

DBU Promoted Polysubstituted Arene Formation via a Michael Addition/Cyclization/Elimination Cascade Reaction

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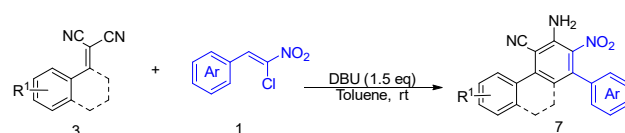
1. General information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. Column chromatography was performed on silica gel (200–300 mesh). All ¹H NMR spectra were recorded on a Bruker AvanceII 500 MHz or Bruker AvanceII400 MHz respectively, ¹³C NMR spectra were recorded on a Bruker AvanceII 101 MHz or Bruker Avance III 126 MHz with chemical shifts reported as ppm (in CDCl₃ or DMSO-d₆, TMS as internal standard). Data for ¹H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad singlet, dd = doublet doublet, coupling constants in Hz, integration). HRMS (ESI) was obtained with a HRMS/MS instrument (LTQ Orbitrap XL TM).

Vinylogous malononitrile derivative **3** were prepared according to the literature^[1]. Chloronitroalkenes **1** were prepared from various substituted aldehyde according to the literature^[2]. Catalysts **Cat.5-10** were synthesized according to literature procedures^[3-4].

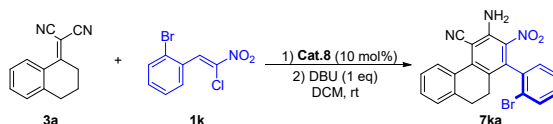
2. Experimental procedures and characterization of products

General procedure : synthesis of compound 7aa-7qa, 7ab-7ai



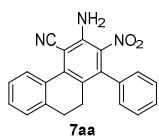
Vinylogous malononitrile derivative **3** (0.2 mmol), chloronitroolefins **1** (0.24 mmol, 1.2equiv) were added to a reaction tube, 2mL toluene were added and the mixture was stirred at rt. DBU (0.3mmol, 1.5 equiv) was added *via* a microsyringe, then the mixture was stirred at room temperature for 15 minutes. The reaction mixture was purified by column chromatography on silica gel directly to give the product **7**.

Enantioselective synthesis of compound 7ka



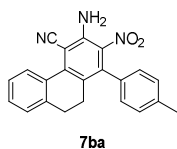
The mixture of α,α -dicyanoolefins **3a** (0.10 mmol), chloronitroolefins **1k** (0.12 mmol), and catalyst **Cat.7** (10 mol %) in DCM (1.0 mL) was stirred for 12 hours at room temperature. After then, DBU (0.1 mmol) was added and stirred for another 40 minutes. The reaction mixture was purified by column chromatography on silica gel directly to give the chiral product **7ka**.

4. -isocyano-2-nitro-1-phenyl-9,10-dihydrophenanthren-3-amine (7aa)



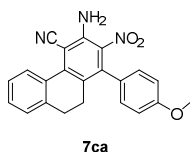
Prepared according to the general procedure as yellow solid (64 mg, 95% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). ^1H NMR (500 MHz, CDCl_3) δ 8.34–8.16 (m, 1H), 7.55–7.30 (m, 6H), 7.25–7.20 (m, 2H), 5.69 (s, 2H), 2.66 (dd, J = 8.3, 5.3 Hz, 2H), 2.47–2.34 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.3, 142.6, 140.37, 139.81, 135.68, 131.13, 130.52, 128.81, 128.59, 128.19, 128.03, 127.96, 127.45, 127.12, 117.24, 95.36, 29.06, 25.99. HRMS (ESI) m/z Calcd. for $\text{C}_{21}\text{H}_{16}\text{N}_3\text{O}_2^+$ ($[\text{M}+\text{H}]^+$) 342.1237, Found 342.1244.

4. -isocyano-2-nitro-1-(p-tolyl)-9,10-dihydrophenanthren-3-amine (7ba)



Prepared according to the general procedure as yellow solid (64 mg, 92% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). ^1H NMR (400 MHz, CDCl_3) δ 8.41–8.06 (m, 1H), 7.46–7.35 (m, 2H), 7.31–7.26 (m, 1H), 7.24 (s, 2H), 7.13–7.03 (m, 2H), 5.60 (s, 2H), 2.652.61 (m, 2H), 2.43–2.38 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.12, 142.35, 140.38, 139.75, 138.52, 135.79, 132.54, 131.17, 130.40, 129.49, 128.31, 127.88, 127.39, 127.06, 117.24, 95.14, 29.05, 25.96, 21.35. HRMS (ESI) m/z Calcd. for $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}_2^+$ ($[\text{M}+\text{H}]^+$) 356.1394, Found 356.1395.

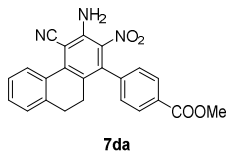
4. -isocyano-1-(4-methoxyphenyl)-2-nitro-9,10-dihydrophenanthren-3-amine (7ca)



Prepared according to the general procedure as yellow solid (62 mg, 85% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). ^1H NMR (400 MHz, DMSO) δ 8.17–8.07 (m, 1H), 7.47–7.30 (m, 3H), 7.27–6.89 (m, 4H), 6.39 (s, 2H), 3.80 (s, 3H), 2.65–2.57 (m, 2H), 2.31–2.22 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 159.81, 143.03, 141.06, 140.22, 138.59, 137.25, 131.40, 130.48, 130.09, 128.37, 127.55, 127.07, 126.98, 126.96, 117.65, 114.53,

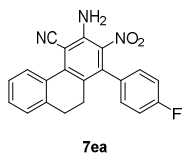
94.22, 55.62, 28.75, 25.98. HRMS (ESI) m/z Calcd. for $C_{22}H_{18}N_3O_3^+([M+H]^+)$ 372.1343, Found 372.1347.

methyl 4-(3-amino-4-isocyano-2-nitro-9,10-dihydrophenanthren-1-yl)benzoate (7da)



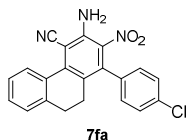
Prepared according to the general procedure as yellow solid (64 mg, 81% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). 1H NMR (400 MHz, $CDCl_3$) δ 8.32–8.19 (m, 1H), 8.18–8.02 (m, 2H), 7.47–7.36 (m, 2H), 7.33–7.27 (m, 3H), 5.84 (s, 2H), 3.95 (s, 3H), 2.64–2.63 (m, 2H), 2.44–2.23 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.52, 143.74, 143.10, 140.74, 139.77, 139.57, 134.65, 130.88, 130.75, 130.25, 130.07, 128.14, 127.99, 127.76, 127.52, 127.20, 117.03, 95.90, 52.36, 28.94, 25.96. HRMS (ESI) m/z Calcd. for $C_{23}H_{18}N_3O_4^+([M+H]^+)$ 400.1292, Found 400.1297.

1. -(4-fluorophenyl)-4-isocyano-2-nitro-9,10-dihydrophenanthren-3-amine (7ea)



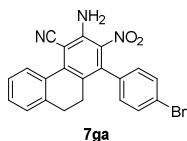
Prepared according to the general procedure as yellow solid (64 mg, 91% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). 1H NMR (400 MHz, $CDCl_3$) δ 8.37–8.06 (m, 1H), 7.48–7.34 (m, 2H), 7.28–7.29 (m, 1H), 7.23–7.07 (m, 4H), 5.68 (s, 2H), 2.79–2.47 (m, 2H), 2.47–2.17 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.72 (d, J = 249.47 Hz), 143.31, 142.67, 139.69, 139.28, 131.50 (d, J = 3.7 Hz), 130.99, 130.59, 129.90, 129.82, 128.23, 127.94, 127.44, 127.15, 117.09, 115.99, (d, J = 22.2 Hz) 95.58, 28.98, 25.94. HRMS (ESI) m/z Calcd. for $C_{21}H_{15}FN_3O_2^+([M+H]^+)$ 360.1143, Found 360.1151.

1. -(4-chlorophenyl)-4-isocyano-2-nitro-9,10-dihydrophenanthren-3-amine (7fa)



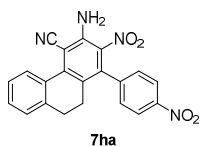
Prepared according to the general procedure as yellow solid (73 mg, 97% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). 1H NMR (500 MHz, $CDCl_3$) δ 8.33–8.15 (m, 1H), 7.49–7.39 (m, 4H), 7.33–7.28 (m, 1H), 7.20–7.12 (m, 2H), 5.76 (s, 2H), 2.78–2.57 (m, 2H), 2.48–2.22 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.46, 142.83, 139.69, 139.16, 135.10, 134.69, 134.16, 130.92, 130.64, 129.38, 129.12, 128.01, 127.95, 127.45, 127.15, 117.04, 95.69, 28.93, 25.93. HRMS (ESI) m/z Calcd. for $C_{21}H_{15}ClN_3O_2^+([M+H]^+)$ 376.0847, Found 376.0854.

1. -(4-bromophenyl)-4-isocyano-2-nitro-9,10-dihydrophenanthren-3-amine (7ga)



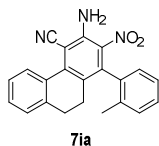
Prepared according to the general procedure as yellow solid (76 mg, 90% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). ^1H NMR (500 MHz, CDCl_3) δ 8.30–8.19 (m, 1H), 7.63–7.56 (m, 2H), 7.47–7.39 (m, 2H), 7.33–7.29 (m, 1H), 7.13–7.07 (m, 2H), 5.76 (s, 2H), 2.74–2.56 (m, 2H), 2.45–2.28 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.48, 139.69, 139.18, 134.68, 132.06, 130.91, 130.66, 129.64, 127.96, 127.64, 127.46, 127.16, 122.86, 117.03, 95.72, 28.93, 25.94. HRMS (ESI) m/z Calcd. for $\text{C}_{21}\text{H}_{15}\text{BrN}_3\text{O}_2$ ($[\text{M}+\text{H}]^+$) 420.0342, Found 420.0352.

4. -isocyano-2-nitro-1-(4-nitrophenyl)-9,10-dihydrophenanthren-3-amine (7ha)



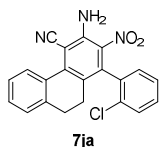
Prepared according to the general procedure as yellow solid (74 mg, 97% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). ^1H NMR (500 MHz, CDCl_3) δ 8.37–8.31 (m, 2H), 8.29–8.23 (m, 1H), 7.49–7.44 (m, 2H), 7.44–7.40 (m, 2H), 7.34–7.29 (m, 1H), 6.04 (s, 2H), 2.76–2.60 (m, 2H), 2.41–2.24 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.74, 144.16, 143.68, 143.15, 139.68, 138.41, 133.86, 131.03, 130.61, 129.08, 128.06, 127.60, 127.44, 127.31, 124.10, 116.79, 96.52, 28.82, 26.00. HRMS (ESI) m/z Calcd. for $\text{C}_{21}\text{H}_{15}\text{N}_4\text{O}_4$ ($[\text{M}+\text{H}]^+$) 387.1088, Found 387.1094.

4. -isocyano-2-nitro-1-(o-tolyl)-9,10-dihydrophenanthren-3-amine (7ia)



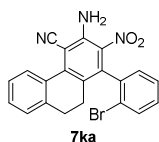
Prepared according to the general procedure as yellow solid (53 mg, 74% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). ^1H NMR (400 MHz, CDCl_3) δ 8.28 (dd, J = 7.4, 1.8 Hz, 1H), 7.41 (tt, J = 7.5, 5.9 Hz, 2H), 7.33–7.25 (m, 3H), 7.237.20 (m, 1H), 7.00 (d, J = 7.5 Hz, 1H), 5.72 (s, 2H), 2.65 (t, J = 6.8 Hz, 2H), 2.25 (td, J = 6.4, 3.3 Hz, 2H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.59, 142.25, 140.16, 139.90, 136.31, 135.33, 131.03, 130.48, 130.14, 128.63, 128.13, 127.97, 127.43, 127.31, 127.10, 126.14, 117.22, 95.29, 28.97, 25.19, 19.69. HRMS (ESI) m/z Calcd. for $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}_2$ ($[\text{M}+\text{H}]^+$) 356.1394, Found 356.1400.

1. -(2-chlorophenyl)-4-isocyano-2-nitro-9,10-dihydrophenanthren-3-amine (7ja)

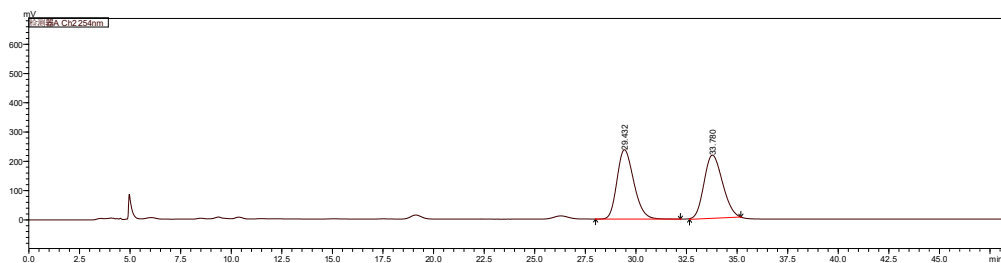


Prepared according to the general procedure as yellow solid (56 mg, 75% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). ^1H NMR (400 MHz, CDCl_3) δ 8.54–8.04 (m, 1H), 7.62–7.46 (m, 1H), 7.46–7.26 (m, 5H), 7.13 (dd, J = 7.4, 2.0 Hz, 1H), 5.99 (s, 2H), 2.79–2.57 (m, 2H), 2.47–2.12 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.20, 140.05, 133.25, 130.86, 130.69, 129.84, 129.69, 129.03, 128.39, 127.99, 127.54, 127.19, 127.12, 117.11, 28.87, 25.36. HRMS (ESI) m/z Calcd. for $\text{C}_{21}\text{H}_{15}\text{ClN}_3\text{O}_2^+([\text{M}+\text{H}]^+)$ 376.0847, Found 376.0855.

1. -(2-bromophenyl)-4-isocyano-2-nitro-9,10-dihydrophenanthren-3-amine (7ka)

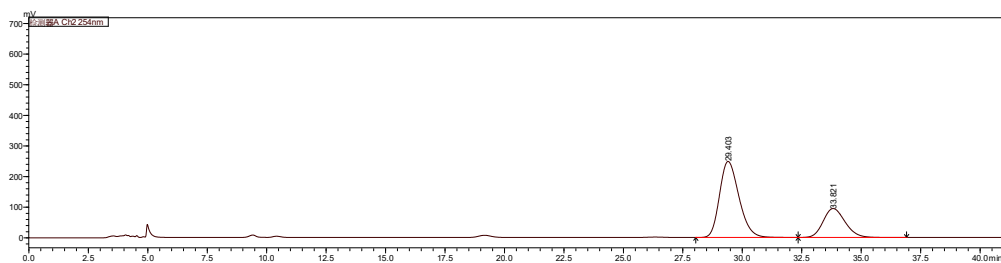


Prepared according to the general procedure as yellow solid (60 mg, 70% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). ^1H NMR (500 MHz, CDCl_3) δ 8.34–8.27 (m, 1H), 7.71 (dd, J = 8.0, 1.2 Hz, 1H), 7.50–7.36 (m, 3H), 7.35–7.28 (m, 2H), 7.15 (dd, J = 7.6, 1.7 Hz, 1H), 6.03 (s, 2H), 2.71 (qdd, J = 14.7, 8.6, 5.0 Hz, 2H), 2.47–2.14 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 144.26, 143.08, 140.10, 139.49, 137.40, 134.14, 132.84, 130.89, 130.71, 129.89, 129.13, 128.24, 128.00, 127.75, 127.54, 127.13, 123.19, 117.12, 96.11, 28.91, 25.48. HRMS (ESI) m/z Calcd. for $\text{C}_{21}\text{H}_{15}\text{BrN}_3\text{O}_2^+([\text{M}+\text{H}]^+)$ 420.0342, Found 420.0349. Enantiomeric excess was determined to be 40% (determined by HPLC using chiral IC column, hexane/2-propanol = 7/3, λ = 254 nm, 1.0 mL/min, t_{major} = 29.4 min, t_{minor} = 33.7 min).



Detector A 254nm

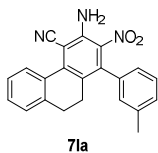
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1	29.432	13756612	237204		49.926				49.926
2	33.780	13797213	216014	M	50.074				50.074
总计		27553826	453218		100.000				100.000



Detector A 254nm

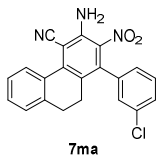
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	29.402	38694715	680368	■	69.941				69.941
2	33.820	16630336	260344	■	30.059				30.059
总计		55325051	940712		100.000				100.000

4. -isocyano-2-nitro-1-(m-tolyl)-9,10-dihydrophenanthren-3-amine (7ia)



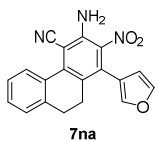
Prepared according to the general procedure as yellow solid (63 mg, 88% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 8.33–8.06 (m, 1H), 7.48–7.36 (m, 2H), 7.35–7.26 (m, 2H), 7.257.15 (m, 1H), 7.06–6.92 (m, 2H), 5.63 (s, 2H), 2.72–2.54 (m, 2H), 2.44–2.39 (m, 2H), 2.38 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 143.18, 142.41, 140.51, 139.78, 138.50, 135.58, 135.51, 131.14, 130.42, 129.33, 128.62, 128.45, 128.22, 127.89, 127.39, 127.06, 125.14, 117.23, 95.17, 29.05, 25.97, 21.48. HRMS (ESI) m/z Calcd. for C₂₂H₁₈N₃O₂⁺ ([M+H]⁺) 356.1394, Found 356.1401.

1. -(3-chlorophenyl)-4-isocyano-2-nitro-9,10-dihydrophenanthren-3-amine (7ma)



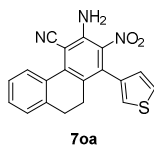
Prepared according to the general procedure as yellow solid (66 mg, 88% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 8.29–8.17 (m, 1H), 7.47–7.34 (m, 4H), 7.32–7.26 (m, 1H), 7.23–7.16 (m, 1H), 7.09 (dt, J = 6.5, 1.9 Hz, 1H), 5.79 (s, 2H), 2.73–2.59 (m, 2H), 2.45–2.26 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 143.58, 139.73, 138.90, 137.55, 134.82, 134.75, 130.87, 130.69, 130.10, 128.73, 128.06, 127.98, 127.96, 127.47, 127.16, 126.23, 117.01, 28.94, 25.95. HRMS (ESI) m/z Calcd. For C₂₁H₁₅ClN₃O₂⁺ ([M+H]⁺) 376.0847, Found 376.0856.

1. -(furan-3-yl)-4-isocyano-2-nitro-9,10-dihydrophenanthren-3-amine (7na)



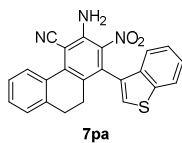
Prepared according to the general procedure as yellow solid (57 mg, 87% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 8.25–8.05 (m, 1H), 7.54 (d, J = 1.8 Hz, 1H), 7.46–7.37 (m, 2H), 7.35–7.27 (m, 1H), 6.61–6.45 (m, 2H), 5.77 (s, 2H), 2.70 (s, 4H). ¹³C NMR (101 MHz, DMSO) δ 146.13, 145.11, 143.61, 142.38, 140.21, 135.11, 131.17, 130.73, 128.31, 127.95, 127.66, 127.09, 126.90, 117.43, 113.62, 112.29, 95.90, 28.68, 25.67. HRMS (ESI) m/z Calcd. for C₁₉H₁₄N₃O₃⁺ ([M+H]⁺) 332.1030, Found 332.1037.

4. -isocyano-2-nitro-1-(thiophen-3-yl)-9,10-dihydrophenanthren-3-amine (7oa)



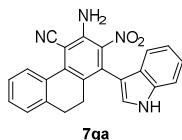
Prepared according to the general procedure as yellow solid (65 mg, 93% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). ^1H NMR (400 MHz, CDCl_3) δ 8.41–7.96 (m, 1H), 7.54–7.44 (m, 1H), 7.44–7.35 (m, 2H), 7.33–7.27 (m, 1H), 7.147.05 (m, 1H), 7.016.92 (m, 1H), 5.58 (s, 2H), 2.78–2.45 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 142.93, 142.32, 139.70, 136.24, 134.86, 132.88, 130.94, 130.56, 129.74, 128.13, 127.94, 127.67, 127.40, 127.12, 117.00, 96.12, 28.96, 26.03. HRMS (ESI) m/z Calcd. for $\text{C}_{19}\text{H}_{14}\text{N}_3\text{O}_2\text{S}^+([\text{M}+\text{H}]^+)$ 348.0801, Found 348.0805.

1. -(benzo[b]thiophen-3-yl)-4-isocyano-2-nitro-9,10-dihydrophenanthren-3-amine (7pa)



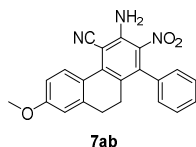
Prepared according to the general procedure as yellow solid (70 mg, 88% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). ^1H NMR (500 MHz, CDCl_3) δ 8.47 (s, 1H), 8.28 (dd, J = 7.6, 1.5 Hz, 1H), 7.48–7.38 (m, 3H), 7.34–7.28 (m, 2H), 7.20 (d, J = 2.6 Hz, 1H), 7.15 (ddd, J = 8.0, 7.1, 1.0 Hz, 1H), 5.46 (s, 2H), 2.68–2.57 (m, 3H), 2.512.41 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.57, 139.89, 130.92, 130.87, 130.62, 129.39, 128.00, 127.46, 127.16, 125.01, 124.83, 124.47, 124.44, 122.96, 122.30, 117.11, 28.97, 25.67. HRMS (ESI) m/z Calcd. for $\text{C}_{23}\text{H}_{16}\text{N}_3\text{O}_2\text{S}^+([\text{M}+\text{H}]^+)$ 398.0958, Found 398.0963.

1. -(1H-indol-3-yl)-4-isocyano-2-nitro-9,10-dihydrophenanthren-3-amine (7qa)



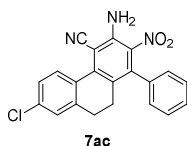
Prepared according to the general procedure as yellow solid (36 mg, 27% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). ^1H NMR (500 MHz, CDCl_3) δ 8.47 (s, 1H), 8.28 (dd, J = 7.6, 1.5 Hz, 1H), 7.48–7.38 (m, 3H), 7.34–7.28 (m, 2H), 7.277.25 (m, 1H), 7.20 (d, J = 2.6 Hz, 1H), 7.15 (ddd, J = 8.0, 7.1, 1.0 Hz, 1H), 5.46 (s, 2H), 2.68–2.57 (m, 3H), 2.51–2.43 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 142.69, 141.74, 139.85, 135.79, 133.24, 131.40, 130.23, 129.96, 127.86, 127.34, 127.03, 126.63, 123.23, 122.99, 120.75, 119.43, 117.43, 111.65, 110.72, 94.88, 29.16, 26.03. HRMS (ESI) m/z Calcd. for $\text{C}_{23}\text{H}_{17}\text{N}_4\text{O}_2^+([\text{M}+\text{H}]^+)$ 381.1346, Found 381.1352.

4. -isocyano-7-methoxy-2-nitro-1-phenyl-9,10-dihydrophenanthren-3-amine (7ab)



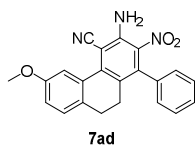
Prepared according to the general procedure as yellow solid (58 mg, 80% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). ^1H NMR (500 MHz, CDCl_3) δ 8.22 (d, J = 8.8 Hz, 1H), 7.50–7.39 (m, 3H), 7.24–7.18 (m, 2H), 6.96 (dd, J = 8.7, 2.7 Hz, 1H), 6.81 (d, J = 2.7 Hz, 1H), 5.73 (s, 2H), 3.88 (s, 3H), 2.71–2.55 (m, 2H), 2.46–2.30 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.28, 143.49, 142.78, 141.98, 140.32, 135.94, 134.68, 129.13, 128.72, 128.40, 127.96, 127.29, 123.87, 117.49, 113.64, 112.04, 94.48, 55.42, 29.43, 25.89. HRMS (ESI) m/z Calcd. for $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}_3^+([\text{M}+\text{H}]^+)$ 372.1343, Found 372.1347.

7. -chloro-4-isocyano-2-nitro-1-phenyl-9,10-dihydrophenanthren-3-amine (7ac)



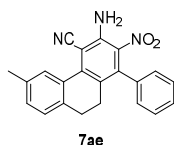
Prepared according to the general procedure as yellow solid (66 mg, 89% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). ^1H NMR (400 MHz, CDCl_3) δ 8.17 (d, J = 8.5 Hz, 1H), 7.52–7.41 (m, 3H), 7.39 (dd, J = 8.5, 2.3 Hz, 1H), 7.28 (d, J = 2.2 Hz, 1H), 7.24–7.11 (m, 2H), 5.64 (s, 2H), 2.61 (dd, J = 8.4, 5.3 Hz, 2H), 2.43–2.30 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.26, 141.60, 141.37, 140.47, 136.29, 135.69, 135.39, 129.59, 128.83, 128.67, 128.64, 128.02, 127.94, 127.81, 127.24, 116.98, 95.16, 28.92, 25.73. HRMS (ESI) m/z Calcd. for $\text{C}_{21}\text{H}_{15}\text{ClN}_3\text{O}_2^+([\text{M}+\text{H}]^+)$ 376.0847, Found 376.0855.

4. -isocyano-6-methoxy-2-nitro-1-phenyl-9,10-dihydrophenanthren-3-amine (7ad)



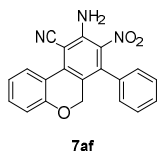
Prepared according to the general procedure as yellow solid (66 mg, 89% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.82 (d, J = 2.5 Hz, 1H), 7.49–7.40 (m, 3H), 7.25–7.17 (m, 3H), 6.97 (dd, J = 8.3, 2.6 Hz, 1H), 5.67 (s, 2H), 3.93 (s, 3H), 2.65–2.51 (m, 2H), 2.47–2.30 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.43, 143.20, 142.52, 140.32, 135.64, 131.84, 131.77, 128.76, 128.54, 128.32, 127.99, 117.23, 117.01, 112.20, 95.30, 55.64, 28.05, 26.28. HRMS (ESI) m/z Calcd. for $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}_3^+([\text{M}+\text{H}]^+)$ 372.1343, Found 372.1347.

4. -isocyano-6-methyl-2-nitro-1-phenyl-9,10-dihydrophenanthren-3-amine (7ae)



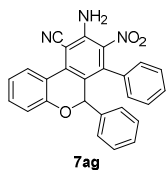
Prepared according to the general procedure as yellow solid (64 mg, 95% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). ^1H NMR (500 MHz, CDCl_3) δ 8.14–8.02 (m, 1H), 7.50–7.41 (m, 3H), 7.26–7.16 (m, 4H), 5.70 (s, 2H), 2.65–2.57 (m, 2H), 2.48 (s, 3H), 2.42–2.35 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.32, 142.73, 140.32, 136.81, 136.74, 135.77, 135.43, 131.23, 131.00, 128.80, 128.55, 128.25, 128.03, 127.80, 117.26, 95.30, 28.60, 26.23, 21.35. HRMS (ESI) m/z Calcd. for $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}_2^+([\text{M}+\text{H}]^+)$ 356.1394, Found 356.1398.

10. -isocyano-8-nitro-7-phenyl-6H-benzo[c]chromen-9-amine (7af)



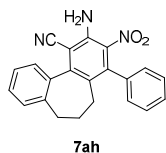
Prepared according to the general procedure as yellow solid (59 mg, 86% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). ^1H NMR (500 MHz, CDCl_3) δ 8.41 (dd, J = 8.0, 1.5 Hz, 1H), 7.55–7.37 (m, 4H), 7.24–7.13 (m, 3H), 7.05 (dd, J = 8.2, 1.2 Hz, 1H), 5.86 (s, 2H), 4.63 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.71, 144.61, 139.03, 137.50, 134.76, 134.01, 132.87, 129.09, 129.00, 127.64, 126.58, 122.66, 122.58, 120.32, 117.85, 116.65, 93.71, 65.59. HRMS (ESI) m/z Calcd. for $\text{C}_{20}\text{H}_{14}\text{N}_3\text{O}_3^+([\text{M}+\text{H}]^+)$ 344.1030, Found 344.1038.

10. -isocyano-8-nitro-6,7-diphenyl-6H-benzo[c]chromen-9-amine (7ag)



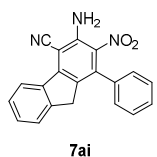
Prepared according to the general procedure as yellow solid (57 mg, 68% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). ^1H NMR (500 MHz, CDCl_3) δ 8.42 (dd, J = 8.0, 1.5 Hz, 1H), 7.44 (tdd, J = 7.7, 1.5, 0.6 Hz, 1H), 7.36 (tt, J = 7.5, 1.3 Hz, 1H), 7.23–7.10 (m, 4H), 7.07 (ddd, J = 8.1, 7.4, 1.2 Hz, 1H), 7.04–6.96 (m, 2H), 6.86 (dd, J = 8.1, 1.2 Hz, 1H), 6.80–6.73 (m, 1H), 5.88 (s, 2H), 5.83 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 153.91, 144.80, 137.87, 133.59, 132.97, 128.94, 128.80, 128.61, 128.55, 128.20, 127.13, 126.03, 123.45, 122.40, 119.08, 116.76, 75.18. HRMS (ESI) m/z Calcd. for $\text{C}_{26}\text{H}_{18}\text{N}_3\text{O}_3^+([\text{M}+\text{H}]^+)$ 420.1343, Found 420.1350.

2. -amino-3-nitro-4-phenyl-6,7-dihydro-5H-dibenzo[a,c][7]annulene-1-carbonitrile (7ah)



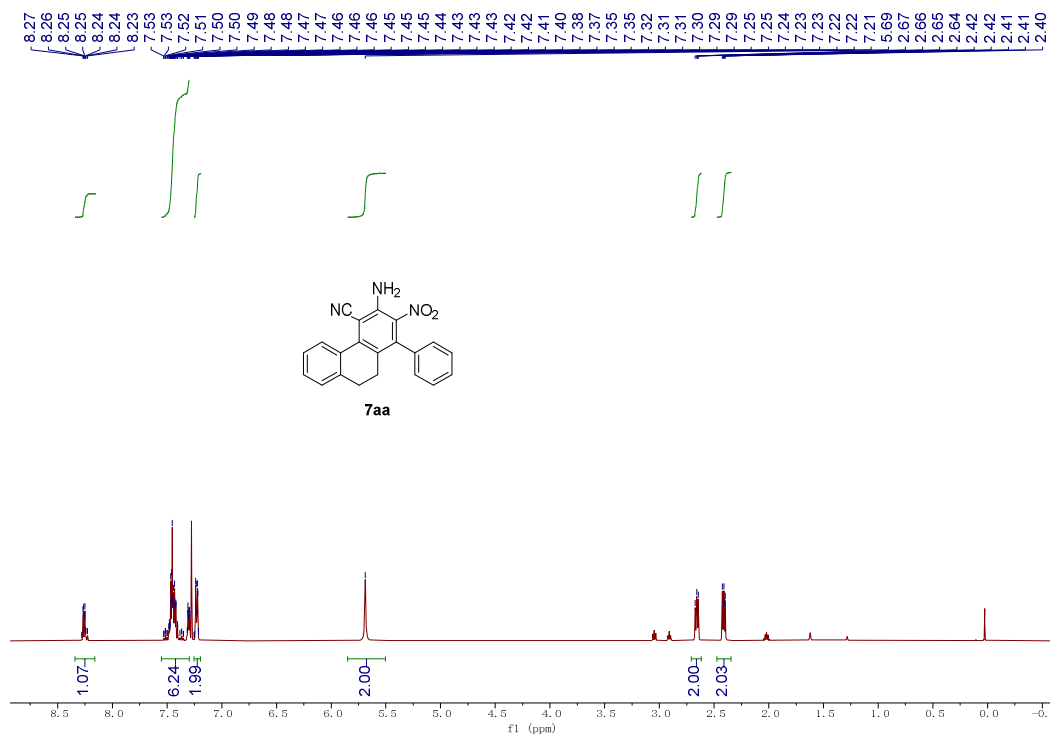
Prepared according to the general procedure as yellow solid (70 mg, 97% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). ^1H NMR (500 MHz, CDCl_3) δ 7.67–7.61 (m, 1H), 7.51–7.39 (m, 5H), 7.35–7.31 (m, 1H), 7.31–7.28 (m, 1H), 7.21–7.15 (m, 1H), 5.51 (s, 2H), 2.72–2.60 (m, 1H), 2.56–2.43 (m, 1H), 2.29–2.17 (m, 1H), 1.96–1.83 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.56, 142.09, 140.52, 139.94, 136.23, 135.67, 135.62, 130.15, 129.19, 128.97, 128.65, 128.58, 128.42, 128.32, 128.29, 127.94, 126.69, 116.11, 98.51, 32.59, 30.79, 26.84. HRMS (ESI) m/z Calcd. for $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}_2^+([\text{M}+\text{H}]^+)$ 356.1394, Found 356.1400.

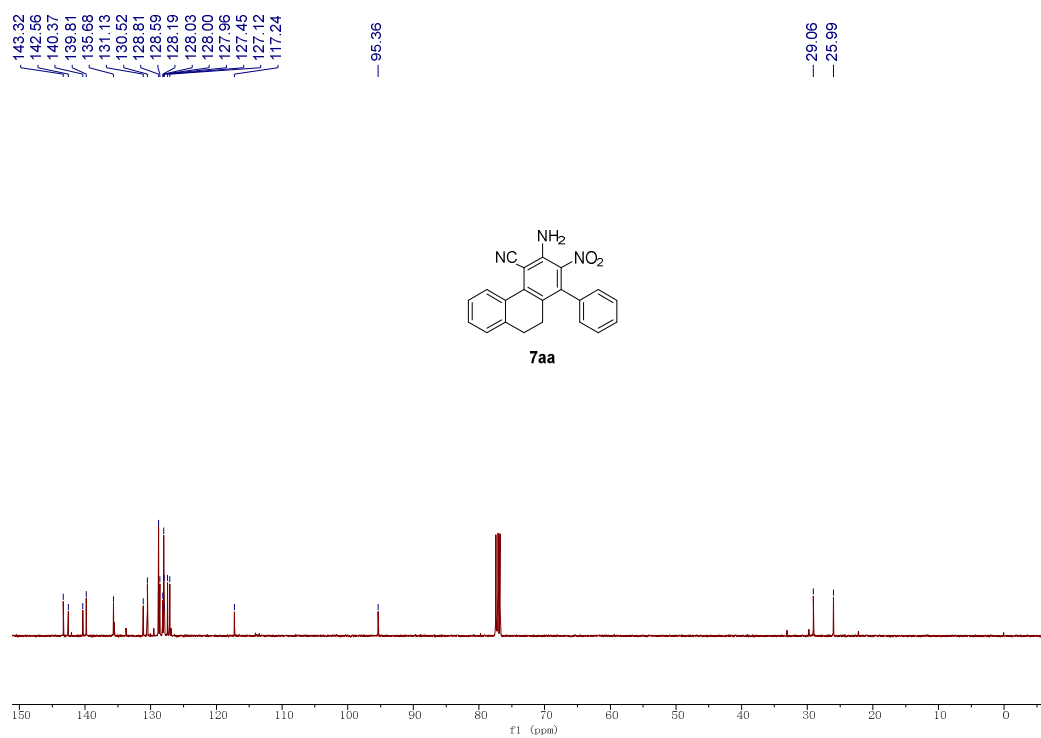
4. -isocyano-2-nitro-1-phenyl-9H-fluoren-3-amine (7ai)

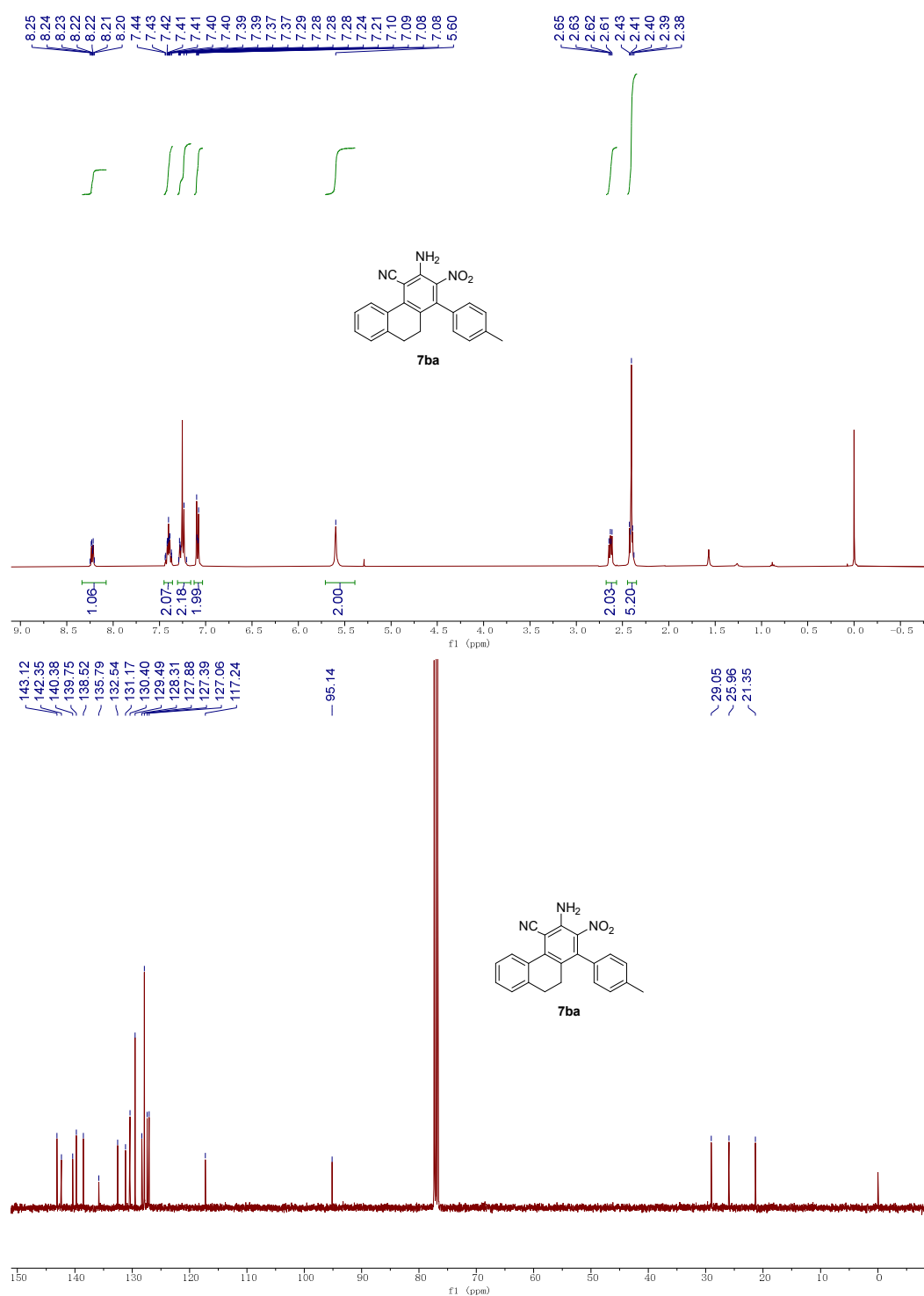


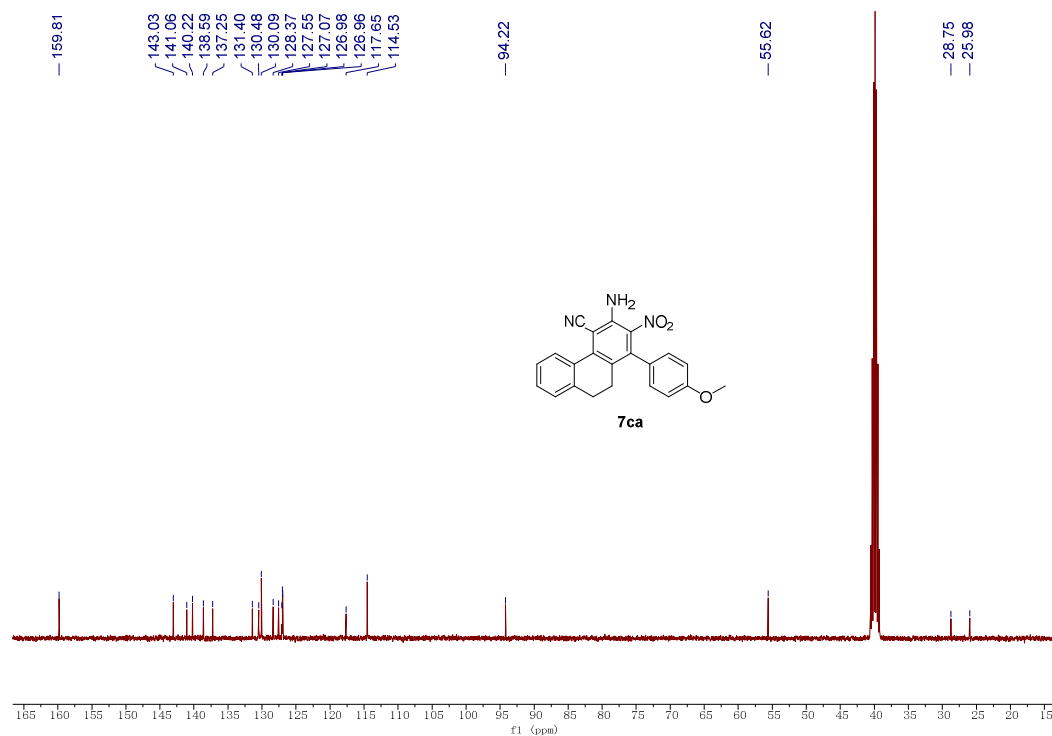
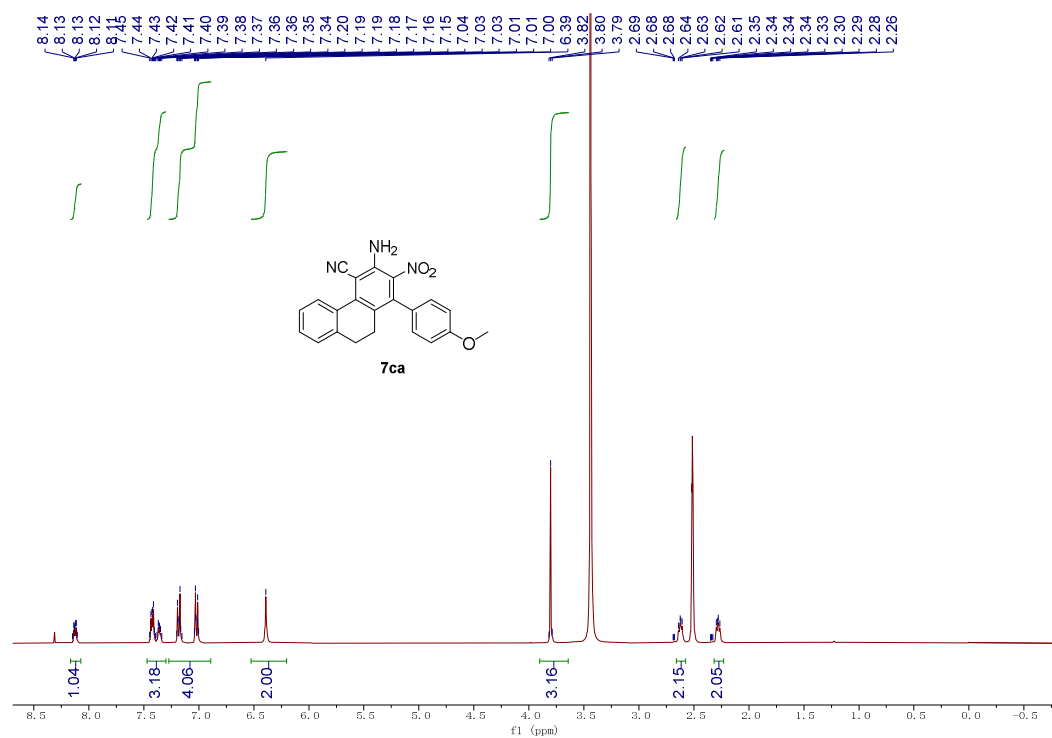
Prepared according to the general procedure as yellow solid (8 mg, 13% yield) after silica gel chromatography (petroleum ether/EtOAc = 10:1). ^1H NMR (400 MHz, DMSO) δ 8.27 (dd, J = 7.1, 1.7 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.50–7.39 (m, 5H), 7.36–7.30 (m, 2H), 6.63 (s, 2H), 2.45 (p, J = 1.8 Hz, 12H). ^{13}C NMR (101 MHz, DMSO) δ 146.76, 145.52, 144.54, 138.00, 137.77, 135.56, 135.51, 131.24, 130.09, 129.26, 129.11, 128.05, 127.92, 126.06, 122.33, 116.17, 89.58, 36.12. HRMS (ESI) m/z Calcd. for $\text{C}_{20}\text{H}_{14}\text{N}_3\text{O}_2^+([\text{M}+\text{H}]^+)$ 328.1081, Found 328.1090.

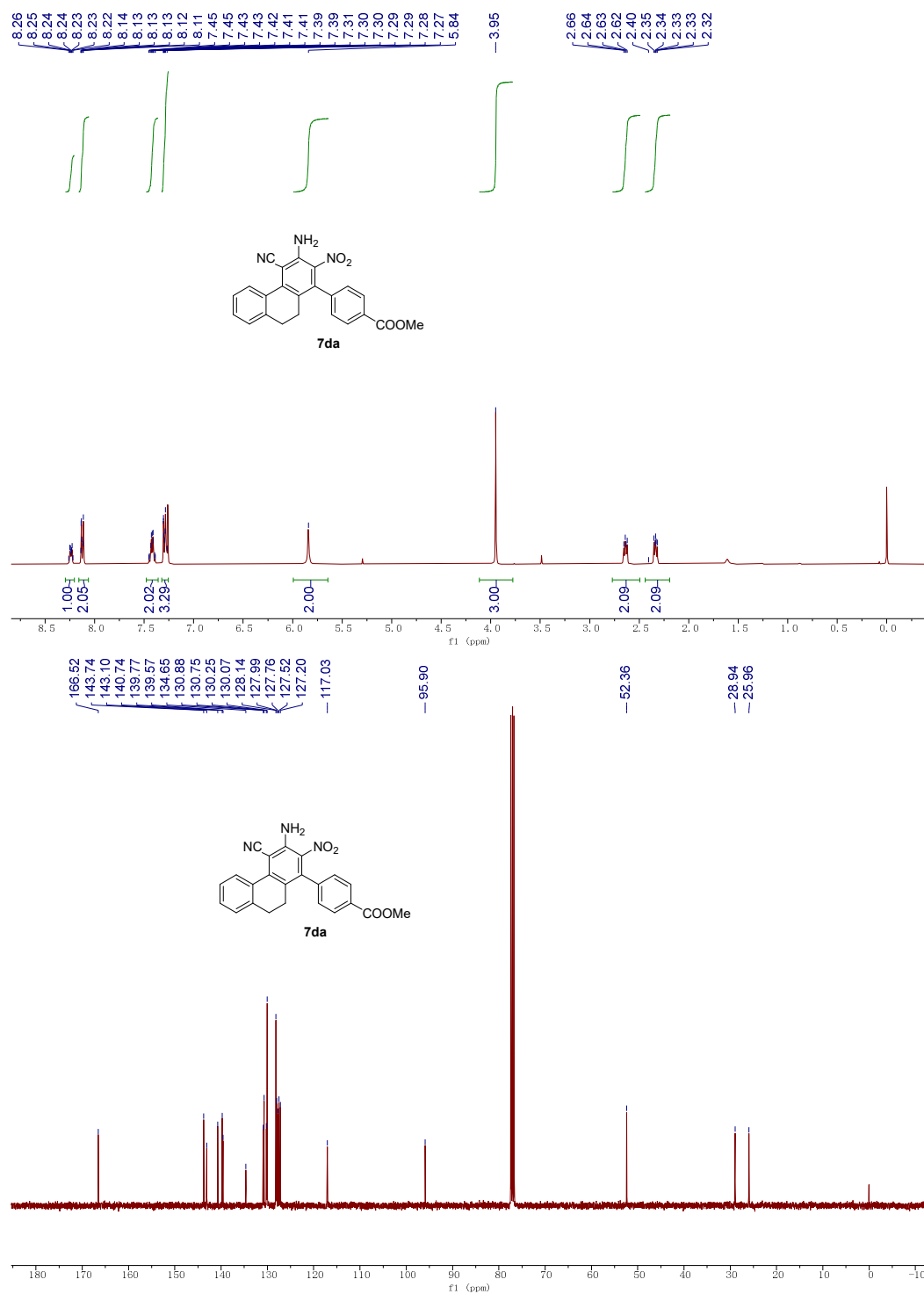
3. NMR spectra for compounds

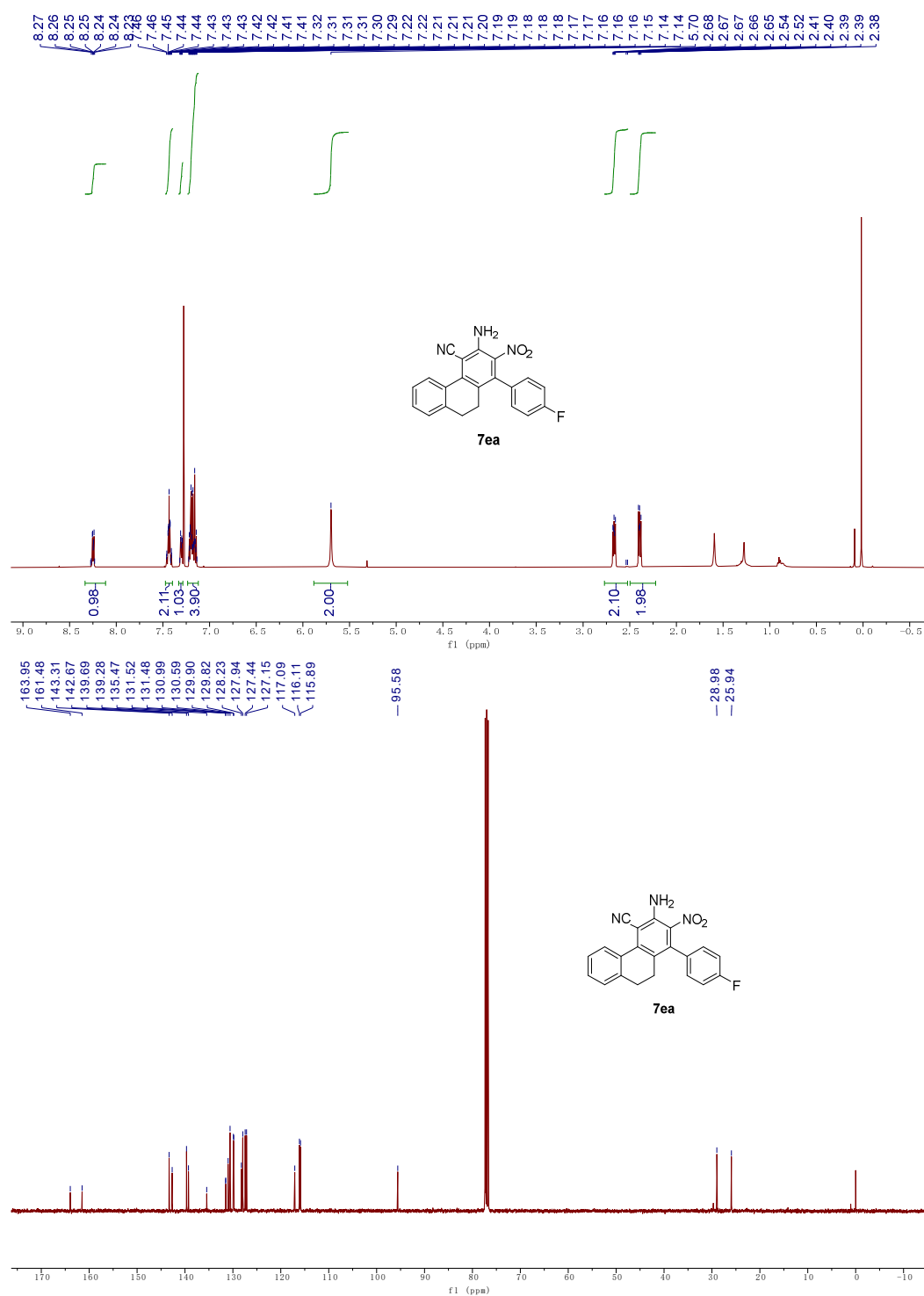


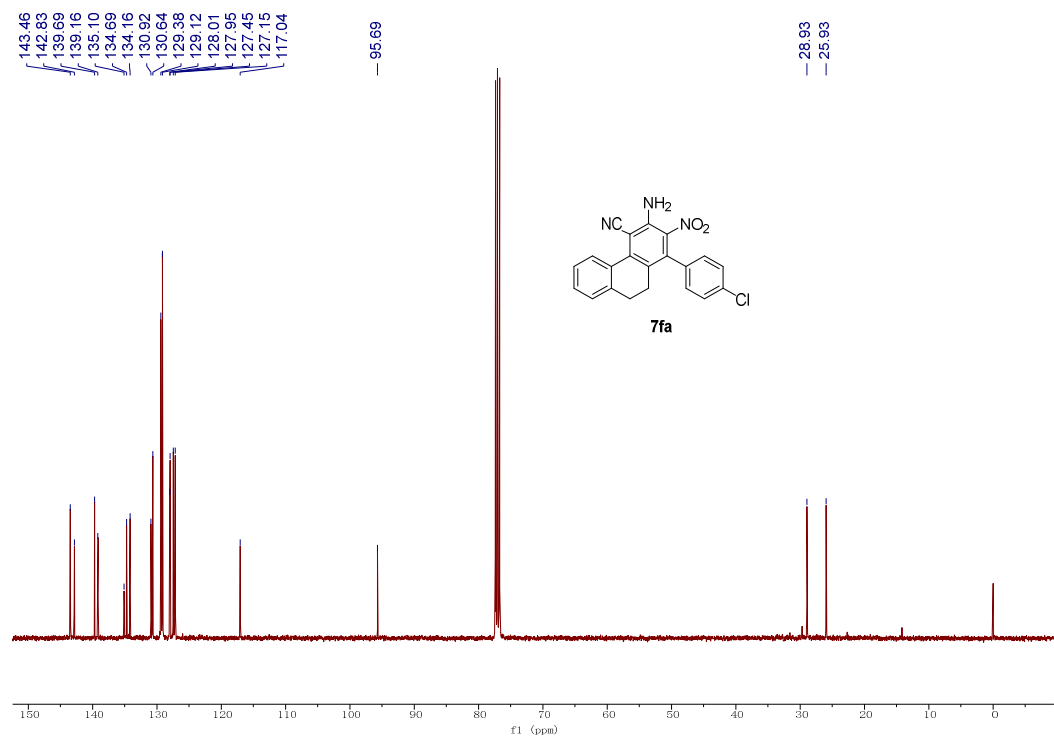
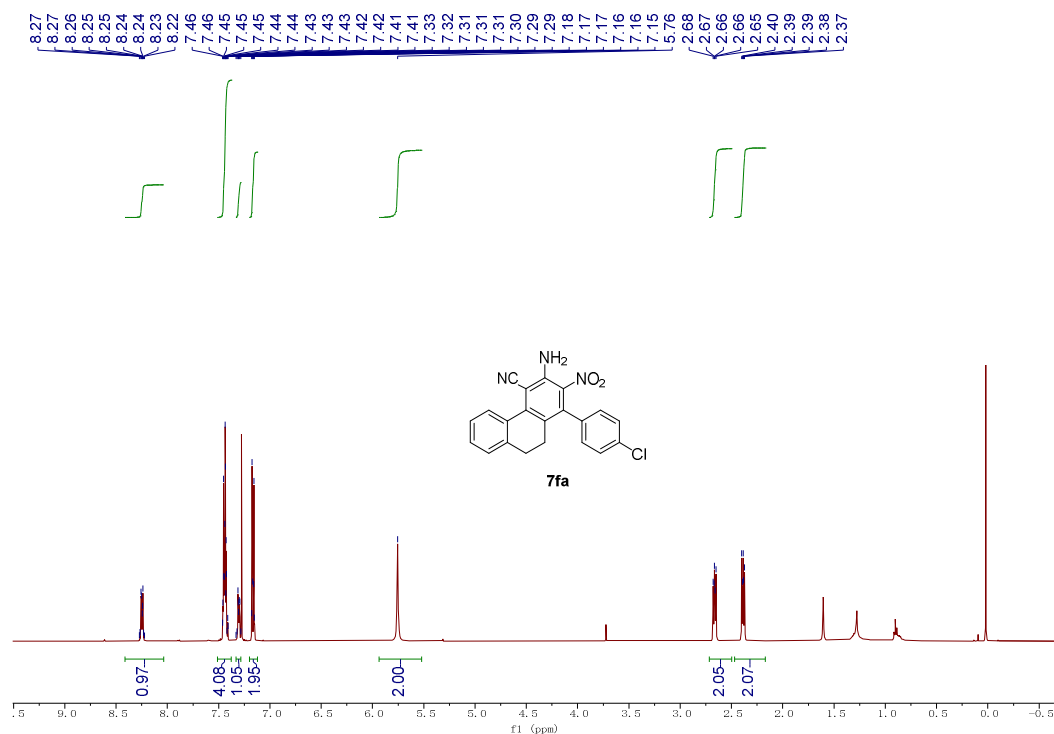


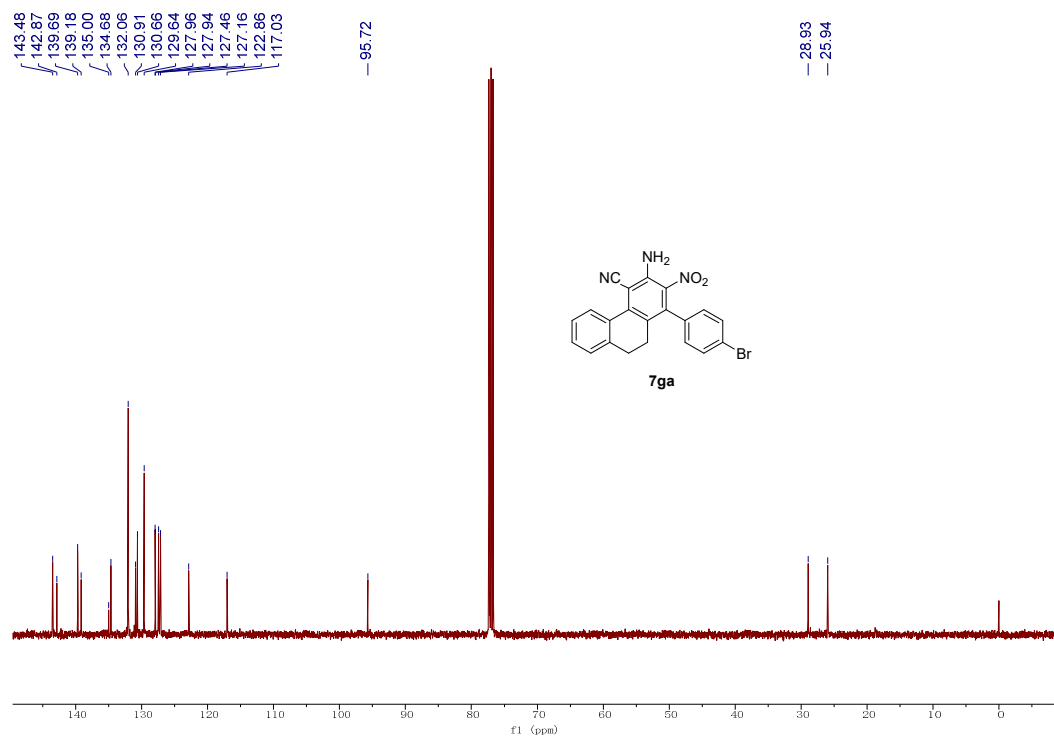
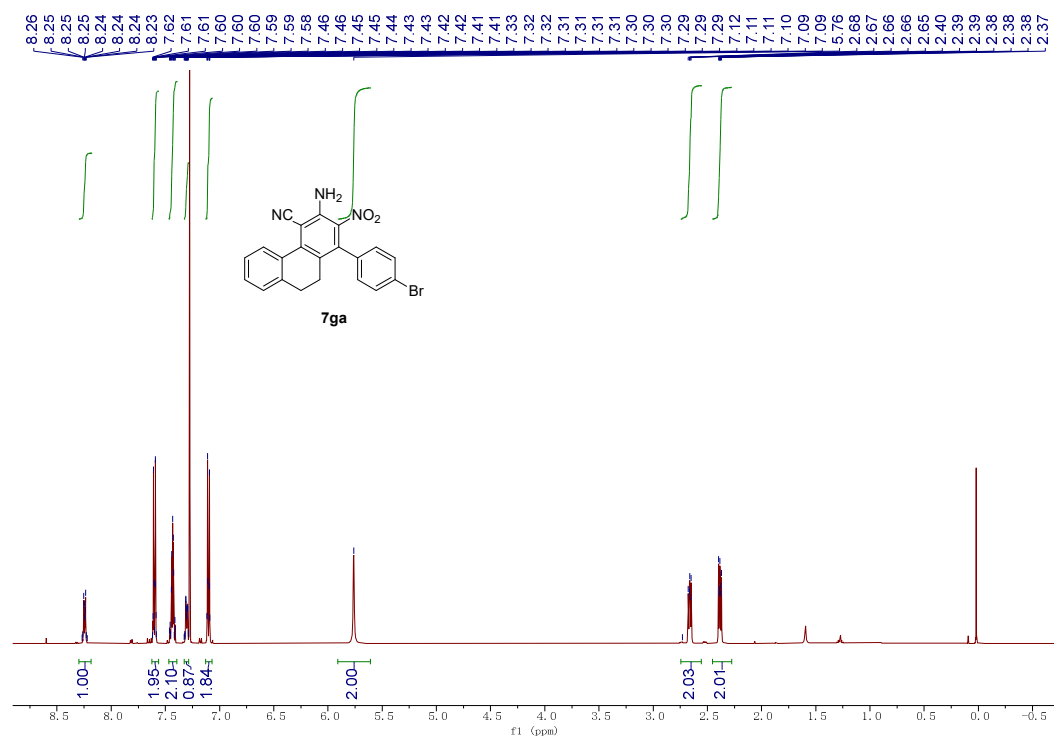


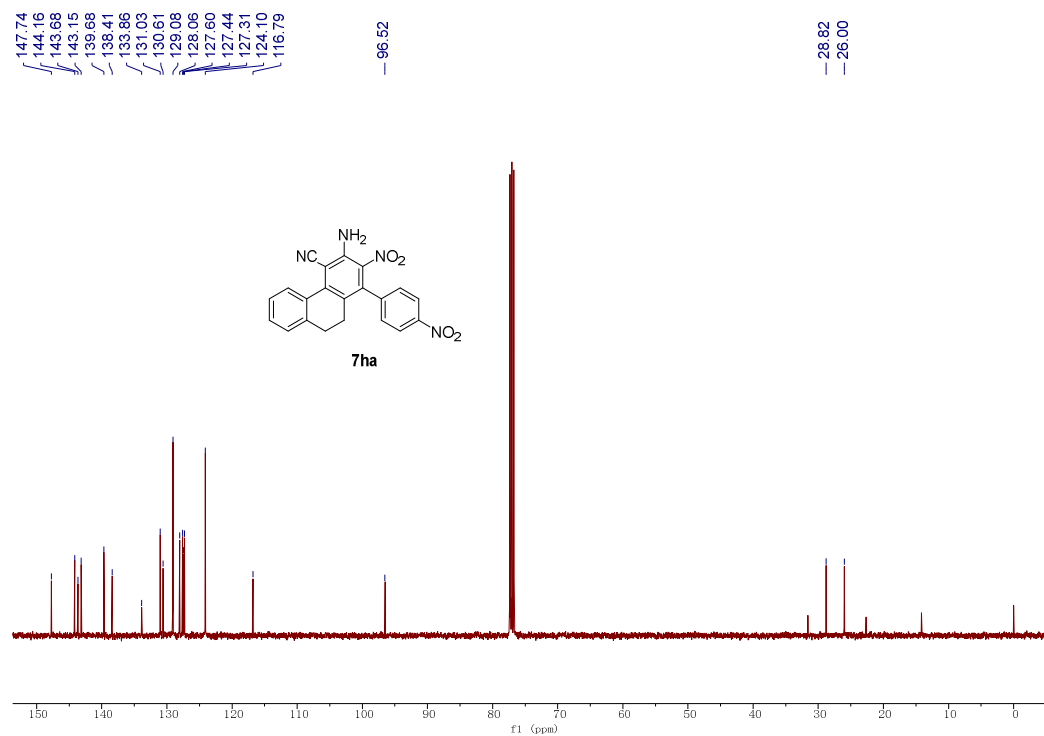
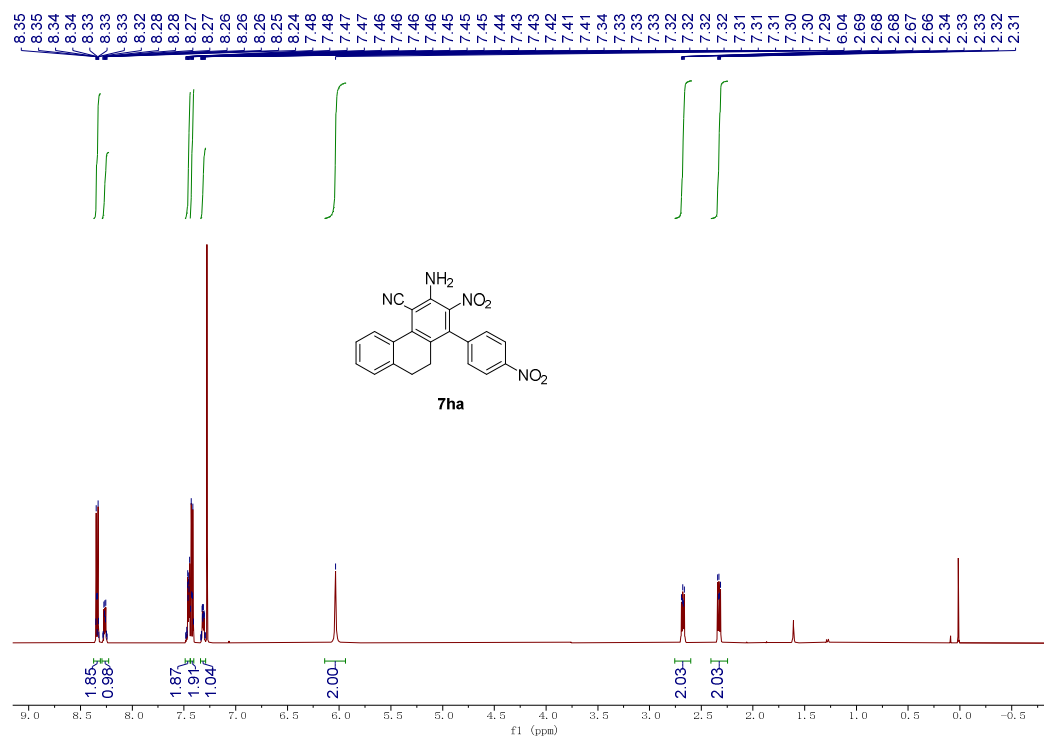


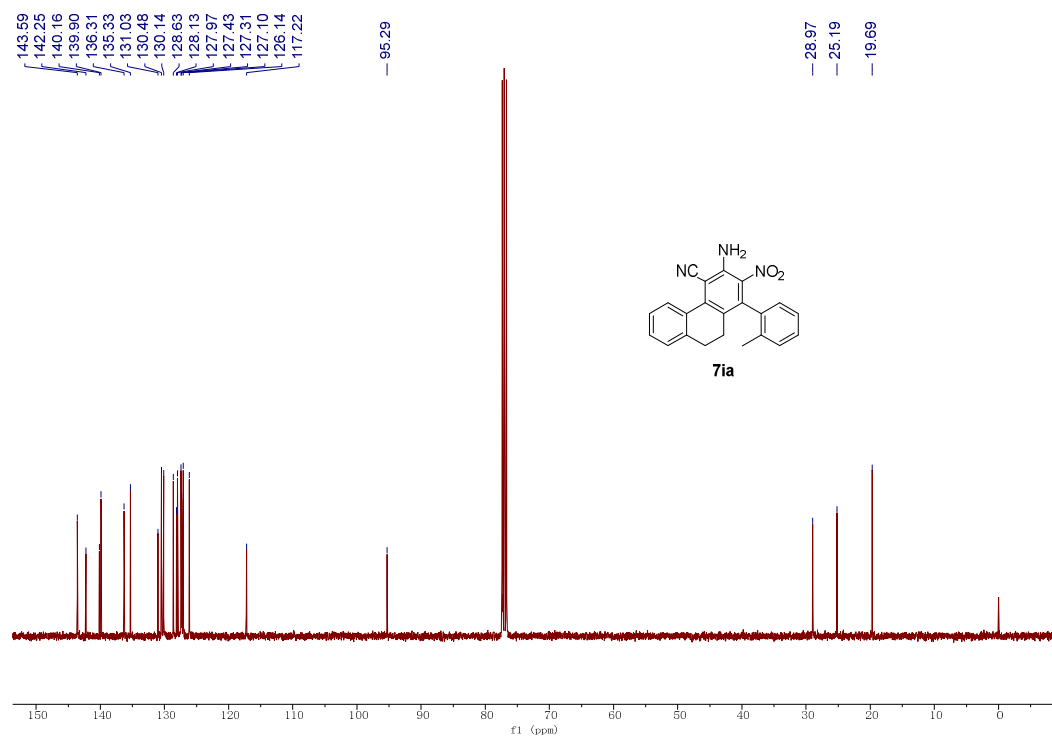
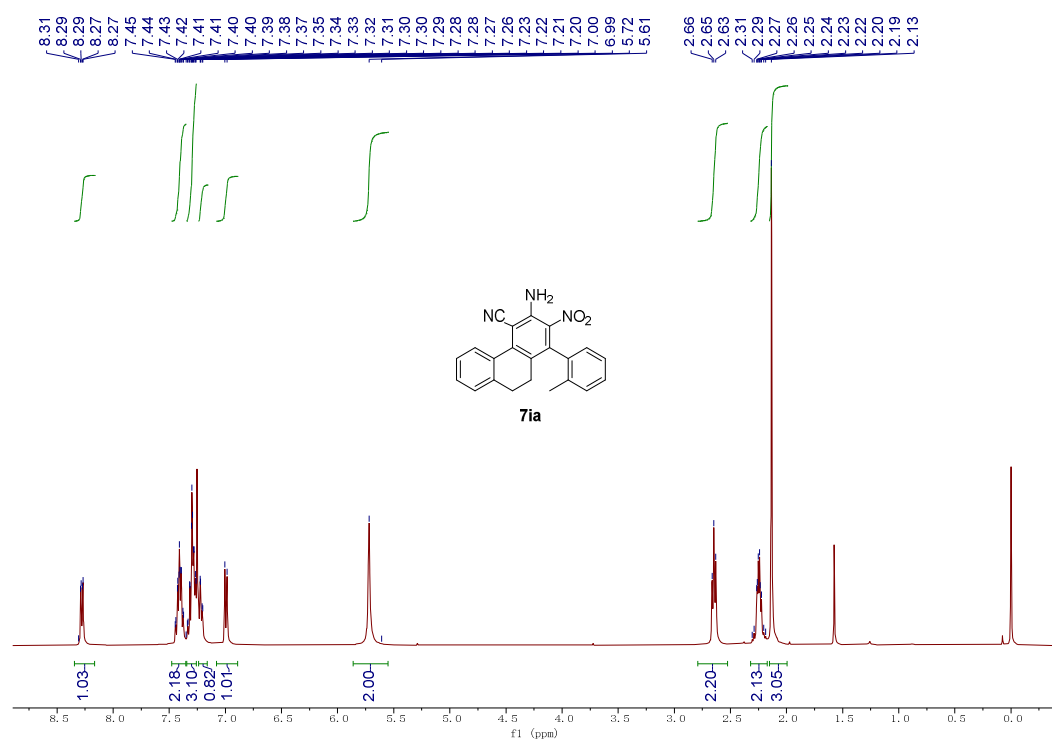


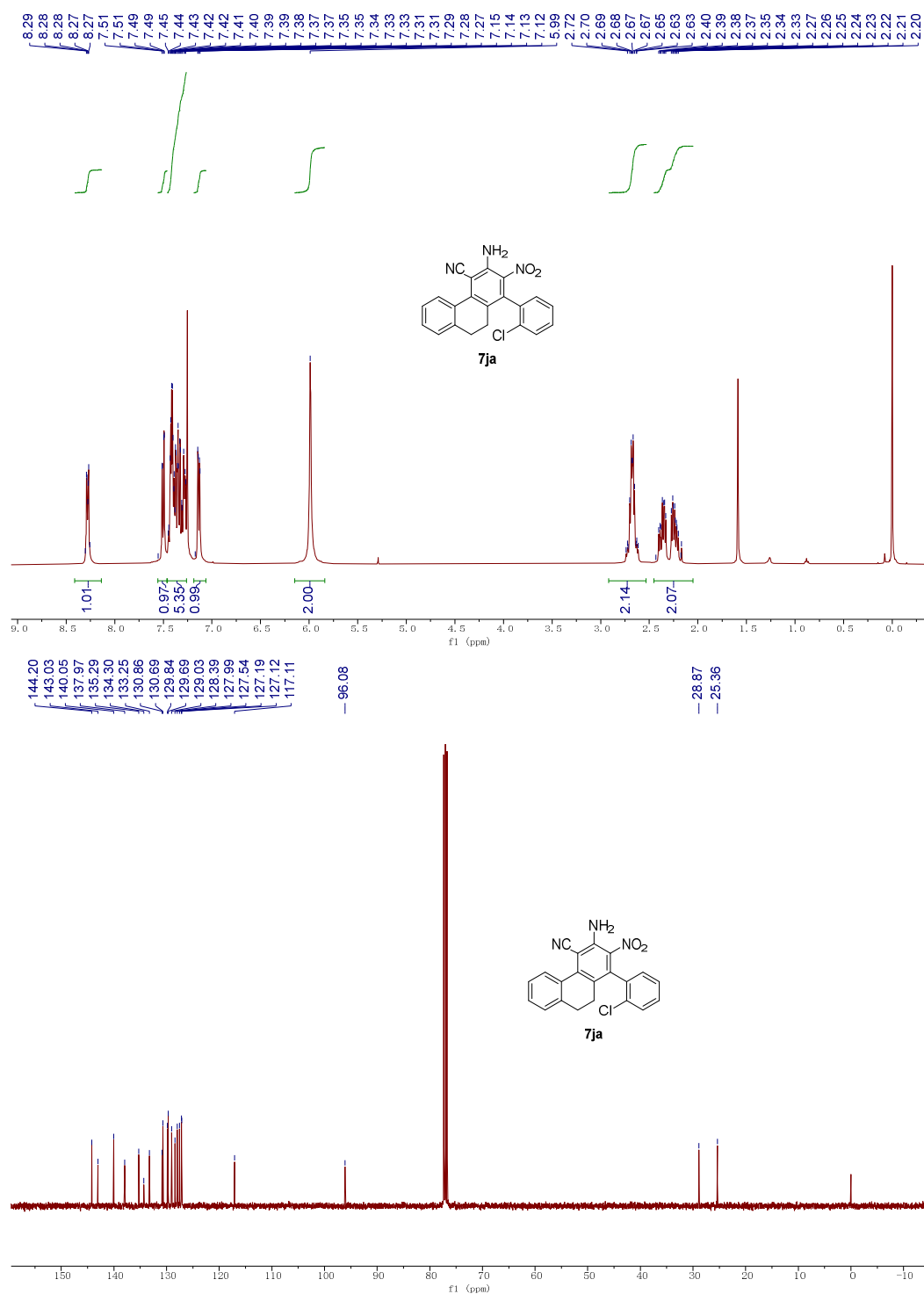


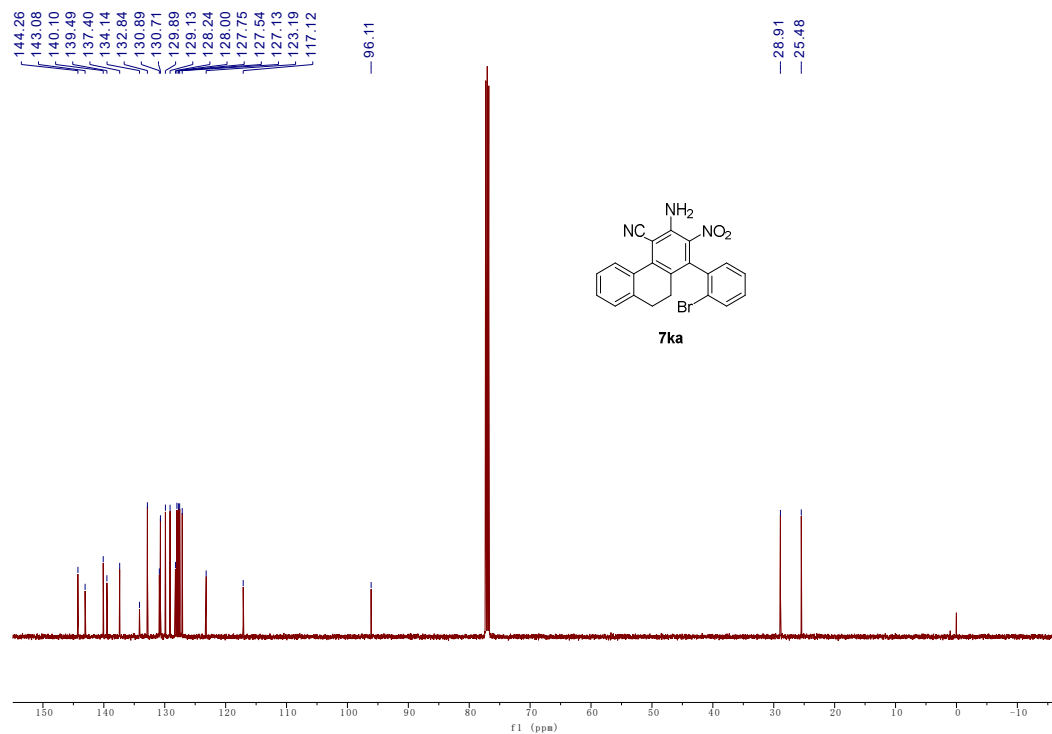
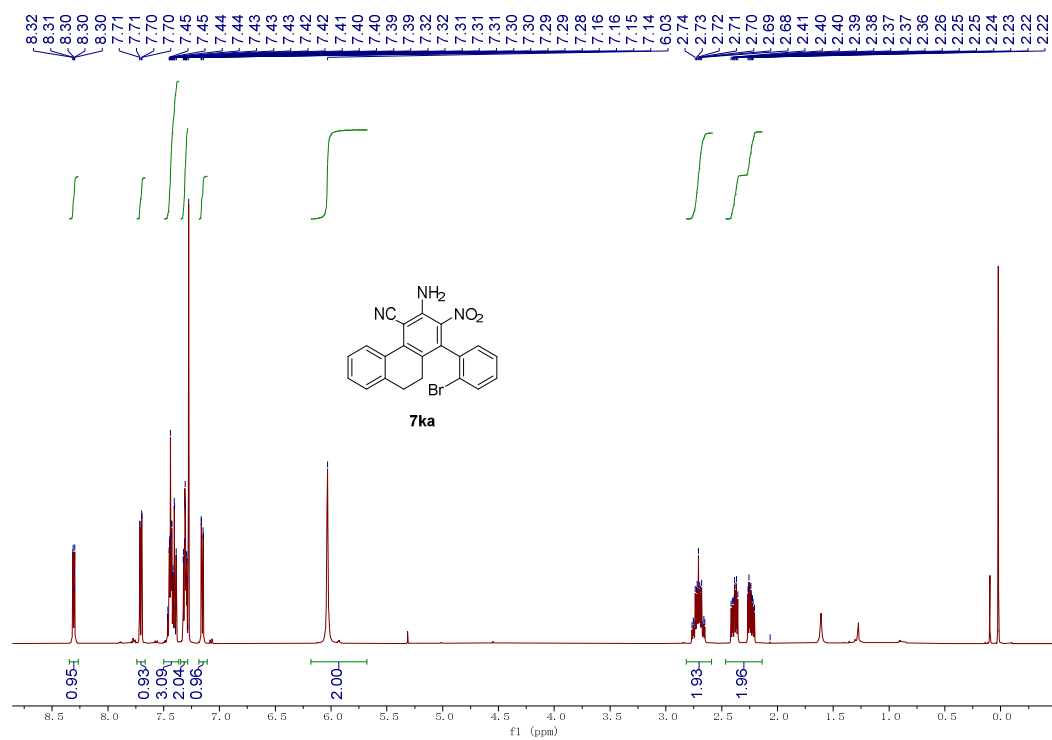


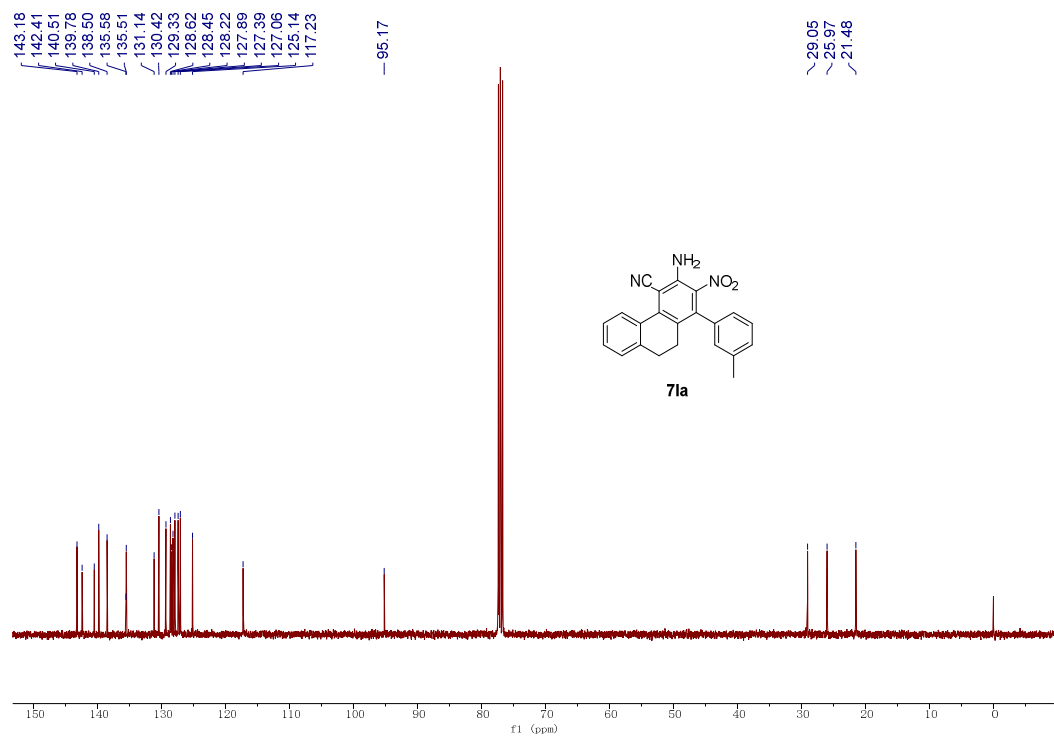
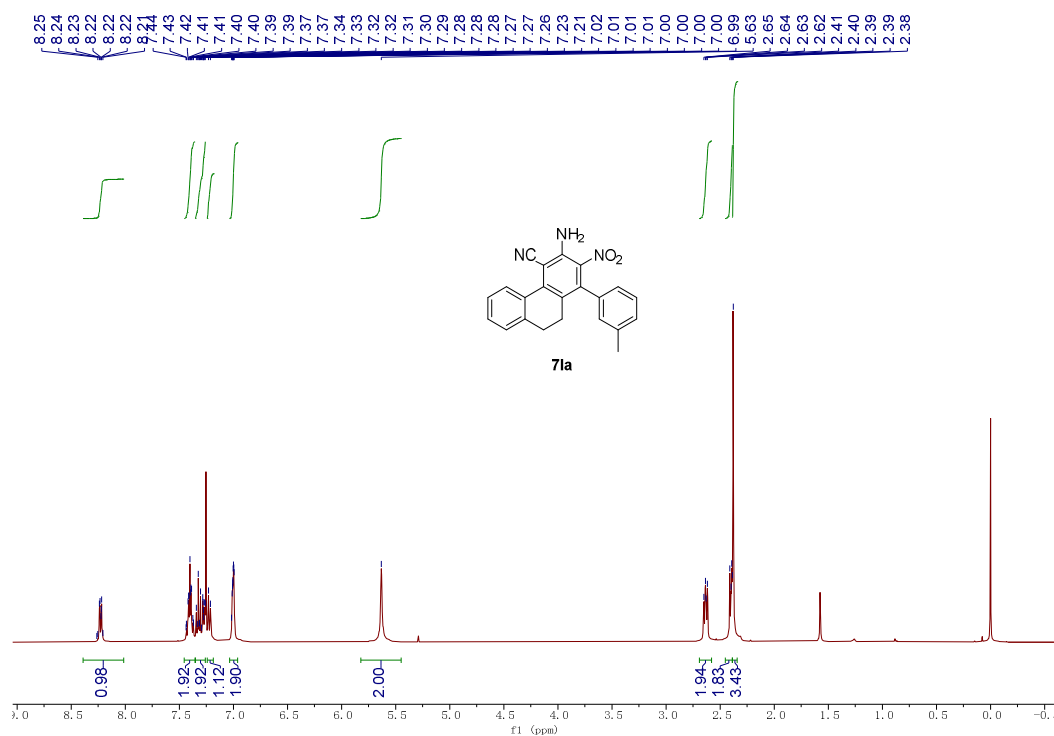


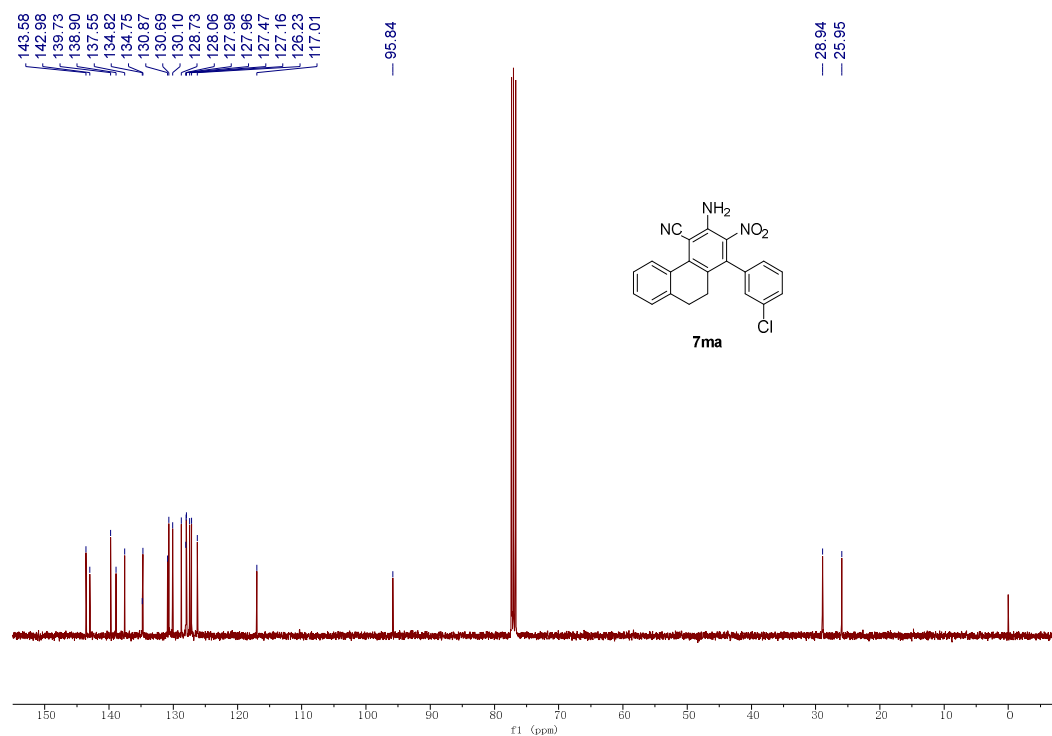
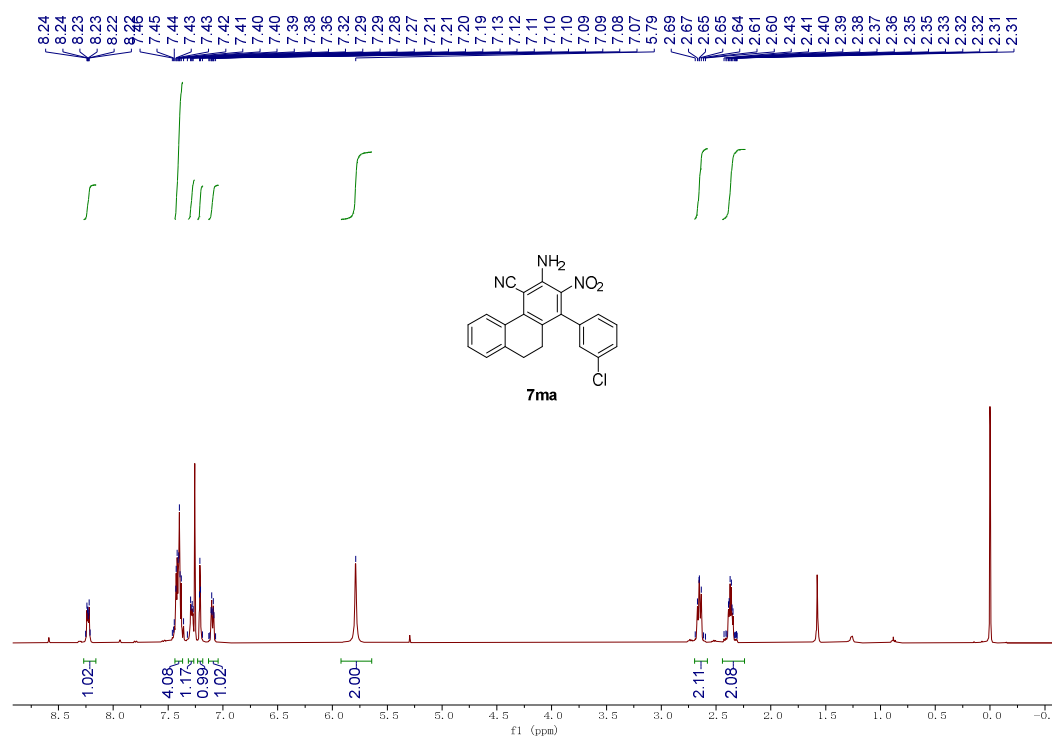


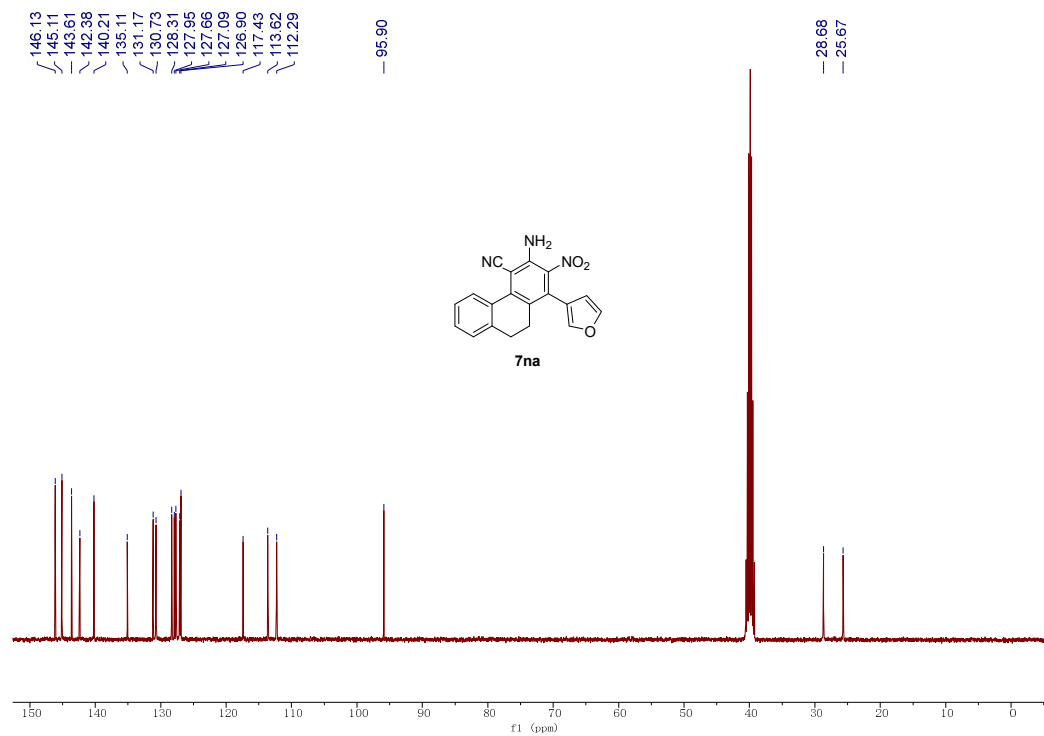
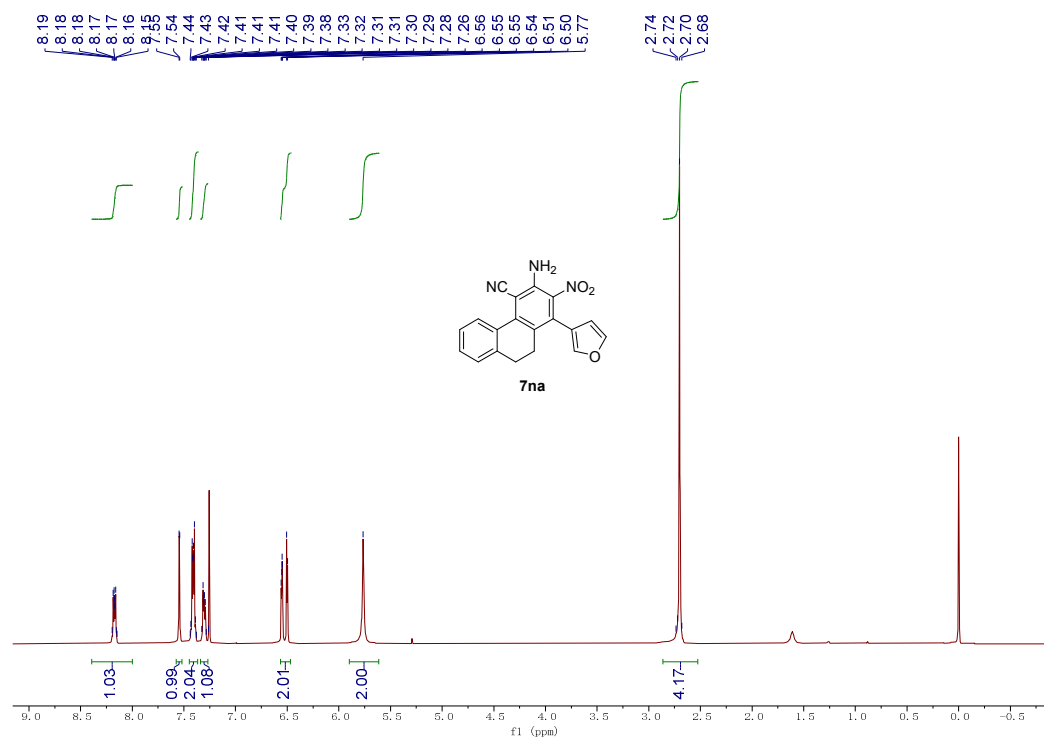


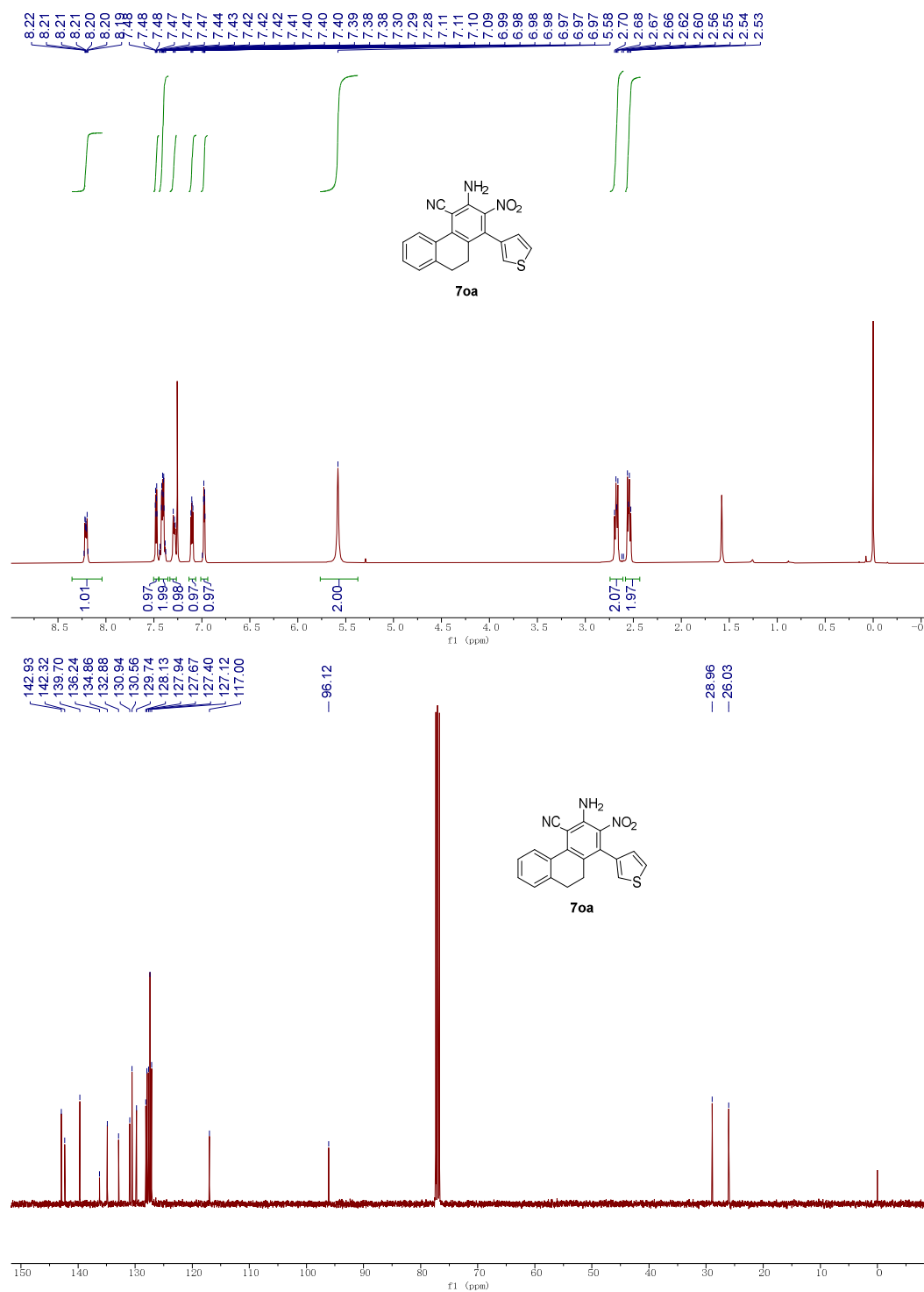


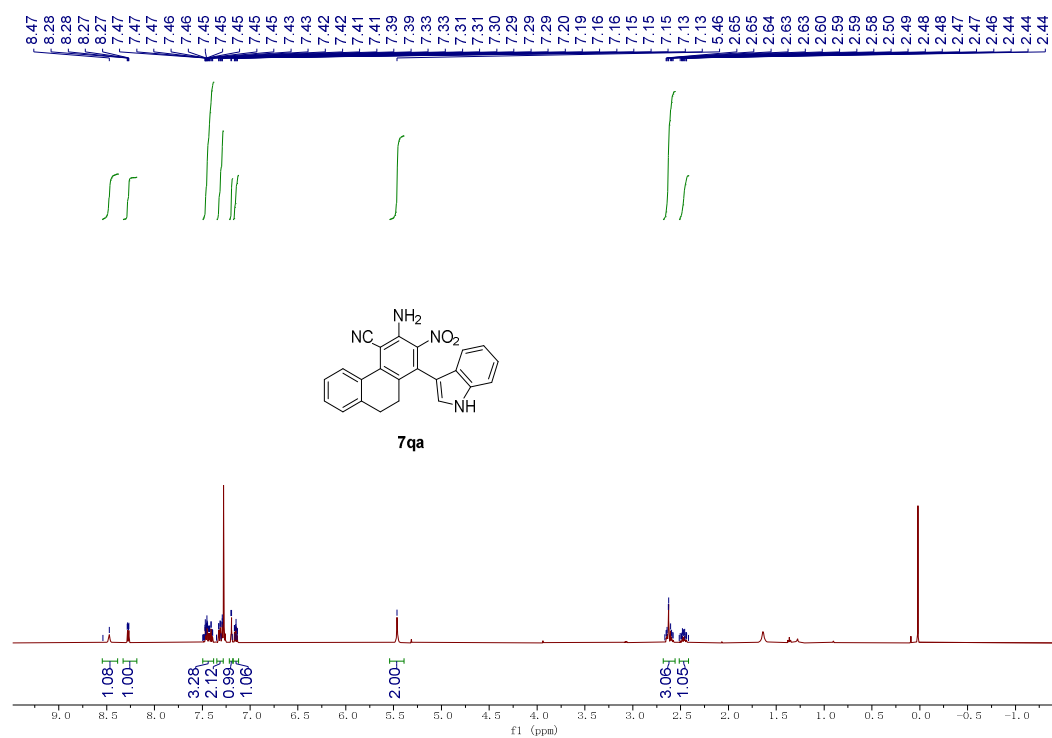


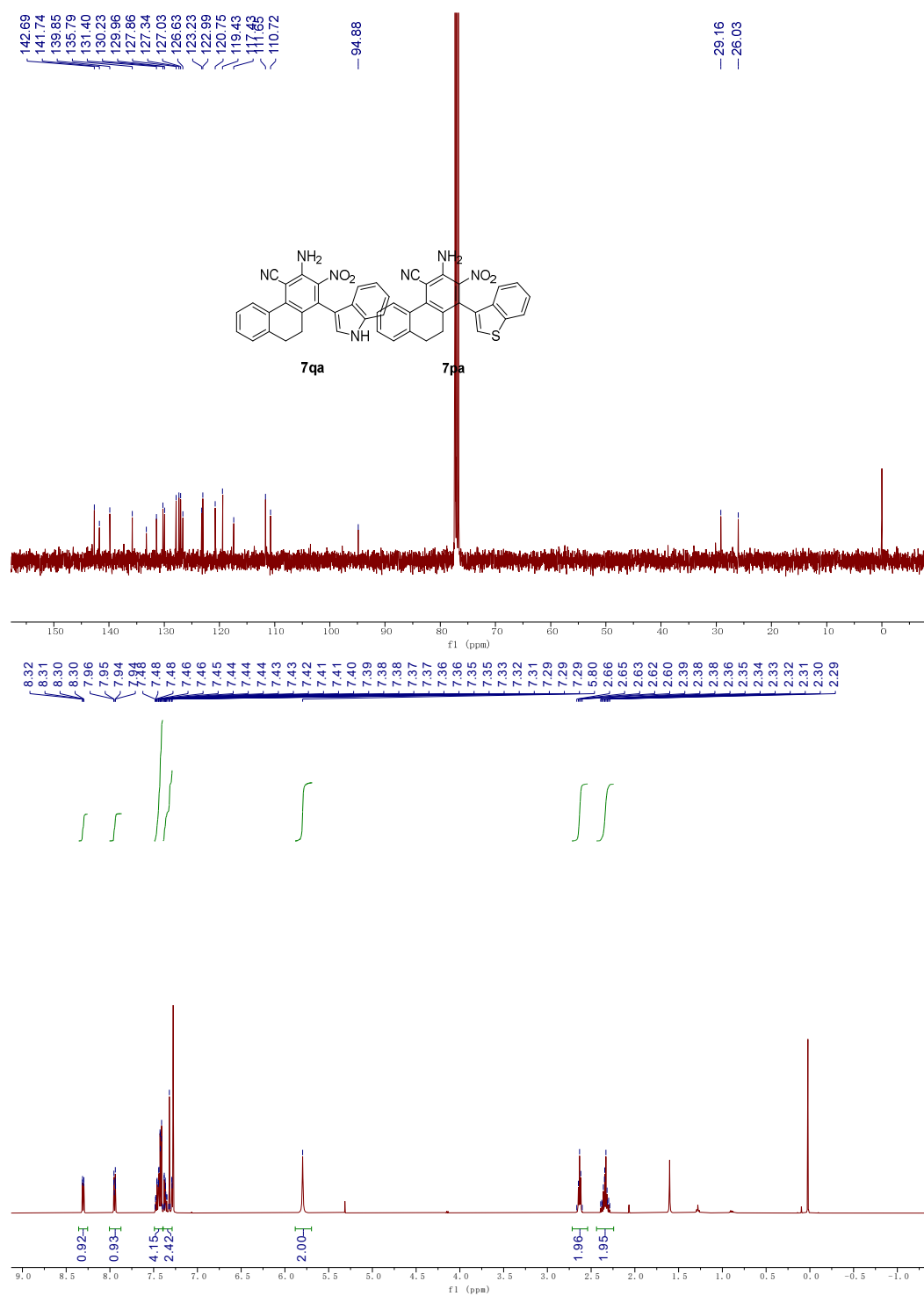


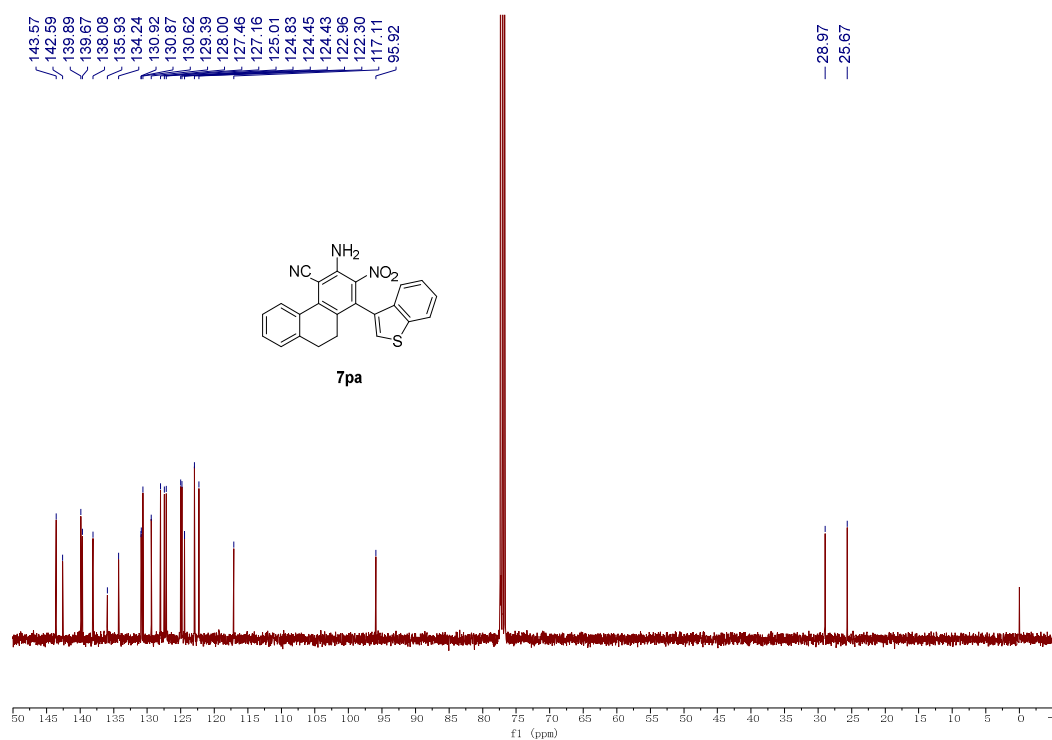


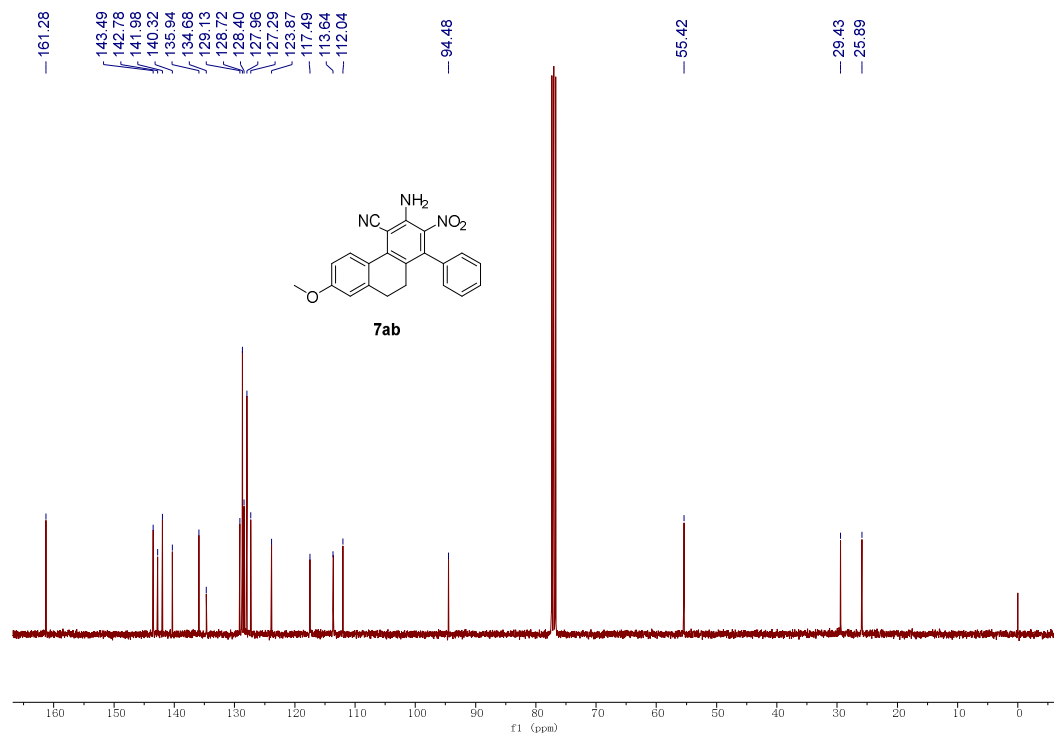
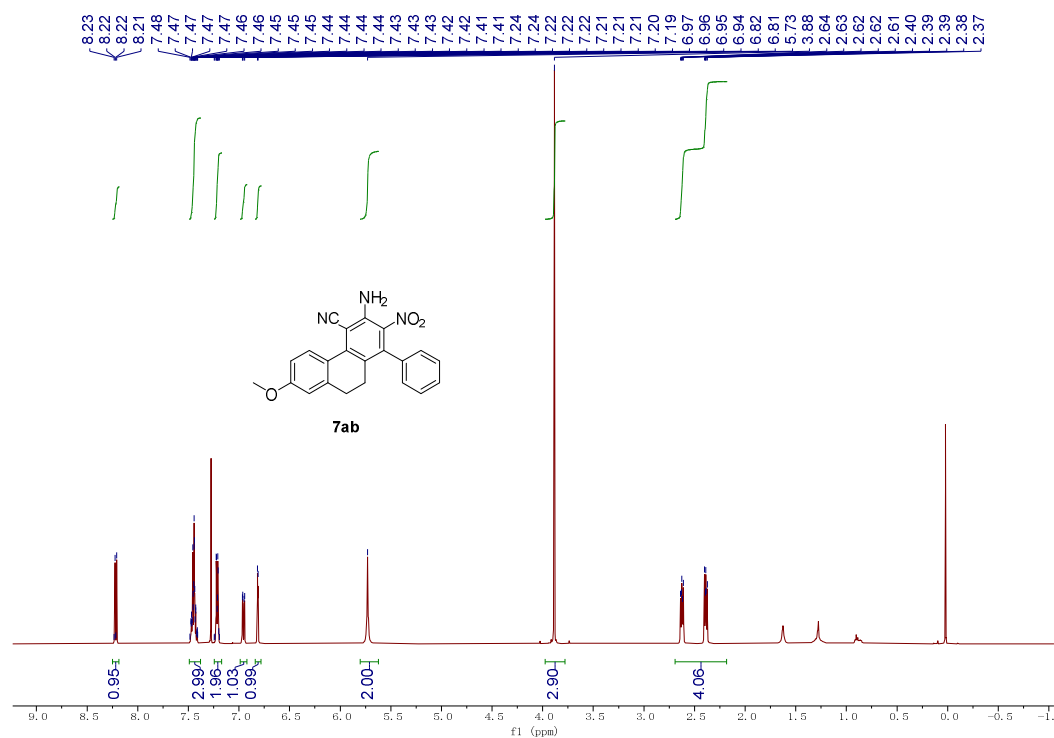


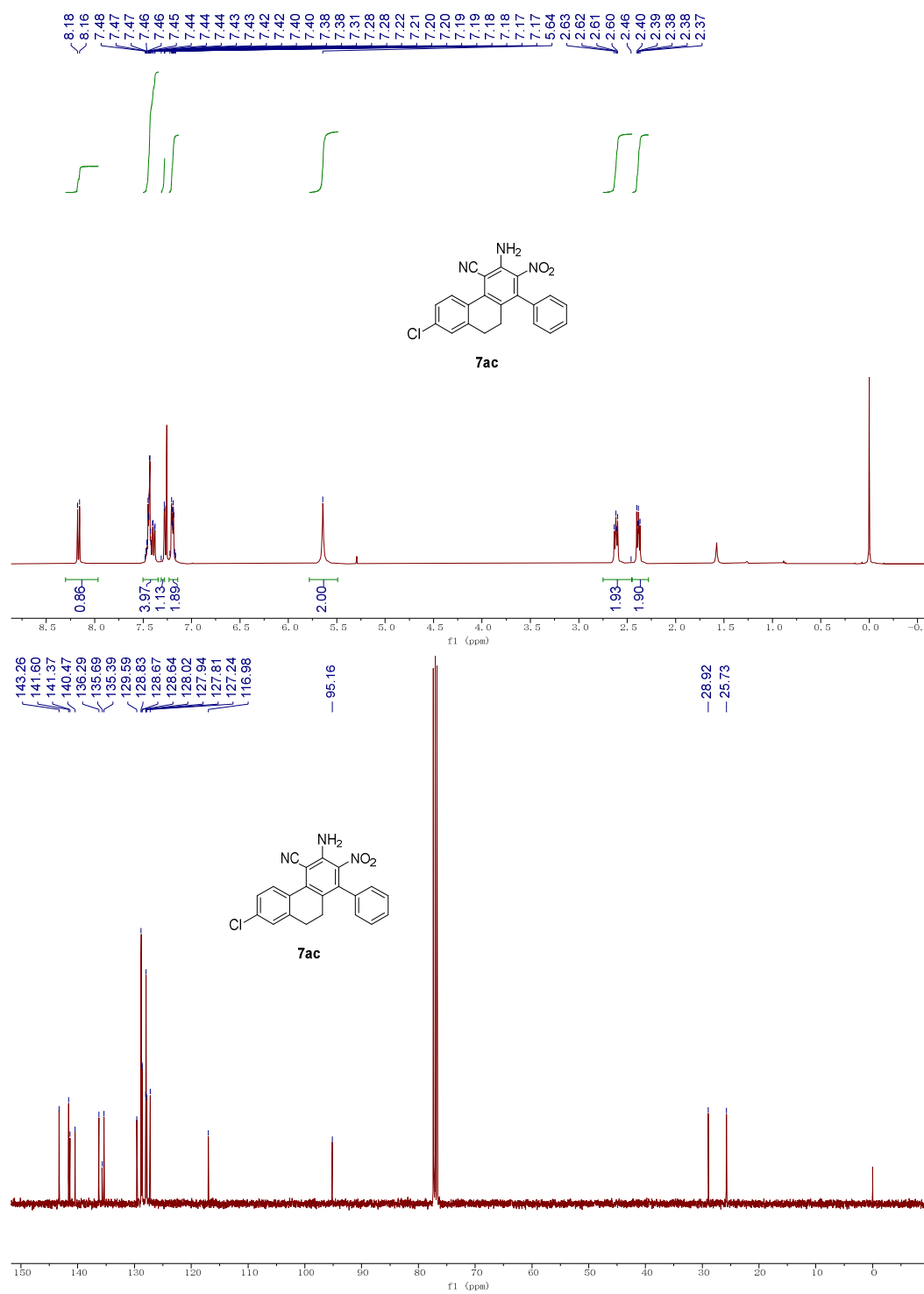


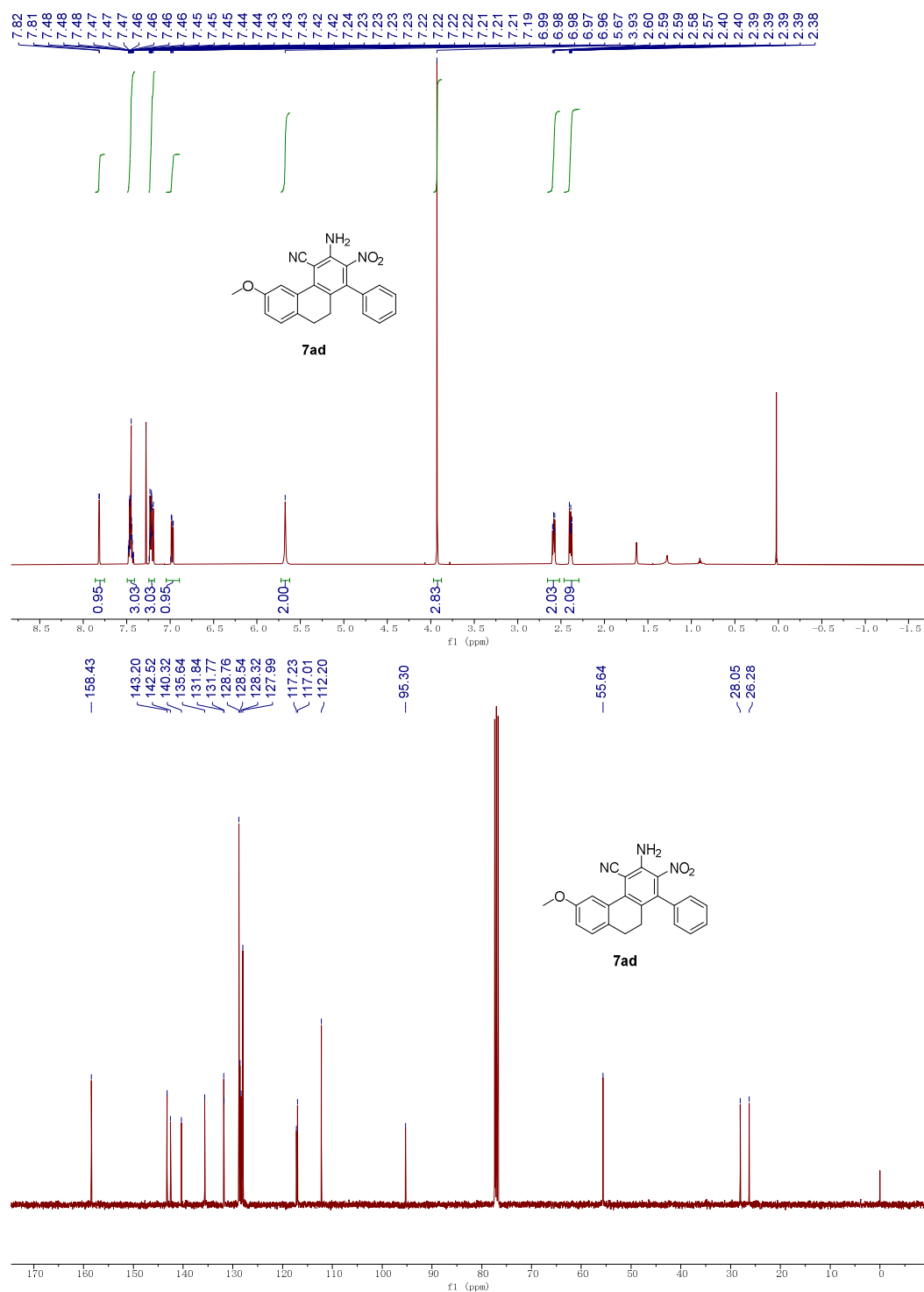


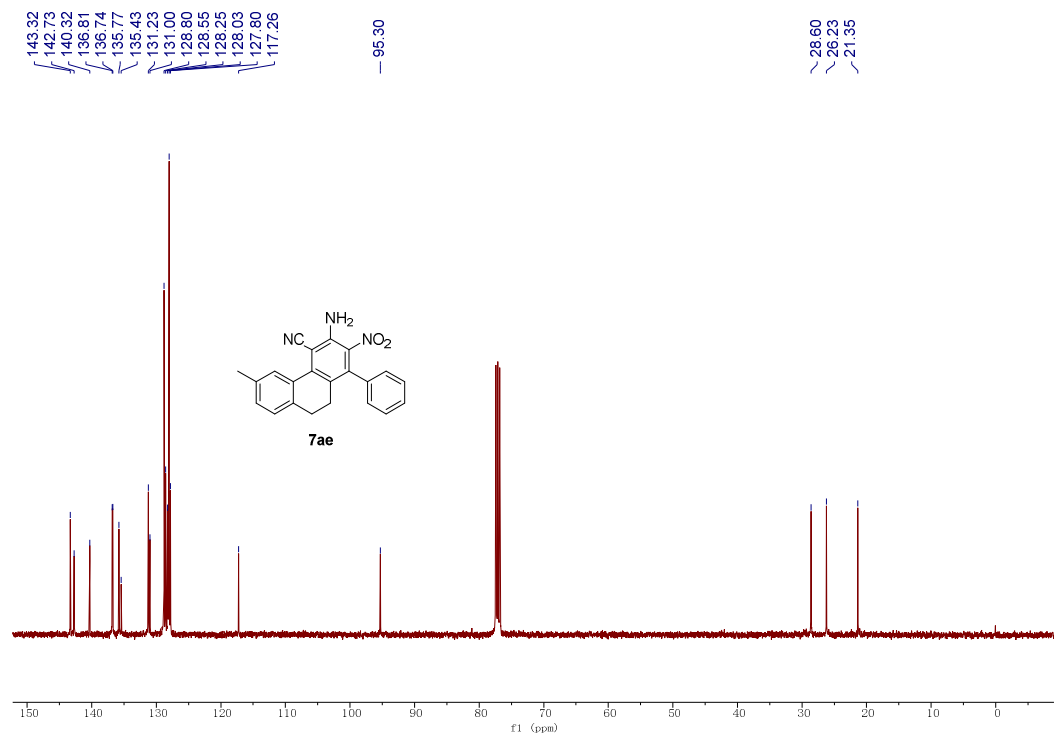
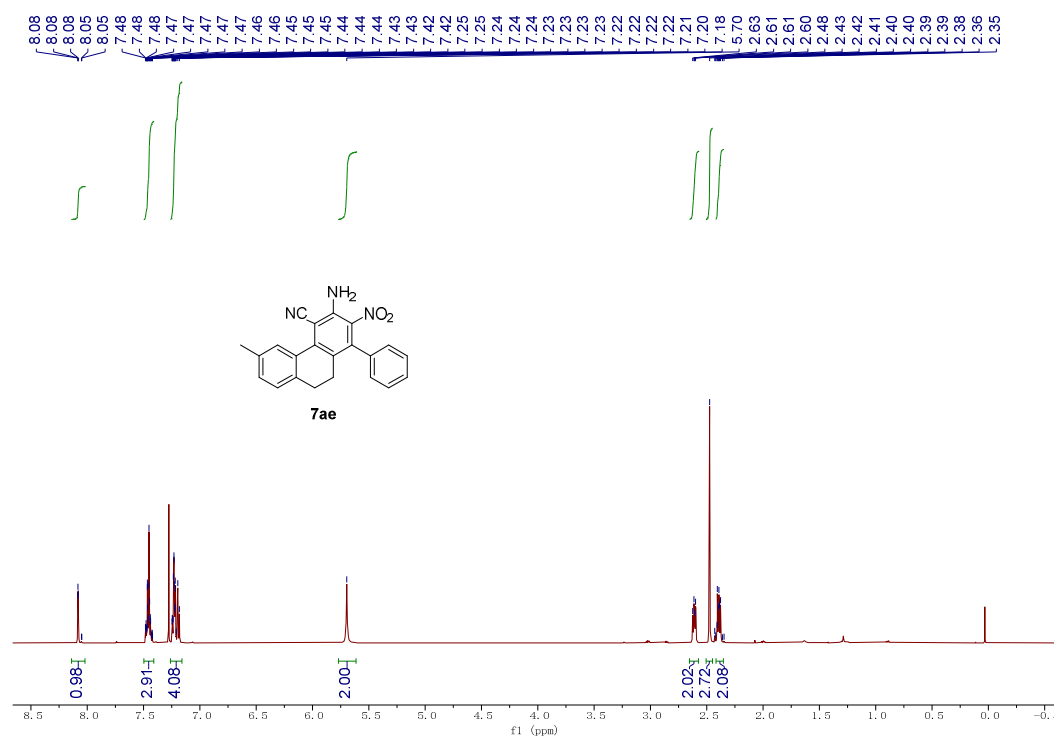


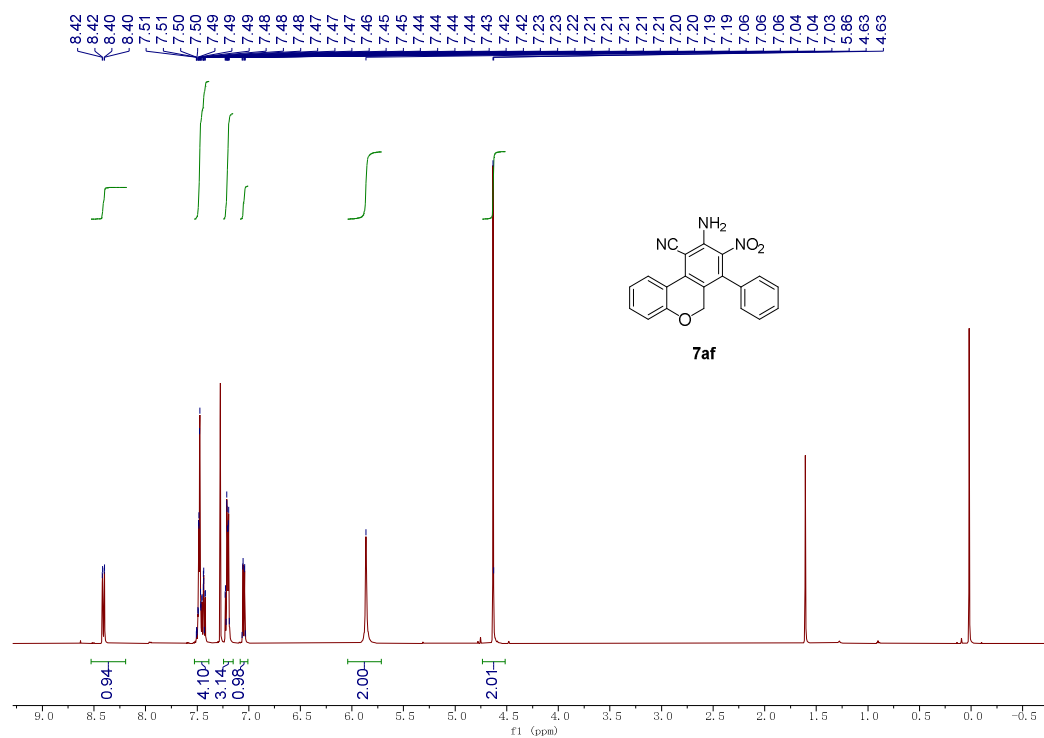


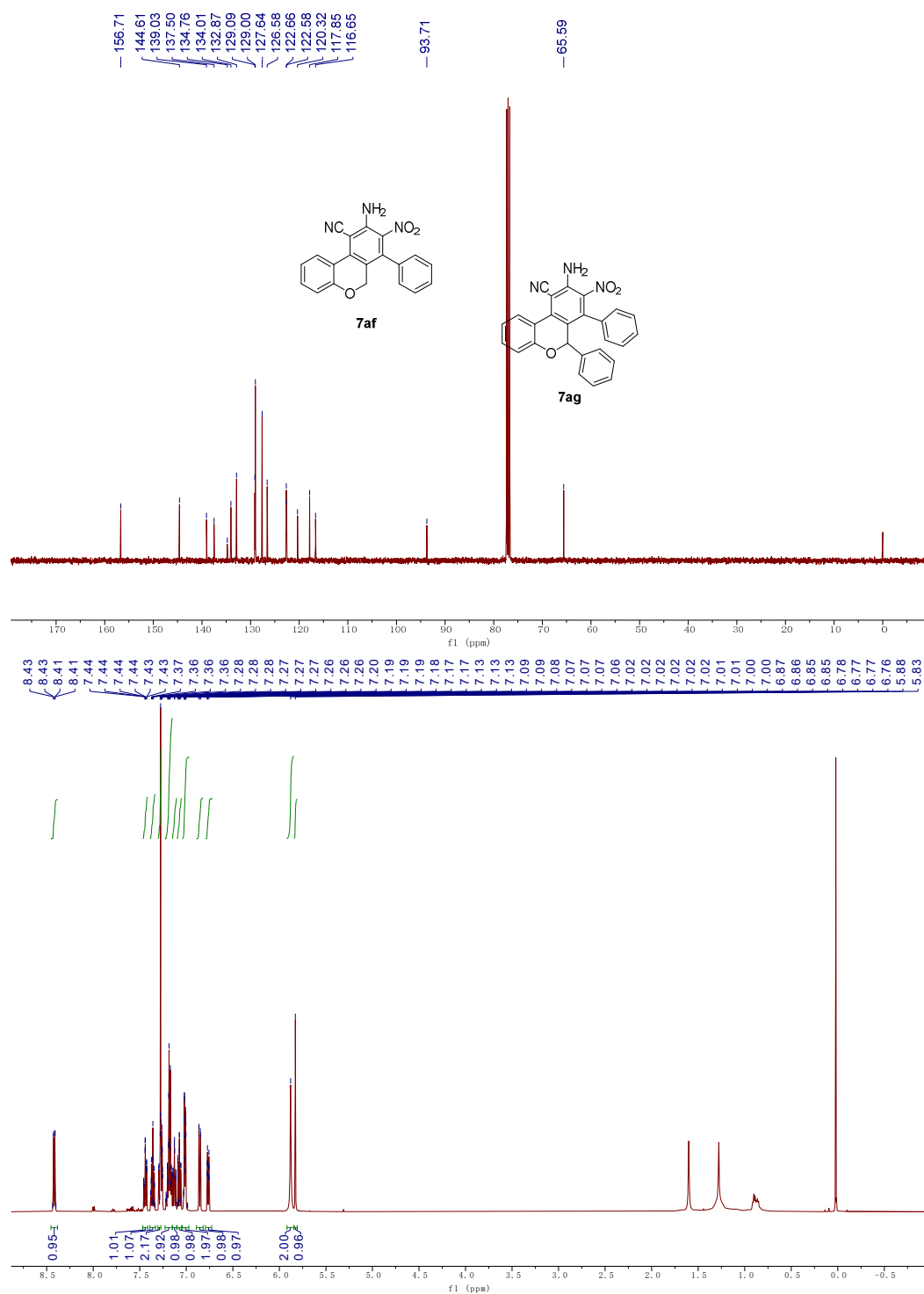


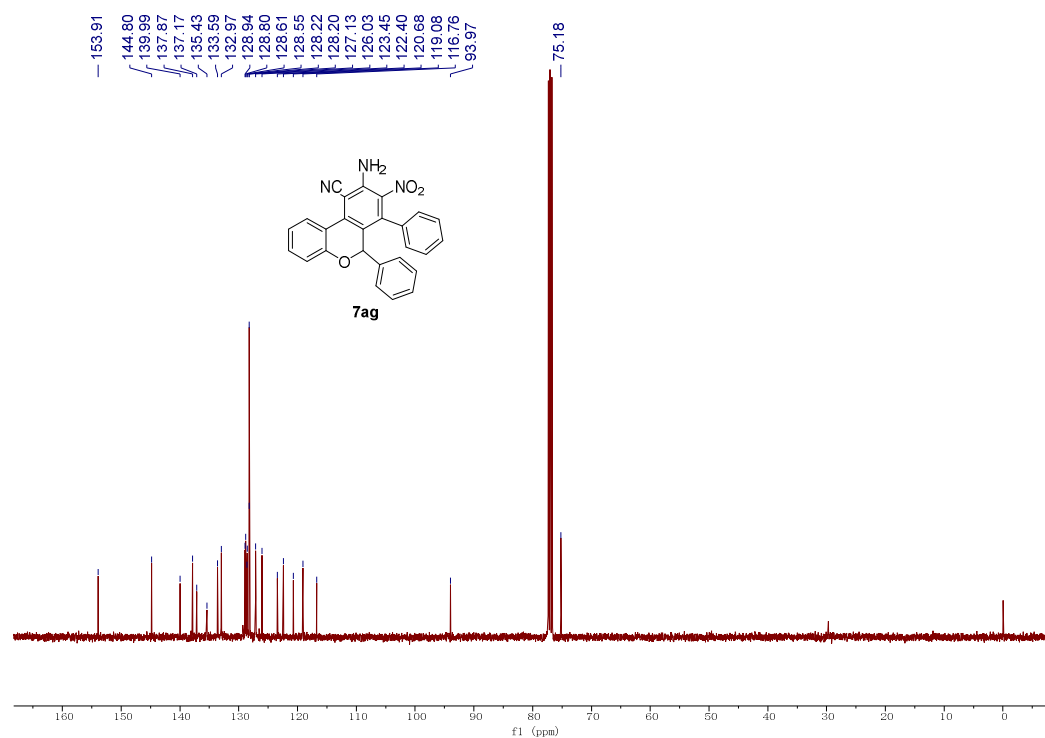


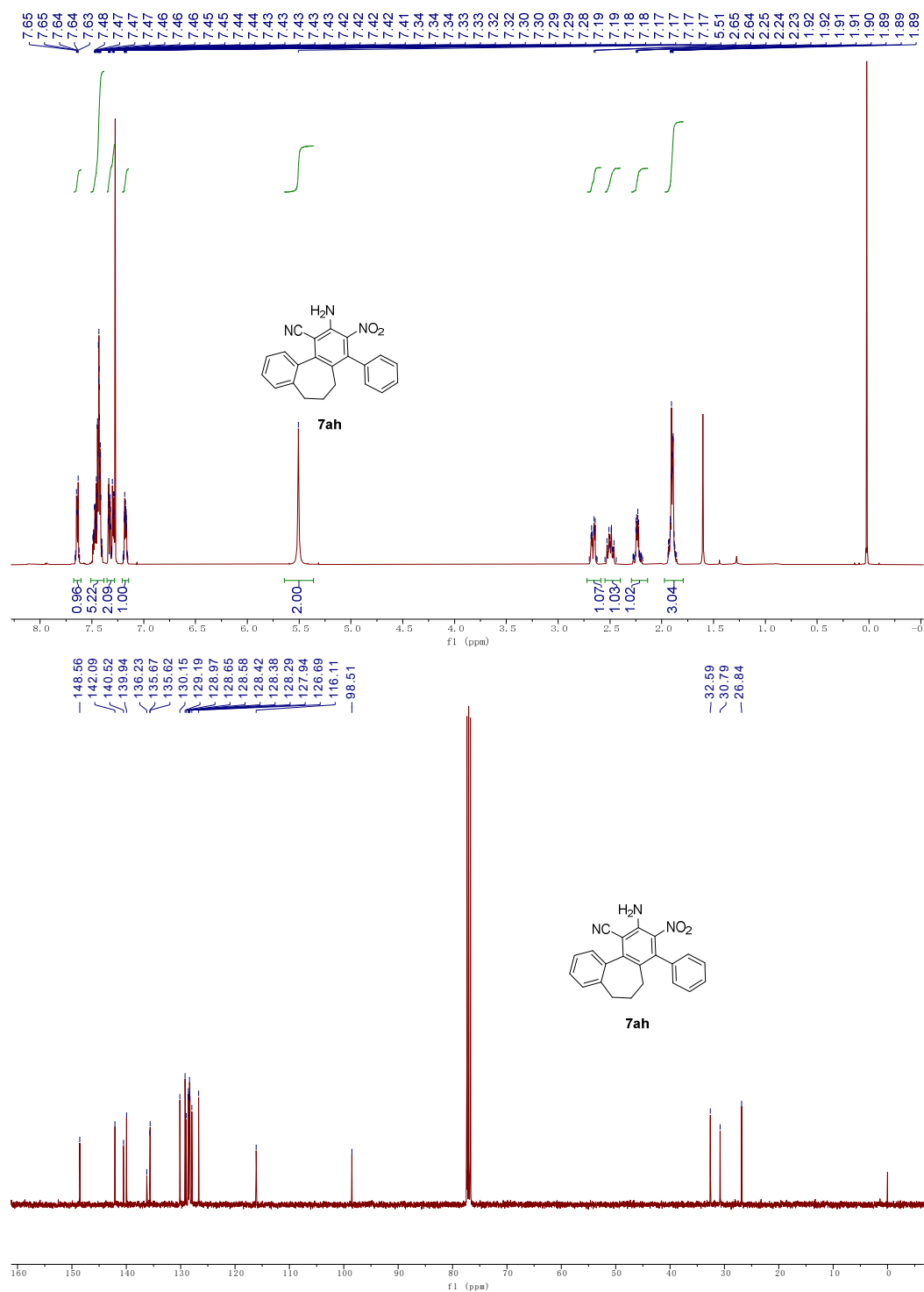


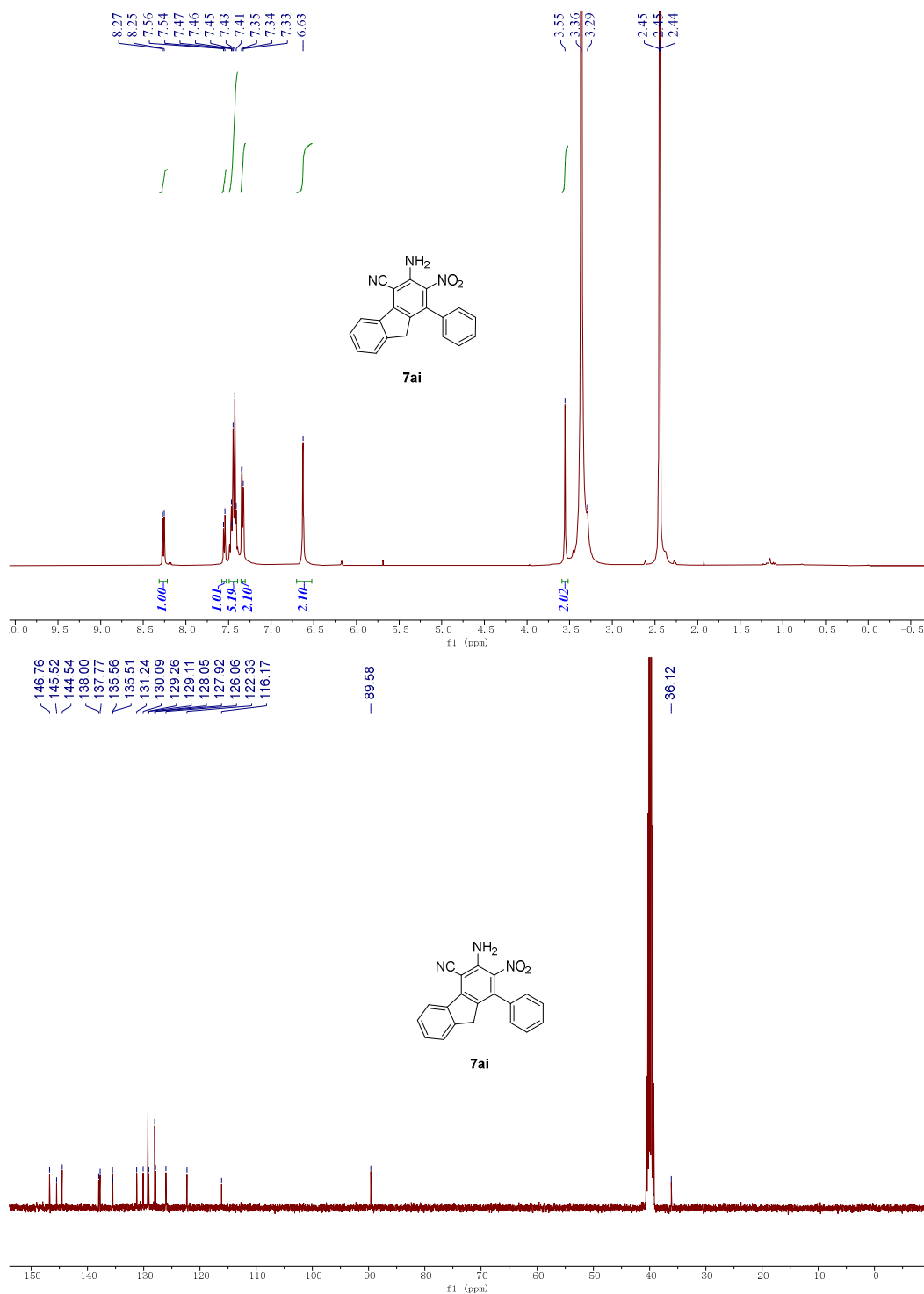












4. Reference

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