Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information for

Rhodium-Catalyzed Oxidative Coupling of N-Acyl Anilines with Alkynes Using an Acylamino Moiety as the Traceless Directing Group

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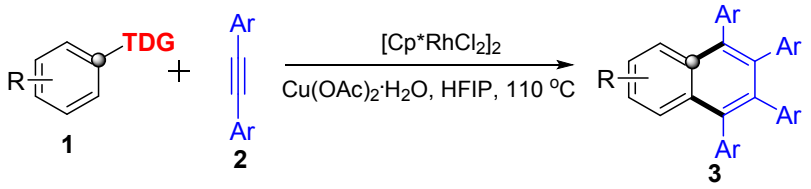
1. General Experimental Information

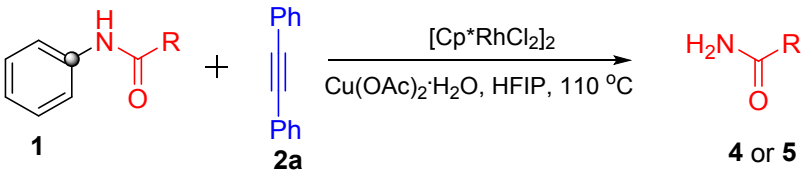
All reactions were performed in flame-dried glassware using sealed tube or Schlenk tube. Liquids and solutions were transferred with syringes. All solvents and chemical reagents were obtained from commercial sources and used without further purifications. ^{1}H and ^{13}C NMR spectra were recorded with tetramethylsilane as an internal reference. Low and high-resolution mass spectra were obtained in the EI mode. Flash column chromatography on silica gel (200-300 mesh) was used for the routine purification of reaction products. The column output was monitored by TLC on silica gel (100-200 mesh) precoated on glass plates (15 x 50 mm), and spots were visualized by UV light at 254 or 365 nM. Commercially available chemicals were obtained from Adamas-beta, Acros Organics, Strem Chemicals, Alfa Aesar, J&K and TCI. Starting materials (amides and alkynes) were prepared according to the literature procedures.[1,2]

2. General Procedure for the Oxidative Coupling of Amides with Alkynes



$Cu(OAc)_2$•H_2O (100 mg, 0.50 mmol), $[Cp^*RhCl_2]_2$ (15 mg, 5 mol%) and internal alkynes **2** (1.00 mmol) were added to a stirred solution of amides **1** (0.50 mmol) in HFIP (2.5 mL), the mixture was heated at 110 °C in a sealed tube till the starting material disappeared. After cooled to room temperature, the reaction mixture was filtered and the filtrate was concentrated. The residue was purified on a silica gel column with petroleum ether as the eluent to afford highly substituted naphthalenes **3**.

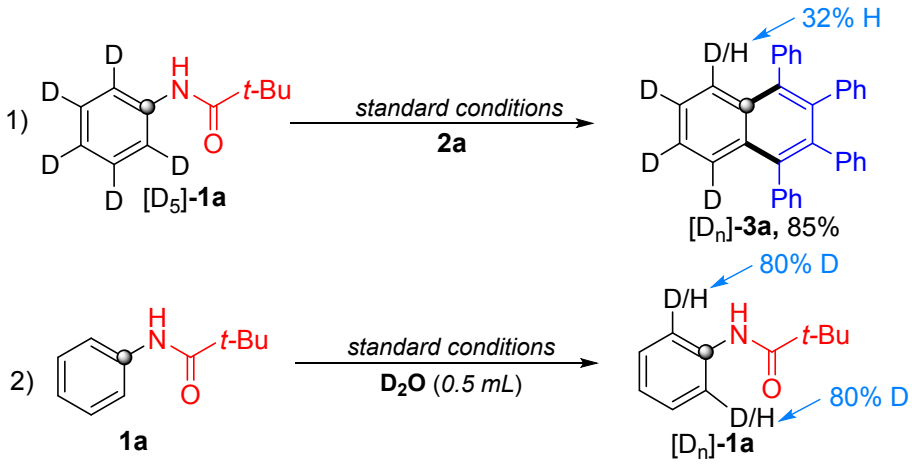
3. General Procedure for Synthesis of 4 and 5



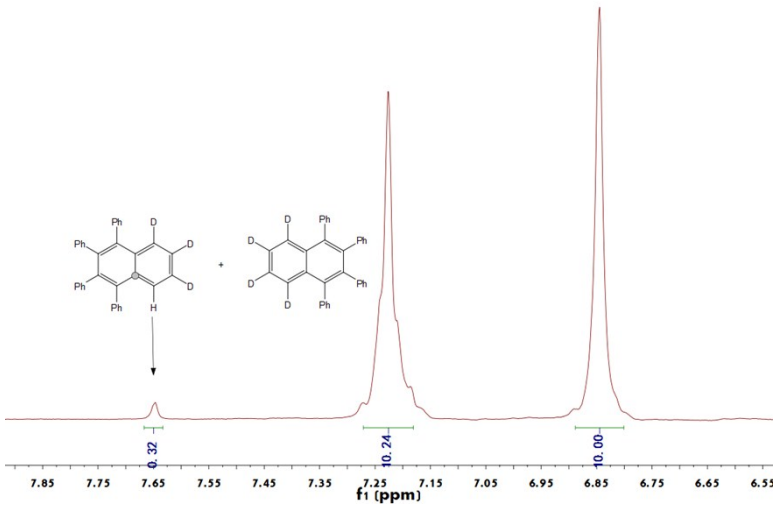
$Cu(OAc)_2$•H_2O (100 mg, 0.50 mmol), $[Cp^*RhCl_2]_2$ (15 mg, 5 mol%) and diphenylacetylene (**2a)**

(178 mg, 1.00 mmol) were added to a stirred solution of amides **1** (0.50 mmol) in HFIP (2.5 mL), the mixture was heated at 110 °C in a sealed tube till the starting material disappeared. After cooled to room temperature, the reaction mixture was filtered and the filtrate was concentrated. The residue was purified on a silica gel column using petroleum ether/ethyl acetate (2:1, v/v) as eluent to afford the *N*-dearylated product **4** or **5**.

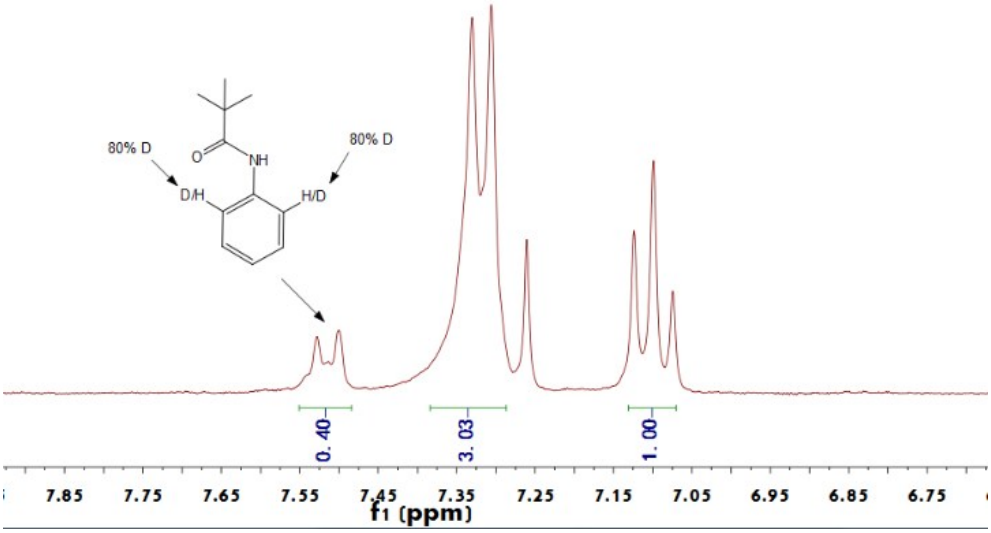
4. Isotopic Labeling Studies



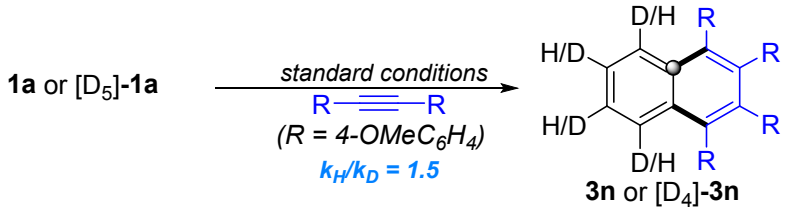
1) $Cu(OAc)_2 \cdot H_2O$ (10 mg, 0.05 mmol), $[Cp^*RhCl_2]_2$ (2 mg, 5 mol%) and diphenylacetylene (**2a)** (18 mg, 0.10 mmol) were added to a stirred solution of $[D_5]$-**1a** (9 mg, 0.05 mmol) in HFIP (1.5 mL), the mixture was heated at 110 °C in a sealed tube till the starting material disappeared. After cooled to room temperature, the reaction mixture was filtered and the filtrate was concentrated. The residue was purified on a silica gel column with petroleum ether as the eluent to afford $[D_n]$-**3a** (18 mg, 85%).



2) $Cu(OAc)_2 \cdot H_2O$ (10 mg, 0.05 mmol) and $[Cp^*RhCl_2]_2$ (2 mg, 5 mol%) were added to a stirred solution of *N*-phenylpivalamide (**1a)** (9 mg, 0.05 mmol) in HFIP (1.5 mL) and D_2O (0.5 ml), the mixture was heated at 110 °C in a sealed tube for 5 h. After 5 h, purification by column chromatography (petroleum ether/ethyl acetate 10:1) to afford $[D_n]$-**1a**.



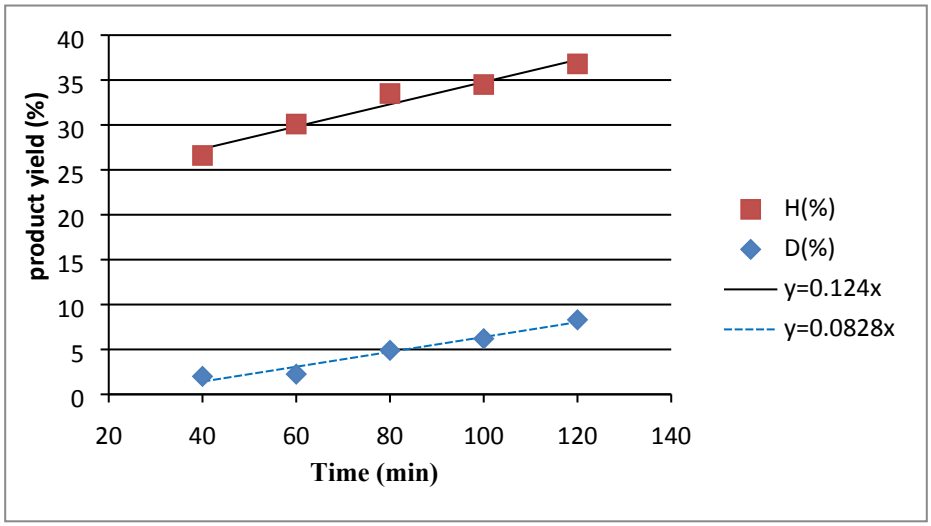
5. KIE Determined By Two Parallel Reactions



Two parallel reactions of 1,2-bis(4-methoxyphenyl)ethyne (**2b**) with *N*-phenylpivalamide (**1a**) and $[D_5]$-**1a** respectively were performed to determine the KIE value by comparison of the initial rates. $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.50 mmol), $[Cp^*RhCl_2]_2$ (15 mg, 5 mol%) and 1,2-bis(4-methoxyphenyl)ethyne (**2b**) (238 mg, 1.00 mmol) were added to a stirred solution of *N*-phenylpivalamide (**1a**) (89 mg, 0.50 mmol) or $[D_5]$-**1a** (91 mg, 0.50 mmol) in HFIP (5 mL), the mixture was heated at 110 °C in a sealed tube. A periodic aliquot (0.5 mL) was removed by a syringe and analyzed by ^1H NMR to provide the following conversions.

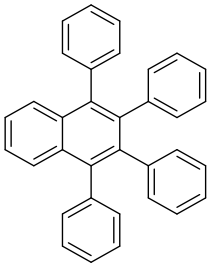
t/min	40	60	80	100	120
3n/%	2.00	2.25	4.90	6.20	8.30

[D_4]-**3n**/%	26.60	30.10	33.50	34.50	36.80



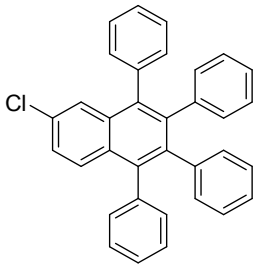
6. Spectroscopic Data of All Products[3]

1,2,3,4-Tetraphenylnaphthalene (3a)



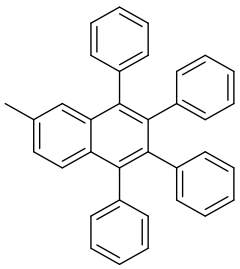
White solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 6.4, 3.3 Hz, 2H), 7.39 (dd, *J* = 6.5, 3.3 Hz, 2H), 7.28 – 7.17 (m, 10H), 6.84 (s, 10H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.53, 139.59, 138.90, 138.42, 132.03, 131.32, 127.54, 127.00, 126.58, 126.44, 125.89, 125.34; **EI-MS** (m/z) 432 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{34}H_{24}$, 432.1878; found, 432.1883.

6-Chloro-1,2,3,4-tetraphenylnaphthalene (3b)



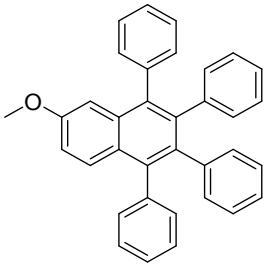
White solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 1.7 Hz, 1H), 7.58 (d, *J* = 9.1 Hz, 1H), 7.31 (dd, *J* = 9.1, 2.1 Hz, 1H), 7.27 – 7.15 (m, 10H), 6.88 – 6.78 (m, 10H);**^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.18, 140.15, 140.07, 139.20, 139.11, 138.84, 138.47, 137.75, 132.90, 132.00, 131.19, 131.17, 131.14, 130.39, 128.82, 127.74, 127.65, 126.74, 126.66, 126.64, 125.68, 125.51, 125.48; **EI-MS** (m/z) 466 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{34}H_{23}{}^{35}Cl$, 466.1488; found, 466.1486.

6-Methyl-1,2,3,4-tetraphenylnaphthalene (3c)



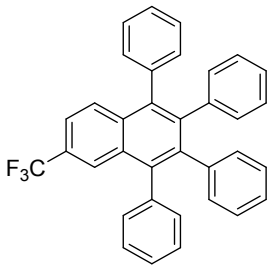
White solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.6 Hz, 1H), 7.40 (s, 1H), 7.21 (s, 11H), 6.83 (s, 10H), 2.37 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.73, 140.66, 139.78, 139.77, 139.00, 138.26, 138.03, 137.80, 135.64, 132.19, 131.42, 131.39, 131.36, 131.33, 130.30, 128.15, 127.54, 127.53, 126.95, 126.56, 126.39, 126.37, 125.89, 125.28, 21.88; **EI-MS** (m/z) 446 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{35}H_{26}$, 446.2035; found, 446.2037.

6-Methoxy-1,2,3,4-tetraphenylnaphthalene (3d)



White solid (112 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 9.2 Hz, 1H), 7.24 – 7.19 (m, 10H), 7.06 (dd, *J* = 9.2, 2.5 Hz, 1H), 6.95 (d, *J* = 2.3 Hz, 1H), 6.83 (s, 10H), 3.68 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.57, 140.74, 140.60, 139.79, 139.73, 139.44, 138.36, 137.30, 136.80, 133.29, 131.49, 131.29, 131.27, 131.22, 128.72, 127.65, 127.51, 126.55, 126.43, 126.41, 125.29, 125.22, 118.03, 105.68, 55.16; **EI-MS** (m/z) 462 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{35}H_{26}O$, 462.1984; found, 462.1982.

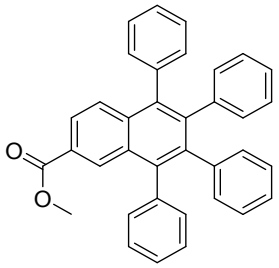
1,2,3,4-Tetraphenyl-6-(trifluoromethyl)naphthalene (3e)



White solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.76 (d, *J* = 8.9 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.32 – 7.14 (m, 10H), 6.85 (d, *J* = 4.0 Hz, 10H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.07, 140.31, 139.97, 139.96, 139.45, 138.89, 138.54, 138.47, 133.34, 131.16, 131.14, 131.13, 131.05, 128.21, 127.79, 127.73, 127.48, 126.95, 126.80, 126.72, 125.65, 125.63, 125.31, 124.68, 124.65,

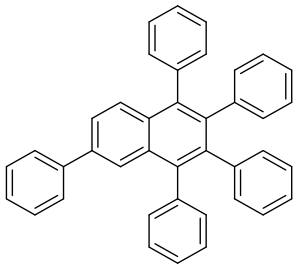
123.51, 121.36, 121.34; **EI-MS** (m/z) 500 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{35}H_{23}F_3$, 500.1752; found, 500.1756.

Methyl 5,6,7,8-tetraphenyl-2-naphthoate (3f)



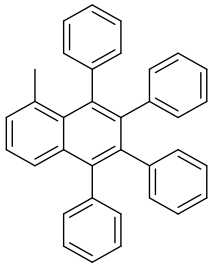
White solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.42 (d, 1H), 7.96 (dd, 1H), 7.69 (d, 1H), 7.25 – 7.15 (m, 10H), 6.85 (d, *J* = 3.6 Hz, 10H), 3.87 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.83, 140.72, 139.62, 139.60, 139.40, 139.32, 138.57, 138.22, 137.93, 133.69, 130.84, 130.75, 130.70, 130.55, 129.50, 127.18, 127.17, 126.85, 126.81, 126.30, 126.16, 125.07, 125.02, 124.67, 51.67; **EI-MS** (m/z) 490 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{36}H_{26}O_2$, 490.1933; found, 490.1934.

1,2,3,4,6-Pentaphenylnaphthalene (3g)



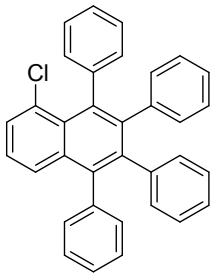
White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.68 – 7.62 (m, 1H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.32 (d, *J* = 7.1 Hz, 1H), 7.22 (dd, *J* = 12.0, 2.9 Hz, 10H), 6.86 (s, 10H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.18, 140.50, 140.47, 139.52, 139.39, 138.97, 138.72, 138.43, 138.26, 132.26, 131.29, 131.28, 131.20, 128.77, 127.58, 127.57, 127.39, 127.25, 126.50, 126.47, 125.49, 125.34, 124.93; **EI-MS** (m/z) 508 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{40}H_{28}$, 508.2191; found, 508.2193.

5-Methyl-1,2,3,4-tetraphenylnaphthalene (3h)



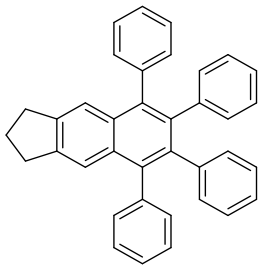
White solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.2, 2.3 Hz, 1H), 7.26 – 7.00 (m, 12H), 6.85 – 6.68 (m, 10H), 1.92 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.94, 140.75, 140.67, 140.46, 140.34, 139.08, 138.49, 138.07, 135.93, 133.40, 131.64, 131.39, 131.30, 131.12, 130.92, 130.32, 127.48, 126.82, 126.47, 126.33, 126.27, 126.18, 125.45, 125.22, 125.02, 25.36; **EI-MS** (m/z) 446 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{35}H_{26}$, 446.2035; found, 446.2035.

5-Chloro-1,2,3,4-tetraphenylnaphthalene(3i)



Orange solid; **^{1}H NMR** (300 MHz, CDCl3) δ 7.59 (d, J = 8.5 Hz, 1H), 7.52 (d, J = 7.4 Hz, 1H), 7.26 – 7.16 (m, 7H), 7.10 (s, 4H), 6.78 (m, 10H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.86, 141.28, 140.19, 139.65, 139.06, 137.08, 134.62, 131.99, 131.53, 131.24, 131.19, 130.95, 129.96, 128.56, 127.62, 127.12, 126.65, 126.58, 126.35, 126.11, 125.47, 125.46, 125.25; **EI-MS** (m/z) 466 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{34}H_{23}{}^{35}Cl$, 466.1488; found, 466.1479.

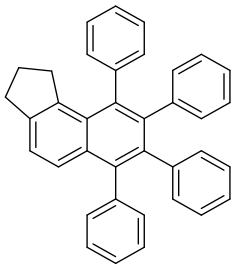
5,6,7,8-Tetraphenyl-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalene (3j)



White solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.44 (s, 2H), 7.22 (s, 10H), 6.83 (s, 10H), 2.93 (t, *J* = 7.2 Hz, 4H), 2.17 – 1.96 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.52, 140.82, 140.13, 137.95,

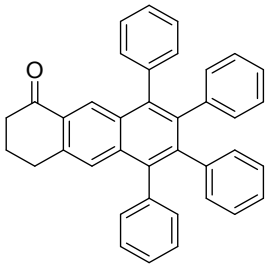
137.93, 131.40, 131.36, 127.46, 126.45, 126.22, 125.13, 121.17, 32.80, 26.18; **EI-MS** (m/z) 472 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{37}H_{28}$, 472.2191; found, 472.2182.

6,7,8,9-Tetraphenyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene (3k)



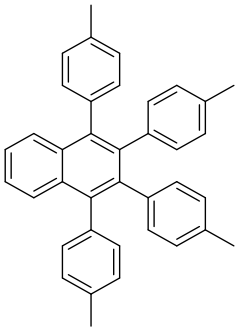
White solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.5 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 7.26 – 7.07 (m, 10H), 6.80 (d, *J* = 4.2 Hz, 10H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.27 (t, *J* = 7.2 Hz, 2H), 1.90 – 1.74 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.36, 142.16, 140.76, 140.73, 140.49, 140.14, 139.97, 139.06, 137.72, 137.36, 131.84, 131.67, 131.34, 131.28, 131.25, 129.29, 127.46, 126.72, 126.57, 126.45, 126.28, 125.16, 125.05, 123.47, 35.16, 33.35, 25.60; **EI-MS** (m/z) 472 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{37}H_{28}$, 472.2191; found, 472.2182.

5,6,7,8-Tetraphenyl-3,4-dihydroanthracen-1(*2H*)-one (3l)



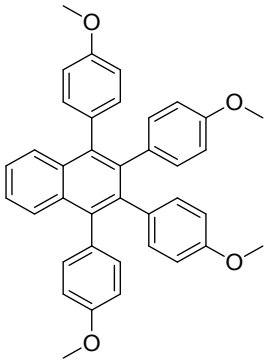
Yellow solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.47 (s, 1H), 7.24 – 7.15 (m, 10H), 6.83 (d, *J* = 2.0 Hz, 10H), 2.97 (t, *J* = 5.5 Hz, 2H), 2.66 (d, *J* = 6.3 Hz, 2H), 2.14 – 2.08 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 198.49, 141.61, 140.54, 140.24, 140.12, 139.32, 139.24, 139.09, 138.69, 137.68, 134.57, 131.25, 131.23, 131.21, 131.02, 130.66, 130.55, 128.10, 127.68, 127.68, 126.84, 126.63, 125.88, 125.54, 125.46, 39.74, 30.19, 23.32; **EI-MS** (m/z) 500 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{38}H_{28}O$, 500.2140; found, 500.2141.

1,2,3,4-Tetra-p-tolylnaphthalene (3m)



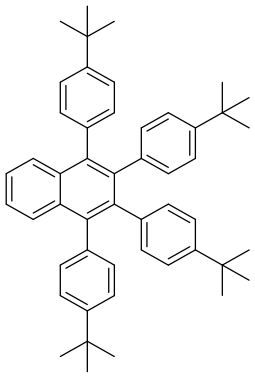
Yellow solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.61 (dd, 2H), 7.33 (dd, 2H), 7.09 – 7.02 (m, 8H), 6.72 – 6.64 (m, 8H), 2.31 (s, 6H), 2.10 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 139.10, 138.28, 137.73, 136.78, 135.60, 134.29, 132.18, 131.14, 131.12, 128.19, 127.24, 126.97, 125.51, 21.26, 21.09; **EI-MS** (m/z) 488 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{38}H_{32}$, 488.2504; found, 488.2505.

1,2,3,4-Tetrakis(4-methoxyphenyl)naphthalene (3n)



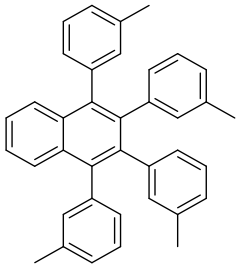
White solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 6.5, 3.3 Hz, 2H), 7.36 (dd, *J* = 6.5, 3.3 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 4H), 6.79 (d, *J* = 8.6 Hz, 4H), 6.71 (d, *J* = 8.5 Hz, 4H), 6.43 (d, *J* = 8.6 Hz, 4H), 3.79 (s, 6H), 3.62 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.90, 156.89, 139.14, 138.17, 133.37, 132.38, 132.30, 132.27, 132.14, 126.96, 125.59, 113.03, 112.16, 55.14, 54.90; **EI-MS** (m/z) 552 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{38}H_{32}O_4$, 552.2301; found, 552.2302.

1,2,3,4-Tetrakis(4-(tert-butyl)phenyl)naphthalene (3o)



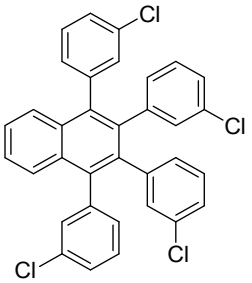
White solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.76 (dd, 2H), 7.37 (dd, 2H), 7.24 (d, *J* = 5.2 Hz, 2H), 7.20 (s, 2H), 7.11 (d, *J* = 8.2 Hz, 4H), 6.81 (d, *J* = 8.3 Hz, 4H), 6.68 (d, *J* = 8.2 Hz, 4H), 1.27 (s, 18H), 1.09 (s, 18H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.85, 147.53, 139.43, 138.33, 137.78, 136.72, 131.96, 131.02, 130.97, 127.09, 125.52, 124.13, 123.02, 34.40, 34.05, 31.36, 31.18; **EI-MS** (m/z) 656 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{50}H_{56}$, 656.4382; found, 656.4388.

1,2,3,4-Tetra-m-tolylnaphthalene (3p)



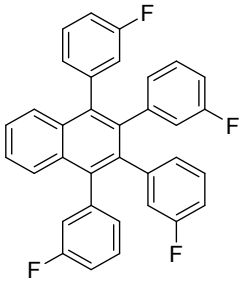
White solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.37 (dd, *J* = 6.5, 3.3 Hz, 2H), 7.11 (t, *J* = 7.5 Hz, 2H), 7.00 (t, *J* = 7.5 Hz, 6H), 6.77 – 6.68 (m, 3H), 6.62 (d, *J* = 6.9 Hz, 5H), 2.26 (s, 6H), 2.01 (t, *J* = 5.4 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.42, 139.58, 139.02, 138.99, 138.27, 138.23, 138.20, 136.76, 136.71, 135.59, 135.53, 135.46, 132.31, 132.26, 132.23, 132.18, 132.16, 132.11, 132.06, 131.94, 128.44, 128.42, 128.36, 128.29, 127.26, 127.22, 127.02, 126.98, 126.23, 126.17, 126.09, 125.81, 125.58, 21.38, 21.35, 21.08; **EI-MS** (m/z) 488 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{38}H_{32}$, 488.2504; found, 488.2503.

1,2,3,4-Tetrakis(3-chlorophenyl)naphthalene (3q)



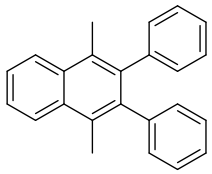
White solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.58 (dd, 2H), 7.47 (dd, *J* = 6.4, 3.3 Hz, 2H), 7.25 – 7.16 (m, 6H), 7.12 – 7.02 (m, 2H), 6.92 – 6.80 (m, 6H), 6.79 – 6.67 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.31, 140.61, 137.59, 137.09, 133.85, 133.69, 133.65, 133.00, 132.96, 132.79, 131.79, 131.11, 131.08, 131.05, 130.97, 130.95, 130.92, 130.87, 129.28, 129.18, 129.14, 129.10, 129.06, 128.43, 128.38, 128.31, 128.27, 128.23, 128.15, 128.11, 127.21, 126.82, 126.79, 126.28; **EI-MS** (m/z) 568 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{34}H_{20}{}^{35}Cl_4$, 568.0319; found, 568.0319.

1,2,3,4-Tetrakis(3-fluorophenyl)naphthalene (3r)



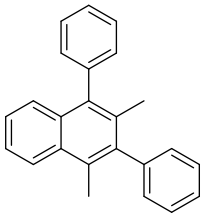
White solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 6.4, 3.3 Hz, 2H), 7.45 (dd, *J* = 6.5, 3.3 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.02 – 6.87 (m, 8H), 6.67 – 6.54 (m, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.15, 163.12, 162.55, 162.51, 162.46, 161.51, 161.48, 160.91, 160.88, 160.84, 141.89, 141.83, 141.11, 141.06, 137.62, 137.15, 131.79, 129.40, 129.35, 129.32, 129.30, 129.25, 128.61, 128.58, 128.55, 128.53, 128.49, 128.47, 128.44, 128.41, 128.38, 128.35, 128.32, 126.90, 126.81, 126.68, 118.10, 118.08, 118.05, 117.96, 117.93, 117.81, 117.79, 117.77, 114.00, 113.99, 113.87, 113.85, 113.07, 112.93; **EI-MS** (m/z) 504 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{34}H_{20}F_4$, 504.1501; found, 504.1494.

1,4-Dimethyl-2,3-diphenylnaphthalene (3s)



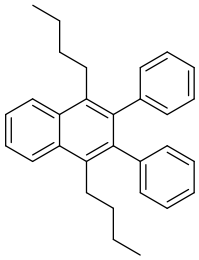
White solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 6.5, 3.4 Hz, 2H), 7.54 (dd, *J* = 6.6, 3.4 Hz, 2H), 7.06 (p, *J* = 6.6 Hz, 6H), 6.92 (d, *J* = 7.2 Hz, 4H), 2.39 (s, 6H); **^{13}C NMR** (126 MHz, CDCl3) δ 141.23, 138.92, 131.54, 129.91, 128.91, 126.74, 125.34, 125.26, 124.52, 16.36; **EI-MS** (m/z) 308 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{24}H_{20}$, 308.1565; found, 308.1562.

1,3-Dimethyl-2,4-diphenylnaphthalene (3s')



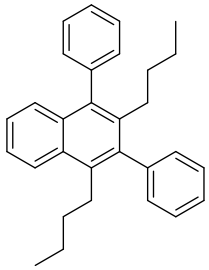
White solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.53 – 7.35 (m, 9H), 7.31 (d, *J* = 1.7 Hz, 2H), 7.24 (d, *J* = 6.8 Hz, 2H), 2.41 (s, 3H), 1.84 (s, 3H); **^{13}C NMR** (126 MHz, CDCl3) δ 141.78, 140.14, 139.79, 136.26, 131.83, 131.59, 130.49, 130.45, 129.95, 128.96, 127.92, 127.90, 126.46, 126.38, 126.18, 124.88, 124.59, 123.81, 19.46, 16.41; **EI-MS** (m/z) 308 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{24}H_{20}$, 308.1565; found, 308.1566.

1,4-Dibutyl-2,3-diphenylnaphthalene (3t)



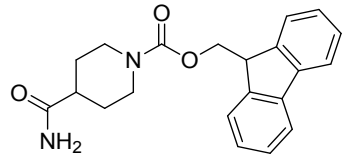
Colourless oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.19 – 8.11 (m, 2H), 7.56 (dd, *J* = 6.7, 3.3 Hz, 2H), 7.15 – 7.03 (m, 6H), 7.01 – 6.96 (m, 4H), 2.80 (t, *J* = 8.3 Hz, 4H), 1.63 – 1.50 (m, 4H), 1.25 (q, *J* = 7.5 Hz, 4H), 0.77 (t, *J* = 7.3 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.01, 138.80, 134.09, 131.04, 129.74, 126.58, 125.29, 125.00, 124.75, 32.95, 29.45, 22.67, 13.21; **EI-MS** (m/z) 392 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{24}H_{20}$, 392.2504; found, 392.2504.

1,3-Dibutyl-2,4-diphenylnaphthalene (3t')



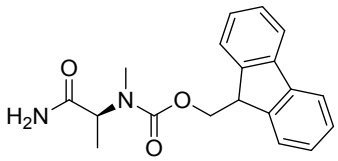
Colourless oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.56 – 7.25 (m, 13H), 2.77 (dd, *J* = 10.1, 6.7 Hz, 2H), 2.29 – 2.14 (m, 2H), 1.65 – 1.50 (m, 2H), 1.27 (q, *J* = 7.4 Hz, 2H), 1.14 (td, *J* = 7.3, 3.0 Hz, 2H), 0.78 (tt, *J* = 7.4, 3.7 Hz, 5H), 0.41 (td, *J* = 7.3, 2.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.84, 139.82, 139.25, 136.81, 136.22, 135.98, 132.48, 130.15, 129.60, 129.42, 127.59, 127.33, 126.76, 126.33, 126.17, 124.61, 124.50, 123.82, 32.86, 32.47, 31.03, 29.58, 22.76, 22.27, 13.24, 12.64; **EI-MS** (m/z) 392 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{24}H_{20}$, 392.2504; found, 392.2505.

(9*H*-Fluoren-9-yl) methyl 4-carbamoylpiperidine-1-carboxylate (4)



White solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.4 Hz, 2H), 7.57 (d, *J* = 7.3 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 5.61 – 5.41 (m, 2H), 4.43 (s, 2H), 4.24 (t, 1H), 4.22 – 3.99 (m, 2H), 2.93 – 2.75 (m, 2H), 2.40 – 2.23 (m, 1H), 1.93 – 1.79 (m, 2H), 1.71 – 1.54 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.20, 155.10, 144.03, 141.35, 127.69, 127.06, 124.96, 119.99, 67.26, 47.38, 43.39, 42.56, 28.47; **EI-MS** (m/z) 350 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{21}H_{22}N_2O_3$, 350.1630; found, 350.1651.

(*S*)-(9*H*-Fluoren-9-yl) methyl (1-amino-1-oxopropan-2-yl)(methyl)carbamate (5)



White solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.4 Hz, 2H), 7.56 (d, *J* = 7.1 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.1 Hz, 2H), 5.92 (d, *J* = 35.1 Hz, 2H), 4.78 (s, 1H), 4.53 (s, 2H),

4.23 (t, J = 6.0 Hz, 1H), 2.76 (s, 3H), 1.27 (s, 3H); **^{13}C NMR (**151 MHz, $CDCl_3$) δ 173.57, 156.90, 143.79, 143.71, 141.37, 127.79, 127.14, 124.95, 124.81, 120.05, 120.04, 67.54, 53.99, 47.37, 29.48, 13.49; **EI-MS** (m/z) 324 (M^+); **HRMS** (EI): m/z [M^+] calcd for $C_{19}H_{20}N_2O_3$, 324.1474; found, 324.1470.

7. Supplementary References

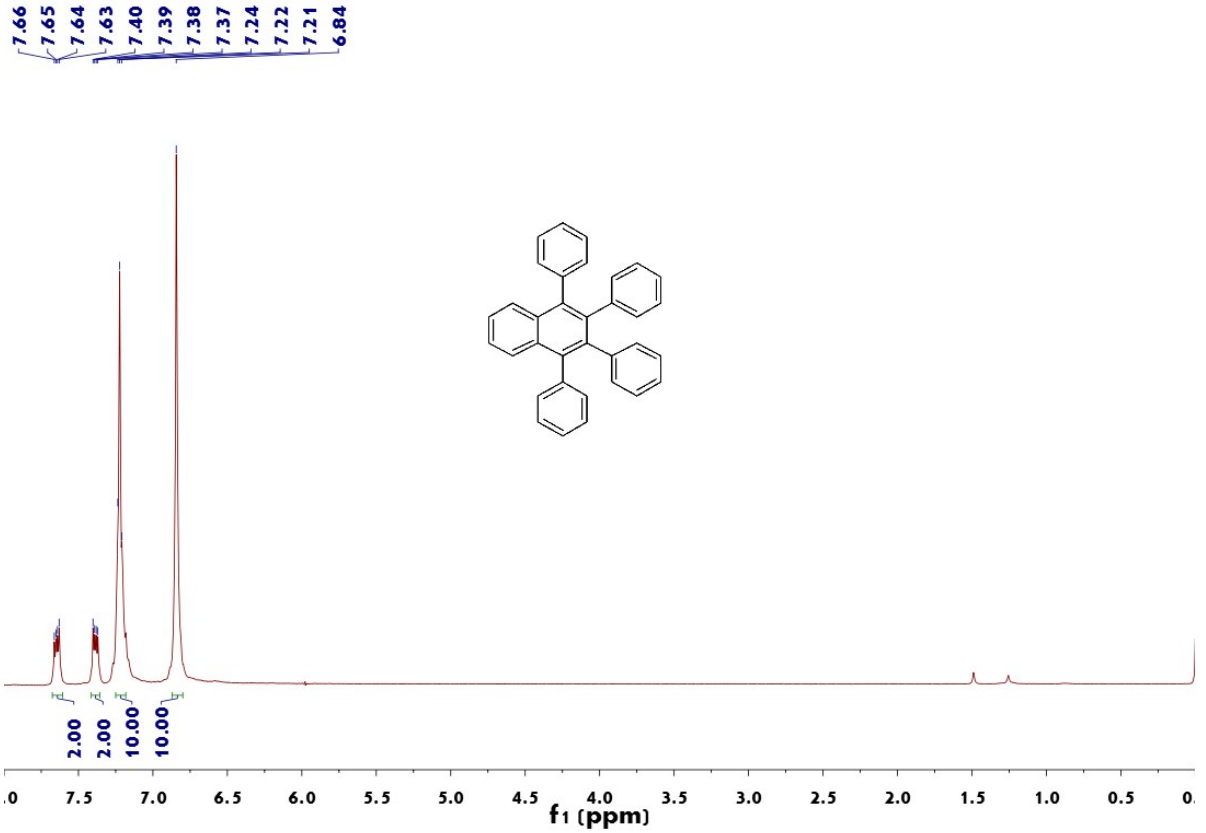
1. Mio, M. J.; Kopel, L. C.; Braun, J. B.; Gadzikwa, T. L.; Hull, K. L.; Brisbois, R. G.; Markworth, C.J.; Grieco, P. A. *Org. Lett.* **2002**, *4*, 3199.

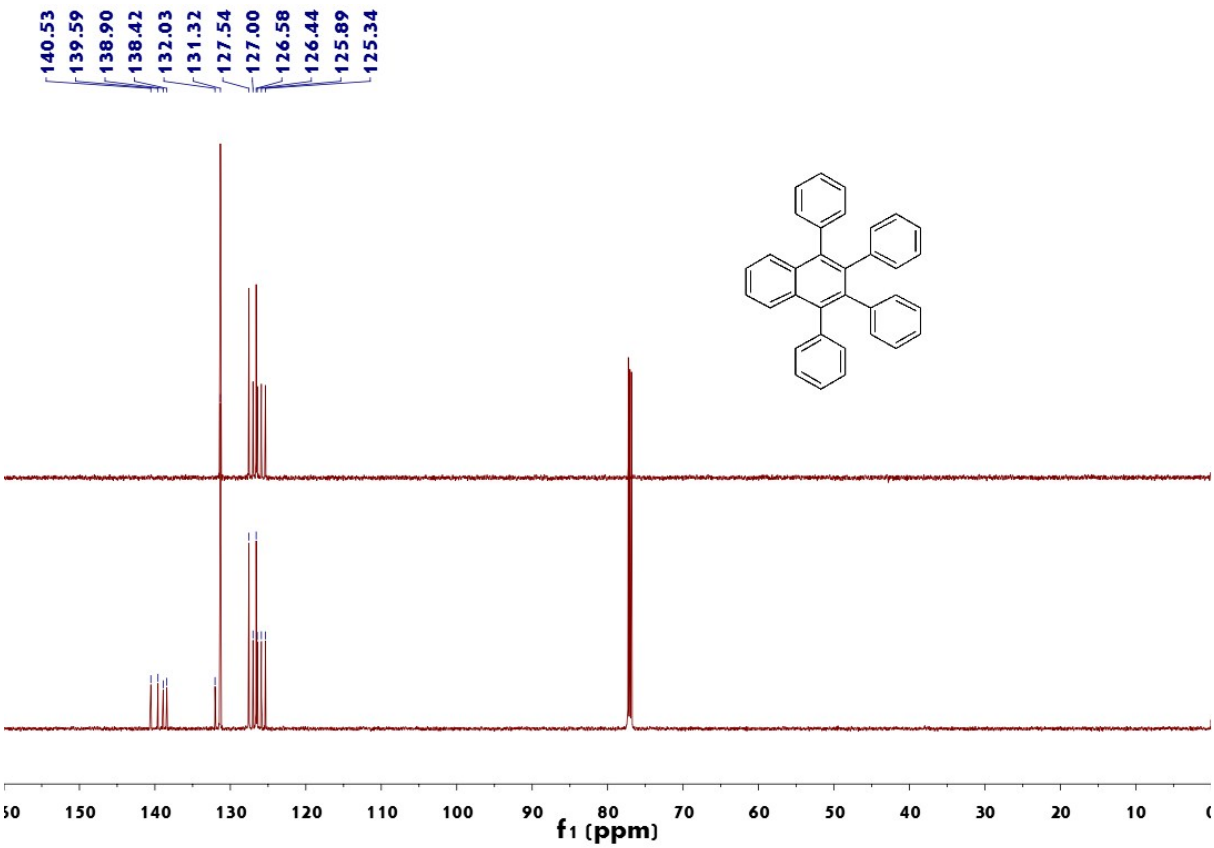
2. Vermaa, A.; Patela, S.; Meenakshia.; Kumara, A.; Yadava, A.;Kumara, S.; Janaa, S.; Sharmaa, S.; Prasada, ChD.; Kumar, S. *Chem. Commun*. **2015**, *51*, 1371.

3. (a) Fukutani, T; Hirano, K; Satoh, T; Miura, M. *Org. Lett.* **2009**, *11*, 5198. (b) Fukutani, T; Hirano, K; Satoh, T; Miura, M. *J. Org. Chem*. **2011**, *76*, 2867.

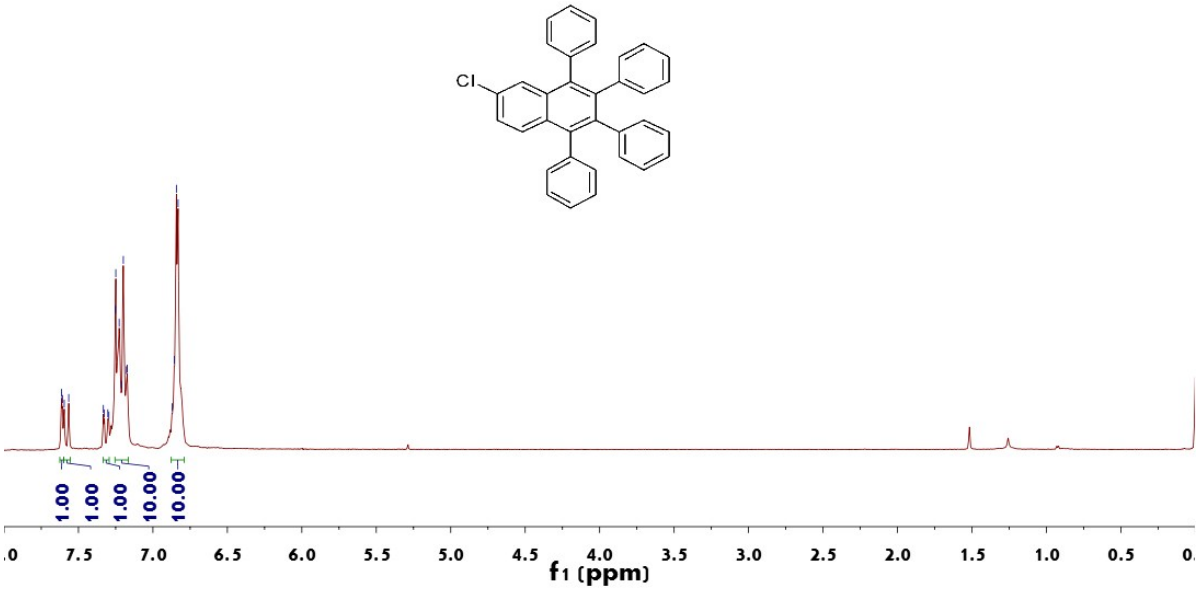
8. Copies of NMR Spectra Data

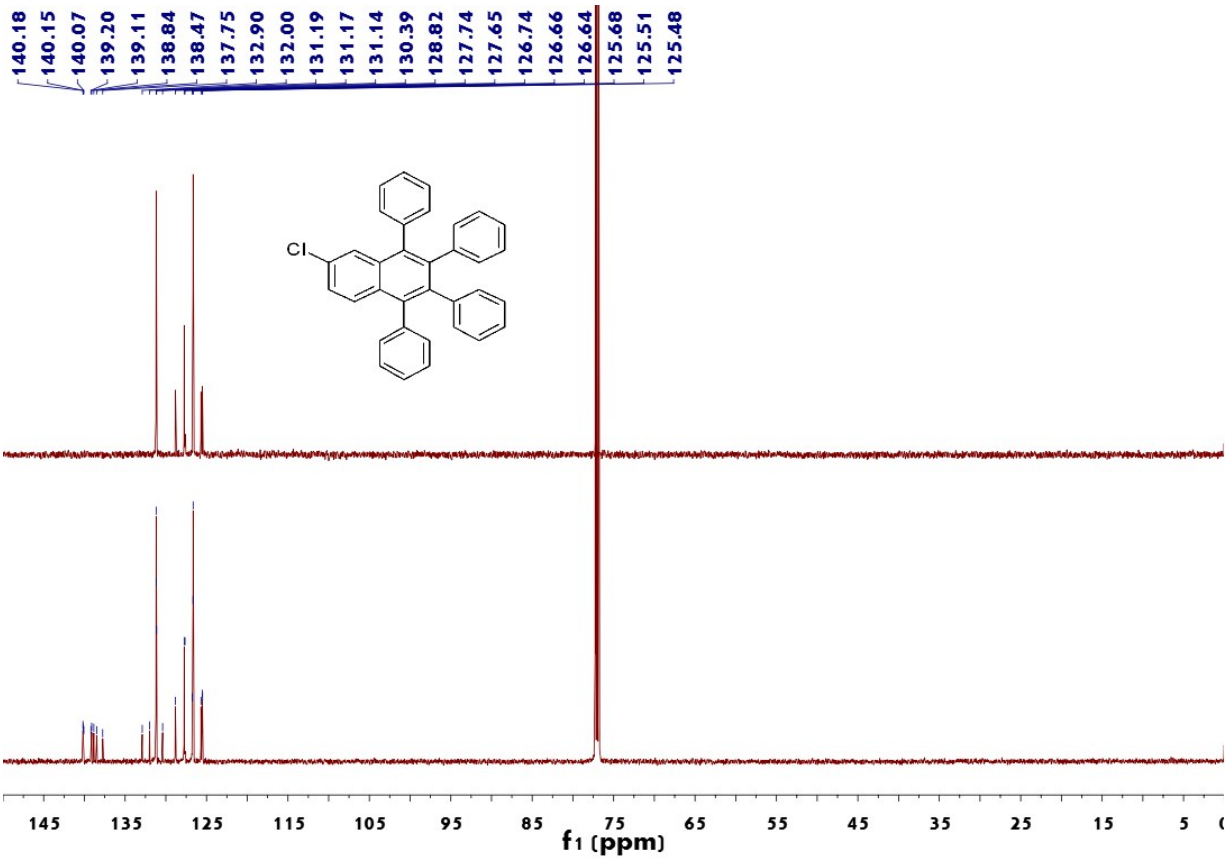
^{1}H and ^{13}C NMR spectra of compound **3a**



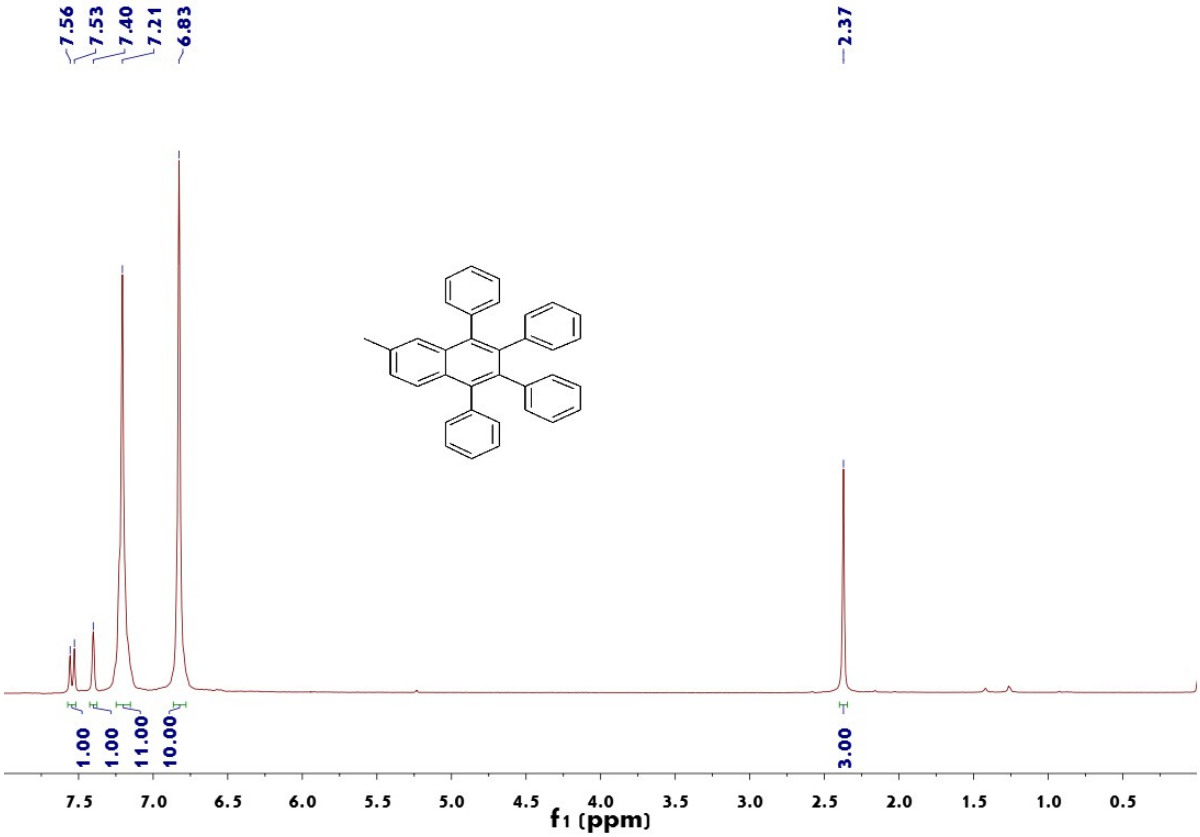


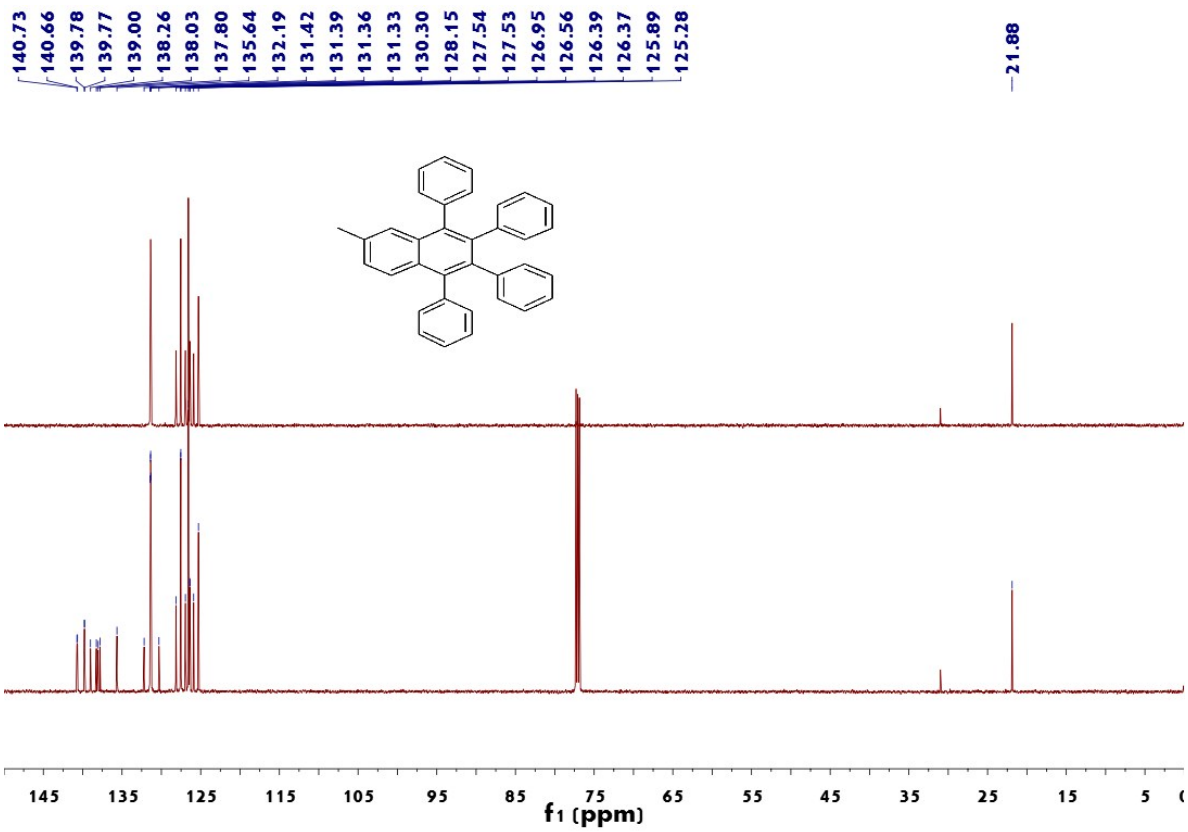
^{1}H and ^{13}C NMR spectra of compound **3b**



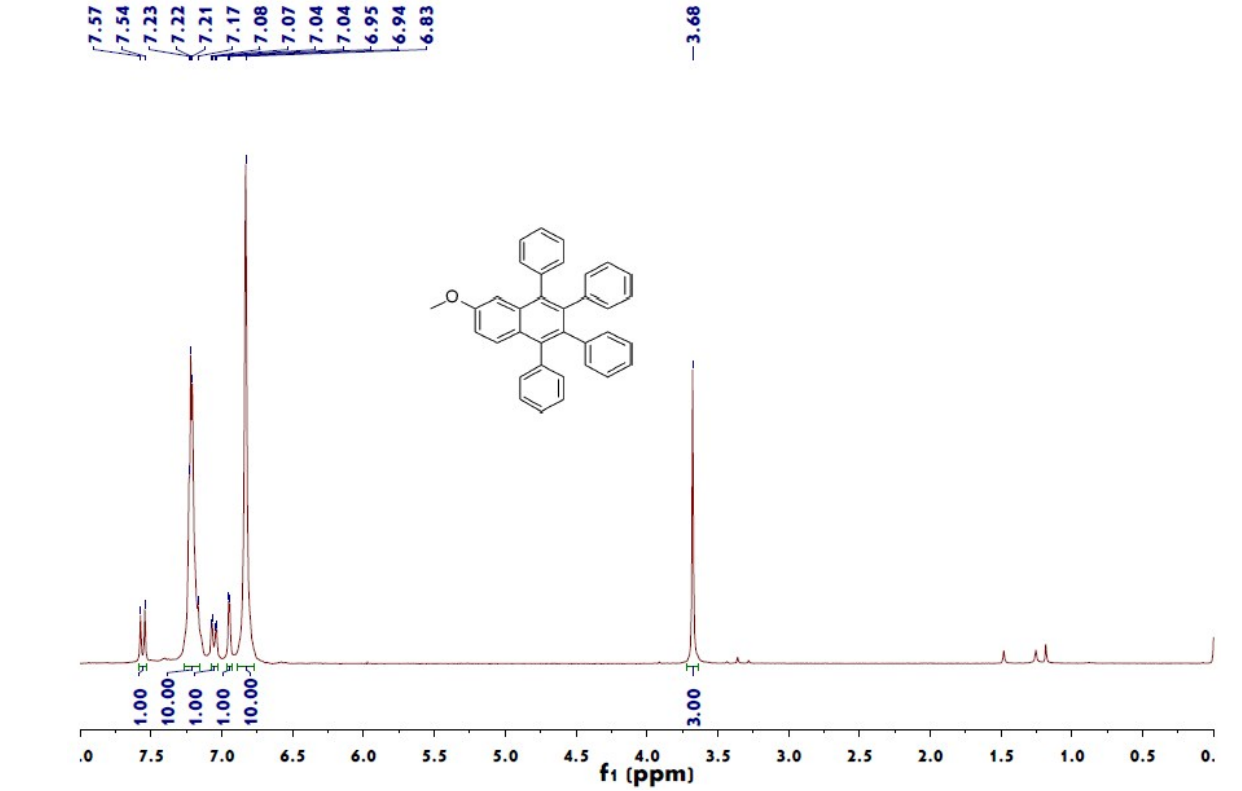


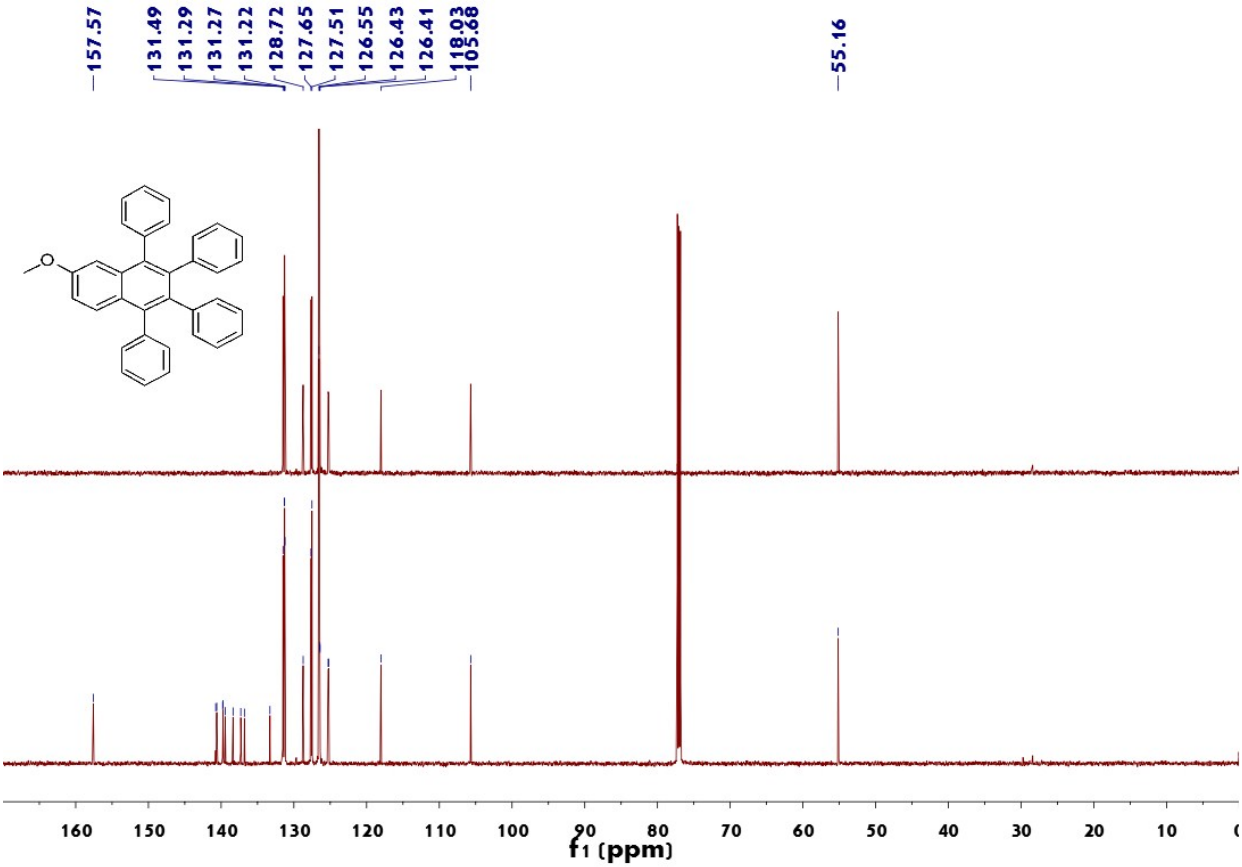
^{1}H and ^{13}C NMR spectra of compound **3c**



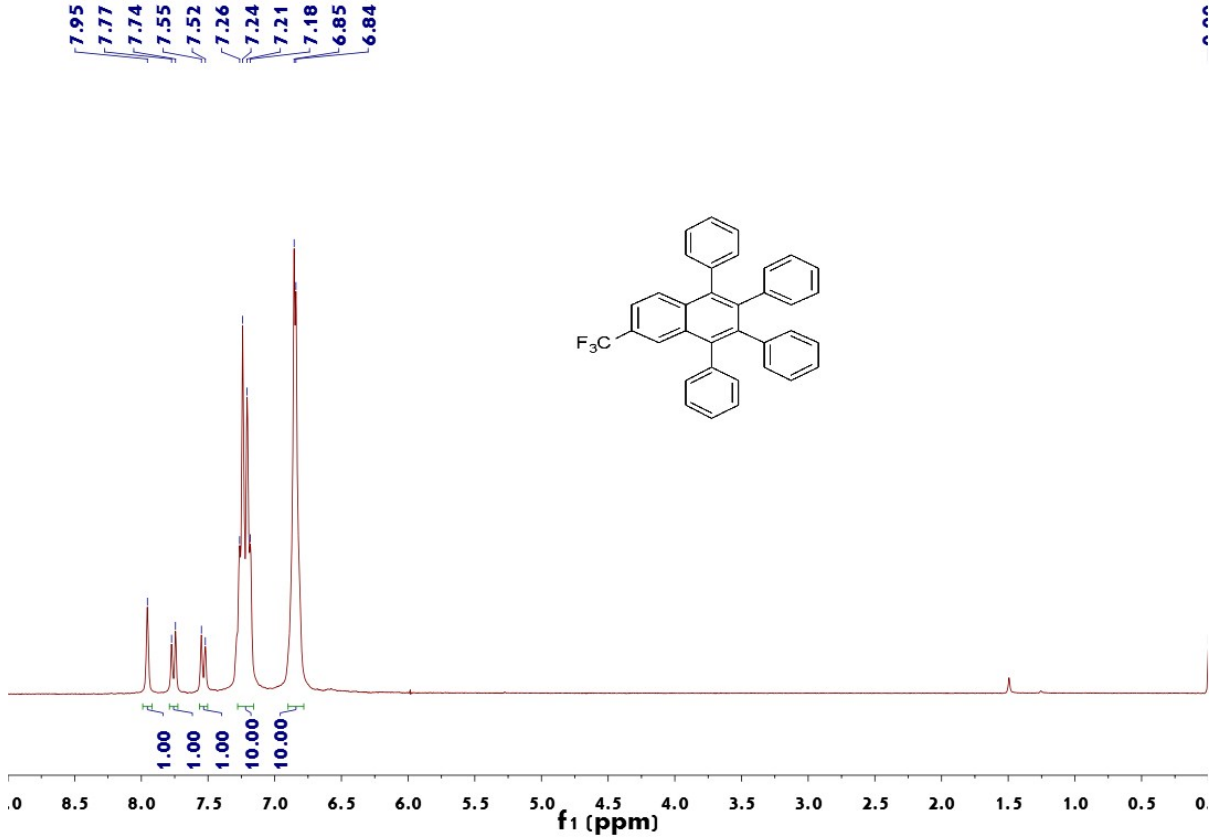


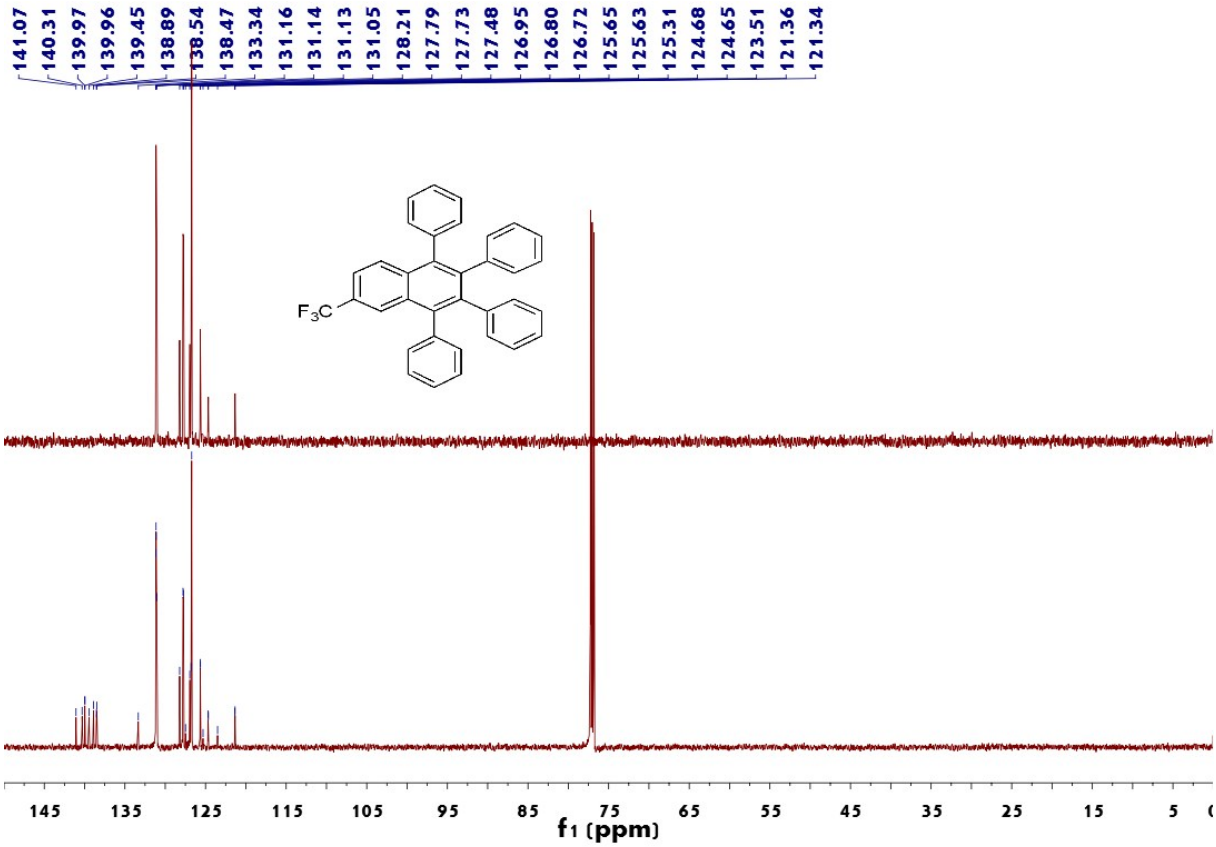
^{1}H and ^{13}C NMR spectra of compound **3d**



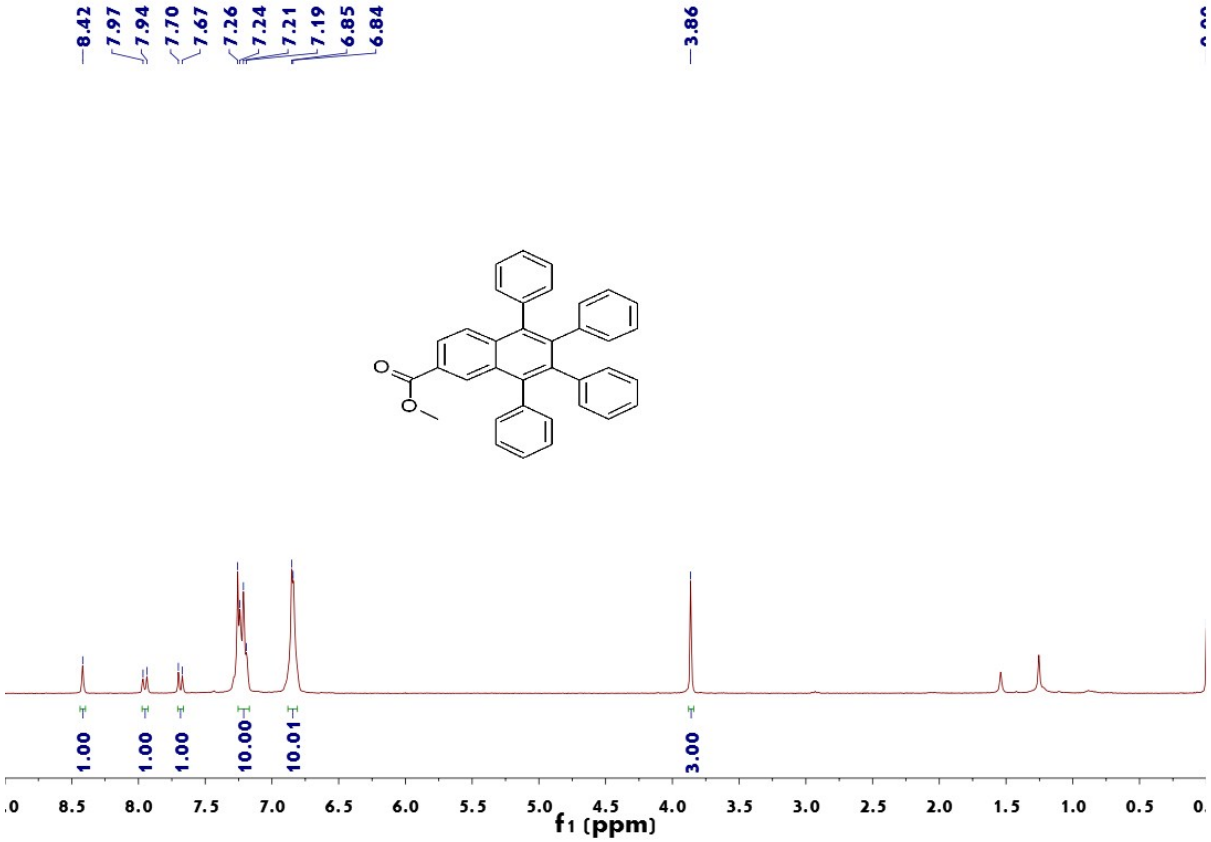


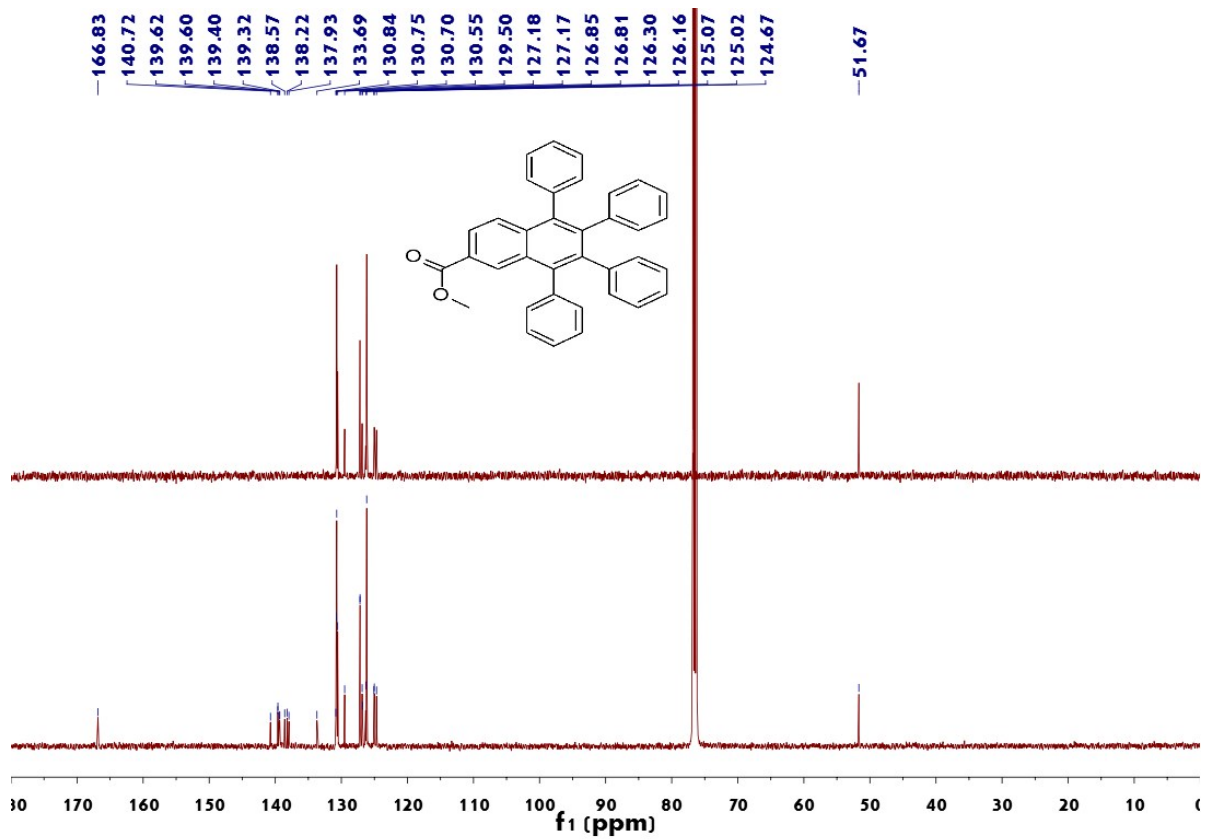
^{1}H and ^{13}C NMR spectra of compound **3e**



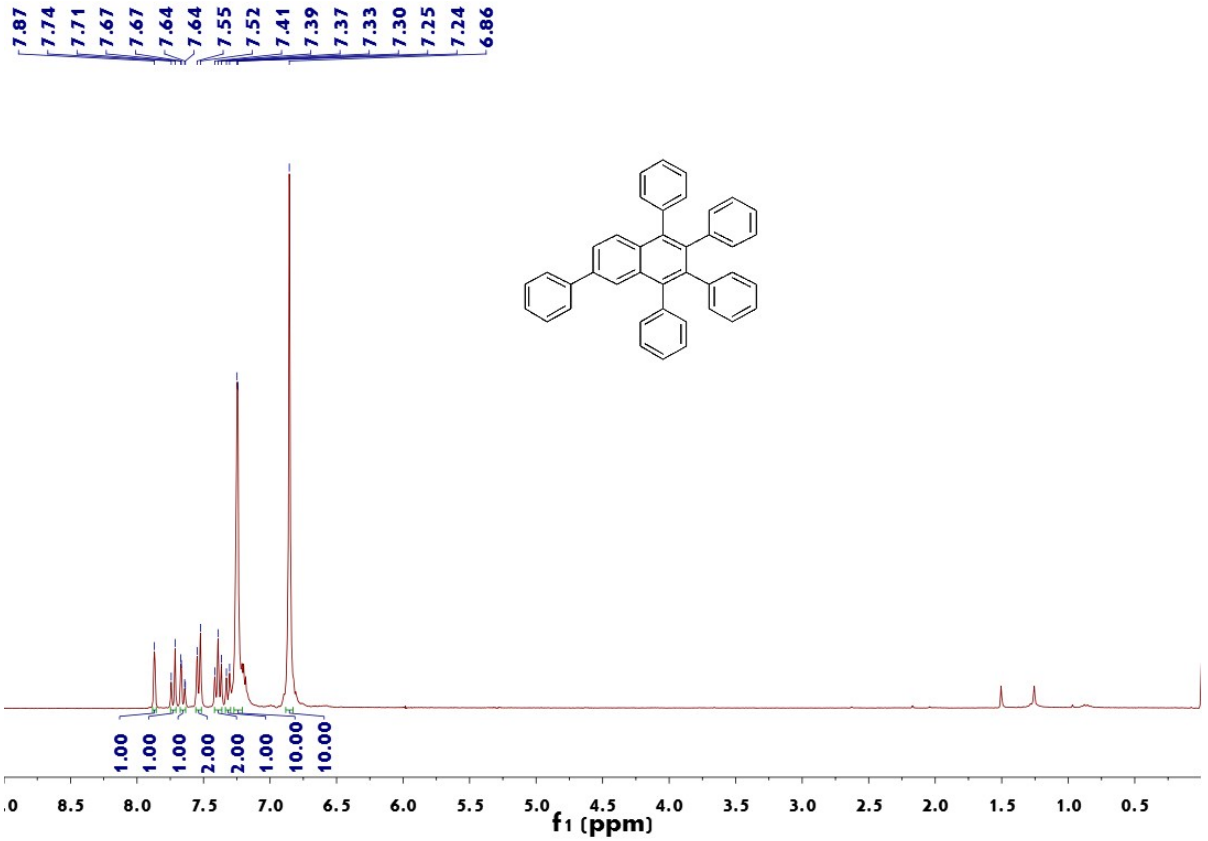


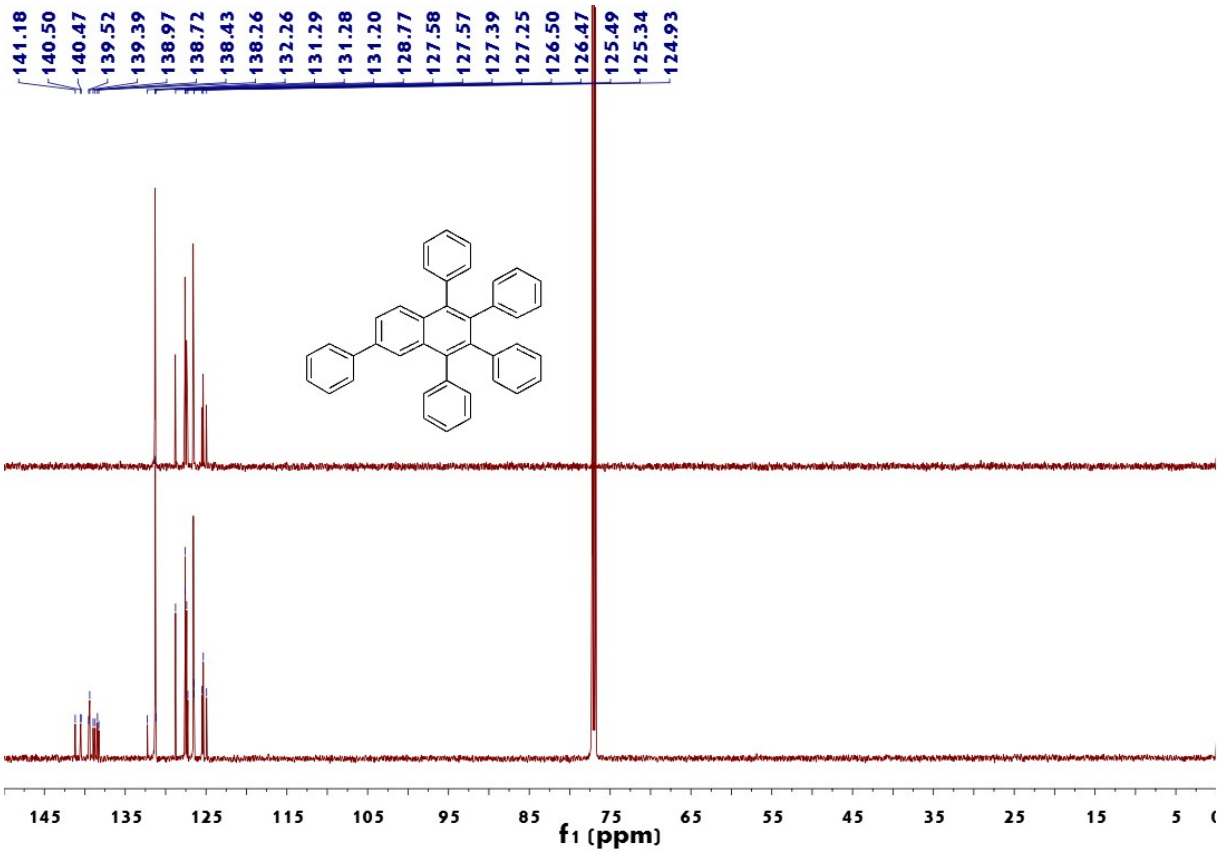
^{1}H and ^{13}C NMR spectra of compound **3f**



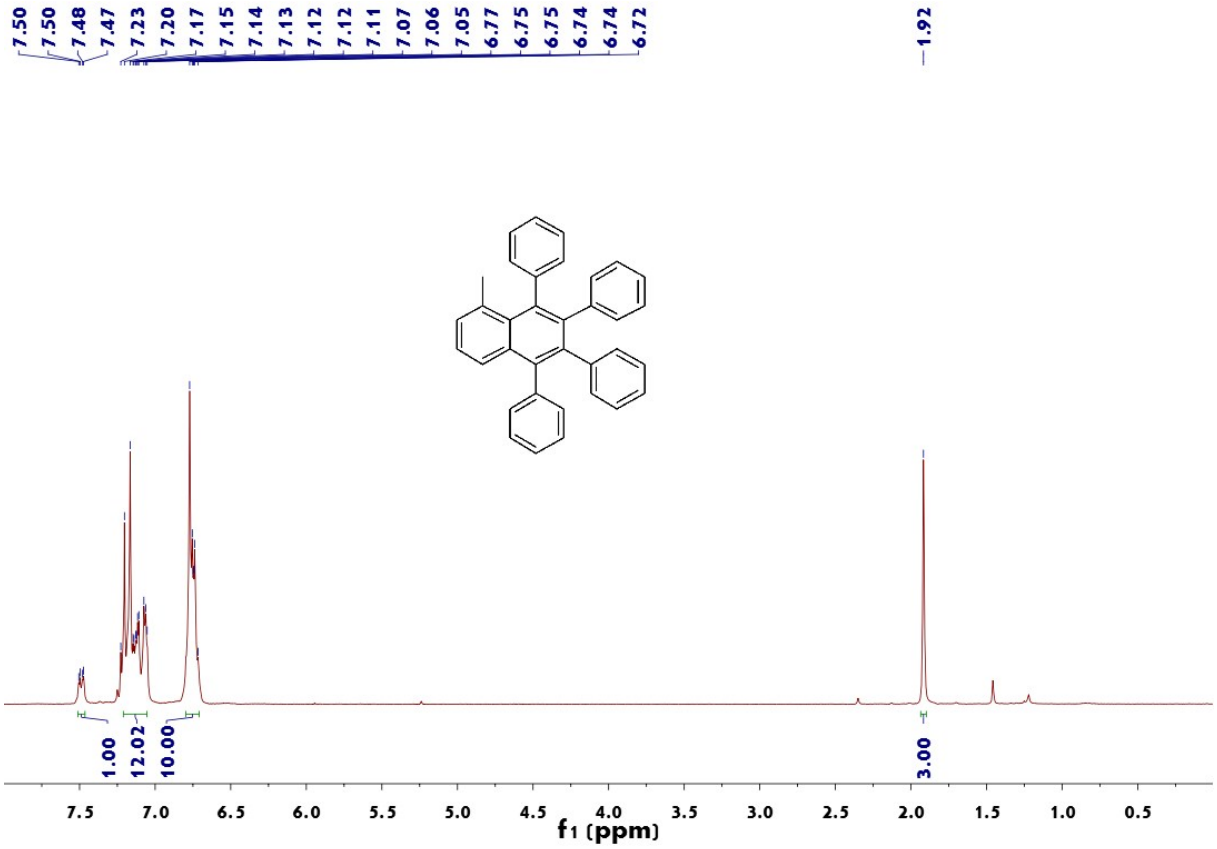


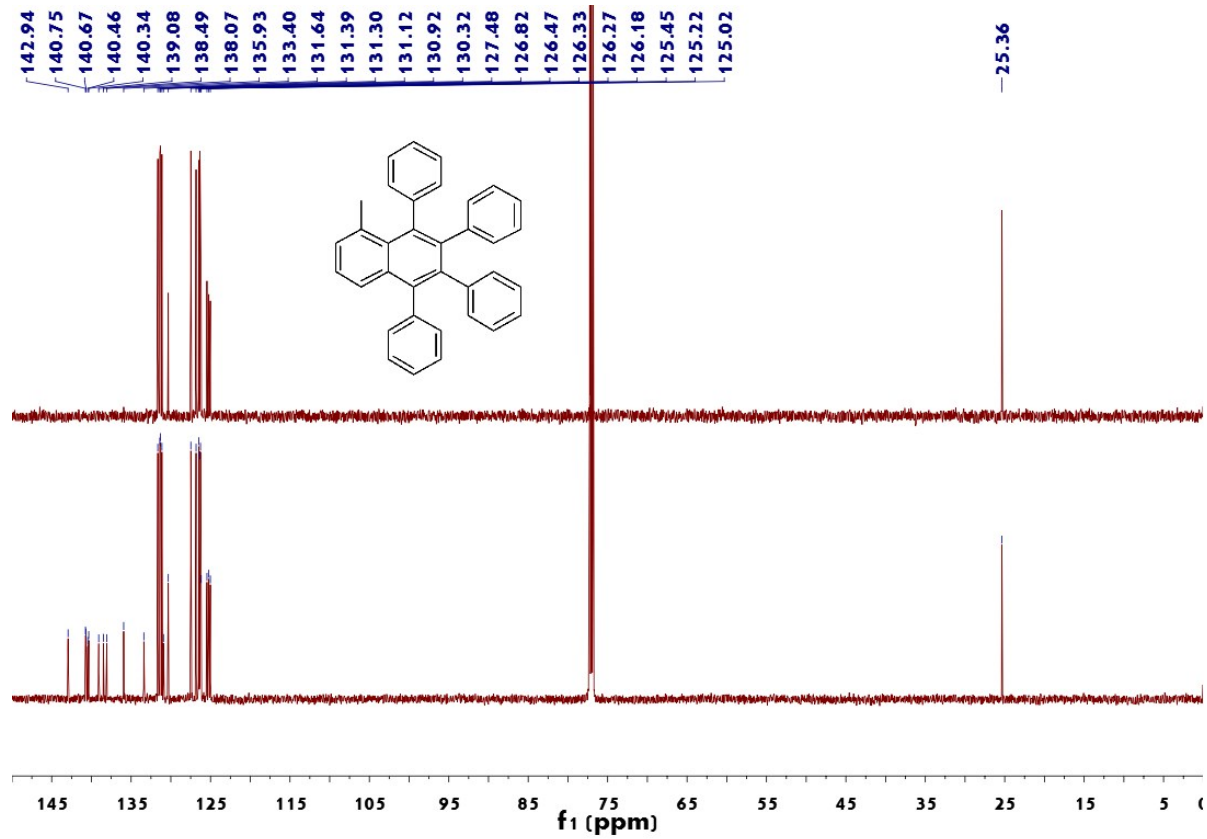
^{1}H and ^{13}C NMR spectra of compound **3g**



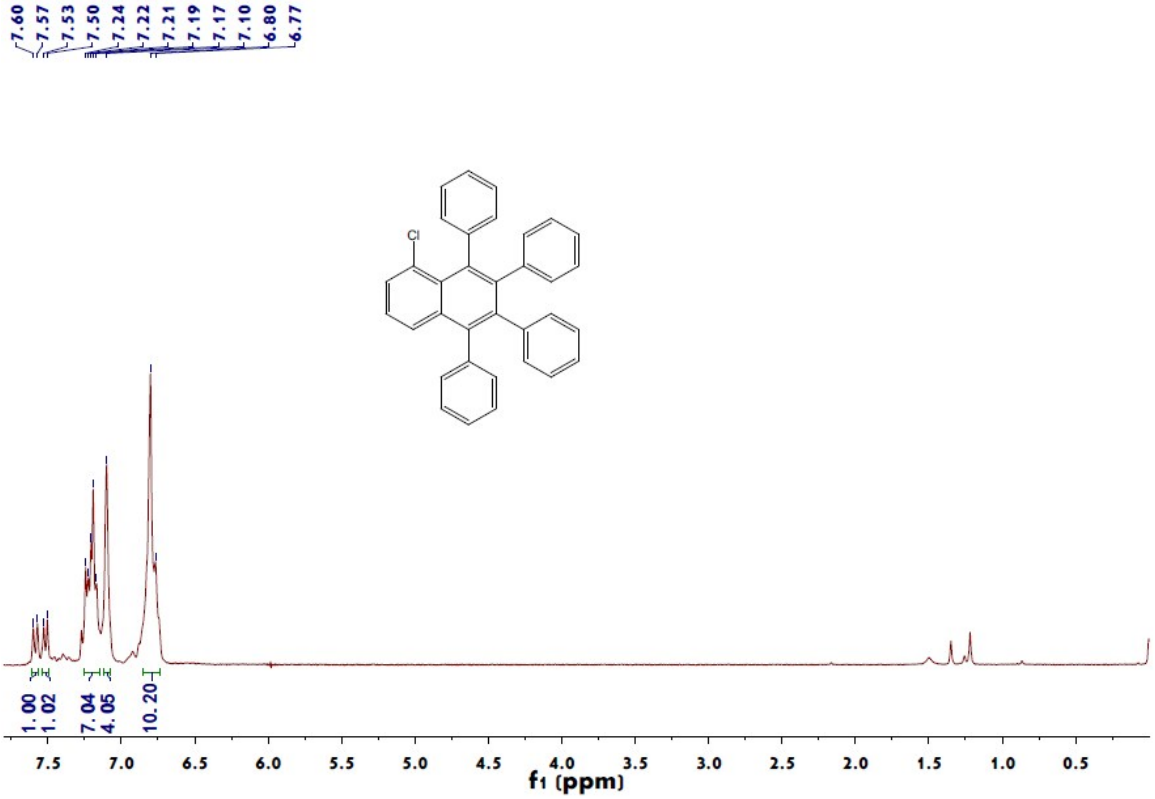


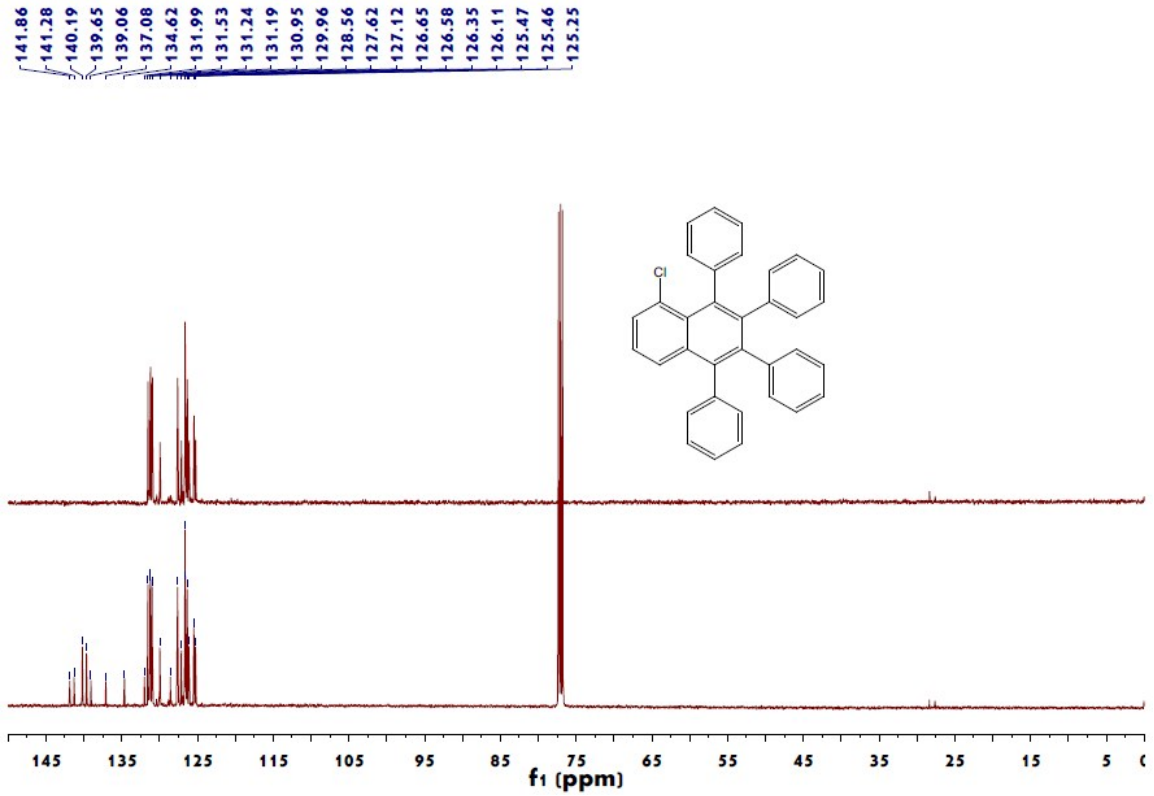
^{1}H and ^{13}C NMR spectra of compound **3h**



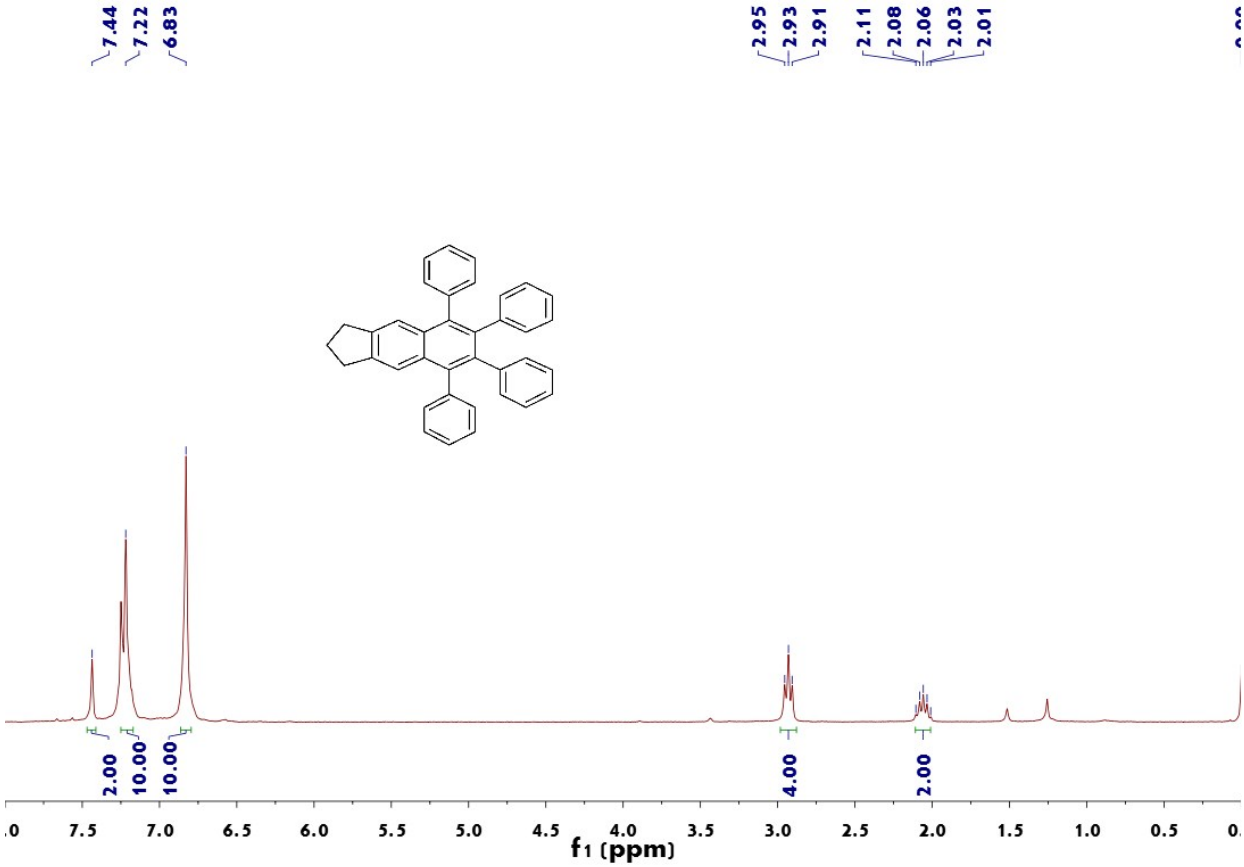


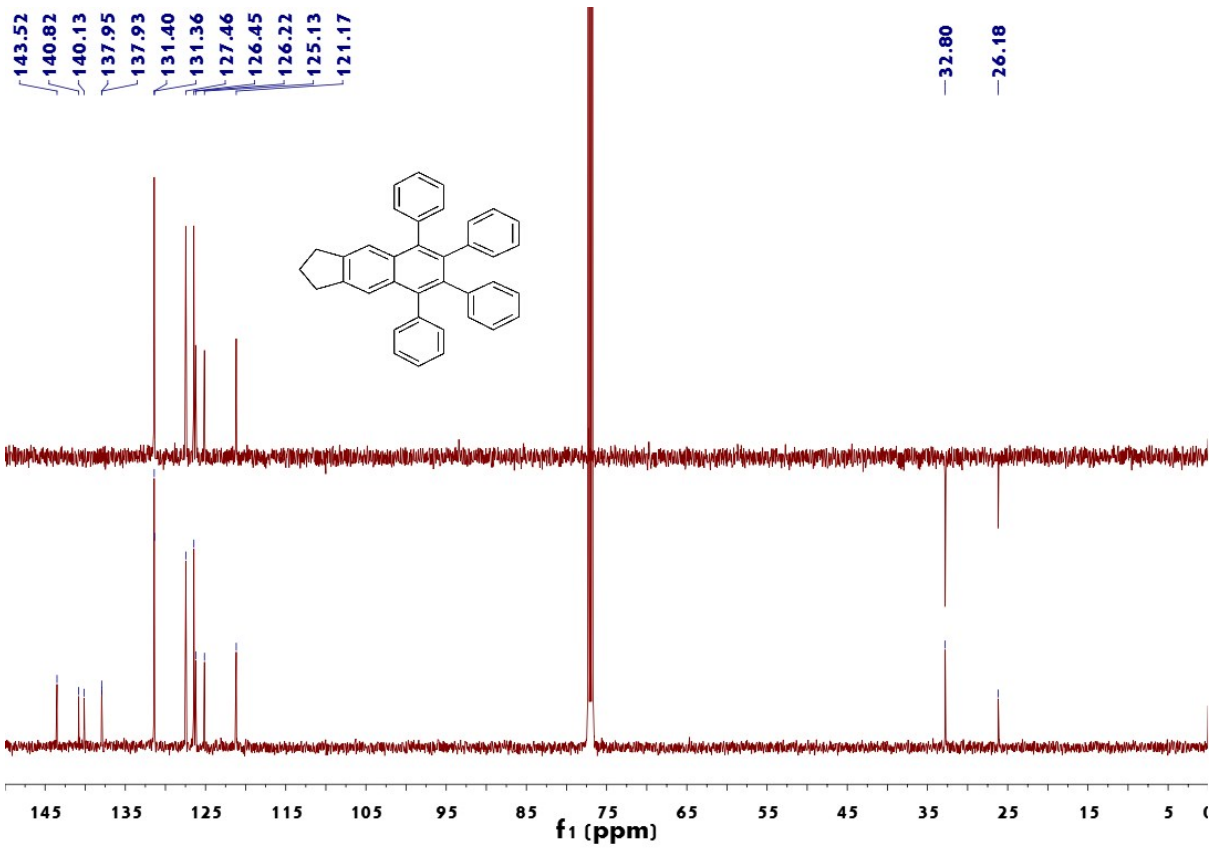
^{1}H and ^{13}C NMR spectra of compound **3i**



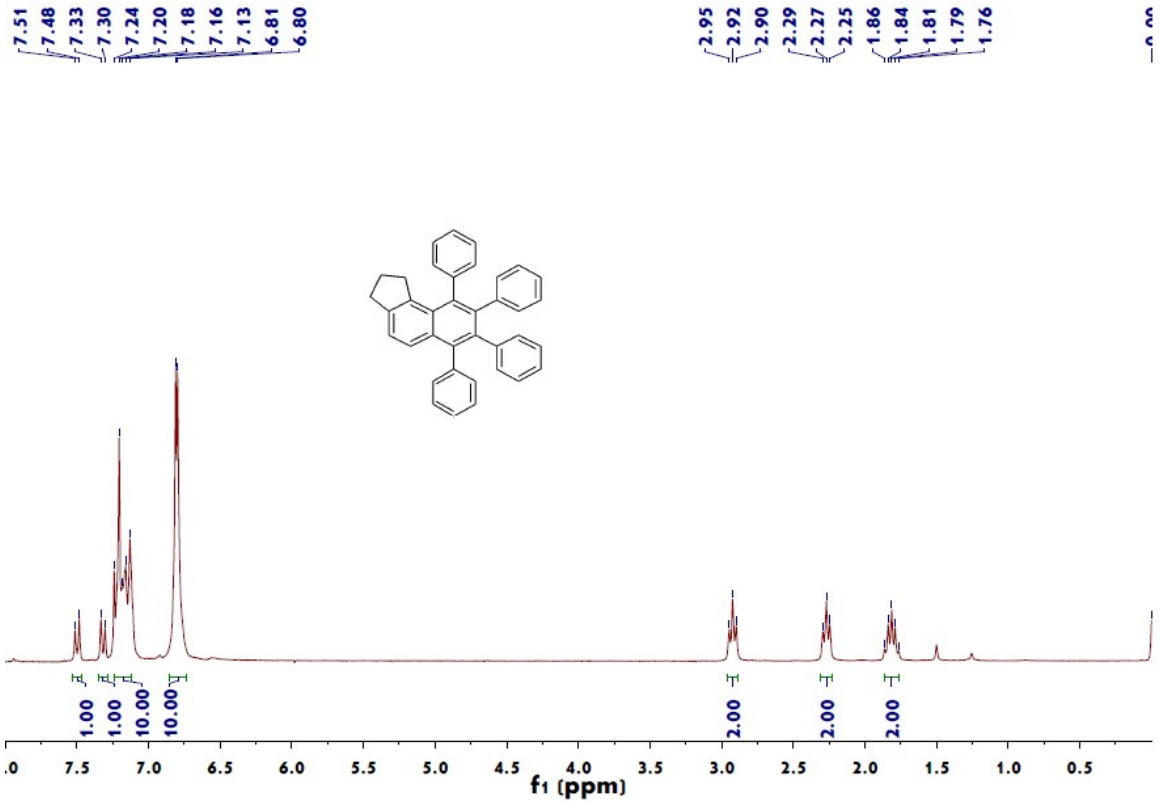


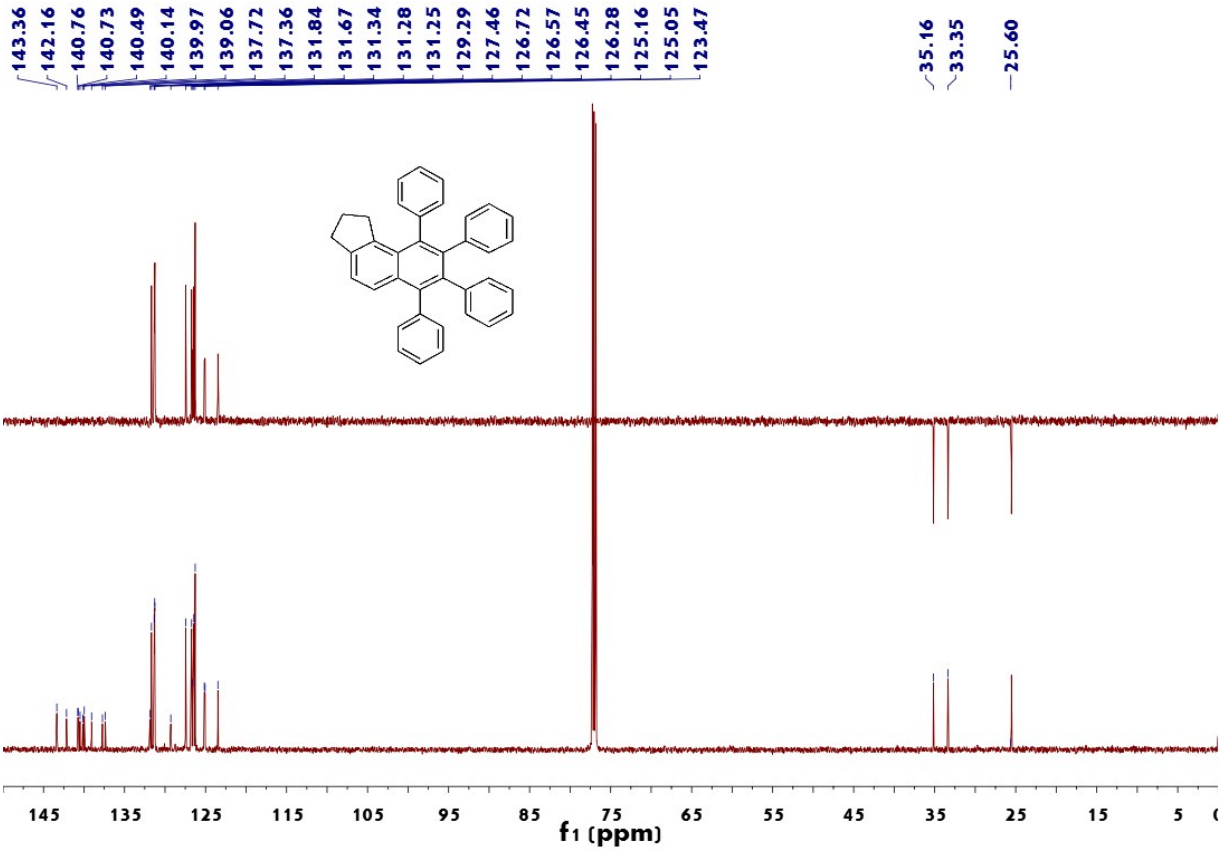
^{1}H and ^{13}C NMR spectra of compound **3j**



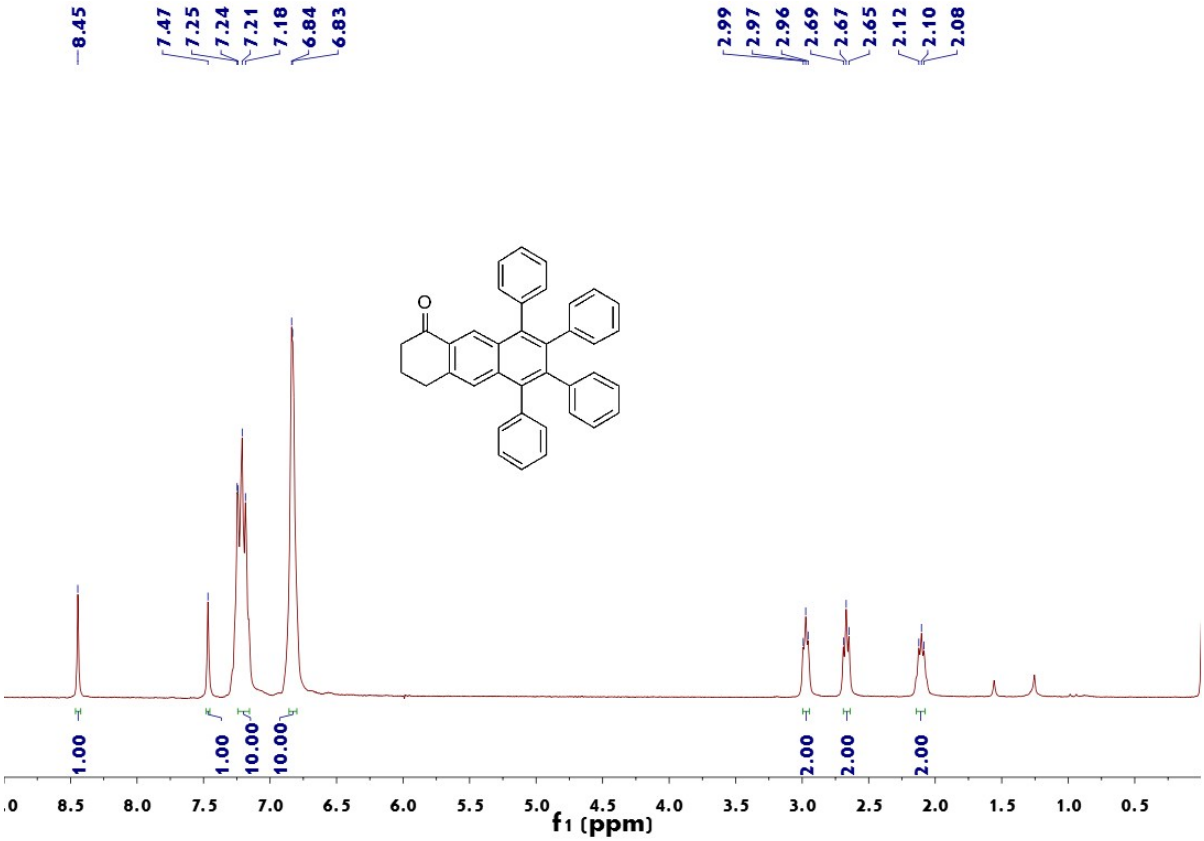


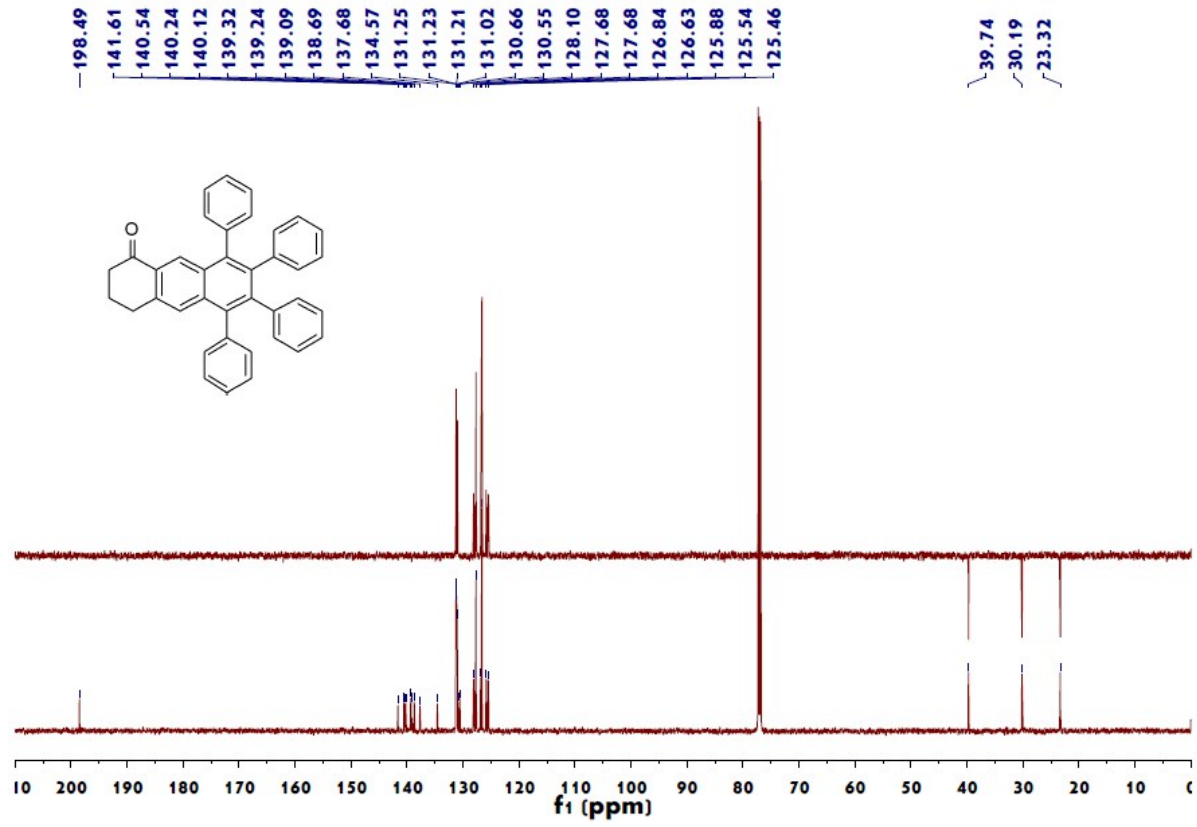
^{1}H and ^{13}C NMR spectra of compound **3k**



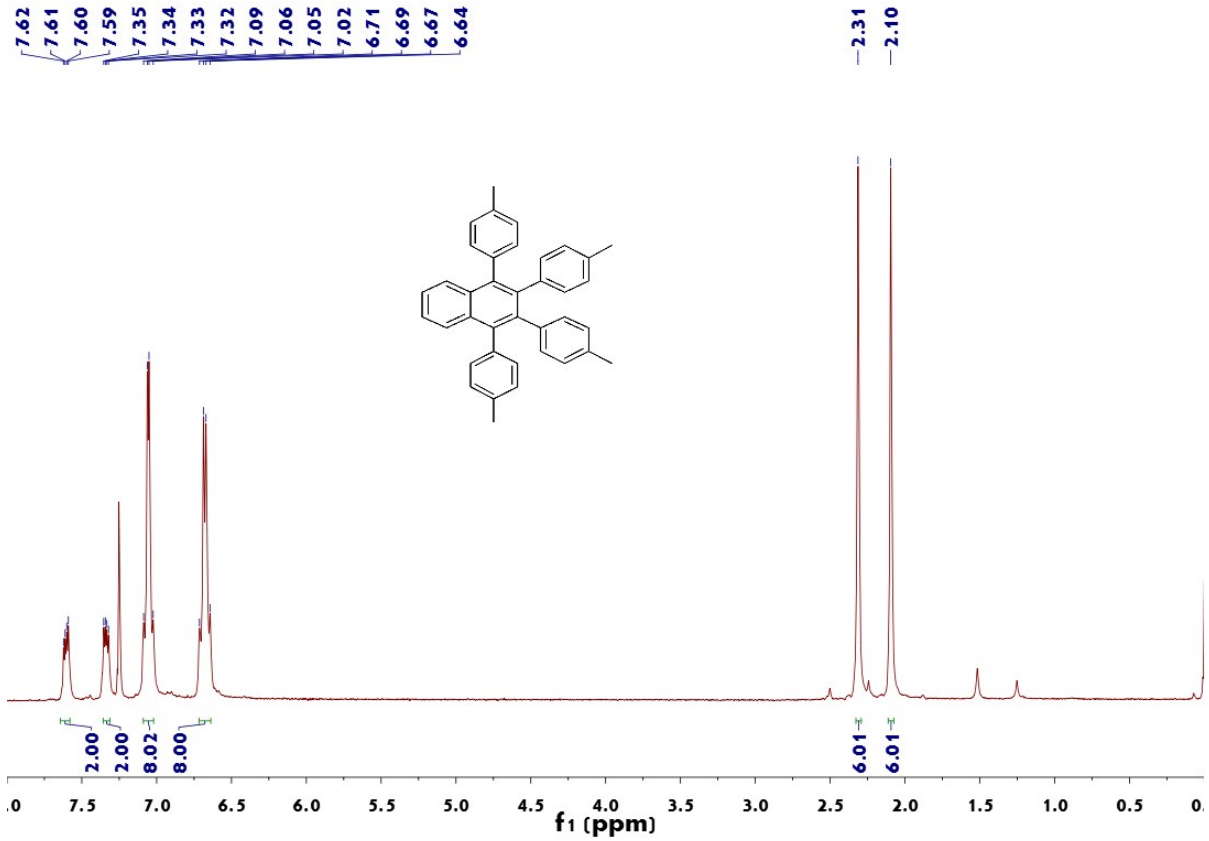


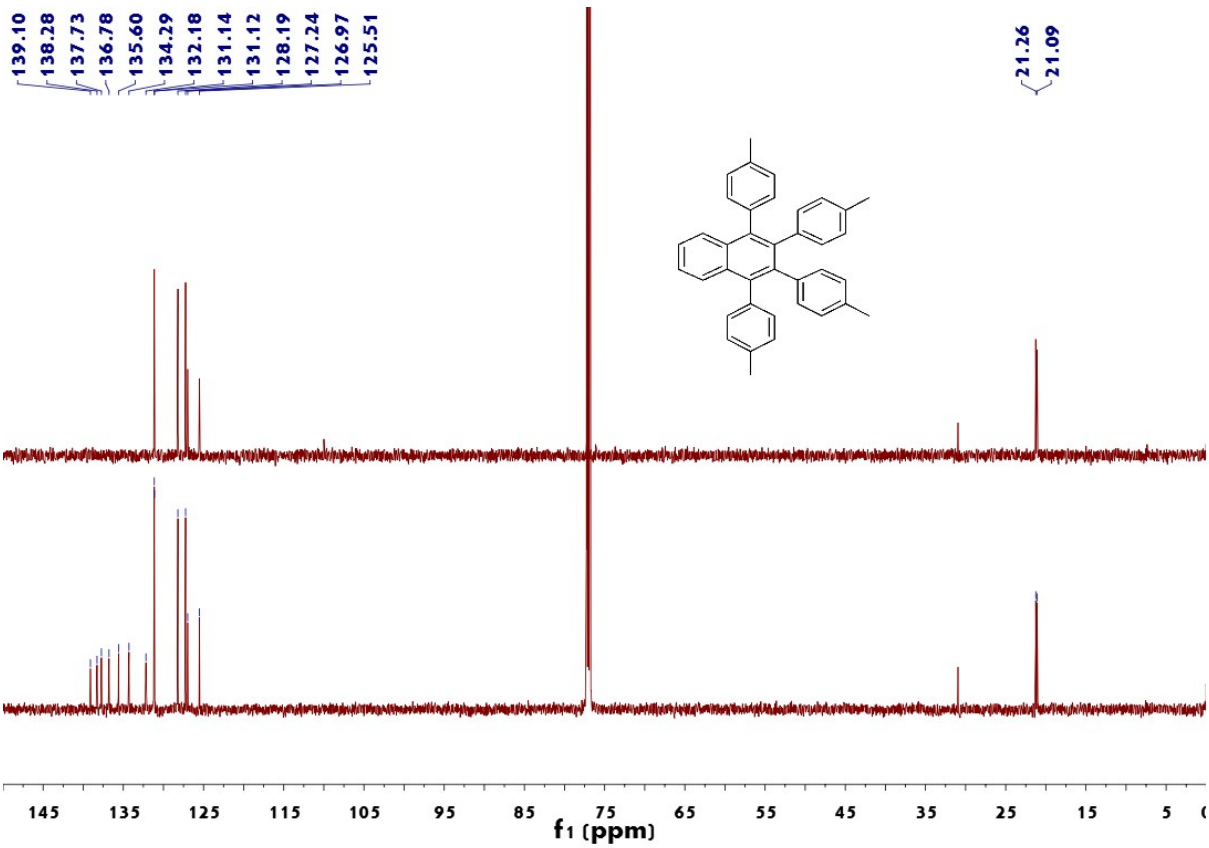
^{1}H and ^{13}C NMR spectra of compound **3l**



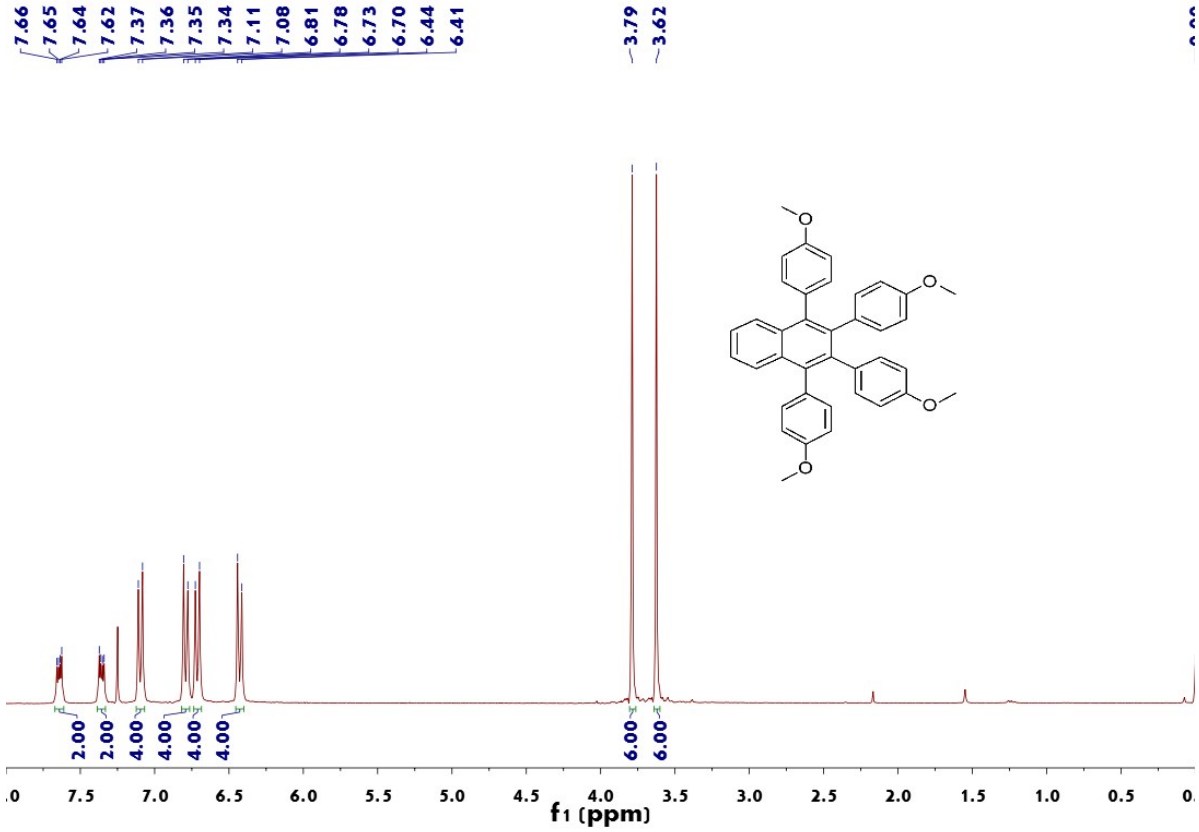


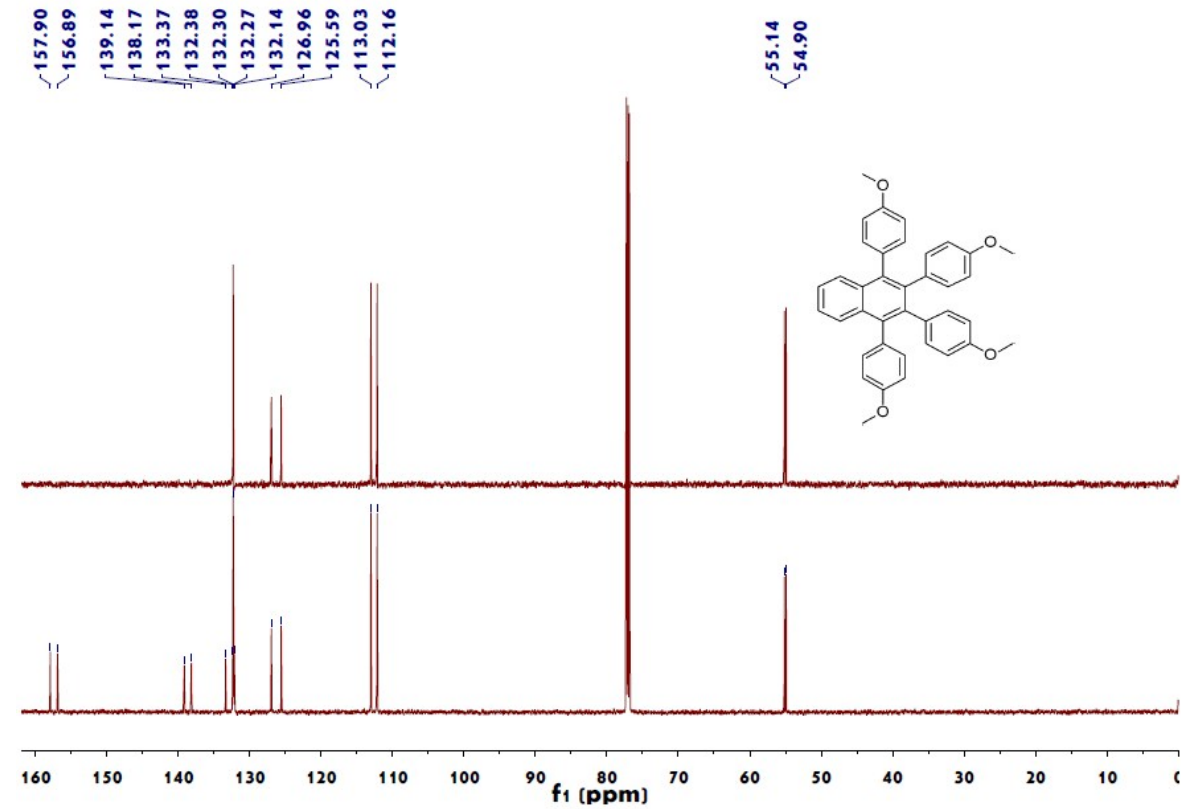
^{1}H and ^{13}C NMR spectra of compound **3m**



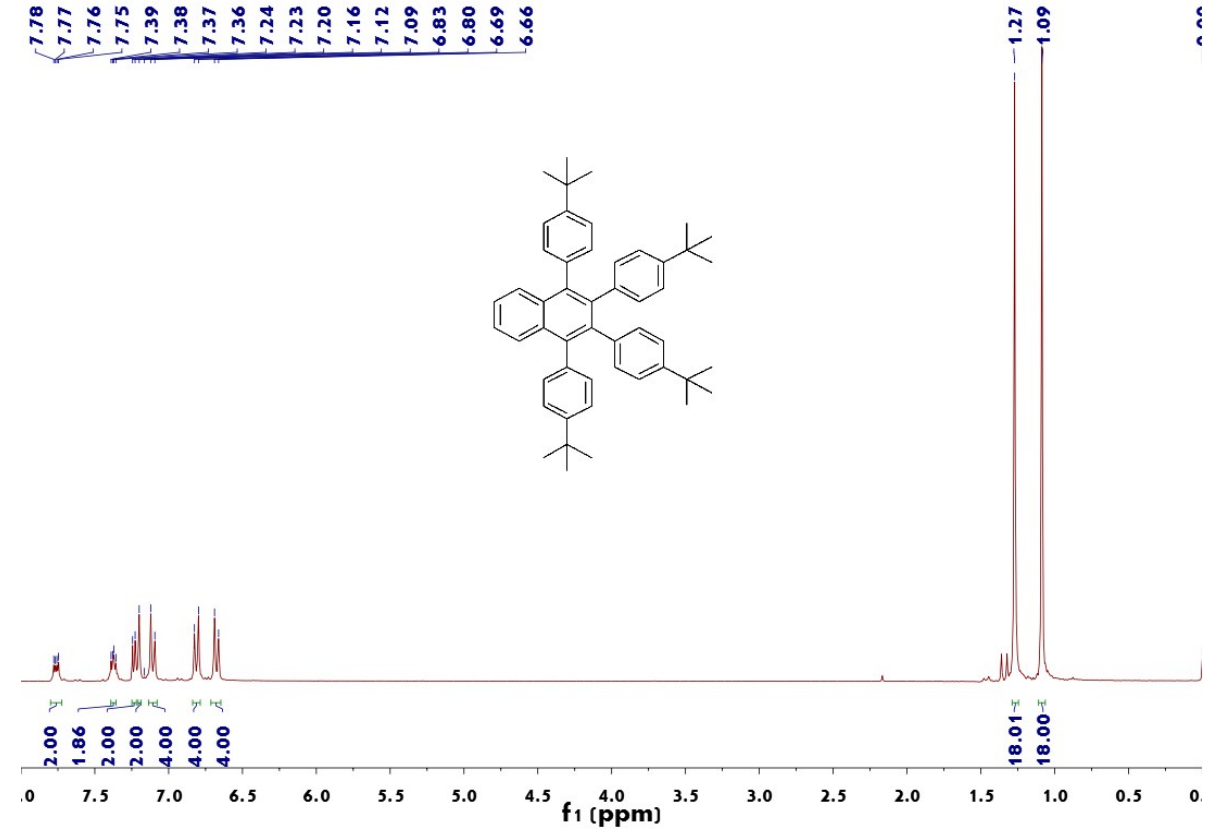


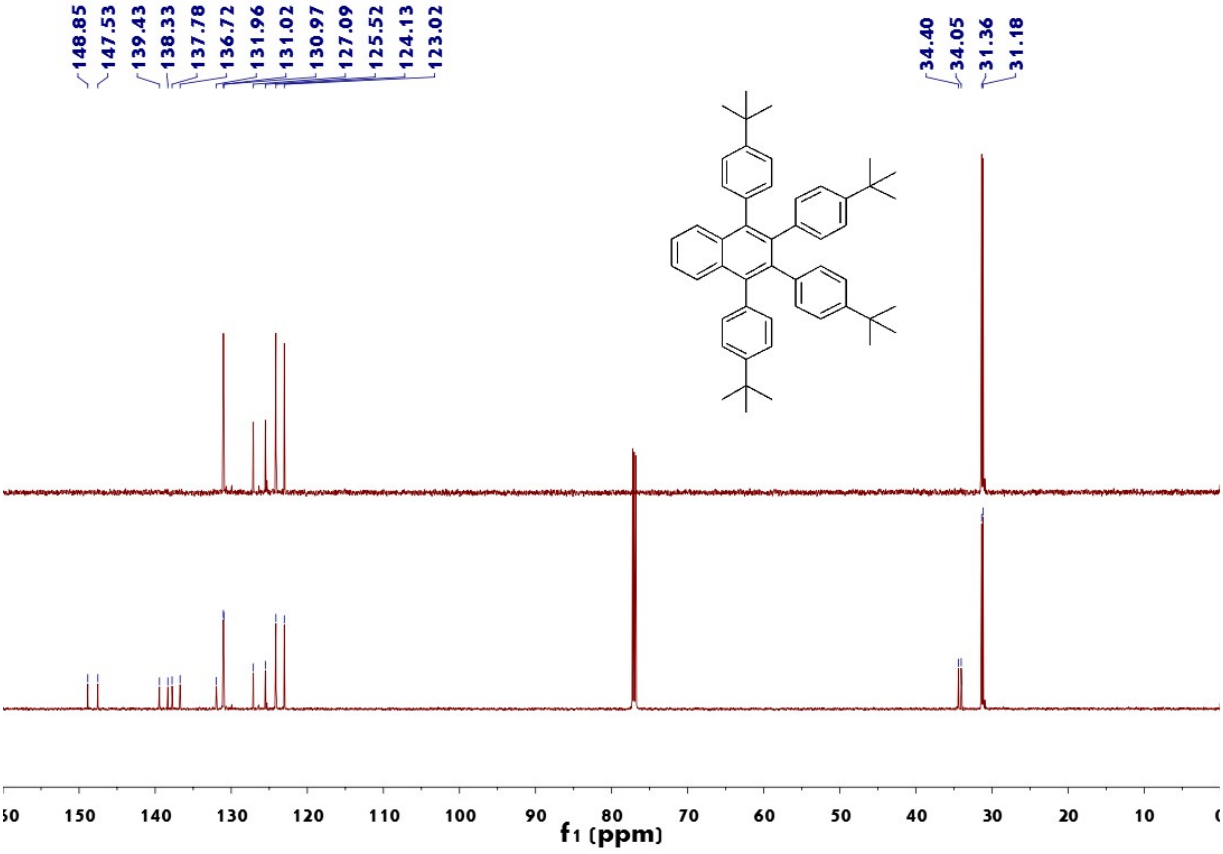
^{1}H and ^{13}C NMR spectra of compound **3n**



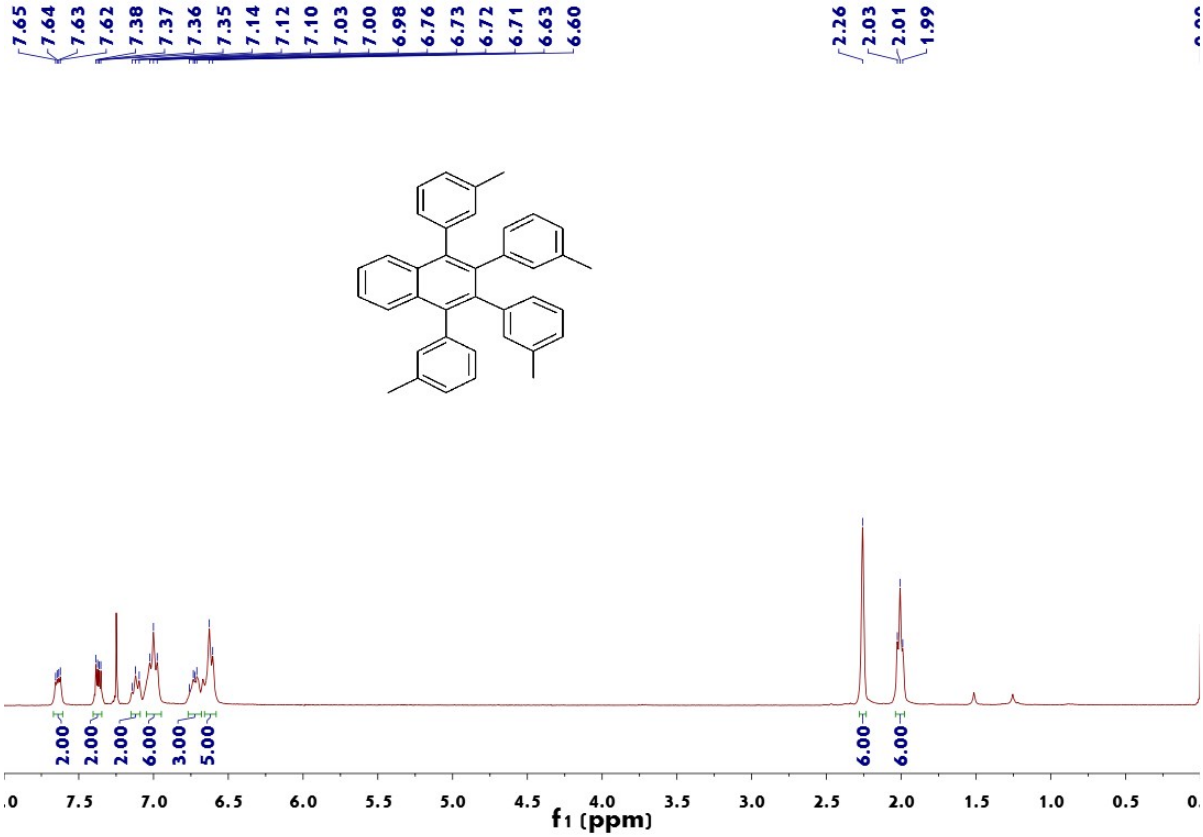


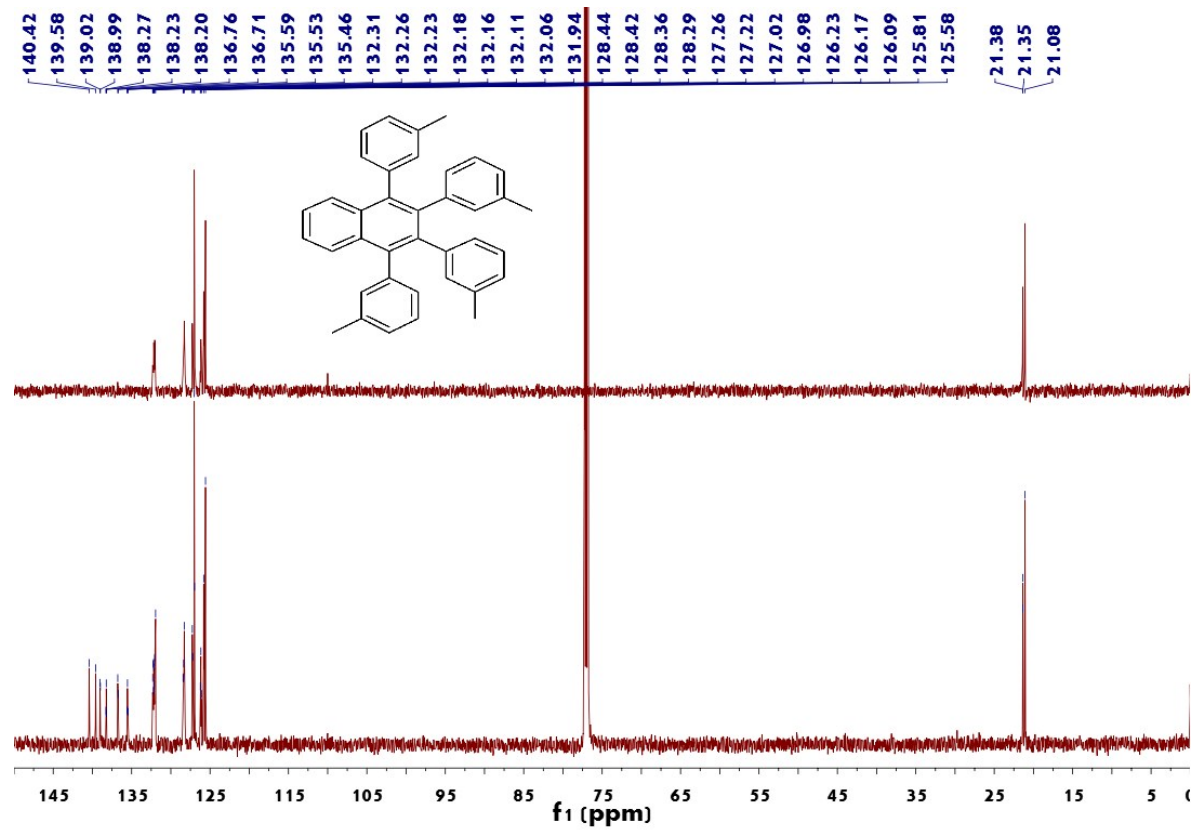
^{1}H and ^{13}C NMR spectra of compound **3o**



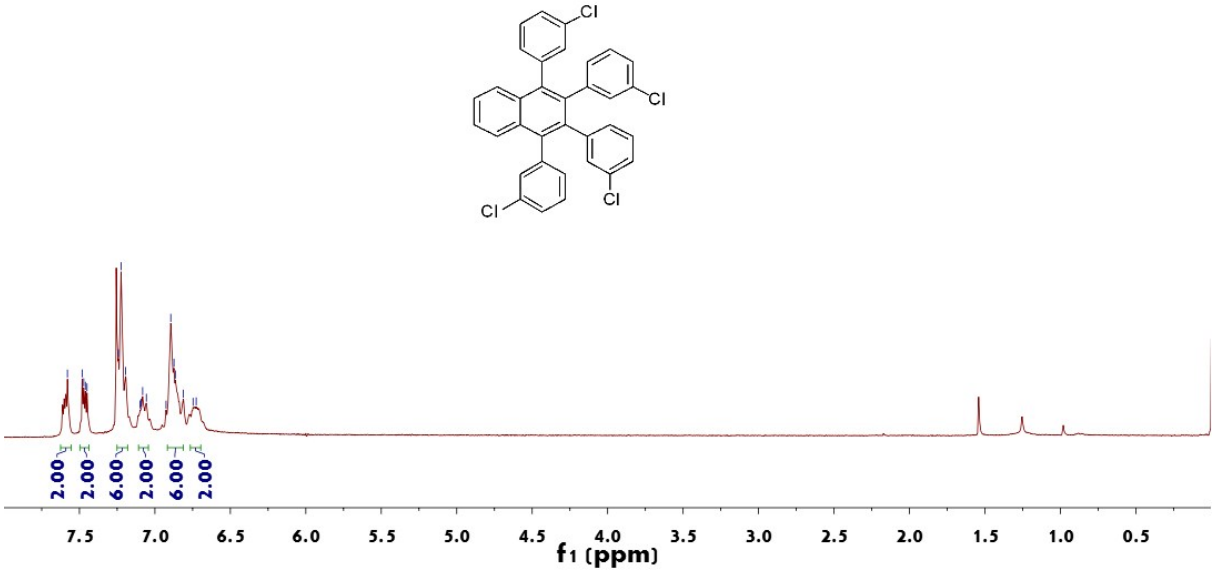


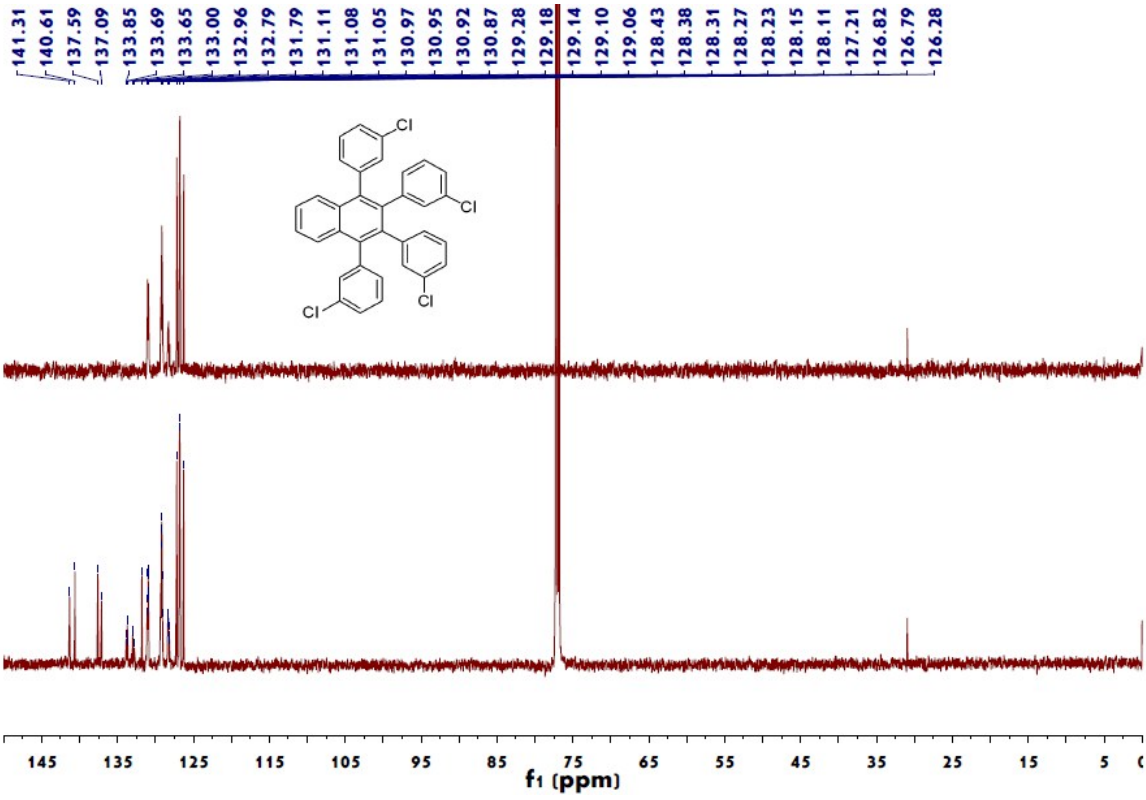
^{1}H and ^{13}C NMR spectra of compound **3p**



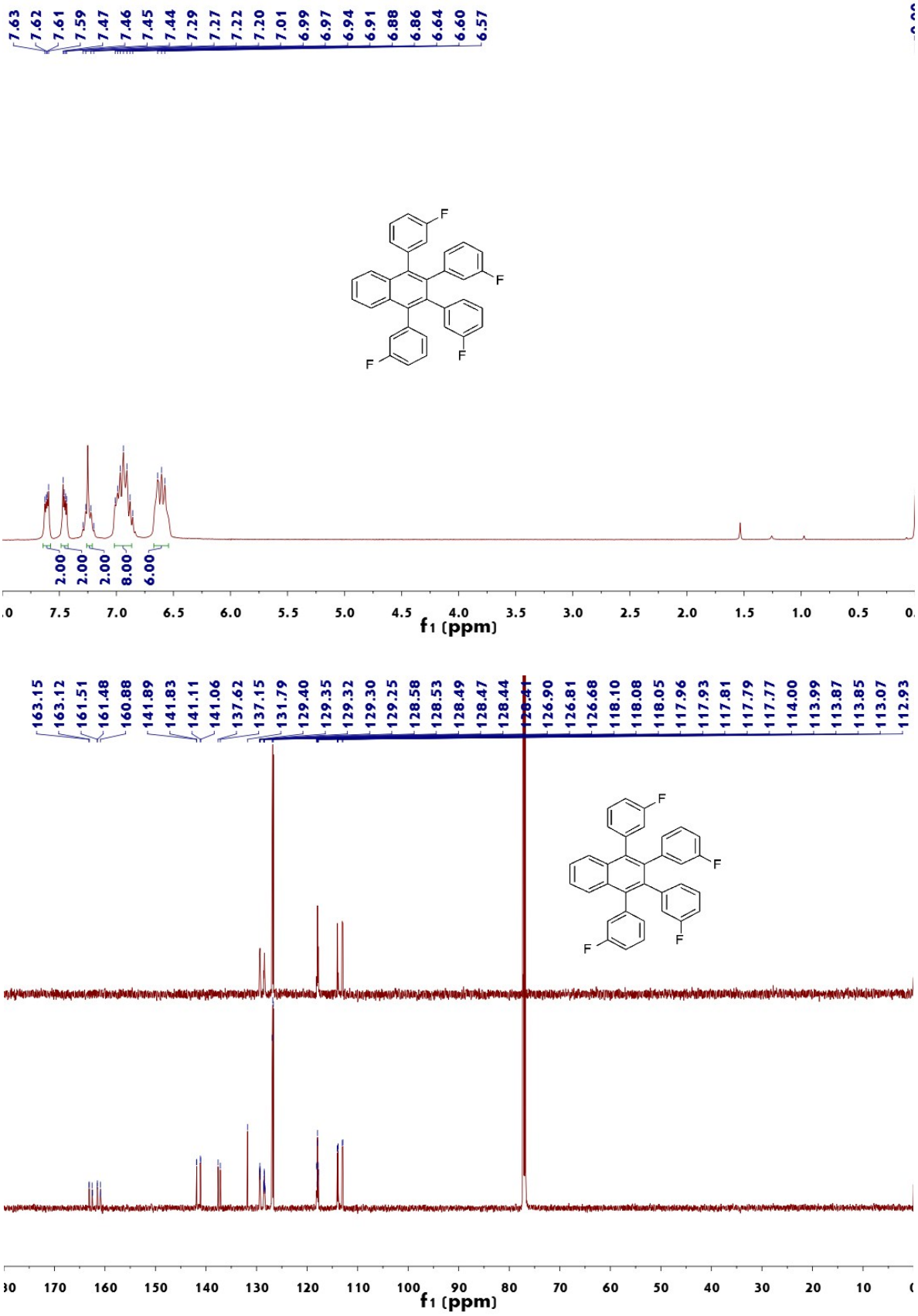


^{1}H and ^{13}C NMR spectra of compound **3q**

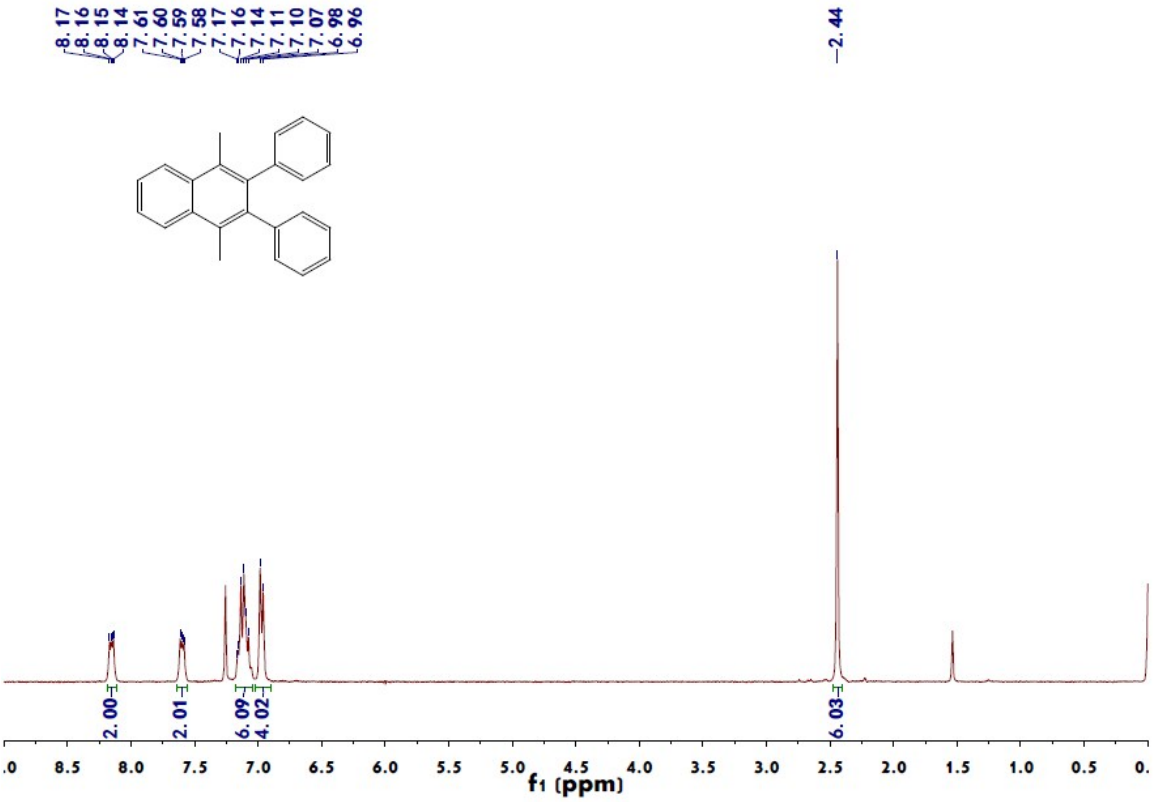


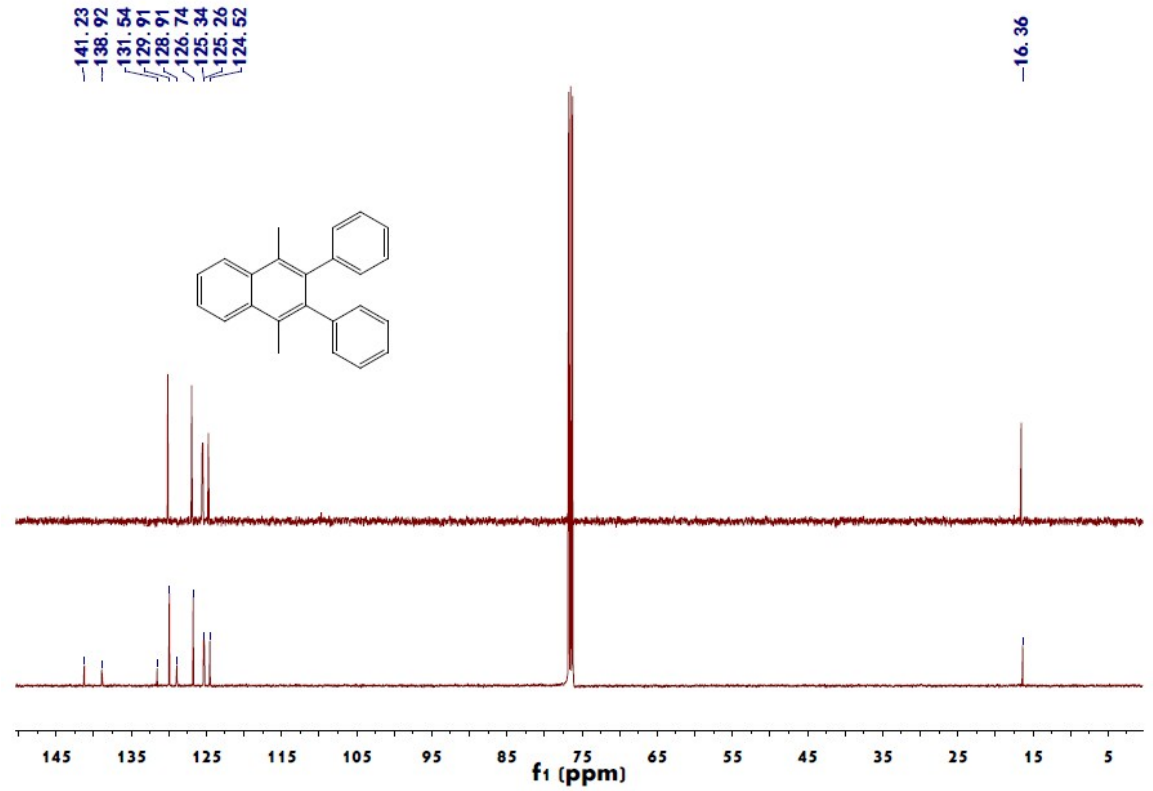


^{1}H and ^{13}C NMR spectra of compound **3r**

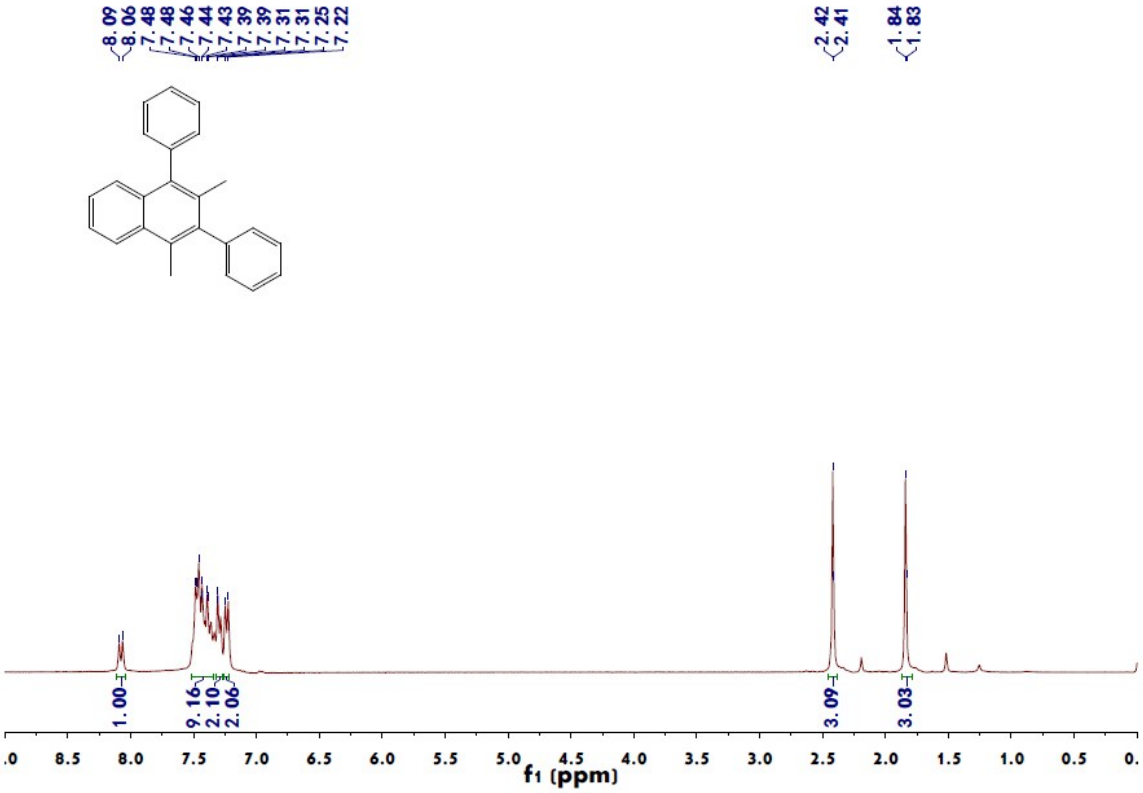


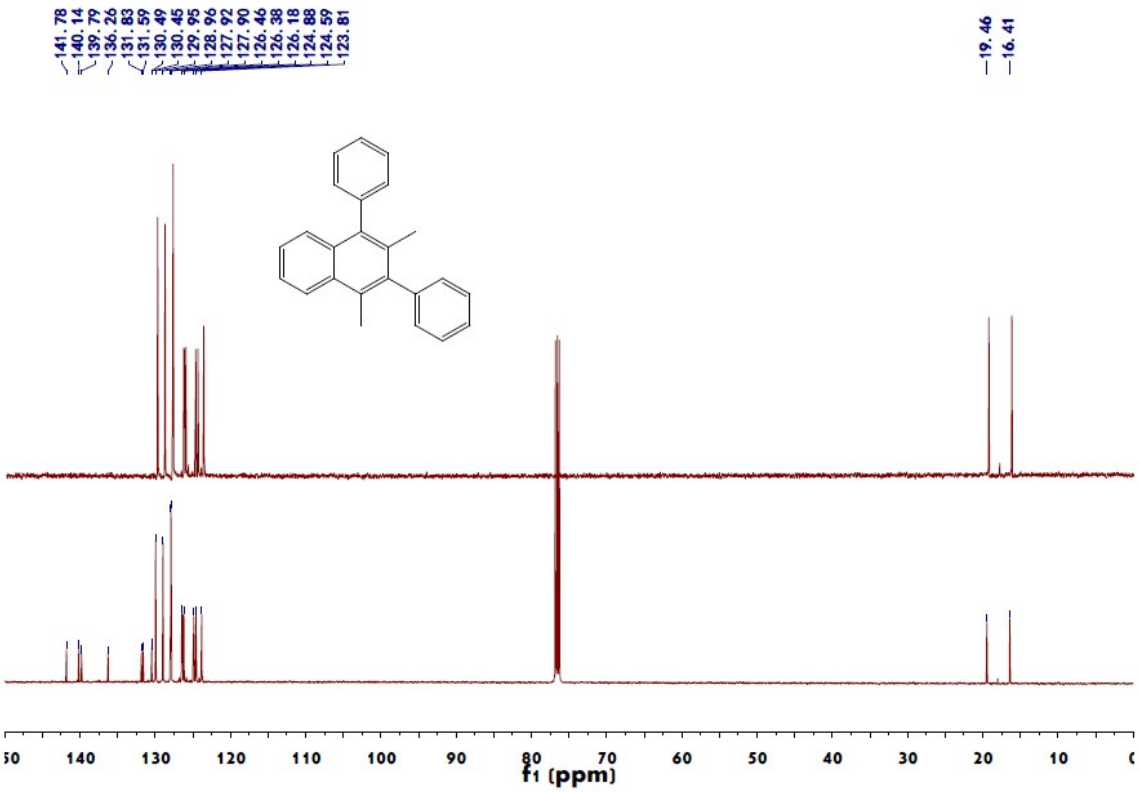
^{1}H and ^{13}C NMR spectra of compound (**3s**)



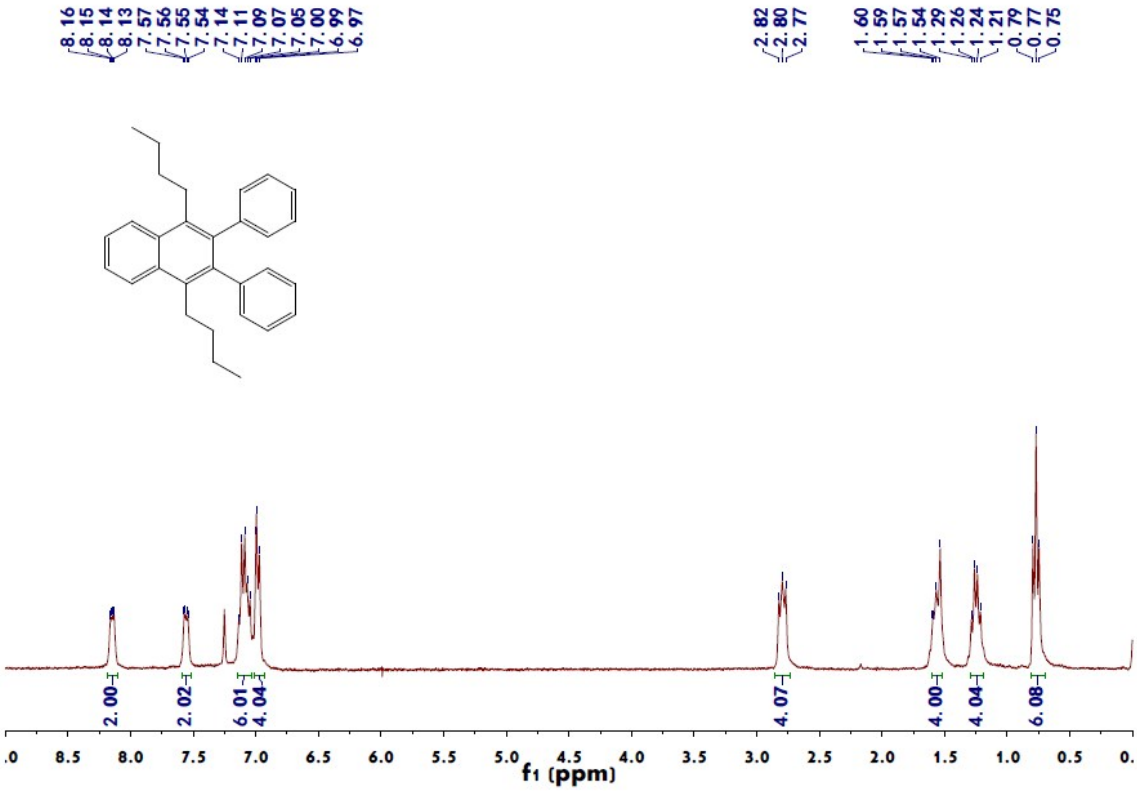


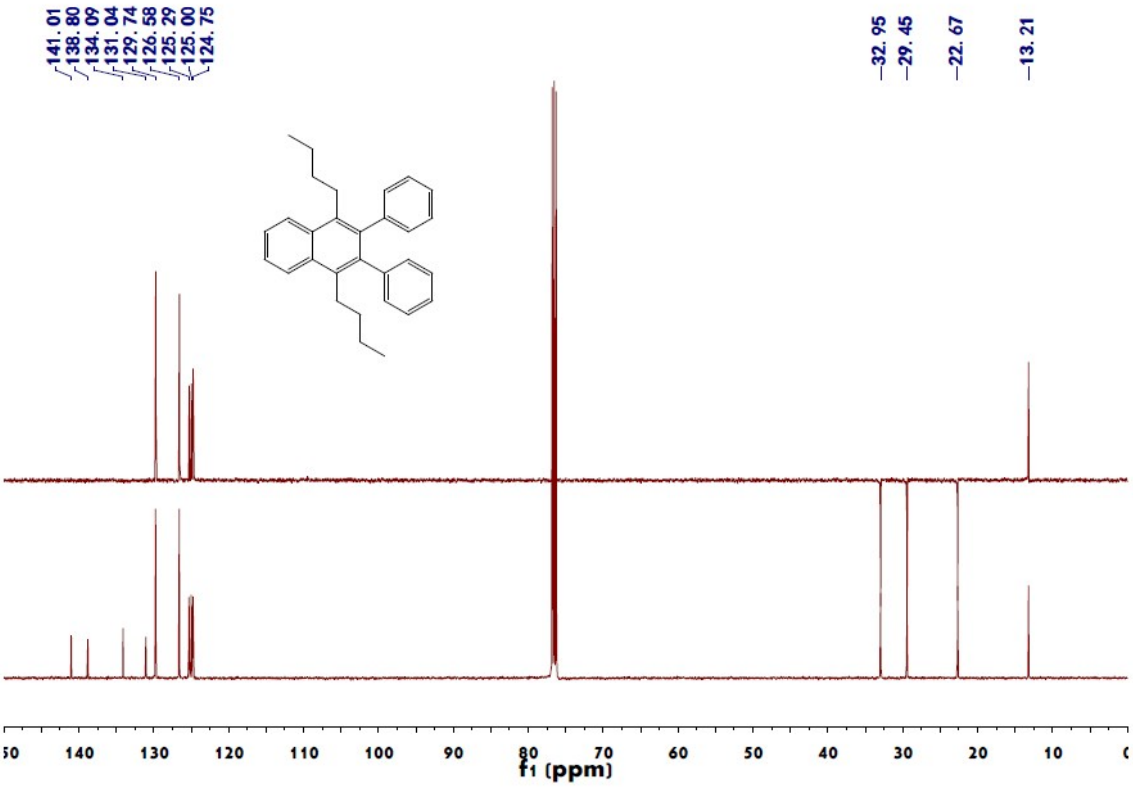
^{1}H and ^{13}C NMR spectra of compound (**3s'**)



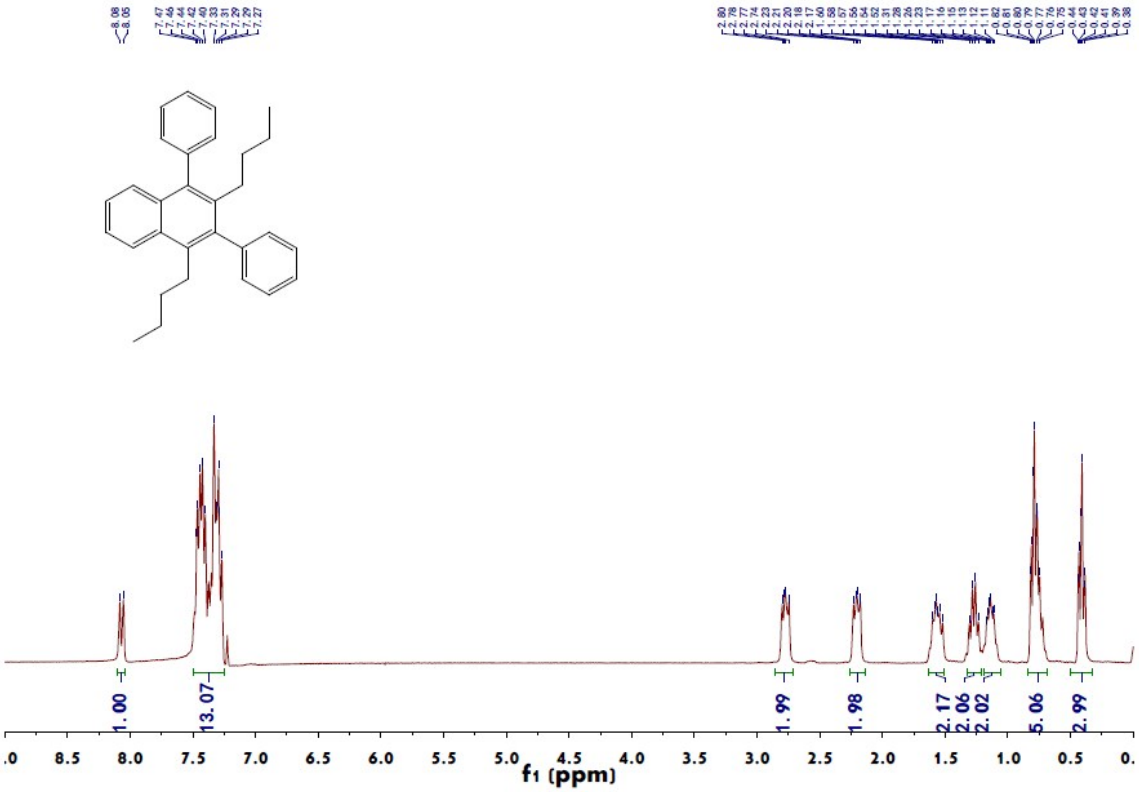


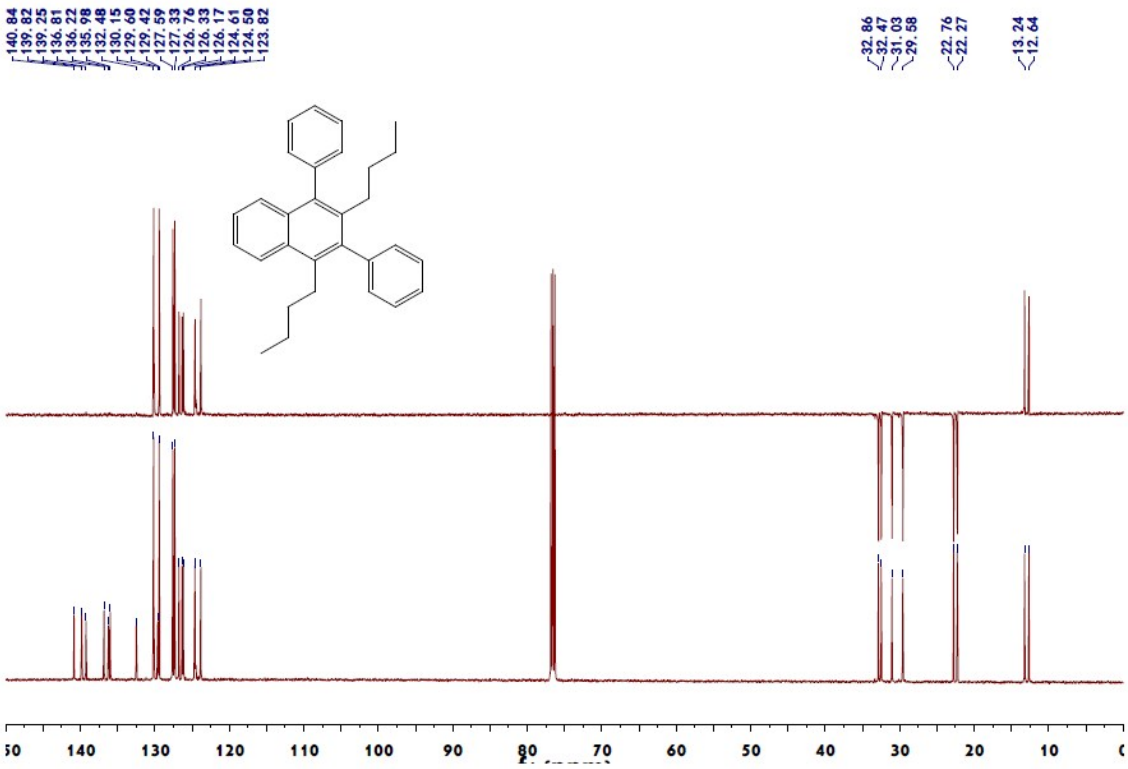
^{1}H and ^{13}C NMR spectra of compound(**3t**)



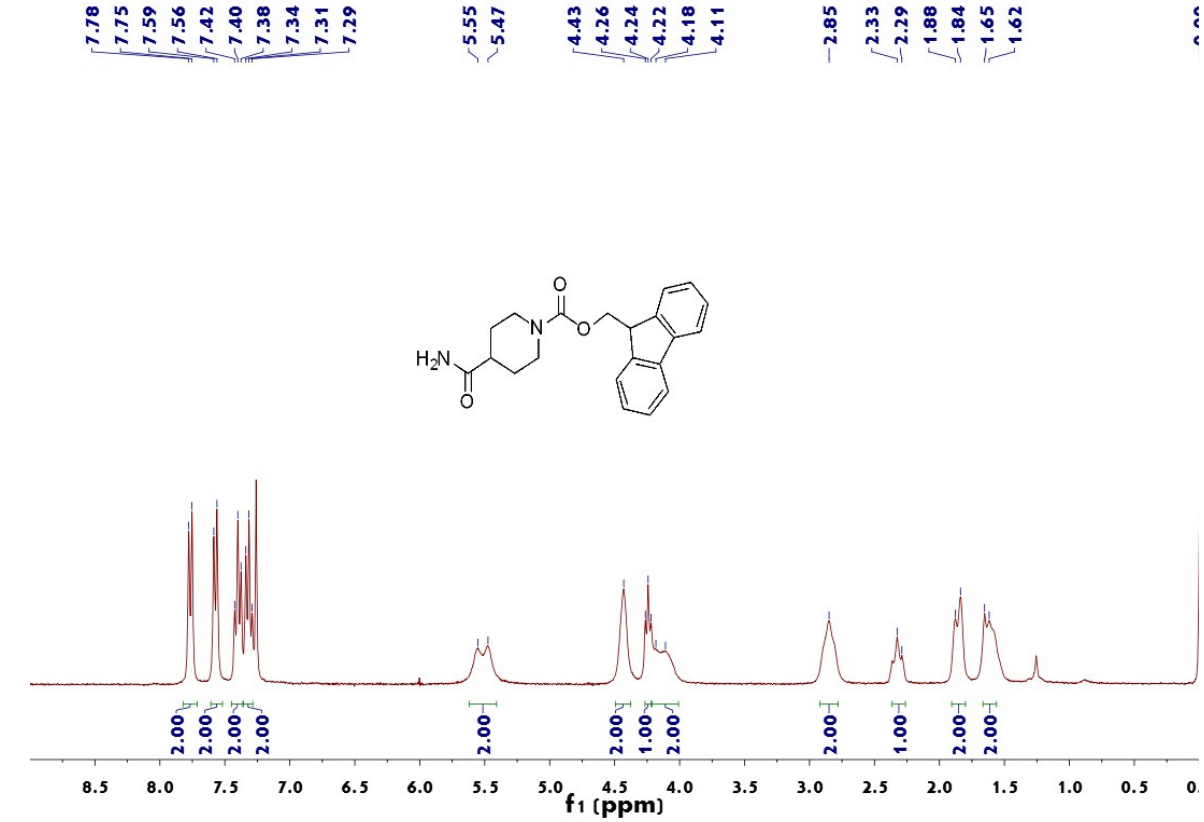


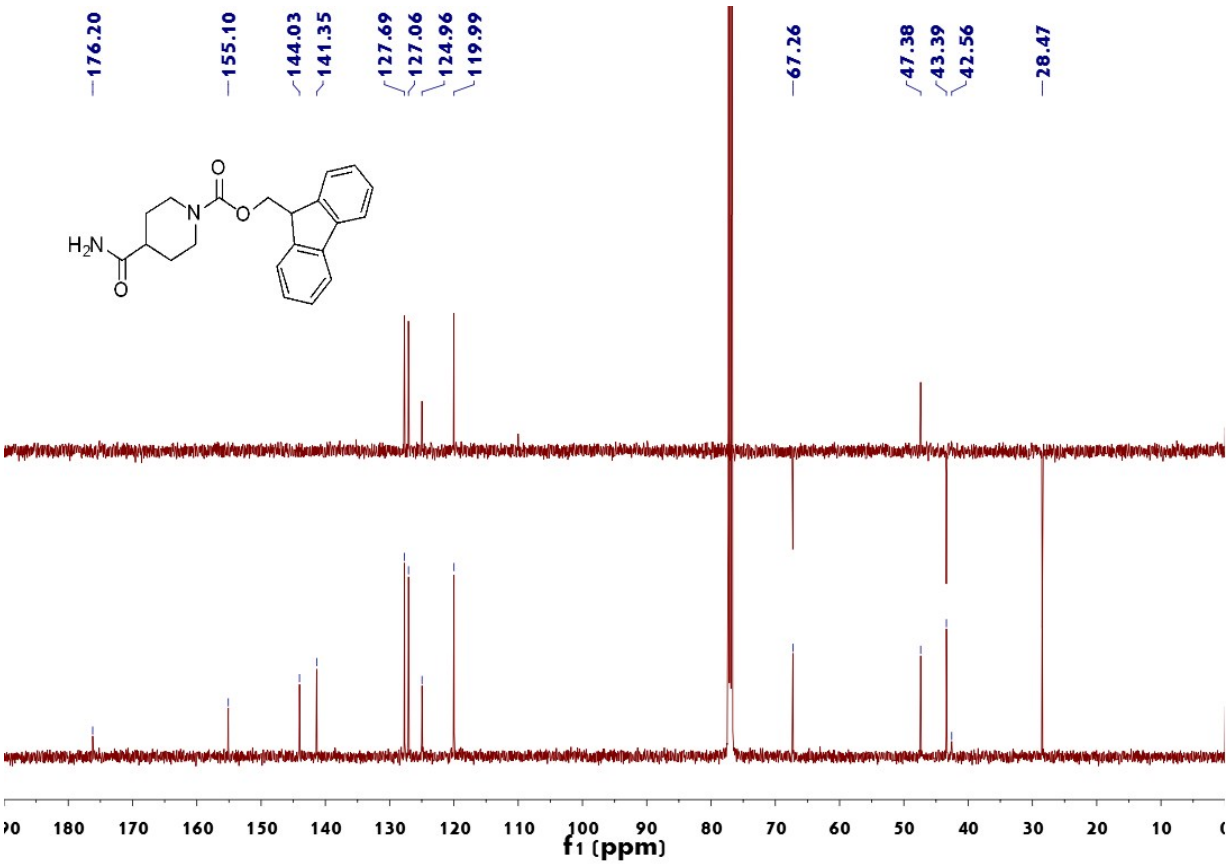
^{1}H and ^{13}C NMR spectra of compound(**3t'**)



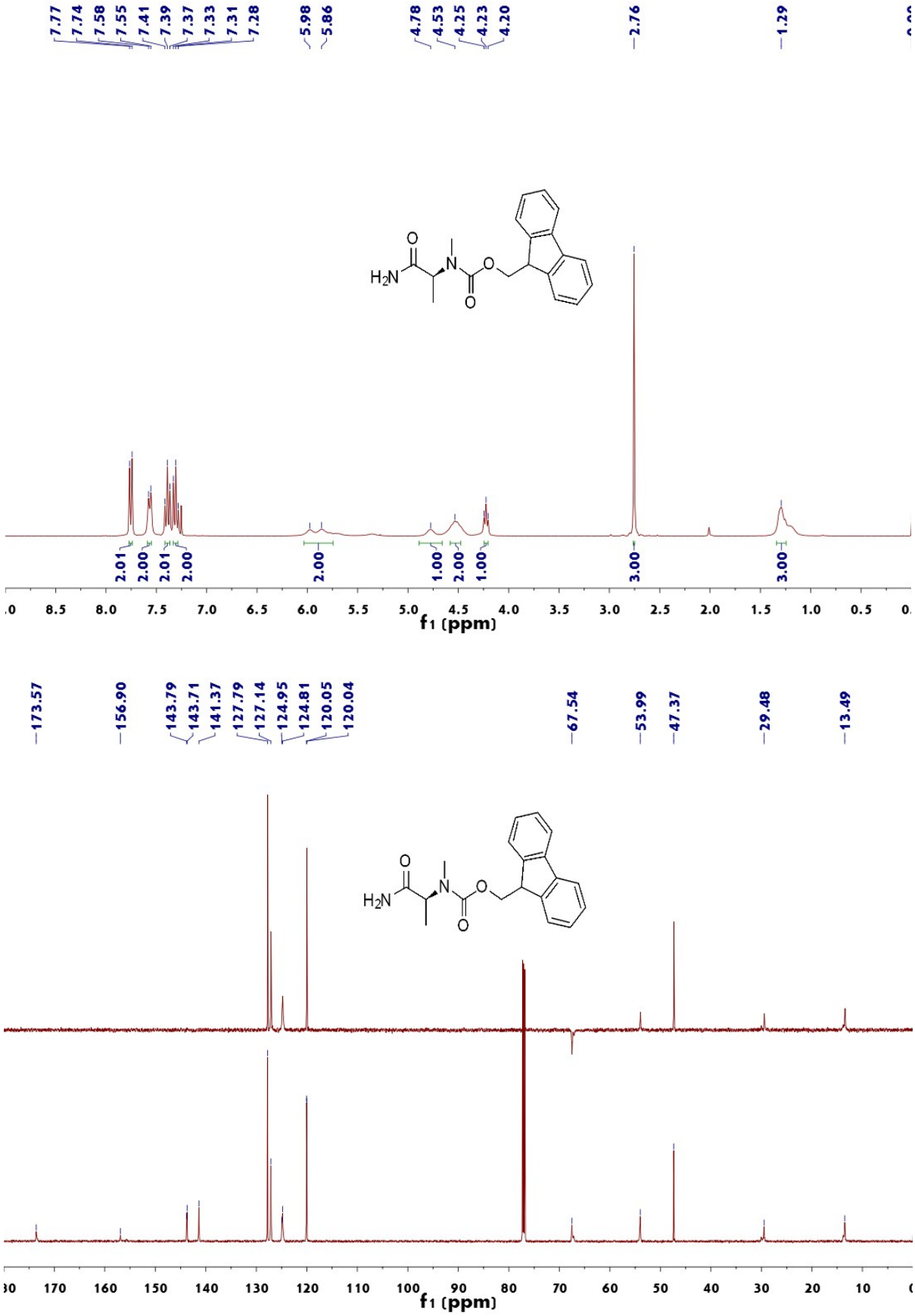


^{1}H and ^{13}C NMR spectra of compound **4**



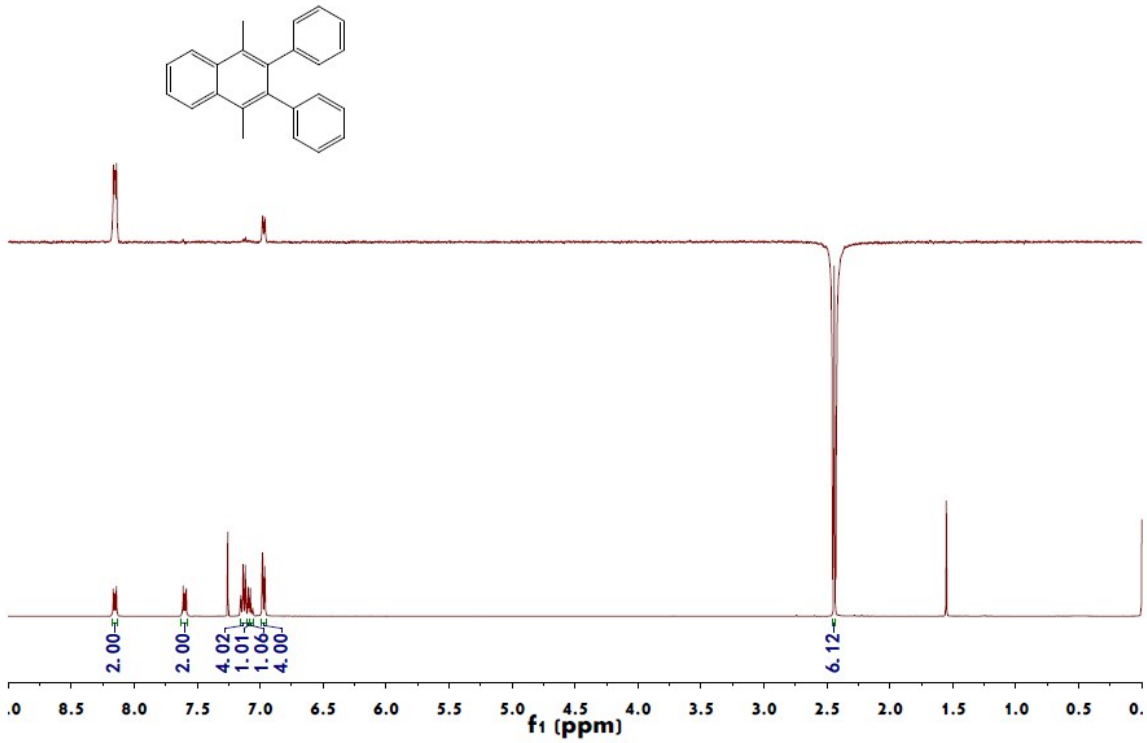


^{1}H and ^{13}C NMR spectra of compound **5**



9. Copies of NOE Spectra of Compounds 3s and 3t

compound **3s:**



compound **3t:**