

Supplementary Information

For

Further Insight into the Photochemical Behavior of 3-aryl-*N*-(arylsulfonyl) propiolamides: Tunable Synthetic Route to Phenanthrenes†

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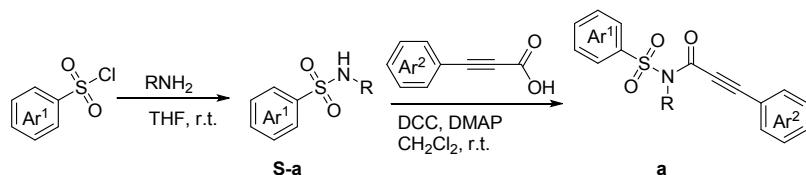
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1. General information

All the starting materials were purchased from Aldrich, EnergyChemical Chemicals and Aladdin, and all were used as received. All the relevant solvents were dried and purified according to the procedure from “Purification of Laboratory Chemicals book”. ^1H NMR (400 MHz or 600 MHz) and ^{13}C NMR (151 MHz) spectra were recorded on Bruker AV-400 instrument in CDCl_3 with TMS as internal standard. Chemical shift in parts per million relative to the chemical shift of CDCl_3 at 7.26 ppm integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m= multiplet) and for ^{13}C NMR spectra were relative to the center line signal of the CDCl_3 triplet at 77.16 ppm. HRMS (ESI) spectra were recorded on a Bruker Esquire LC mass spectrometer using electrospray ionization. GC-MS analysis was performed on a 7890A-5975C/Agilent and GC analysis on a 7890B/Agilent. Melting points were determined using a capillary melting point apparatus and are uncorrected. Flash column chromatography was performed using 200-300 mesh silica gel and eluted with petroleum/ ethyl acetate.

3-(*p*-tolyl)propiolic acid, 3-(*m*-tolyl)propiolic acid and 3-(4-methoxyphenyl)propiolic acid were synthesized according to literature procedures¹. The 3-(thiophen-2-yl)propiolic acid and 3-(3,4,5-trimethoxyphenyl)propiolic acid were prepared according to literature procedures².

2. Typical procedure for preparation of substrates



Synthesis of S-a.

For substrates **1a**, **6a**, **7a** and **9a-30a, 23a-28a**: MeNH_2 (3eq., 33% solution in methanol) was added to solution of arylsulfonyl chloride (1.0 eq.) in THF (0.2 mol/L). The mixture was stirred at room temperature for 10 minutes, poured into water and extracted with ethyl acetate, then the organic layer was dried over MgSO_4 for 8 hours, filtered and concentrated to furnish the **S-a**, that was submitted to the next step without any purification.

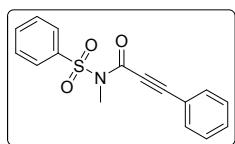
For substrate **4a**, **5a** and **8a**, **S-a** was synthesized according to reported literature procedures³.

For substrate **2a** and **3a**, **S-a** was synthesized according to previous literature procedures⁴.

Synthesis of a.

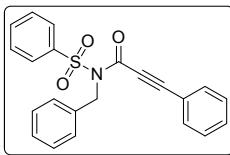
To a solution of 3-arylpropiolic acid (1.1 eq.) in CH_2Cl_2 (0.2 mol/L), DMAP (0.1 eq.) was added, then the solution was cooled to 0 °C. **S-a** (1.0 eq.) and DCC (1.2 eq.) were added sequentially. The resulting solution was stirred at room temperature until completion. The precipitated urea was then filtered off by celite and the filtrate was concentrated, the residue was purified by column chromatography on silica gel with petroleum/ethyl acetate to provide compound **a**.

3. Characterization of substrates

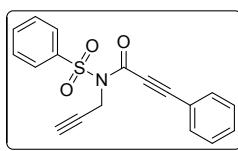


N-methyl-3-phenyl-N-(phenylsulfonyl)propiolamide (1a). White solid, m.p. = 112.9–114.3 °C. The compound was prepared following the typical procedure. Yield 80% (239.3 mg, 1.0 mmol); ^1H NMR (600 MHz, CDCl_3): δ 8.02 (dd, J = 8.4, 1.0 Hz, 2H), 7.69 – 7.62 (m, 1H), 7.61 – 7.51 (m, 4H), 7.51 – 7.45 (m, 1H), 7.44 – 7.36 (m, 2H), 3.53 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 152.84, 138.73, 134.19, 132.92, 131.19, 129.24, 128.84, 128.21, 119.55, 93.99, 81.61, 33.55; GC-MS (EI):

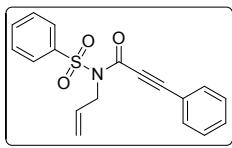
299.0, 235.1, 178.1, 142.1, 129.1; HRMS (ESI): calc. for $C_{16}H_{13}NNaO_3S$ [M+Na]⁺: 322.0508, found: 322.0517.



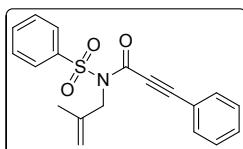
N-benzyl-3-phenyl-N-(phenylsulfonyl)propiolamide (2a). White solid, m.p. = 126.1–127.0°C. The compound was prepared following the typical procedure. Yield 70% (525.0 mg, 2.0 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 7.9 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.29 (m, 12H), 5.31 (s, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 153.04, 138.86, 136.26, 134.00, 132.88, 131.21, 128.85, 128.82, 128.75, 128.27, 128.18, 119.38, 94.05, 81.74, 50.54; GC-MS (EI): 375.1, 311.2, 234.1, 129.1, 91.1; HRMS (ESI): calc. for $C_{22}H_{17}NNaO_3S$ [M+Na]⁺: 398.0821, found: 398.0825.



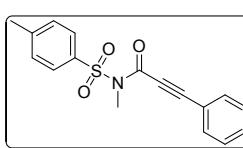
3-phenyl-N-(phenylsulfonyl)-N-(prop-2-yn-1-yl)propiolamide (3a). White solid, m.p. = 62.3–63.1°C. The compound was prepared following the typical procedure. Yield 60% (387.6 mg, 2.0 mmol); ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 7.9 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.51 (dt, *J* = 15.6, 7.5 Hz, 5H), 7.39 (t, *J* = 7.5 Hz, 2H), 4.88 (s, 2H), 2.37 (s, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 152.01, 138.49, 134.32, 133.00, 131.36, 128.99, 128.85, 119.23, 94.35, 81.12, 77.92, 73.26, 36.33; GC-MS (EI): 323.1, 258.1, 182.1, 127.1, 77.1, 28.1; HRMS (ESI): calc. for $C_{18}H_{13}NNaO_3S$ [M+Na]⁺: 346.0508, found: 346.0513.



N-allyl-3-phenyl-N-(phenylsulfonyl)propiolamide (4a). White solid, m.p. = 67.4–68.5°C. The compound was prepared following the typical procedure. Yield 45% (292.5 mg, 2.0 mmol); ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 7.9 Hz, 2H), 7.62 (d, *J* = 7.3 Hz, 1H), 7.58 – 7.43 (m, 5H), 7.38 (t, *J* = 7.4 Hz, 2H), 5.99 (dq, *J* = 10.5, 5.6 Hz, 1H), 5.41 (d, *J* = 17.1 Hz, 1H), 5.32 (d, *J* = 10.2 Hz, 1H), 4.71 (d, *J* = 5.3 Hz, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 152.66, 138.90, 134.09, 132.80, 132.43, 131.18, 128.94, 128.81, 128.76, 119.34, 119.16, 93.23, 81.50, 49.56; GC-MS (EI): 325.2, 260.1, 184.1, 129.1, 77.1; HRMS (ESI): calc. for $C_{18}H_{15}NNaO_3S$ [M+Na]⁺: 348.0665, found: 348.0662.

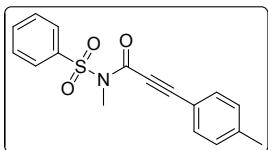


N-(2-methylallyl)-3-phenyl-N-(phenylsulfonyl)propiolamide (5a). White solid, m.p. = 107.3–108.2°C. The compound was prepared following the typical procedure. Yield 55% (372.9 mg, 2.0 mmol); ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 7.7 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.58 – 7.43 (m, 5H), 7.38 (t, *J* = 7.4 Hz, 2H), 5.02 (d, *J* = 9.5 Hz, 2H), 4.65 (s, 2H), 1.82 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 153.06, 139.91, 138.83, 134.13, 132.87, 131.17, 128.99, 128.89, 128.85, 119.46, 113.13, 92.96, 81.54, 52.61, 20.37; GC-MS (EI): 339.2, 274.1, 198.2, 155.2, 129.1, 77.1; HRMS (ESI): calc. for $C_{19}H_{17}NNaO_3S$ [M+Na]⁺: 362.0821, found: 362.0823.

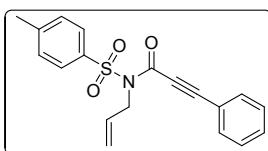


N-methyl-3-phenyl-N-tosylpropiolamide (6a). White solid, m.p. = 78.4–79.3°C. The compound was prepared following the typical procedure. Yield 85% (266.2 mg, 1.0 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 7.7 Hz, 2H), 7.57 (d, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.32 (d, *J* = 7.7 Hz, 2H), 3.50 (s, 3H), 2.43 (s, 3H); ¹³C NMR (151

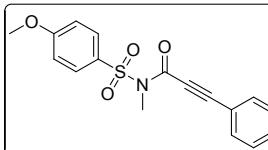
MHz, CDCl₃) δ 152.87, 145.36, 135.75, 132.92, 131.13, 129.83, 128.83, 128.26, 119.63, 93.81, 81.69, 33.49, 21.80; GC-MS (EI): 313.1, 249.1, 236.1, 192.1, 142.1, 129.1; HRMS (ESI): calc. for C₁₇H₁₅NNaO₃S [M+Na]⁺: 336.0665, found: 336.0672.



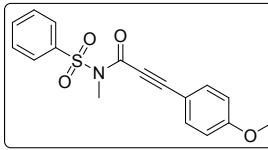
N-methyl-N-(phenylsulfonyl)-3-(p-tolyl)propiolamide (7a). White solid, m.p. = 140.4–141.1°C. The compound was prepared following the typical procedure. Yield 85% (2.0 mg, 1.0 mmol); ¹H NMR (600 MHz, CDCl₃) δ 8.08 – 7.98 (m, 2H), 7.64 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.9 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 3.52 (s, 3H), 2.39 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 152.97, 141.99, 138.79, 134.13, 132.95, 129.64, 129.21, 128.22, 116.43, 94.61, 81.39, 33.56, 21.92; GC-MS (EI): 313.2, 298.1, 248.2, 192.1, 156.2, 143.1, 77.1; HRMS (ESI): calc. for C₁₇H₁₅NNaO₃S [M+Na]⁺: 336.0665, found: 336.0672.



N-allyl-3-phenyl-N-tosylpropiolamide (8a). White solid, m.p. = 44.4–45.9°C. The compound was prepared following the typical procedure. Yield 65% (440.7 mg, 2.0 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, J = 8.1 Hz, 2H), 7.52 (d, J = 7.9 Hz, 2H), 7.47 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 5.98 (dq, J = 10.6, 5.7 Hz, 1H), 5.40 (d, J = 17.1 Hz, 1H), 5.31 (d, J = 11.1 Hz, 1H), 4.69 (d, J = 5.4 Hz, 2H), 2.42 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 152.72, 145.27, 135.96, 132.83, 132.55, 131.14, 129.56, 128.89, 128.83, 119.49, 119.08, 93.07, 81.61, 49.56, 21.80; GC-MS (EI): 339.1, 192.1, 168.1, 129.0, 91.1, 75.1; HRMS (ESI): calc. for C₁₉H₁₇NNaO₃S [M+K]⁺: 362.0821, found: 362.0822.

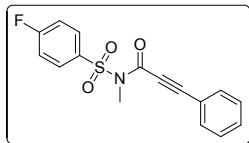


N-((4-methoxyphenyl)sulfonyl)-N-methyl-3-phenylpropiolamide (9a). White solid, m.p. = 55.9–57.3°C. The compound was prepared following the typical procedure. Yield 70% (276.4 mg, 1.2 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, J = 8.7 Hz, 2H), 7.58 (d, J = 7.9 Hz, 2H), 7.48 (t, J = 7.3 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 6.97 (d, J = 8.7 Hz, 2H), 3.87 (s, 3H), 3.50 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 164.14, 152.93, 132.93, 131.12, 130.67, 130.08, 128.84, 119.68, 114.37, 93.70, 81.72, 55.88, 33.55; GC-MS (EI): 329.0, 265.1, 208.1, 193.0, 142.1, 129.1; HRMS (ESI): calc. for C₁₇H₁₅NNaO₄S [M+Na]⁺: 352.0614, found: 352.0618.

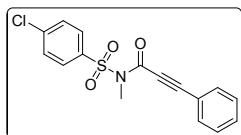


3-(4-methoxyphenyl)-N-methyl-N-(phenylsulfonyl)propiolamide (10a). White solid, m.p. = 120.5–121.8°C. The compound was prepared following the typical procedure. Yield 75% (370.1 mg, 1.5 mmol); ¹H NMR (600 MHz, CDCl₃) δ 8.07 – 7.97 (m, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.57 – 7.48 (m, 4H), 6.95 – 6.85 (m, 2H), 3.84 (s, 3H), 3.51 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 161.99, 153.05, 138.82, 134.96, 134.09, 129.19, 128.17, 114.56, 111.27, 95.02, 81.33, 55.58, 33.53; GC-MS (EI): 329.0, 264.0, 208.0, 159.0, 144.0; HRMS (ESI): calc. for C₁₇H₁₅NNaO₄S [M+Na]⁺: 352.0614, found: 352.0619.

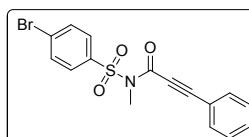
N-((4-fluorophenyl)sulfonyl)-N-methyl-3-phenylpropiolamide (11a). White solid, m.p. = 91.1–92.2°C. The compound was prepared following the typical procedure. Yield 65% (309.0 mg, 1.5 mmol); ¹H NMR (600 MHz, CDCl₃) δ 8.05 (dd, J = 8.8, 5.0 Hz, 2H), 7.56 (d, J = 7.3 Hz, 2H),



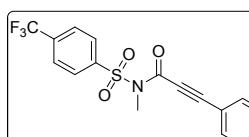
7.48 (t, $J = 7.5$ Hz, 1H), 7.40 (t, $J = 7.6$ Hz, 2H), 7.20 (t, $J = 8.5$ Hz, 2H), 3.54 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 166.01 (d, $J = 257.3$ Hz), 152.84, 134.59 (d, $J = 3.2$ Hz), 132.90, 131.37, 131.30, 128.88, 119.34, 116.58, 116.43, 94.08, 81.41, 33.76; GC-MS (EI): 317.2, 253.2, 142.1, 129.1, 95.1; HRMS (ESI): calc. for C₁₆H₁₂FNNaO₃S [M+Na]⁺: 340.0414, found: 340.0420.



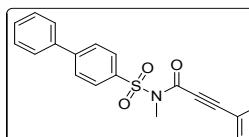
N-(4-chlorophenyl)-N-methyl-3-phenylpropiolamide (12a). White solid, m.p. = 68.8-70.1°C. The compound was prepared following the typical procedure. Yield 75% (374.7 mg, 1.5 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, $J = 8.4$ Hz, 2H), 7.57 (d, $J = 7.7$ Hz, 2H), 7.49 (t, $J = 8.7$ Hz, 3H), 7.40 (t, $J = 7.5$ Hz, 2H), 3.54 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 152.83, 140.97, 137.06, 132.94, 131.34, 129.86, 129.52, 128.91, 119.35, 94.22, 81.41, 33.79; GC-MS (EI): 333.1, 256.1, 234.2, 142.1, 129.1, 111.1; HRMS (ESI): calc. for C₁₆H₁₂ClNNaO₃S [M+Na]⁺: 356.0119, found: 356.0118.



N-(4-bromophenyl)-N-methyl-3-phenylpropiolamide (13a). White solid, m.p. = 77.2-78.5 °C. The compound was prepared following the typical procedure. Yield 80% (330.8mg, 1.1mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, $J = 8.3$ Hz, 2H), 7.67 (d, $J = 8.3$ Hz, 2H), 7.56 (d, $J = 7.5$ Hz, 2H), 7.49 (t, $J = 7.4$ Hz, 1H), 7.40 (t, $J = 7.5$ Hz, 2H), 3.54 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 152.79, 137.57, 132.92, 132.49, 131.33, 129.85, 129.54, 128.89, 119.31, 94.20, 81.38, 33.78; GC-MS (EI): 376.1, 300.1, 256.1, 143.1, 129.1; HRMS (ESI): calc. for C₁₆H₁₂BrNNaO₃S [M+Na]⁺: 399.9613, found: 399.9617.

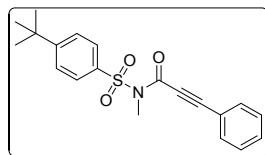


N-methyl-3-phenyl-N-(4-(trifluoromethyl)phenyl)sulfonylpropiolamide (14a). White solid, m.p. = 71.3-72.3°C. The compound was prepared following the typical procedure. Yield 70% (385.4mg, 1.5mmol); ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, $J = 8.1$ Hz, 2H), 7.80 (d, $J = 8.1$ Hz, 2H), 7.55 (d, $J = 7.4$ Hz, 2H), 7.49 (t, $J = 7.4$ Hz, 1H), 7.40 (t, $J = 7.5$ Hz, 2H), 3.58 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 152.81, 142.06, 135.68 (q, $J = 33.3$ Hz), 132.94, 131.45, 129.00, 128.92, 126.34 (q, $J = 3.6$ Hz), 123.13 (q, $J = 273.1$ Hz), 119.17, 94.50, 81.23, 33.92; GC-MS (EI): 367.2, 303.1, 246.1, 142.1, 129.1, 75.1; HRMS (ESI): calc. for C₁₇H₁₂F₃NNaO₃S [M+Na]⁺: 390.0382, found: 390.0387.

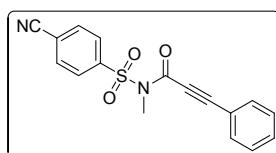


N-([1,1'-biphenyl]-4-ylsulfonyl)-N-methyl-3-phenylpropiolamide (15a). White solid, m.p. = 104.6-105.4°C. The compound was prepared following the typical procedure. Yield 65% (243.8mg, 1.0mmol); ¹H NMR (600 MHz, CDCl₃) δ 8.13 – 8.04 (m, 2H), 7.77 – 7.69 (m, 2H), 7.64 – 7.56 (m, 4H), 7.52 – 7.46 (m, 3H), 7.45 – 7.37 (m, 3H), 3.56 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 152.92, 147.19, 139.13, 137.16, 132.95, 131.20, 129.24, 128.90, 128.87, 128.82, 127.83, 127.54, 119.59, 94.02, 81.67, 33.63; GC-MS (EI): 375.2, 311.2, 254.1, 142.1, 129.1; HRMS (ESI): calc. for C₂₂H₁₇NNaO₃S [M+Na]⁺: 398.0821, found: 398.0823.

N-((4-(tert-butyl)phenyl)sulfonyl)-N-methyl-3-phenylpropiolamide (16a). White solid, m.p. =

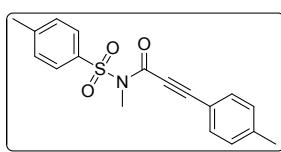


93.4-94.6°C. The compound was prepared following the typical procedure. Yield 40% (355.0 mg, 2.5 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.6 Hz, 2H), 7.55 (dd, *J* = 16.6, 7.9 Hz, 4H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 3.51 (s, 3H), 1.34 (d, *J* = 5.4 Hz, 9H); ¹³C NMR (151 MHz, CDCl₃) δ 158.20, 152.91, 135.63, 132.94, 131.13, 128.83, 128.10, 126.29, 119.68, 93.83, 81.75, 35.45, 33.47, 31.13; GC-MS (EI): 355.1, 340.1, 278.1, 263.1, 235.1 142.1, 118.1; HRMS (ESI): calc. for C₂₀H₂₂NO₃S [M+H]⁺: 356.1315, found: 356.1323.



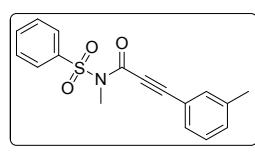
N-((4-cyanophenyl)sulfonyl)-N-methyl-3-phenylpropiolamide (17a).

White solid, m.p. = 145.3-146.8°C. The compound was prepared following the typical procedure. Yield 60% (291.6 mg, 1.5 mmol); ¹H NMR (600 MHz, CDCl₃) δ 8.14 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 3.59 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 152.83, 142.65, 132.99, 132.91, 131.58, 129.17, 128.99, 119.06, 117.84, 117.15, 94.77, 81.11, 34.07; GC-MS (EI): 323.1, 247.1, 203.1, 142.1, 129.1, 75.1; HRMS (ESI): calc. for C₁₇H₁₂N₂NaO₃S [M+Na]⁺: 347.0461, found: 347.0462.



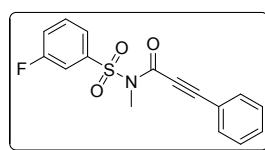
N-methyl-3-(p-tolyl)-N-tosylpropiolamide (18a).

White solid, m.p. = 123.4-124.6°C. The compound was prepared following the typical procedure. Yield 80% (392.4 mg, 1.5 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 3.50 (s, 3H), 2.41 (d, *J* = 14.0 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 153.01, 145.29, 141.92, 135.82, 132.95, 129.80, 129.62, 128.28, 116.53, 94.43, 81.47, 33.51, 21.92, 21.81; GC-MS (EI): 327.2, 250.2, 206.2, 148.1, 115.1, 91.1; HRMS (ESI): calc. for C₁₈H₁₇NNaO₃S [M+Na]⁺: 350.0821, found: 350.0825.



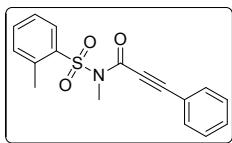
N-methyl-N-(phenylsulfonyl)-3-(m-tolyl)propiolamide (19a).

White solid, m.p. = 107.2-108.3°C. The compound was prepared following the typical procedure. Yield 65% (305.2 mg, 1.5 mmol); ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 7.7 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.37 (d, *J* = 6.8 Hz, 2H), 7.31 – 7.23 (m, 2H), 3.52 (s, 3H), 2.35 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 152.88, 138.73, 138.70, 134.15, 133.35, 132.13, 130.06, 129.21, 128.72, 128.21, 119.32, 94.34, 81.33, 33.55, 21.30; GC-MS (EI): 313.2, 249.2, 192.2, 156.2, 143.1, 77.1; HRMS (ESI): calc. for C₁₇H₁₅NNaO₃S [M+Na]⁺: 336.0665, found: 336.0672.

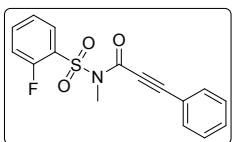


N-((3-fluorophenyl)sulfonyl)-N-methyl-3-phenylpropiolamide (20a).

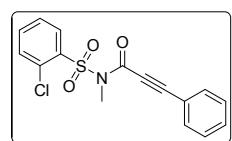
White solid, m.p. = 126.0-127.1°C. The compound was prepared following the typical procedure. Yield 50% (317.0 mg, 2.0 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.7 Hz, 2H), 7.54 – 7.45 (m, 2H), 7.44 – 7.31 (m, 3H), 3.54 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 162.27 (d, *J* = 252.4 Hz), 152.78, 140.53 (d, *J* = 7.1 Hz), 132.96, 131.35, 131.05 (d, *J* = 7.7 Hz), 128.91, 124.08 (d, *J* = 3.3 Hz), 121.52 (d, *J* = 21.2 Hz), 119.35, 115.81 (d, *J* = 24.9 Hz), 94.38, 81.40, 33.76; GC-MS (EI): 317.0, 253.1, 196.0, 129.0, 95.1, 75.1; HRMS (ESI): calc. for C₁₆H₁₂FNNaO₃S [M+Na]⁺: 340.0414, found: 340.0420.



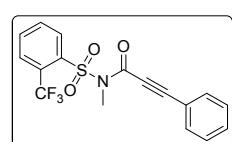
N-methyl-3-phenyl-N-(o-tolylsulfonyl)propiolamide (21a). White solid, m.p. = 61.2-62.3°C. The compound was prepared following the typical procedure. Yield 80% (375.6mg, 1.5mmol); ¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.41 (m, 4H), 7.34 (dt, *J* = 18.7, 8.3 Hz, 4H), 3.56 (s, 3H), 2.60 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 152.84, 137.71, 137.43, 134.03, 132.82, 132.75, 131.42, 131.11, 128.76, 126.35, 119.49, 94.33, 81.44, 33.09, 20.34; GC-MS (EI): 313.2, 248.2, 234.2, 192.2, 142.1; HRMS (ESI): calc. for C₁₇H₁₅NNaO₃S [M+Na]⁺: 336.0670, found: 336.0664.



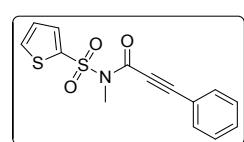
N-((2-fluorophenyl)sulfonyl)-N-methyl-3-phenylpropiolamide (22a). White solid, m.p. = 132.2-133.5°C. The compound was prepared following the typical procedure. Yield 55% (261.5mg, 1.5mmol); ¹H NMR (400 MHz, CDCl₃) δ 8.09 (t, *J* = 7.3 Hz, 1H), 7.62 (d, *J* = 6.2 Hz, 1H), 7.49 (dd, *J* = 19.6, 7.4 Hz, 3H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.30 – 7.19 (m, 3H), 3.61 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 159.09 (d, *J* = 256.7 Hz), 152.77, 136.40 (d, *J* = 8.7 Hz), 132.83, 132.12, 131.22, 128.83, 127.10 (d, *J* = 13.7 Hz), 124.43 (d, *J* = 3.6 Hz), 119.40, 117.33 (d, *J* = 20.8 Hz), 94.35, 81.27, 33.48; GC-MS (EI): 317.1, 240.1, 196.1, 142.1, 129.1, 118.1; HRMS (ESI): calc. for C₁₆H₁₂FNNaO₃S [M+Na]⁺: 340.0414, found: 340.0422.



N-((2-chlorophenyl)sulfonyl)-N-methyl-3-phenylpropiolamide (23a). White solid, m.p. = 110.2-111.5°C. The compound was prepared following the typical procedure. Yield 60% (299.7 mg, 1.5 mmol); ¹H NMR (400 MHz, CDCl₃) δ 8.35 – 8.23 (m, 1H), 7.58 – 7.44 (m, 5H), 7.44 – 7.34 (m, 3H), 3.66 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 152.75, 136.77, 134.88, 133.55, 132.81, 132.06, 131.88, 131.22, 128.80, 127.10, 119.29, 94.31, 81.16, 33.91; GC-MS (EI): 333.0, 298.0, 268.1, 234.1, 212.1, 129.1, 75.1; HRMS (ESI): calc. for C₁₆H₁₂ClNNaO₃S [M+Na]⁺: 356.0119, found: 356.0123.

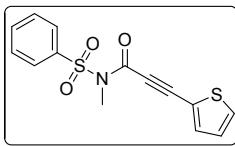


N-methyl-3-phenyl-N-(2-(trifluoromethyl)phenylsulfonyl)propiolamide (24a). White solid, m.p. = 86.3-87.1°C. The compound was prepared following the typical procedure. Yield 65% (477.1mg, 2.0mmol); ¹H NMR (600 MHz, CDCl₃) δ 8.52 (d, *J* = 5.6 Hz, 1H), 7.87 (d, *J* = 4.9 Hz, 1H), 7.80 – 7.67 (m, 2H), 7.48 (dd, *J* = 19.7, 7.5 Hz, 3H), 7.38 (t, *J* = 7.5 Hz, 2H), 3.63 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 153.15, 137.55, 134.80, 134.04, 132.90, 132.29, 131.33, 128.83, 128.29 (q, *J* = 6.2 Hz), 127.71 (q, *J* = 33.5 Hz), 122.58 (q, *J* = 273.8 Hz), 119.15, 94.28, 81.02, 33.92; GC-MS (EI): 367.2, 302.1, 246.2, 145.1, 129.1; HRMS (ESI): calc. for C₁₇H₁₂F₃NNaO₃S [M+Na]⁺: 390.0382, found: 390.0388.



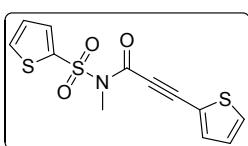
N-methyl-3-phenyl-N-(thiophen-2-ylsulfonyl)propiolamide (25a). White solid, m.p. = 108.6-109.4°C. The compound was prepared following the typical procedure. Yield 65% (495.6 mg, 2.5 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.85 (s, 1H), 7.69 (d, *J* = 4.7 Hz, 1H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.13 (d, *J* = 3.7 Hz, 1H), 3.50 (s,

3H); ^{13}C NMR (151 MHz, CDCl_3) δ 152.76, 138.44, 134.93, 134.25, 133.11, 131.29, 128.88, 127.60, 119.59, 94.43, 81.63, 33.44; GC-MS (EI): 305.1, 272.1, 184.1, 142.1, 129.1, 75.1; HRMS (ESI): calc. for $\text{C}_{14}\text{H}_{11}\text{NNaO}_3\text{S}_2$ [$\text{M}+\text{Na}]^+$: 328.0073, found: 328.0080.



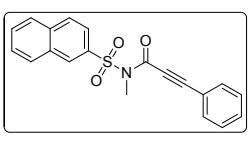
N-methyl-N-(phenylsulfonyl)-3-(thiophen-2-yl)propiolamide (26a).

White solid, m.p. = 109.5–110.2°C. The compound was prepared following the typical procedure. Yield 60% (366.0 mg, 2.0 mmol); ^1H NMR (600 MHz, CDCl_3) δ 8.01 (d, J = 7.5 Hz, 2H), 7.65 (t, J = 7.5 Hz, 1H), 7.57 – 7.47 (m, 4H), 7.08 (dd, J = 4.8, 4.0 Hz, 1H), 3.50 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 152.64, 138.73, 136.92, 134.22, 131.98, 129.31, 128.17, 127.91, 119.29, 88.16, 85.98, 33.38; GC-MS (EI): 305.0, 240.1, 184.0, 135.0, 77.1; HRMS (ESI): calc. for $\text{C}_{14}\text{H}_{11}\text{NNaO}_3\text{S}_2$ [$\text{M}+\text{Na}]^+$: 328.0073, found: 328.0080.



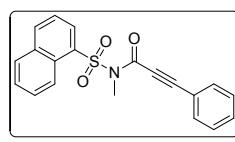
N-methyl-3-(thiophen-2-yl)-N-(thiophen-2-ylsulfonyl)propiolamide (27a).

Slight brown solid, m.p. = 137.5–138.7°C. The compound was prepared following the typical procedure. Yield 65% (404.3 mg, 2.0 mmol); ^1H NMR (600 MHz, CDCl_3) δ 7.85 (d, J = 3.6 Hz, 1H), 7.70 (d, J = 4.9 Hz, 1H), 7.54 (t, J = 4.8 Hz, 2H), 7.13 (t, J = 4.4 Hz, 1H), 7.11 – 7.06 (m, 1H), 3.47 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 152.56, 138.40, 137.11, 134.90, 134.27, 132.16, 127.94, 127.64, 119.32, 88.63, 86.01, 33.27; GC-MS (EI): 311.0, 279.0, 187.0, 158.0, 132.0; HRMS (ESI): calc. for $\text{C}_{12}\text{H}_9\text{NNaO}_3\text{S}_3$ [$\text{M}+\text{Na}]^+$: 333.9637, found: 333.9643.



N-methyl-N-(naphthalen-2-ylsulfonyl)-3-

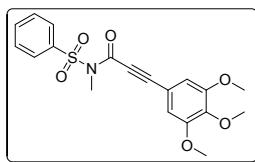
phenylpropiolamide (28a). White solid, m.p. = 107.2–108.1°C. The compound was prepared following the typical procedure. Yield 50% (349.0 mg, 2.0 mmol); ^1H NMR (600 MHz, CDCl_3) δ 8.62 (s, 1H), 8.02 – 7.85 (m, 4H), 7.72 – 7.64 (m, 1H), 7.60 (dd, J = 11.1, 3.9 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.47 (t, J = 7.5 Hz, 1H), 7.38 (t, J = 7.7 Hz, 2H), 3.58 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 152.83, 135.49, 135.39, 132.88, 131.90, 131.15, 130.54, 129.65, 129.62, 129.59, 128.81, 128.07, 127.91, 122.43, 119.54, 93.98, 81.67, 33.61; GC-MS (EI): 349.1, 285.1, 228.1, 142.1, 127.1; HRMS (ESI): calc. for $\text{C}_{20}\text{H}_{15}\text{NNaO}_3\text{S}$ [$\text{M}+\text{Na}]^+$: 372.0665, found: 372.0670.



N-methyl-N-(naphthalen-1-ylsulfonyl)-3-phenylpropiolamide (29a).

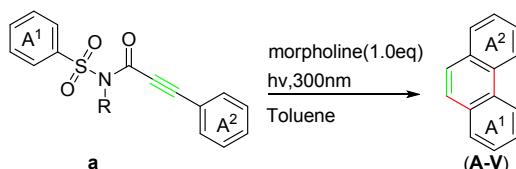
White solid, m.p. = 107.3–108.5°C. The compound was prepared following the typical procedure. Yield 45% (314.1 mg, 2.0 mmol); ^1H NMR (600 MHz, CDCl_3) δ 8.48 (d, J = 6.5 Hz, 2H), 8.12 (d, J = 8.1 Hz, 1H), 7.97 (d, J = 8.1 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.62 (t, J = 7.3 Hz, 1H), 7.57 – 7.42 (m, 4H), 7.36 (t, J = 7.5 Hz, 2H), 3.66 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 152.74, 135.76, 134.29, 133.61, 132.83, 132.75, 131.11, 129.54, 129.02, 128.78, 128.40, 127.18, 124.15, 123.67, 119.52, 94.27, 81.59, 33.37; GC-MS (EI): 349.2, 285.1, 228.2, 215.2, 142.1, 129.1; HRMS (ESI): calc. for $\text{C}_{20}\text{H}_{15}\text{NNaO}_3\text{S}$ [$\text{M}+\text{Na}]^+$: 372.0665, found: 372.0671.

N-methyl-N-(phenylsulfonyl)-3-(3,4,5-trimethoxyphenyl)propiolamide (30a). Brown solid, m.p. = 63.5–65.0°C; ^1H NMR (600 MHz, CDCl_3) δ 8.01 (d, J = 7.6 Hz, 2H), 7.69 – 7.61 (m, 1H),



7.53 (dd, $J = 16.9, 9.2$ Hz, 2H), 6.80 (s, 2H), 3.88 (s, 3H), 3.85 (s, 6H), 3.50 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 153.37, 152.82, 141.36, 138.71, 134.17, 129.26, 128.14, 114.17, 110.22, 94.51, 80.98, 61.16, 56.40, 33.50; GC-MS (EI): 389.0, 324.1, 253.1, 208.1, 77.0, 51.0; HRMS (ESI): calc. for $\text{C}_{19}\text{H}_{19}\text{NNaO}_6\text{S} [\text{M}+\text{Na}]^+$: 412.0825, found: 412.0826.

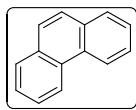
4. Photoinduced synthesis of phenanthrenes.



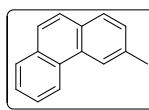
General procedure:

The solution of substrate **a** (0.2mmol) in anhydrous toluene (40mL) was placed in a dry quartz tube, then the organic base morpholine (0.2mmol) was added and well mixed, the reaction system was irradiated under the 300nm UV light. After the reaction finished, the solvent was removed in vacuo, the residue was purified by silica gel column chromatograph using petroleum elutent to afford the phenanthrenes product.

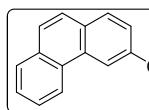
5. Characterization of phenanthrenes and otherinvolved compounds.



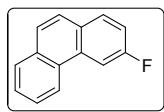
Phenanthrene (A). Substrate **1a** was irradiated for 0.9 h, 28.5 mg, 80% yield; Substrate **2a** was irradiated for 1.2 h, 26.7 mg, 75% yield; Substrate **3a** was irradiated for 1.0 h, 25.0 mg, 70% yield; Substrate **4a** was irradiated for 1.1 h, 26.7 mg, 75% yield; Substrate **5a** was irradiated for 1.0 h, 31.0 mg, 87% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.71 (d, $J = 8.1$ Hz, 2H), 7.91 (d, $J = 7.6$ Hz, 2H), 7.76 (s, 2H), 7.65 (dd, $J = 16.1, 7.6$ Hz, 4H); ^{13}C NMR (151 MHz, CDCl_3) δ 132.17, 130.42, 128.70, 127.05, 126.70, 122.79. The analytical data match those reported in the literature⁵.



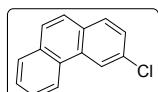
3-methylphenanthrene (B). Substrate **6a** was irradiated for 1.0 h, 32.6 mg, 85% yield; Substrate **7a** was irradiated for 1.2 h, 34.6 mg, 90% yield; Substrate **8a** was irradiated for 1.2 h, 30.8 mg, 80% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.71 (d, $J = 8.2$ Hz, 1H), 8.51 (s, 1H), 7.90 (d, $J = 7.8$ Hz, 1H), 7.81 (d, $J = 8.1$ Hz, 1H), 7.77 – 7.57 (m, 4H), 7.46 (d, $J = 8.0$ Hz, 1H), 2.65 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 136.40, 132.33, 130.46, 130.15, 130.10, 128.65, 128.53, 128.43, 126.86, 126.54, 126.45, 126.09, 122.75, 122.54, 22.27. The analytical data match those reported in the literature⁶.



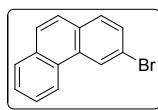
3-methoxyphenanthrene (C). Substrate **9a** was irradiated for 2.5 h, 22.9 mg, 55% yield; Substrate **10a** was irradiated for 2.5 h, 27.1 mg, 65% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.55 (d, $J = 8.0$ Hz, 1H), 7.99 (d, $J = 2.3$ Hz, 1H), 7.85 – 7.79 (m, 1H), 7.74 (d, $J = 8.7$ Hz, 1H), 7.62 (d, $J = 8.8$ Hz, 1H), 7.60 – 7.49 (m, 3H), 7.19 (dd, $J = 8.6, 2.3$ Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 158.55, 132.51, 131.70, 130.08, 129.85, 128.71, 126.84, 126.72, 126.67, 126.22, 124.65, 122.77, 116.81, 104.04, 55.55. The analytical data match those reported in the literature⁵.



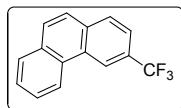
3-fluorophenanthrene (D**)**. Substrate **11a** was irradiated for 1.2 h, 21.6 mg, 55% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.61 – 8.51 (m, 1H), 8.30 (dd, *J* = 11.1, 2.4 Hz, 1H), 7.96 – 7.83 (m, 2H), 7.77 – 7.59 (m, 4H), 7.36 (td, *J* = 8.5, 2.5 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 161.71 (d, *J* = 245.3 Hz), 132.33, 131.93 (d, *J* = 8.4 Hz), 130.68 (d, *J* = 8.9 Hz), 129.81 (d, *J* = 4.3 Hz), 128.81 (d, *J* = 1.4 Hz), 128.75, 127.29, 126.73, 126.42, 126.26 (d, *J* = 2.6 Hz), 122.97, 115.72 (d, *J* = 23.9 Hz), 107.89 (d, *J* = 22.1 Hz). The analytical data match those reported in the literature⁷.



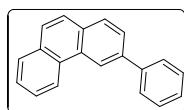
3-chlorophenanthrene (E**)**. Substrate **12a** was irradiated for 1.2 h, 30.5 mg, 72% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.65 (s, 1H), 8.60 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.77 – 7.59 (m, 4H), 7.55 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 132.70, 132.36, 131.52, 130.42, 130.06, 129.44, 128.77, 127.37, 127.34, 127.22, 127.01, 126.35, 122.83, 122.52. The analytical data match those reported in the literature⁵.



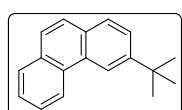
3-bromophenanthrene (F**)**. White solid, m.p. = 81.2-82.8 °C; Substrate **13a** was irradiated for 2.5 h, 15.4 mg, 30% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.81 (d, *J* = 1.4 Hz, 1H), 8.58 (d, *J* = 8.0 Hz, 1H), 7.93 – 7.86 (m, 1H), 7.74 (dd, *J* = 8.7, 2.3 Hz, 2H), 7.71 – 7.59 (m, 4H); ¹³C NMR (151 MHz, CDCl₃) δ 132.31, 131.86, 130.65, 130.17, 129.82, 129.31, 128.74, 127.52, 127.33, 127.02, 126.37, 125.66, 122.80, 120.95; GC-MS (EI): 258.0, 256.0, 176.1, 150.0, 98.0, 88.1, 74.1. The analytical data match those reported in the literature⁸.



3-(trifluoromethyl)phenanthrene (G**)**. White solid, m.p. = 54.0-55.8°C; Substrate **14a** was irradiated for 1.5 h, 34.5 mg, 70% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.96 (s, 1H), 8.71 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 8.9 Hz, 1H), 7.78 (t, *J* = 9.6 Hz, 2H), 7.73 (t, *J* = 7.3 Hz, 1H), 7.67 (t, *J* = 7.3 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 133.97, 132.36, 130.19, 129.89, 129.44, 129.40, 128.95, 128.37 (q, *J* = 32.1 Hz), 127.55, 127.42, 126.27, 124.76 (q, *J* = 272.2 Hz), 122.81, 122.61 (q, *J* = 3.3 Hz), 120.35 (q, *J* = 4.4 Hz); GC-MS (EI): 246.1, 227.1, 196.1, 176.1, 123.1, 98.1; HRMS (ESI): calc. for C₁₅H₁₀F₃ [M+H]⁺: 247.0729, found: 247.0734.

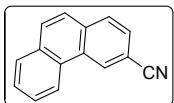


3-phenylphenanthrene (H**)**. Substrate **15a** was irradiated for 2.5 h, 28.5 mg, 56% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.94 (s, 1H), 8.82 (d, *J* = 8.2 Hz, 1H), 7.97 (dd, *J* = 16.2, 8.0 Hz, 2H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 7.7 Hz, 2H), 7.83 – 7.76 (m, 2H), 7.69 (dt, *J* = 14.6, 7.1 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 141.65, 139.49, 132.41, 131.29, 130.64, 130.51, 129.15, 129.04, 128.80, 127.73, 127.53, 127.14, 126.81, 126.73, 126.69, 126.12, 122.79, 121.24. The analytical data match those reported in the literature⁵.

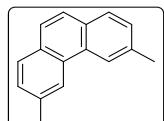


3-(tert-butyl)phenanthrene(I**)**.White solid, m.p. = 54.0-55.0°C;Substrate **16a** was irradiated for 1.2 h, 39.4 mg, 84% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.76 (d, *J* = 8.2 Hz, 1H), 8.73 (d, *J* = 1.1 Hz, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.78 – 7.65 (m, 4H), 7.61 (dd, *J* = 10.9, 3.9 Hz, 1H), 1.54 (s, 9H);¹³C NMR (151

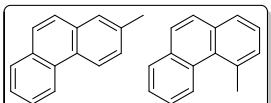
MHz, CDCl₃) δ 149.48, 132.35, 130.58, 130.09, 130.02, 128.75, 128.36, 126.67, 126.46, 126.44, 126.38, 125.06, 122.64, 118.38, 35.37, 31.69; GC-MS (EI): 234.2, 219.2, 202.1, 191.1, 178.1, 95.5. The analytical data match those reported in the literature⁹.



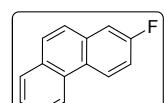
phenanthrene-3-carbonitrile (J). Substrate **17a** was irradiated for 2.0 h, 22.4 mg, 55% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.91 (s, 1H), 8.55 (d, *J* = 7.8 Hz, 1H), 8.05 – 7.81 (m, 3H), 7.80 – 7.60 (m, 4H); ¹³C NMR (151 MHz, CDCl₃) δ 134.27, 132.24, 130.41, 129.97, 129.51, 129.35, 128.96, 128.21, 127.97, 127.89, 127.76, 126.09, 122.60, 119.65, 109.78. The analytical data match those reported in the literature¹⁰.



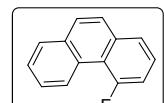
3,6-dimethylphenanthrene (K). Substrate **18a** was irradiated for 1.2 h, 27.6 mg, 67% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.49 (s, 2H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.66 (s, 2H), 7.43 (dd, *J* = 8.1, 1.0 Hz, 2H), 2.65 (s, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 136.13, 130.26, 130.19, 128.48, 128.28, 125.90, 122.49, 22.25. The analytical data match those reported in the literature¹¹.



2-methylphenanthrene (L)and 4-methylphenanthrene (L'). Substrate **19a** was irradiated for 2.0 h, 29.6 mg, the total yield of both the regioisomer is 77%, the ratio of **J/J'** is 4/3; ¹H NMR (400 MHz, CDCl₃) δ 8.96 (d, *J* = 8.2 Hz, 0.60H), 8.68 (d, *J* = 8.2 Hz, 1H), 8.60 (d, *J* = 8.4 Hz, 1H), 7.95 (dd, *J* = 7.6, 1.7 Hz, 0.60H), 7.93 – 7.88 (m, 1H), 7.84 – 7.79 (m, 0.6H), 7.77 – 7.47 (m, 9.6H), 3.19 (s, 1.8H), 2.59 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 136.43, 135.66, 133.86, 133.61, 132.32, 131.84, 131.80, 131.36, 130.47, 130.21, 128.84, 128.65, 128.46, 128.26, 128.14, 127.65, 127.58, 127.22, 127.04, 126.80, 126.60, 126.24, 126.01, 125.91, 125.70, 122.68, 122.58, 27.55, 21.60. The analytical data match those reported in the literature¹⁰.

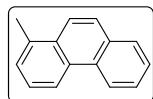


2-fluorophenanthrene (M). ¹H NMR (400 MHz, CDCl₃) δ 8.66 (dd, *J* = 9.1, 5.4 Hz, 1H), 8.62 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 8.9 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.60 (dd, *J* = 10.9, 4.0 Hz, 1H), 7.53 (dd, *J* = 9.4, 2.7 Hz, 1H), 7.40 (td, *J* = 8.7, 2.7 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 161.45 (d, *J* = 246.1 Hz), 133.57 (d, *J* = 8.8 Hz), 131.65 (d, *J* = 1.2 Hz), 130.25, 128.85, 128.38, 127.13, 127.05 (d, *J* = 2.0 Hz), 126.55 (d, *J* = 0.5 Hz), 126.27 (d, *J* = 3.7 Hz), 125.11 (d, *J* = 8.8 Hz), 122.58, 115.61 (d, *J* = 23.7 Hz), 112.70 (d, *J* = 20.5 Hz). The analytical data match those reported in the literature⁷.

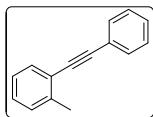


4-fluorophenanthrene (M'). Substrate **20a** was irradiated for 1.0 h, the total weight of **M** and **M'** is 29.1 mg, the total yield is 74 %, the ratio of **M/M'** is 8/1; ¹H NMR (400 MHz, CDCl₃) δ 9.21 – 9.07 (m, 1H), 7.92 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.82 – 7.60 (m, 5H), 7.54 (td, *J* = 7.9, 4.9 Hz, 1H), 7.37 (ddd, *J* = 14.2, 7.8, 1.2 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 161.63 (d, *J* = 253.0 Hz), 134.92 (d, *J* = 4.6 Hz), 132.65, 128.51 (d, *J* = 5.2 Hz), 128.41 (d, *J* = 1.1 Hz), 127.93, 127.77, 127.28 (d, *J* = 2.4 Hz), 126.94 (d, *J* = 2.1 Hz), 126.73 (d, *J* = 10.1 Hz), 126.59 (d, *J* = 3.1 Hz), 124.65 (d, *J* = 3.6 Hz), 119.66 (d, *J* = 9.2 Hz), 113.47 (d, *J* = 24.9 Hz). The analytical data match those reported in the literature¹².

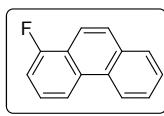
1-methylphenanthrene (N). ¹H NMR (400 MHz, CDCl₃) δ 8.72 (d, *J* = 8.3 Hz, 1H), 8.60 (d, *J* =



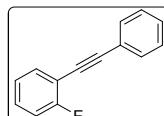
8.4 Hz, 1H), 7.97 (d, J = 9.1 Hz, 1H), 7.94 – 7.88 (m, 1H), 7.80 (d, J = 9.1 Hz, 1H), 7.72 – 7.52 (m, 3H), 7.46 (d, J = 7.1 Hz, 1H), 2.78 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 135.02, 131.78, 130.93, 130.78, 130.46, 128.61, 127.90, 126.82, 126.68, 126.55, 126.28, 123.08, 123.00, 121.00, 20.12. The analytical data match those reported in the literature¹³.



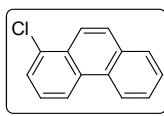
1-methyl-2-(phenylethynyl)benzene (N'). Substrate **21a** was irradiated for 2.3 h, the total weight of **N** and **N'** is 17.3 mg, the total yield is 45%, the ratio of **N/N'** is 3/5; ^1H NMR (400 MHz, CDCl_3) δ 7.60 – 7.52 (m, 2H), 7.50 (d, J = 7.4 Hz, 1H), 7.40 – 7.31 (m, 3H), 7.24 (d, J = 3.9 Hz, 2H), 7.18 (dq, J = 8.6, 4.1 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 140.33, 131.97, 131.65, 129.60, 128.49, 128.44, 128.32, 125.72, 123.67, 123.14, 93.46, 88.45, 20.90. The analytical data match those reported in the literature¹⁴.



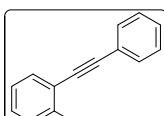
1-fluorophenanthrene (O). ^1H NMR (400 MHz, CDCl_3) δ 8.66 (d, J = 8.1 Hz, 1H), 8.46 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 9.1 Hz, 1H), 7.98 – 7.89 (m, 1H), 7.81 (d, J = 9.1 Hz, 1H), 7.74 – 7.54 (m, 3H), 7.30 (dd, J = 9.7, 8.2 Hz, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 159.43 (d, J = 249.9 Hz), 132.29 (d, J = 4.3 Hz), 132.21, 129.77 (d, J = 2.6 Hz), 128.93, 127.53 (d, J = 1.9 Hz), 127.26, 127.15, 126.62 (d, J = 8.7 Hz), 123.16, 121.70 (d, J = 15.4 Hz), 118.66 (d, J = 7.0 Hz), 118.54 (d, J = 3.8 Hz), 111.16 (d, J = 20.3 Hz). The analytical data match those reported in the literature¹⁵.



1-fluoro-2-(phenylethynyl)benzene (O'). Substrate **22a** was irradiated for 1.0 h, the total weight of **O** and **O'** is 36.5 mg, the total yield is 93%, the ratio of **O/O'** is 3/1; ^1H NMR (400 MHz, CDCl_3) δ 7.65 – 7.49 (m, 3H), 7.43 – 7.28 (m, 4H), 7.20 – 7.06 (m, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 162.74 (d, J = 251.6 Hz), 133.56, 131.82, 130.09 (d, J = 7.9 Hz), 128.72, 128.49, 124.09 (d, J = 3.7 Hz), 123.00, 115.65 (d, J = 20.9 Hz), 112.02 (d, J = 15.7 Hz), 94.53 (d, J = 3.2 Hz), 82.80. The analytical data match those reported in the literature¹⁴.

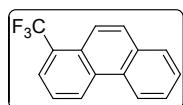


1-chlorophenanthrene (P). ^1H NMR (400 MHz, CDCl_3) δ 8.68 (d, J = 8.1 Hz, 1H), 8.64 (d, J = 8.3 Hz, 1H), 8.24 (d, J = 9.2 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 9.2 Hz, 1H), 7.67 (tdd, J = 15.8, 10.7, 5.2 Hz, 3H), 7.57 (t, J = 8.0 Hz, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 132.85, 132.04, 132.03, 130.07, 129.47, 128.86, 128.36, 127.33, 127.22, 127.21, 126.59, 123.11, 122.65, 121.78. The analytical data match those reported in the literature⁵.

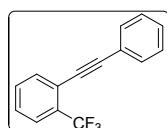


1-chloro-2-(phenylethynyl)benzene (P'). Substrate **23a** was irradiated for 1.8 h, the total weight of **P** and **P'** is 29.7 mg, the total yield is 70%, the ratio of **P/P'** is 6/5; ^1H NMR (400 MHz, CDCl_3) δ 7.61 – 7.53 (m, 3H), 7.45 – 7.40 (m, 1H), 7.38 – 7.33 (m, 3H), 7.28 – 7.20 (m, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 136.05, 133.35, 131.87, 129.43, 129.39, 128.78, 128.51, 126.59, 123.33, 123.02, 94.65, 86.29. The analytical data match those reported in the literature¹⁶.

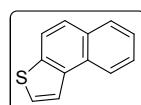
1-(trifluoromethyl)phenanthrene (Q). White solid, m.p. = 55.2–56.7°C; ^1H NMR (400 MHz,



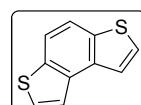
CDCl_3) δ 8.93 (d, $J = 8.4$ Hz, 1H), 8.71 (d, $J = 8.3$ Hz, 1H), 8.12 (dd, $J = 9.3$, 1.9 Hz, 1H), 8.02 – 7.87 (m, 3H), 7.76 – 7.63 (m, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 131.66, 131.37, 130.04, 129.03, 128.81, 128.46, 127.53, 127.41, 127.05, 126.87 (q, $J = 29.9$ Hz), 125.26, 124.99 (q, $J = 273.8$ Hz), 124.96 (q, $J = 6.0$ Hz), 122.95, 122.24 (q, $J = 2.7$ Hz); GC-MS (EI): 246.1, 225.1, 196.1, 176.1, 150.0, 69.0; HRMS (ESI): calc. for $\text{C}_{15}\text{H}_{10}\text{F}_3$ $[\text{M}+\text{H}]^+$: 247.0729, found: 247.0726.



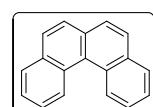
1-(phenylethynyl)-2-(trifluoromethyl)benzene(Q'). Substrate **24a** was irradiated for 2.0 h, the total weight of **Q** and **Q'** is 24.6 mg, the total yield is 50%, the ratio of **Q/Q'** is 1/7; ^1H NMR (400 MHz, CDCl_3) δ 7.69 (t, $J = 7.4$ Hz, 2H), 7.57 (dd, $J = 6.5$, 3.0 Hz, 2H), 7.52 (t, $J = 7.7$ Hz, 1H), 7.46 – 7.34 (m, 4H); ^{13}C NMR (151 MHz, CDCl_3) δ 133.84, 131.84, 131.65 (q, $J = 30.3$ Hz), 131.54, 128.97, 128.54, 128.06, 126.03 (q, $J = 5.0$ Hz), 123.77 (d, $J = 273.4$ Hz), 122.87, 121.71 (q, $J = 2.0$ Hz), 95.07, 85.50. The analytical data match those reported in the literature¹⁴.



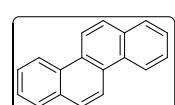
naphtho[2,1-b]thiophene (R). Substrate **25a** was irradiated for 2.5 h, 12.9 mg, 35% yield; Substrate **26a** was irradiated for 3.0 h, 18.4 mg, 50% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.35 (d, $J = 8.2$ Hz, 1H), 8.04 – 7.87 (m, 3H), 7.76 (d, $J = 8.8$ Hz, 1H), 7.59 (tt, $J = 14.8$, 7.2 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 137.39, 135.94, 130.98, 129.36, 128.56, 126.48, 125.84, 125.30, 125.07, 123.62, 122.04, 120.70. The analytical data match those reported in the literature⁵.



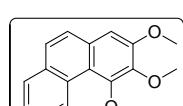
benzo[1,2-b:4,3-b']dithiophene(S). White solid, m.p.= 112.3-113.8 °C; Substrate **27a** was irradiated for 2.5 h, 22.1 mg, 58% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.83 (s, 2H), 7.72 (d, $J = 5.4$ Hz, 2H), 7.57 (d, $J = 5.4$ Hz, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 136.54, 134.75, 126.61, 122.04, 118.88; GC-MS (EI): 190.0, 158.0, 145.0, 114.1, 95.0; HRMS (ESI): calc. for $\text{C}_{10}\text{H}_6\text{NaS}_2$ $[\text{M}+\text{Na}]^+$: 212.9803, found: 212.9798.



benzo[c]phenanthrene (T). Substrate **28a** was irradiated for 3.0 h, 16.9 mg, 37% yield; ^1H NMR (400 MHz, CDCl_3) δ 9.16 (d, $J = 8.4$ Hz, 2H), 8.04 (d, $J = 7.8$ Hz, 2H), 7.92 (d, $J = 8.5$ Hz, 2H), 7.85 (d, $J = 8.5$ Hz, 2H), 7.68 (dt, $J = 14.7$, 7.1 Hz, 4H); ^{13}C NMR (151 MHz, CDCl_3) δ 133.62, 131.11, 130.43, 128.68, 128.03, 127.60, 127.47, 126.98, 126.26, 125.98. The analytical data match those reported in the literature⁶.

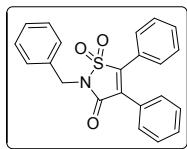


chrysene (U). Substrate **29a** was irradiated for 2.5 h, 11.5 mg, 25% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.80 (d, $J = 8.4$ Hz, 2H), 8.74 (d, $J = 9.0$ Hz, 2H), 8.02 (t, $J = 7.6$ Hz, 4H), 7.77 – 7.69 (m, 2H), 7.65 (dd, $J = 10.9$, 4.0 Hz, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 132.31, 130.70, 128.71, 128.36, 127.49, 126.82, 126.52, 123.30, 121.36. The analytical data match those reported in the literature⁶.

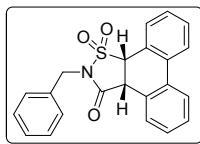


2,3,4-trimethoxyphenanthrene (V). Substrate **30a** (0.31g, 0.8mmol) was irradiated for 3.5 h, 0.11g, 50% yield; ^1H NMR (600 MHz, CDCl_3) δ 9.52 (d, $J = 8.6$ Hz, 1H), 7.86 (d, $J = 7.7$ Hz, 1H), 7.73 – 7.59 (m, 3H), 7.55 (dd, $J = 10.8$, 3.9 Hz, 1H), 7.11 (s, 1H), 4.11 – 3.98 (m, 9H); ^{13}C NMR (151 MHz, CDCl_3) δ 152.64,

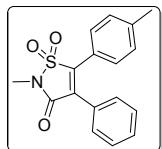
152.55, 142.93, 131.93, 130.27, 129.99, 128.55, 127.29, 126.86, 126.84, 126.60, 125.65, 119.03, 105.30, 61.42, 60.42, 55.98. The analytical data match those reported in the literature¹⁷.



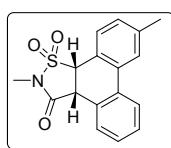
2-benzyl-4,5-diphenylisothiazol-3(2H)-one 1,1-dioxide (2c). White solid, m.p. = 164.5–165.9°C. Substrate **2a** was irradiated for 0.2 h; ¹H NMR (400 MHz, CDCl₃) δ 7.58 – 7.50 (m, 4H), 7.49 – 7.31 (m, 11H), 4.91 (s, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 160.38, 144.13, 134.50, 132.79, 131.62, 130.58, 130.35, 129.56, 129.45, 129.10, 128.87, 128.86, 128.51, 127.12, 124.92, 43.64; GC-MS (EI): 375.1, 311.2, 282.1, 234.1, 178.1, 91.1. HRMS (ESI): calc. for C₂₂H₁₅NNaO₃S [M+Na]⁺: 398.0821, found: 398.0817.



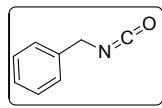
(3aR,11bS)-2-benzyl-3a,11b-dihydrophenanthro[9,10-d]isothiazol-3(2H)-one 1,1-dioxide(2d). White solid, m.p. = 143.9–145.2°C; Substrate **2a** was irradiated for 0.2 h. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (dd, J = 15.9, 7.8 Hz, 2H), 7.68 (d, J = 7.8 Hz, 1H), 7.60 – 7.51 (m, 2H), 7.45 – 7.39 (m, 2H), 7.38 – 7.26 (m, 6H), 5.07 (d, J = 8.5 Hz, 1H), 4.83 – 4.73 (m, 2H), 4.61 (d, J = 8.5 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 167.20, 134.57, 134.16, 131.47, 131.39, 131.00, 129.28, 129.14, 128.85, 128.77, 128.53, 128.28, 127.11, 125.45, 124.81, 124.30, 120.44, 63.00, 44.62, 44.02; GC-MS (EI): 311.1, 205.0, 177.1, 151.0, 91.1; HRMS (ESI): calc. for C₂₂H₁₅NNaO₃S [M+Na]⁺: 398.0821, found: 398.0819.



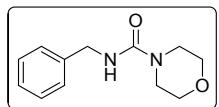
2-methyl-4-phenyl-5-(p-tolyl)isothiazol-3(2H)-one 1,1-dioxide (7c). White solid, m.p. = 173.0–174.2°C. Substrate **14a** was irradiated for 0.2 h; ¹H NMR (600 MHz, CDCl₃) δ 7.45 – 7.40 (m, 3H), 7.40 – 7.36 (m, 4H), 7.18 (d, J = 8.1 Hz, 2H), 3.27 (s, 3H), 2.37 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 160.44, 144.32, 142.42, 132.22, 130.46, 130.24, 130.21, 129.41, 128.91, 127.45, 121.91, 24.27, 21.76; GC-MS (EI): 313.1, 298.0, 248.0, 192.1, 132.1, 119.0; HRMS (ESI): calc. for C₁₇H₁₅NNaO₃S [M+Na]⁺: 336.0665, found: 336.0669.



(3aR,11bS)-2,9-dimethyl-3a,11b-dihydrophenanthro[9,10-d]isothiazol-3(2H)-one 1,1-dioxide(7d). White solid, m.p. = 207.2–208.7°C; Substrate **7a** was irradiated for 0.2 h. ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 7.8 Hz, 1H), 7.81 (s, 1H), 7.73 (d, J = 7.7 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.34 (t, J = 7.2 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 5.01 (d, J = 8.7 Hz, 1H), 4.58 (d, J = 8.6 Hz, 1H), 3.13 (s, 3H), 2.47 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 167.22, 141.46, 133.71, 131.41, 130.81, 129.67, 129.13, 129.01, 127.17, 125.60, 125.49, 124.08, 117.33, 62.47, 44.74, 25.10, 21.88; GC-MS (EI): 249.1, 219.1, 191.1, 165.1, 123.6, 94.7; HRMS (ESI): calc. for C₁₇H₁₅NNaO₃S [M+Na]⁺: 336.0665, found: 336.0673.



(isocyanatomethyl)benzene (2e). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.36 (m, 2H), 7.33 (dd, J = 6.9, 4.3 Hz, 3H), 4.50 (s, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 137.01, 128.96, 128.08, 126.84, 46.62; GC-MS (EI): 133.0, 104.0, 91.1, 77.0, 32.0, 28.1.

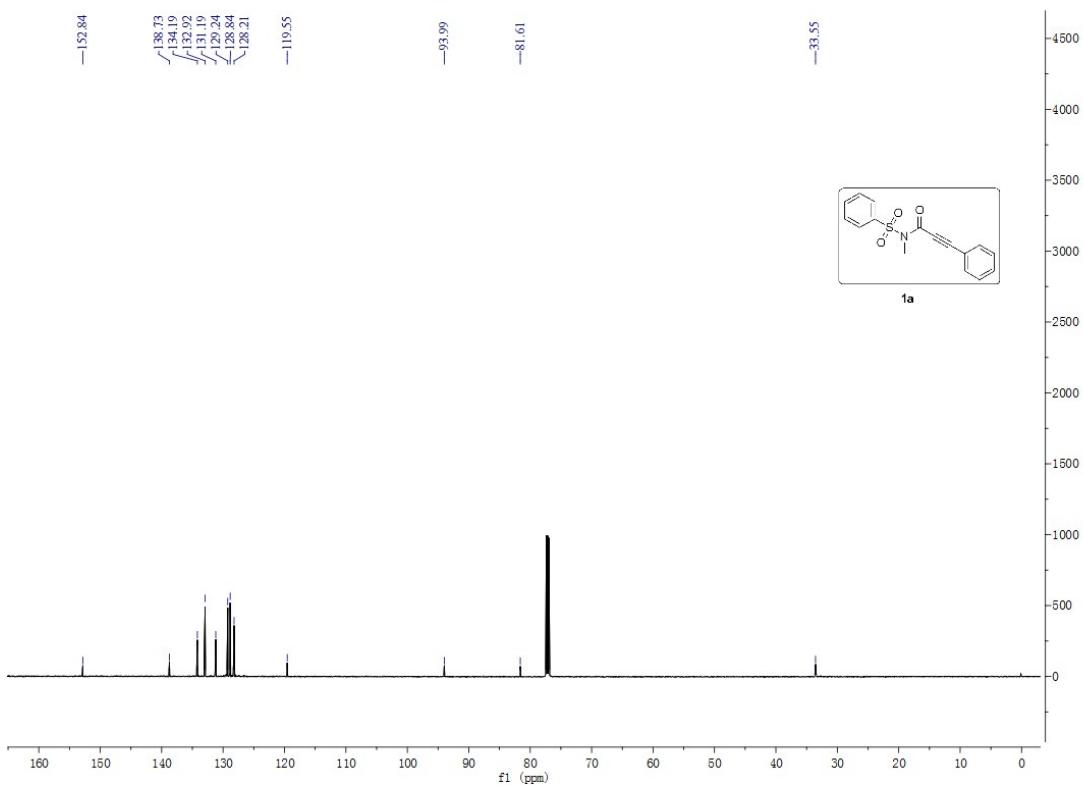
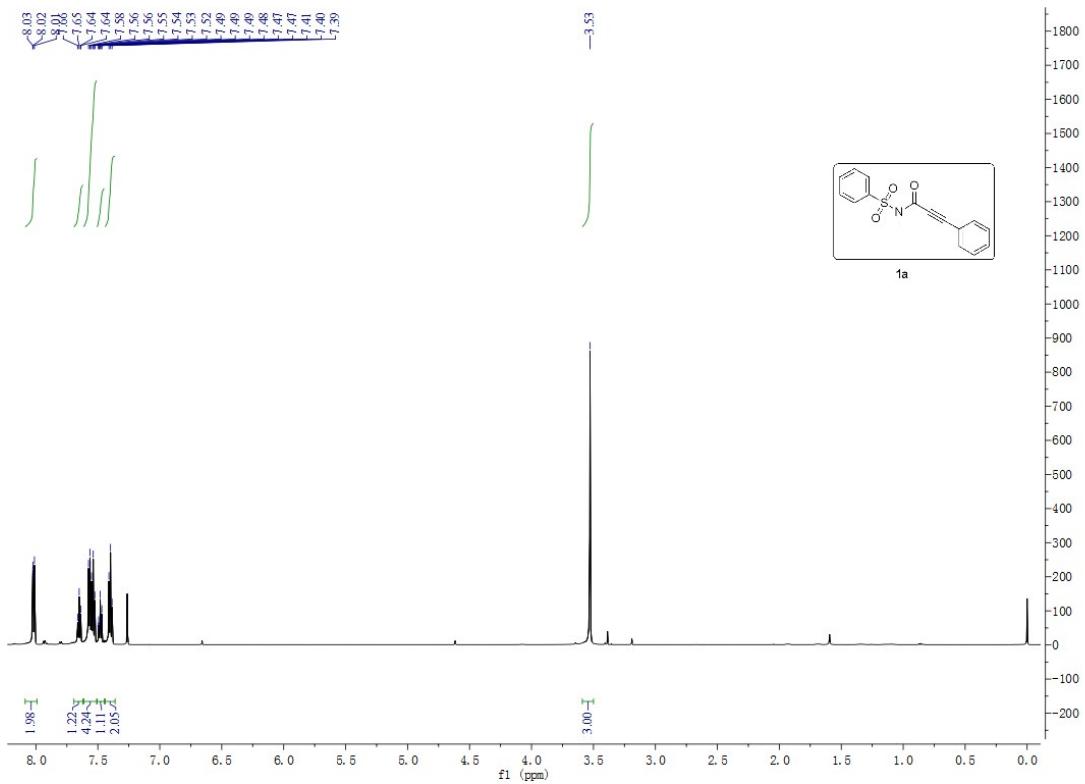


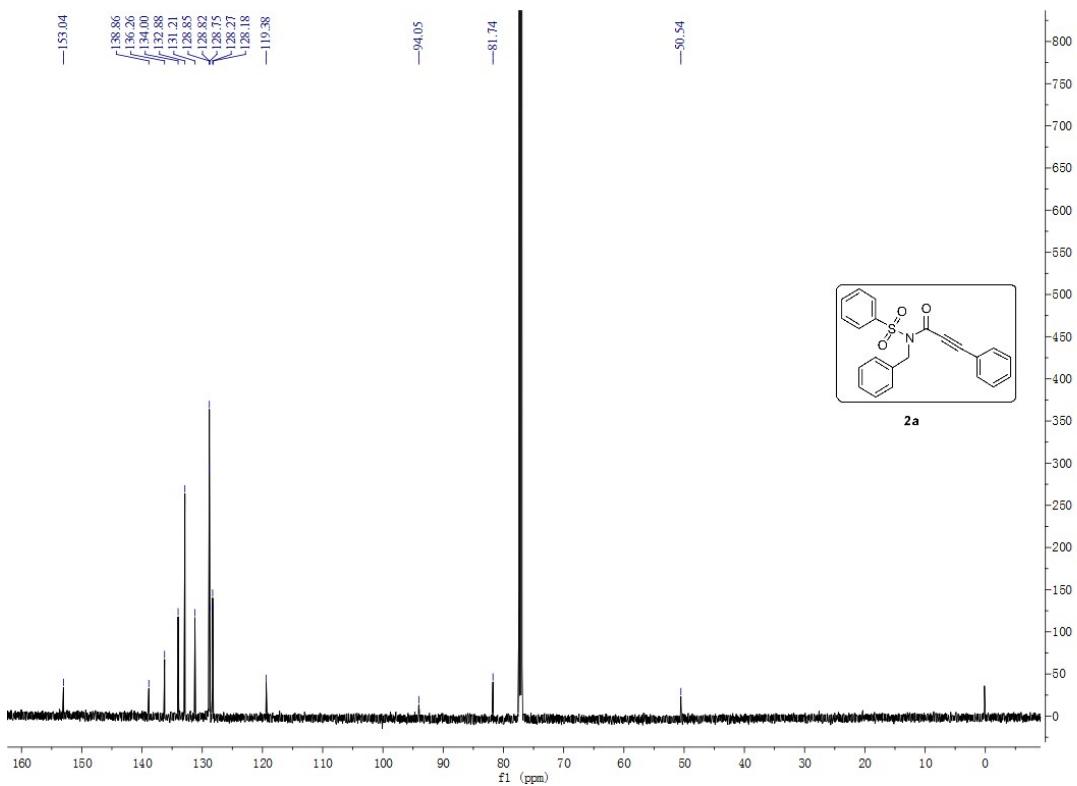
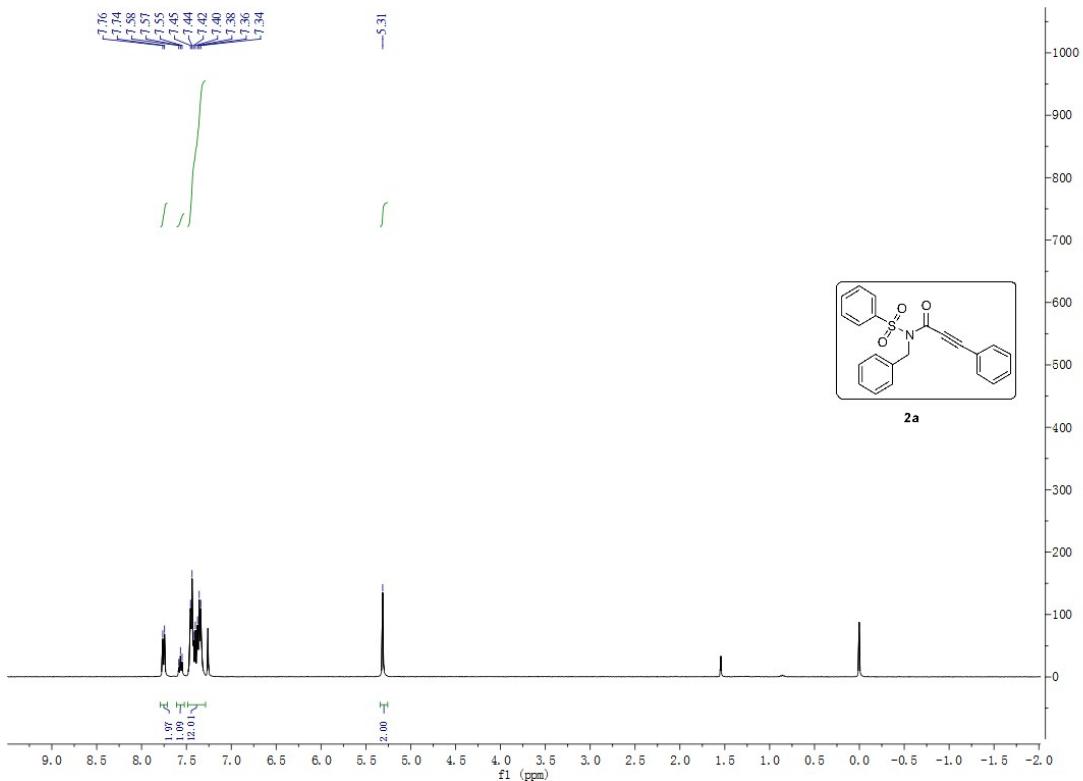
N-benzylmorpholine-4-carboxamide (2f). Brown solid, m.p.= 138.2–139.8°C, 40% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.24 (m, 5H), 4.75 (s, 1H), 4.43 (d, *J*= 5.5 Hz, 2H), 3.72 – 3.62 (m, 4H), 3.40 – 3.31 (m, 4H); ¹³C NMR (151 MHz, CDCl₃) δ 156.78, 138.30, 127.80, 126.93, 126.55, 65.61, 44.11, 43.14; GC-MS (EI): 220.1, 189.1, 133.0, 91.1, 57.1; HRMS (ESI): calc. for C₁₂H₁₇N₂O₂ [M+H]⁺= 221.1285; found: 221.1286. The analytical data match those reported in the literature¹⁸.

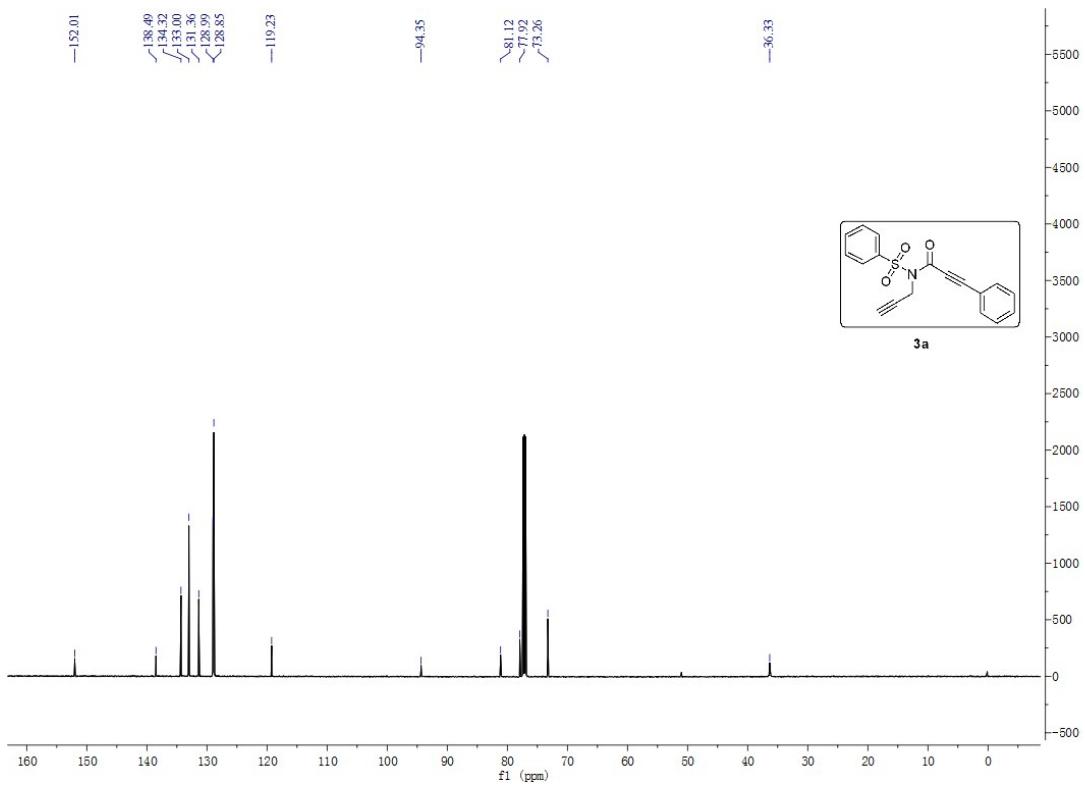
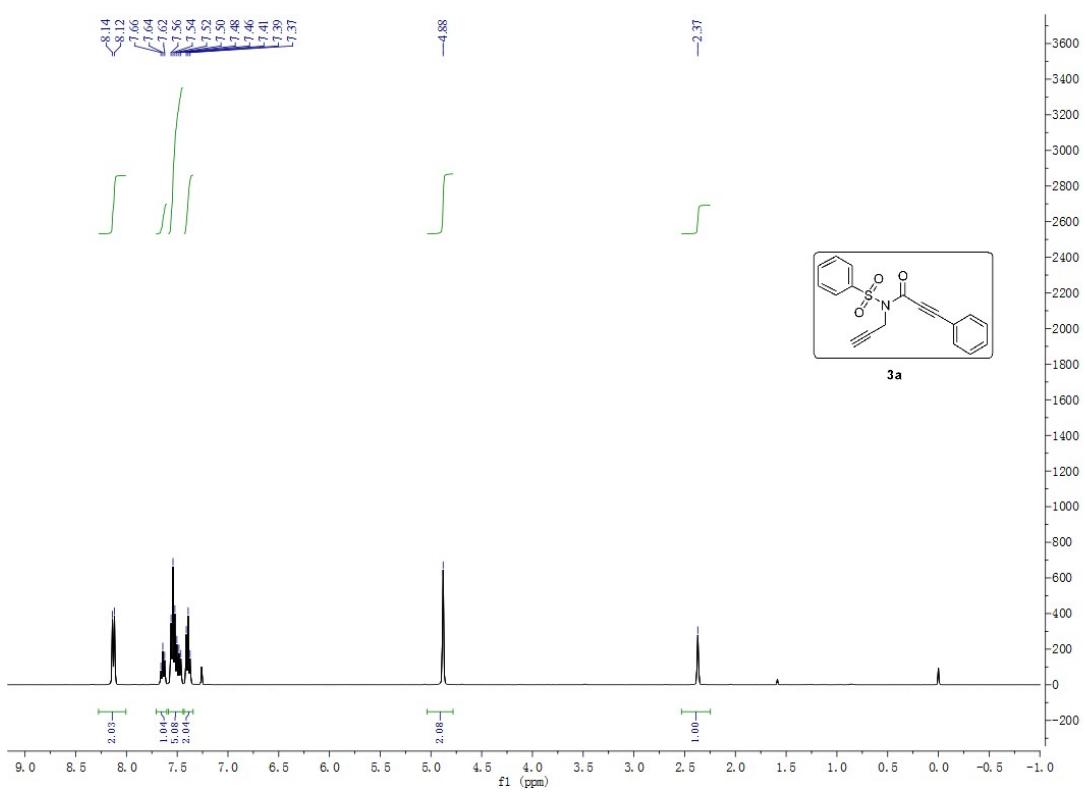
6. Reference

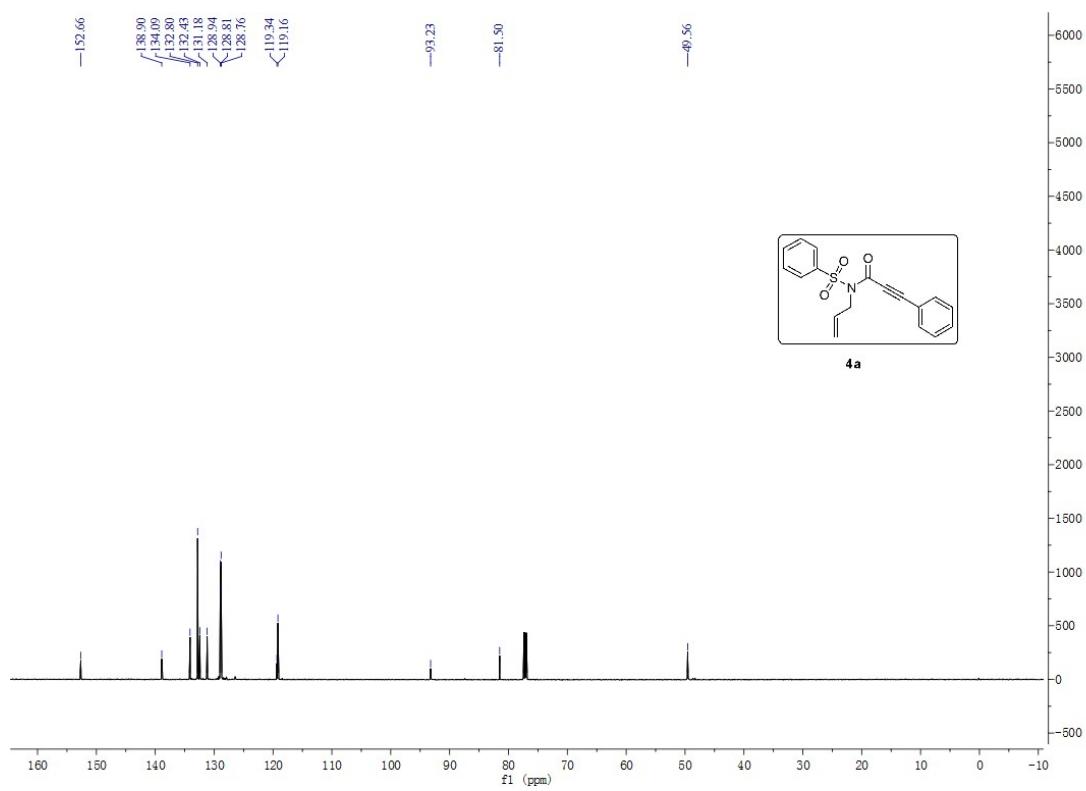
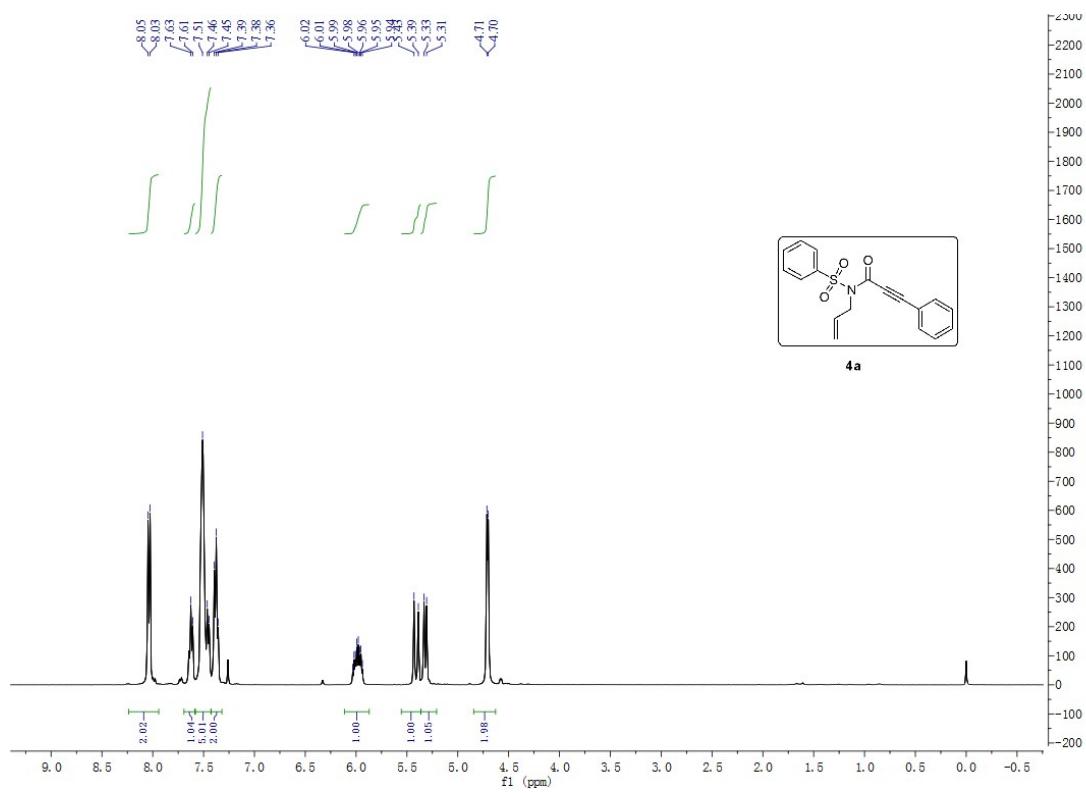
- 1K.Park,T.Palani,A.Pyo,S.Lee, *Tetrahedron Lett.*,2012,**53**, 733.
- 2K.Park,J. M. You,S.Jeon,S.Lee, *Eur. J. Org. Chem.*, 2013,**2013**, 1973.
- 3A. K.Ganguly,S. S.Alluri,D.Caroccia,D.Biswas,C. H.Wang,E.Kang,C.Strickland, *J. Med. Chem.*,2011,**54**,7176.
- 4a) D.Campolo,T.Arif,C.Borie,D.Mouysset,N.Vanthuyne,J. V.Naubron,M.Nechab, *Angew. Chem. Int. Ed.*,2014, **53**, 3227;b) B.Nyasse,L.Grehn,U.Ragnarsson,H.L.S.Maia,L.S.Monteiro,I.Leito,I.Koppel,J.Koppel, *J. Chem. Soc., Perkin Trans. 1* 1995, 2025.
- 5Y.Xia,Z.Liu,Q.Xiao,P.Qu,R.Ge,Y.Zhang,J.Wang, *Angew. Chem. Int. Ed.*,2012, **51**, 5714.
- 6M.Murai,N.Hosokawa,D.Roy,K.Takai, *Org. Lett.*,2014, **16**,4134.
- 7Y.Yamamoto,K.Matsui,M.Shibuya, *Chem. Eur. J.*, 2015,**21**, 7245.
- 8Q.Lefebvre,M.Jentsch,M.Rueping, *Beilstein J. Org. Chem.*,2013, **9**, 1883.
- 9D. W. Cameron and M. Mingin, *Aust. J. Chem.*, 1977, **30**, 859.
- 10H.Li,K. H.He,J.Liu,B. Q.Wang,K. Q.Zhao,P.Hu,Z. J. Shi, *Chem. Commun.*, 2012, **48**, 7028.
- 11S.Moussa,F.Aloui, B.Ben Hassine, *Synth.Commun.*, 2011, **41**, 1006.
- 12M. Yokota, D. Fujita and J. Ichikawa, *Org. Lett.*, 2007, **9**, 4639.
- 13W.Krasodomski,M. K.Luczynski,J.Wilamowski,J. J. Sepiol, *Tetrahedron*, 2003, **59**, 5677.
- 14M. Rubin, A. Trofimov and V. Gevorgyan, *J. Am. Chem. Soc.*, 2005, **127**, 10243.
- 15Z. Li and R. J. Twieg, *Chem. Eur. J.*, 2015, **21**,15534.
- 16M. R. Eberhard, Z. Wang and C. M. Jensen, *Chem. Commun.*, 2002, 818.
- 17V.Mamane,P.Hannen,A.Fürstner, *Chem. Eur. J.*, **2004**, 10, 4556 – 4575.
- 18A.Yagodkin,K.Löschcke,J.Weisell,A. Azhayev, *Tetrahedron*, **2010**, 66, 2210-2221.

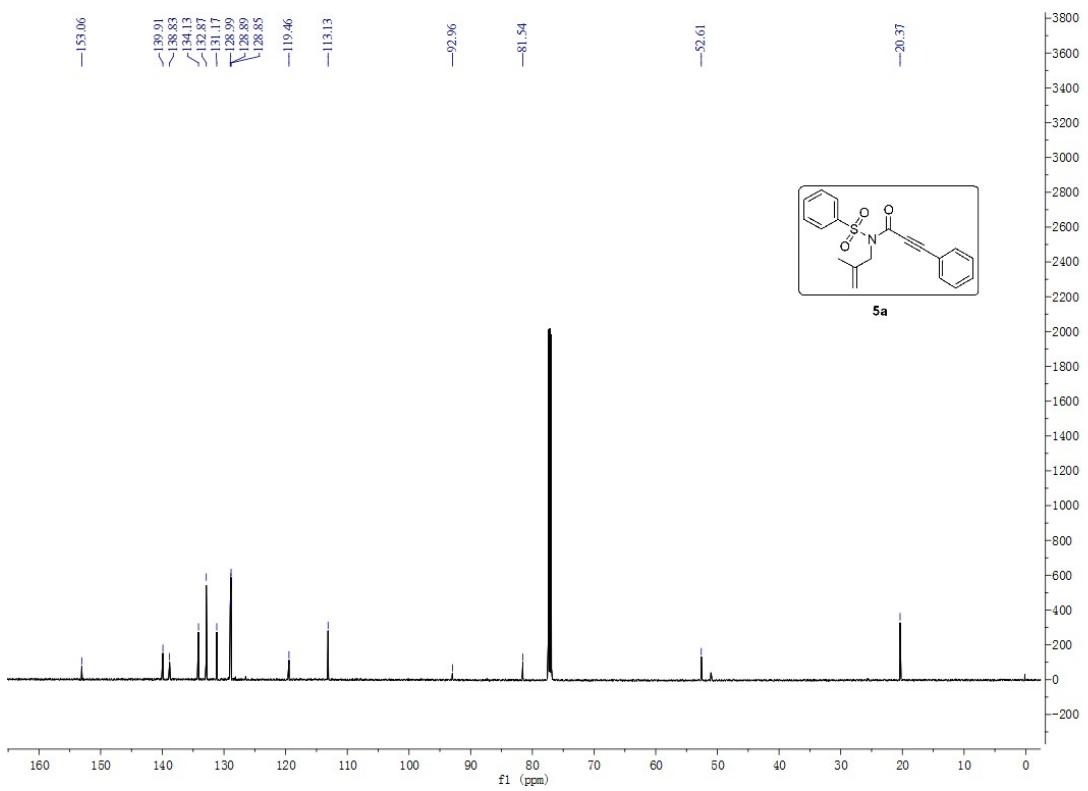
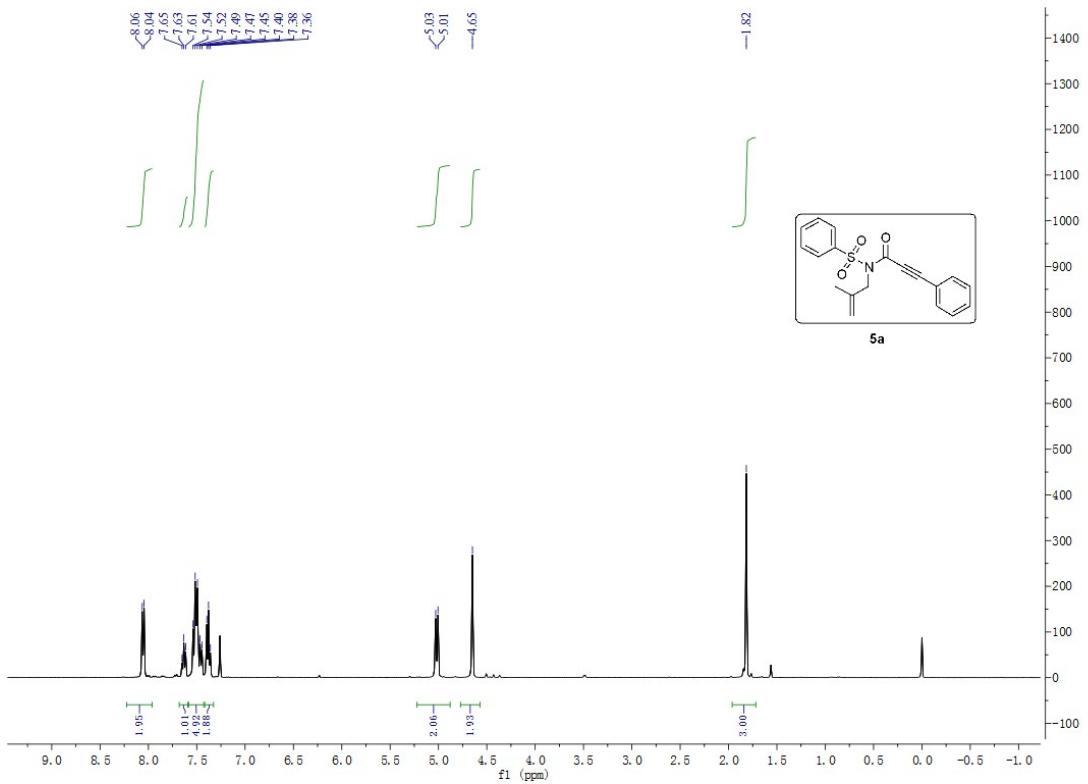
7. ¹H and ¹³C spectrum for all the related compounds

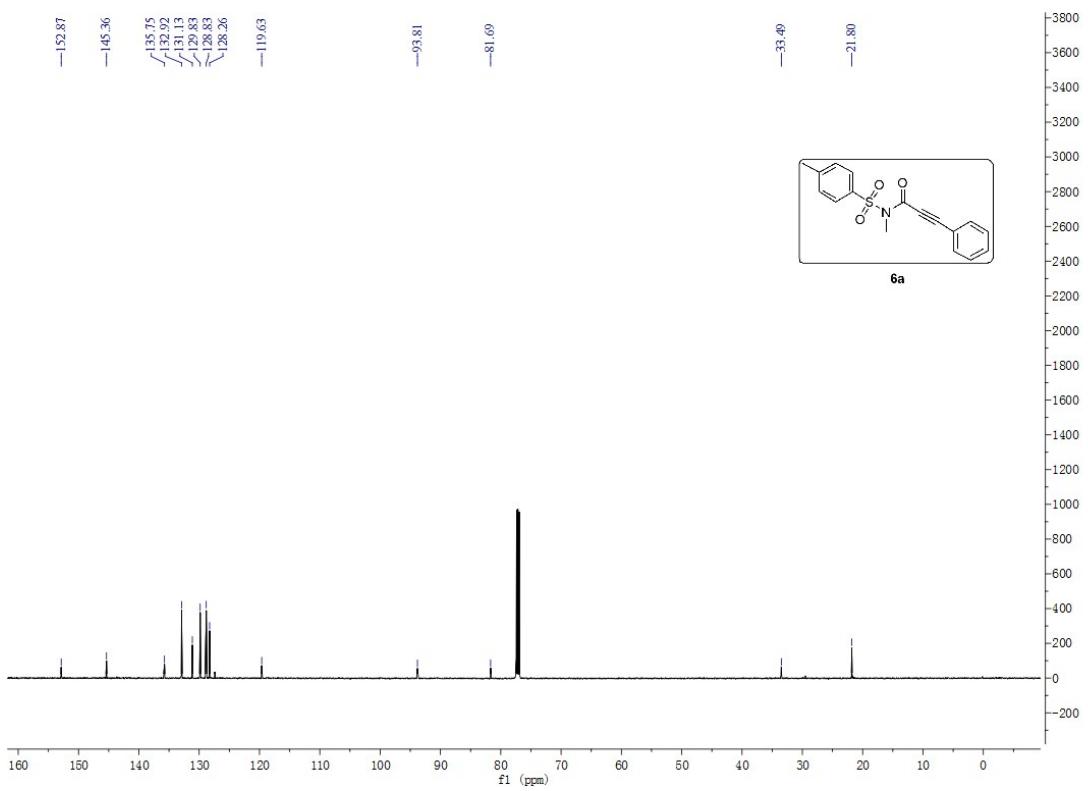
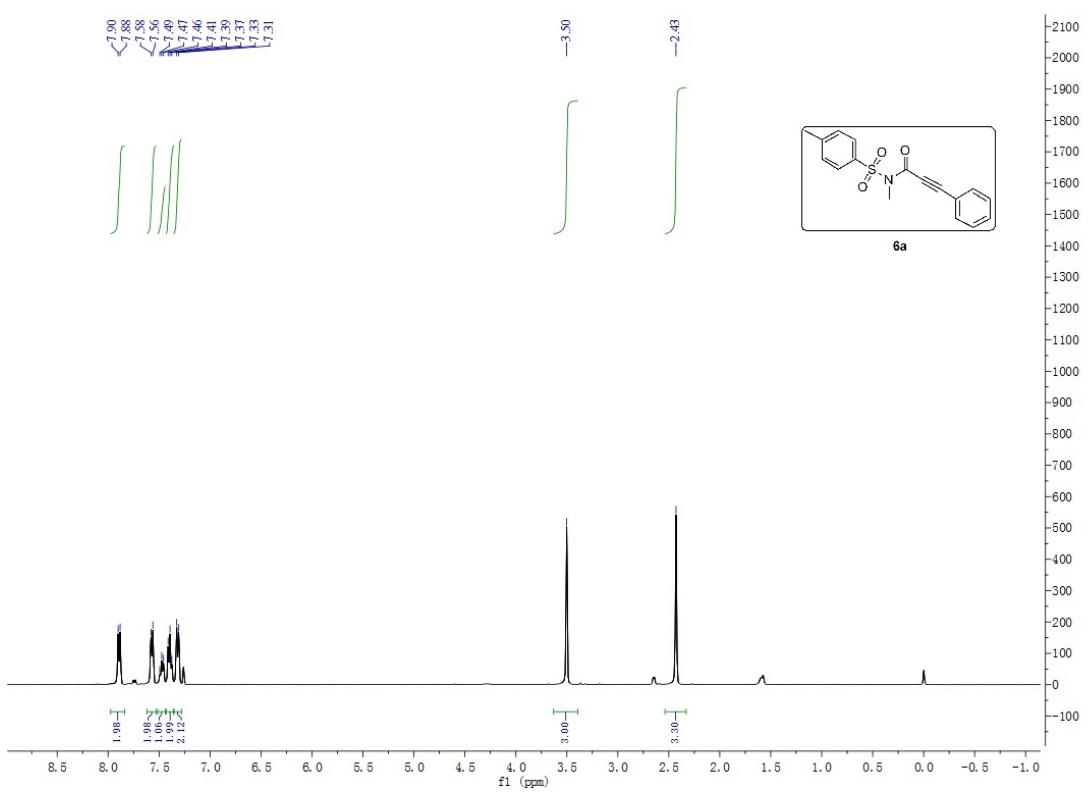


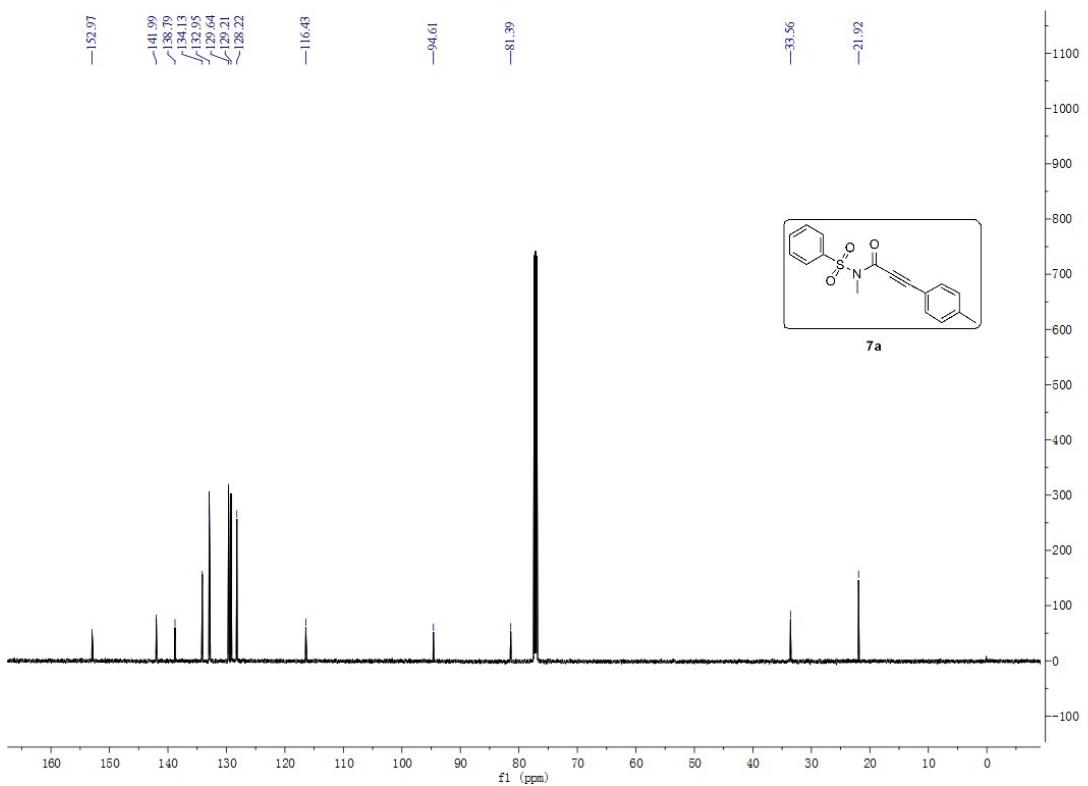
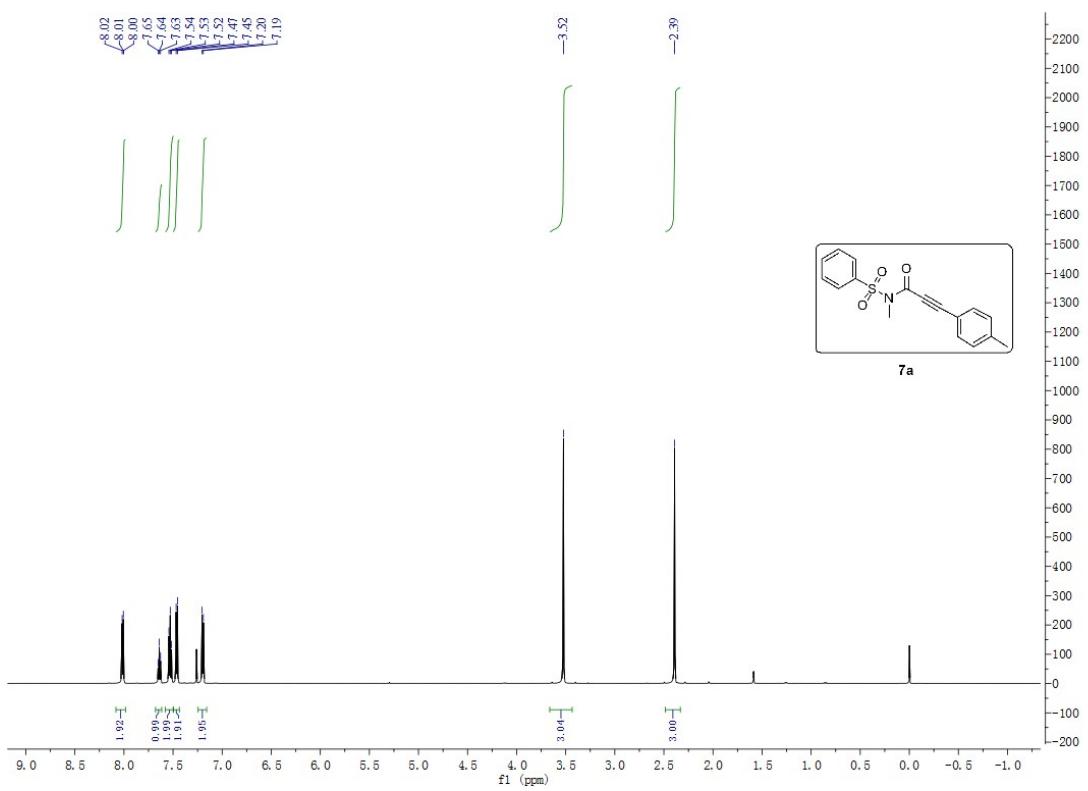


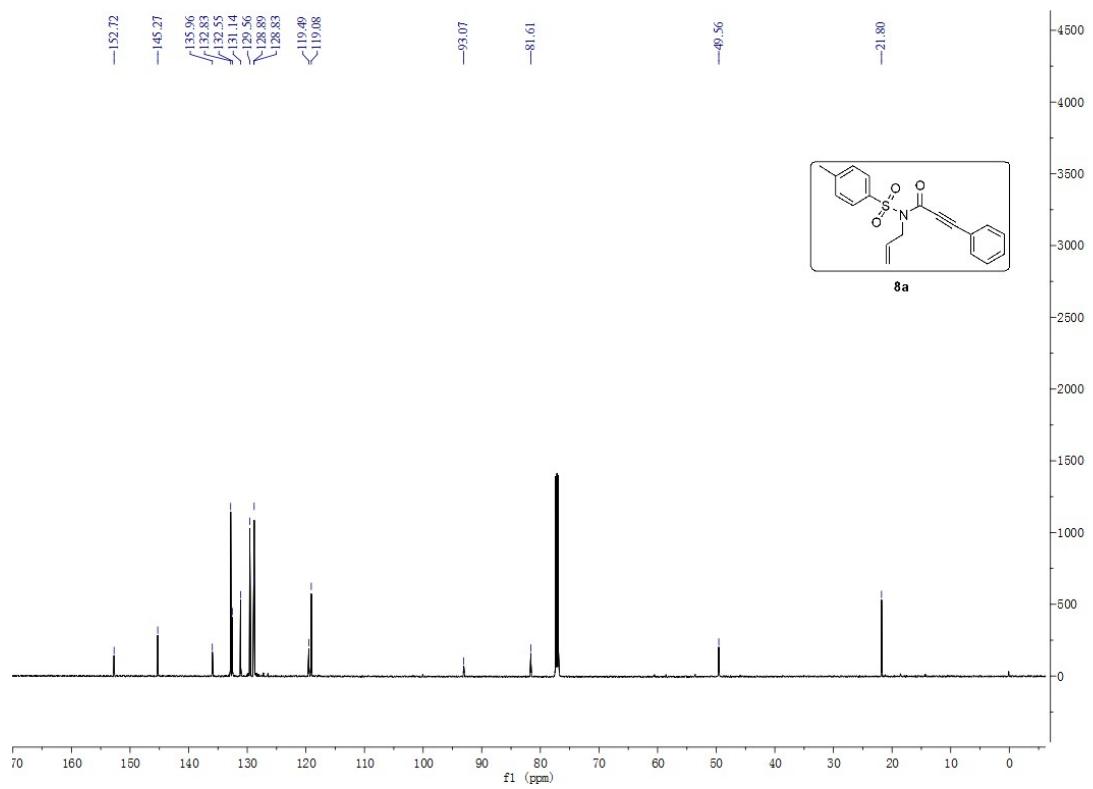
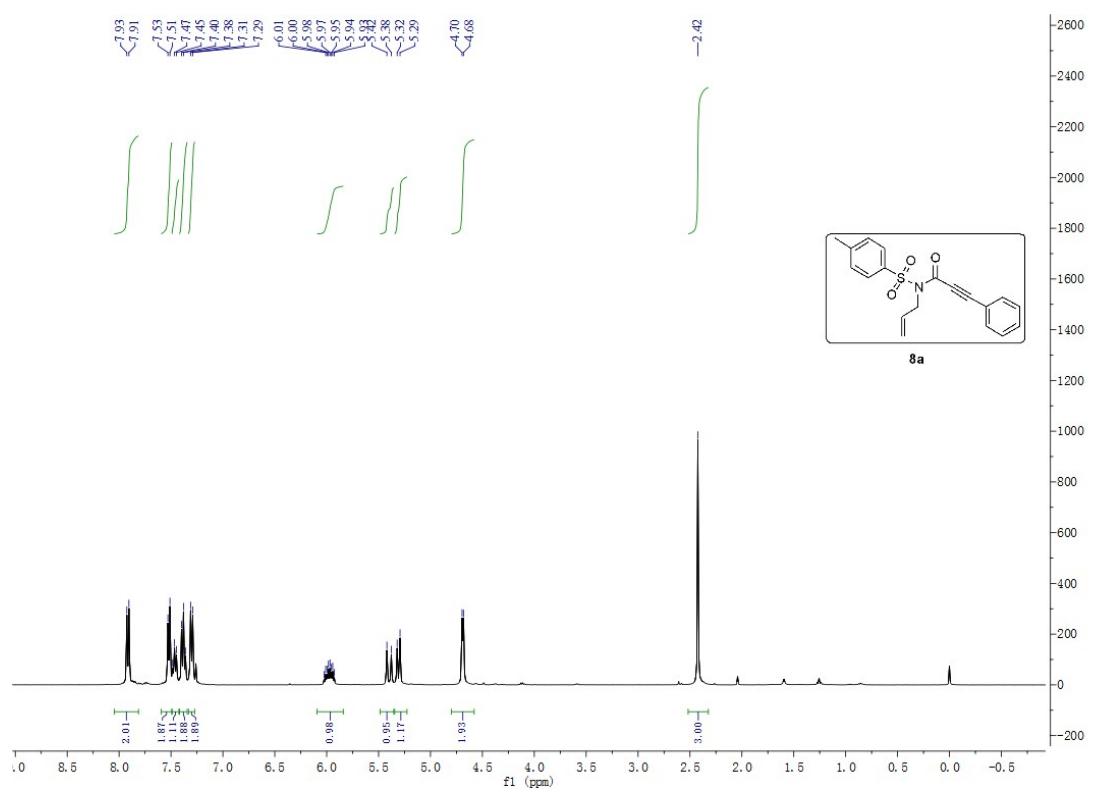


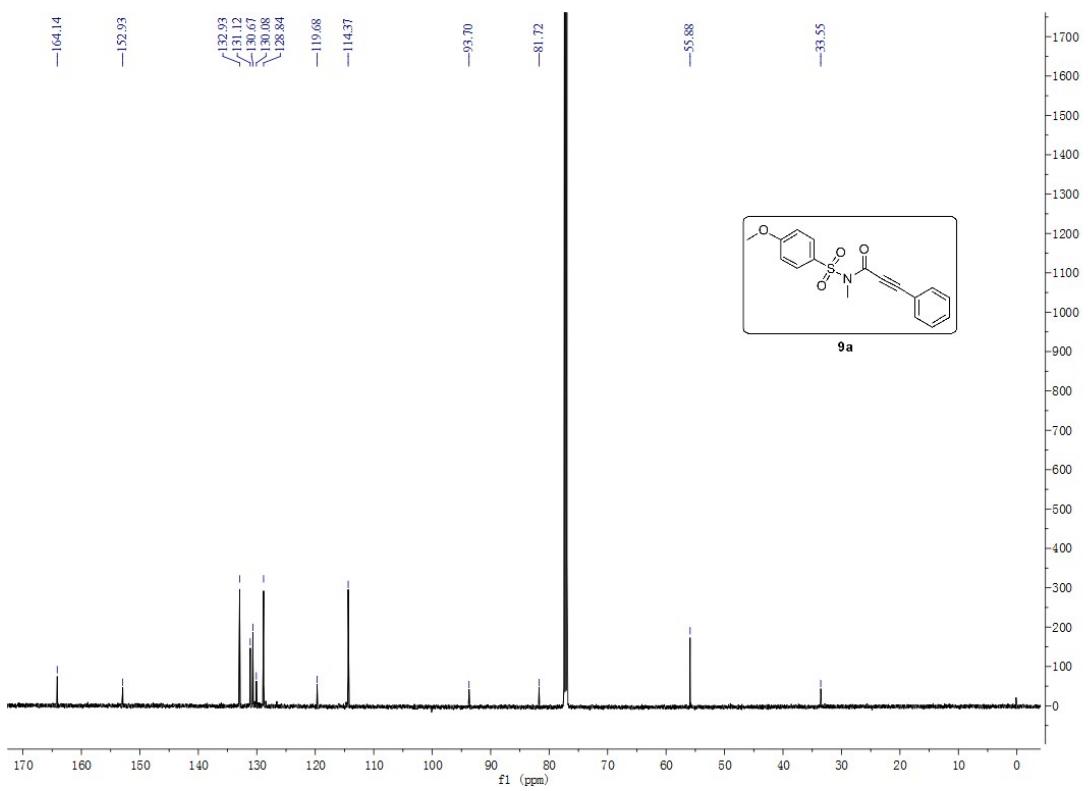
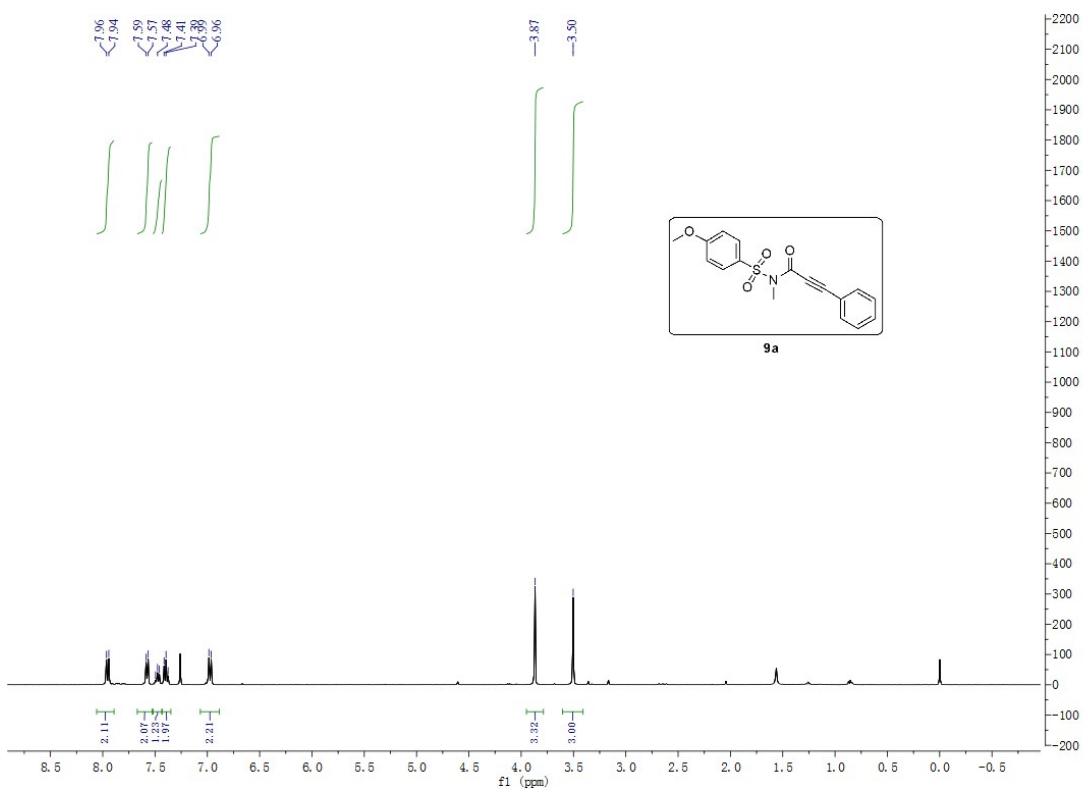


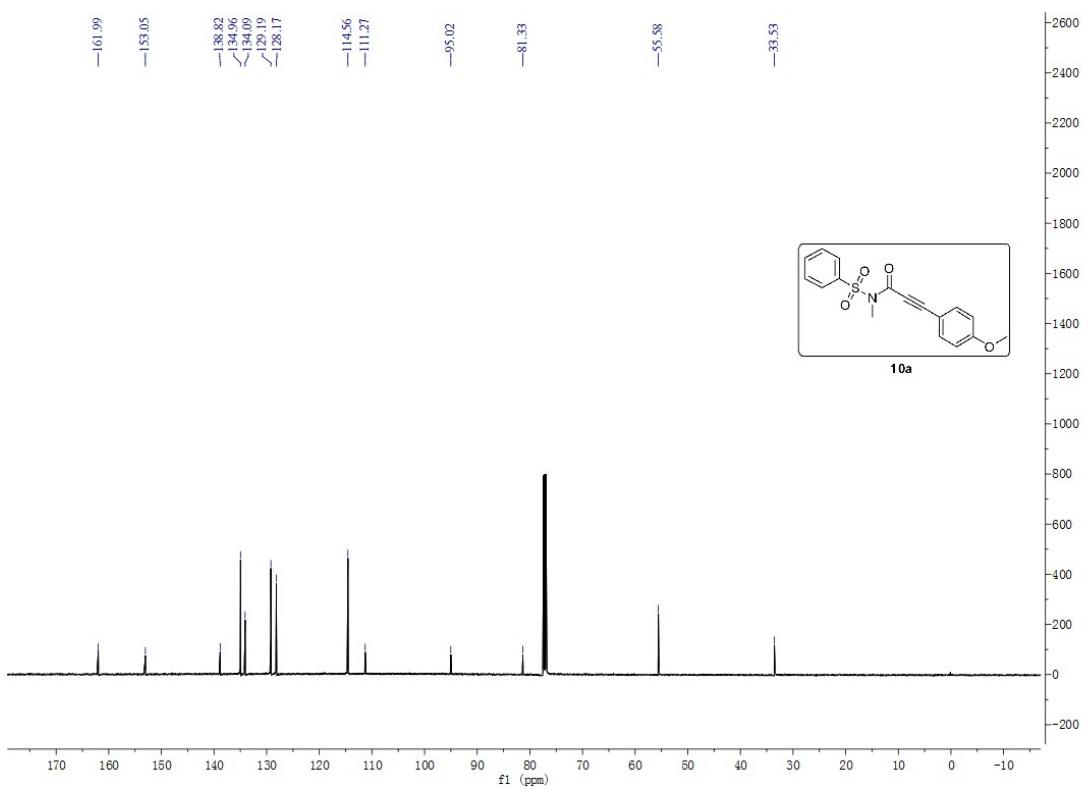
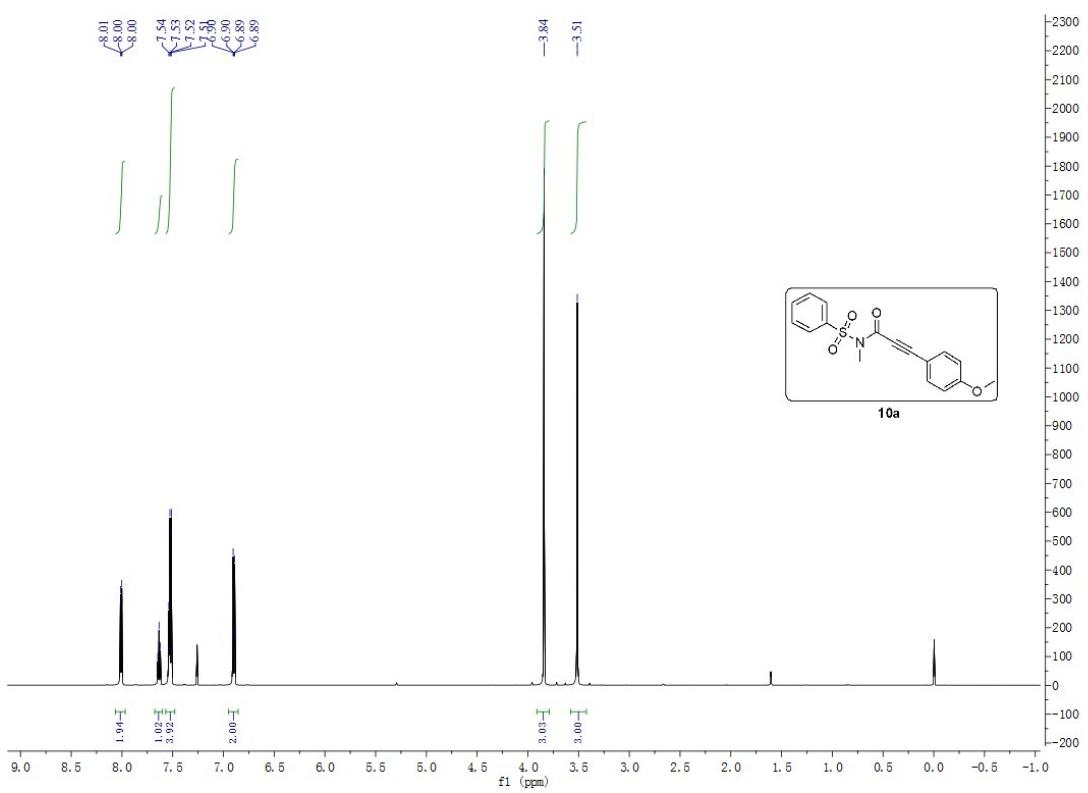


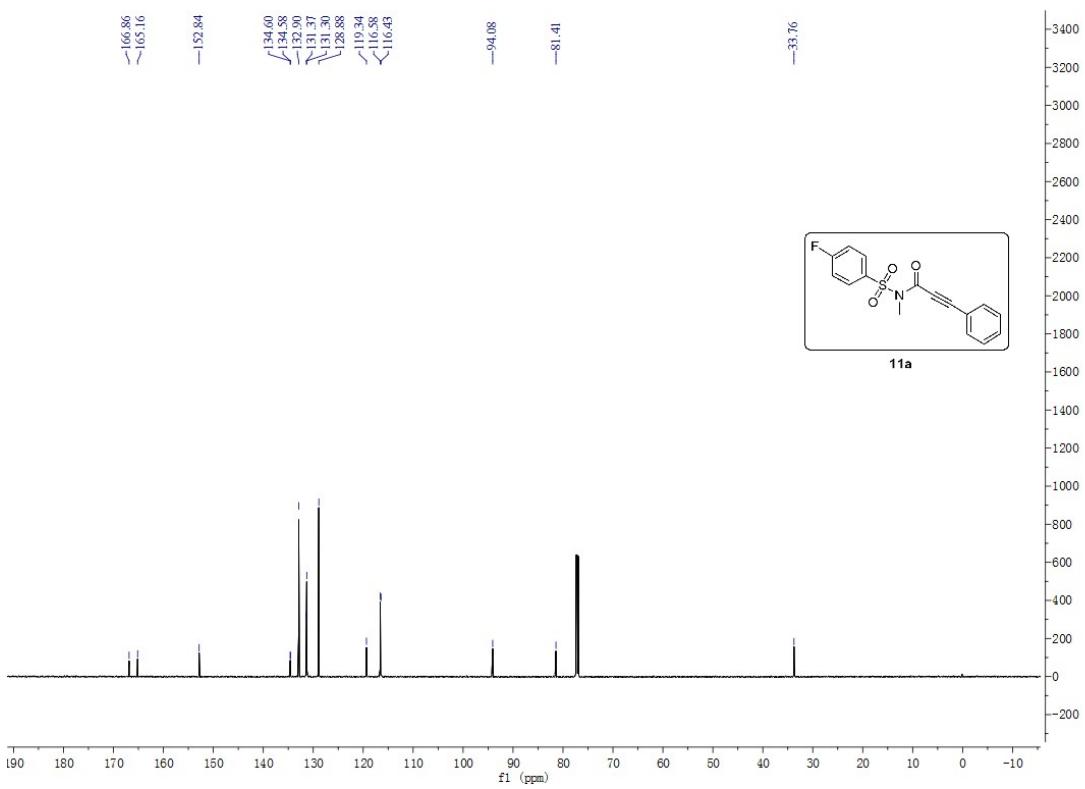
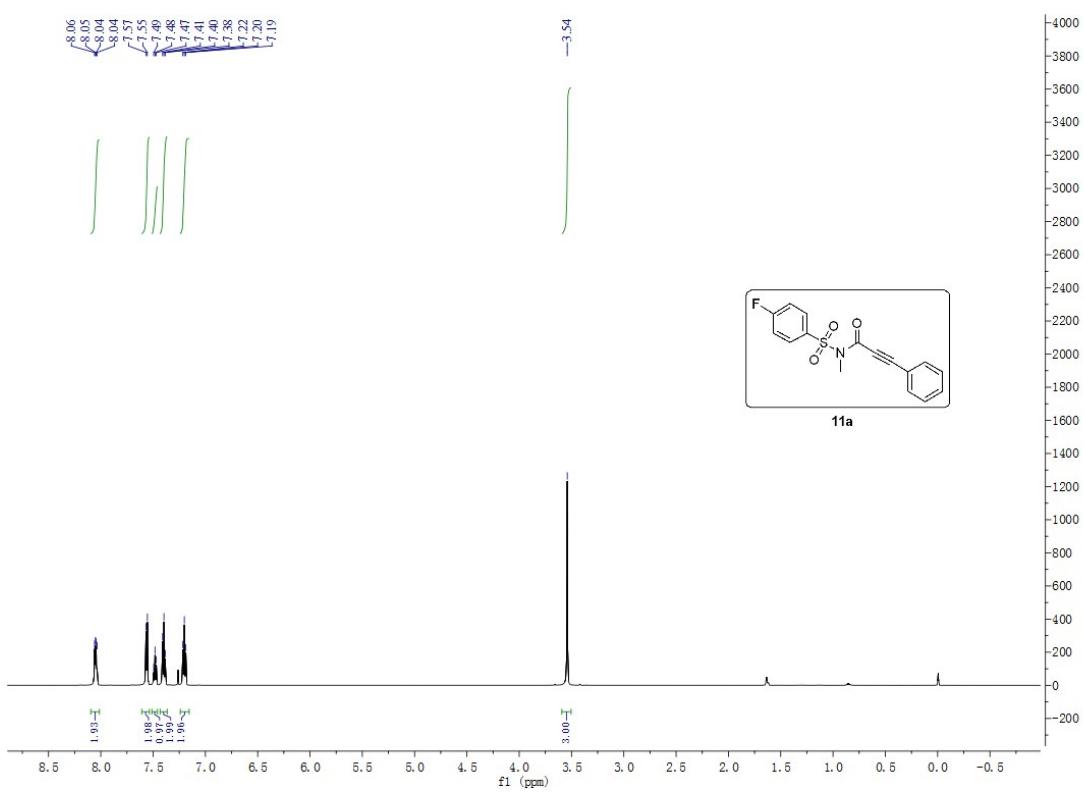


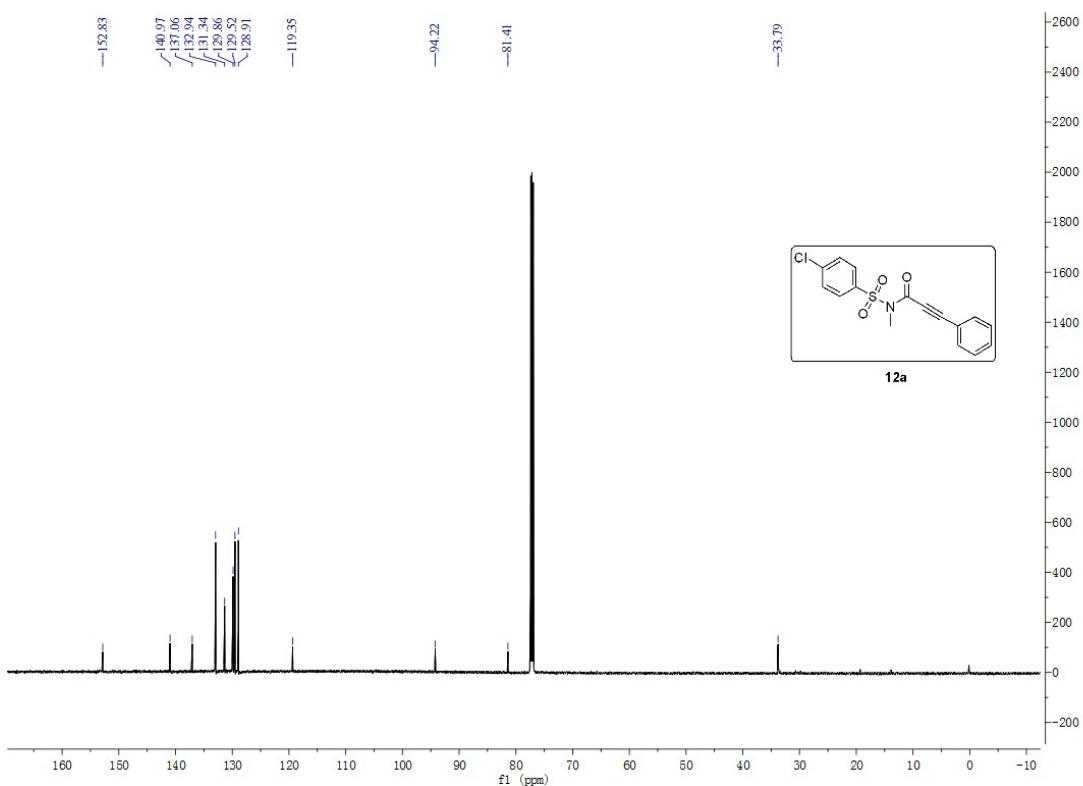
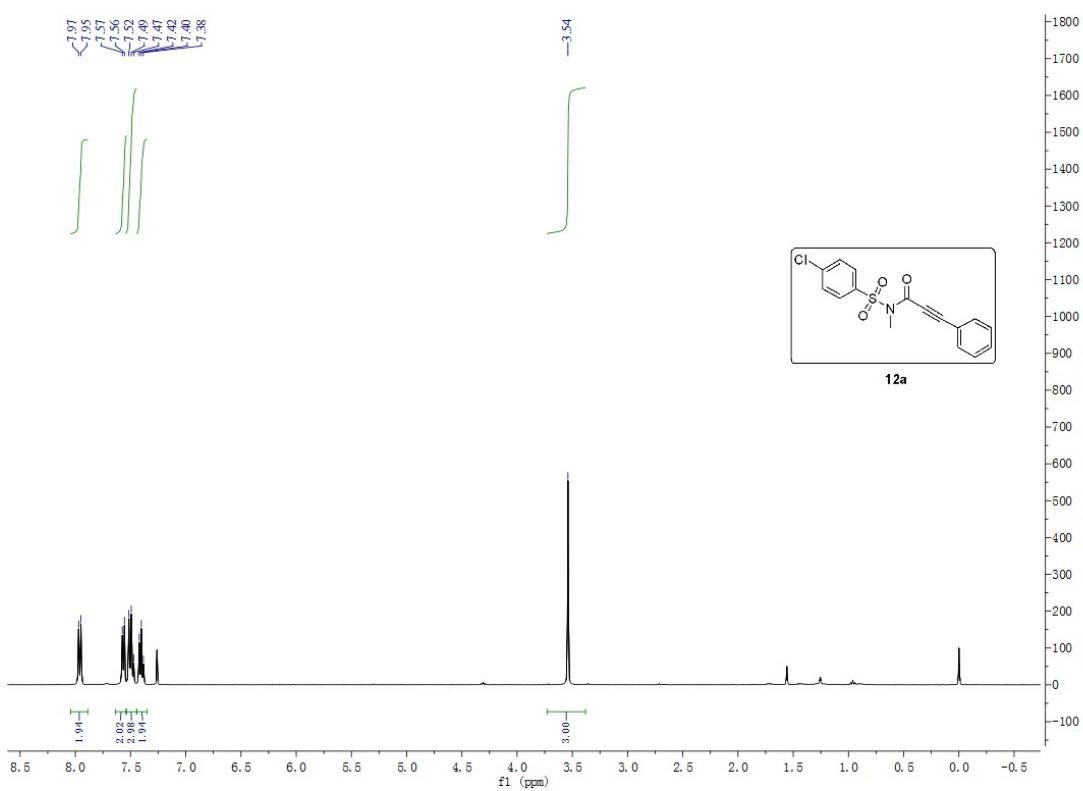


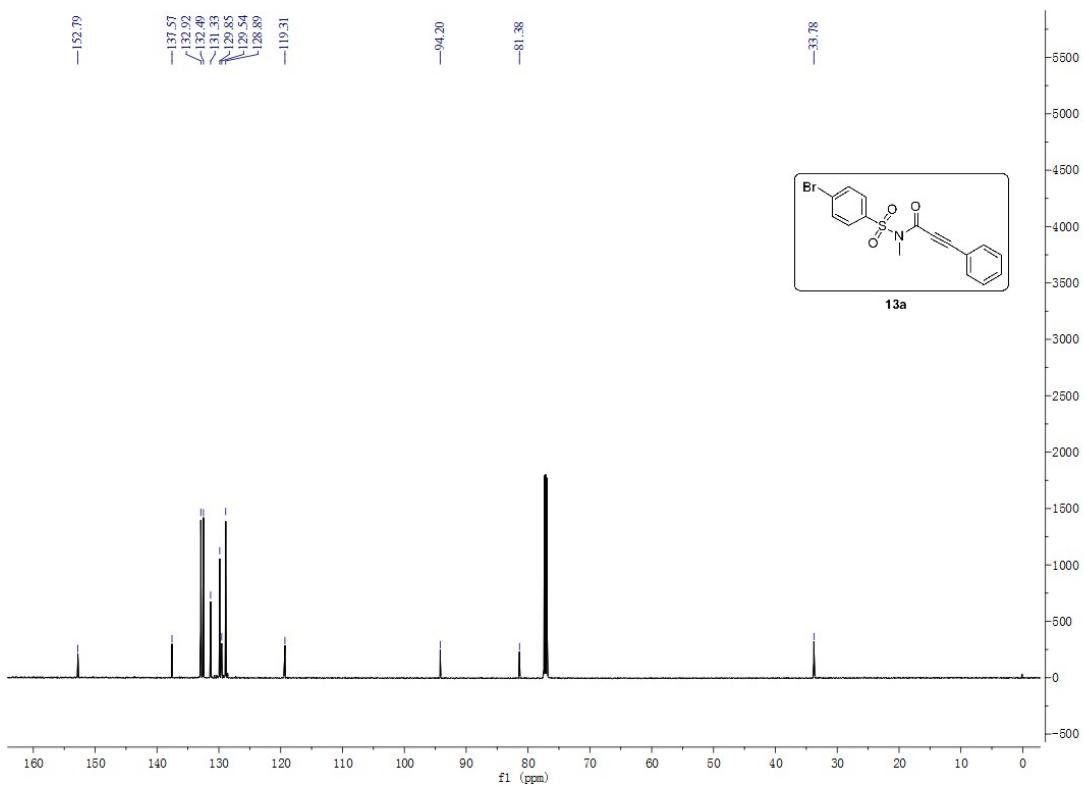
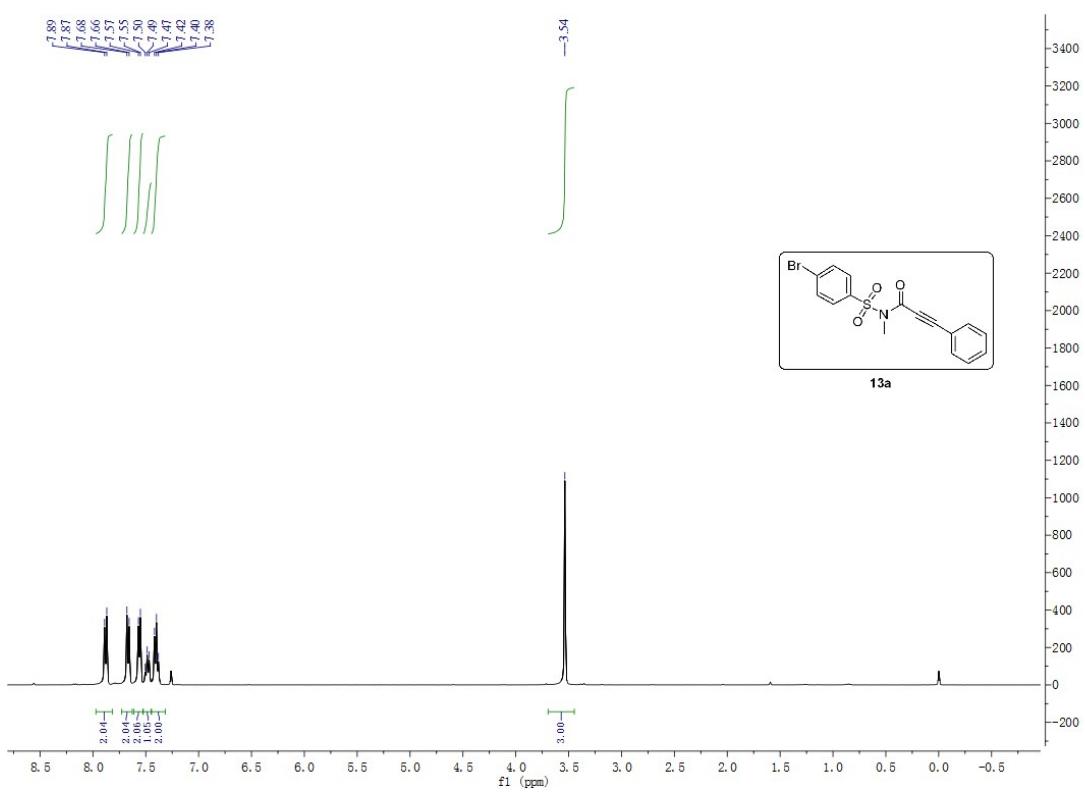


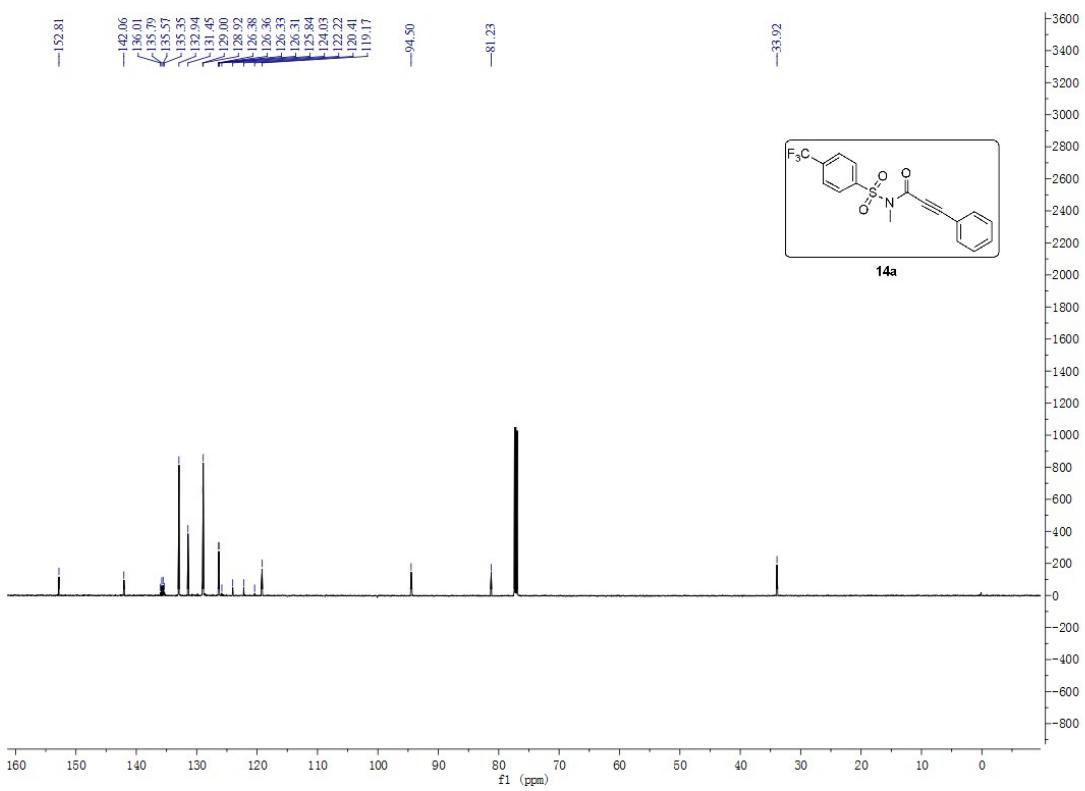
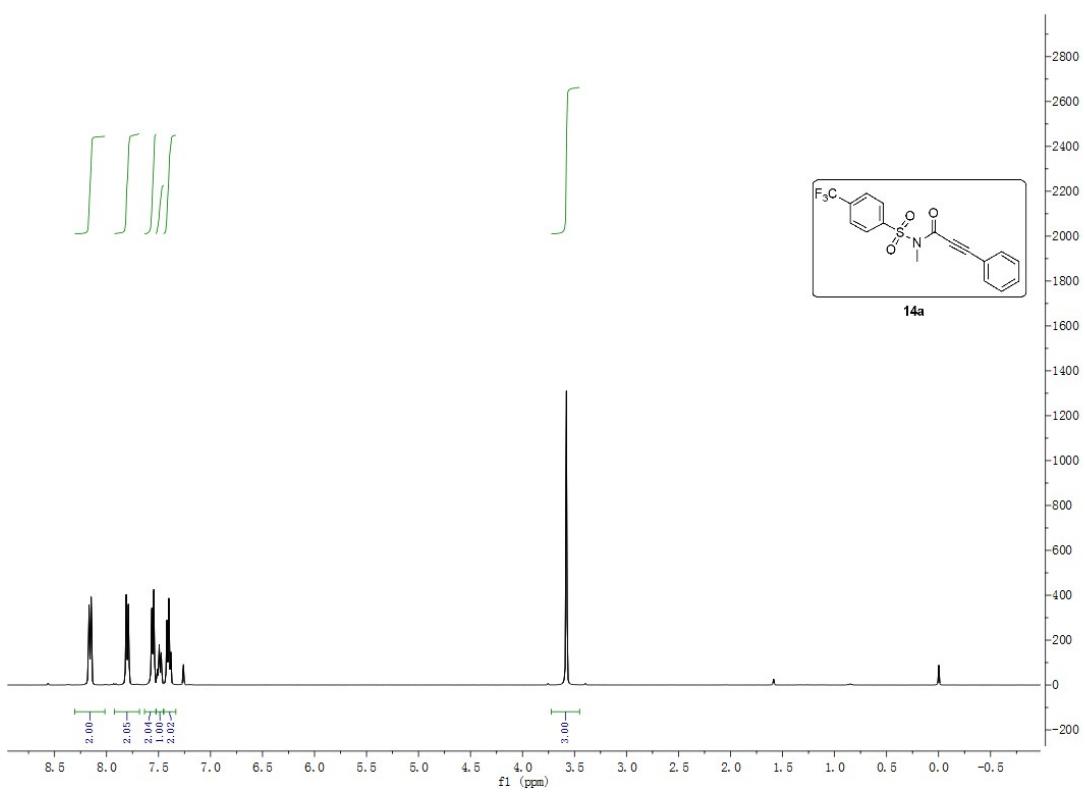


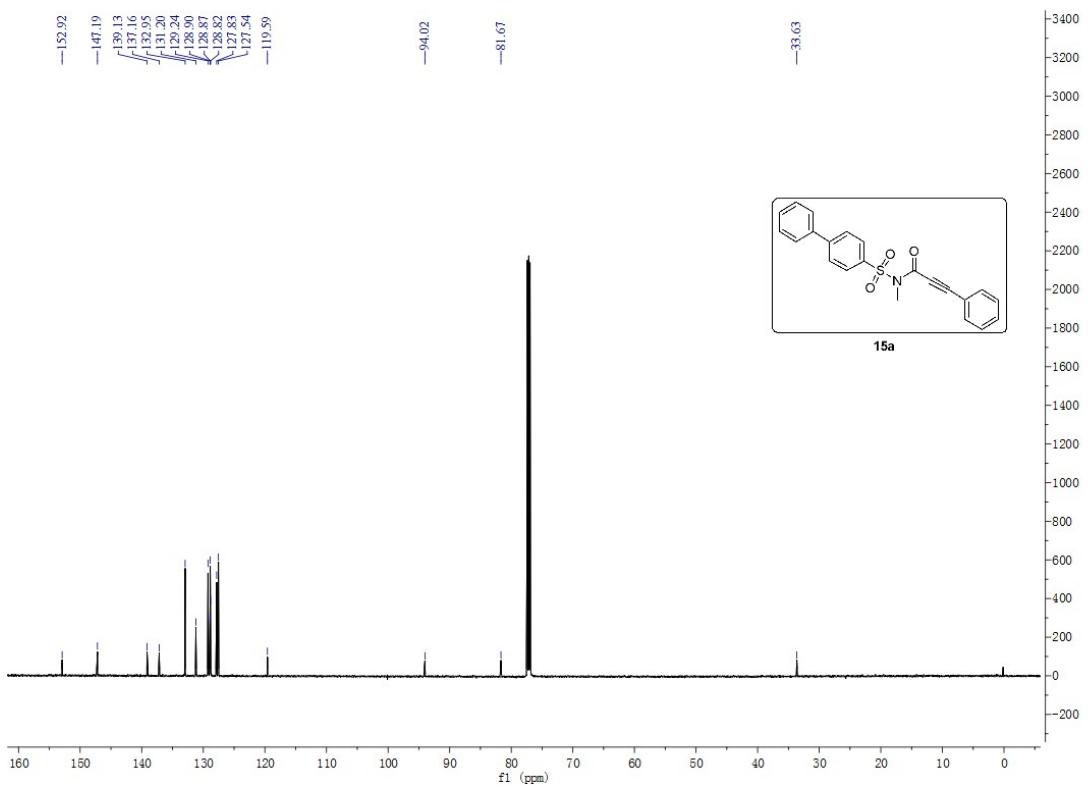
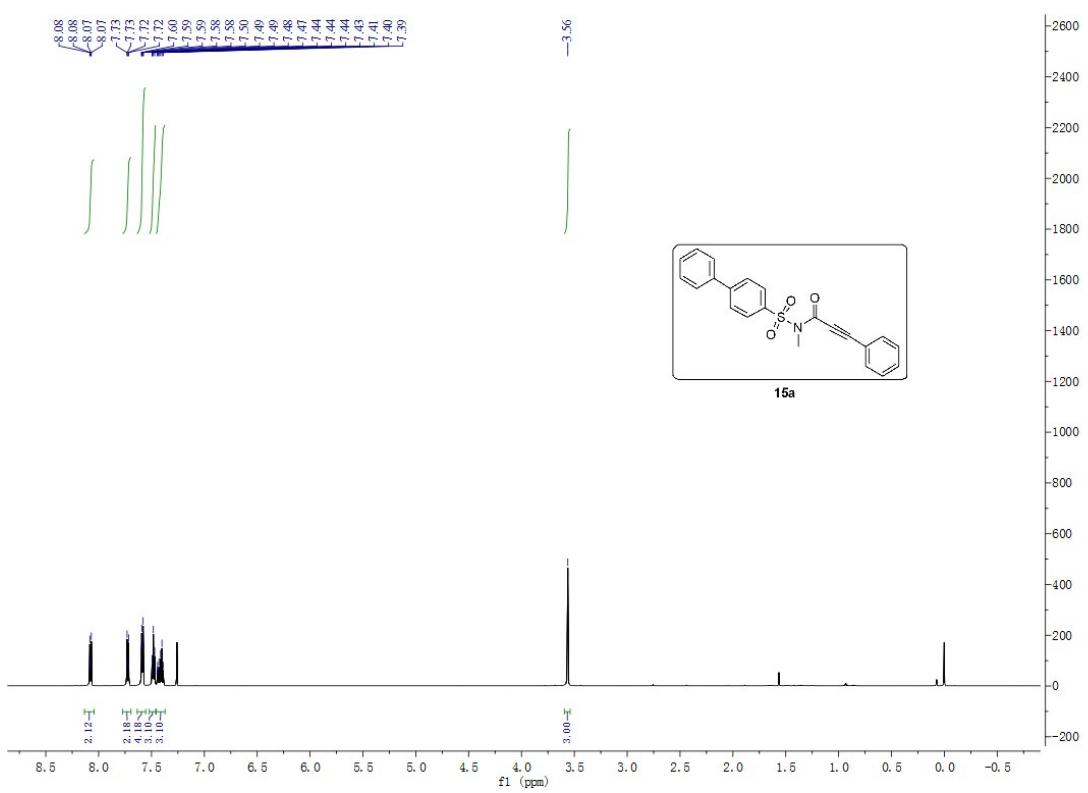


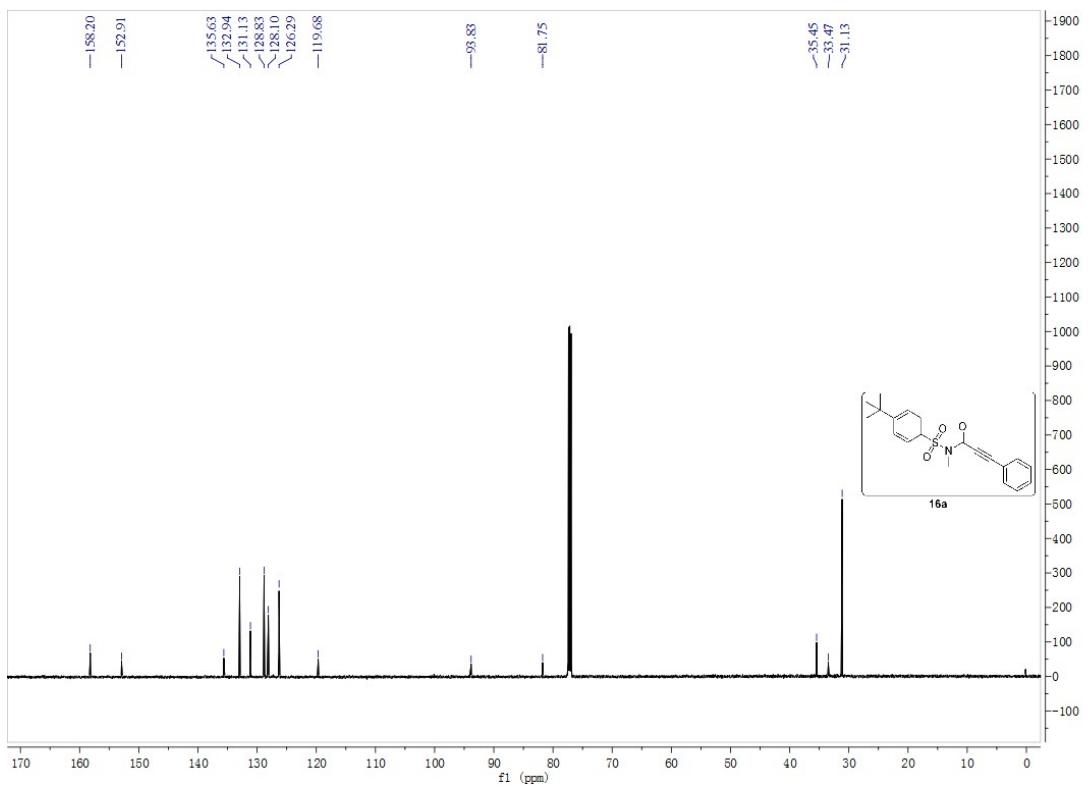
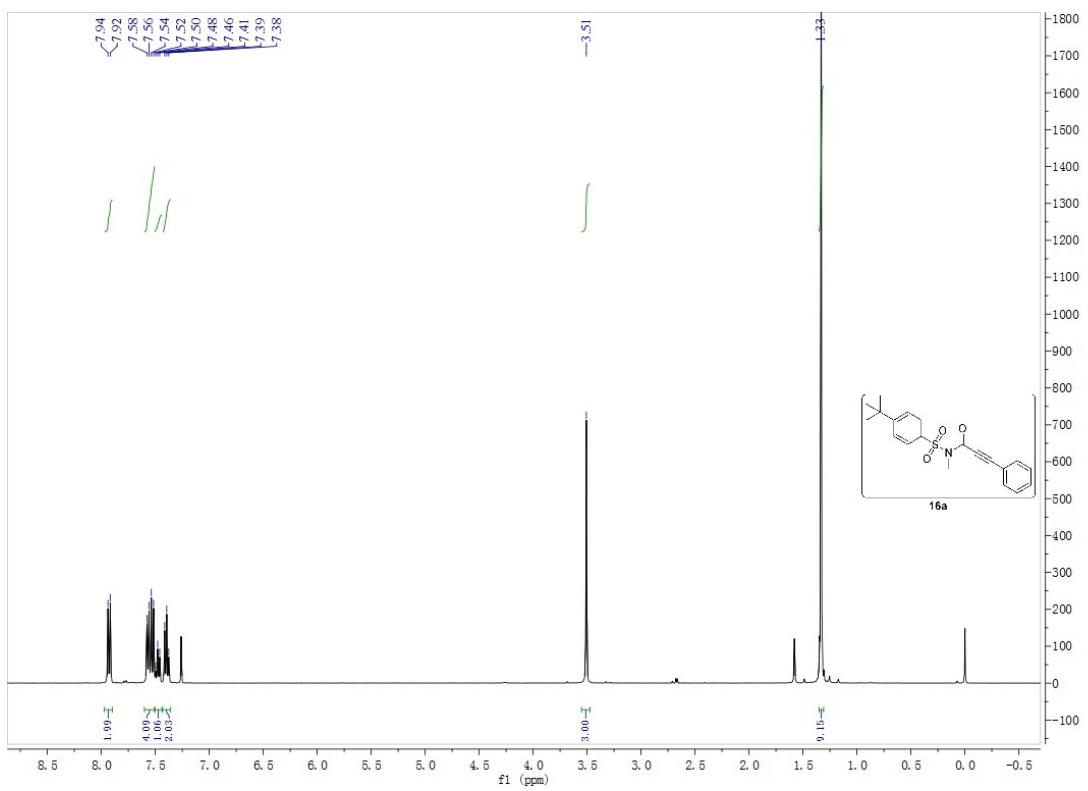


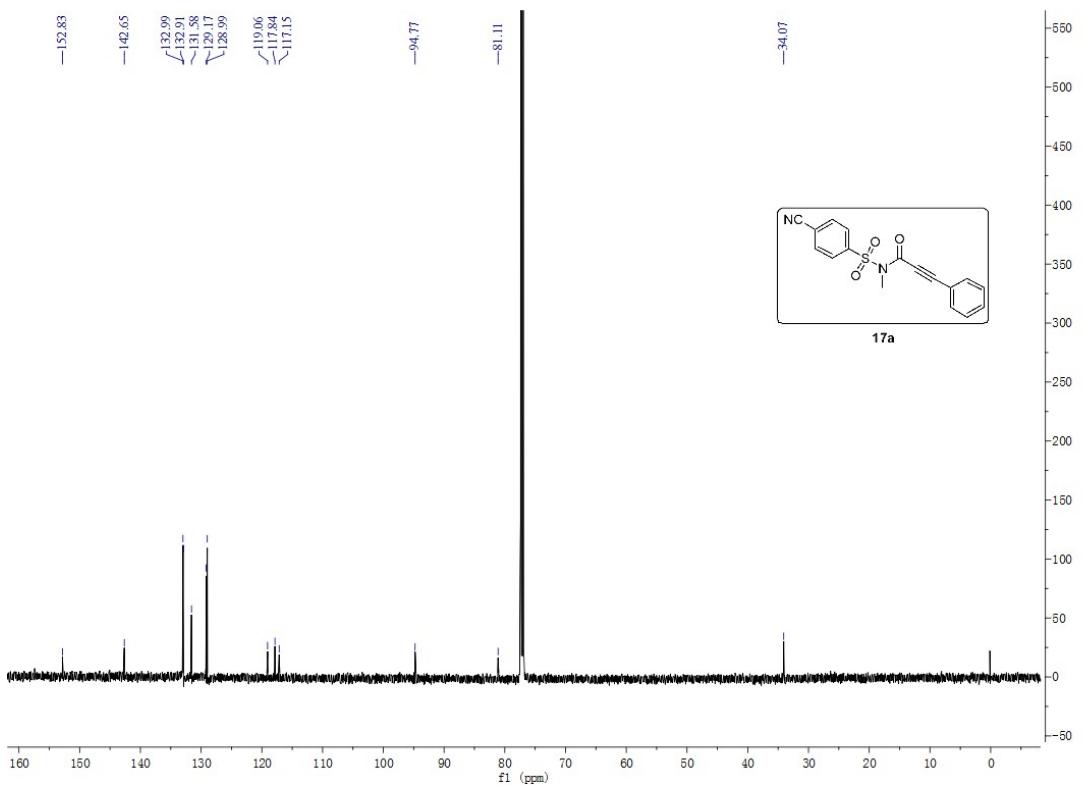
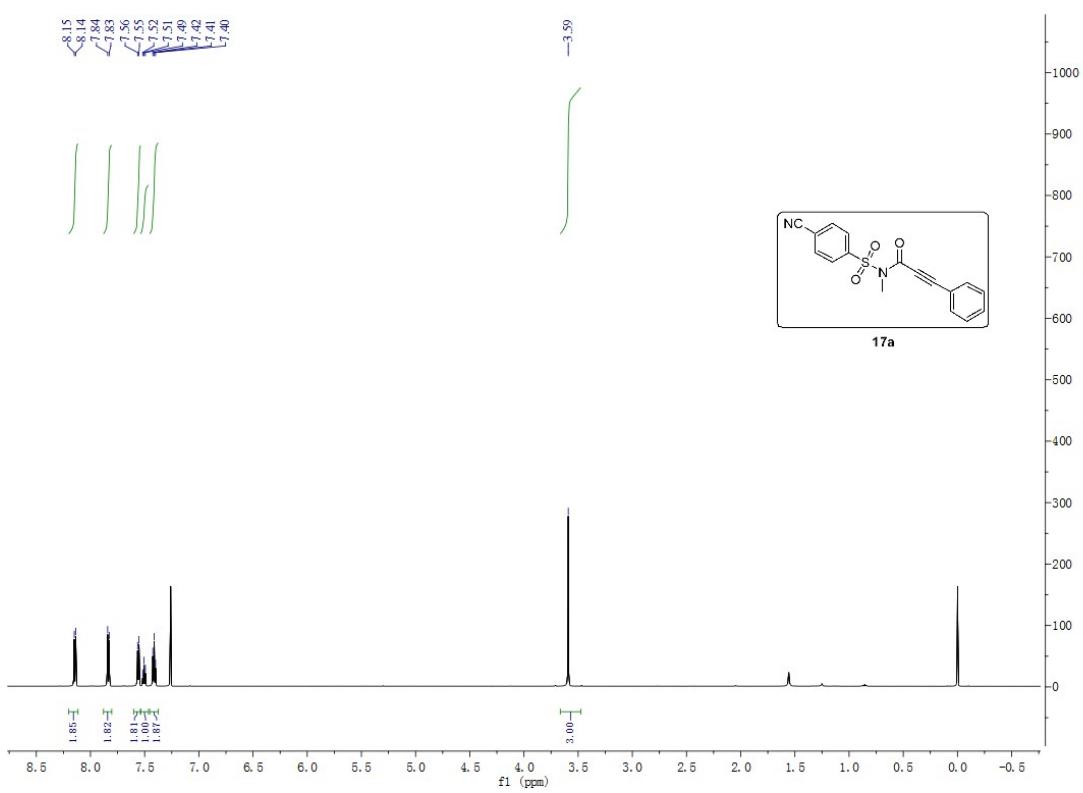


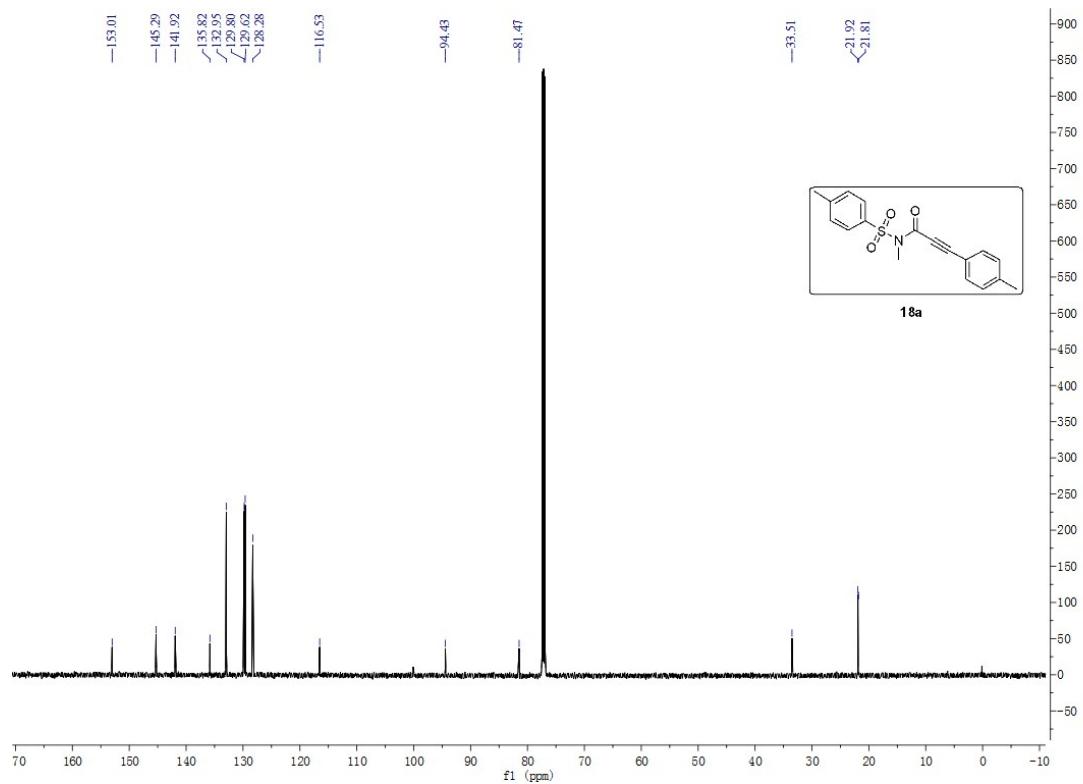
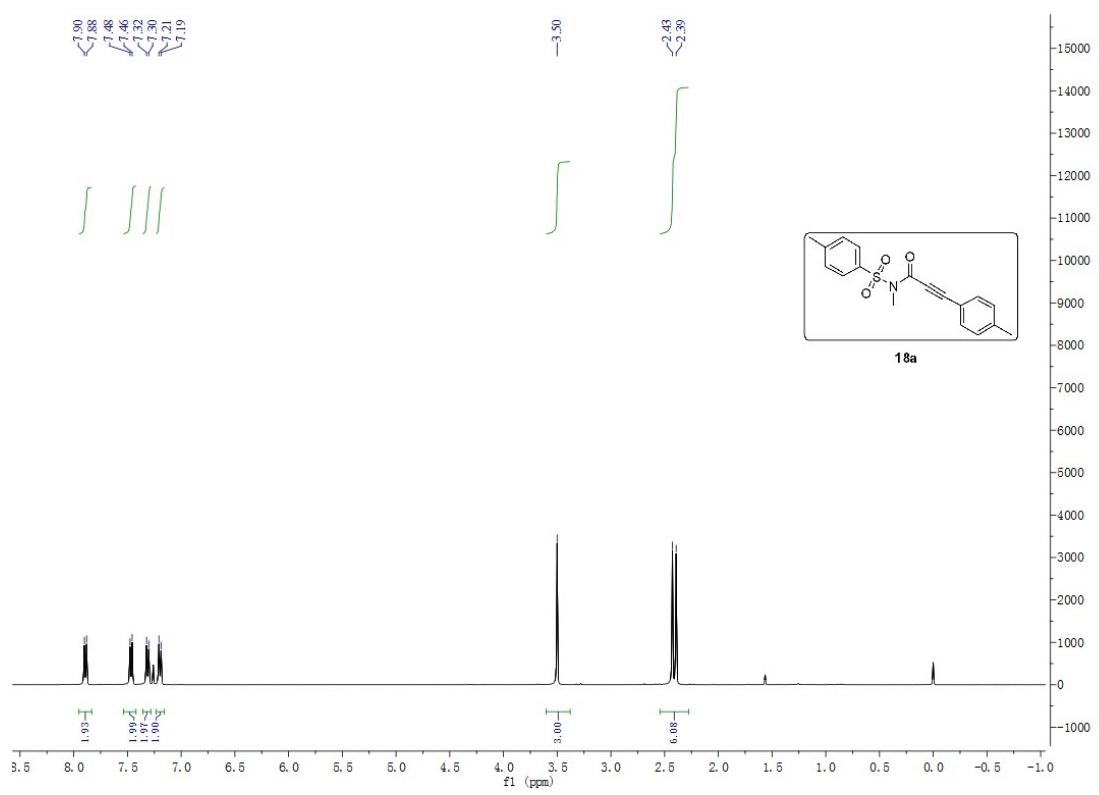


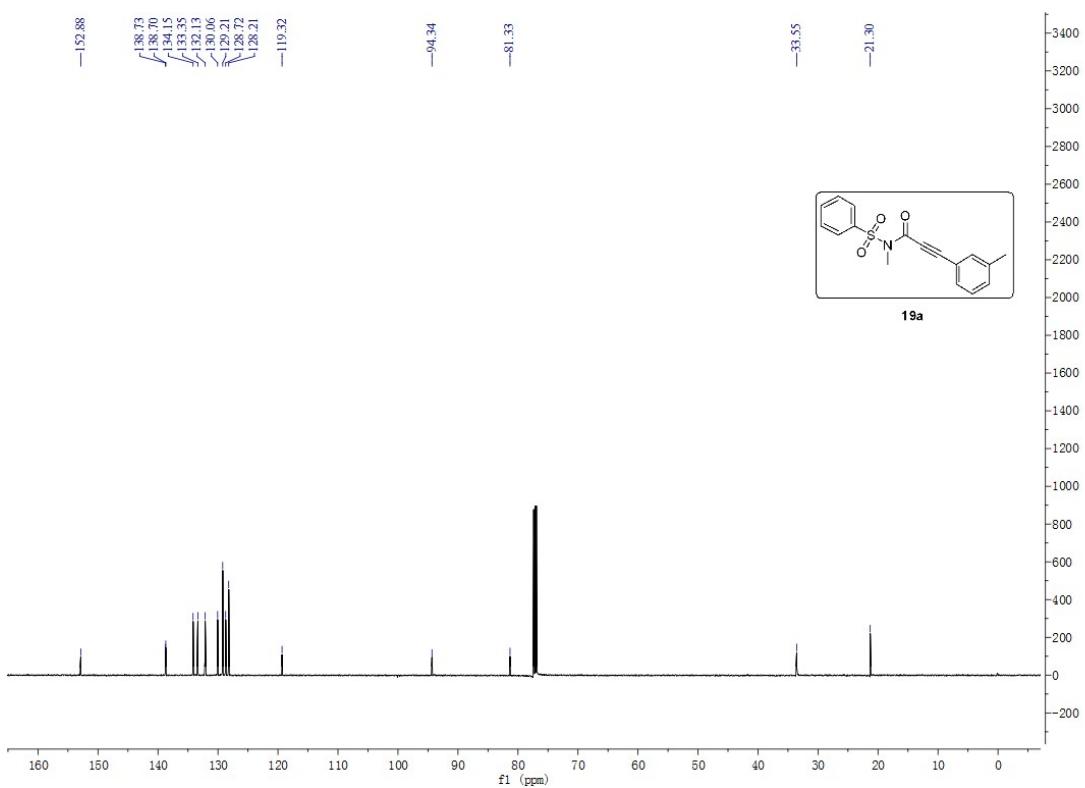
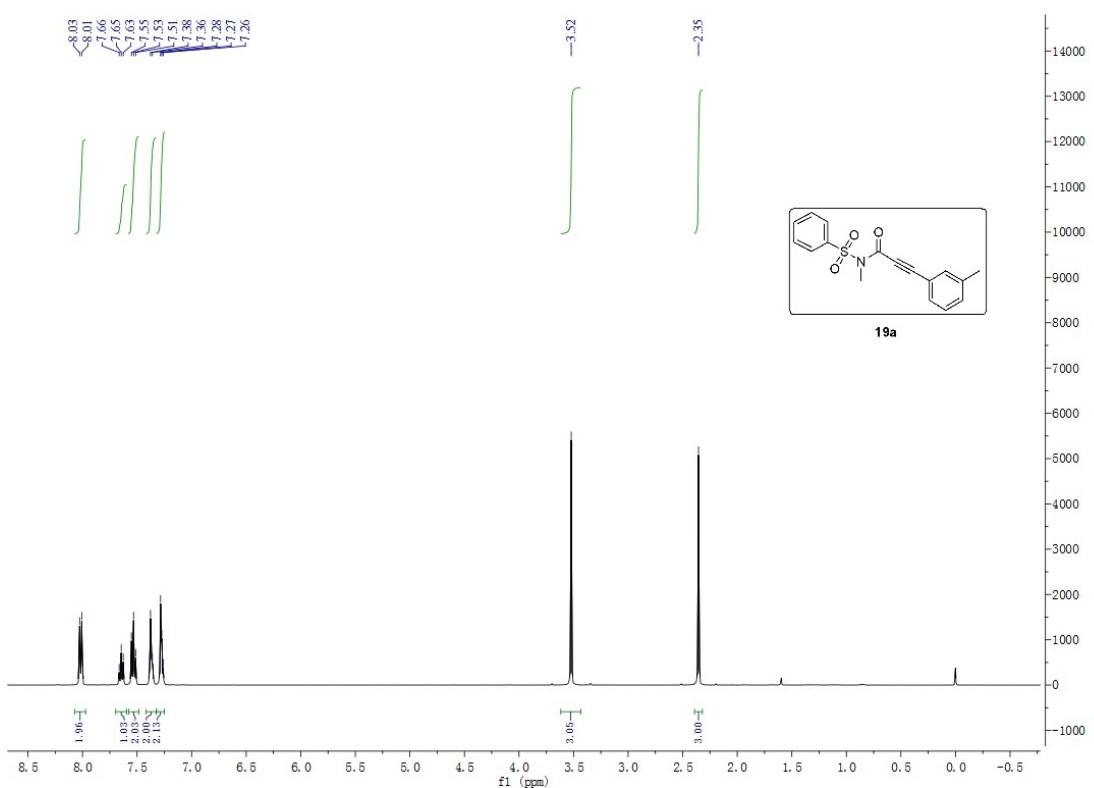


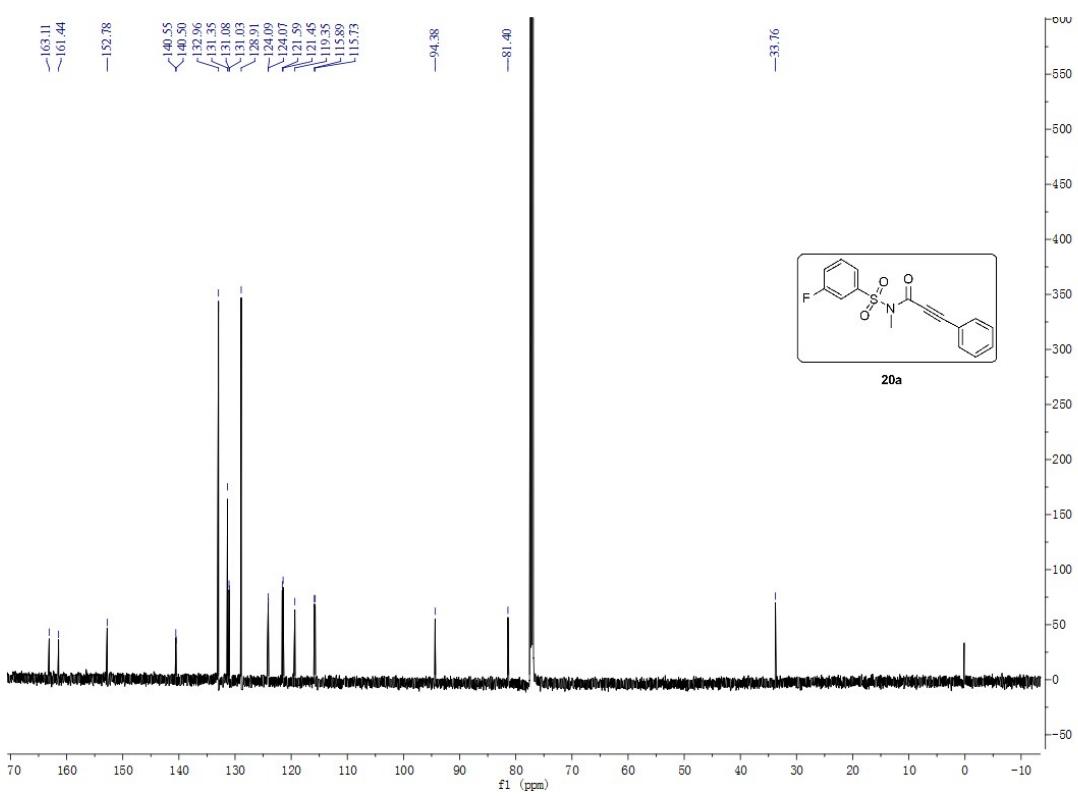
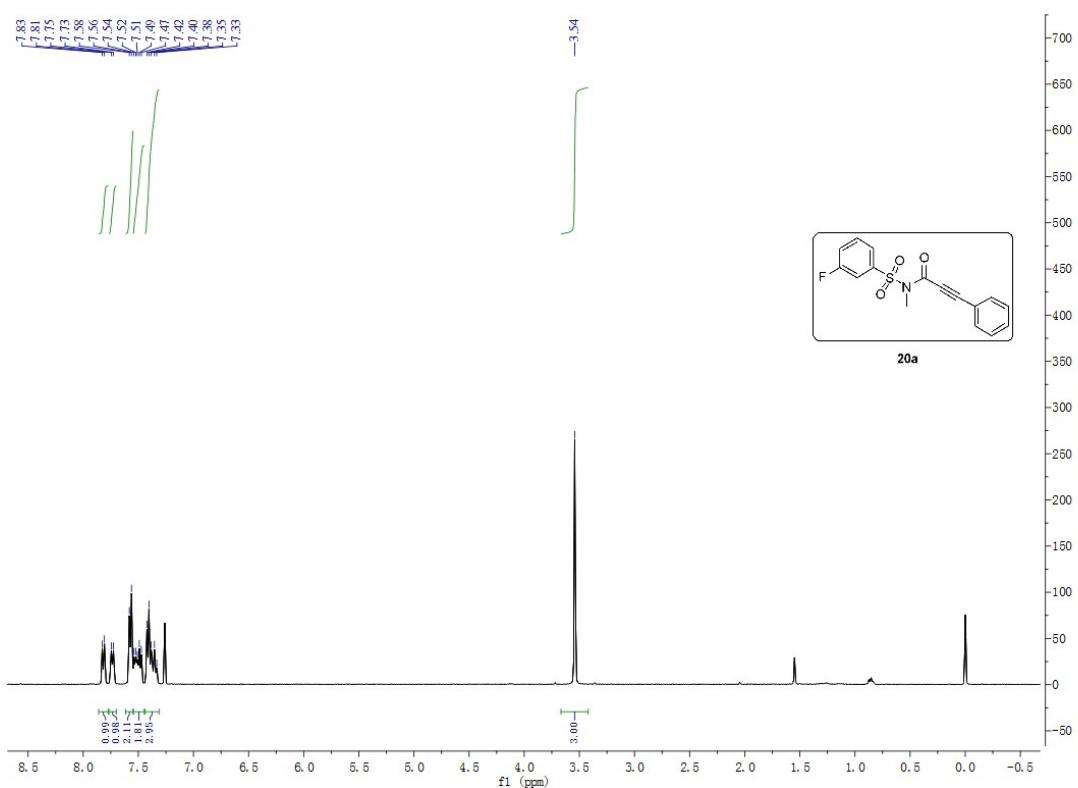


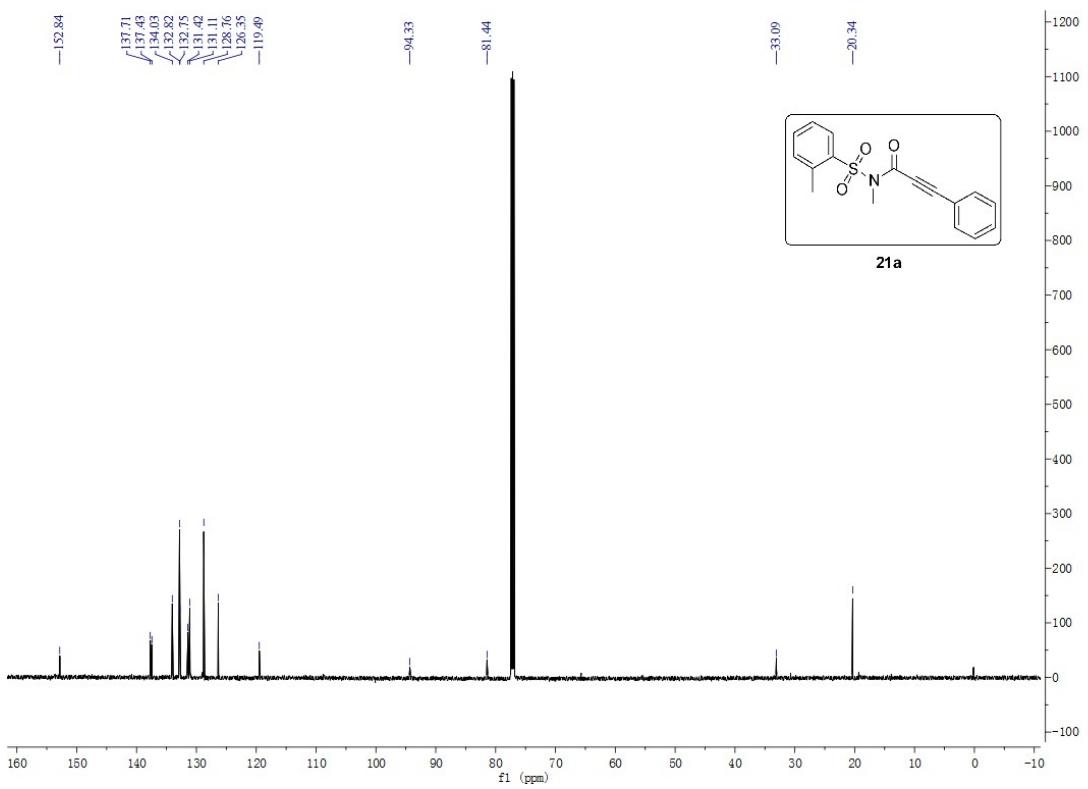
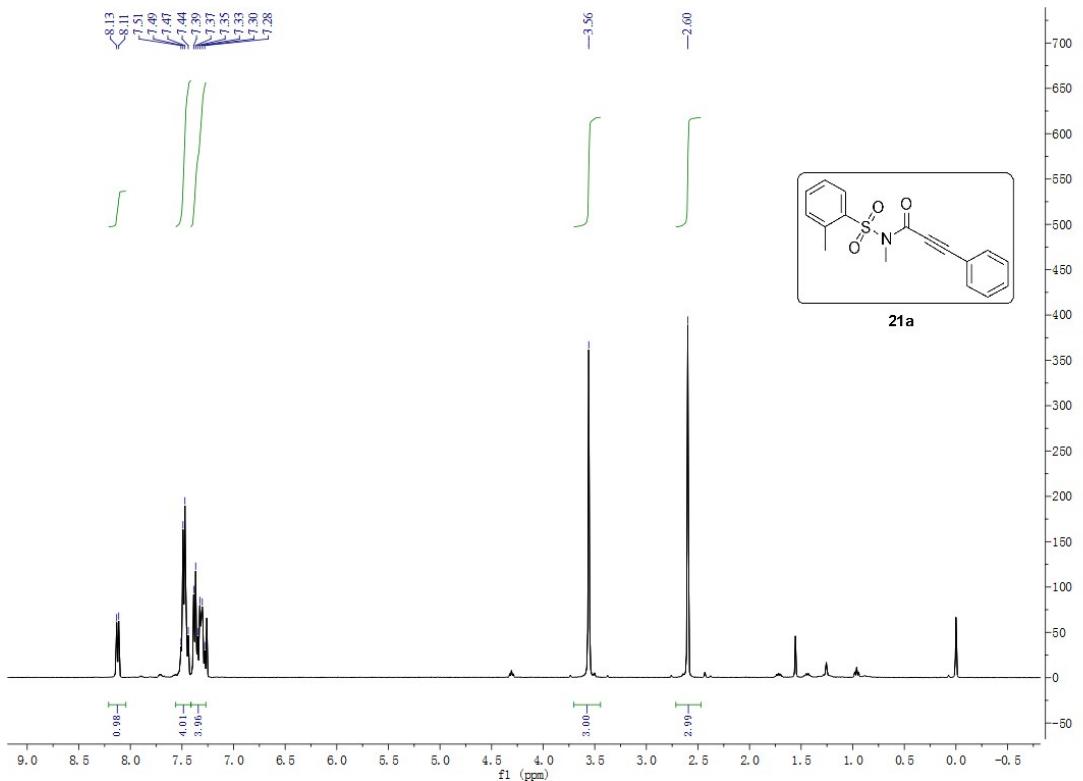


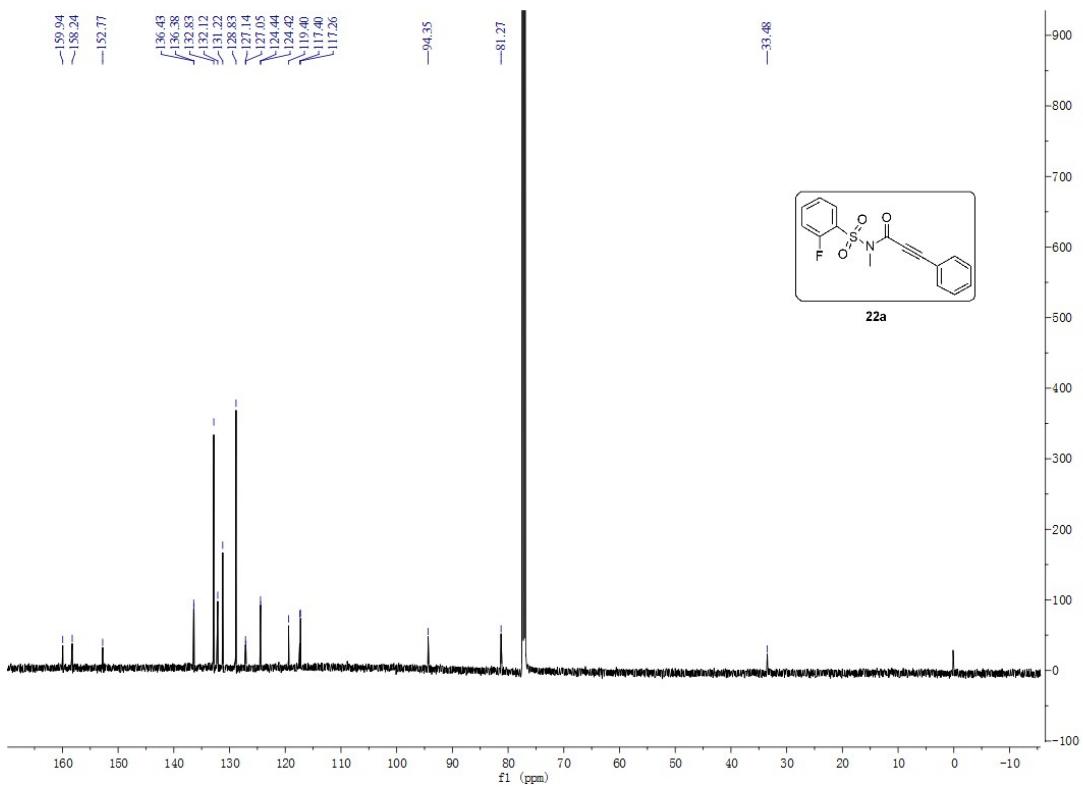
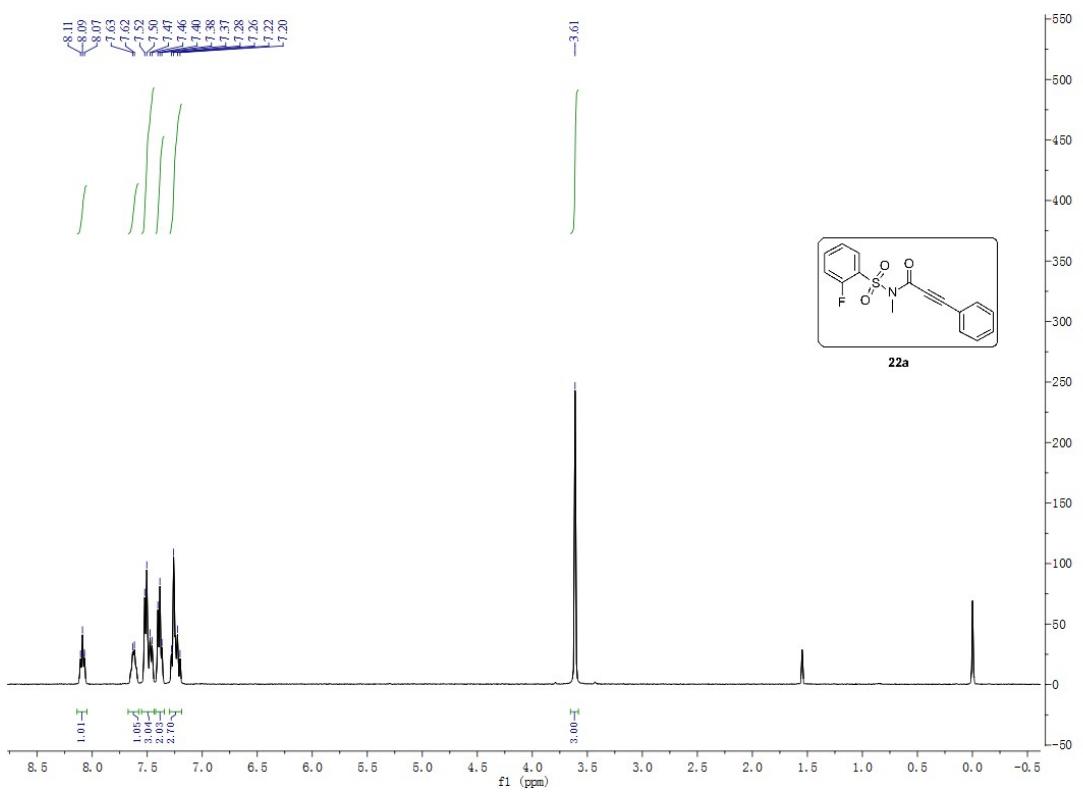


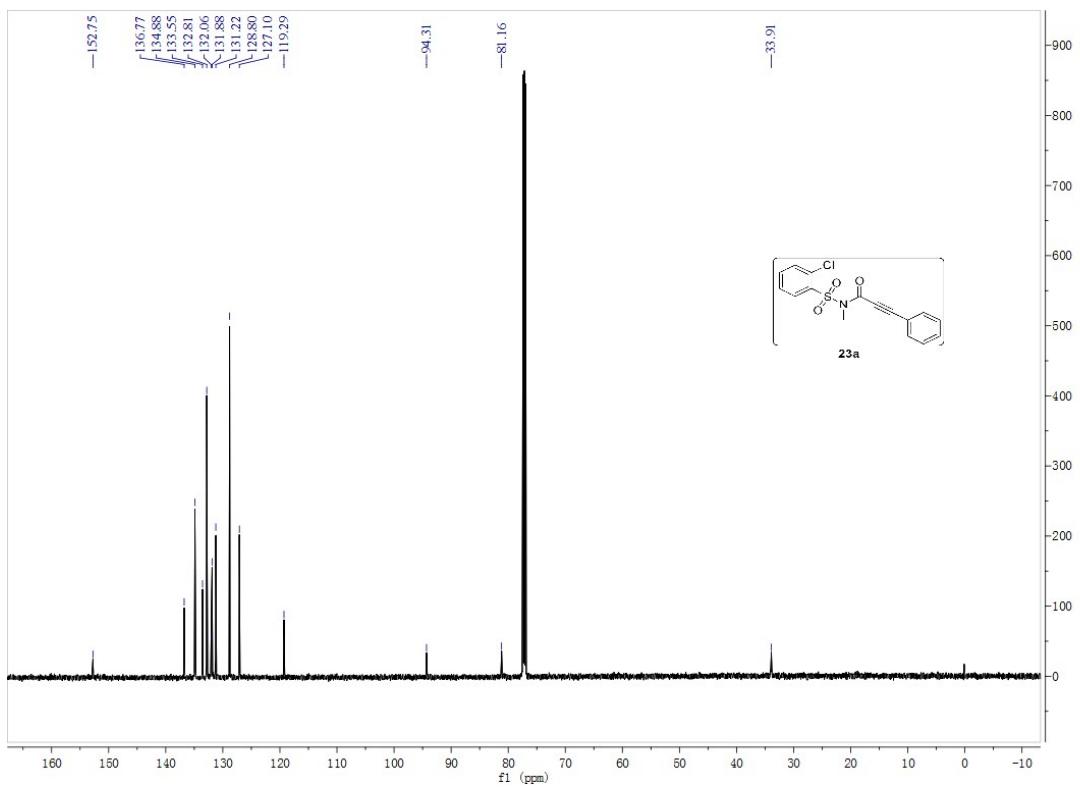
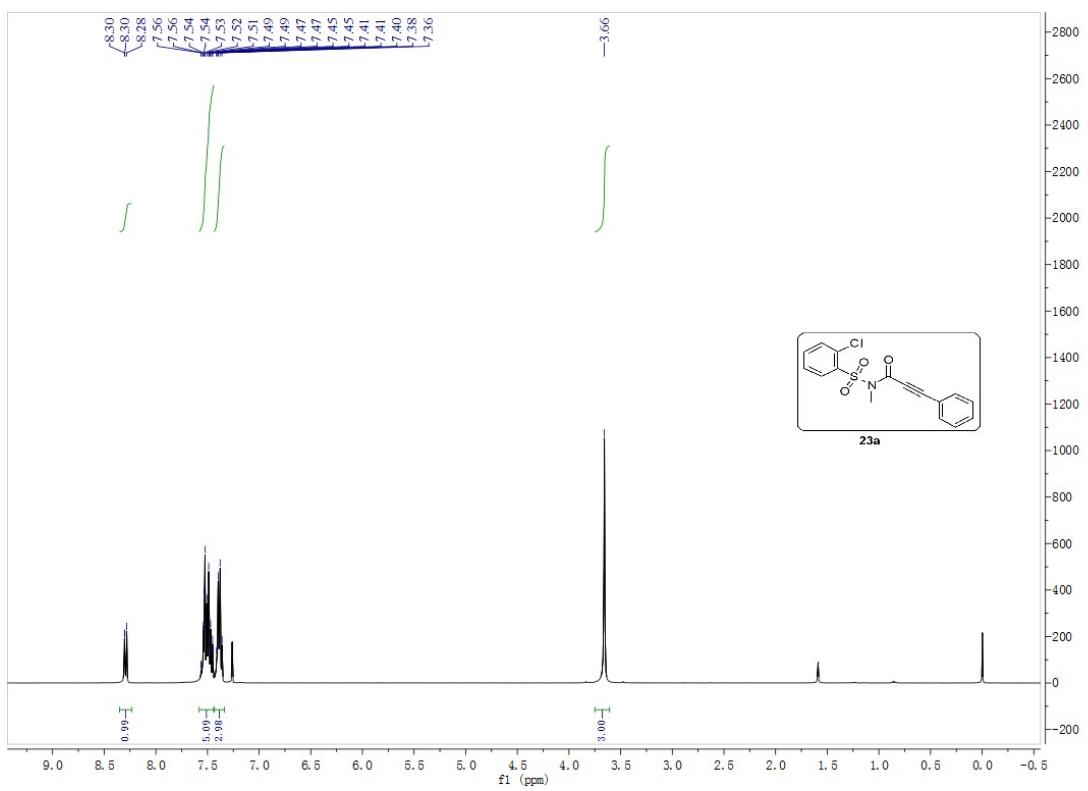


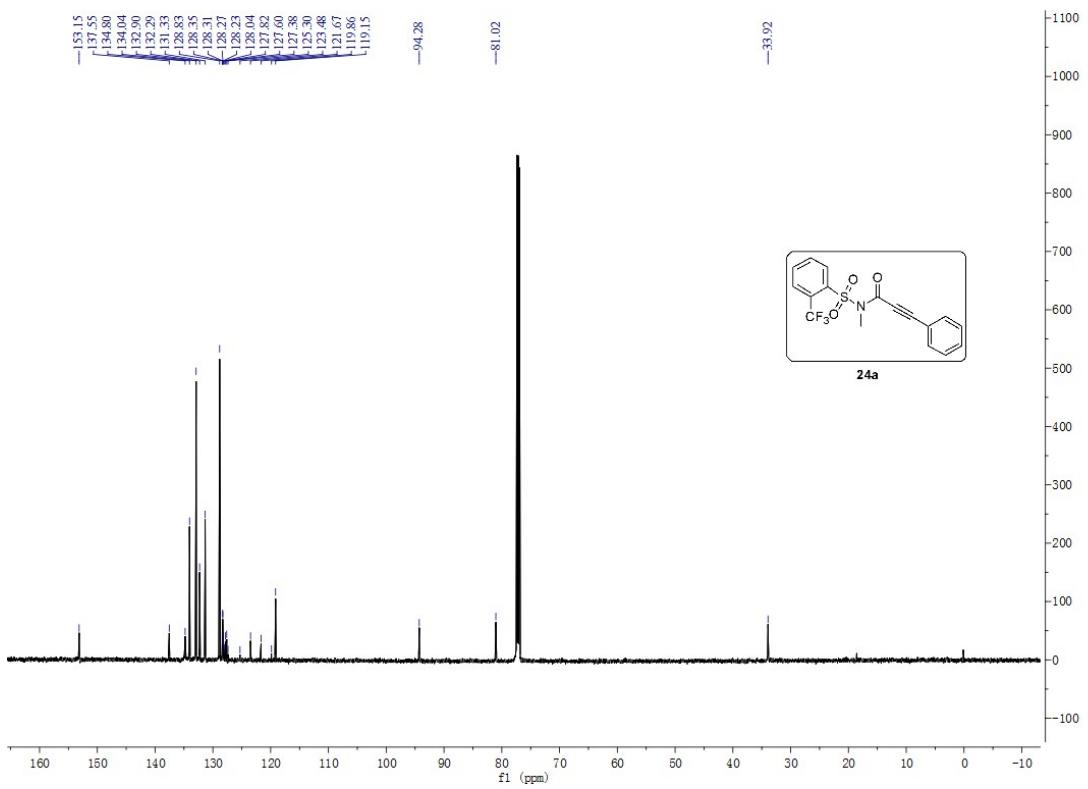
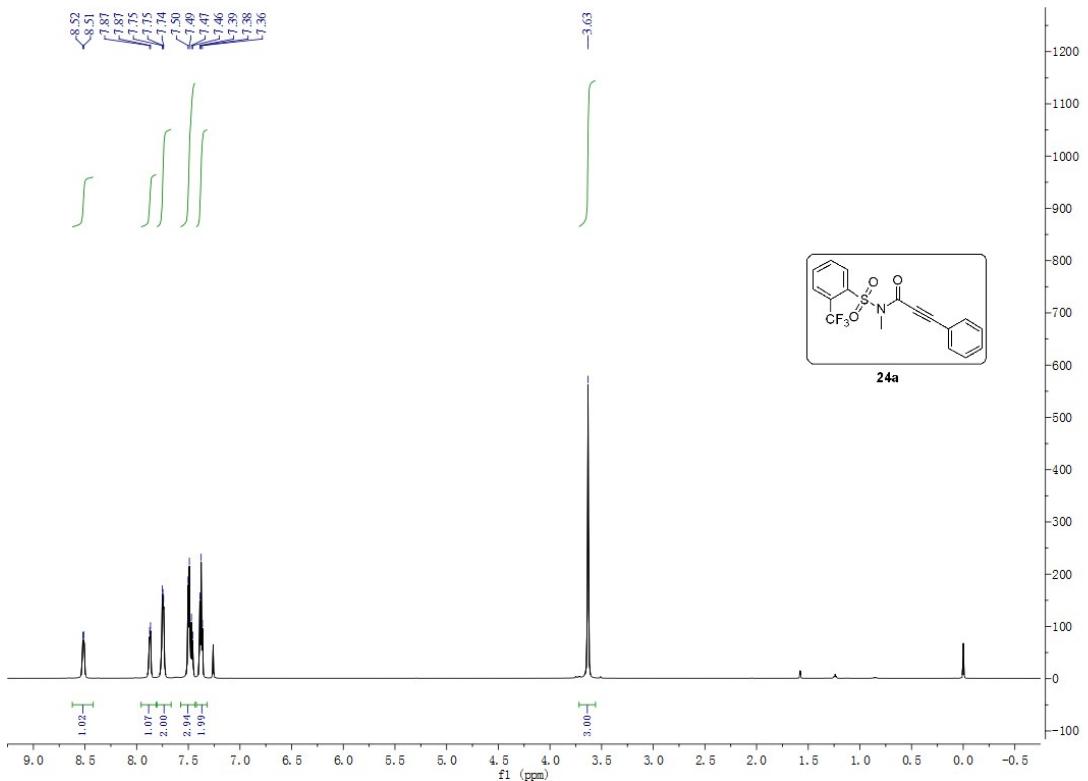


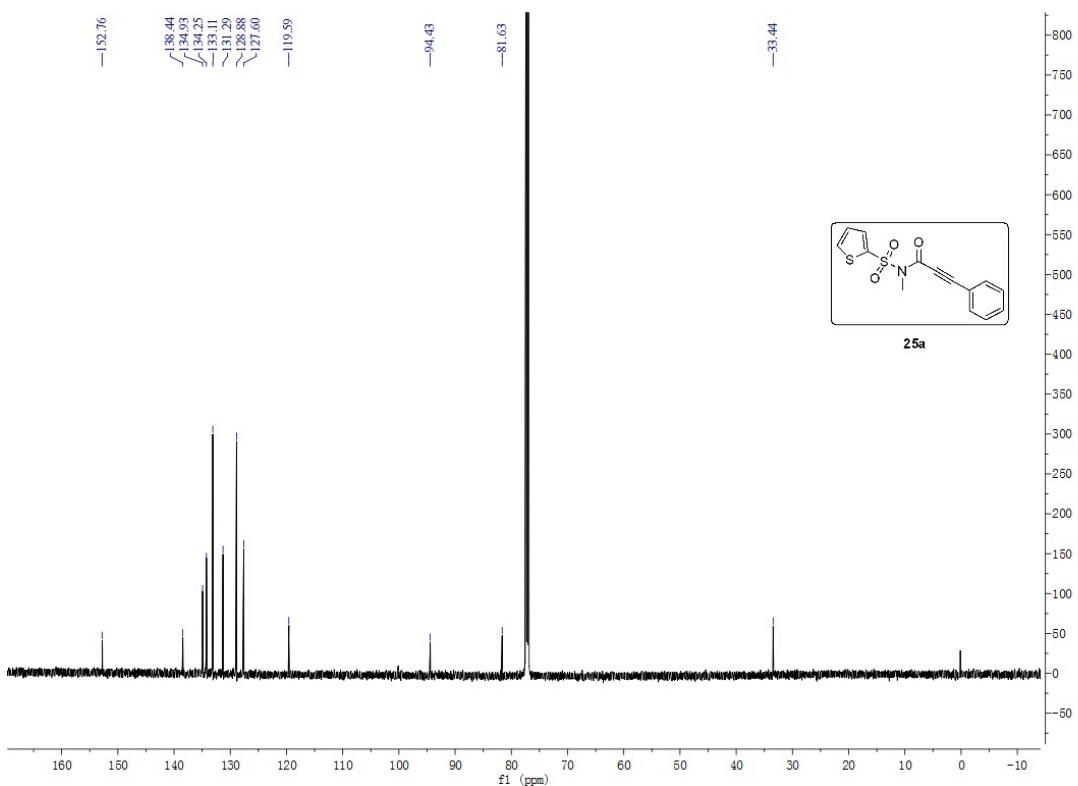
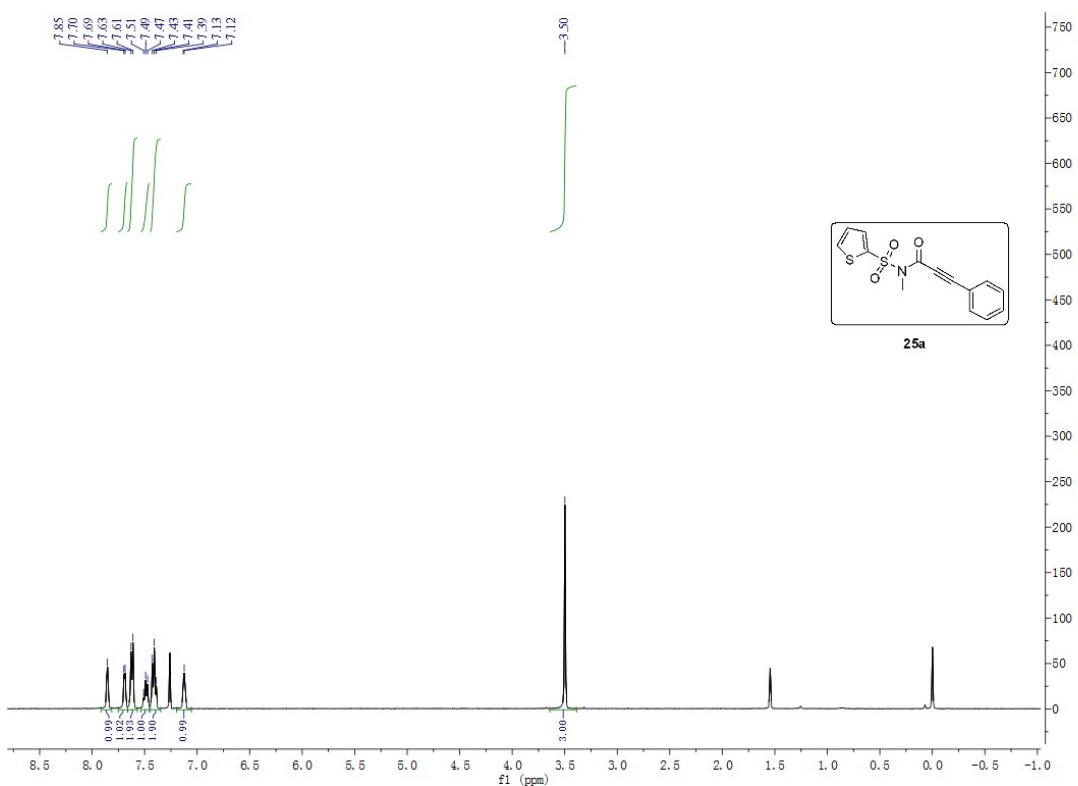


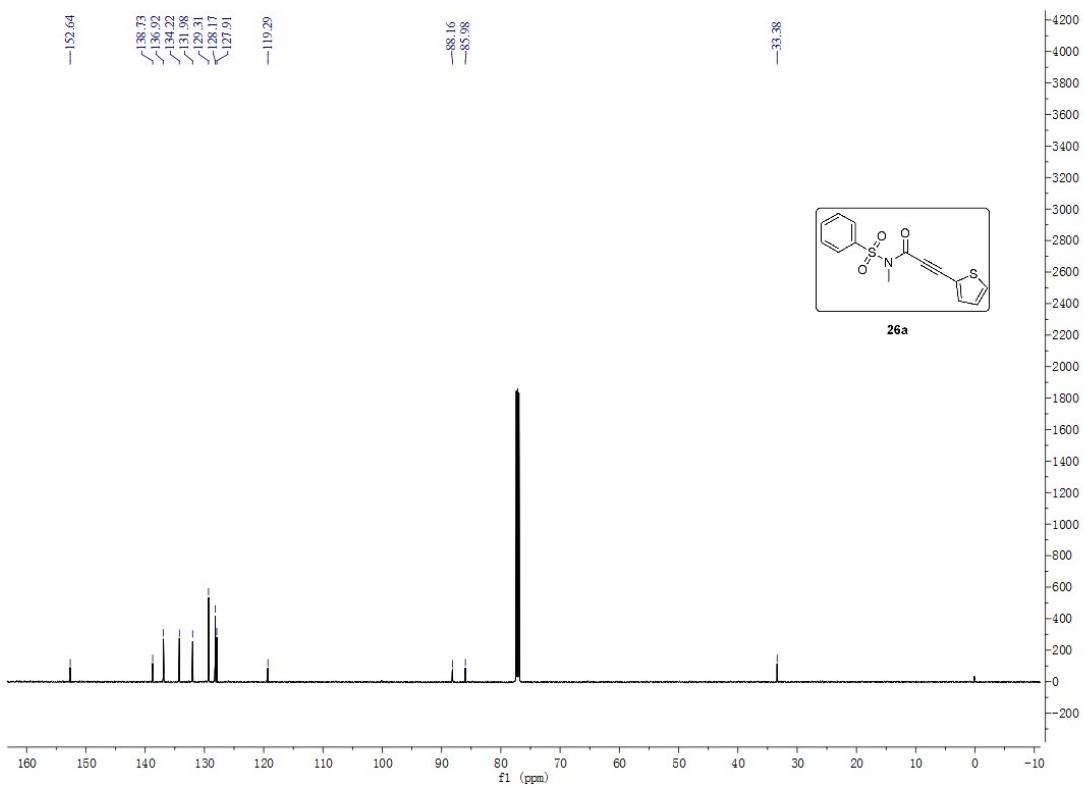
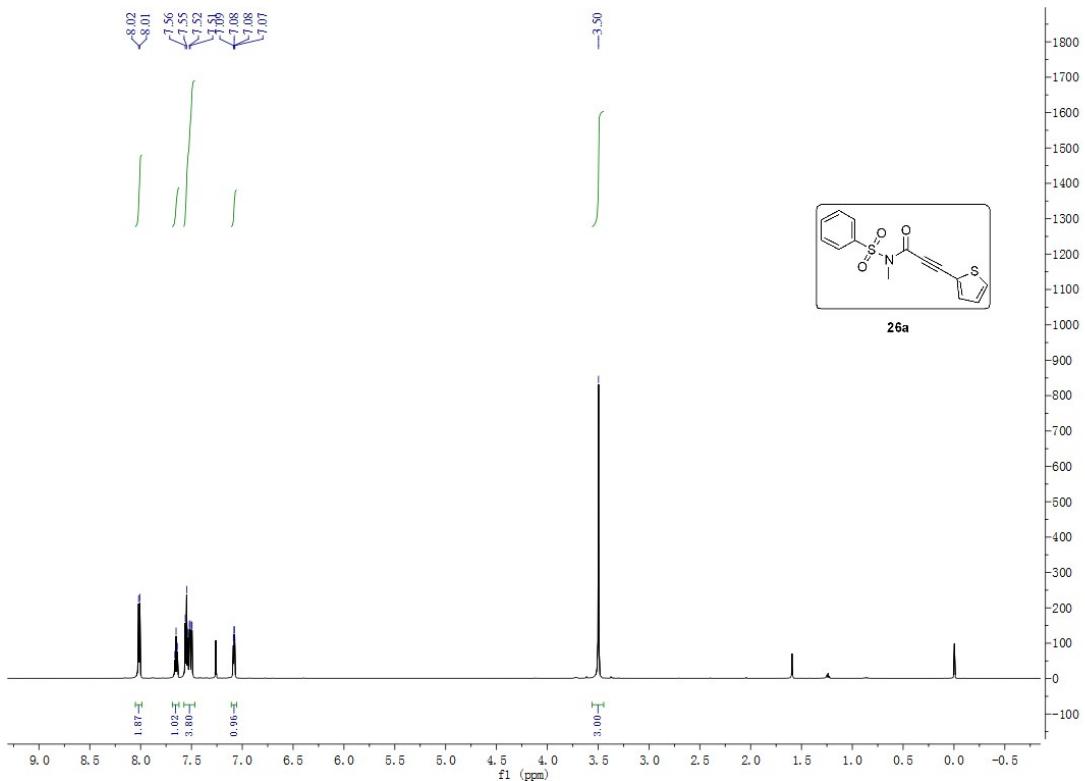


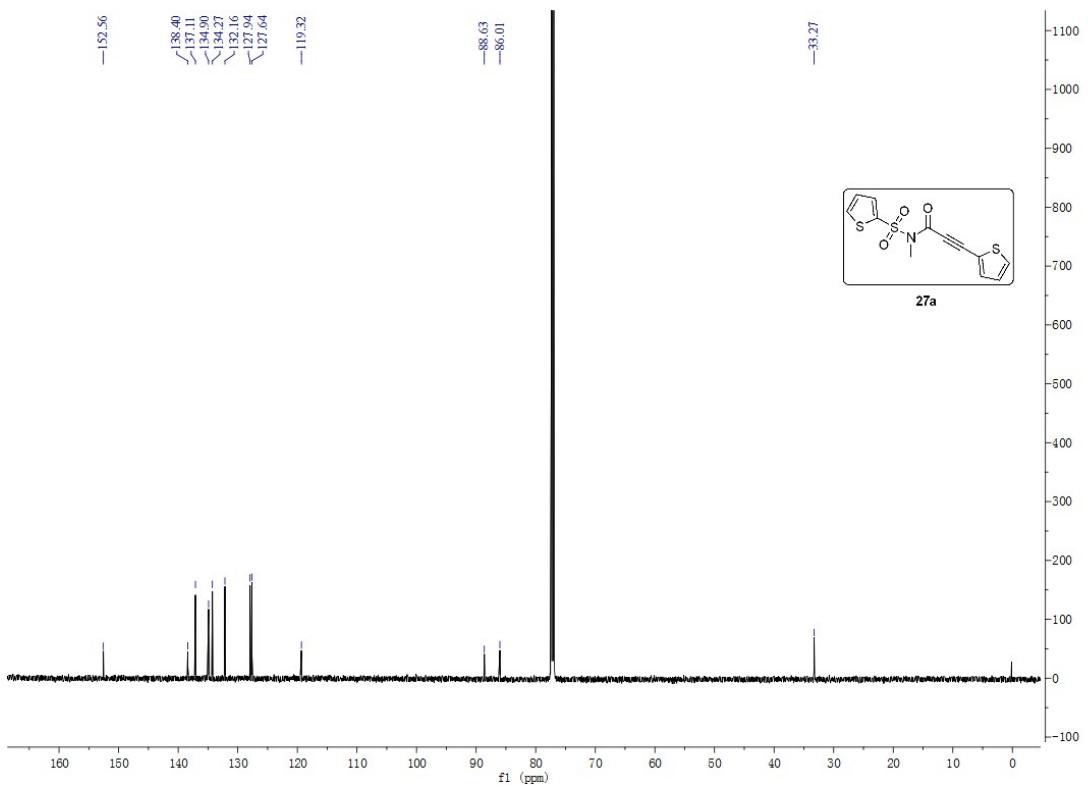
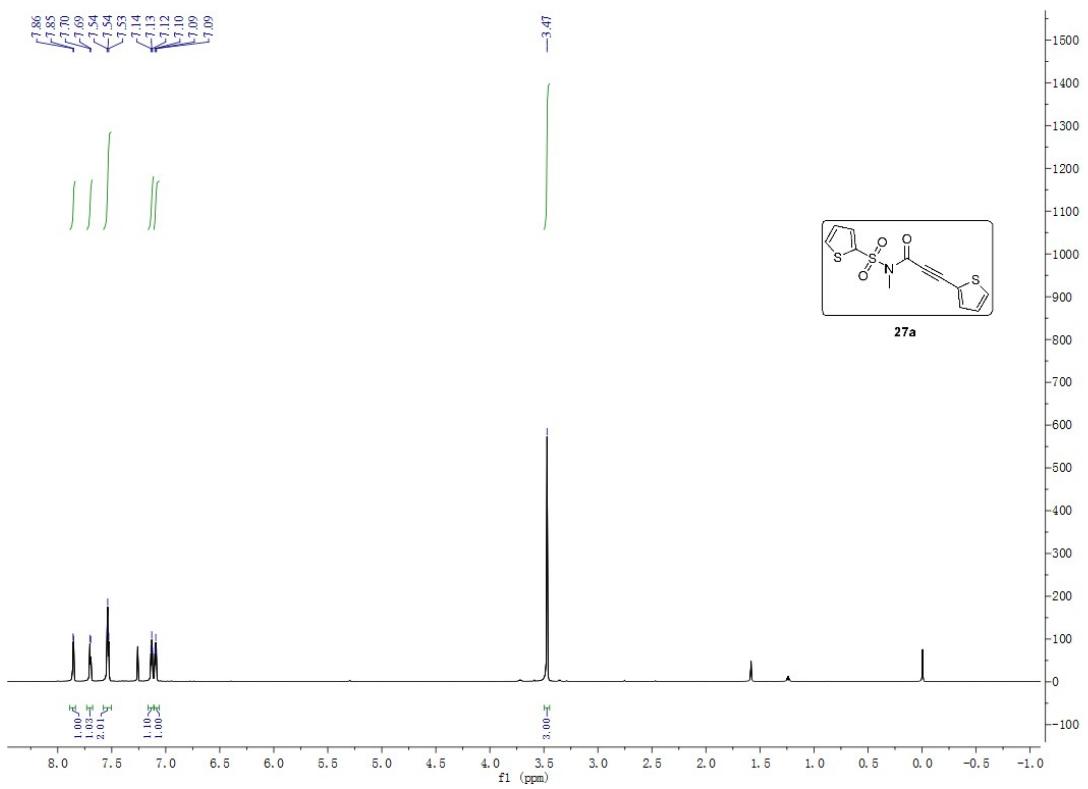


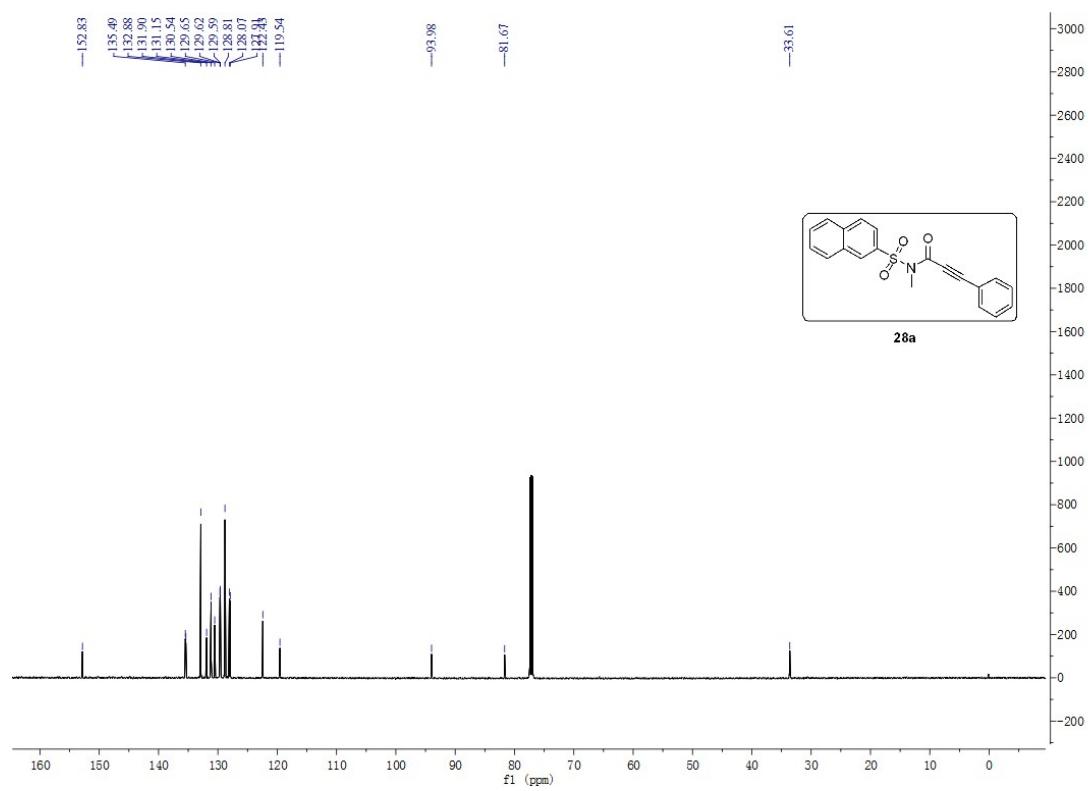
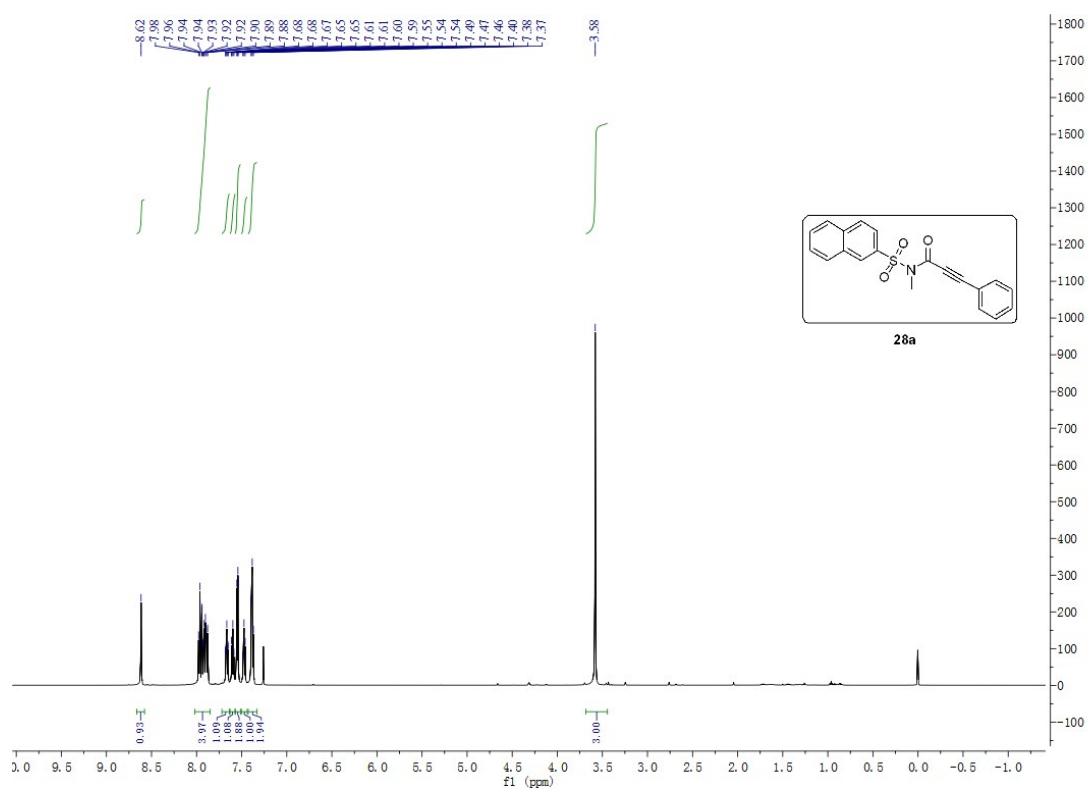


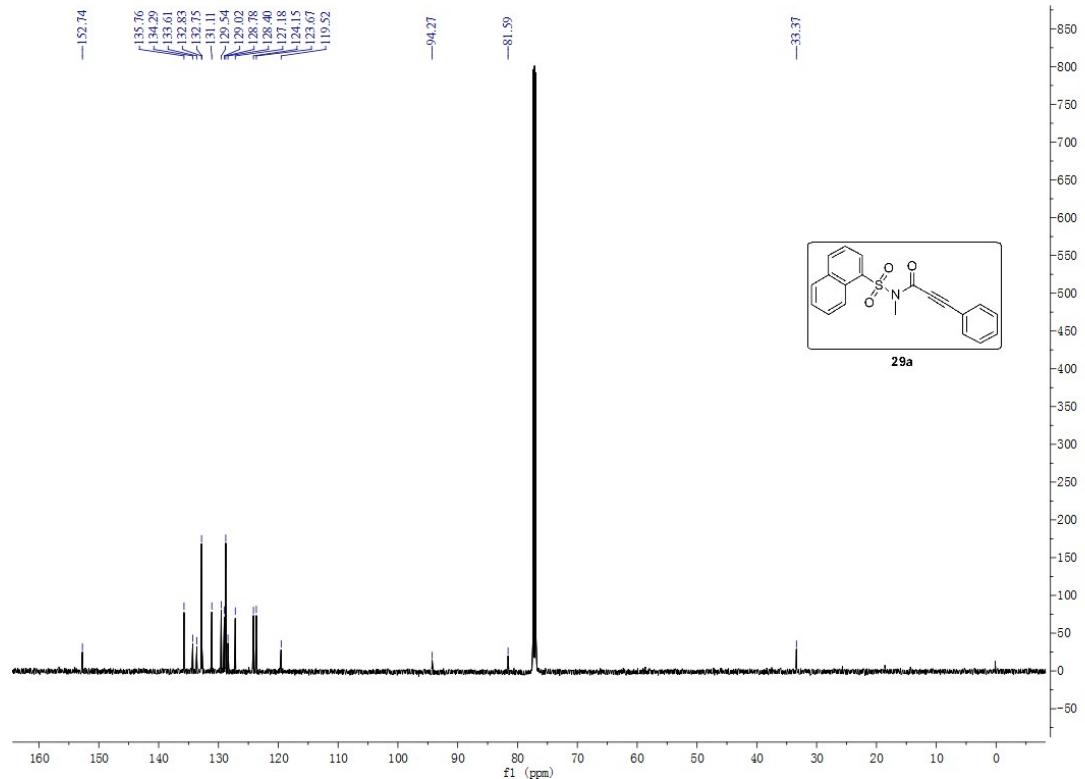
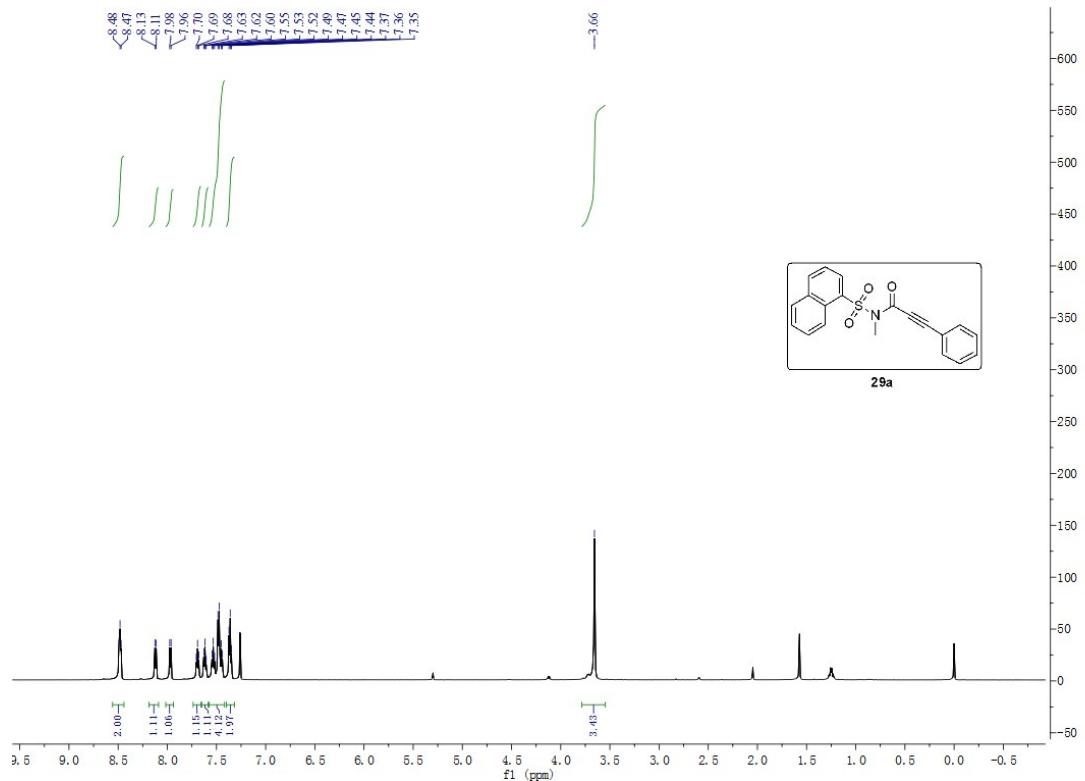


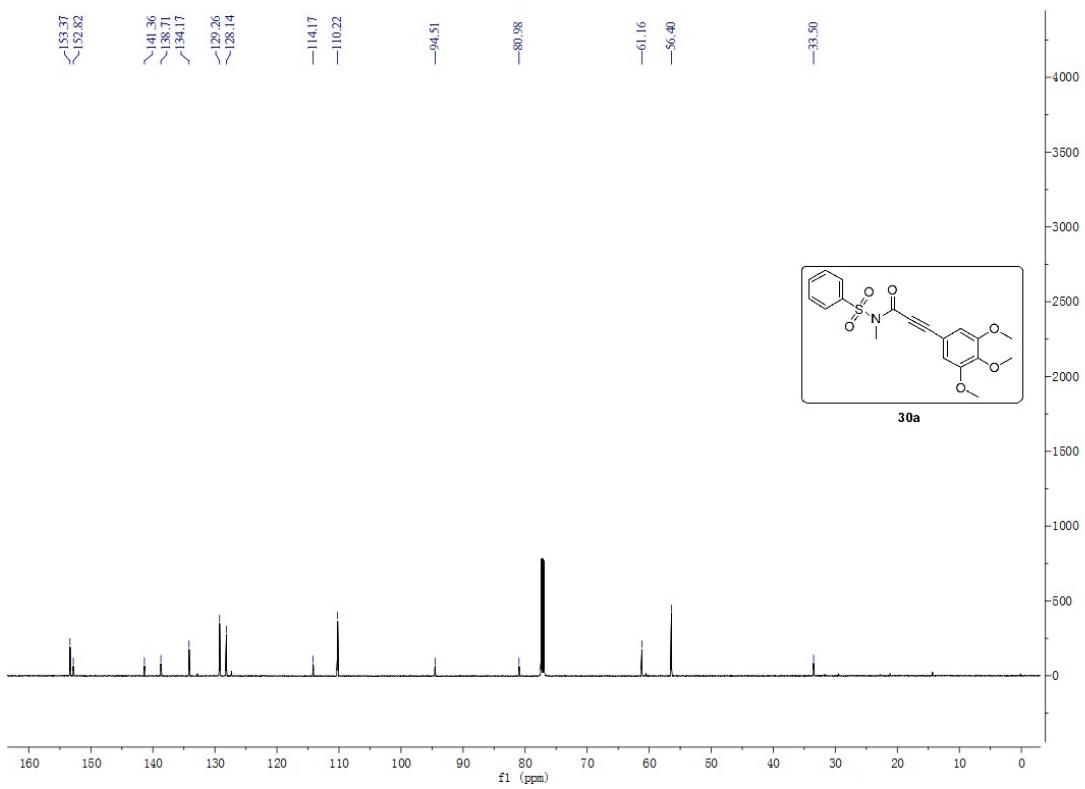
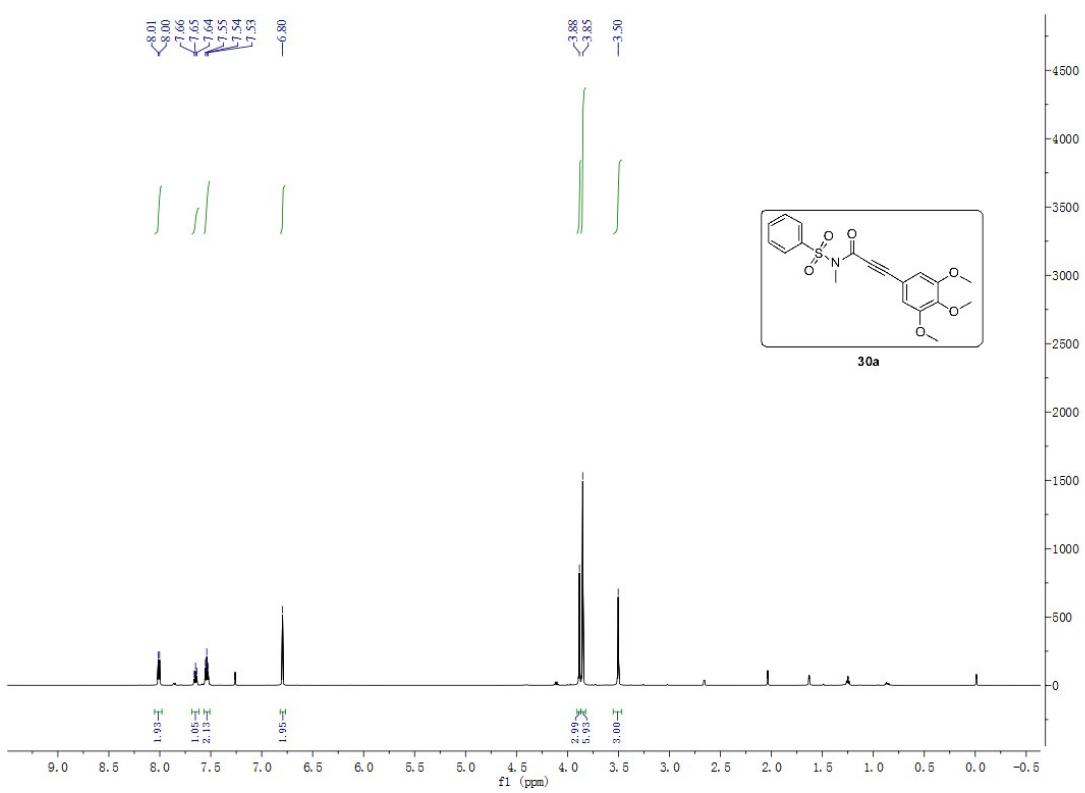


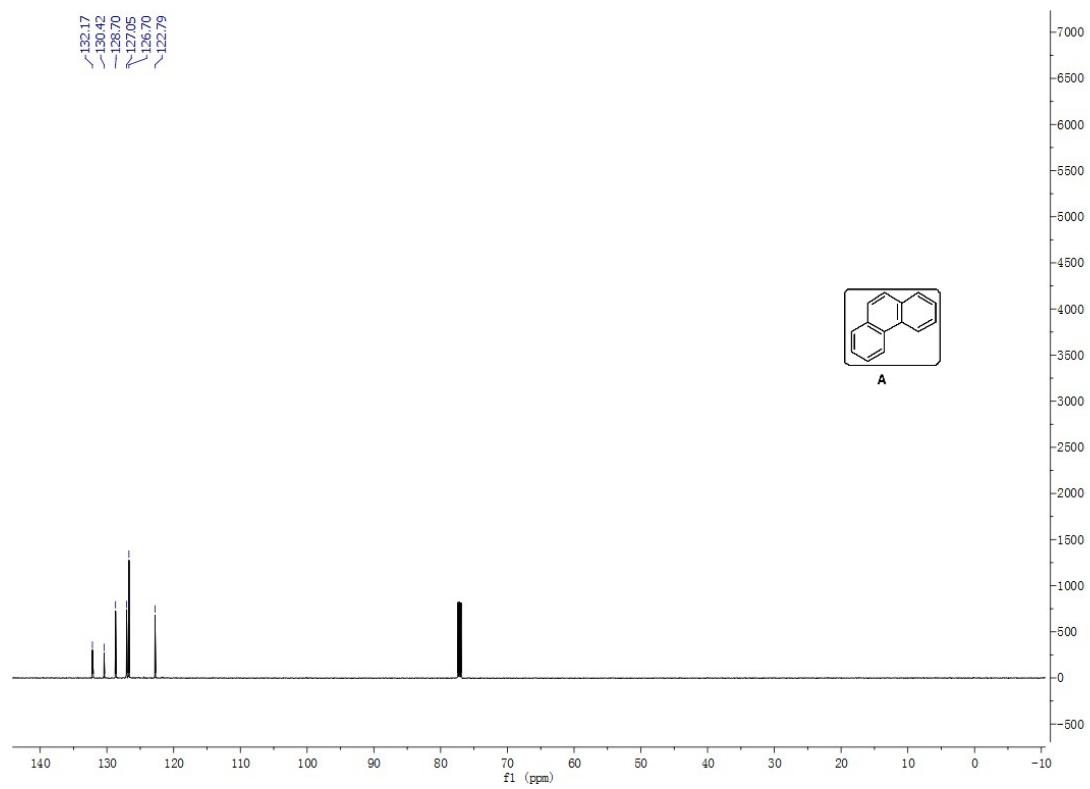
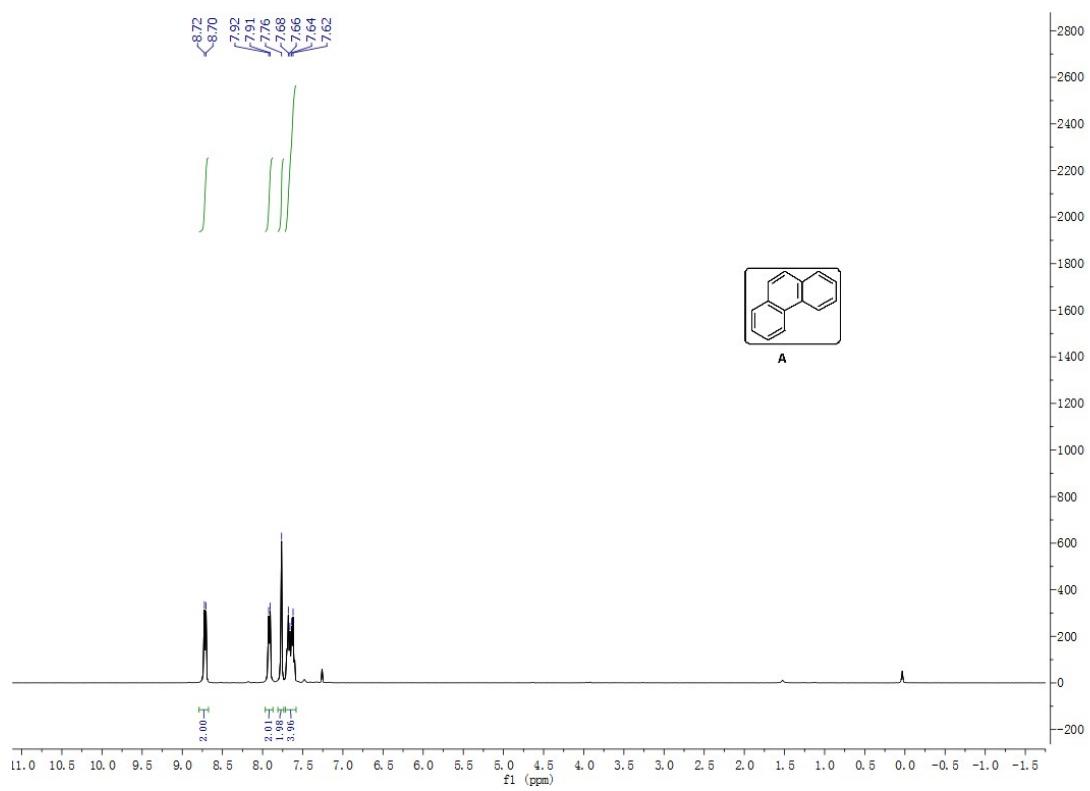


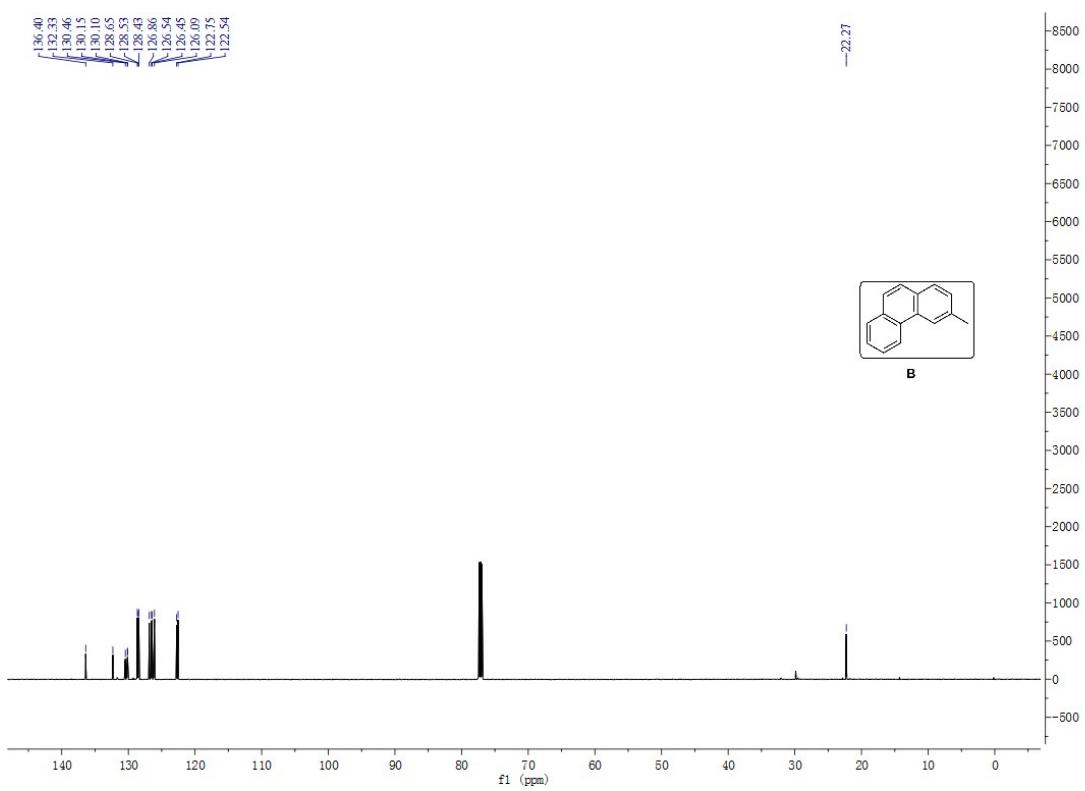
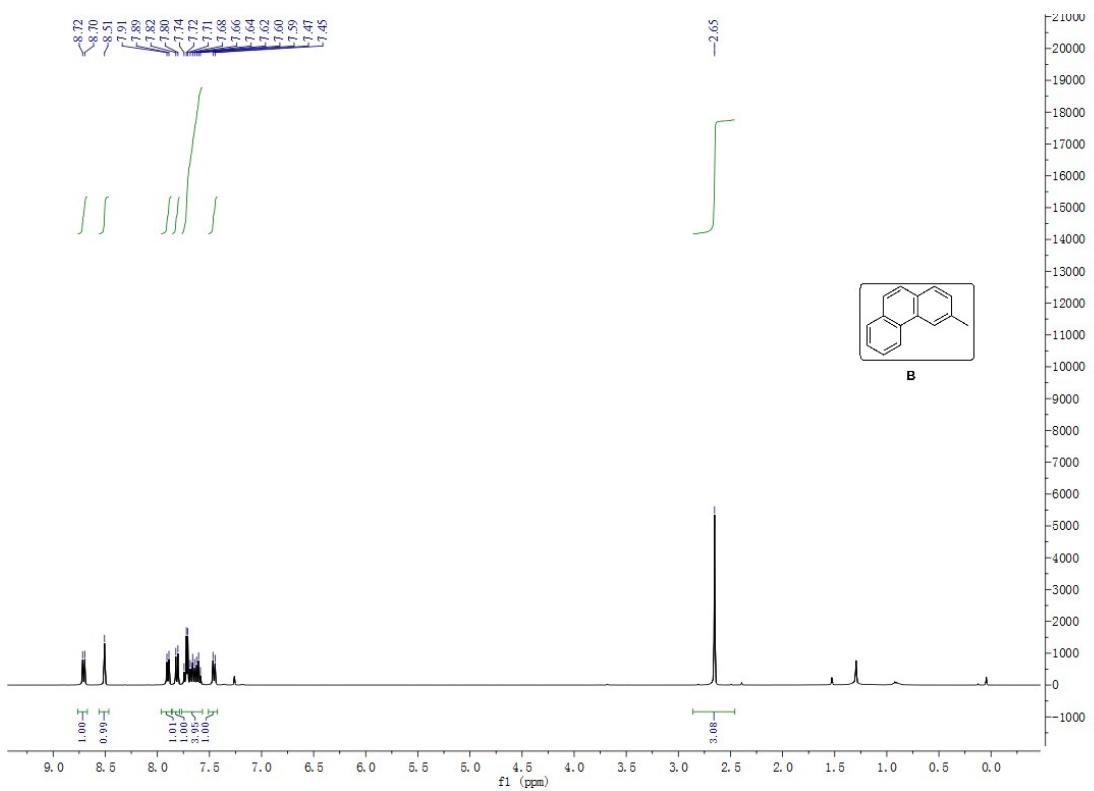


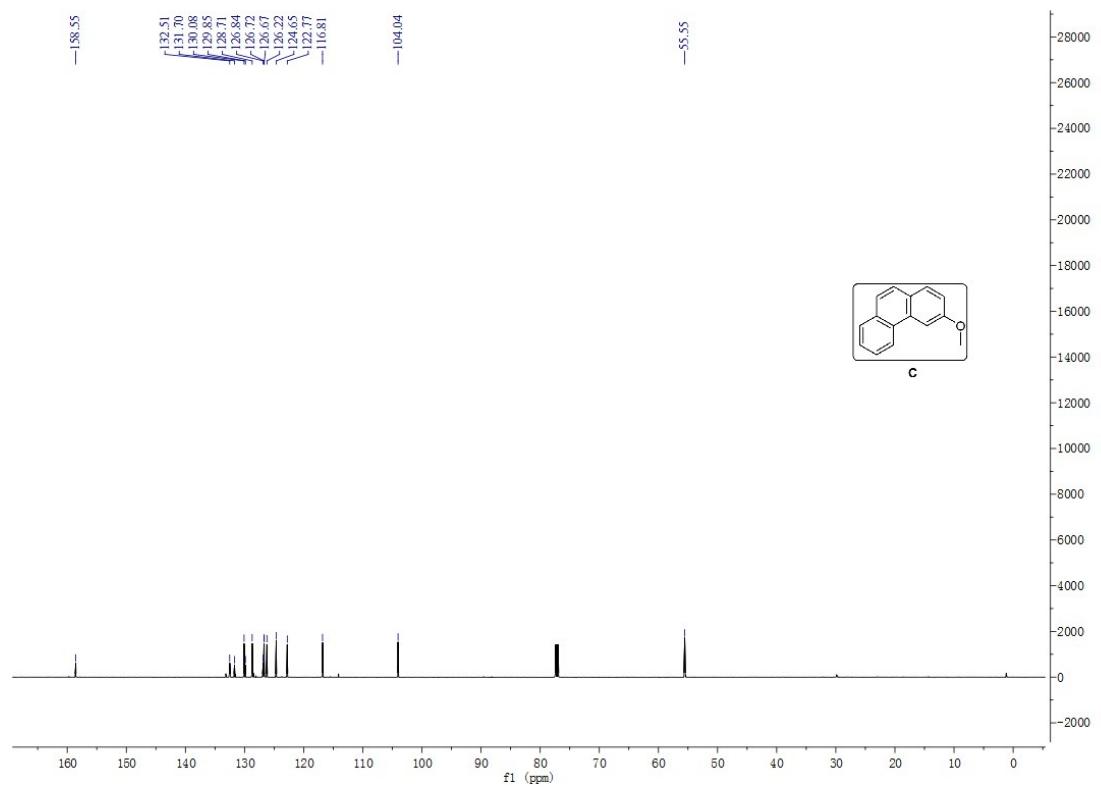
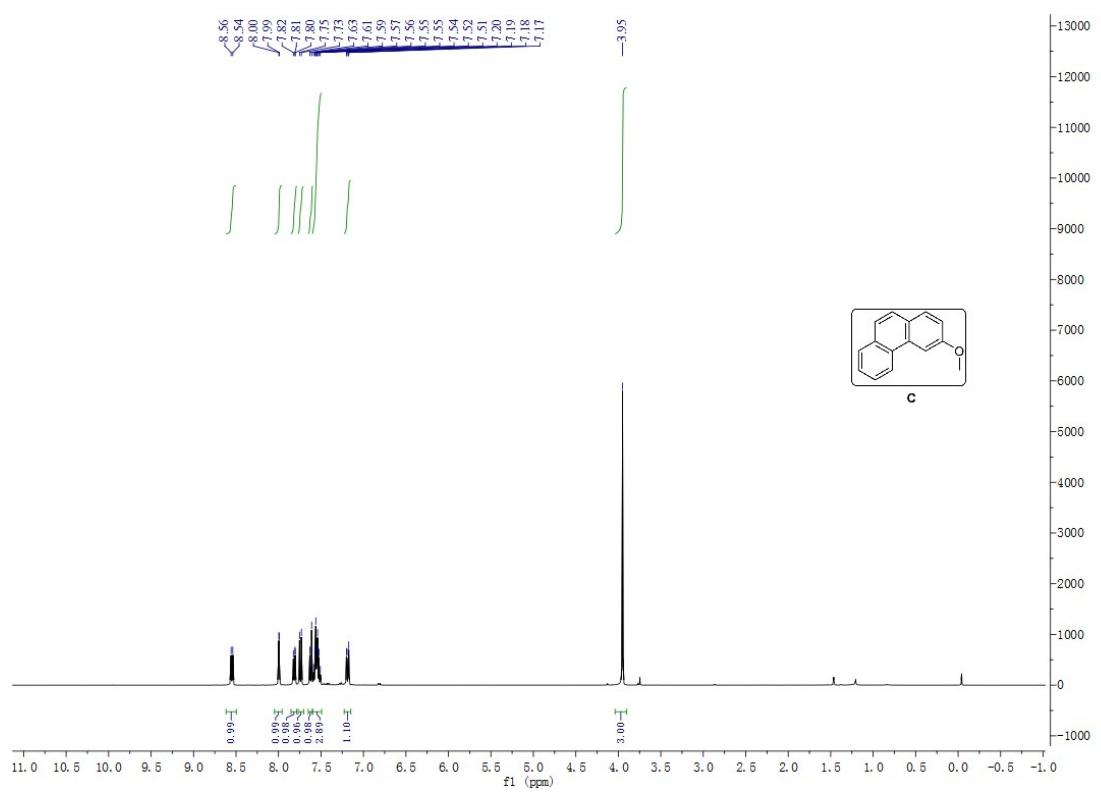


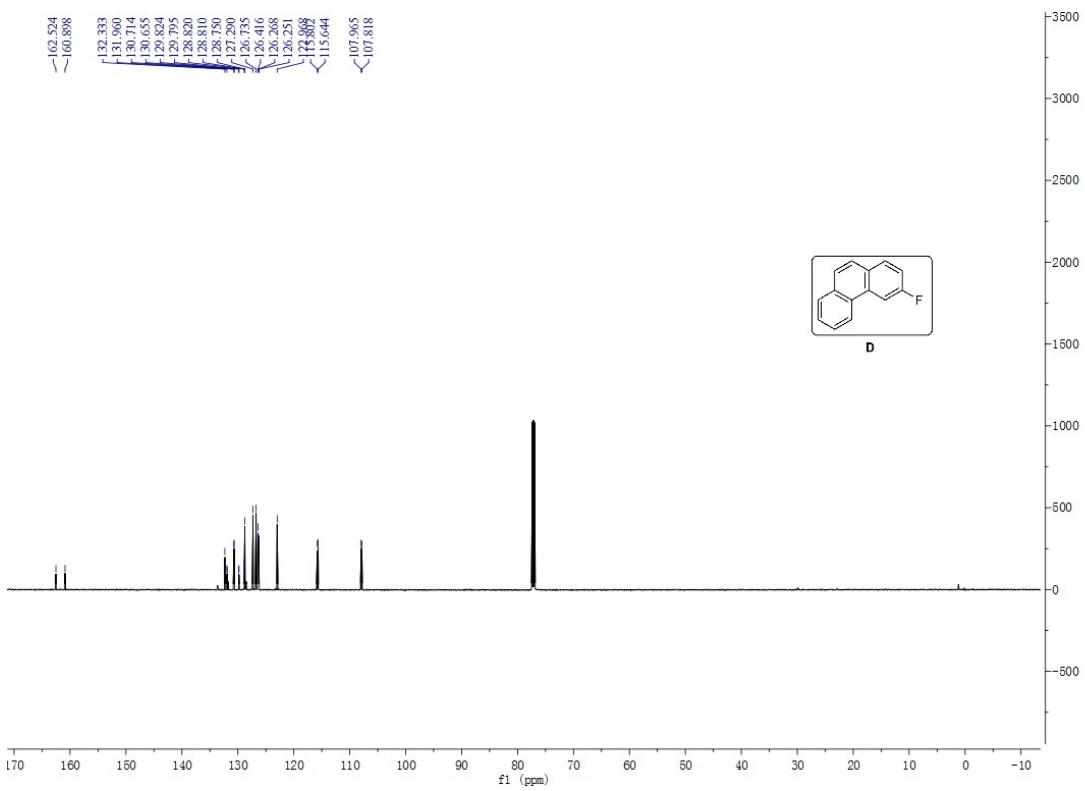
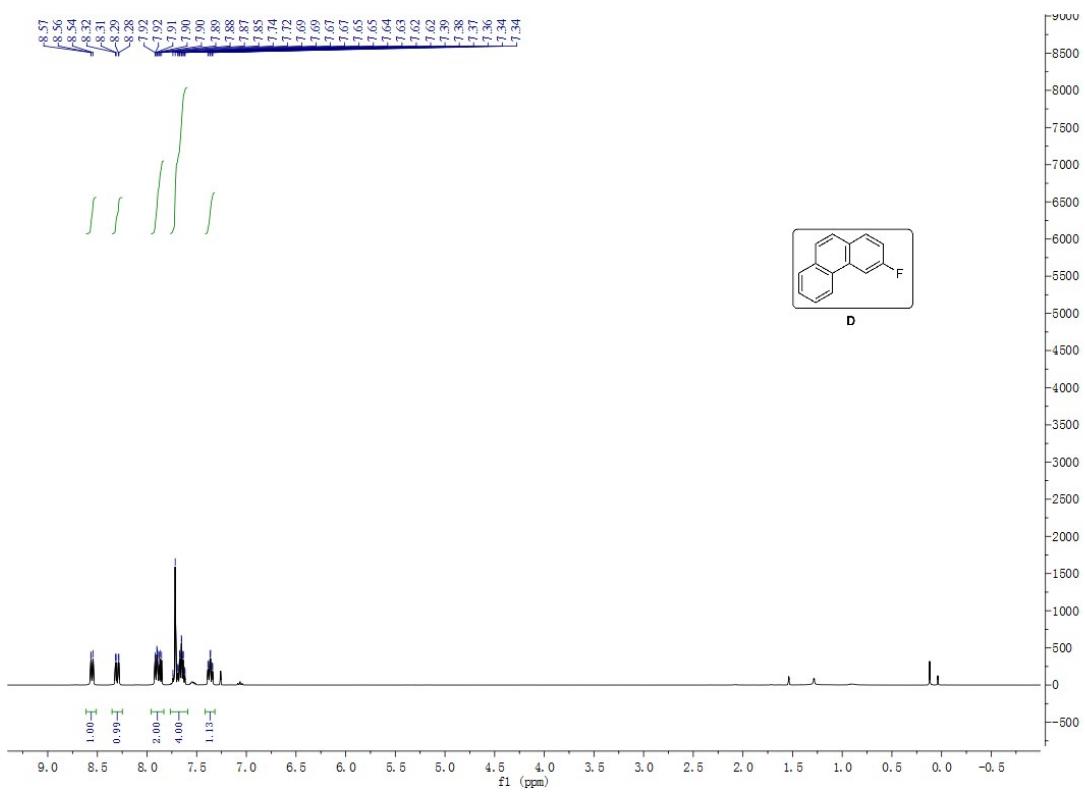


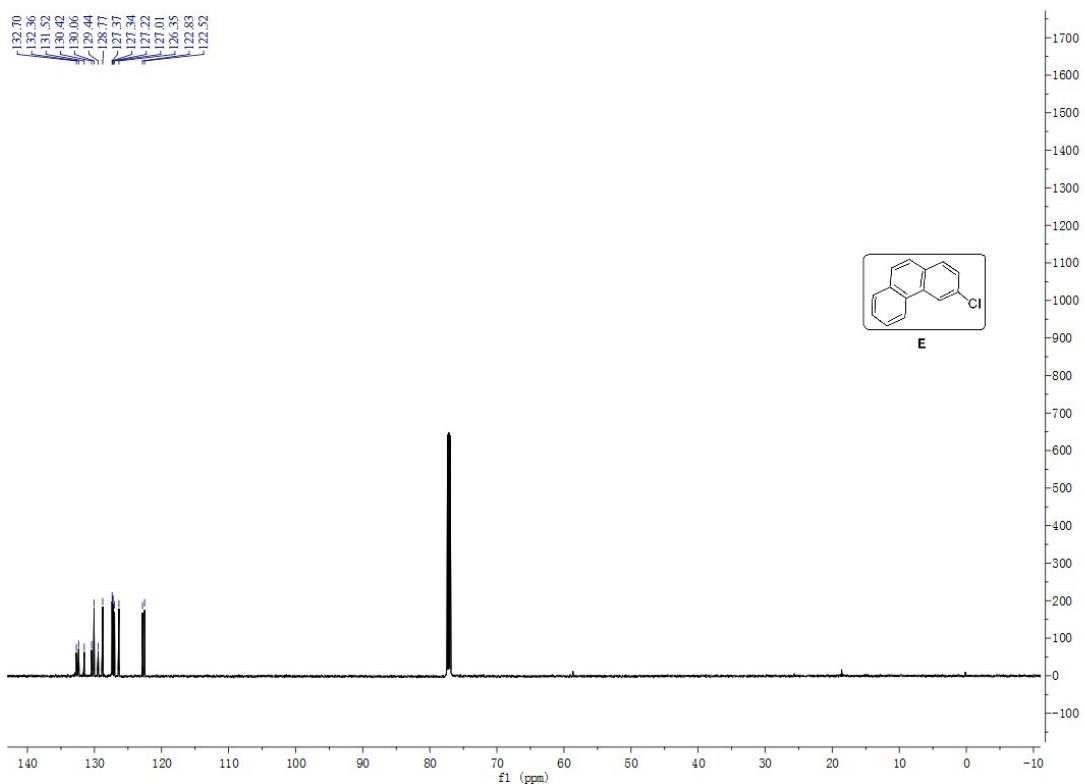
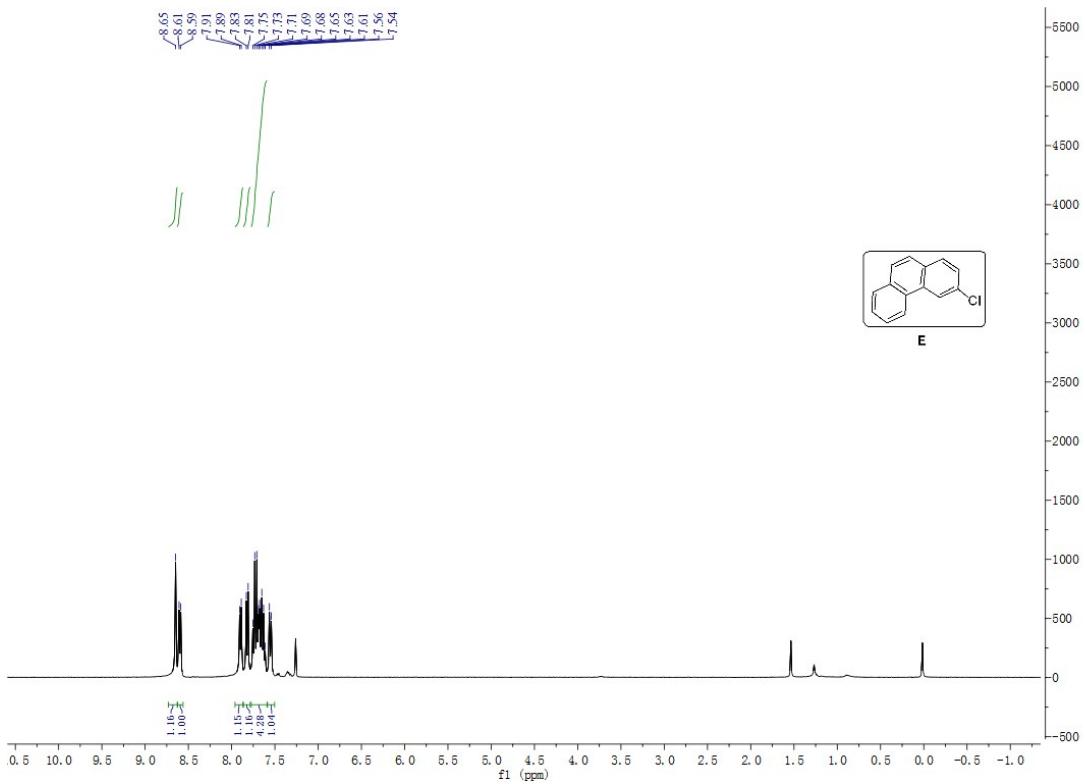


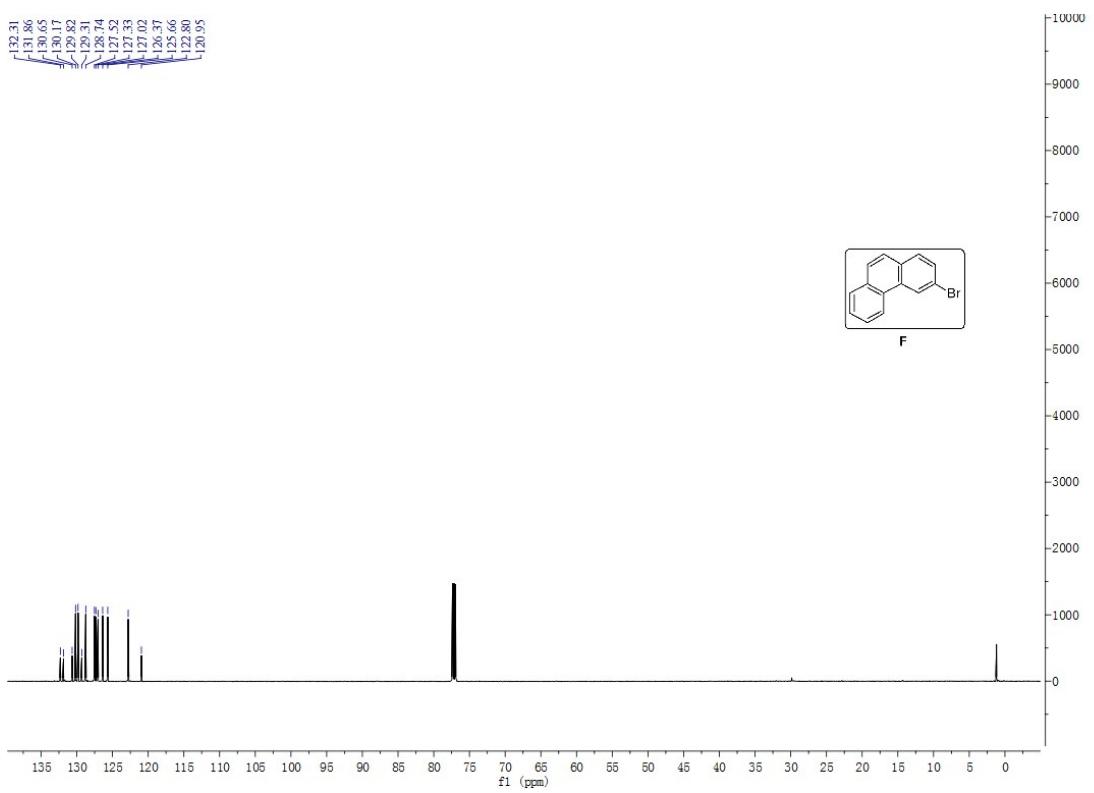
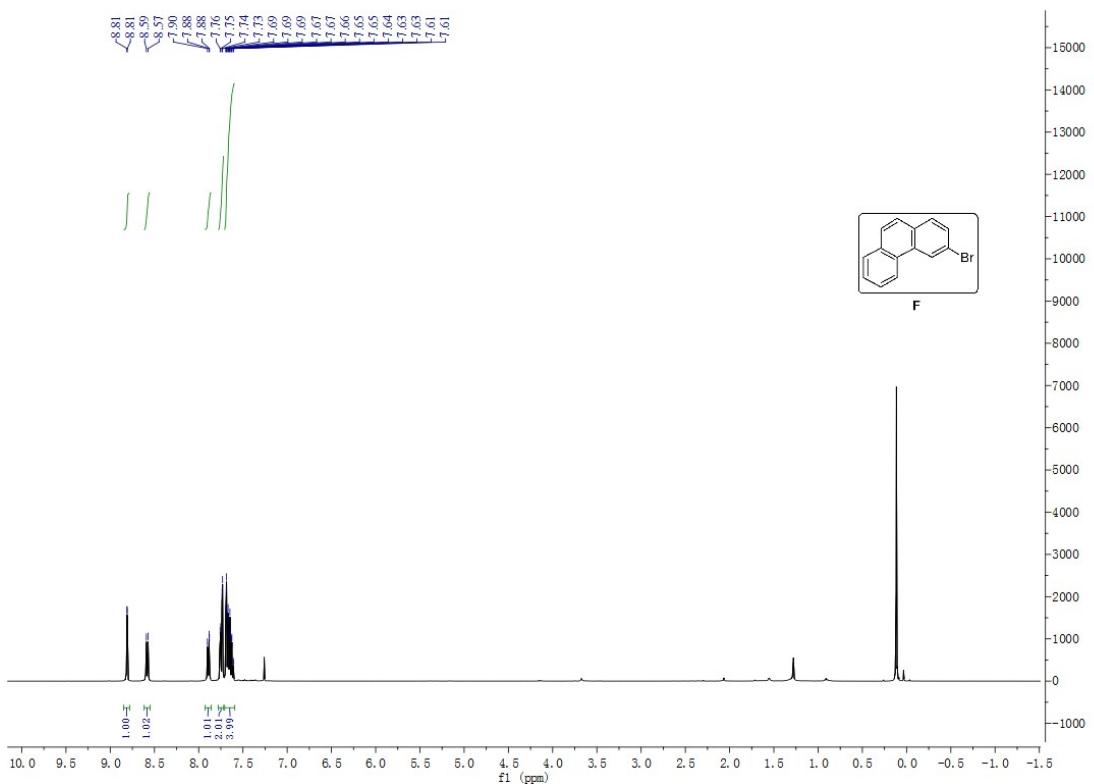


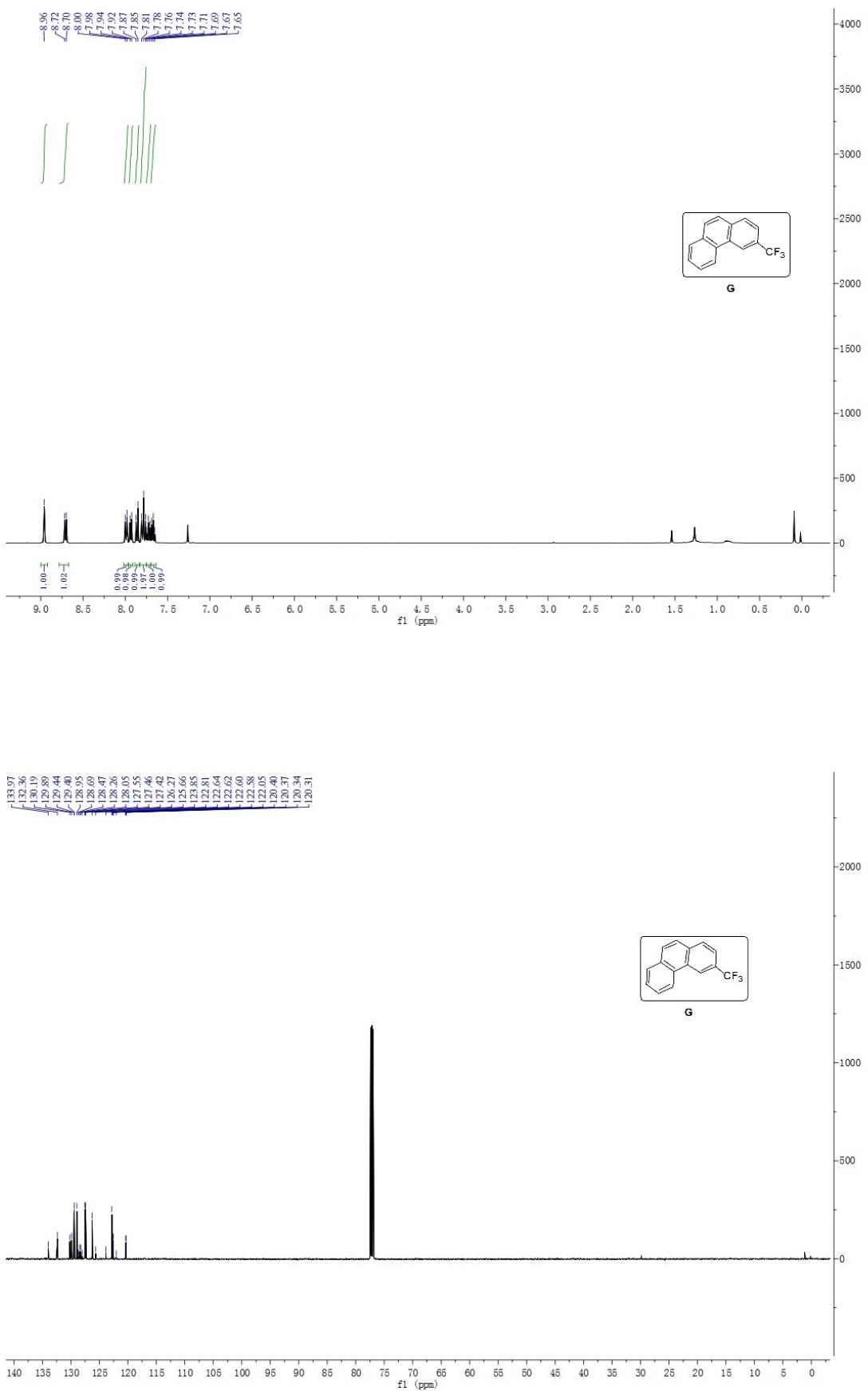


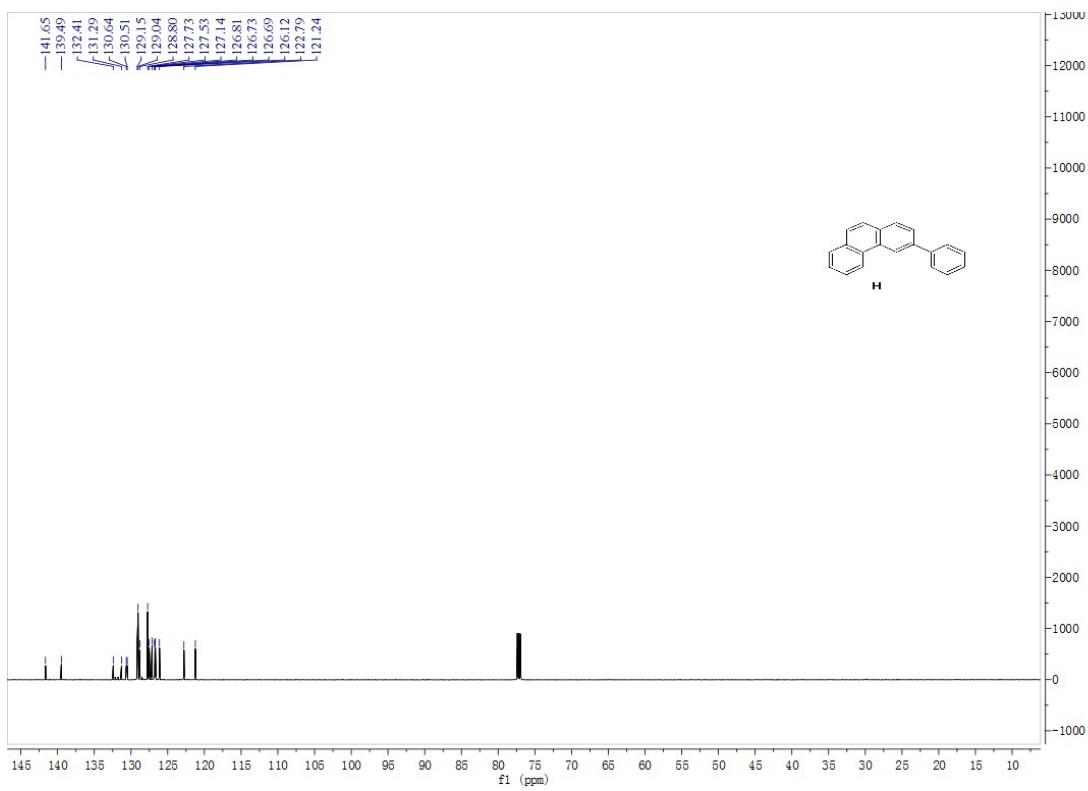
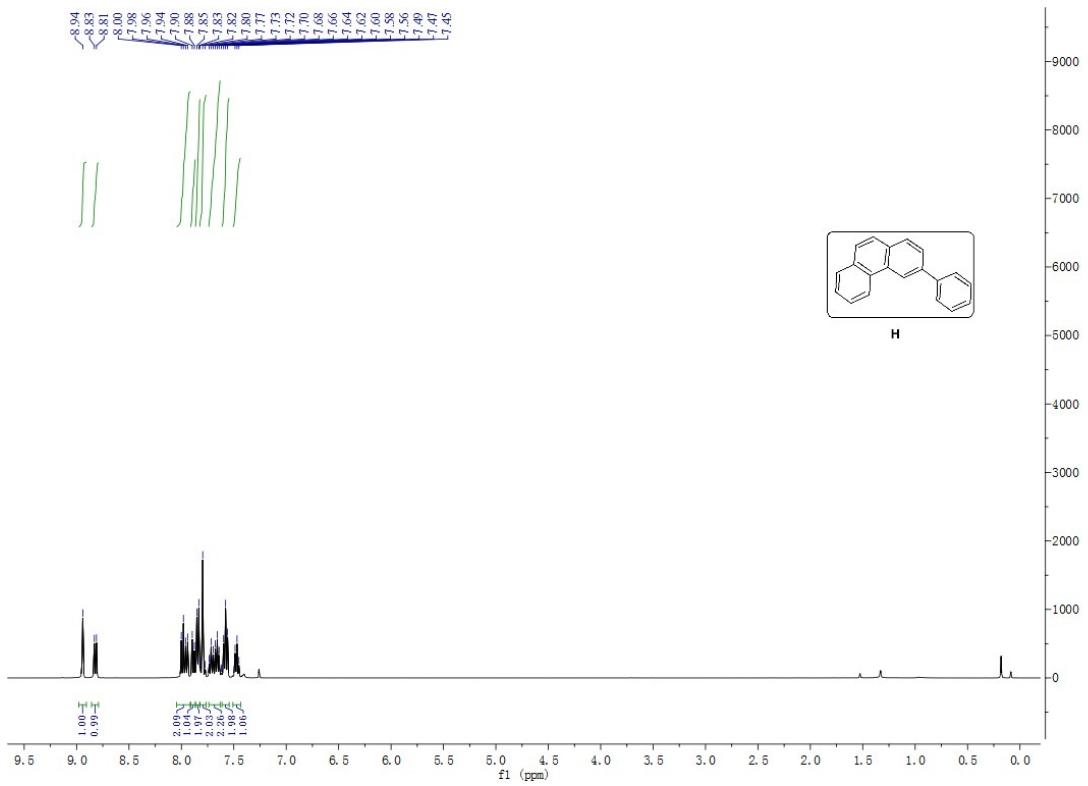


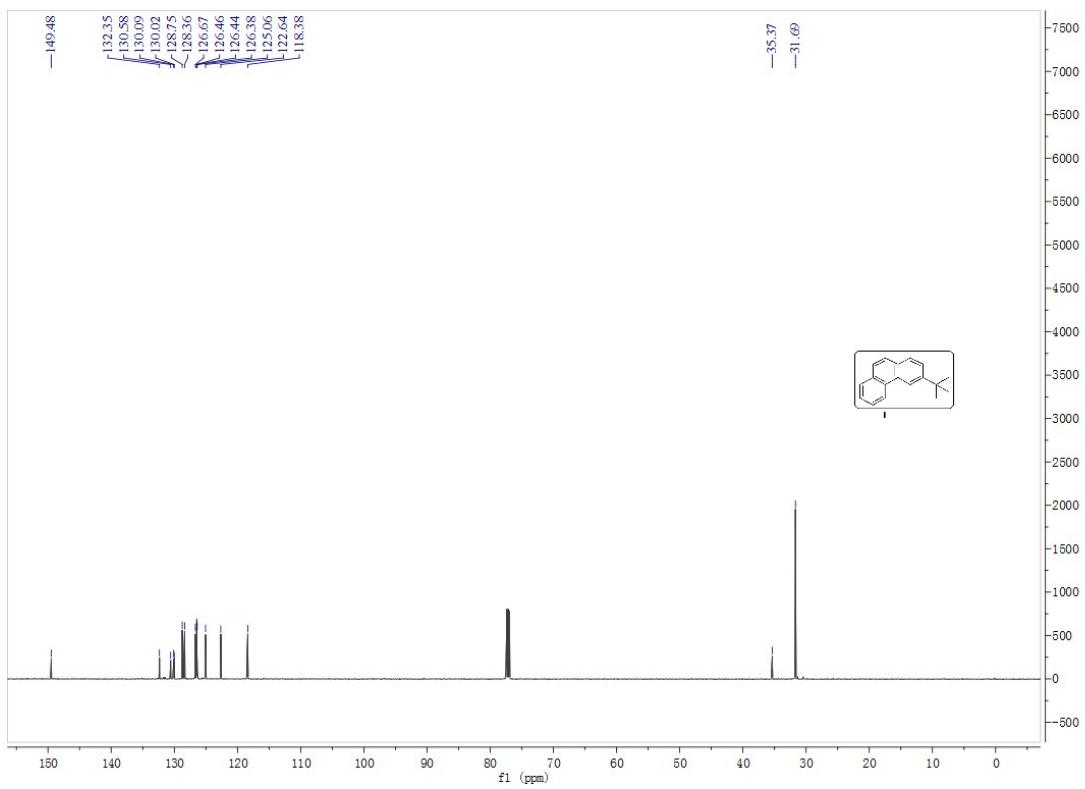
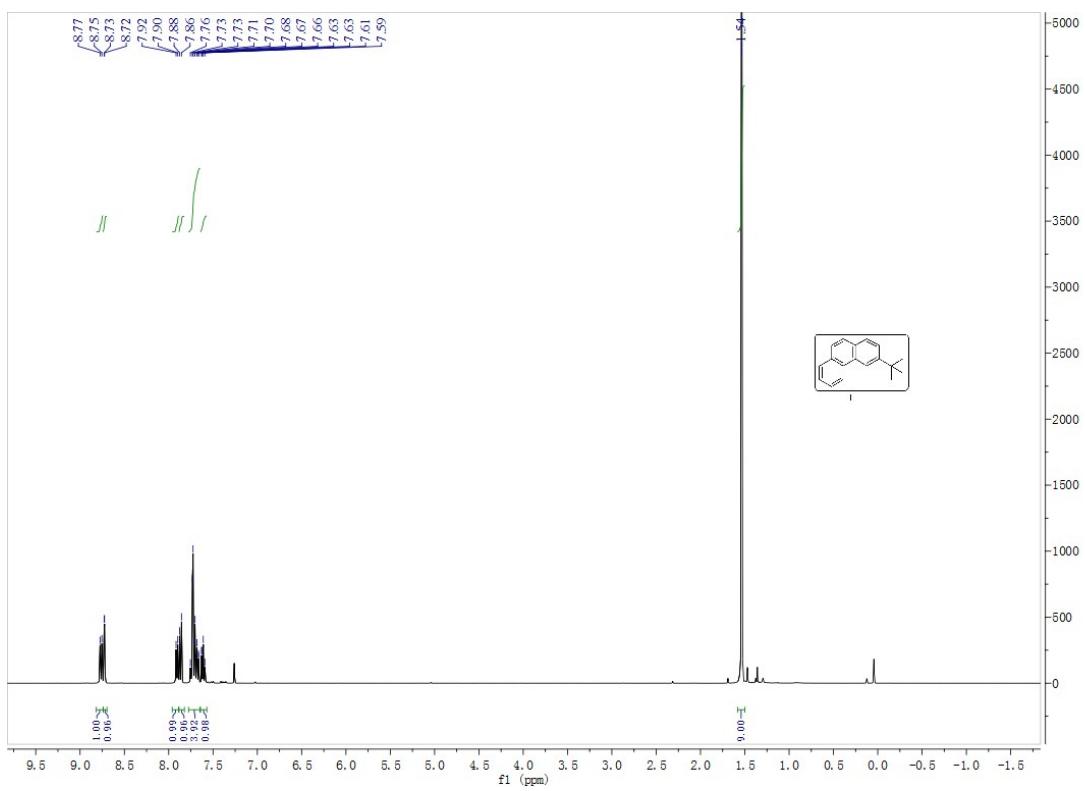


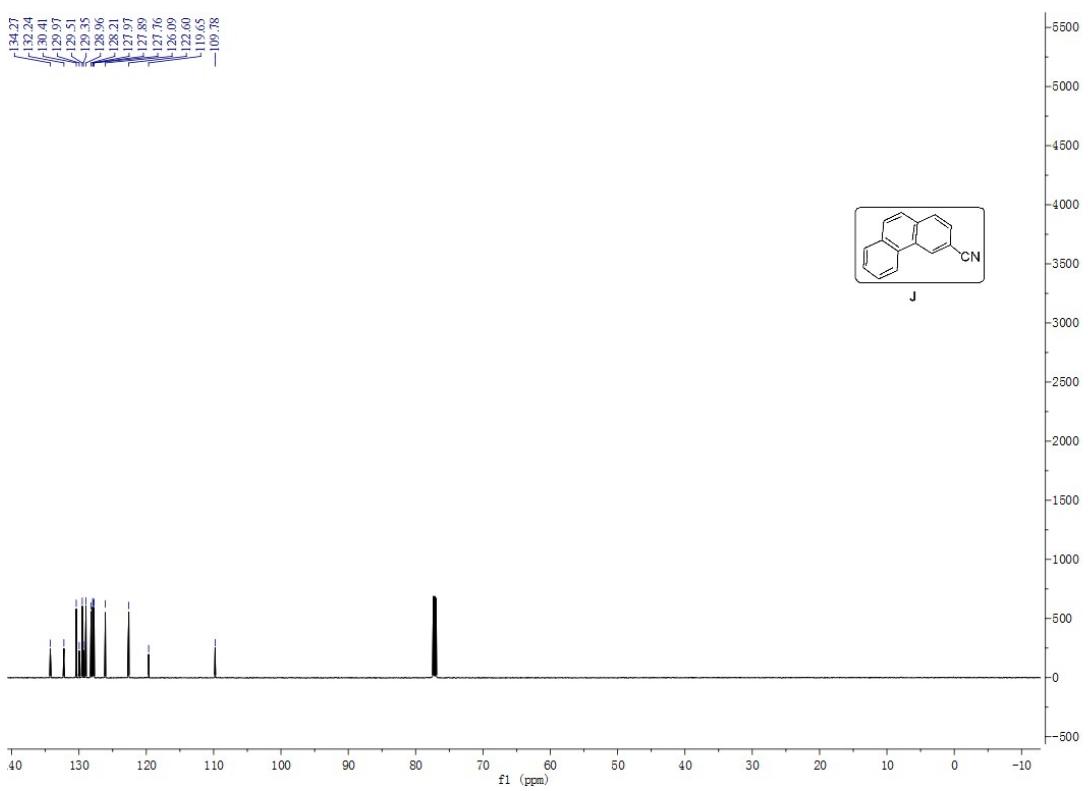
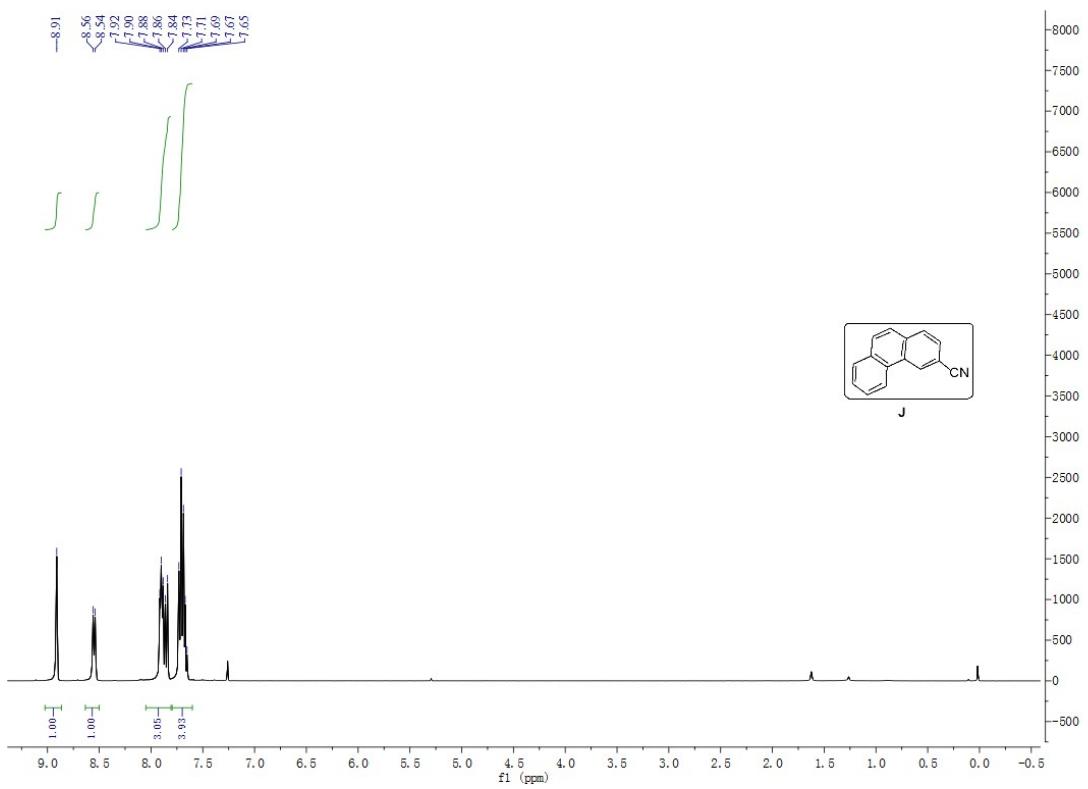


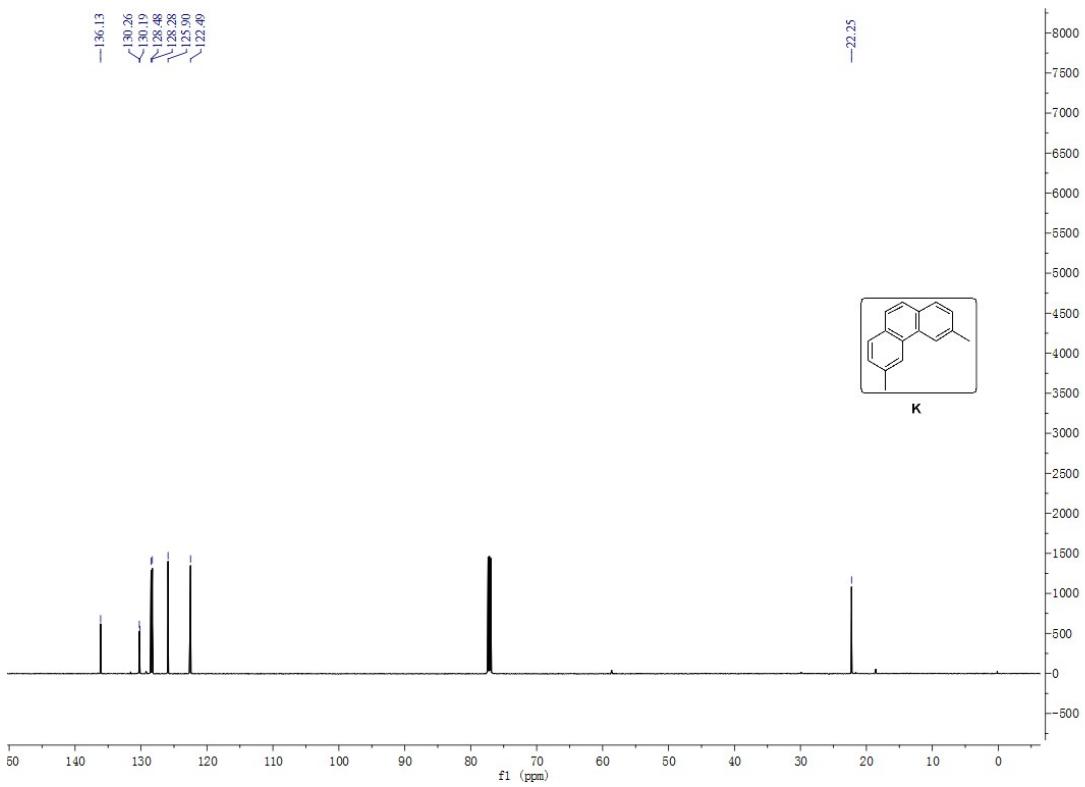
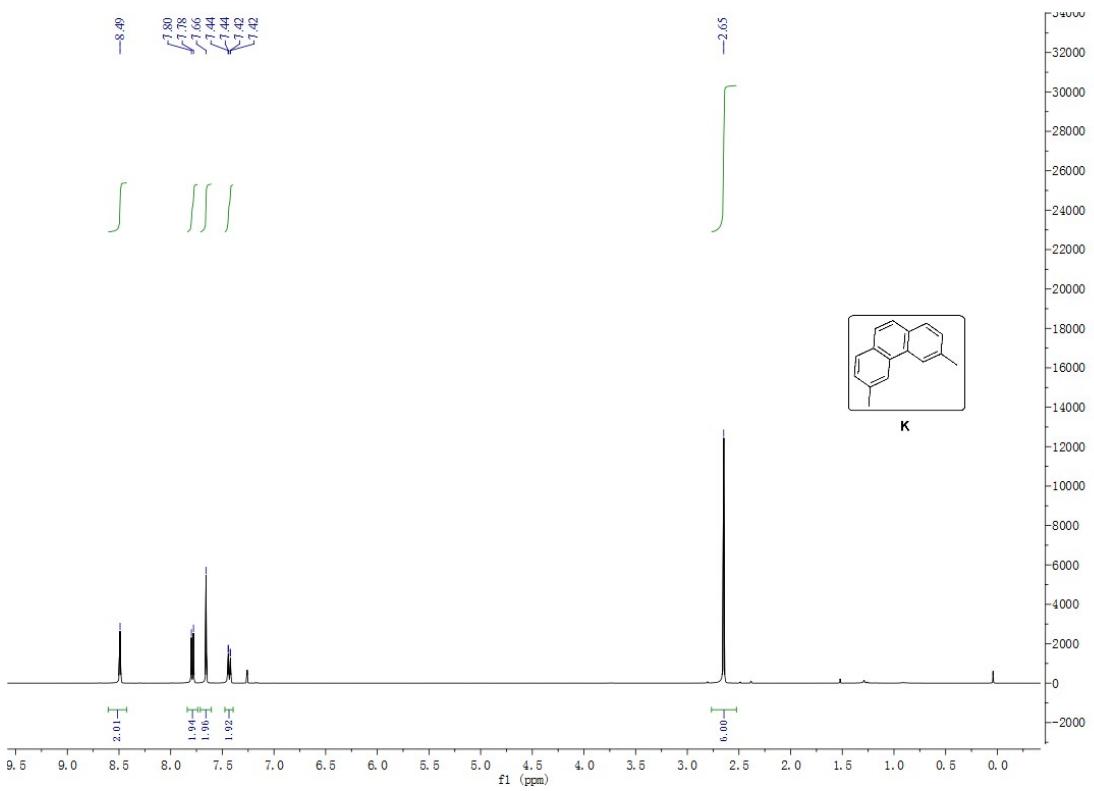


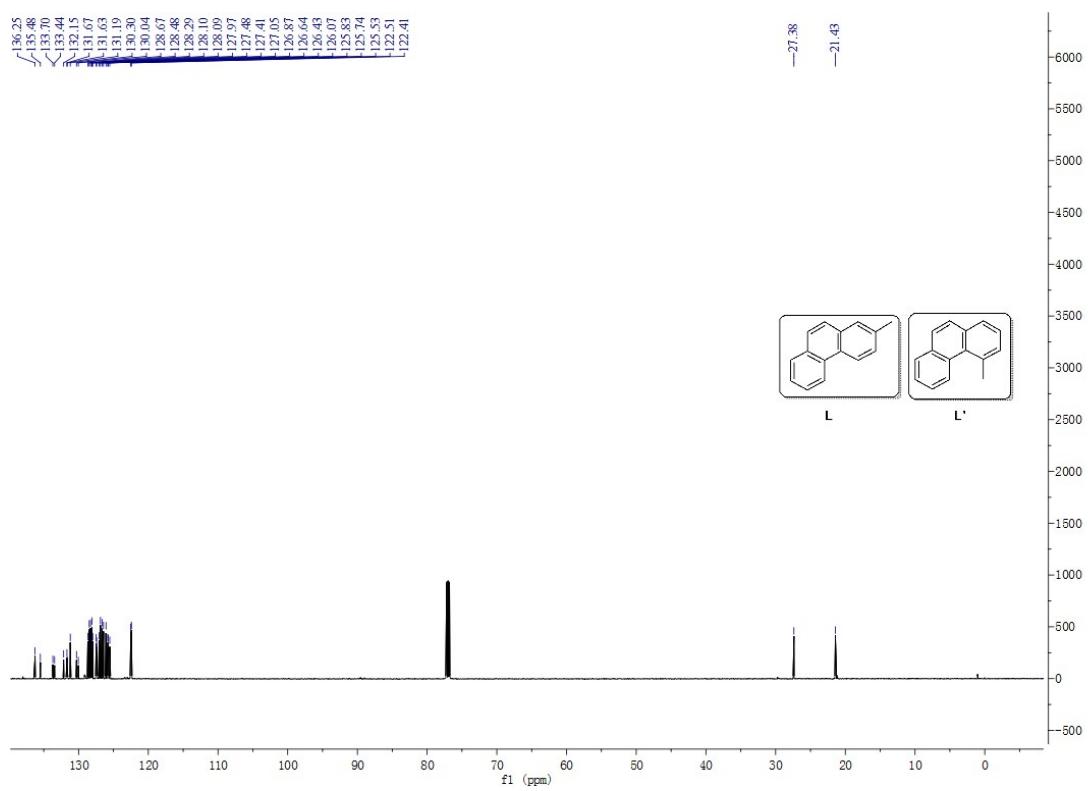
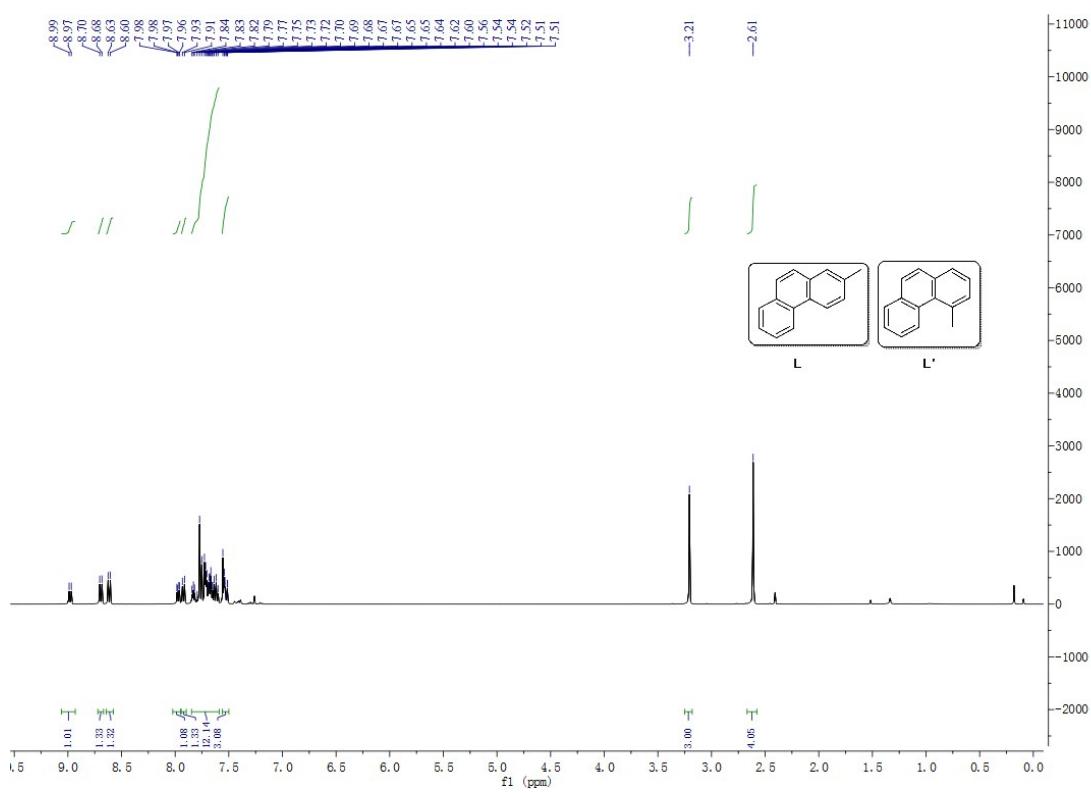


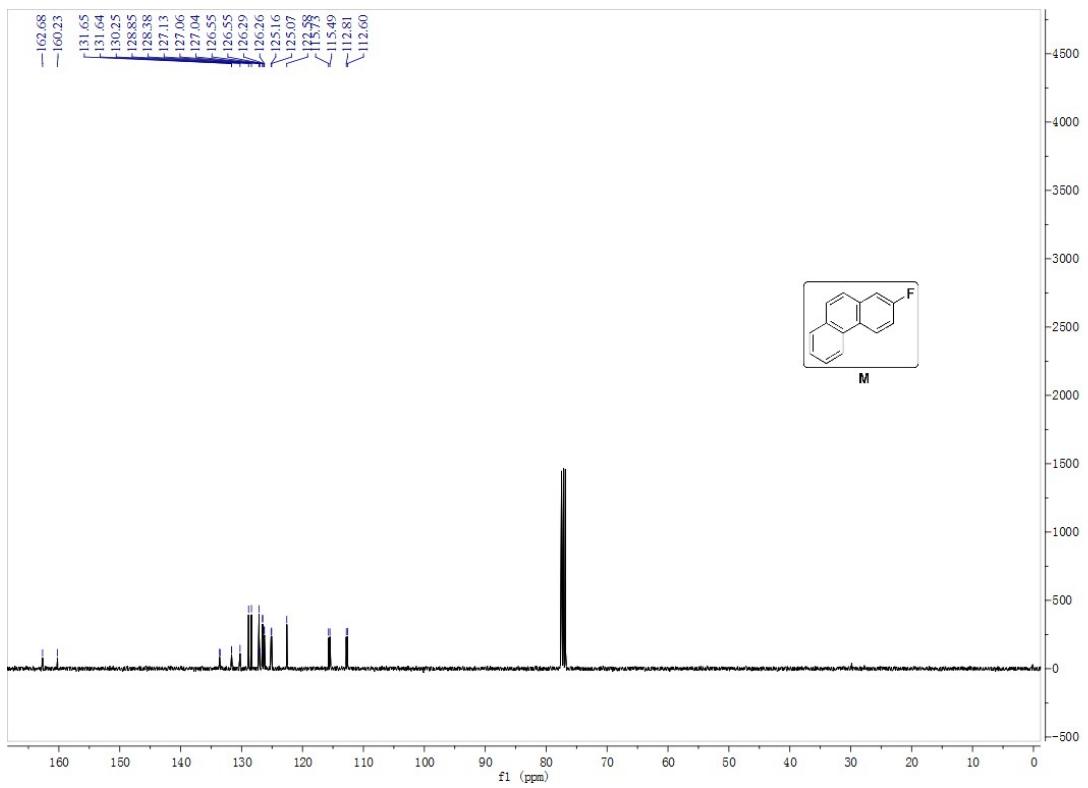
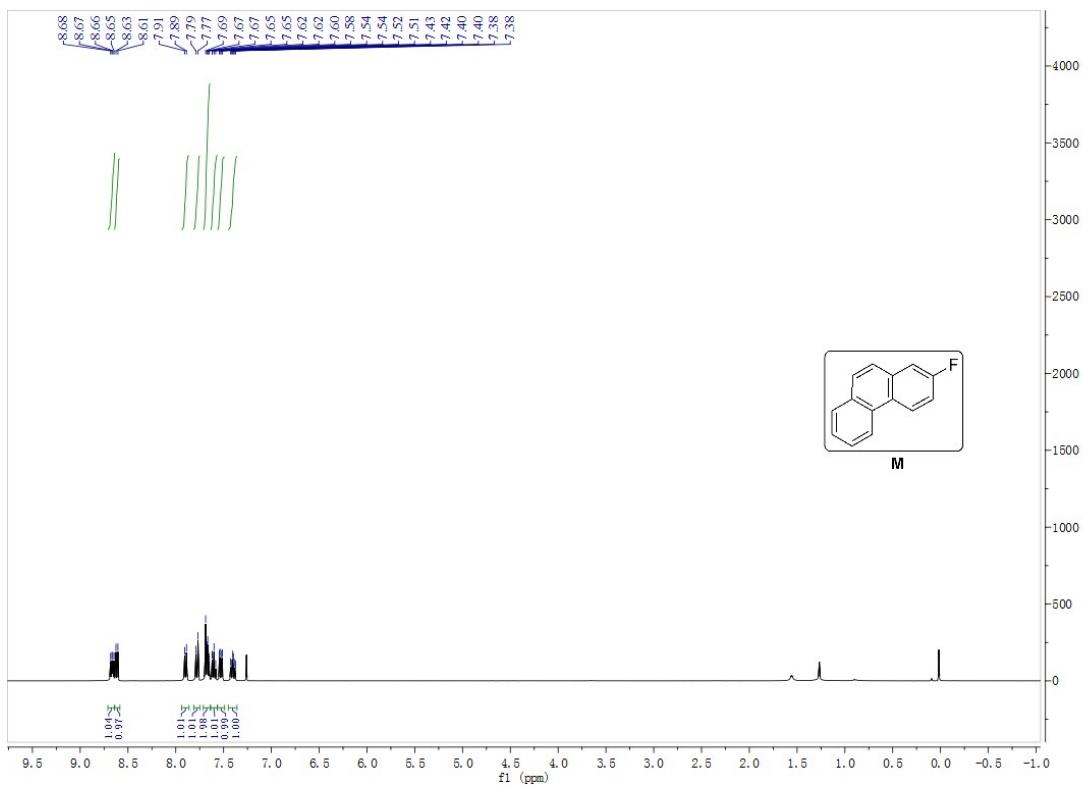


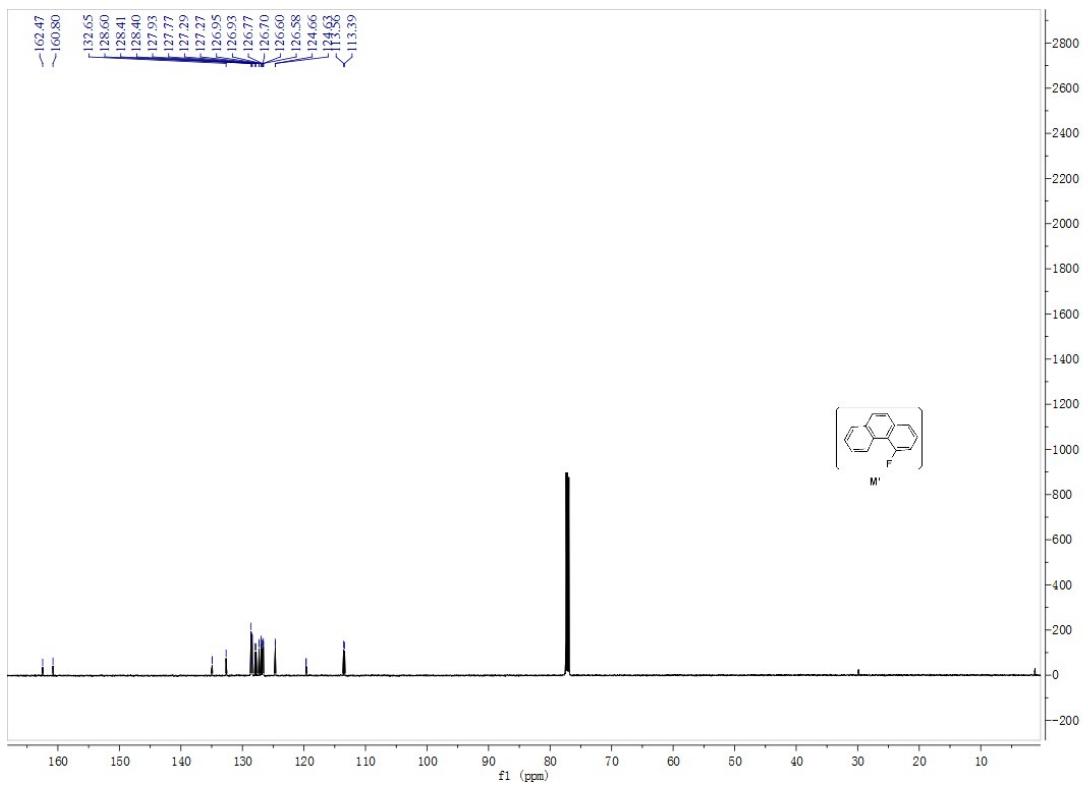
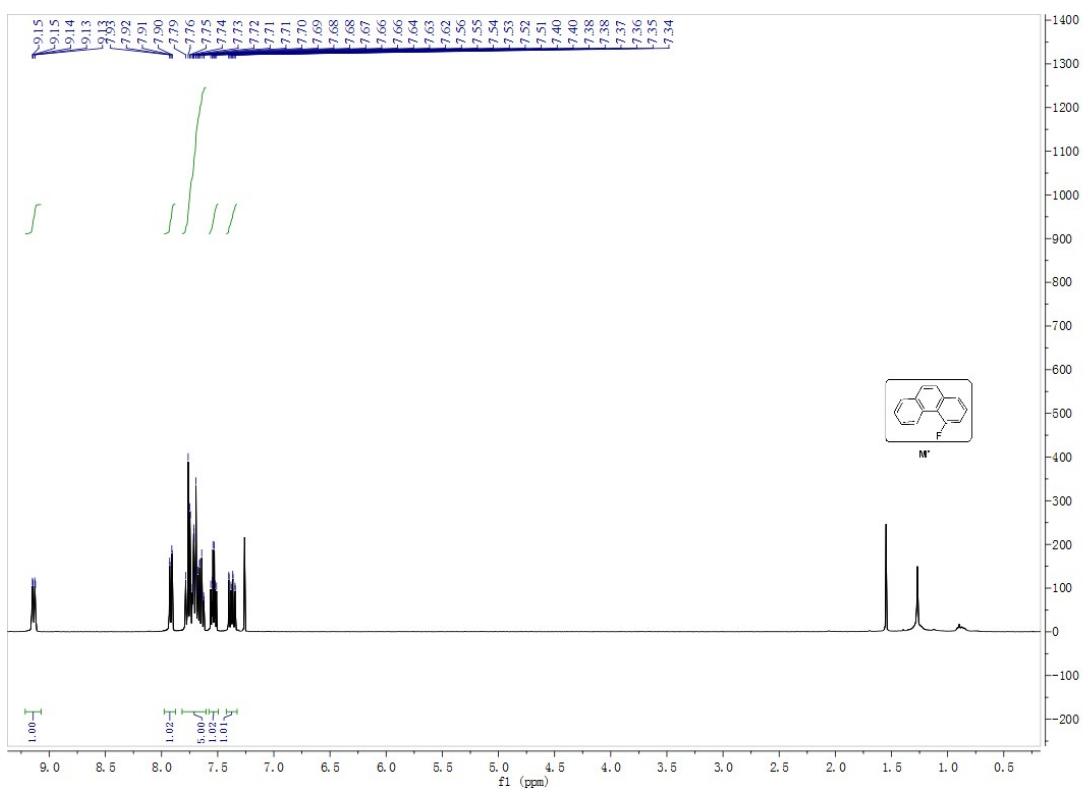


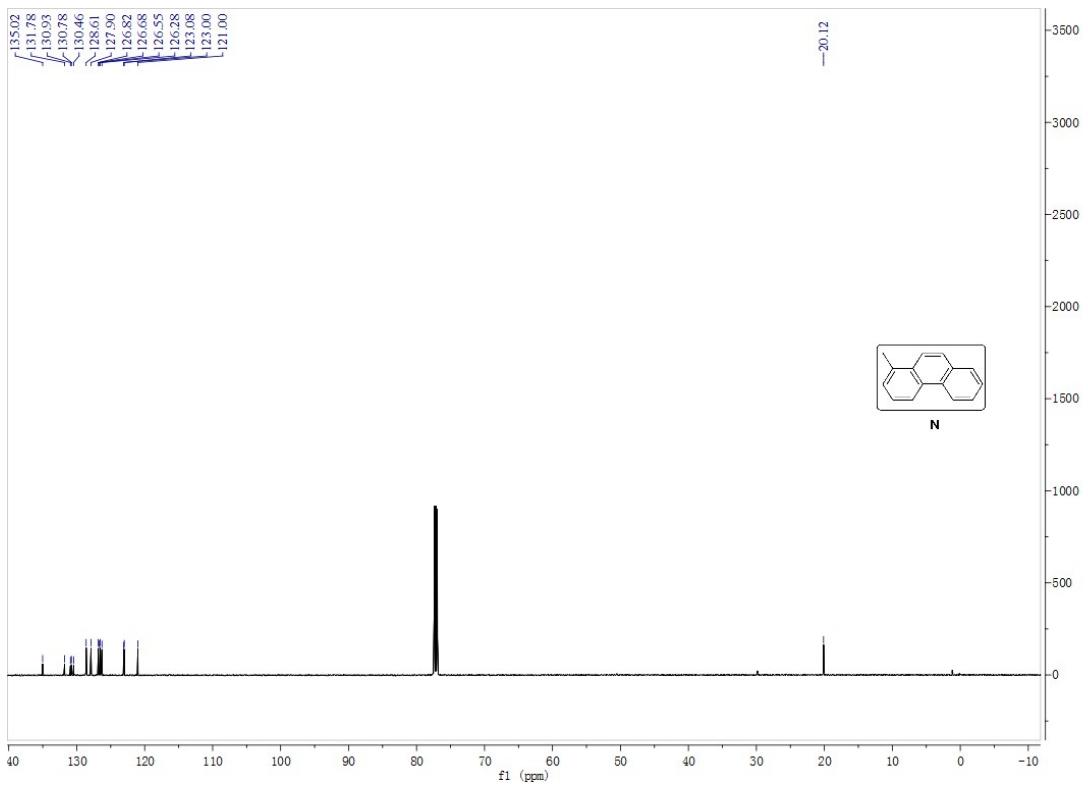
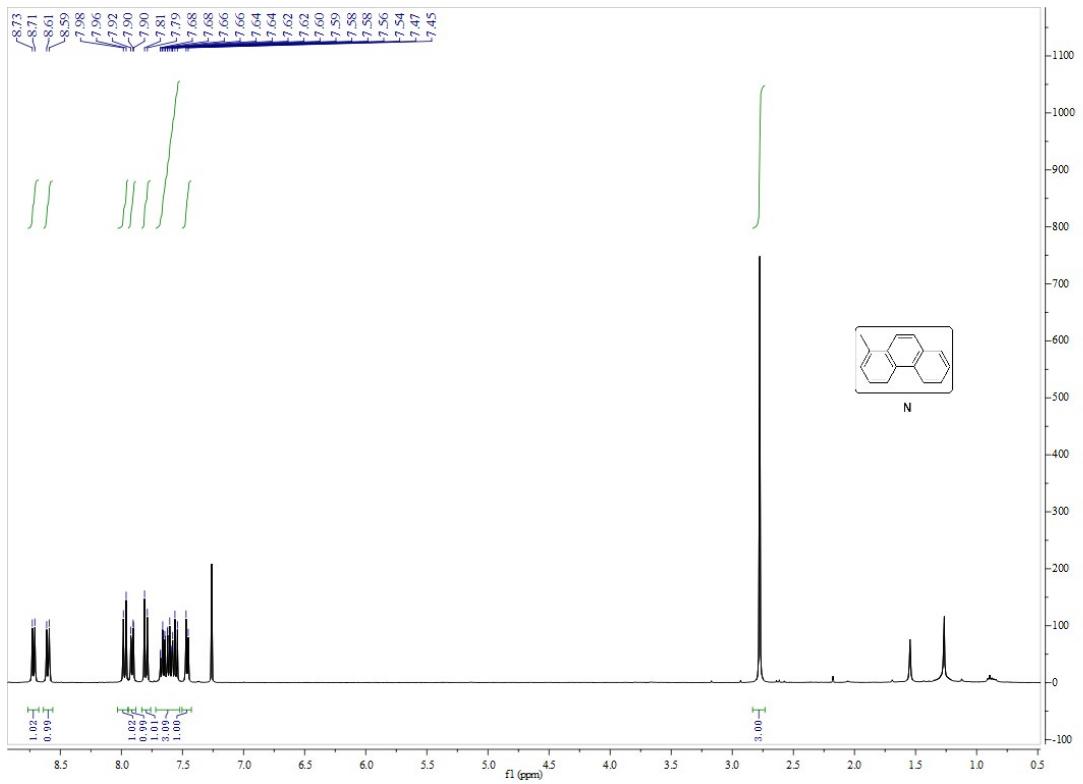


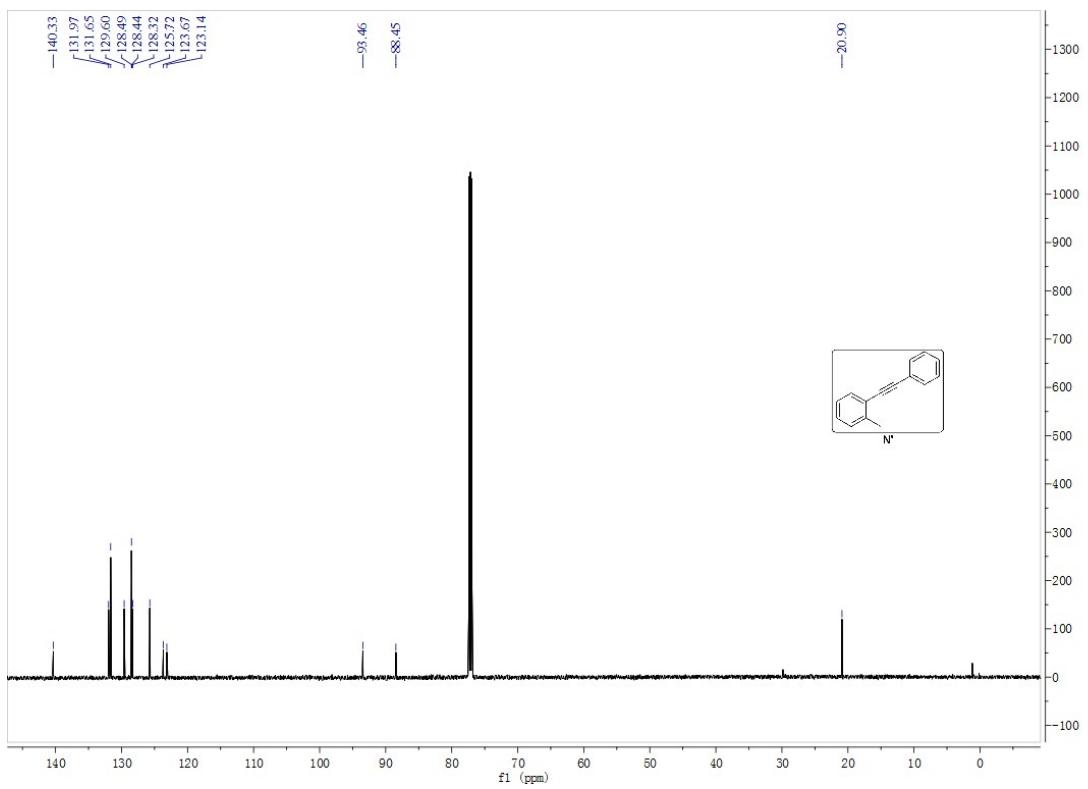
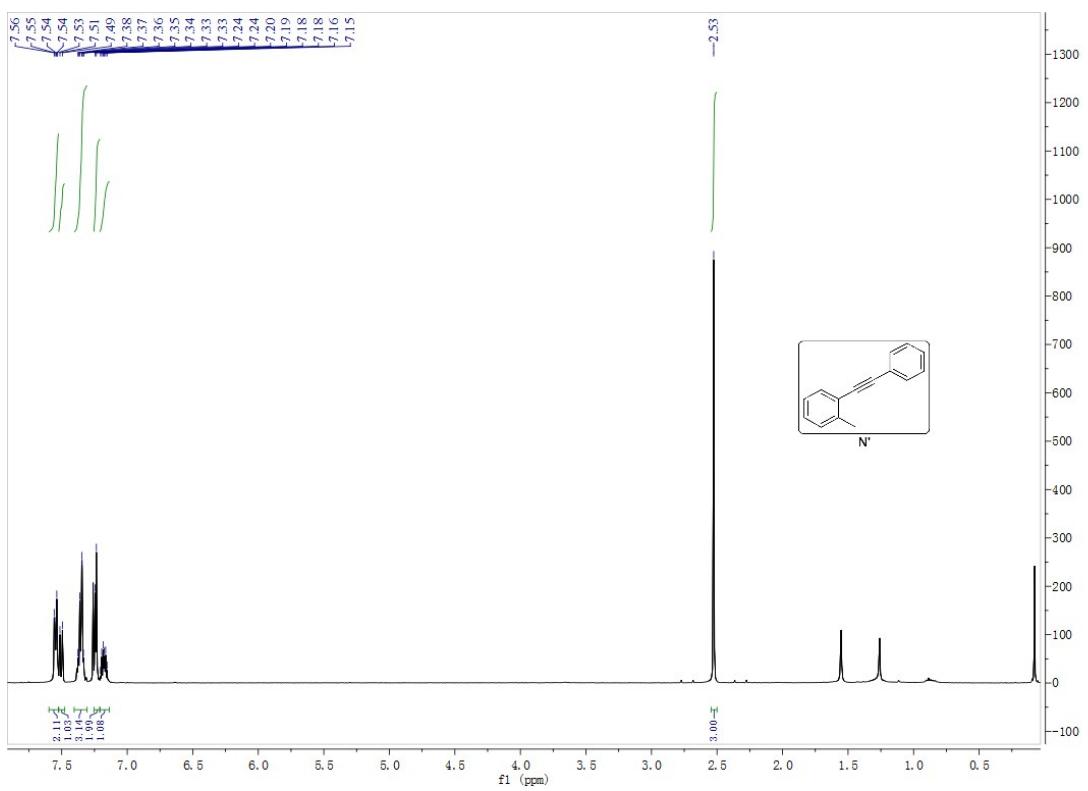


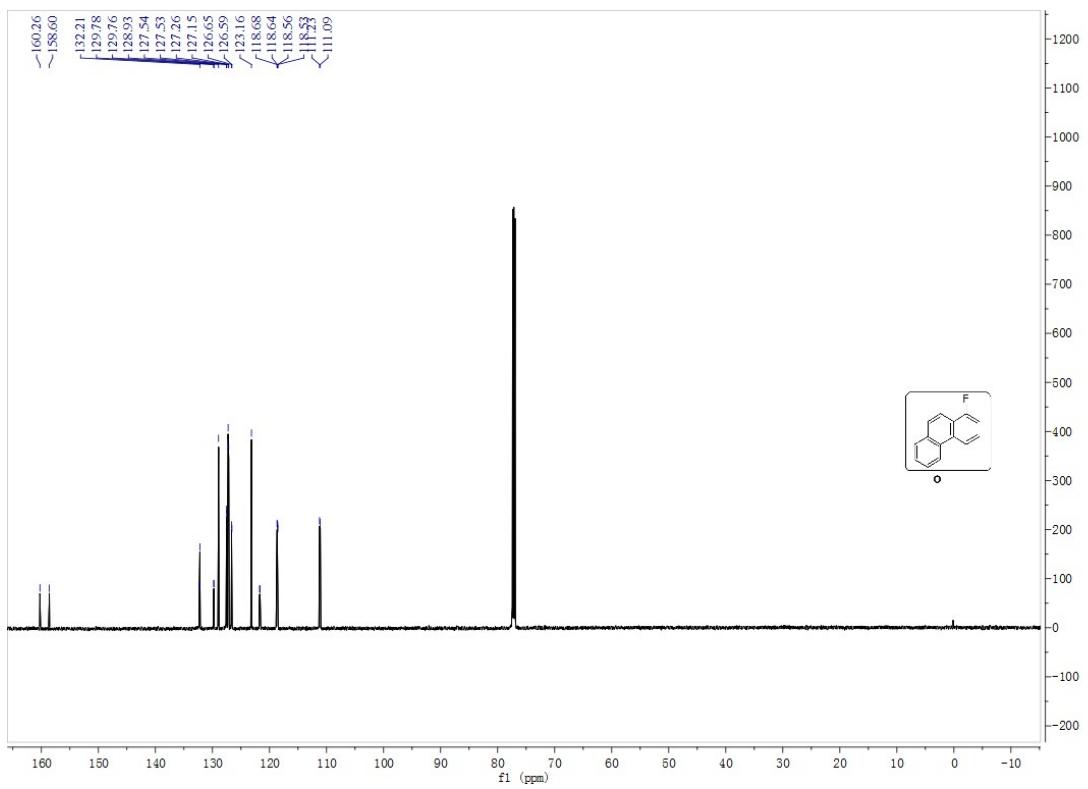
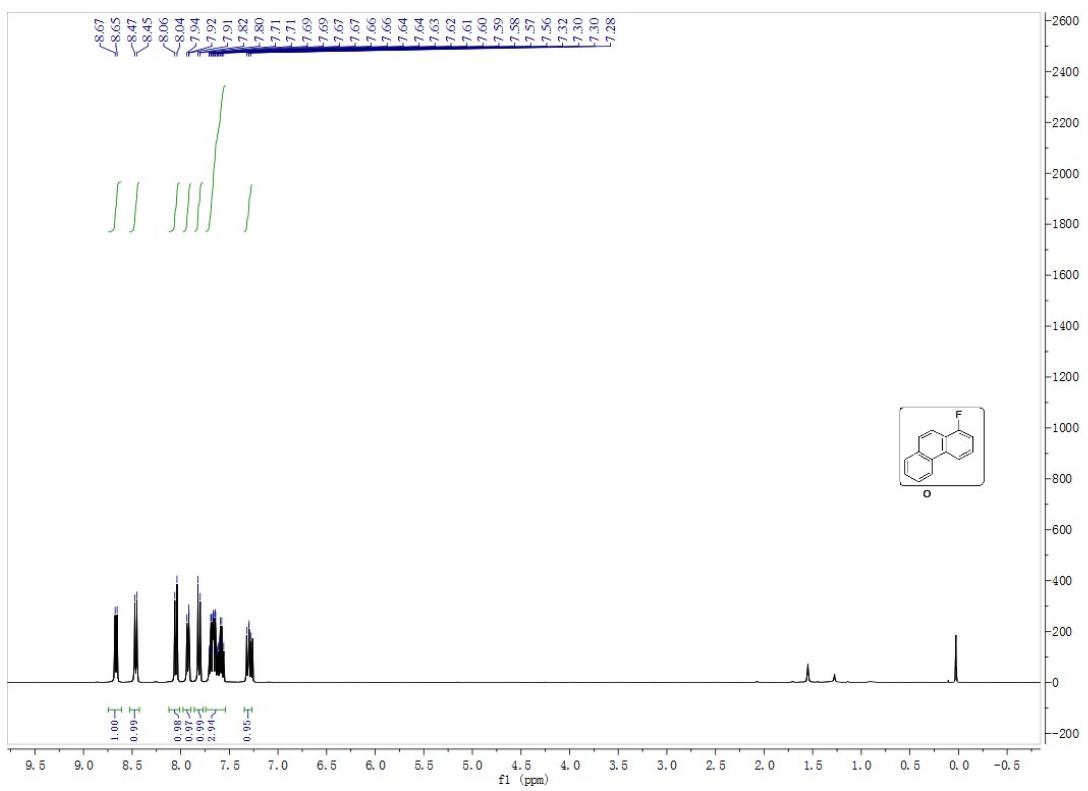


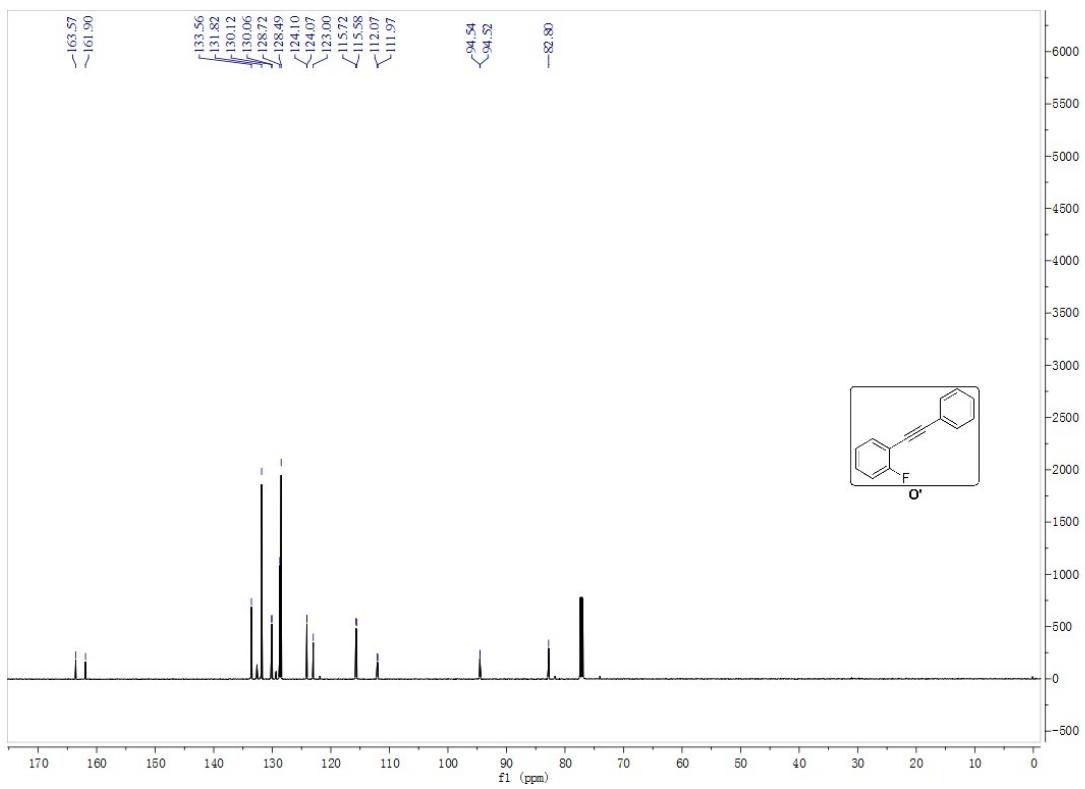
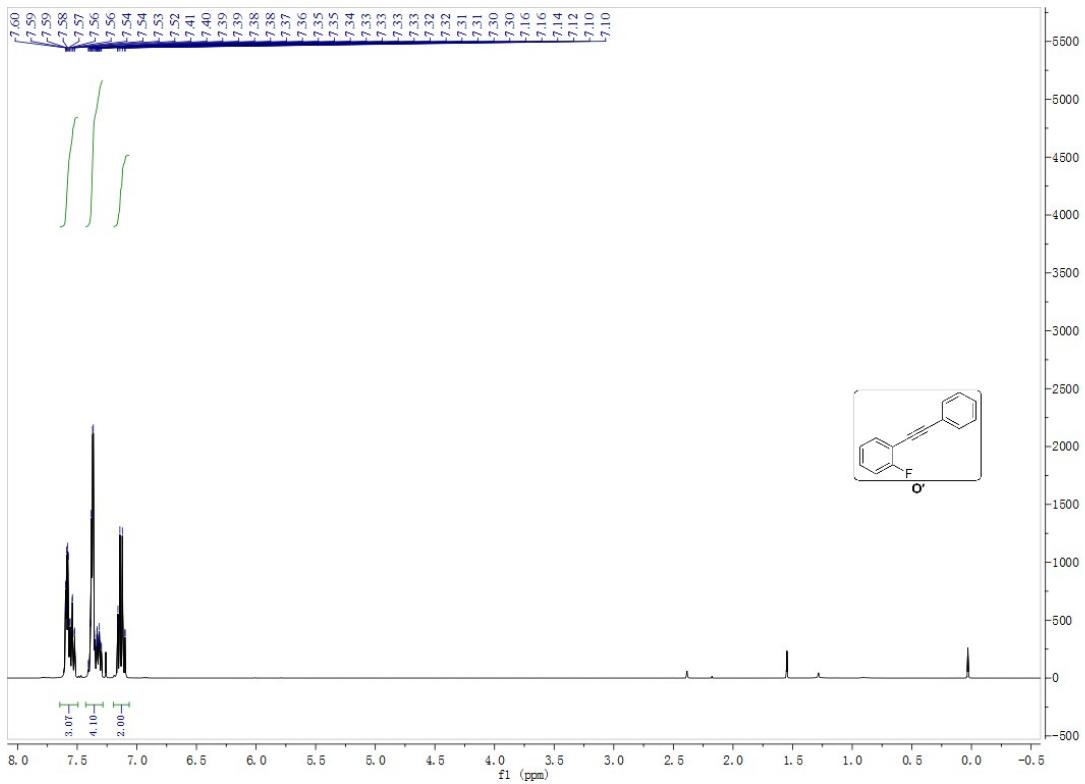


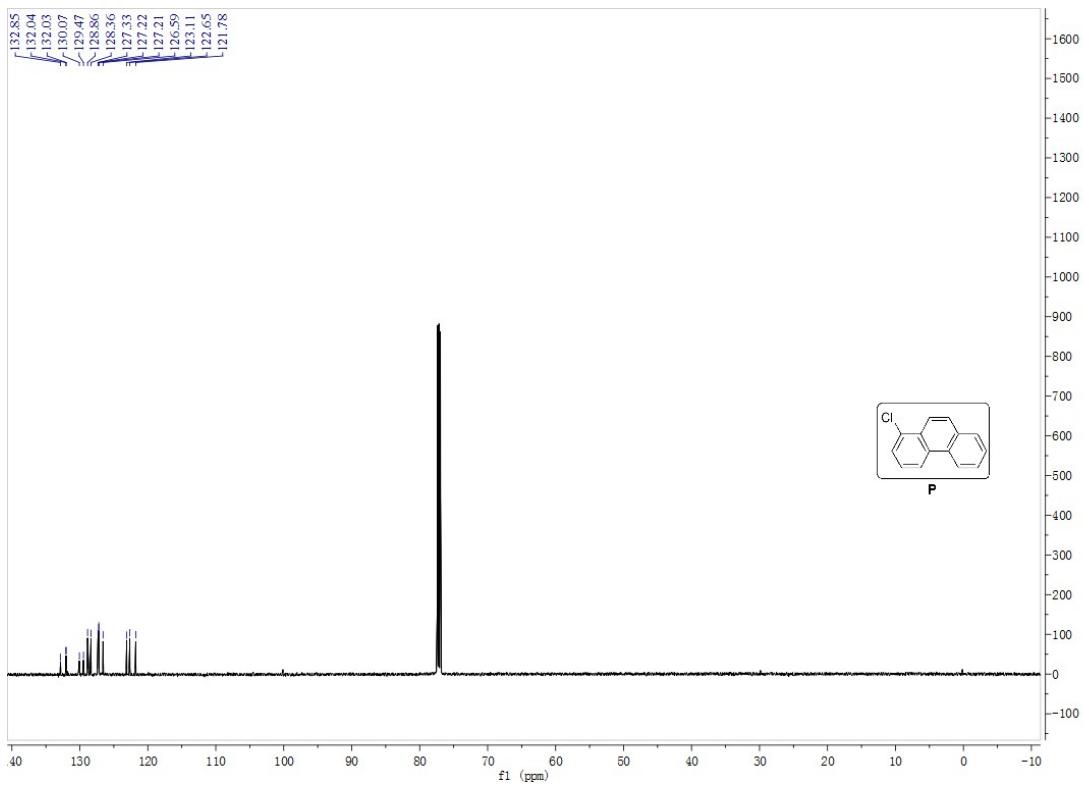
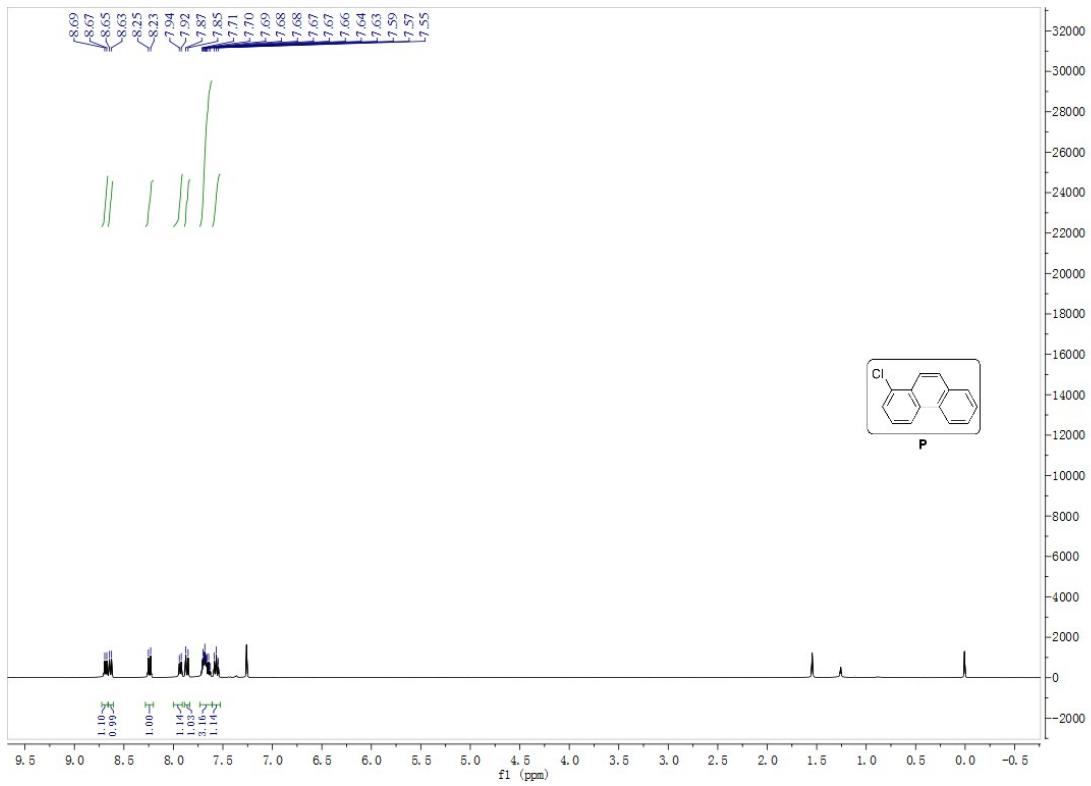


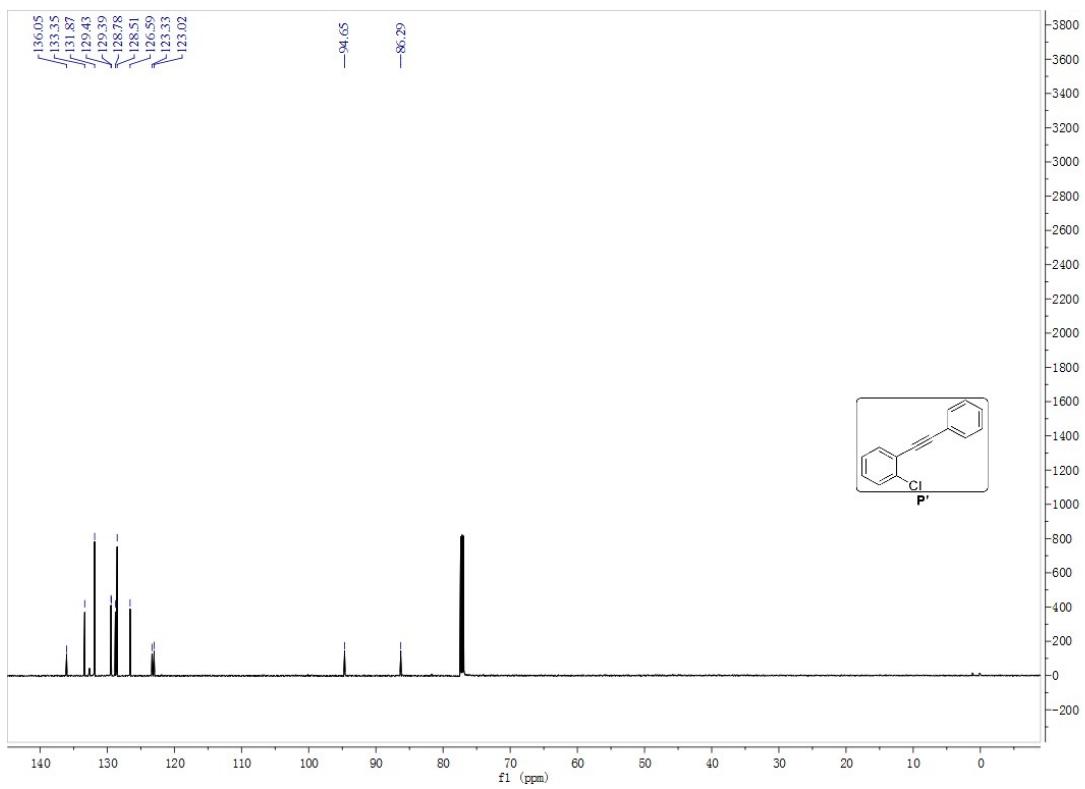
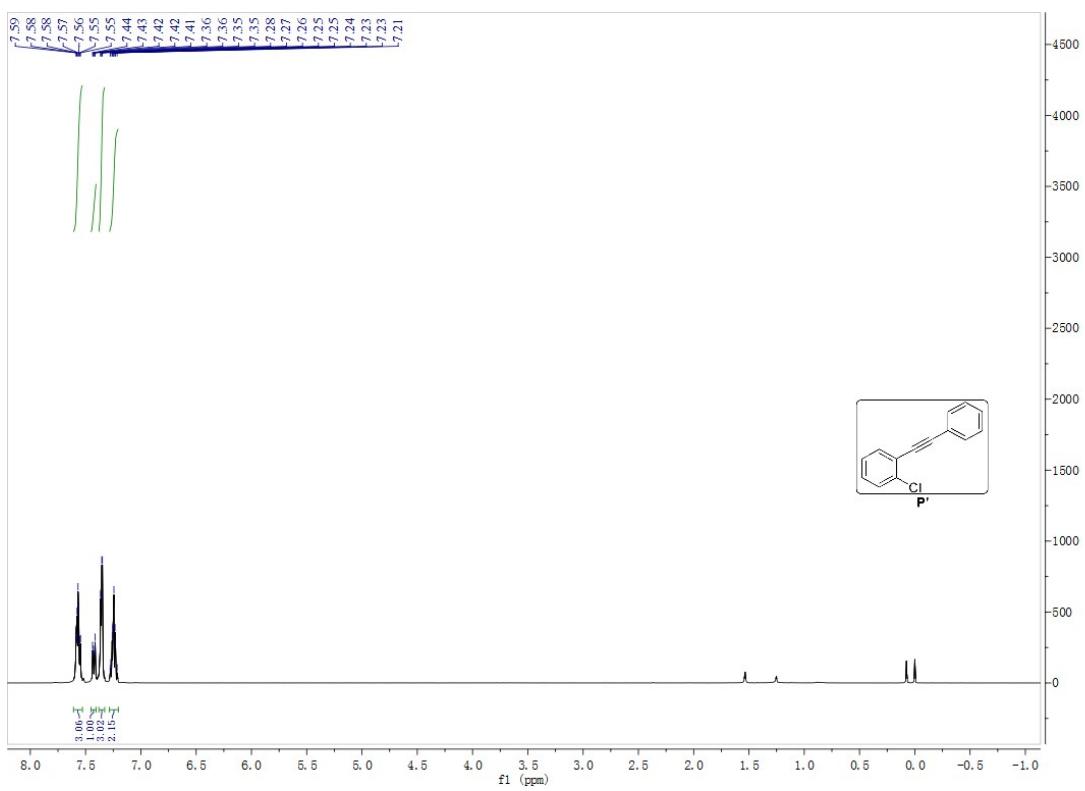


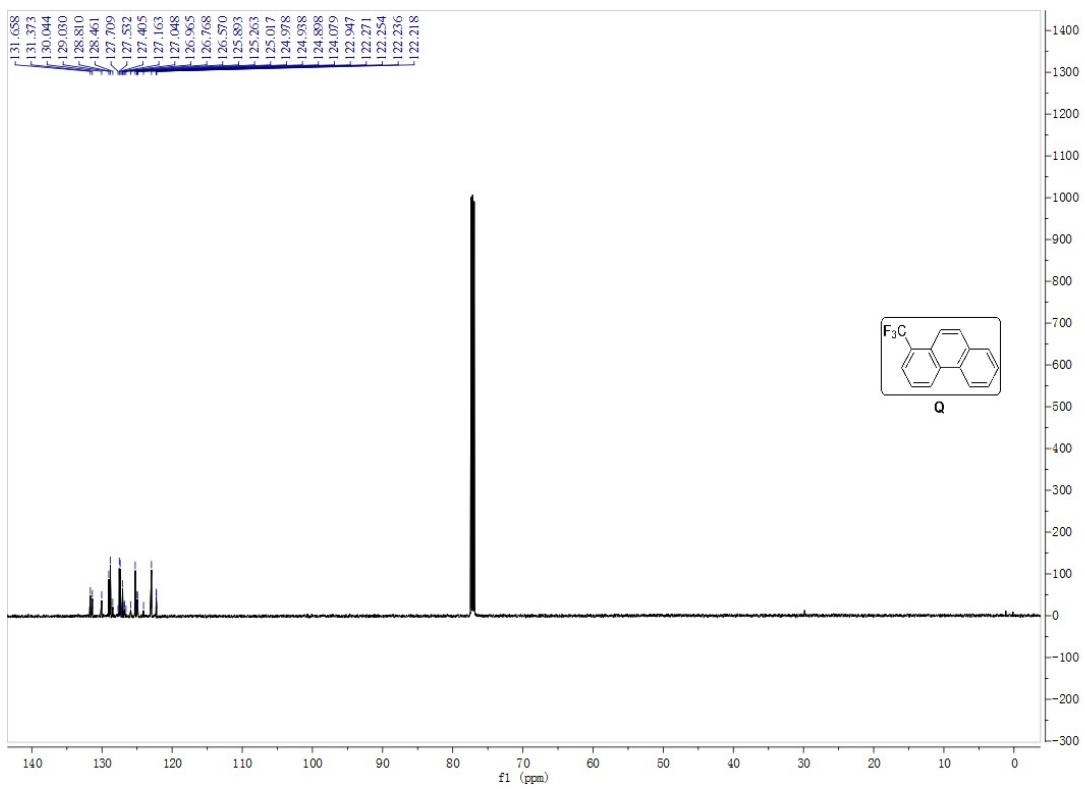
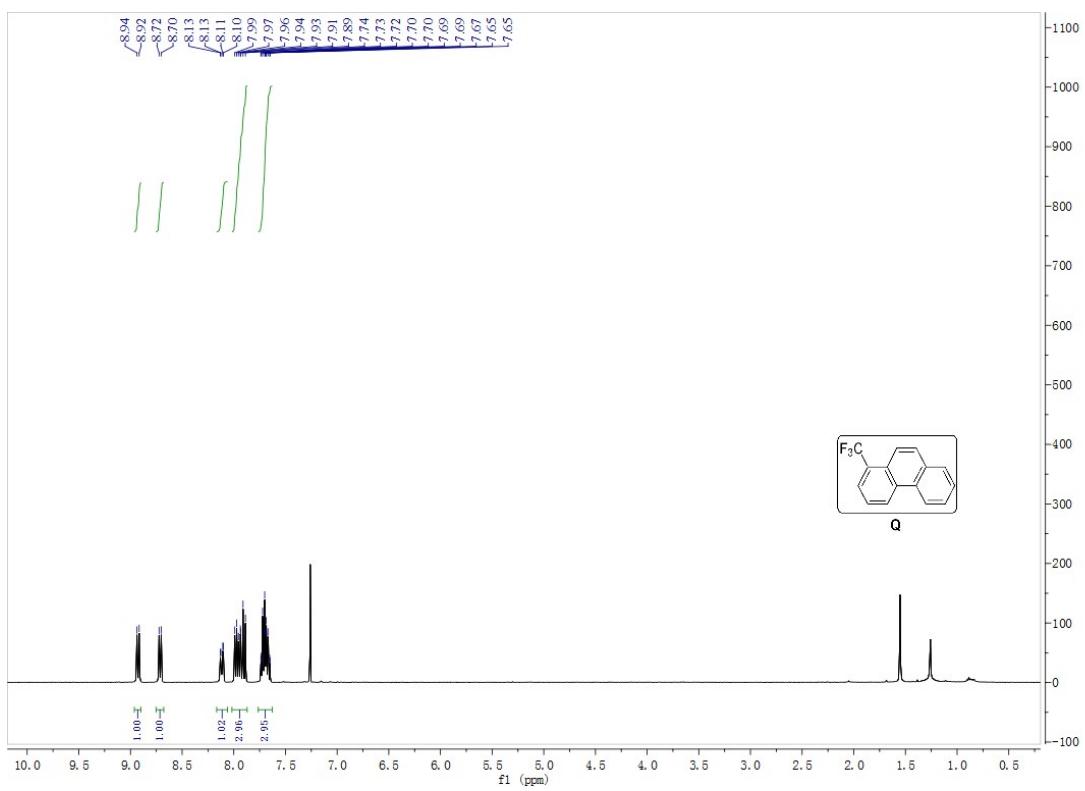


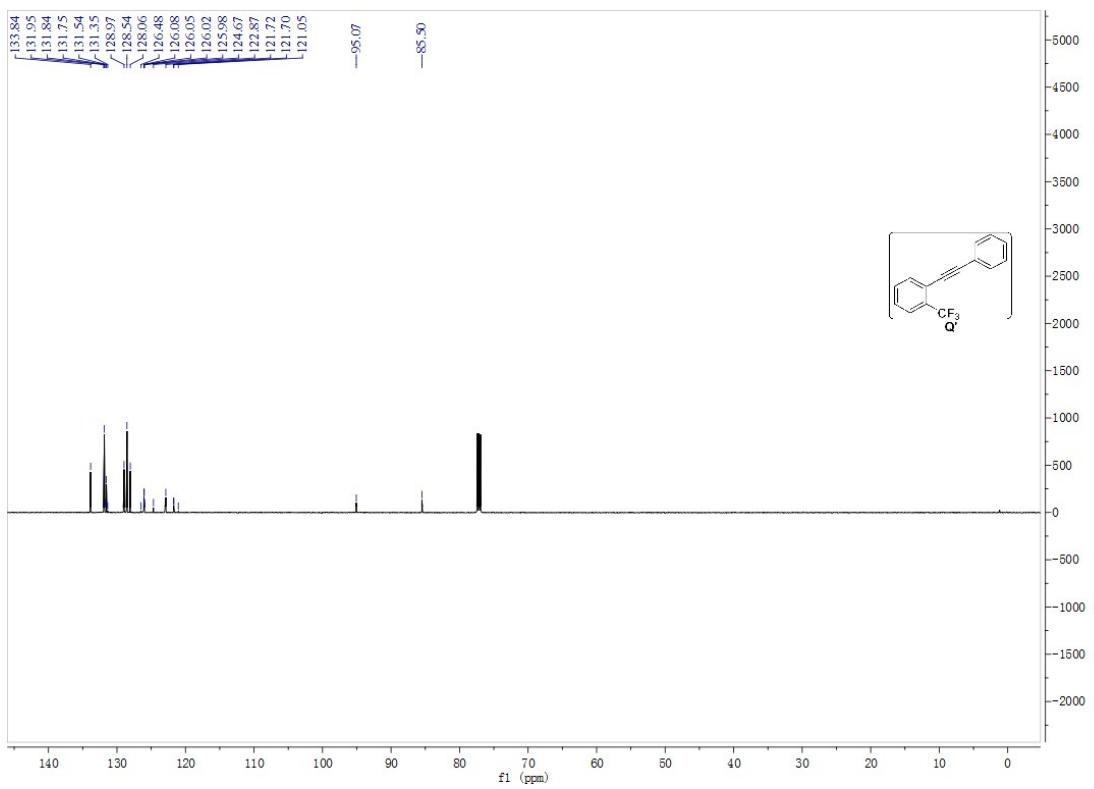
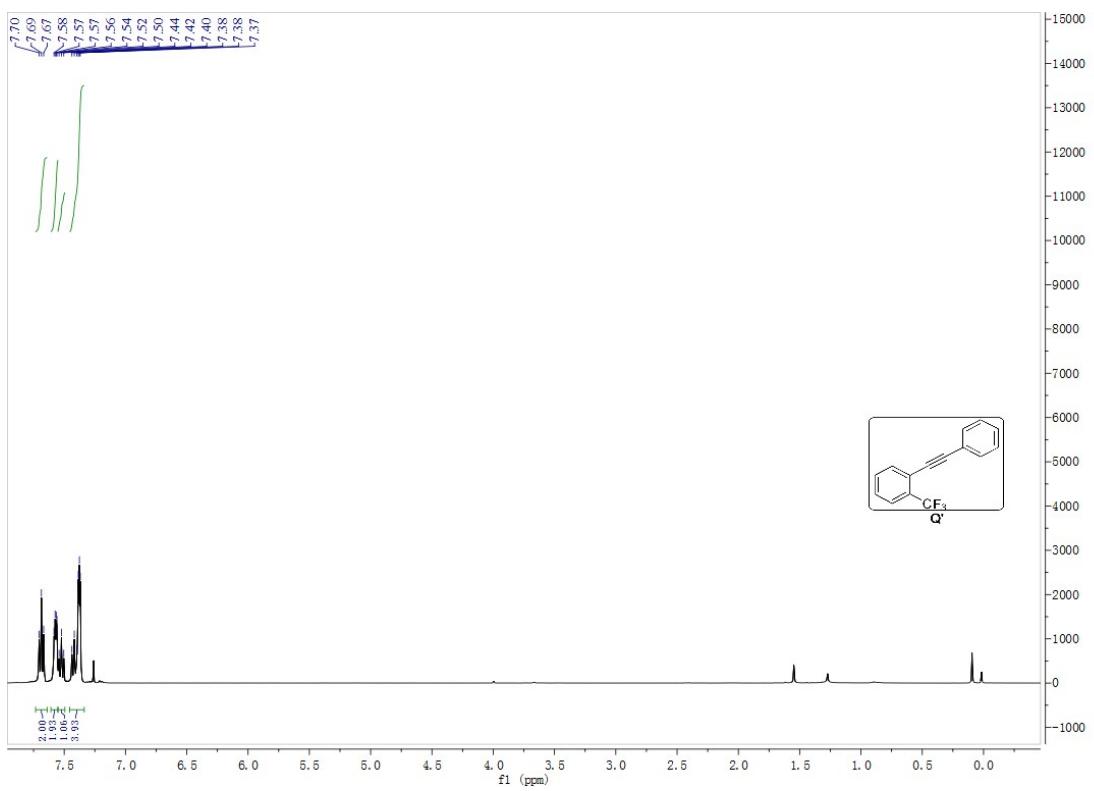


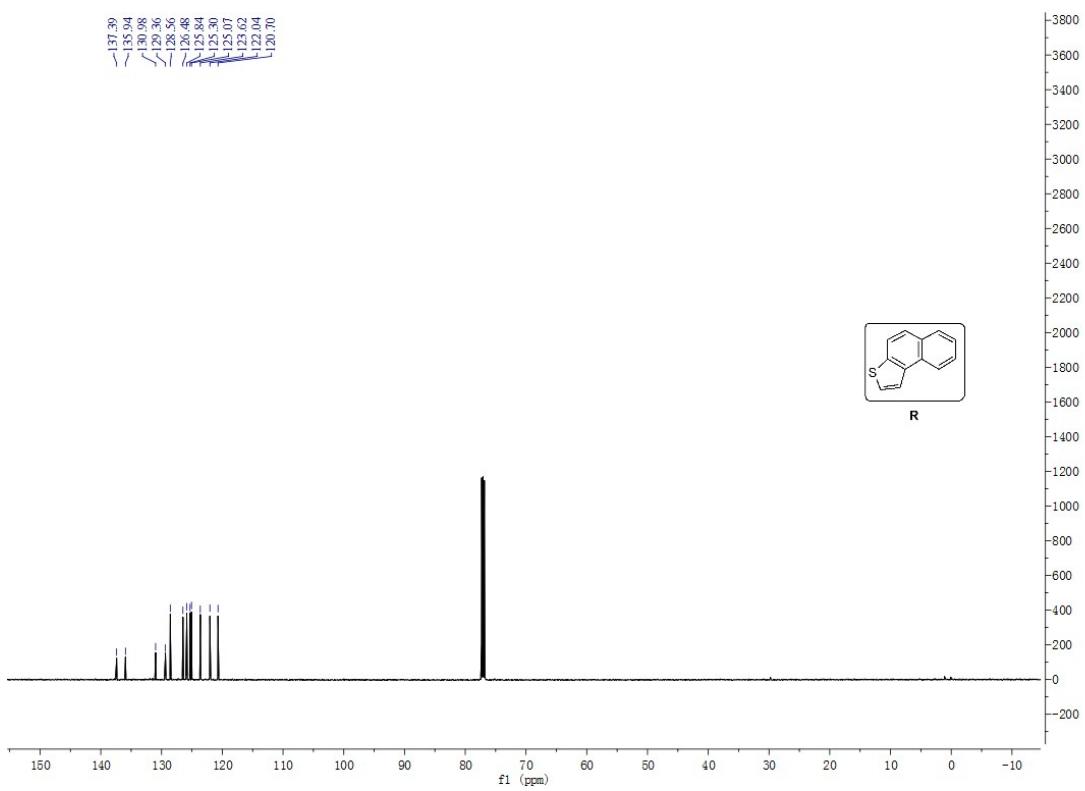
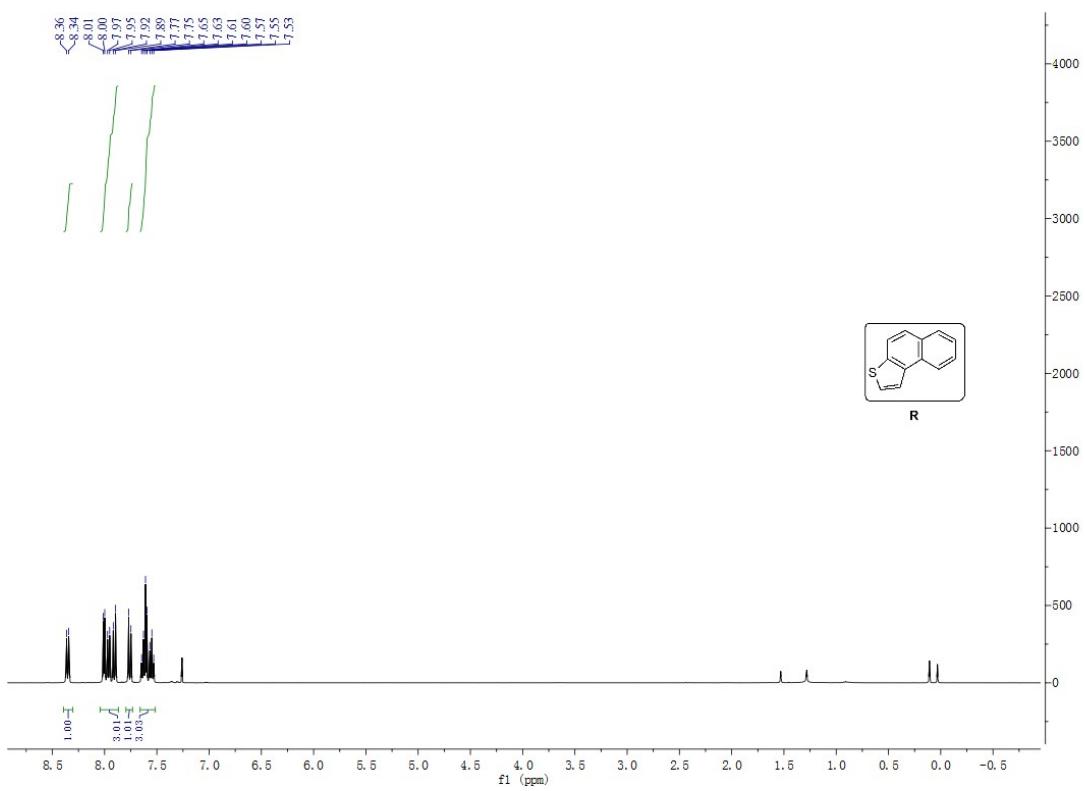


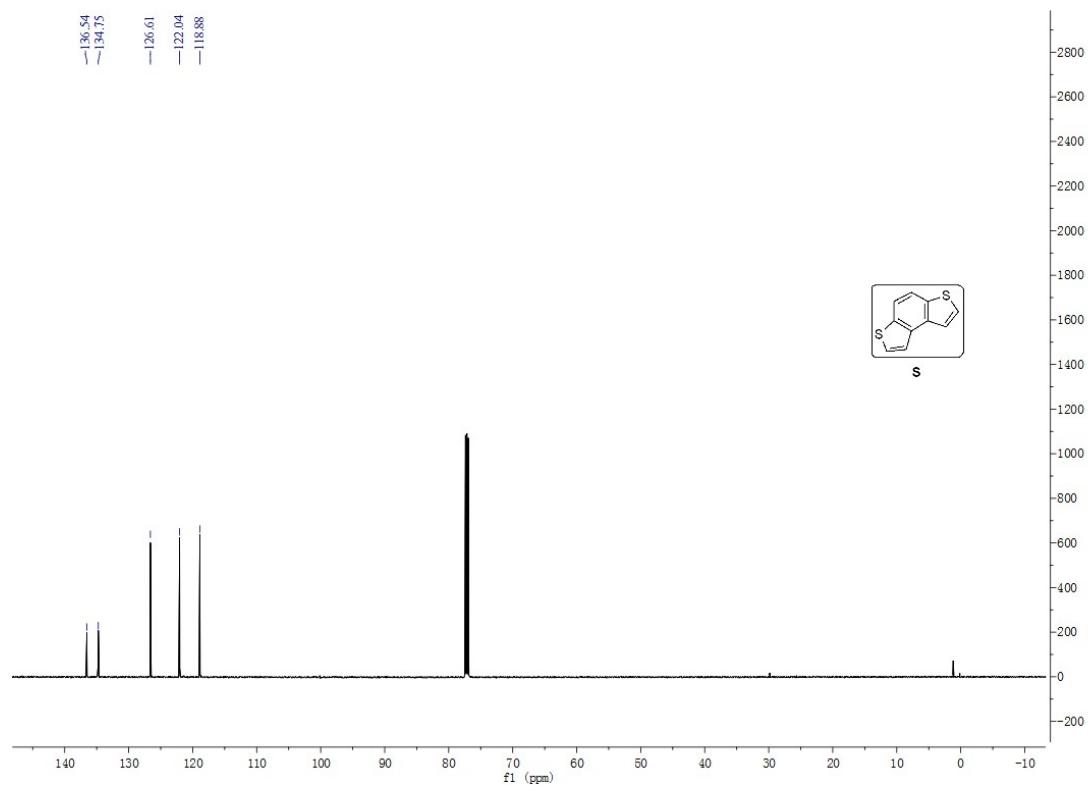
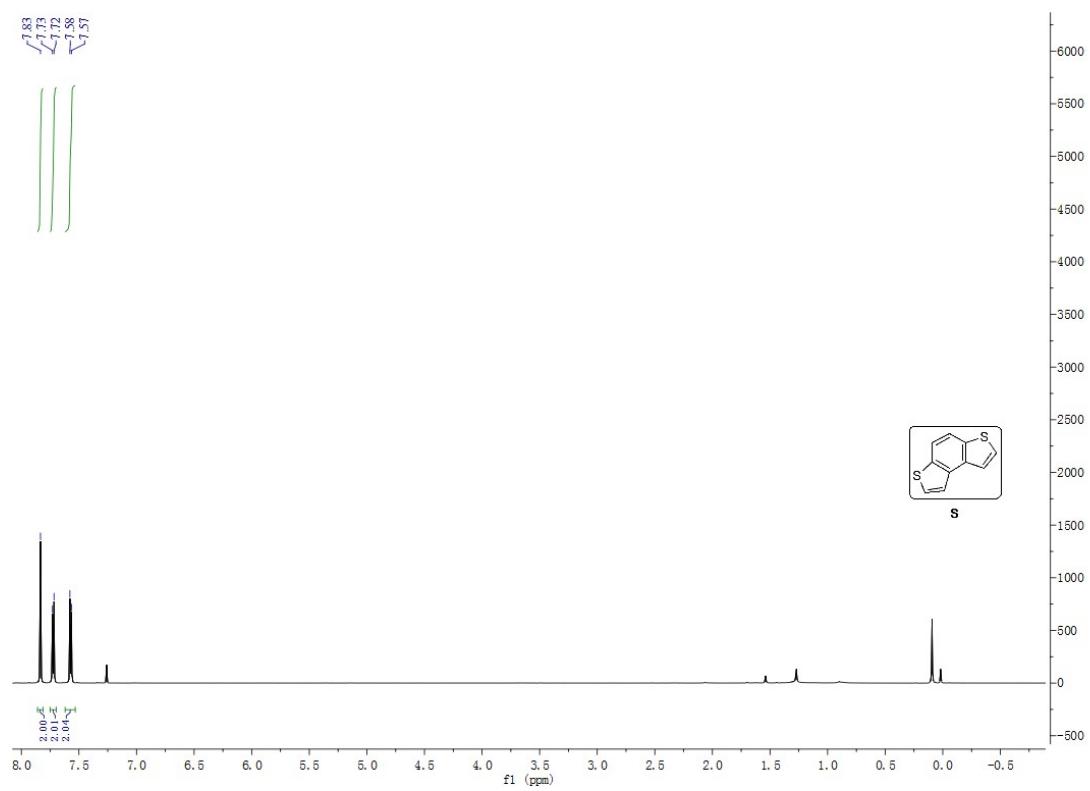


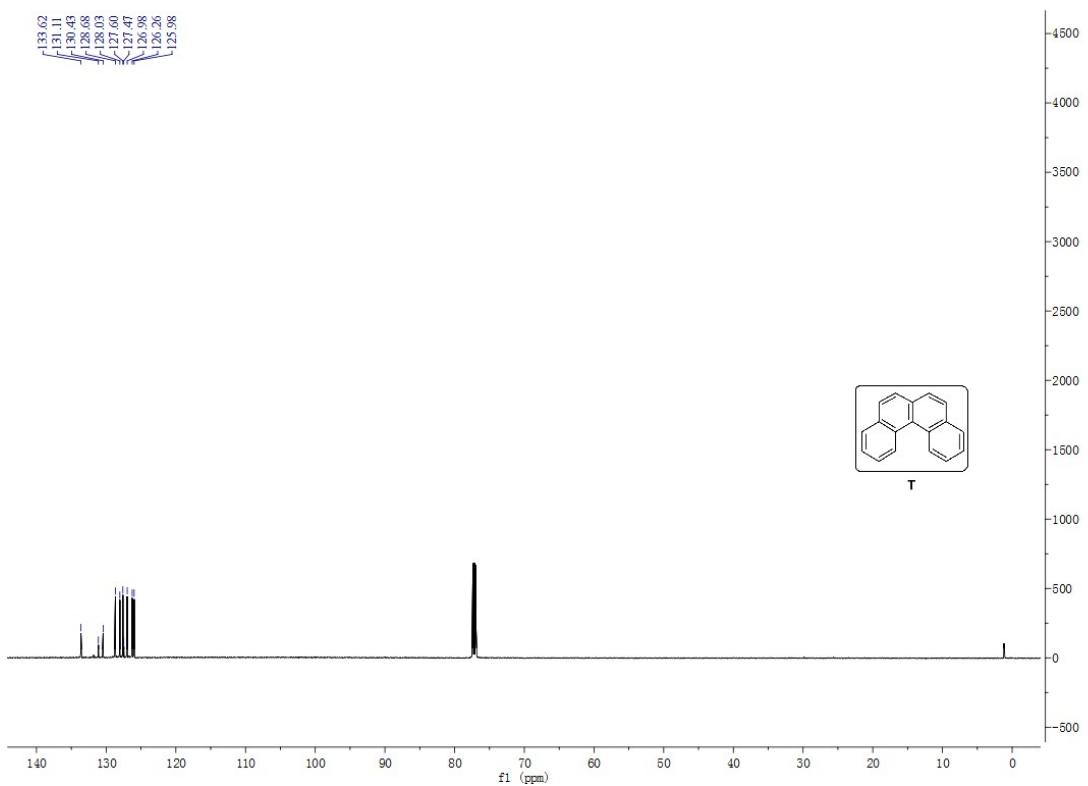
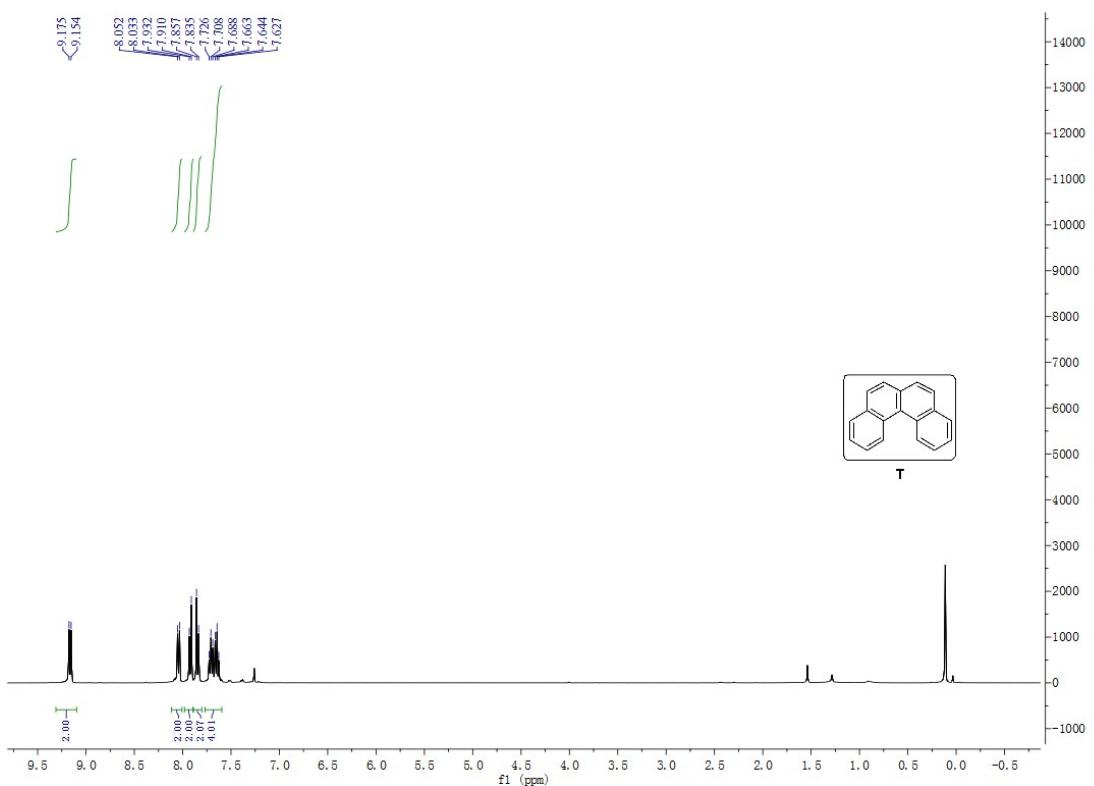


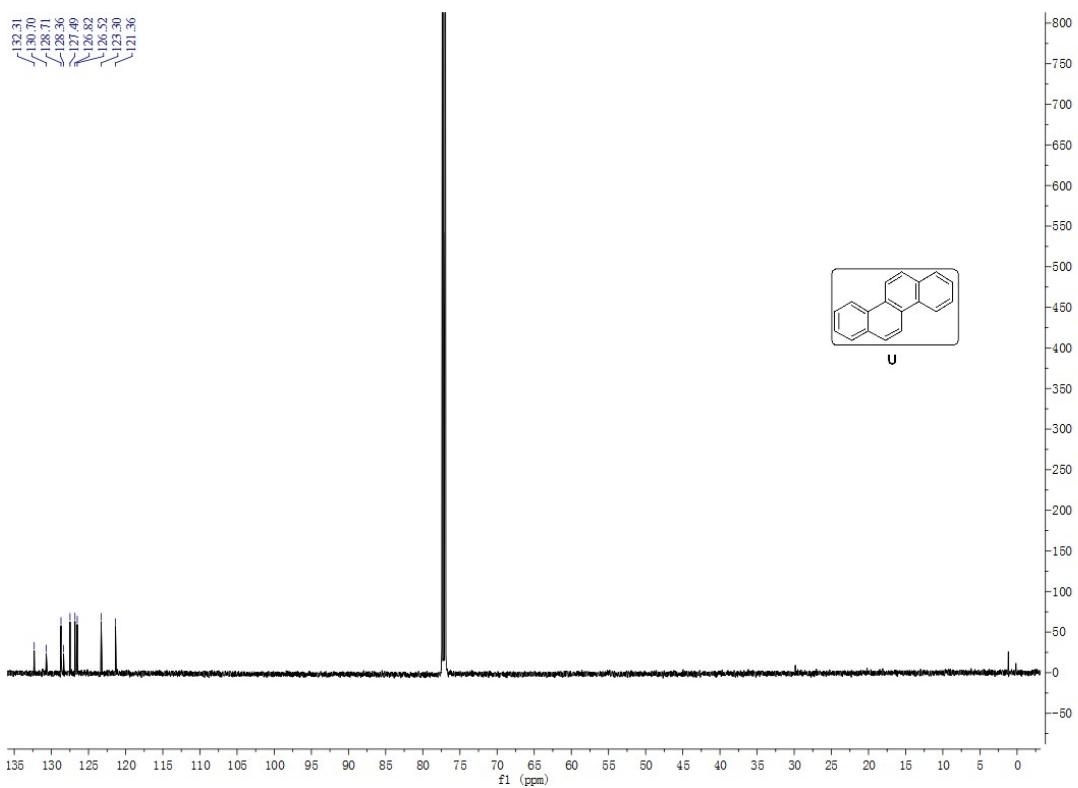
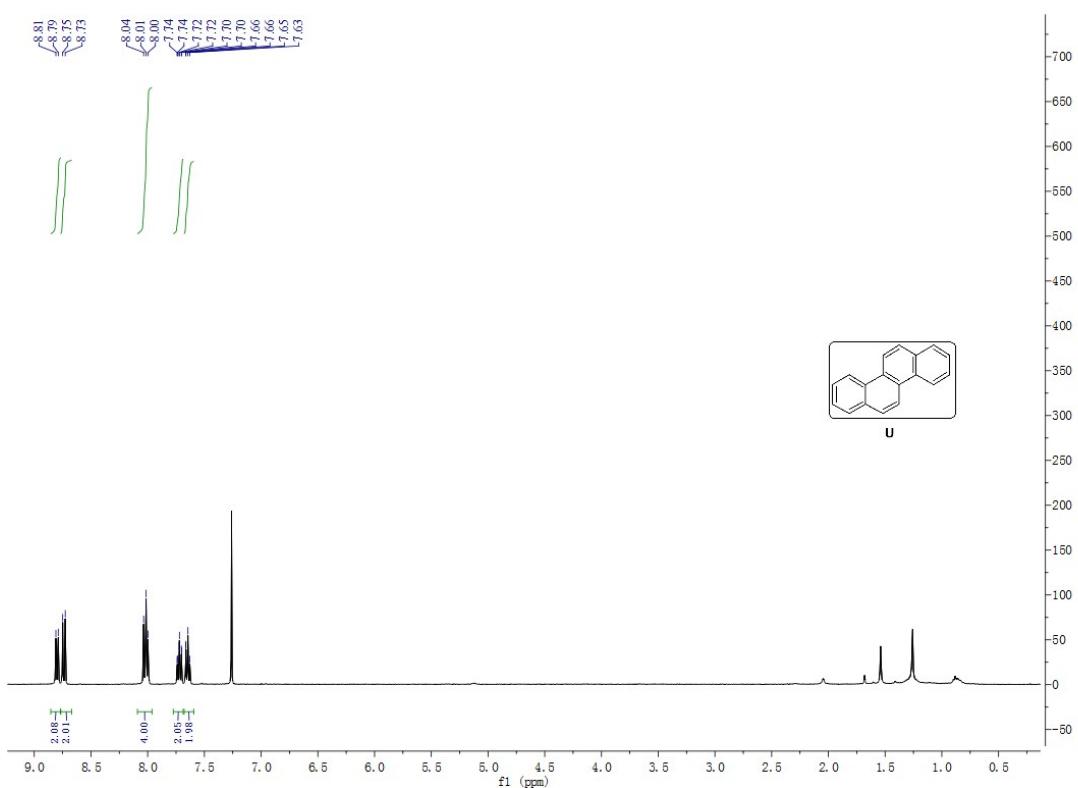


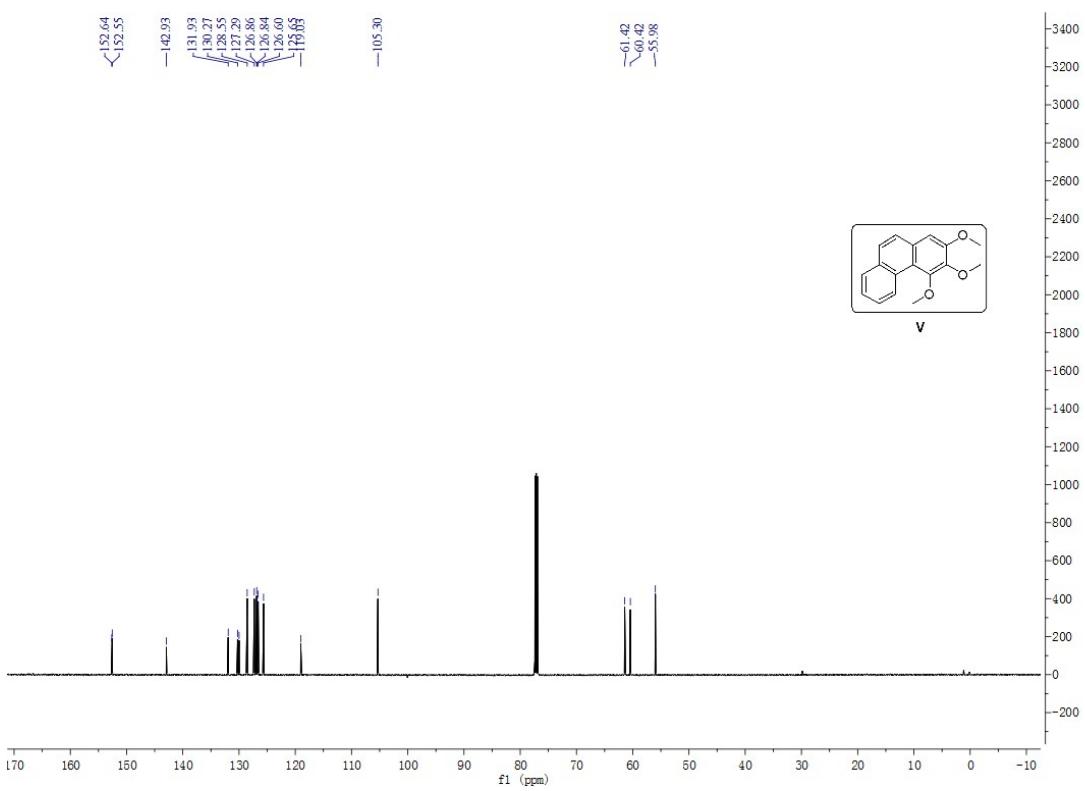
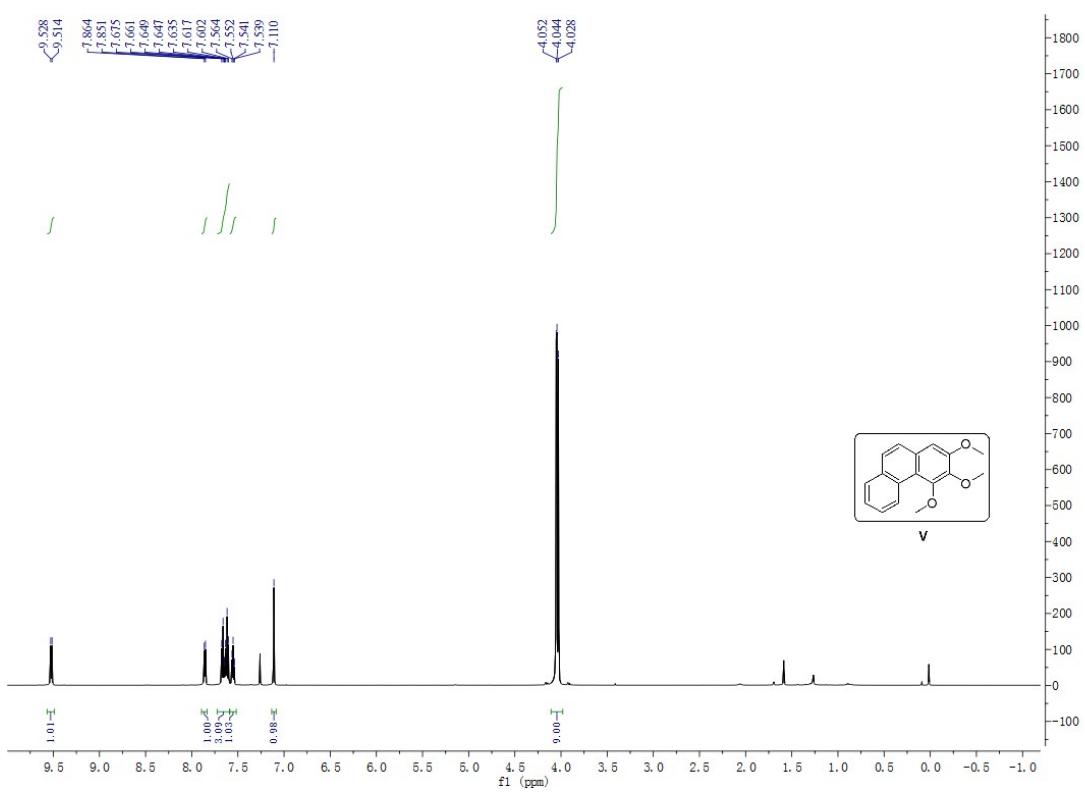


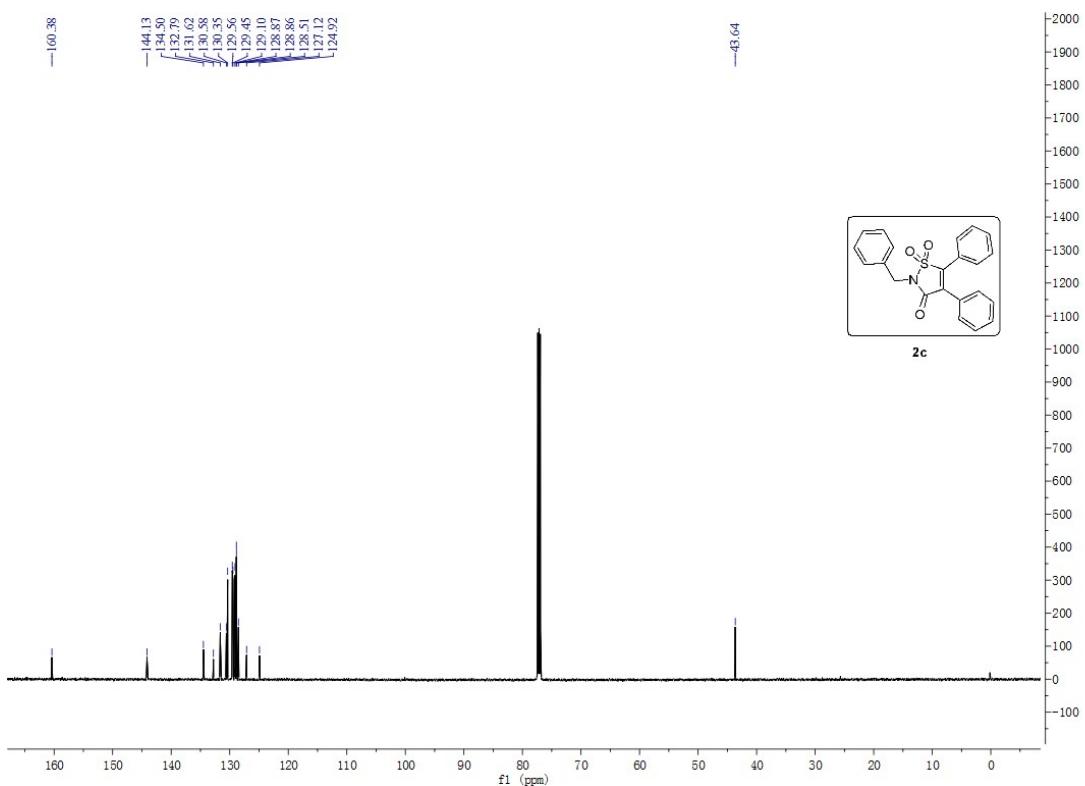
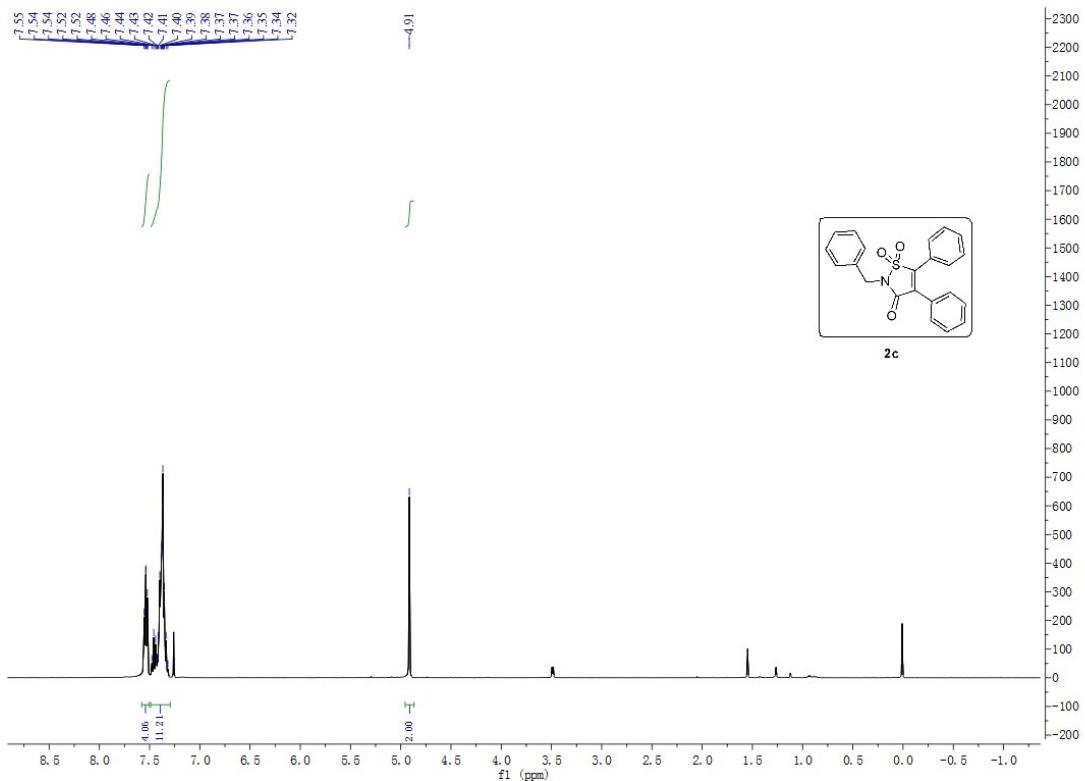


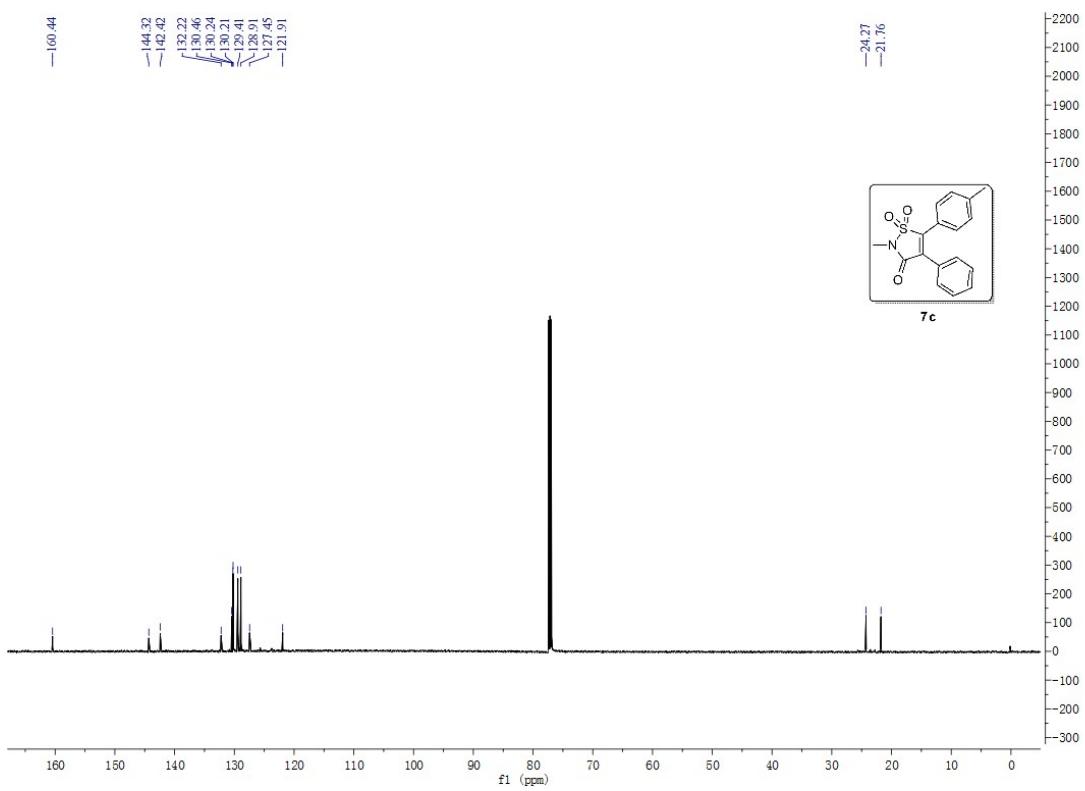
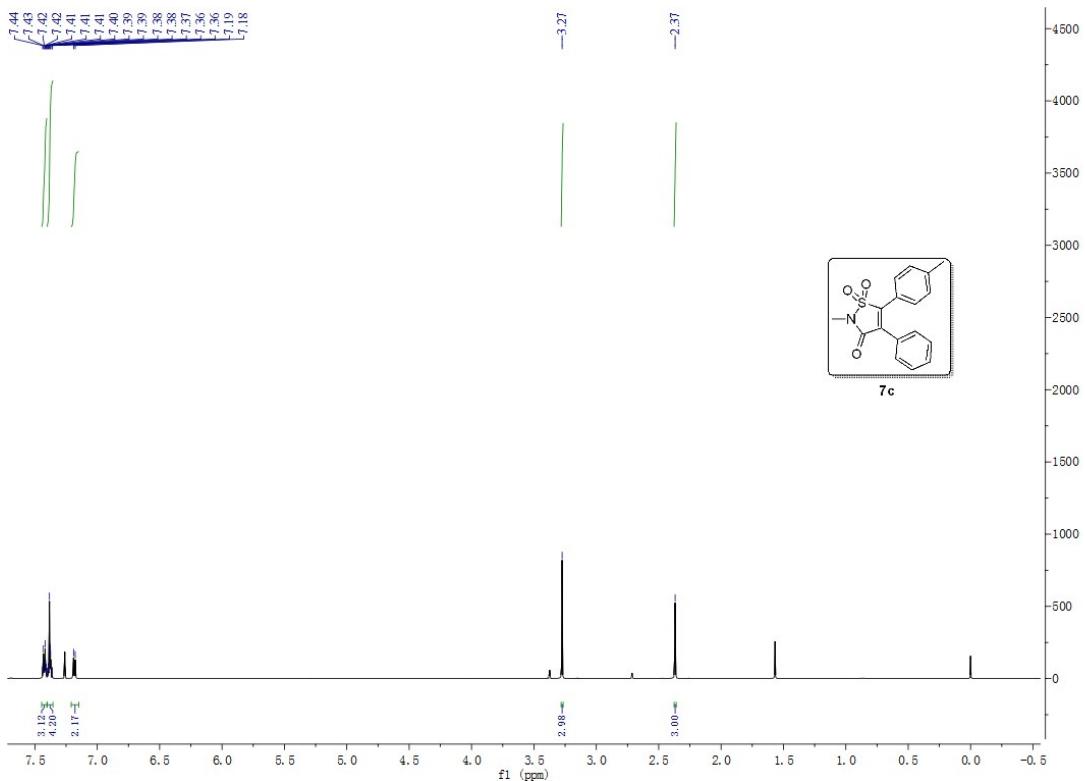


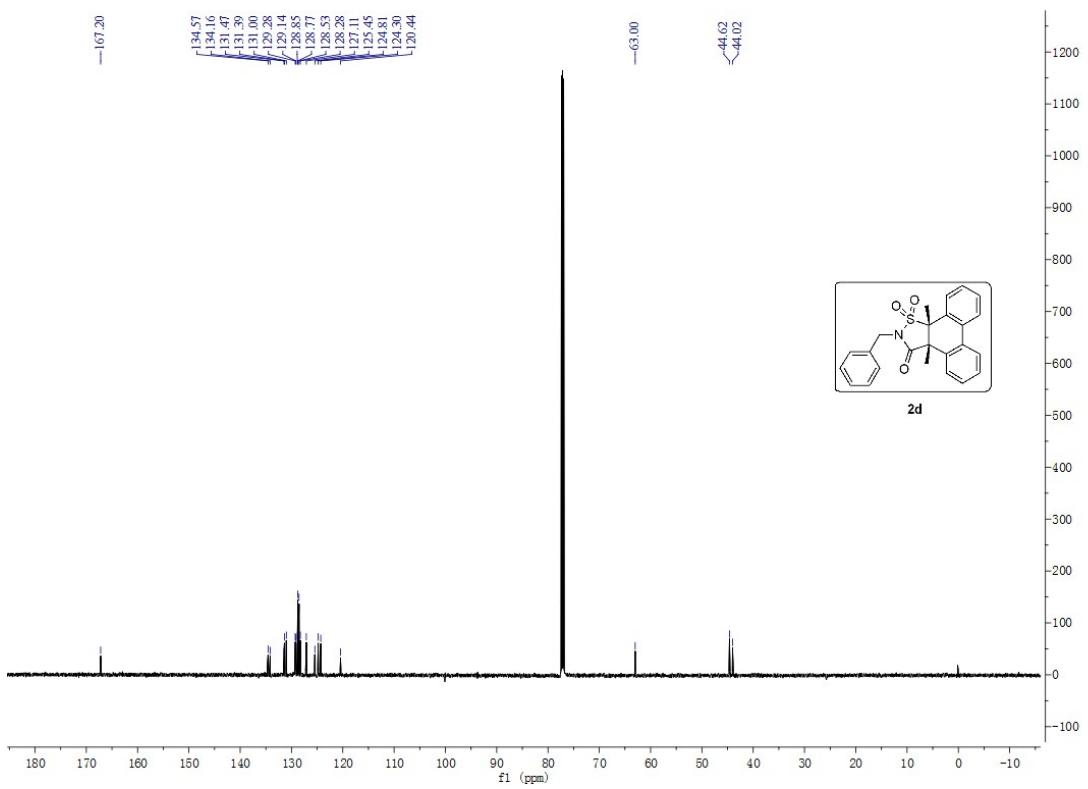
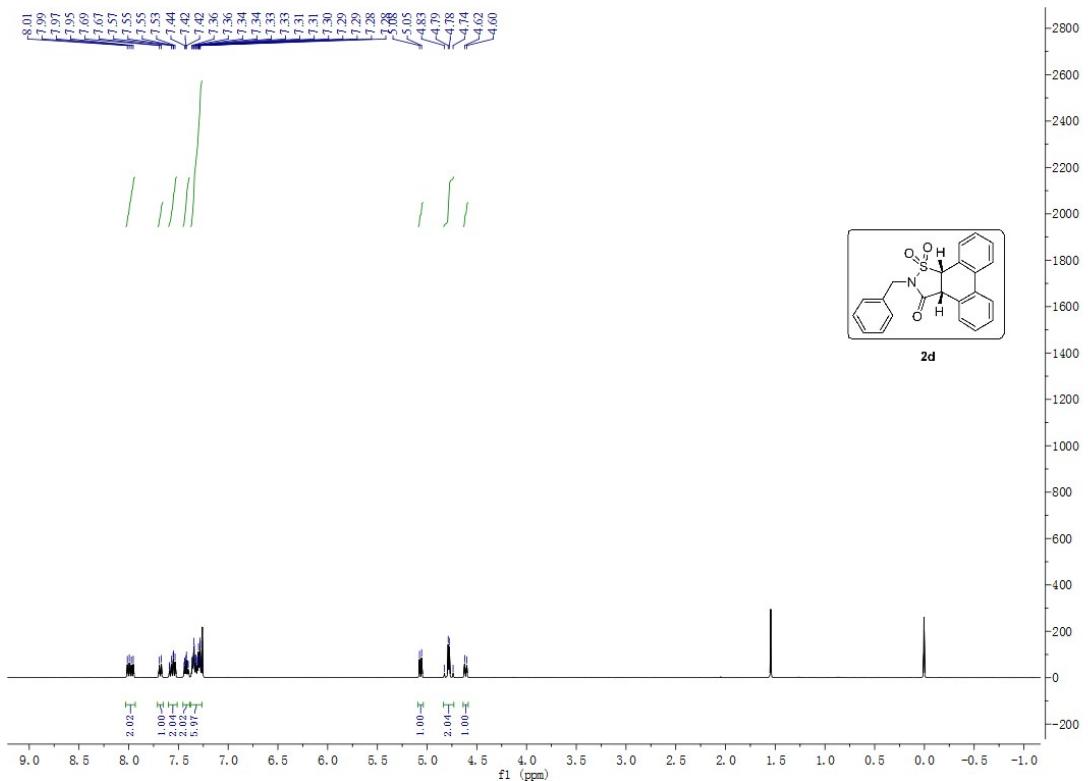




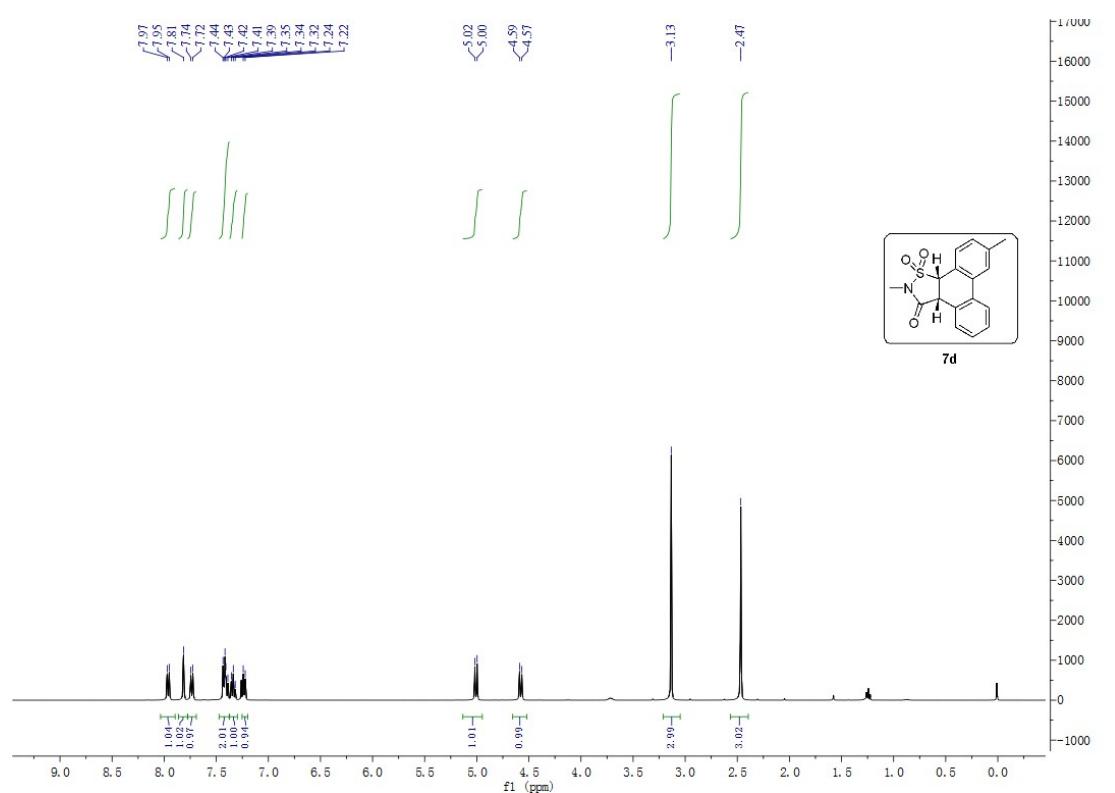
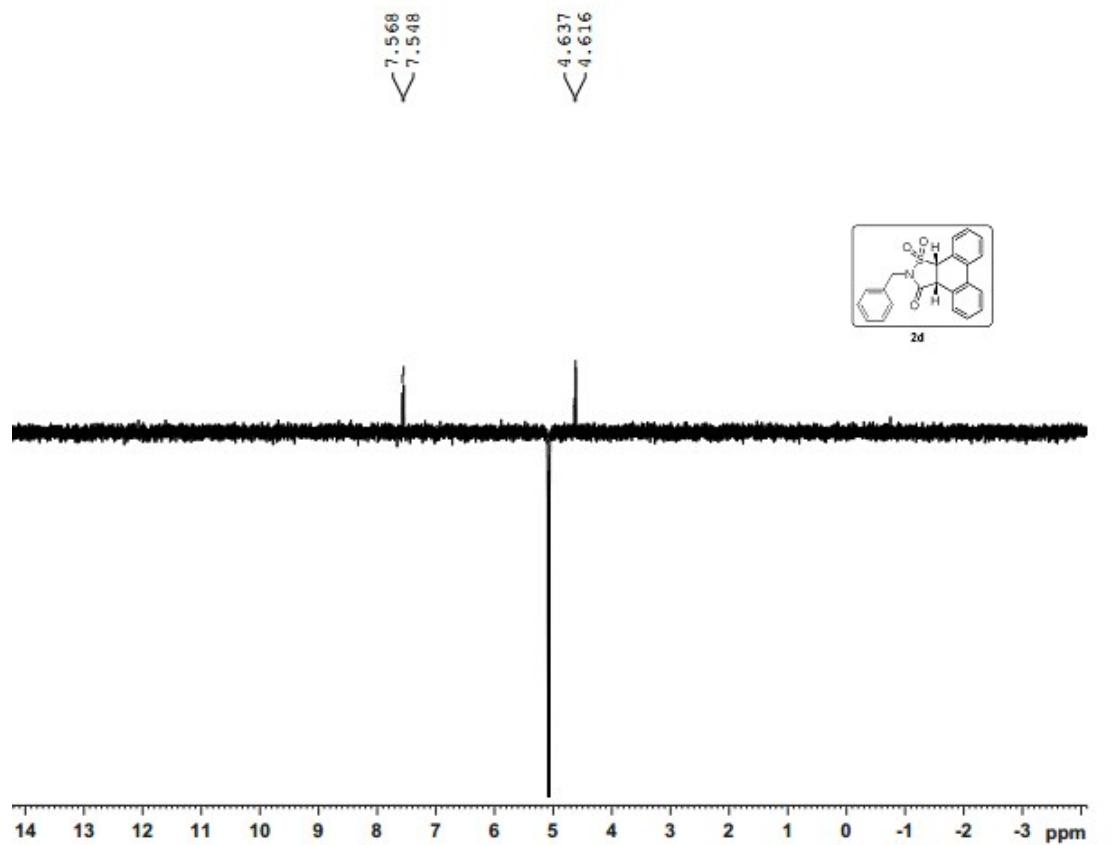


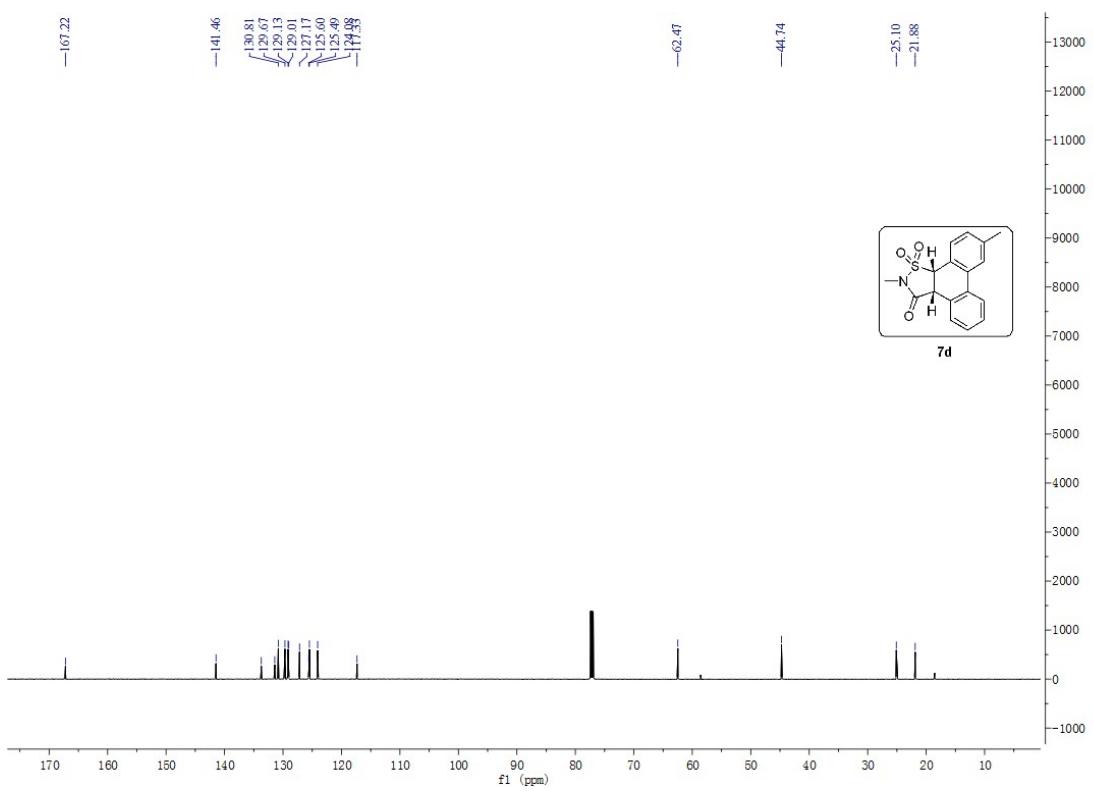






The NOE spectrum of **2d**.





The NOE spectrum of **7d**.

