Supporting Information

Decarbonylative/decarboxylative [4 + 2] annulation of phthalic anhydrides and cyclic iodoniums towards triphenylenes

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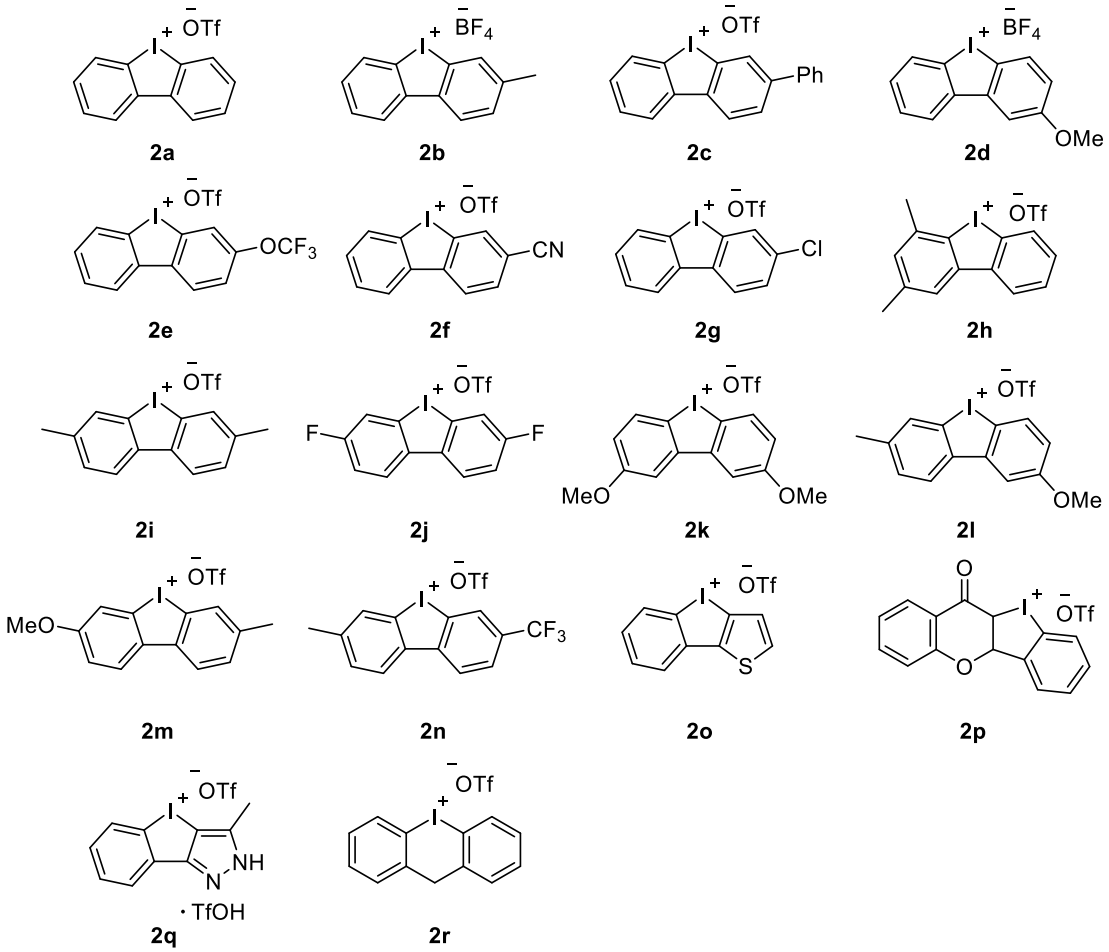
I. General remarks

NMR spectra were obtained on a BRUKER Ascend500 and Ascend400. The ^{1}H NMR (500 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm). The ^{13}C NMR (125 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 the internal standard ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm). High-resolution mass spectra (HR-MS) were obtained with a BRUKER solanX 70 FT-MS (ESI^+). Melting points were determined with SGW® X-4 and are uncorrected. The gas chromatography (GC) was detected with SHIMADZU GC-2014.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Phthalic anhydride and palladium were purchased from Beijing InnoChem Science & Technology (China) Co., Ltd. TfOH and *m*-CPBA (purity of 75%) were purchased from Adamas-Beta Co., Ltd.

II. General procedure for the synthesis of the cyclic diaryliodonium salts



2a **2b** **2c** **2d**

2e **2f** **2g** **2h**

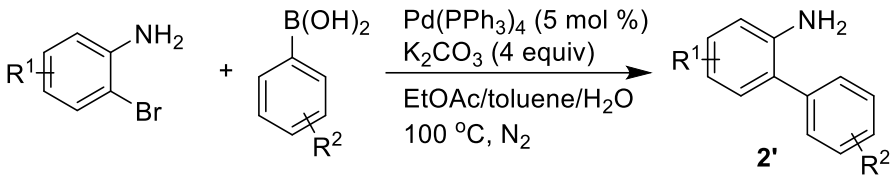
2i **2j** **2k** **2l**

2m **2n** **2o** **2p**

2q **2r**

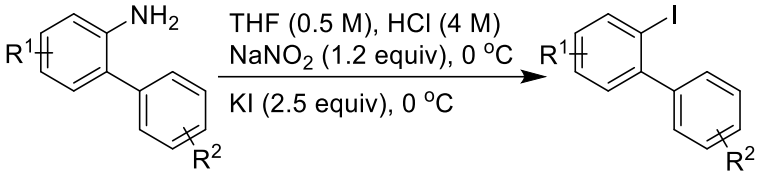
Compounds **2a-e, 2g, 2i-k** and **2o**;[1] **2f** and **2m**;[2] **2h**;[3] **2p**;[4a] **2q**[4b] and **2r**[4c] were prepared according to modified literature procedures. Compounds **2l** and **2n** are prepared as follows:

General procedure for the preparation of 2-aminobiaryl derivatives (2')



2-Bromonaniline derivatives (5 mmol, 1 equiv), arylboronic acids (7.5 mmol, 1.5 equiv), K_2CO_3 (2.76 g, 20 mmol, 4 equiv), $Pd(PPh_3)_4$ (289 mg, 5 mol %), EtOH (10 mL), toluene (20 mL) and H_2O (8 mL) were added to a round-bottom flask. The mixture was stirred at 100 ℃ for 16 h under nitrogen atmosphere. After being cooled down to room temperature, the mixture was extracted with EtOAc (3 × 30 mL). The combined organic phase was dried by Na_2SO_4, and filtered. After removal of volatile components from the filtrate, the resulting crude products was purified by column chromatography on a silica gel to afford the desired 2-aminobiaryl derivatives (**2'**).

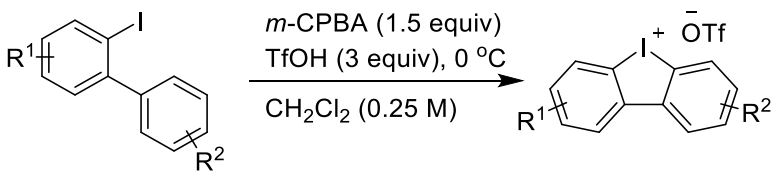
General procedure for the preparation of 2-iodobiaryl (2'') from 2-aminobiaryl



2' **2''**

To a solution of **2'** (5 mmol, 1 equiv) in THF (10 mL) was added 4 M aqueous HCl (10 mL). After cooled down to 0 ℃ in an ice water bath, an aqueous solution of $NaNO_2$ (414 mg, 6 mmol, 1.2 equiv) in water (6 mL) was added dropwise. After 20 min stirring under the same temperature, a solution of KI (2.08 g, 12.5 mmol, 2.5 equiv) in H_2O (10 mL) was added. The reaction mixture was stirred at 0 ℃ for 10 min, then removed the ice water bath. The reaction was stirred overnight at room temperature before 1 M aqueous $Na_2S_2O_3$ was added until the color of the mixture didn't change. The phases were separated, and the aqueous phase was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with H_2O (3 × 10 mL), dried over anhydrous Na_2SO_4, concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel to afford the desired 2-iodobiaryl derivatives (**2''**).

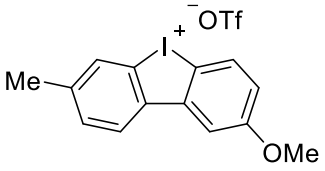
General procedure of the preparation of cyclic diaryliodonium salts (2)



2'' **2**

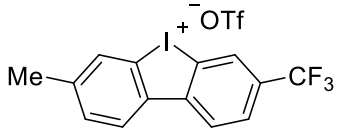
To a stirred solution of **2''** (5 mmol, 1 equiv) in CH_2Cl_2 (20 mL) was added *m*-CPBA (1.73g, 75%, 7.5 mmol, 1.5 equiv), and TfOH (3 equiv) at ice-bath. The solution was stirred for 3 h at room temperature before CH_2Cl_2 was removed by rotary evaporation. To the residue was added Et_2O (20 mL), and the resulting mixture was stirred for 20 min. The solid precipitate was collected by vacuum filtration, washed with Et_2O for three times, and dried under vacuum to afford cyclic diaryliodonium salt derivatives (**2**).

2-methoxy-7-methyldibenzo[*b,d*]iodol-5-ium triflate (2l)



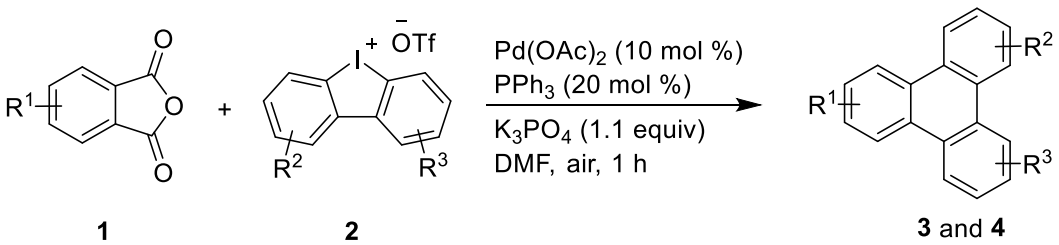
A gray solid (800 mg, 34% yield). M.p.: > 240 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 8.12–8.38 (m, 1H), 8.01–7.95 (m, 3H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.28–7.25 (m, 1H), 3.93 (s, 3H), 2.49 (s, 3H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 161.63, 143.28, 141.62, 138.95, 131.60, 131.20, 130.28, 126.96, 121.83, 118.02, 111.24, 110.21, 56.12, 21.22 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{14}H_{12}IO^+$ ([M−OTf$^-$]$^+$) 322.9928, found 322.9925.

3-methyl-7-(trifluoromethyl)dibenzo[*b,d*]iodol-5-ium triflate (2n)



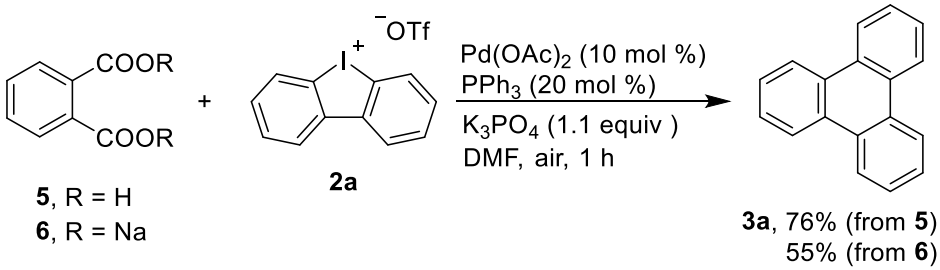
A white solid (1100 mg, 43% yield). M.p.: > 240 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 8.62 (d, *J* = 8.0 Hz, 1H), 8.50–8.48 (m, 2H), 8.20 (d, *J* = 7.5 Hz, 2H), 8.01 (s, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 2.52 (s, 3H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 146.11, 143.47, 138.17, 132.37, 130.80, 130.07 (d, $J_{C\text{-}F}$ = 32.6 Hz), 128.11, 127.95 (d, $J_{C\text{-}F}$ = 4.0 Hz), 127.72, 122.84 (q, $J_{C\text{-}F}$ = 168.6 Hz), 122.73, 122.42, 119.86, 21.79.ppm. **HRMS (ESI) *m/z*:** calcd for $C_{14}H_9F_3I^+$ ([M−OTf$^-$]$^+$) 360.9696, found 360.9697.

III. General procedure for the synthesis of triphenylenes

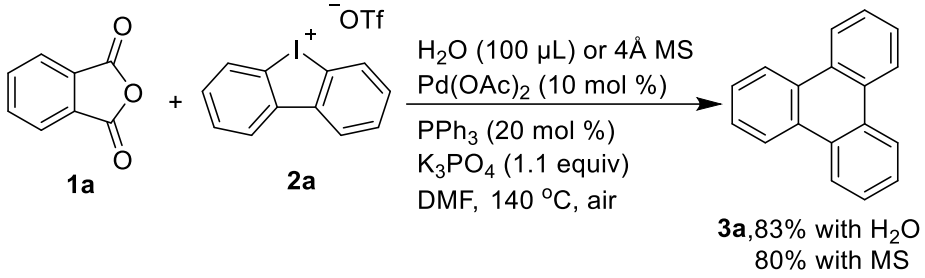


To a dry Schlenk tube containing a magnetic stir bar was added **1** (0.2 mmol), cyclic diaryliodonium salt **2** (0.2 mmol, 1 equiv), K_3PO_4 (46.7 mg, 0.22 mmol, 1.1 equiv), $Pd(OAc)_2$ (4.5 mg, 10 mol %), PPh_3 (10.5 mg, 20 mol %) and DMF (1 mL). The mixture was stirred at 140 ℃ for 1 h under air. After being cooled down to room temperature, the mixture was purified by a silica gel column (200-300 mesh), eluting with petroleum ether/EtOAc (100/1→5/1, v/v) to afford products **3** and **4**.

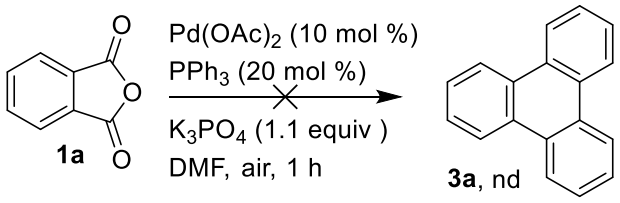
IV. Mechanistic studies



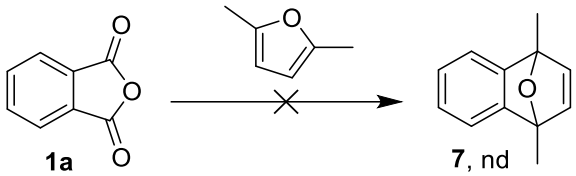
To a dry Schlenk tube with a magnetic stir bar was added **8** or **9** (0.2 mmol, 1 equiv), **2a** (0.2 mmol, 1 equiv), K_3PO_4 (46.7 mg, 0.22 mmol, 1.1 equiv), $Pd(OAc)_2$ (4.5 mg, 10 mol %), PPh_3 (10.5 mg, 20 mol %) and DMF (1.0 mL). The mixture was stirred at 140 ℃ for 1 h under air before it cooled down to room temperature. The mixture was purified by a silica gel column (200-300 mesh), eluting with petroleum ether to afford **3a** (35 mg, 76 % yield from **8**; 25 mg, 55 % yield from **9**).



The mixture of **1a**, **2a** (0.2 mmol), K_3PO_4 (46.7 mg, 0.22 mmol, 1.1 equiv), $Pd(OAc)_2$ (4.5 mg, 10 mol %), PPh_3 (10.5 mg, 20 mol %), DMF(1.0 mL) and H_2O (100 μL) or 4 ÅMS (50 mg). The mixture was stirred at 140 ℃ for 1 h under air. After being cooled down to room temperature, and the mixture was purified by a silica gel column (200-300 mesh), eluting with petroleum ether to afford **3a** (38 mg, 83% with H_2O; 37 mg, 80% with 4 ÅMS).

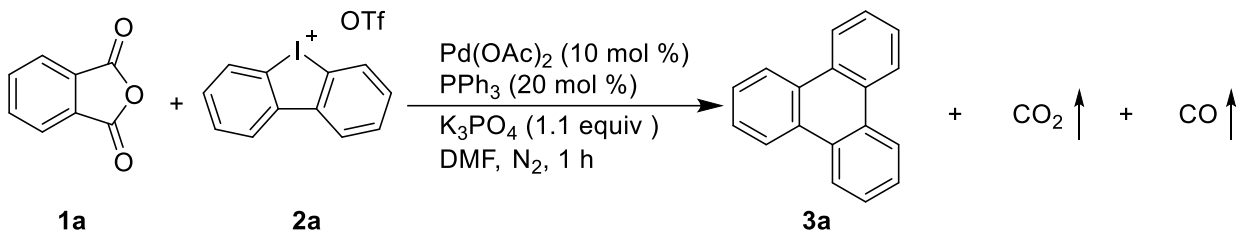


The mixture of **1a** (30 mg, 0.2 mmol), K_3PO_4 (46.7 mg, 0.22 mmol, 1.1 equiv), $Pd(OAc)_2$ (4.5 mg, 10 mol %), PPh_3 (10.5 mg, 20 mol %) and DMF (1.0 mL) were reacted at 140 ℃ for 1 h, triphenylene **3a** was not detected by thin-layer chromatography (TLC).



The DMF (1.0 mL) solution of **1a** (30 mg, 0.2 mmol), 2,5-dimethylfuran (21 μL, 0.2 mmol), K_3PO_4 (46.7 mg, 0.22 mmol, 1.1 equiv), $Pd(OAc)_2$ (4.5 mg, 10 mol %) and PPh_3 (10.5 mg, 20 mol %) was stirred at 140 ℃ for 1 h under air, Diels-Alder addition product **7** was not detected.

GC detection:



Two groups of parallel tests were conducted. Each dry Schlenk tube (25 mL) containing a magnetic stir bar was added **1a** (0.2 mmol), cyclic iodonium salt **2a** (0.2 mmol, 1 equiv), K_3PO_4 (46.7 mg, 0.22 mmol, 1.1 equiv), $Pd(OAc)_2$ (4.5 mg, 10 mol %), PPh_3 (10.5 mg, 20 mol %), and DMF (1 mL). The tubes were filled with nitrogen. Before the reaction, 10 mL gas of one group was extracted and injected into a gas sampling bag filling with nitrogen for GC detection (*Figure S1*, a). The other group was stirred at 140 ℃ for 1 h before extracting 10 mL gas sample for GC analysis (*Figure S1*, b). Before the reaction, both CO_2 and CO were not detected (*Figure S1*, a). After the reaction, CO_2 was detected with retention time at 6.443 min, while CO was not detected (*Figure S1*, b).

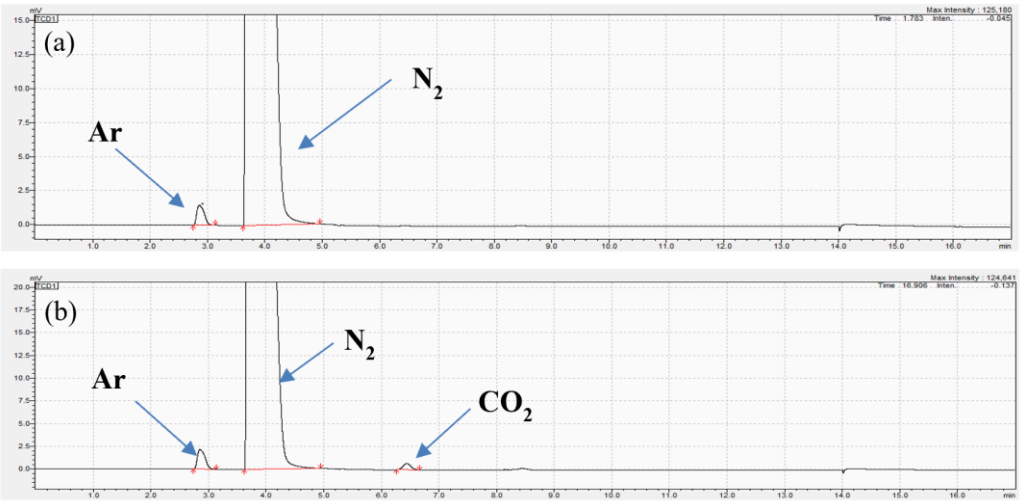


Figure S1. GC spectra of **1a** + **2a** (a) before and (b) after the reaction

5 **2a** **3a**

Two groups of parallel tests were conducted. Each dry Schlenk tube containing a magnetic stir bar was added phthalic acid **5** (0.2 mmol), cyclic diaryliodonium salt **2a** (0.2 mmol, 1 equiv), K_3PO_4 (46.7 mg, 0.22 mmol, 1.1 equiv), $Pd(OAc)_2$ (4.5 mg, 10 mol %), PPh_3 (10.5 mg, 20 mol %), and DMF (1 mL). The tubes were filled with nitrogen. Before the reaction, 10 mL gas of one group was extracted and injected into a gas sampling bag filling with nitrogen for GC detection (*Figure S2*, a). The other group was stirred at 140 ℃ for 1 h before extracting 10 mL gas sample for GC analysis (*Figure S2*, b). Before the reaction, both CO_2 and CO were not detected (*Figure S2*, a). After the reaction, CO_2 was detected with retention time at 6.448 min (*Figure S2*, b).

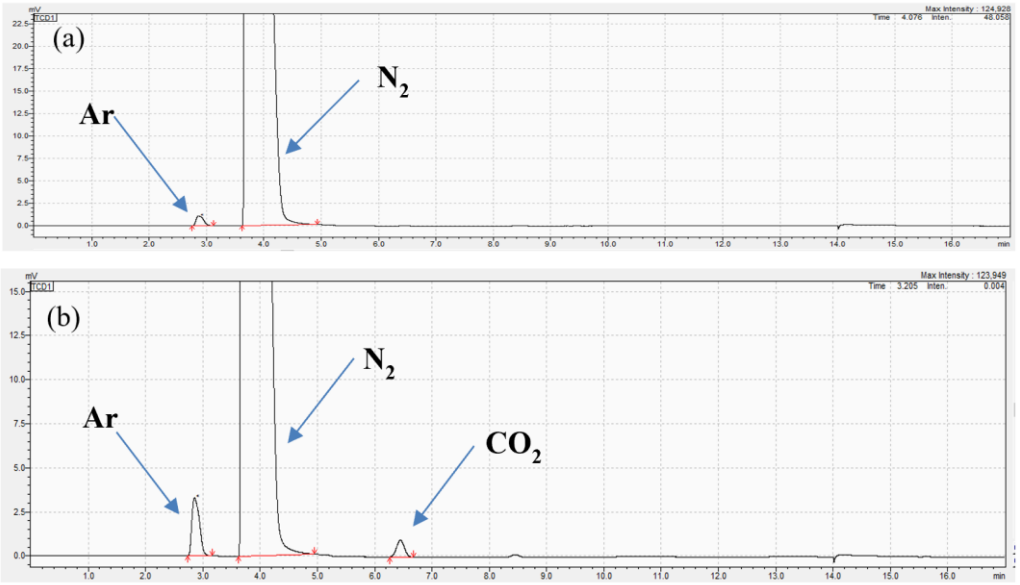
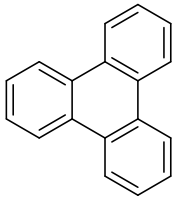


Figure S2. GC spectra of **5** + **2a** (a) before and (b) after the reaction

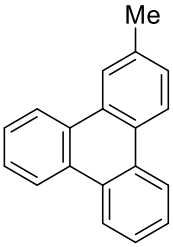
V. Experimental data for the described substances

triphenylene (3a)[2]



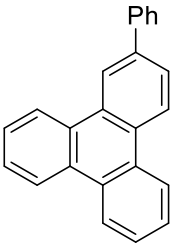
A white solid (41 mg, 90% yield), purification via a silica (200-300 mesh) gel column (petroleum ether, v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.68–8.66 (m, 6H), 7.68–7.66 (m, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 129.95, 127.37, 123.45 ppm.

2-methyltriphenyd lene (3b and 4e)[2]



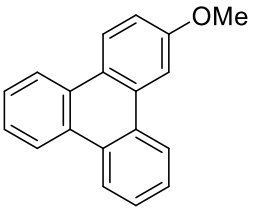
A white solid (**3b:** 44 mg, 92% yield; **4e:**47 mg, 99% yield), purification via a silica (200-300 mesh) gel column (petroleum ether, v). **^{1}H NMR (500 MHz, CDCl$_3$):** δ = 8.67–8.61 (m, 4H), 8.55 (d, *J* = 8.5 Hz, 1H), 8.45 (s, 1H), 7.67–7.62 (m, 4H), 7.49 (dd, *J* = 8.3 Hz, 1.3 Hz, 1H), 2.62 (s, 3H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** δ = 137.02, 130.04, 129.90, 129.84, 129.54, 128.83, 127.62, 127.30, 127.23, 126.92, 123.46, 123.43, 123.39, 123.22, 21.99 ppm.

2-phenyltriphenylene (3c)[2]



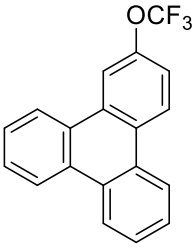
A white solid (28 mg, 46% yield), purification via a silica (200-300 mesh) gel column (petroleum ether, v). **^{1}H NMR (500 MHz, CDCl$_3$):** δ = 8.86 (s, 1H), 8.75–8.67 (m, 5H), 7.91–7.90 (m, 1H), 7.82 (d, *J* = 7.5 Hz, 2H), 7.80 (s, 4H), 7.55 (t, *J* = 7.3 Hz, 2H), 7.46–7.43 (m, 1H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** δ = 141.44, 140.16, 130.34, 130.30, 130.07, 130.05, 129.88, 129.20, 128.94, 127.78, 127.68, 127.61, 127.56, 127.52, 127.50, 127.18, 126.63, 124.14, 123.65, 123.60, 123.59, 122.05 ppm.

2-methoxytriphenylene (3d and 4f)[2]



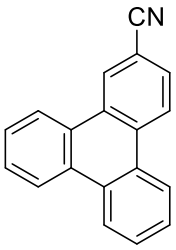
A white solid (**3d:** 50 mg, 96% yield; **4f:** 49 mg, 95% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 80/1, v/v). **^{1}H NMR (500 MHz, CDCl$_3$):** δ = 8.67–8.63 (m, 2H), 8.59–8.55 (m, 3H), 8.06 (d, *J* = 2.5 Hz, 1H), 7.68–7.59 (m, 4H), 7.29 (dd, *J* = 9.0 Hz, 2.5 Hz, 1H), 4.04 (s, 3H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** δ = 159.08, 131.42, 130.37, 130.08, 129.64, 128.91, 127.47, 127.41, 127.20, 126.41, 125.11, 123.96, 123.54, 123.47, 123.43, 122.93, 116.00, 105.95, 55.63 ppm.

2-(trifluoromethoxy)triphenylene (3e)[5]



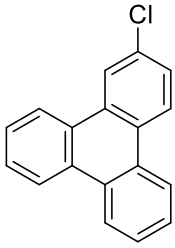
A white solid (26 mg, 41% yield), purification via a silica (200-300 mesh) gel column (petroleum ether, v). **^{1}H NMR (500 MHz, CDCl$_3$):** δ = 8.69–8.66 (m, 3H), 8.61–8.60 (m, 1H), 8.57–8.55 (m, 1H), 8.45 (s, 1H), 7.73–7.67 (m, 4H), 7.52 (d, *J* = 9.0 Hz, 1H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** δ = 148.60, 131.45, 130.37, 129.90, 129.13, 129.00, 128.53, 128.20, 127.77, 127.69, 127.63, 125.43, 123.59, 123.52, 121.87, 120.21, 119.82, 115.35 ppm. **^{19}F NMR (376 MHz, CDCl$_3$)**: δ = -57.50 (s) ppm.

triphenylene-2-carbonitrile (3f)[6]



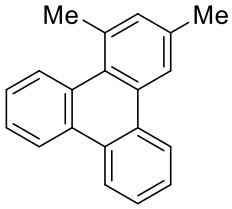
A white solid (49 mg, 96% yield) , purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 80/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.96 (d, *J*=1.0 Hz, 1H), 8.72 (d, *J* = 8.5 Hz, 1H), 8.69–8.67 (m, 2H), 8.64 (d, *J* = 8.0 Hz, 1H), 8.60 (dd, *J* = 7.0 Hz, 2.5 Hz, 1H), 7.86 (dd, *J* = 9.3 Hz, 1.5 Hz, 1H), 7.78–7.70 (m, 4H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 133.06, 130.95, 130.26, 130.11, 129.09, 129.04, 128.61, 128.49, 128.45, 128.33, 128.02, 127.88, 124.44, 124.06, 123.69, 123.63, 123.41, 119.50, 110.71 ppm.

2-chlorotriphenylene (3g and 4g)[2]



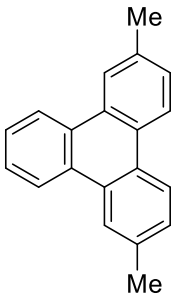
A white solid (**3g**: 31 mg, 59% yield; **4f:** 32 mg, 61% yield), purification via a silica (200-300 mesh) gel column (petroleum ether, v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.65–8.63 (m, 2H), 8.59–8.55 (m, 4H), 7.70–7.65 (m, 4H), 7.60–7.58 (m, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 139.03, 133.51, 131.35, 130.28, 130.04, 129.81, 129.51, 129.25, 128.81, 128.34, 128.18, 128.00, 127.64, 127.58, 125.06, 123.51, 123.36, 123.21 ppm.

1,3-dimethyltriphenylene (3h)[7]



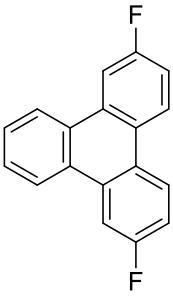
A white solid (30 mg, 59% yield), purification via a silica (200-300 mesh) gel column (petroleum ether, v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.64–8.58 (m, 4H), 8.34 (s, 1H), 7.62–7.55 (m, 4H), 7.35 (s, 1H), 3.03 (s, 3H), 3.57 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 135.93, 135.37, 133.30, 131.51, 130.98, 130.81, 130.46, 130.21, 128.38, 128.18, 127.29, 127.14, 126.32, 125.73, 123.78, 123.35, 123.18, 121.43, 26.70, 21.65 ppm.

2,7-dimethyltriphenylene (3i)[2]



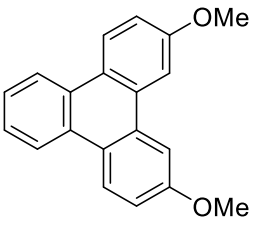
A white solid (26 mg, 51% yield), purification via a silica (200-300 mesh) gel column (petroleum ether, v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.68–8.63 (m, 2H), 8.51 (d, *J* = 8.0 Hz, 2H), 8.43 (s, 2H), 7.65–7.62 (m, 2H), 7.47 (dd, *J* = 8.3 Hz, 1.3 Hz, 2H), 2.61 (s, 6H) ppm. **^{13}C NMR(125 MHz, $CDCl_3$):** δ = 136.53, 129.96, 129.52, 128.78, 127.72, 127.10, 123.41, 123.39, 123.16, 21.97 ppm.

2,7-difluorotriphenylene (3j)[2]



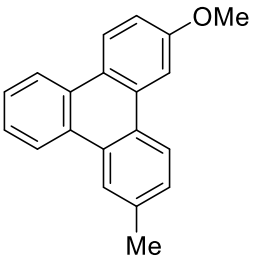
A white solid (28 mg, 53% yield), purification via a silica (200-300 mesh) gel column (petroleum ether, v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.55–8.51 (m, 4H), 8.26 (dd, J = 11.0 Hz, 2.0 Hz, 2H), 7.71–7.69 (m, 2H), 7.41–7.37 (m, 2H) ppm. **^{13}C NMR(125 MHz, $CDCl_3$):** δ = 162.199 (d, $J_{C\text{-}F}$ = 244.13 Hz), 131.42 (d, $J_{C\text{-}F}$ = 8.6 Hz), 129.63, 128.12, 126.03, 125.54 (d, $J_{C\text{-}F}$ = 9.3 Hz), 123.76, 115.87 (d, $J_{C\text{-}F}$ = 22.9 Hz), 109.03 (d, $J_{C\text{-}F}$ = 21.6 Hz) ppm. **^{19}F NMR (376 MHz, $CDCl_3$)**: δ = -114.27 (s) ppm.

2,11-dimethoxytriphenylene (3k)[8]



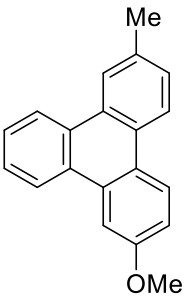
A white solid (38 mg, 66% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 60/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.57 (d, J = 9.0 Hz, 2H), 8.54–8.52 (m, 2H), 7.97 (d, J = 2.5 Hz, 2H), 7.59–7.57 (m, 2H), 7.28 (dd, J = 13.0 Hz, 4.0 Hz, 2H), 4.03 (s, 6H) ppm. **^{13}C NMR(125 MHz, $CDCl_3$):** δ = 158.92, 131.08, 129.04, 126.46, 125.18, 124.38, 122.89, 115.74, 106.34, 55.67 ppm.

6-methoxy-2-methyltriphenylene (3l)[9]



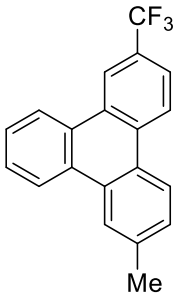
A white solid (54 mg, 99% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.63 (d, J = 8.0 Hz, 1H), 8.56–8.55 (m, 2H), 8.47–8.45 (m, 2H), 8.02 (s, 1H), 7.64–7.57 (m, 2H), 7.48 (d, J = 8.5 Hz, 1H), 7.24 (s, 1H), 4.03 (s, 3H), 2.62 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 159.04, 137.15, 131.52, 130.34, 130.19, 128.81, 128.66, 127.34, 127.26, 126.28, 125.05, 123.59, 123.55, 123.41, 123.38, 122.91, 115.54, 105.71, 55.61, 22.00 ppm.

2-methoxy-7-methyltriphenylene (3m)[2]



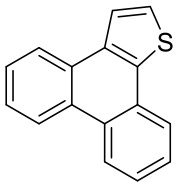
A white solid (16 mg, 30% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 100/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.66–8.65 (m, 1H), 8.58–8.57 (m, 1H), 8.54 (d, J = 9.0 Hz, 1H), 8.45–8.42 (m, 2H), 8.04 (d, J = 2.5 Hz, 1H), 7.67–7.64 (m, 2H), 7.46 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 2.5 Hz, 1H), 4.03 (s, 3H), 2.06 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 158.72, 135.96, 130.97, 130.26, 129.73, 128.87, 127.74, 127.33, 127.04, 124.84, 124.07, 123.49, 123.45, 123.41, 122.86, 115.94, 105.87, 55.62, 21.93 ppm.

2-methyl-7-(trifluoromethyl)triphenylene (3n)



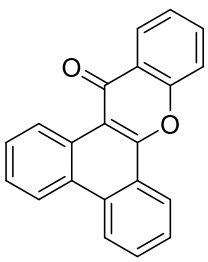
A white solid (36 mg, 58% yield), purification via a silica (200-300 mesh) gel column (petroleum ether, v). M.p.:119.2–121.2 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.88 (s, 1H), 8.70–8.64 (m, 3H), 8.54 (d, J = 8.5), 8.46 (s, 1H), 7.84 (d, J = 9.0 Hz, 1H), 7.72–7.68 (m, 2H), 7.52 (d, J = 8.0 Hz, 1H), 2.64 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 138.38, 133.86, 132.51, 130.63, 130.15, 129.41, 129.28, 129.19, 128.76, 128.50, 128.08, 127.64, 126.62, 125.83, 123.93 (d, $J_{C\text{-}F}$ = 18.3 Hz), 123.63, 123.53 (d, $J_{C\text{-}F}$ = 4.5 Hz), 123.28 (d, $J_{C\text{-}F}$ = 3.5 Hz), 120.77 (q, $J_{C\text{-}F}$ = 4.1 Hz), 22.06. ppm. **^{19}F NMR (376 MHz, $CDCl_3$)**: δ = -62.01 (s) ppm. **HRMS (ESI) *m/z*:** calcd for $C_{20}H_{14}F_3$ (M+H) 311.1048, found 311.1045.

phenanthro[9,10-*b*]thiophene (3o)[5]



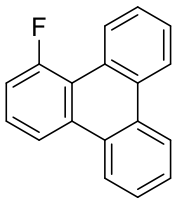
A white solid (17 mg, 36% yield). purification via a silica (200-300 mesh) gel column (petroleum ether, v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.72–8.67 (m, 2H), 8.34–8.32 (m, 1H), 8.16–8.15 (m, 1H), 7.98 (d, J = 5.5 Hz, 1H), 7.68–7.62 (m, 4H), 7.57 (d, J = 5.5 Hz, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 136.79, 135.18, 129.21, 129.00, 128.77, 128.49, 127.38, 127.26, 126.50, 126.18, 125.10, 124.46, 124.44, 123.76, 123.65, 123.36 ppm.

14*H*-dibenzo[*a*,*c*]xanthen-14-one (3p)[10]



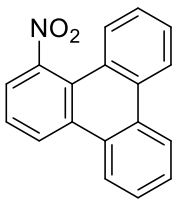
A yellow solid (28 mg, 48% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 40/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 10.20 (d, J = 8.5 Hz,1H), 8.80 (d, J = 8.0 Hz, 1H), 8.73–8.69 (m, 2H), 8.48 (d, J = 8.0 Hz), 7.87 (t, J = 7.5 Hz, 1H), 7.79–7.77 (m, 3H), 7.73–7.70 (m, 2H), 7.50 (t, J = 7.5 Hz, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 178.55, 154.59, 134.10, 133.99, 130.82, 129.15, 128.75, 127.90, 127.67, 127.51, 126.87, 124.89, 124.29, 124.14, 123.09, 122.50, 117.67, 112.87 ppm.

1-fluorotriphenylene (4b)[11]



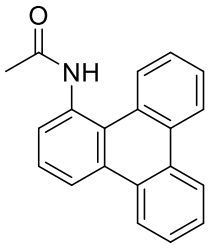
A white solid (34 mg, 69% yield). purification via a silica (200-300 mesh) gel column (petroleum ether, v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 9.13–9.10 (m, 1H), 8.70–8.60 (m, 3H), 8.49 (d, J = 8.0 Hz, 1H), 7.71–7.65 (m, 4H), 7.62–7.57 (m, 1H), 7.41–7.36 (m, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 162.84, 160.84, 132.80 (d, $J_{C\text{-}F}$ = 3.9 Hz), 130.22 (d, $J_{C\text{-}F}$ = 4.0 Hz), 129.14 (d, $J_{C\text{-}F}$ = 2.6 Hz), 128.51, 128.28, 127.86, 127.71 (d, $J_{C\text{-}F}$ = 5.4 Hz), 127.47, 127.29, 127.21, 123.87, 123.39, 123.03, 119.16 (d, $J_{C\text{-}F}$ = 3.4 Hz), 114.70, 114.49 ppm. **^{19}F NMR (471 MHz, $CDCl_3$)**: δ = -108.32 (s) ppm.

1-nitrotriphenylene (4c)[6]



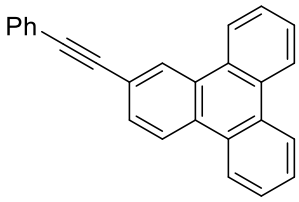
A yellow solid (36 mg, 66% yield). purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 60/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.80 (d, J = 8.0 Hz, 1H), 8.64 (d, J = 8.5 Hz, 2H), 8.59 (d, J = 7.5 Hz, 1H), 8.03 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 7.5 Hz, 1H), 7.72–7.67 (m, 4H), 7.54 (t, J = 7.5 Hz, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 132.61, 131.19, 130.53, 129.18, 128.88, 128.77, 128.31, 128.08, 127.25, 126.63, 126.55, 126.43, 125.46, 123.87, 123.72, 123.61, 123.43, 122.57 ppm.

***N*-(triphenylen-1-yl)acetamide (4d)**



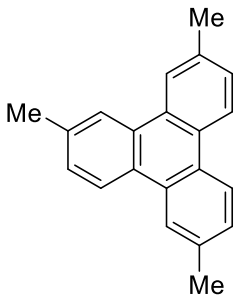
A white solid (56 mg, 98% yield). purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 5/1, v/v). M.p.: 225.6–227.6 ºC. **^{1}H NMR (500 MHz, DMSO-d_6):** δ = 10.29 (s, 1H), 9.02 (d, J = 8.0 Hz, 1H), 8.75–8.73 (m, 3H), 8.67 (d, J = 8.0 Hz, 1H), 7.70–7.58 (m, 6H), 2.16 (s, 3H) ppm. **^{13}C NMR (125 MHz, DMSO-d_6):** δ = 168.44, 135.00, 131.14, 129.88, 129.39, 129.28, 128.98, 127.78, 127.73, 127.69, 127.35, 126.96, 126.54, 126.28, 125.18, 123.91, 123.63, 123.38, 121.24 , 23.42 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{20}H_{16}NO$ (M+H) 286.1232, found 286.1235.

2-(phenylethynyl)triphenylene (4h)[12]



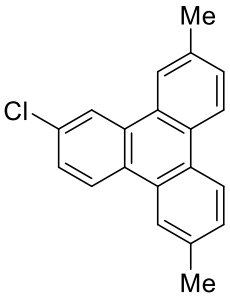
A white solid (20 mg, 30% yield). purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 40/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.84 (s, 1H), 8.67–8.60 (m, 5H), 7.80–7.78 (m, 1H), 7.69–7.63 (m, 6H), 7.42–7.38 (m, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 131.86, 130.21, 130.13, 130.08, 129.88, 129.70, 129.47, 129.27, 128.59, 128.55, 127.74, 127.53, 127.51, 126.99, 123.66, 123.59, 123.57, 123.51, 123.46, 123.42, 122.08, 90.36, 89.99 ppm.

2,6,11-trimethyltriphenylene (4i)[13]



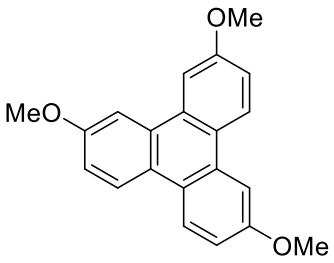
A white solid (40 mg, 74% yield). purification via a silica (200-300 mesh) gel column (petroleum ether, v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.53 (d, J = 8.5 Hz, 1H), 8.50–8.48 (m, 2H), 8.43 (s, 2H), 8.39 (s, 1H), 7.47–7.43 (m, 3H), 2.62–2.60 (m, 9H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 136.72, 136.45, 136.38, 129.94, 129.64, 129.45, 128.63, 128.57, 128.33, 127.86, 127.66, 127.36, 123.40, 123.34, 123.18, 123.16, 123.12, 21.96 ppm.

2-chloro-6,11-dimethyltriphenylene (4j)



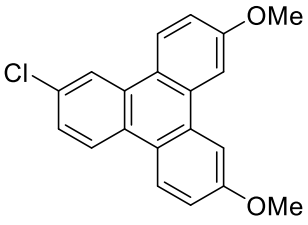
A white solid (44 mg, 76% yield). purification via a silica (200-300 mesh) gel column (petroleum ether, v). M.p.: 158.7–160.7 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.57 (s, 1H), 8.54 (d, *J* = 9.0 Hz, 1H), 8.48 (d, *J* = 8.0 Hz, 2H), 8.33 (d, *J* = 12.5 Hz, 2H), 7.57 (dd, *J* = 9.0 Hz, 2.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 2H), 2.61 (s, 3H), 2.60 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** *δ* = 136.82, 133.23, 131.41, 129.42, 129.06, 128.87, 128.43, 128.39, 128.10, 127.63, 127.28, 125.03, 123.45, 123.32, 123.24, 123.14, 21.94, 21.91 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{20}H_{16}Cl$ (M+H) 291.0941, found 291.0940.

2,6,11-trimethoxytriphenylene (4k)[14]



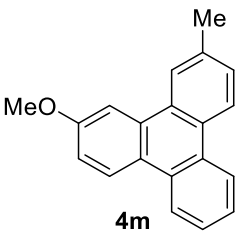
A white solid (32 mg, 50% yield). purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 60/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** *δ* = 8.50–8.43 (m, 3H), 7.96–7.93 (m, 3H), 7.28–7.25 (m, 3H), 7.20 (dd, *J* = 9.0 Hz, 2.5 Hz, 1H), 4.03–4.01 (m, 9H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** *δ* = 158.99, 158.43, 158.22, 131.53, 130.42, 129.95, 128.99, 125.22, 124.60, 124.55, 124.49, 124.09, 123.12, 115.83, 115.63, 115.07, 106.33, 105.48, 55.68, 55.67, 55.61 ppm.

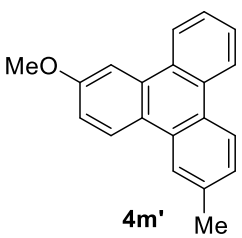
6-chloro-2,11-dimethoxytriphenylene (4l)



A white solid (30 mg, 46% yield). purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 60/1, v/v). M.p.: 150.3–153.3 ºC.**^{1}H NMR (500 MHz, $CDCl_3$):** *δ* = 8.50–8.42 (m, 4H), 7.95 (s, 1H), 7.50 (dd, *J* = 9.0 Hz, 2.0 Hz, 1H), 7.30–7.27 (m, 2H), 4.03 (d, *J* = 1.5 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** *δ* = 159.38, 159.11, 132.50, 131.52, 131.00, 130.46, 127.46, 126.63, 125.30, 125.13, 124.50, 123.69, 123.25, 122.62, 115.99, 115.90, 106.44, 106.41, 55.69 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{20}H_{16}ClO_2$ (M+H) 323.0839, found 323.0840.

2-methoxy-11-methyltriphenylene and 2-methoxy-6-methyltriphenylene (4m and 4m')

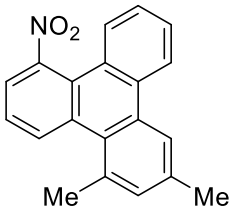




A white solid (24 mg, with a ratio of 1/1) purification via a silica (200-300 mesh) gel column (petroleum ether, v). **^{1}H NMR (500 MHz, $CDCl_3$):** *δ* = 8.62–8.50 (m, 4H), 8.35 (s, 1H), 8.05–8.04 (m, 1H), 7.66–7.57 (m, 2H), 7.48 (d, *J* = 8.5 Hz, 0.5H), 7.43 (d, *J* = 8.0 Hz, 0.5H), 7.27–7.26 (m, 0.9H, cover the solvent),4.04 (d, *J* = 6.0 Hz, 3H), 2.61 (d, *J* = 9.0 Hz, 3H) ppm. **^{13}C NMR (125 MHz,**

$CDCl_3$): δ = 158.97, 158.94, 137.04, 136.83, 131.51, 131.30, 130.46, 130.03, 129.67, 129.59, 129.24, 129.00, 128.94, 128.03, 127.88, 127.39, 126.95, 126.73, 126.60, 126.33, 125.07, 125.03, 124.06, 123.85, 123.47, 123.42, 123.40, 123.35, 123.30, 123.18, 122.93, 122.86, 115.86, 115.83, 105.88, 105.87, 55.64, 55.59, 21.99, 21.97 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{20}H_{17}O$ (M+H) 273.1279, found 273.1278.

1,3-dimethyl-9-nitrotriphenylene (4n)



A yellow solid (47 mg, 78% yield). purification via a silica (200-300 mesh) gel column (petroleum ether, v). M.p.: 120.1–122.1 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.67 (d, *J* = 8.0 Hz, 1H), 8.53 (d, *J* = 8.5 Hz, 1H), 8.27 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.76–7.75 (m, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.49–7.46 (m, 1H), 7.37 (s, 1H), 2.96 (s, 3H), 2.57 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 149.79, 137.58, 135.24, 133.94, 133.47, 132.11, 131.76, 130.85, 128.81, 126.91, 126.83, 126.27, 125.50, 124.96, 124.28, 123.32, 122.28, 121.56, 26.33, 21.68 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{20}H_{16}NO_2$ (M+H) 302.1181, found 302.1180.

VI. References

[1] Xie, R.; Lv, H.; Ye, X.; Kong, X.; Li, S. Cu-Catalyzed Tandem N-arylation of Phthalhydrazides with Cyclic Iodoniums to Yield Dihydrobenzo[*c*]cinnolines. *Org. Biomol. Chem.* **2020**, *18*, 4824–4830.

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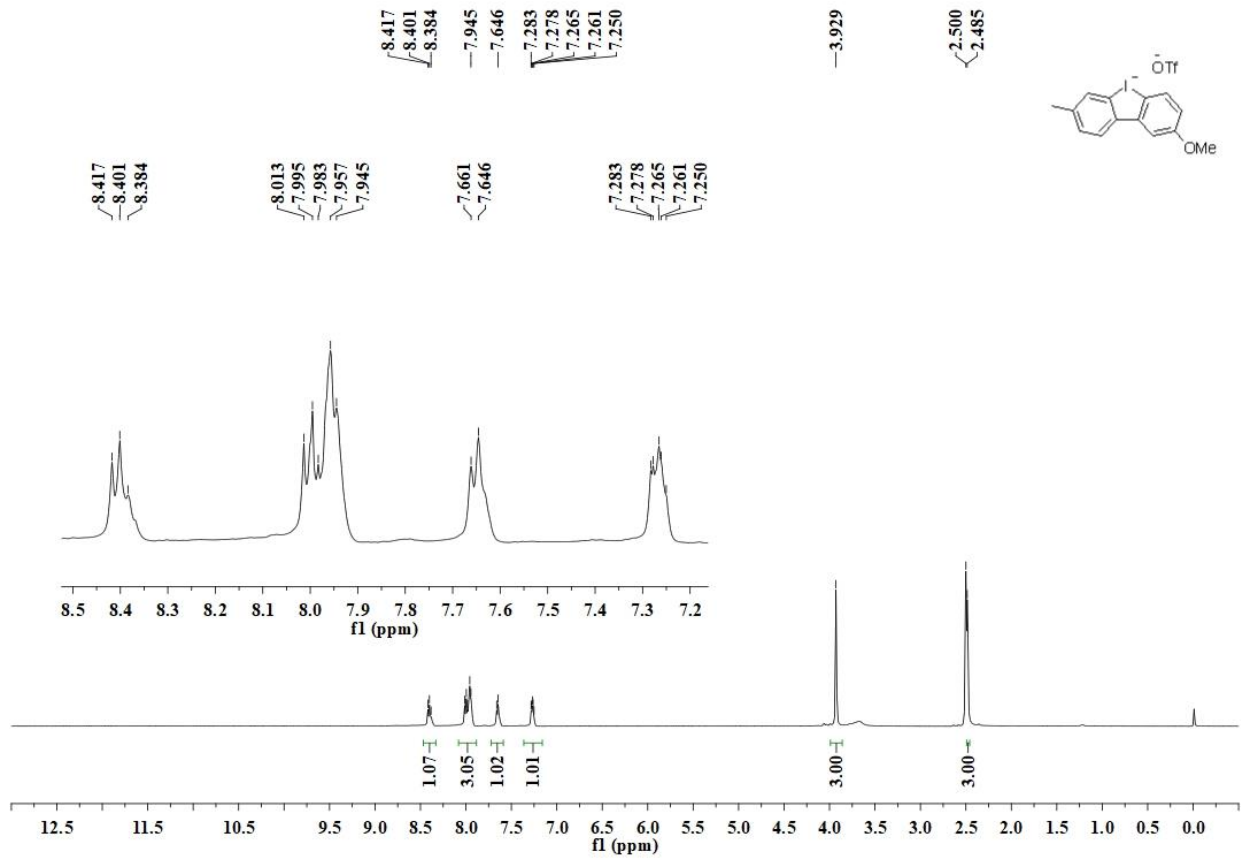
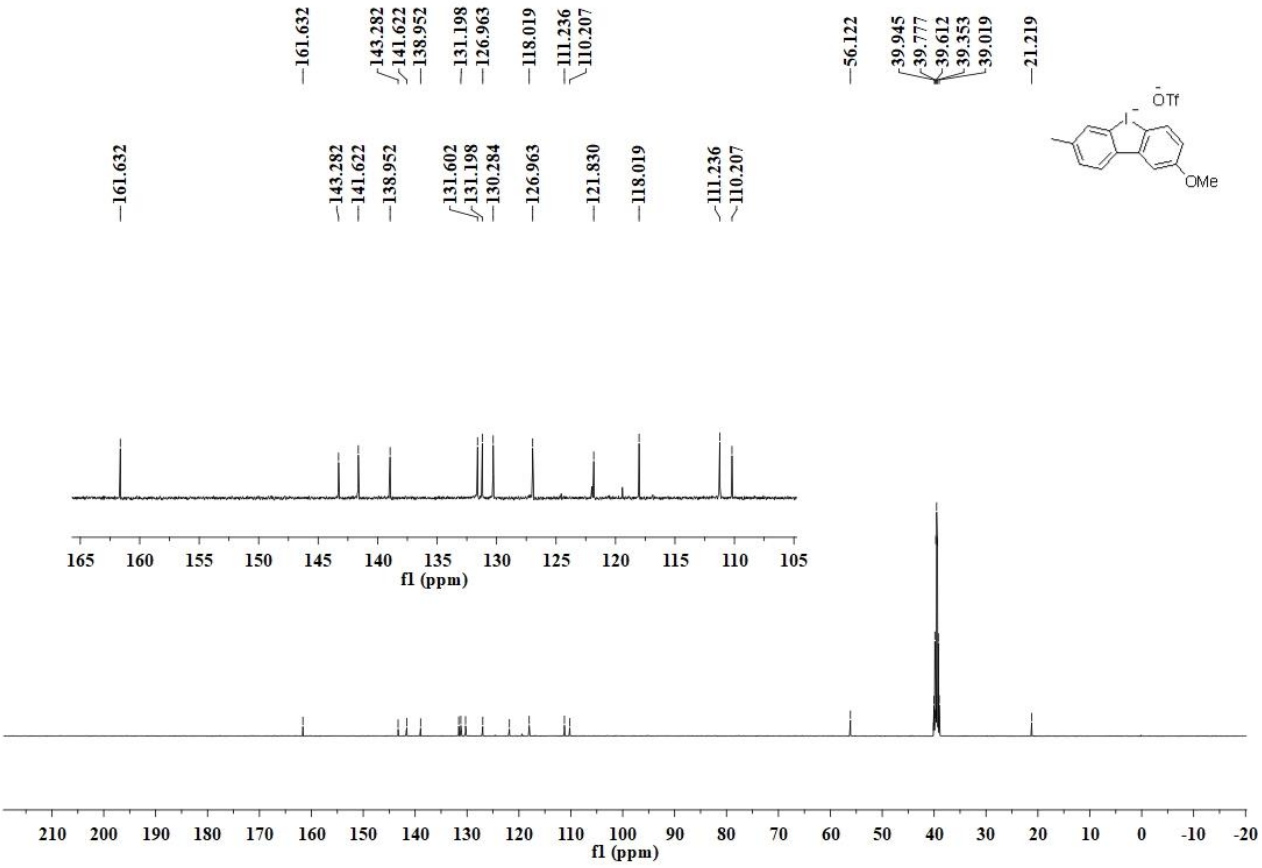
VII. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra

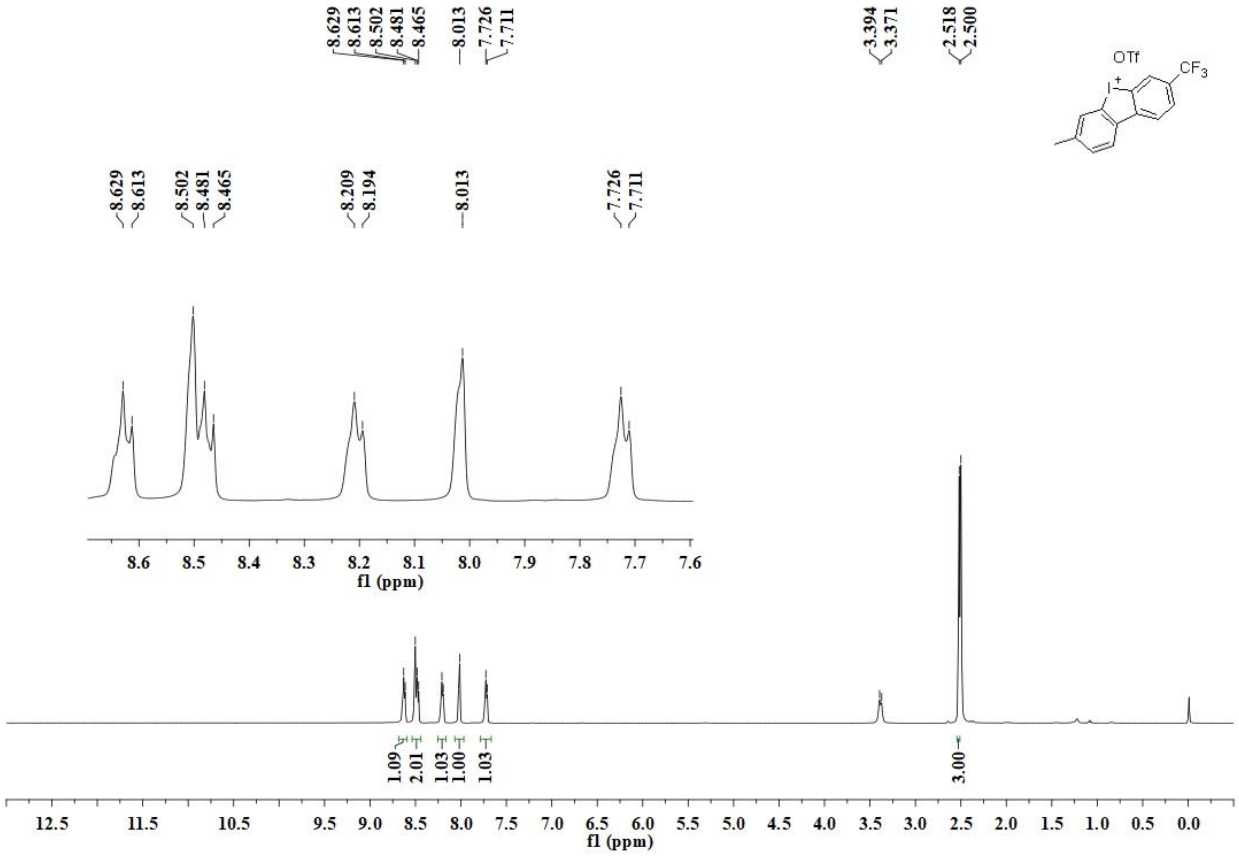
^{1}H NMR (500 MHz, DMSO-d_6) of **2l**



^{13}C NMR (125 MHz, DMSO-d_6) of **2l**



^{1}H NMR (500 MHz, DMSO-d_6) of **2n**



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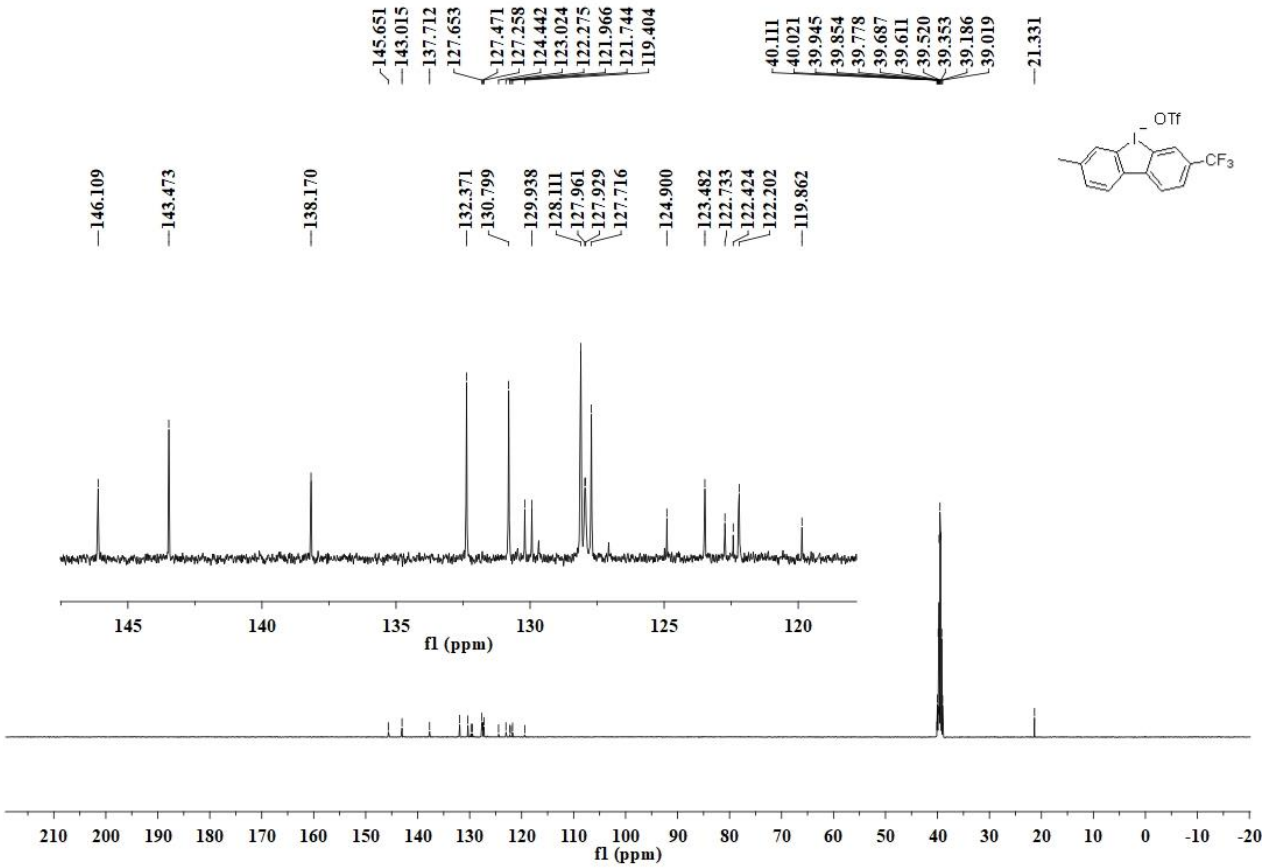
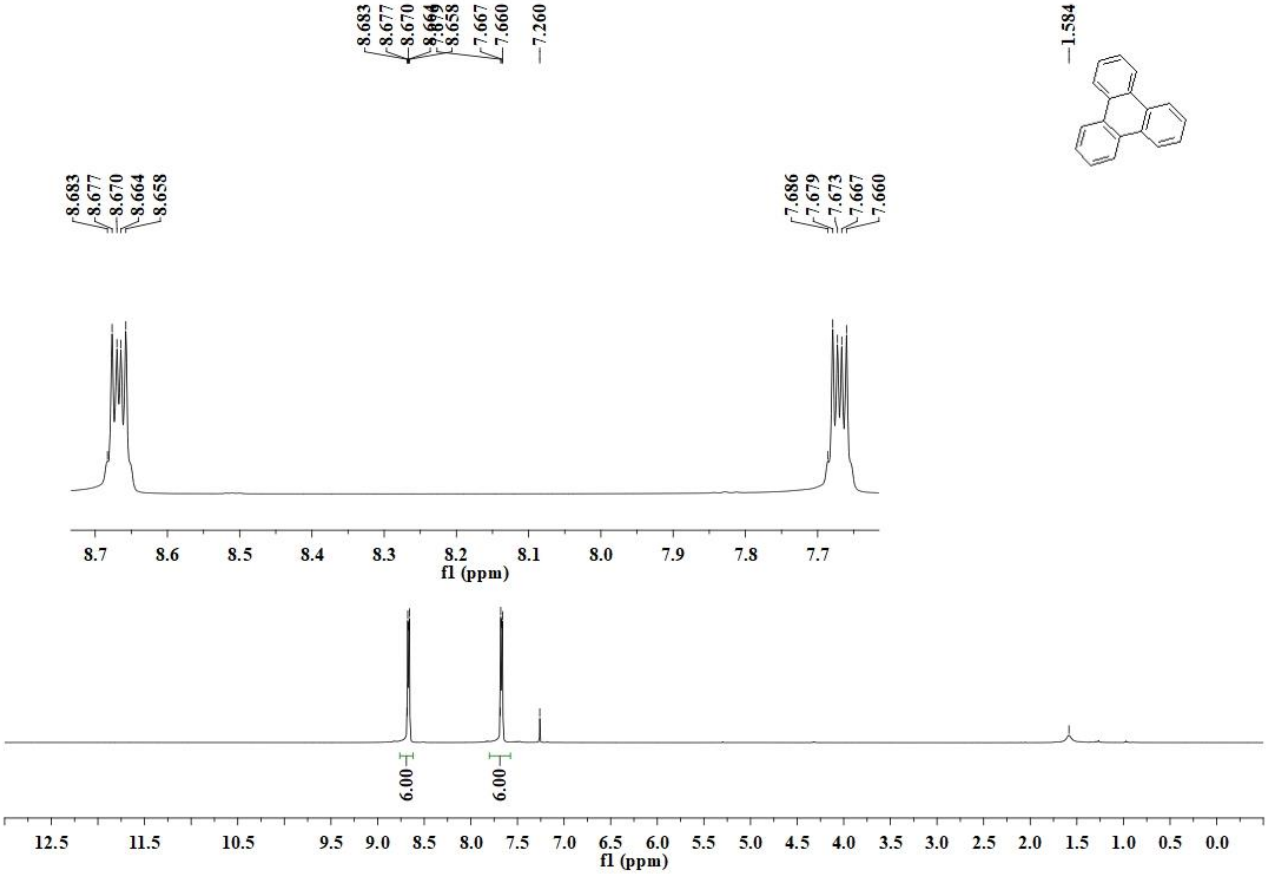


^{1}H NMR (500 MHz, $CDCl_3$) of **3a**



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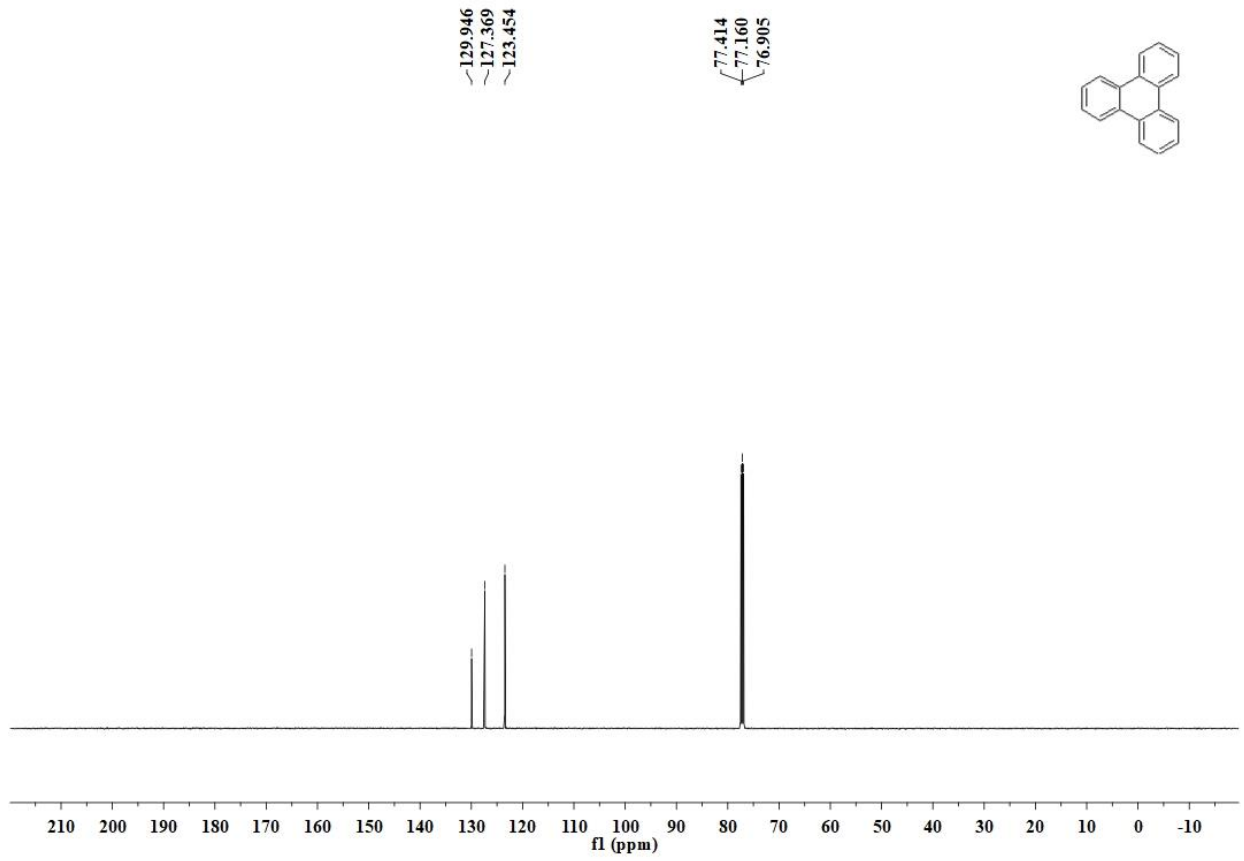
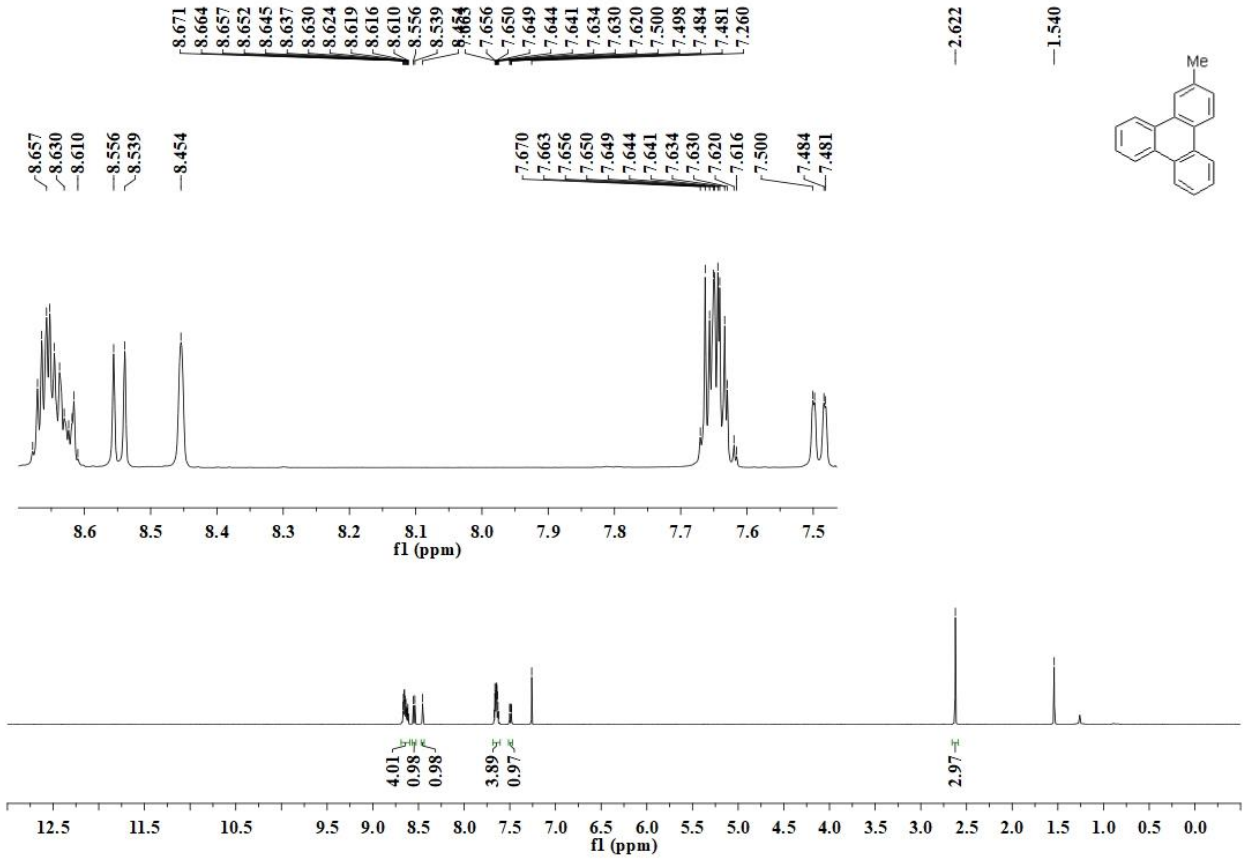
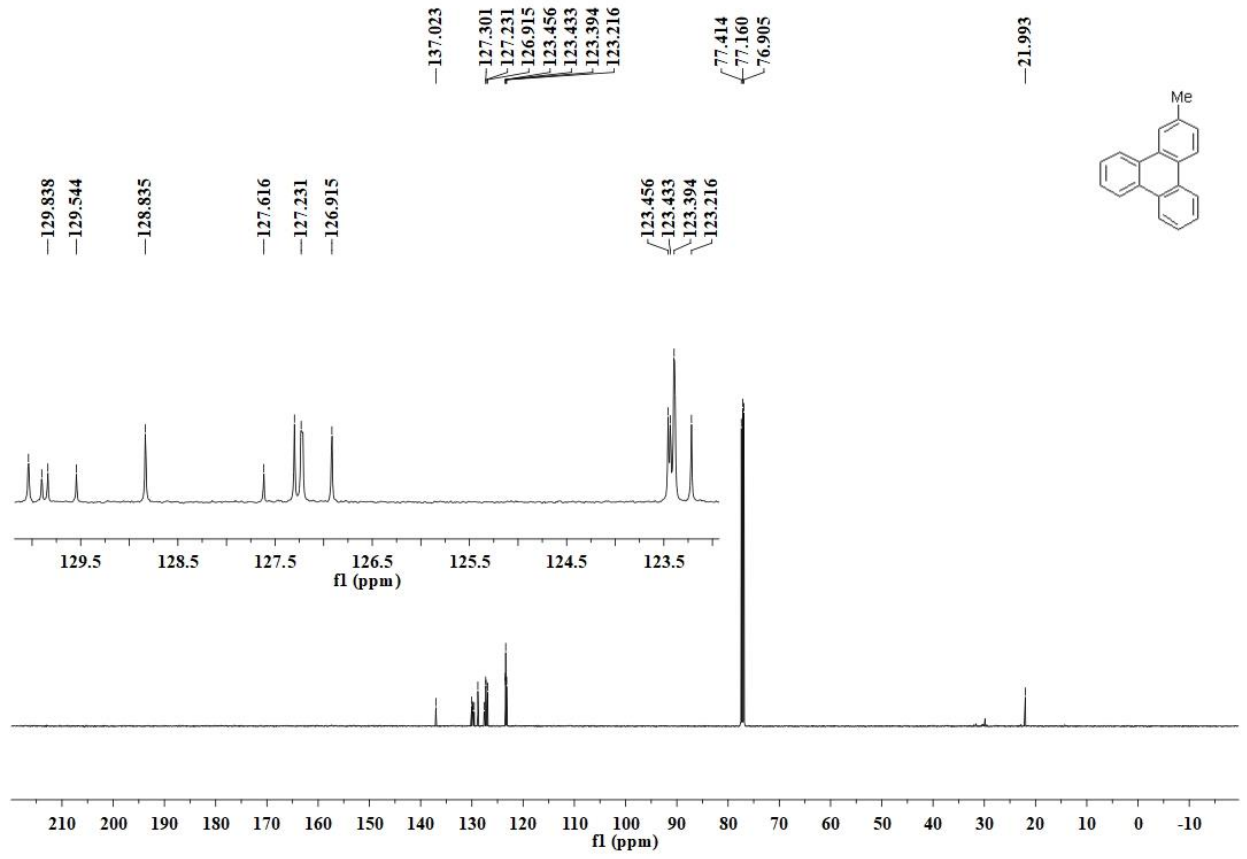


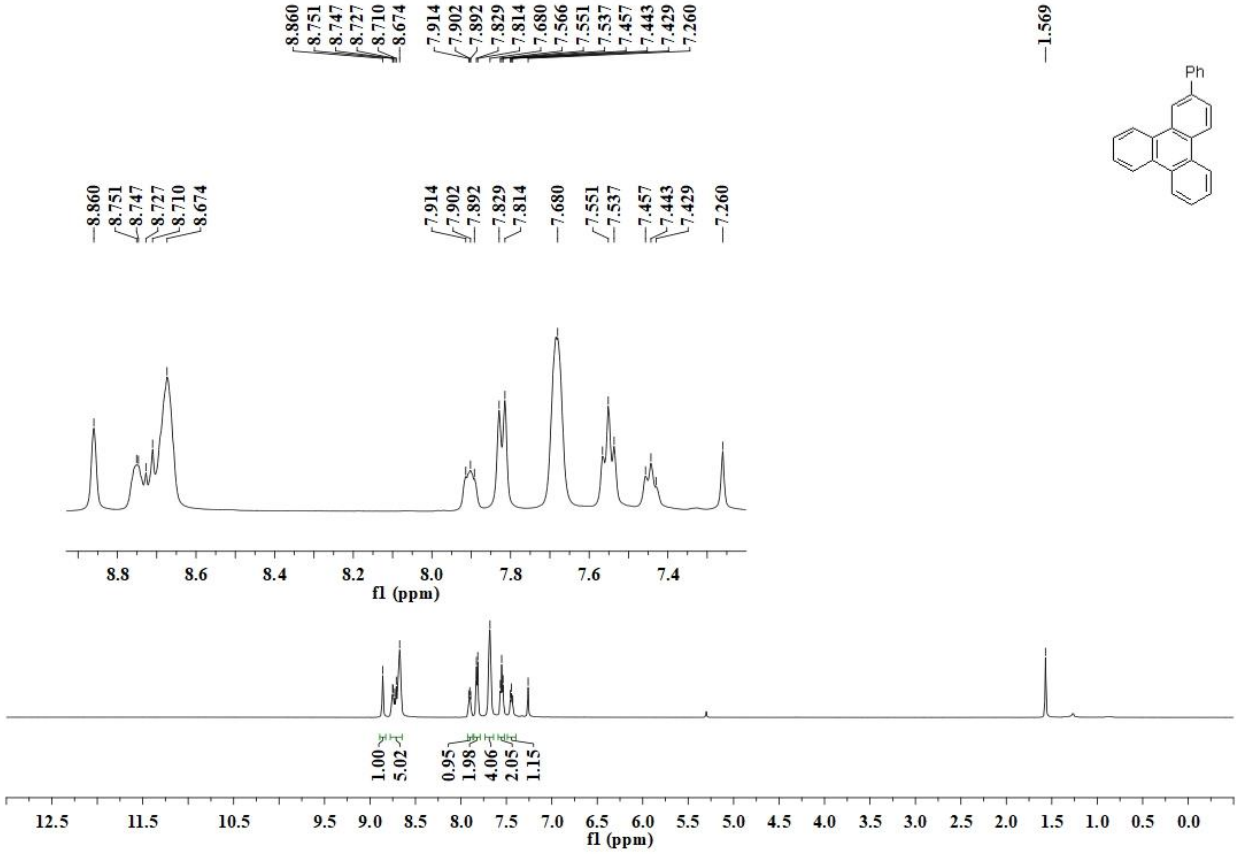
^{1}H NMR (500 MHz, $CDCl_3$) of **3b** and **4e**



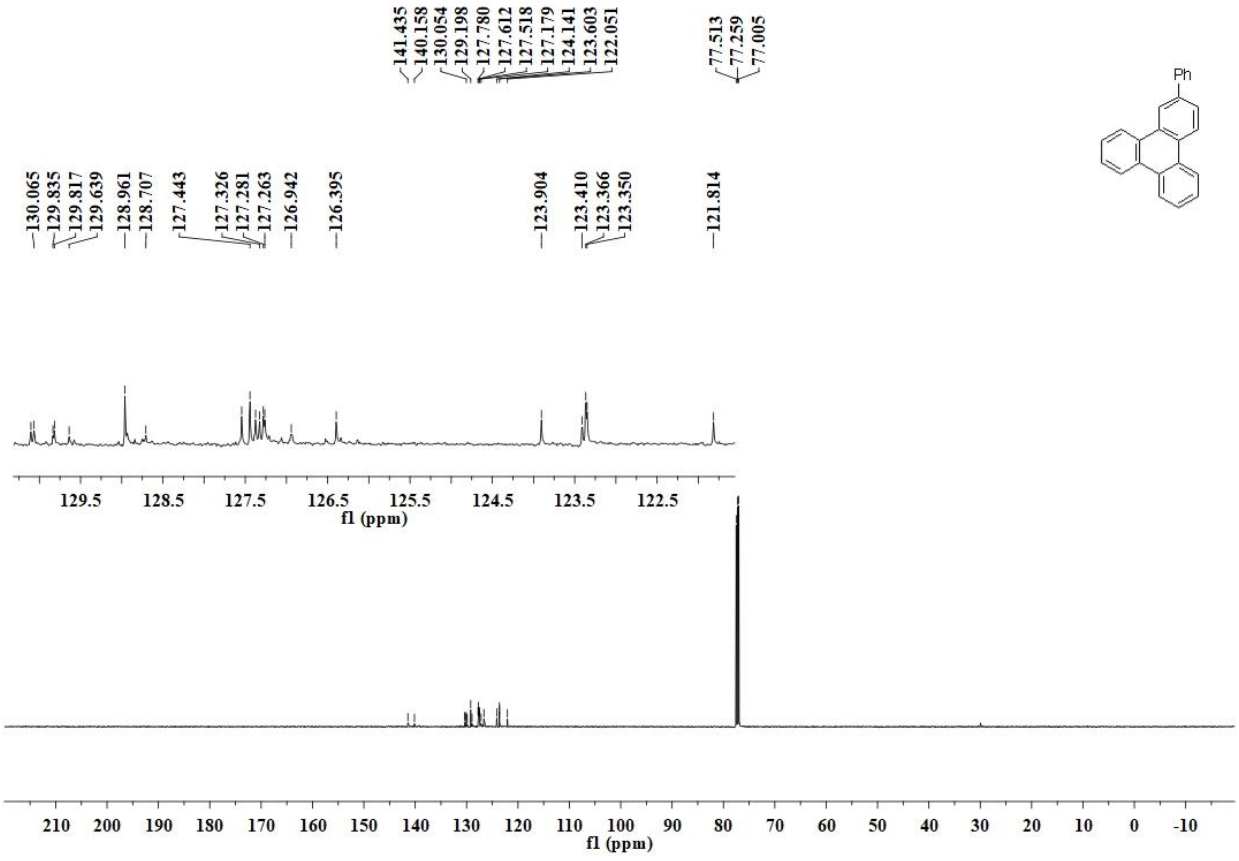
^{13}C NMR (125 MHz, $CDCl_3$) of **3b** and **4e**



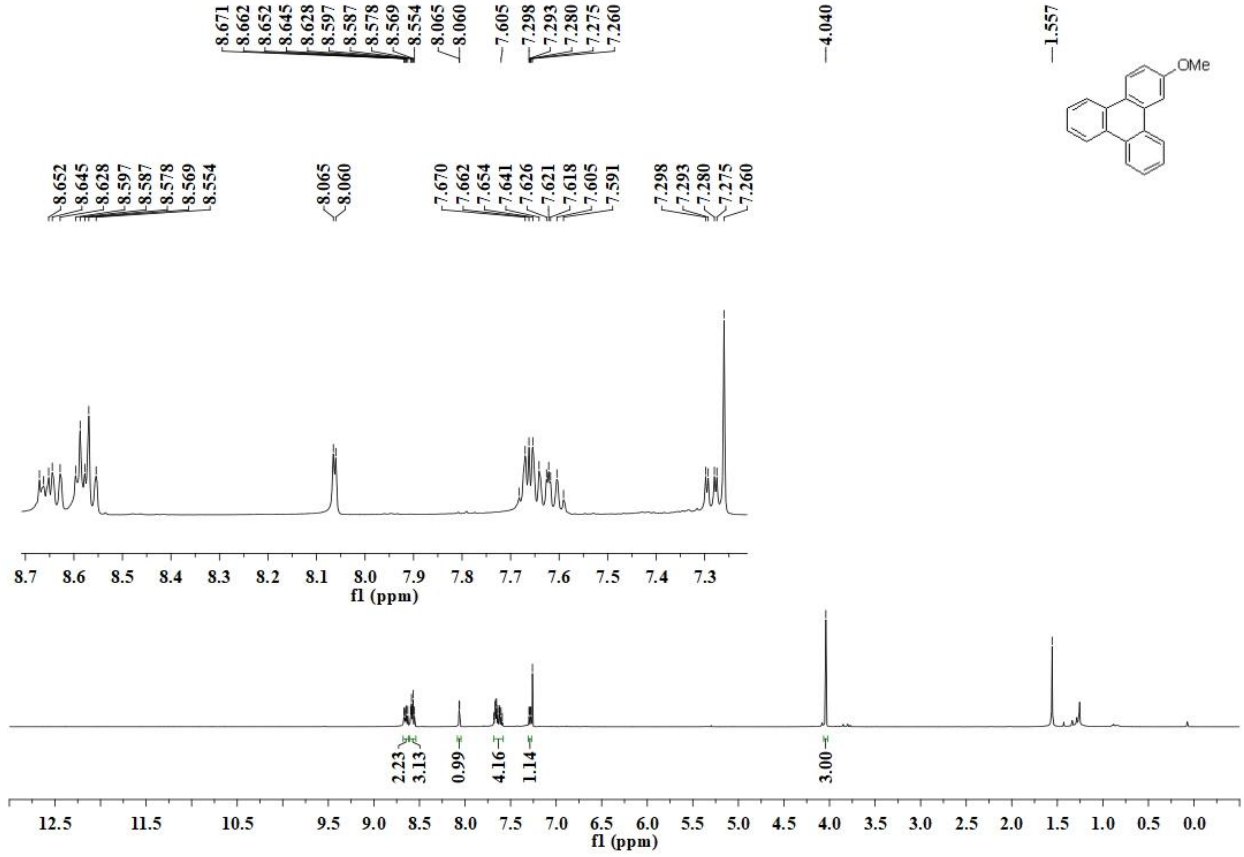
^{1}H NMR (500 MHz, $CDCl_3$) of **3c**



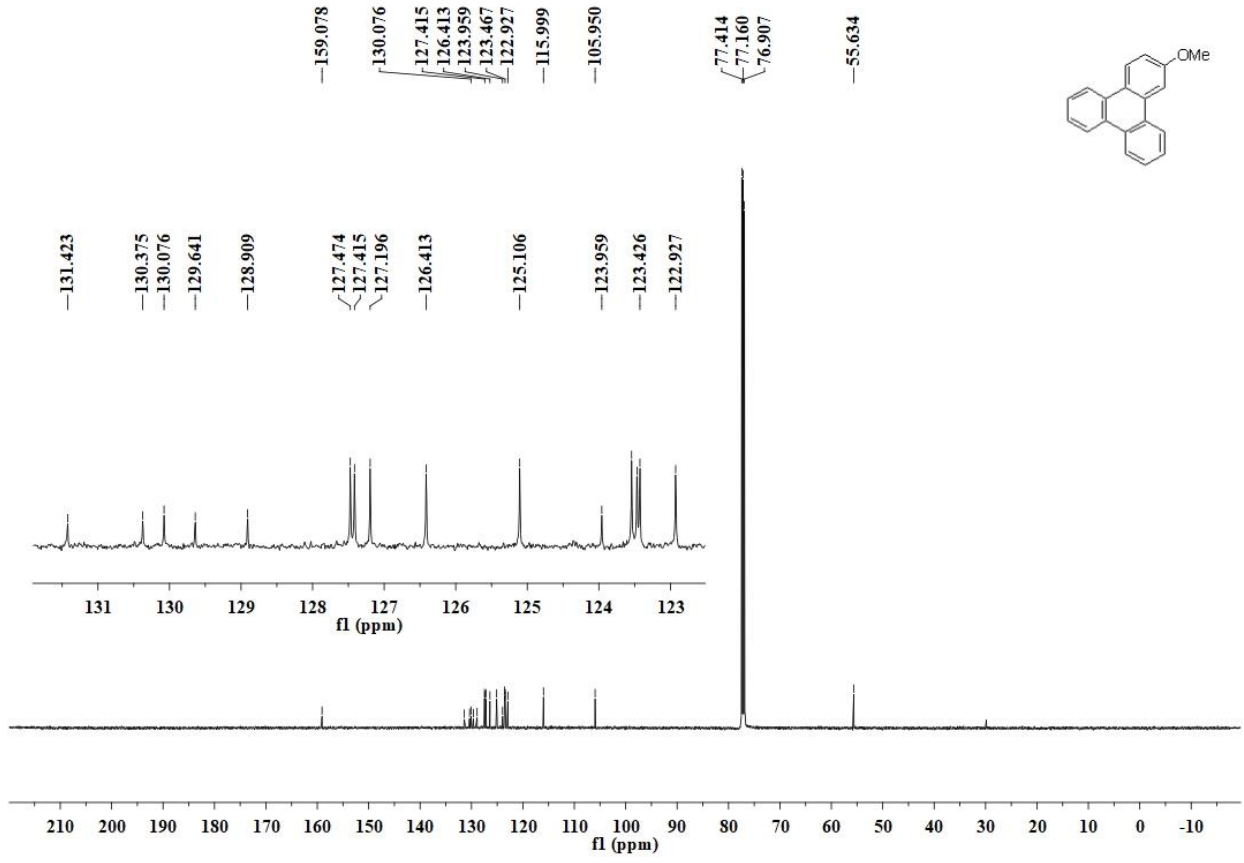
^{13}C NMR (125 MHz, $CDCl_3$) of **3c**



^{1}H NMR (500 MHz, $CDCl_3$) of **3d** and **4f**



^{13}C NMR (125 MHz, $CDCl_3$) of **3d** and **4f**



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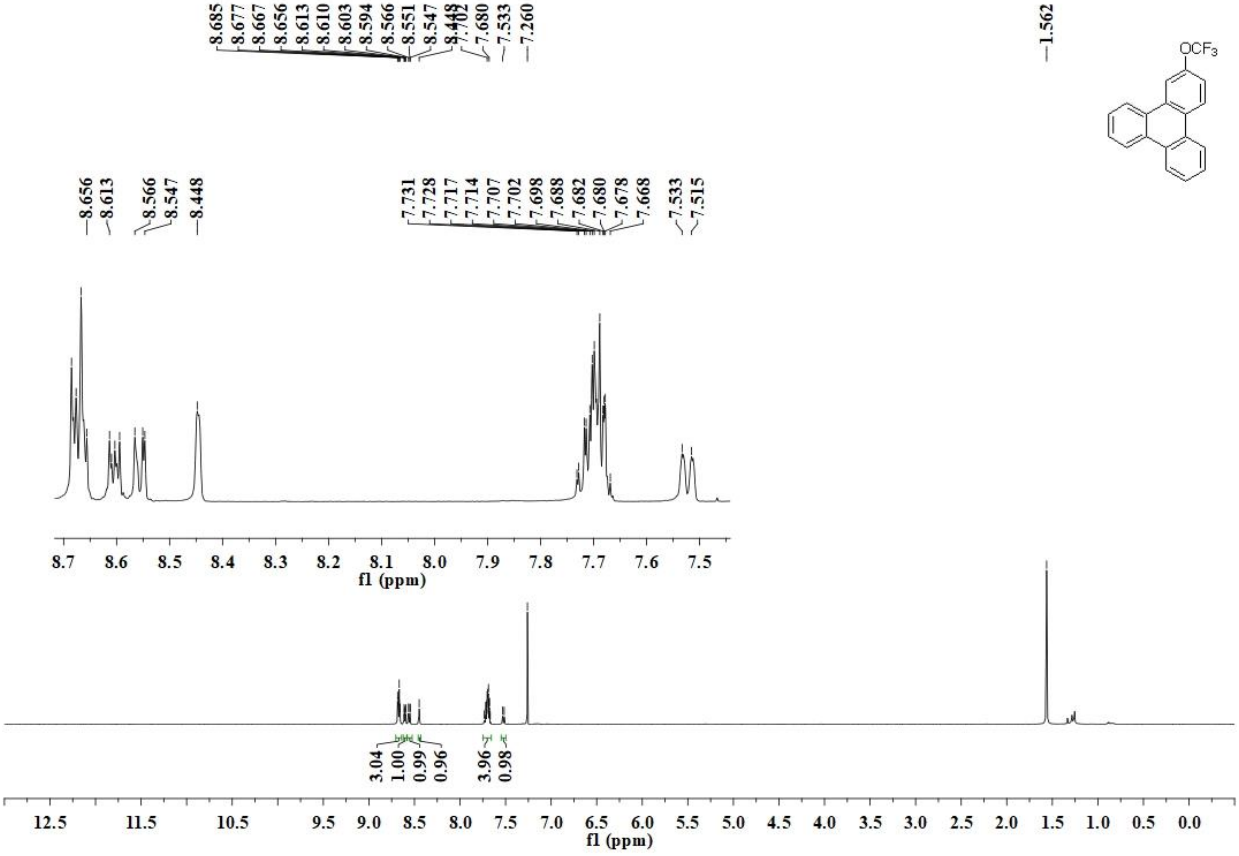
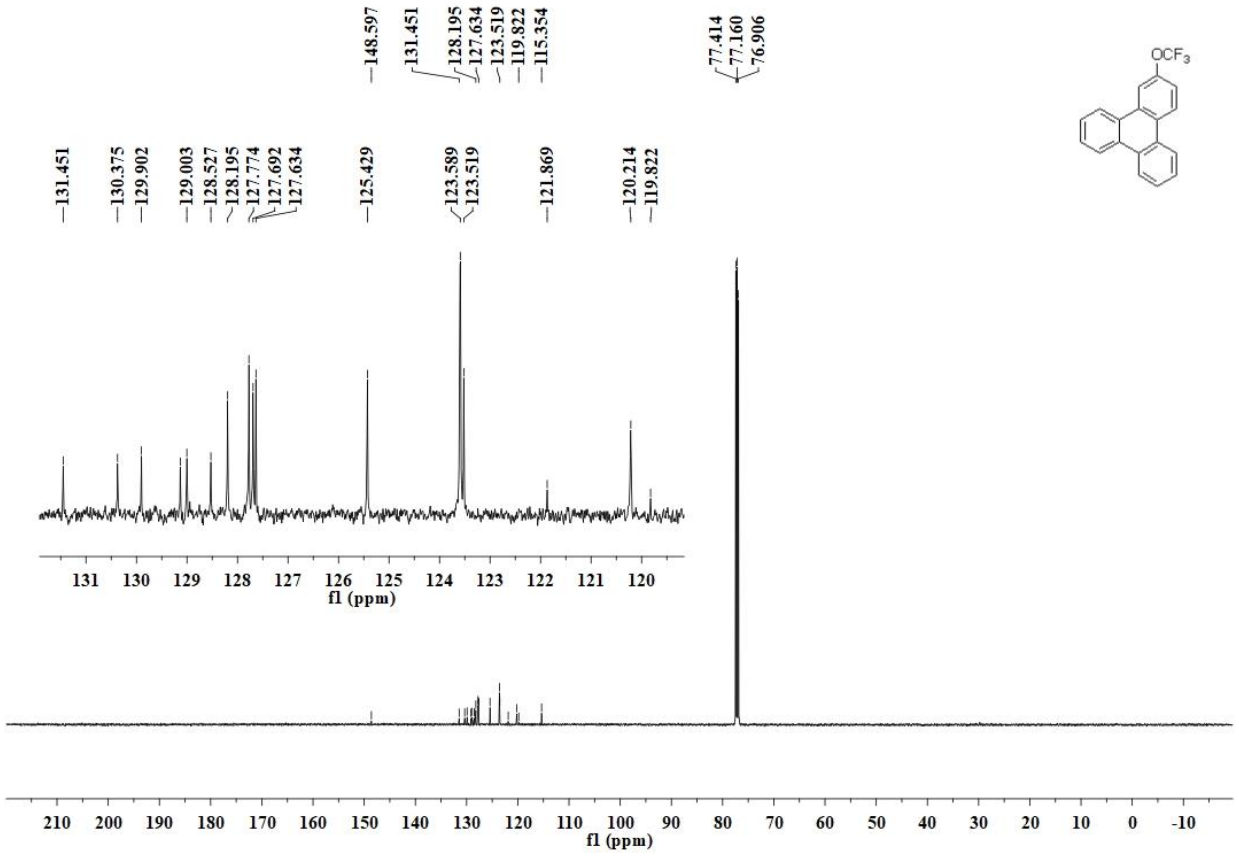
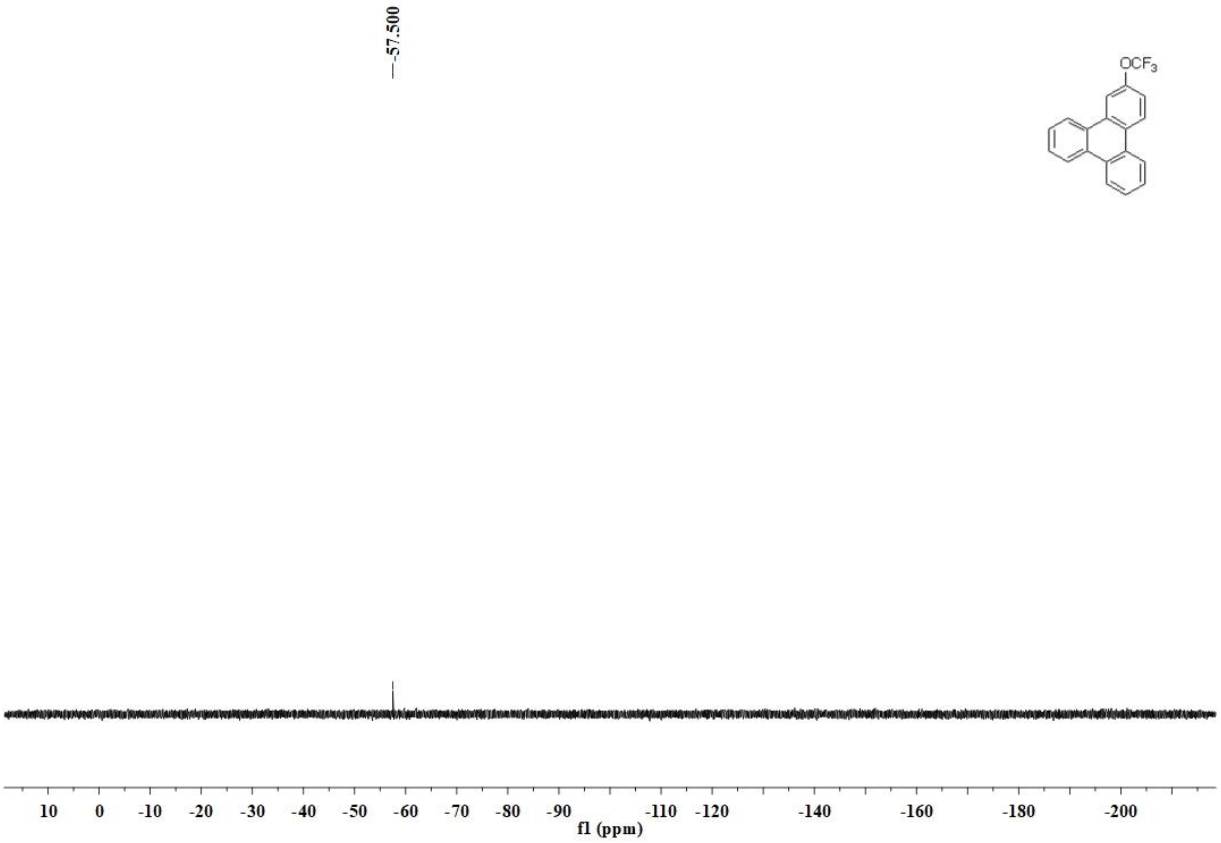


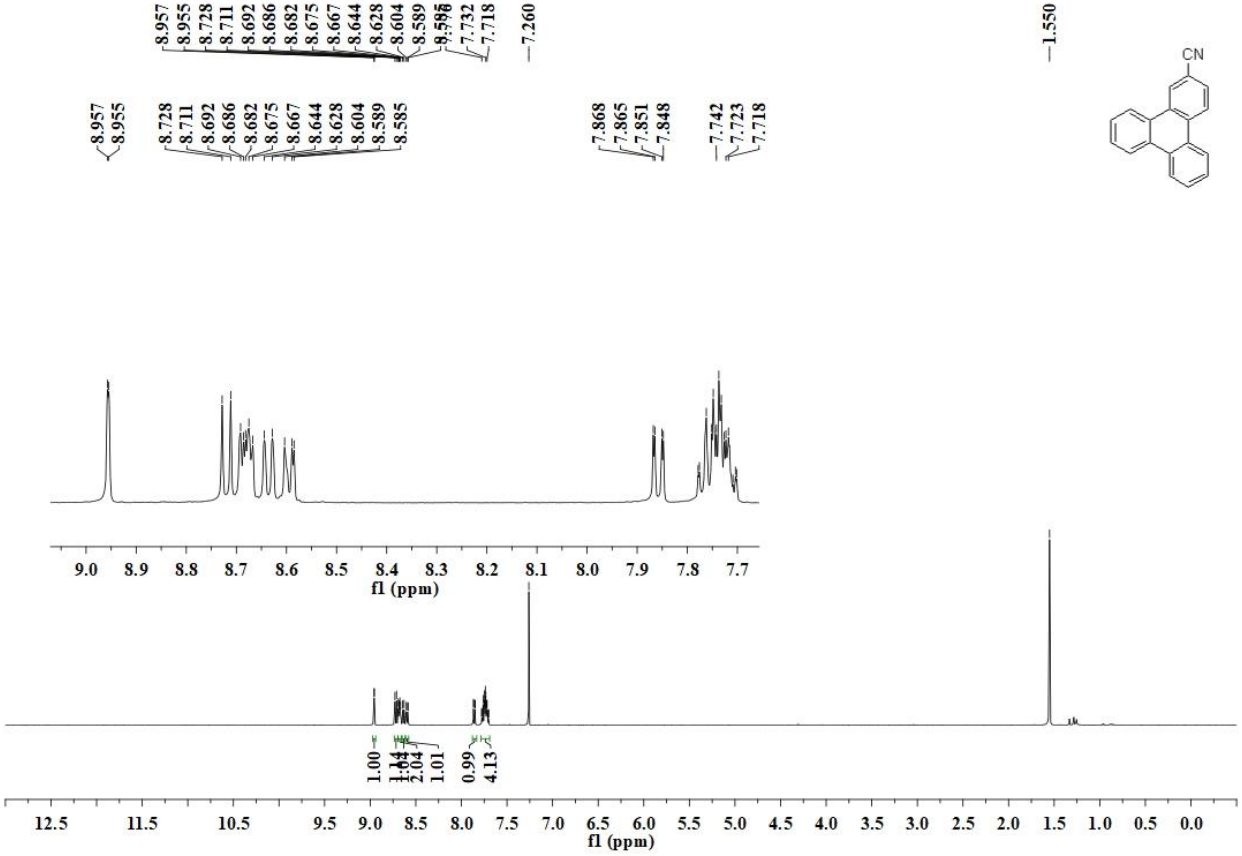
^{13}C NMR (125 MHz, $CDCl_3$) of **3e**



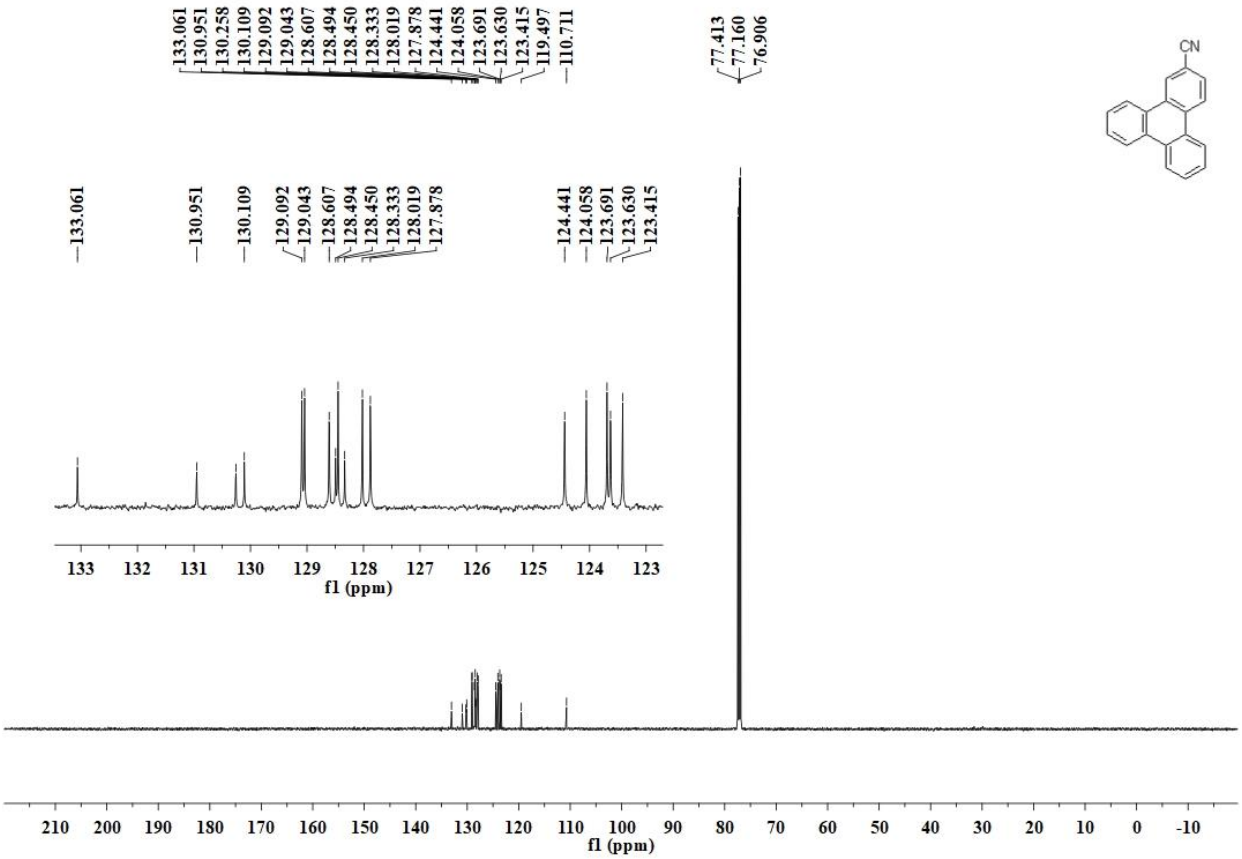
^{19}F NMR (376 MHz, $CDCl_3$) of **3e**



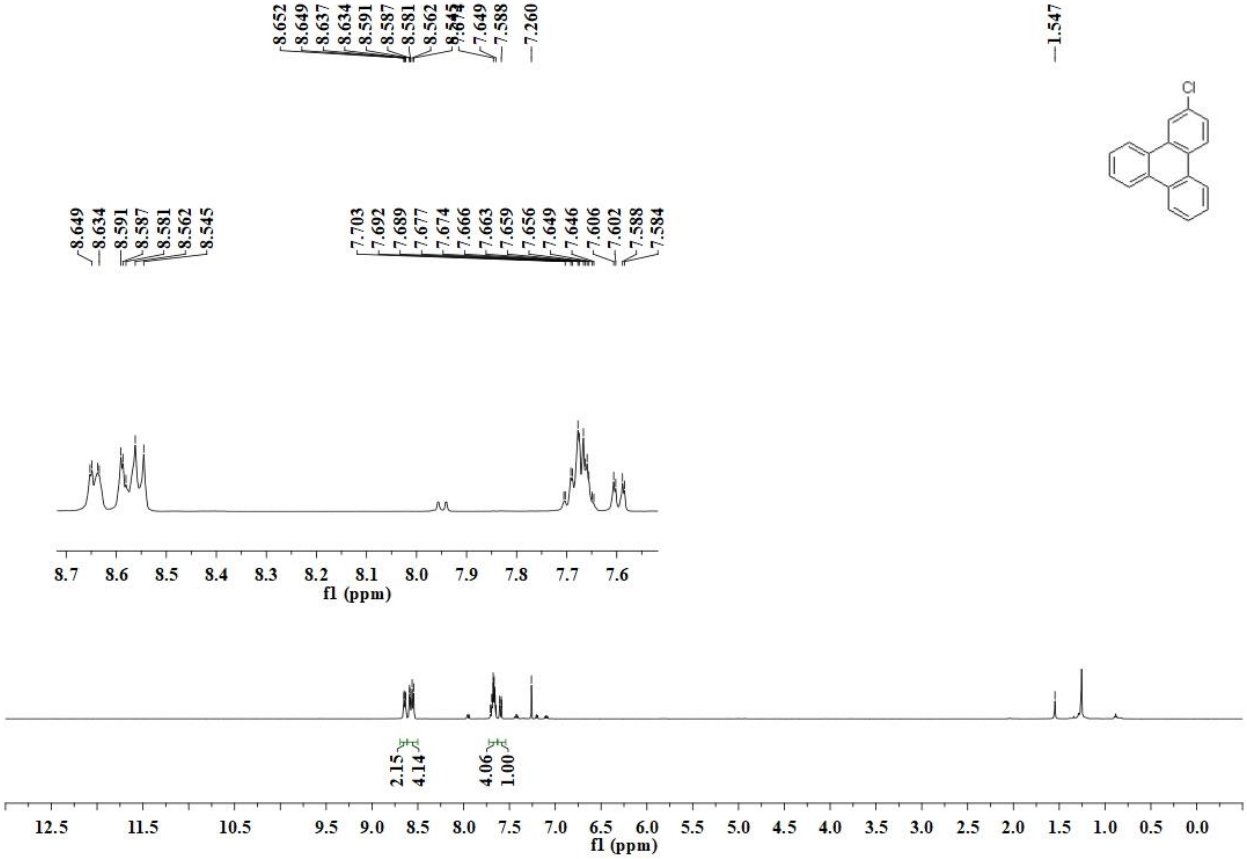
^{1}H NMR (500 MHz, $CDCl_3$) of **3f**



^{13}C NMR (125 MHz, $CDCl_3$) of **3f**



^{1}H NMR (500 MHz, $CDCl_3$) of **3g** and **4g**



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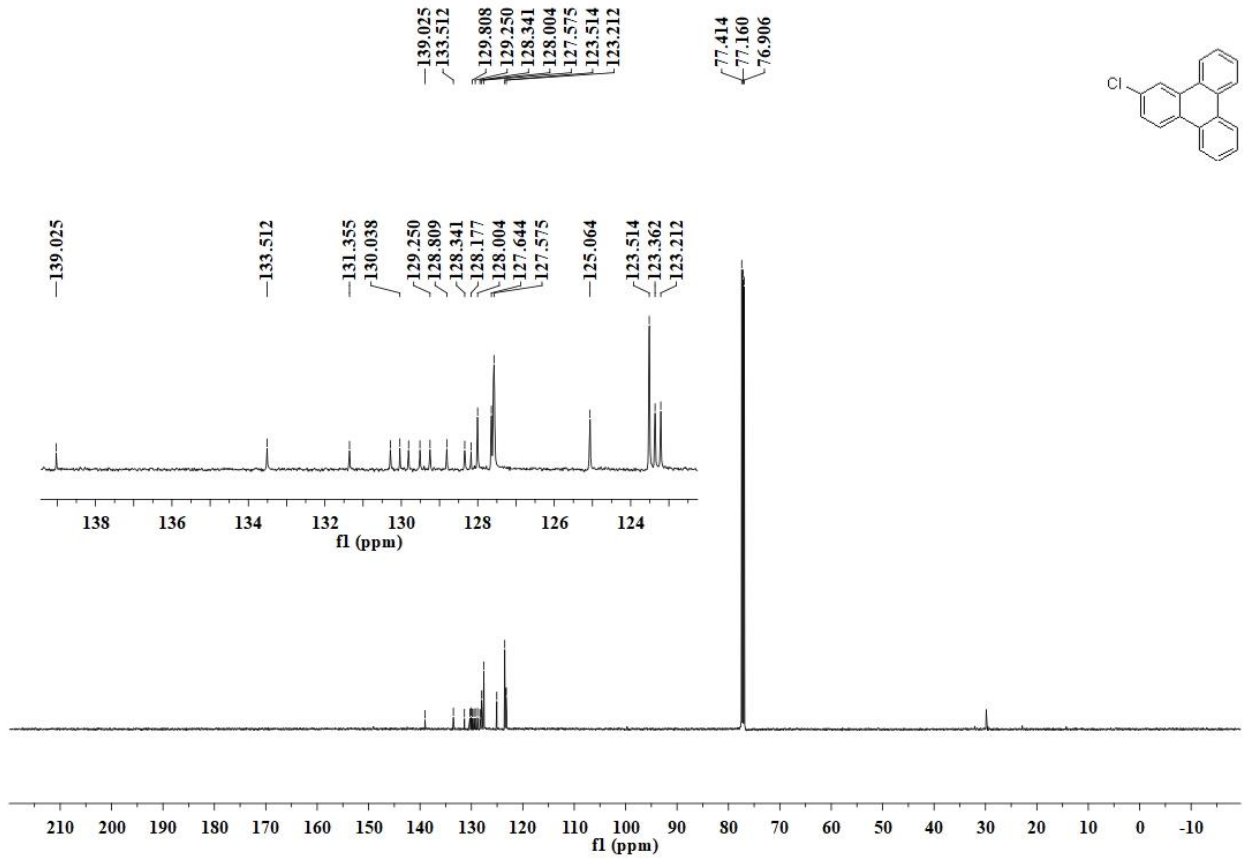

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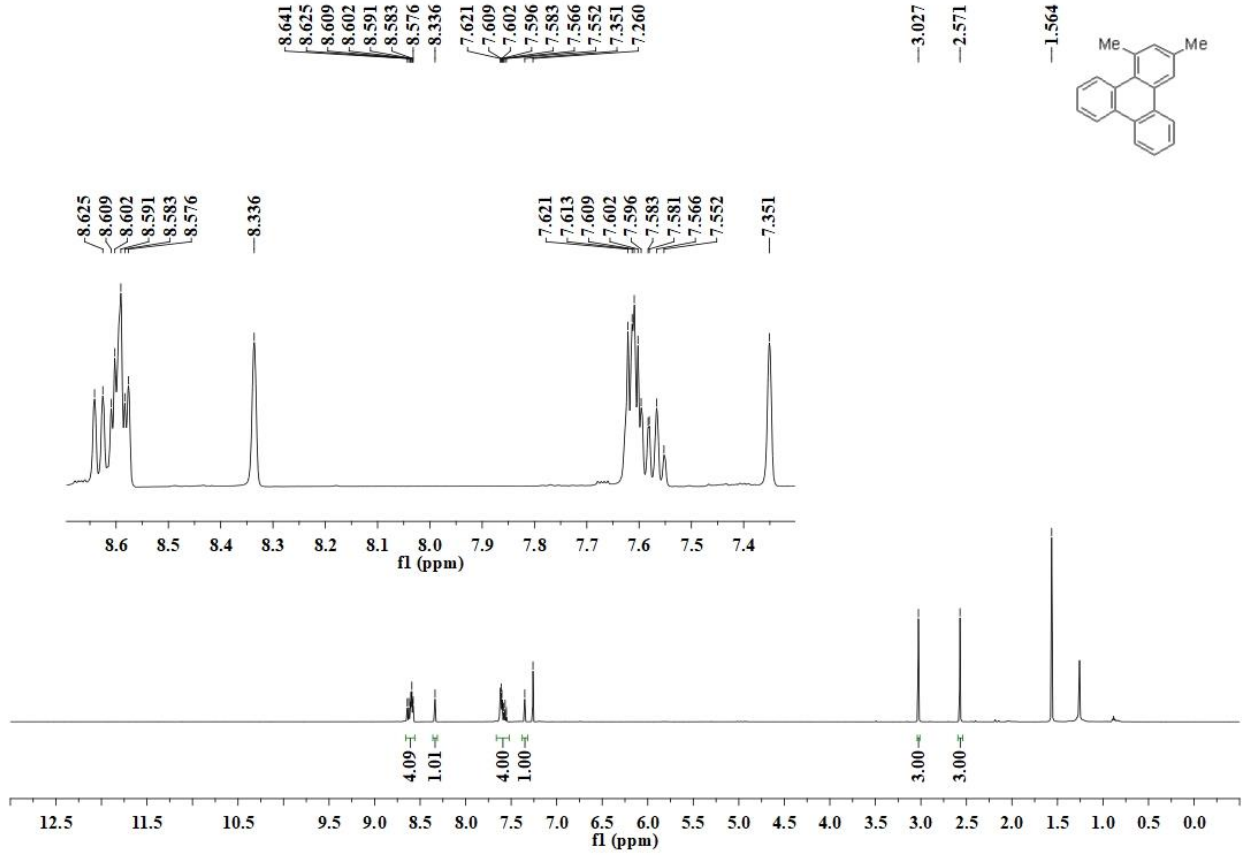
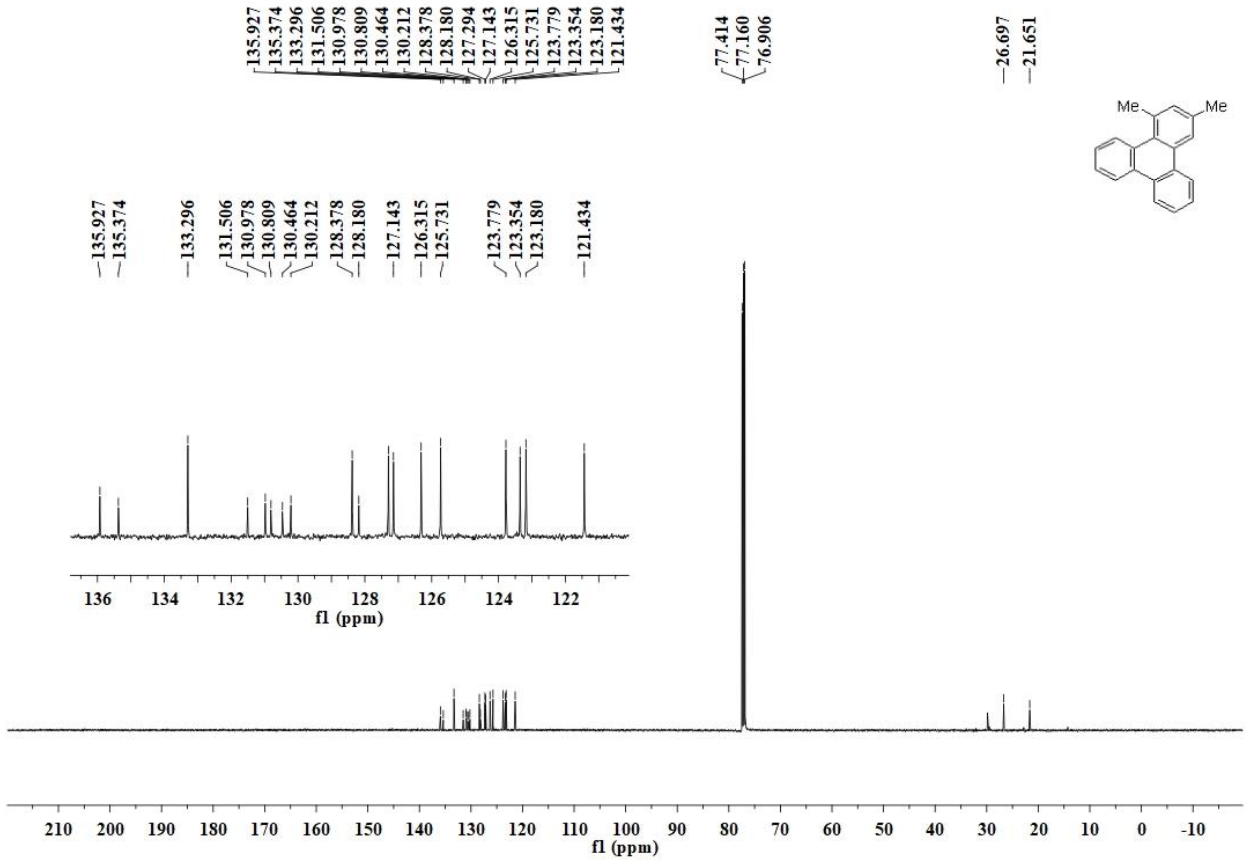
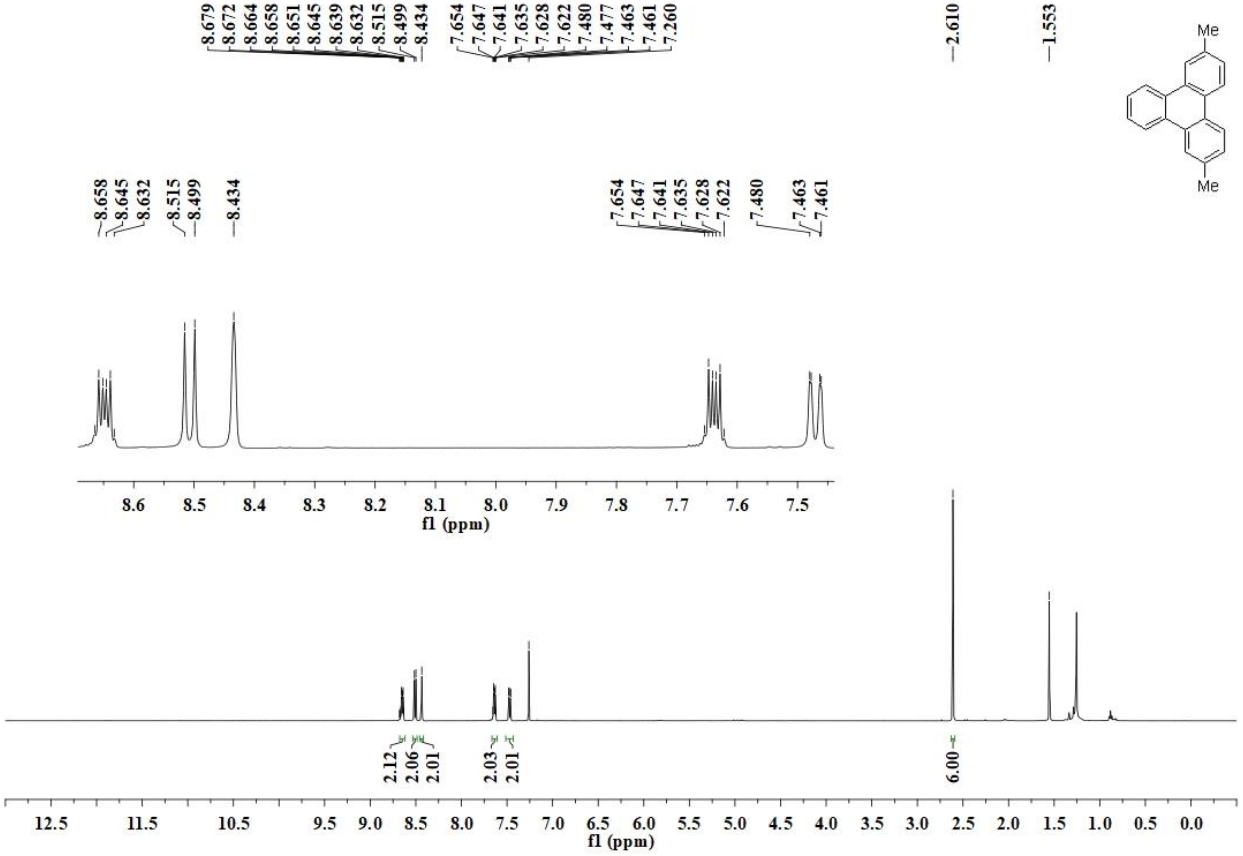


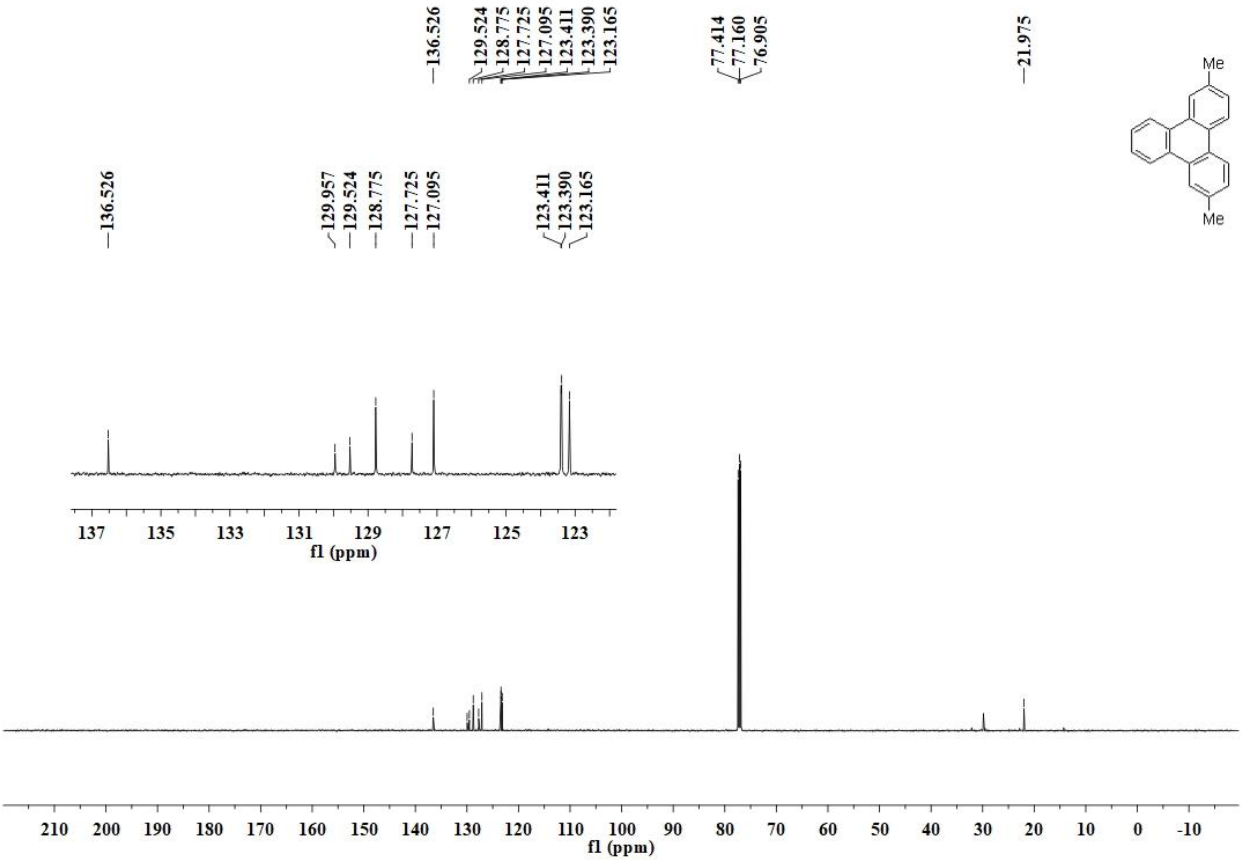
^{13}C NMR (125 MHz, $CDCl_3$) of **3h**



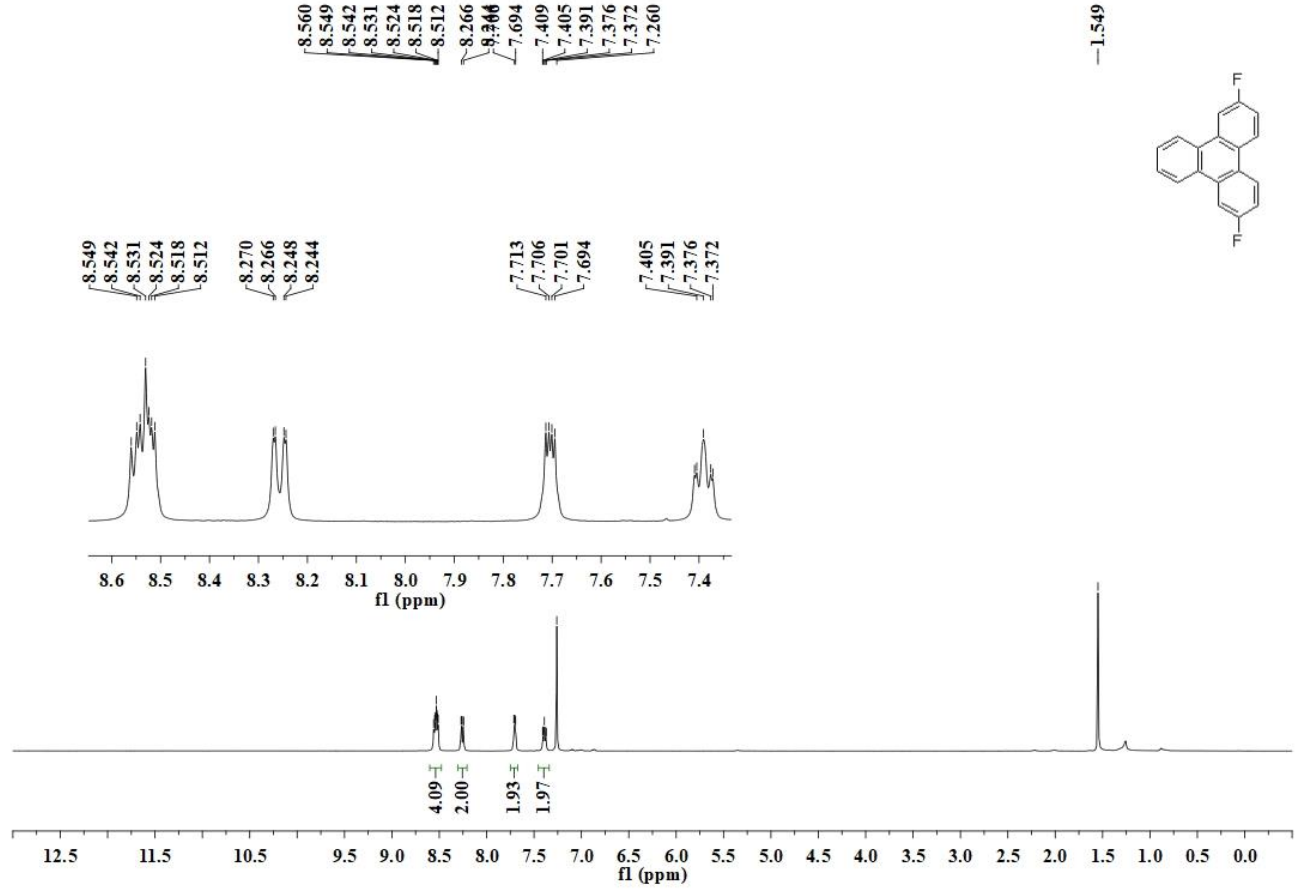
^{1}H NMR (500 MHz, $CDCl_3$) of **3i**



^{13}C NMR (125 MHz, $CDCl_3$) of **3i**



^{1}H NMR (500 MHz, $CDCl_3$) of **3j**



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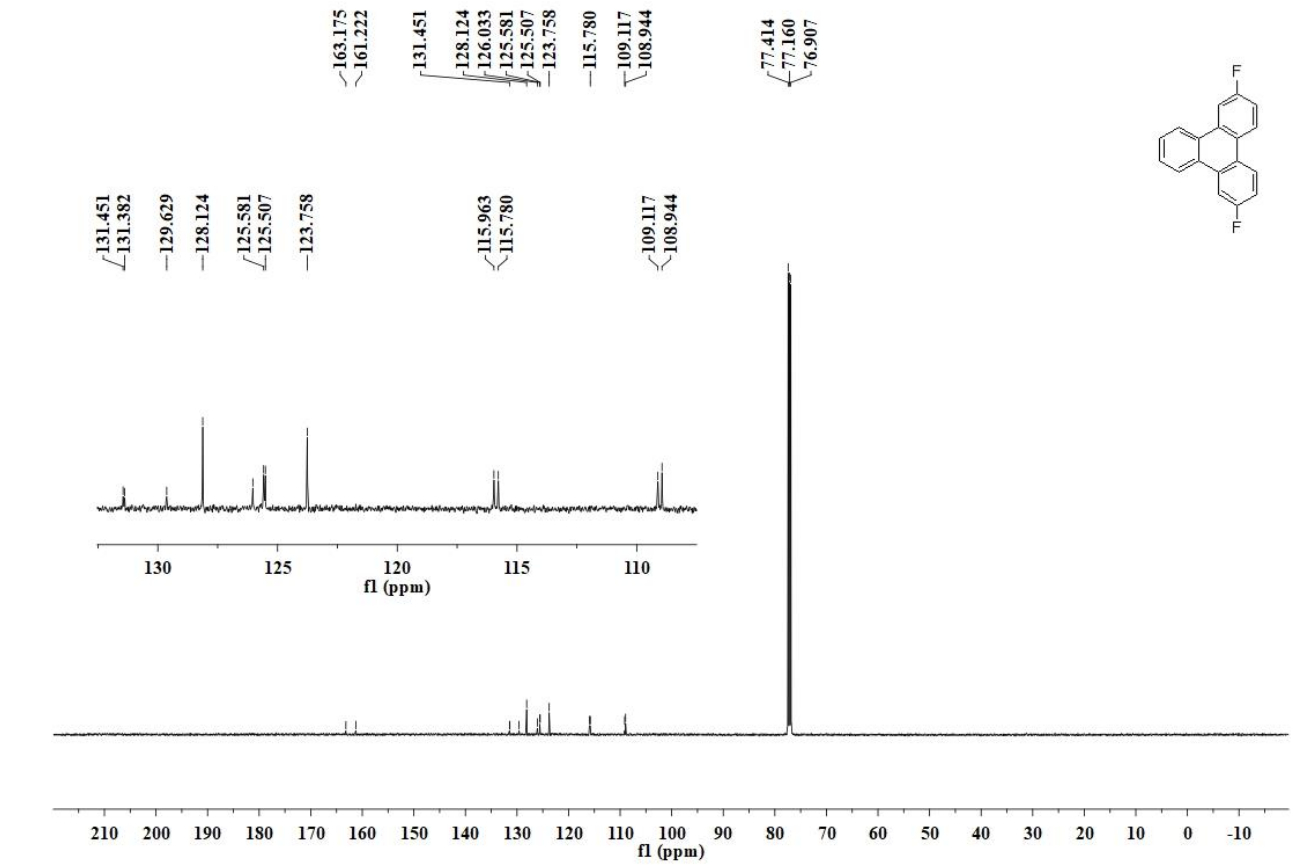
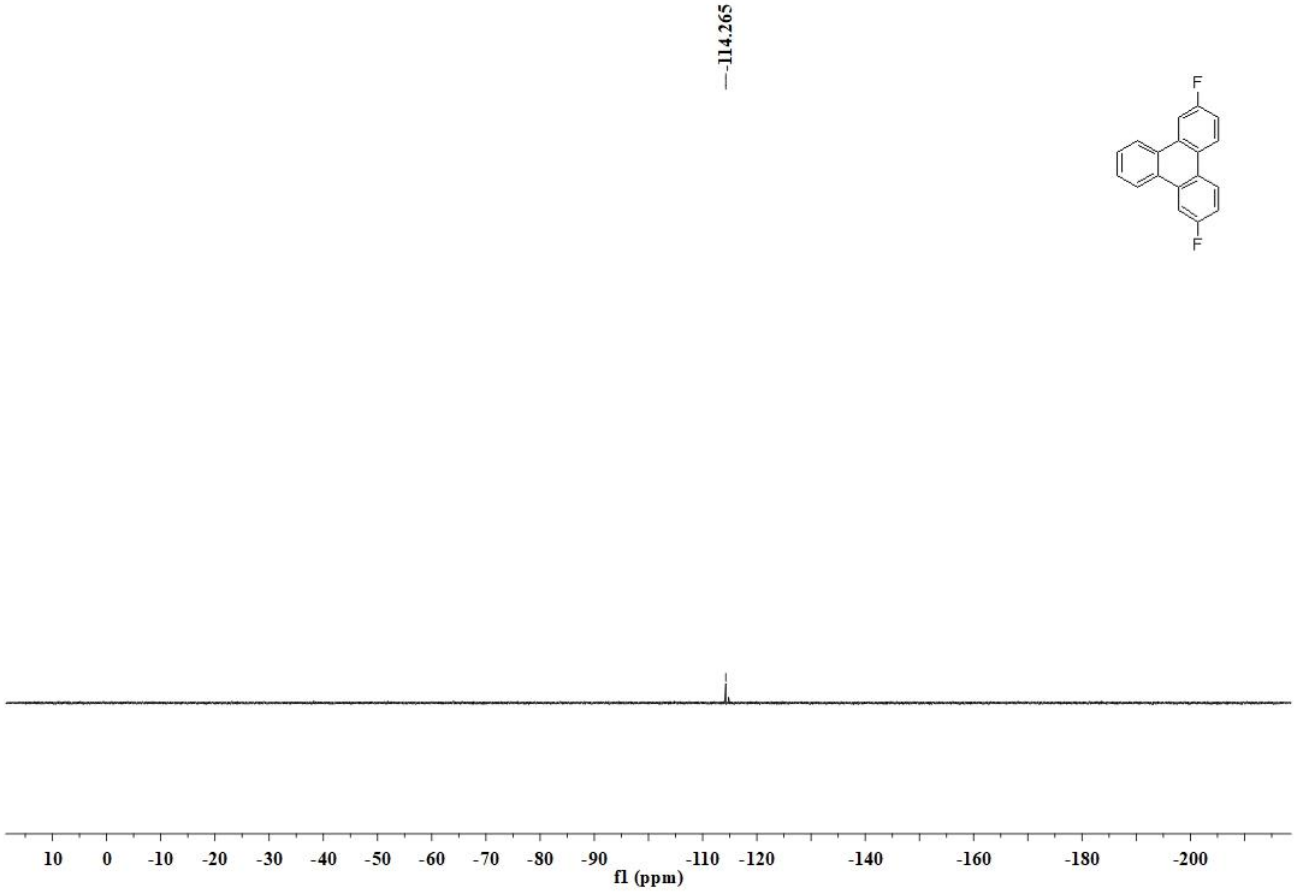
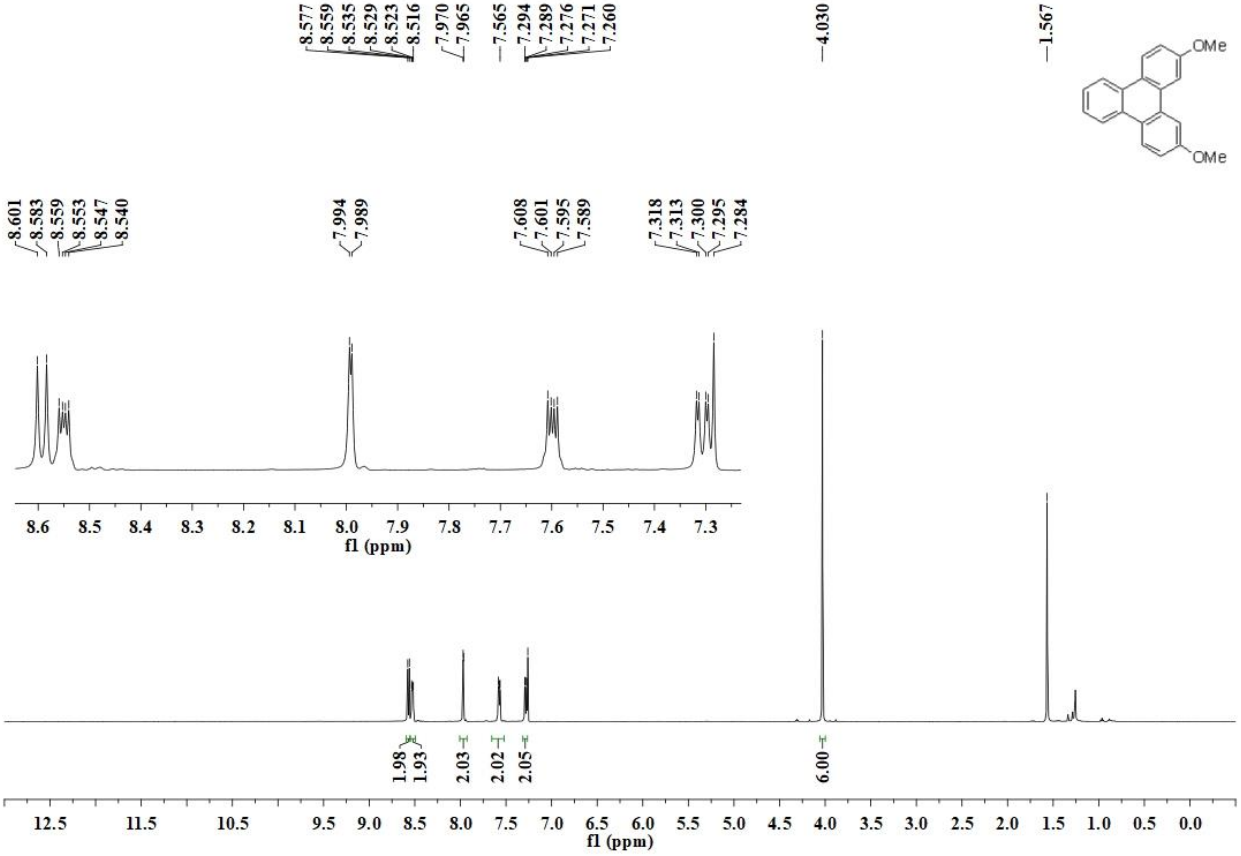


^{19}F NMR (376 MHz, $CDCl_3$) of **3j**



^{1}H NMR (500 MHz, $CDCl_3$) of **3k**



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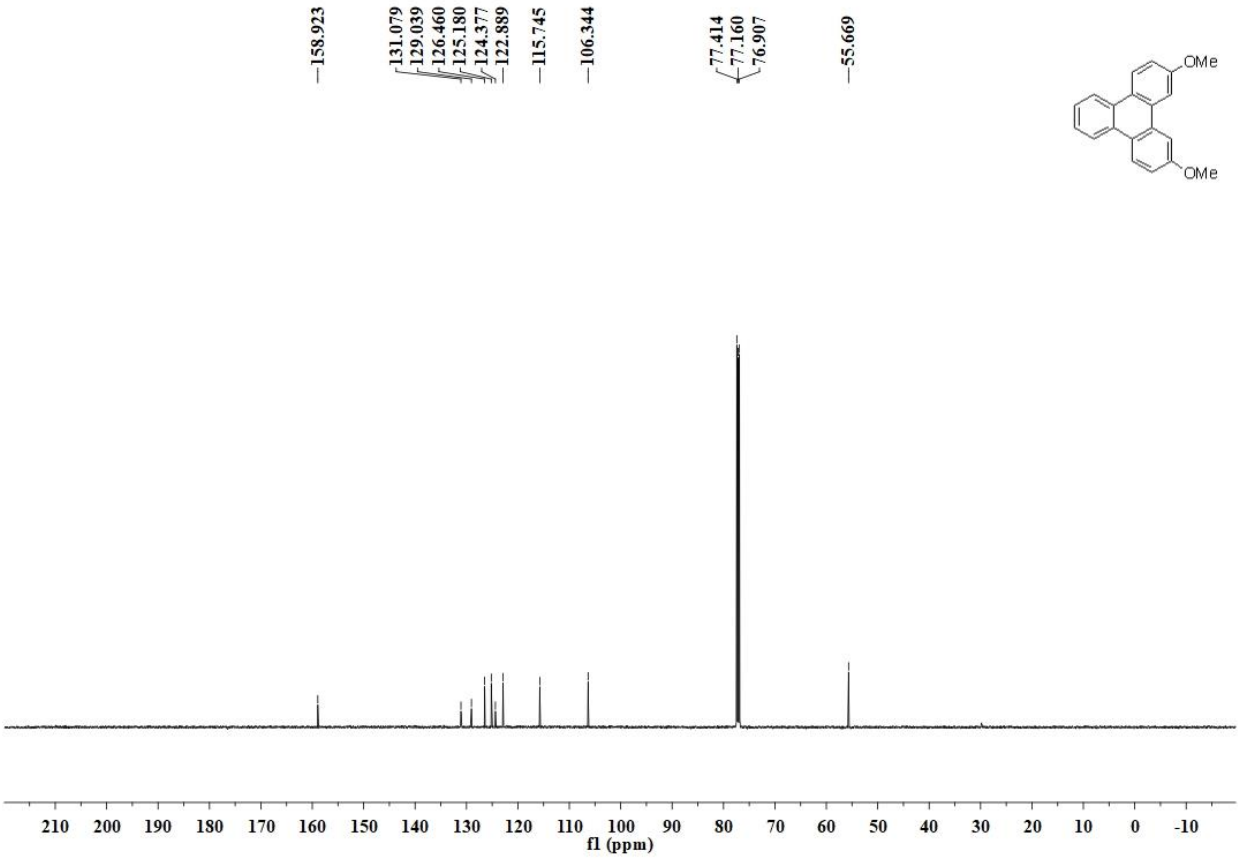

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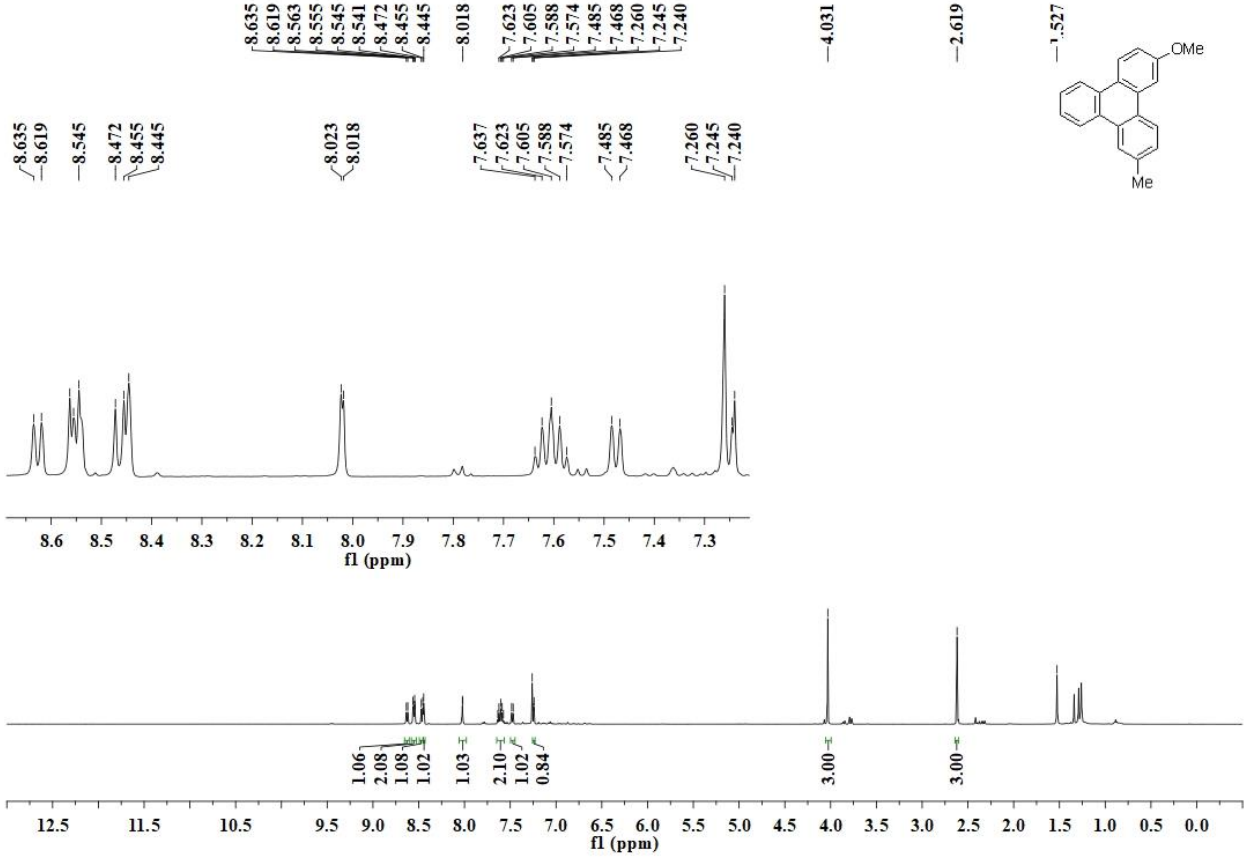

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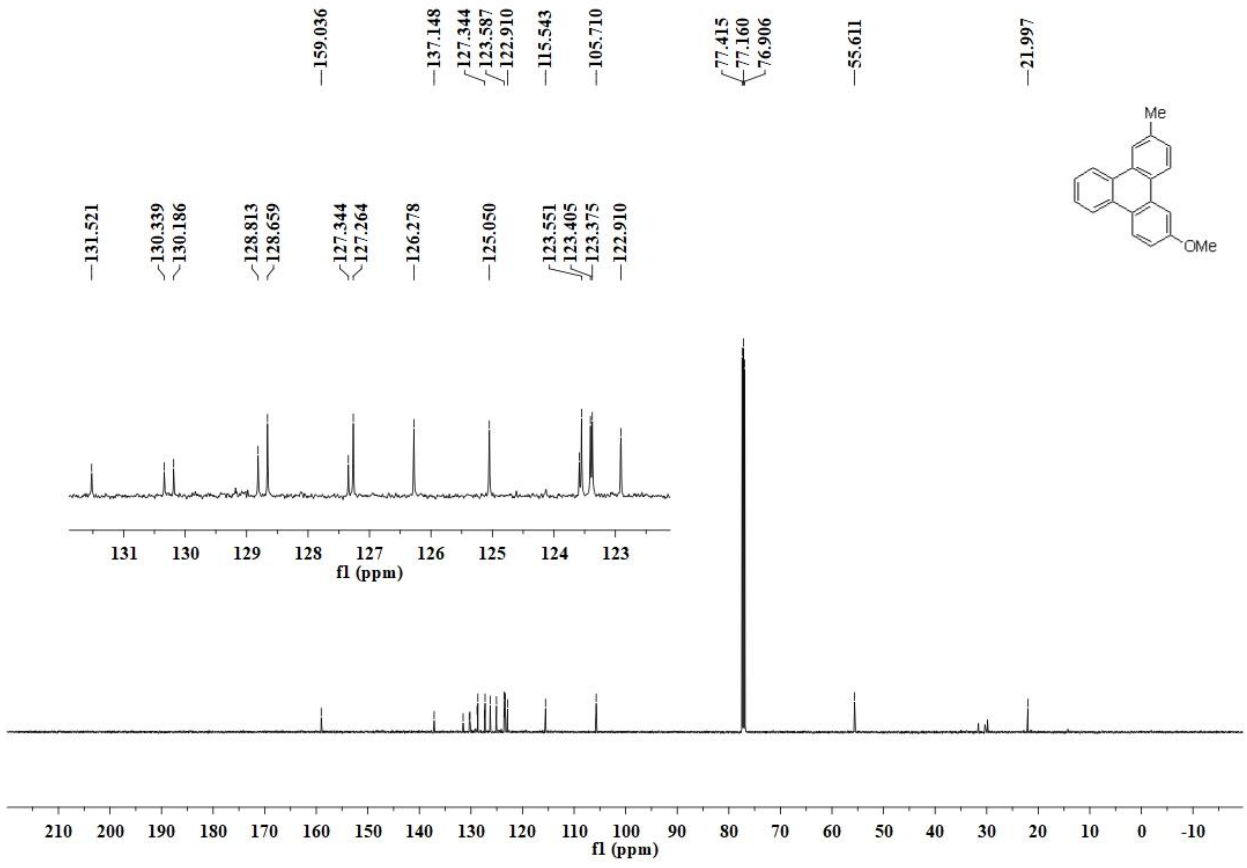
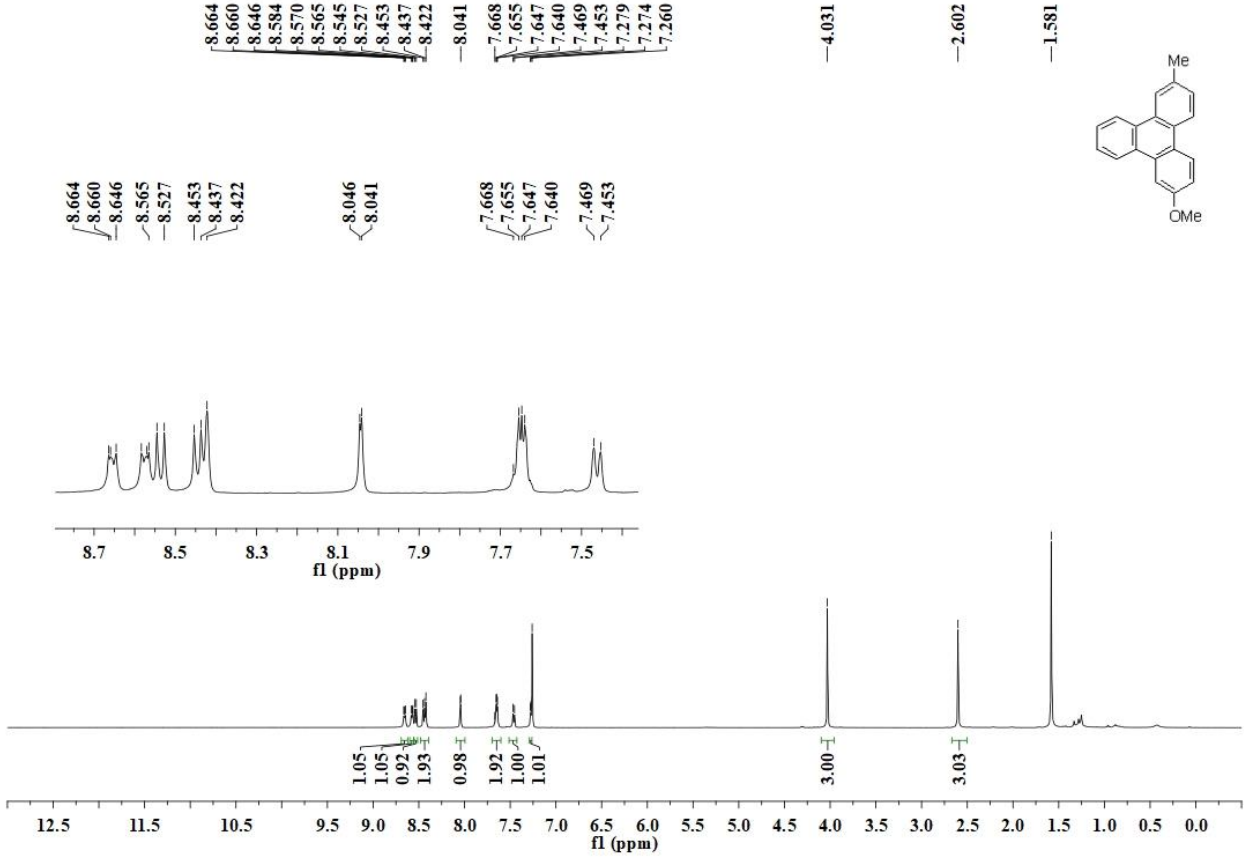


^{1}H NMR (500 MHz, $CDCl_3$) of **3m**



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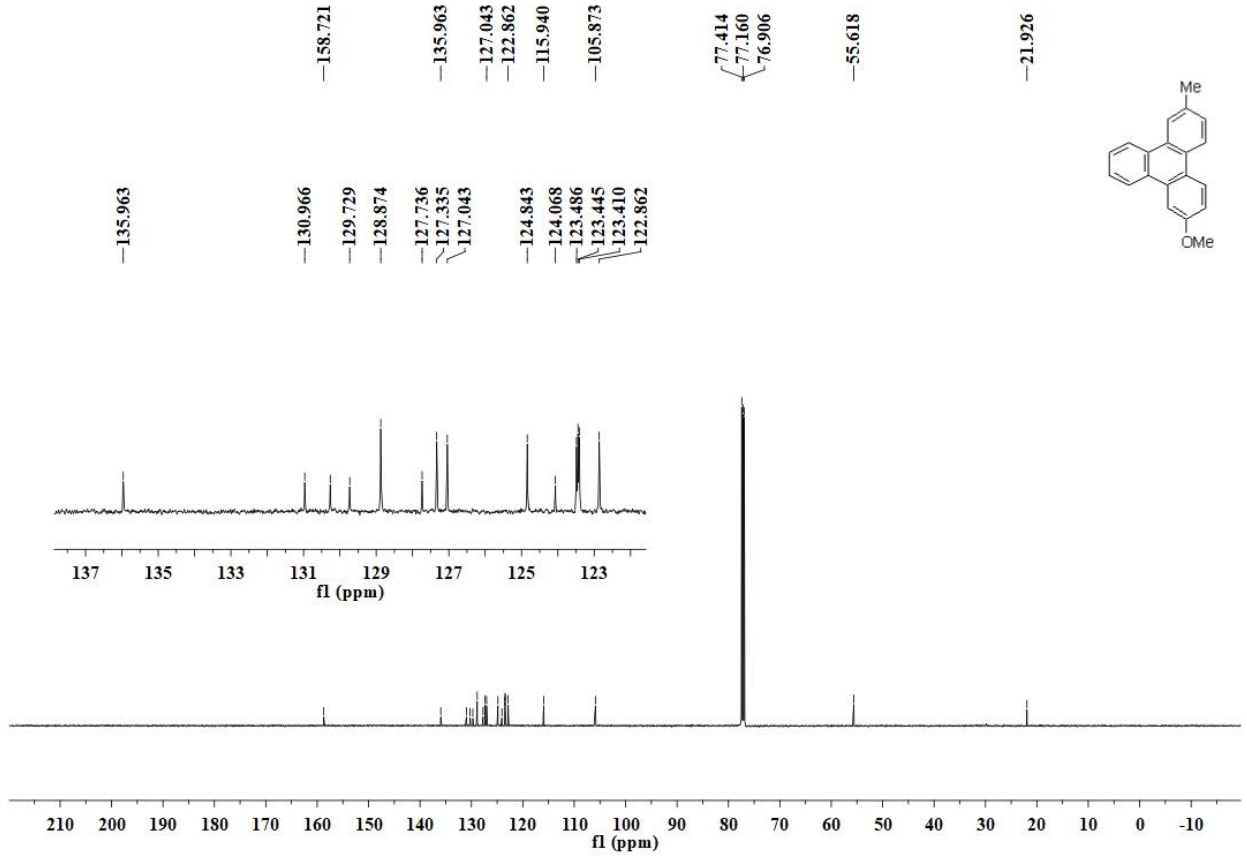

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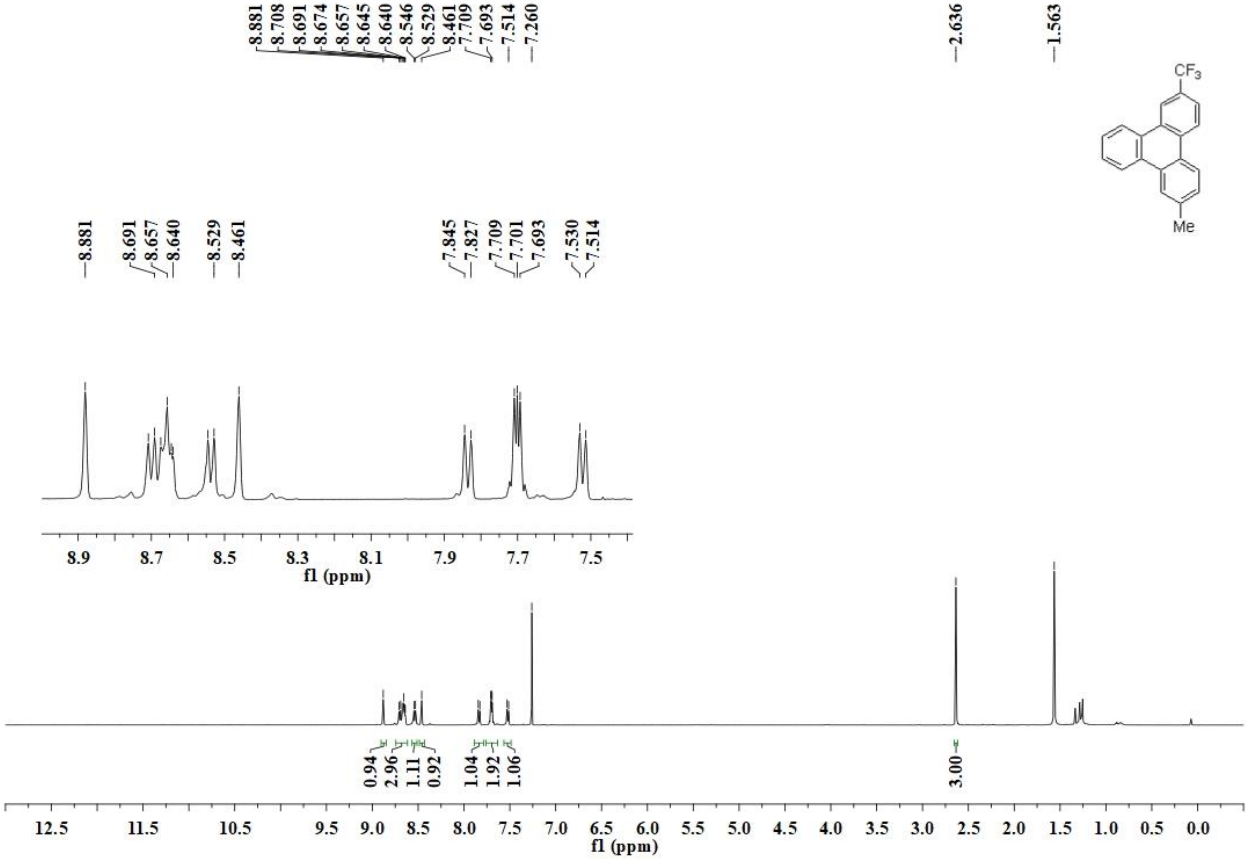

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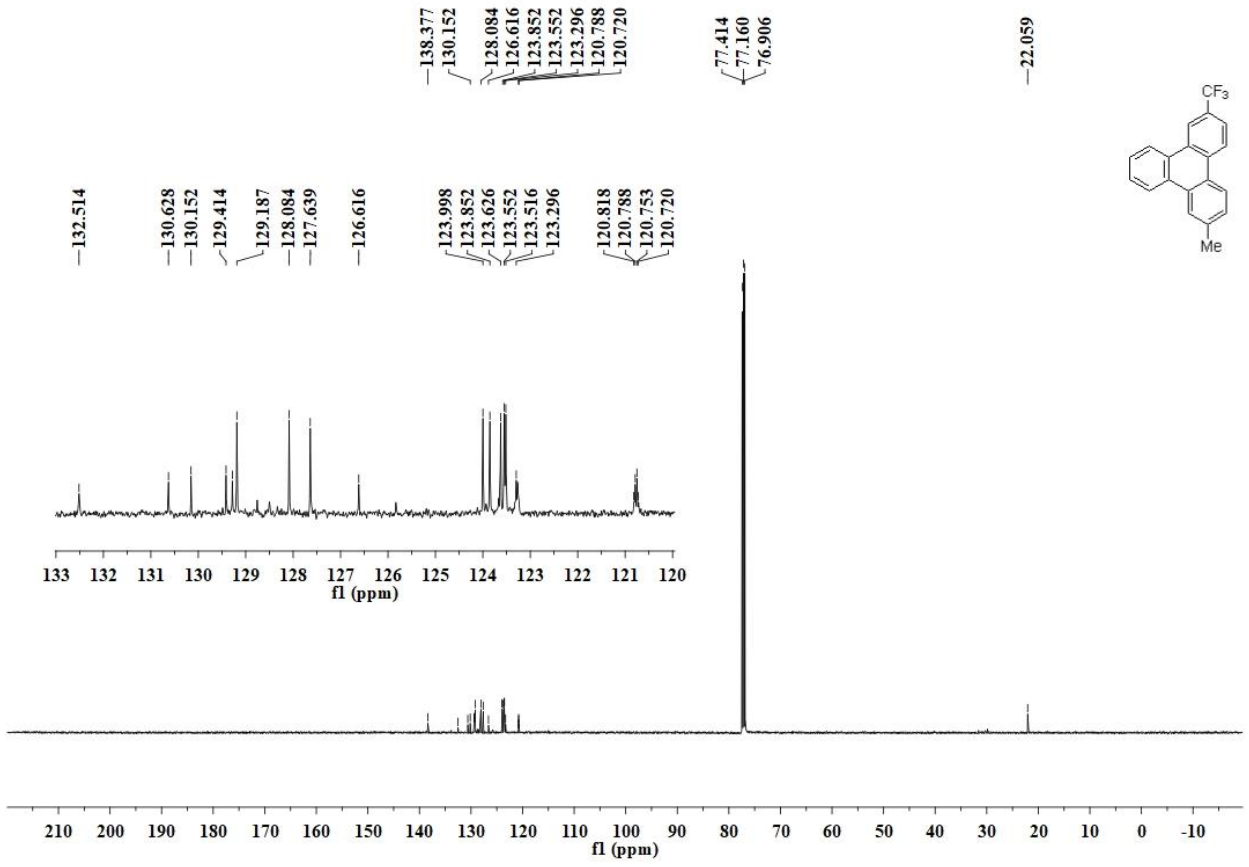
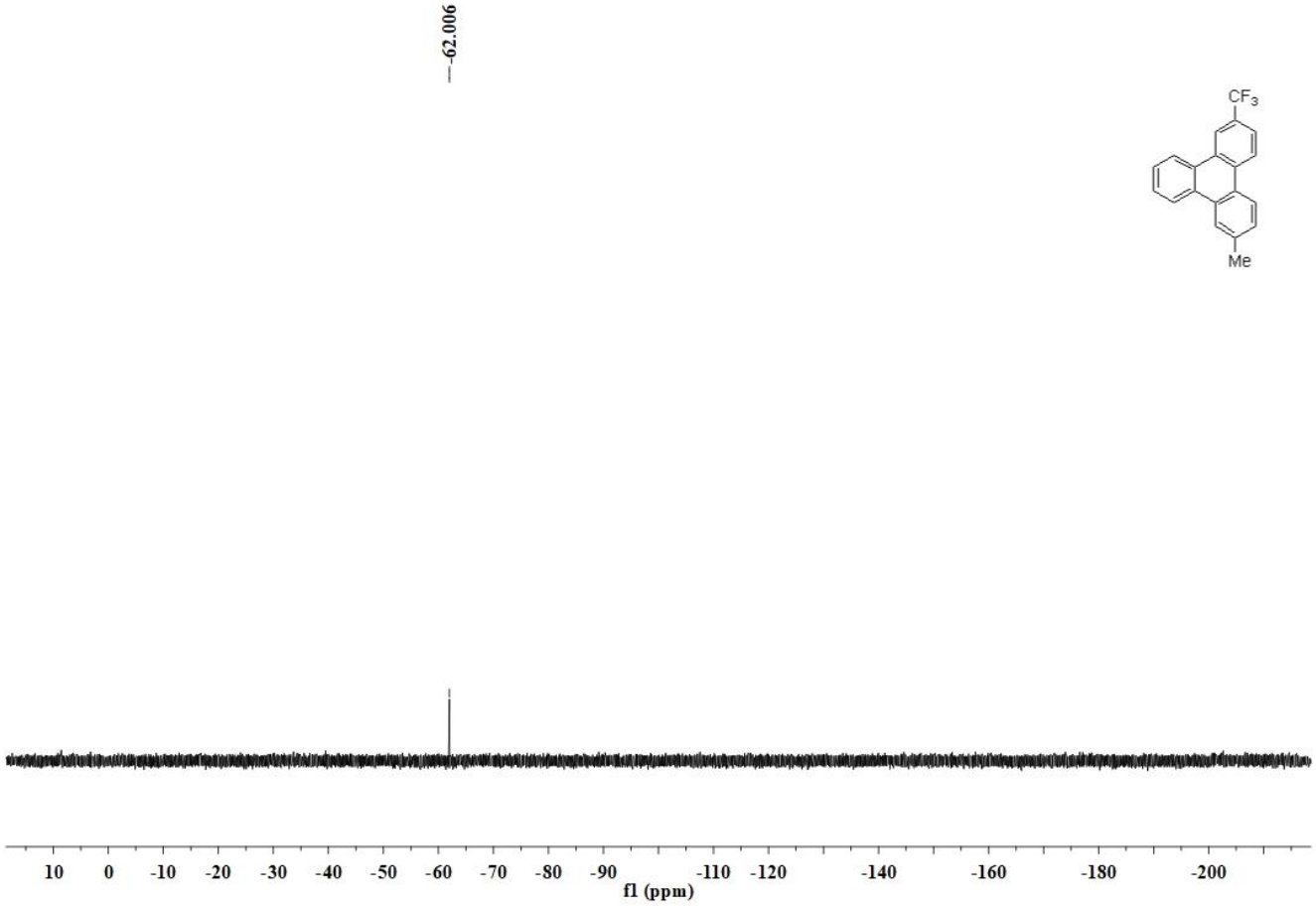


^{19}F NMR (376 MHz, $CDCl_3$) of **3n**



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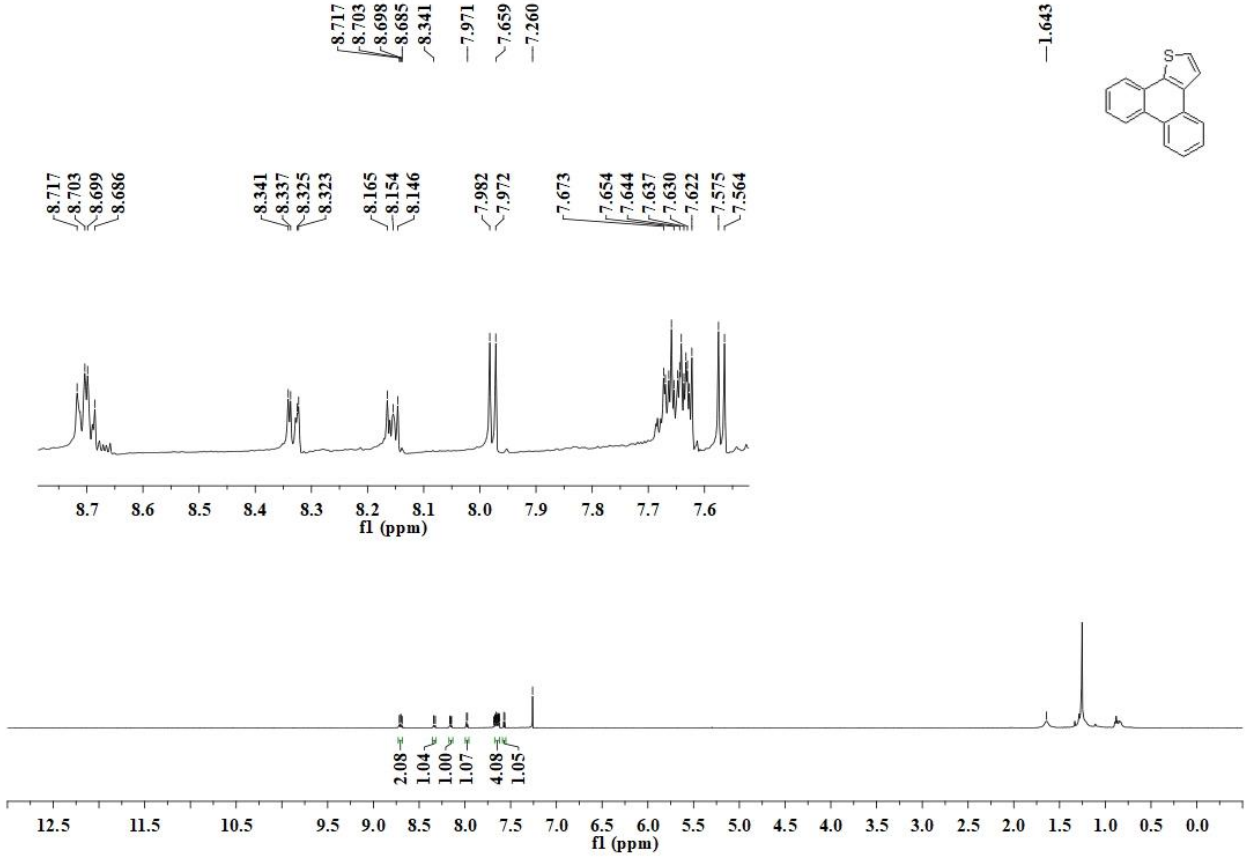

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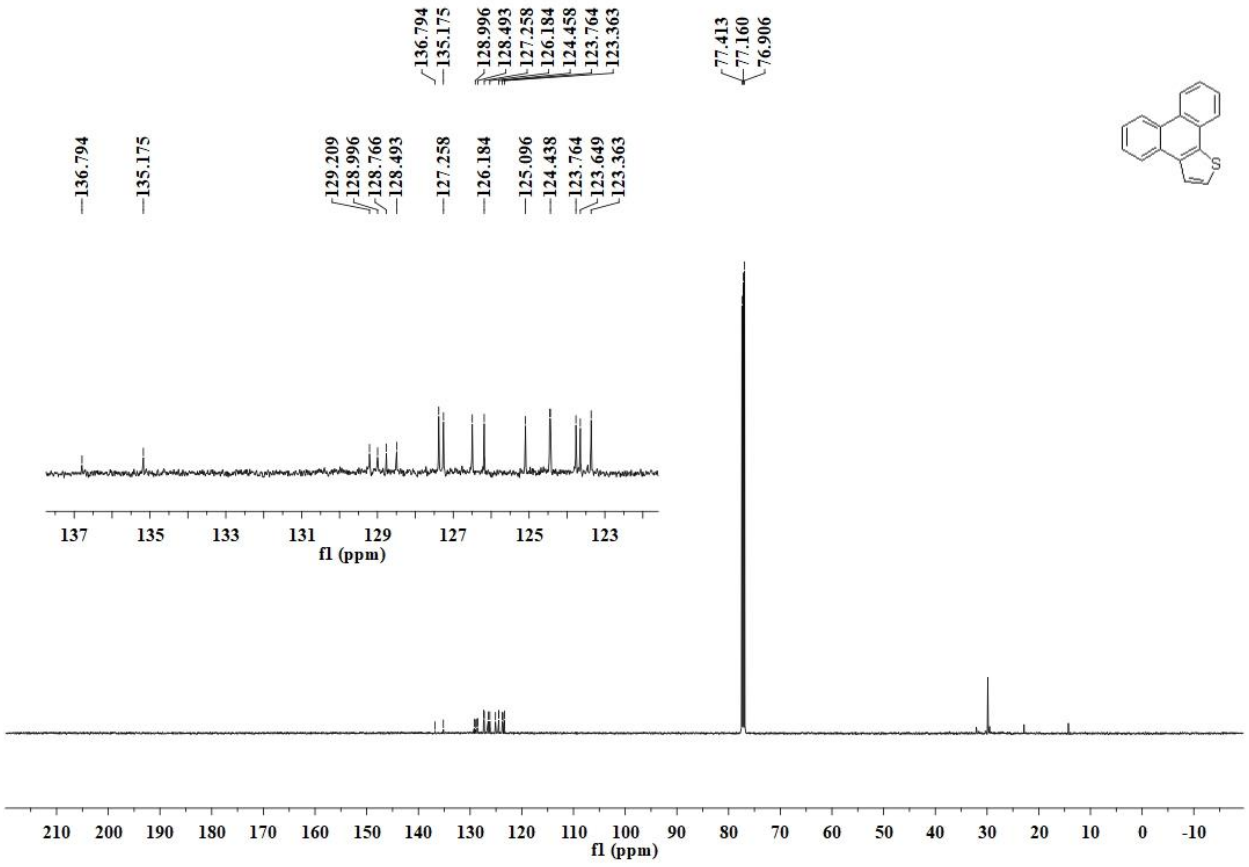

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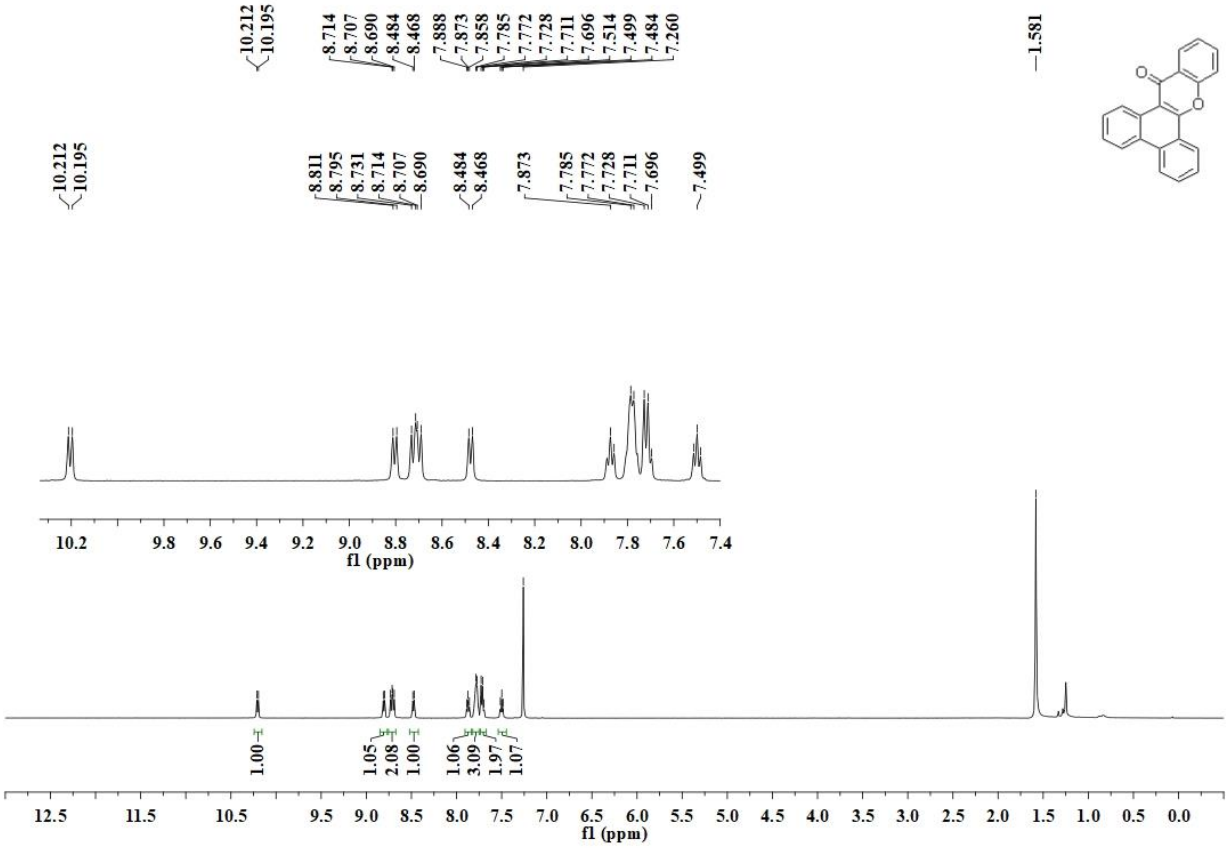

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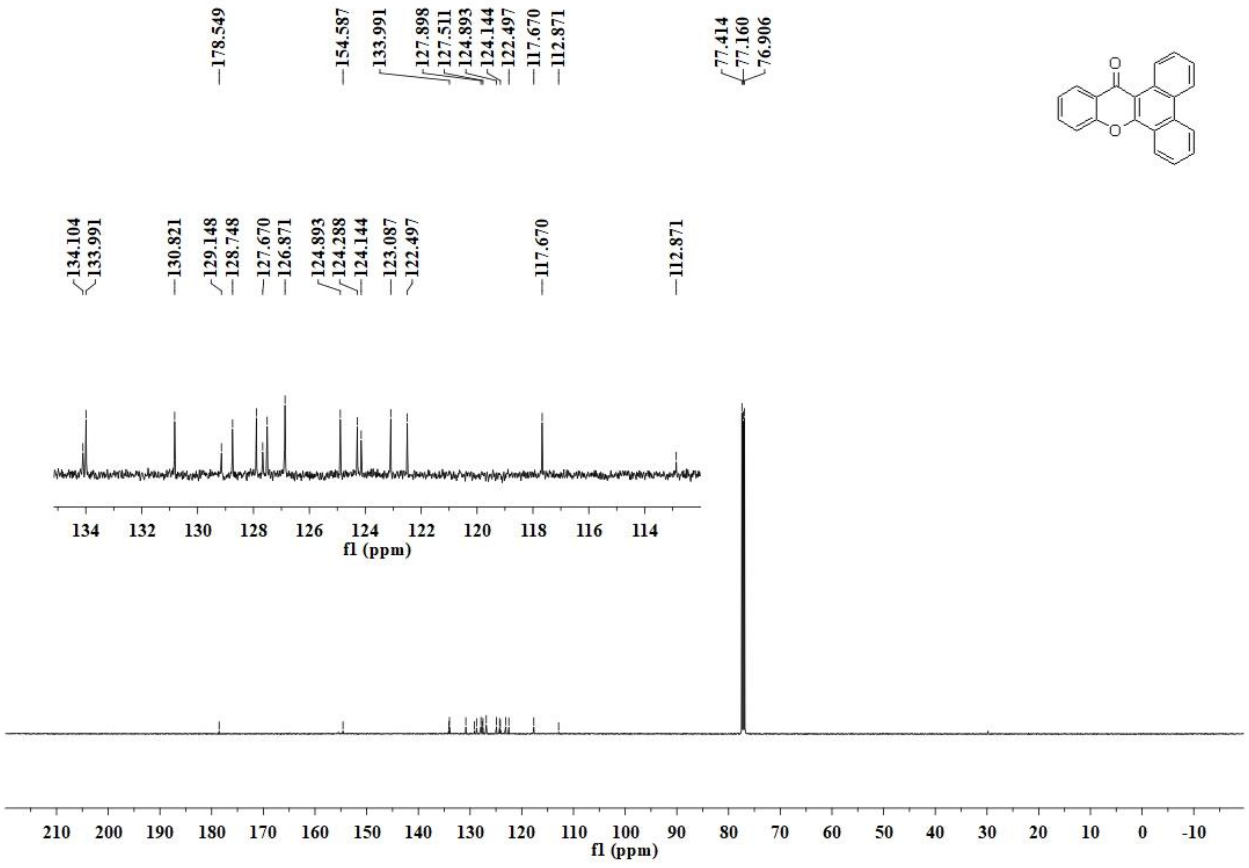
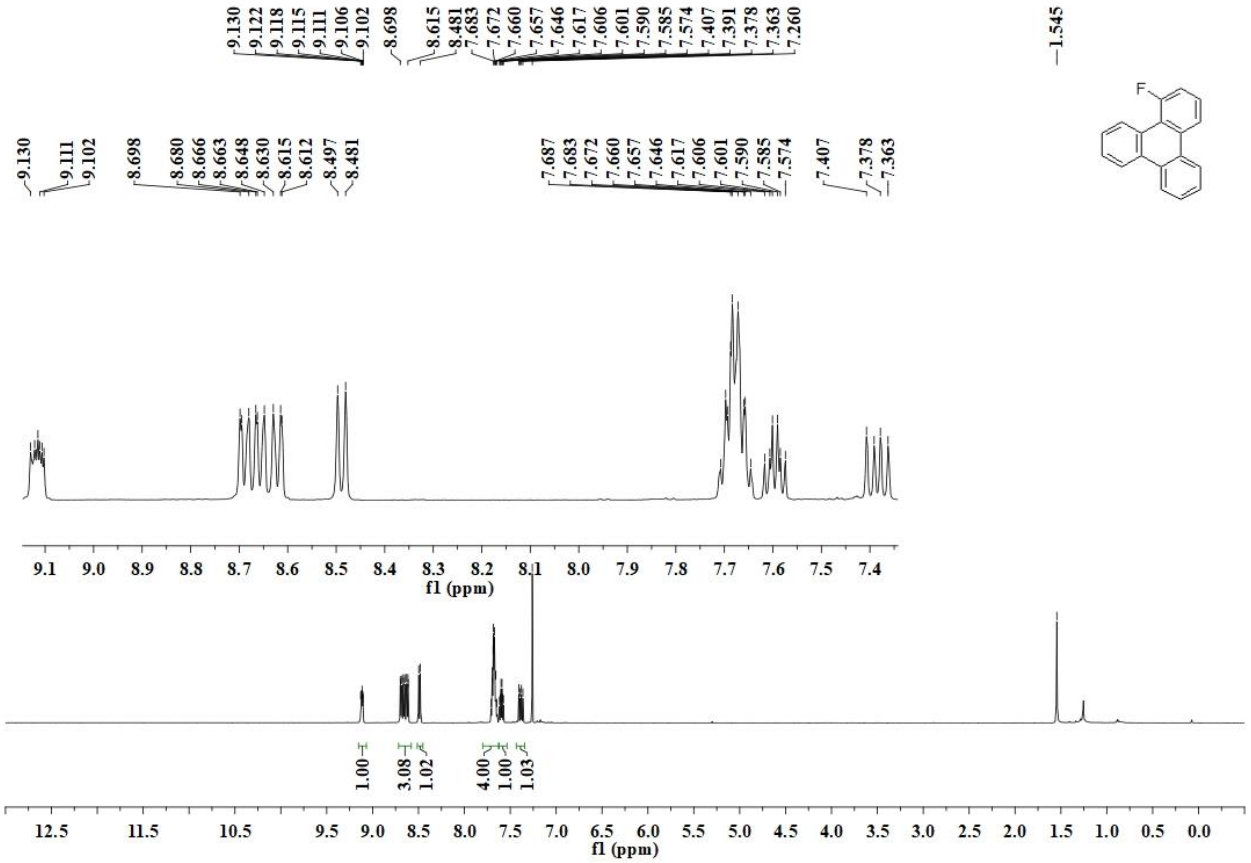


^{1}H NMR (500 MHz, $CDCl_3$) of **4b**



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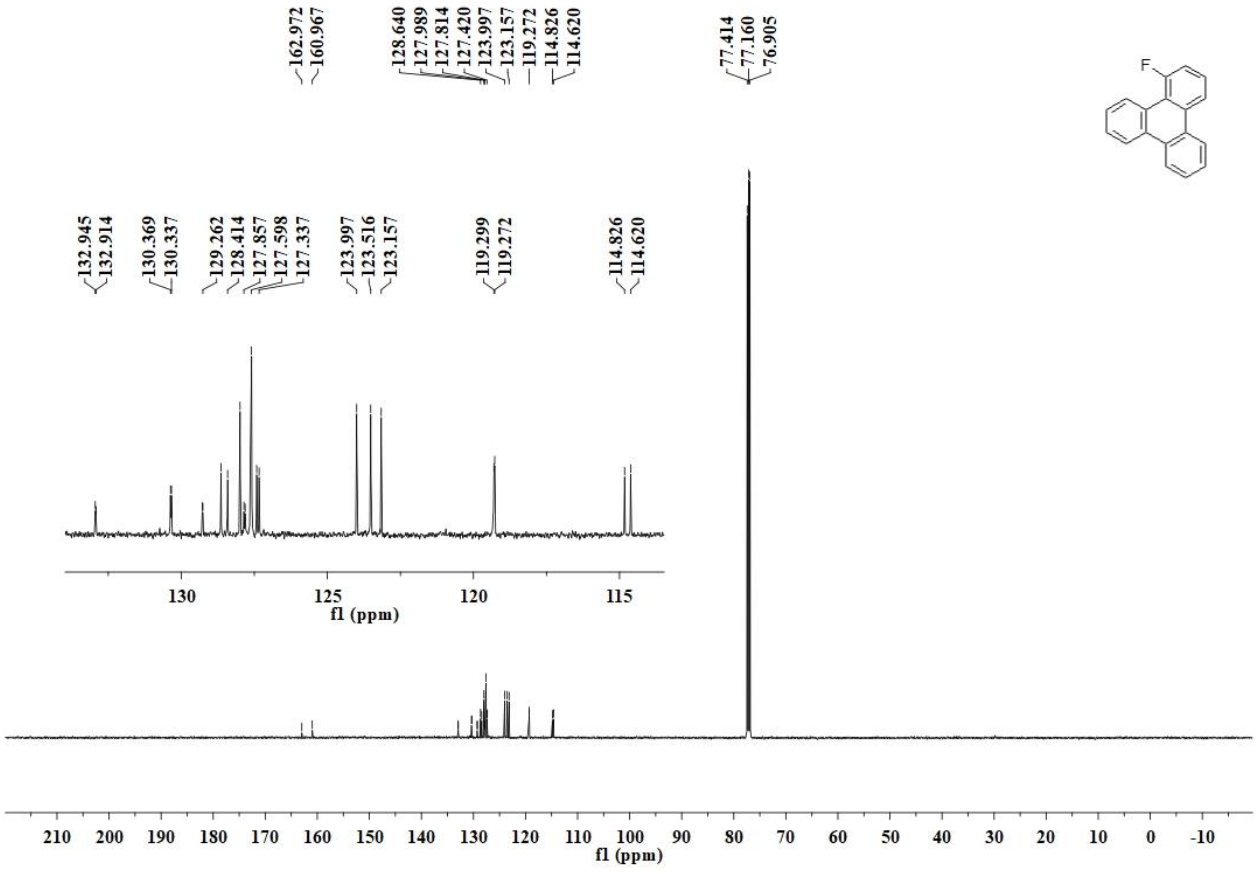

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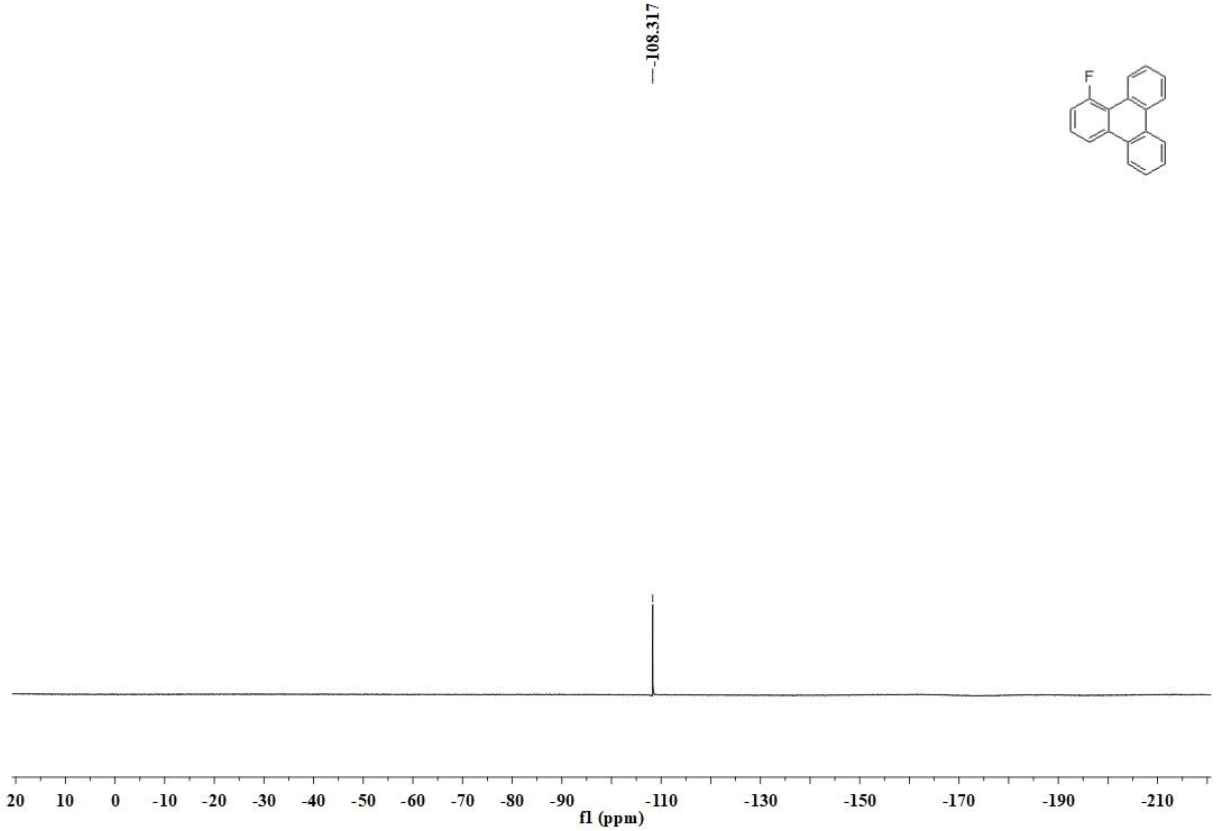

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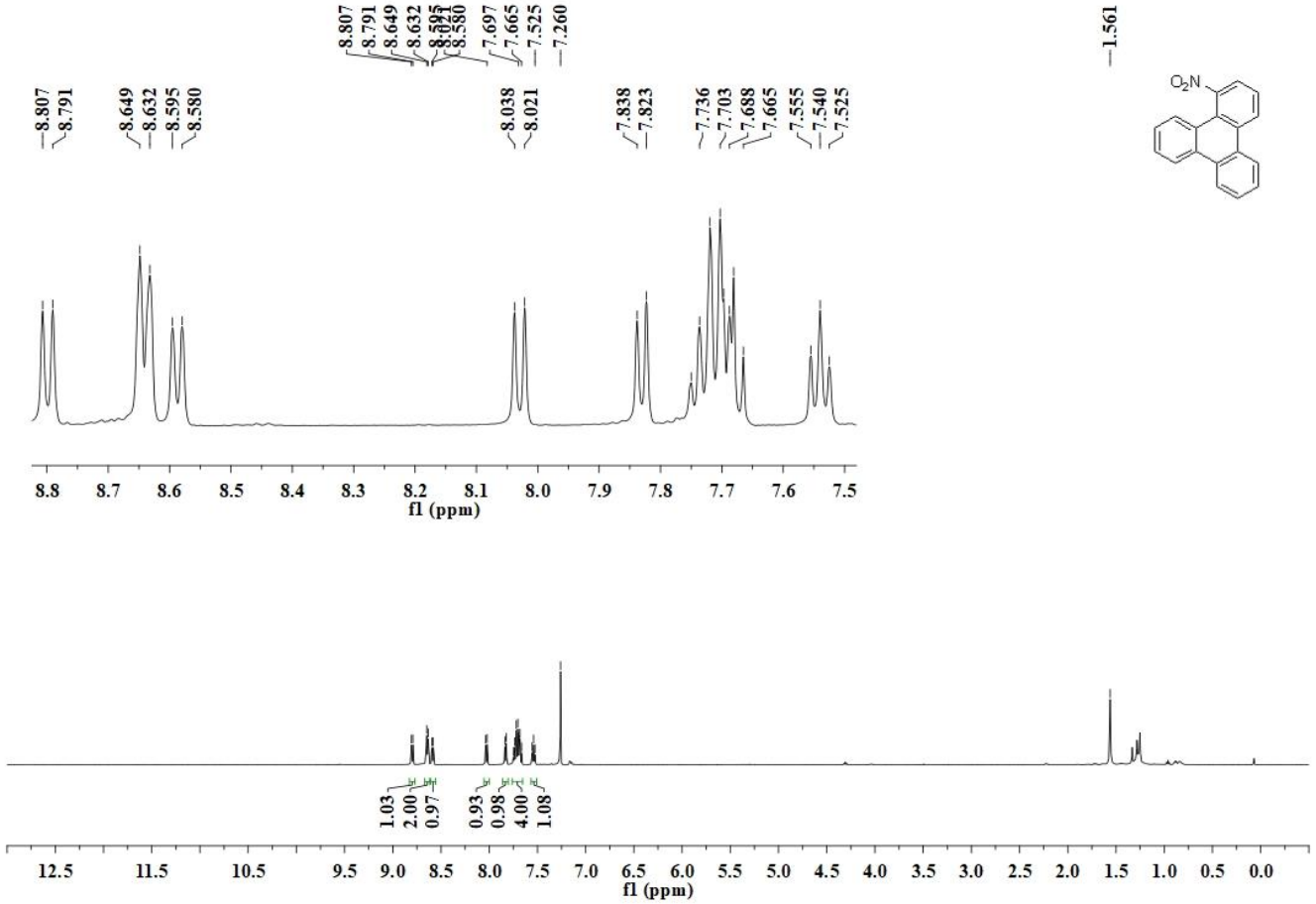

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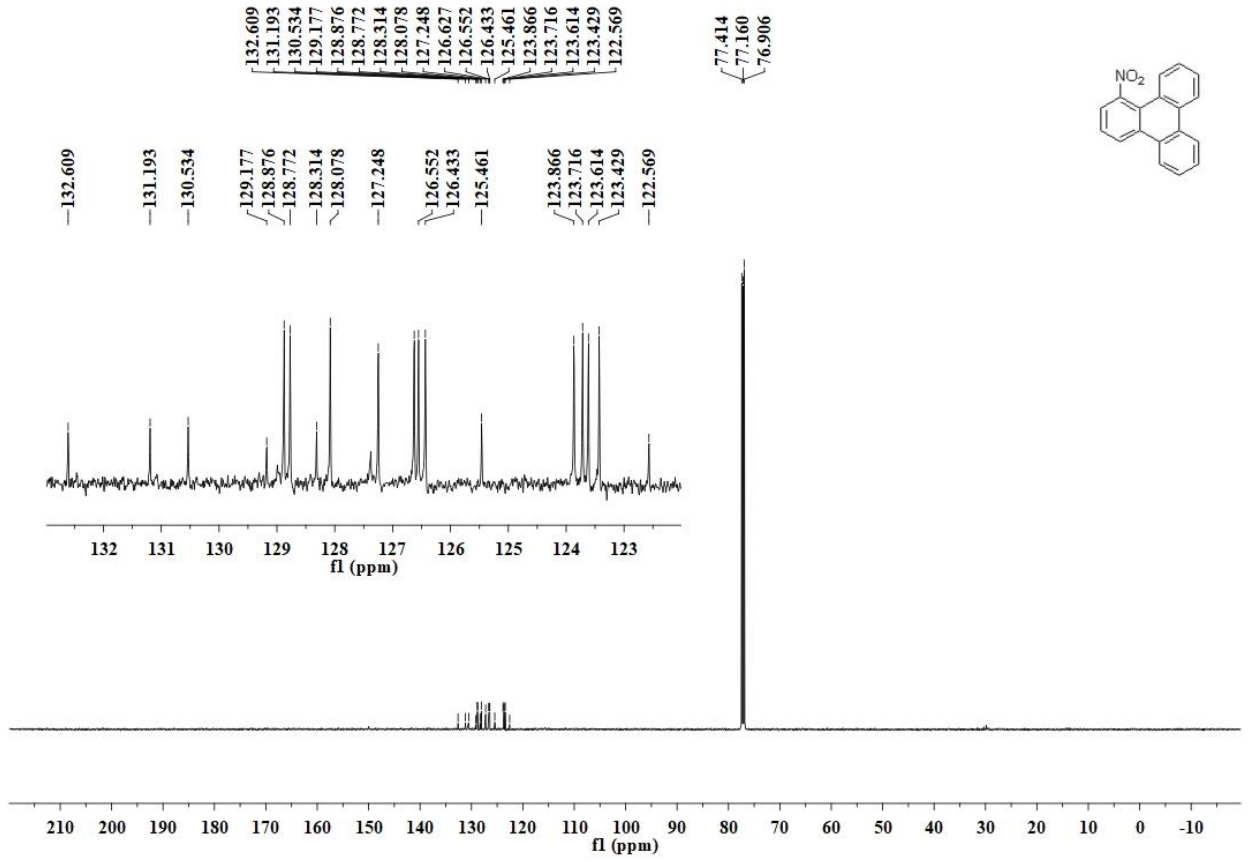

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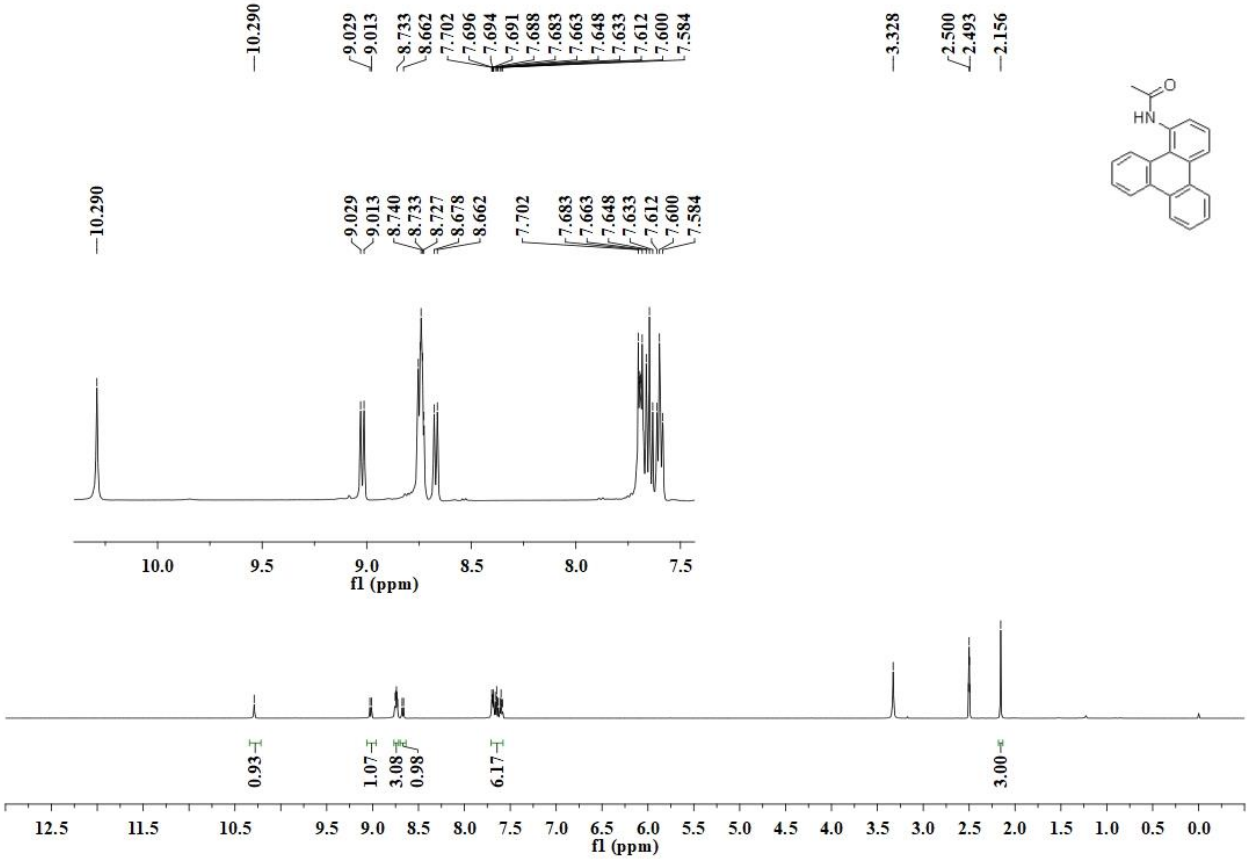
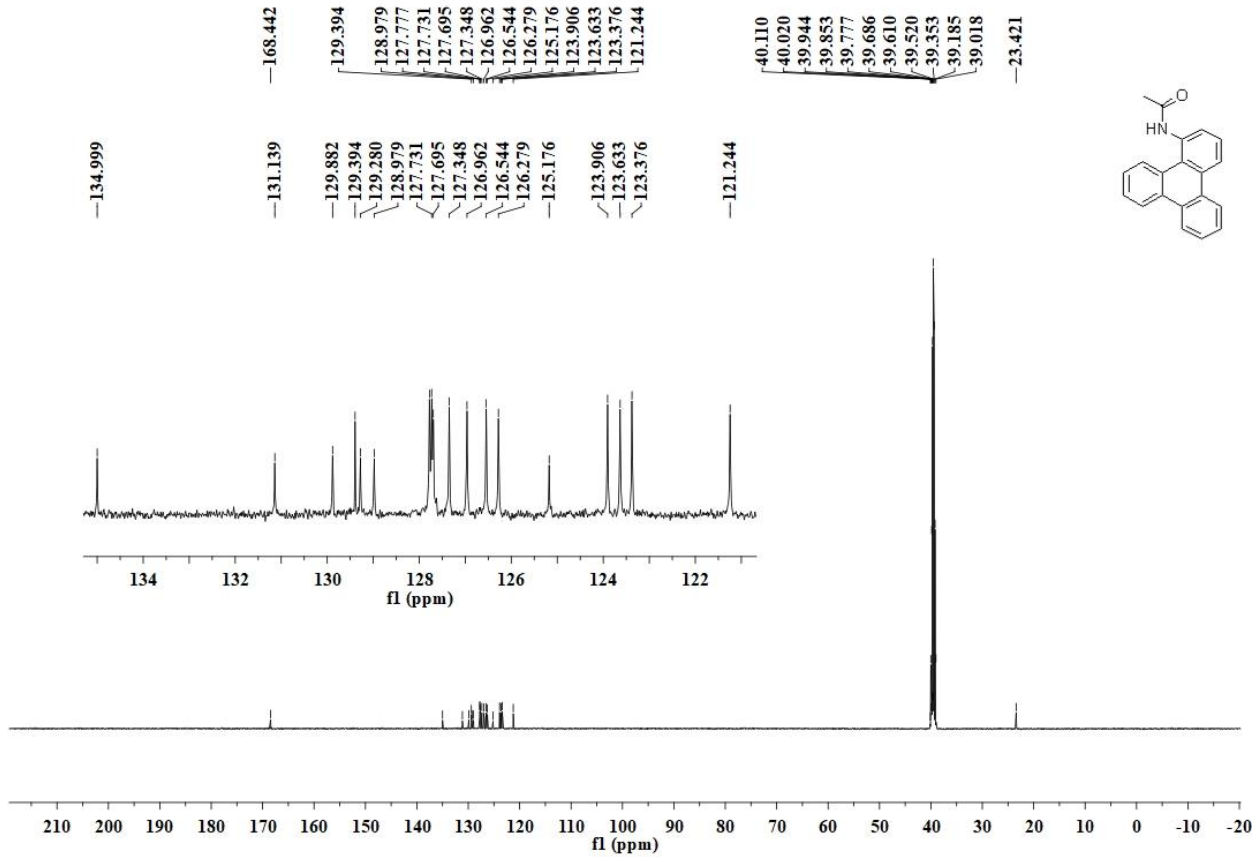
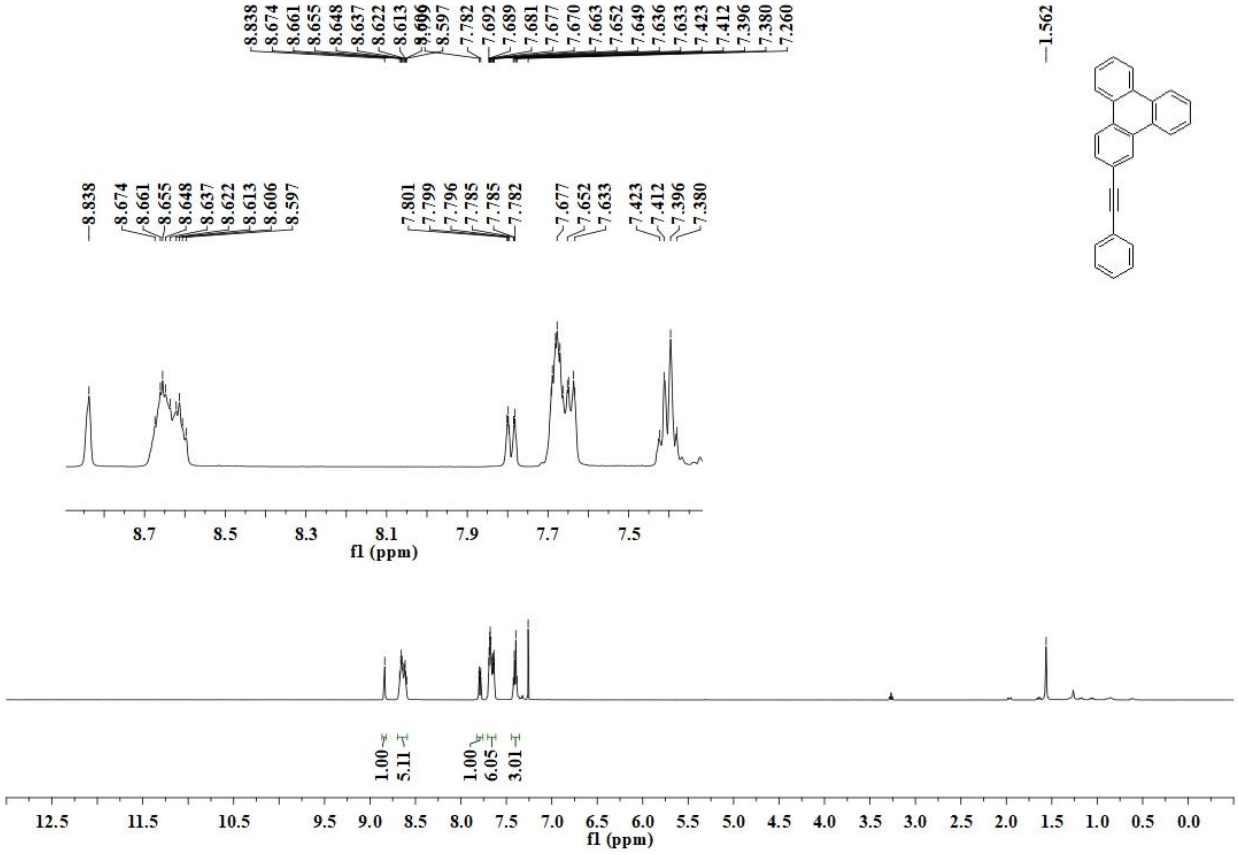


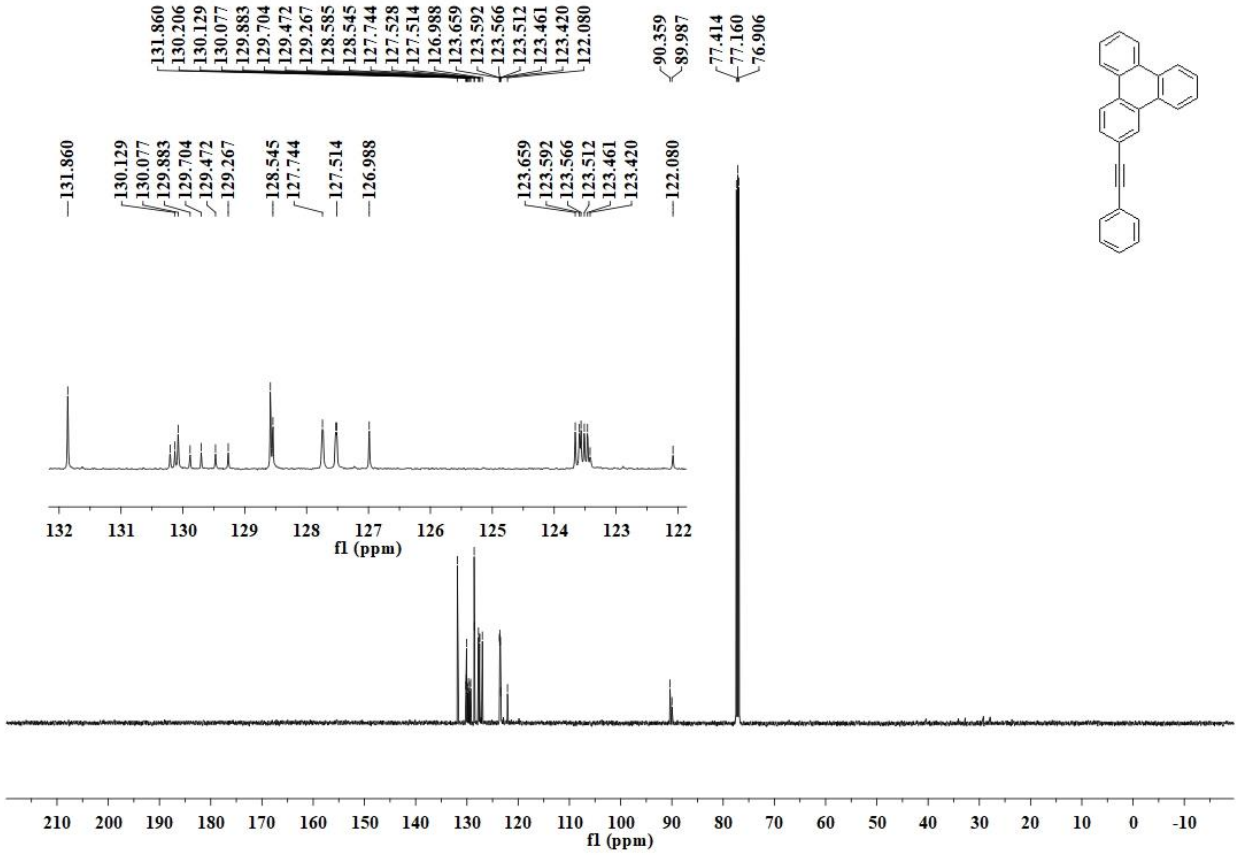
^{13}C NMR (125 MHz, DMSO-*d6*) of **4d**



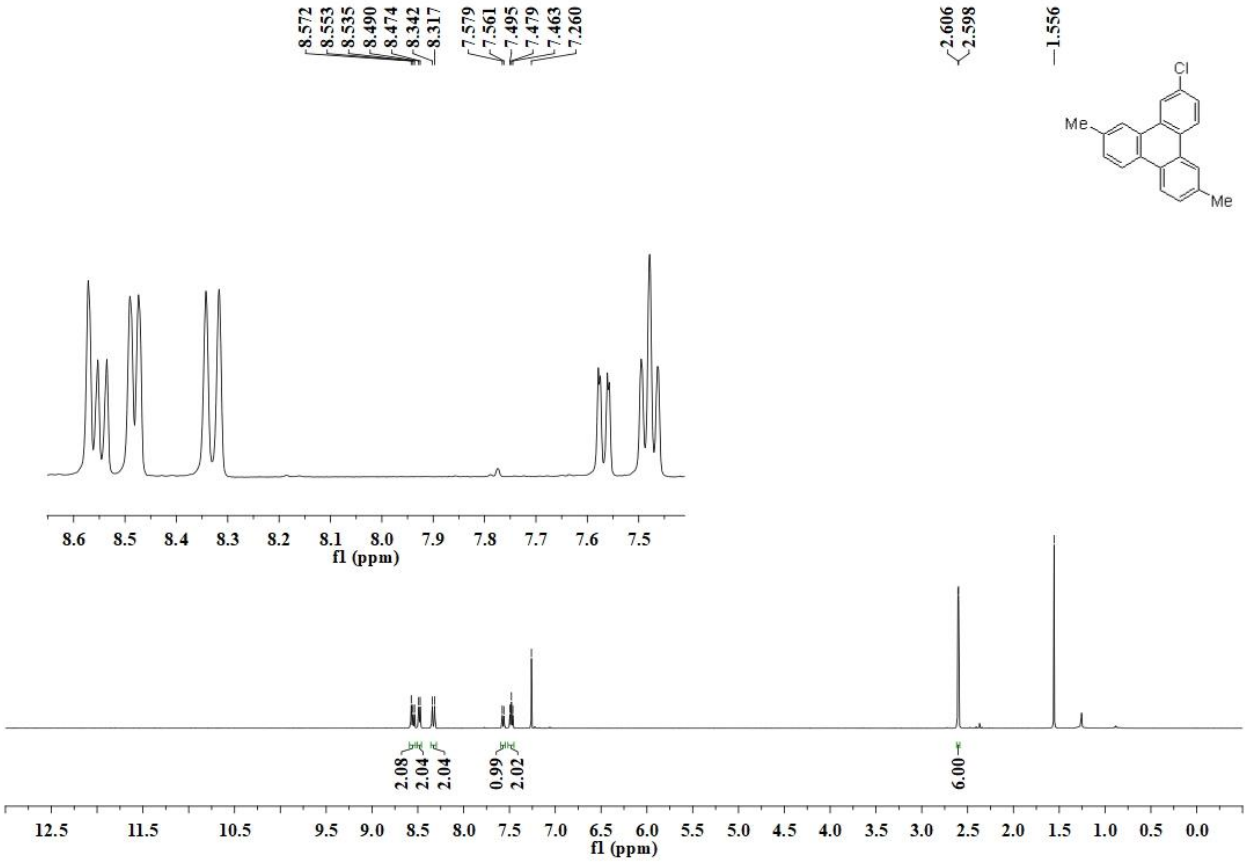
^{1}H NMR (500 MHz, $CDCl_3$) of **4h**



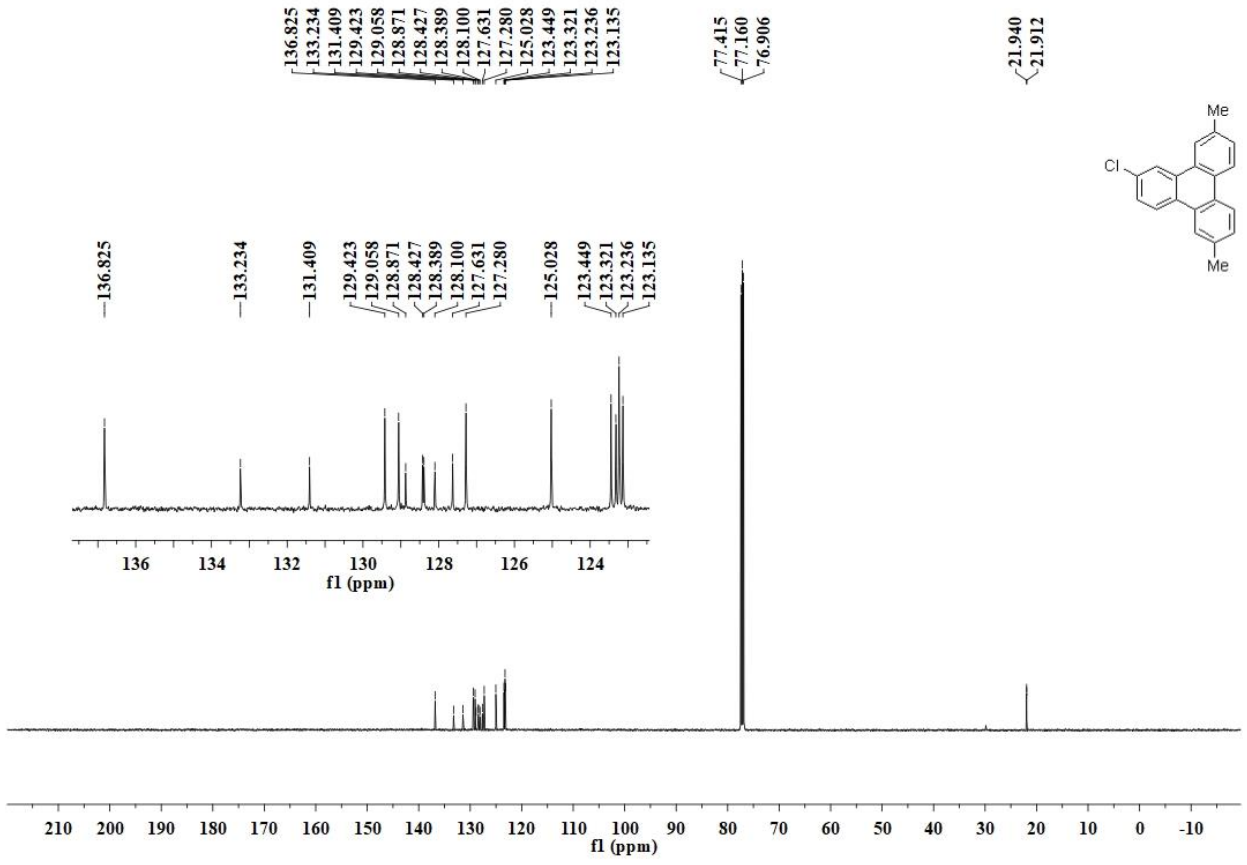
^{13}C NMR (125 MHz, $CDCl_3$) of **4h**



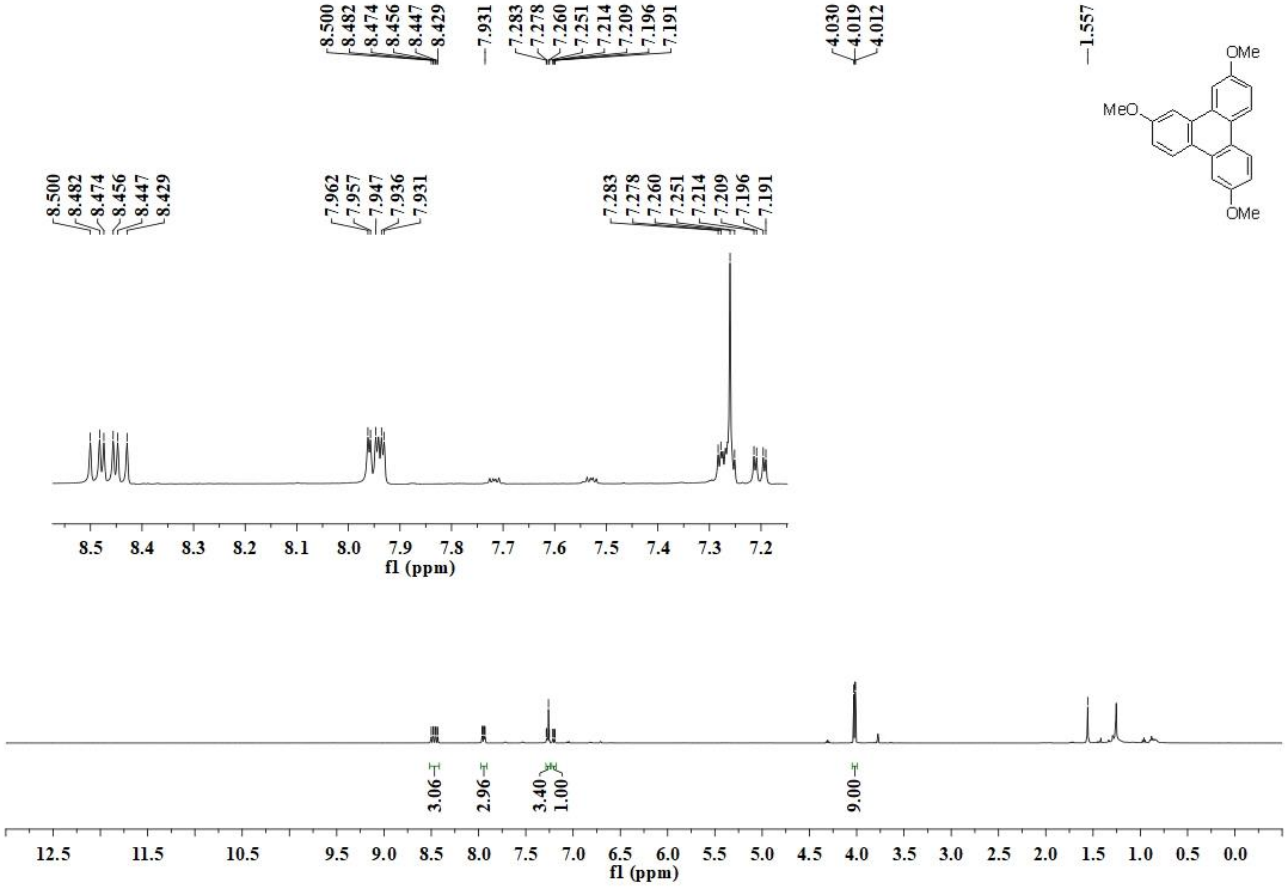
^{1}H NMR (500 MHz, $CDCl_3$) of **4j**



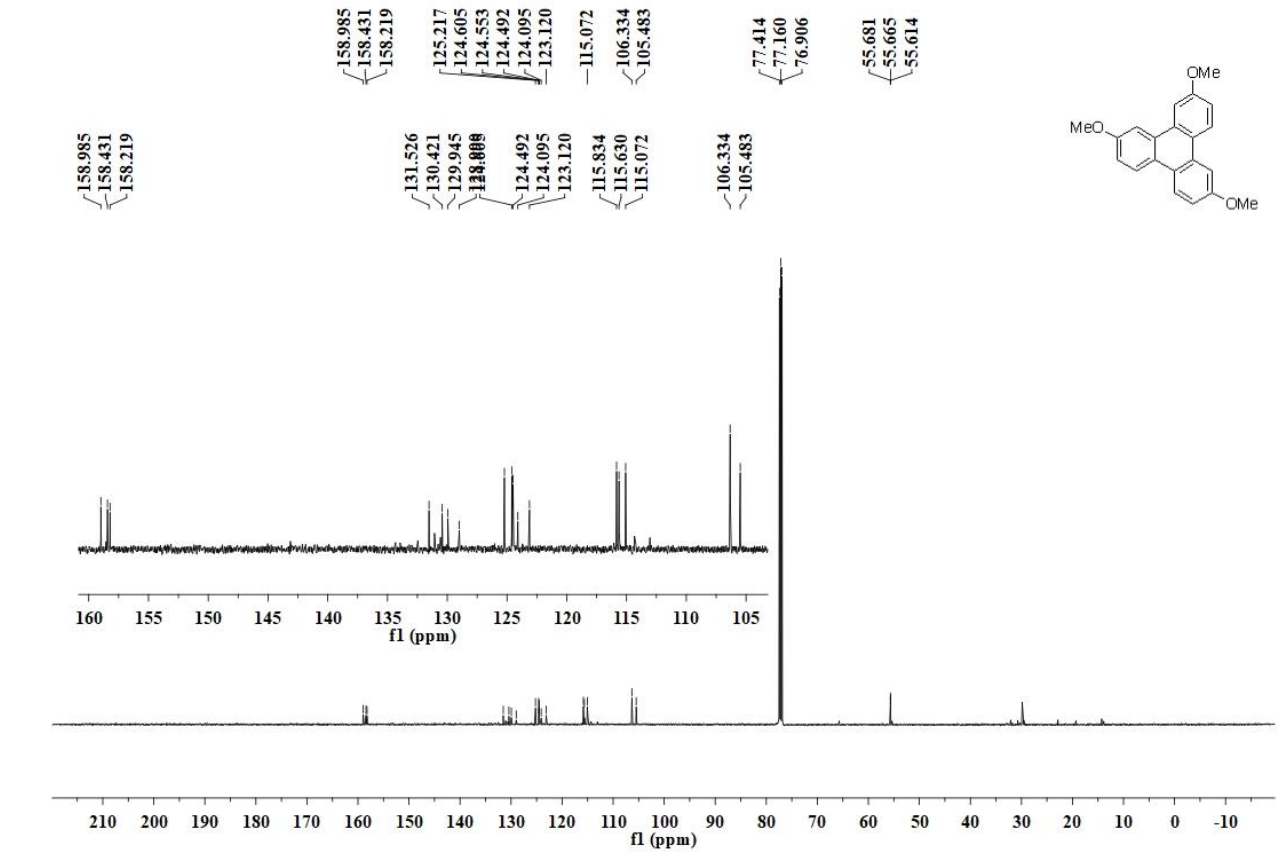
^{13}C NMR (125 MHz, $CDCl_3$) of **4j**



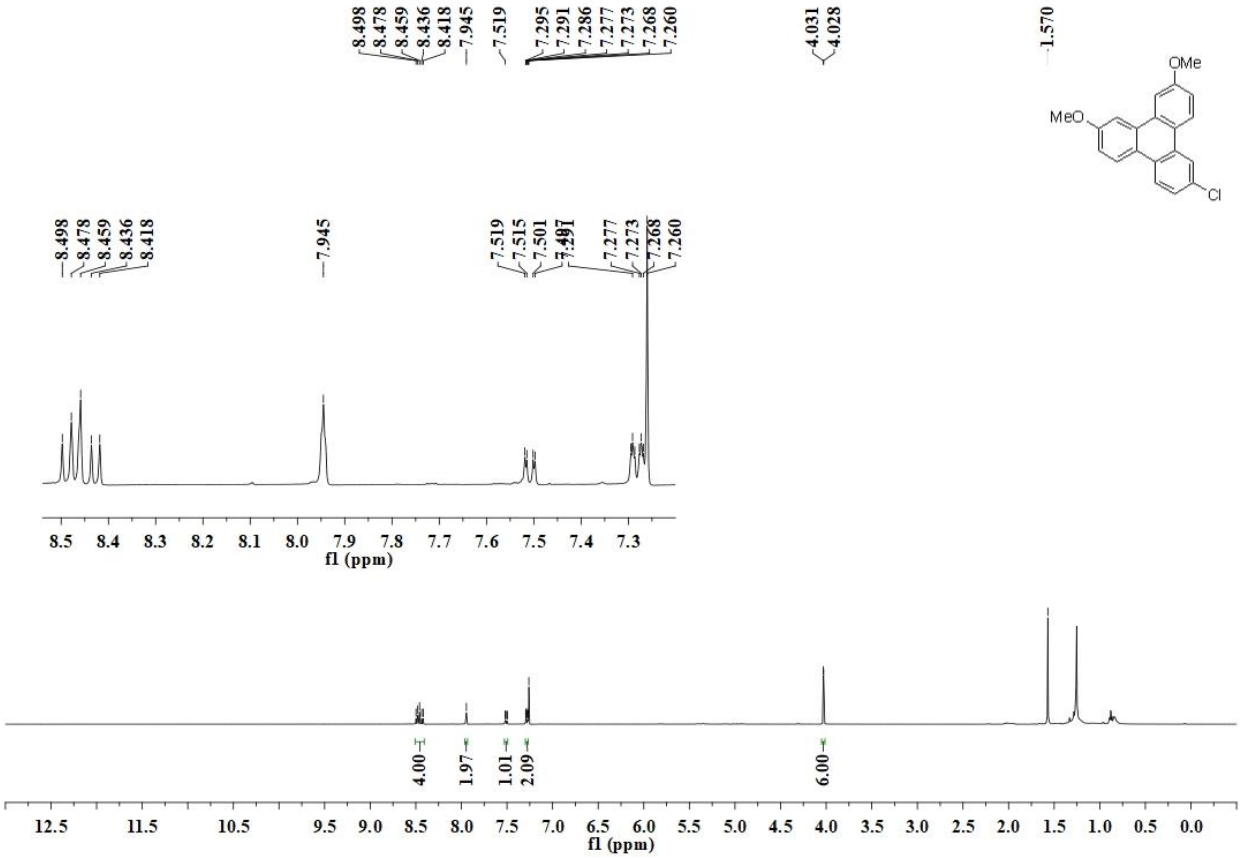
^{1}H NMR (500 MHz, $CDCl_3$) of **4k**



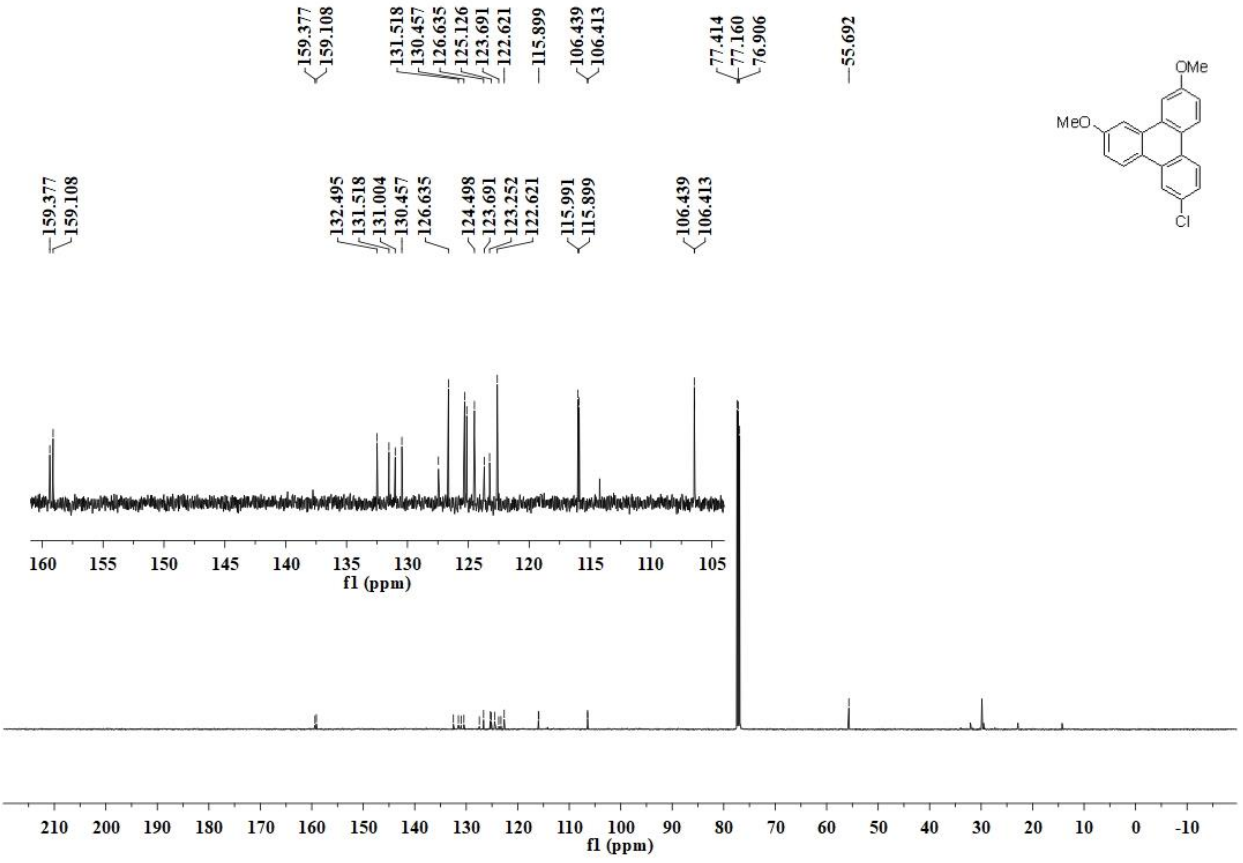
^{13}C NMR (125 MHz, $CDCl_3$) of **4k**



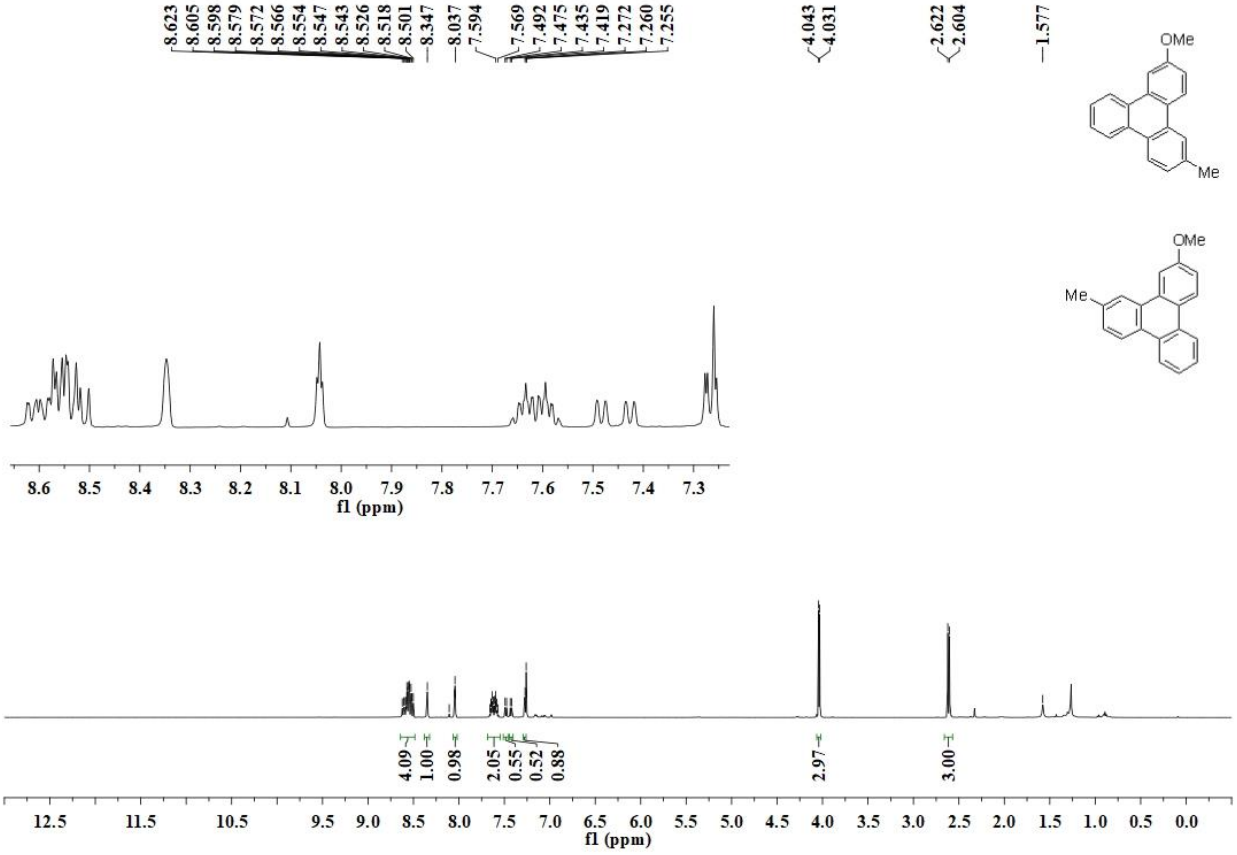
^{1}H NMR (500 MHz, $CDCl_3$) of **4l**



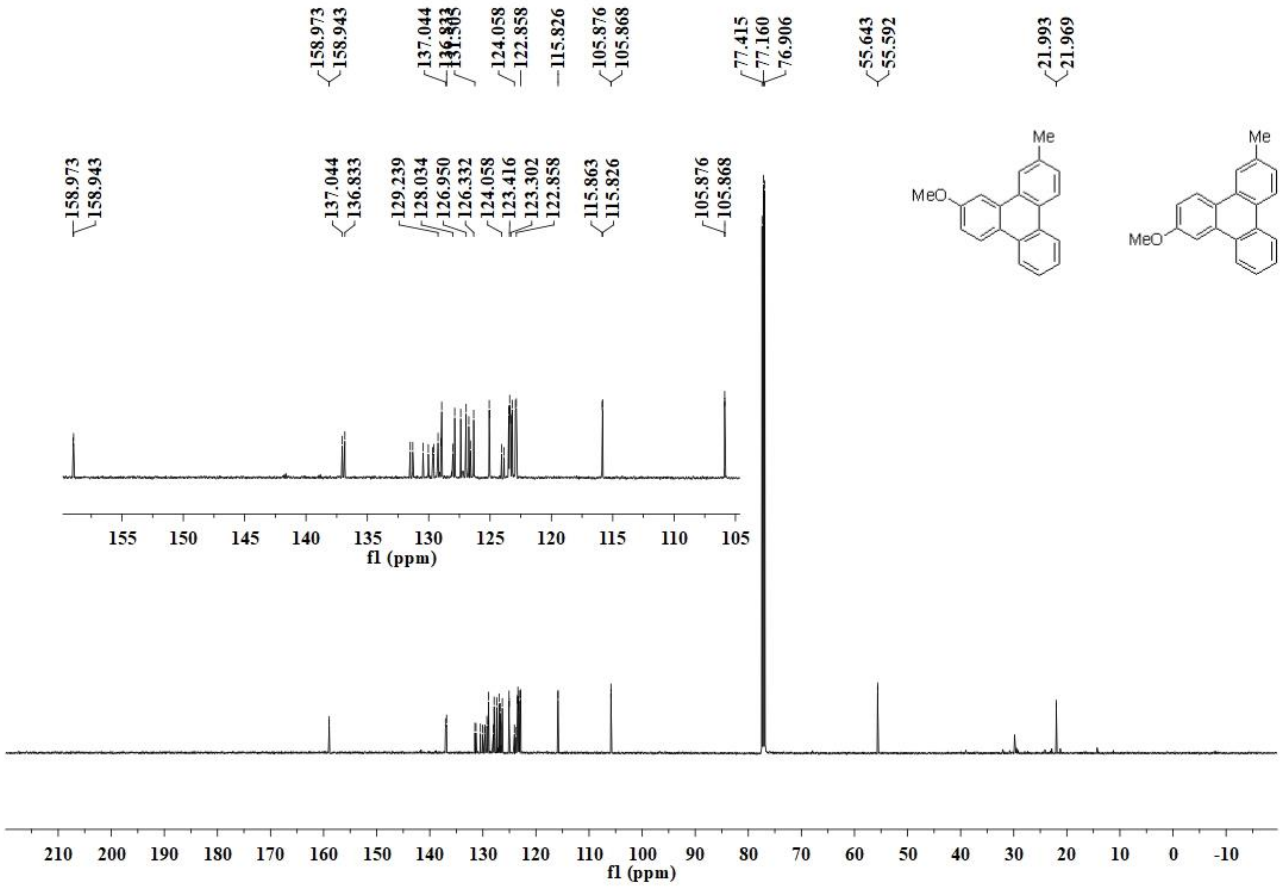
^{13}C NMR (125 MHz, $CDCl_3$) of **4l**



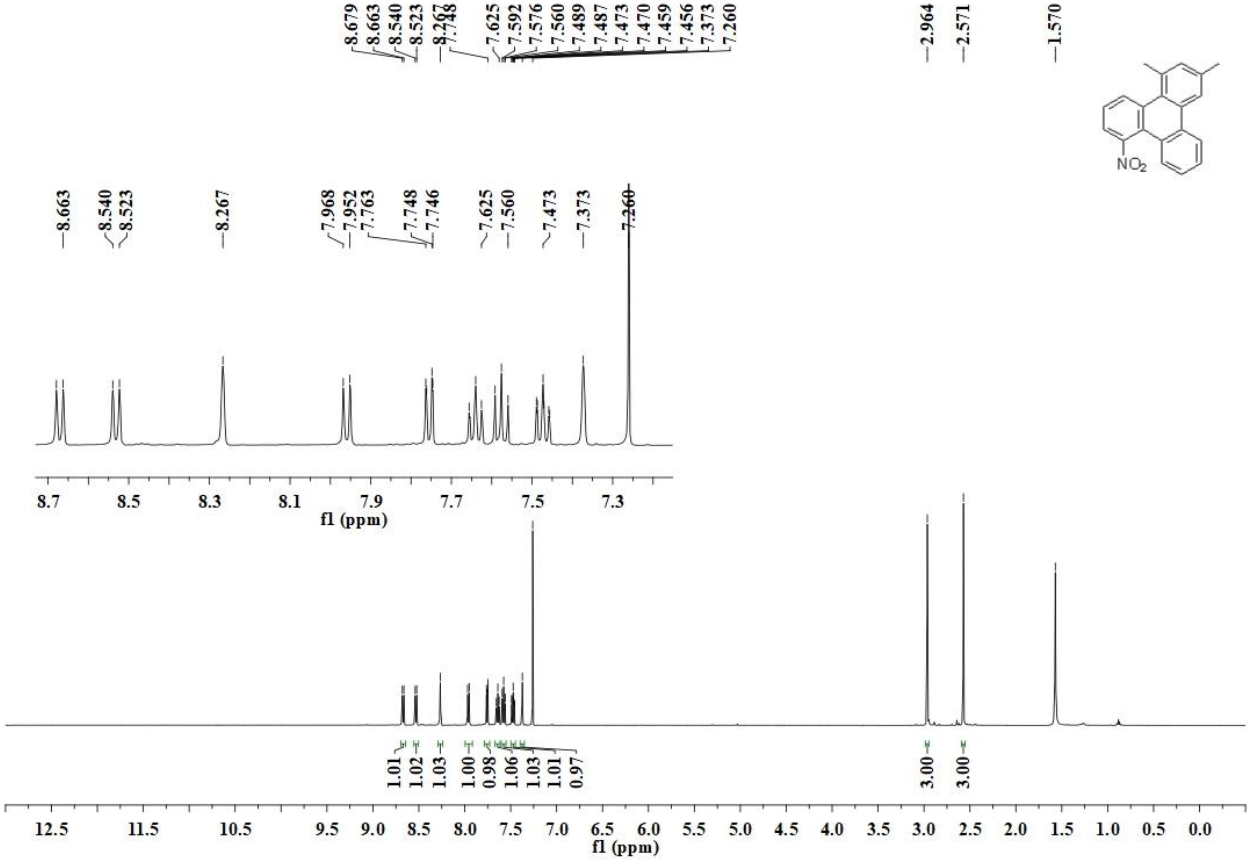
^{1}H NMR (500 MHz, $CDCl_3$) of **4m**



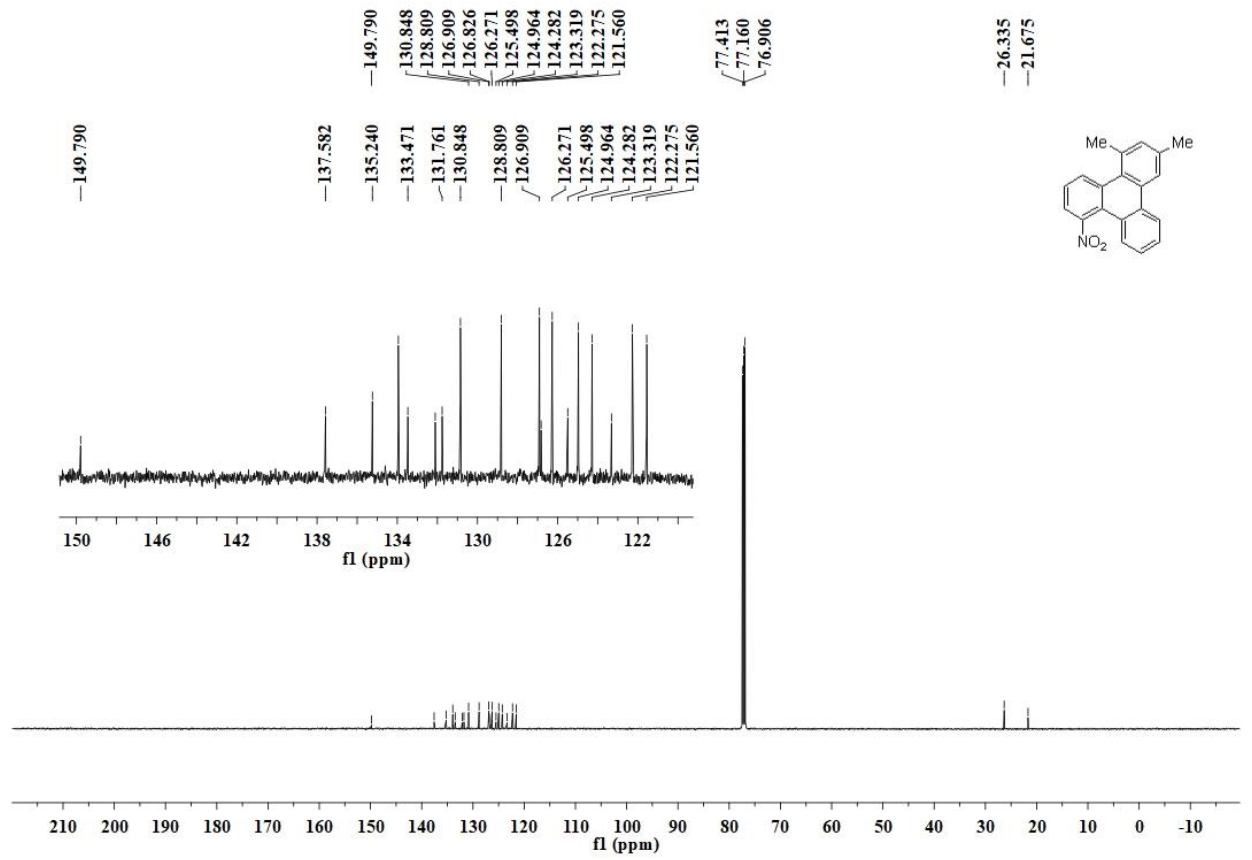
^{13}C NMR (125 MHz, $CDCl_3$) of **4m**



^{1}H NMR (500 MHz, $CDCl_3$) of **4n**



^{13}C NMR (125 MHz, $CDCl_3$) of **4n**



H-H NOESY (500 MHz, $CDCl_3$) of **4n**