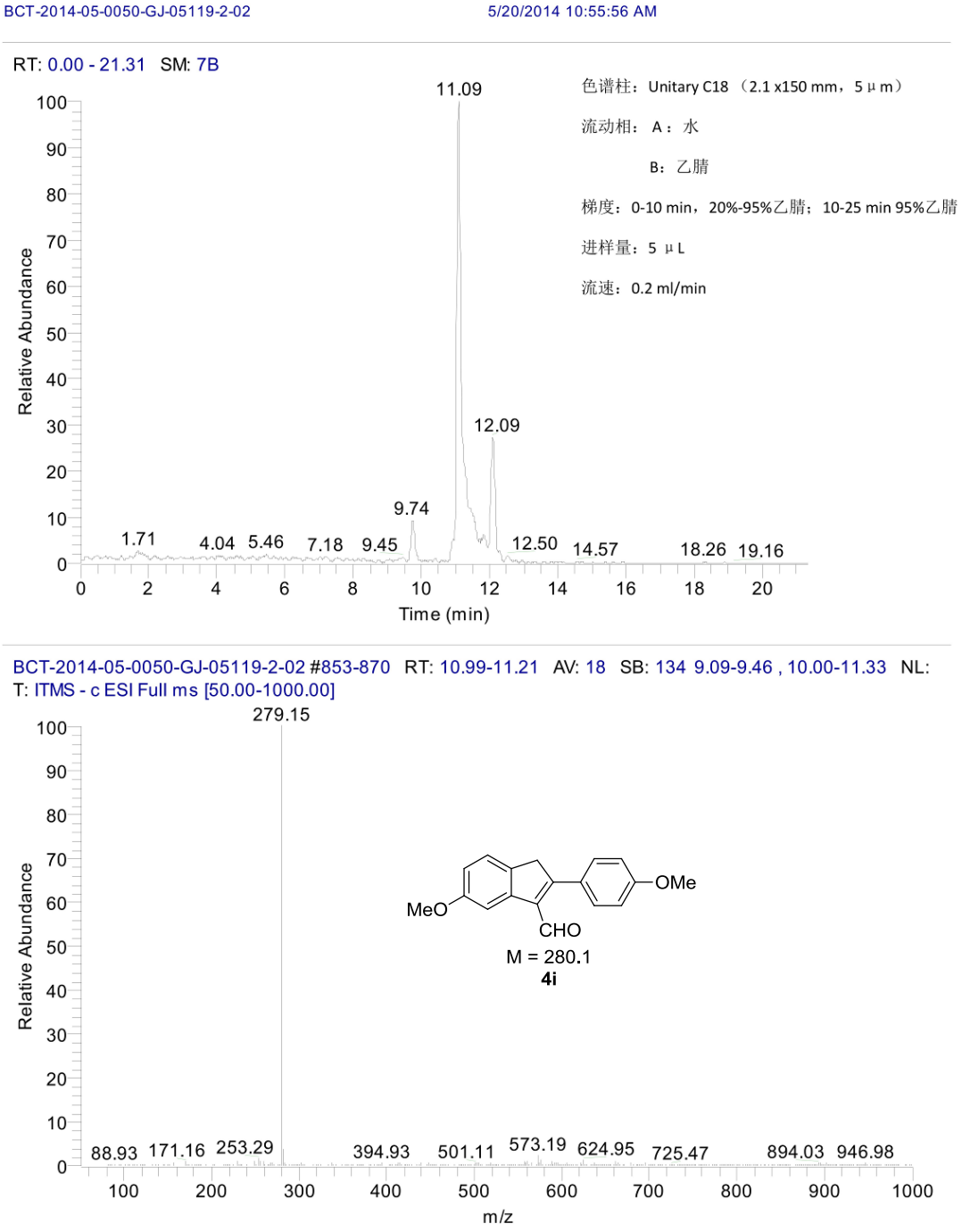




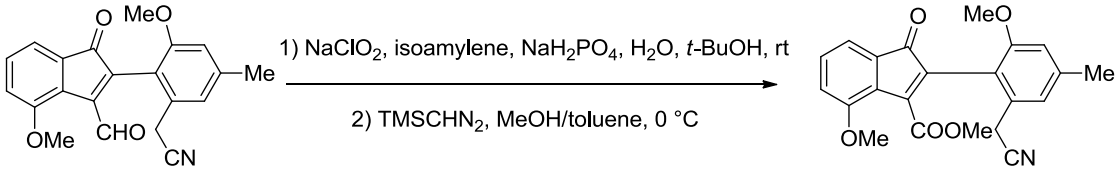


1i (1 mmol) and the $Ph_3PAuNTf_2$ (0.1 mmol, 73.8 mg) in toluene (2 mL) were placed in a screw-cap vial containing a stirring bar. The reaction vial was fitted with a cap, filled with $^{18}O_2$ and heated with stirring at 80 ℃ for 10 h. The reaction mixture was cooled, filtered through a plug of silica gel. The filtrate was concentrated and the obtained residue was purified by flash column chromatography to afford the desired

product **4i** with a yield of 75%.



10. Preparation of 5 and Characterization Data



3s **5**

To a stirred solution of the aldehyde **3s** (0.21 mmol, 74 mg) in *t*-BuOH (0.8 mL) was added phosphate buffer (0.4 mL) (pH ~ 3.6) and 2-methyl-2-butene (1.06 mmol, 0.11 mL) at room temperature. After that a solution of $NaClO_2$ (0.32 mmol, 29 mg) in H_2O (0.40 mL) was added to the reaction mixture and stirred at room temperature for 3 h. After completion of the reaction it was acidified with 1 N HCl to pH 4. Most of the solvent was evaporated off and EtOAc (10 mL) and brine (8 mL) were added to the residue. The organic layer was separated off and the aqueous layer was extracted with EtOAc (2 ×10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and the crude acid thus obtained after evaporation of the solvent was mixed in MeOH/toluene (v:v = 1:1) at 0 ℃, and a solution of (trimethylsilyl)diazomethane (2.0 M in hexanes) was slowly added dropwise via syringe over 30 min until effervescence ceased. The reaction mixture was stirred for 1 h and then concentrated under reduced pressure to afford the crude ester as a pale yellowish oil. The resulting oil was purified by chromatography (3:1 to 1:1 petroleum ether:EtOAc). Pure fractions were evaporated to dryness to afford compound **5** as a yellowish solid (64 mg, 80%); Data were in agreement with those reported previously.[2] TLC (petroleum ether:ethyl acetate, 3:1, v/v): R_f=0.3; yellowish solid, 80%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.29 (m, 1H), 7.21 (d, J = 6.0 Hz, 1H), 7.04 (d, J = 6.0 Hz, 1H), 6.97 (s, 1H), 6.69 (s, 1H), 3.87 (s, 3H), 3.77 (s, 3H), 3.76 (d, J = 18.0 Hz, 1H), 3.72 (s, 3H), 3.66 (d, J = 18.0 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 195.2, 166.1, 158.3, 153.0, 148.4, 141.2, 131.9, 131.2, 131.0, 130.6, 128.2, 121.4, 119.1, 118.1, 117.2, 115.2, 111.5, 56.3, 55.9, 52.5, 22.1, 21.9.

11. References

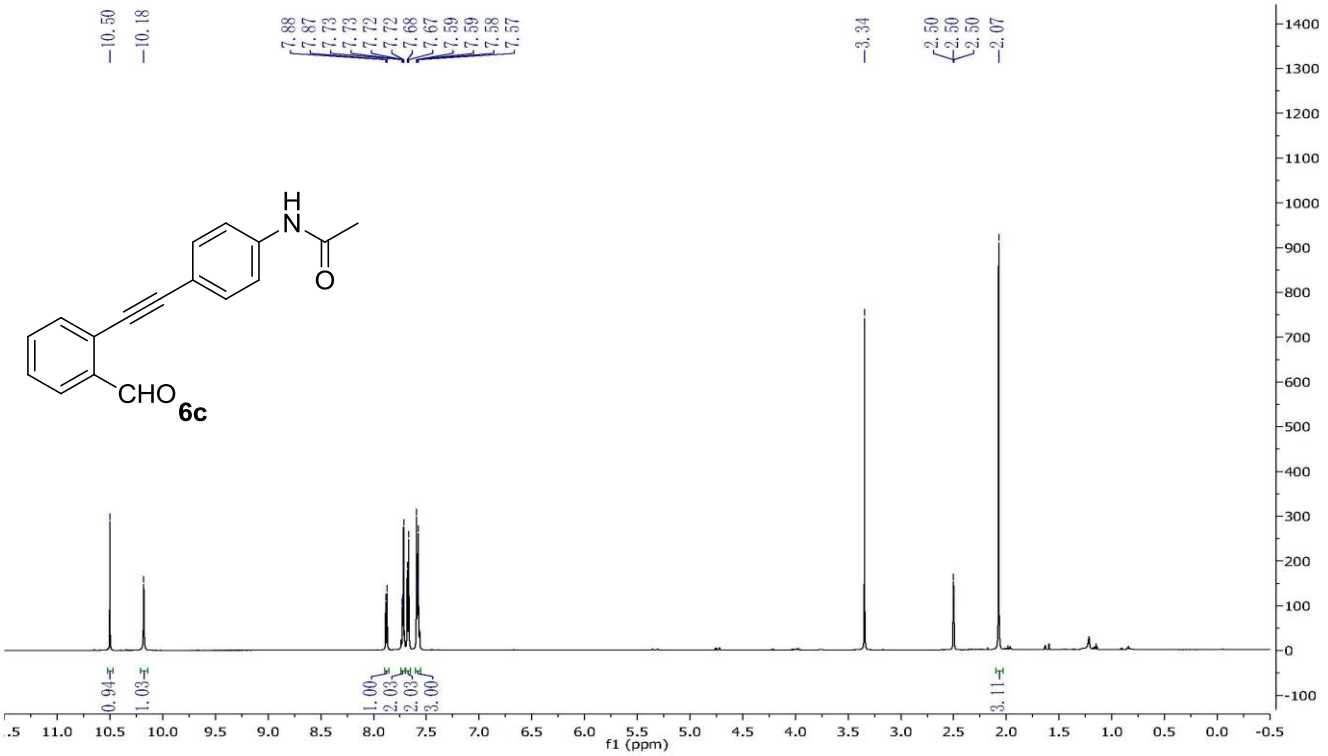
[1] a) J. H. Park, S. V. Bhilare, S. W. Youn, *Org. Lett.* **2011**, *13*, 2228-2231; b) Y. Ohta, Y. Kubota, T. Watabe, H. Chiba, S. Oishi, N. Fujii, H. Ohno, *J. Org. Chem.* **2009**, *74*, 6299-6302; c) C. Inga, B. Rita, S. Rokas, *Tetrahedron.* **2011**, *67*, 706-717; d) K. Yoshida, H. Shida, H. Takahashi, A. Yanagisawa, *Chem. Eur. J.* **2011**, *17*, 344-349; e) M. M. Li, P. Xing, Z. G. Huang, B. Jiang, *Chin. J. Chem.* **2013,** *31*, 49-54.

[2] a) H. Tsukamoto, T. Ueno, Y. Kondo, *J. Am. Chem. Soc.* **2006**, *128*, 1406-1407; b) T. Enomoto, A. L. Girard, Y. Yasui, Y. Takemoto, *J. Org. Chem.* **2009**, *74*, 9158-9164; c) Y. Liu, J. Guo, Y. Liu, X. Wang, Y. Wang, X. Jia, G. Wei, L. Chen, J. Xiao, M. Cheng, *Chem. Commun.* **2014**, *50*, 6243-6245.

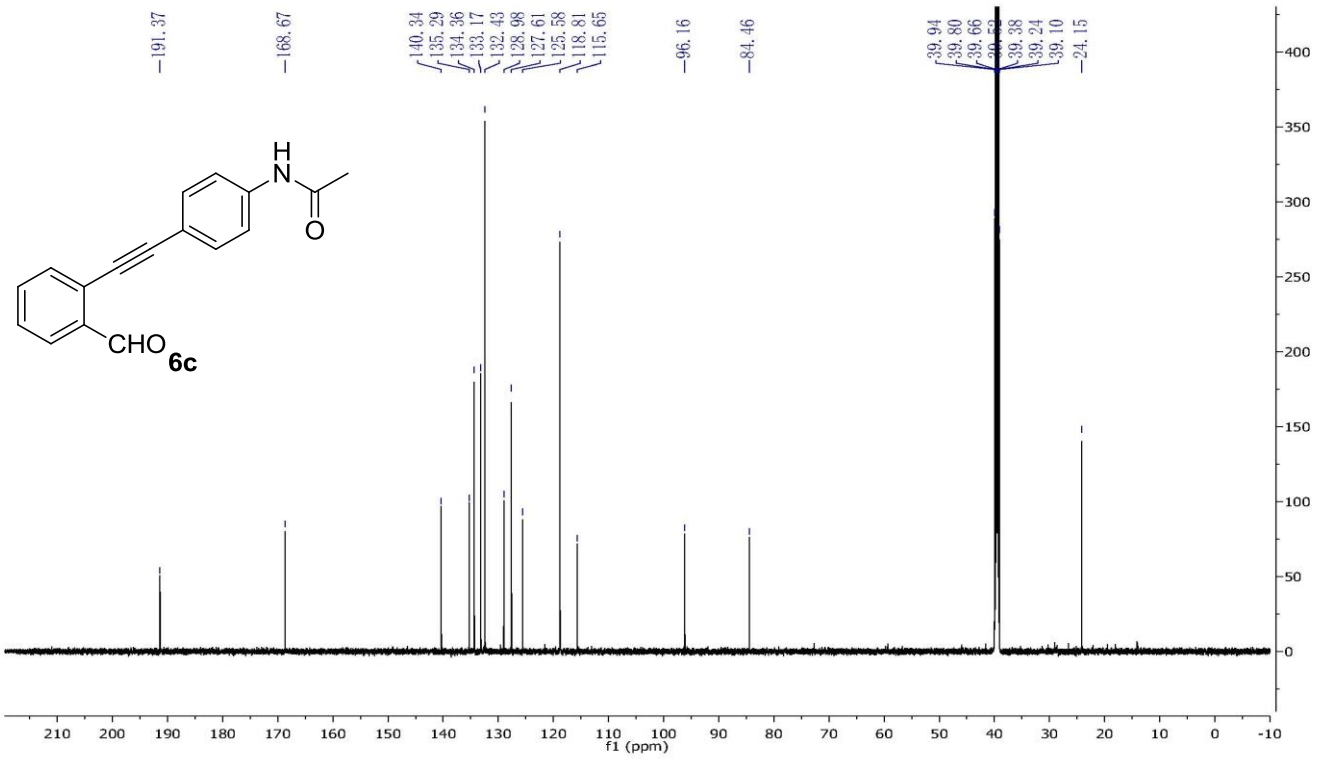
[3] a) X. P. Chen, J. Jin, N. N. Wang, P. Lu, Y. G. Wang, *Eur. J. Org. Chem.* **2012**, *4*, 824-830; b) C. Y. Lee, M. J. Wu, *Eur. J. Org. Chem.* **2007**, *21*, 3463-3467; c) Zhang, J.; Wu, D.; Chen, X. L.; Liu, Y. K.; Xu, Z. Y. *J. Org. Chem.*, **2014**, *79*, 4799-4808.

[4] W. Liu, M. Buck, N. Chen, M. Shang, N. J. Taylor, J. Asoud, X. Wu, B. B. Hasinoff, G. I. Dmitrienko, *Org. Lett.*, **2007**, *9*, 2915-2918.

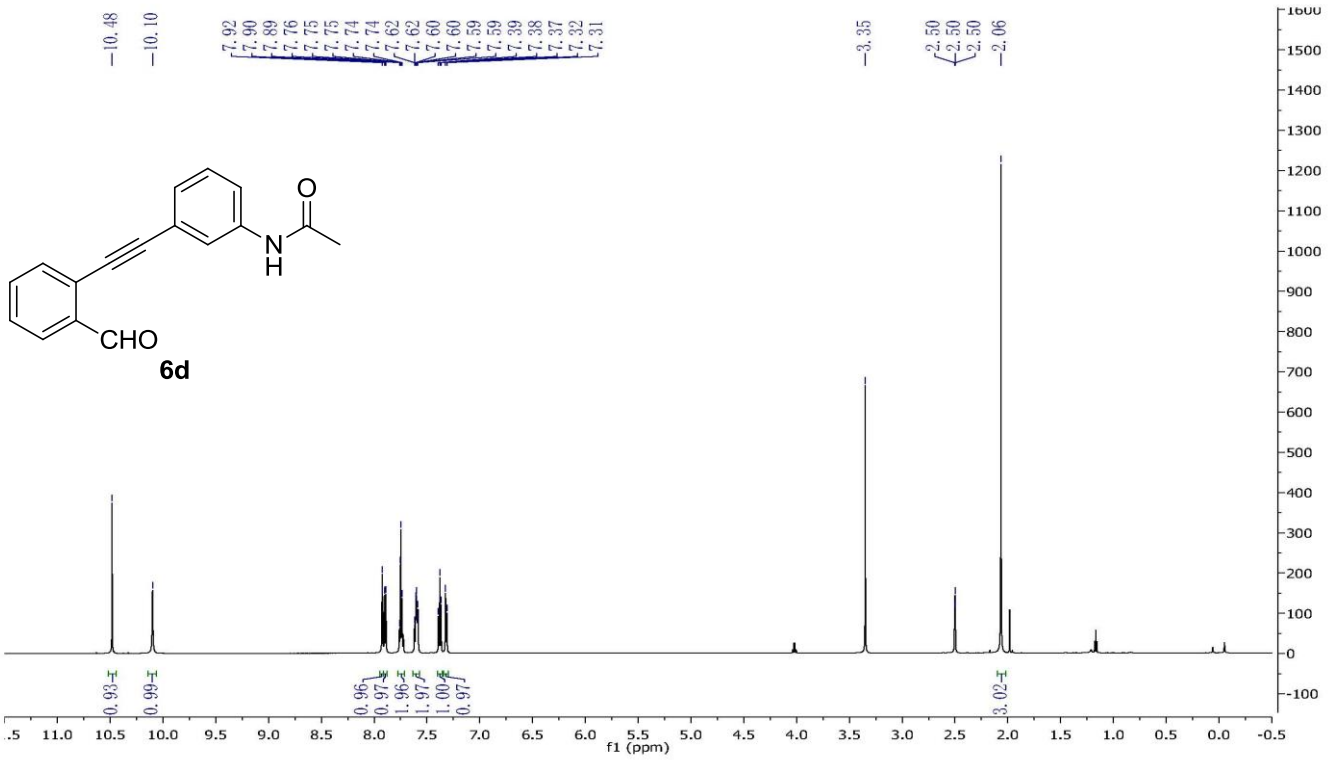
12. NMR Spectra



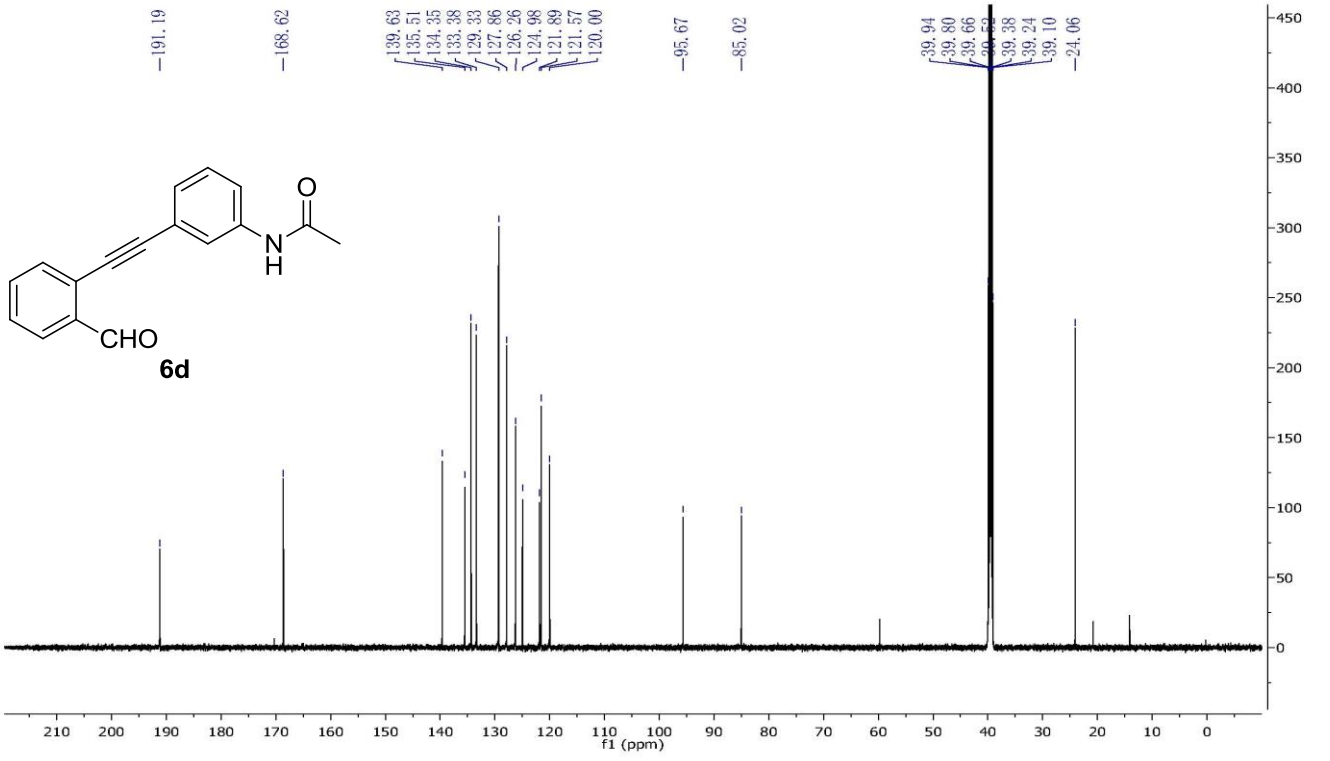
^{1}H NMR Spectrum of Compound **6c** (DMSO-d_6, 600 MHz)



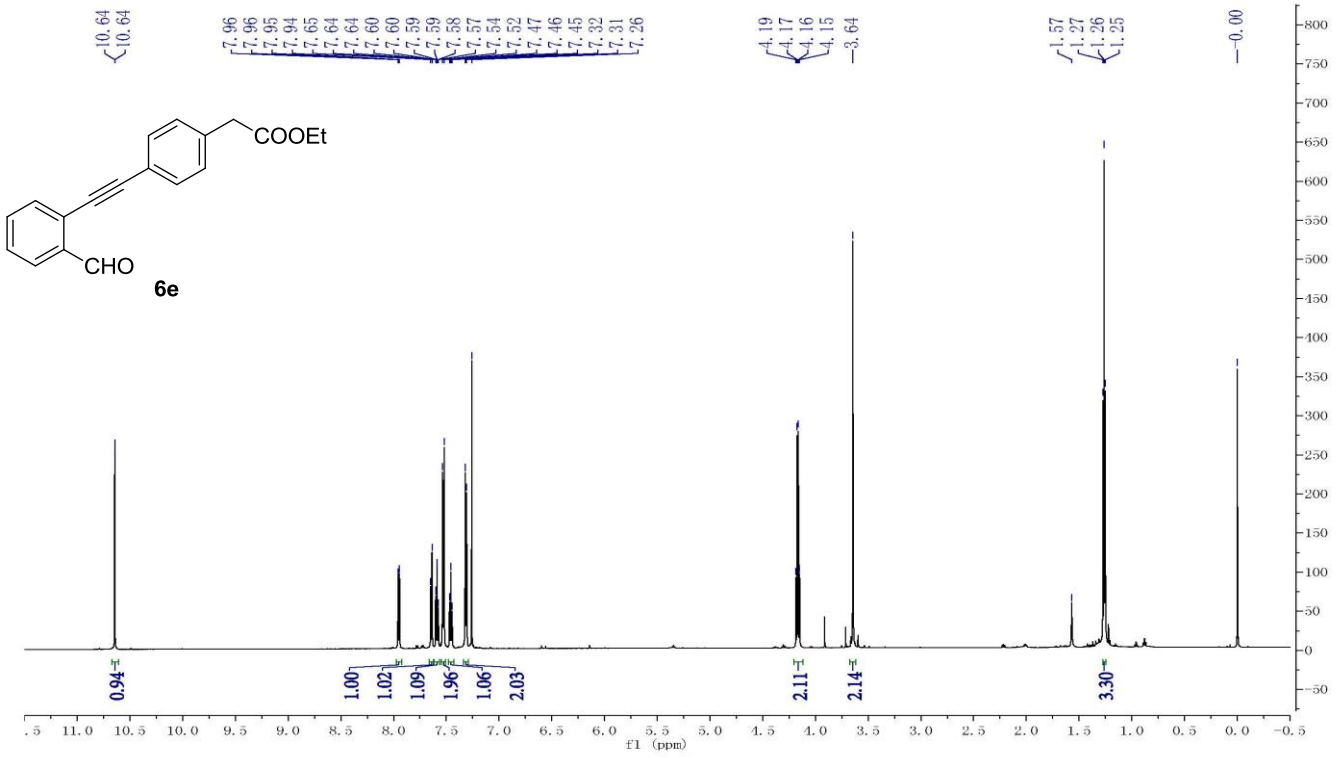
^{13}C NMR Spectrum of Compound **6c** (DMSO-d_6, 150 MHz)



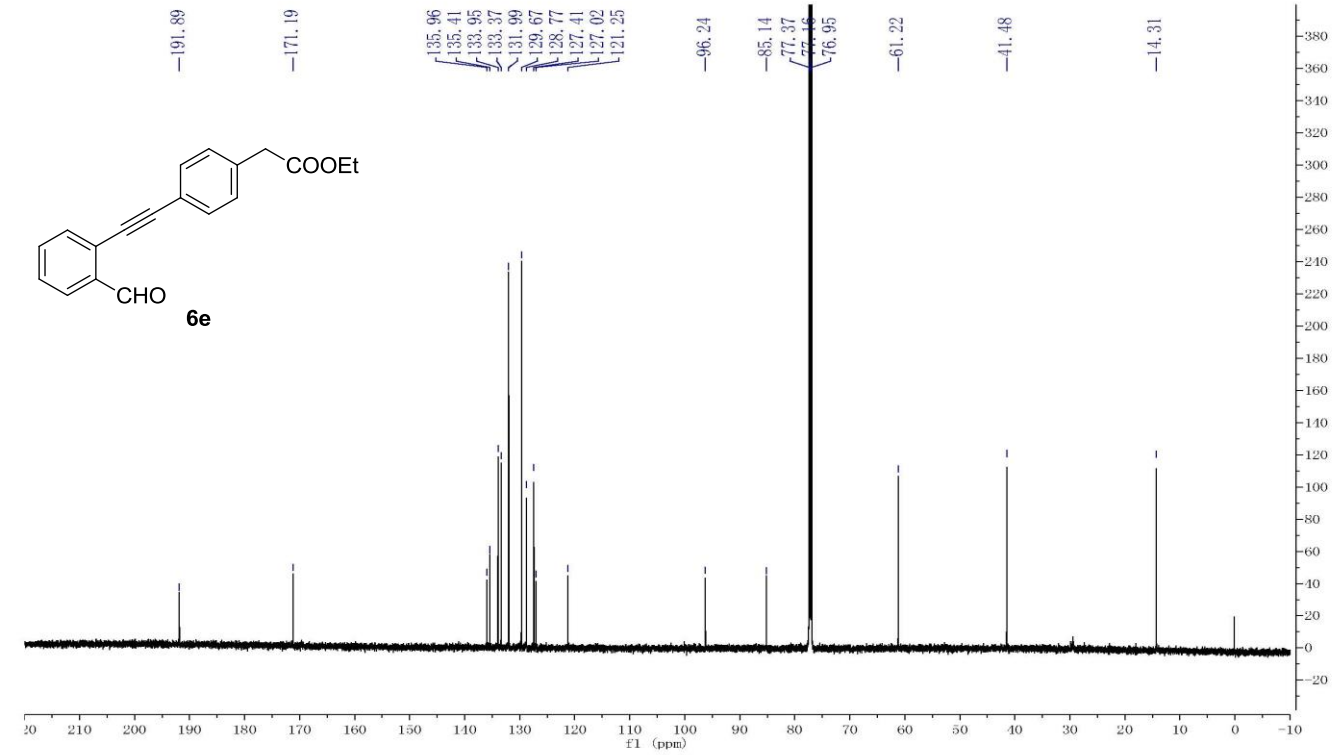
^{1}H NMR Spectrum of Compound **6d** (DMSO-d_6, 600 MHz)



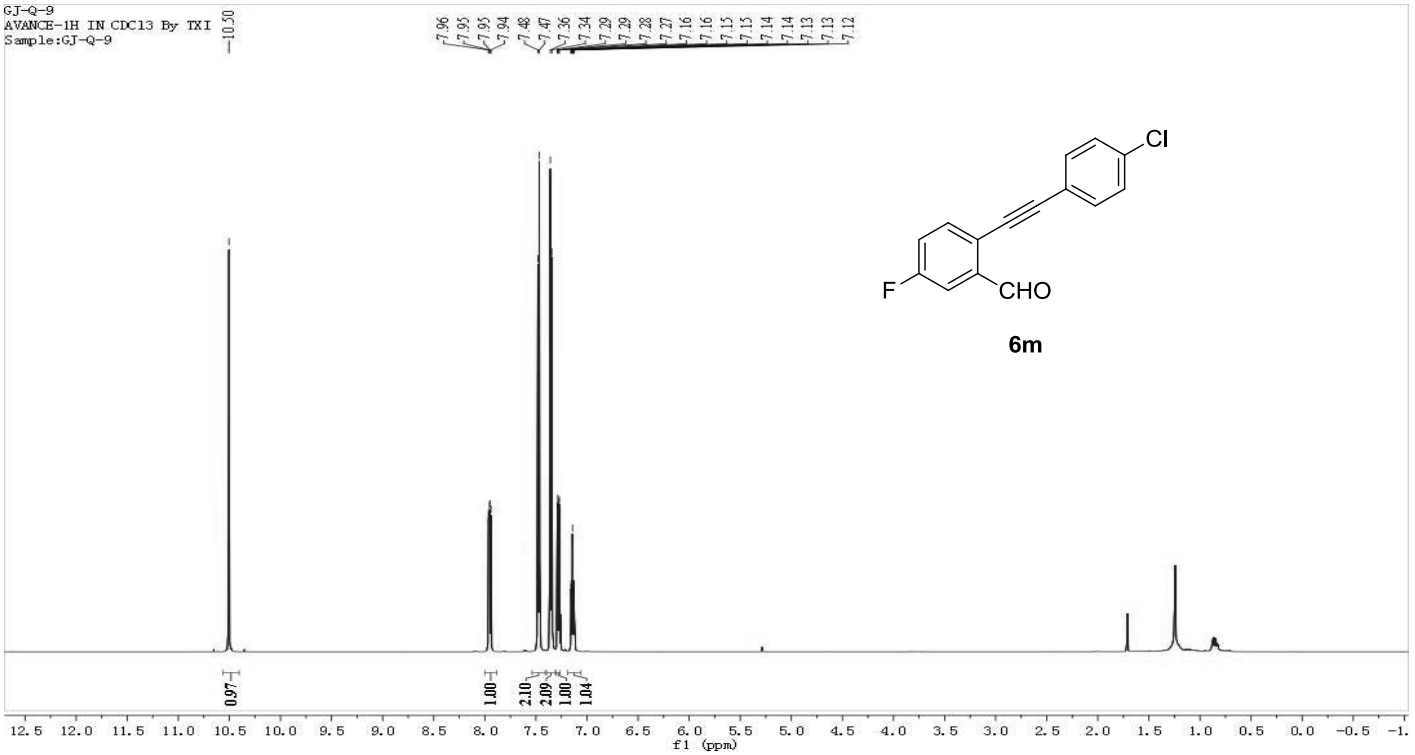
^{13}C NMR Spectrum of Compound **6d** (DMSO-d_6, 150 MHz)



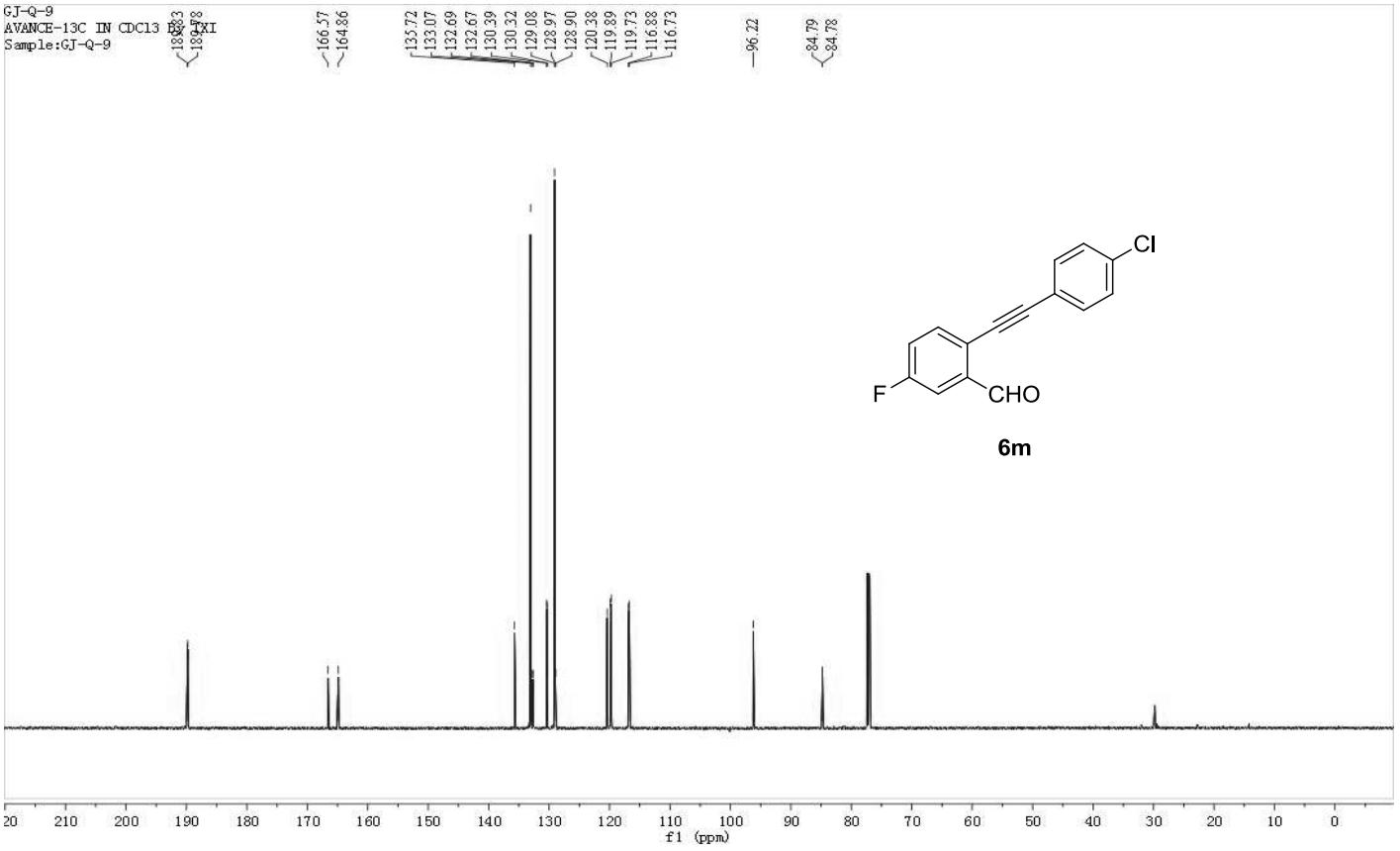
^{1}H NMR Spectrum of Compound **6a** ($CDCl_3$, 600 MHz)



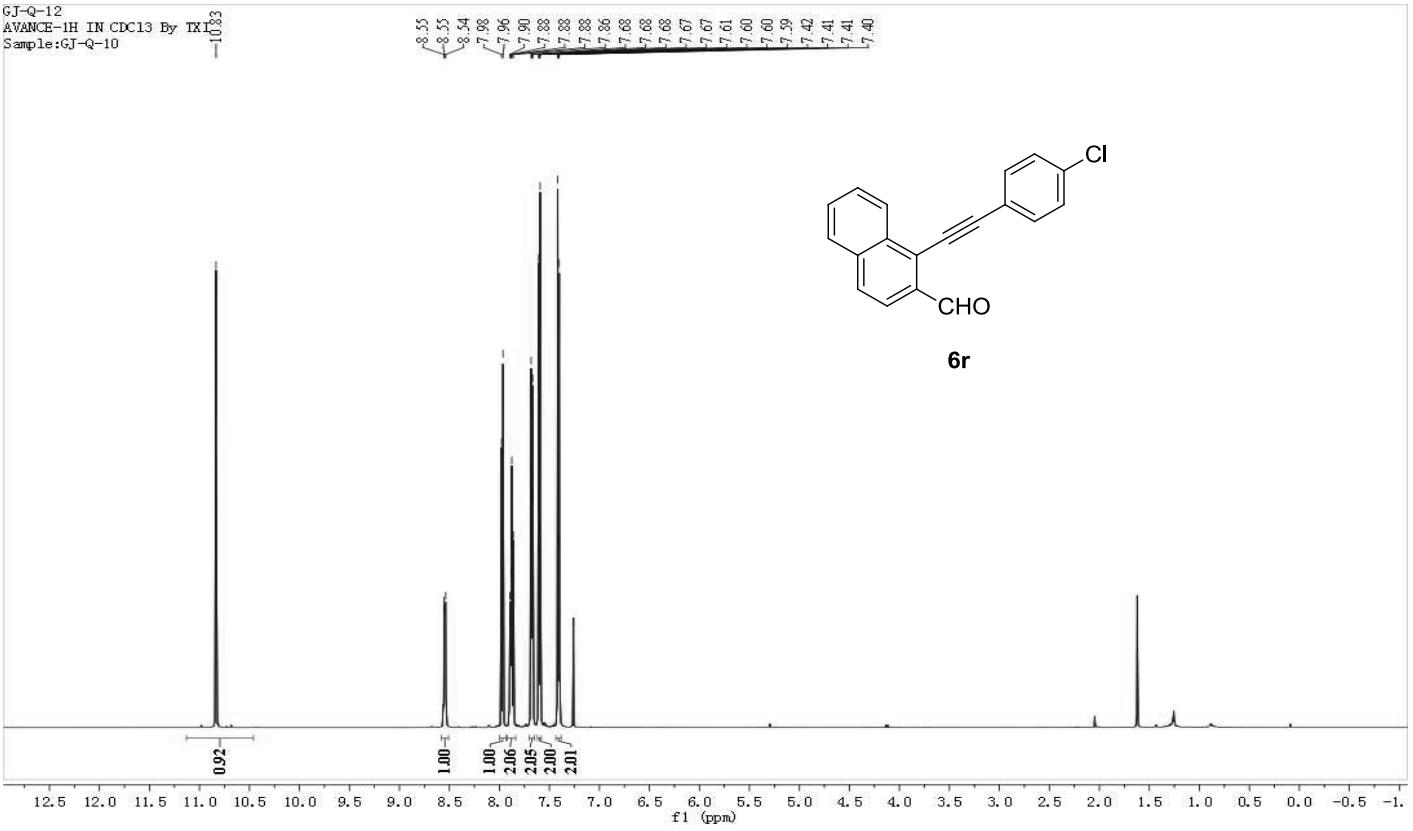
^{13}C NMR Spectrum of Compound **6a** ($CDCl_3$, 150 MHz)



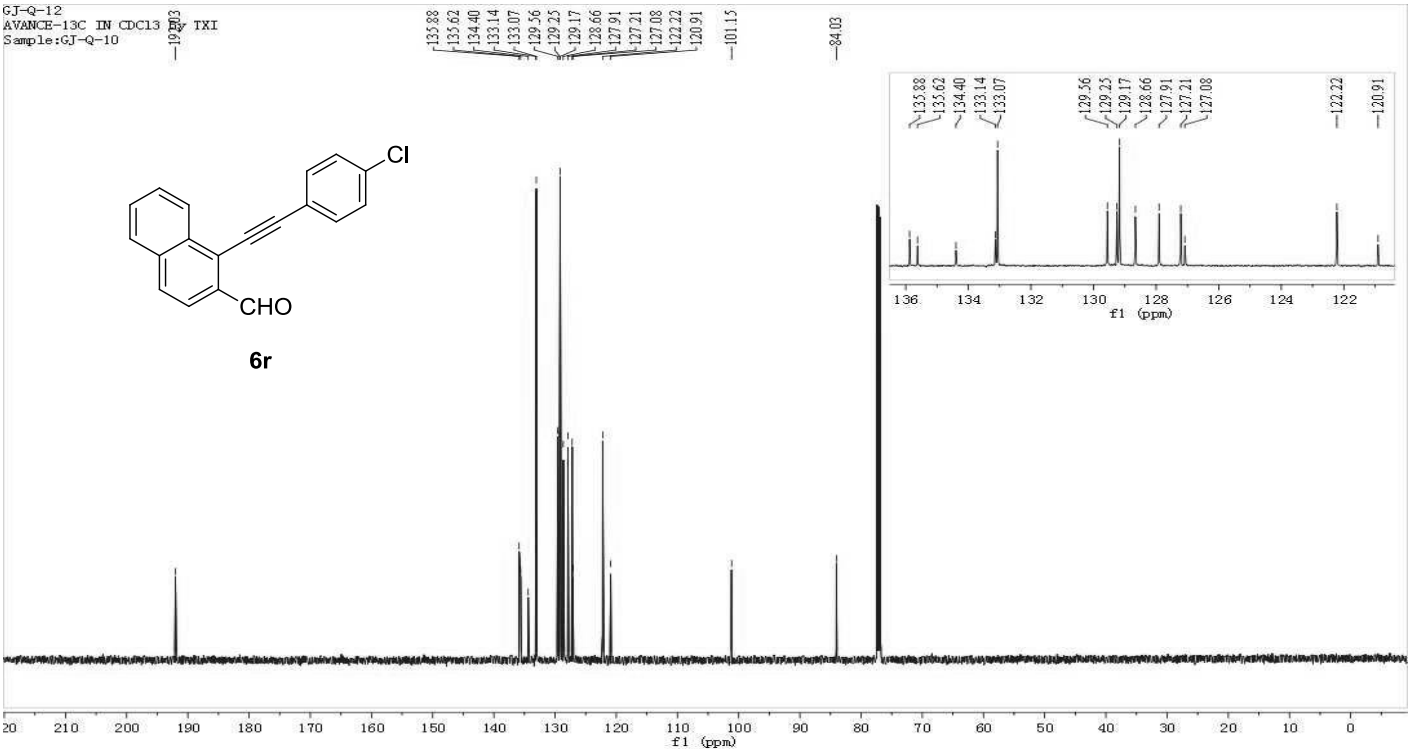
^{1}H NMR Spectrum of Compound **6m** ($CDCl_3$, 600 MHz)



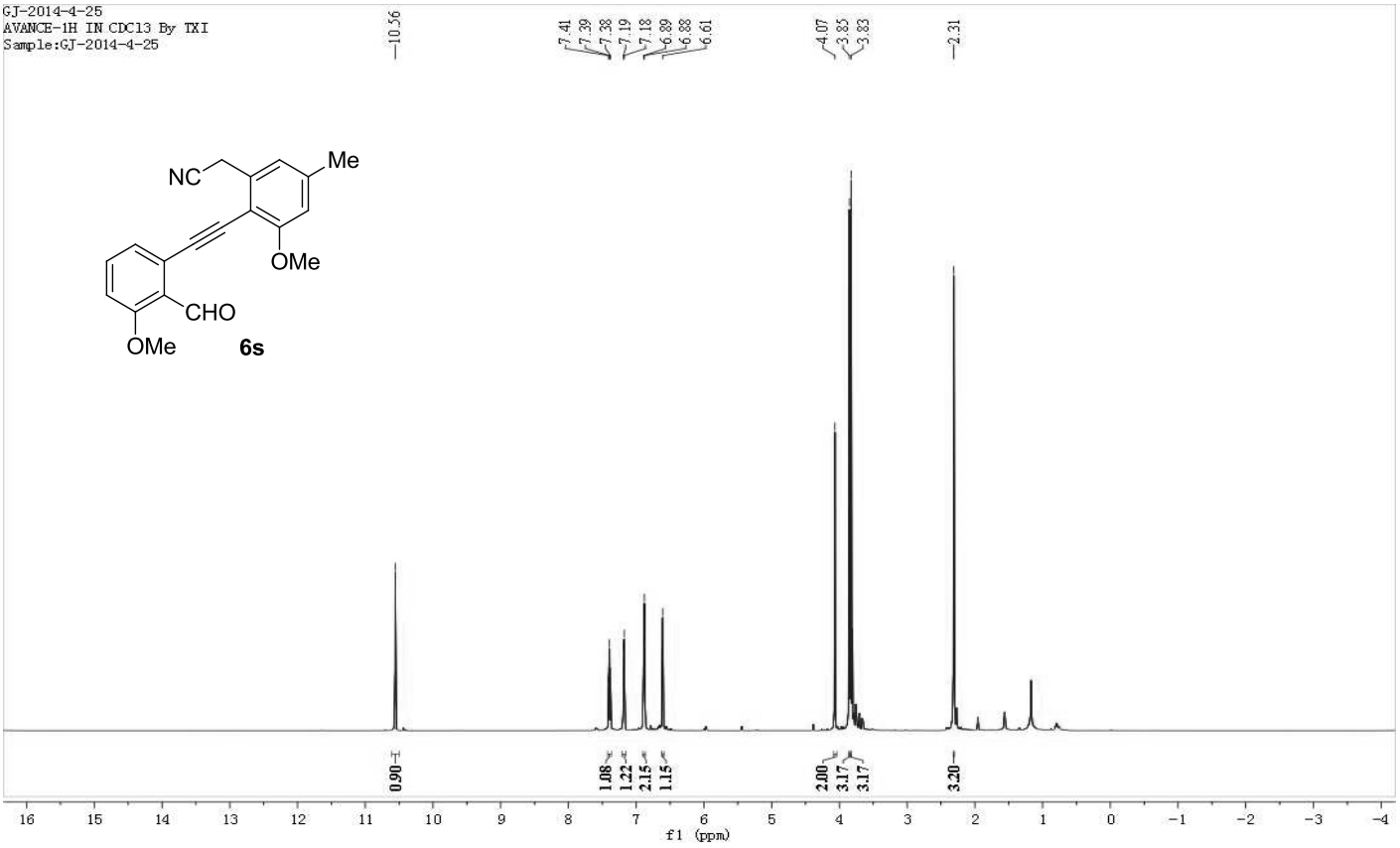
^{13}C NMR Spectrum of Compound **6m** ($CDCl_3$, 150 MHz)



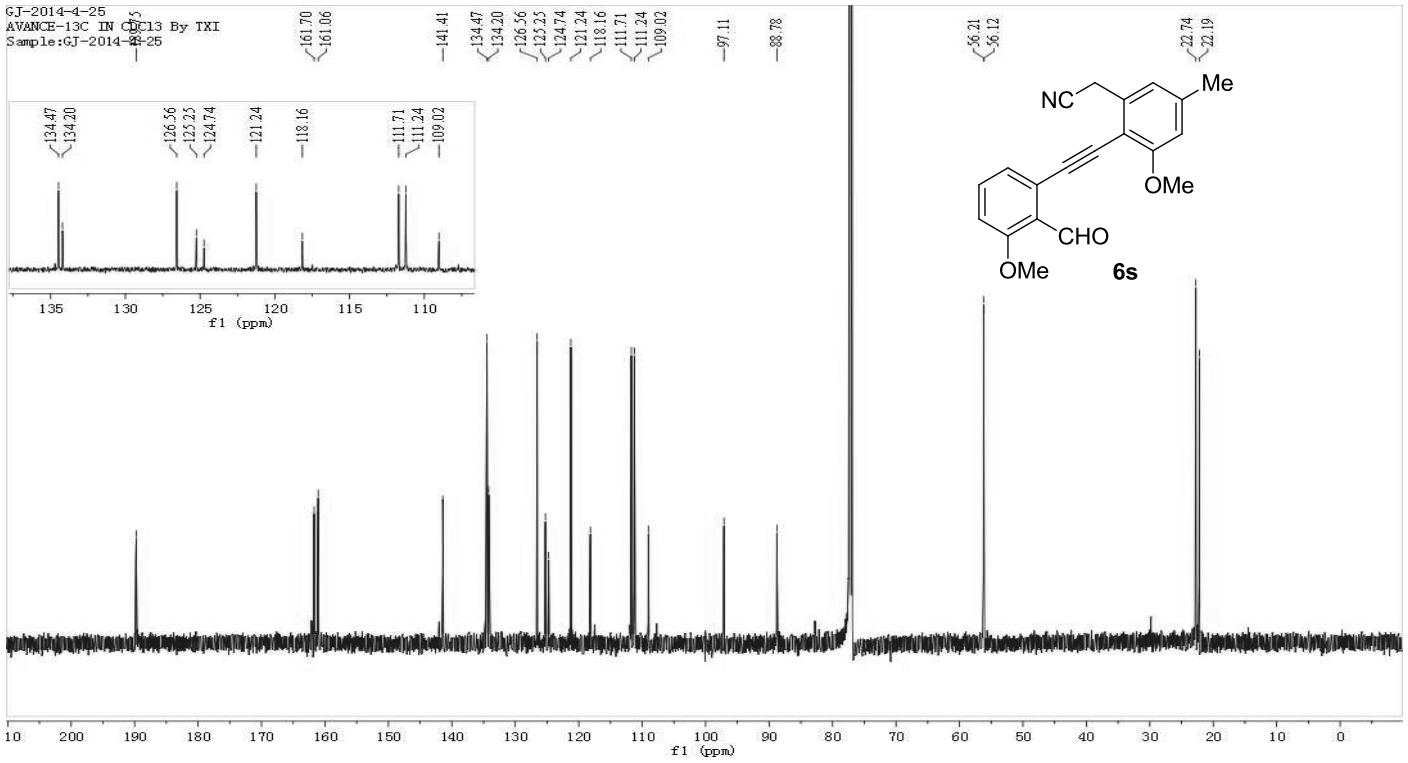
^{1}H NMR Spectrum of Compound **6r** ($CDCl_3$, 600 MHz)



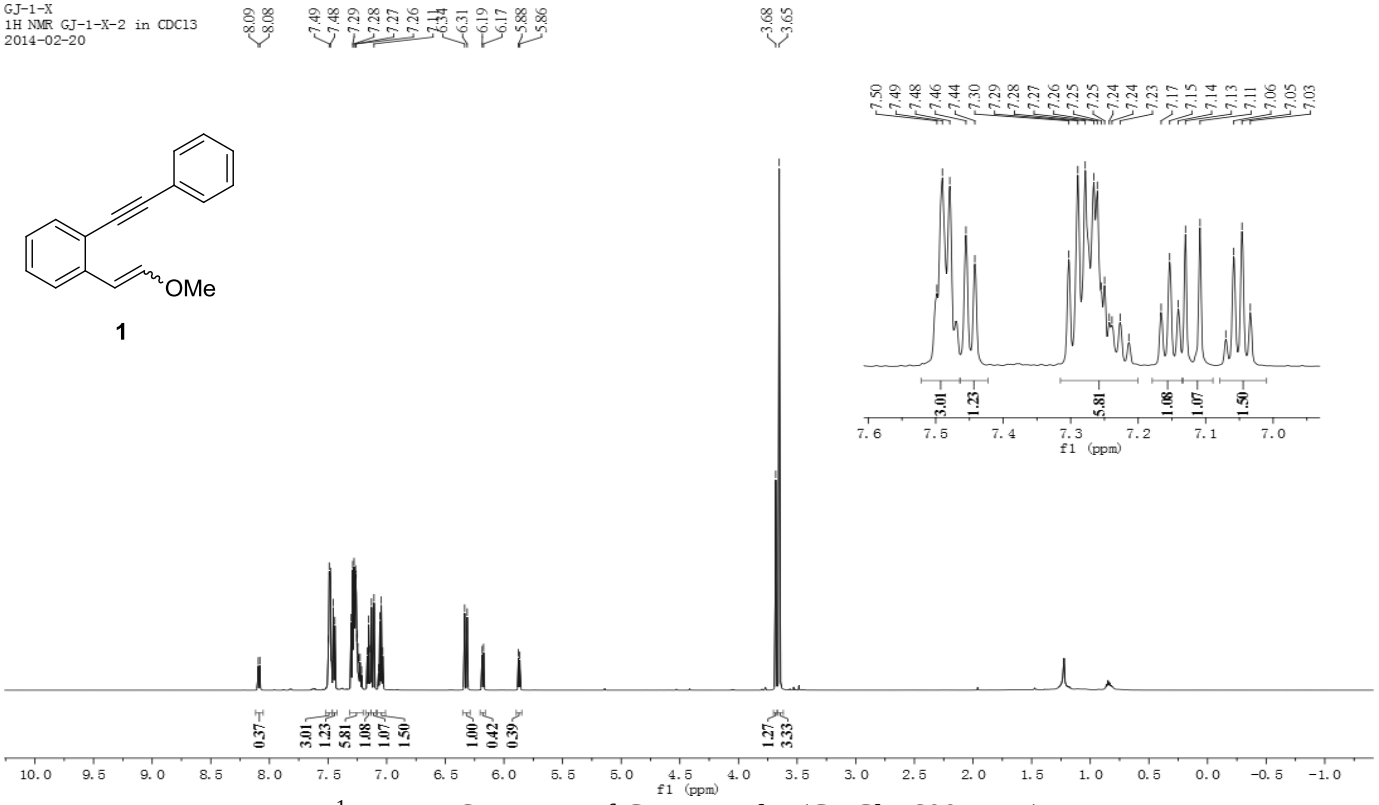
^{13}C NMR Spectrum of Compound **6r** ($CDCl_3$, 150 MHz)



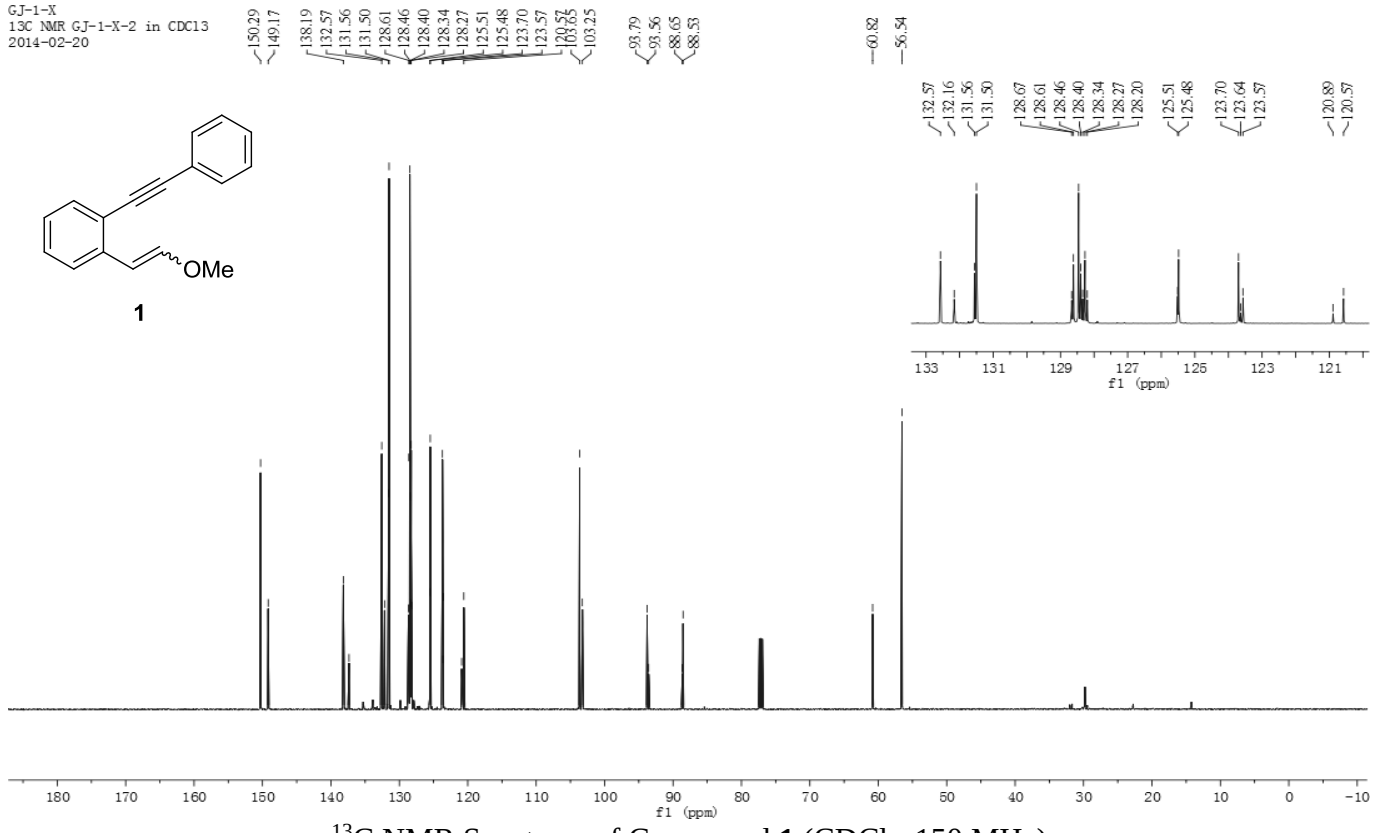
^{1}H NMR Spectrum of Compound **6s** ($CDCl_3$, 600 MHz)



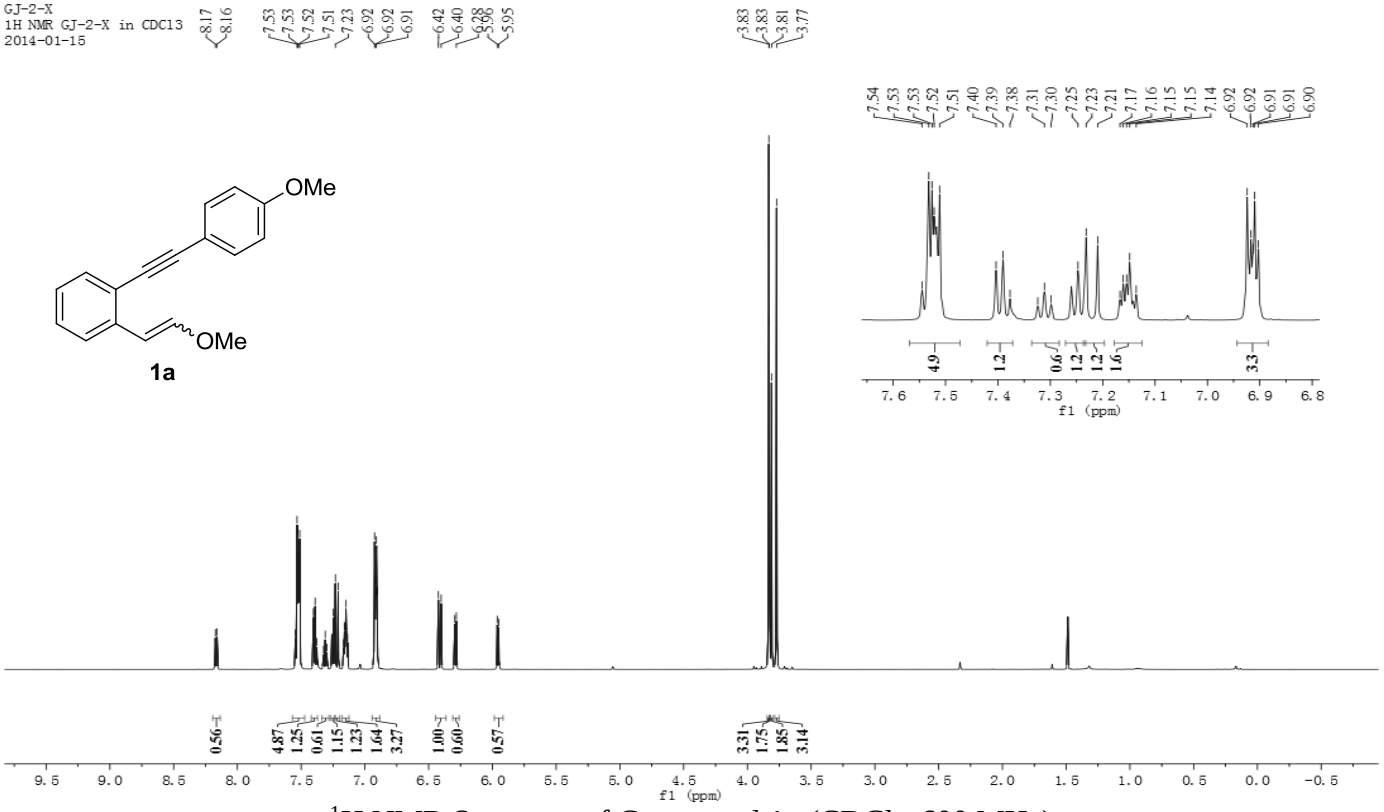
^{13}C NMR Spectrum of Compound **6s** ($CDCl_3$, 150 MHz)



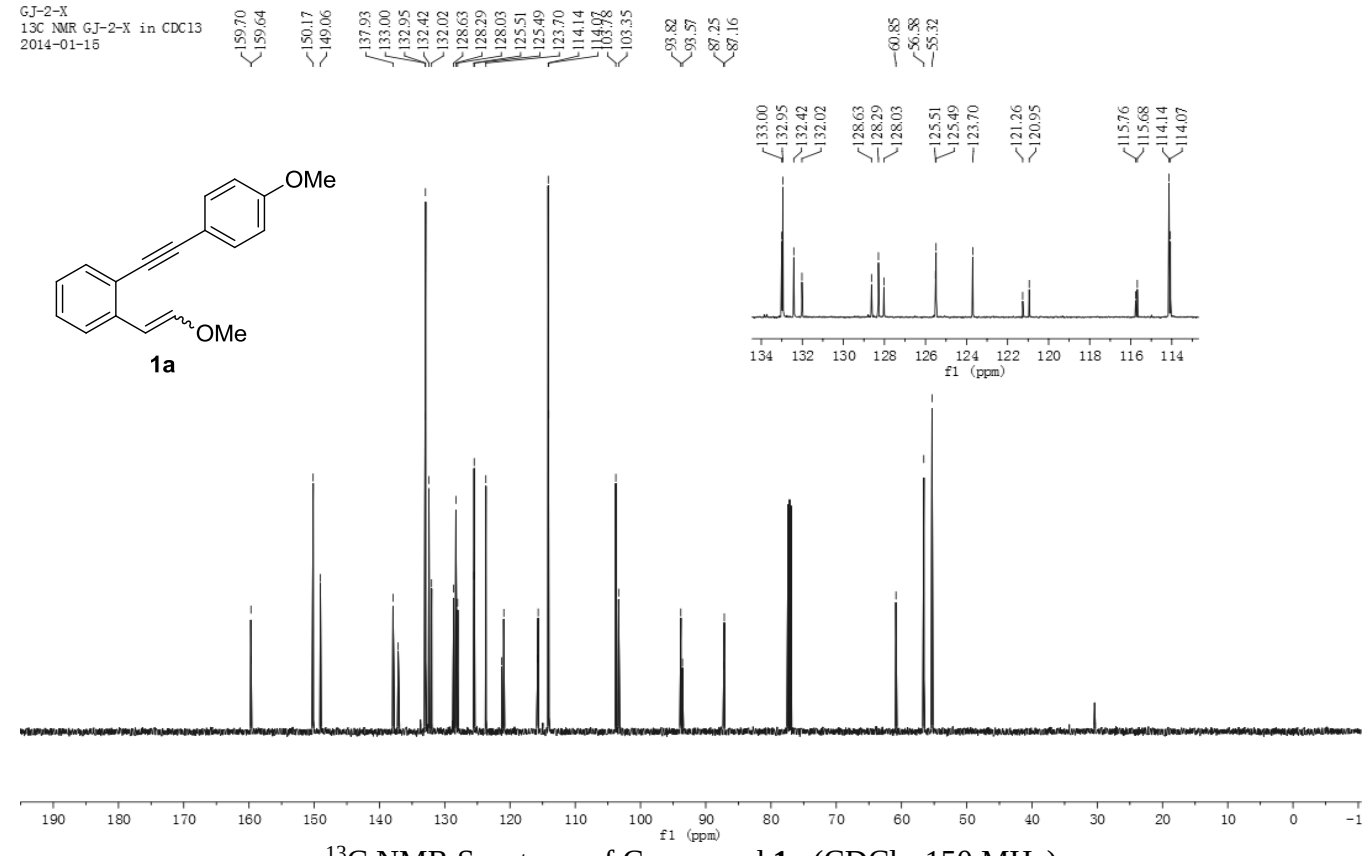
^{1}H NMR Spectrum of Compound **1** ($CDCl_3$, 600 MHz)



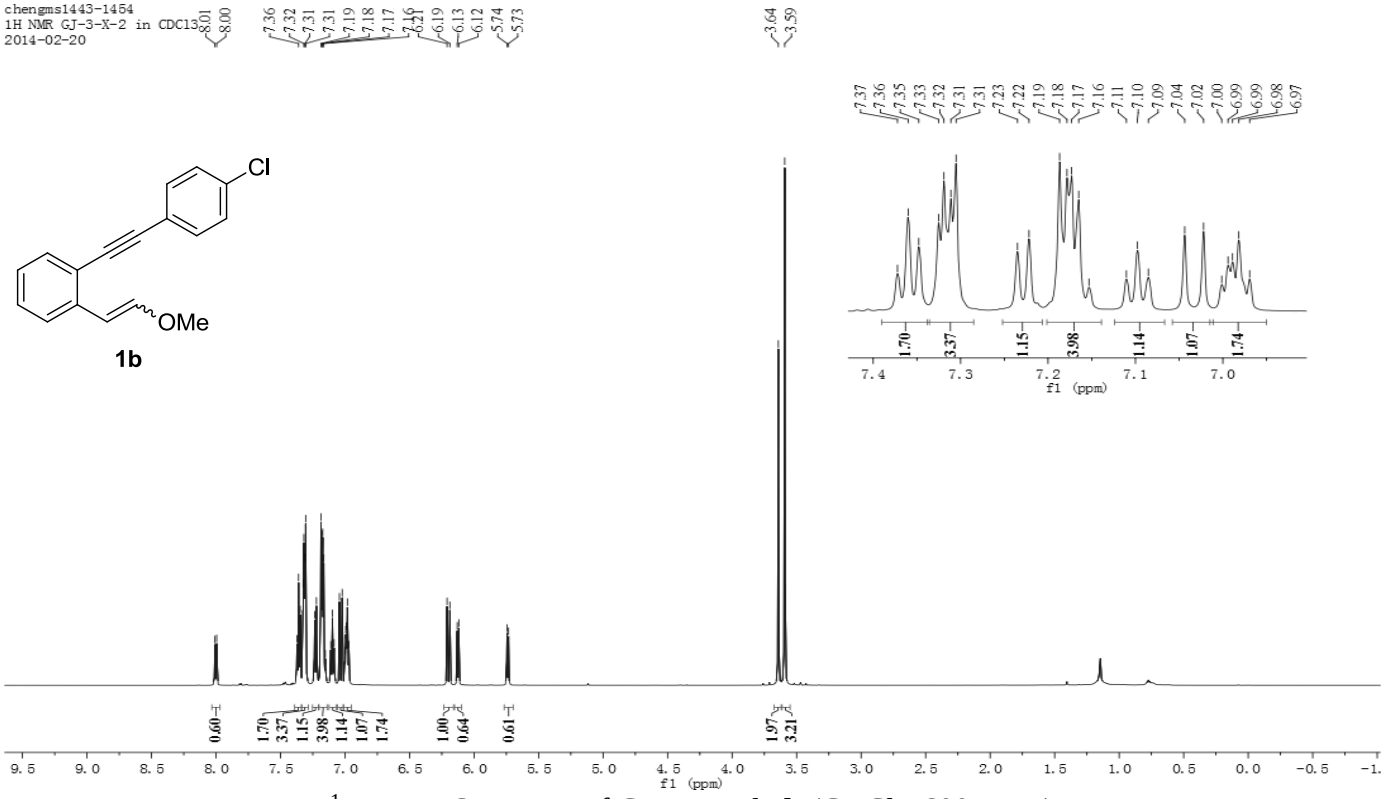
^{13}C NMR Spectrum of Compound **1** ($CDCl_3$, 150 MHz)



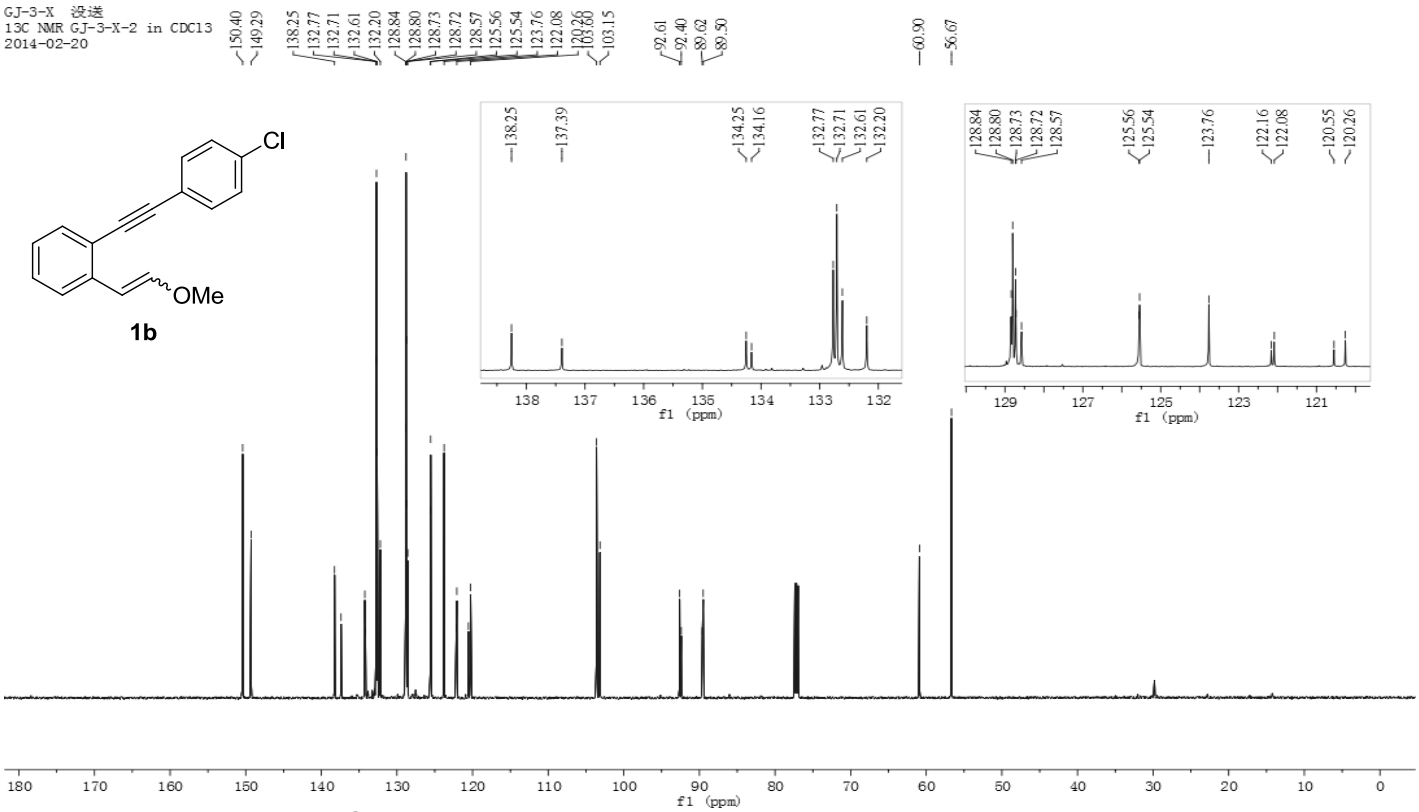
^{1}H NMR Spectrum of Compound **1a** ($CDCl_3$, 600 MHz)



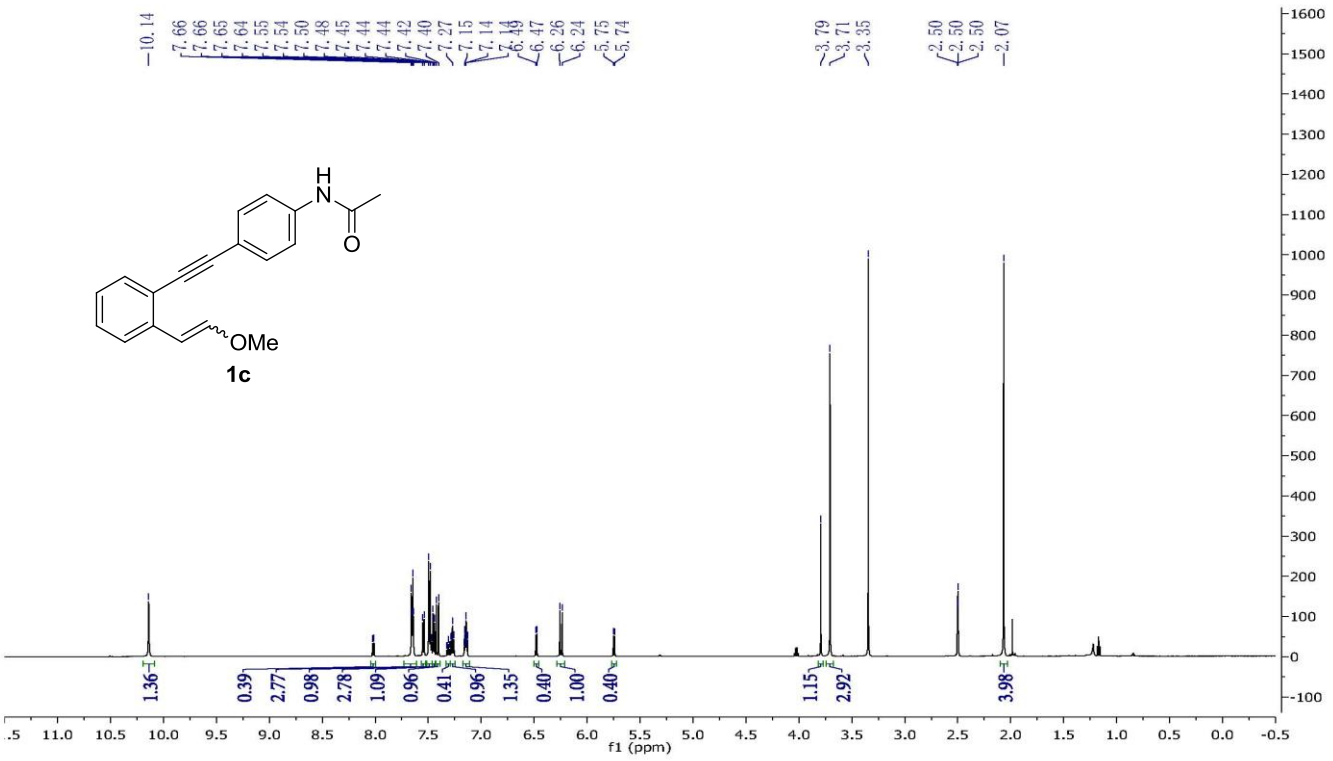
^{13}C NMR Spectrum of Compound **1a** ($CDCl_3$, 150 MHz)



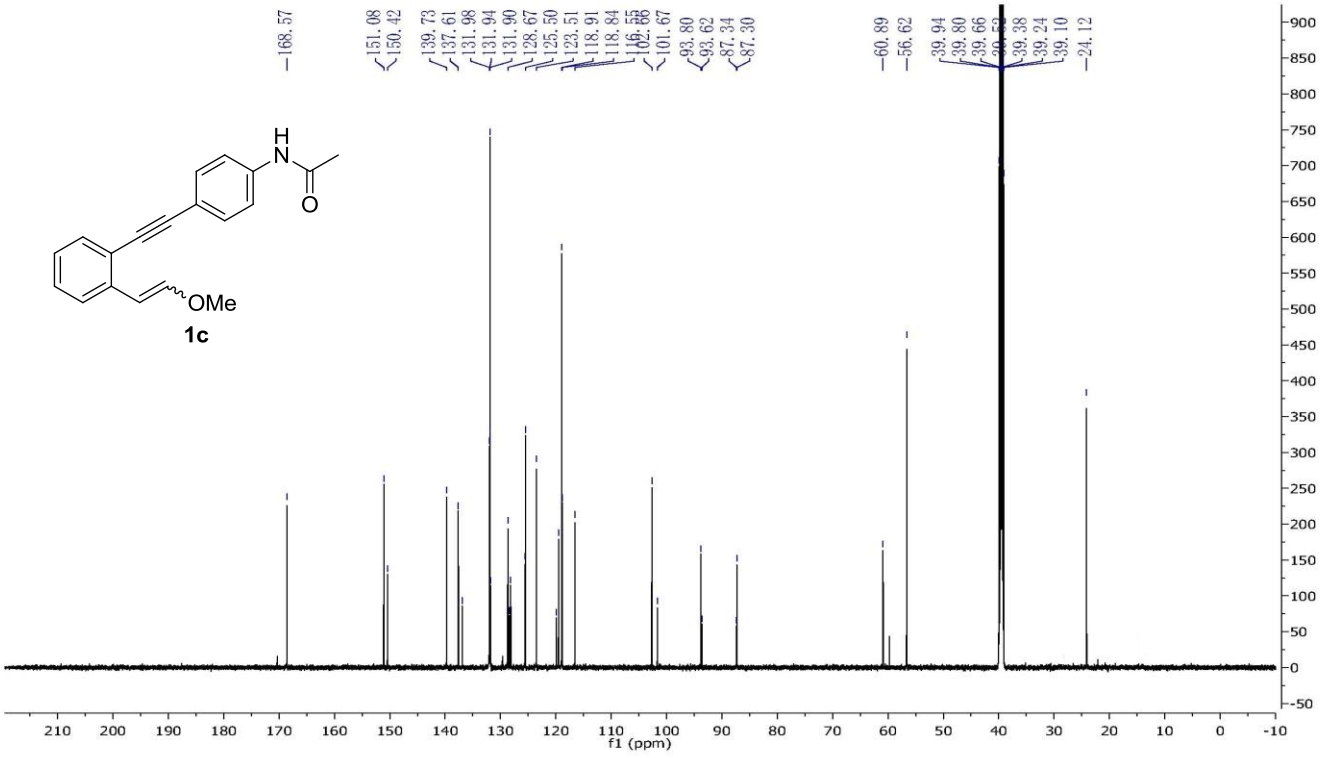
^{1}H NMR Spectrum of Compound **1b** ($CDCl_3$, 600 MHz)



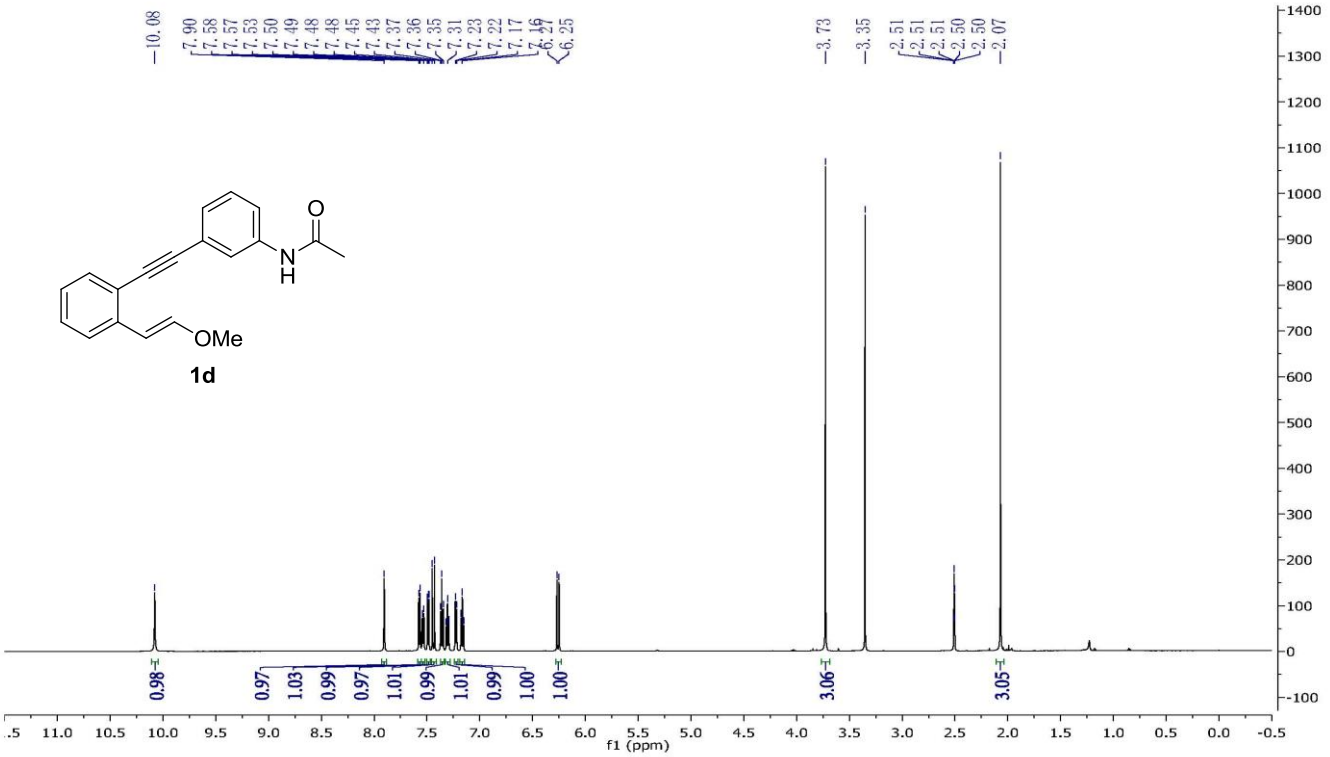
^{13}C NMR Spectrum of Compound **1b** ($CDCl_3$, 150 MHz)



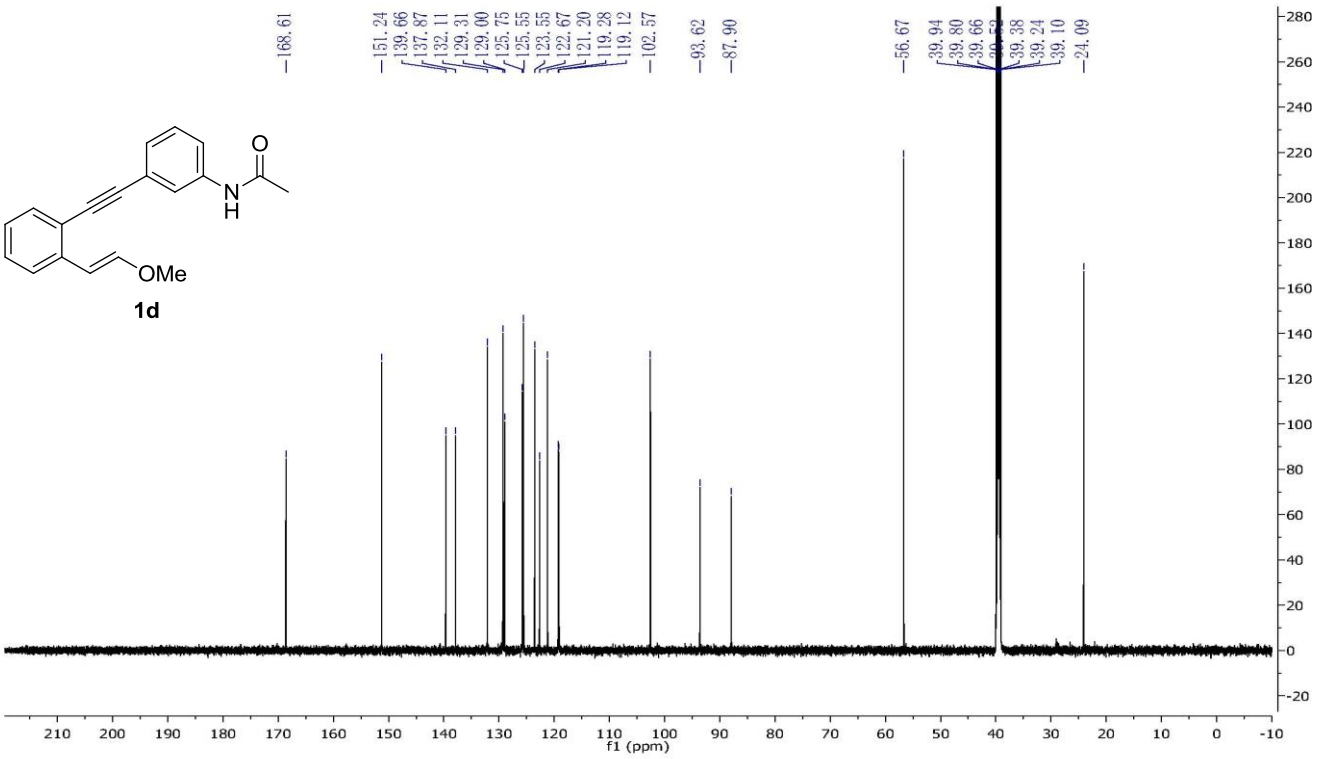
^{1}H NMR Spectrum of Compound **1c** (DMSO-*d*$_6$, 600 MHz)



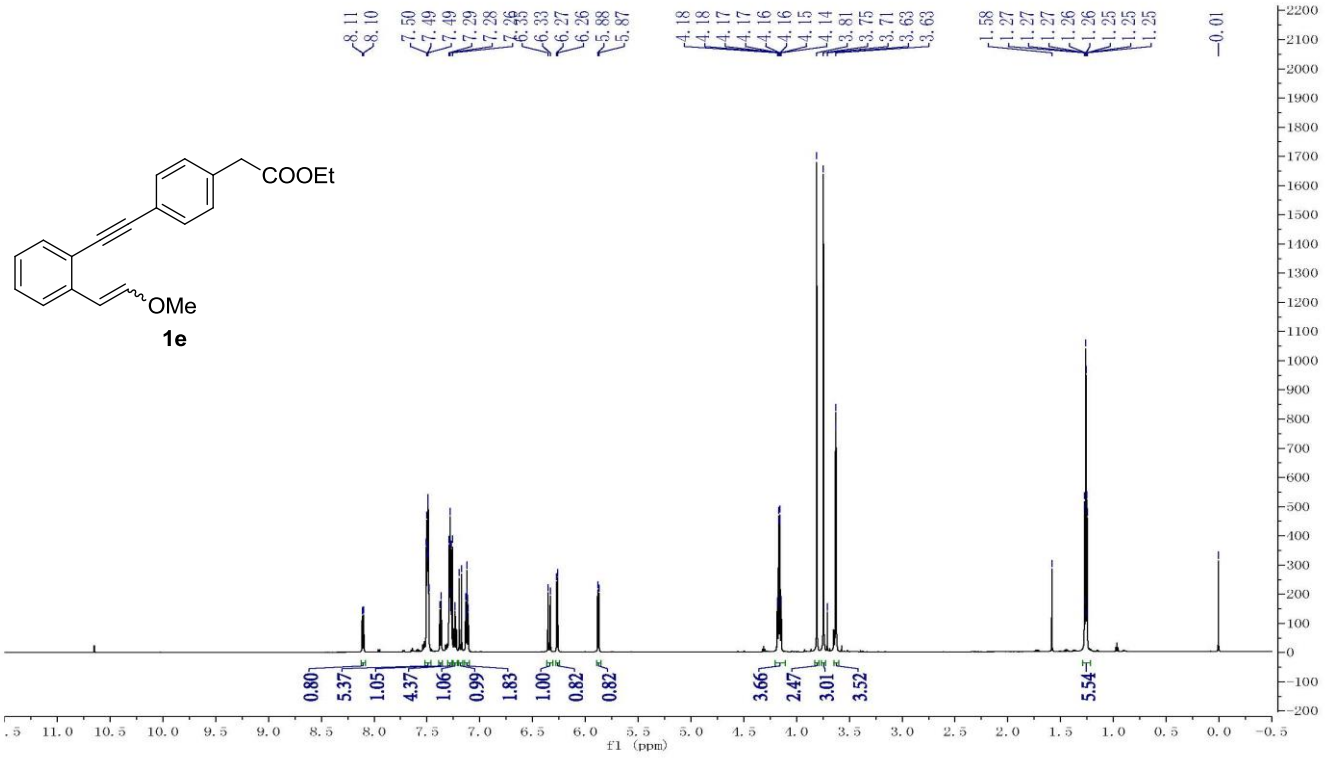
^{13}C NMR Spectrum of Compound **1c** (DMSO-*d*$_6$, 150 MHz)



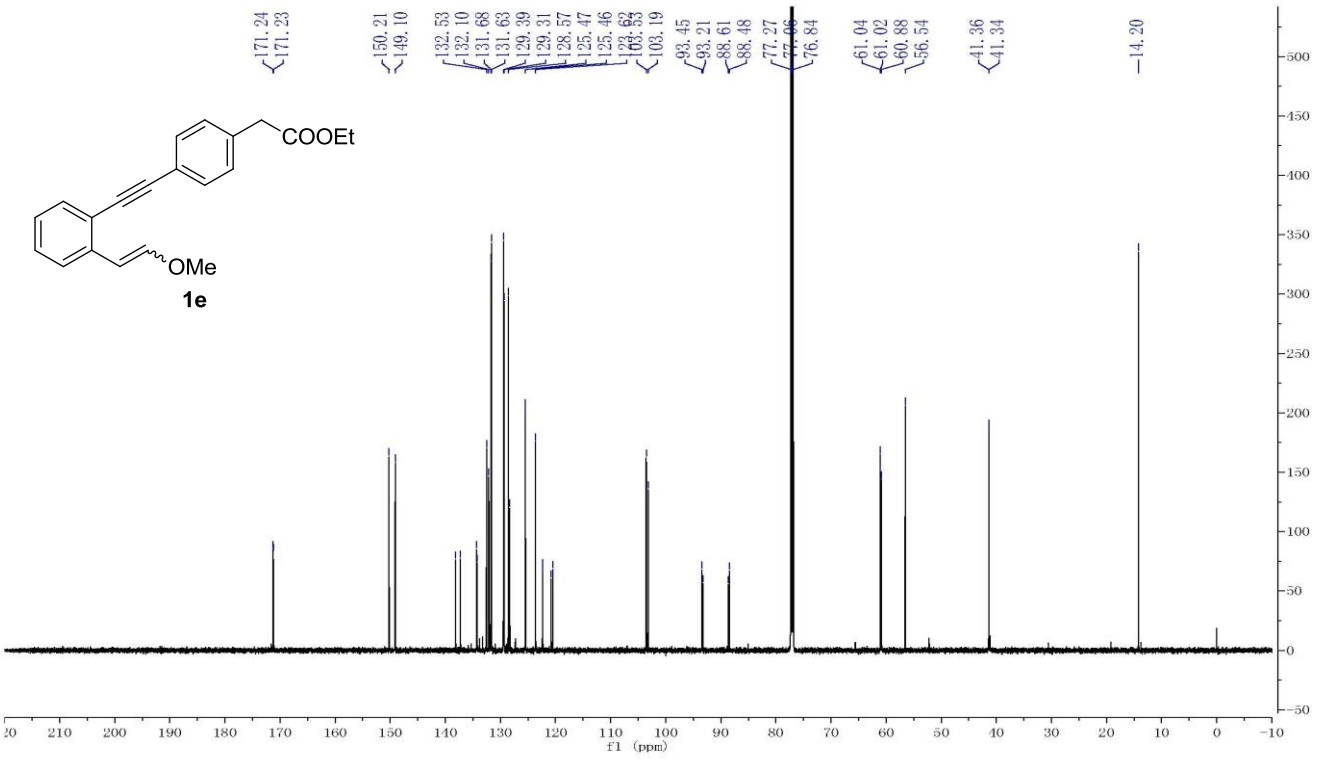
^{1}H NMR Spectrum of Compound **1d** (DMSO-d_6, 600 MHz)



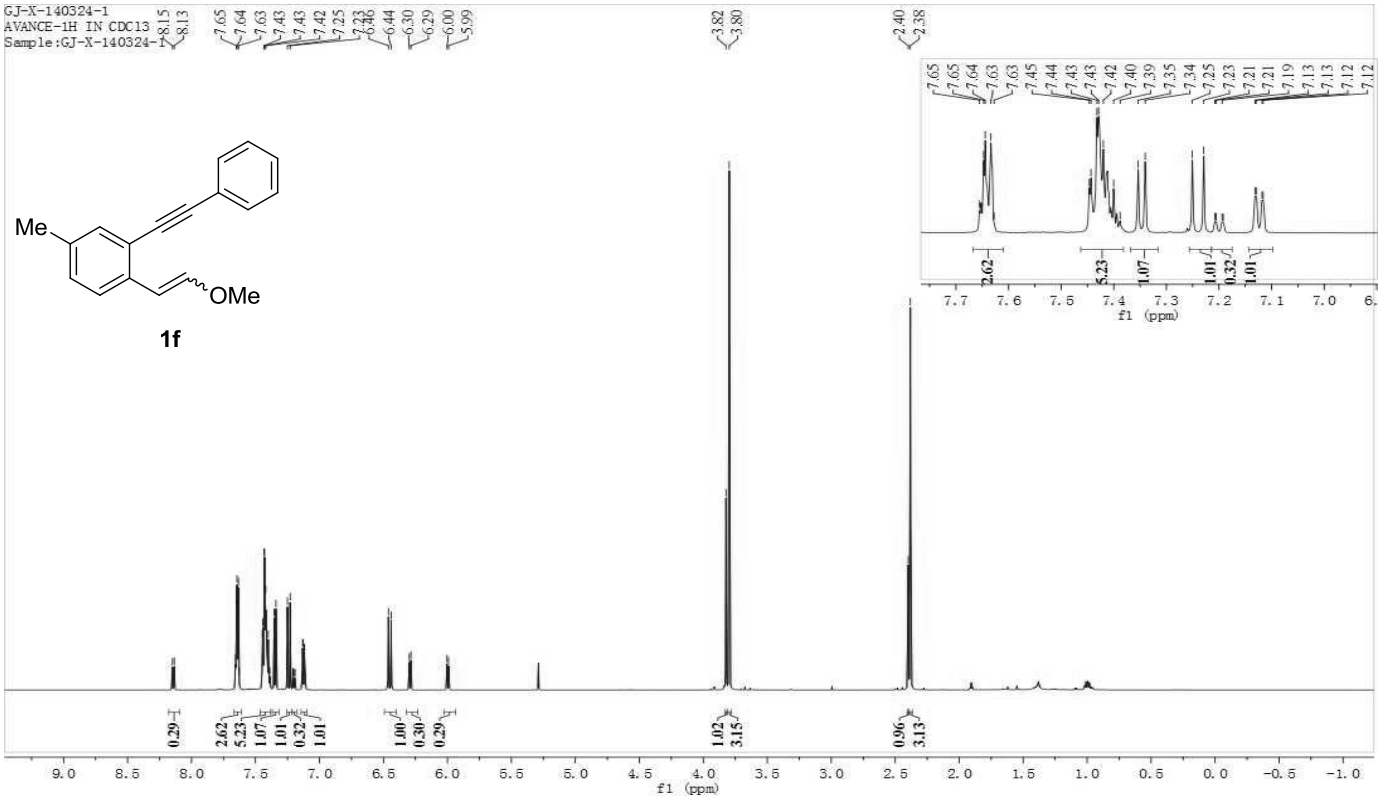
^{13}C NMR Spectrum of Compound **1d** (DMSO-d_6, 150 MHz)



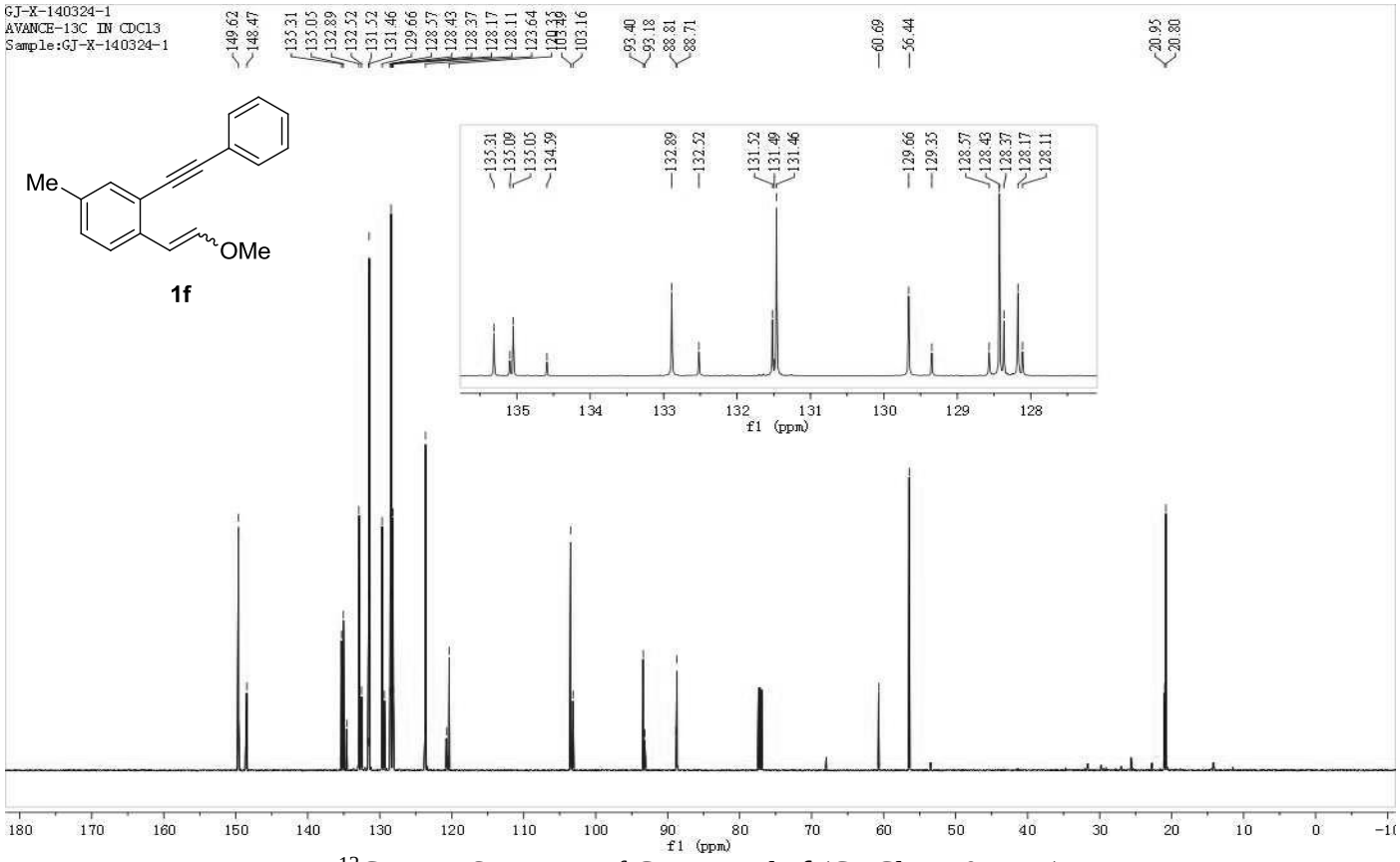
^{1}H NMR Spectrum of Compound **1e** ($CDCl_3$, 600 MHz)



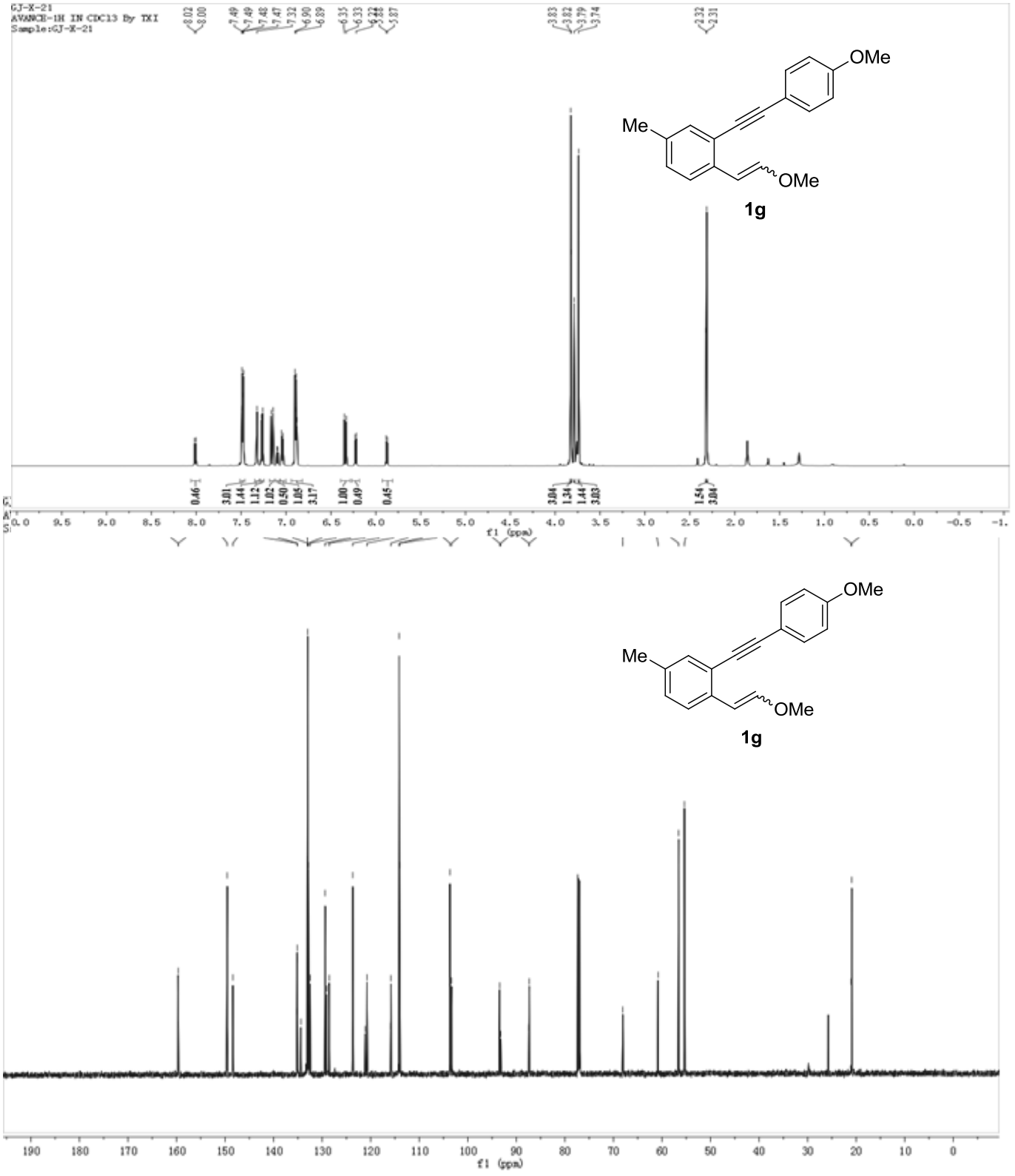
^{13}C NMR Spectrum of Compound **1e** ($CDCl_3$, 150 MHz)

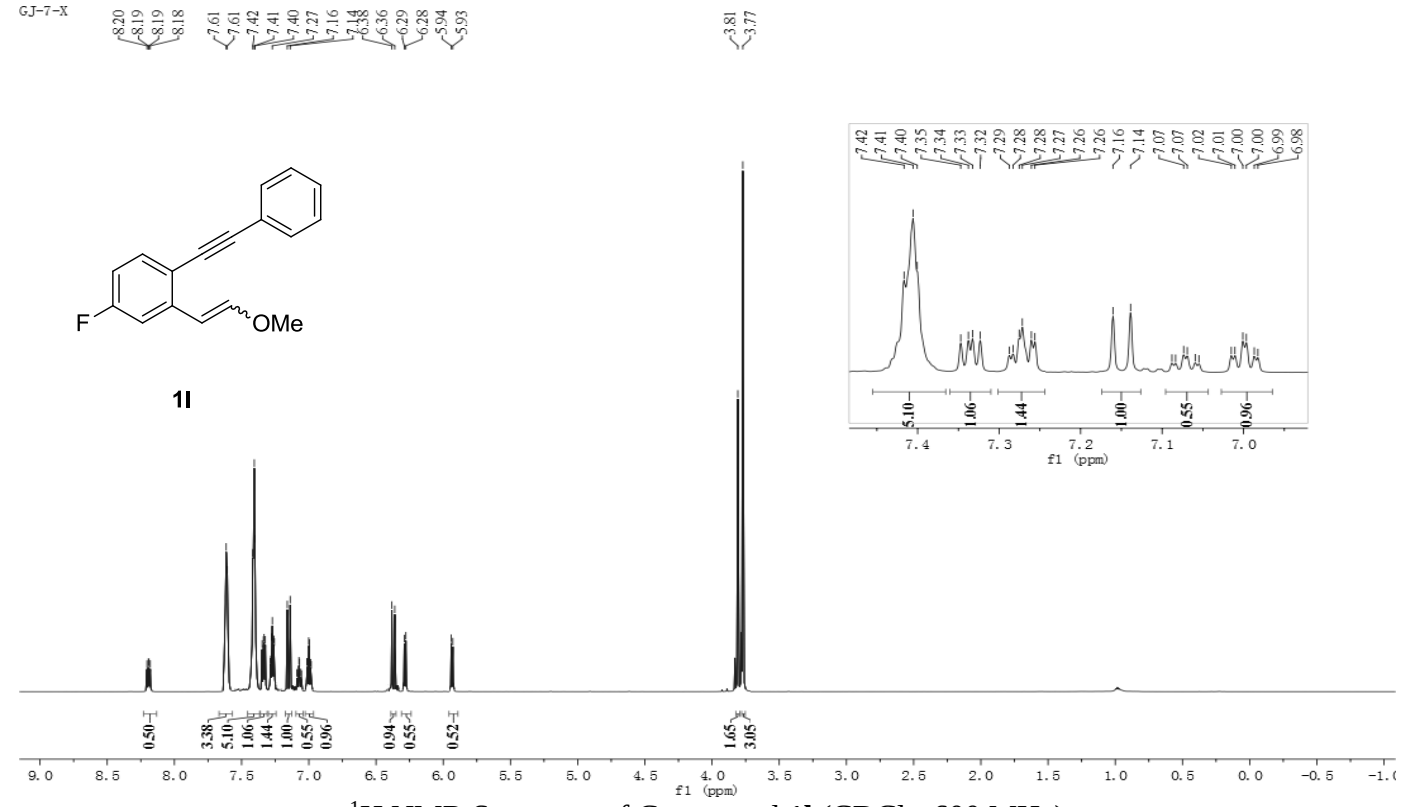


^{1}H NMR Spectrum of Compound **1f** ($CDCl_3$, 600 MHz)

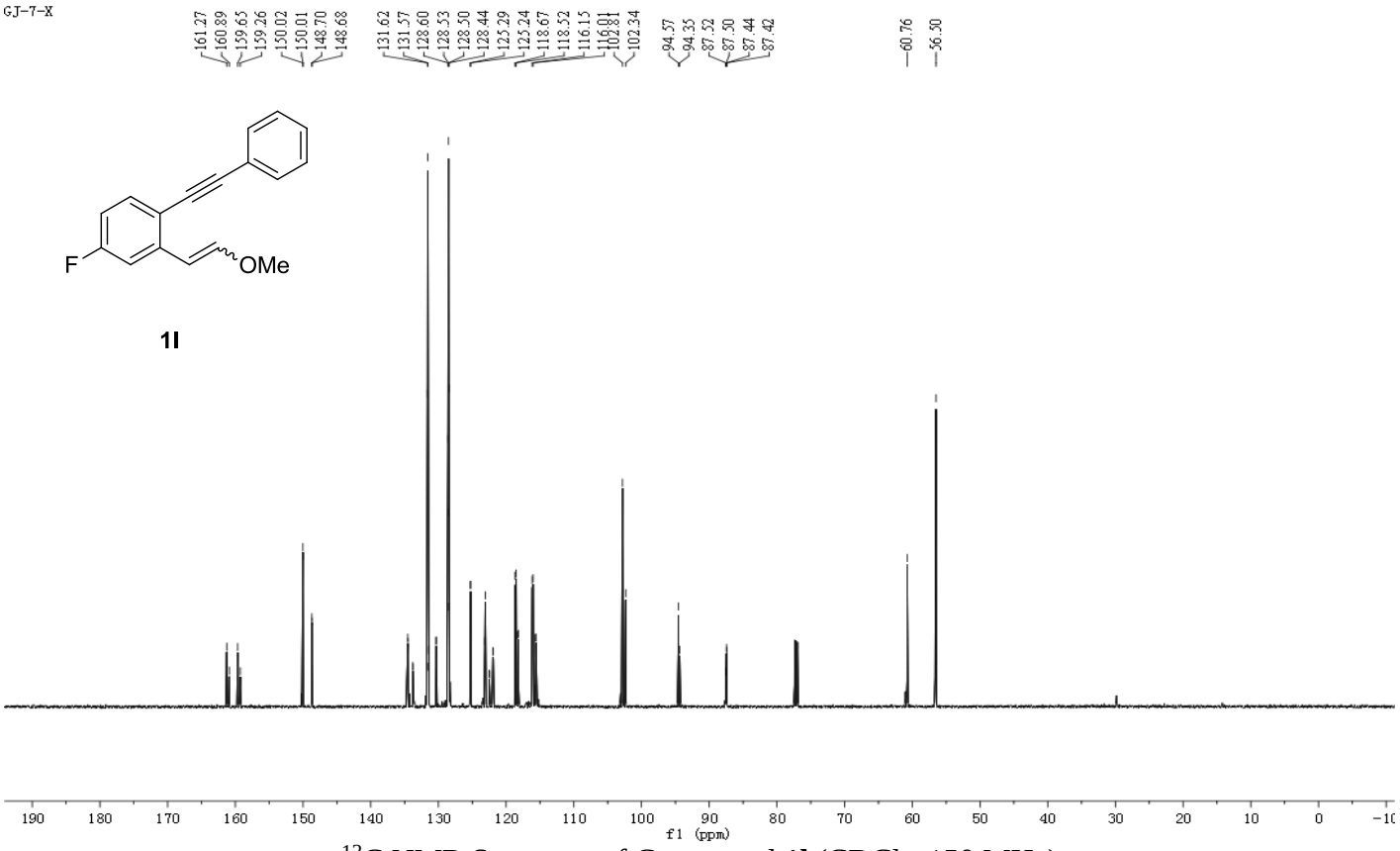


^{13}C NMR Spectrum of Compound **1f** ($CDCl_3$, 150 MHz)

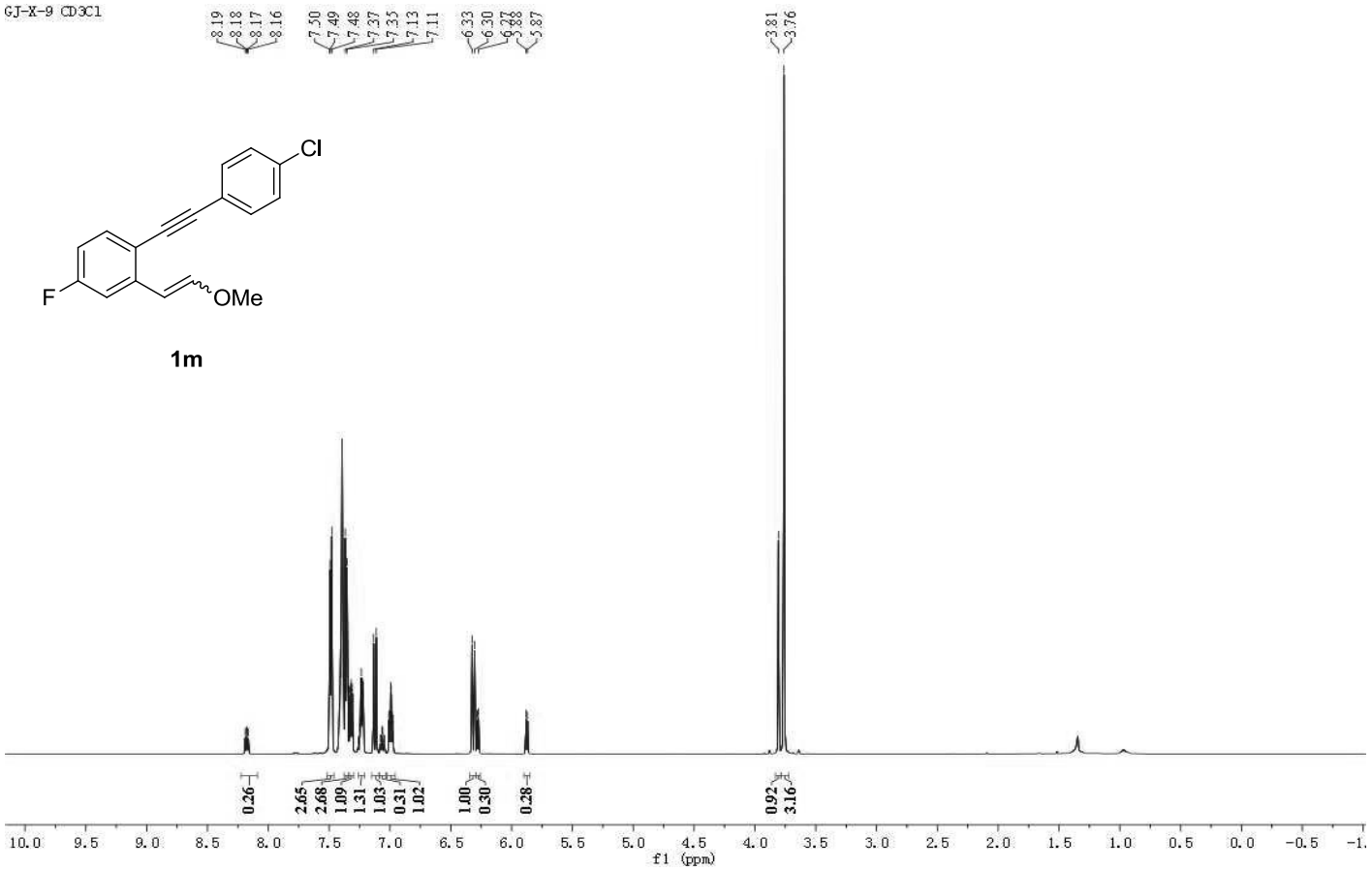

GJ-X-21
AVANCE-1H IN CDCl3 By TXI
Sample:GJ-X-21
OMe
Me
OMe
1g
f1 (ppm)
OMe
Me
OMe
1g
f1 (ppm)



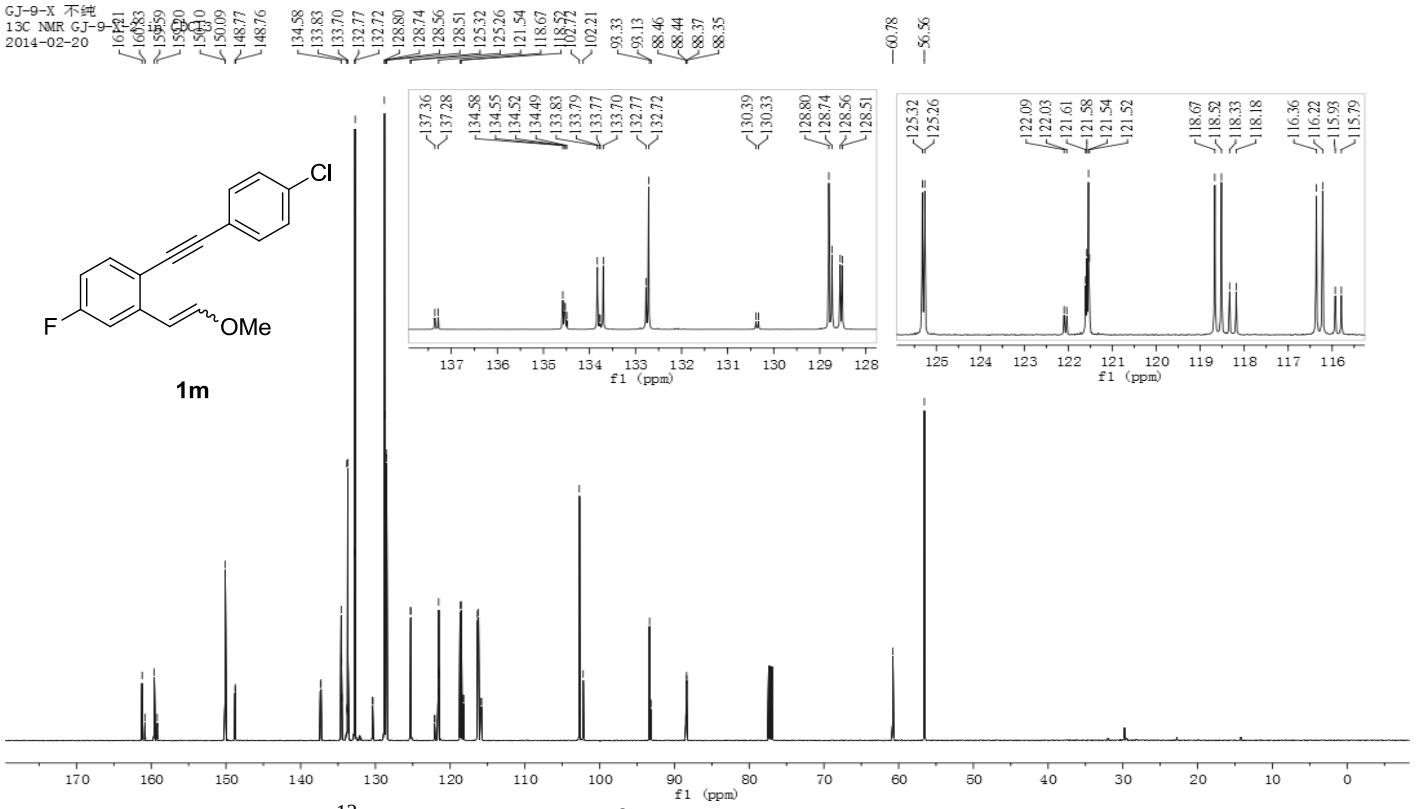
^{1}H NMR Spectrum of Compound **1l** ($CDCl_3$, 600 MHz)



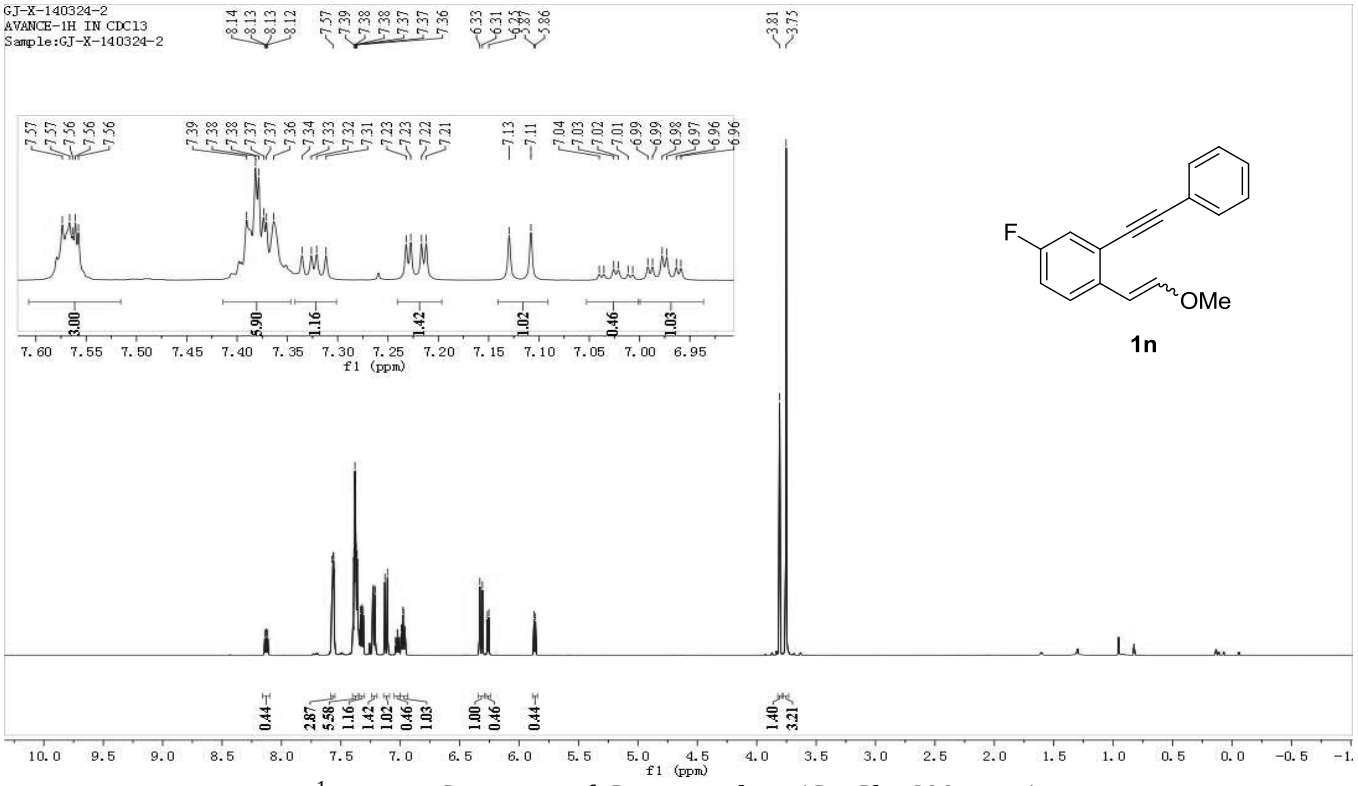
^{13}C NMR Spectrum of Compound **1l** ($CDCl_3$, 150 MHz)



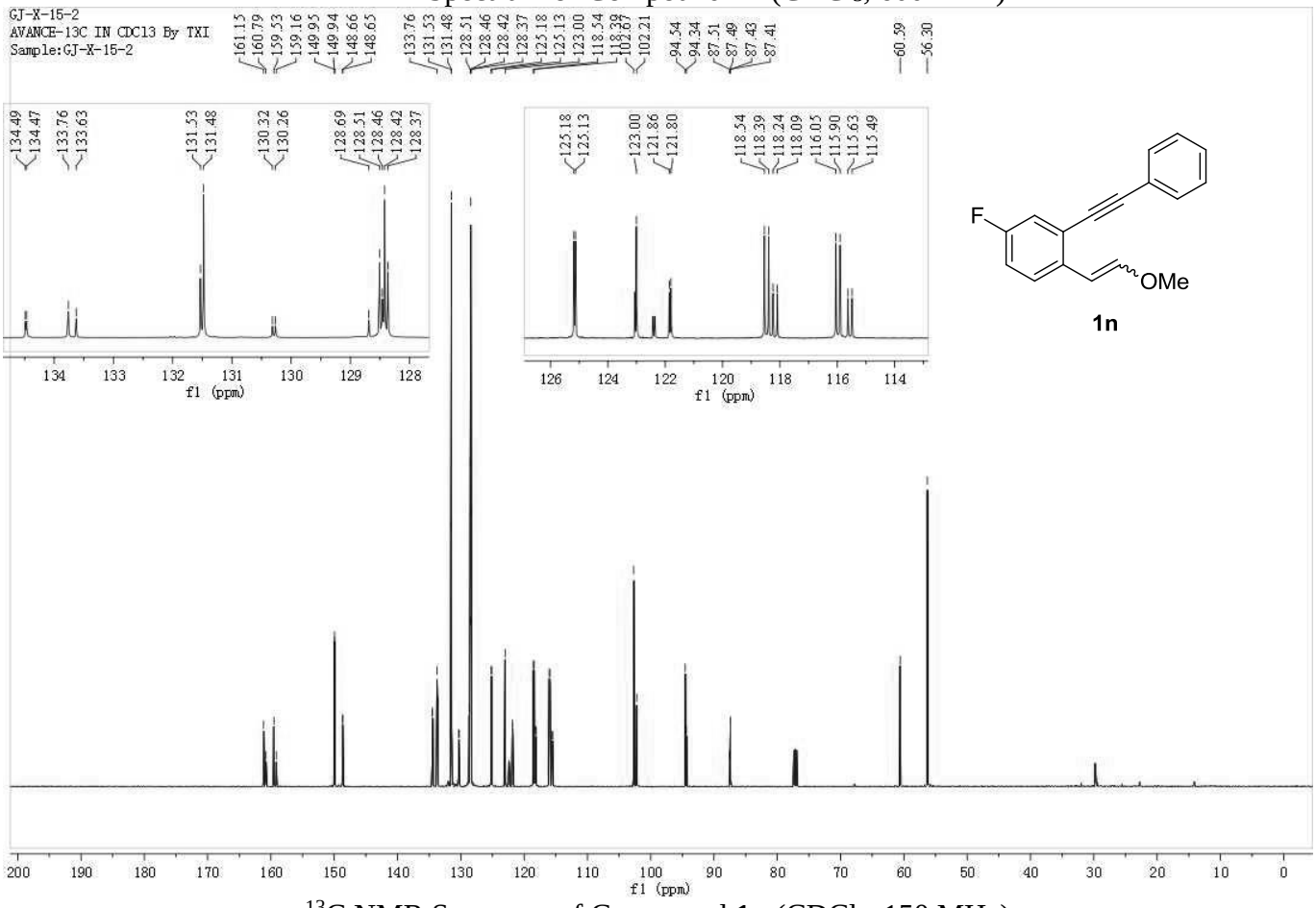
^{1}H NMR Spectrum of Compound **1m** ($CDCl_3$, 600 MHz)



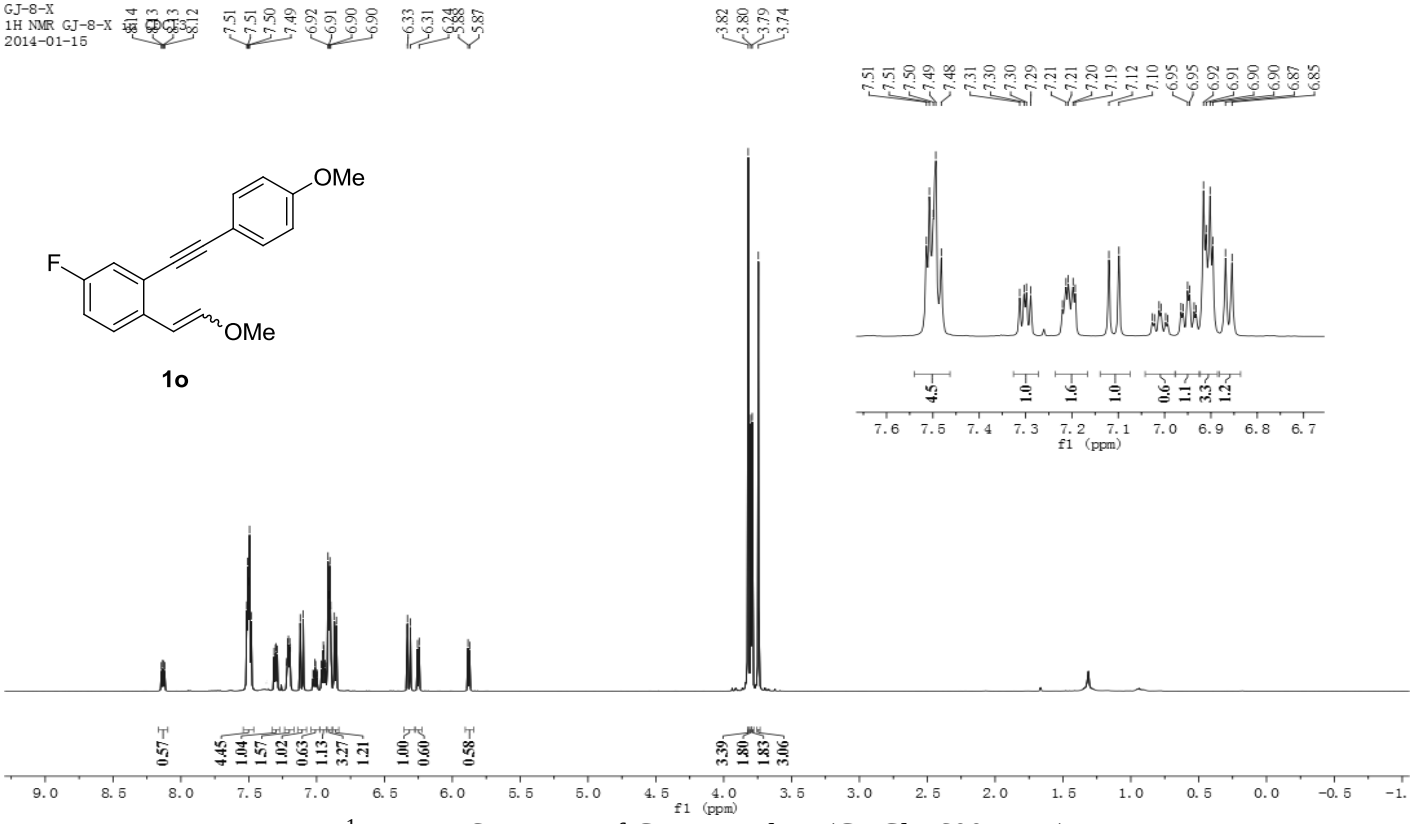
^{13}C NMR Spectrum of Compound **1m** ($CDCl_3$, 150 MHz)



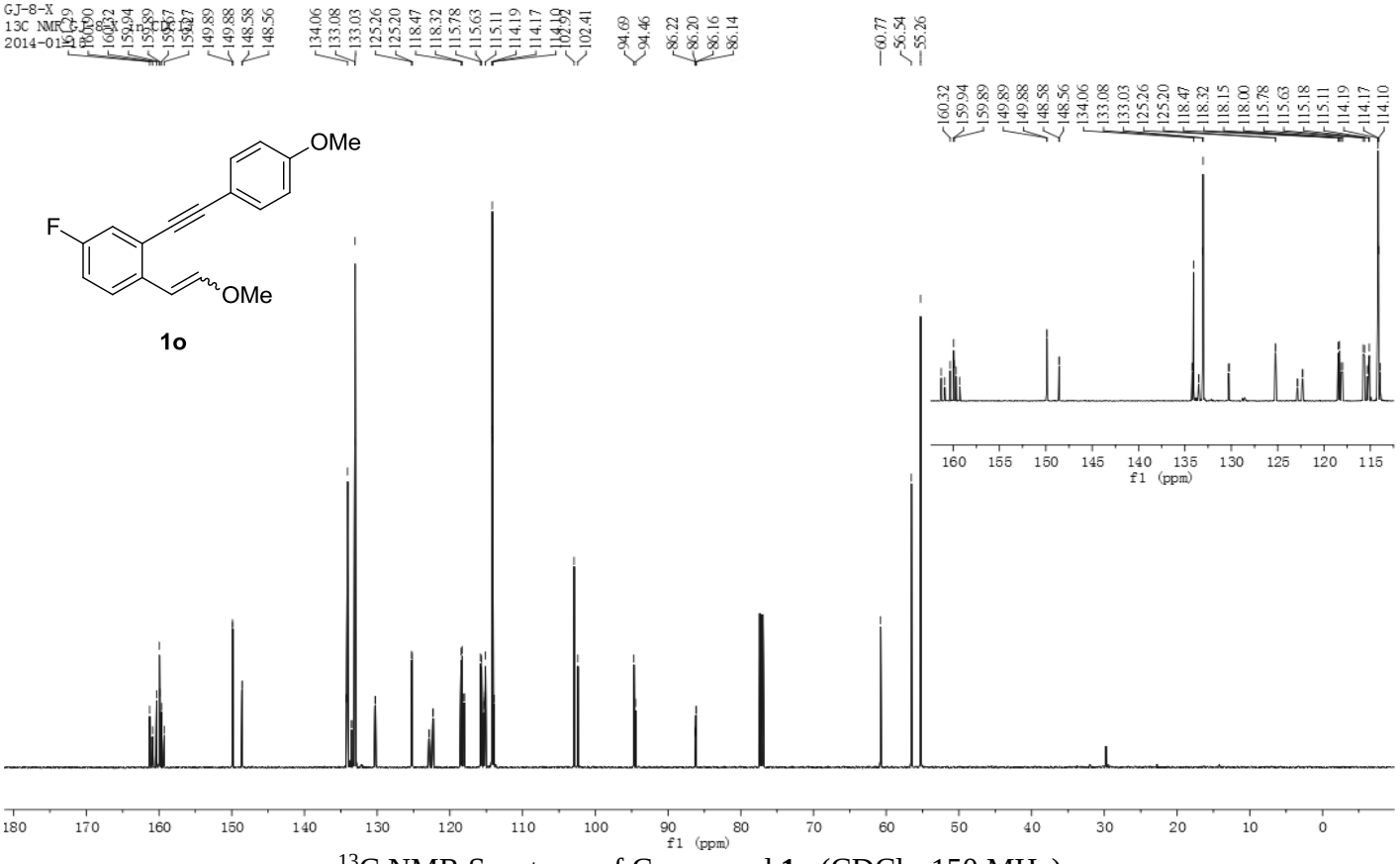
^{1}H NMR Spectrum of Compound **1n** ($CDCl_3$, 600 MHz)



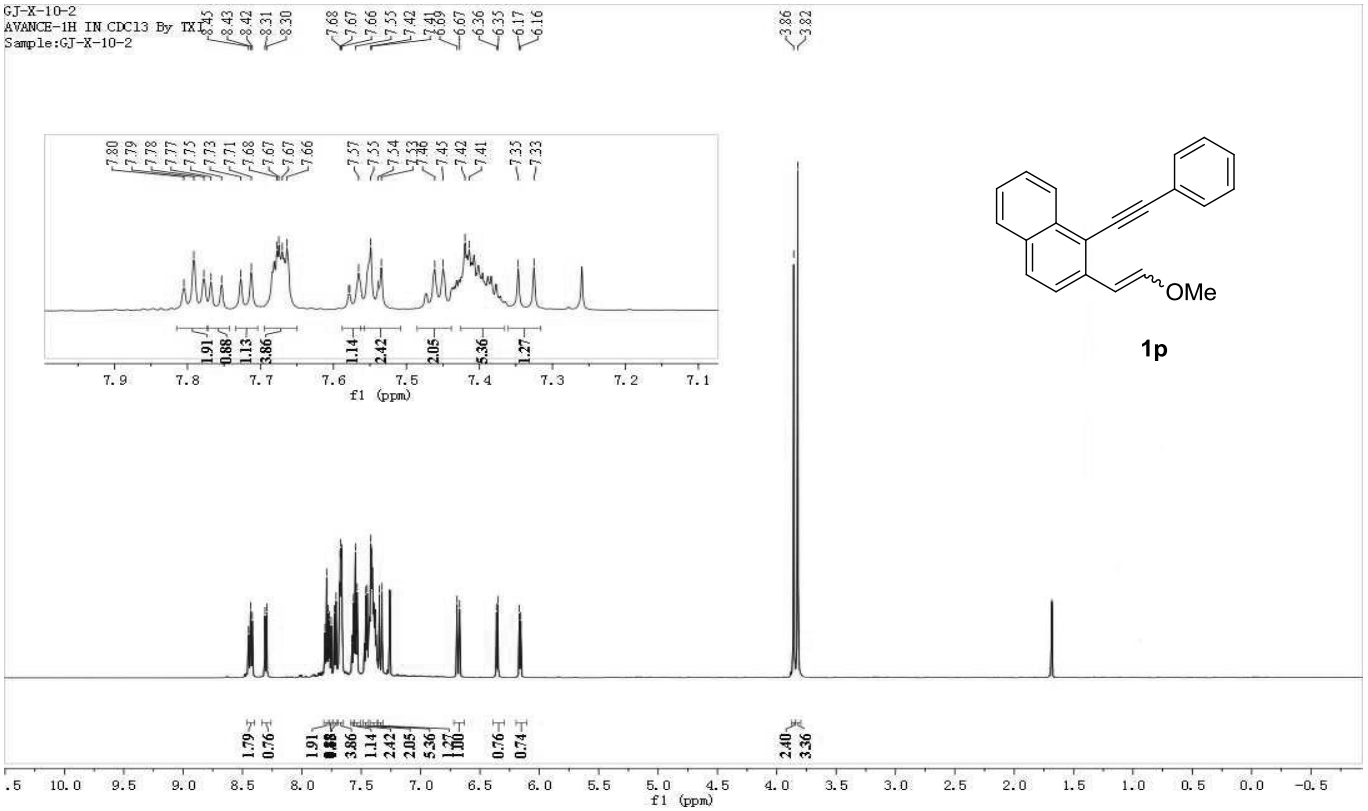
^{13}C NMR Spectrum of Compound **1n** ($CDCl_3$, 150 MHz)



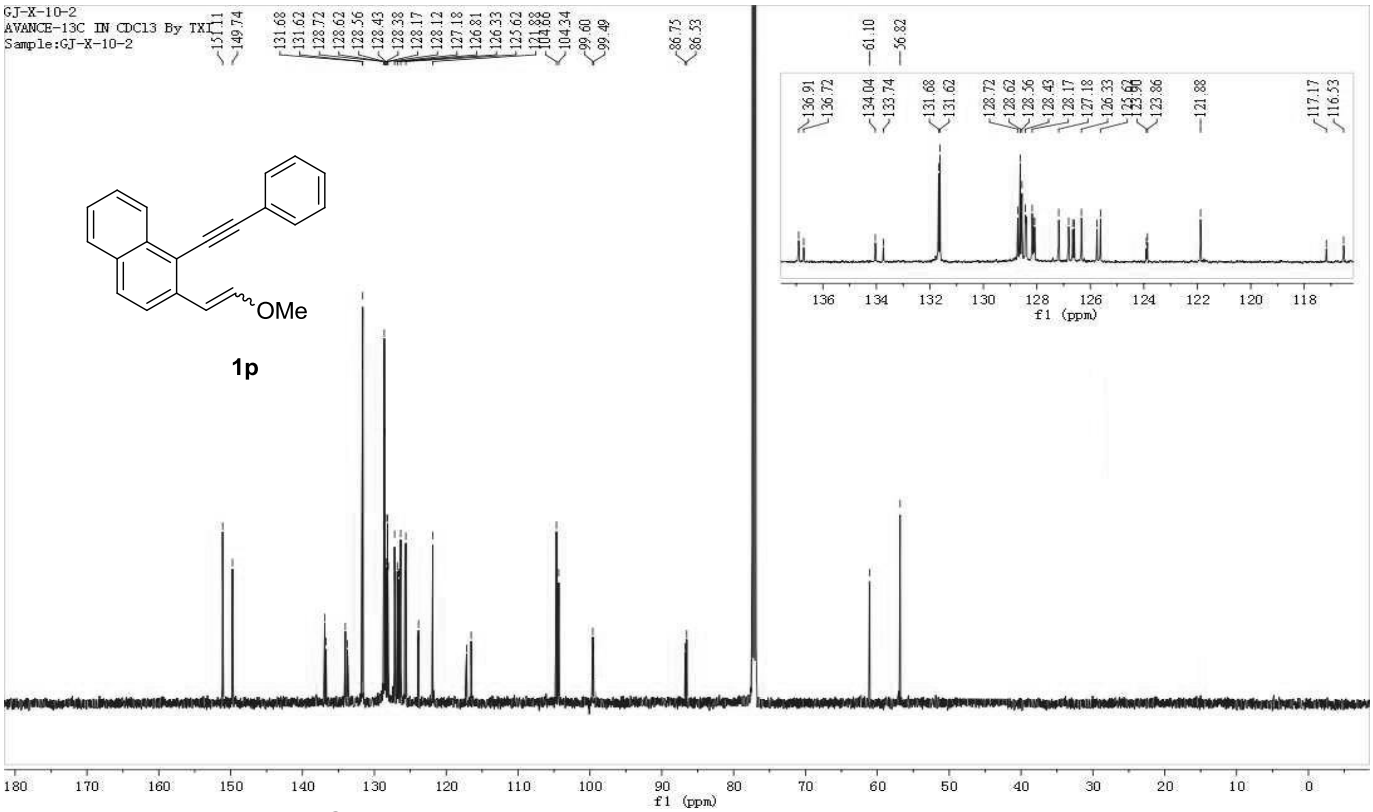
^{1}H NMR Spectrum of Compound **1o** ($CDCl_3$, 600 MHz)



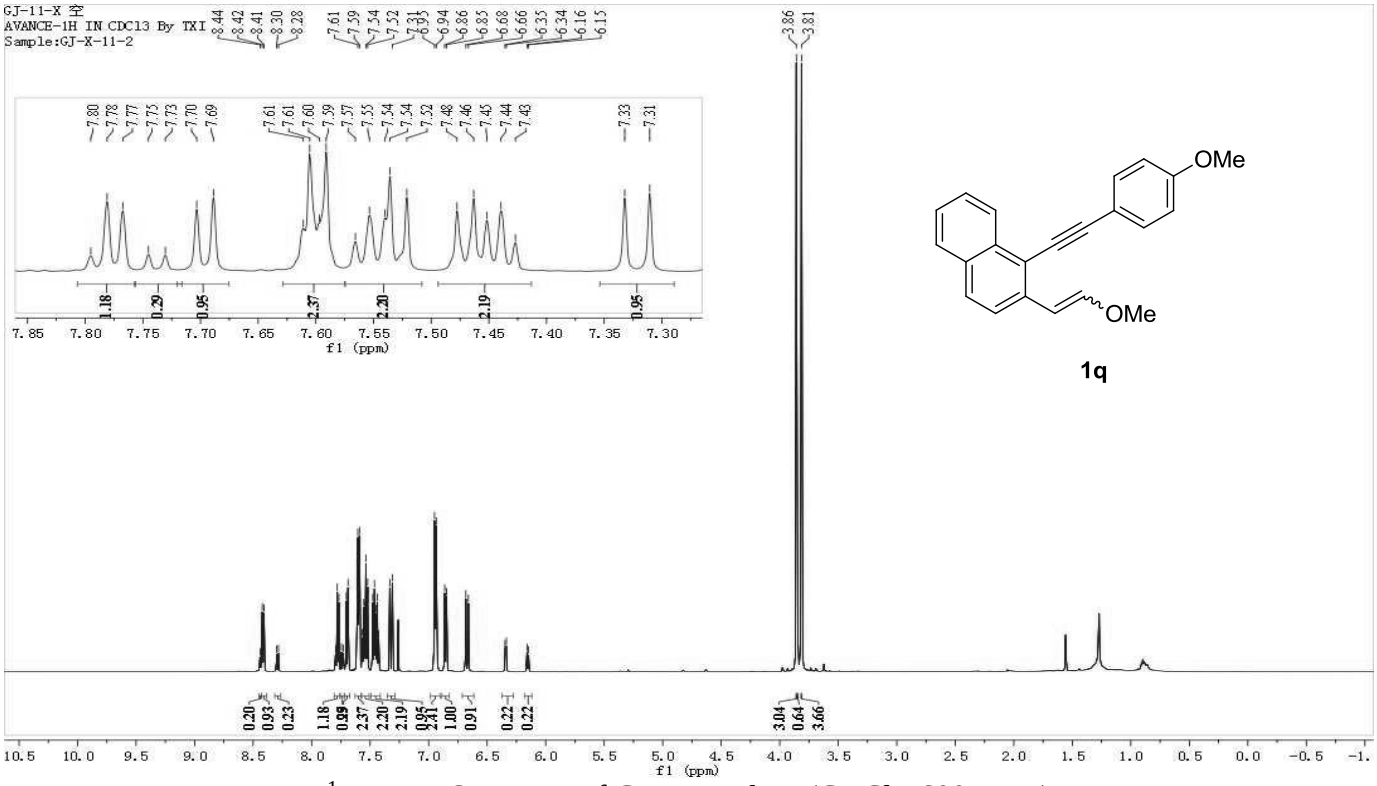
^{13}C NMR Spectrum of Compound **1o** ($CDCl_3$, 150 MHz)



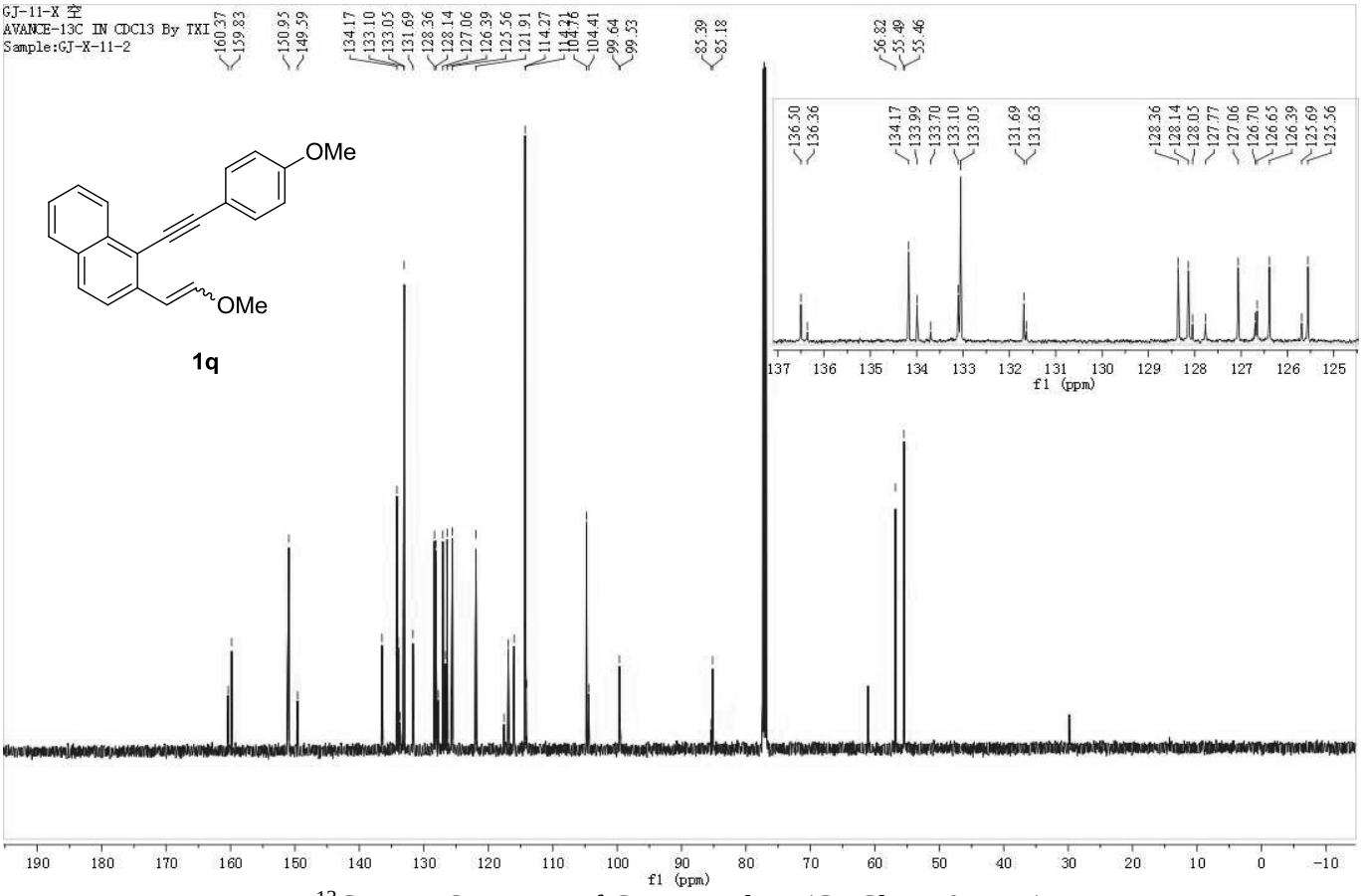
^{1}H NMR Spectrum of Compound **1p** ($CDCl_3$, 600 MHz)



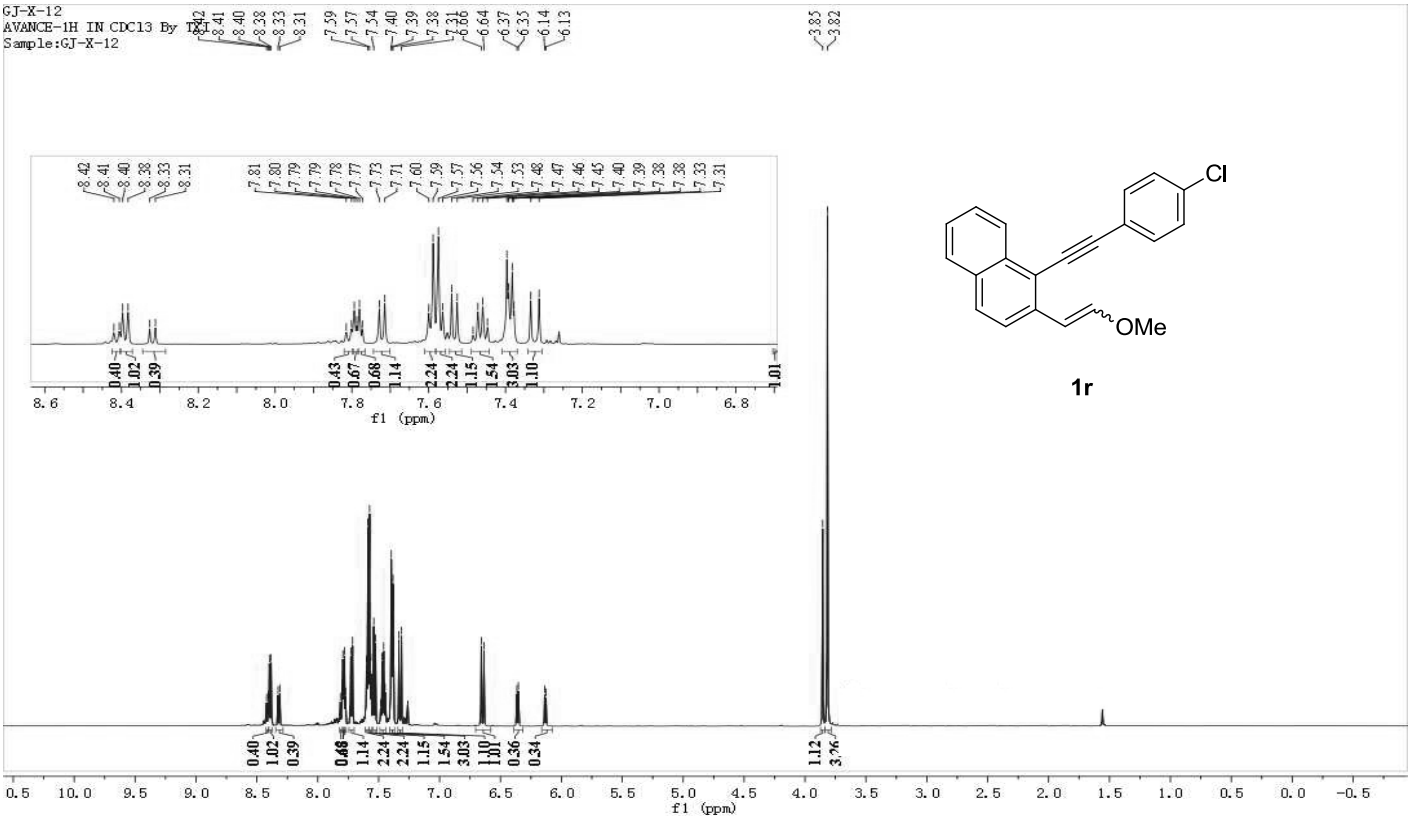
^{13}C NMR Spectrum of Compound **1p** ($CDCl_3$, 150 MHz)



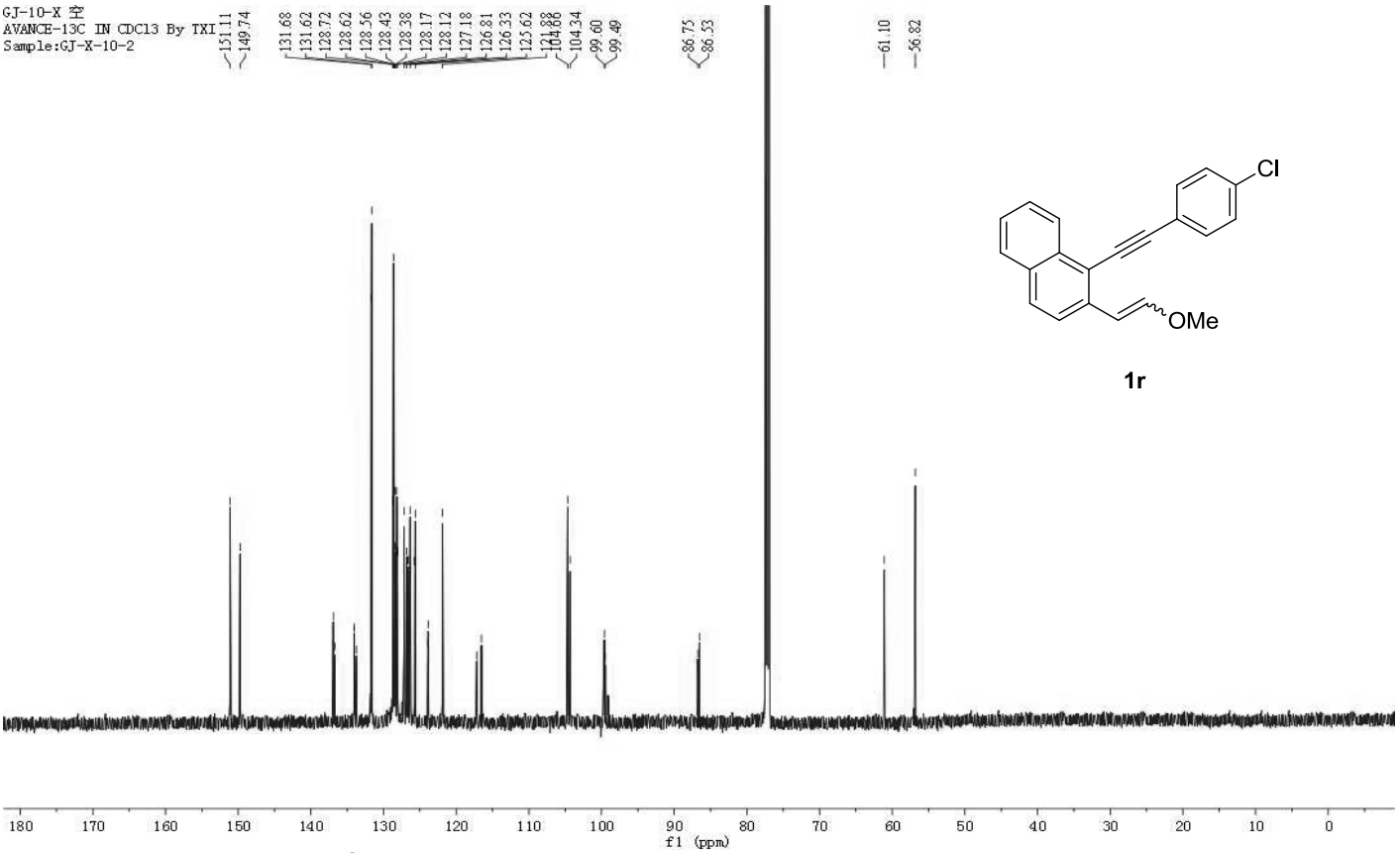
^{1}H NMR Spectrum of Compound **1q** ($CDCl_3$, 600 MHz)



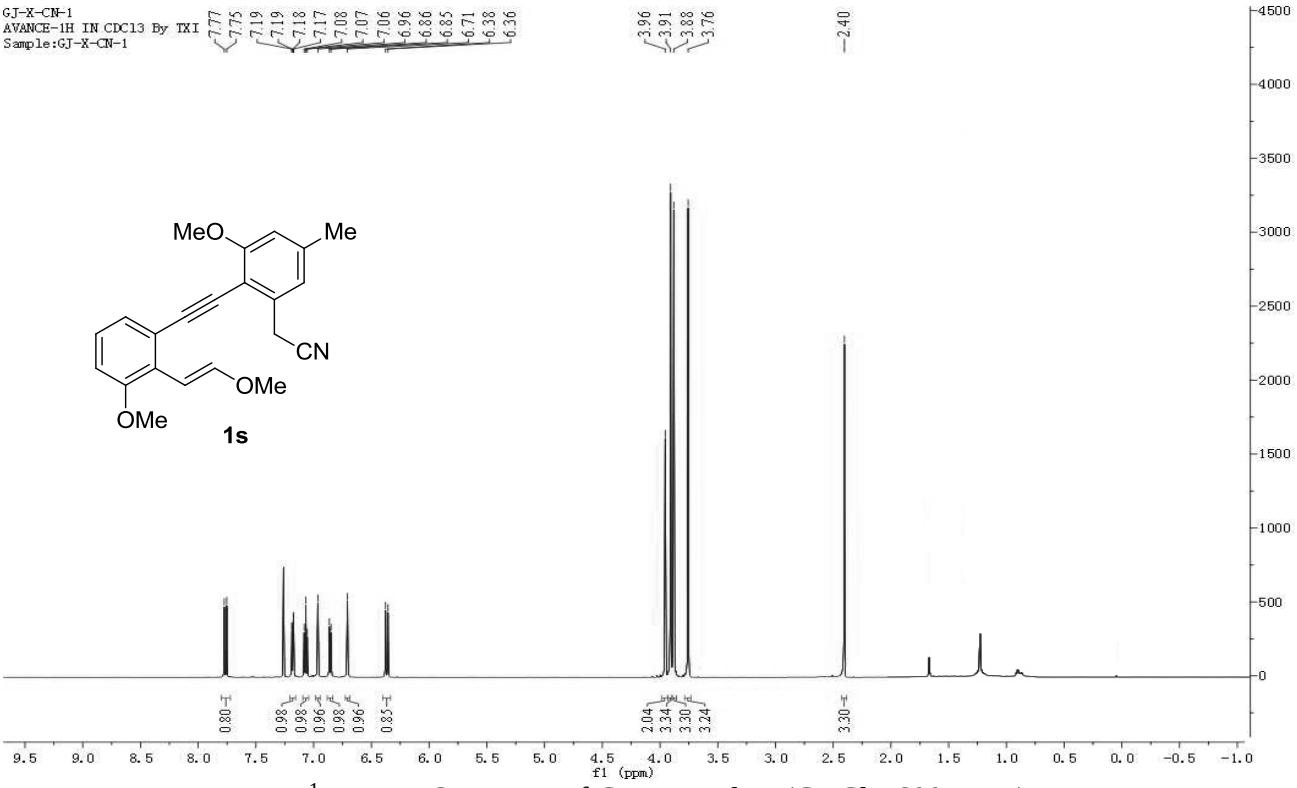
^{13}C NMR Spectrum of Compound **1q** ($CDCl_3$, 150 MHz)



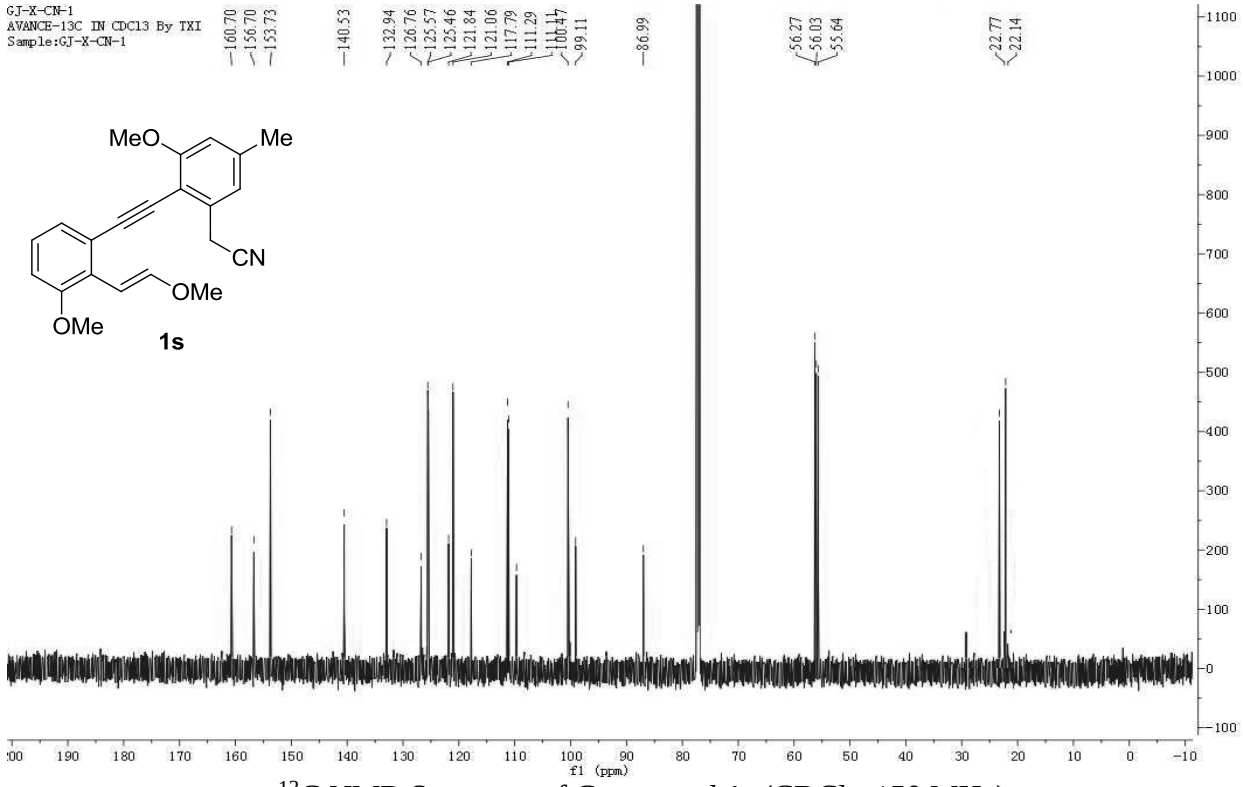
^{1}H NMR Spectrum of Compound **1r** ($CDCl_3$, 600 MHz)



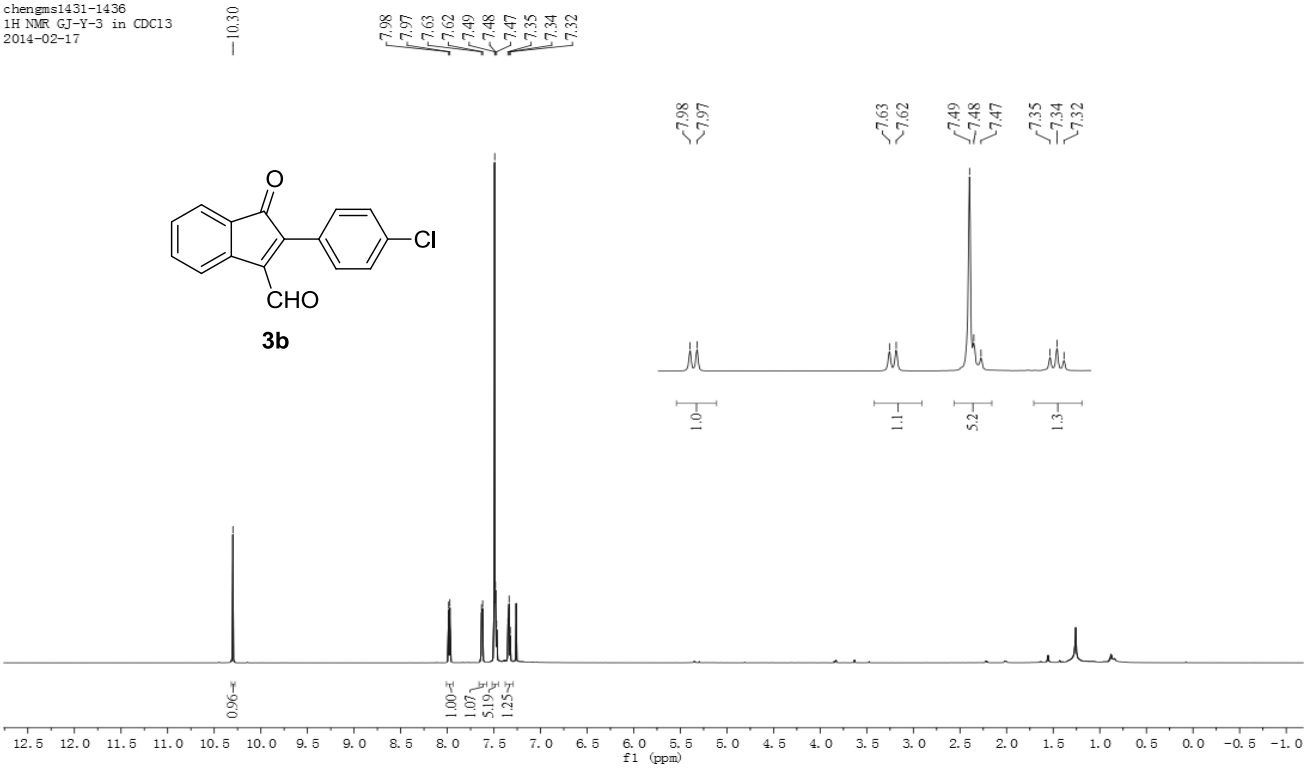
^{13}C NMR Spectrum of Compound **1r** ($CDCl_3$, 150 MHz)



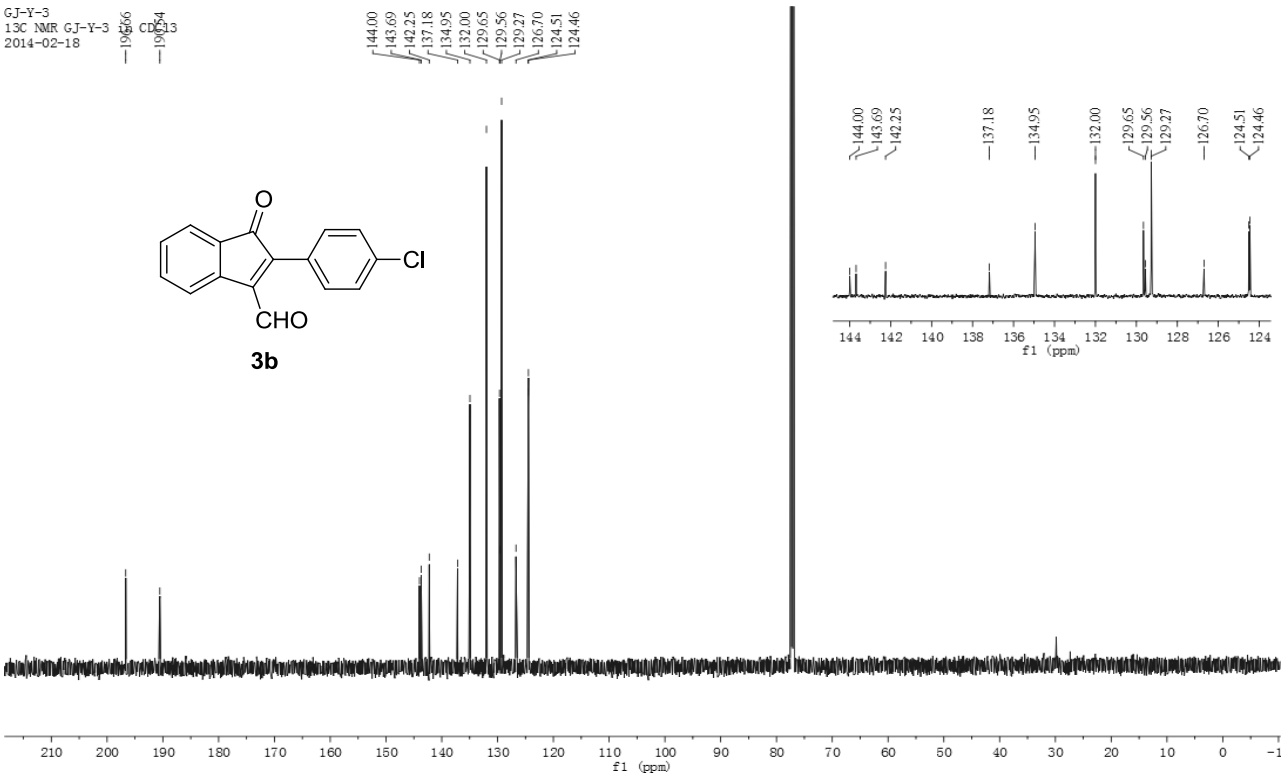
^{1}H NMR Spectrum of Compound **1s** ($CDCl_3$, 600 MHz)



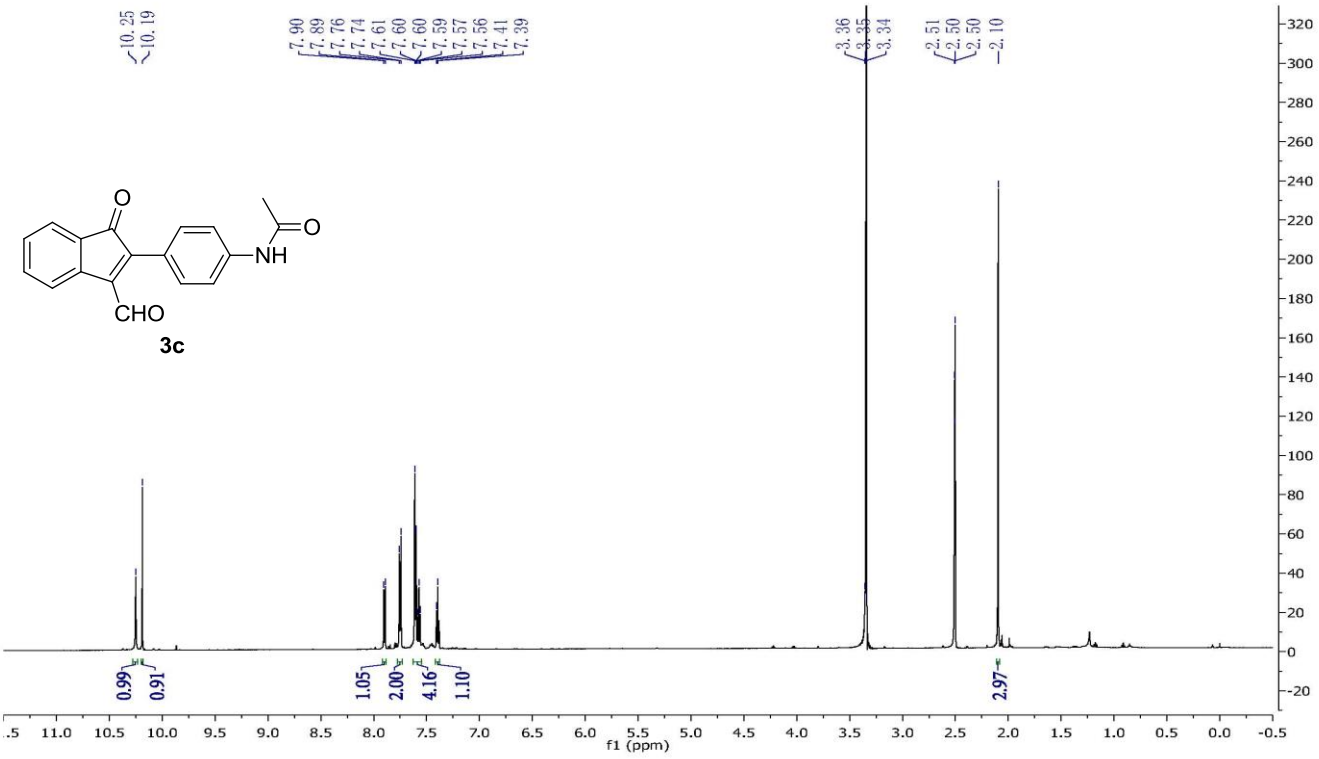
^{13}C NMR Spectrum of Compound **1s** ($CDCl_3$, 150 MHz)



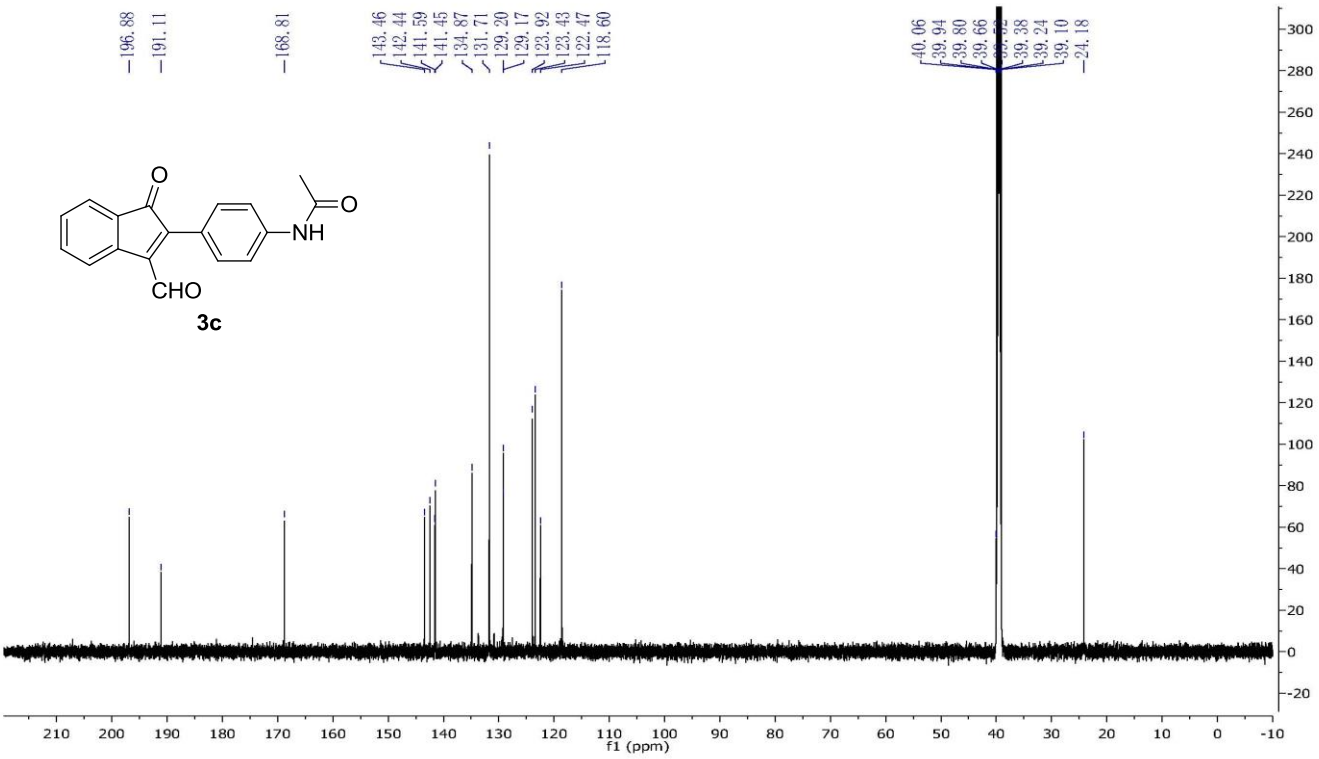
^{1}H NMR Spectrum of Compound **3b** ($CDCl_3$, 600 MHz)



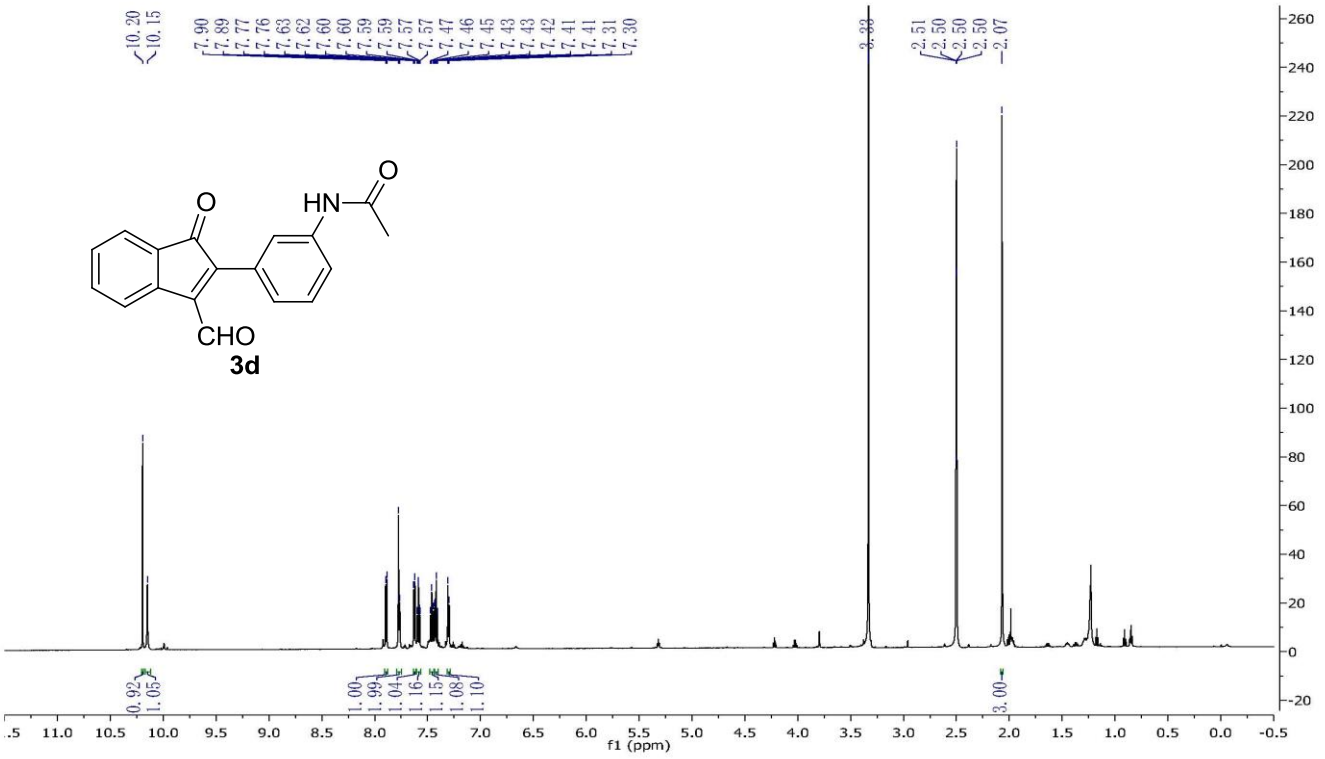
^{13}C NMR Spectrum of Compound **3b** ($CDCl_3$, 150 MHz)



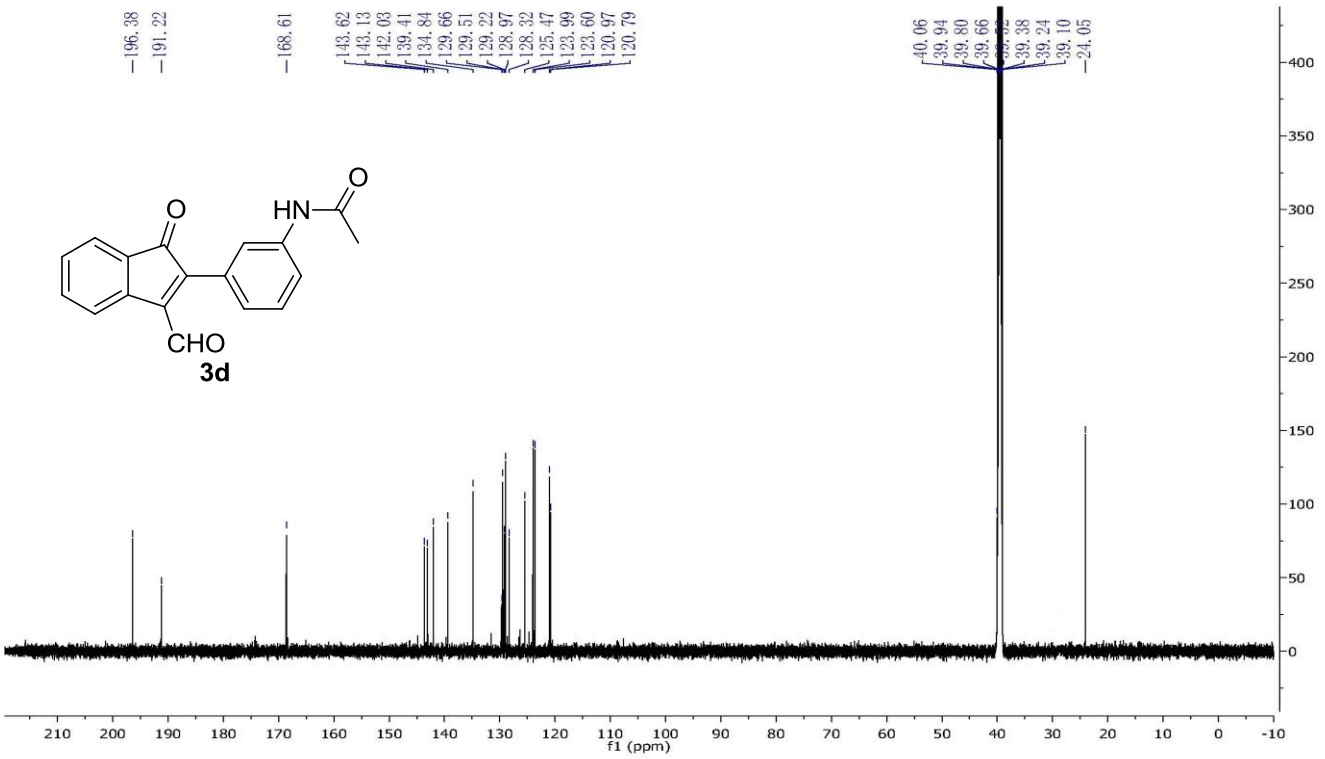
^{1}H NMR Spectrum of Compound **3c** (DMSO-d_6, 600 MHz)



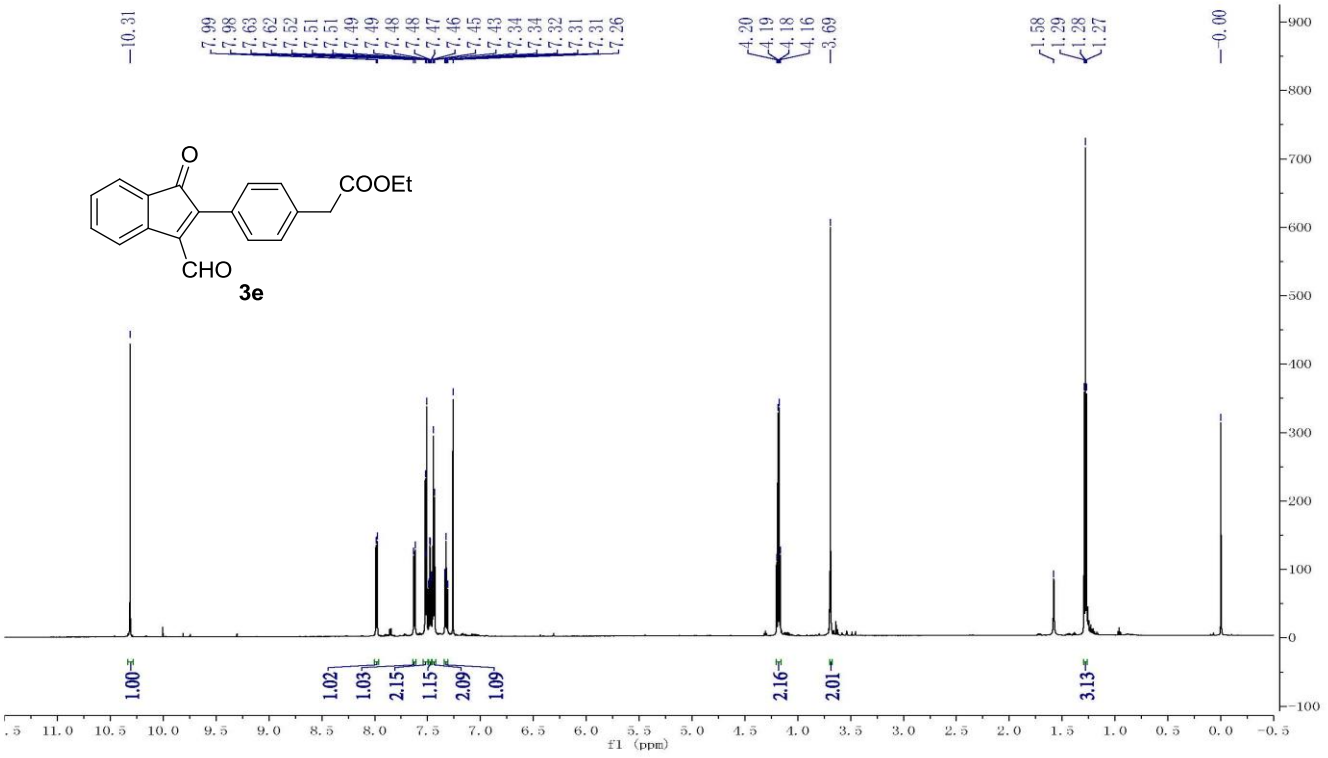
^{13}C NMR Spectrum of Compound **3c** (DMSO-d_6, 150 MHz)



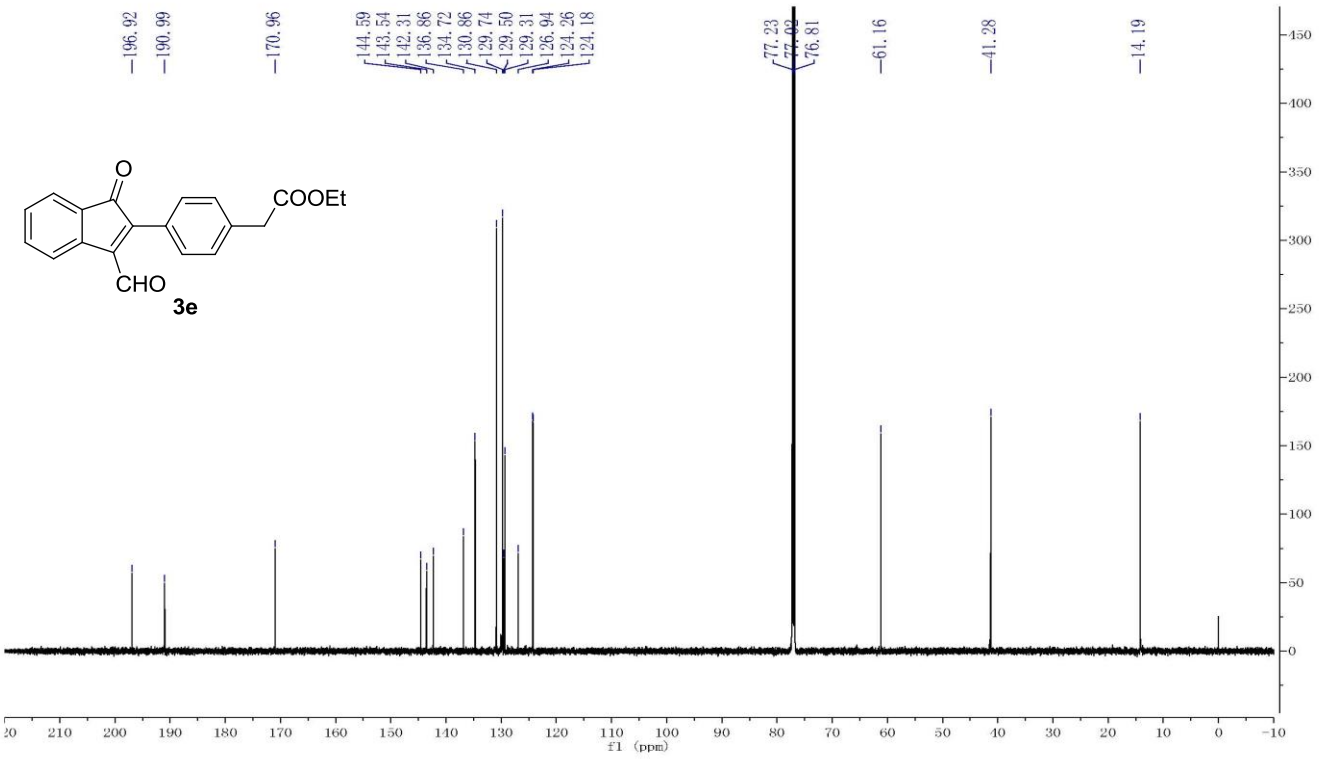
^{1}H NMR Spectrum of Compound **3d** (DMSO-d_6, 600 MHz)



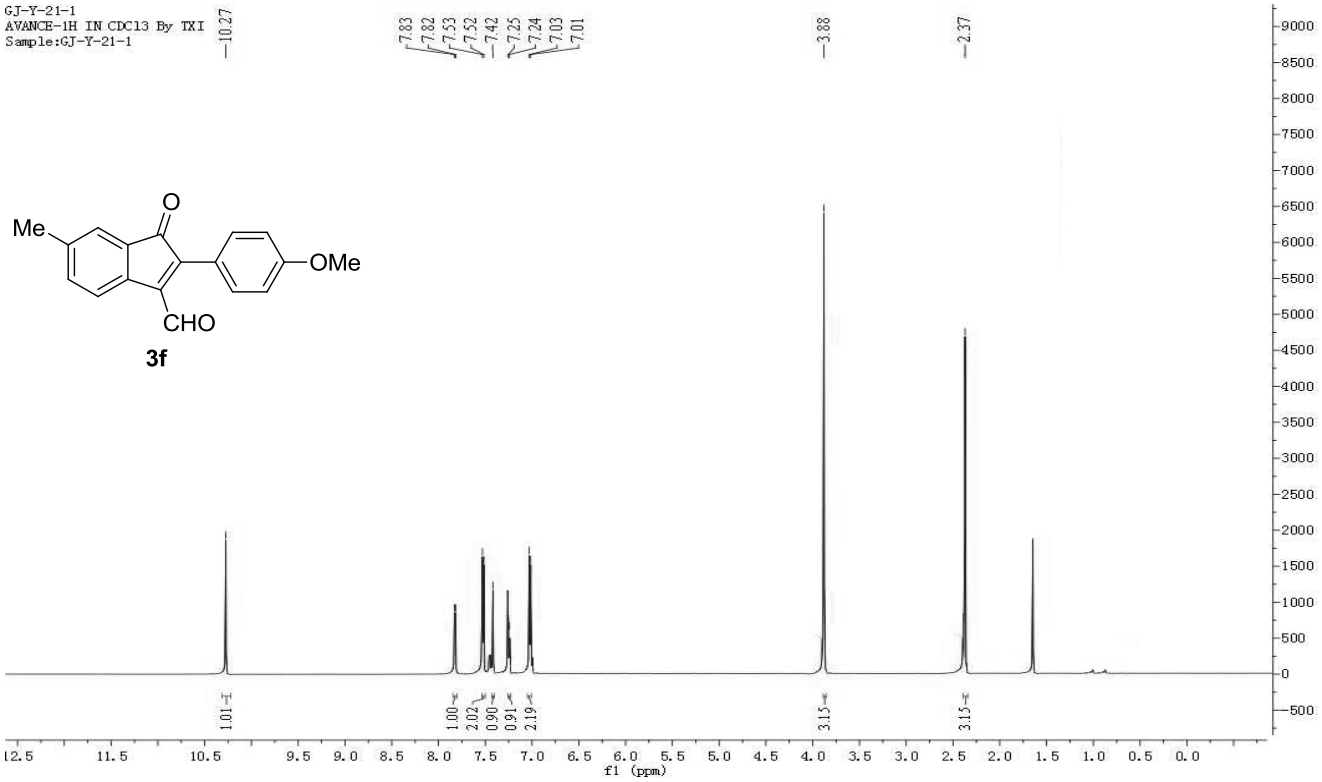
^{13}C NMR Spectrum of Compound **3d** (DMSO-d_6, 150 MHz)



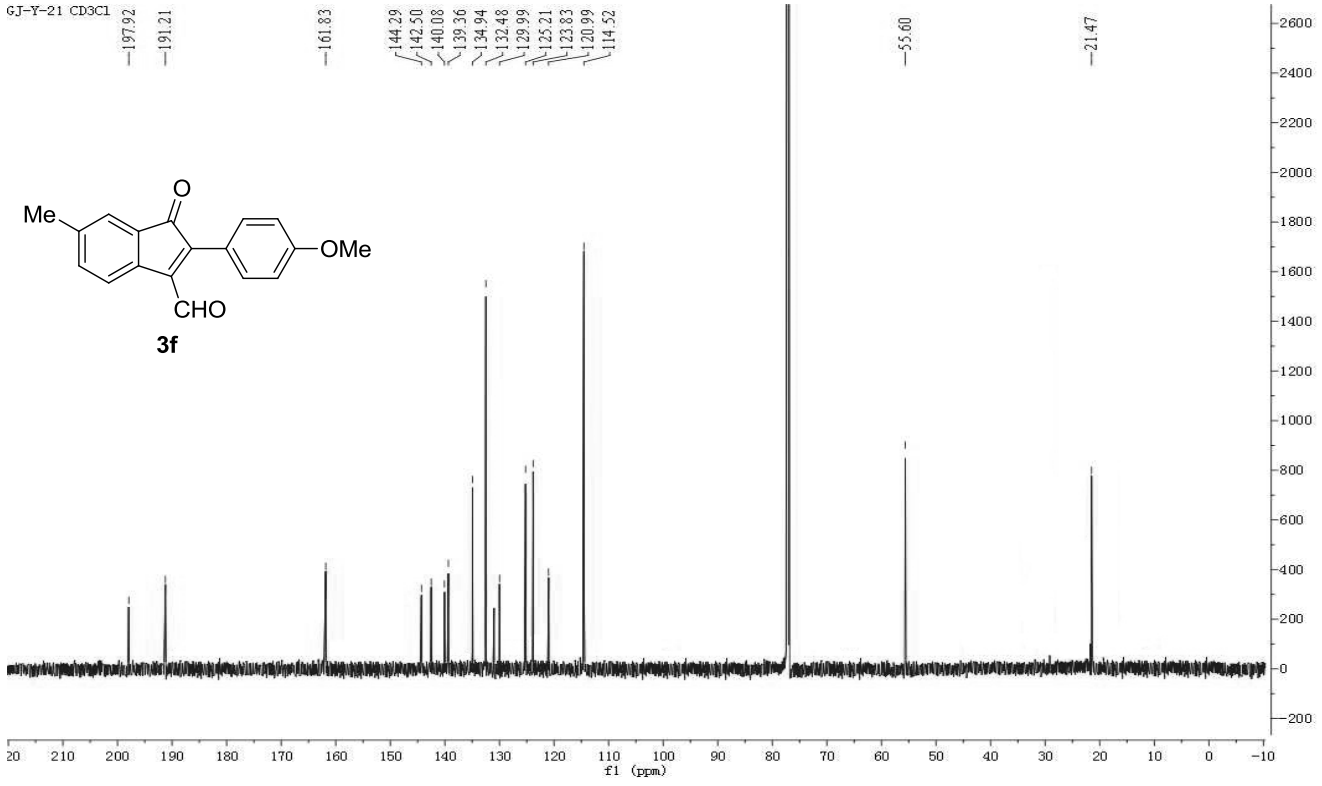
^{1}H NMR Spectrum of Compound **3e** ($CDCl_3$, 600 MHz)



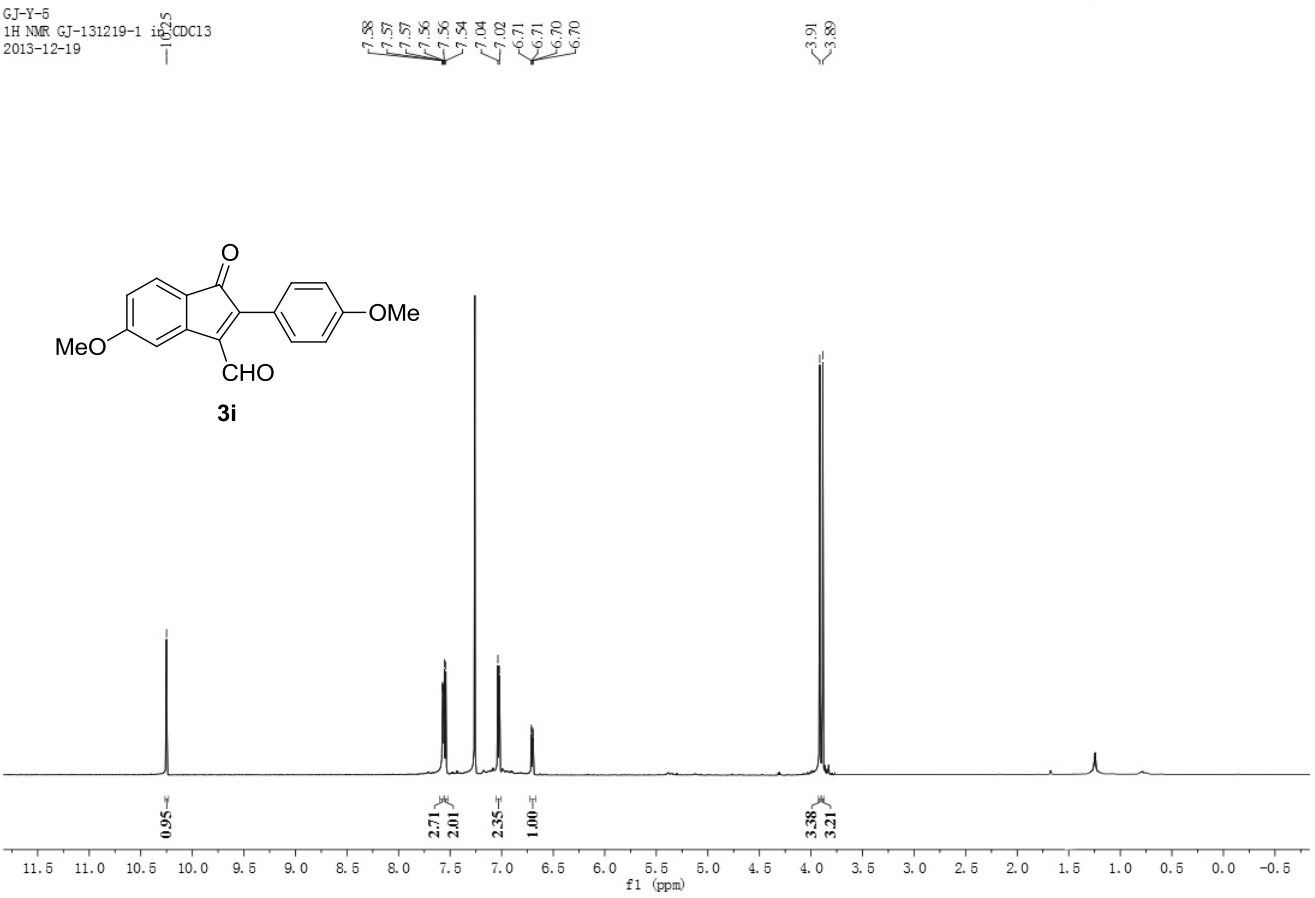
^{13}C NMR Spectrum of Compound **3e** ($CDCl_3$, 150 MHz)



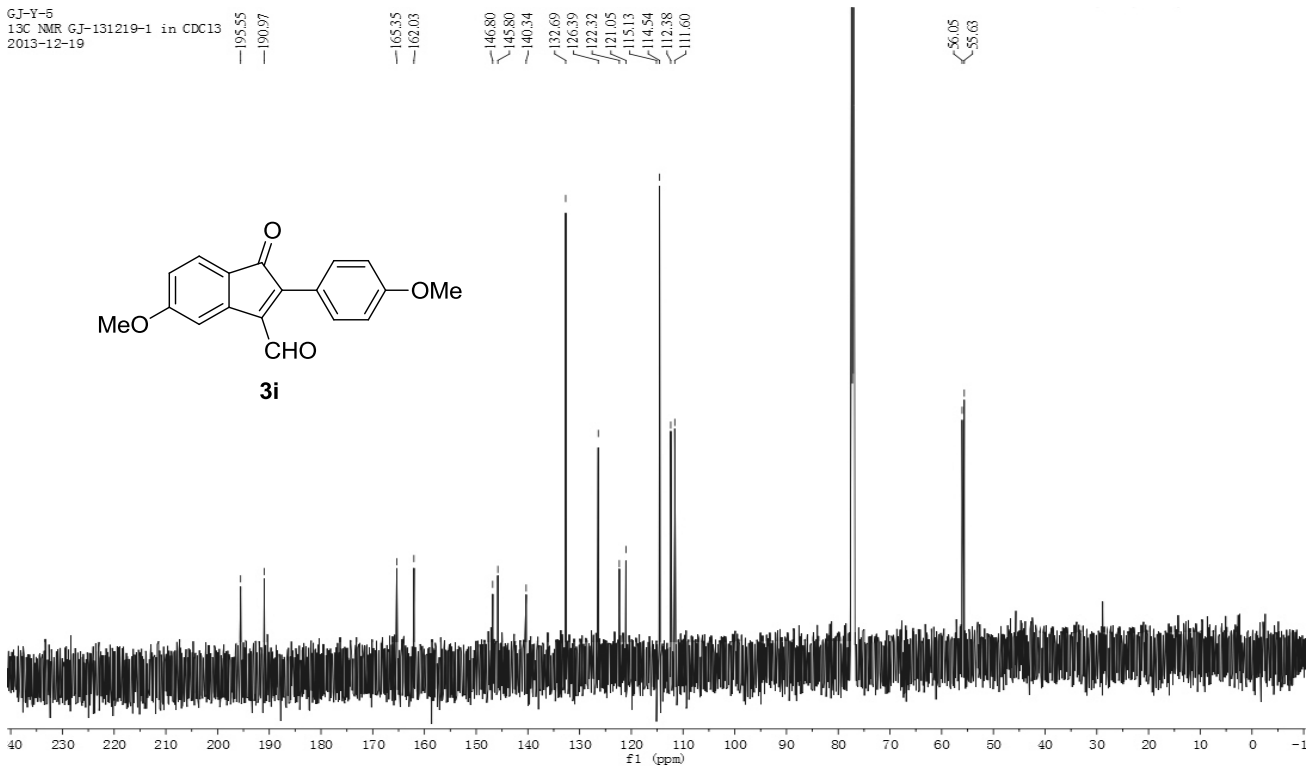
^{1}H NMR Spectrum of Compound **3f** ($CDCl_3$, 600 MHz)



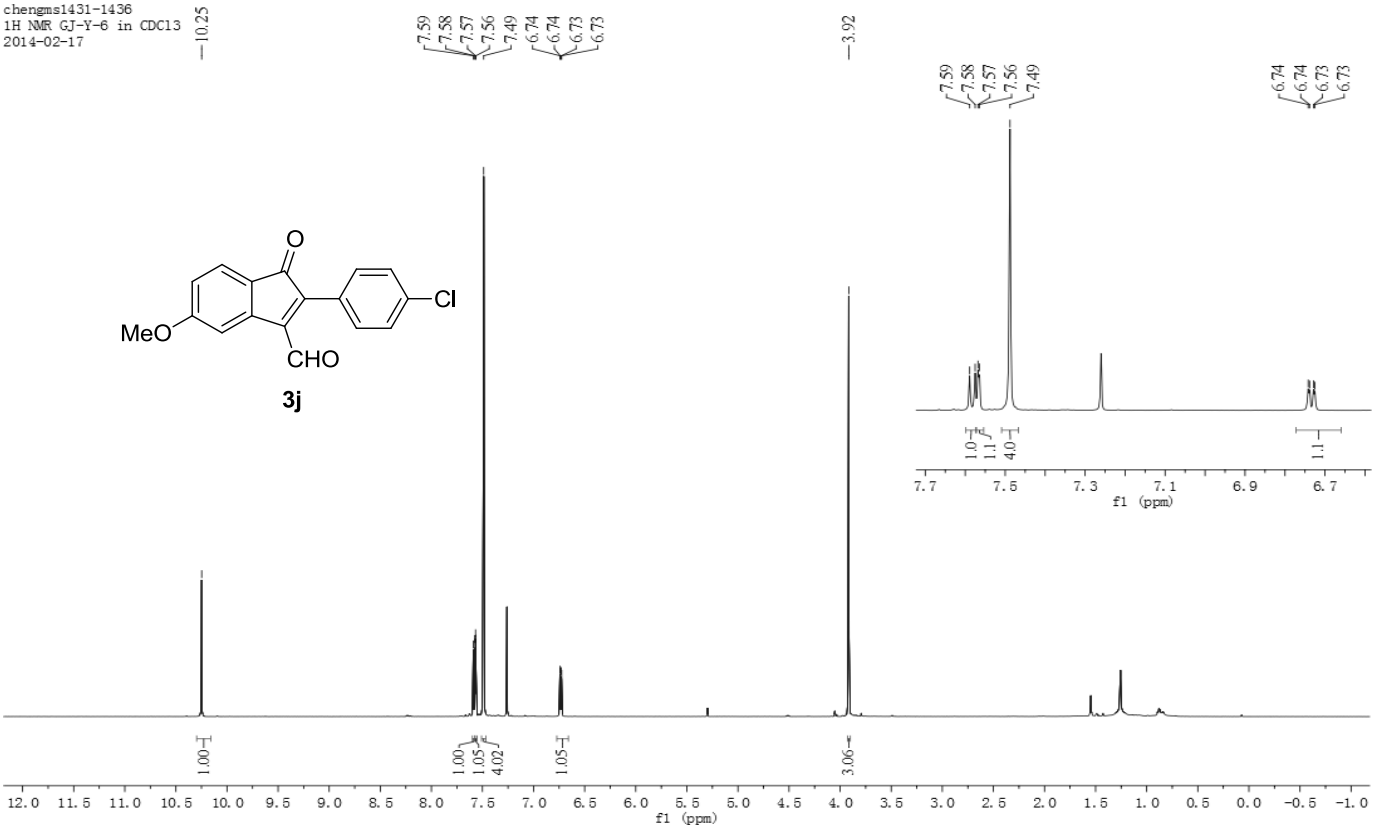
^{13}C NMR Spectrum of Compound **3f** ($CDCl_3$, 150 MHz)



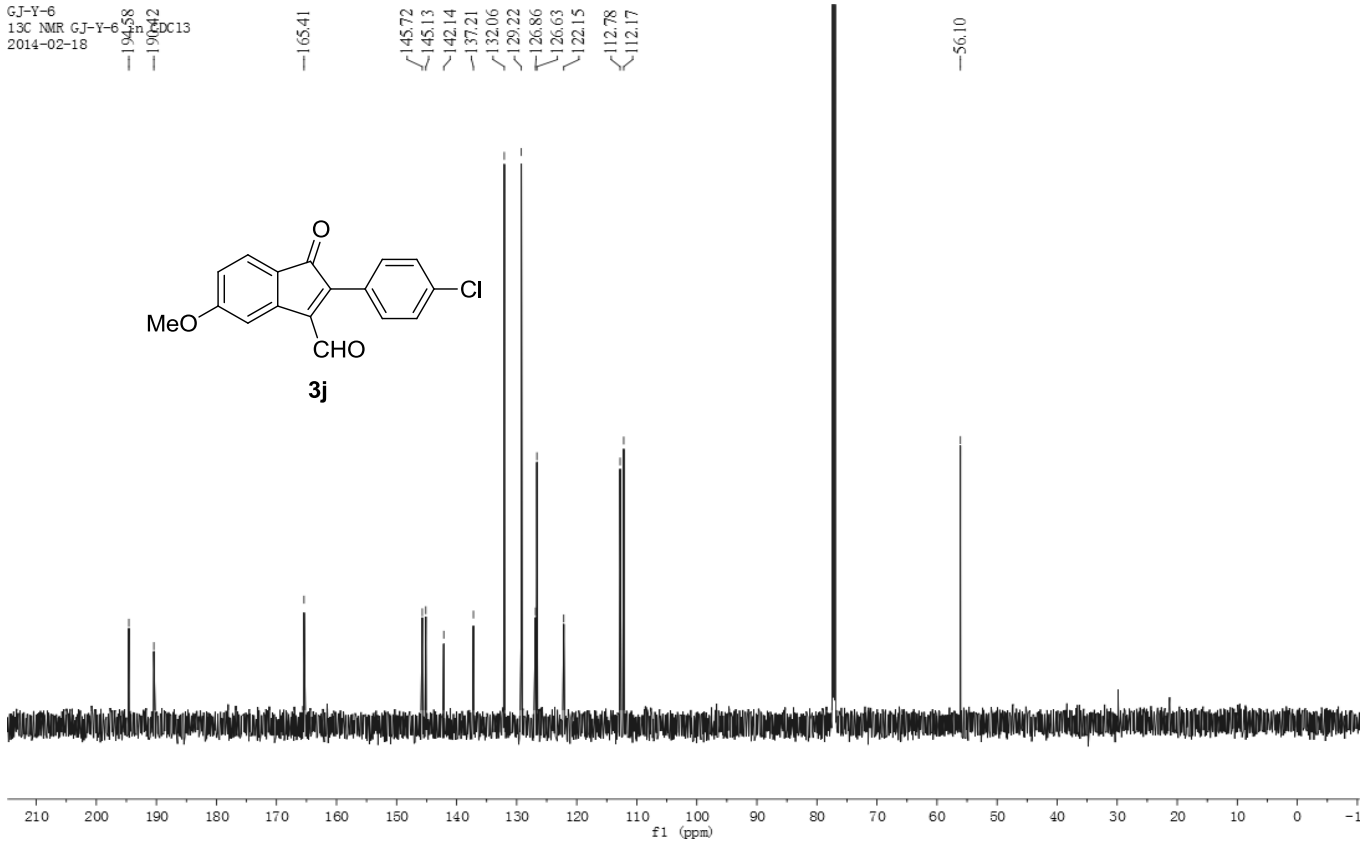
^{1}H NMR Spectrum of Compound **3i** ($CDCl_3$, 600 MHz)



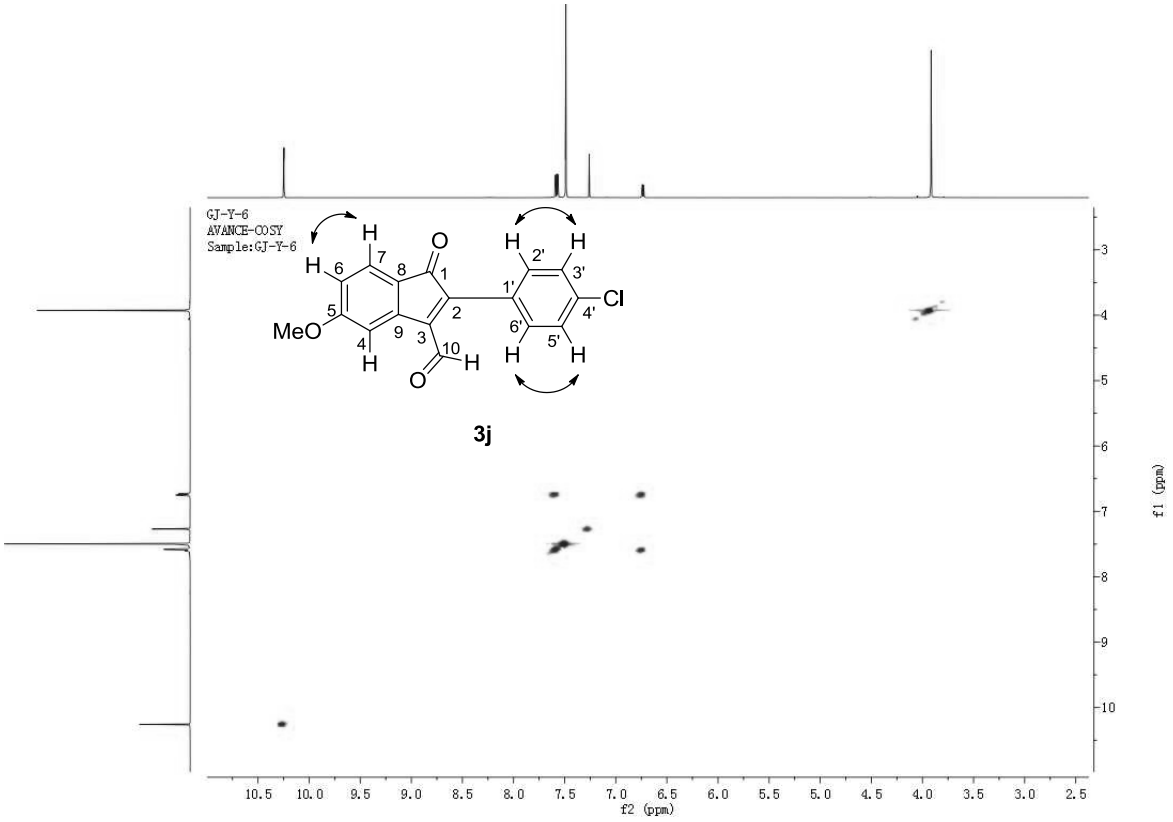
^{13}C NMR Spectrum of Compound **3i** ($CDCl_3$, 150 MHz)



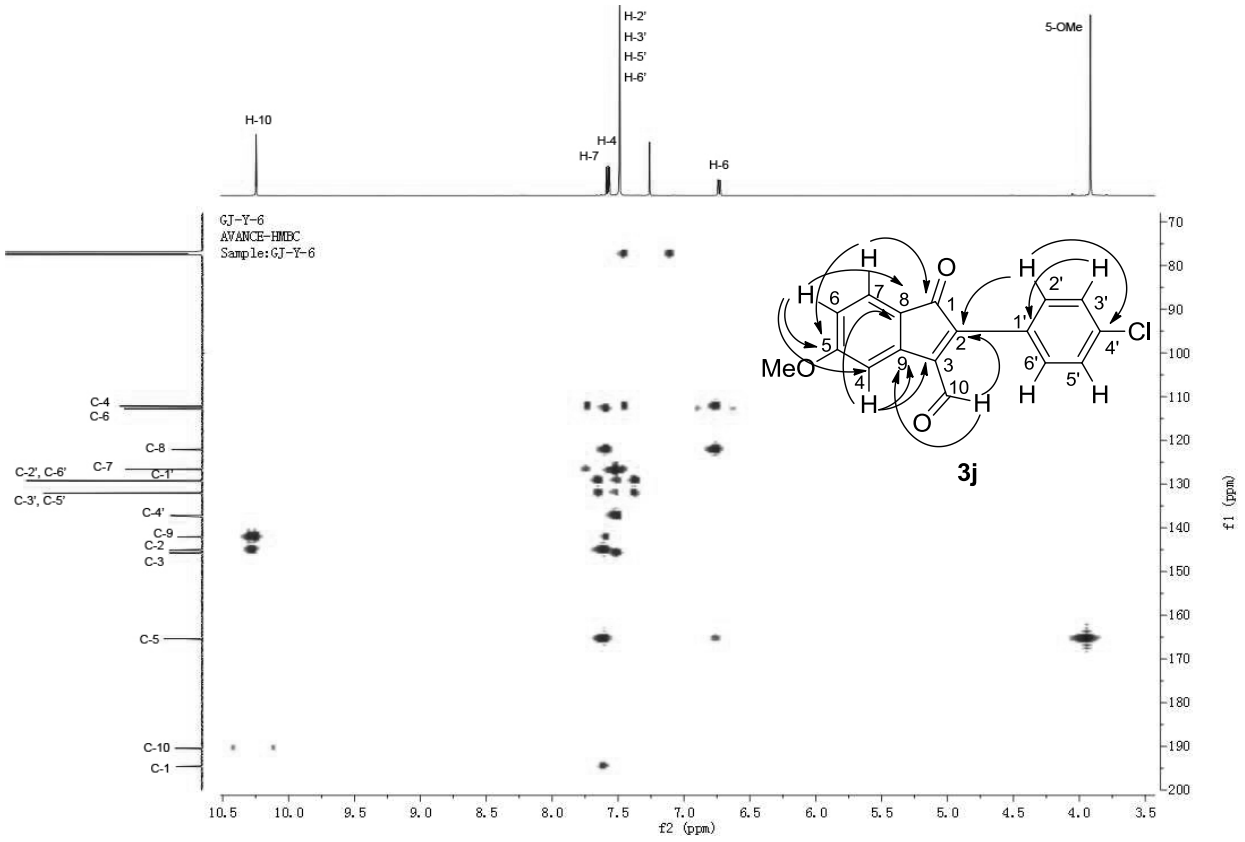
^{1}H NMR Spectrum of Compound **3j** ($CDCl_3$, 600 MHz)



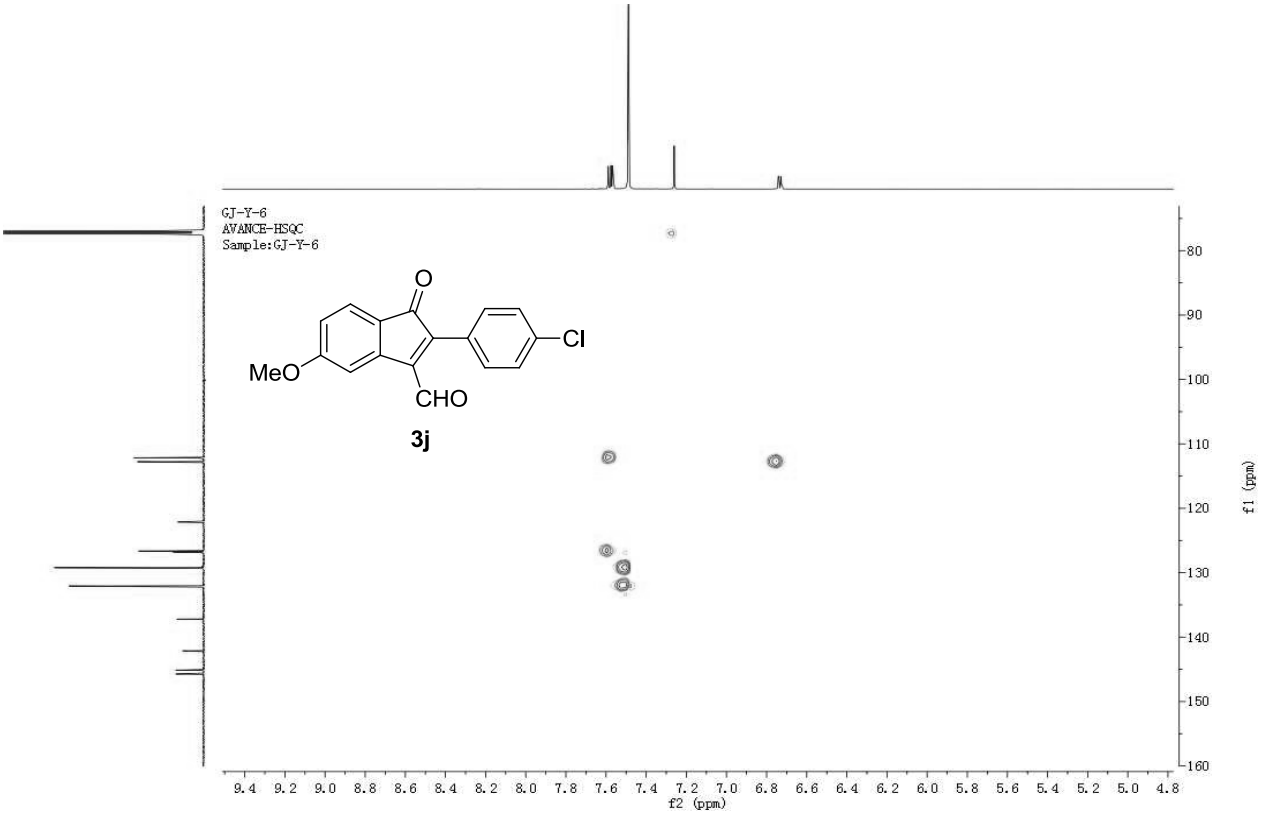
^{13}C NMR Spectrum of Compound **3j** ($CDCl_3$, 150 MHz)



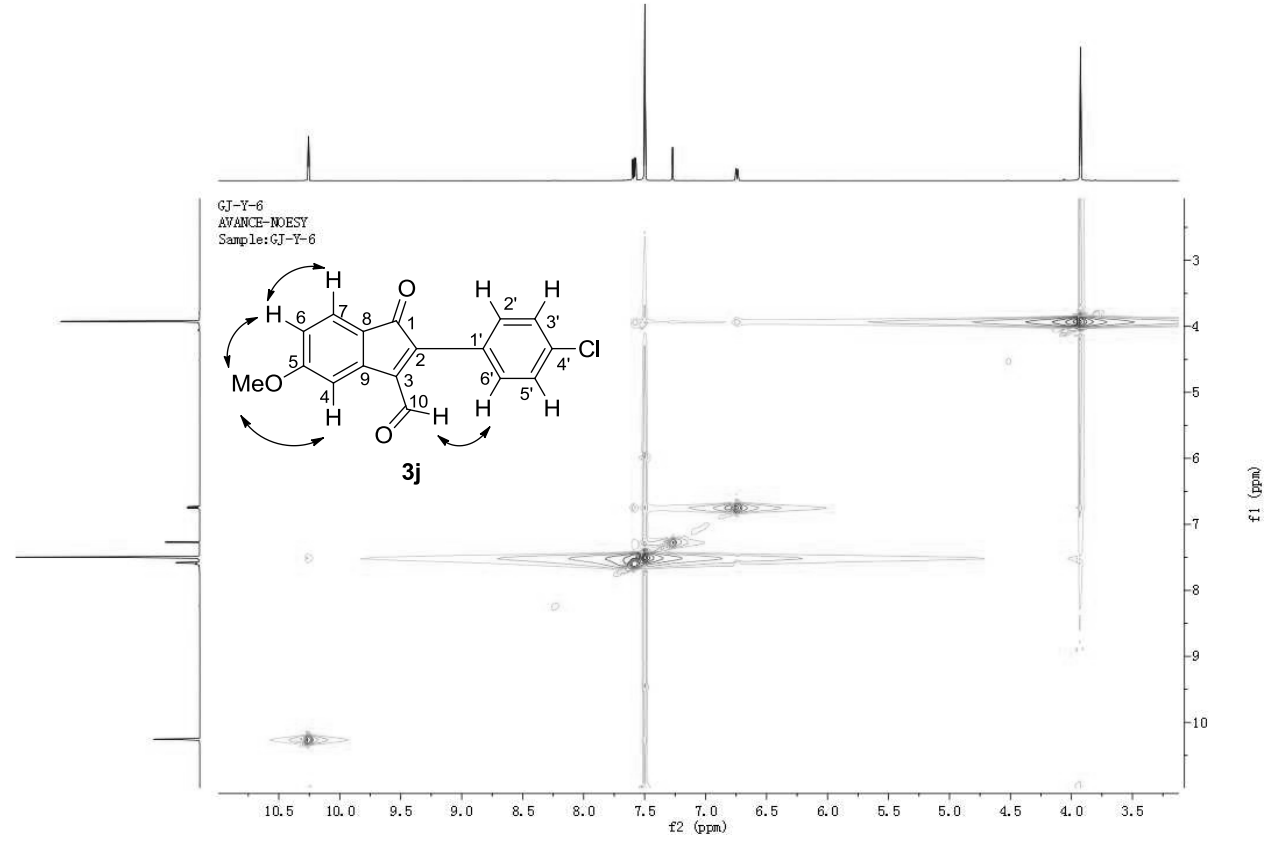
HSQC Spectrum of Compound **3j** ($CDCl_3$, 600 MHz)



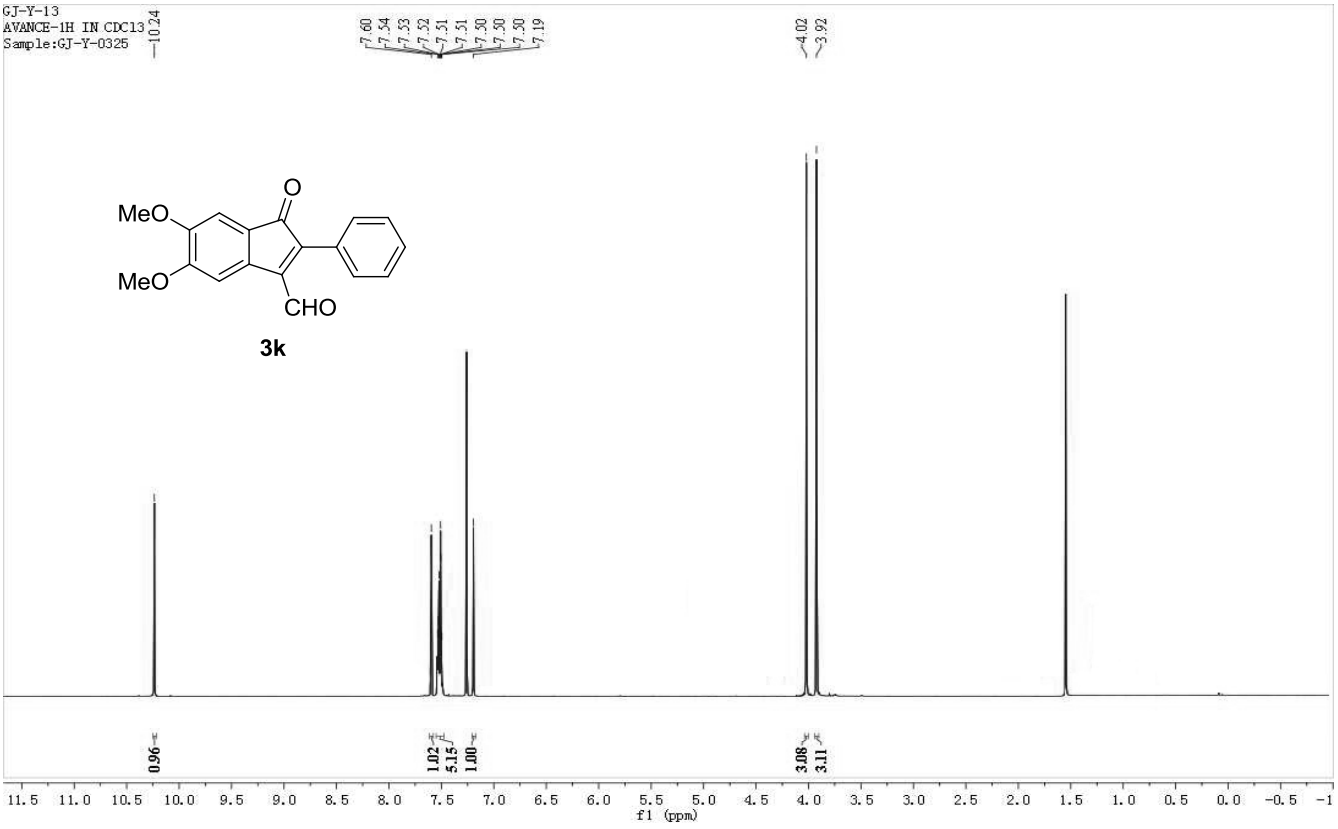
HMBC Spectrum of Compound **3j** ($CDCl_3$, 600 MHz)



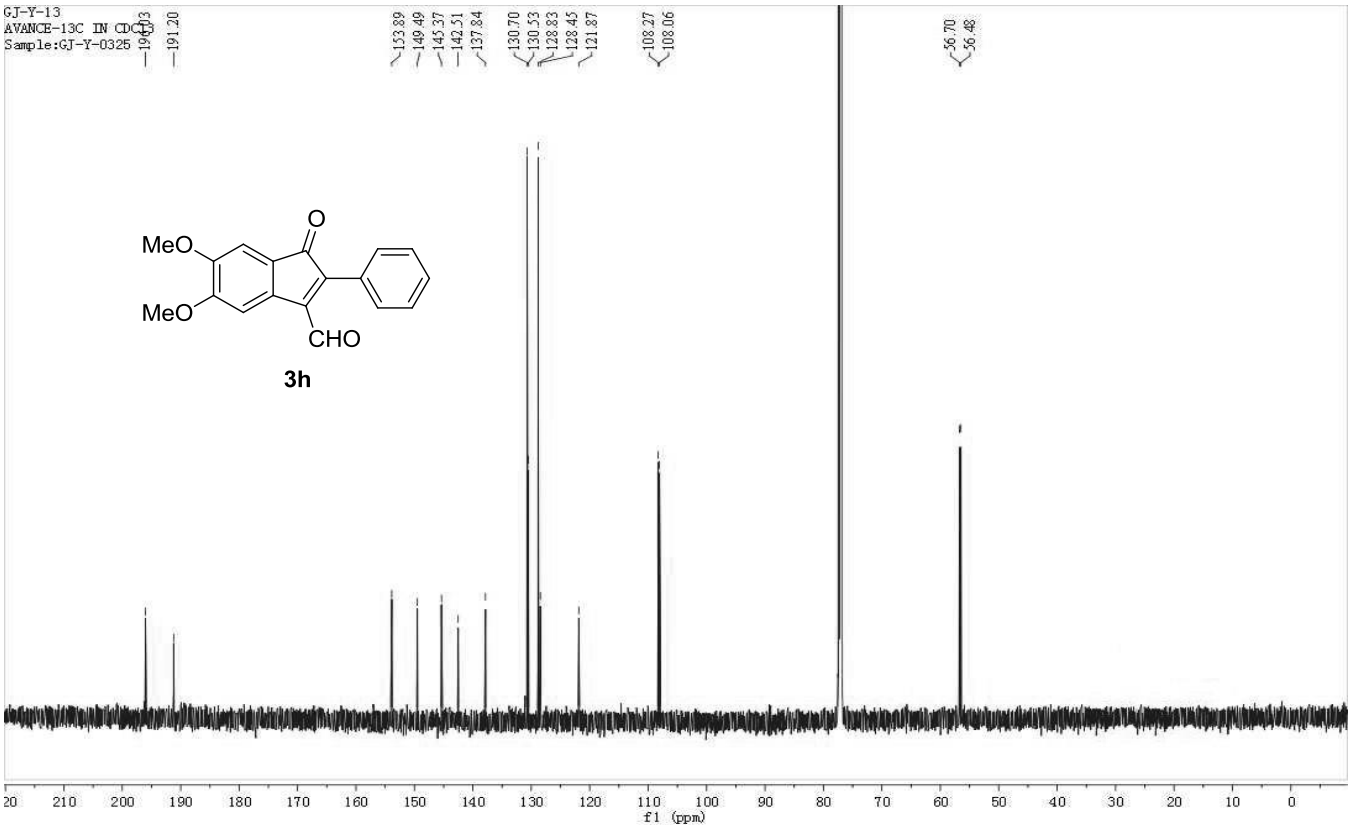
HSQC Spectrum of Compound **3j** ($CDCl_3$, 600 MHz)



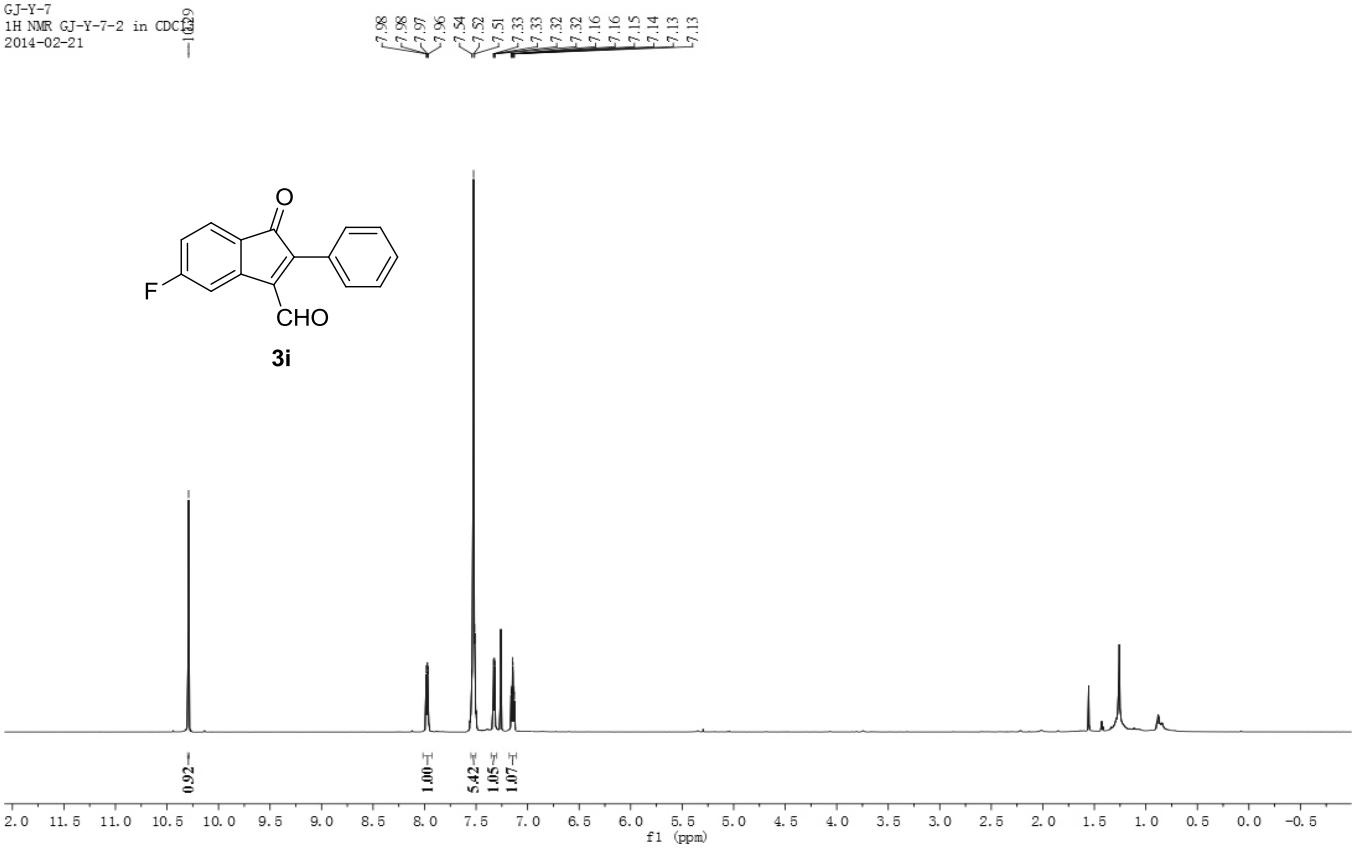
NOESY Spectrum of Compound **3j** ($CDCl_3$, 600 MHz)



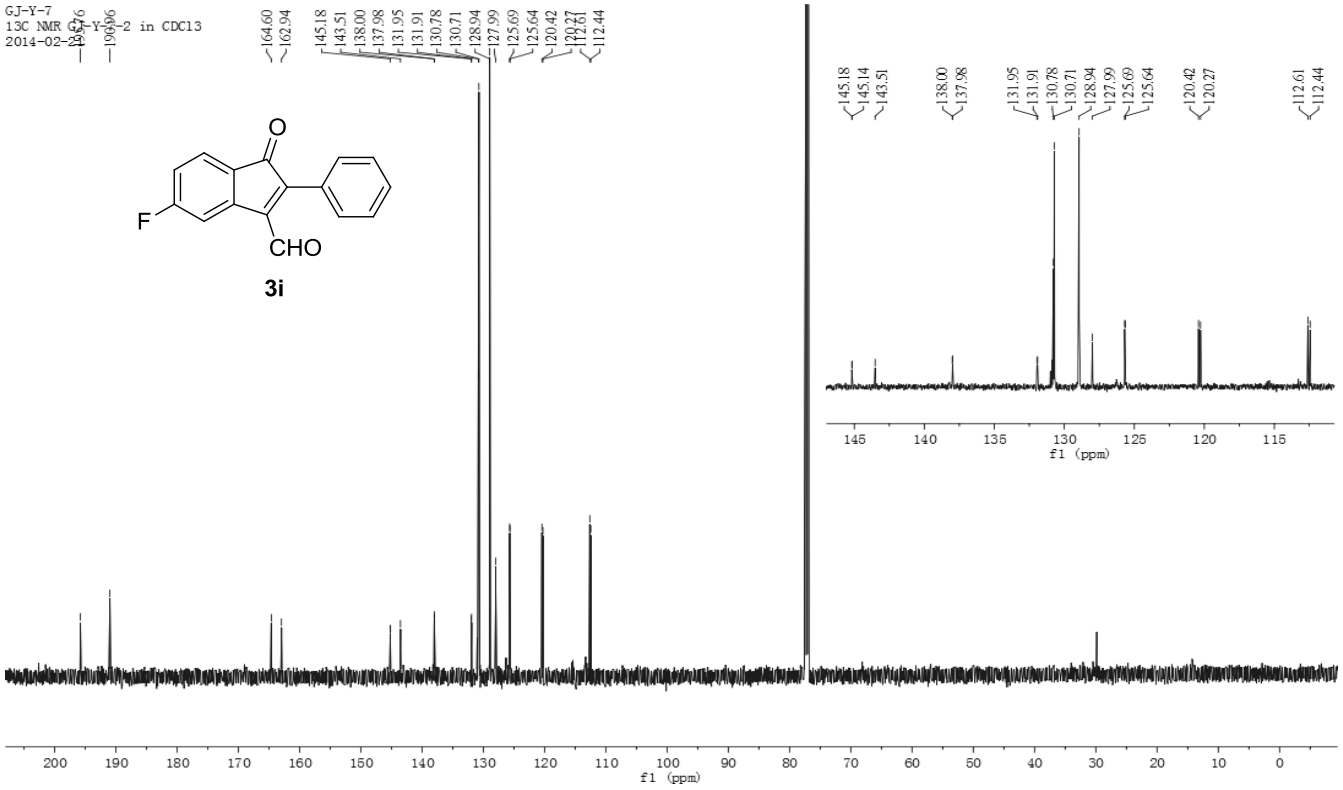
^{1}H NMR Spectrum of Compound **3k** ($CDCl_3$, 600 MHz)



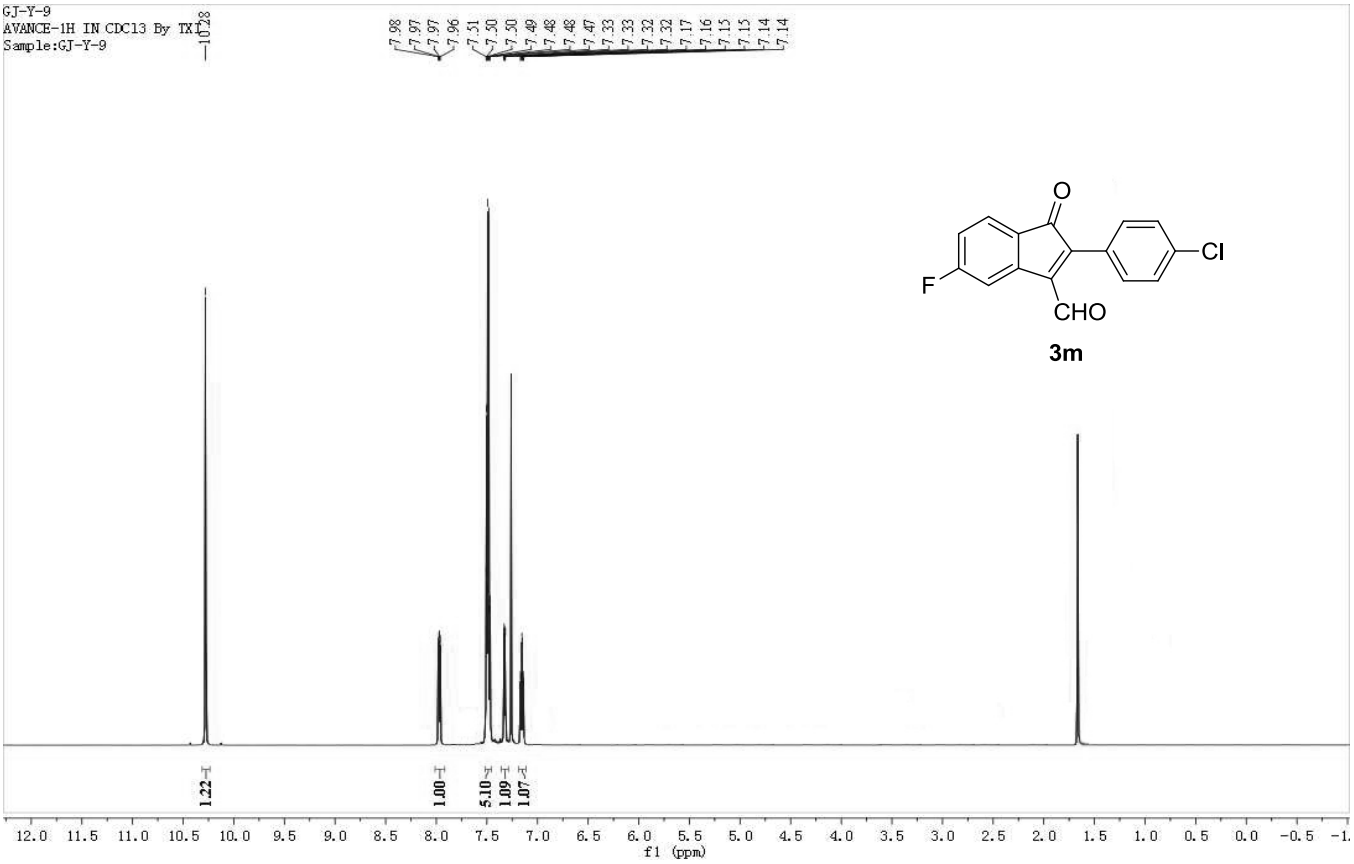
^{13}C NMR Spectrum of Compound **3h** ($CDCl_3$, 150 MHz)



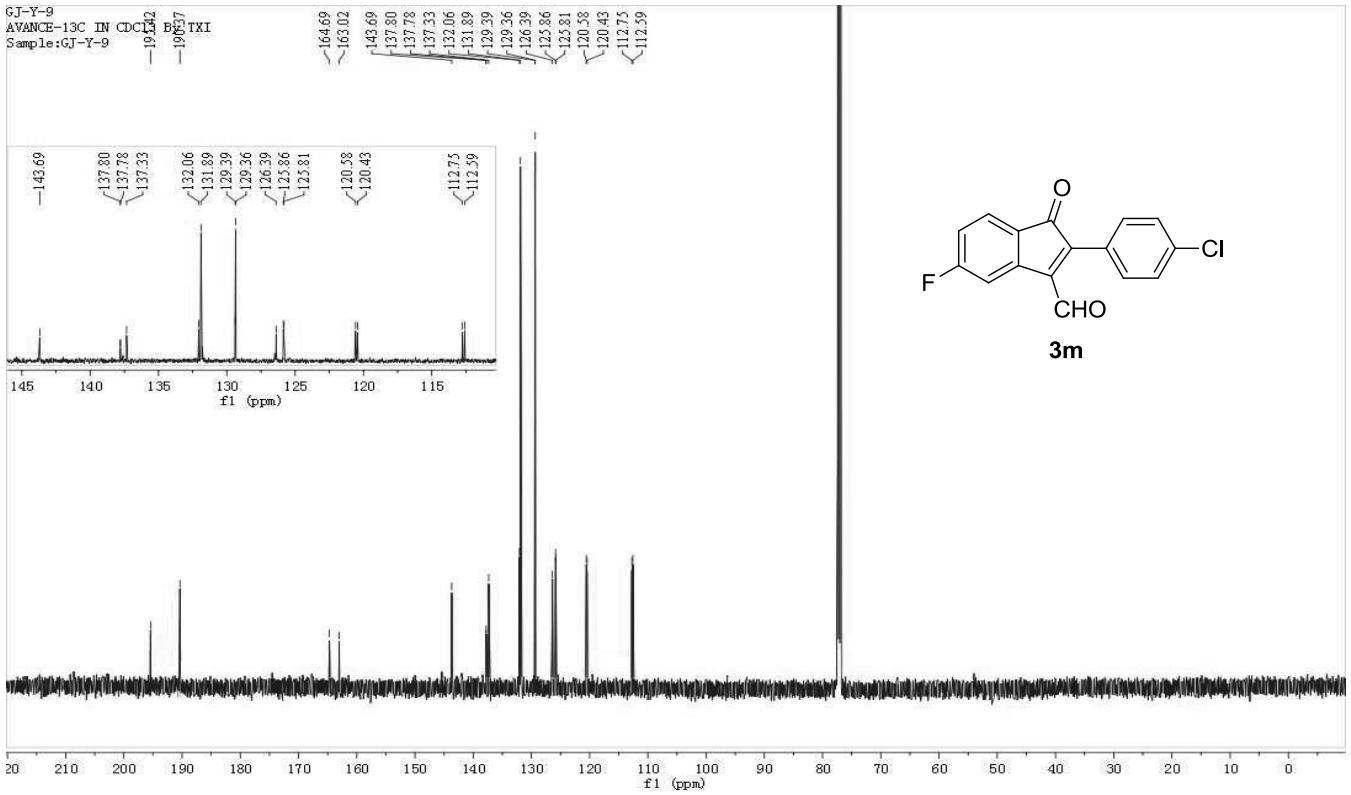
^{1}H NMR Spectrum of Compound **3i** ($CDCl_3$, 600 MHz)



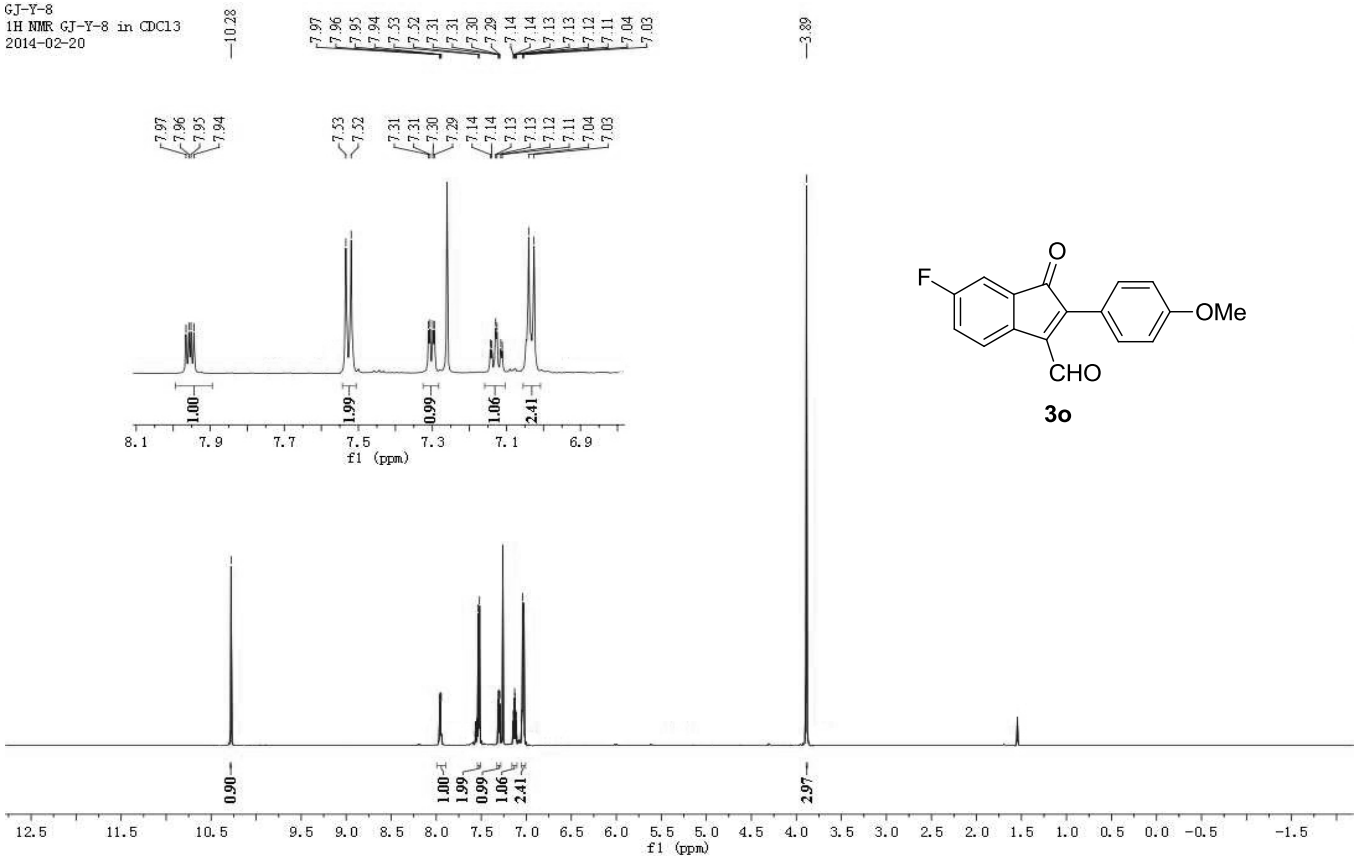
^{13}C NMR Spectrum of Compound **3i** ($CDCl_3$, 150 MHz)



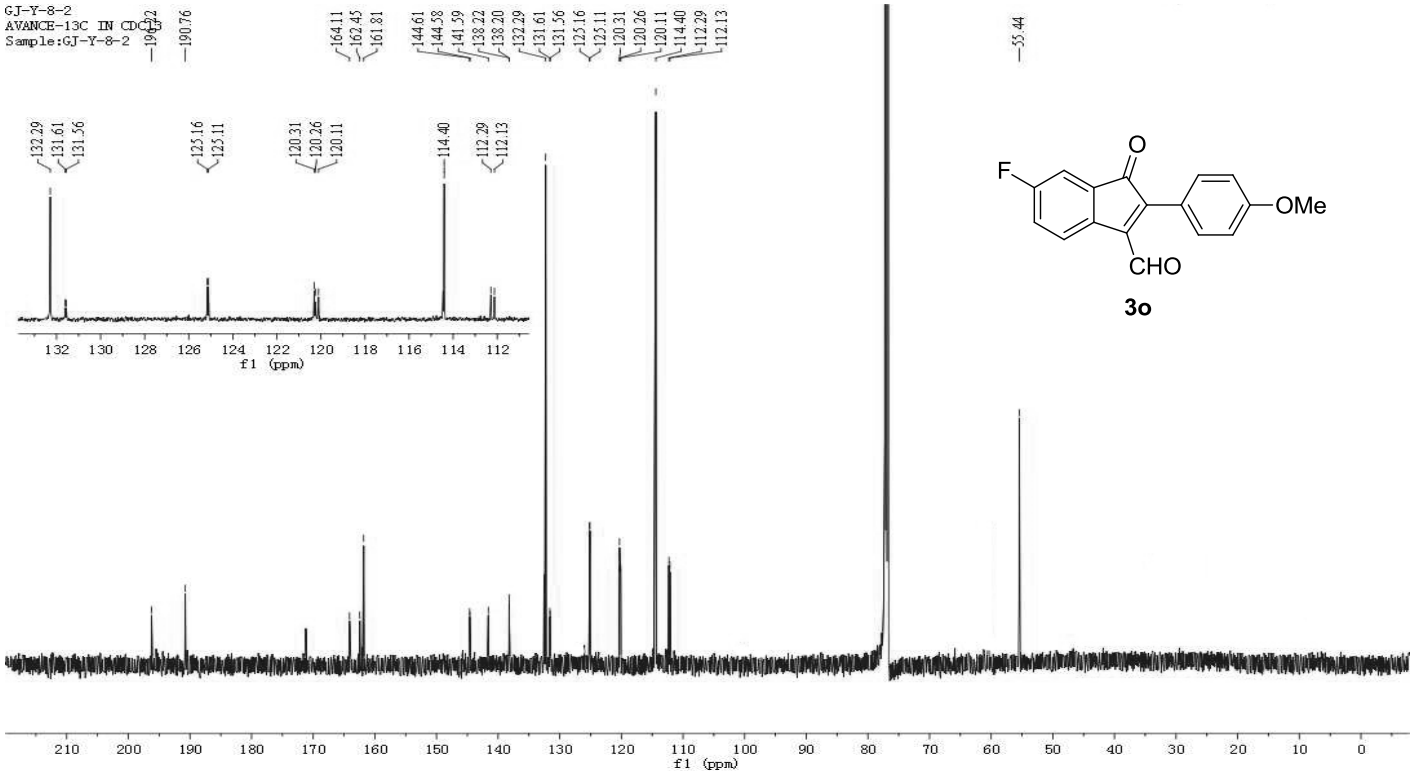
^{1}H NMR Spectrum of Compound **3m** ($CDCl_3$, 600 MHz)



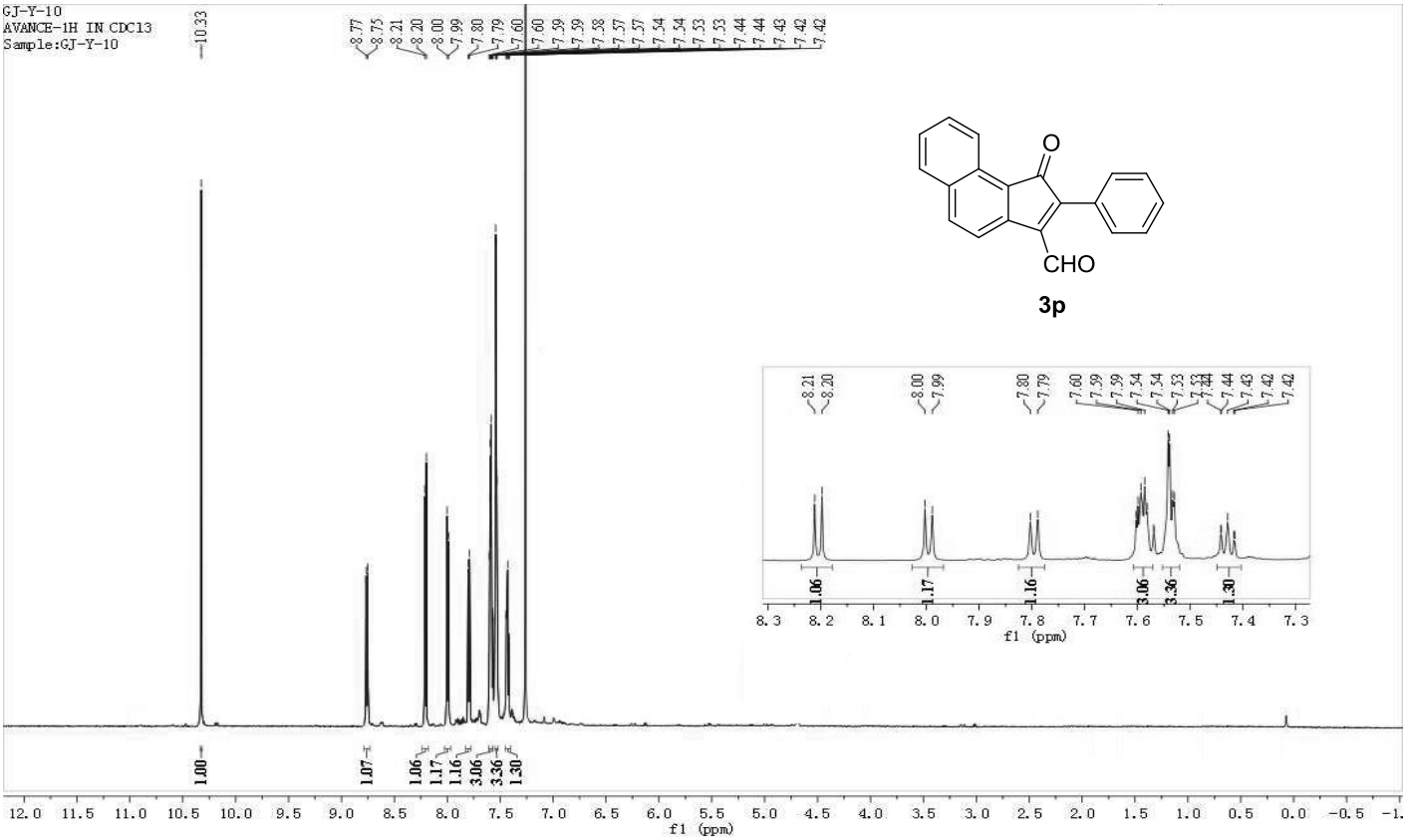
^{13}C NMR Spectrum of Compound **3m** ($CDCl_3$, 150 MHz)



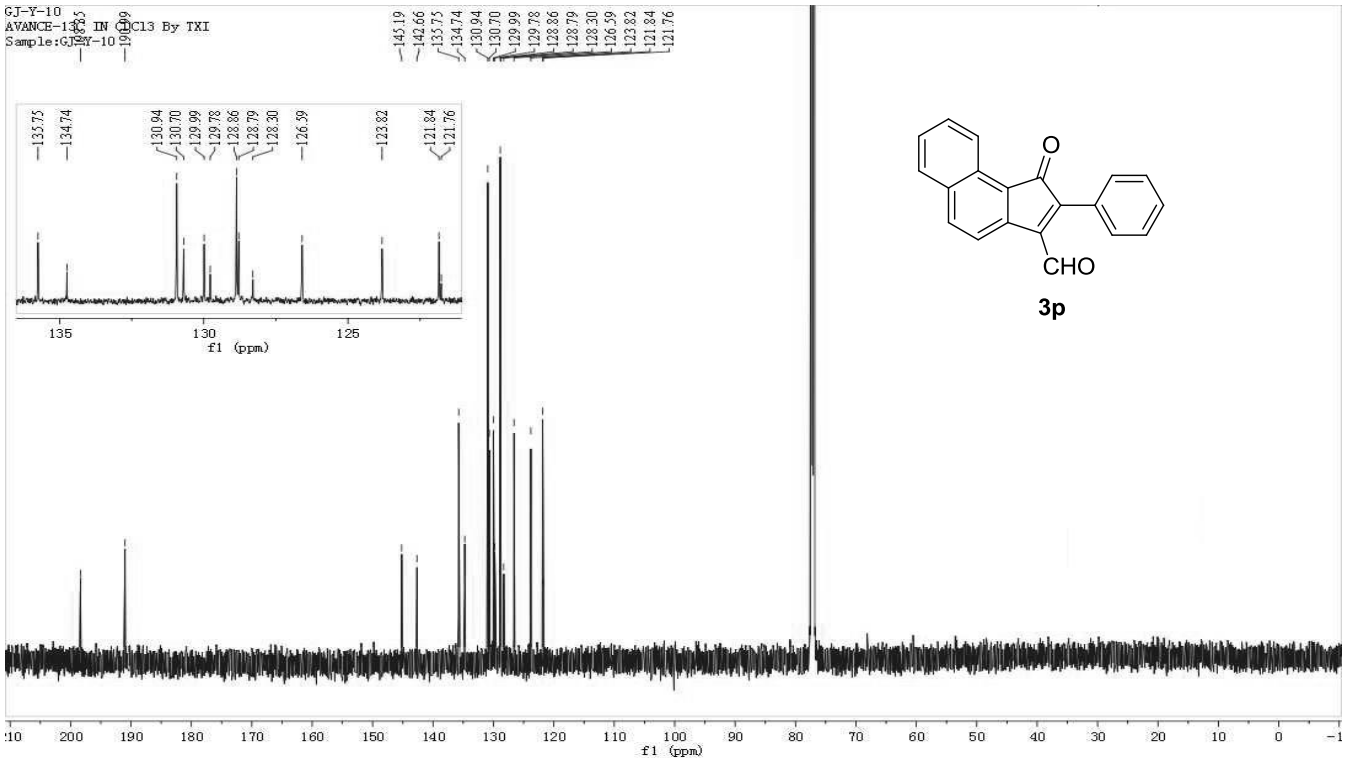
^{1}H NMR Spectrum of Compound **3o** ($CDCl_3$, 600 MHz)



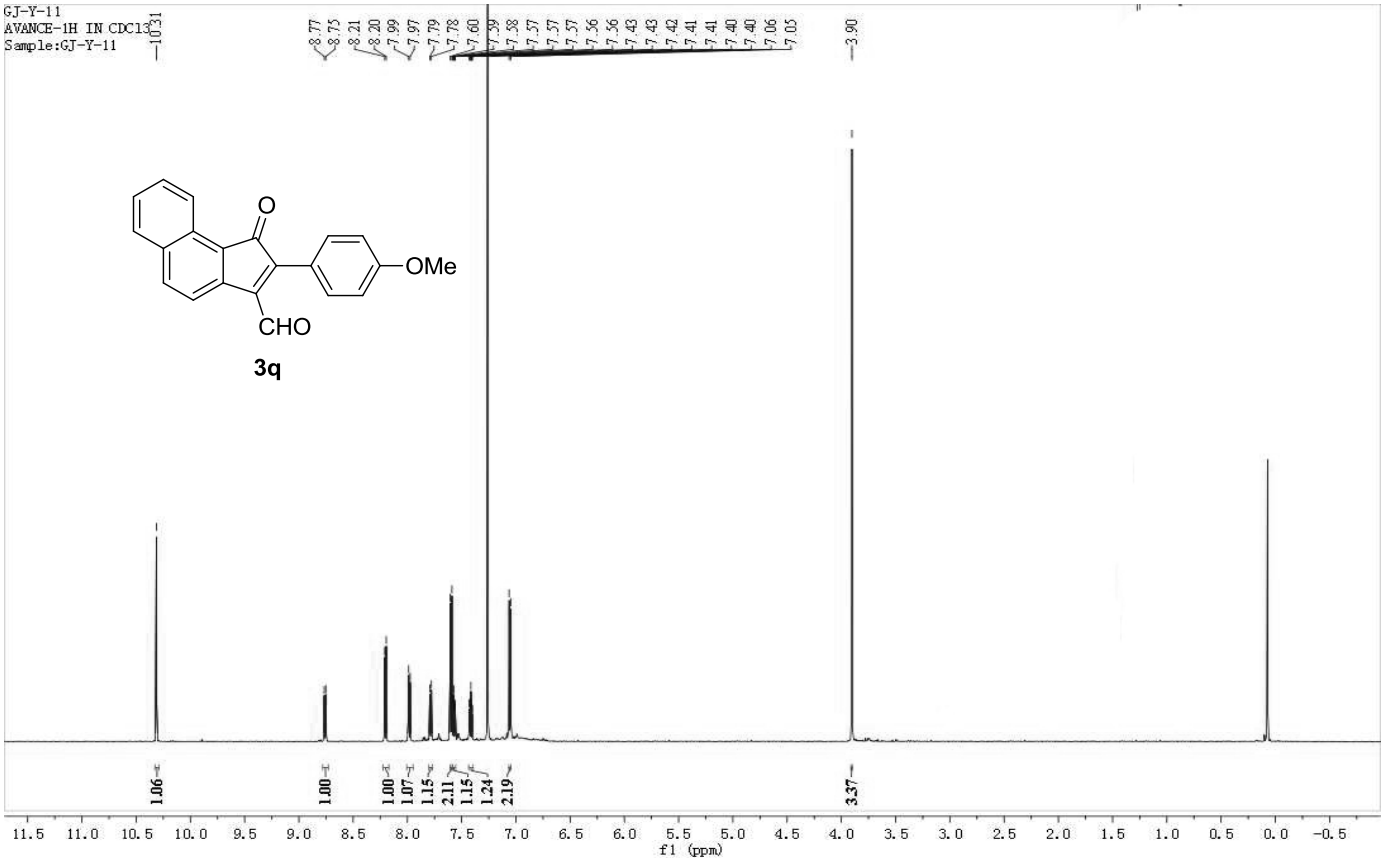
^{13}C NMR Spectrum of Compound **3o** ($CDCl_3$, 150 MHz)



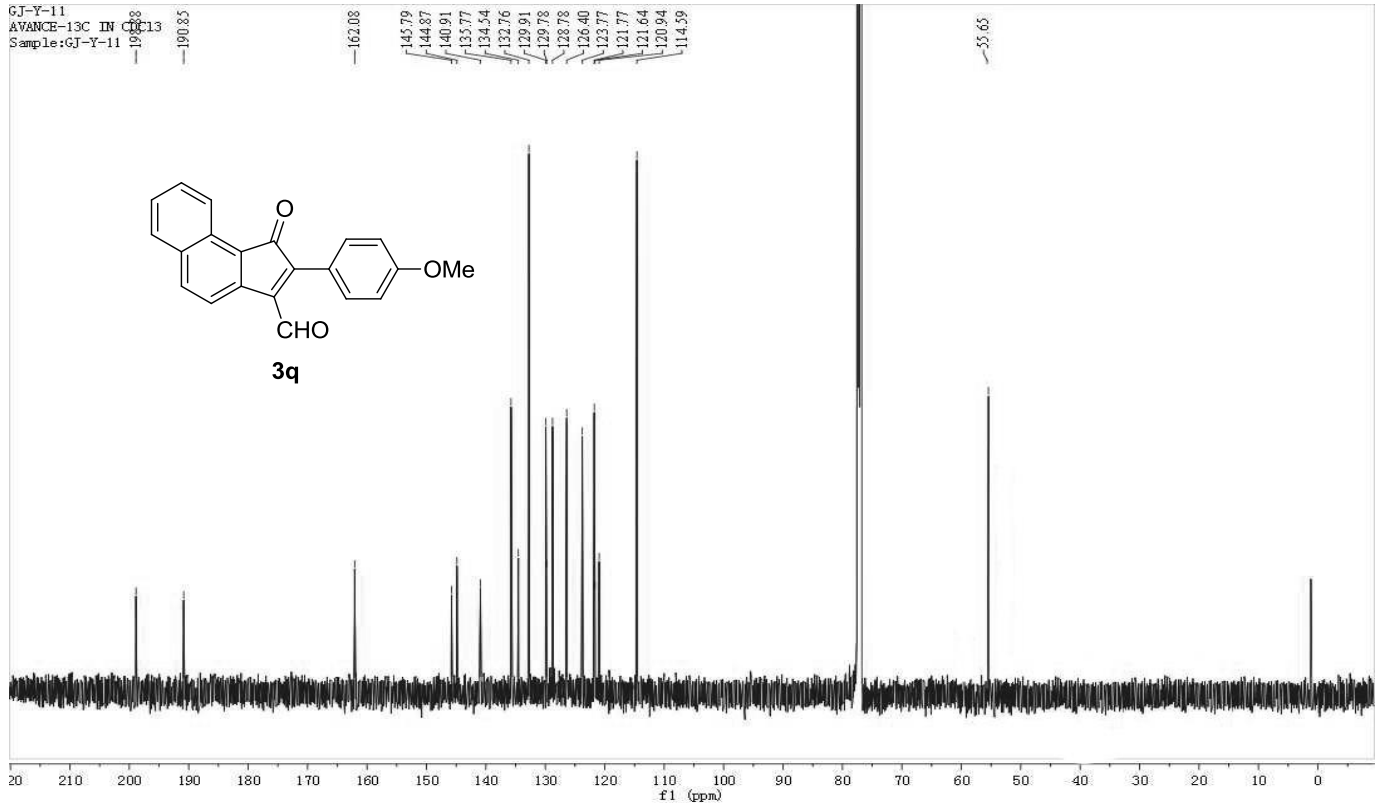
^{1}H NMR Spectrum of Compound **3p** ($CDCl_3$, 600 MHz)



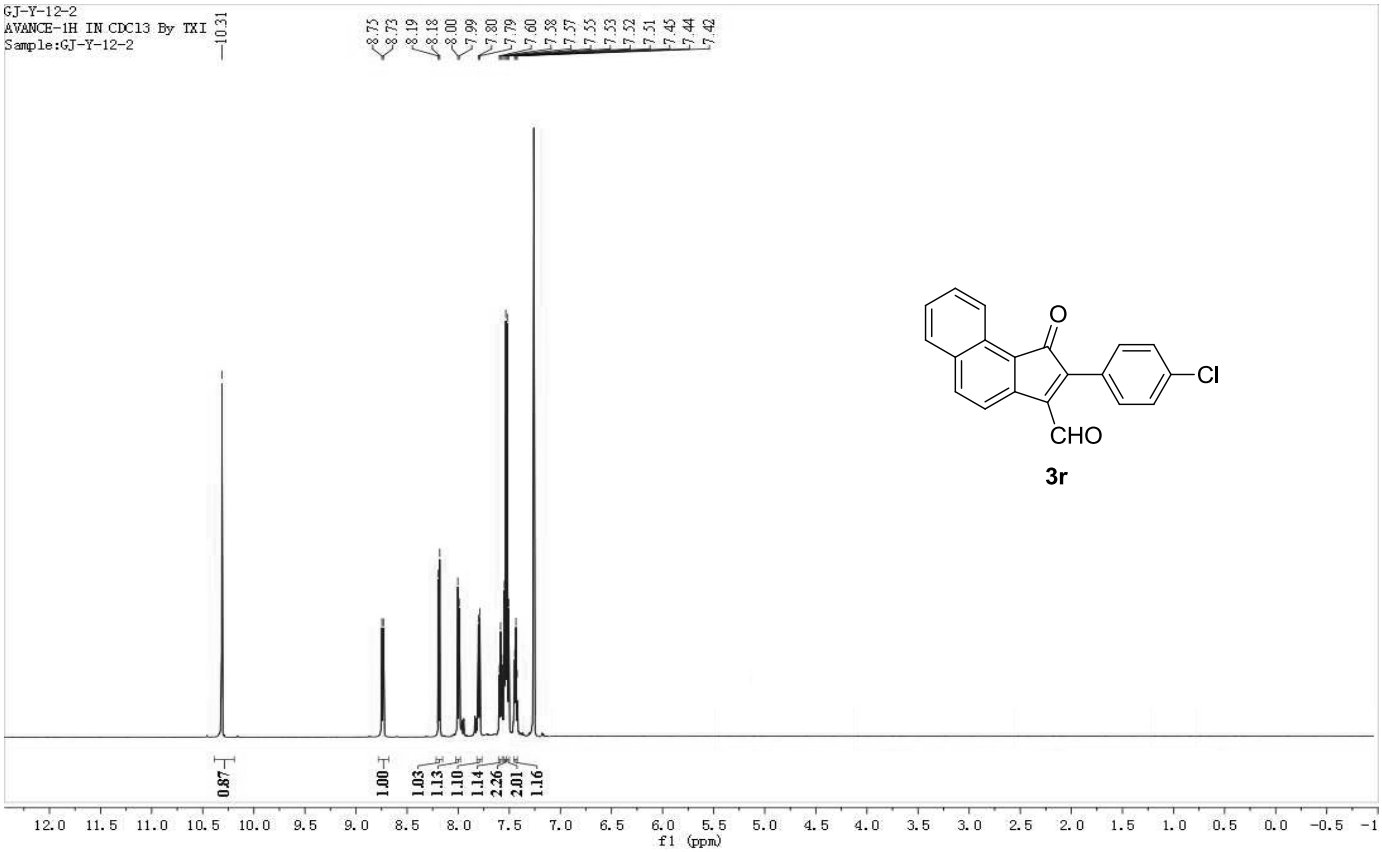
^{13}C NMR Spectrum of Compound **3p** ($CDCl_3$, 150 MHz)



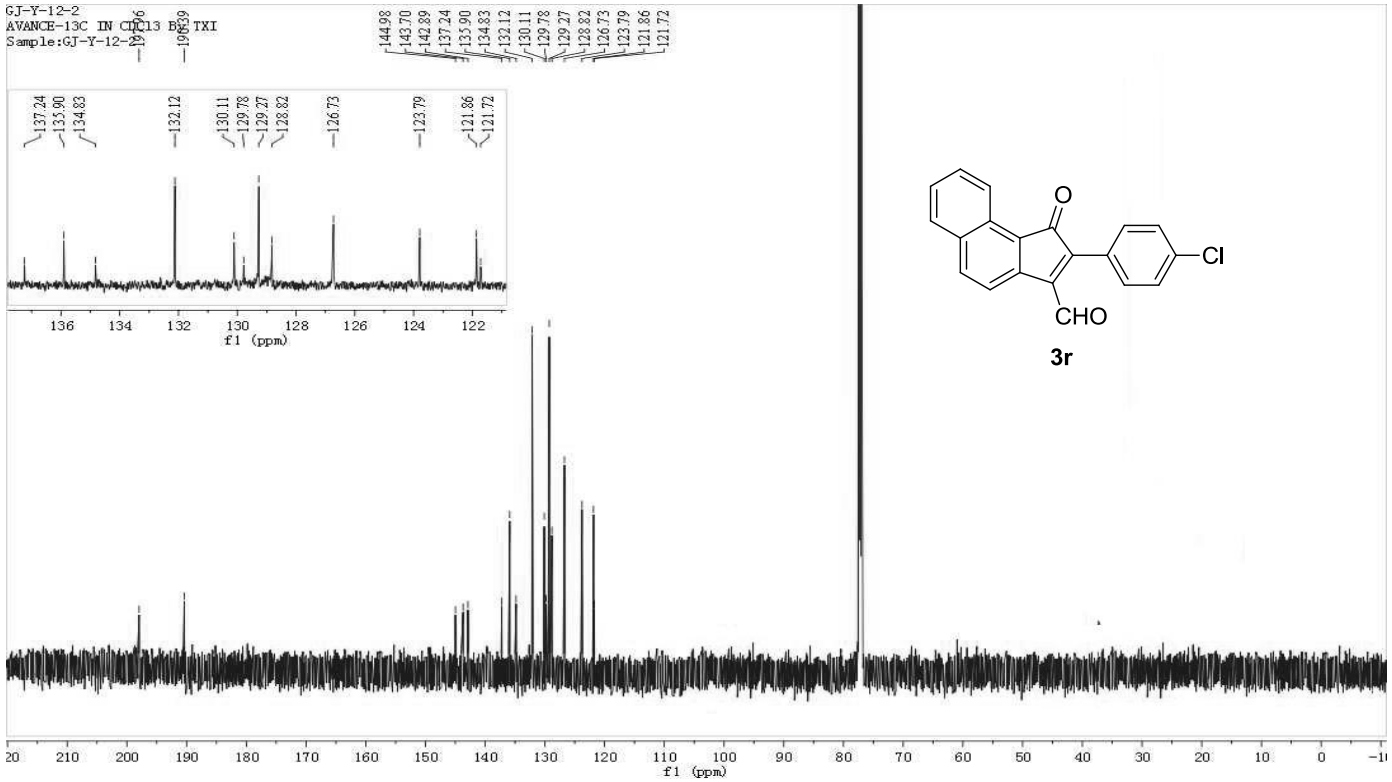
^{1}H NMR Spectrum of Compound **3q** ($CDCl_3$, 600 MHz)



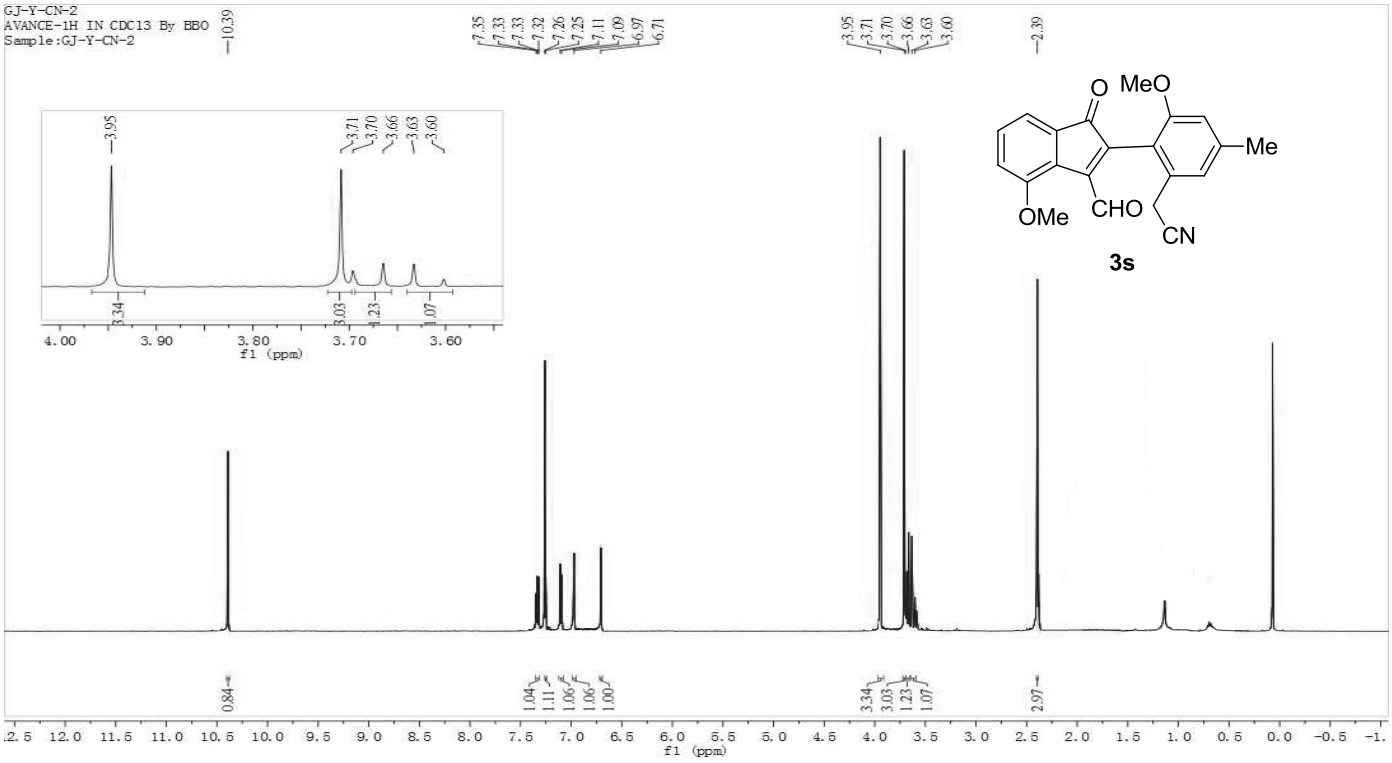
^{13}C NMR Spectrum of Compound **3q** ($CDCl_3$, 150 MHz)



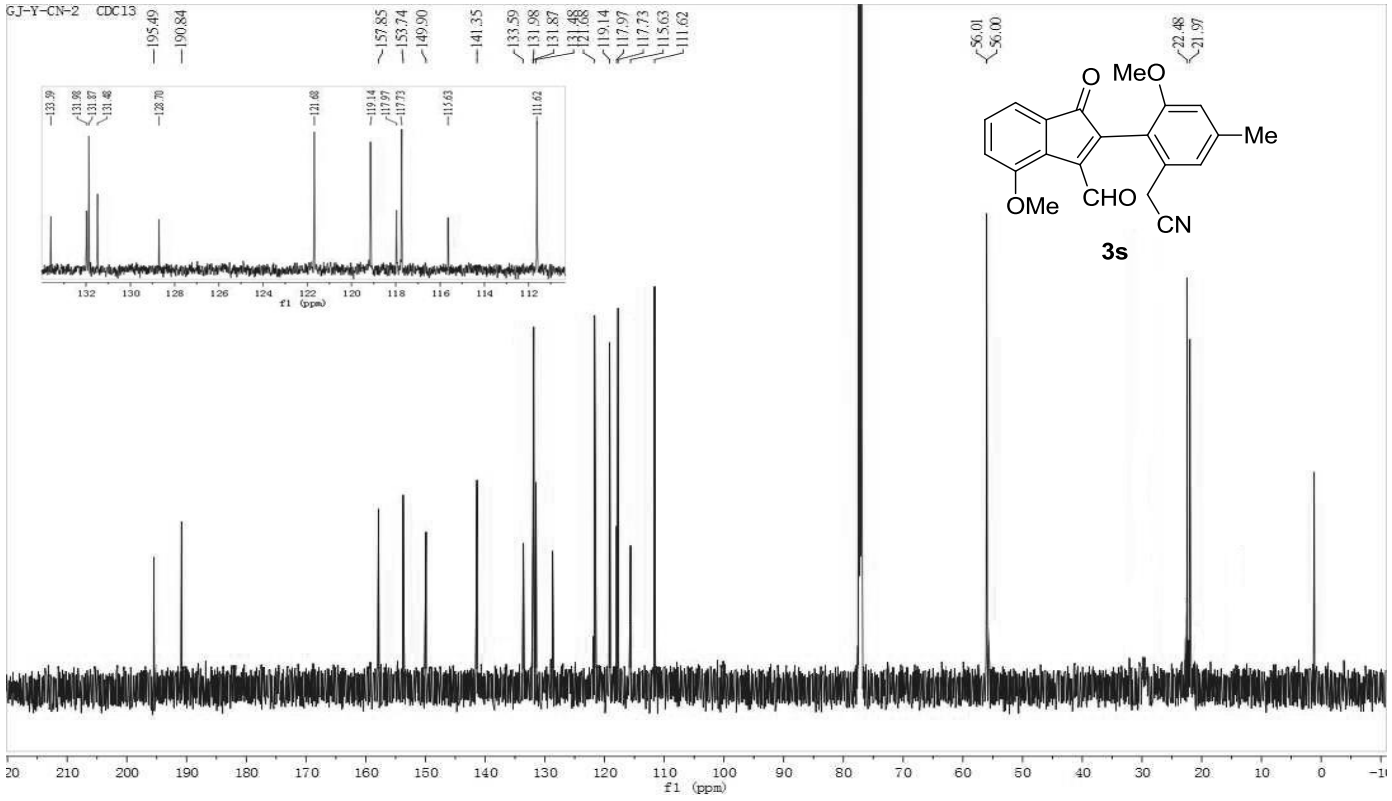
^{1}H NMR Spectrum of Compound **3o** ($CDCl_3$, 600 MHz)



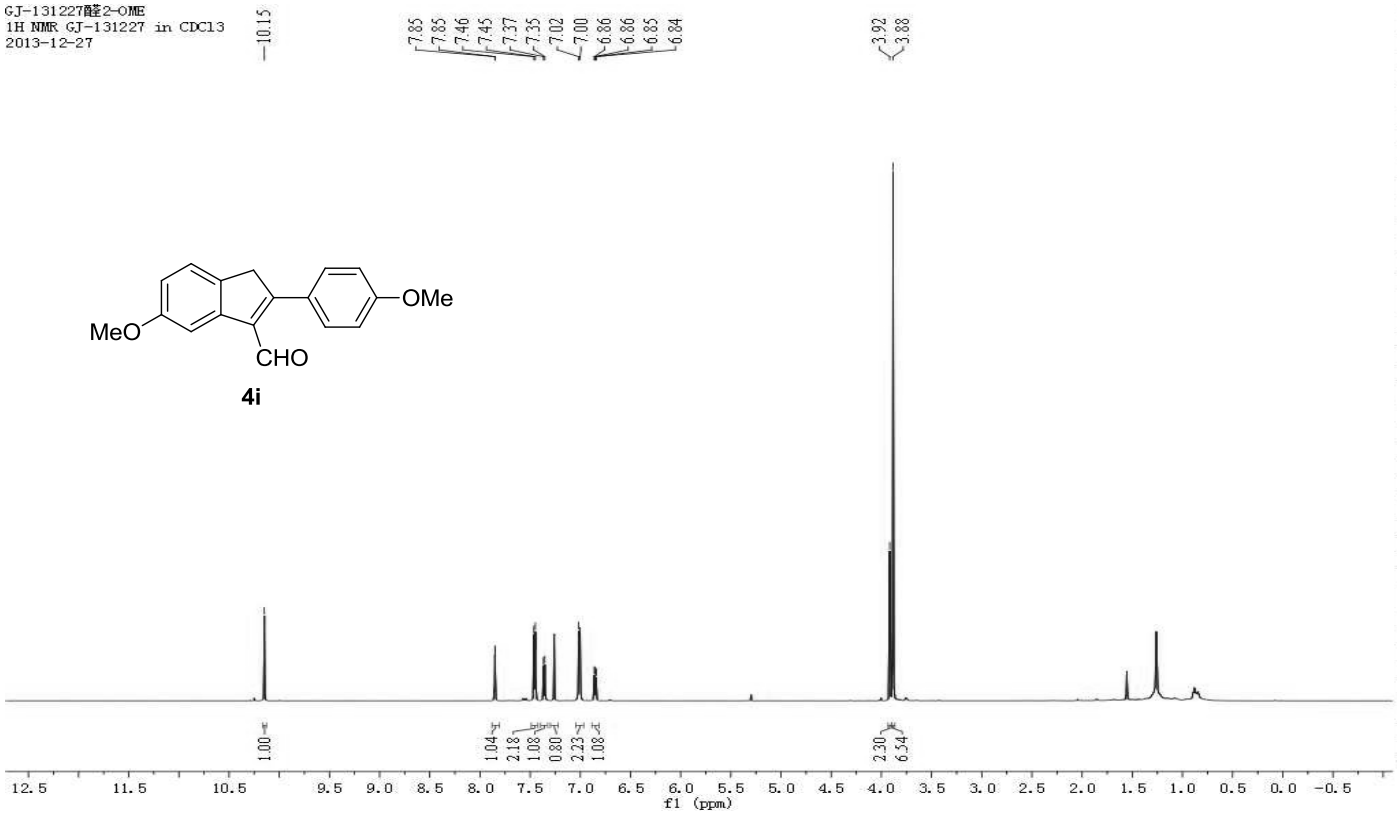
^{13}C NMR Spectrum of Compound **3o** ($CDCl_3$, 150 MHz)



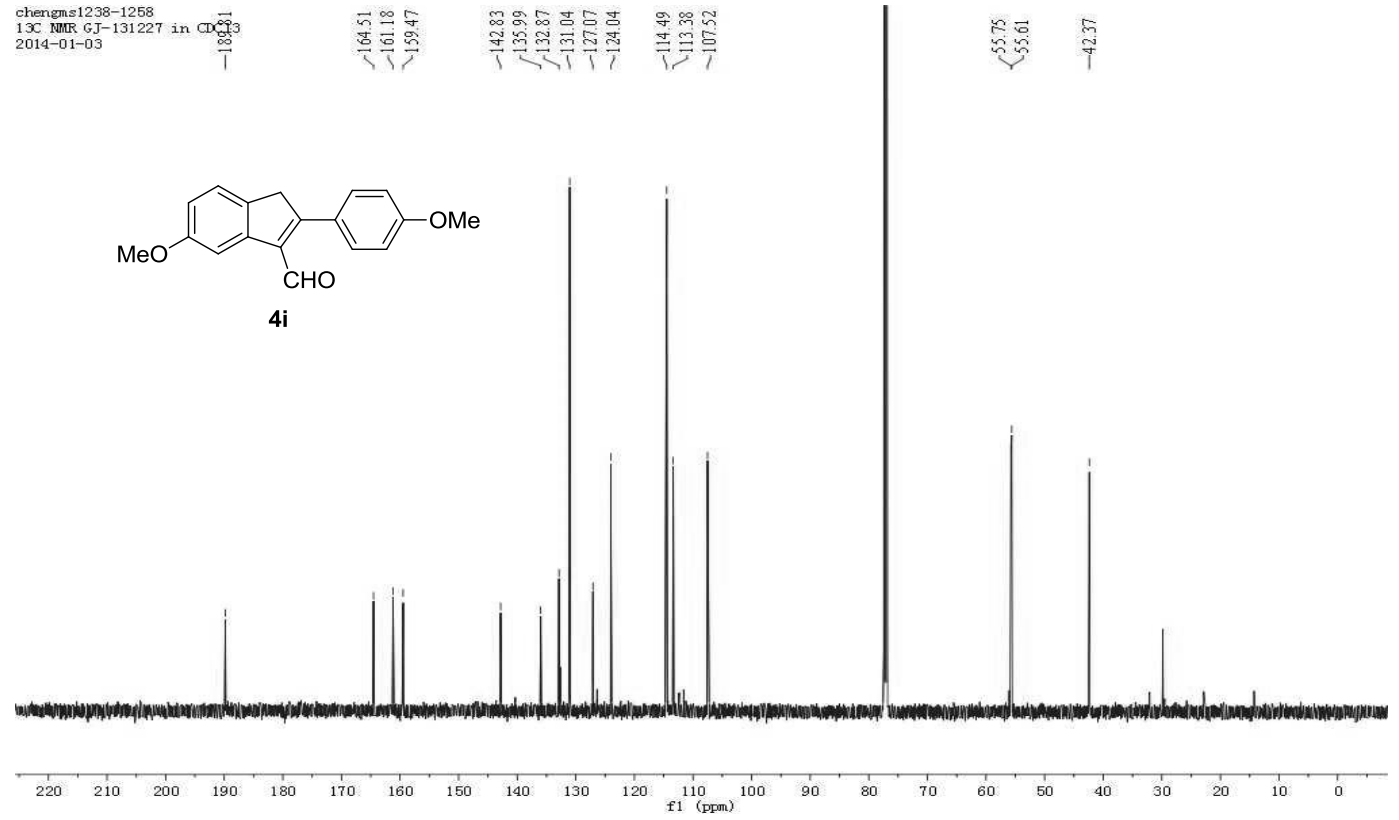
^{1}H NMR Spectrum of Compound **3p** ($CDCl_3$, 600 MHz)



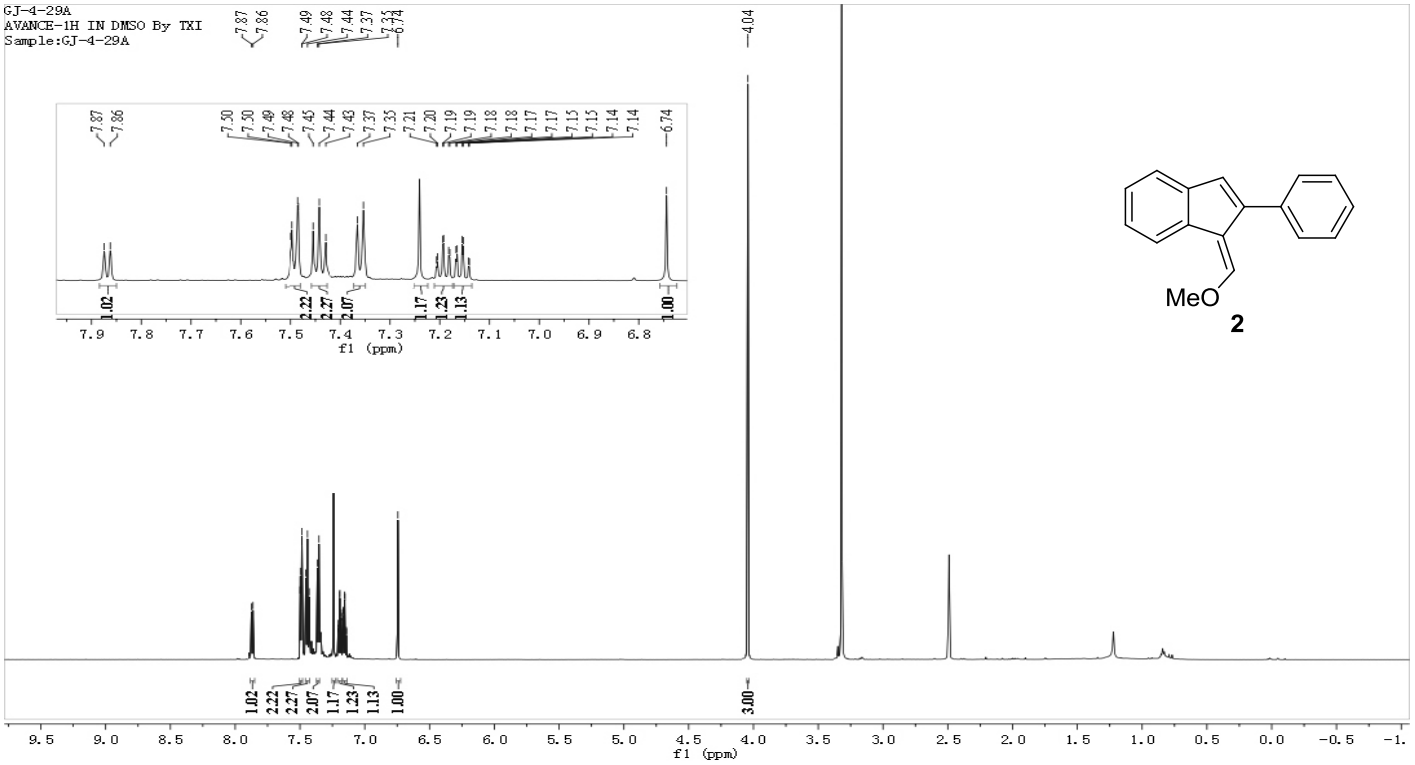
^{13}C NMR Spectrum of Compound **3p** ($CDCl_3$, 150 MHz)



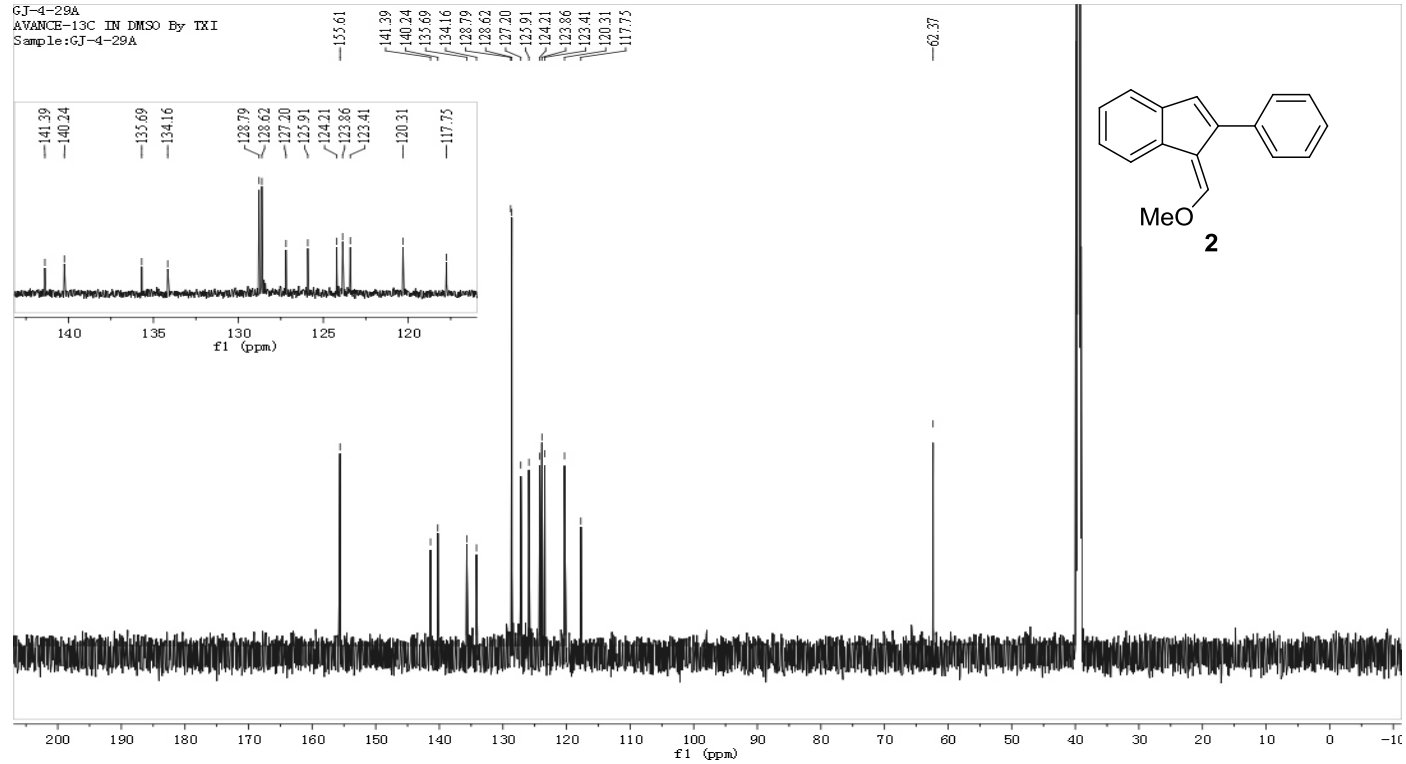
^{1}H NMR Spectrum of Compound **4i** ($CDCl_3$, 600 MHz)



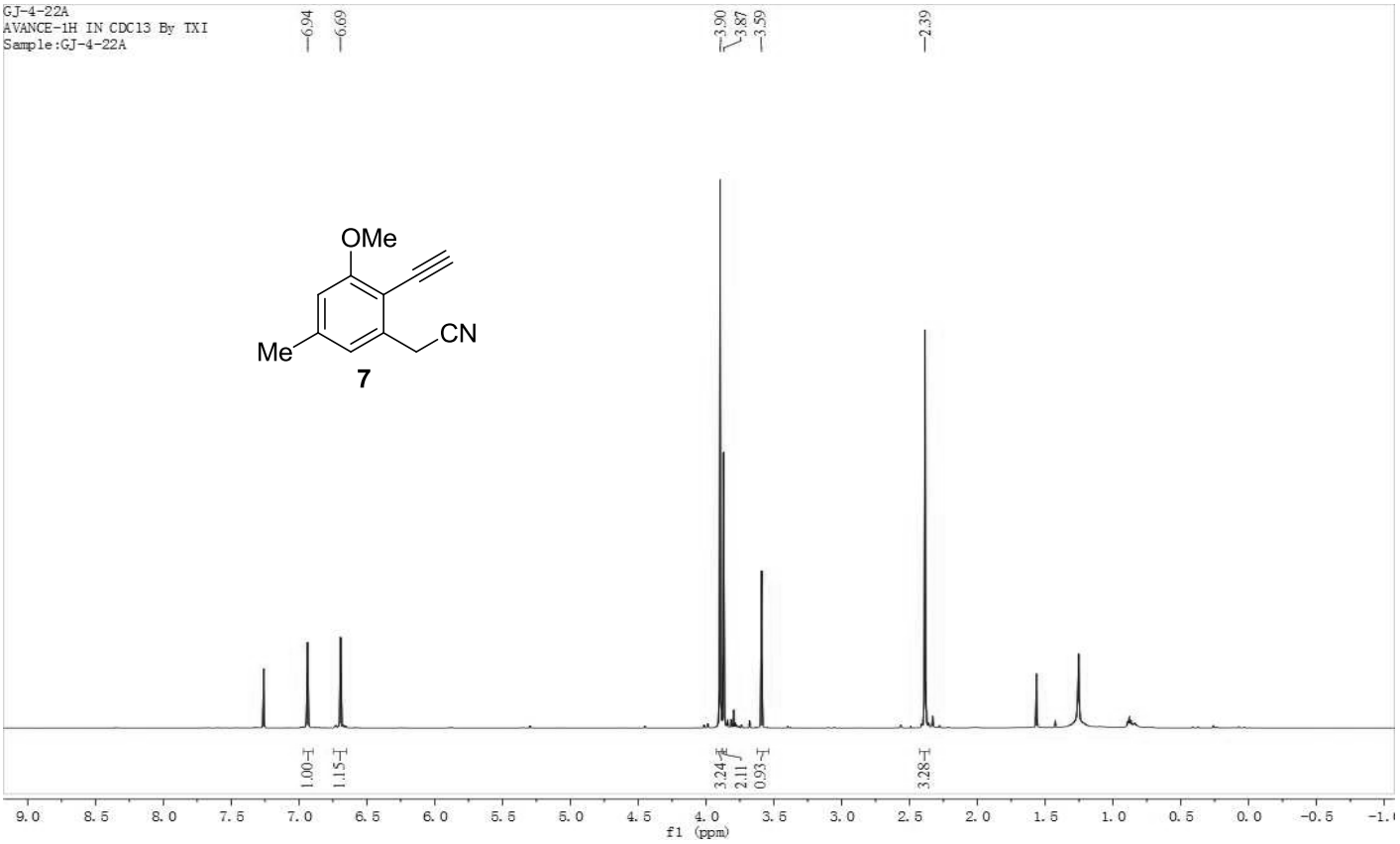
^{13}C NMR Spectrum of Compound **4i** ($CDCl_3$, 150 MHz)



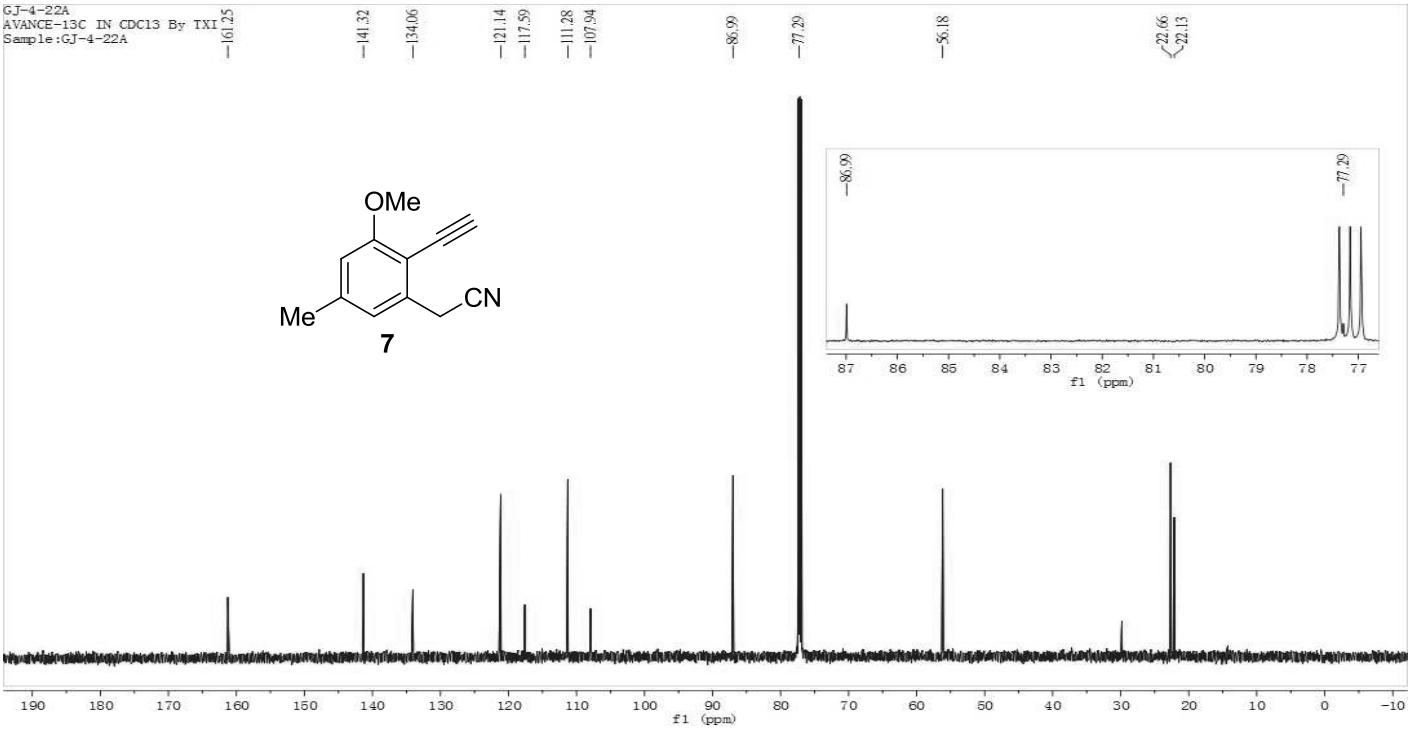
^{1}H NMR Spectrum of Compound **2** ($CDCl_3$, 600 MHz)



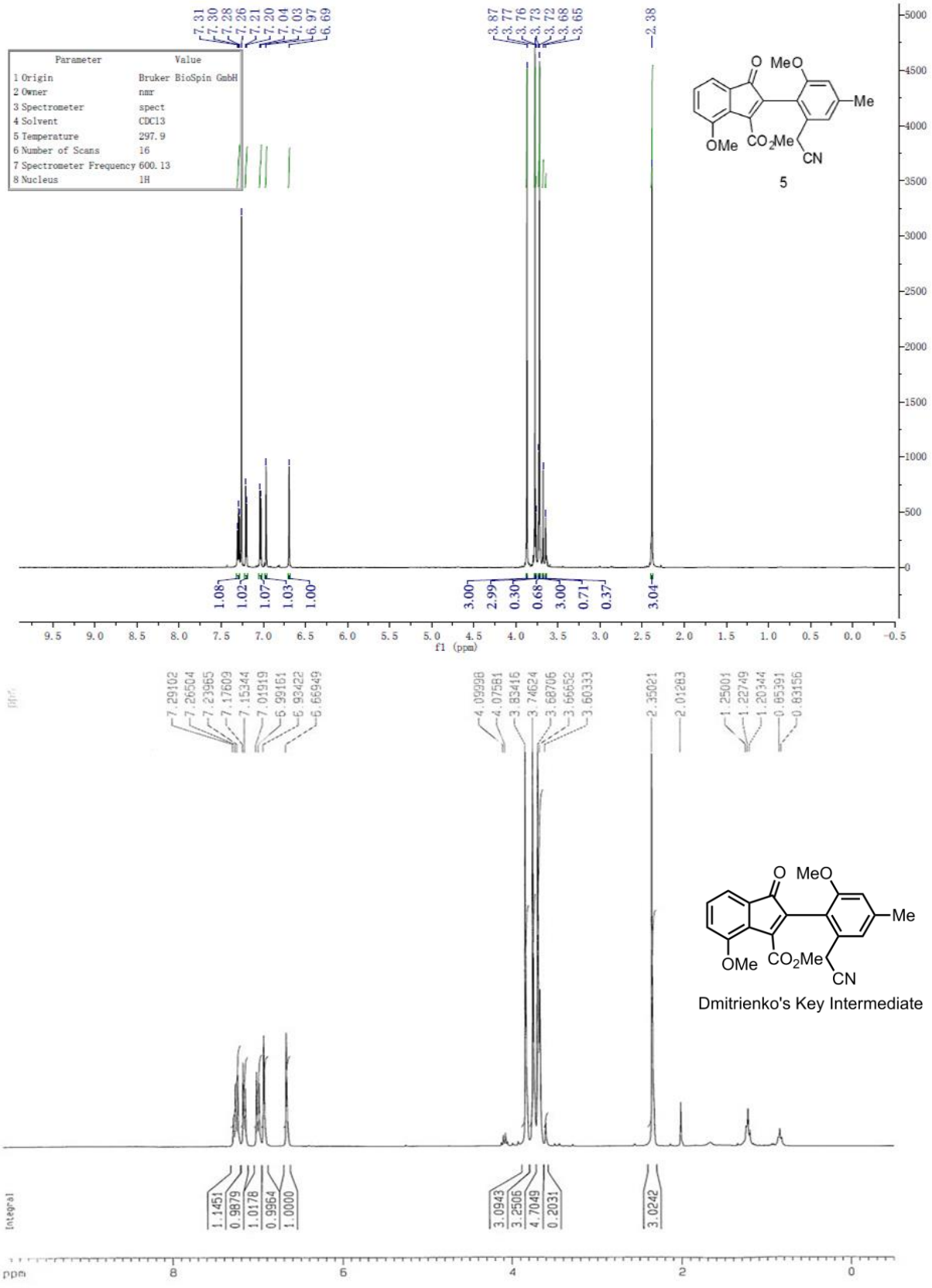
^{13}C NMR Spectrum of Compound **2** ($CDCl_3$, 150 MHz)



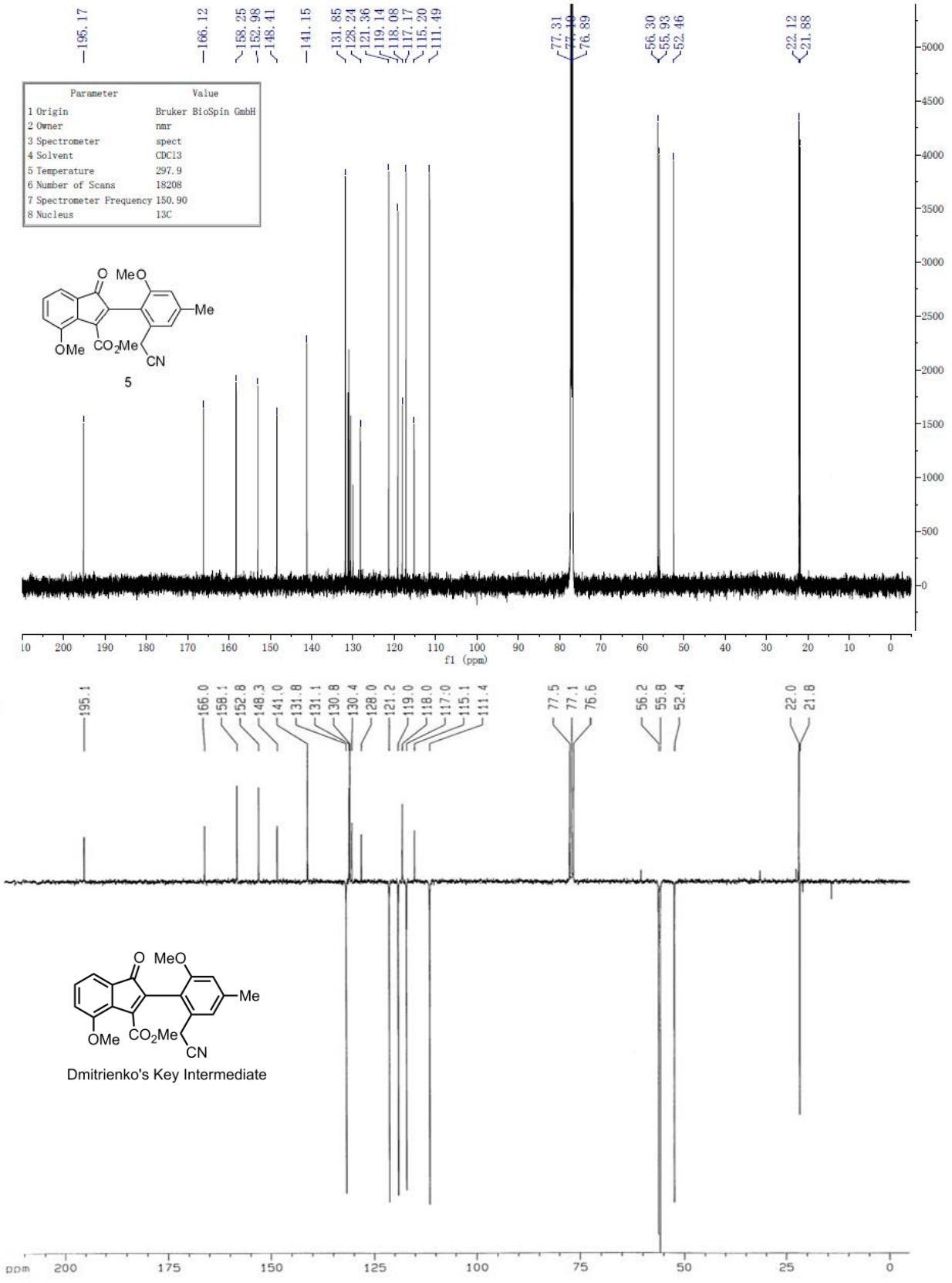
^{1}H NMR Spectrum of Compound **7** ($CDCl_3$, 600 MHz)



^{13}C NMR Spectrum of Compound **7** ($CDCl_3$, 150 MHz)



^{1}H-NMR Spectrum of Compound **5** and Dmitrienko's Key Intermediate



^{13}C-NMR Spectrum of Compound **5** and Dmitrienko's Key Intermediate