Electronic Supplementary Material (ESI) for RSC Advances.

Ligand-Enabled and Magnesium-Activated Hydrogenation with Earth-Abundant Cobalt Catalysts

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Supporting Information

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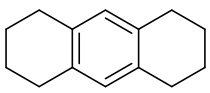
1. Materials and Methods

General. All reactions dealing with air or moisture-sensitive compounds were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck). Flash silica gel column chromatography was performed on silica gel 60N (spherical and neutral, 140–325 mesh) as described by Still.[1] NMR spectra were measured on a Bruker AV-400 spectrometer and reported in parts per million. ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ were referenced internally to tetramethylsilane as a standard, and ^{13}C NMR spectra were recorded at 100 MHz and referenced to the solvent resonance. Analytical gas chromatography (GC) was carried out on a Thermo Trace 1300 gas chromatograph, equipped with a flame ionization detector. Mass spectra (GC-MS) were taken at Thermo Trace 1300 gas chromatograph mass spectrometer. High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (Thermo Scientific, USA) equipped with ESI ionization source. Melting points were determined with a Hanon MP-300. X-ray photoelectron spectroscopy (XPS) data were collected with a Thermo Fisher ESCALAB Xi^{+} spectrometer equipped with monochromatic Al Kα radiation. The analyzer was in the constant analyzer energy (CAE) mode at a pass energy of 20 eV for all the valence-band XPS measurements. The binding energies were measured with an accuracy of 0.1 eV. The binding energy scales were calibrated using the C1s peak at 284.8 eV from carbon contamination.

Materials. Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., Alfa Aesar, Adamas-beta., and other commercial suppliers and used as received. Solvents were dried over sodium (for THF) by refluxing for overnight and freshly distilled prior to use. $Co(acac)_2$ (99.9%), $CoCl_2$ (99.9%), $CoBr_2$ (99.9%), $NiCl_2$(>98%) and $FeBr_2$ (>98%) were purchased from Aldrich Inc. and used as received. Ligands of diketimine, Me-diketimine were prepared according to the related literature procedures[2–4].

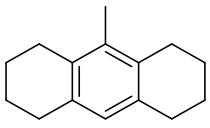
2. General Procedure for Cobalt-Catalyzed Hydrogenation of PAHs

In a Schlenk tube were placed Mg turnings (10 mg, 0.4 mmol) and $CoBr_2$ (5 mg, 0.02mmol). The solids were heated using a heat gun at around 300 °C under vacuum for 5 min. After cooling down under a nitrogen atmosphere, PAH (0.2 mmol), diketimine (8 mg, 0.02 mmol) and THF (2.0ml) were added. The resulting mixture was heated at 80 °C for 2 hours, during which the color of the mixture turned dark. Then the resulting mixture was quickly moved to a high-pressure autoclave. The reaction mixture was stirred under an atmosphere of H_2 (8 Mpa) at 60 °C for 50 h. After quenching with saturated NH_4Cl/H_2O (4 mL), the crude product was extracted with EtOAc (3 × 4 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum. After removal of the volatiles under vacuum, the crude product was purified by column chromatography to afford the desired hydrogenation compound .



1,2,3,4,5,6,7,8-Octahydroanthracene (3a)[5]

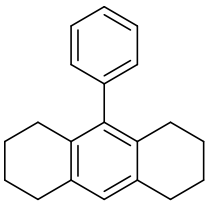
The general procedure was applied to anthracene (36 mg, 0.2 mmol) under an atmosphere of H_2 (8 Mpa) at 60 °C for 48 h. The crude product was purified by column chromatography on silica gel (Petroleum ether) to afford the title compound as a white solid (31 mg, 84% yield). Melting point: 77–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.82 (s, 2H), 2.73 (s, 8H), 1.82–1.76 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.4, 129.6, 29.1, 23.6; IR (neat): 2991, 2902, 2828, 1491, 1407, 970, 902, 849, 802 cm^{-1}; HRMS (EI): calcd for $C_{14}H_{18}$ $[M]^{+}$ 186.1409 found186.1407.



9-Methyl-1,2,3,4,5,6,7,8-octahydroanthracene (3b)[5]

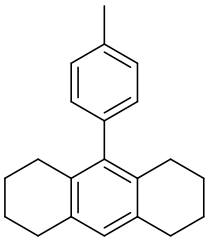
The general procedure was applied to 9-methylanthracene (38 mg, 0.2 mmol) under an atmosphere of H_2 (8 Mpa) at 60 °C for 48 h. The crude product was purified by column chromatography on silica gel (Petroleum

ether) to afford the title compound as a white solid (32 mg, 81% yield). Melting point: 50–52 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.79 (s, 1H), 2.80 (t, J = 6.1 Hz, 4H), 2.72 (t, J = 6.3 Hz, 4H), 2.16 (s, 3H), 1.94–1.77 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.9, 134.3, 132.8, 127.6, 30.2, 27.4, 24.0, 23.1, 14.3; IR (neat): 2986, 2923, 2833, 1418, 975, 849, 807, 702 cm^{-1}. HRMS (EI): calcd for $C_{15}H_{20}$ [M]$^+$ 200.1565 found 200.1564.



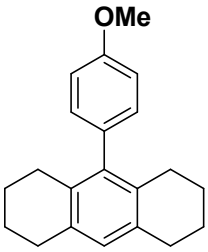
9-Phenyl-1,2,3,4,5,6,7,8-octahydroanthracene (3c)[6]

The general procedure was applied to 9-phenylanthracene (51 mg, 0.2 mmol) under an atmosphere of H_2 (8 Mpa) at 60 °C for 48 h. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid (42 mg, 80% yield). Melting point: 81–82 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (t, J = 7.4 Hz, 2H), 7.36–7.30 (m, 1H), 7.13 (d, J = 5.1, 2H), 6.89 (s, 1H), 2.79 (t, J = 6.2 Hz, 4H), 2.27 (t, J = 6.3 Hz, 4H), 1.77–1.62 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.7, 141.1, 134.3, 132.4, 129.1, 128.5, 126.4, 29.7, 28.2, 23.6, 23.1; IR (neat): 2933, 2823, 1433, 902, 734, 697 cm^{-1}. HRMS (EI): calcd for $C_{20}H_{22}$ [M$^+$] 262.1722, found 262.1719.



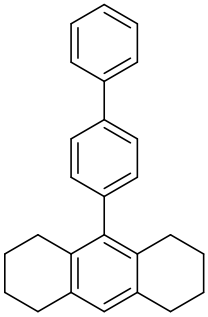
9-(4-Methylphenyl)-1,2,3,4,5,6,7,8-octahydroanthracene (3d)[6]

The general procedure was applied to 9-(4-methylphenyl)anthracene (54 mg, 0.2 mmol) under an atmosphere of H_2 (8 Mpa) at 60 °C for 48 h. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid (45 mg, 81% yield). Melting point: 80–81 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (d, J = 7.8 Hz, 2H), 7.00 (d, J = 7.9 Hz, 2H), 6.87 (s, 1H), 2.78 (t, J = 6.2 Hz, 4H), 2.40 (s, 3H), 2.28 (t, J = 6.3 Hz, 4H), 1.77–1.63 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.6, 138.0, 135.9, 134.3, 132.6, 129.2, 129.0, 128.9, 29.7, 28.2, 23.6, 23.1, 21.3; IR (neat): 3344, 2907, 2849, 1528, 1428, 1097, 870, 813, 770 cm^{-1}. HRMS (EI): calcd for $C_{21}H_{24}$ [M$^+$] 276.1878, found 276.1879.



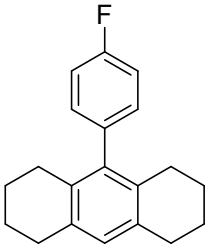
9-(4-Methoxyphenyl)-1,2,3,4,5,6,7,8-octahydroanthracene (3e)[6]

The general procedure was applied to 9-(4-methoxyphenyl)anthracene (57 mg, 0.2 mmol) under an atmosphere of H_2 (8 Mpa) at 60 °C for 48 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a white solid (46 mg, 79% yield). Melting point: 88–89 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.03 (d, J = 8.7 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 6.88 (s, 1H), 3.85 (s, 3H), 2.78 (t, J = 6.1 Hz, 4H), 2.28 (t, J = 6.2 Hz, 4H), 1.75–1.60 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 141.3, 134.3, 133.2, 132.9, 130.1, 129.0, 113.9, 55.2, 29.7, 28.3, 23.7, 23.1. IR (neat): 2933, 2823, 1433, 902, 734, 697 cm^{-1}. HRMS (EI): calcd for $C_{21}H_{24}O$ [M$^+$] 292.1827, found 292.1824.



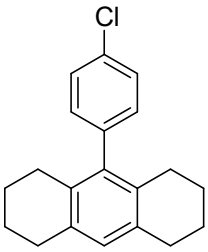
9-([1,1'-Biphenyl]-4-yl)-1,2,3,4,5,6,7,8-octahydroanthracene (3f)[6]

The general procedure was applied to 9-([1,1'-biphenyl]-4-yl)anthracene (66 mg, 0.2 mmol) under an atmosphere of H_2 (8 Mpa) at 60 °C for 48 h. The crude product was purified by column chromatography on silica gel (CH_2Cl_2/PE = 1/50) to afford the title compound as a white solid (53 mg, 78% yield). Melting point: 101–102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.62 (m, 4H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 6.90 (s, 1H), 2.80 (t, *J* = 6.1 Hz, 4H), 2.33 (t, *J* = 6.2 Hz, 4H), 1.80–1.66 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.3, 140.9, 140.1, 139.2, 134.3, 132.5, 129.5, 129.2, 128.7, 127.1, 127.0, 29.7, 28.3, 23.6, 23.1; IR (neat): 2923, 2849, 1475,1454, 1244, 1102, 997, 770, 765, 681 cm^{-1}. HRMS (EI): calcd for $C_{26}H_{26}$ [M$^+$] 338.2035, found 338.2035.



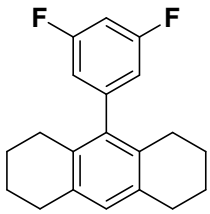
9-(4-Fluorophenyl)-1,2,3,4,5,6,7,8-octahydroanthracene (3g)[6]

The general procedure was applied to 9-(4-fluorophenyl)anthracene (54 mg, 0.2 mmol) under an atmosphere of H_2 (8 Mpa) at 60 °C for 48 h. The crude product was purified by column chromatography on silica gel (Petroleum ether) to afford the title compound as a white solid (46 mg, 82% yield). Melting point: 157–158 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13–7.04 (m, 4H), 6.88 (s, 1H), 2.78 (t, *J* = 6.1 Hz, 4H), 2.24 (t, *J* = 6.2 Hz, 4H), 1.74–1.64 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6 (d, *J* = 243.0 Hz), 140.6, 136.8 (d, *J* = 3.0 Hz), 134.4, 132.6, 130.6 (d, *J* = 7.0 Hz), 129.3, 115.4 (d, *J* = 21.0 Hz), 29.7, 28.2, 23.6, 23.0; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –116.6; IR (neat): 2933, 2823, 1433, 902, 734, 697 cm^{-1}. HRMS (EI): calcd for $C_{20}H_{21}F$ [M$^+$] 280.1627, found 280.1625.



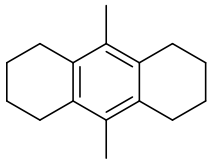
9-(4-Chlorophenyl)-1,2,3,4,5,6,7,8-octahydroanthracene(3h)[6]

The general procedure was applied to 9-(4-chlorophenyl)anthracene (58 mg, 0.2 mmol) using Mg (3.5 equiv) under an atmosphere of H_2 (8.0 Mpa) at 60 °C for 60 h. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid (27 mg, 46% yield). Melting point: 170–171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 6.88 (s, 1H), 2.77 (t, *J* = 6.1 Hz, 4H), 2.23 (t, *J* = 6.2 Hz, 4H), 1.76–1.61 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.4, 139.5, 134.4, 132.4, 132.4, 130.5, 129.4, 128.7, 29.7, 28.2, 23.5, 22.9; IR (neat): 2938, 2839, 1445, 922, 744, 711 cm^{-1}. HRMS (EI): calcd for $C_{20}H_{21}Cl$ [M$^+$] 296.1332, found 296.1330.



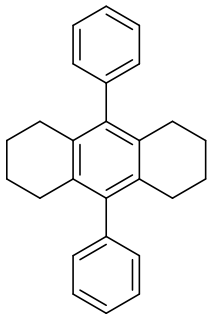
9-(3,5-Difluorophenyl)-1,2,3,4,5,6,7,8-octahydroanthracene (3i)[6]

The general procedure was applied to 9-(3,5-difluorophenyl)anthracene (58 mg, 0.2 mmol) under an atmosphere of H_2 (8 Mpa) at 60 °C for 48 h. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid (43 mg, 72% yield). Melting point: 121–123 °C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.90 (s, 1H), 6.78 (tt, J = 9.1, 2.3 Hz, 1H), 6.71–6.62 (m, 2H), 2.78 (t, J = 6.1 Hz, 4H), 2.28 (t, J = 6.1 Hz, 4H), 1.78–1.64 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.2 (d, J = 246.0 Hz), 144.7 (d, J = 9.0 Hz), 139.5, 134.6, 132.0, 129.7, 112.2 (d, J = 24.0 Hz, 11.0 Hz), 102.0 (t，J = 25.0 Hz), 29.6, 27.9, 23.5, 22.9; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –110.1; IR (neat): 3054, 2907, 2854, 1597, 1418, 1328, 1102, 970, 839, 697 cm^{-1}. HRMS (EI): calcd for $C_{20}H_{20}F_2$ [M$^+$] 298.1533, found 298.1535.



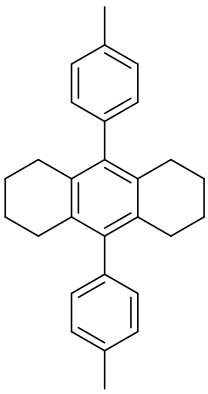
9,10-Dimethyl-1,2,3,4,5,6,7,8-octahydroanthracene (3j)[6]

The general procedure was applied to 9,10-dimethylanthracene (41 mg, 0.2mmol) under an atmosphere of H_2 (8 Mpa) at 60 °C for 48 h. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid (36 mg, 84% yield). Melting point: 151–152 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.67 (s, 8H), 2.10 (s, 6H), 1.81–1.75 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.7, 132.2, 28.1, 23.3, 14.2; IR (neat): 2907, 2839, 2812, 1449, 1412, 1255, 965, 875, 823 cm^{-1}. HRMS (EI): calcd for $C_{16}H_{22}$ [M]$^+$ 214.1722 found 214.1723.



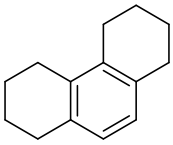
9,10-Diphenyl-1,2,3,4,5,6,7,8-octahydroanthracene (3k)[6]

The general procedure was applied to 9,10-diphenylanthracene (66 mg, 0.2 mmol) under an atmosphere of H_2 (8 Mpa) at 60 °C for 60 h. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid (54 mg, 80% yield). Melting point: >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (t, 4H), 7.34 (t, 2H), 7.24–7.17 (m, 4H), 2.33 (s, 8H), 1.60 (s, 8H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 141.7, 141.3, 132.7, 129.6, 128.8, 126.7, 29.2, 23.5; IR (neat): 3054, 2918, 2839, 1581, 1444, 1023, 792, 739, 681 cm^{-1}. HRMS (EI): calcd for $C_{26}H_{26}$ [M$^+$] 338.2035 found 338.2036.



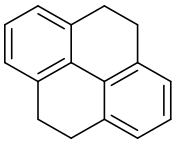
9,10-Di-(4-Methylphenyl)-1,2,3,4,5,6,7,8-octahydroanthracene(3l)[6]

The general procedure was applied to 9,10-di(4-methylphenyl)anthracene (72 mg, 0.2 mmol) under an atmosphere of H_2 (8.0 Mpa) at 60 °C for 60 h. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid (56 mg, 76% yield). Melting point: >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.24 (d, *J* = 7.7 Hz, 4H), 7.08 (d, *J* = 7.8 Hz, 4H), 2.41 (s, 6H), 2.33 (s, 8H), 1.59 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.8, 138.3, 135.9, 132.5, 129.2, 129.1, 29.0, 23.2, 21.3; IR (neat): 3044, 2931, 2822, 1580, 1434, 1016, 787, 753, 677 cm^{-1}. HRMS (EI): calcd for $C_{28}H_{30}$ [M$^+$] 366.2348, found 366.2346.



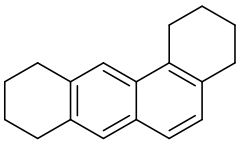
1,2,3,4,5,6,7,8-Octahydrophenanthrene (3m)[7]

The general procedure was applied to phenanthrene (36 mg, 0.2 mmol) under an atmosphere of H_2 (8 Mpa) at 60 °C for 60 h. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as colorless oil (20 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 6.88 (s, 2H), 2.76 (t, *J* = 6.2 Hz, 4H), 2.58 (t, *J* = 6.4 Hz, 4H), 1.86–1.74(m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 135.3, 134.3, 126.4, 30.1, 26.3, 23.5, 22.9; IR (neat): 2912, 2849, 1244, 1060, 997 cm^{-1}. HRMS (EI): calcd for $C_{14}H_{18}$ [M]$^+$ 186.1409, found 186.1411.



4,5,9,10-Tetrahydropyrene (3n)[8]

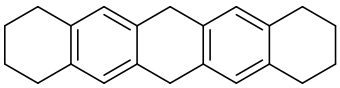
The general procedure was applied to pyrene (40 mg, 0.2 mmol) under an atmosphere of H_2 (8 Mpa) at 60 °C for 60 h. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid (31 mg, 76% yield). Melting point: 138–139 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.16–7.06 (m, 6H), 2.89 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 135.4, 130.6, 127.1, 125.9, 28.3; IR (neat): 3060, 2918, 2823, 1907, 1444, 1149, 776, 739, 628 cm^{-1}; HRMS (EI): calcd for $C_{16}H_{14}$ [M$^+$] 206.1096, found 206.1094.



1,2,3,4,8,9,10,11-Octahydrotetraphene (3o)[6]

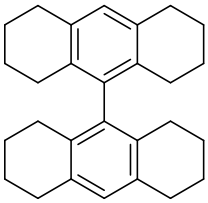
The general procedure was applied to tetraphene (46 mg, 0.2 mmol) under an atmosphere of H_2 (8 Mpa) at 60 °C for 60 h. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid (35 mg, 74% yield). Melting point: 51–52 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.65 (s, 1H), 7.48 (d, *J* = 6.1 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 1H), 3.07 (t, *J* = 6.2 Hz, 2H), 2.99–2.95 (m, 4H), 2.88 (t, *J* = 6.0 Hz, 2H), 1.99–1.82 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 135.9, 134.8, 133.2, 131.1, 130.7,

130.6, 127.4, 127.3, 124.8, 121.9, 30.4, 30.2, 29.5, 25.7, 23.6, 23.5, 23.3, 23.1; IR (neat): 2918, 2844, 1591, 1497, 1423, 1239, 923, 855, 792 cm^{-1}. HRMS (EI): calcd for $C_{18}H_{20}$ [M^+] 236.1565, found 236.1568.



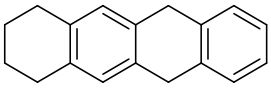
1,2,3,4,6,8,9,10,11,13-Decahydropentacene (3p)[6]

The general procedure was applied to pentacene (56 mg, 0.2 mmol) under an atmosphere of H_2 (8 Mpa) at 60 °C for 48 h. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid (24 mg, 41% yield). Melting point: 174–175 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.98 (s, 4H), 3.81 (s, 4H), 2.74 (s, 8H), 1.80–1.77 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 134.7, 134.2, 128.0, 35.4, 29.2, 23.6; IR (neat): 2986, 2902, 2839, 1497, 1349, 1244, 1249, 928, 818 cm^{-1}. HRMS (EI): calcd for $C_{22}H_{24}$ [M^+] 288.1878, found 288.1880.



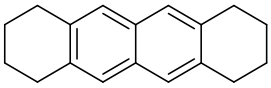
1,1',2,2',3,3',4,4',5,5',6,6',7,7',8,8'-Hexadecahydro-9,9'-bianthracene (3q)[6]

The general procedure was applied to 9,9'-bianthracene (71 mg, 0.2 mmol) under an atmosphere of H_2 (8.0 Mpa) at 60 °C for 60 h. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid (27 mg, 37% yield). Melting point: 170–171 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.85 (s, 2H), 2.76 (t, J = 6.1 Hz, 8H), 2.06 (t, J = 6.3 Hz, 8H), 1.73–1.60 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.7, 134.4, 131.4, 128.4, 29.8, 27.1, 23.7, 23.3; IR (neat): 2912, 2839, 1460, 1418, 1286, 1234, 912, 849 cm^{-1}. HRMS (EI): calcd for $C_{28}H_{34}$ [M^+] 370.2661, found 370.2660.



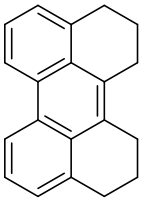
1,2,3,4,6,11-Hexahydrotetracene (3r)[6]

The general procedure was applied to tetracene (46 mg, 0.2 mmol) under an atmosphere of H_2 (8 Mpa) at 60 °C for 48 h. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid (13 mg, 28% yield). Melting point: 128–129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.27 (m, 2H), 7.18 (dd, J = 5.6, 3.3 Hz, 2H), 7.03 (s, 2H), 3.88 (s, 4H), 2.76 (s, 4H), 1.80 (s, 4H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 137.2, 134.9, 134.0, 128.0, 127.5, 126.1, 35.9, 29.3, 23.6; IR (neat): 2965, 2912, 2839, 1475, 1412, 1260, 1081, 797, 713 cm^{-1}. HRMS (EI): calcd for $C_{18}H_{18}$ [M^+] 234.1409, found 234.1411.



1, 2, 3, 4,7,8,9,10-Octahydrotetracene (3r')[6]

The general procedure was applied to tetracene (46 mg, 0.2 mmol) under an atmosphere of H_2 (8 Mpa) at 60 °C for 48 h. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a white solid (20 mg, 42% yield). Melting point: 174–175 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (s, 4H), 2.94 (s, 8H), 1.87–1.84 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.1, 130.9, 125.6, 29.8, 23.5; IR (neat): 3018, 2912, 2833, 2639, 1586, 1491, 1439, 1234, 923, 860, 813 cm^{-1}. HRMS (EI): calcd for $C_{18}H_{20}$ [M^+] 236.1565, found 236.1567.

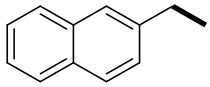


1,2,3,10,11,12-Hexahydroperylene (3s)[6]

The general procedure was applied to perylene (50 mg, 0.2 mmol) under an atmosphere of H_2 (8 Mpa) at 60 °C for 48 h. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford the title compound as a yellow solid (41 mg, 79% yield). Melting point: 184–185 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (d, J = 8.3 Hz, 2H), 7.50–7.41 (m, 2H), 7.33 (d, J = 7.0 Hz, 2H), 3.13–3.06 (m, 8H), 2.15–2.04 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.5, 129.6, 128.9, 128.7, 125.6, 124.9, 120.9, 31.6, 28.2, 23.1; IR (neat): 3007, 2923, 2854, 1597, 1460, 1423,1249, 807, 776, 734 cm^{-1}. HRMS (EI): calcd for $C_{20}H_{18}$ [M$^+$] 258.1409, found 258.1410.

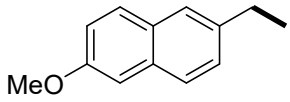
3. General Procedure for Cobalt -catalyzed hydrogenation of olefins

In a Schlenk tube were placed Mg turnings (10 mg, 0.4 mmol) and $CoBr_2$ (5 mg, 0.02 mmol). The solids were heated using a heat gun at around 300 ℃ under vacuum for 5 min. After cooling down under a nitrogen atmosphere, olefins (0.2 mmol), diketimine (8mg, 0.02mmol) and THF (2.0ml) were added, The resulting mixture was heated at 60℃ for 1 hour, during which the color of the mixture turned dark. then the resulting mixture were quickly moved to a high-pressure autoclave. The reaction mixture was stirred under an atmosphere of H_2 (2 Mpa) at room temperature for 24 h. After quenching with saturated NH_4Cl/H_2O (4 mL), the crude product was extracted with EtOAc (3 × 4 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum. After removal of the volatiles under vacuum, the crude product was purified by column chromatography to afford the desired hydrogenation compound.



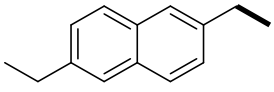
2-ethylnaphthalene (5a)[9]

The general procedure was applied to 2-vinylnaphthalene (31 mg, 0.2mmol) under an atmosphere of H_2 (2.0 Mpa) at room temperature for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether) to afford the title compound as a colorless oil (84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.85 (m, 3H), 7.70 (s, 1H), 7.48 (m, 3H), 2.89 (q , 2H), 1.41 (t, J = 7.6 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ=141.7, 133.7, 131.9, 127.8, 127.6, 127.4, 127.1, 125.8, 125.5, 124.9, 29.0, 15.5. GC-MS (EI): calcd for $C_{12}H_{12}$ [M$^+$] 156.09, found 156.08.



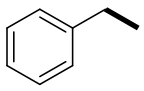
2-ethyl-6-methoxynaphthalene (5b)[10]

The general procedure was applied to 2-methoxy-6-vinylnaphthalene (37 mg, 0.2mmol) under an atmosphere of H_2 (2.0 Mpa) at room temperature for 24 h.The crude product was purified by column chromatography on silica gel (Petroleum ether) to afford the title compound as a yellow solid (89% yield). M.p.:56-57℃;^{1}H NMR (400 MHz, $CDCl_3$) δ=7.68 (d, J = 9.2, 2.7 Hz, 2H), 7.56 (s, 1H), 7.33 (d, J = 8.4, 1.2 Hz, 1H), 7.13 (m, 2H), 3.92 (s, 3H), 2.79 (q, 2H), 1.32 (t, J = 7.6 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ=141.7, 133.7, 131.9, 127.8, 127.6, 127.4, 127.1, 125.8, 125.5, 124.9, 29.0, 15.5. GC-MS (EI): calcd for $C_{13}H_{14}O$ [M$^+$] 186.10, found 186.09.



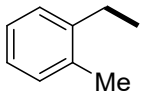
2,6-diethylnaphthalene (5c)[9]

The general procedure was applied to 2-ethyl-6-vinylnaphthalene (36 mg, 0.2mmol) under an atmosphere of H_2 (2.0 Mpa) at room temperature for 24 h.The crude product was purified by column chromatography on silica gel (Petroleum ether) to afford the title compound as a colorless oil (90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.71 (d, J = 8.4 Hz, 2H), 7.59 (s, 2H), 7.32 (d, J = 8.3 Hz, 2H), 2.80 (q, J = 7.6 Hz, 4H), 1.32 (t, J = 7.6 Hz, 6H).; ^{13}C NMR (100MHz, $CDCl_3$) δ = 140.9, 132.1, 127.3, 127.0, 125.3, 28.9, 15.6. GC-MS (EI): calcd for $C_{14}H_{16}$ [M$^+$] 184.13, found 184.13.



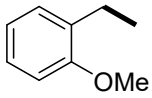
Ethylbenzene (5d)[9]

The general procedure was applied to styrene (0.2mmol) under an atmosphere of H_2 (2.0 Mpa) at room temperature for 24 h.The crude product was purified by column chromatography on silica gel (Petroleum ether) to afford the title compound as a colorless oil (86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.33 –7.10 (m, 2H), 2.65 (q, J = 7.6 Hz, 2H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =144.23, 128.29, 127.84, 125.57, 28.86, 15.61. GC-MS (EI): calcd for C_8H_{10} [M^+] 106.08, found 106.06.



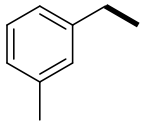
1-ethyl-2-methylbenzene (5e)[9]

The general procedure was applied to 1-methyl-2-vinylbenzene (0.2 mmol) under an atmosphere of H_2 (2.0 Mpa) at room temperature for 24 h.The crude product was purified by column chromatography on silica gel (Petroleum ether) to afford the title compound as a colorless oil (87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.20 –7.09 (m, 4H), 2.65 (q, J = 7.6 Hz, 1H), 2.33 (s, 1H), 1.24 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ =142.29, 135.73, 129.99, 127.86, 125.98, 125.70, 26.15, 19.14, 14.35. GC-MS (EI): calcd for C_9H_{12} [M^+] 120.09, found 120.08.



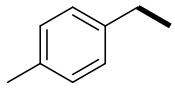
1-ethyl-2-methoxybenzene(5f)[9]

The general procedure was applied to 1-methoxy-2-vinylbenzene (0.2mmol) under an atmosphere of H_2 (2.0 Mpa) at room temperature for 24 h.The crude product was purified by column chromatography on silica gel (Petroleum ether) to afford the title compound as a colorless oil (82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.20 (t, J = 8.6 Hz, 2H), 6.97–6.85 (m, 2H), 3.86 (s, 3H), 2.68 (q, J = 7.5 Hz, 2H), 1.23 (dd, J = 9.0, 6.0 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ = 157.31, 132.56, 128.87, 126.73, 120.39, 110.08, 55.18, 23.19, 14.13. GC-MS (EI): calcd for $C_9H_{12}O$ [M^+] 136.09, found 136.10.



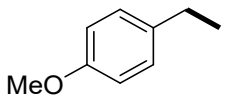
1-ethyl-3-methylbenzene (5g)[9]

The general procedure was applied to 1-methyl-3-vinylbenzene (0.2mmol) under an atmosphere of H_2 (2.0 Mpa) at room temperature for 24 h.The crude product was purified by column chromatography on silica gel (Petroleum ether) to afford the title compound as a colorless oil (85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.20 (t, J = 7.4 Hz, 1H), 7.08–6.98 (m, 3H), 2.64 (q, J = 7.6 Hz, 2H), 2.36 (s, 3H), 1.26 (d, J = 0.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =144.20, 137.82, 128.68, 128.20, 126.31, 124.83, 28.78, 21.40, 15.64. GC-MS (EI): calcd for C_9H_{12} [M^+] 120.09, found 120.05.



1-ethyl-4-methylbenzene (5h)[9]

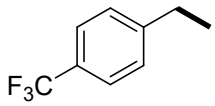
The general procedure was applied to 1-methyl-4-vinylbenzene (0.2mmol) under an atmosphere of H_2 (2.0 Mpa) at room temperature for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether) to afford the title compound as a colorless oil (80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.12 (s, 4H), 2.64 (q, J = 7.6 Hz, 1H), 2.35 (s, 1H), 1.25 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =141.19, 134.97, 128.97, 127.72, 28.41, 20.96, 15.77. GC-MS (EI): calcd for C_9H_{12} [M^+] 120.09, found 120.08.



1-ethyl-4-methoxybenzene(5i)[9]

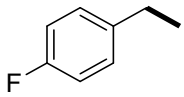
The general procedure was applied to 1-methoxy-4-vinylbenzene (0.2mmol) under an atmosphere of H_2 (2.0 Mpa) at room temperature for 24 h.The crude product was purified by column chromatography on silica gel (Petroleum ether) to afford the title compound as a colorless oil (84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.15 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 3.81 (s, 2H), 2.62 (q, J = 7.6 Hz, 1H), 1.24 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100

MHz, $CDCl_3$) δ =157.58, 136.35, 128.67, 113.68, 55.21, 27.94, 15.88. GC-MS (EI): calcd for $C_9H_{12}O$ [M^+] 136.09, found 136.10.



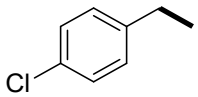
1-ethyl-4-(trifluoromethyl)benzene (5j)[11]

The general procedure was applied to 1-(trifluoromethyl)-4-vinylbenzene (0.2mmol) under an atmosphere of H_2 (2.0 Mpa) at room temperature for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether) to afford the title compound as a colorless oil (87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.54 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 2.71 (q, J = 7.6 Hz, 2H), 1.26 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.28, 128.15, 125.24, 125.20, 28.75, 15.28. ^{19}F NMR (376 MHz, $CDCl_3$) δ =-62.27. GC-MS (EI): calcd for $C_9H_9F_3$ [M^+] 174.07, found 174.09.



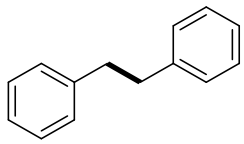
1-ethyl-4-fluorobenzene (5k)[11]

The general procedure was applied to 1-fluoro-4-vinylbenzene (0.2mmol) under an atmosphere of H_2 (2.0 Mpa) at room temperature for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether) to afford the title compound as a colorless oil (80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.52–7.46 (m, 1H), 7.31 (dd, J = 9.8, 7.7 Hz, 1H), 2.97 (q, J = 7.6 Hz, 1H), 1.57 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=161.12(d, J=241Hz), 139.78(d, J=3.0 Hz), 129.10(d, J=8.0 Hz), 115.94(d, J=20 Hz),, 55.24, 28.07, 15.76; ^{19}F NMR (376 MHz, $CDCl_3$) δ=-118.28. GC-MS (EI): calcd for C_8H_9F [M^+] 124.07, found 124.04.



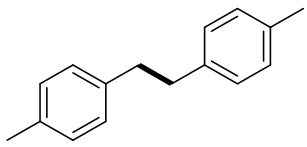
1-chloro-4-ethylbenzene (5l)[9]

The general procedure was applied to 1-chloro-4-vinylbenzene (0.2mmol) under an atmosphere of H_2 (2.0 Mpa) at room temperature for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether) to afford the title compound as a colorless oil (73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.24 (d, J = 8.3 Hz, 1H), 7.11 (d, J = 8.3 Hz, 1H), 2.61 (q, J = 7.6 Hz, 1H), 1.21 (t, J = 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ =142.60, 131.23, 129.19, 128.34, 28.24, 15.51. GC-MS (EI): calcd for C_8H_9Cl [M^+] 140.04, found 140.02.



1,2-diphenylethane (5m)[12]

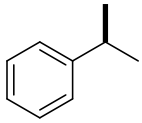
The general procedure was applied to (*E*)-1,2-diphenylethene (36 mg, 0.2mmol) or 1,2-diphenylethyne(35.6 mg, 0.2mmol)under an atmosphere of H_2 (2.0 Mpa) at room temperature for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether) to afford the title compound as a yellow solid (90% yield). Melting point: 53℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.28 (t, J = 7.1 Hz, 4H), 7.22-7.17 (m, 6H), 2.92 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=141.8, 128.4, 128.3, 125.9, 37.9. GC-MS (EI): calcd for $C_{14}H_{14}$ [M^+] 182.11, found 182.11.



1,2-di-*p*-tolylethane (5n)[12]

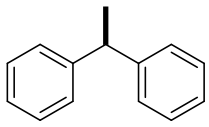
The general procedure was applied to (*E*)-1,2-di-*p*-tolylethene (0.2mmol) under an atmosphere of H_2 (2.0 Mpa) at room temperature for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum

ether) to afford the title compound as a yellow solid (87% yield). Melting point: 86℃-89℃ ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.11 (d, *J* = 0.8 Hz, 8H), 2.87 (s, 4H), 2.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ= 138.9, 135.3, 128.9, 128.3, 37.6, 21.0. GC-MS (EI): calcd for $C_{16}H_{18}$ [M^+] 210.14, found 210.14.



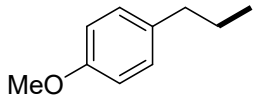
Cumene (5o)[9]

The general procedure was applied to prop-1-en-2-ylbenzene (0.2mmol) under an atmosphere of H_2 (2.0 Mpa) at room temperature for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether) to afford the title compound as a colorless oil (82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*= 7.43–7.03 (m, 1H), 2.90 (t, *J*=6.9 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*= 148.65, 146.96, 135.35, 120.14, 111.73, 111.05, 55.87, 55.74, 37.63, 24.74, 13.79. GC-MS (EI): calcd for C_9H_{12} [M^+] 120.09, found 120.05.



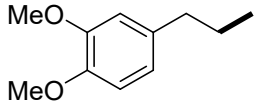
ethane-1,1-diyldibenzene(5p)[13]

The general procedure was applied to ethene-1,1-diyldibenzene (36 mg, 0.2mmol) under an atmosphere of H_2 (2.0 Mpa) at room temperature for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether) to afford the title compound as a colorless oil (85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.31–7.15 (m, 10H), 4.15 (q, 1H), 1.64 (d, *J* = 7.2 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ=146.3, 128.3, 127.6, 126.0, 44.7, 21.8. GC-MS (EI): calcd for $C_{14}H_{14}$ [M^+] 182.11, found 182.09.



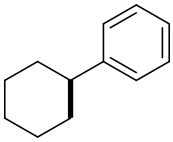
1-methoxy-4-propylbenzene (5q)[9]

The general procedure was applied to 1-allyl-4-methoxybenzene (30 mg, 0.2mmol) under an atmosphere of H_2 (2.0 Mpa) at room temperature for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether) to afford the title compound as a yellow oil (84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.10 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.57 – 2.48 (m, 2H), 1.62-1.57(m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=157.6, 134.8, 129.3, 113.6, 55.2, 37.1, 24.8, 13.8. GC-MS (EI): calcd for $C_{10}H_{14}O$ [M^+] 150.10, found 150.09.



1,2-dimethoxy-4-propylbenzene (5r)[9]

The general procedure was applied to 4-allyl-1,2-dimethoxybenzene (36 mg, 0.2mmol) under an atmosphere of H_2 (4.0 Mpa) at 60ºC for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether) to afford the title compound as a yellow oil (78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ=6.79 (d, *J* = 8.7 Hz, 1H), 6.74–6.69 (m, 2H), 3.87 (d, *J* = 6.8 Hz, 6H), 2.52 (d, *J* = 7.8 Hz, 2H), 1.5-1.59 (m, 2H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=148.6, 146.9, 135.3, 120.1, 111.7, 111.1, 55.9, 55.7, 37.6, 24.7, 13.8. GC-MS (EI): calcd for $C_{11}H_{16}O_2$ [M^+] 180.12, found 180.12.



Cyclohexylbenzene (5s)[13]

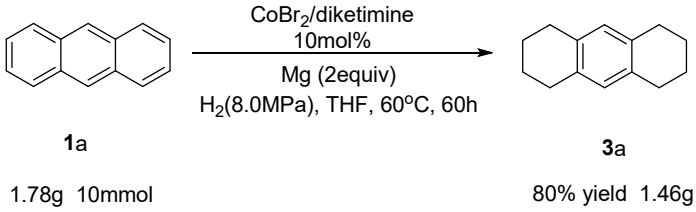
The general procedure was applied to 2,3,4,5-tetrahydro-1,1'-biphenyl (30 mg, 0.2mmol) under an atmosphere of H_2 (2.0 Mpa) at room temperature for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether) to afford the title compound as a colorless oil (79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.31–7.13 (m, 5H), 2.48 (q, 1H), 1.86–1.72 (m, 5H), 1.50 – 1.20 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ= 148.07, 128.25, 126.80, 125.74, 44.58, 34.45, 26.91, 26.16; GC-MS (EI): calcd for $C_{12}H_{16}$ [M^+] 160.13, found 160.09.

4. Preparation of diketimine-Co complex.

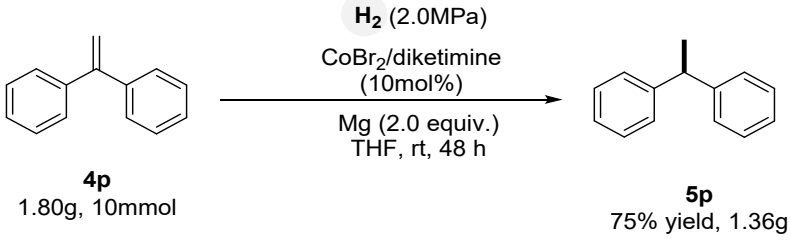
according to reported literature.[14]

To a solution of anhydrous $CoBr_2$ (1.40g, 6.40 mmol) in THF (15 mL) was added diketimine (2.40g, 6.40mmol, in 15 ml THF). The resulting green-brown solution was stirred for 24h at room temperature. After solvent evaporation the greenish brown powder was washed with hexane(4×15ml), filtered, and dried in vacuo. Yield 80%. ^{13}C NMR (THF-d_8): δ=156.6, 142.8, 131.0, 121.8, 116.0, 25.7, 22.8; IR (KBr): 3053 , 2949 , 2913 , 2854 , 1467, 1433 , 1385, 1364, 1347, 1322, 1255, 1181, 1107, 891, 788, 739. UV/vis (THF; λ_{max}): 592, 681.The spectroscopic data were consistent with those previously reported. [14]

5. Gram-Scale Hydrogenation of 1a and 4p



In a 200ml Schlenk tube were placed Mg turnings (0.48 g, 20 mmol) and $CoBr_2$ (22 mg, 1 mmol). The solids were heated using a heat gun at around 300 °C under vacuum for 8 min. After cooling down under a nitrogen atmosphere, anthracene (10 mmol, 1.78 g), diketimine (0.38 g, 1 mmol) and THF (80 mL) were added, The resulting mixture was heated at 80 °C for 12 hours. then the resulting mixture were quickly moved to a high-pressure autoclave. The reaction mixture was stirred under an atmosphere of H_2 (8 Mpa) at 60 °C for 60 h. After quenching with saturated NH_4Cl/H_2O (30 mL), the crude product was extracted with EtOAc (4×50 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum. After removal of the volatiles under vacuum, the crude product was purified by column chromatography to afford the desired hydrogenation compound **3a** (1.46 g, 80% yield).



In a 200ml Schlenk tube were placed Mg turnings (0.48g, 20 mmol) and $CoBr_2$ (22 mg, 1mmol). The solids were heated using a heat gun at around 400°C under vacuum for 8 min. After cooling down under a nitrogen atmosphere, **4p** (10 mmol, 1.80g), diketimine (0.38 g, 1 mmol) and THF (80 ml) were added, The resulting mixture was heated at 60°C for 2hours. then the resulting mixture were quickly moved to a high-pressure autoclave. The reaction mixture was stirred under an atmosphere of H_2 (2 Mpa) at 25 °C for 48 h. After quenching with saturated NH_4Cl/H_2O (30 mL), the crude product was

extracted with EtOAc (4×50 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum. After removal of the volatiles under vacuum, the crude product was purified by column chromatography to afford the desired hydrogenation compound **5p** (1.36 g, 75% yield).

6. Reaction Profile for Hydrogenation of Anthracene

Cobalt catalysis: Kinetic studies were performed by treating **1a** (0.2 mmol) with $CoBr_2$ (0.02 mmol), diketimine (0.02 mmol) and Mg (2 equiv) under the atmosphere of hydrogen (8 Mpa) at 60 °C. The yield of **3a** and the recovery of **1a** were determined by ^1H NMR analysis using 1, 3, 5-trimethoxybenzene as an internal standard. The data points for reaction profiles were collected by performing multiple batches of the reaction with different reaction times.

Table S1. Studying the Reaction profile of Hydrogenation of Anthracene with Cobalt Catalysis

Time (h)	Recovery of **1a** (%)	Yield of **2a** (%)	Yield of **3a** (%)
0	100	0	0
1	89	4	0
2	81	9	0
5	72	24	0
8	57	35	4
10	38	50	6
11	31	46	17
12	27	43	24
16	19	28	41
20	12	18	60
24	9	1	70
36	0	7	81
48	0	0	88

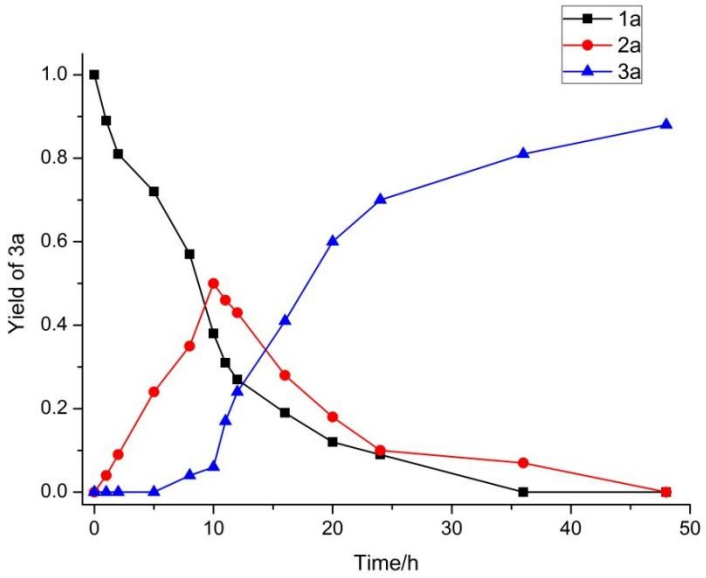


Figure S1. Reaction profile for cobalt-catalyzed hydrogenation of anthracene.

7. Experiments of XPS for Analysis of Active Metal Species

$CoBr_2$+diketimine: XPS studies were performed by $CoBr_2$ (60 mg, 0.276 mmol), diketimine (104 mg, 0.276 mmol) in THF (10 mL) under the nitrogen atmosphere at room temperature for 24 h. After the removal of the volatiles under vacuum.

$CoBr_2$+diketimine+Mg: In a Schlenk tube were placed Mg turnings (19 mg, 0.8 mmol) and $CrCl_2$ (9 mg, 0.04 mmol). The solids were heated using a heat gun at around 300 °C under vacuum for 5 min. After cooling down under a nitrogen atmosphere, diketimine (15 mg, 0.04 mmol) and THF (4 mL) were added, The resulting mixture was heated at 80 °C for 4 hours, mixture was filtered through Celite and the solvent was removed under vacuum.

8. X-Ray Crystal Structure of 3l

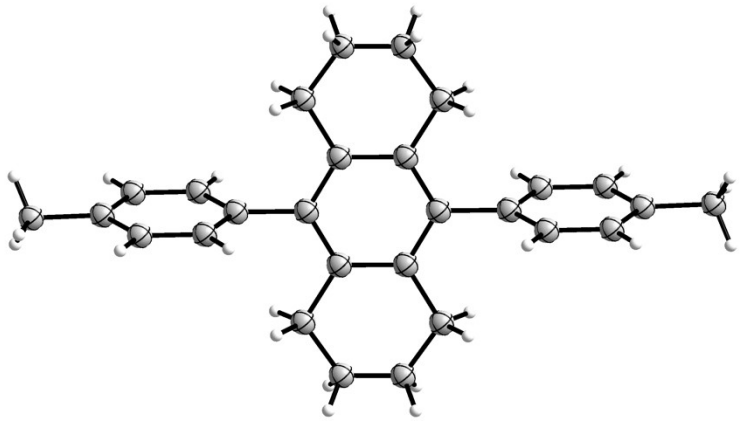


Figure S2. X-Ray Crystal Structure of 3l (CCDC:1840125)

Empirical formula	C_{28} H_{30}
Formula weight	366.52
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a= 9.427(2) A alpha = 112.635(6) deg.
b= 11.348(3) A beta = 97.722(6) deg.	
c = 11.761(5) A gamma = 106.198(4) deg.	
Volume	072.9(5) A^3
Z, Calculated density	2, 1.135 Mg/m^3
Absorption coefficient	0.064 mm^-1
F(000)	396
Crystal size	0.37 x 0.30 x 0.19 mm
Theta range for data collection	2.09 to 25.10 deg.
Limiting indices	-7<=h<=11, -13<=k<=13, -14<=l<=14
Reflections collected / unique	5417 / 3772 [R(int) = 0.0228]
Completeness to theta = 25.10	98.9 %
Absorption correction	None
Max. and min. transmission	0.9881 and 0.9771
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3772 / 0 / 253
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0716, wR2 = 0.2051

R indices (all data)	R1 = 0.1053, wR2 = 0.2378
Largest diff. peak and hole	0.295 and -0.275 e.A^-3

Supplementary References

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9. ^{1}H, ^{13}C and ^{19}F NMR Spectra

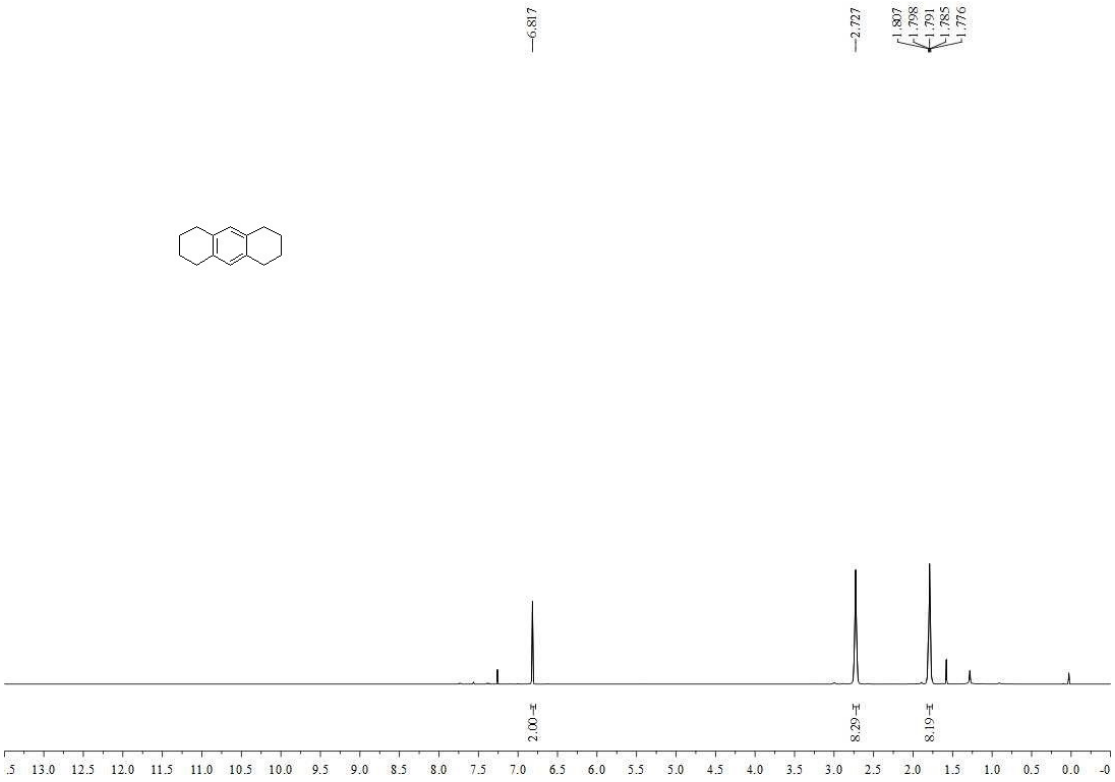

Figure S3. ^{1}H NMR spectrum for compound **3a**.

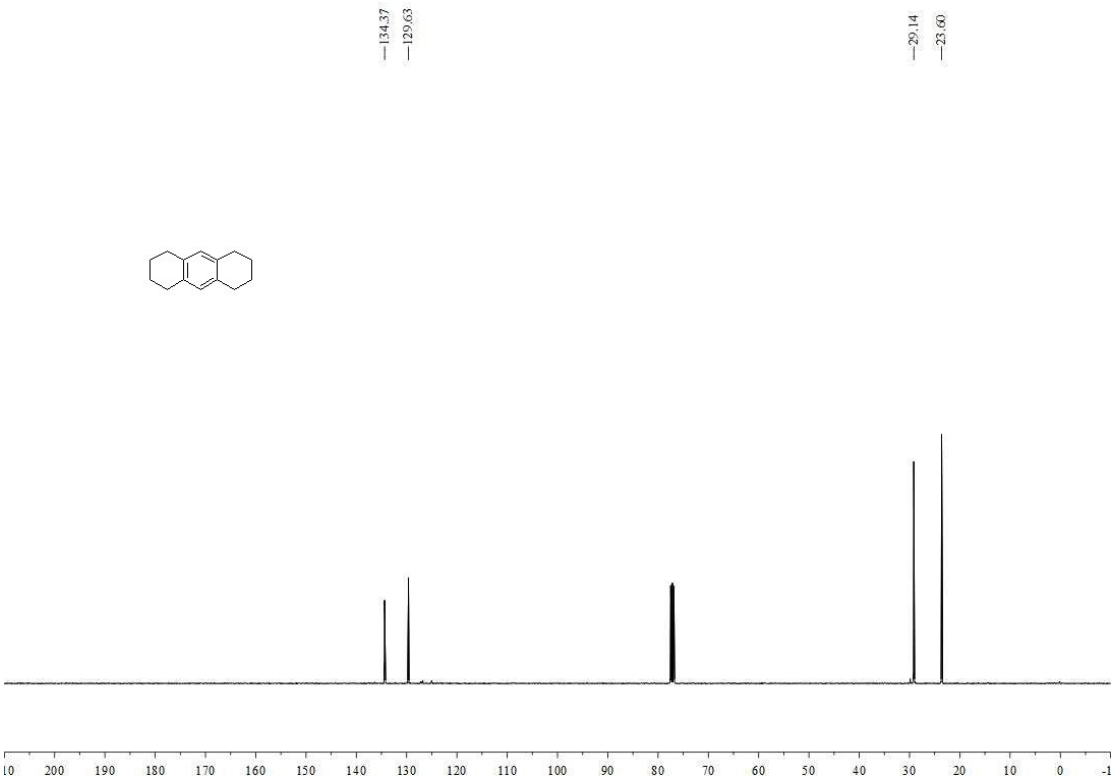

Figure S4. ^{13}C NMR spectrum for compound **3a**.

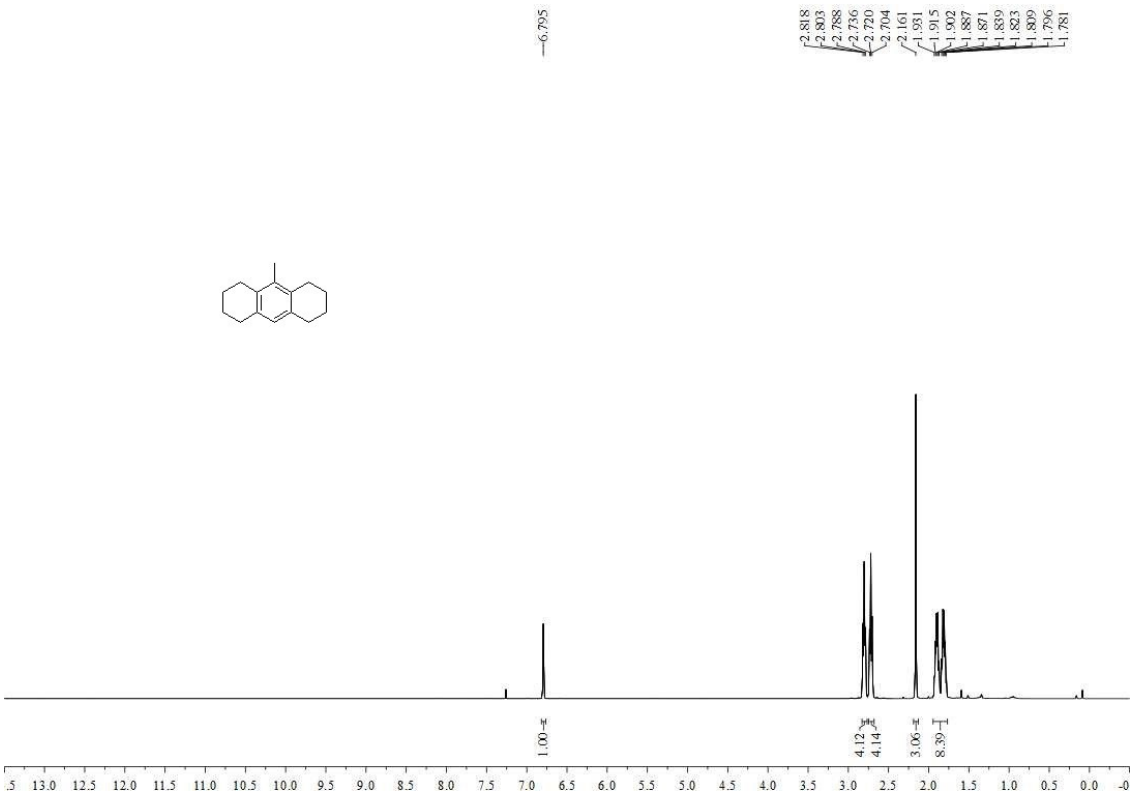

Figure S5. ^{1}H NMR spectrum for compound **3b**.

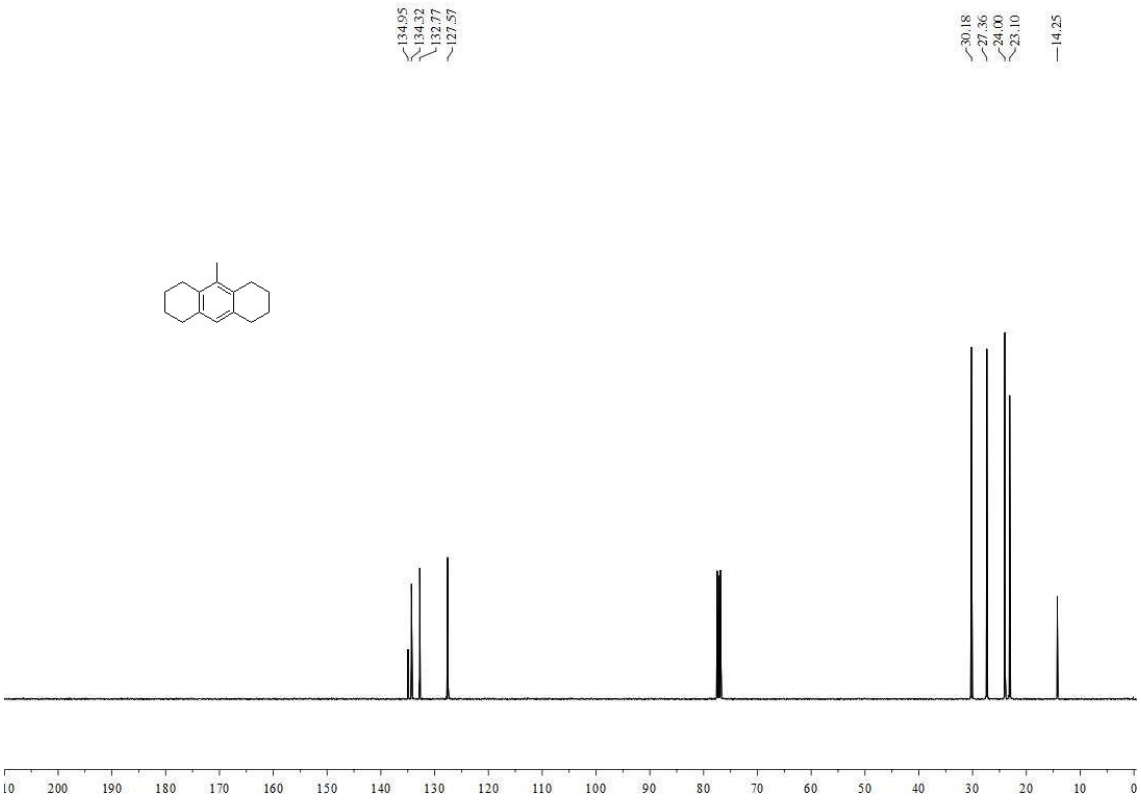

Figure S6. ^{13}C NMR spectrum for compound **3b**.

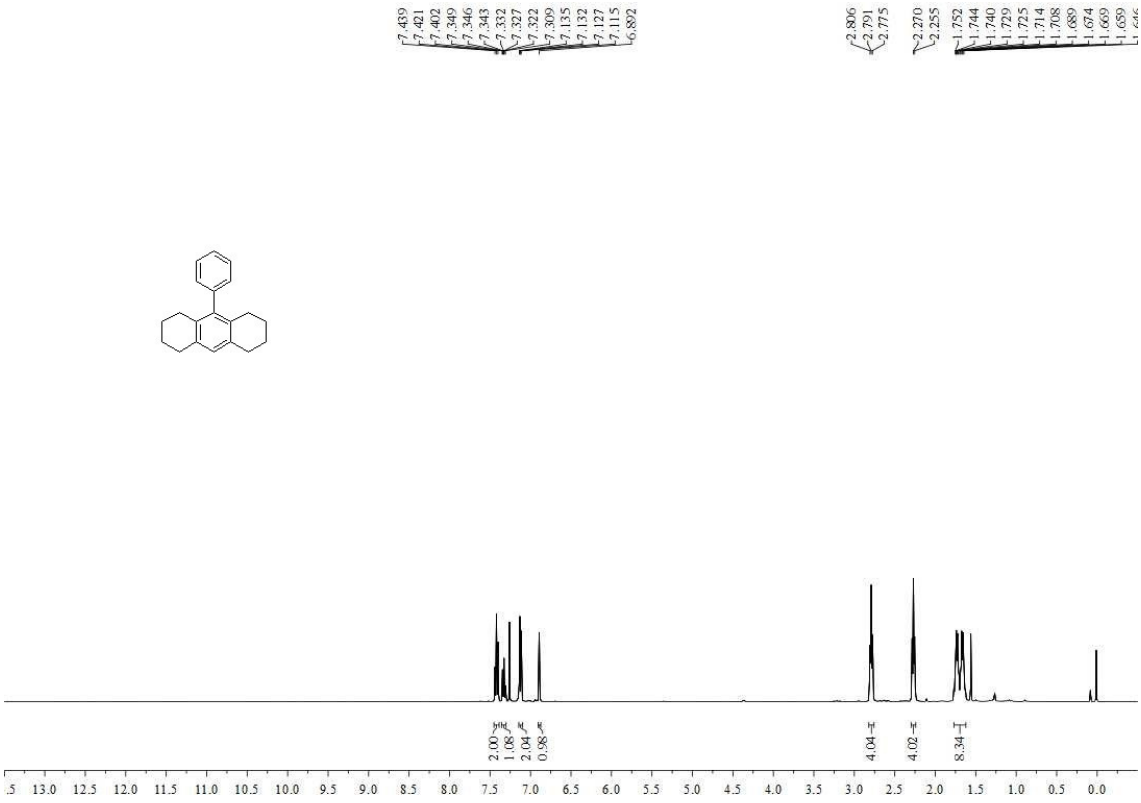

Figure S7. ^{1}H NMR spectrum for compound **3c**.

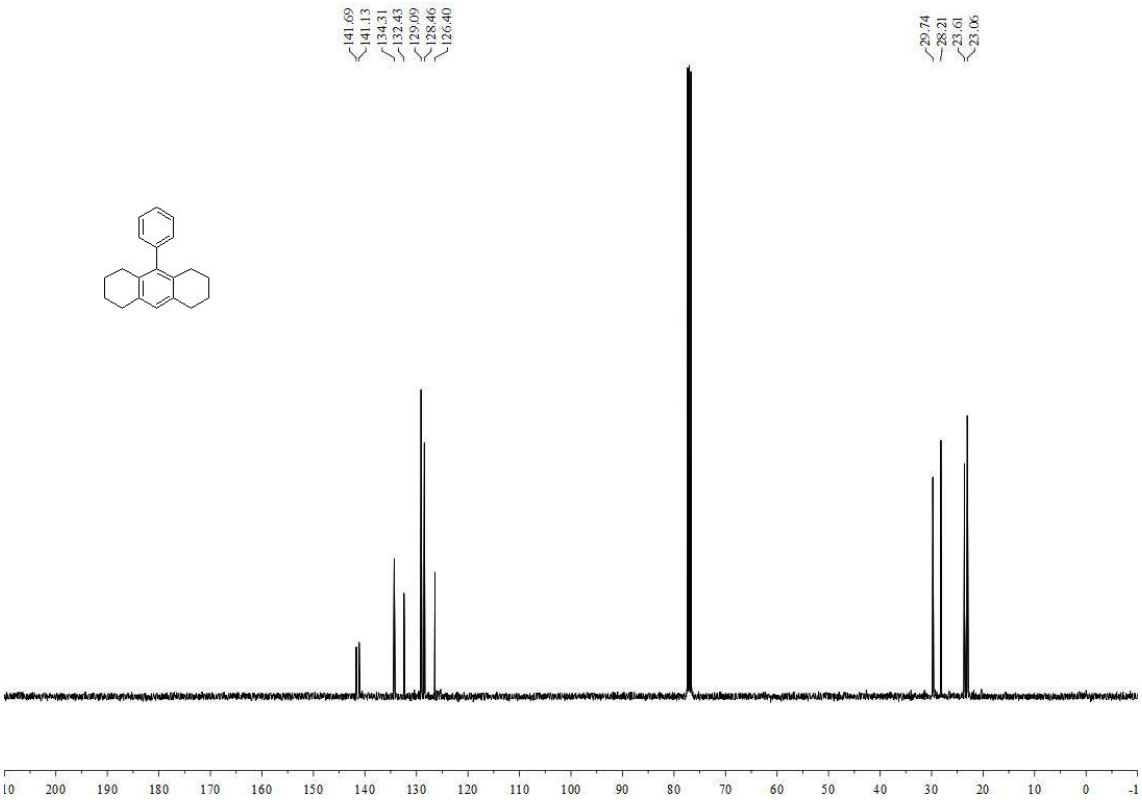

Figure S8. ^{13}C NMR spectrum for compound **3c**.

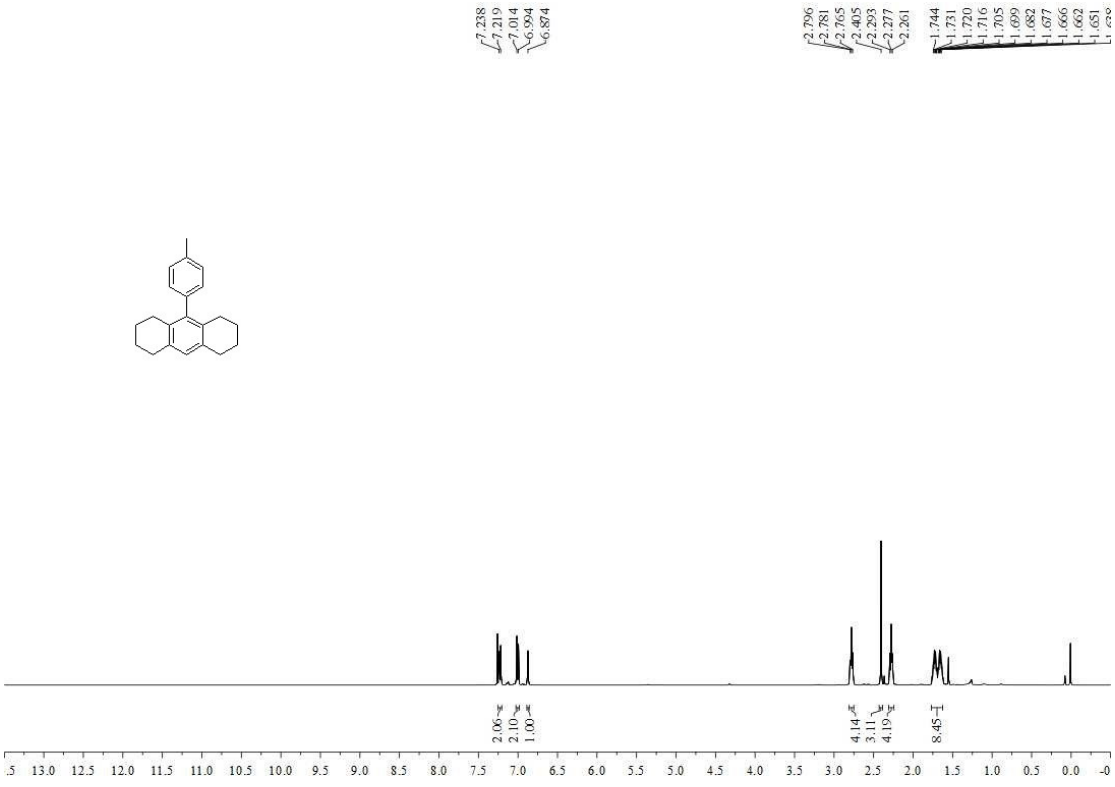

Figure S9. ^{1}H NMR spectrum for compound **3d**.

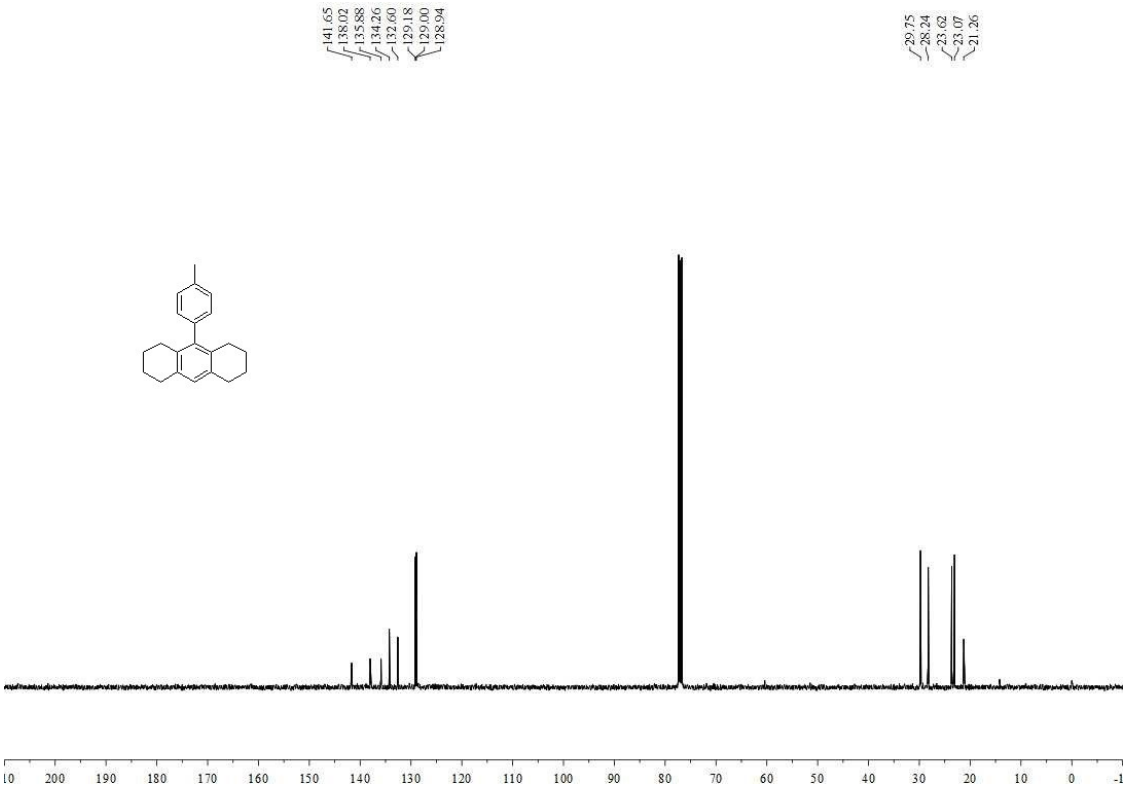

Figure S10. ^{13}C NMR spectrum for compound **3d**.

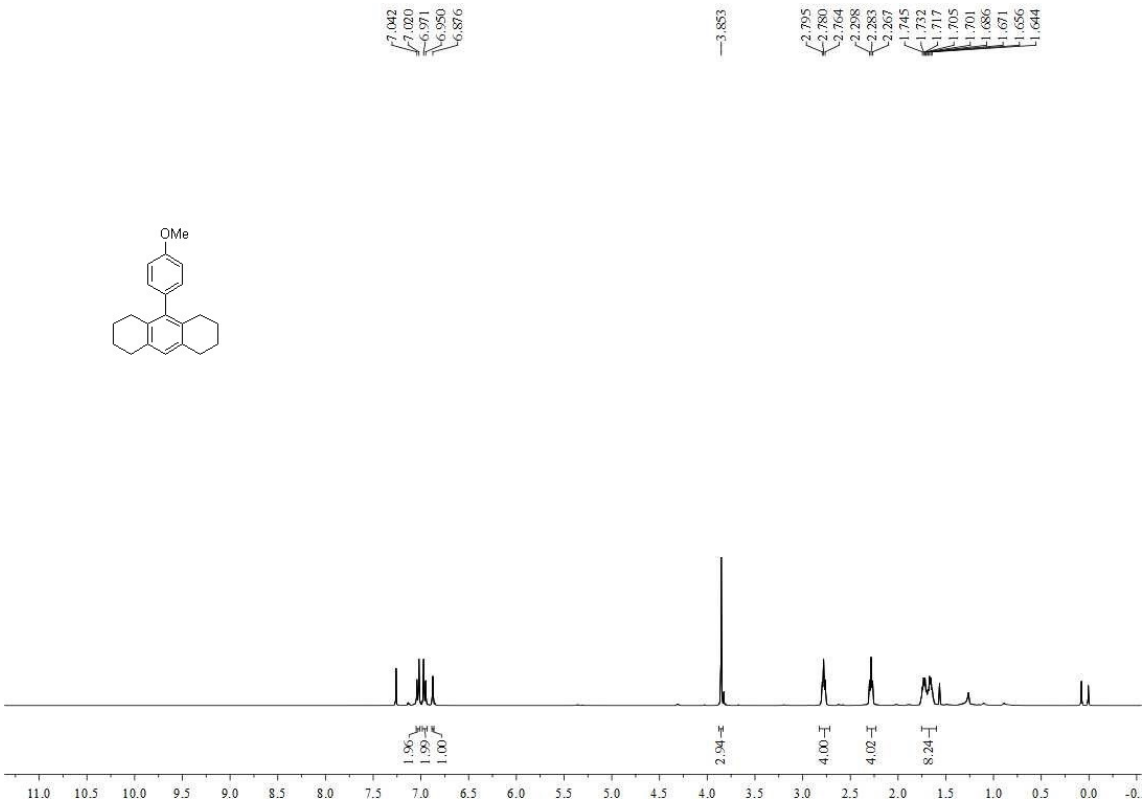

Figure S11. ^{1}H NMR spectrum for compound **3e**.

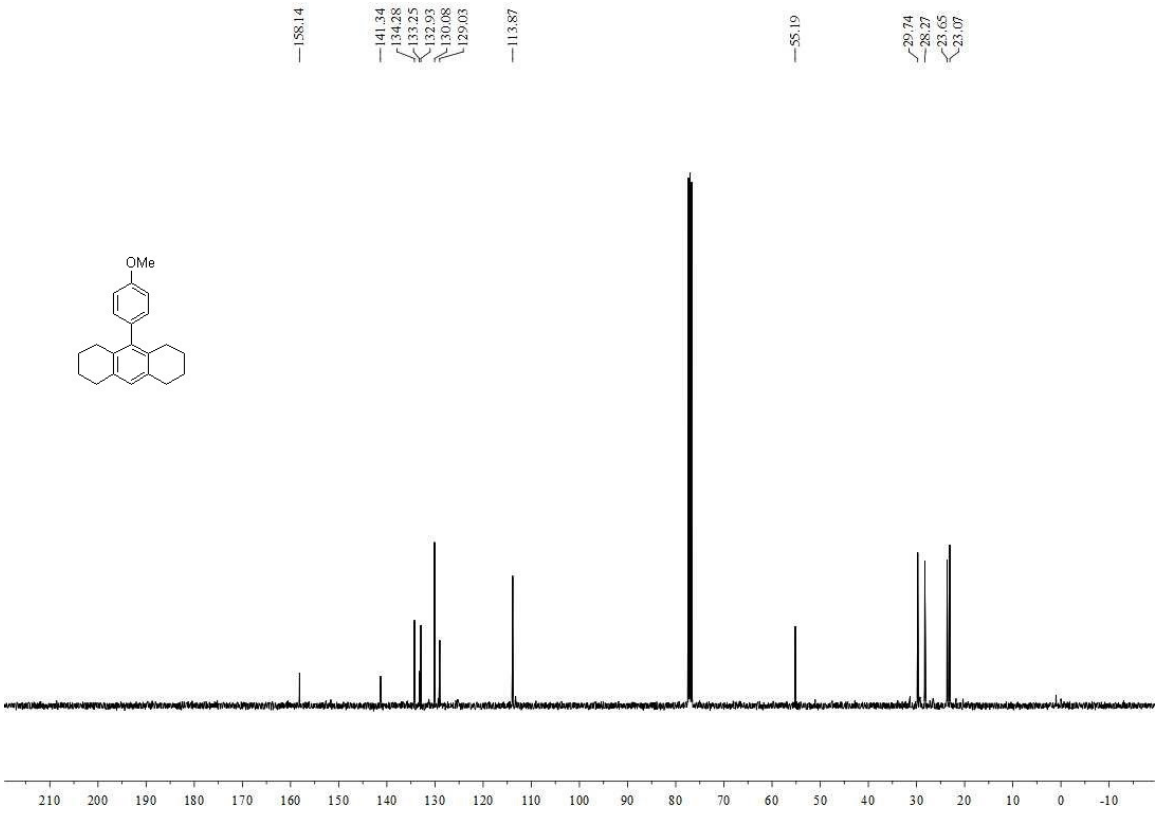

Figure S12. ^{13}C NMR spectrum for compound **3e**.

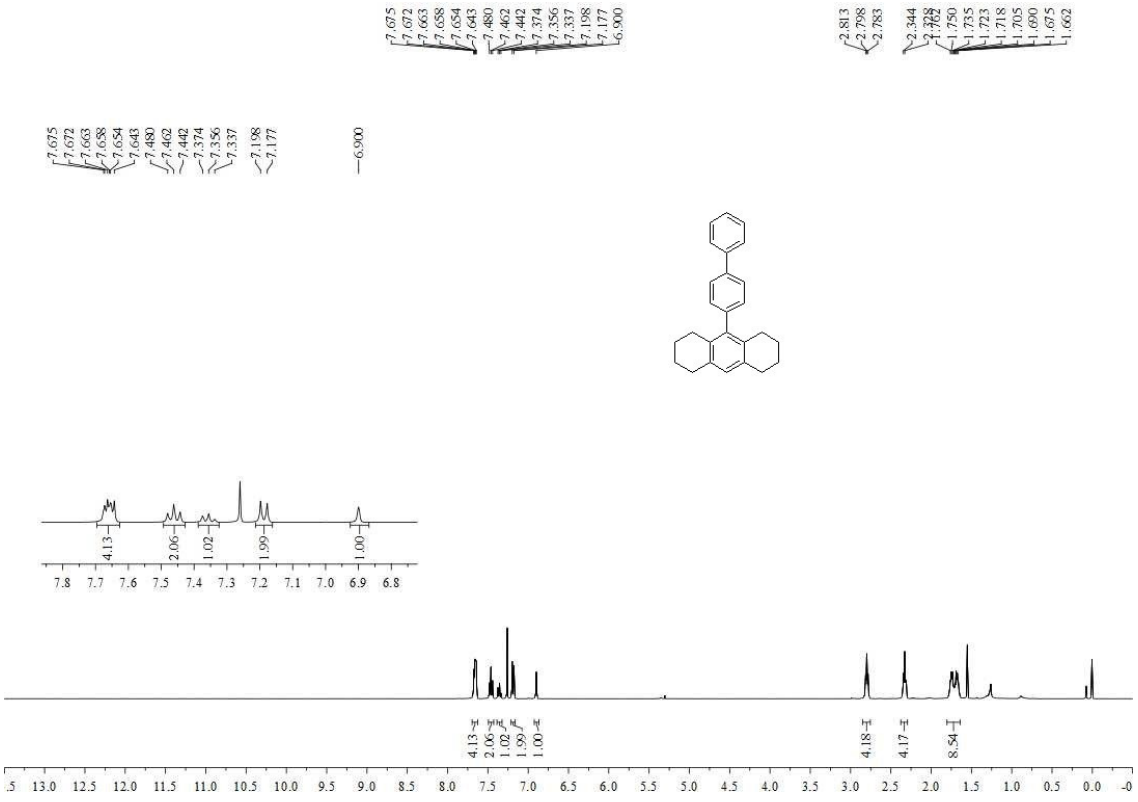

Figure S13. ^{1}H NMR spectrum for compound **3f**.

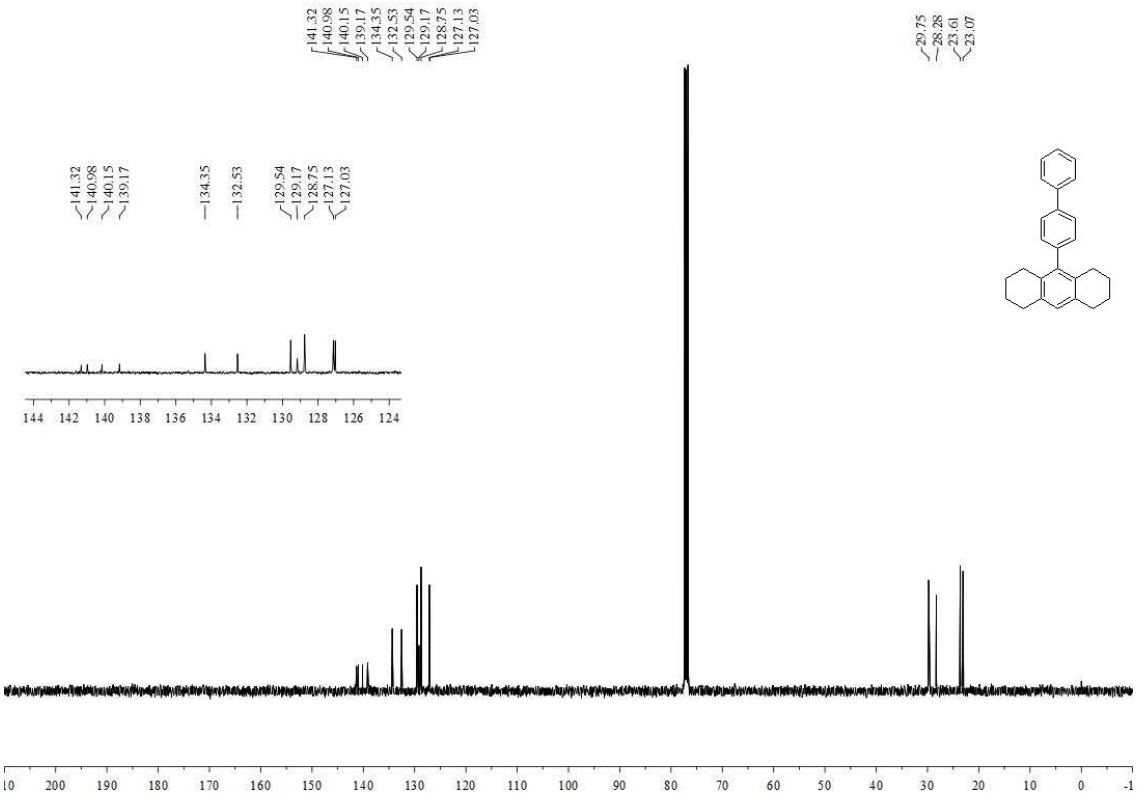

Figure S14. ^{13}C NMR spectrum for compound **3f**.

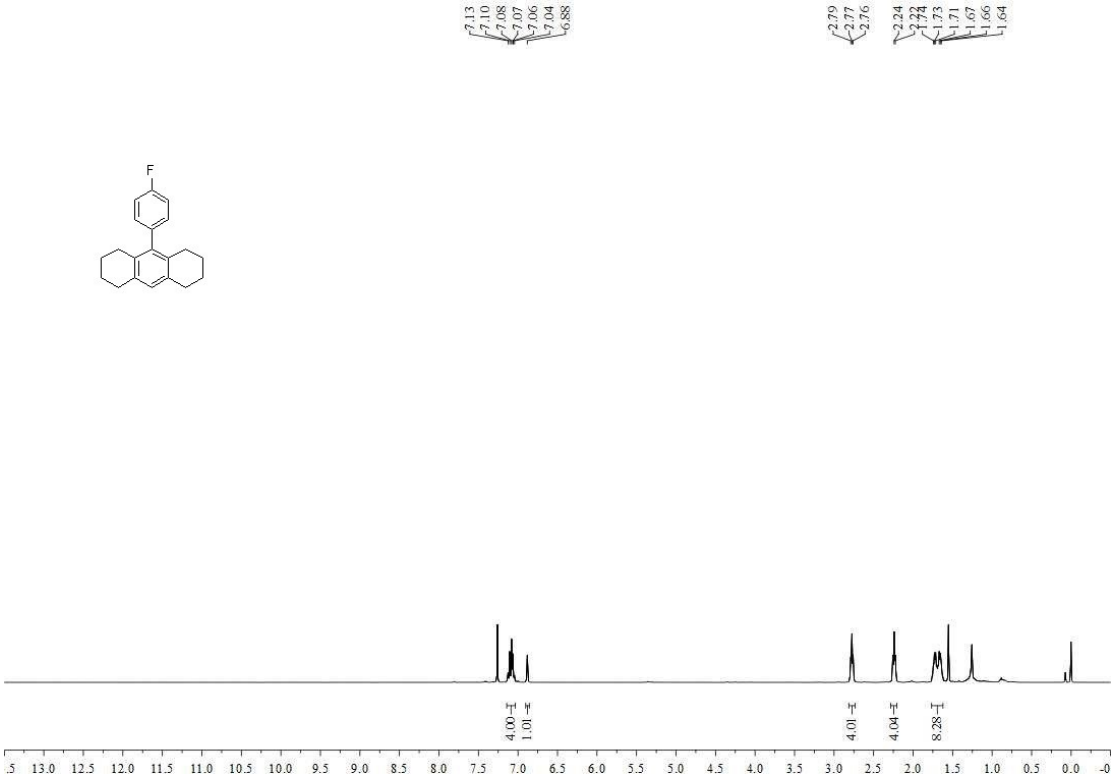

Figure S15. ^{1}H NMR spectrum for compound **3g**.

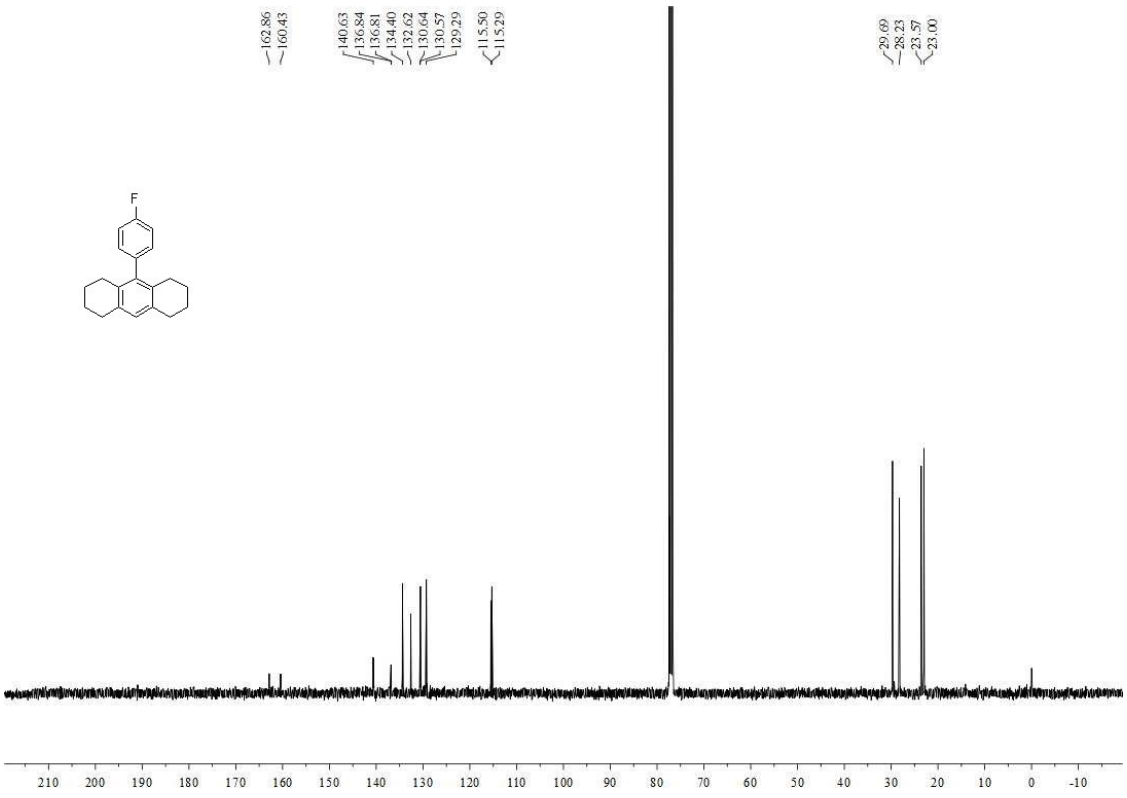

Figure S16. ^{13}C NMR spectrum for compound **3g**.

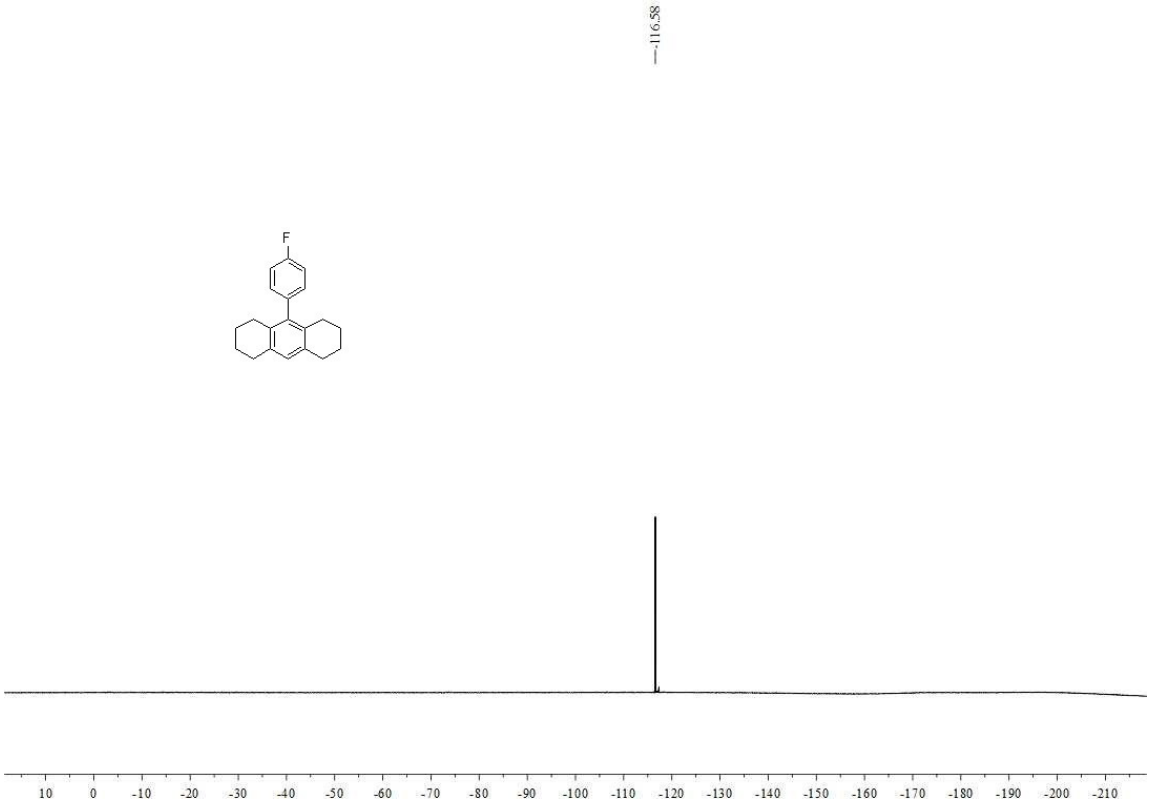

Figure S17. ^{19}F NMR spectrum for compound **3g**.

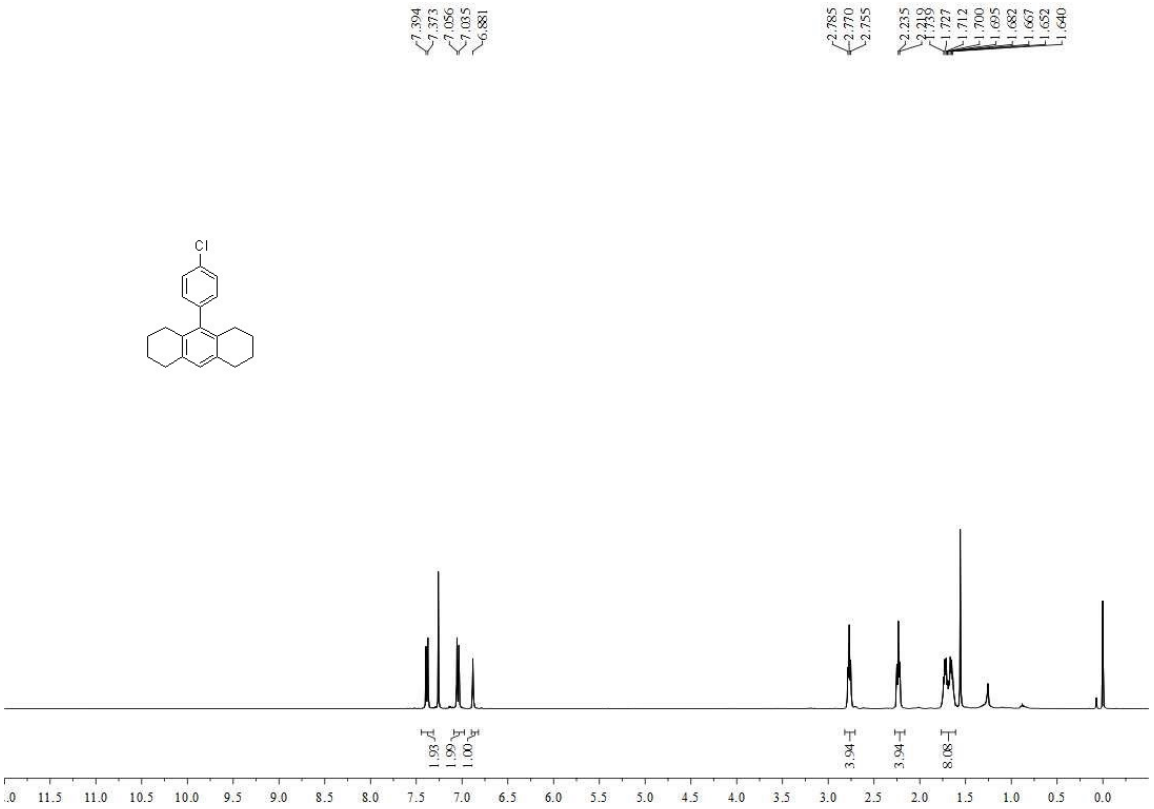

Figure S18. ^{1}H NMR spectrum for compound **3h**.

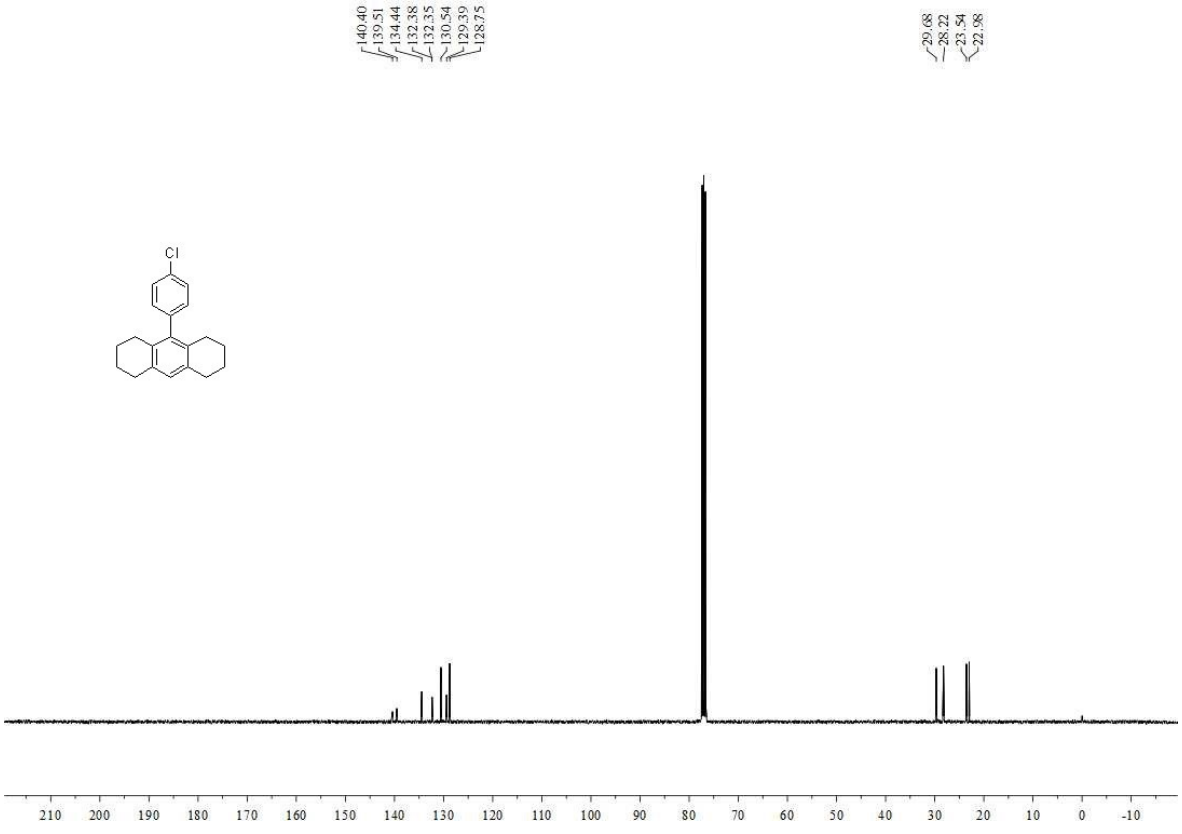

Figure S19. ^{13}C NMR spectrum for compound **3h**.

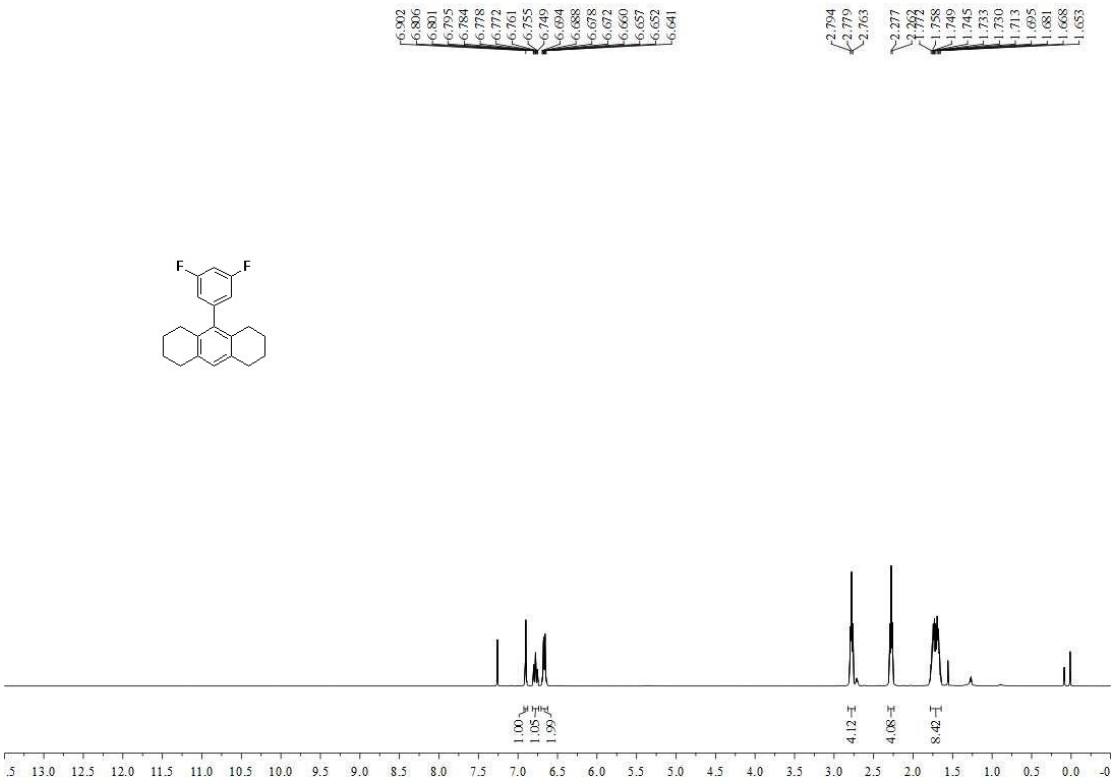

Figure S20. ^{1}H NMR spectrum for compound **3i**.

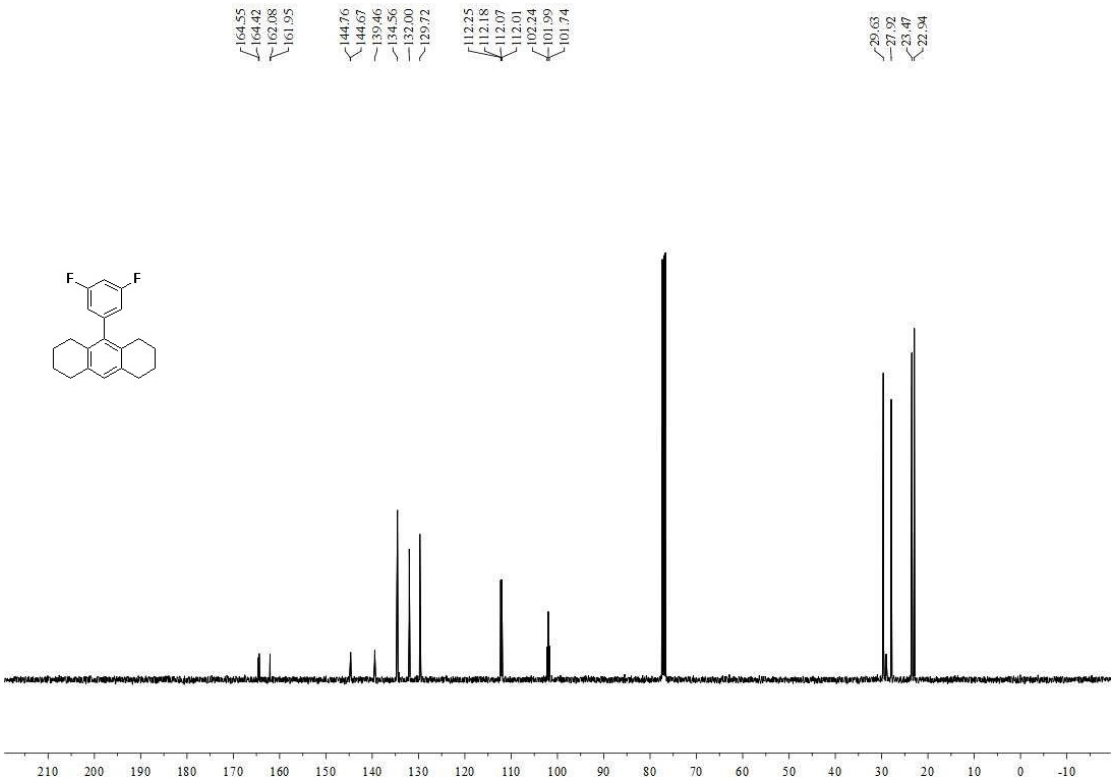

Figure S21. ^{13}C NMR spectrum for compound **3i**.

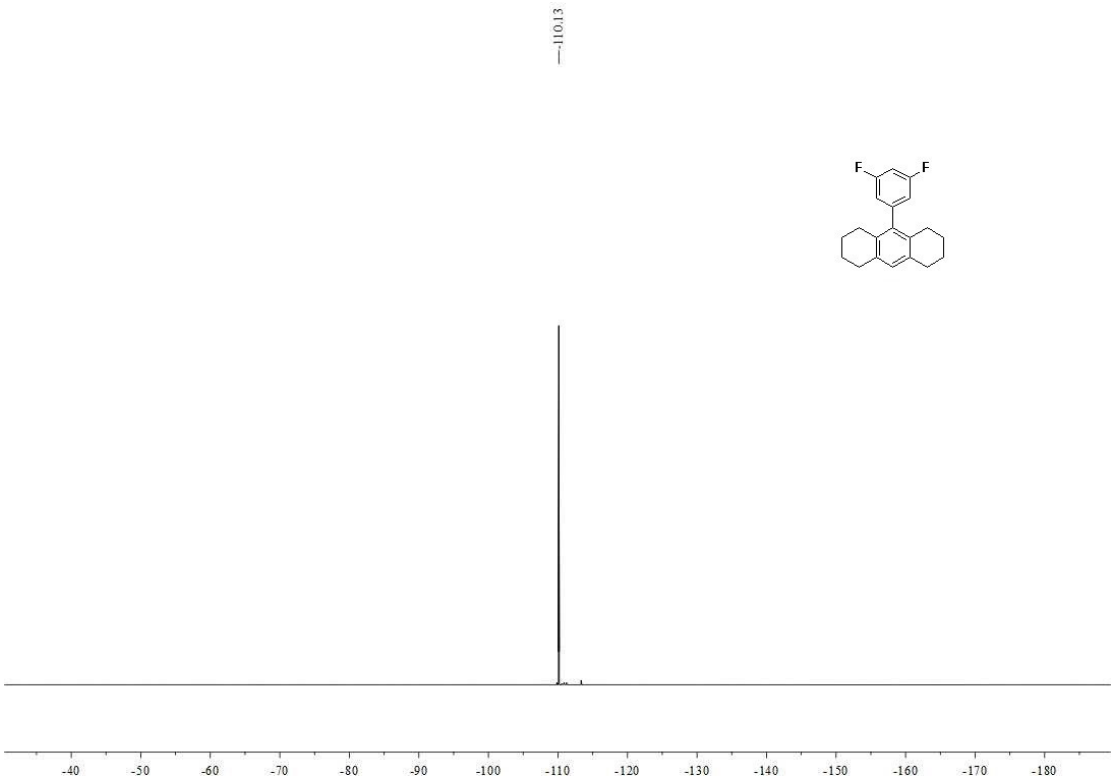

Figure S22. ^{19}F NMR spectrum for compound **3i**.

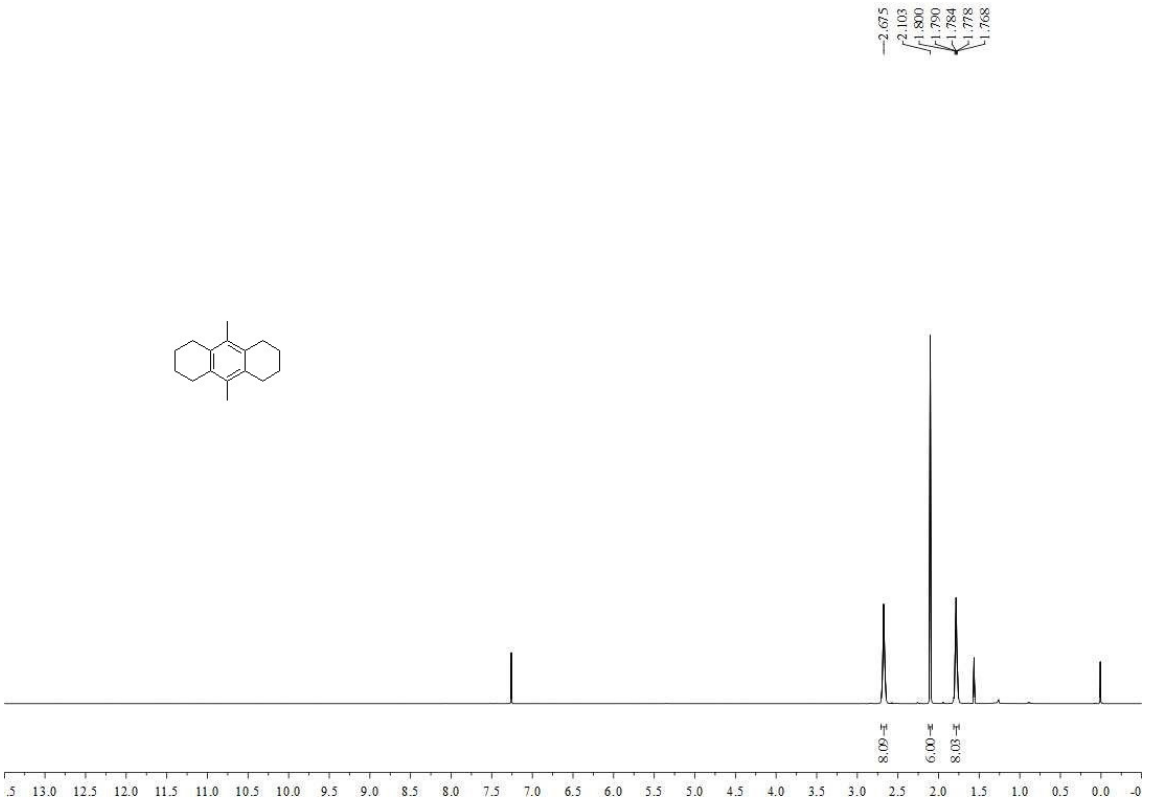

Figure S23. ^{1}H NMR spectrum for compound **3j**.

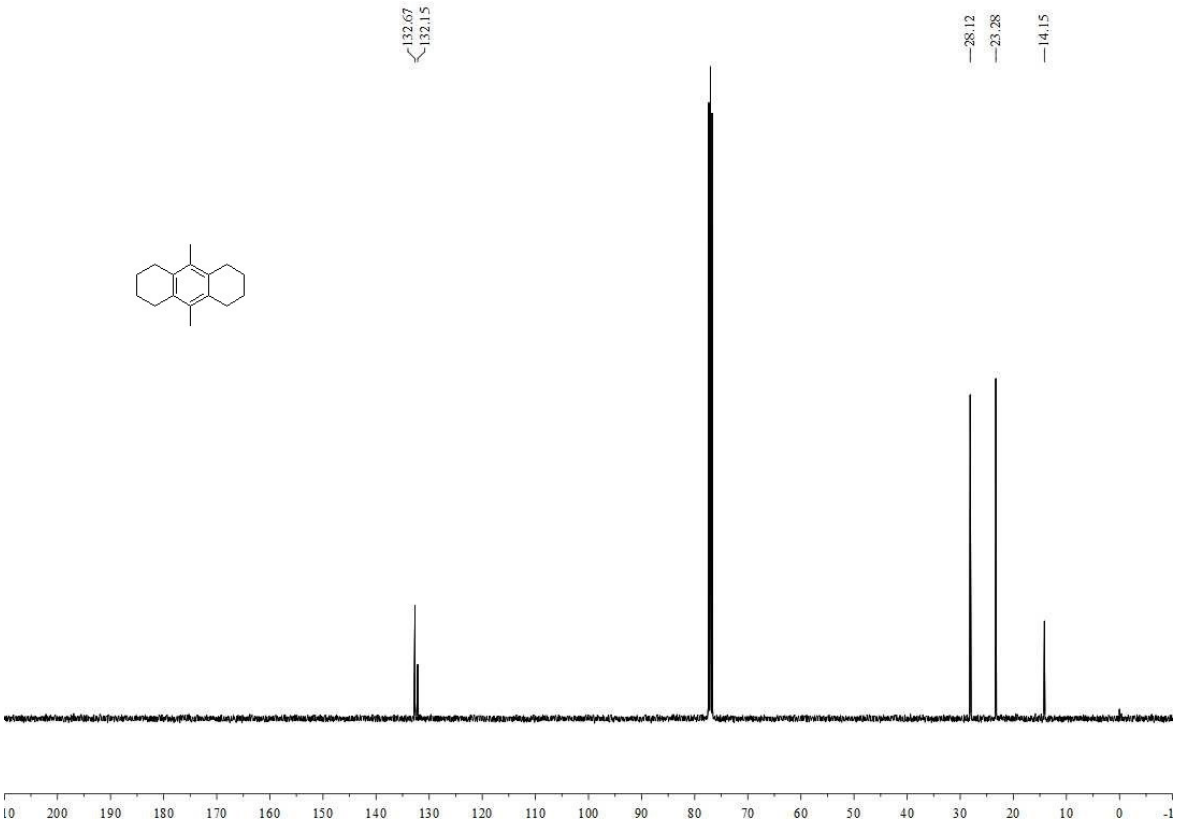

Figure S24. ^{13}C NMR spectrum for compound **3j**.

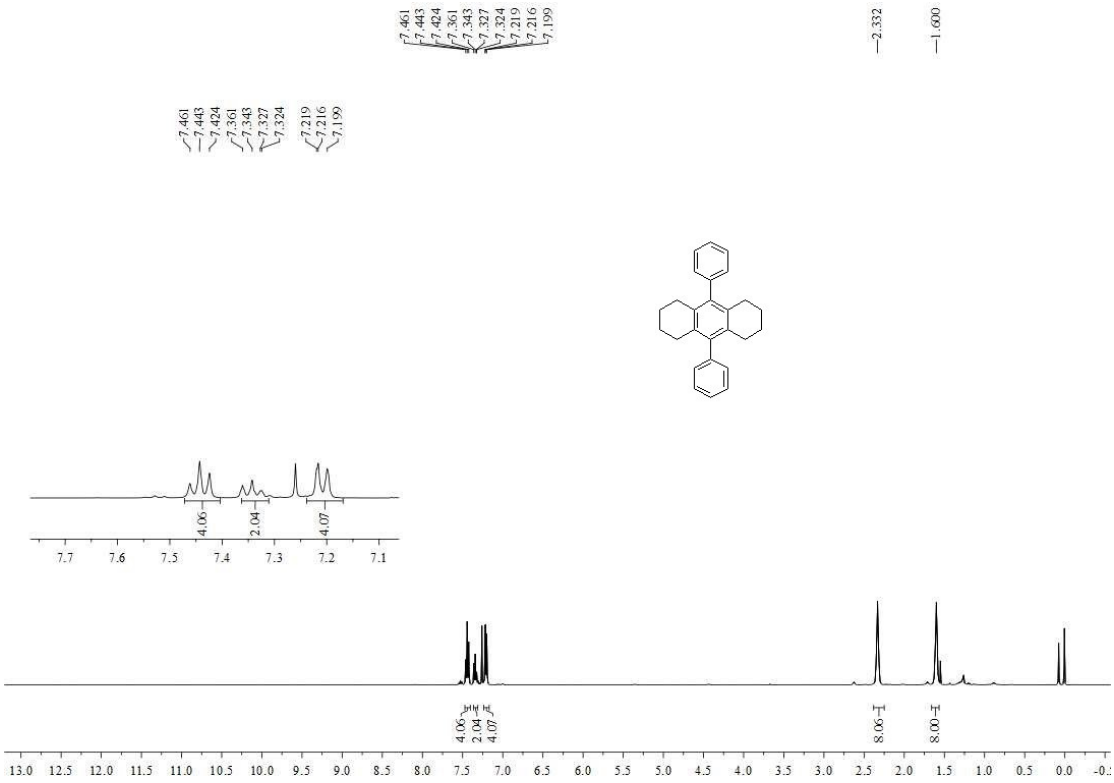

Figure S25. ^{1}H NMR spectrum for compound **3k**.

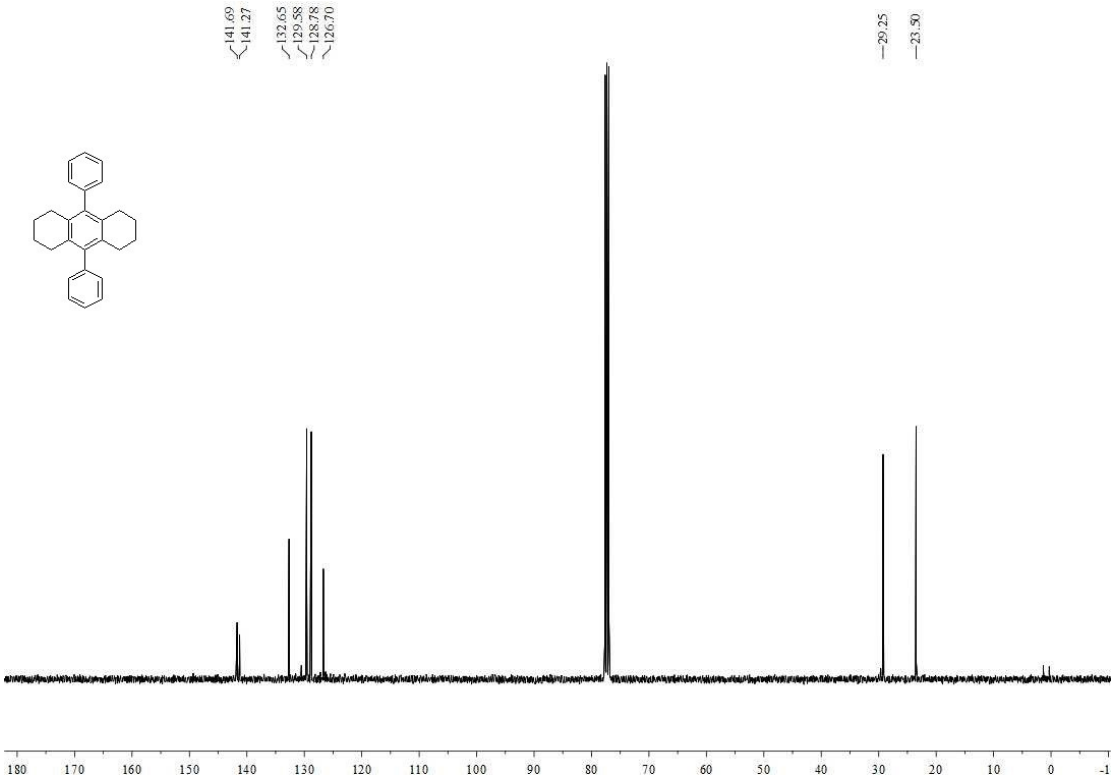

Figure S26. ^{13}C NMR spectrum for compound **3k**.

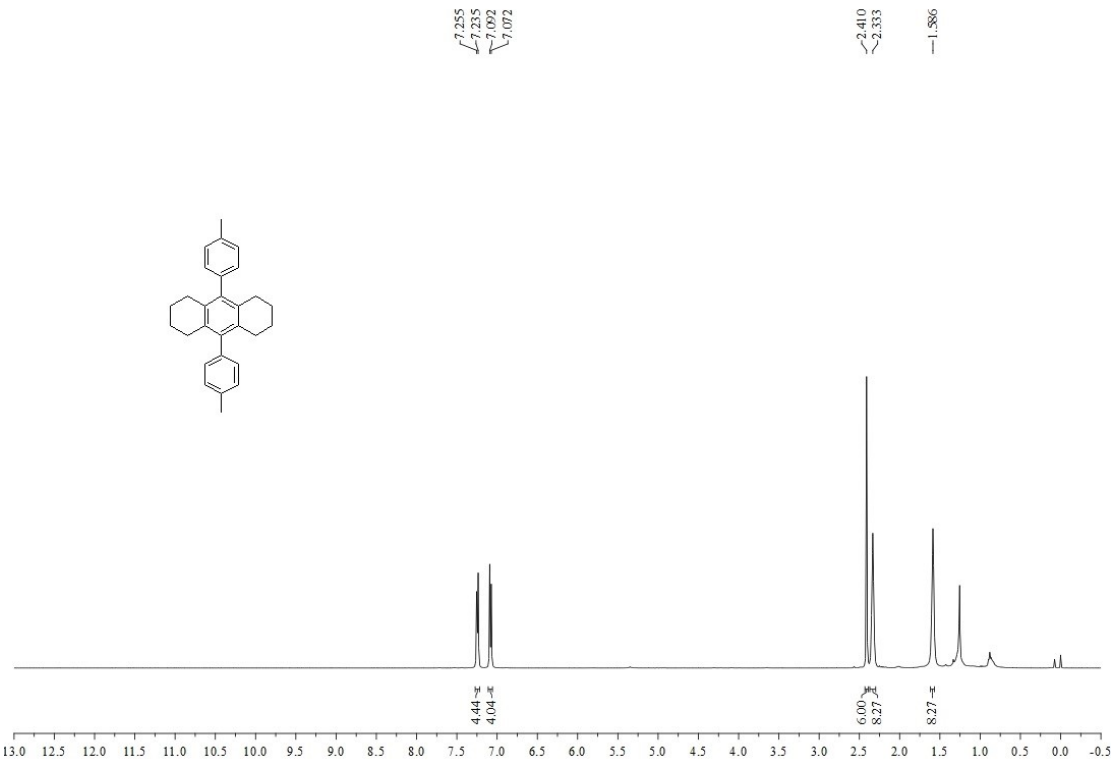

Figure S27. ^{1}H NMR spectrum for compound **3l**.

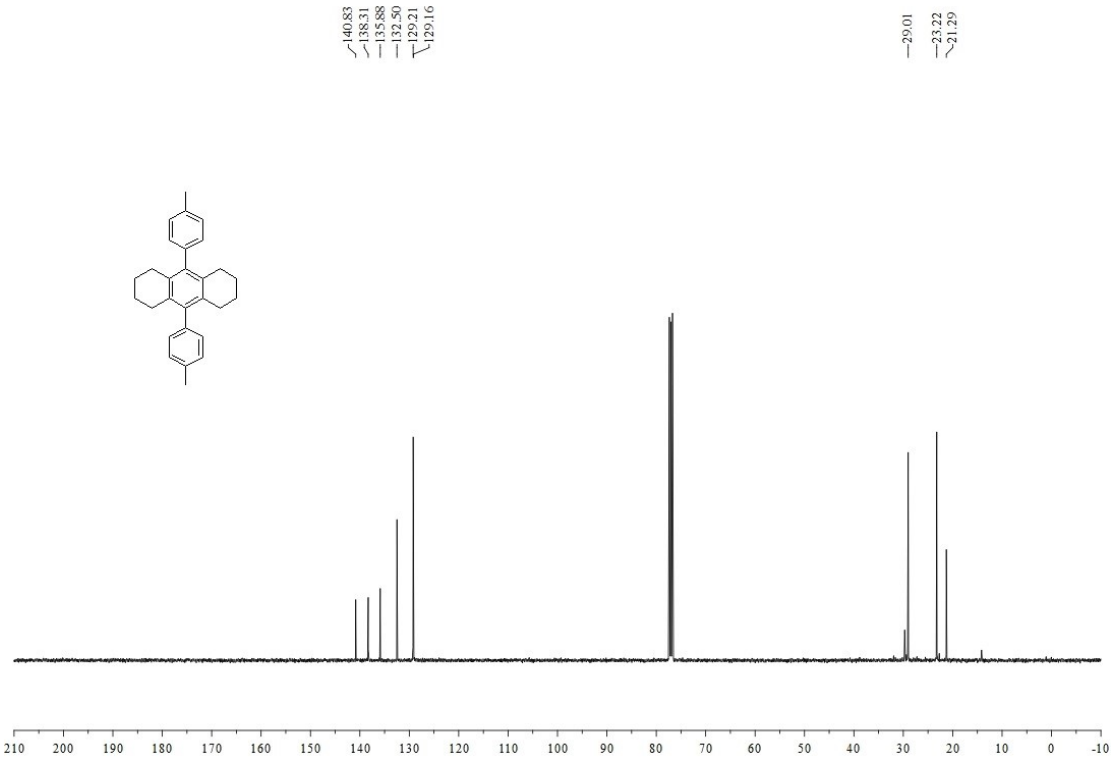

Figure S28. ^{13}C NMR spectrum for compound **3l**.

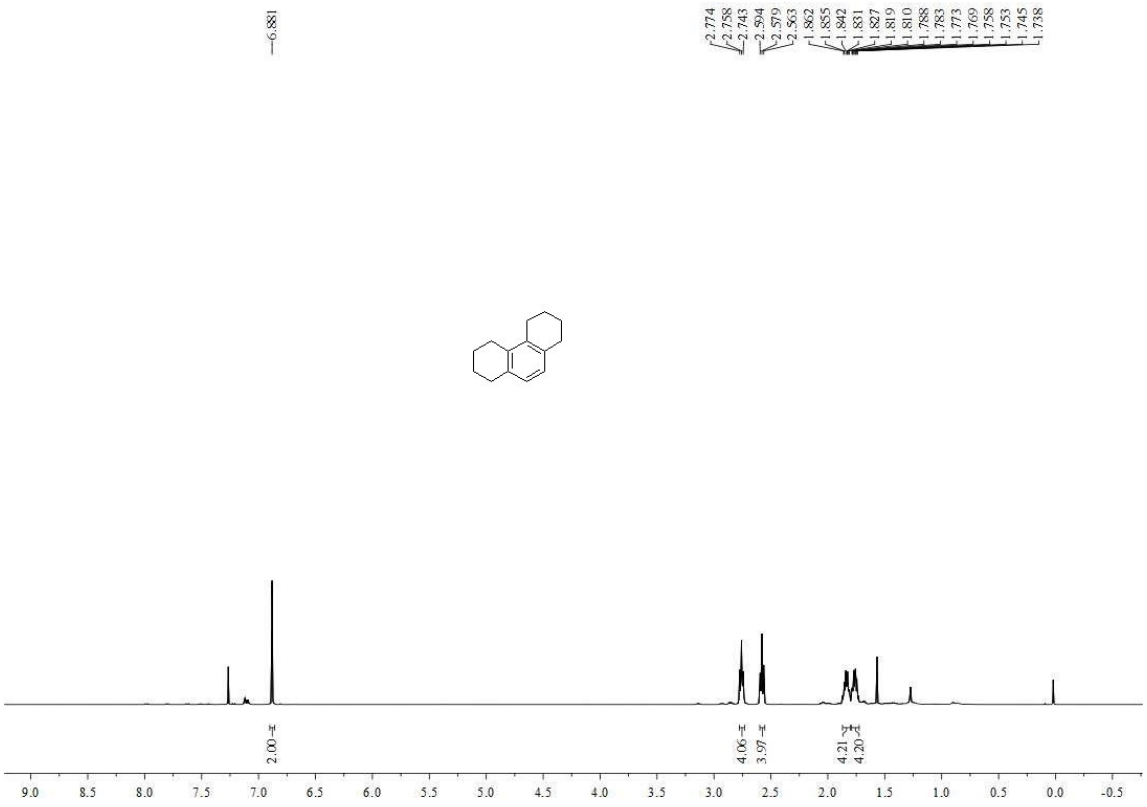

Figure S29. ^{1}H NMR spectrum for compound **3m**.

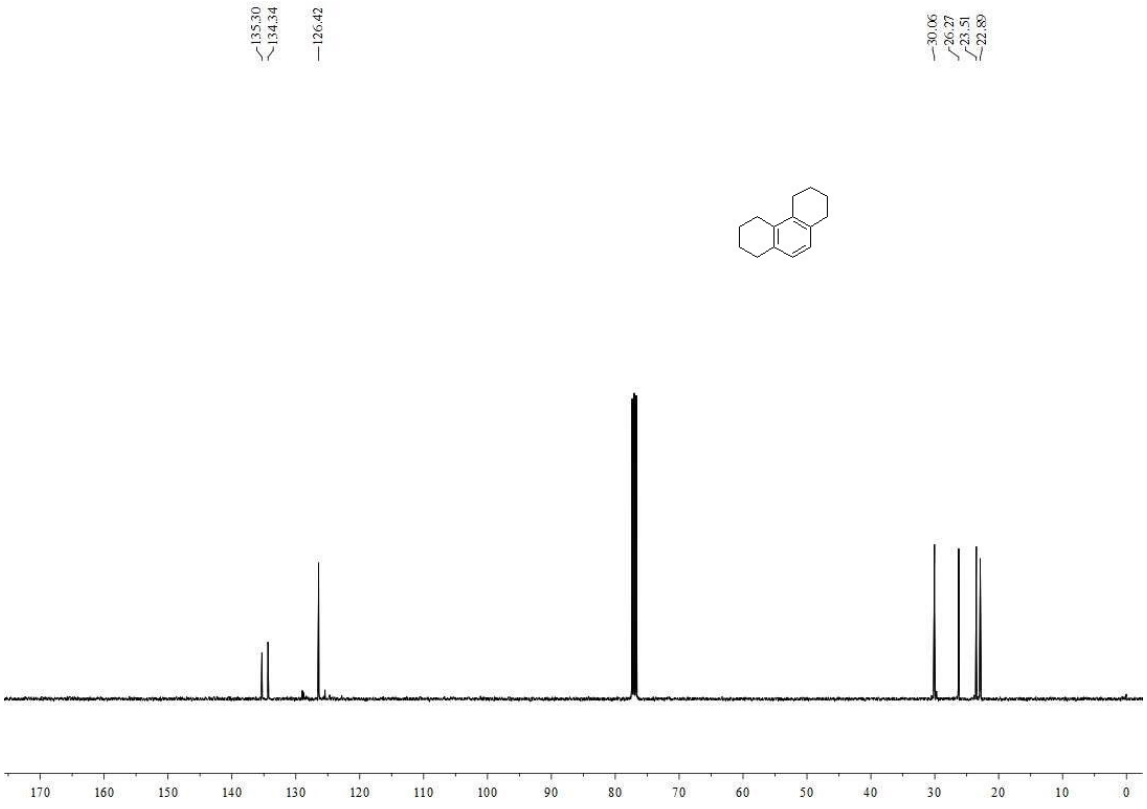

Figure S30. ^{13}C NMR spectrum for compound **3m**.

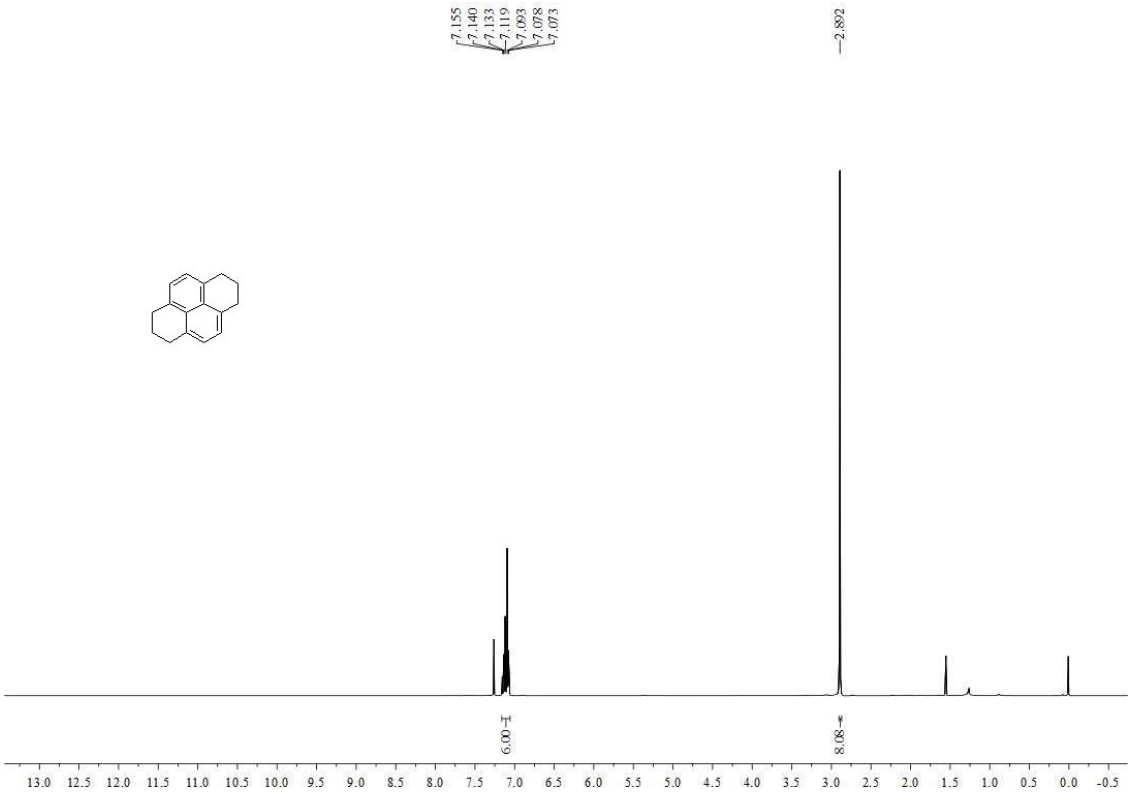

Figure S31. ^{1}H NMR spectrum for compound **3n**.

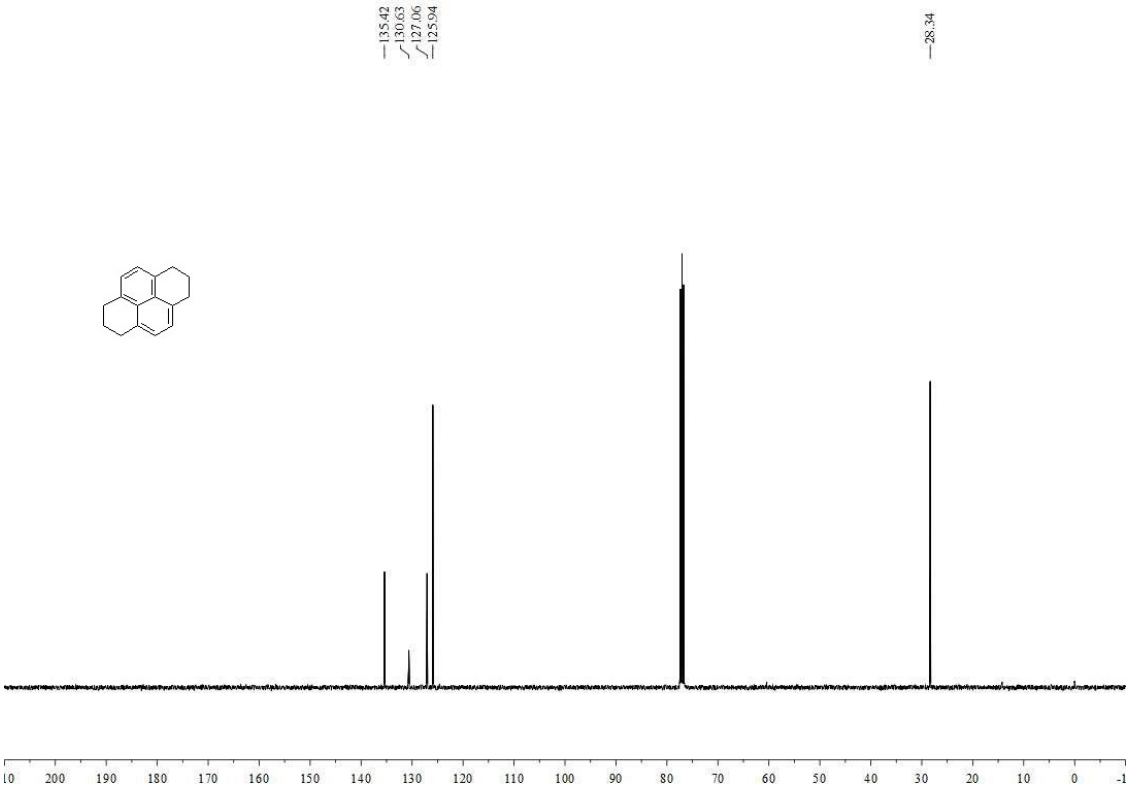

Figure S32. ^{13}C NMR spectrum for compound **3n**.

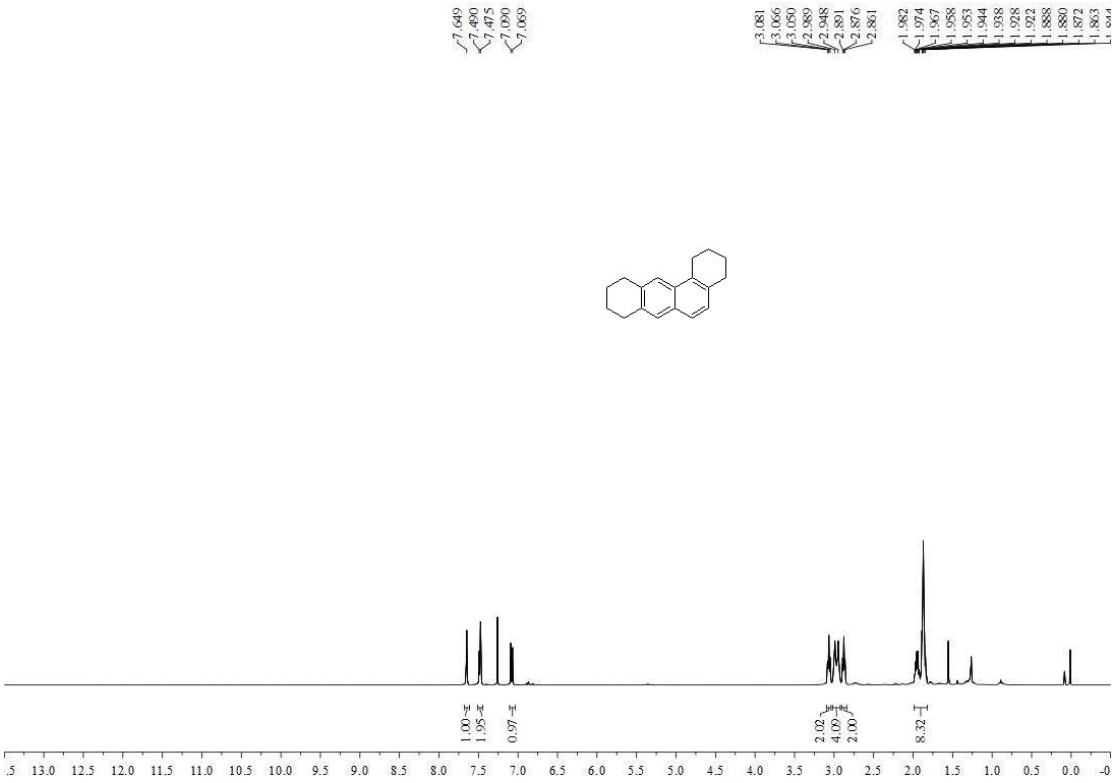

Figure S33. ^{1}H NMR spectrum for compound **3o**.

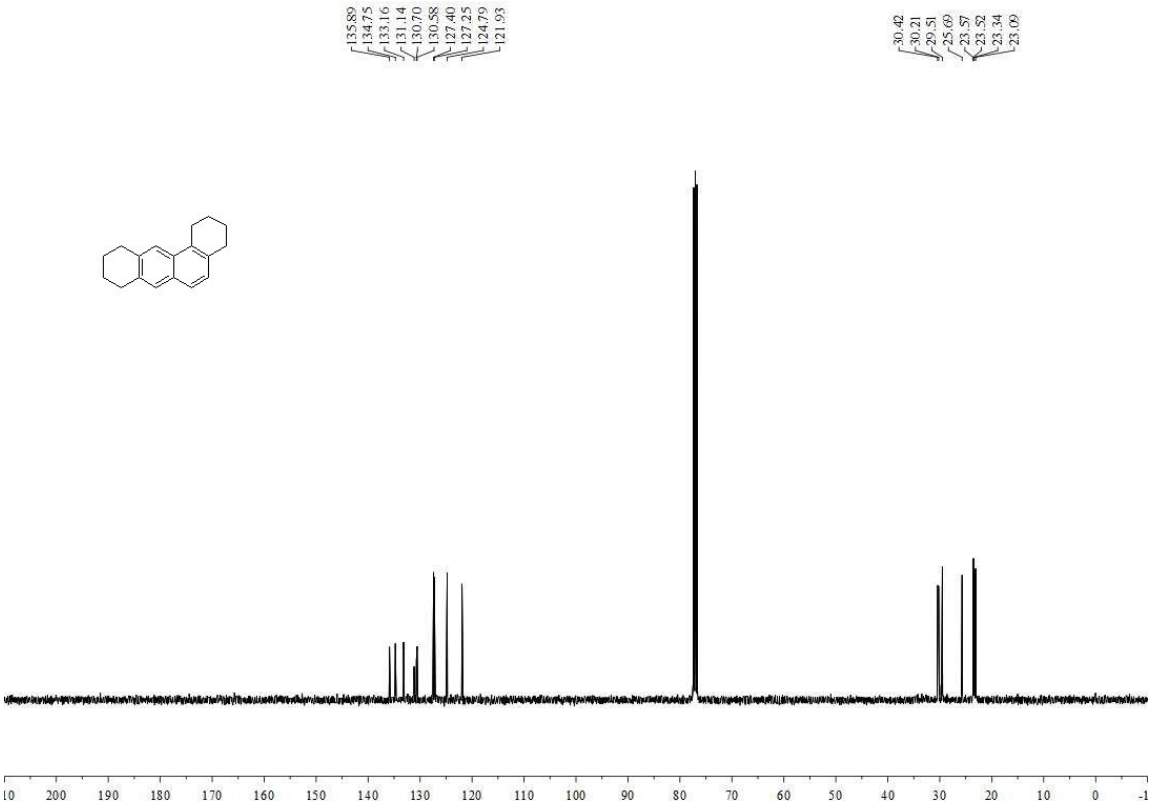

Figure S34. ^{13}C NMR spectrum for compound **3o**.

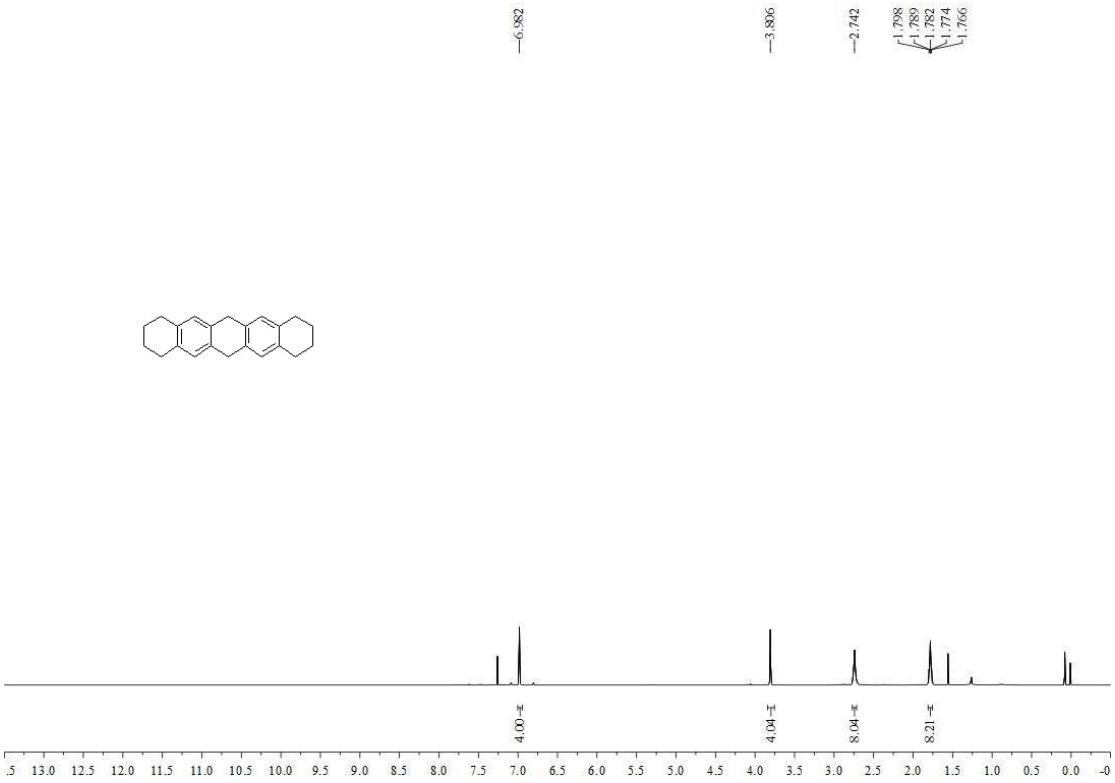

Figure S35. ^{1}H NMR spectrum for compound **3p**.

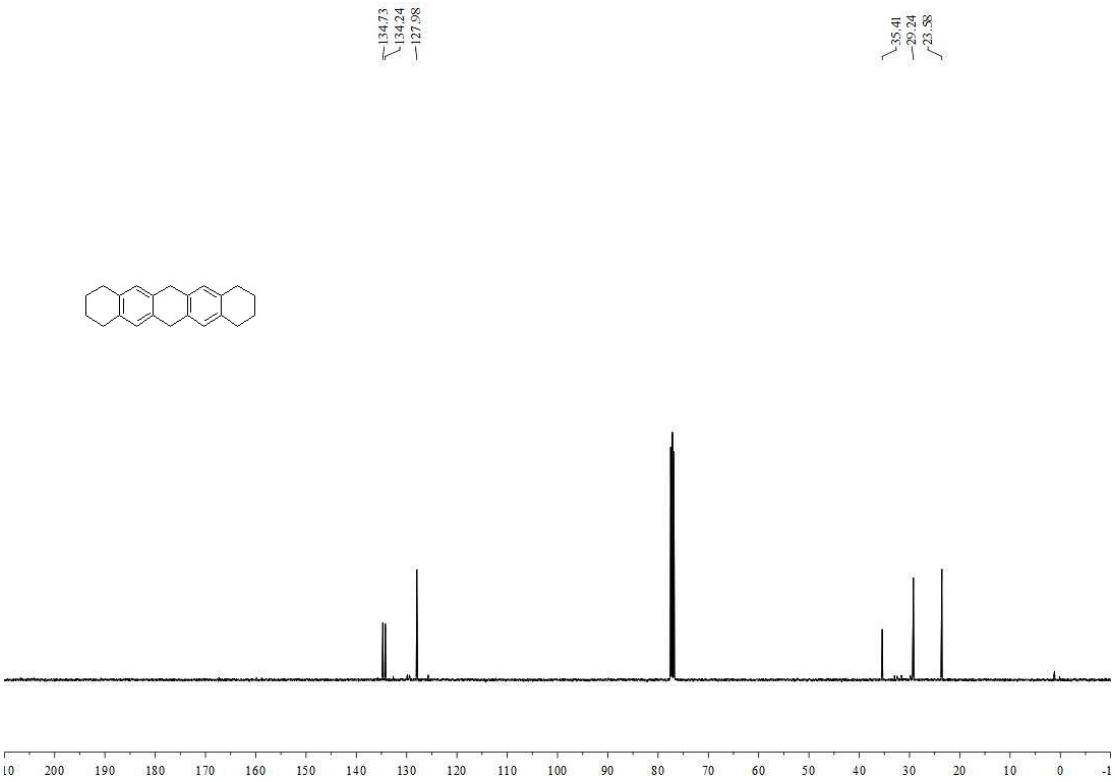

Figure S36. ^{13}C NMR spectrum for compound **3p**.

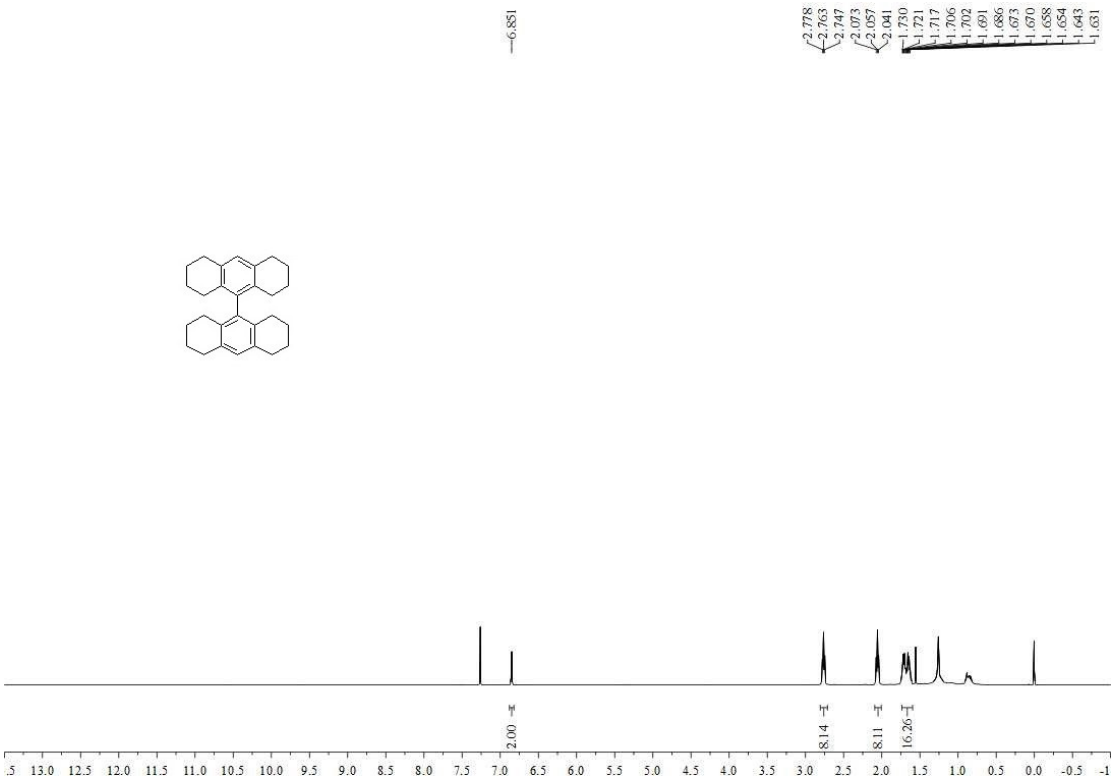

Figure S37. ^{1}H NMR spectrum for compound **3q**.

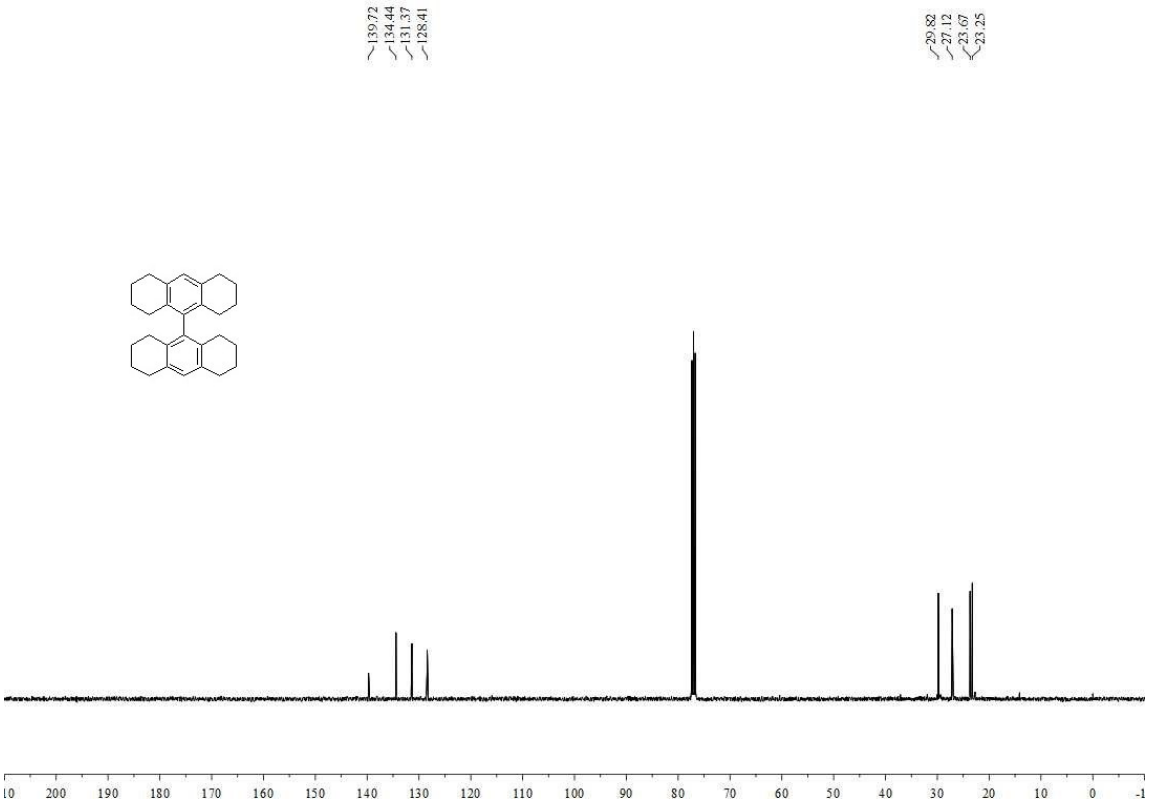

Figure S38. ^{13}C NMR spectrum for compound **3q**.

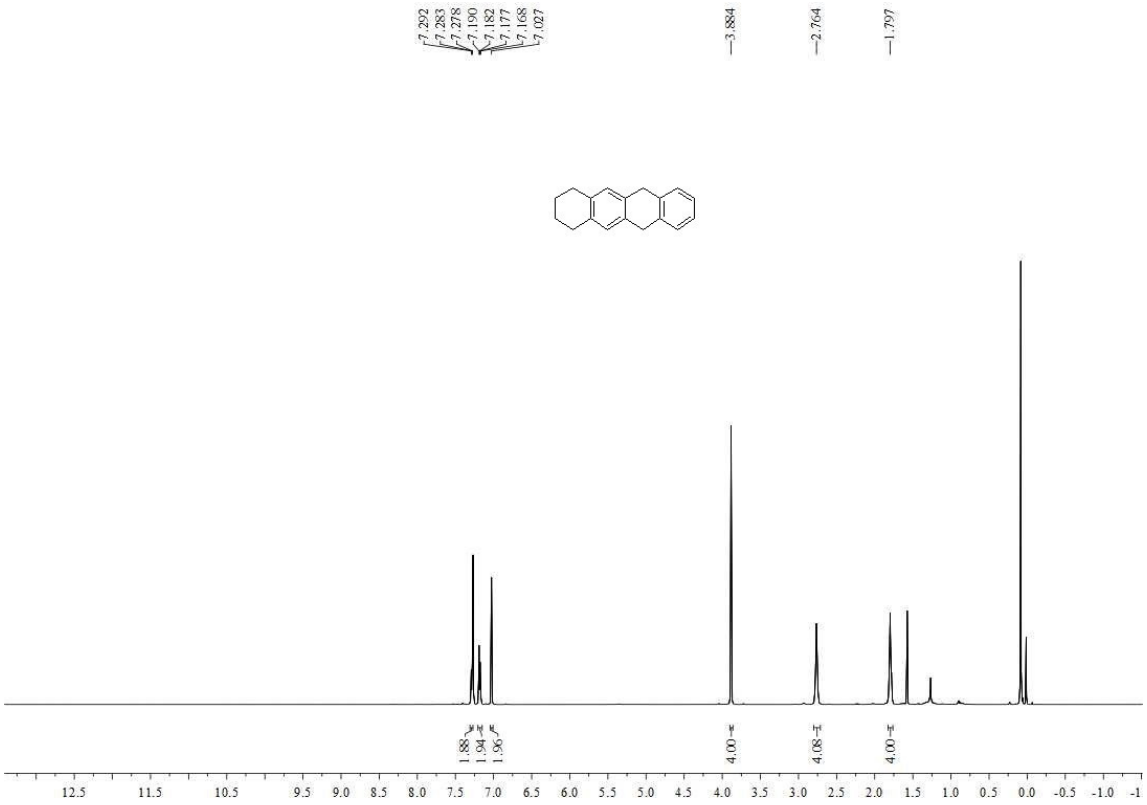

Figure S39. ^{1}H NMR spectrum for compound **3r**.

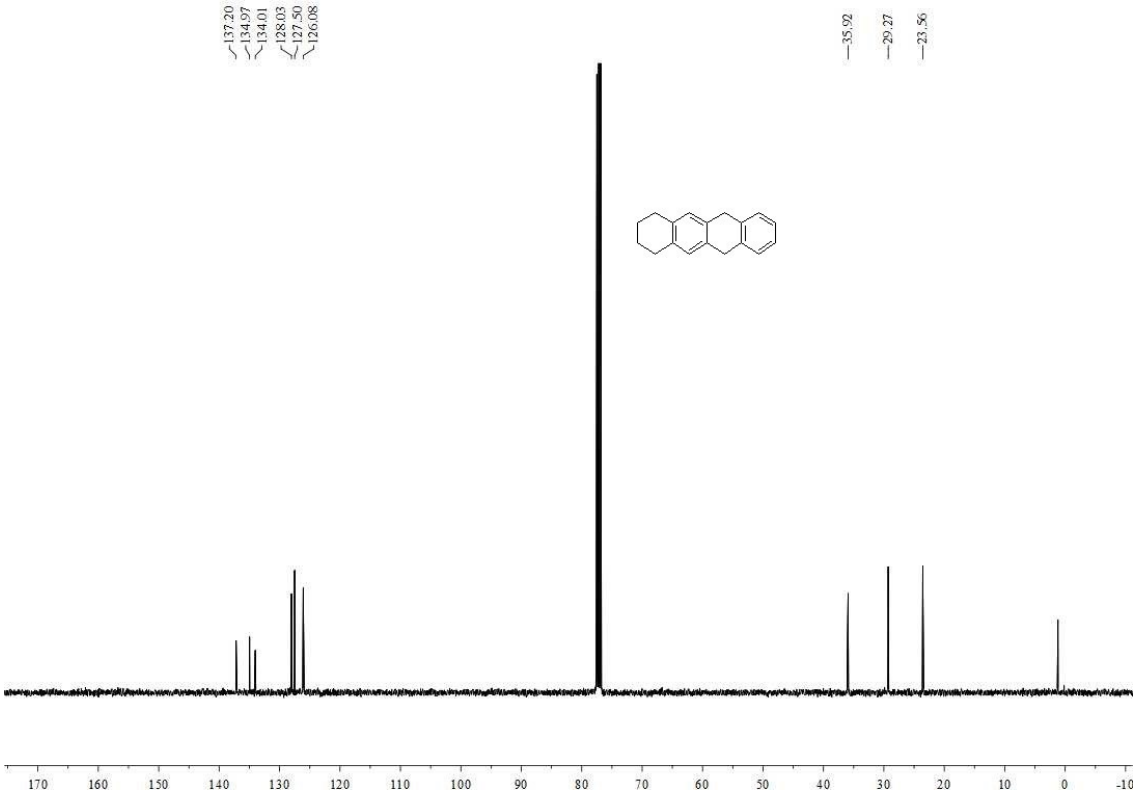

Figure S40. ^{13}C NMR spectrum for compound **3r**.

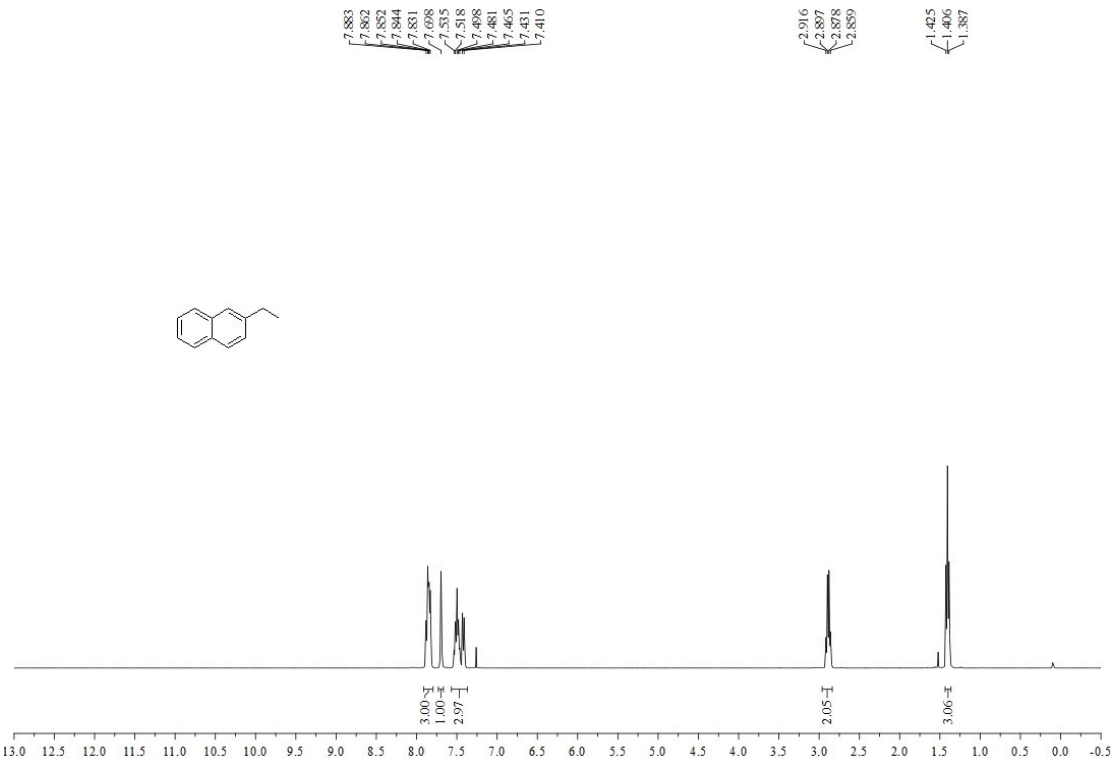

Figure S41. [1]H NMR spectrum for compound **5a**.

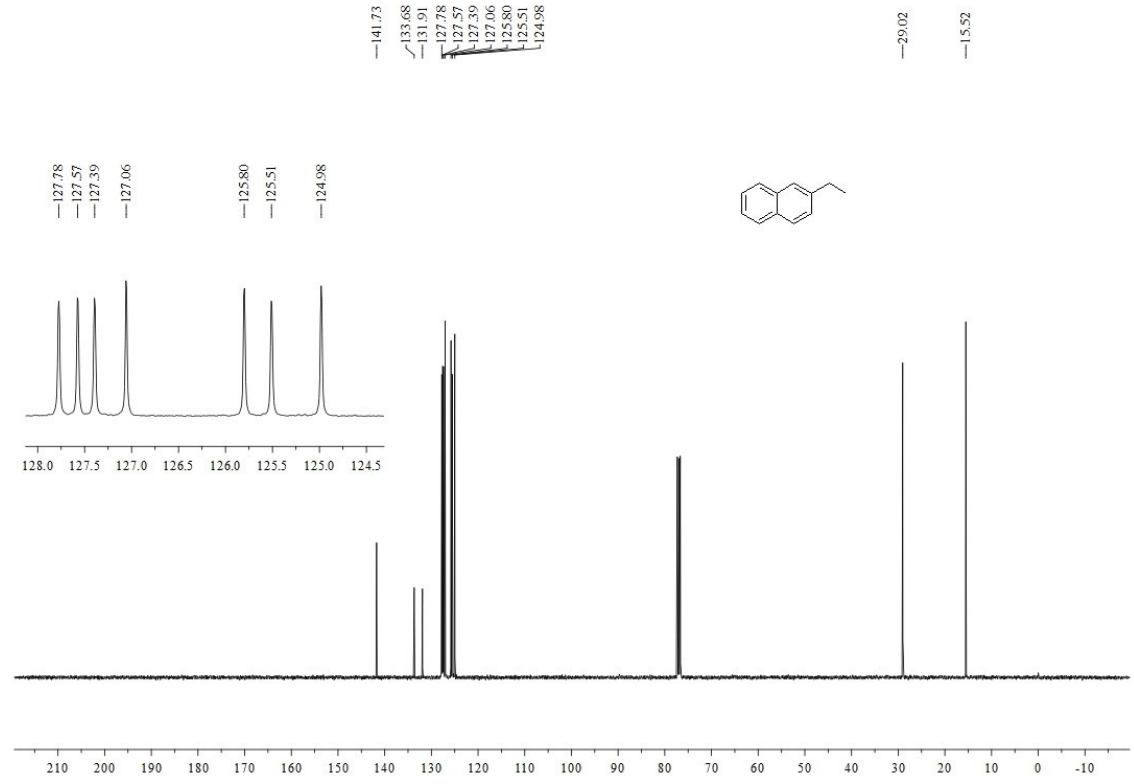

Figure S42. [13]C NMR spectrum for compound **5a**.

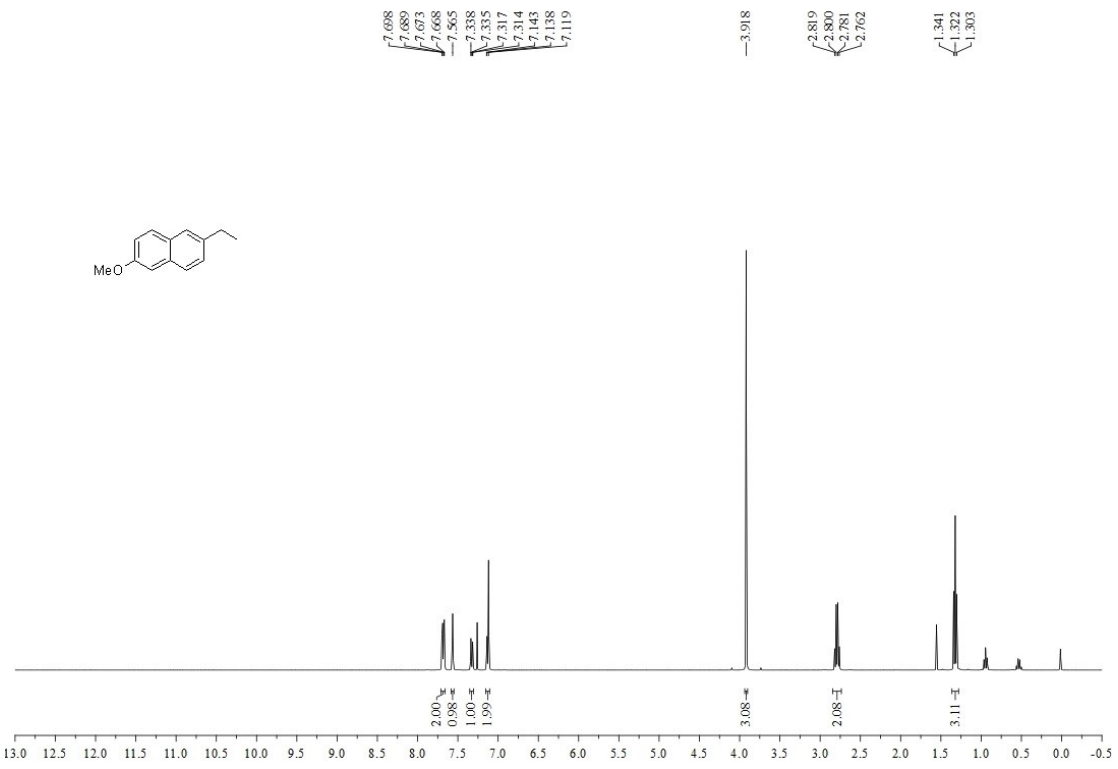

Figure S43. [1]H NMR spectrum for compound **5b**.

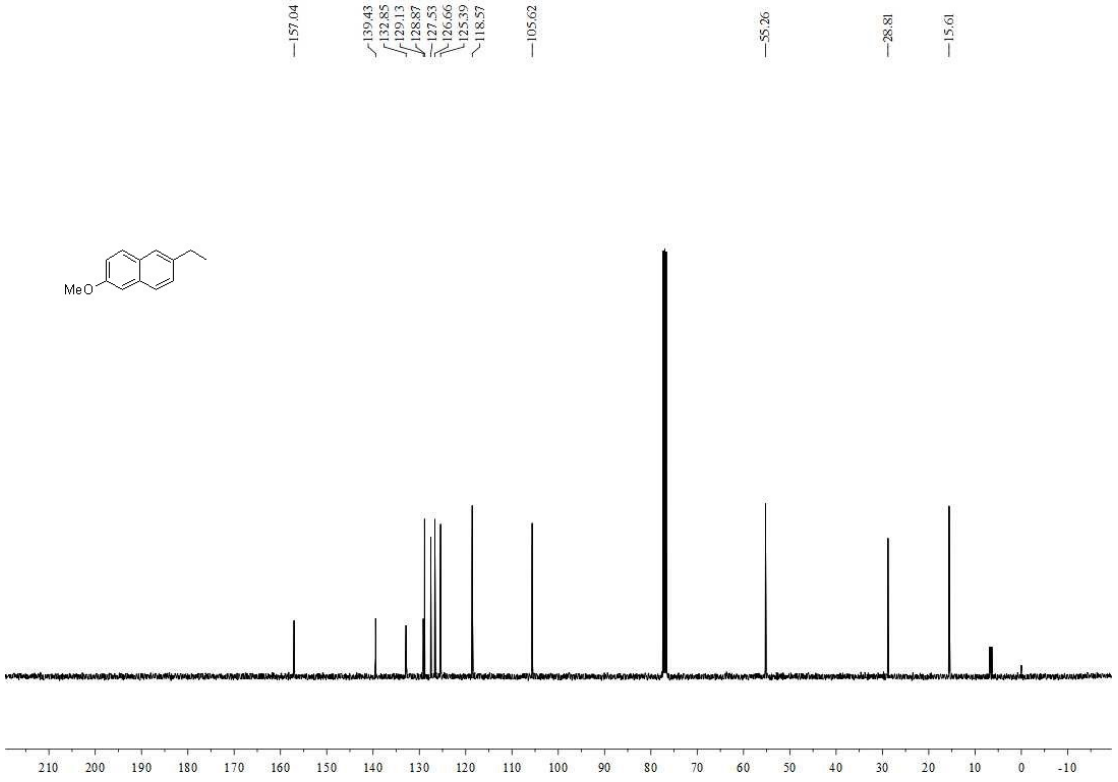

Figure S44. [13]C NMR spectrum for compound **5b**.

Figure S45. [1]H NMR spectrum for compound **5c**.

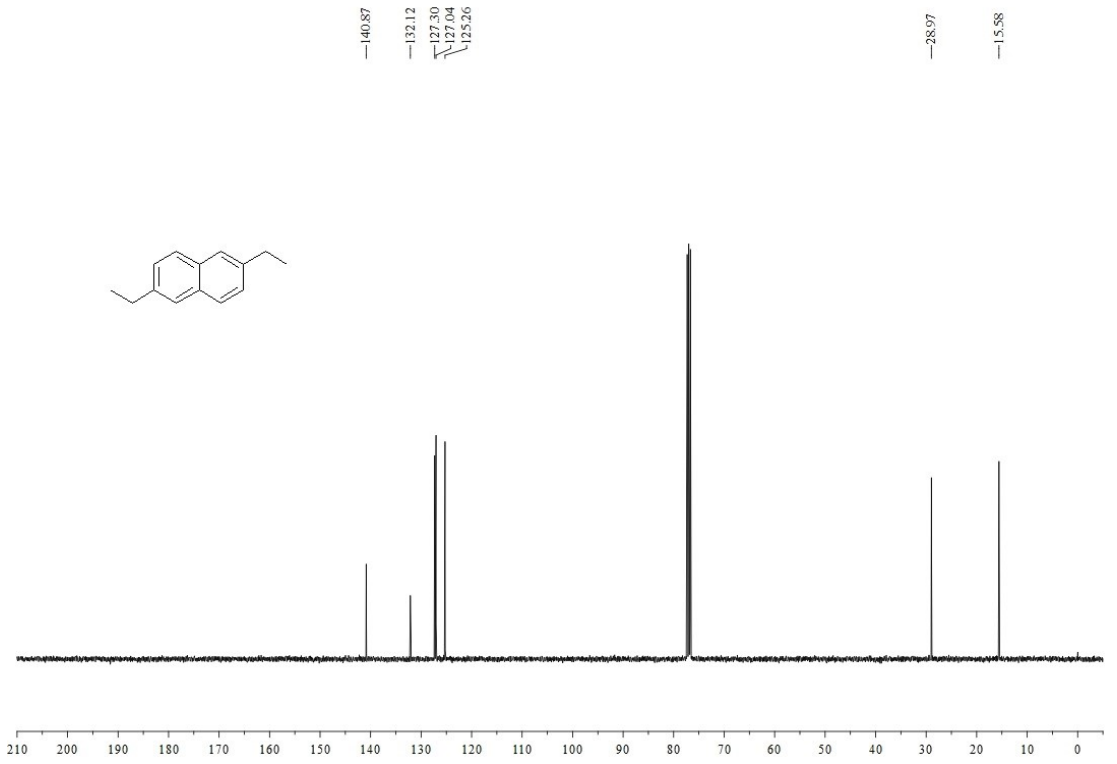

Figure S46. [13]C NMR spectrum for compound **5c**

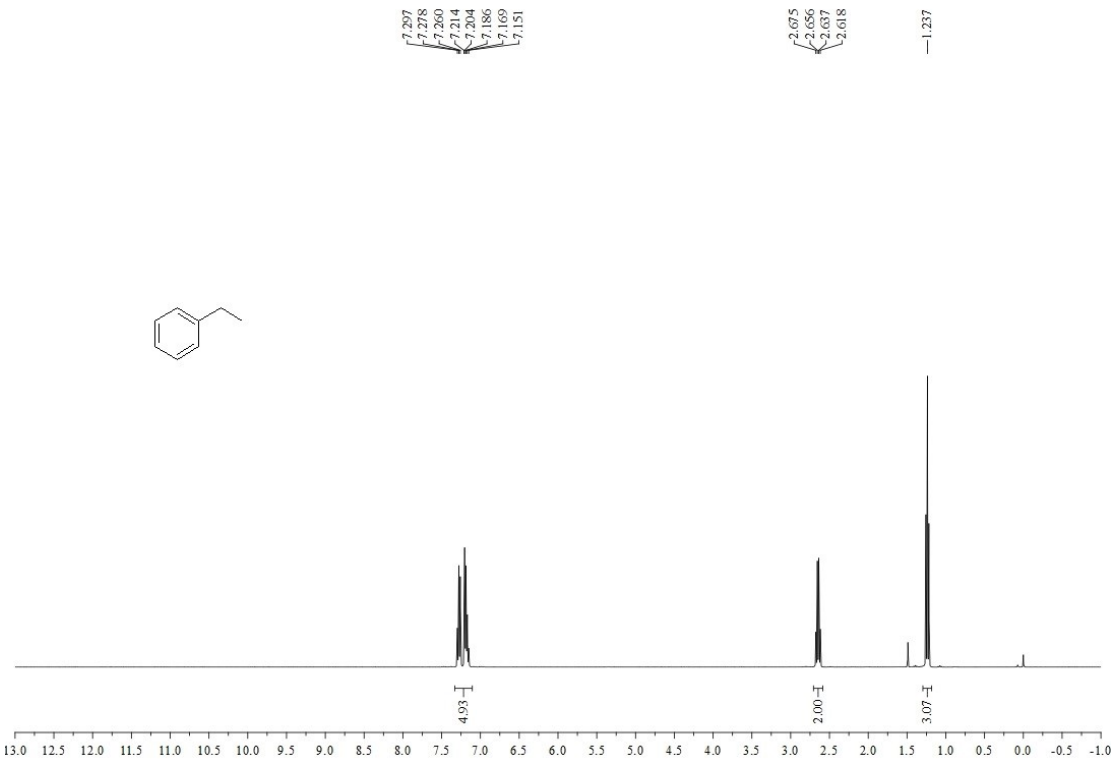

Figure S47. [1]H NMR spectrum for compound **5d**.

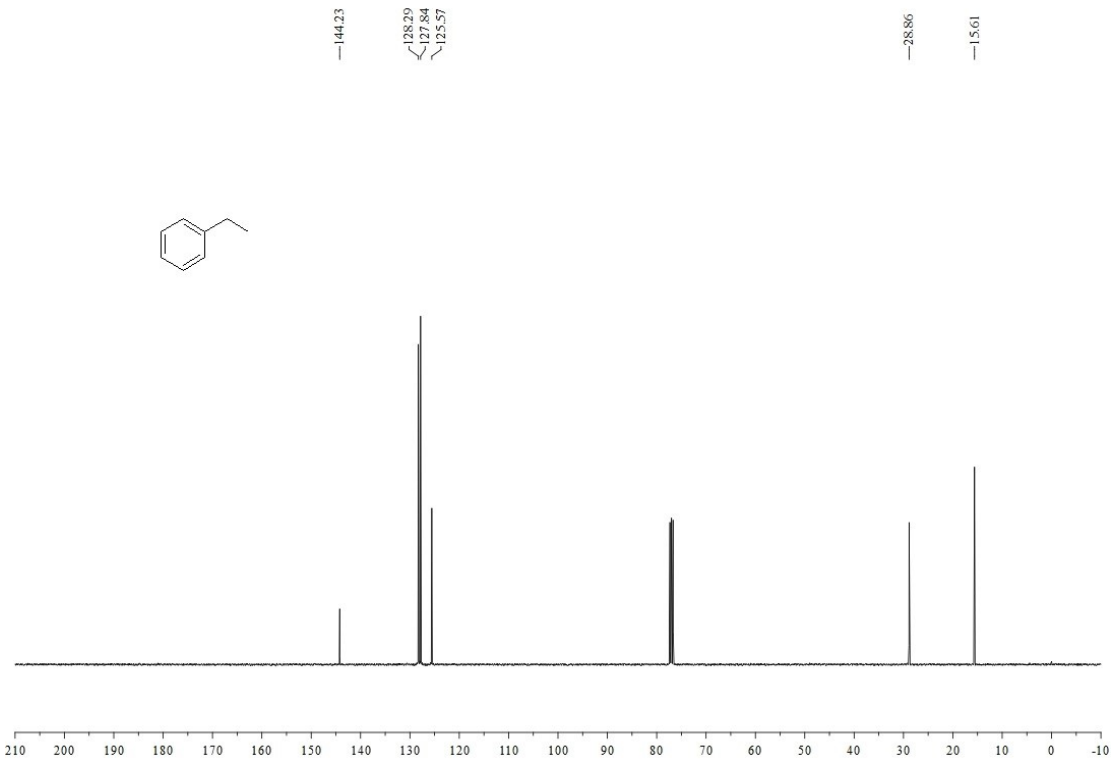

Figure S48. [13]C NMR spectrum for compound **5d**

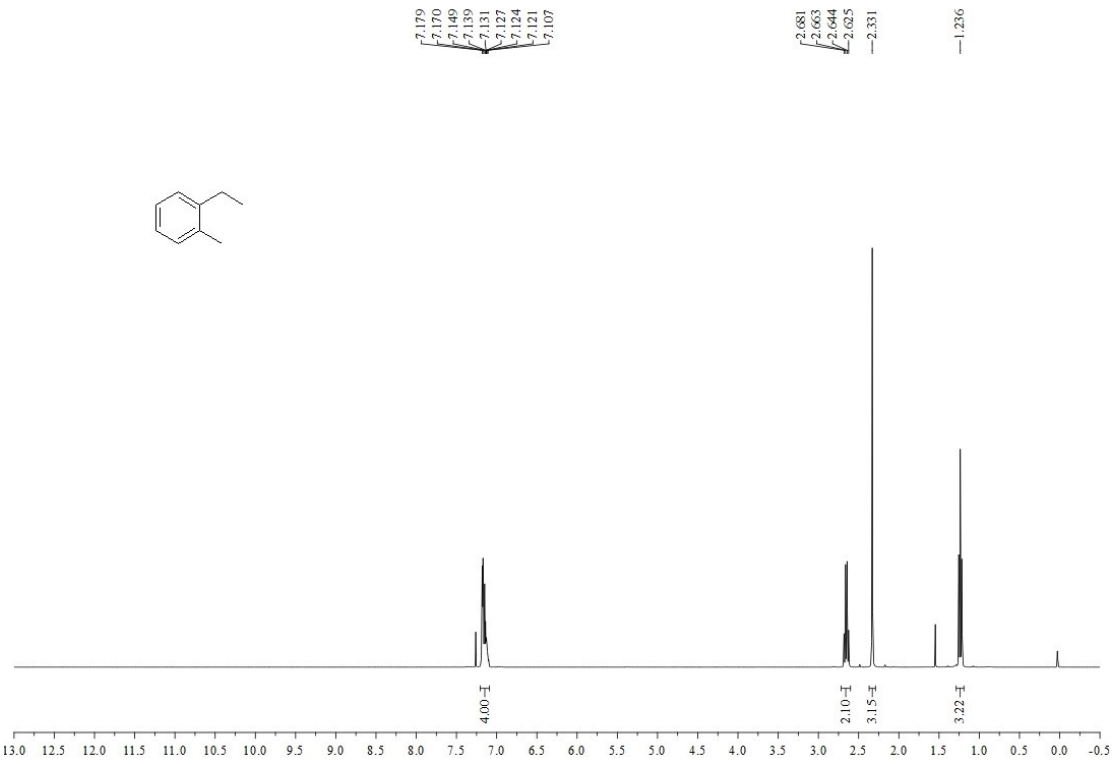

Figure S49. [1]H NMR spectrum for compound **5e**

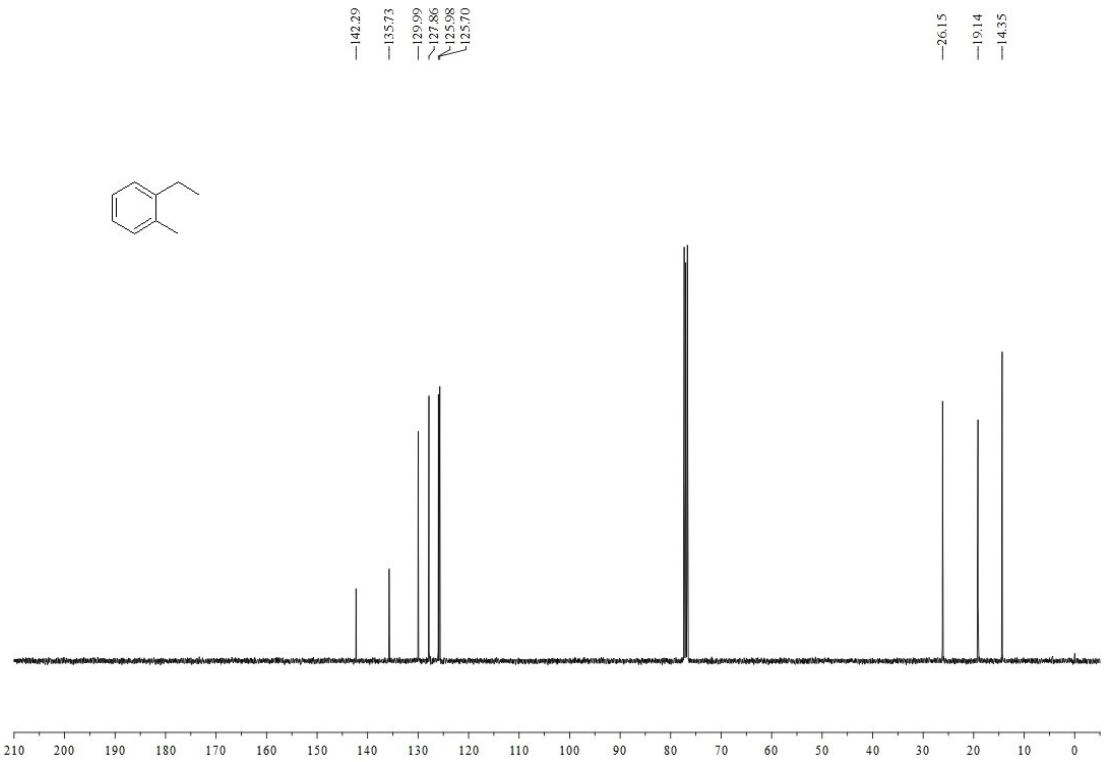

Figure S50. [13]C NMR spectrum for compound **5e**

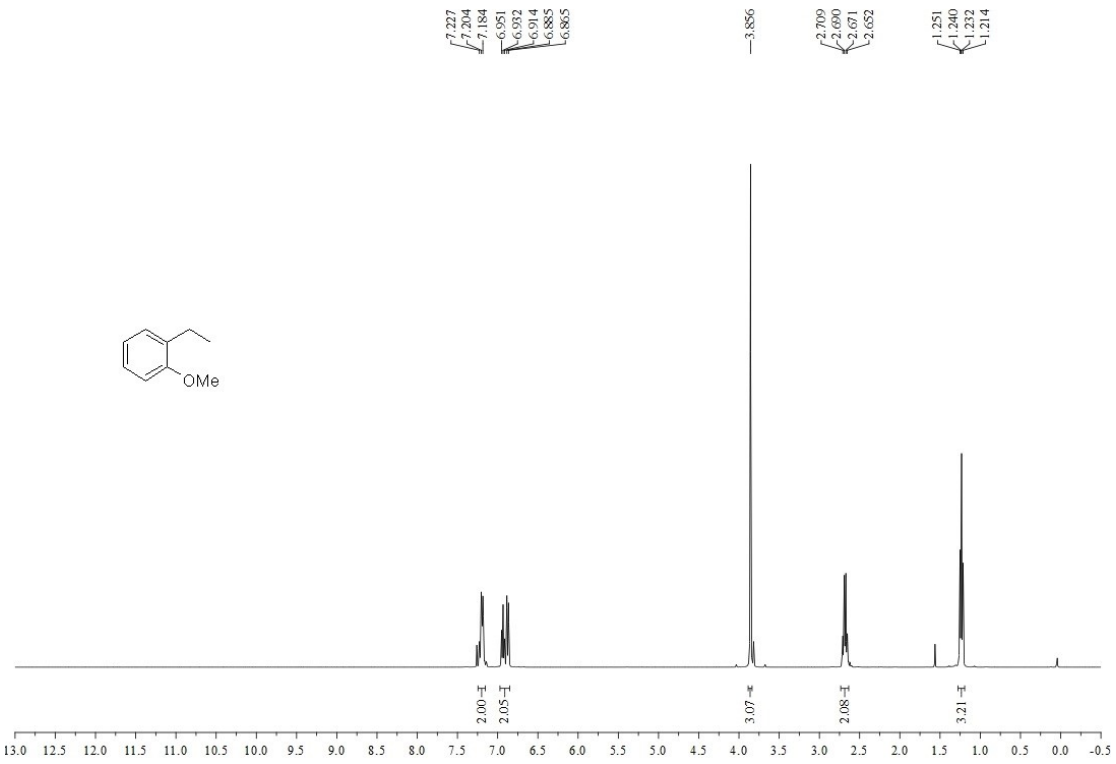

Figure S51. [1]H NMR spectrum for compound **5f**

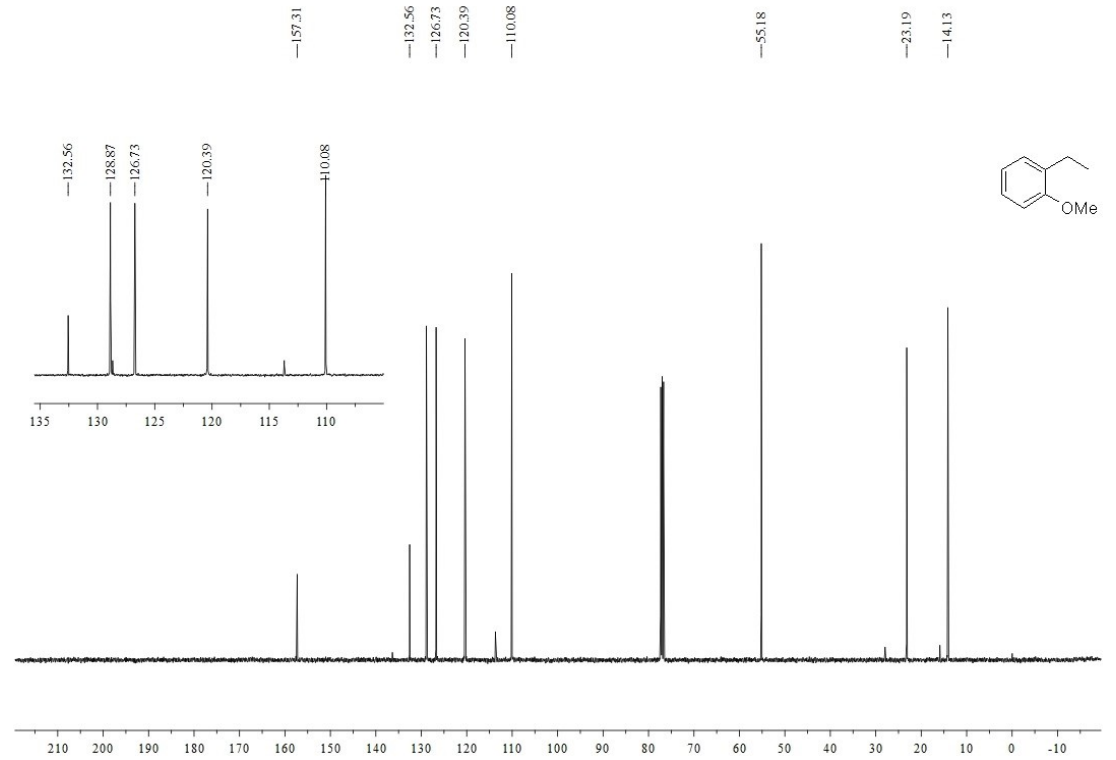

Figure S52. [13]C NMR spectrum for compound **5f**

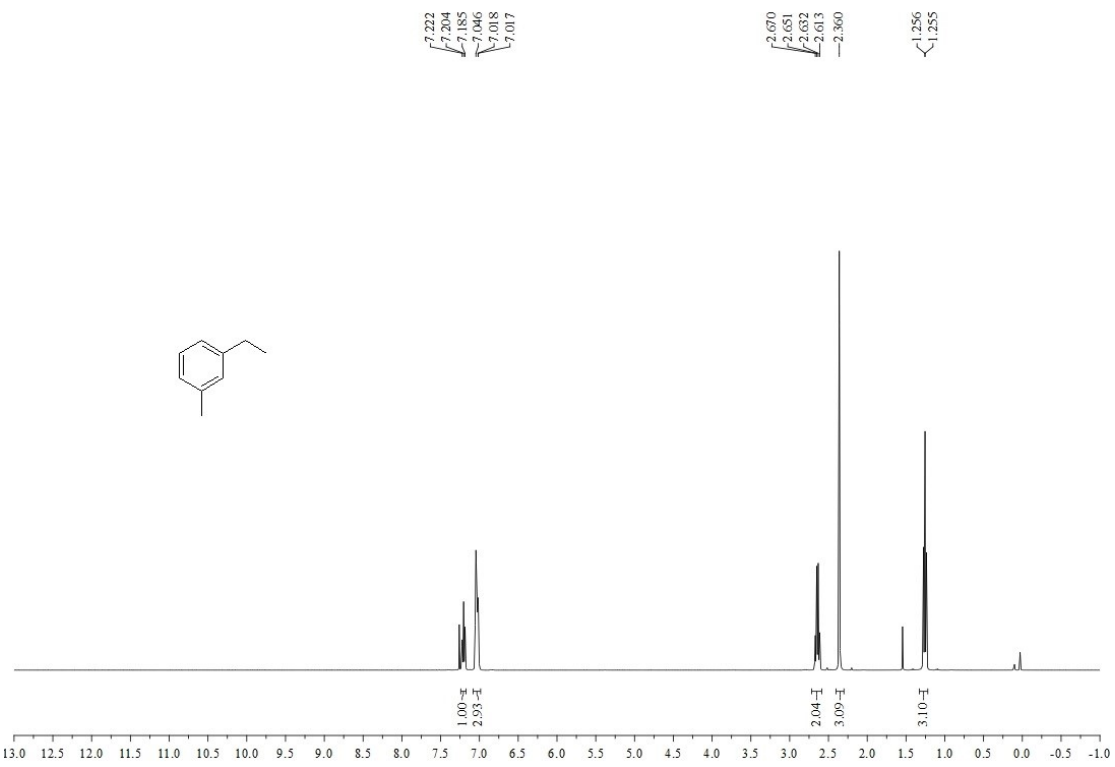

Figure S53. [1]H NMR spectrum for compound **5g**

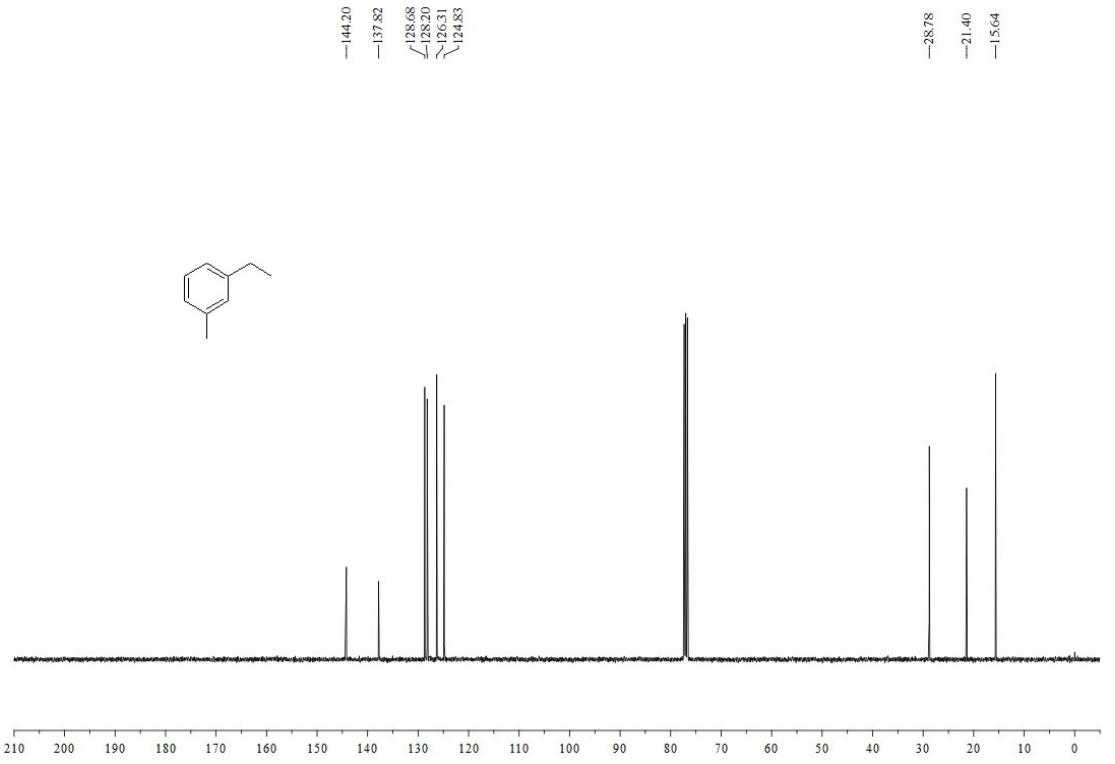

Figure S54. [13]C NMR spectrum for compound **5g**

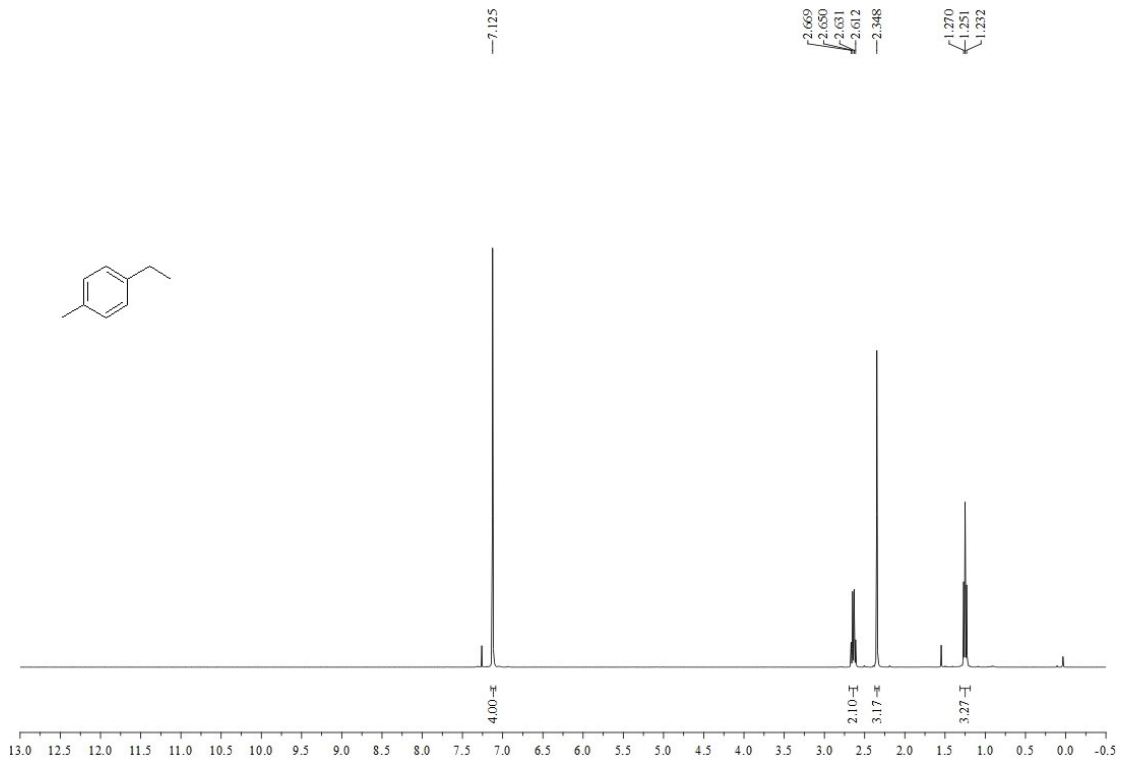

Figure S55. [1]H NMR spectrum for compound **5h**

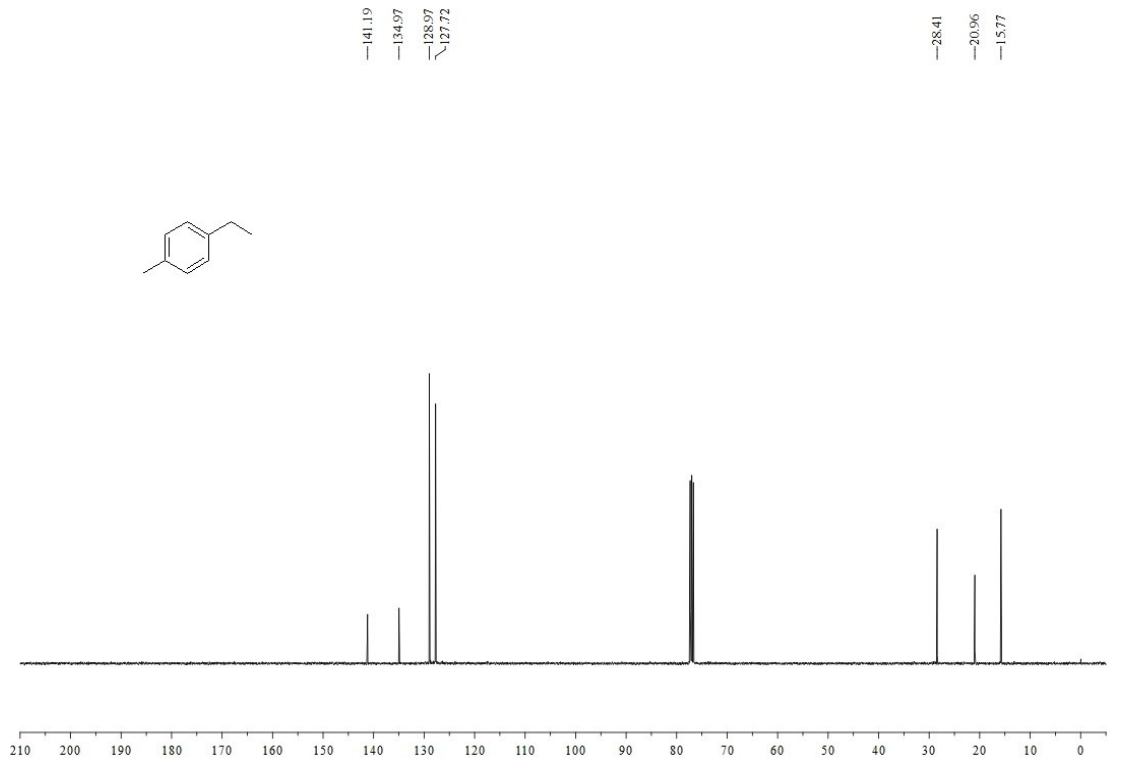

Figure S56. [13]C NMR spectrum for compound **5h**

Figure S57. [1]H NMR spectrum for compound **5i**

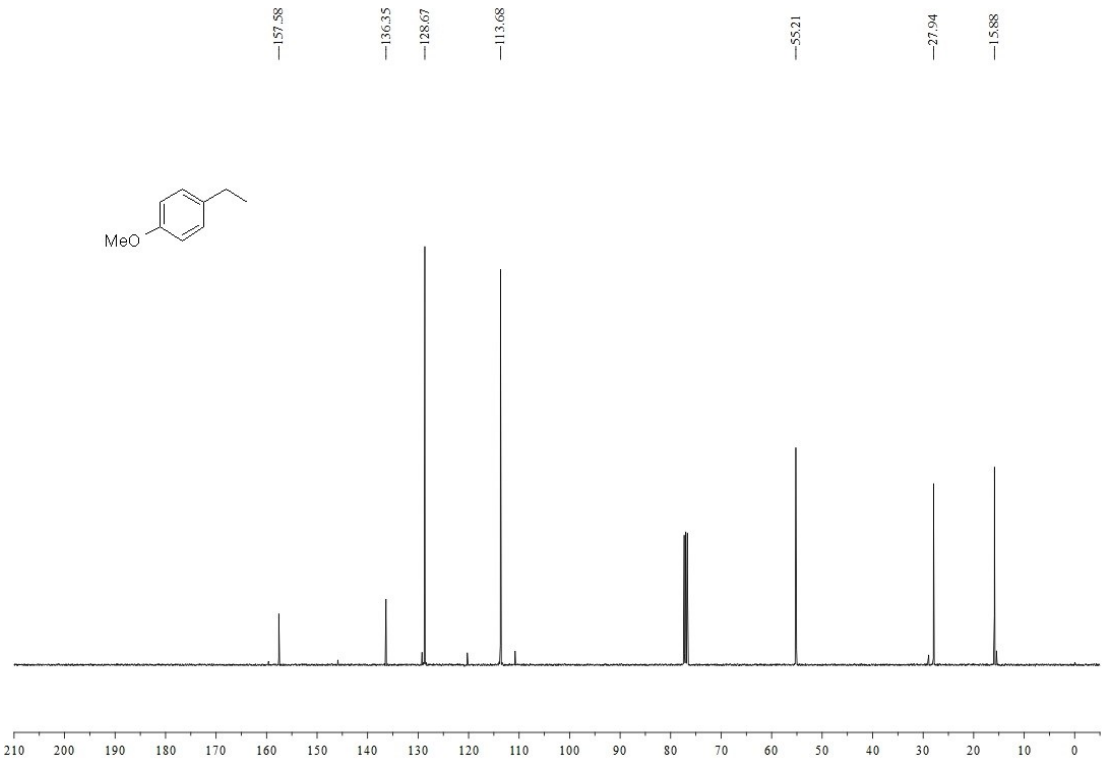

Figure S58. [13]C NMR spectrum for compound **5i**

Figure S59. [1]H NMR spectrum for compound **5j**

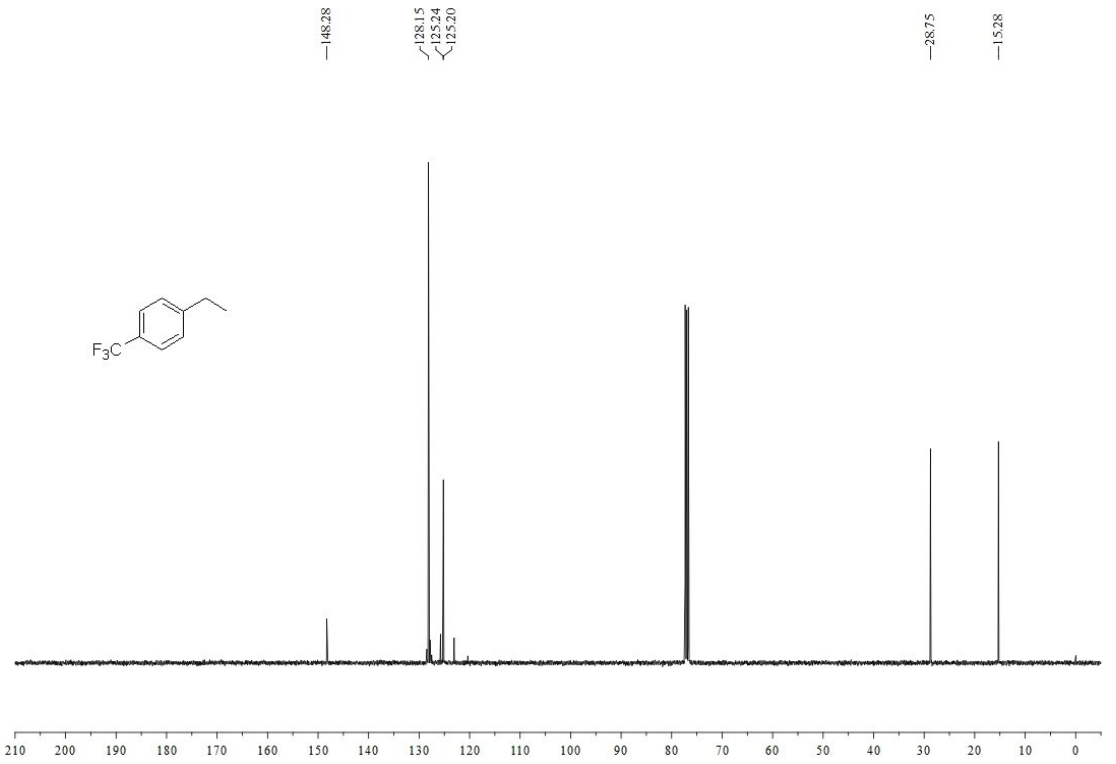

Figure S60. [13]C NMR spectrum for compound **5j**

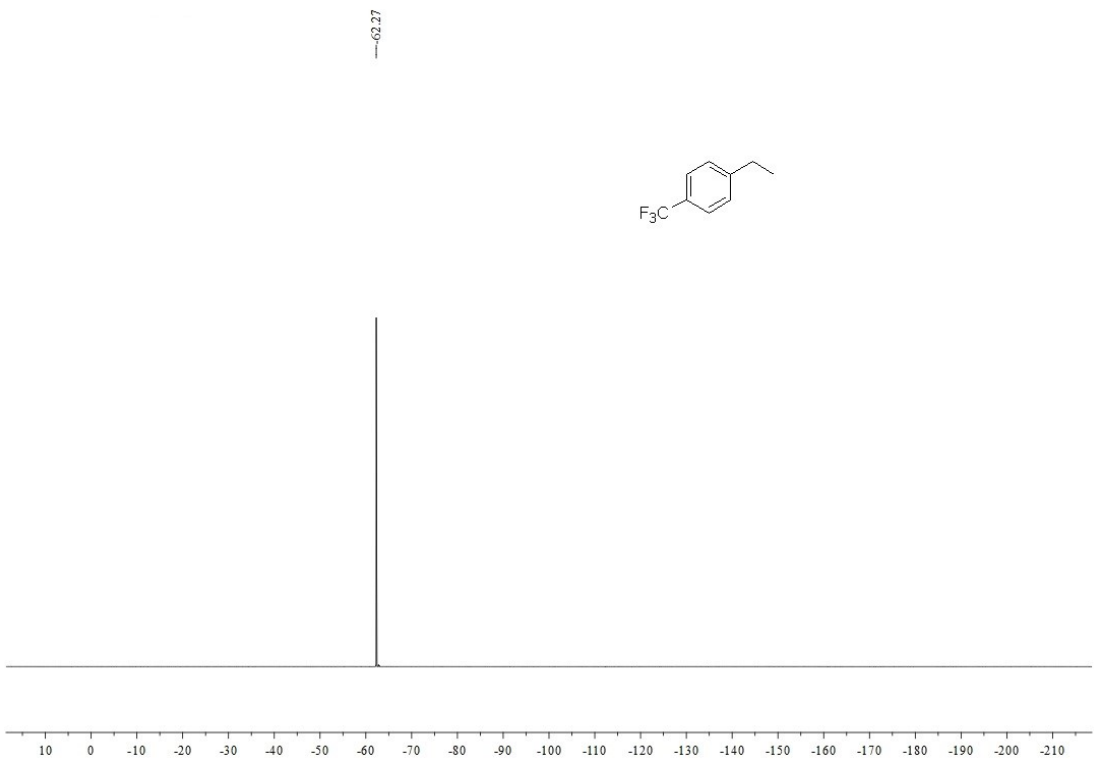

Figure S61. ^{19}F NMR spectrum for compound **5j**

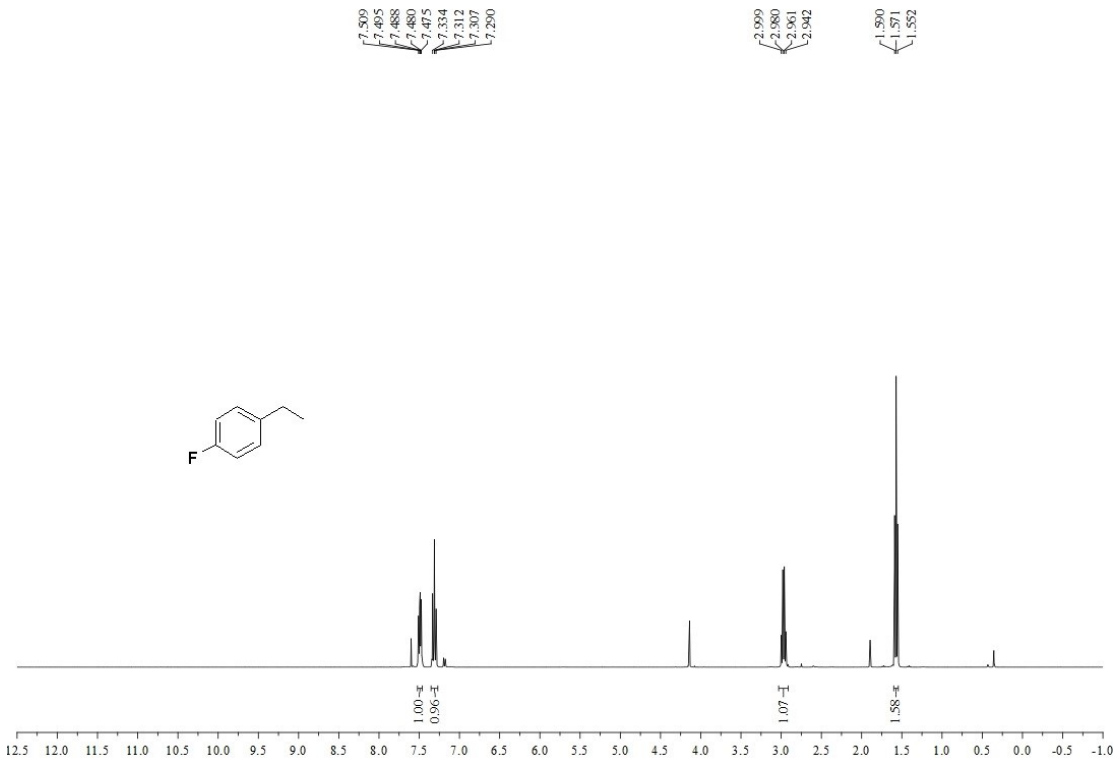

Figure S62. [1]H NMR spectrum for compound **5k**

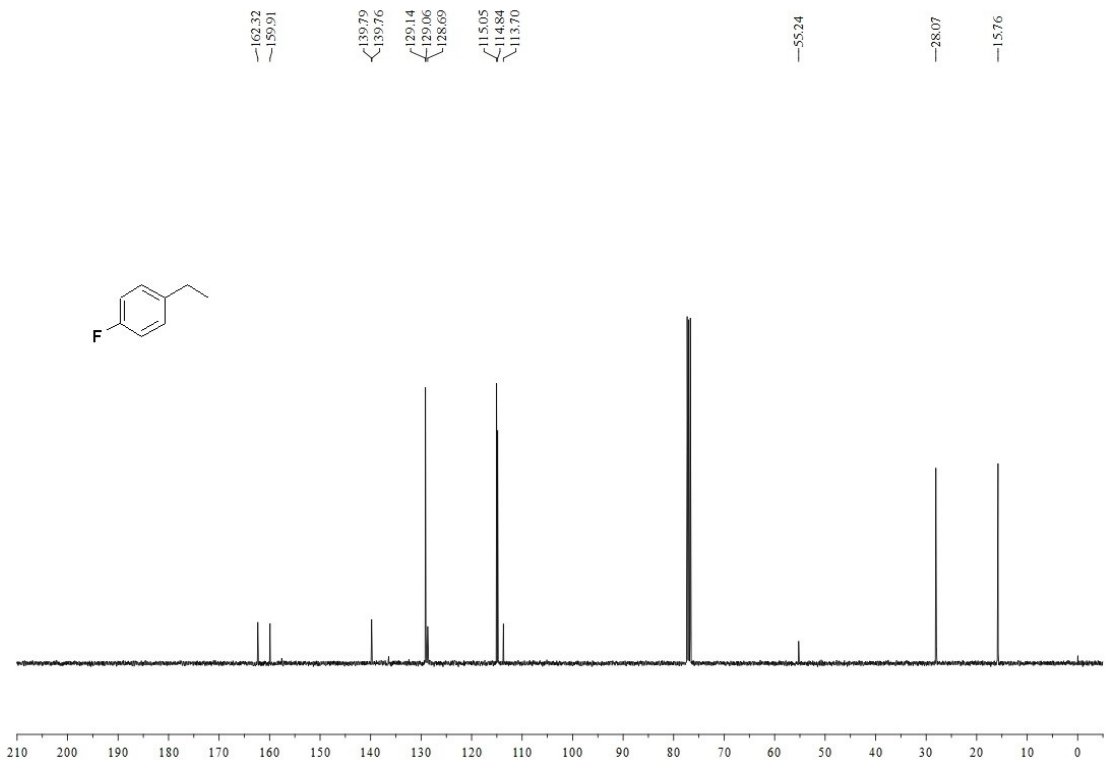

Figure S63. [13]C NMR spectrum for compound **5k**

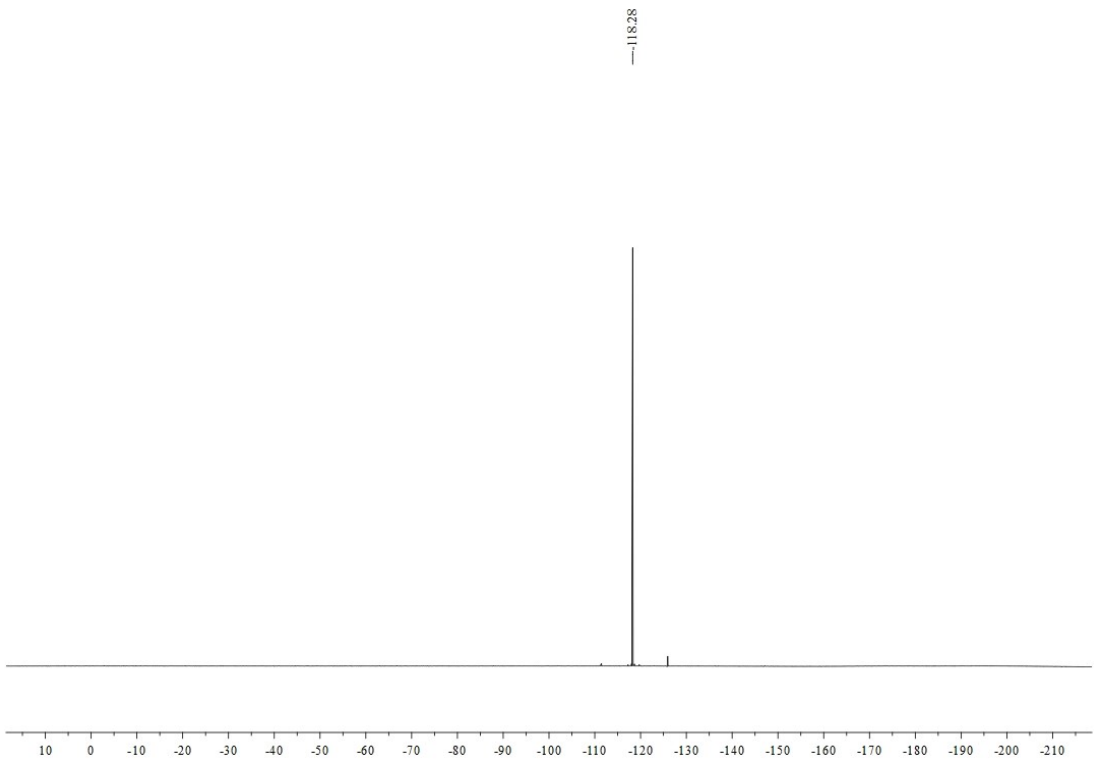

Figure S64. ^{19}F NMR spectrum for compound **5k**

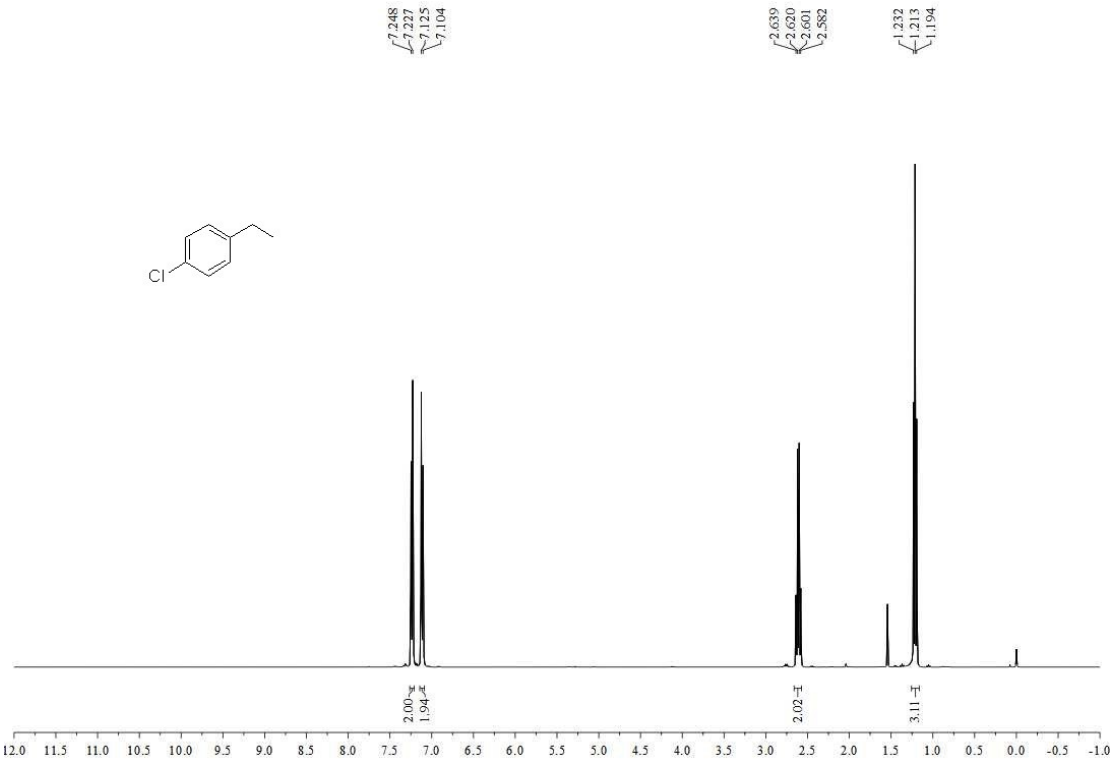

Figure S65. [1]H NMR spectrum for compound **5l**

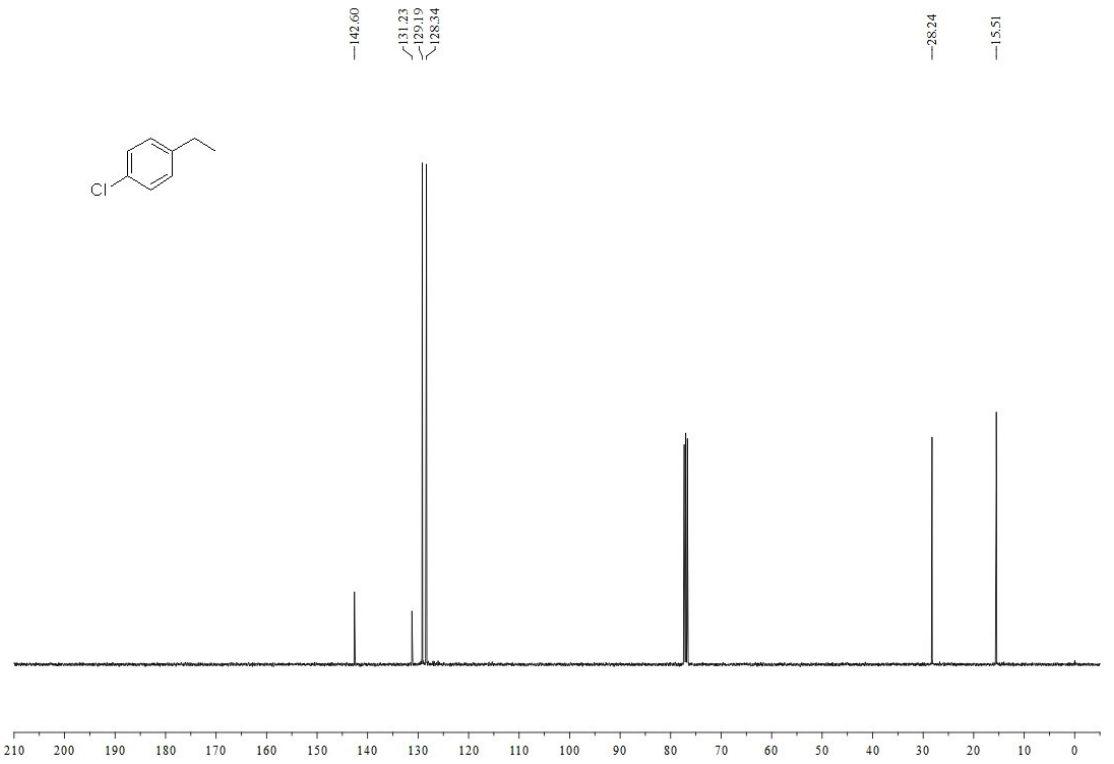

Figure S66. [13]C NMR spectrum for compound **5l**

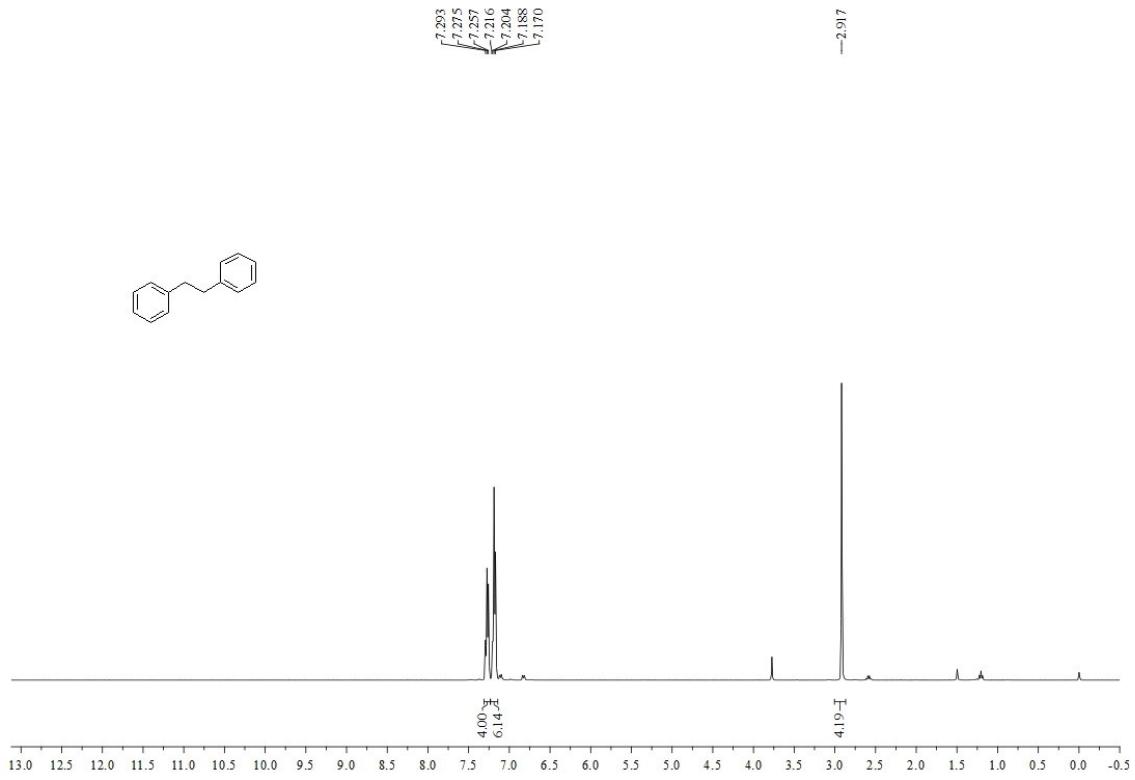

Figure S67. ^{1}H NMR spectrum for compound **5m.**

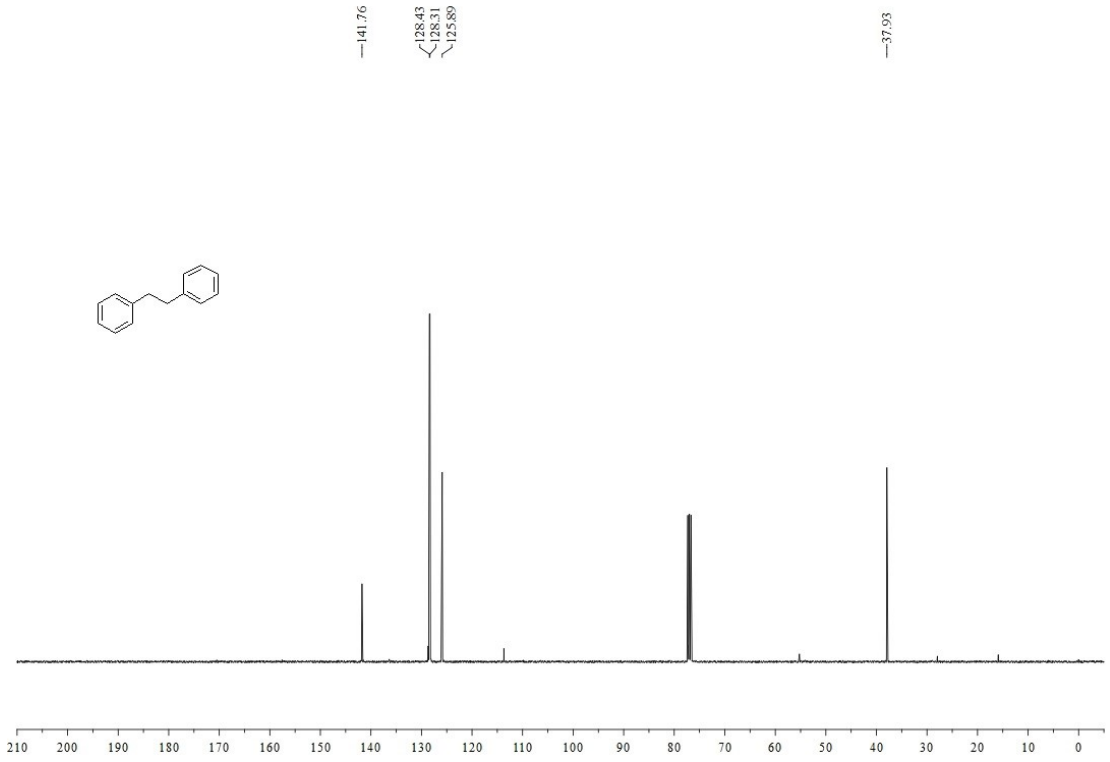

Figure S68. ^{13}C NMR spectrum for compound **5m**.

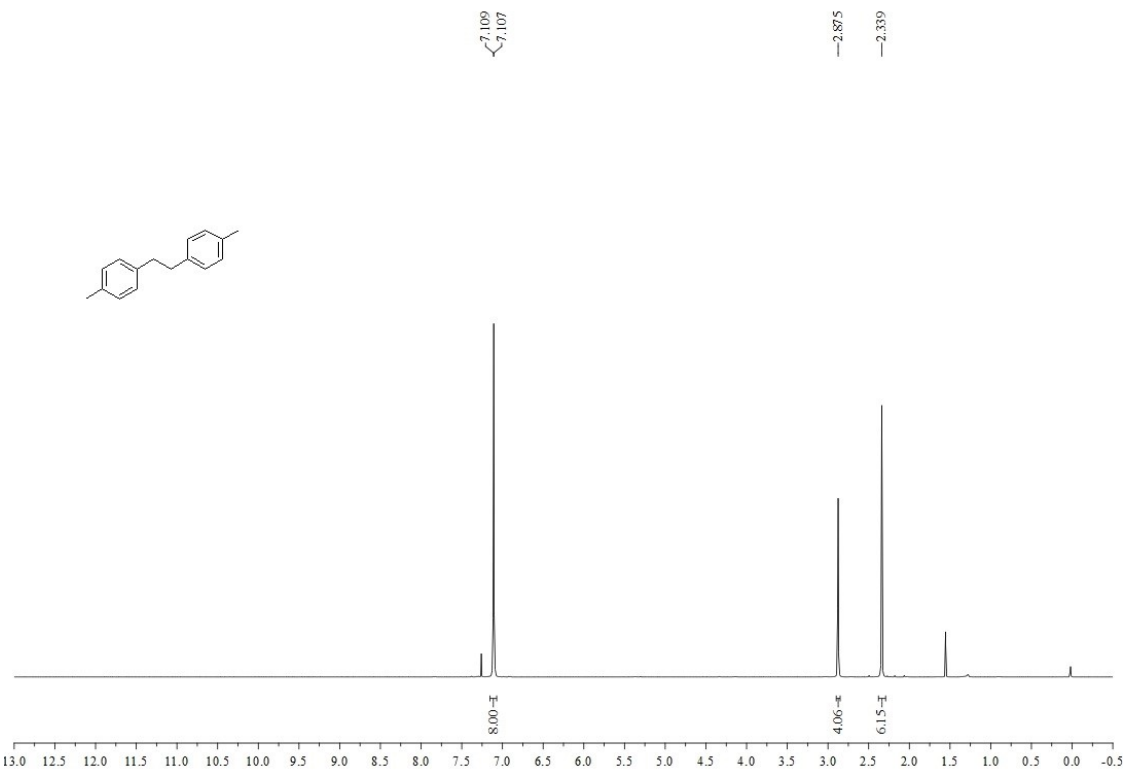

Figure S69. [1]H NMR spectrum for compound **5n**.

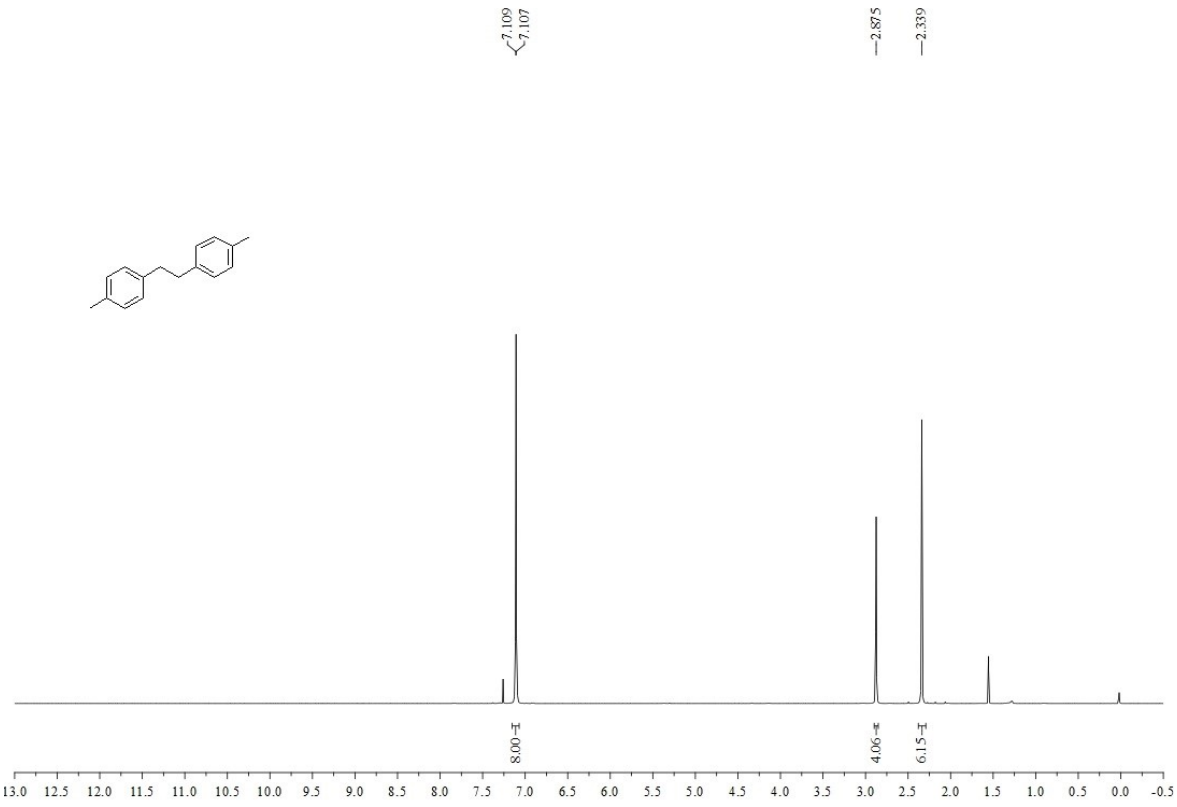

Figure S70. [13]C NMR spectrum for compound **5n**.

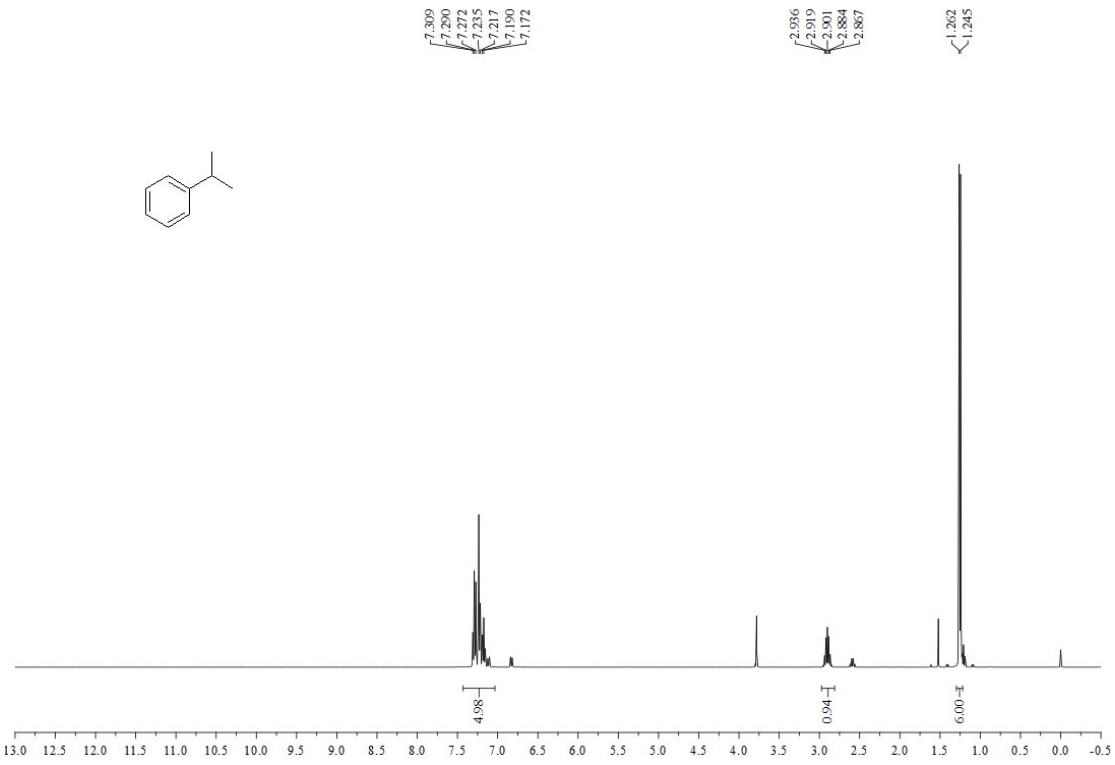

Figure S71. [1]H NMR spectrum for compound **5o**.

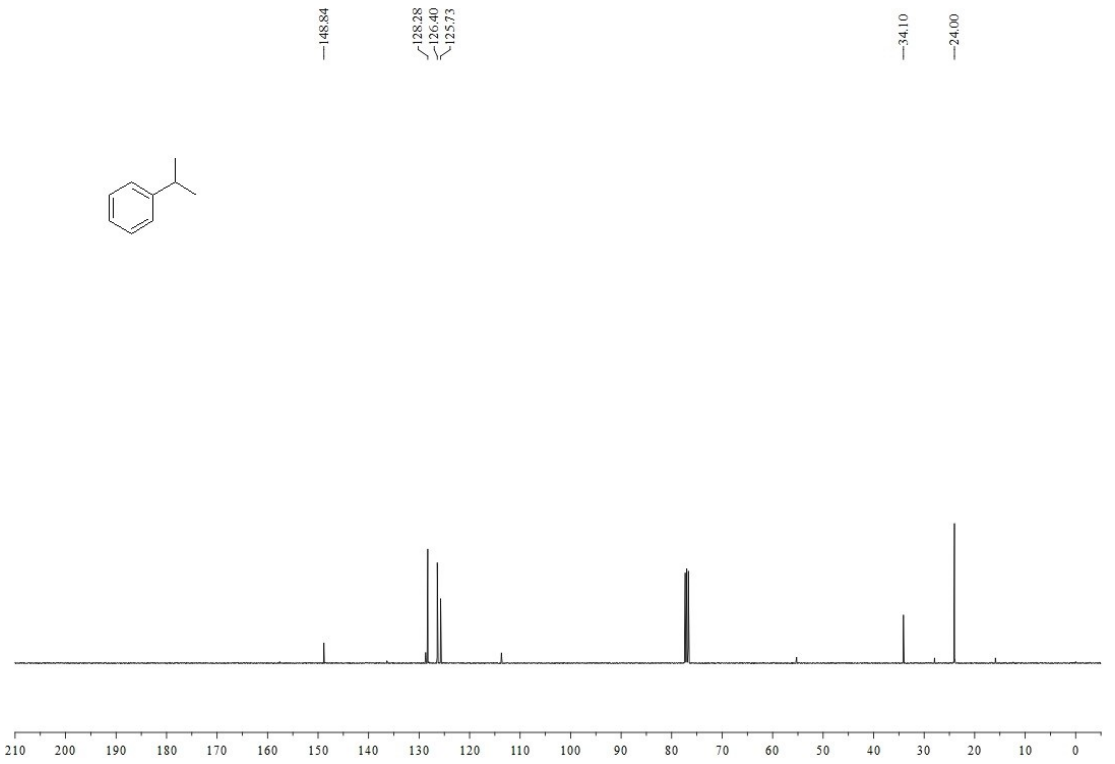

Figure S72. [13]C NMR spectrum for compound **5o**.

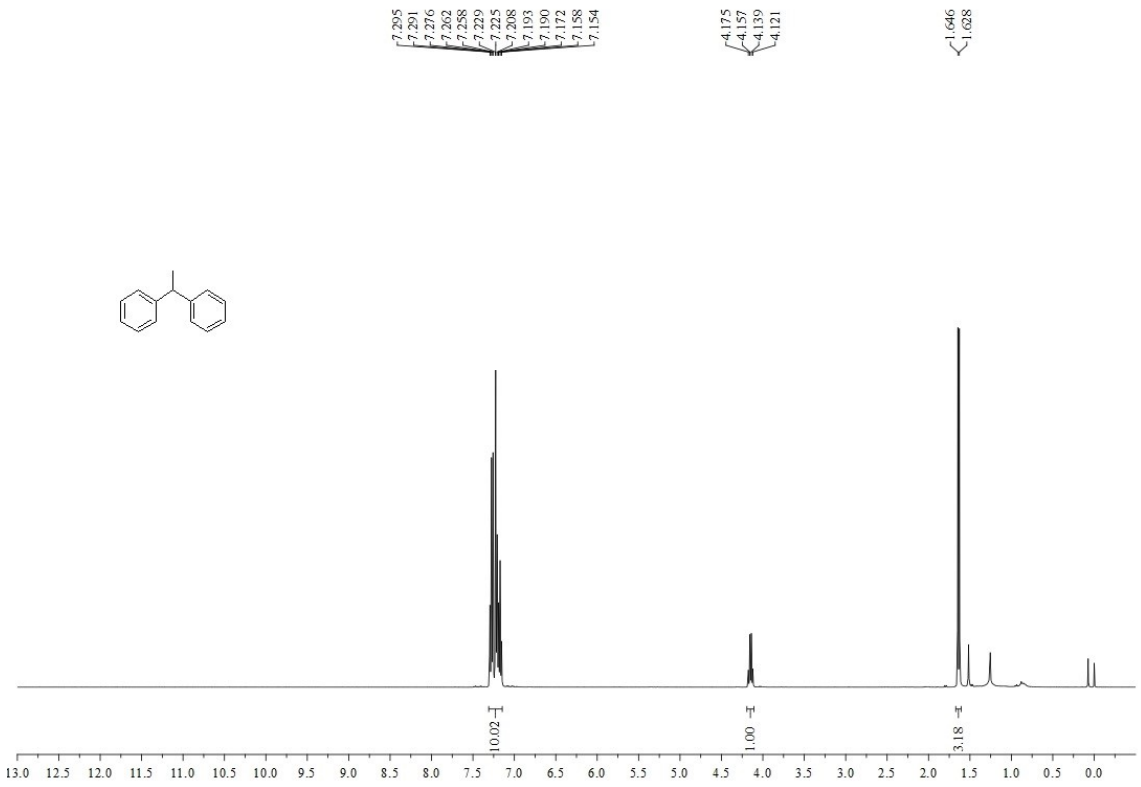

Figure S73. ^{1}H NMR spectrum for compound **5p**

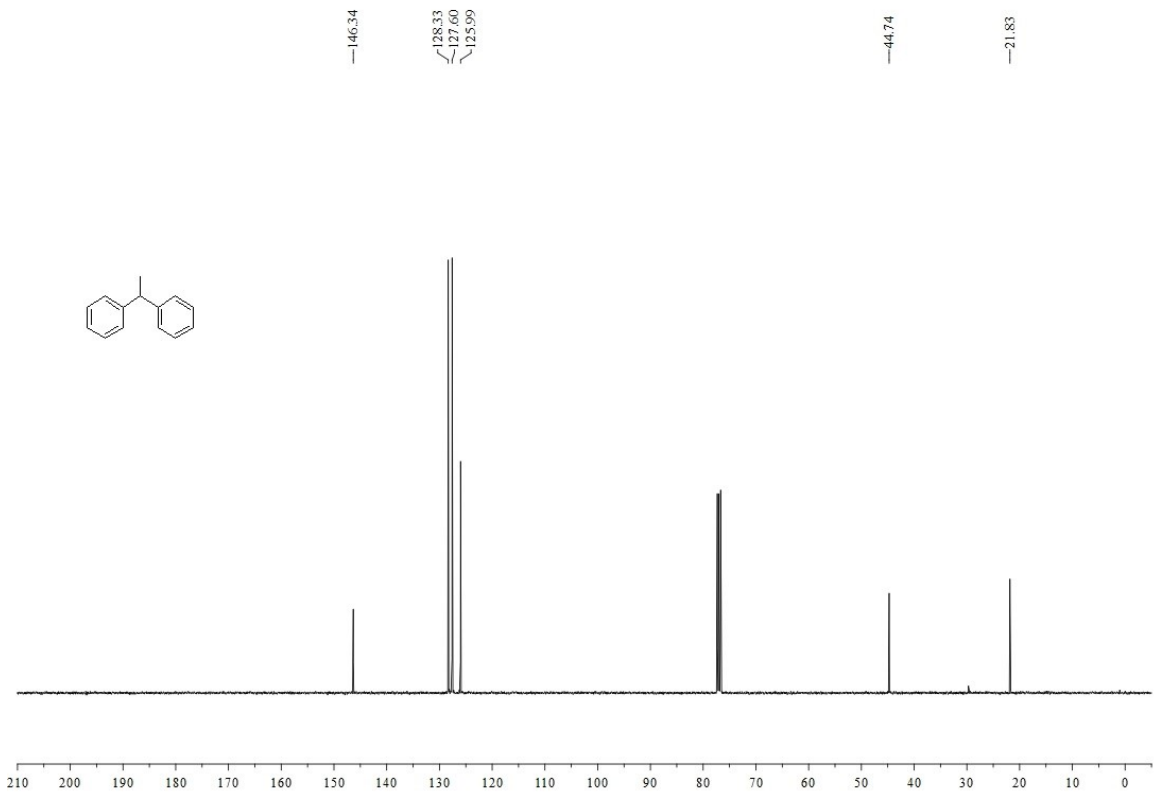

Figure S74. ^{13}C NMR spectrum for compound **5p**.

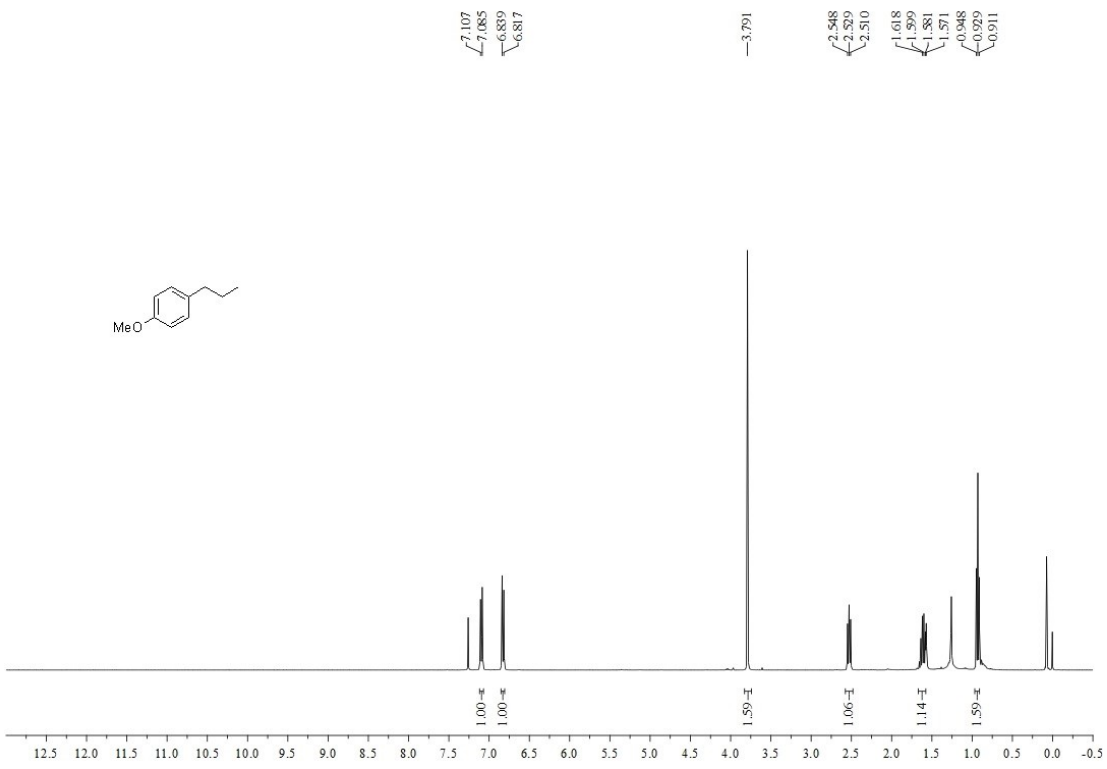

Figure S75. [1]H NMR spectrum for compound **5q**.

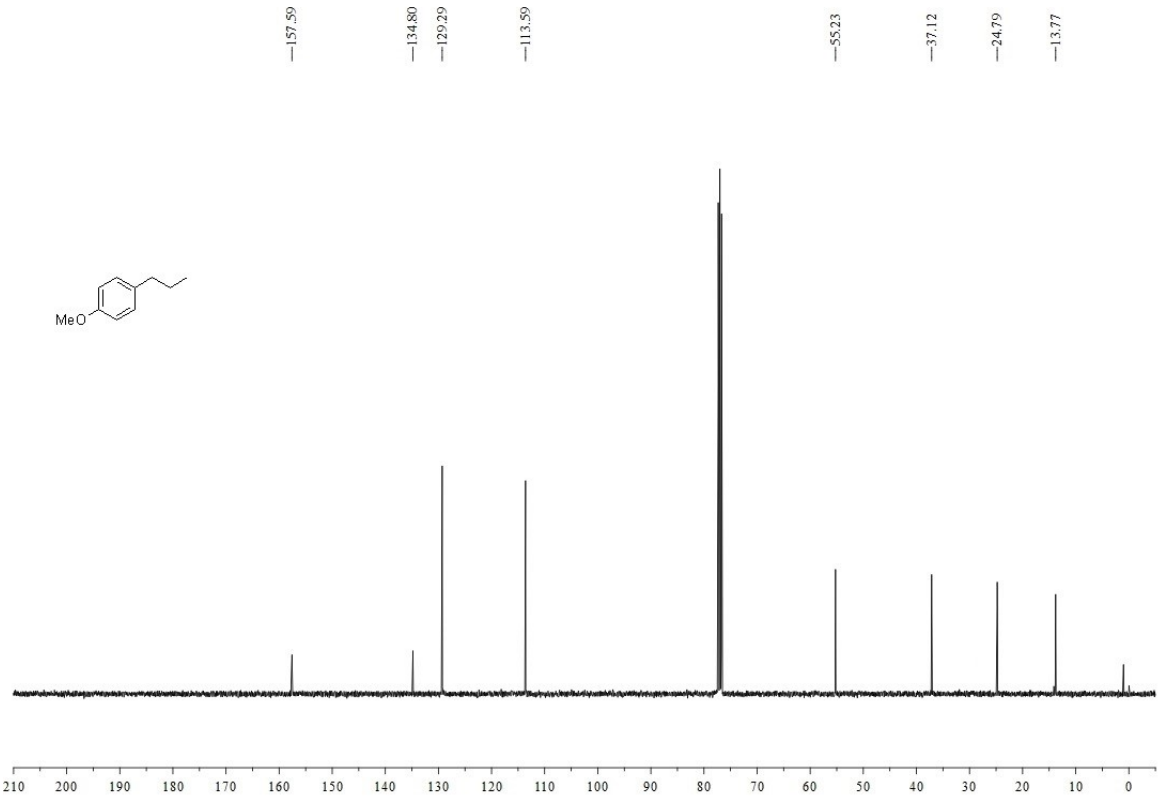

Figure S76. [13]C NMR spectrum for compound **5q**.

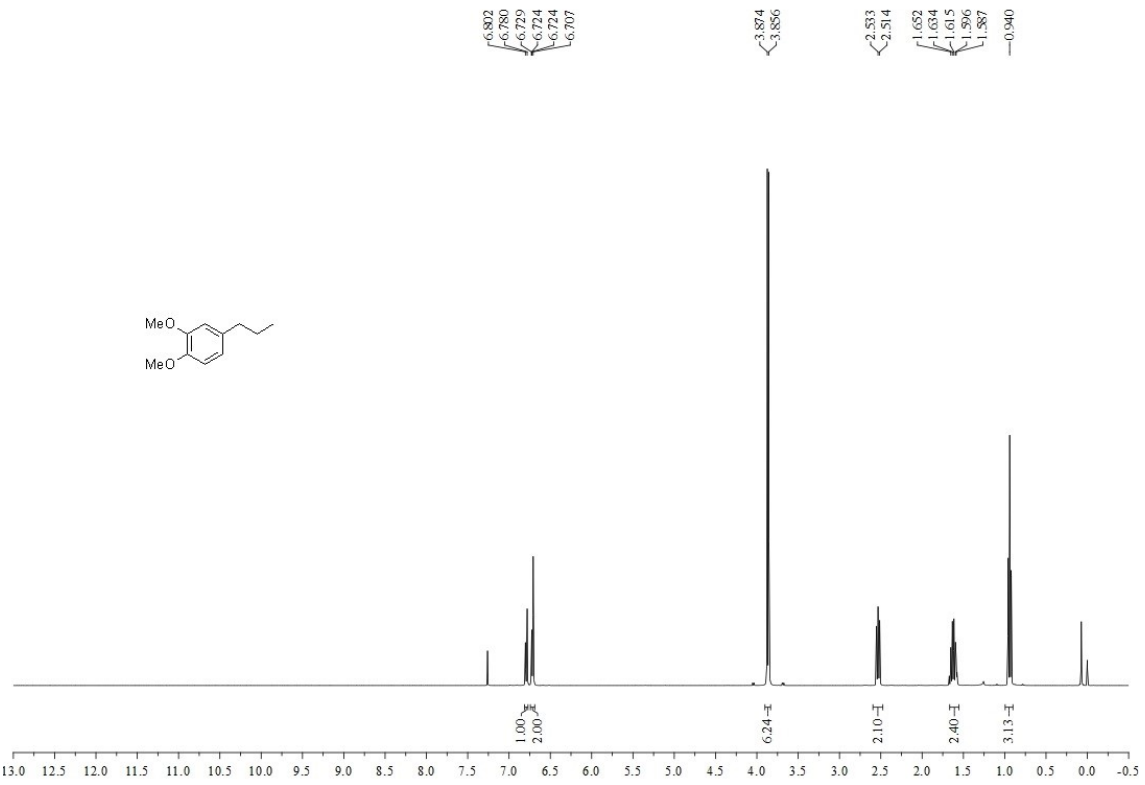

Figure S77. [1]H NMR spectrum for compound **5r**.

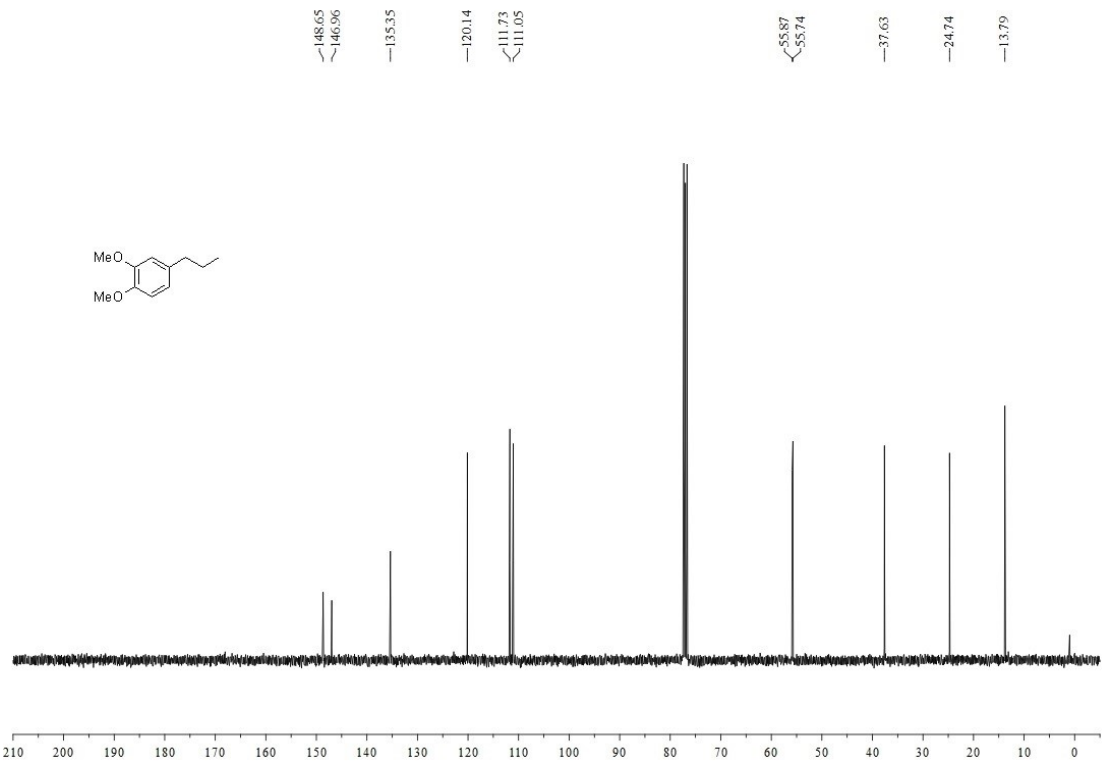

Figure S78. [13]C NMR spectrum for compound **5r**.

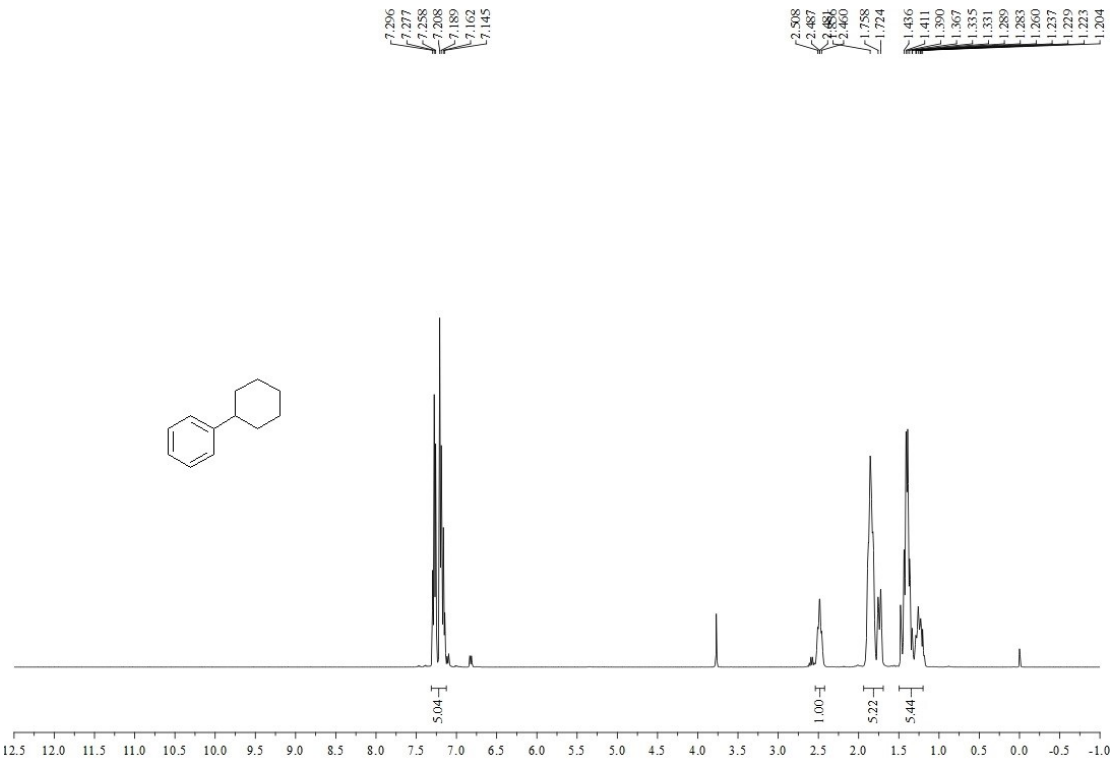

Figure S79. [1]H NMR spectrum for compound **5s**.

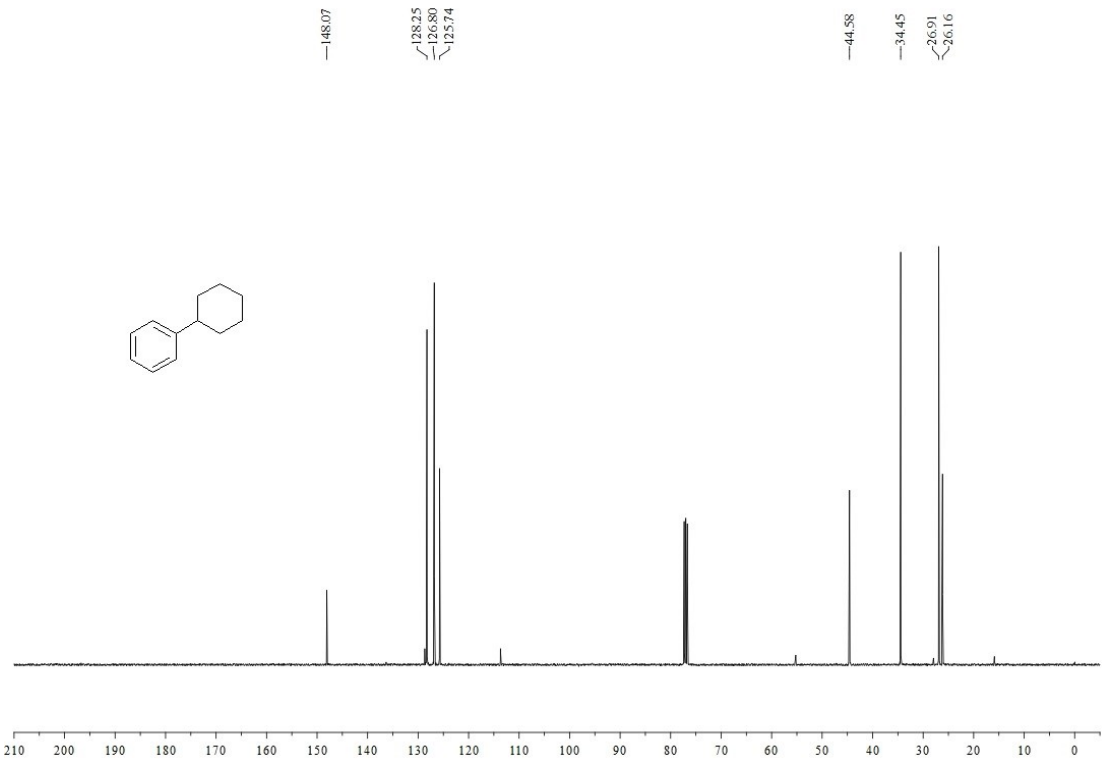

Figure S80. [13]C NMR spectrum for compound **5s.**

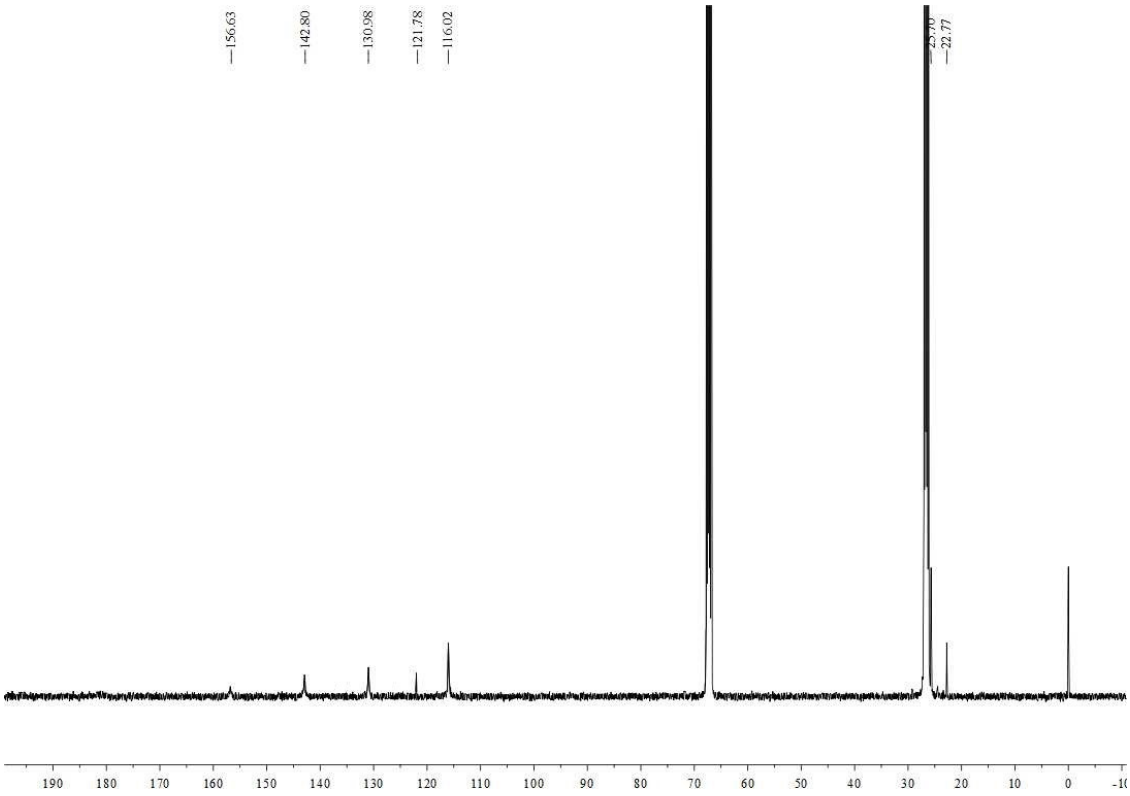

Figure S81. ^{13}C NMR spectrum for complex diketimine-Co.

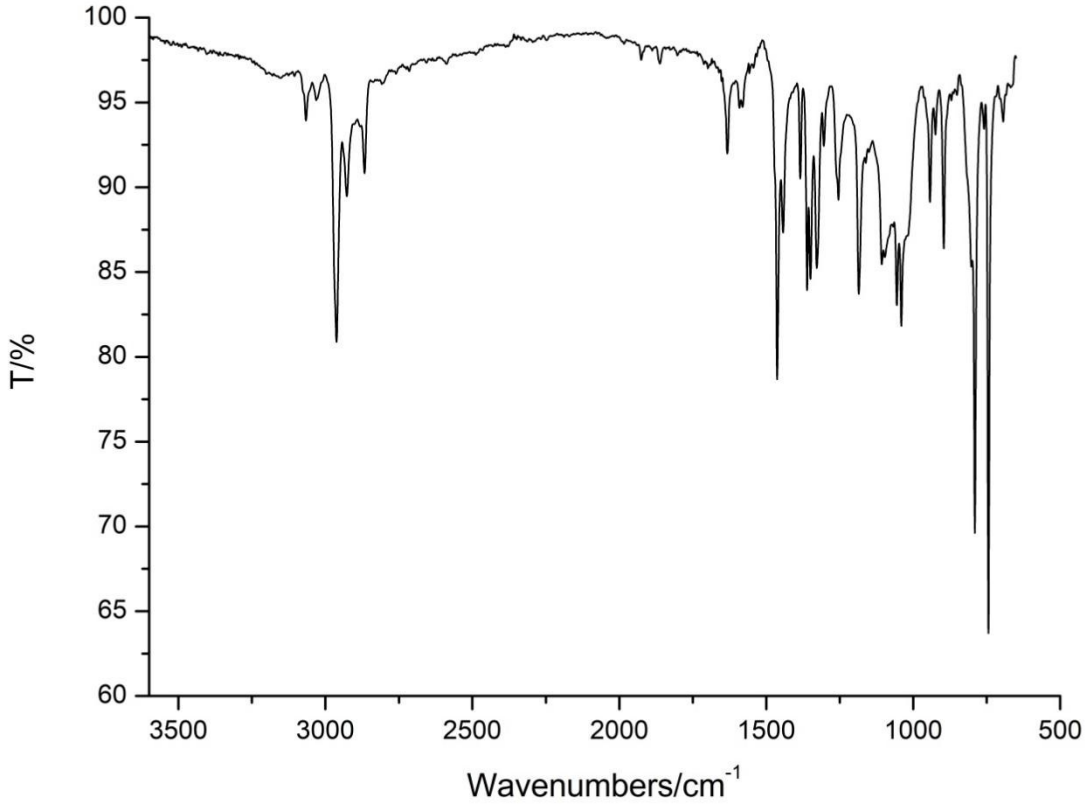

Figure S82. IR spectrum for complex diketimine-Co.

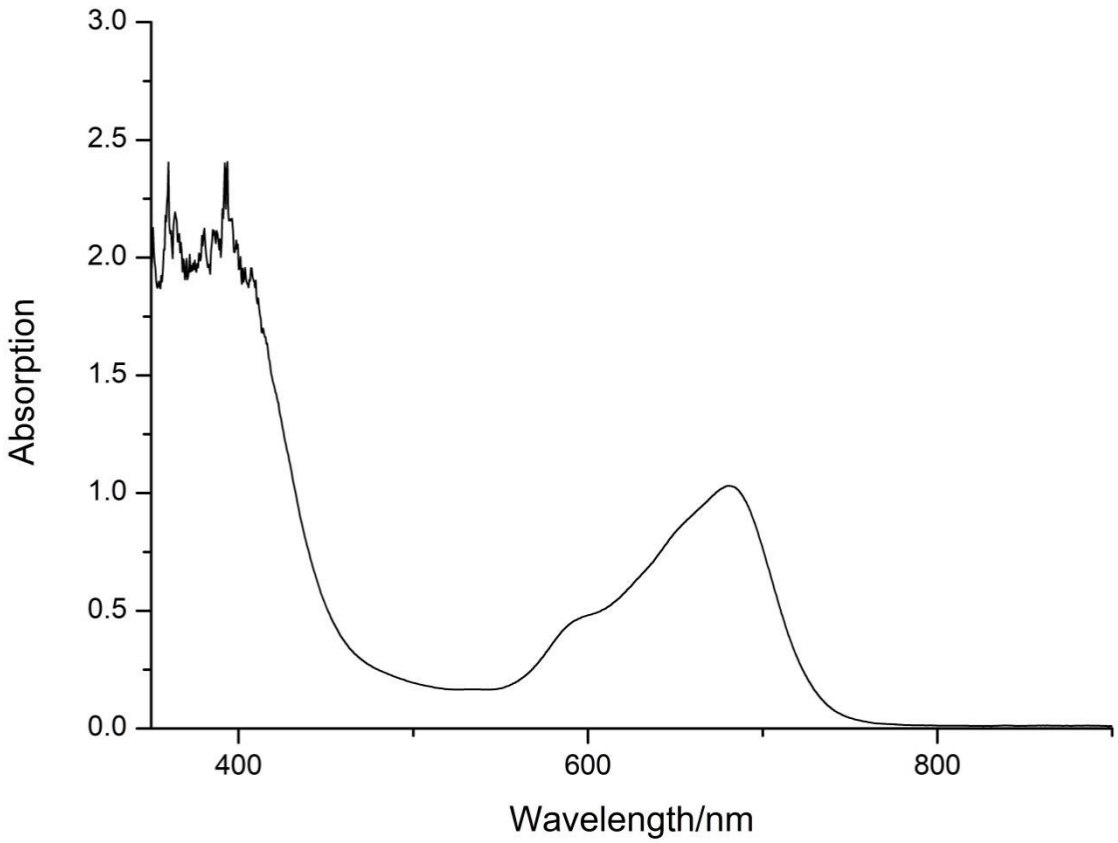

Figure S83. UV spectrum for complex diketimine-Co.