1. General information

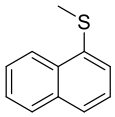
Unless otherwise noted, all reagents were purchased from commercial sources and used without further purification. All of the required non-commercially available Grignard reagents were prepared from the corresponding alkyl halide and magnesium according to standard procedures. The concentrations of the Grignard reagents prepared in the current study were determined by titration with 2-butanol in xylene using 1,10-phenanthroline as an indicator.[1] The reaction solvent, toluene was dried by refluxing over Na, and freshly distilled prior to use. All reactions were monitored by TLC and visualized by UV lamp (254 nm)/or by staining with a solution of 10 g phosphomolybdic acid and 100 mL EtOH followed by heating. Flash column chromatography was performed using 230-400 mesh silica gel. ^{1}H NMR (400 MHz) and ^{13}C NMR (150 MHz) spectra were obtained on Bruker AV-400 instrument. Chemical shifts for ^{1}H NMR spectra were reported in δ ppm referenced to an internal $SiMe_4$ standard. The abbreviations s, brs, d, t, q and m stand for the resonance multiplicity singlet, broad singlet, doublet, triplet, quartet and multiplet, respectively. HR-ESI-MS spectra were recorded on a Bruker Esquire LC mass spectrometer using electrospray ionization.

2. Preparation of substrates[2]

Under air, a sealed tube was charged with aryl iodine or aryl bromine (0.4 mmol), CuBr (10 %), ZnF_2 (0.8 mmol), and DMSO (2 mL). The reaction tube was kept stirring at 150 ºC for 36 h. After the completion of the reaction, as monitored by TLC, brine was added (10 mL), and the reaction mixture was extracted with ethyl acetate (3×5 mL). The ethyl acetate extracts were concentrated in vacuo, and the residue was purified by flash column chromatography on silica gel to give the corresponding products.

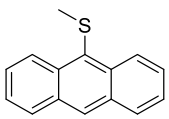
[1] Watson, S. C.; Eastham, J. F. J. Organomet. Chem. 1967, 9, 165.
[2] Chem. Commun., 2011, 47, 5304–5306.

Methyl(naphthalen-1-yl)sulfane (2)



Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.44 (q, *J* = 7.3 Hz, 2H), 2.60 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.9, 133.7, 131.7, 128.6, 126.3, 126.2, 125.9, 125.8, 124.3, 123.6, 16.3; HRMS (ES^+) exact mass calculated for ($C_{11}H_{11}S$) $[M+H]^+$ requires ***m/z*** 175.0576, found ***m/z*** 175.0573.

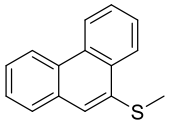
Anthracen-9-yl(methyl)sulfane (3)



Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, *J* = 8.9 Hz, 2H), 8.47 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.82 – 7.42 (m, 4H), 2.43 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.1, 132.0, 131.1, 129.1, 129.0, 127.0, 126.8, 125.4, 20.2; HRMS (ES^+) exact mass calculated for ($C_{15}H_{13}S$) $[M+H]^+$ requires ***m/z***

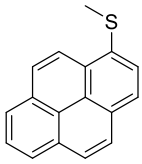
225.0732, found ***m/z*** 225.0738.

Methyl(phenanthren-9-yl)sulfane (4)



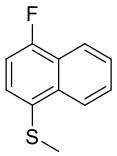
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 9.0 Hz, 1H), 8.63 (d, *J* = 9.0 Hz, 1H), 8.38 (d, *J* = 7.1 Hz, 1H), 7.92 – 7.78 (m, 1H), 7.72 – 7.66 (m, 2H), 7.59 (t, *J* = 3.6 Hz, 3H), 2.66 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.5, 132.1, 130.5, 130.4, 129.0, 127.7, 127.1, 127.1, 126.9, 126.2, 124.9, 123.3, 123.2, 122.7, 16.0; HRMS (ES^+) exact mass calculated for ($C_{15}H_{13}S$) $[M+H]^+$ requires ***m/z*** 225.0732, found ***m/z*** 225.0733.

Methyl(pyren-1-yl)sulfane (5)



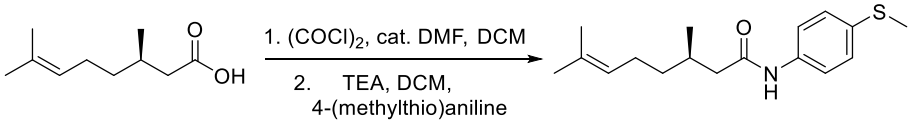
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 9.2 Hz, 1H), 8.36 – 7.77 (m, 8H), 2.70 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.2, 131.6, 131.1, 129.5, 129.4, 127.7, 127.4, 127.0, 126.2, 125.3, 125.2, 125.1, 125.1, 124.6, 123.8, 17.4; HRMS (ES^+) exact mass calculated for ($C_{17}H_{13}S$) $[M+H]^+$ requires ***m/z*** 249.0732, found ***m/z*** 249.0733.

(4-Fluoronaphthalen-1-yl)(methyl)sulfane (6)



Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.9 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 7.64 – 7.57 (m, 2H), 7.41 (dd, *J* = 8.0, 5.2 Hz, 1H), 7.11 (dd, *J* = 10.0, 8.3 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.9 (d, *J* = 251.4 Hz), 133.4 (d, *J* = 5.6 Hz), 130.8 (d, *J* = 5.2 Hz), 127.4, 126.6 (d, *J* = 2.7 Hz), 125.7 (d, *J* = 8.7 Hz), 124.9 (d, *J* = 3.9 Hz), 124.2 (d, *J* = 17.1 Hz), 121.3 (d, *J* = 6.1 Hz), 109.5 (d, *J* = 20.9 Hz), 17.6; HRMS (ES^+) exact mass calculated for ($C_{11}H_{10}FS$) $[M+H]^+$ requires ***m/z*** 193.0482, found ***m/z*** 193.0483.

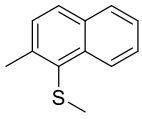
(*R*)-3,7-dimethyl-*N*-(4-(methylthio)phenyl)oct-6-enamide (11)



11

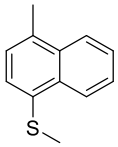
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.6 Hz, 3H), 7.21 (d, *J* = 8.6 Hz, 2H), 5.08 (t, *J* = 7.0 Hz, 1H), 2.45 (s, 3H), 2.40 – 2.27 (m, 1H), 2.21 – 1.89 (m, 4H), 1.67 (s, 3H), 1.59 (s, 3H), 1.49 – 1.34 (m, 1H), 1.31 – 1.14 (m, 1H), 0.98 (d, *J* = 6.3 Hz, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 135.7, 133.5, 131.7, 128.1, 124.3, 120.7, 45.5, 37.0, 30.7, 25.8, 25.6, 19.7, 17.8, 16.8; HRMS (ES^+) exact mass calculated for ($C_{17}H_{26}NOS$) $[M+H]^+$ requires ***m/z*** 292.1730, found ***m/z*** 292.1733.

Methyl(2-methylnaphthalen-1-yl)sulfane (12)



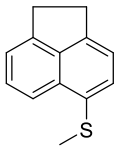
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 8.6 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 2.87 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.1, 135.1, 132.9, 131.9, 128.8, 128.7, 128.5, 126.9, 126.2, 125.2, 22.2, 19.1; HRMS (ES^+) exact mass calculated for ($C_{12}H_{13}S$) $[M+H]^+$ requires ***m/z*** 189.0732, found ***m/z*** 189.0735.

Methyl(4-methylnaphthalen-1-yl)sulfane (13)



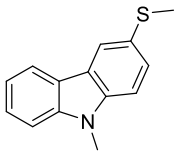
Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.19 (m, 1H), 8.15 – 7.93 (m, 1H), 7.58 – 7.55 (m, 2H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.30 – 7.24 (m, 1H), 2.68 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.5, 133.1, 132.6, 132.1, 126.6, 126.2, 126.0, 125.2, 124.9, 124.8, 19.5, 17.0; HRMS (ES^+) exact mass calculated for ($C_{12}H_{13}S$) $[M+H]^+$ requires ***m/z*** 189.0732, found ***m/z*** 189.0736.

(1,2-Dihydroacenaphthylen-5-yl)(methyl)sulfane (14)



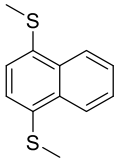
Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 7.1 Hz, 1H), 7.40 (d, *J* = 6.8 Hz, 1H), 7.31 (d, *J* = 7.1 Hz, 1H), 3.91 – 3.18 (m, 4H), 2.65 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 144.7, 139.5, 130.9, 130.0, 128.0, 127.5, 112.0, 119.8, 119.4, 30.7, 29.9, 17.2; HRMS (ES^+) exact mass calculated for ($C_{13}H_{13}S$) $[M+H]^+$ requires ***m/z*** 201.0732, found ***m/z*** 201.0736.

9-Methyl-3-(methylthio)-9H-carbazole (15)[3]



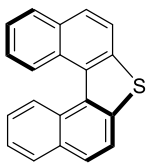
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.03 (m, 2H), 7.60 – 7.47 (m, 2H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.30 – 7.23 (m, 1H), 3.85 (s, 3H), 2.60 (s, 3H).

1,4-Bis(methylthio)naphthalene (16)



Light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.31 (m, 2H), 7.61 – 7.56 (m, 2H), 7.38 (s, 2H), 2.55 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.9, 132.2, 126.7, 125.3, 124.7, 16.9; HRMS (ES^+) exact mass calculated for ($C_{12}H_{13}S_2$) $[M+H]^+$ requires ***m/z*** 221.0453, found ***m/z*** 221.0459.

Dinaphtho[2,1-b:1',2'-d]thiophene (17)[4]



Yellow solid; HRMS (ES^+) exact mass calculated for ($C_{20}H_{13}S$) $[M+H]^+$ requires ***m/z*** 285.0732, found ***m/z*** 285.0730.

[3] Org. Lett., **2012**, *14*, 796–799.
[4] J. Am. Chem. Soc., **2012**, *134*, 20302–20305.

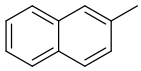
3. General procedure for the Ni-Catalyzed alkylation of arylsulfides

Typical procedure

(a) An oven-dried, argon-flushed Schlenk tube was charged with the arylsulfides (if solid; 0.2 mmol) and $NiCl_2(PPh_3)(IPr)$ (1% mmol). The tube was immediately sealed and again flushed with argon. Subsequently, freshly distilled toluene (1.5 mL), the arylsulfides (if liquid) and a MeMgBr solution in diethyl ether (3.0 M) were added and the mixture was stirred for 8 h at the room temperature. Upon purification via column chromatography the pure product was obtained after solvent removal.

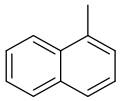
(b) An oven-dried, argon-flushed Schlenk tube was charged with the 2-(methylthio)naphthalene (0.2 mmol), dcype (5% mmol) and $Ni(cod)_2$ (5% mmol). The tube was immediately sealed and again flushed with argon. Subsequently, freshly distilled toluene (1.5 mL) and Grignard reagents were added and the mixture was stirred for 10 h at 90 °C. Upon purification via column chromatography the pure product was obtained after solvent removal.

2-methylnaphthalene (1a)



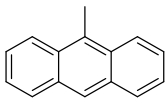
White solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.74 (m, 3H), 7.64 (s, 1H), 7.45 (pd, *J* = 6.9, 1.4 Hz, 2H), 7.35 (dd, *J* = 8.4, 1.5 Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.6, 133.8, 131.8, 128.2, 127.8, 127.7, 127.4, 126.9, 126.0, 125.1, 21.9; HRMS (ES^+) exact mass calculated for ($C_{11}H_{11}$) $[M+H]^+$ requires ***m/z*** 143.0855, found ***m/z*** 143.0857.

1-methylnaphthalene (2a)



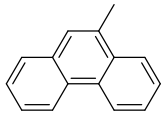
Colorless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.62 – 7.49 (m, 2H), 7.47 – 7.33 (m, 2H), 2.74 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.4, 133.7, 132.7, 128.6, 126.7, 126.5, 125.8, 125.7, 125.7, 124.2, 19.5; HRMS (ES^+) exact mass calculated for ($C_{11}H_{11}$) $[M+H]^+$ requires ***m/z*** 143.0855, found ***m/z*** 143.0857.

9-methylanthracene (3a)



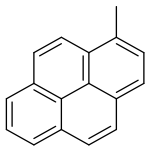
Yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.50 – 8.26 (m, 3H), 8.04 (d, *J* = 7.8 Hz, 2H), 7.70 – 7.38 (m, 4H), 3.13 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 131.6, 130.2, 130.2, 129.2, 125.4, 125.3, 124.9, 124.8, 14.1; HRMS (ES^+) exact mass calculated for ($C_{15}H_{13}$) $[M+H]^+$ requires ***m/z*** 193.1012, found ***m/z*** 193.1015.

9-methylphenanthrene (4a)



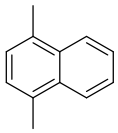
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 – 8.74 (m, 1H), 8.74 – 8.66 (m, 1H), 8.17 – 8.06 (m, 1H), 7.92 – 7.82 (m, 1H), 7.77 – 7.54 (m, 5H), 2.78 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.6, 132.2, 132.1, 130.5, 129.8, 127.9, 126.9, 126.7, 126.6, 126.3, 125.9, 124.8, 123.1, 122.6, 20.2; HRMS (ES^+) exact mass calculated for ($C_{15}H_{13}$) $[M+H]^+$ requires ***m/z*** 193.1012, found ***m/z*** 193.1011.

1-methylpyrene (5a)



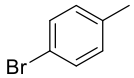
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 9.2 Hz, 1H), 8.20 – 8.18 (m, 2H), 8.13 – 8.09 (m, 2H), 8.06 – 7.98 (m, 3H), 7.88 (d, *J* = 7.5 Hz, 1H), 3.00 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.3, 131.5, 131.1, 129.8, 129.3, 127.9, 127.6, 127.2, 126.5, 125.9, 124.9, 124.9, 124.8, 124.7, 123.8, 19.9; HRMS (ES^+) exact mass calculated for ($C_{17}H_{13}$) $[M+H]^+$ requires ***m/z*** 217.1012, found ***m/z*** 217.1016.

1,4-dimethylnaphthalene (6a)



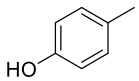
Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.0 – 8.06 (m, 2H), 7.61 – 7.58 (m, 2H), 7.27 (s, 2H), 2.73 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.8, 132.4, 126.4, 125.5, 124.8, 19.5; HRMS (ES^+) exact mass calculated for ($C_{12}H_{13}$) $[M+H]^+$ requires ***m/z*** 157.1012, found ***m/z*** 157.1019.

1-bromo-4-methylbenzene (7a)



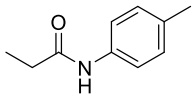
Colorless liquid;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.3 Hz, 2H), 7.04 (d, *J* = 8.1 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 131.4, 130.9, 119.2, 21.1; HRMS (ES^+) exact mass calculated for (C_7H_8Br) $[M+H]^+$ requires ***m/z*** 170.9804, found ***m/z*** 170.9801.

***p*-cresol (8a)**



White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.3 Hz, 1H), 6.75 (d, *J* = 8.5 Hz, 1H), 4.92 (s, 0H), 2.29 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.26, 130.21, 130.16, 115.24, 20.58; HRMS (ES^+) exact mass calculated for (C_7H_9O) $[M+H]^+$ requires ***m/z*** 109.0648, found ***m/z*** 109.0638.

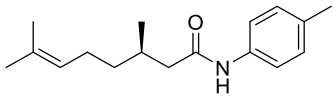
***N*-(*p*-tolyl)propionamide (10a)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 3H), 2.38 (q, *J* = 7.6 Hz, 2H), 2.31 (s, 3H), 1.24 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 135.5, 133.9, 129.6,

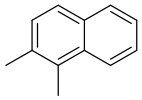
112.0, 30.9, 21.0, 9.9; HRMS (ES^+) exact mass calculated for ($C_{10}H_{14}NO$) $[M+H]^+$ requires ***m/z*** 164.1070, found ***m/z*** 164.1077.

(*R*)-3,7-dimethyl-*N*-(*p*-tolyl)oct-6-enamide (11a)



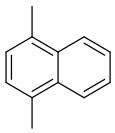
^1H NMR (400 MHz, $CDCl_3$ δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.32 (s, 1H), 7.10 (d, *J* = 8.1 Hz, 2H), 5.09 (t, *J* = 7.0 Hz, 1H), 2.41 – 2.24 (m, 4H), 2.17 – 1.87 (m, 4H), 1.68 (s, 3H), 1.60 (s, 3H), 1.48 – 1.35 (m, 1H), 1.29 – 1.20 (m, 1H), 0.99 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 135.5, 133.9, 131.7, 129.5, 124.4, 120.1, 45.6, 37.0, 30.7, 25.8, 25.6, 21.0, 19.7, 17.8; HRMS (ES^+) exact mass calculated for ($C_{17}H_{26}NO$) $[M+H]^+$ requires ***m/z*** 260.2009, found ***m/z*** 260.2007.

1,2-dimethylnaphthalene (12a)



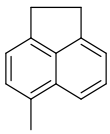
Colorless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.51 (m, 1H), 7.48 (t, *J* = 7.0 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 2.66 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.2, 132.9, 132.4, 131.3, 129.1, 128.5, 125.8, 125.8, 124.6, 123.8, 20.9, 14.6; HRMS (ES^+) exact mass calculated for ($C_{12}H_{13}$) $[M+H]^+$ requires ***m/z*** 157.1012, found ***m/z*** 157.1010.

1,4-dimethylnaphthalene (13a)



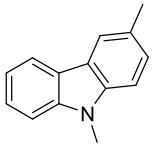
Colorless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.07 (m, 2H), 7.62 – 7.58 (m, 2H), 7.28 (s, 2H), 2.74 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.8, 132.4, 126.4, 125.5, 124.8, 19.5; HRMS (ES^+) exact mass calculated for ($C_{12}H_{13}$) $[M+H]^+$ requires ***m/z*** 157.1012, found ***m/z*** 157.1019.

5-methyl-1,2-dihydroacenaphthylene (14a)



White solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 1H), 7.57 – 7.49 (m, 1H), 7.35 – 7.30 (m, 2H), 7.23 (d, *J* = 6.9 Hz, 1H), 3.73 – 3.27 (m, 4H), 2.68 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.4, 143.9, 139.4, 131.1, 129.9, 127.9, 127.5, 119.6, 119.2, 119.1, 30.7, 29.9, 18.1; HRMS (ES^+) exact mass calculated for ($C_{13}H_{13}$) $[M+H]^+$ requires ***m/z*** 169.1012, found ***m/z*** 169.1010.

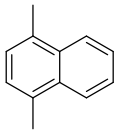
3,9-dimethyl-9*H*-carbazole (15a)



White solid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.7 Hz, 1H), 7.97 (s, 1H), 7.53 (t, *J* = 7.7

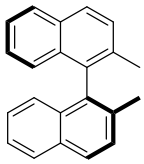
Hz, 1H), 7.45 – 7.22 (m, 4H), 3.84 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.3, 139.4, 128.1, 127.1, 125.5, 122.9, 122.7, 120.4, 120.3, 118.6, 108.4, 108.2, 29.1, 21.5; HRMS (ES^+) exact mass calculated for ($C_{14}H_{14}N$) $[M+H]^+$ requires ***m/z*** 196.1121, found ***m/z*** 196.1125.

1,4-dimethylnaphthalene (16a)



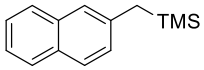
Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.06 (m, 2H), 7.62 – 7.58 (m, 2H), 7.28 (s, 2H), 2.74 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.79, 132.43, 126.38, 125.47, 124.79, 19.5; HRMS (ES^+) exact mass calculated for ($C_{12}H_{13}$) $[M+H]^+$ requires ***m/z*** 157.1012, found ***m/z*** 157.1013.

(*S*)-2,2'-dimethyl-1,1'-binaphthalene (17a)



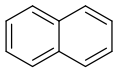
Light yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (t, *J* = 7.9 Hz, 4H), 7.51 (d, *J* = 7.7 Hz, 2H), 7.41 – 7.38 (m, 2H), 7.25 – 7.20 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 2.04 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.2, 134.4, 132.9, 132.3, 128.8, 128.1, 127.6, 126.2, 125.8, 125.0, 20.2; HRMS (ES^+) exact mass calculated for ($C_{22}H_{19}$) $[M+H]^+$ requires ***m/z*** 283.1481, found ***m/z*** 283.1487.

trimethyl(naphthalen-2-ylmethyl)silane (1b)



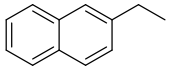
White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 1H), 7.70 – 7.67 (m, 2H), 7.43 – 7.36 (m, 2H), 7.34 – 7.32 (m, 1H), 7.14 – 7.13 (m, 1H), 2.22 (s, 2H), -0.00 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.4, 134.0, 131.1, 128.0, 127.7, 127.6, 127.1, 125.9, 125.3, 124.4, 27.5, -1.7; HRMS (ES^+) exact mass calculated for ($C_{14}H_{19}Si$) $[M+H]^+$ requires ***m/z*** 215.1251, found ***m/z*** 215.1253.

naphthalene (1c)



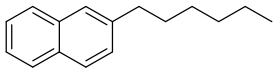
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 6.2, 3.3 Hz, 4H), 7.53 (dd, *J* = 6.3, 3.2 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.6, 128.0, 125.9; HRMS (ES^+) exact mass calculated for ($C_{10}H_9$) $[M+H]^+$ requires ***m/z*** 129.0699, found ***m/z*** 129.0698.

2-ethylnaphthalene (1d)



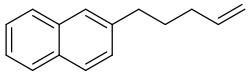
Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.77 (m, 3H), 7.67 (s, 1H), 7.54 – 7.34 (m, 3H), 2.86 (q, *J* = 7.6 Hz, 2H), 1.38 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 133.9, 132.1, 127.9, 127.7, 127.5, 127.2, 126.0, 125.7, 125.1, 29.2, 15.7; HRMS (ES^+) exact mass calculated for ($C_{12}H_{13}$) $[M+H]^+$ requires ***m/z*** 157.1012, found ***m/z*** 157.1013.

2-hexylnaphthalene (1e)



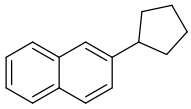
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.73 (m, 3H), 7.61 (s, 1H), 7.47 – 7.39 (m, 2H), 7.35 – 7.33 (m, 1H), 2.88 – 2.65 (m, 2H), 1.71 (p, *J* = 7.5 Hz, 2H), 1.46 – 1.24 (m, 6H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 133.8, 132.1, 127.8, 127.7, 127.6, 127.5, 126.4, 125.9, 125.1, 36.3, 31.9, 31.5, 29.2, 22.8, 14.3; HRMS (ES^+) exact mass calculated for ($C_{16}H_{21}$) $[M+H]^+$ requires ***m/z*** 213.1638, found ***m/z*** 213.1634.

2-(pent-4-en-1-yl)naphthalene (1f)



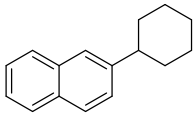
Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.71 (m, 3H), 7.63 (s, 1H), 7.52 – 7.29 (m, 3H), 5.93 – 5.83 (m, 1H), 5.19 – 4.65 (m, 2H), 2.81 (t, *J* = 7.6 Hz, 2H), 2.16 (q, *J* = 7.0 Hz, 2H), 1.97 – 1.73 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 138.7, 133.8, 132.1, 127.9, 127.7, 127.5, 126.5, 126.0, 125.2, 114.9, 35.6, 33.5, 30.6; HRMS (ES^+) exact mass calculated for ($C_{15}H_{17}$) $[M+H]^+$ requires ***m/z*** 197.1325, found ***m/z*** 197.1329.

2-cyclopentylnaphthalene (1g)



White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (t, *J* = 7.8 Hz, 3H), 7.66 (s, 1H), 7.49 – 7.35 (m, 3H), 3.21 – 3.13 (m, 1H), 2.29 – 2.04 (m, 2H), 1.91 – 1.81 (d, *J* = 5.4 Hz, 2H), 1.79 – 1.59 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 133.7, 132.2, 127.9, 127.7, 127.6, 126.4, 125.9, 125.2, 124.9, 46.2, 34.7, 25.8; HRMS (ES^+) exact mass calculated for ($C_{15}H_{17}$) $[M+H]^+$ requires ***m/z*** 197.1325, found ***m/z*** 197.1335.

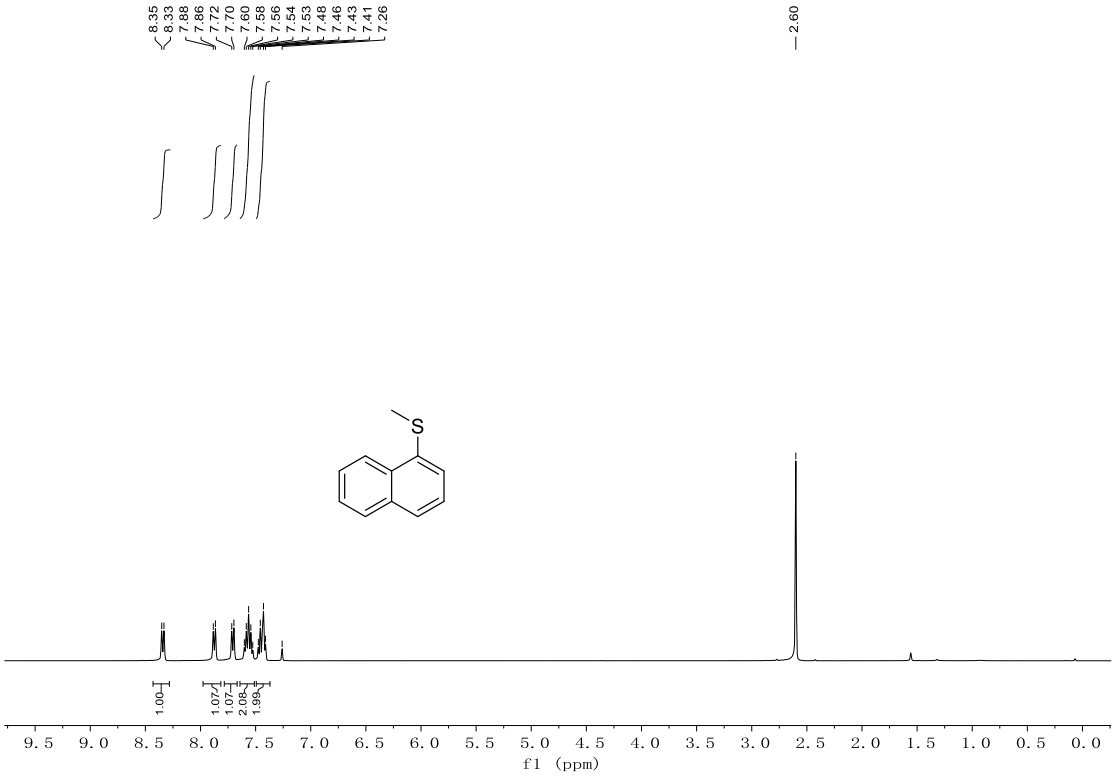
2-cyclohexylnaphthalene (1h)

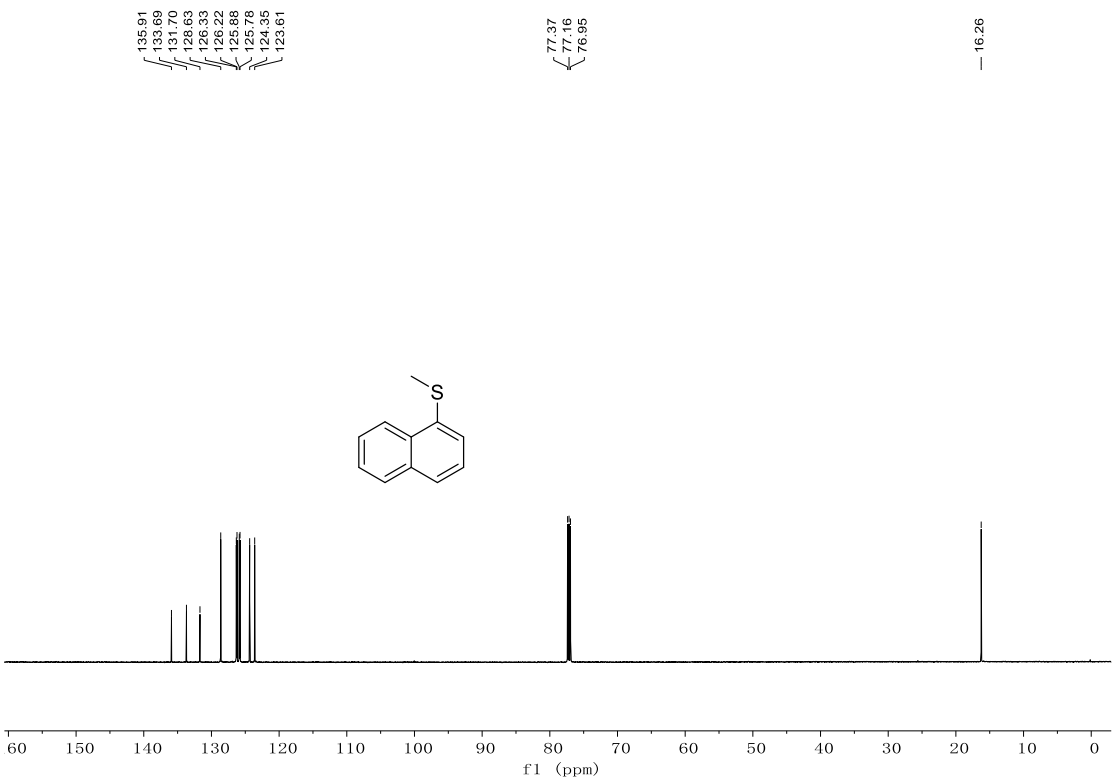


White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 7.74 (m, 3H), 7.66 (s, 1H), 7.4 – 7.39 (m, 3H), 2.69 (t, *J* = 11.5 Hz, 1H), 2.01 – 1.80 (m, 5H), 1.66 – 1.18 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 133.8, 132.3, 127.8, 127.7, 127.7, 126.3, 125.9, 125.1, 124.7, 44.8, 34.6, 27.1, 26.4; HRMS (ES^+) exact mass calculated for ($C_{16}H_{19}$) $[M+H]^+$ requires ***m/z*** 211.1481, found ***m/z*** 211.1484.

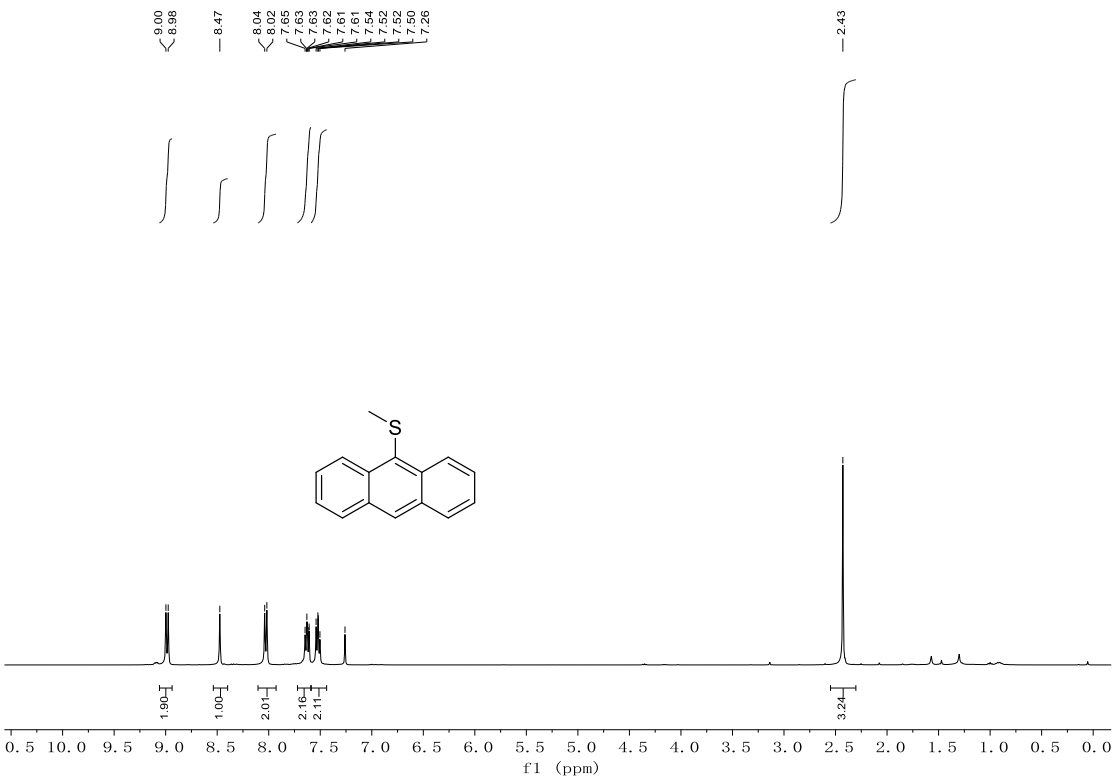
4. NMR Spectra for all the compounds

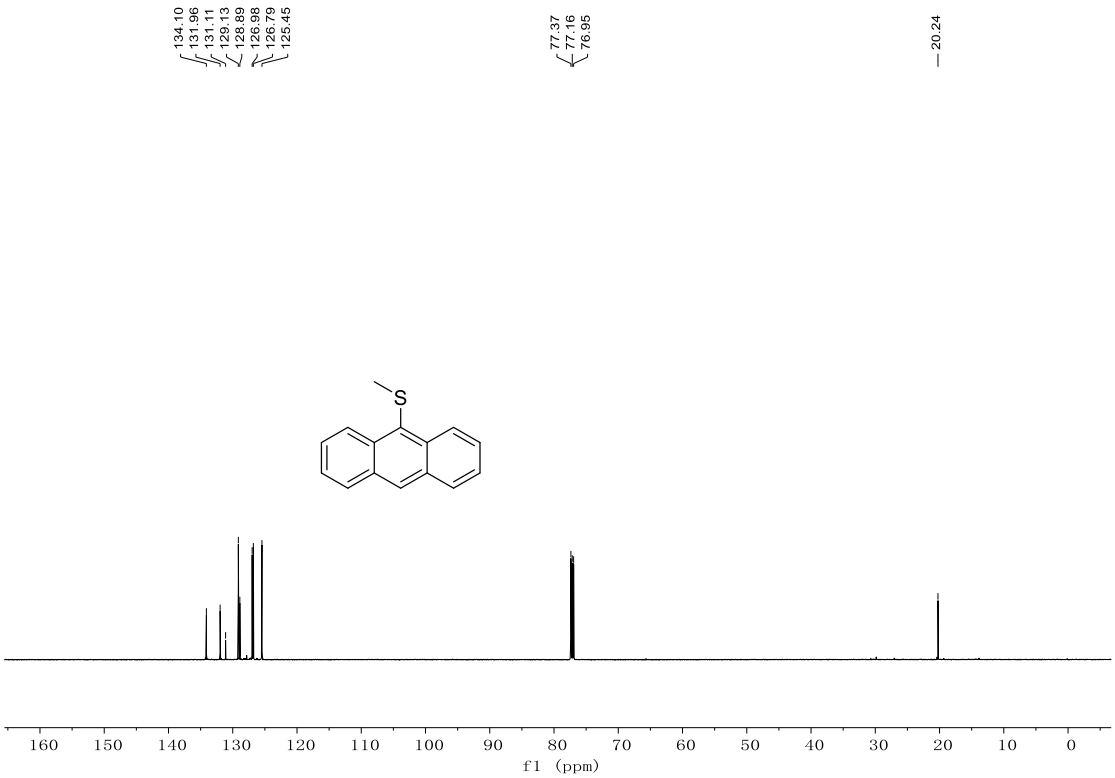
Methyl(naphthalen-1-yl)sulfane (2)



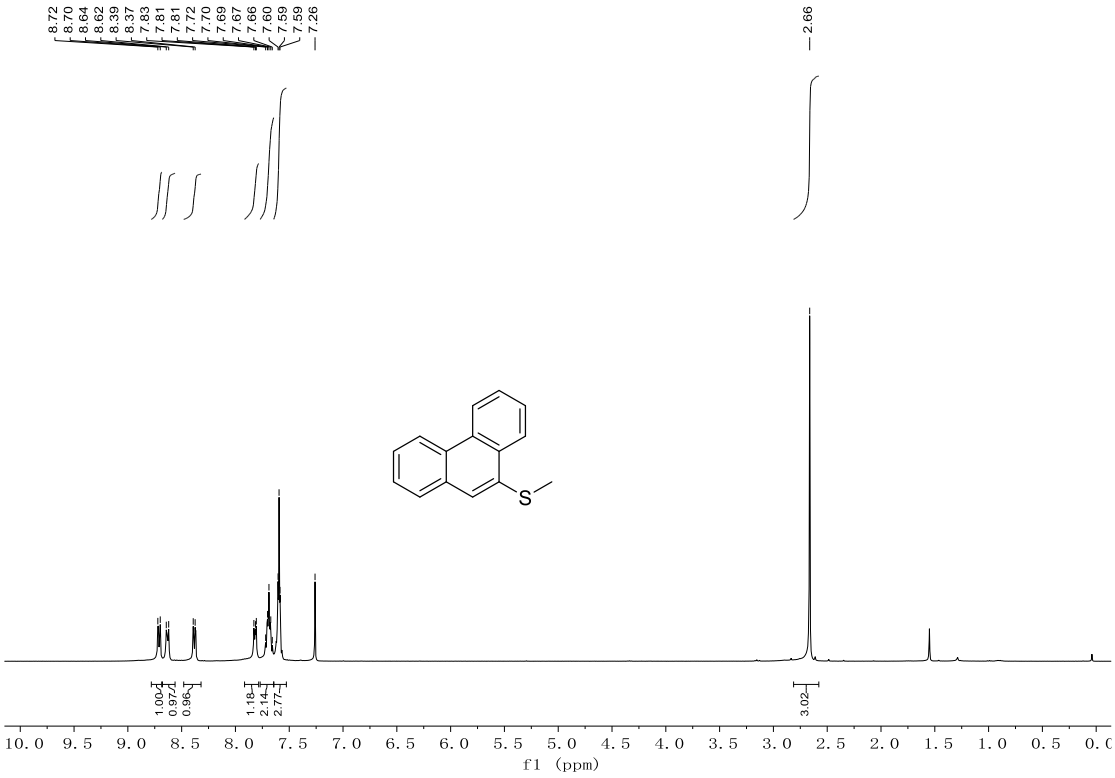


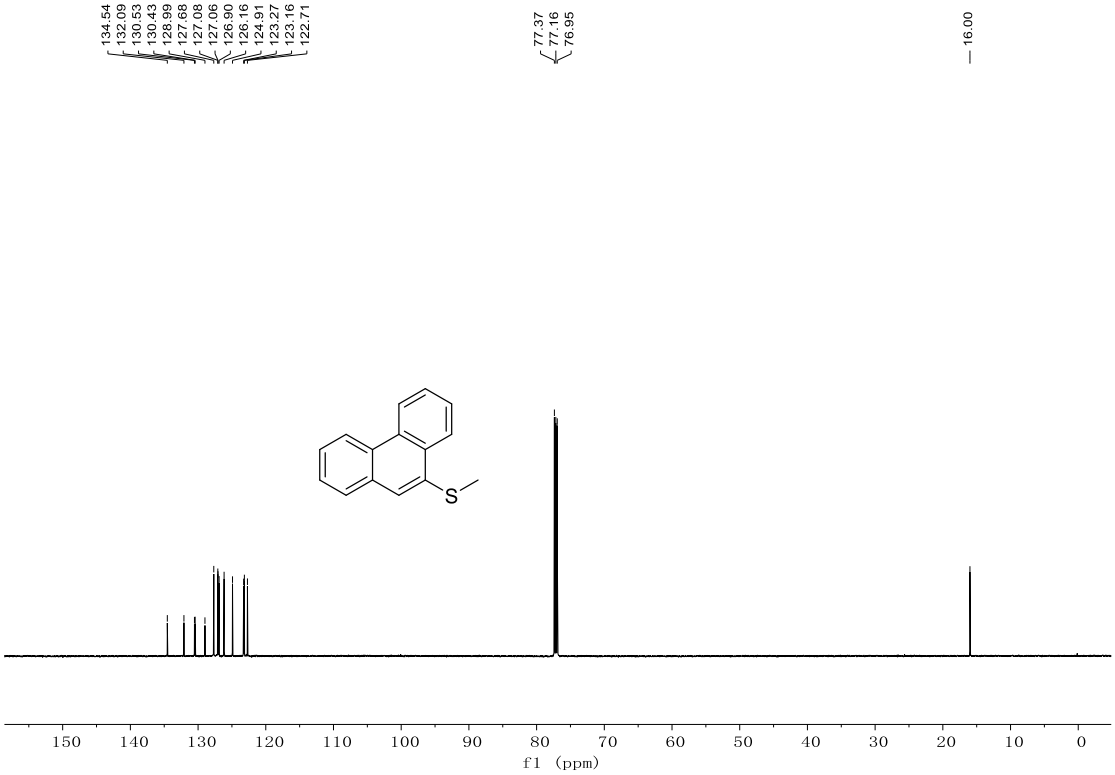
Anthracen-9-yl(methyl)sulfane (3)



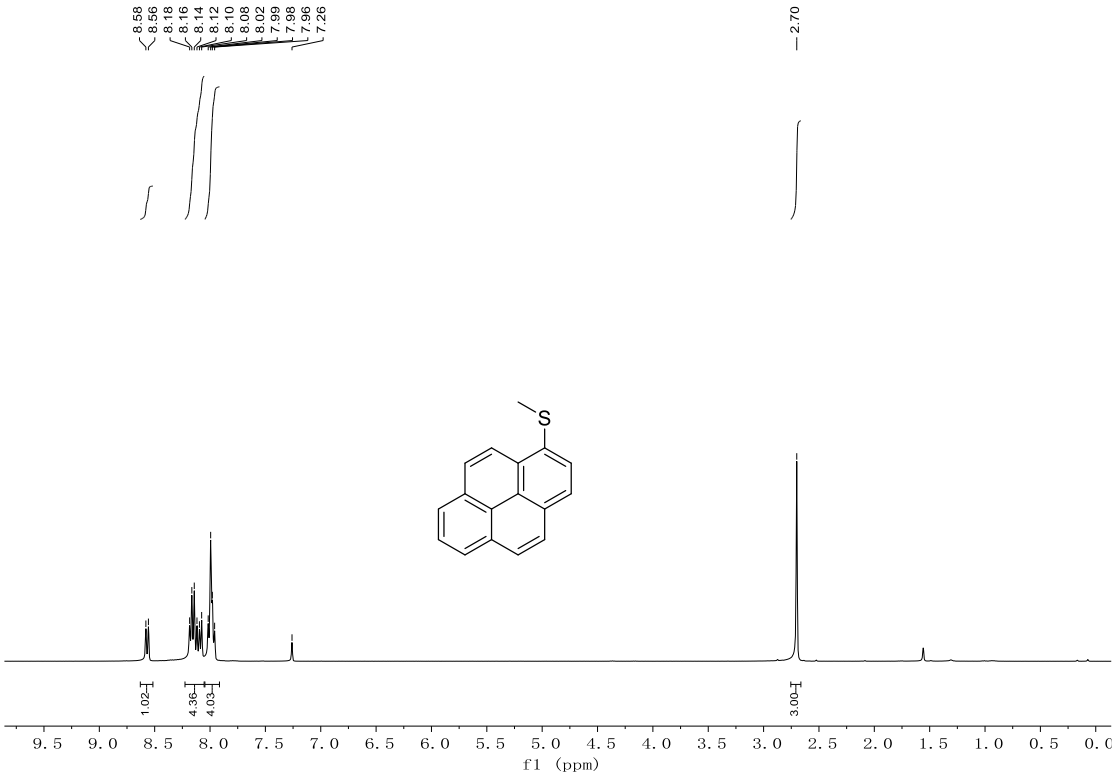


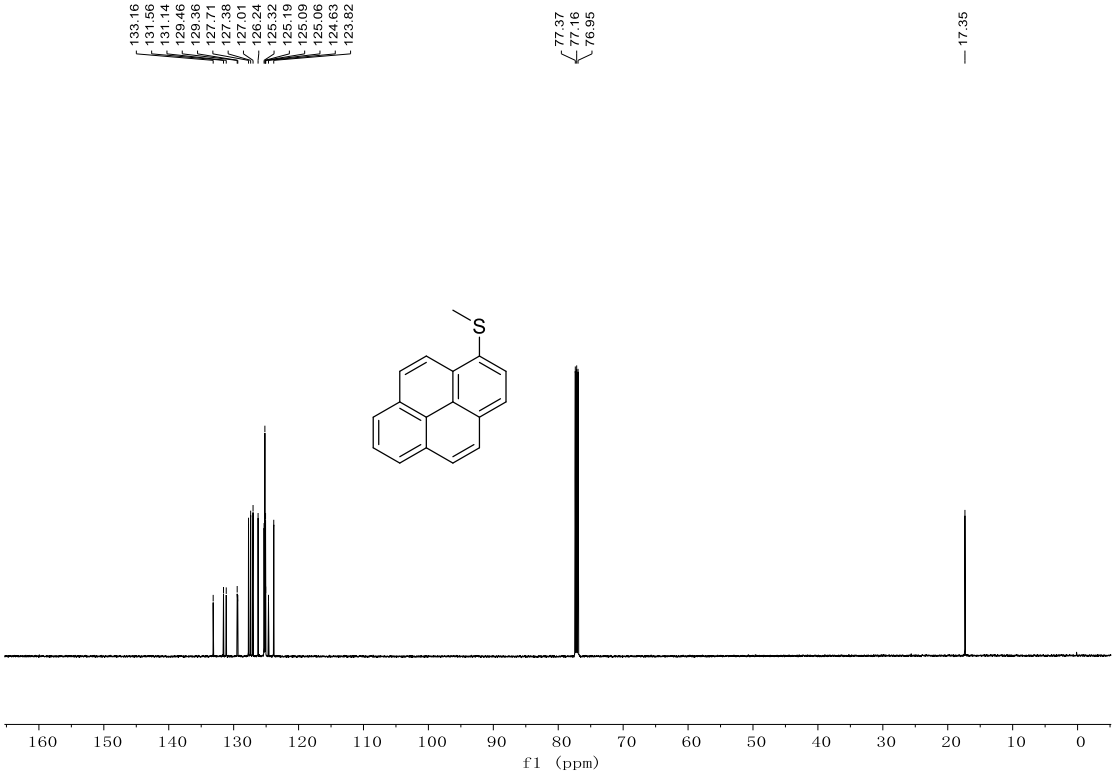
Methyl(phenanthren-9-yl)sulfane (4)



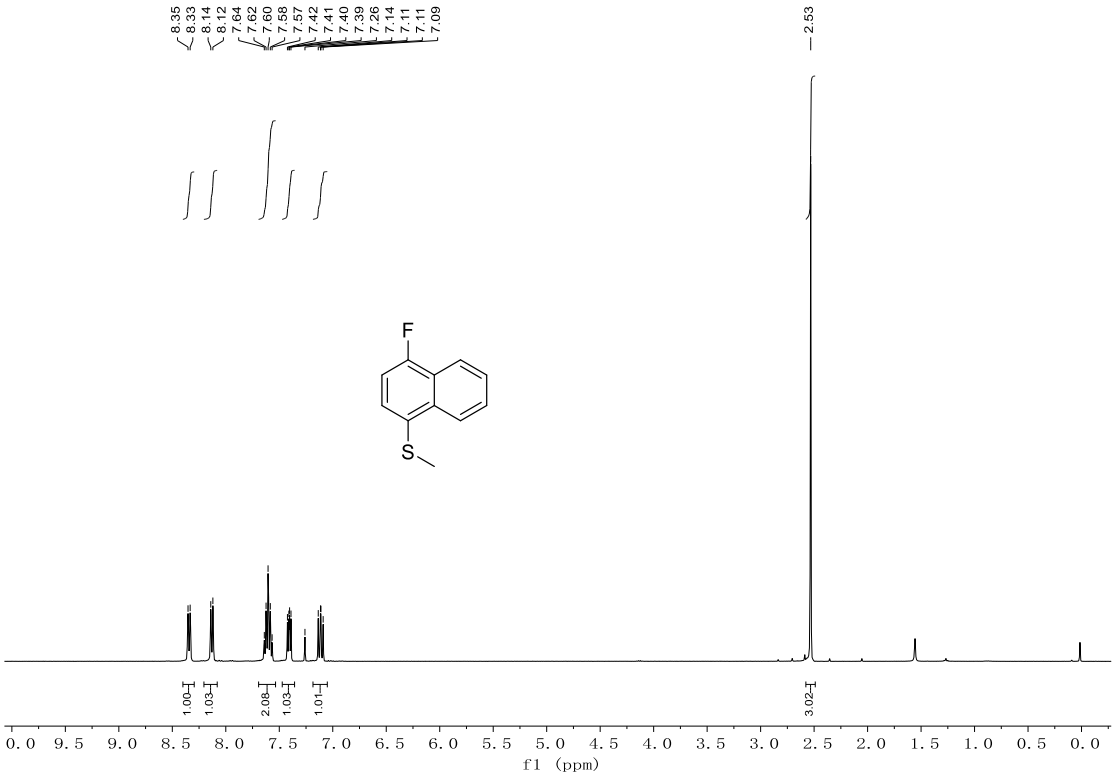


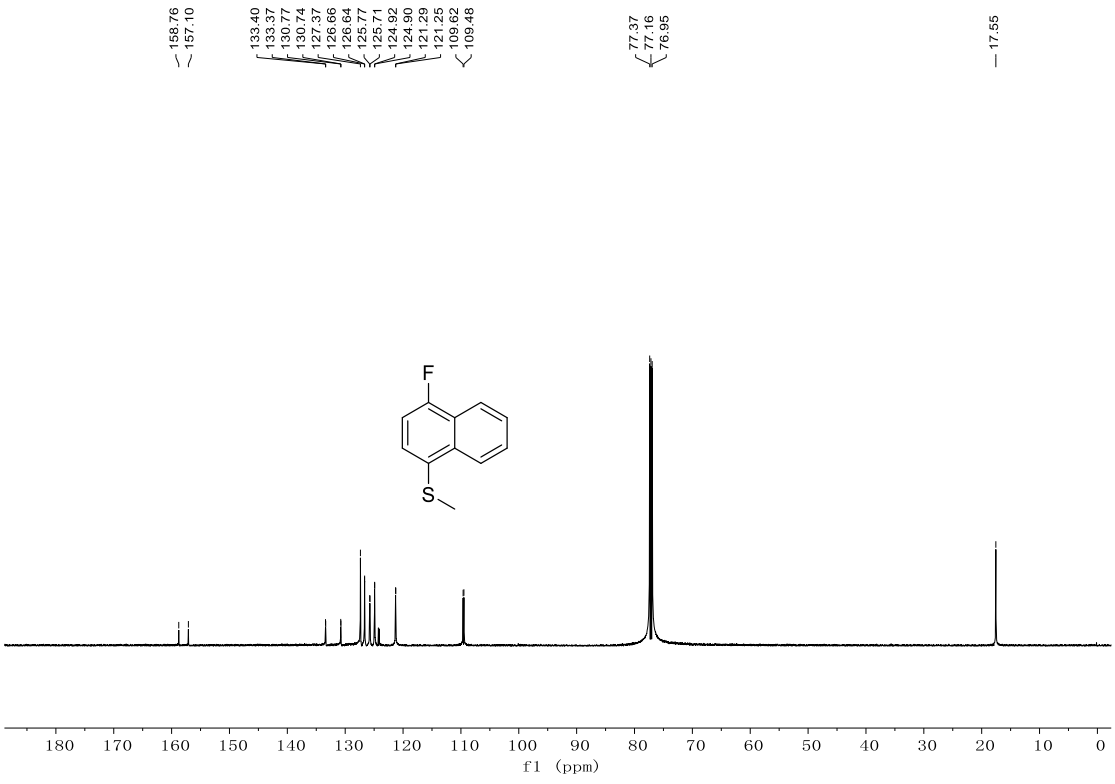
Methyl(pyren-1-yl)sulfane (5)



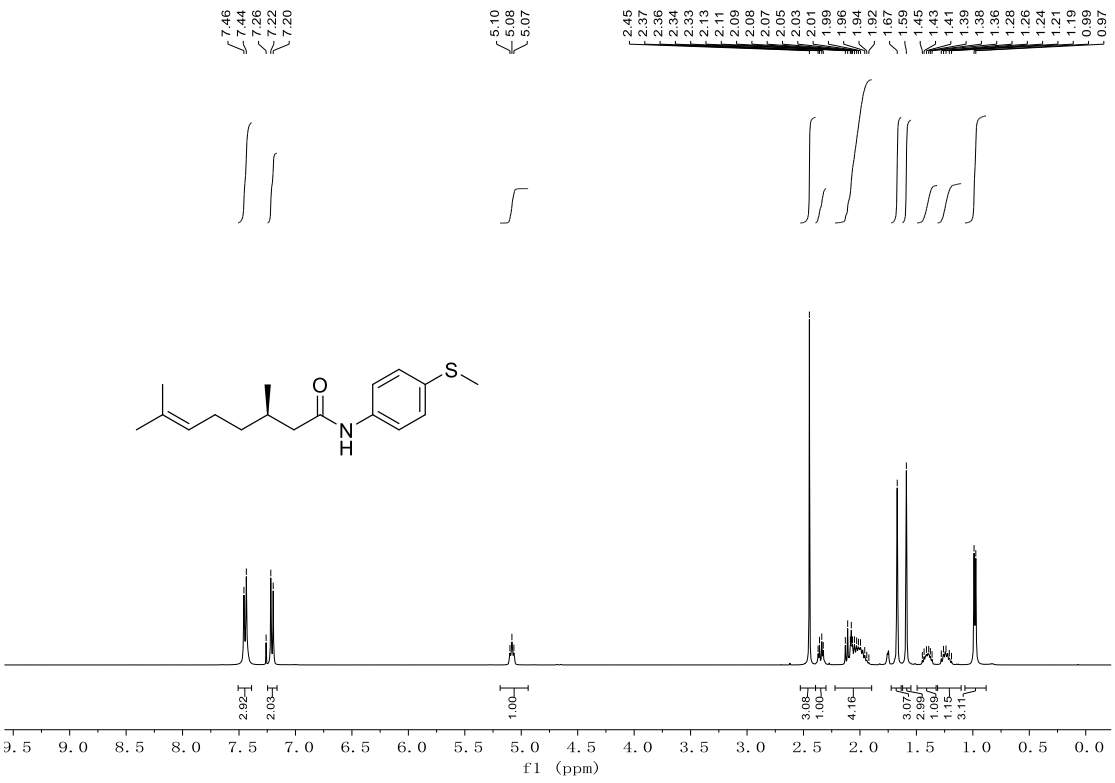


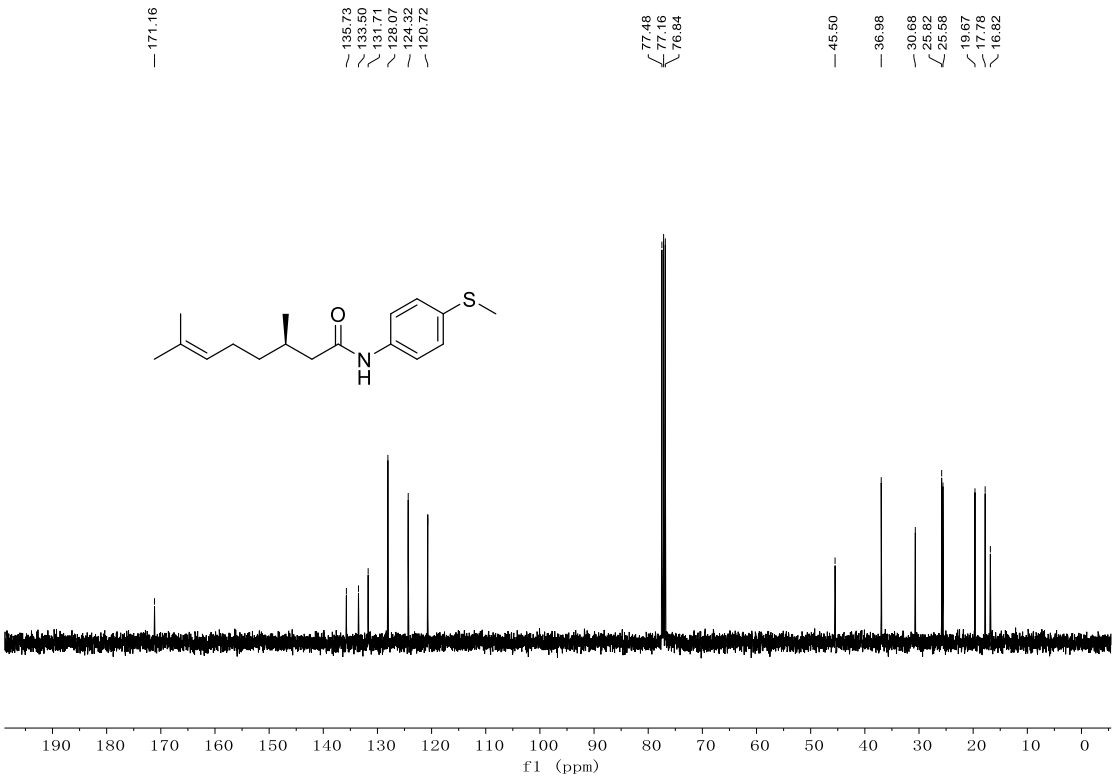
(4-Fluoronaphthalen-1-yl)(methyl)sulfane (6)



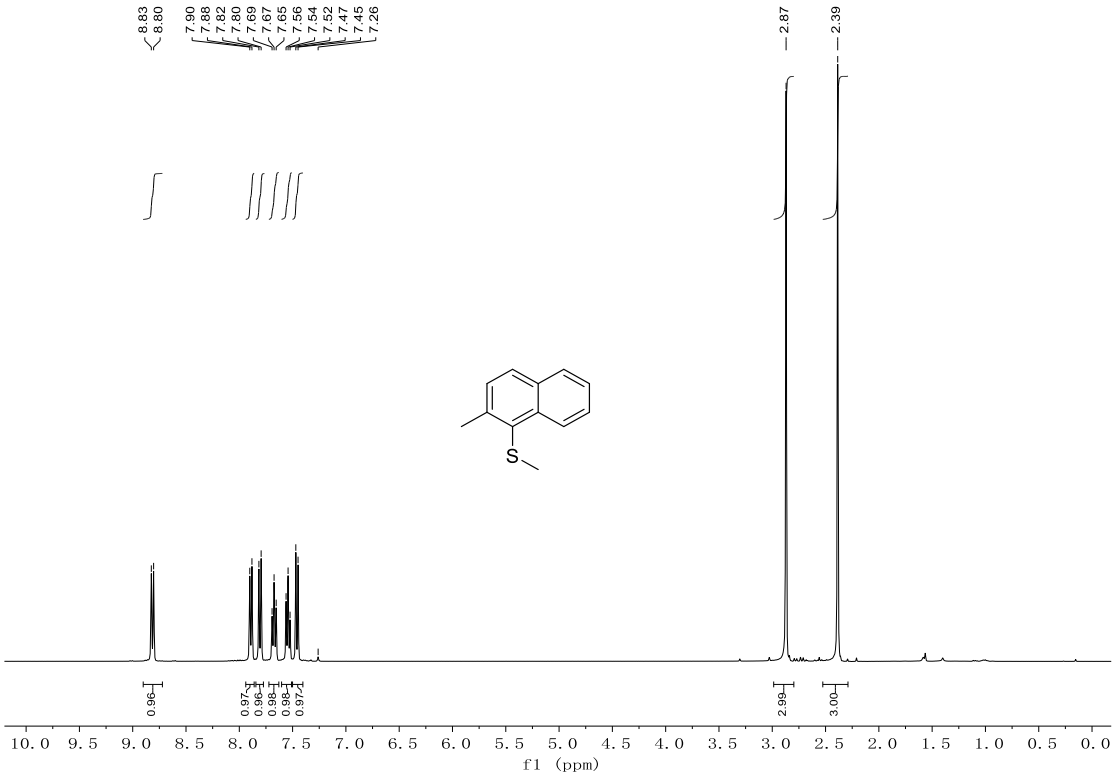


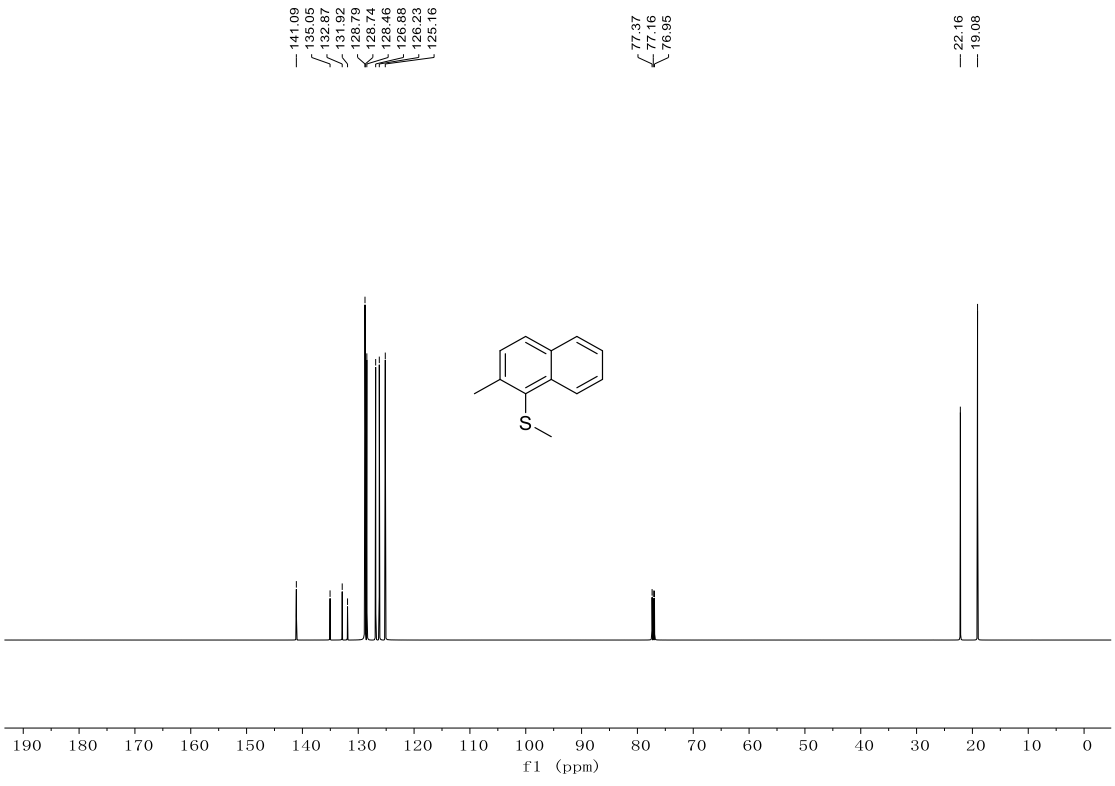
(*R*)-3,7-dimethyl-*N*-(4-(methylthio)phenyl)oct-6-enamide (11)



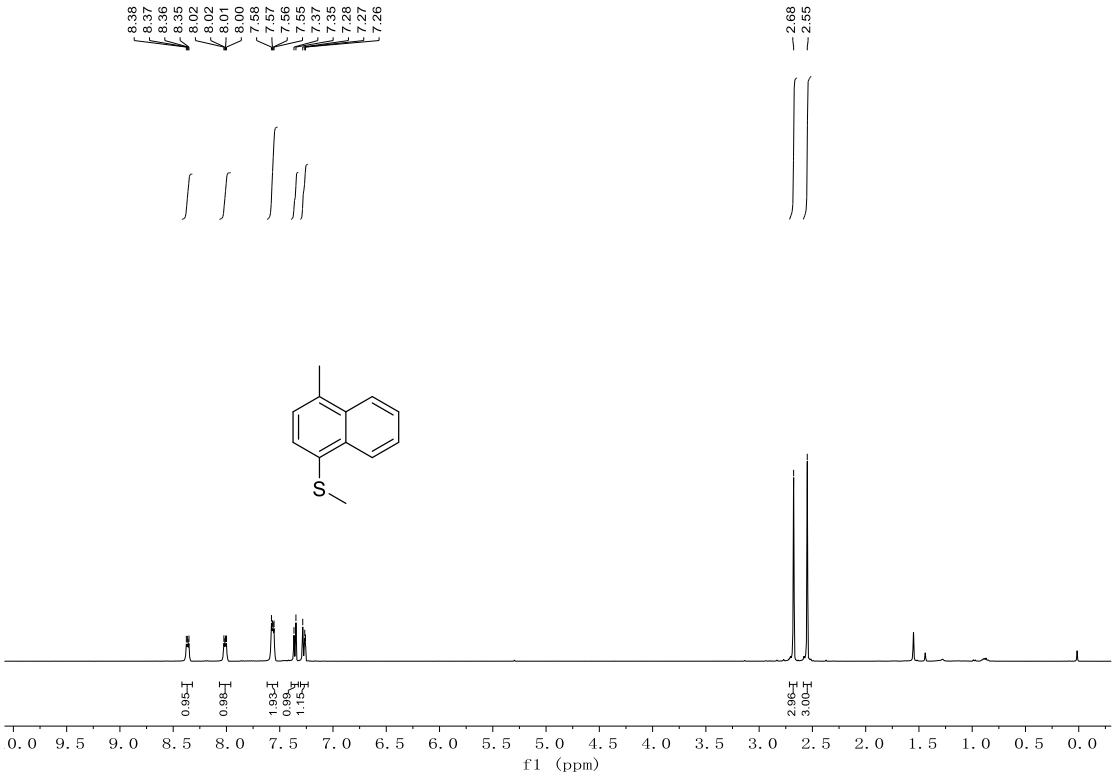


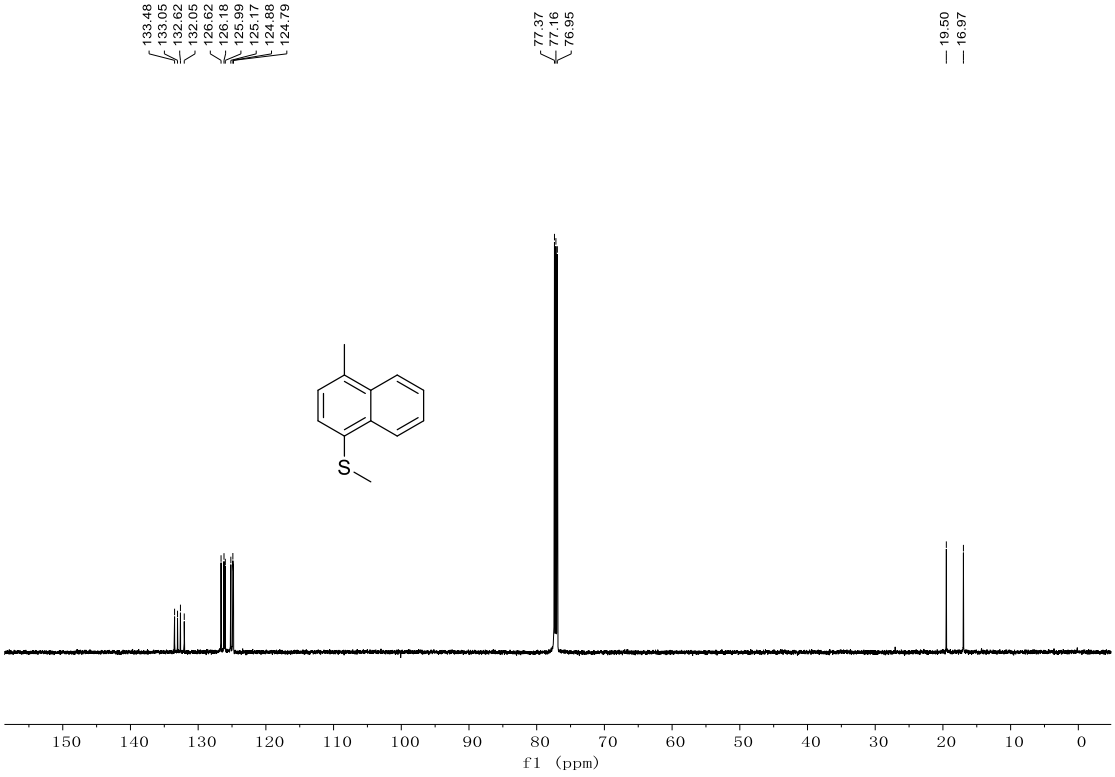
Methyl(2-methylnaphthalen-1-yl)sulfane (12)



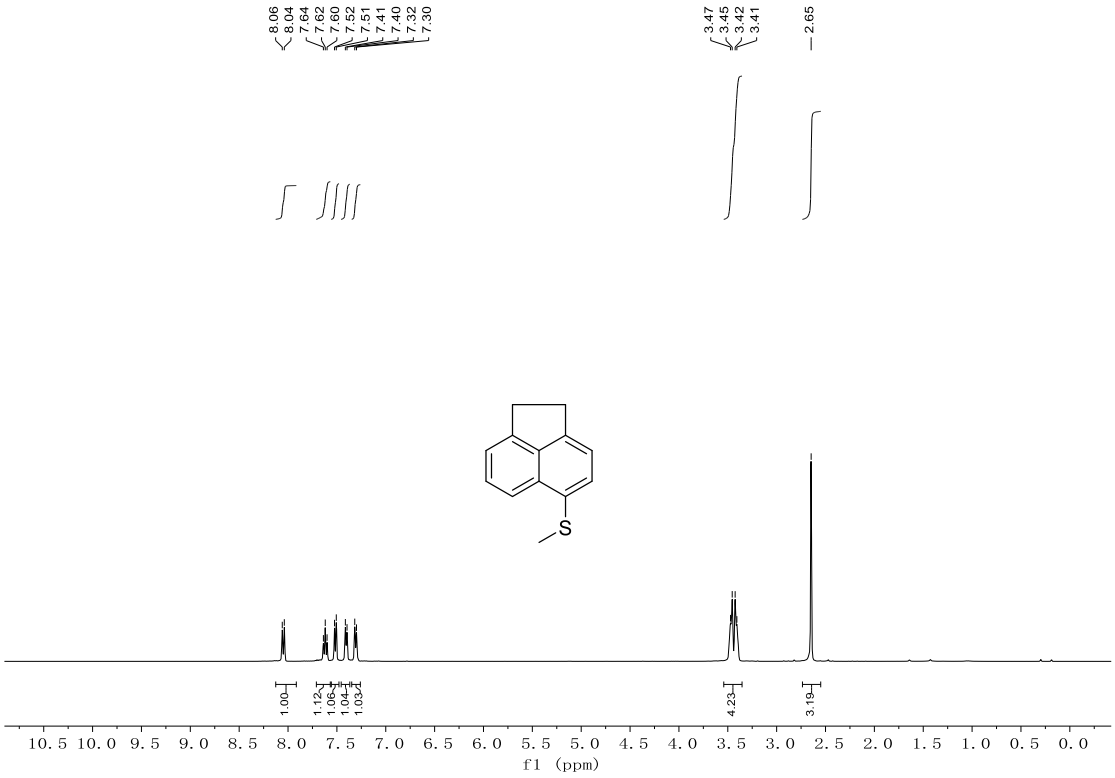


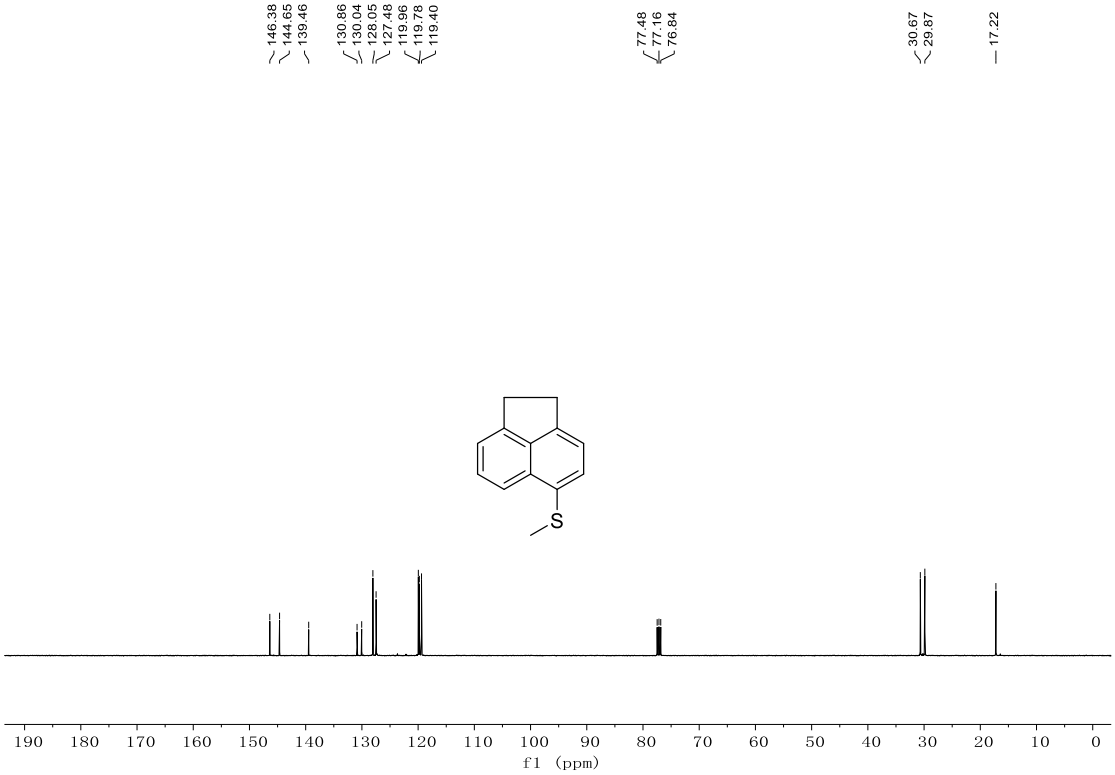
Methyl(4-methylnaphthalen-1-yl)sulfane (13)



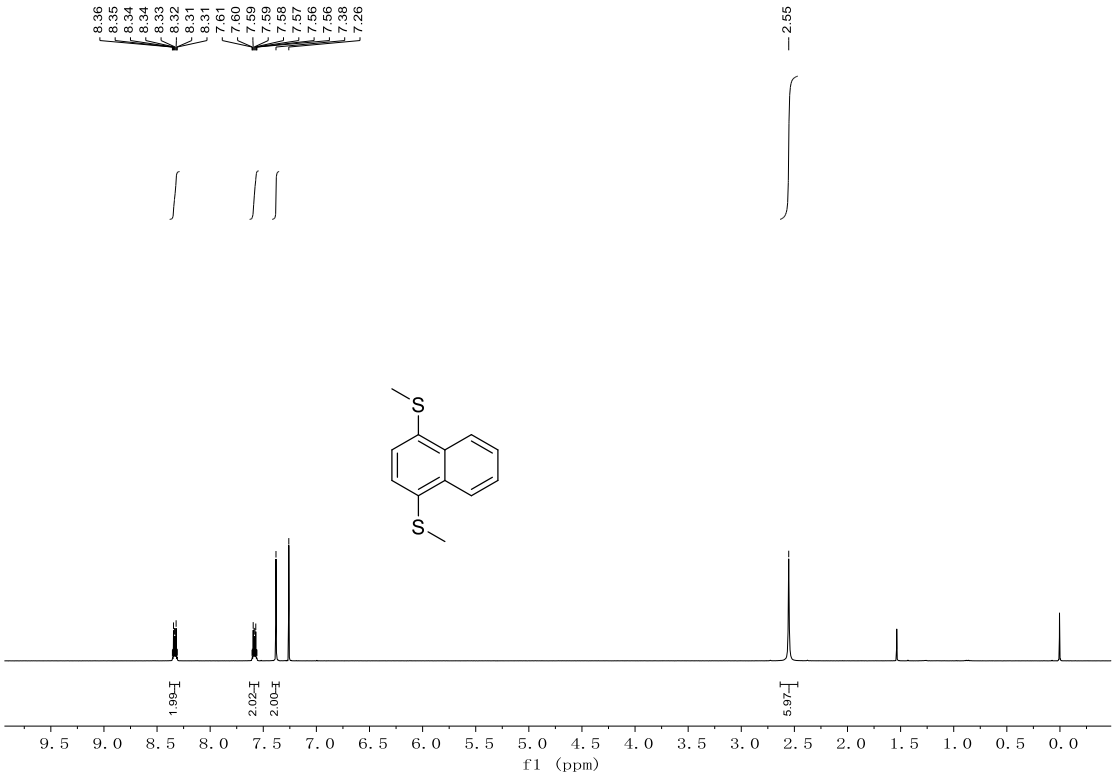


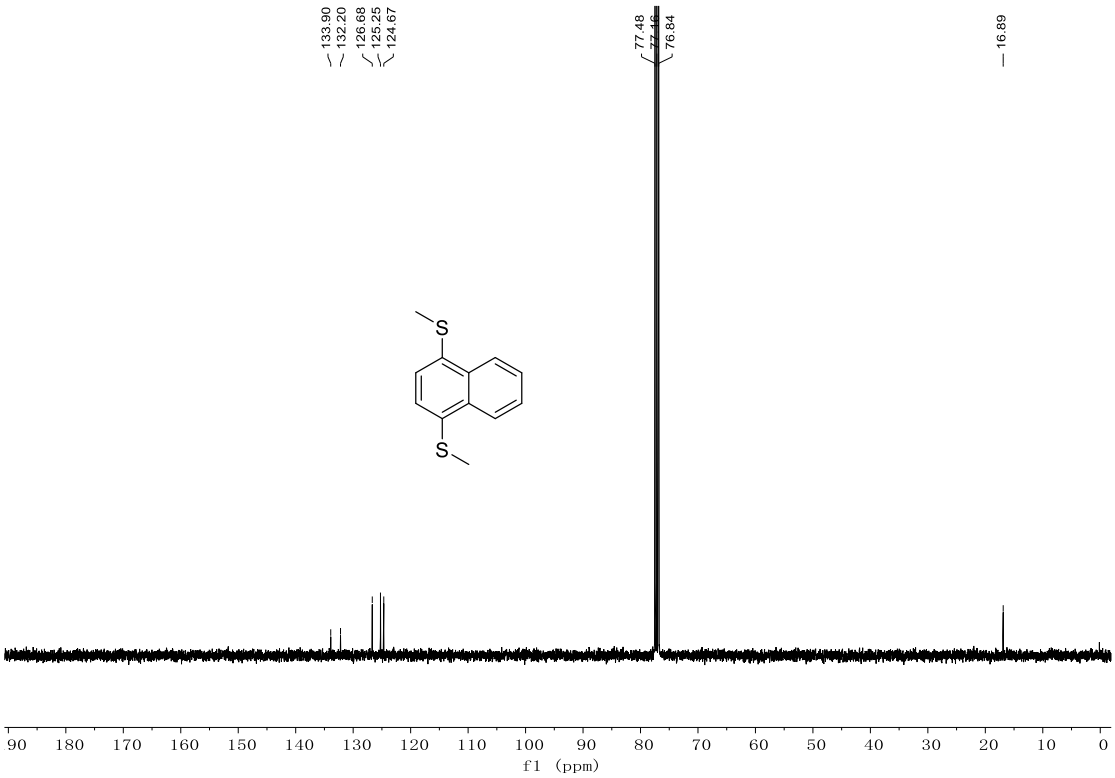
(1,2-Dihydroacenaphthylen-5-yl)(methyl)sulfane (14)



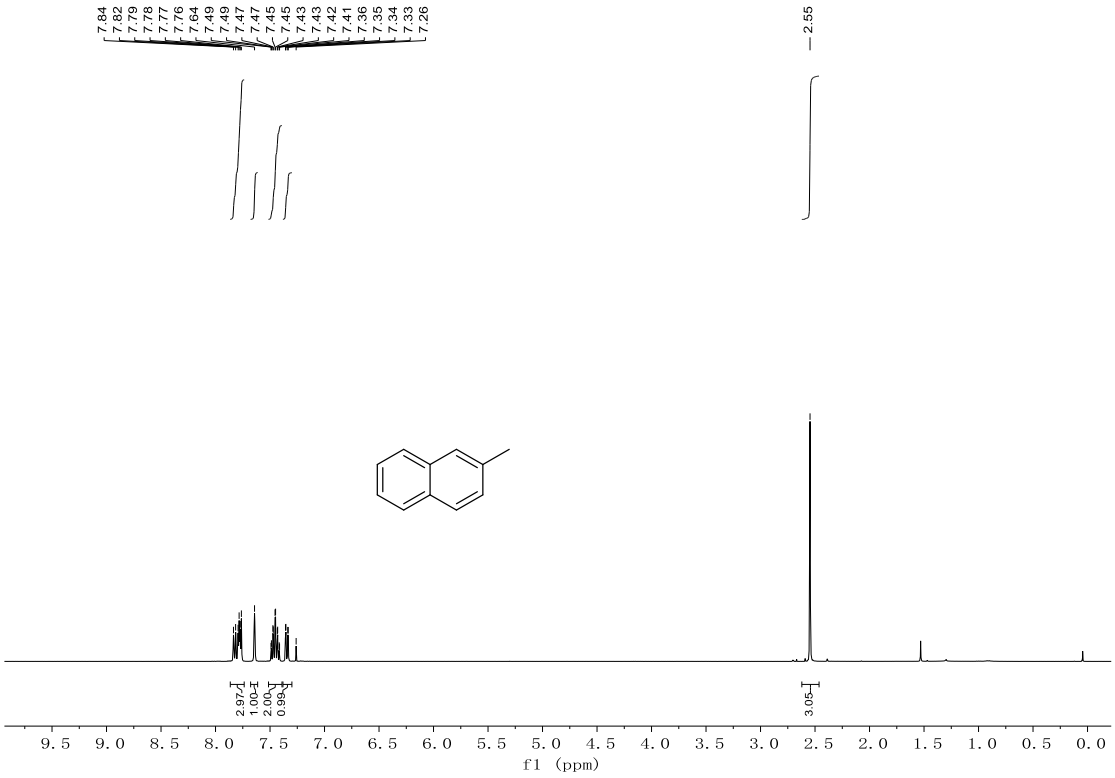


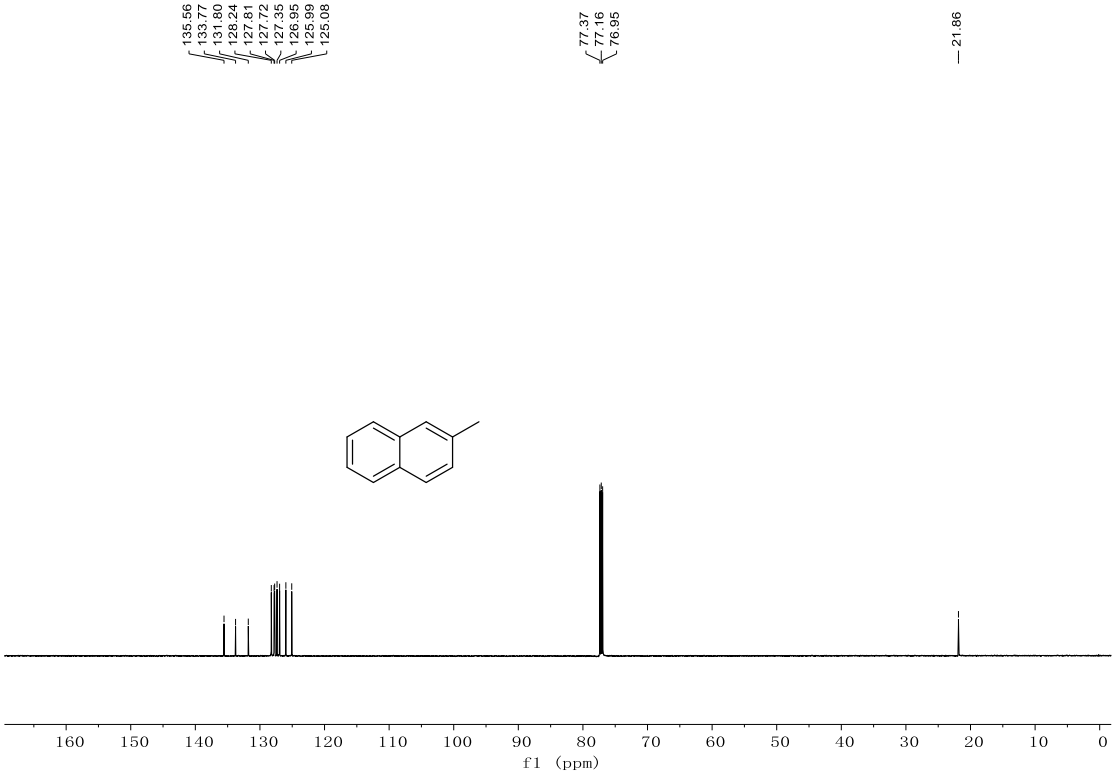
1,4-Bis(methylthio)naphthalene (16)



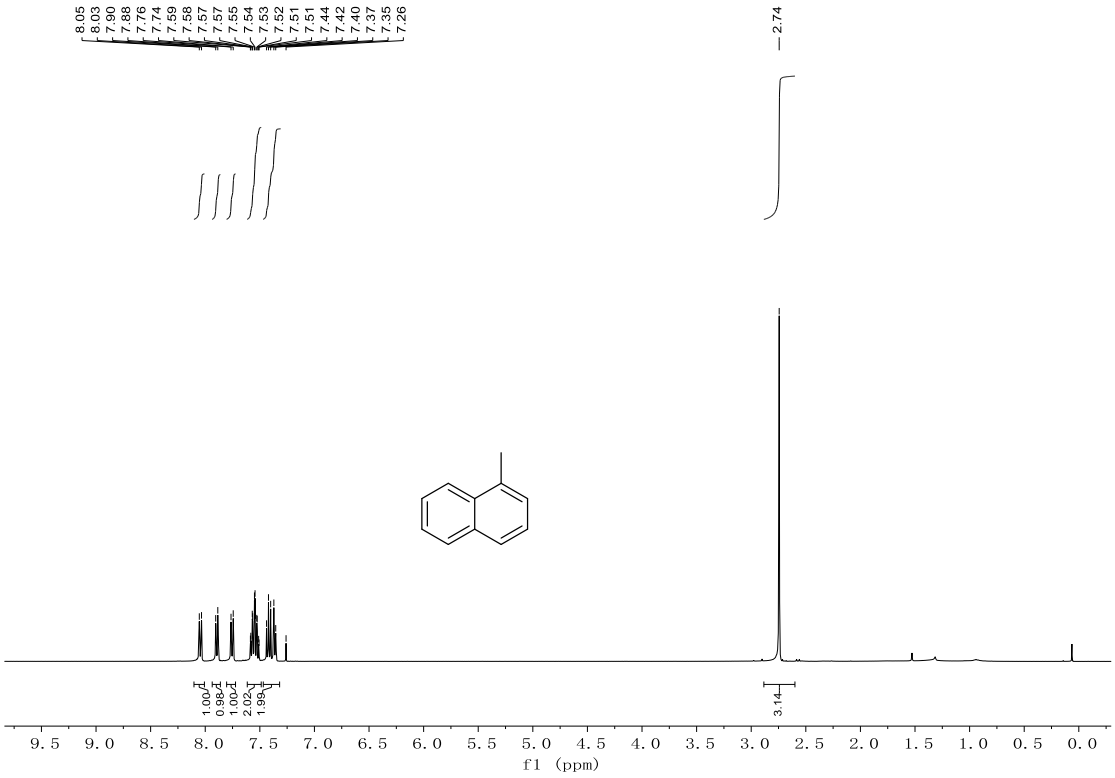


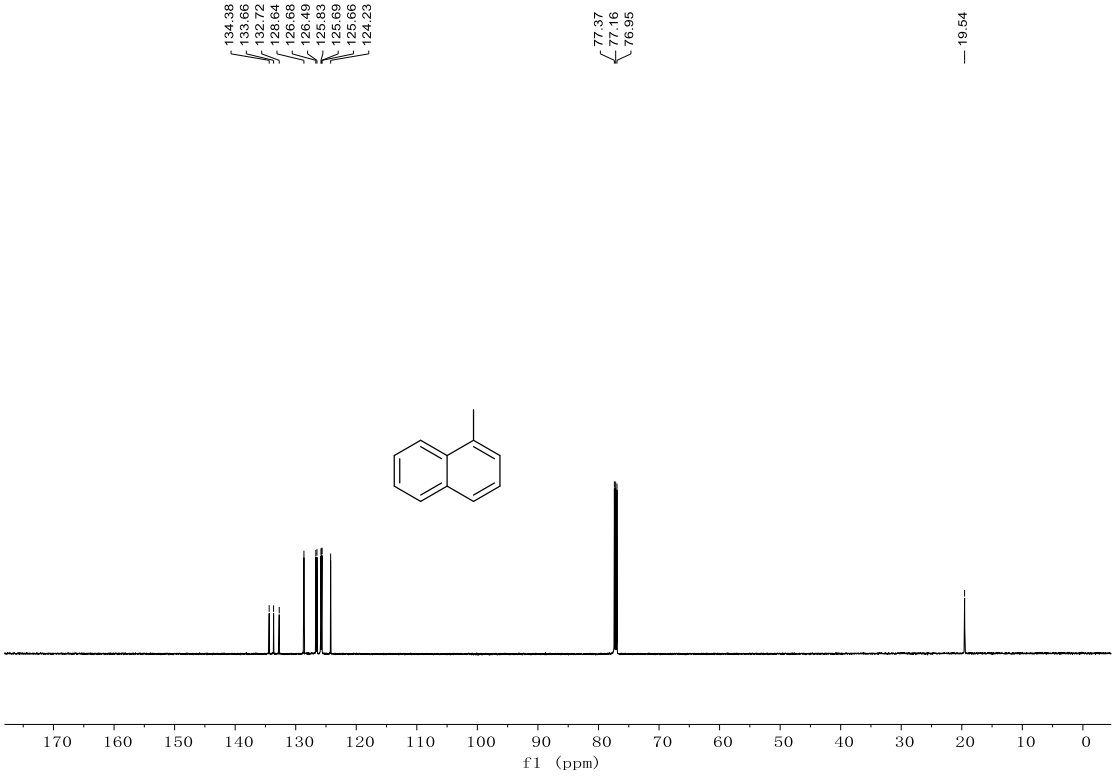
2-methylnaphthalene (1a)



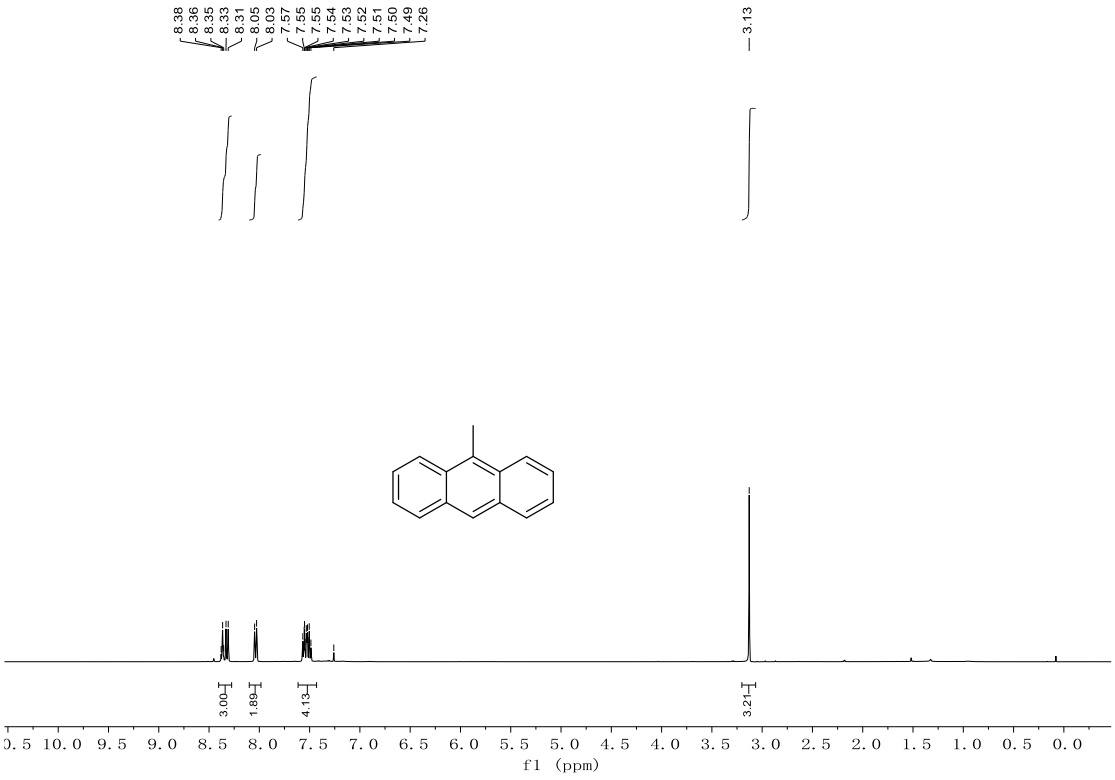


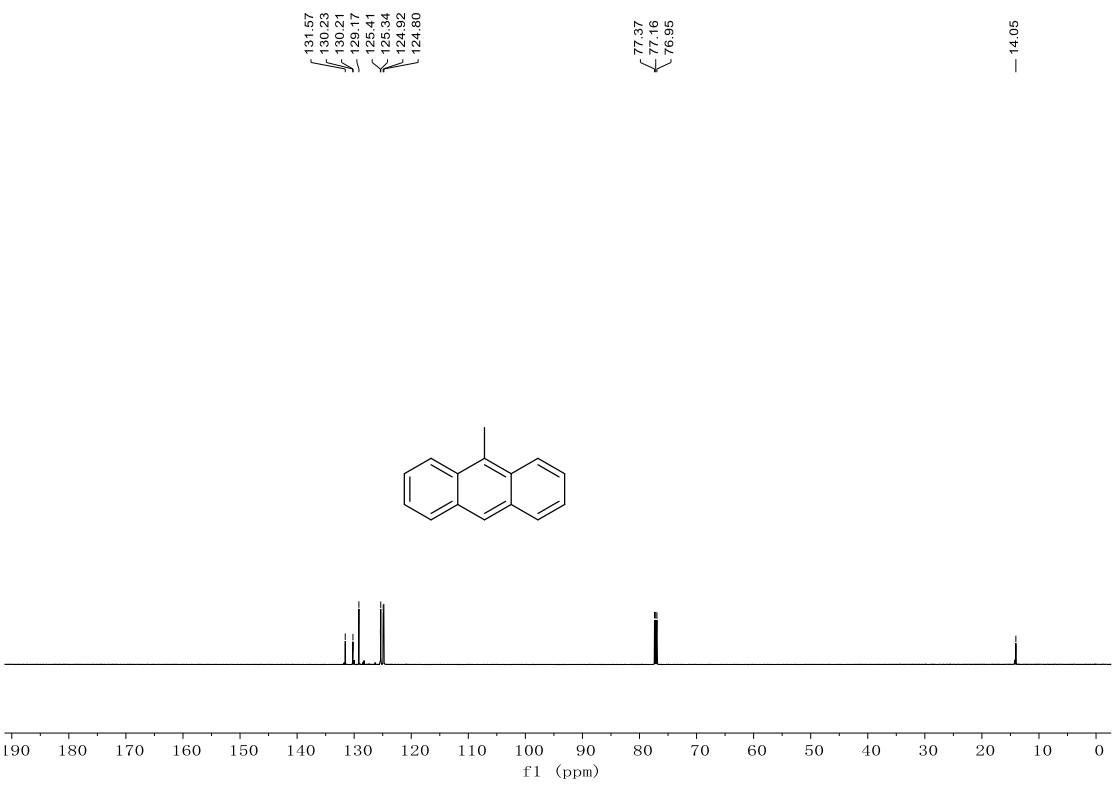
1-methylnaphthalene (2a)



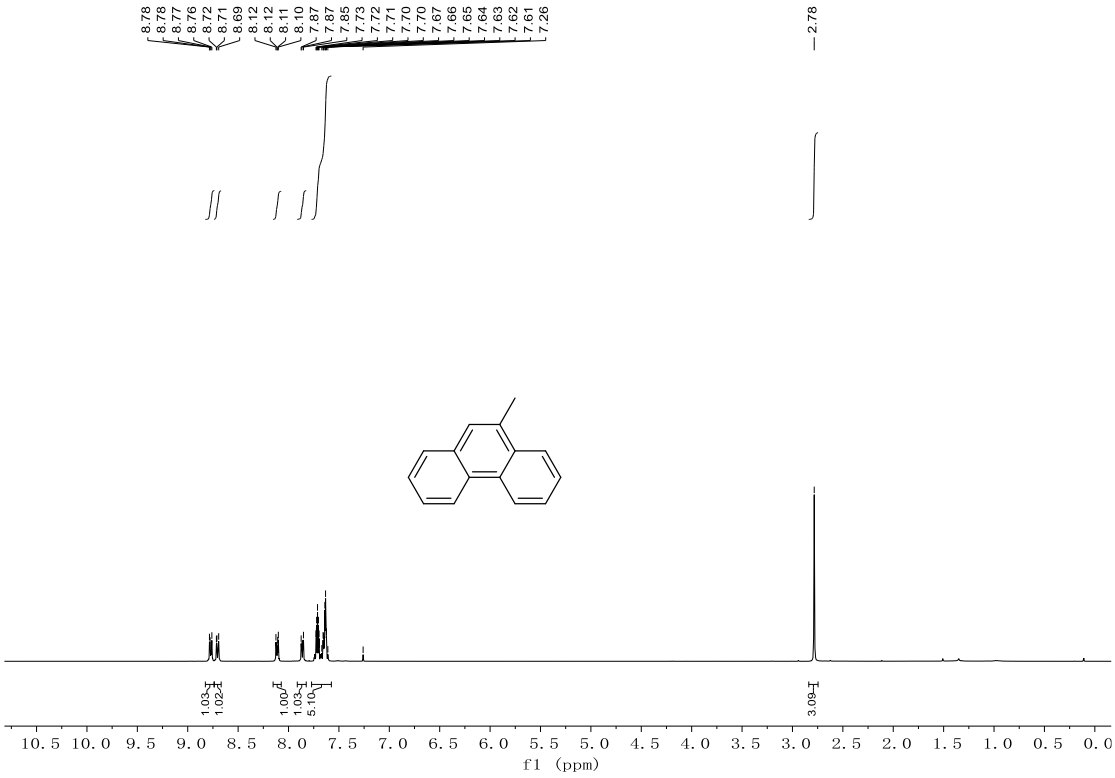


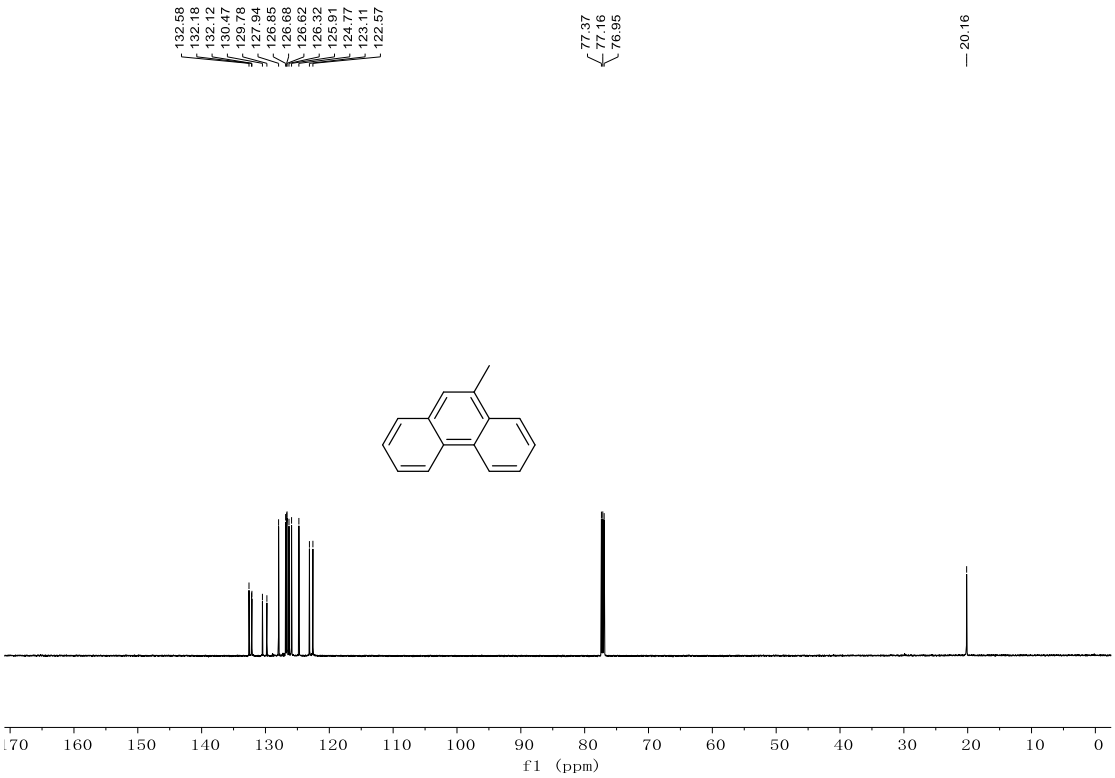
9-methylanthracene (3a)



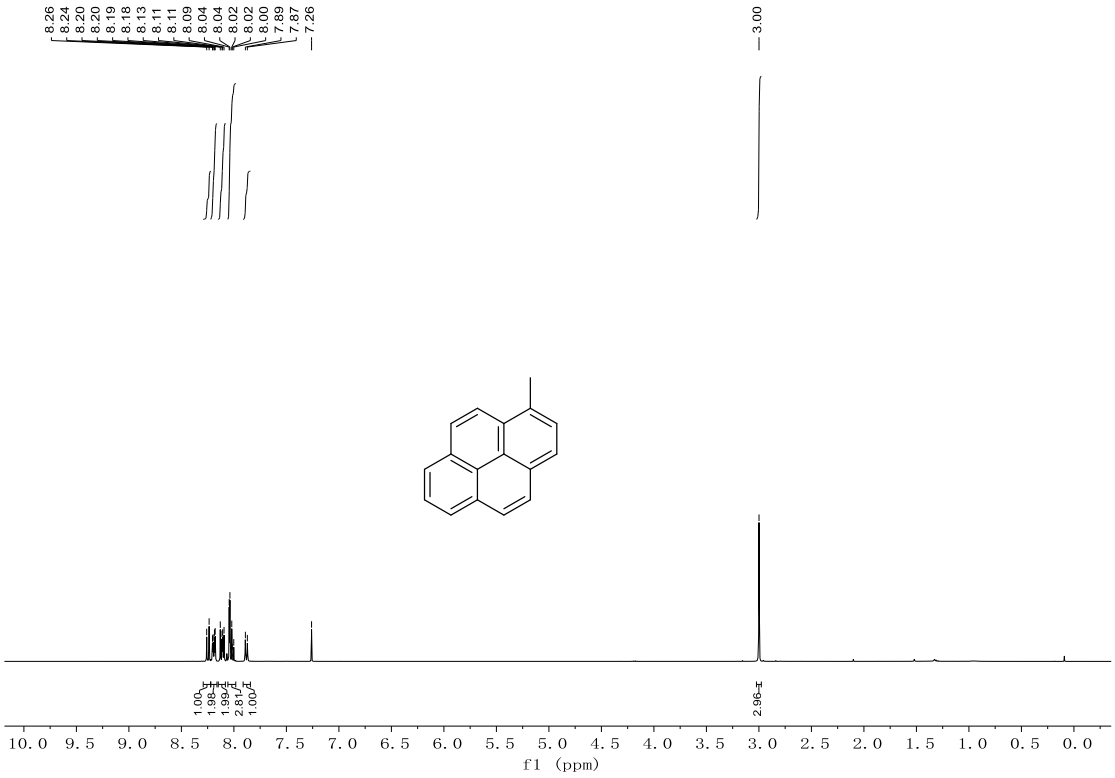


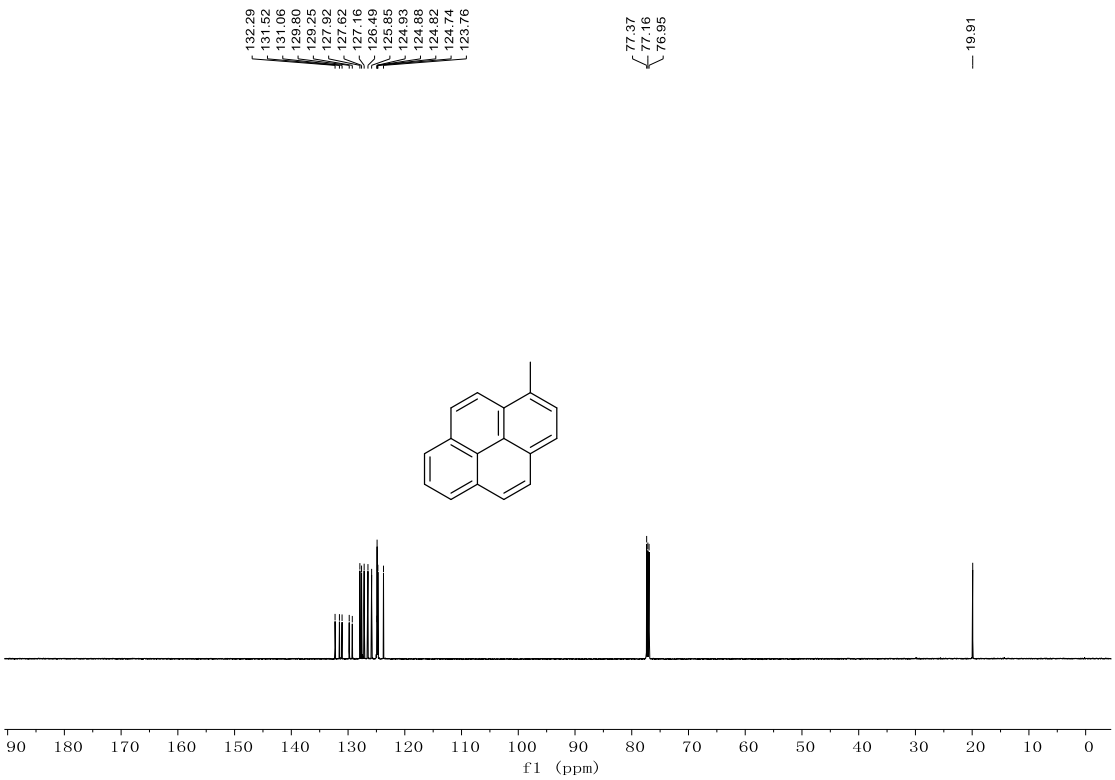
9-methylphenanthrene (4a)



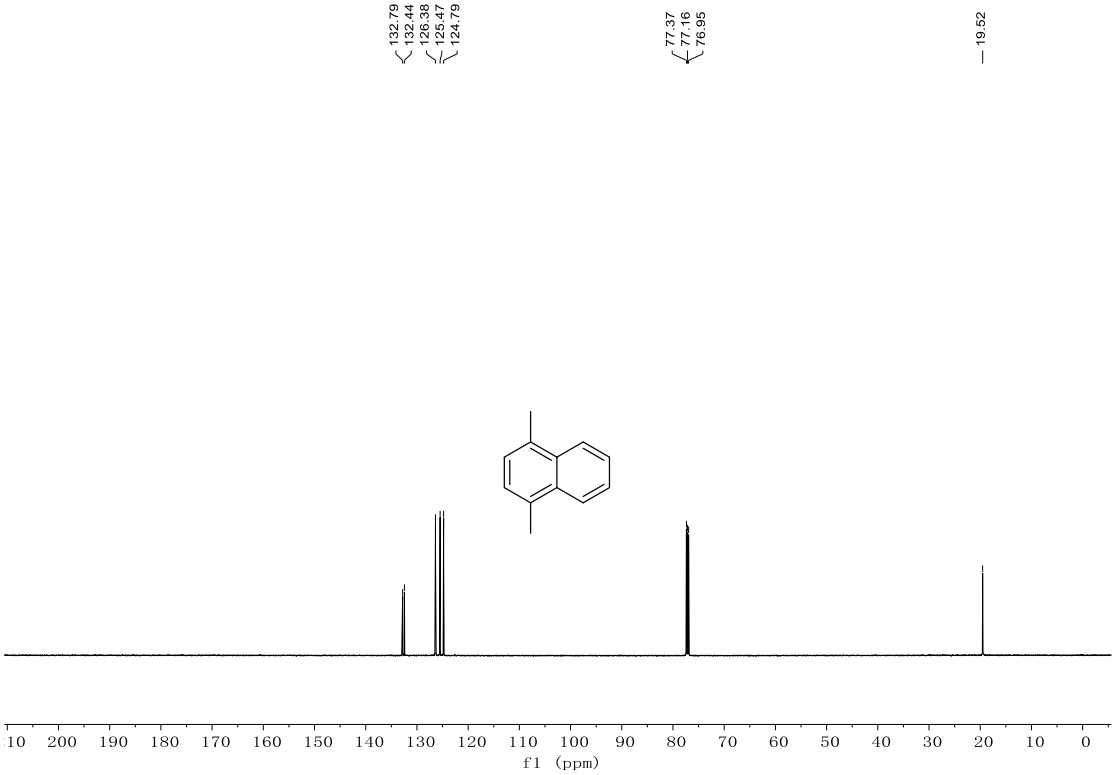


1-methylpyrene (5a)

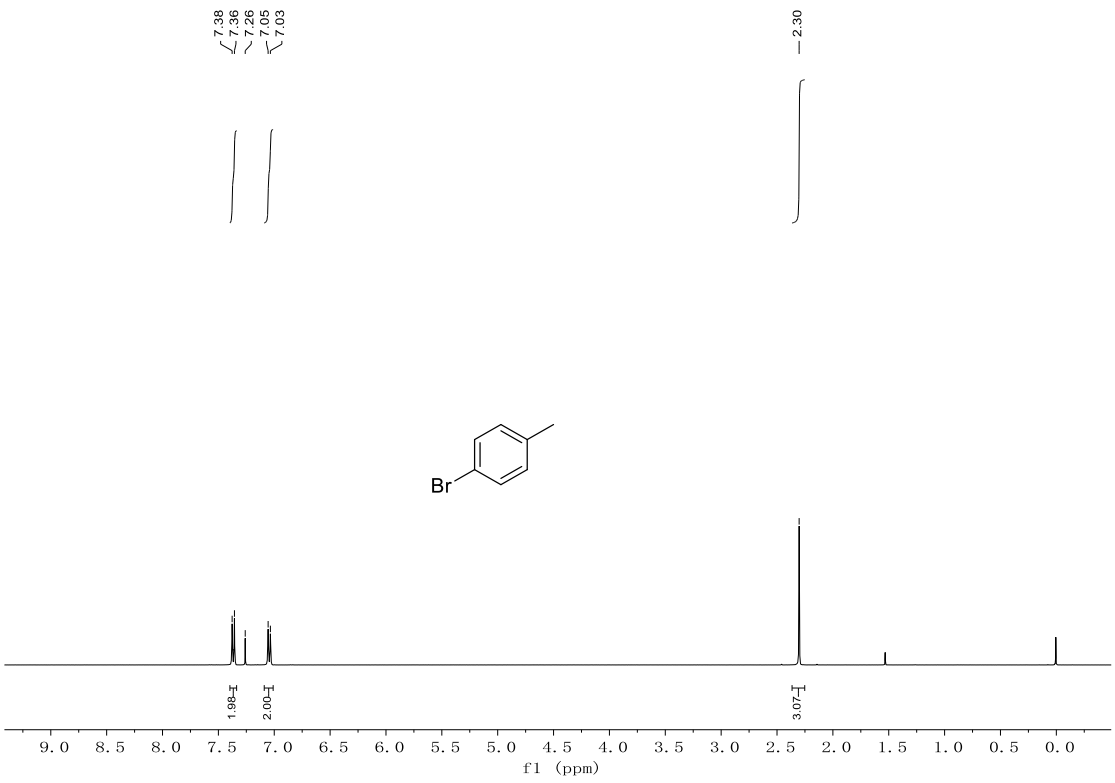


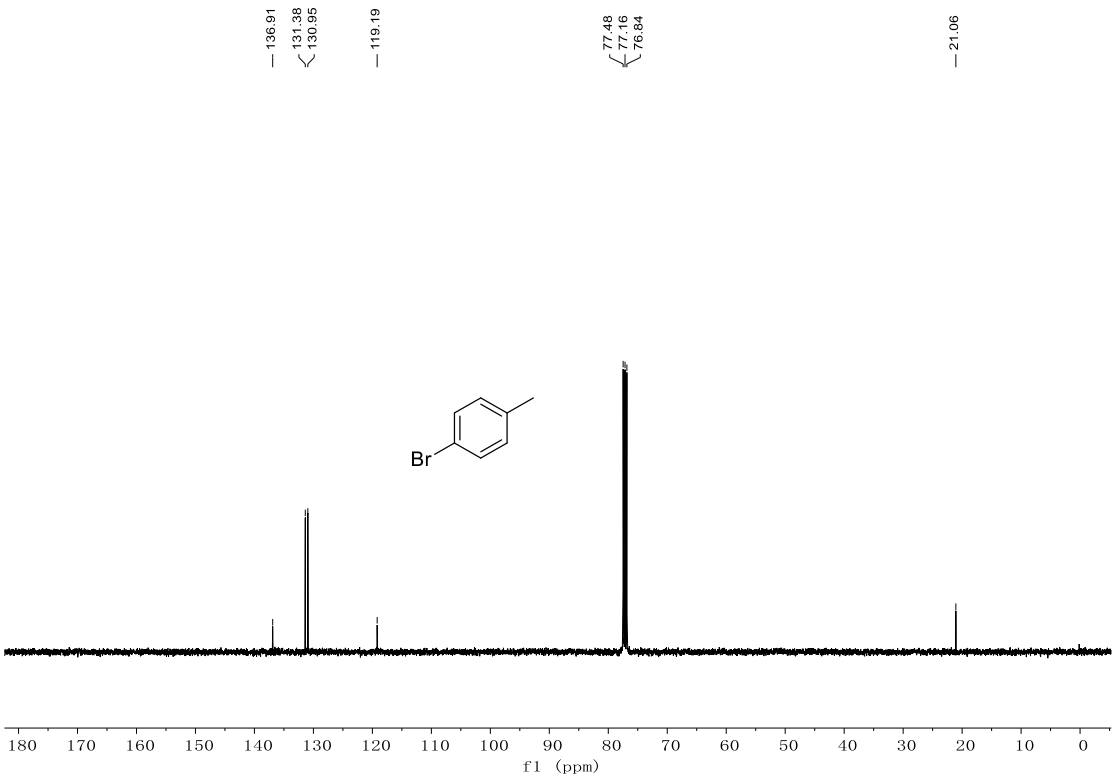


1,4-dimethylnaphthalene (6a)

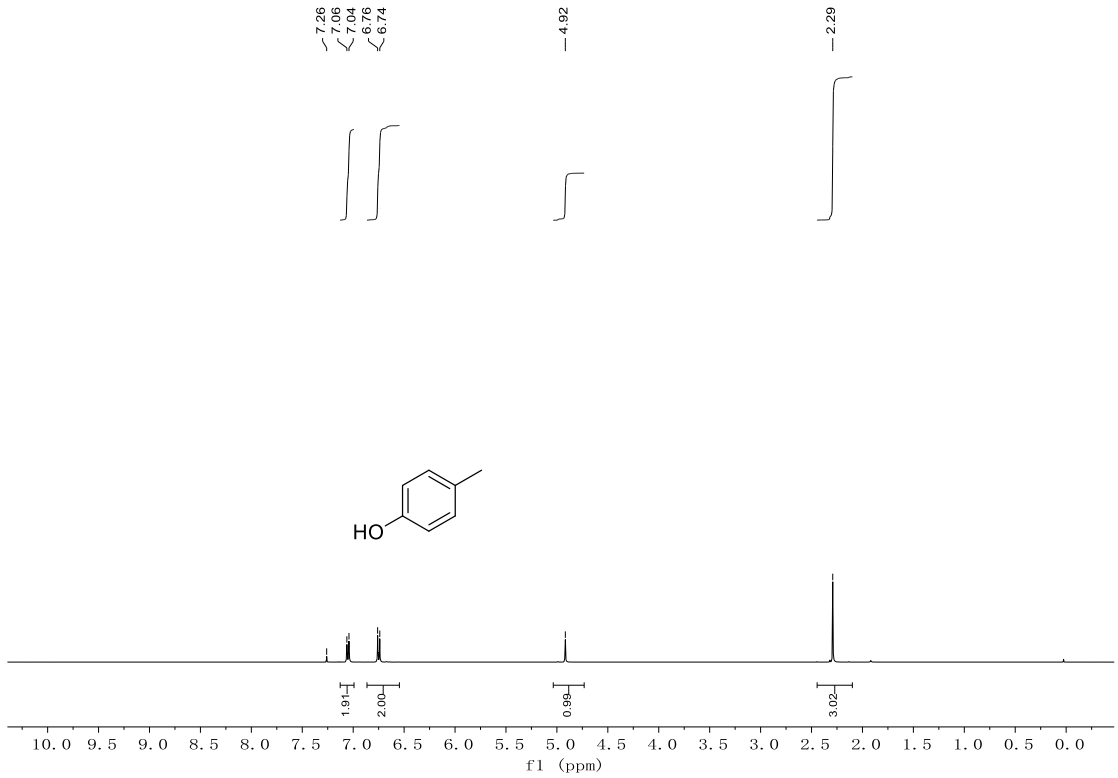


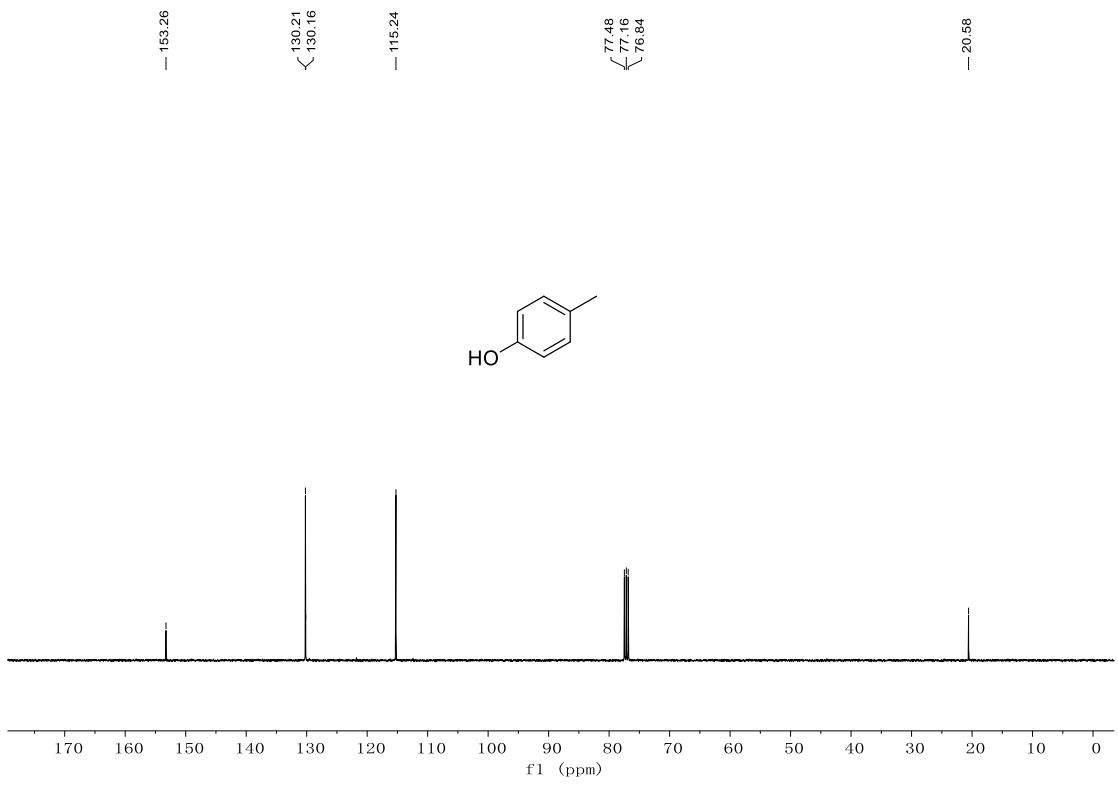
1-bromo-4-methylbenzene (7a)



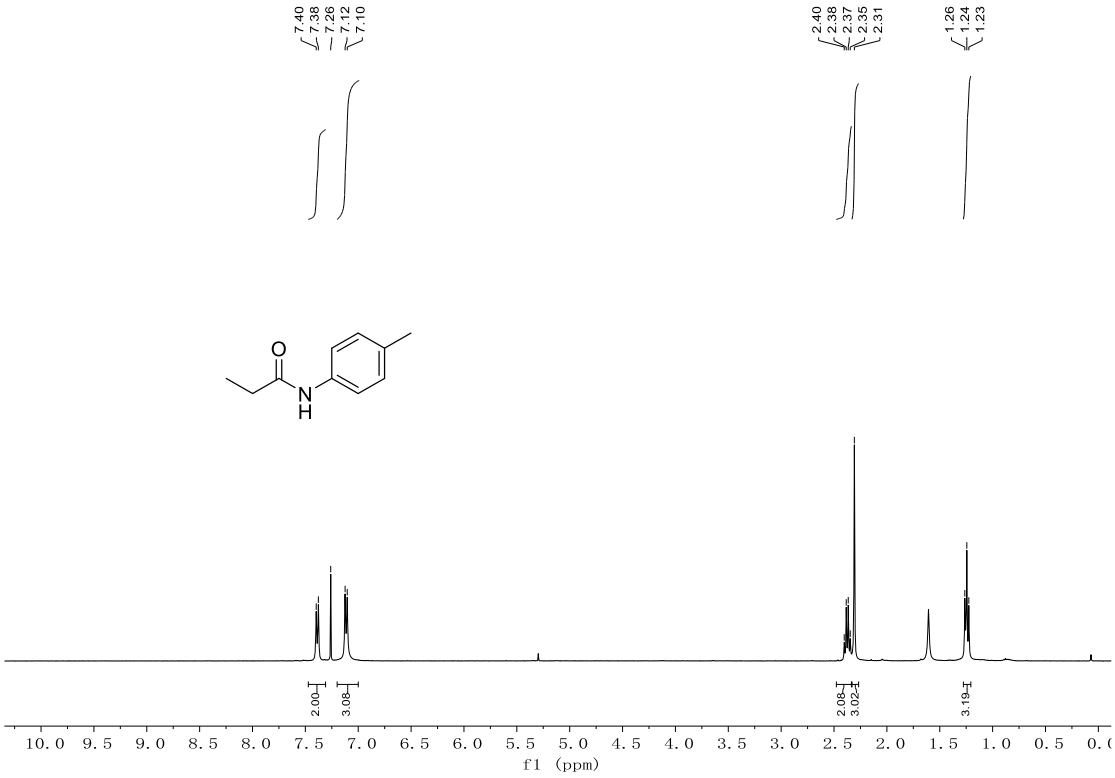


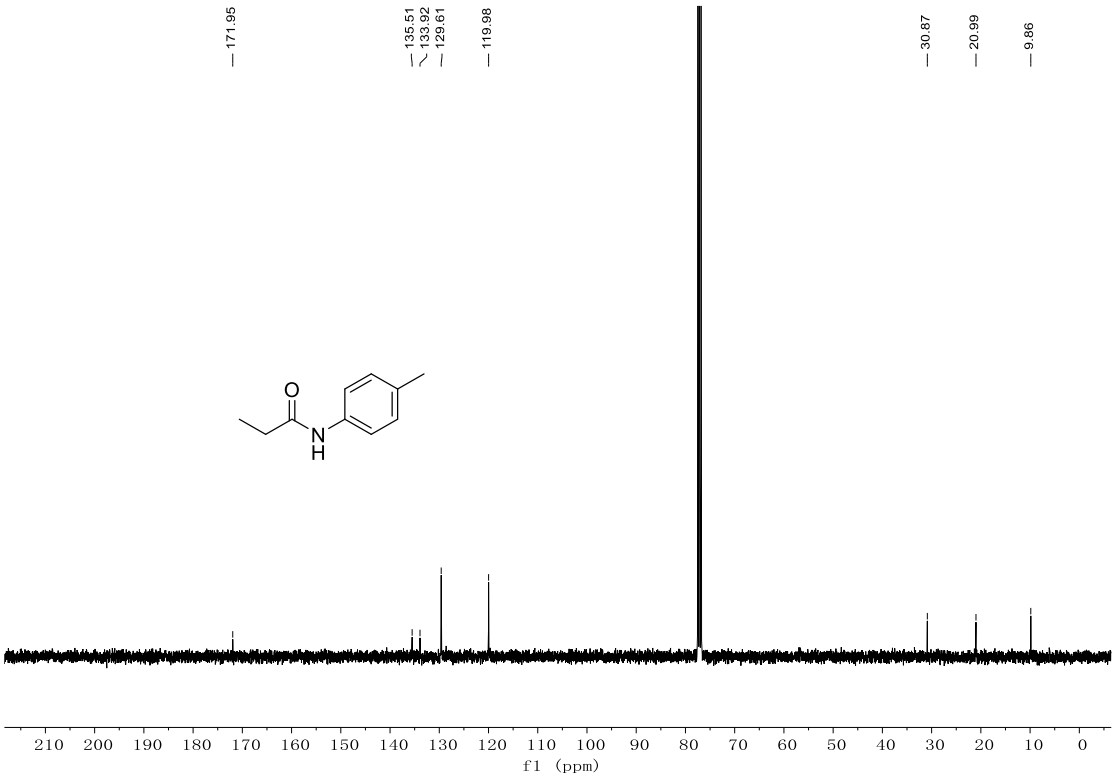
***p*-cresol (8a)**


7.26
7.06
7.04
6.76
6.74
4.92
2.29
HO
1.91
2.00
0.99
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

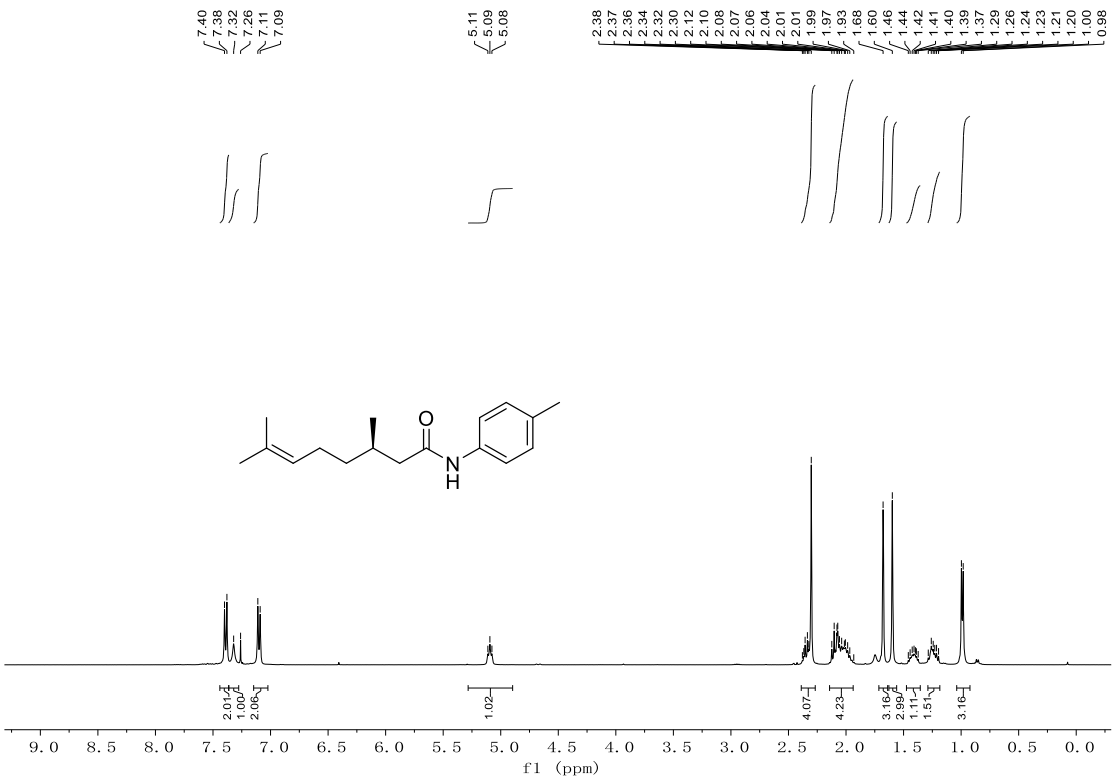

153.26
130.21
130.16
115.24
77.48
77.16
76.84
20.58
HO
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

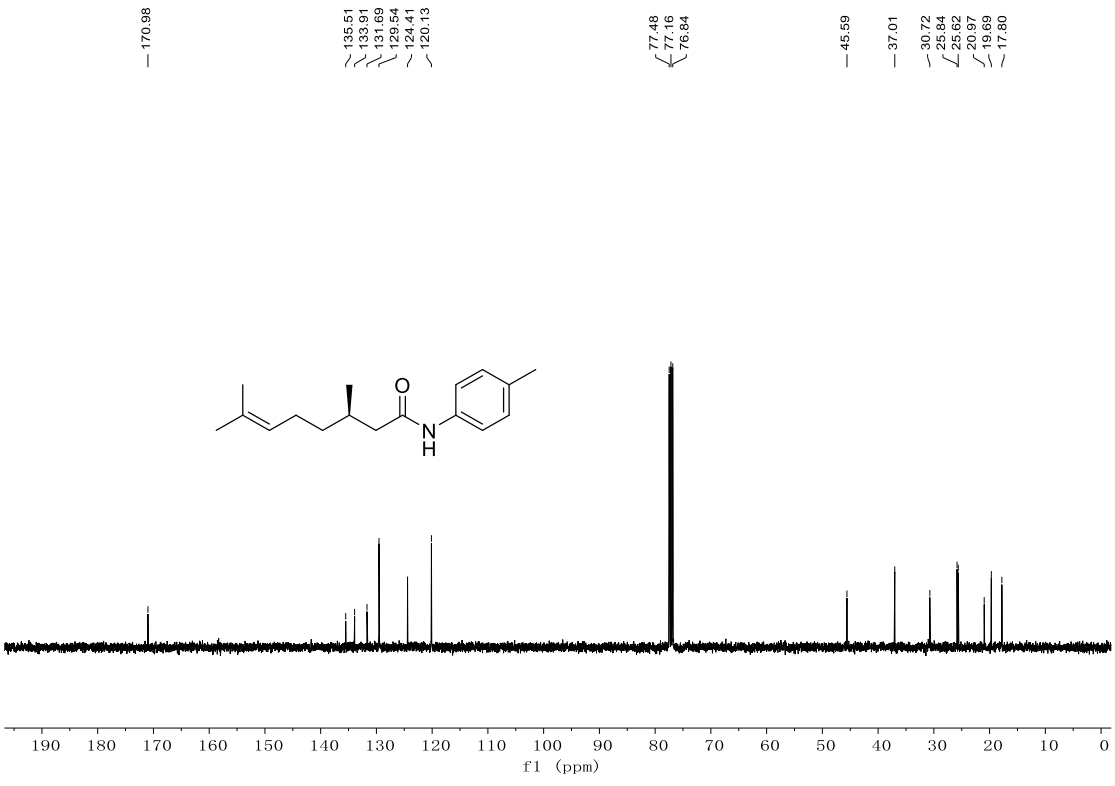
_N_-(_p_-tolyl)propionamide (10a)



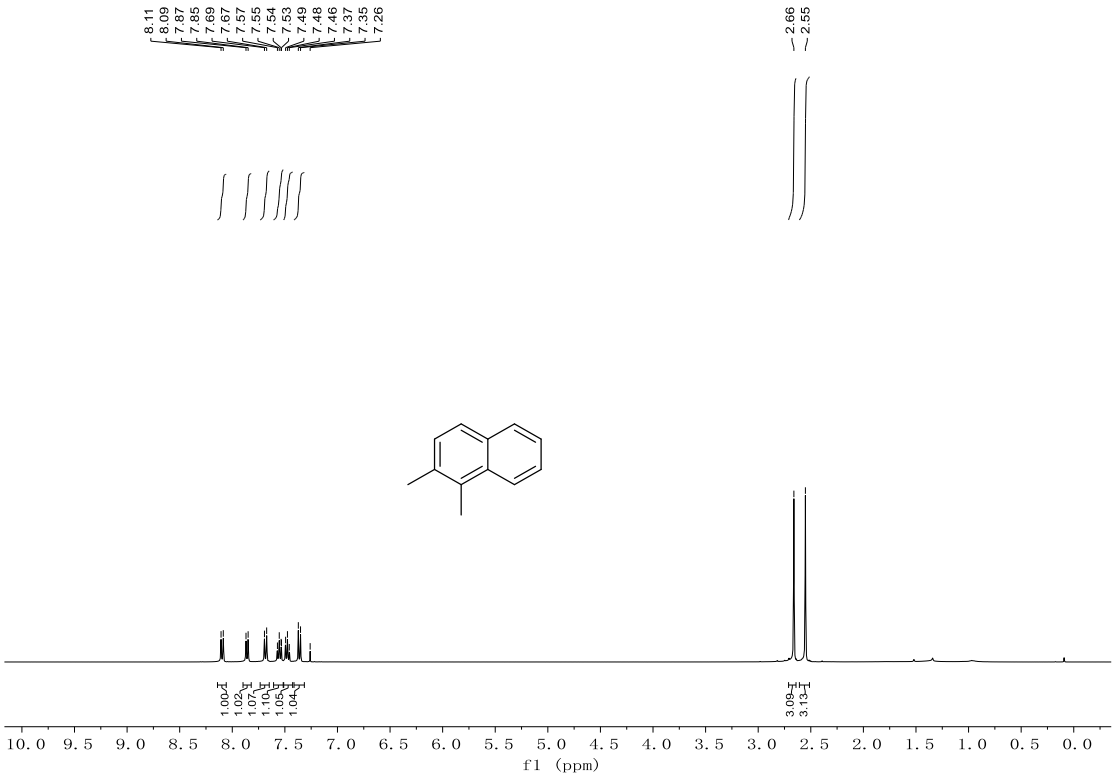


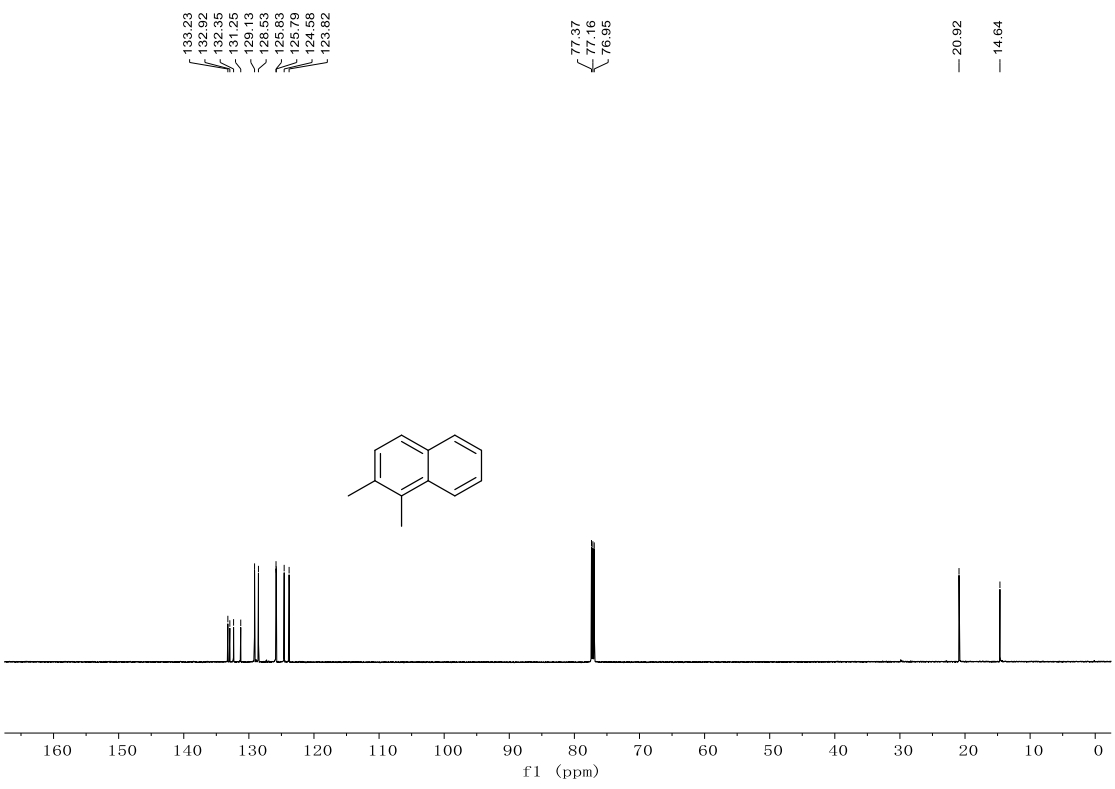
(*R*)-3,7-dimethyl-*N*-(*p*-tolyl)oct-6-enamide (11a)



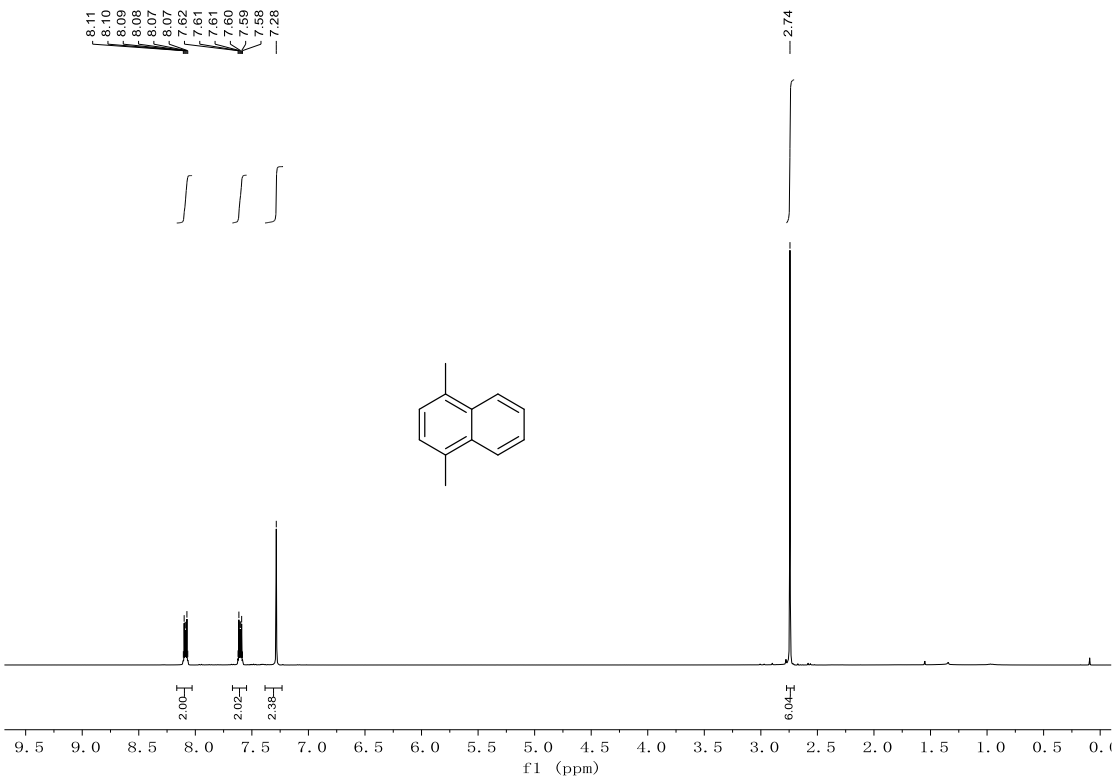


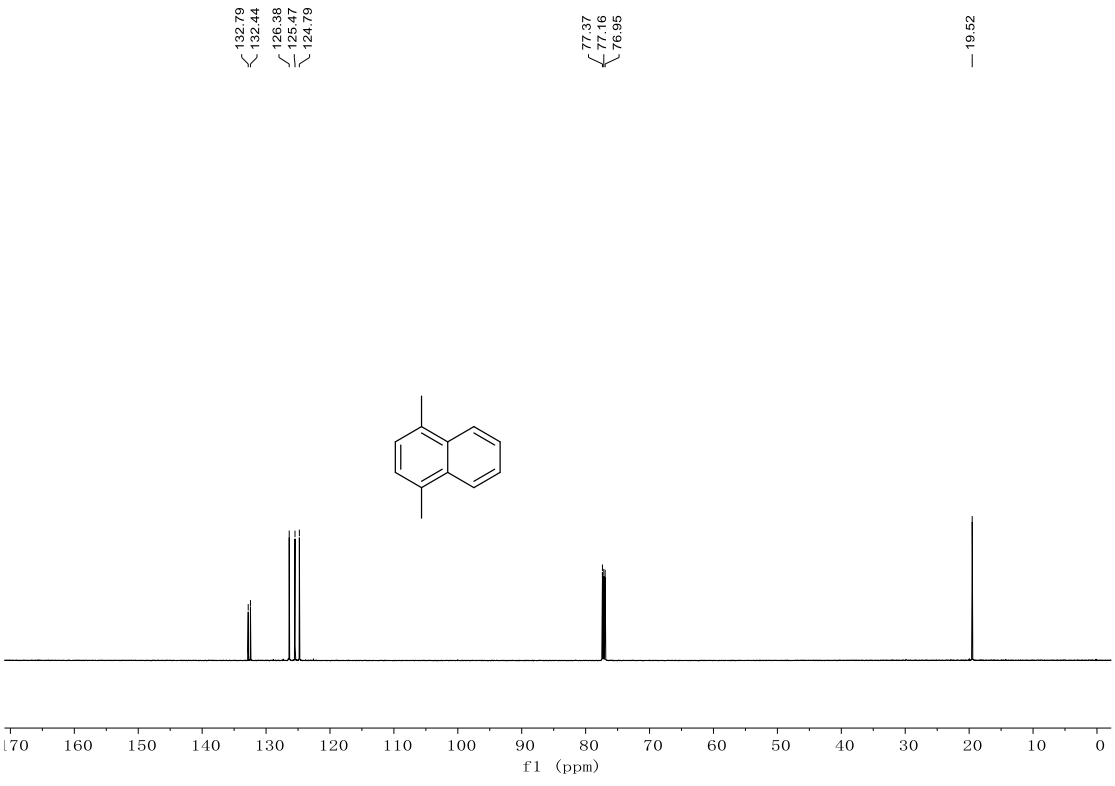
1,2-dimethylnaphthalene (12a)



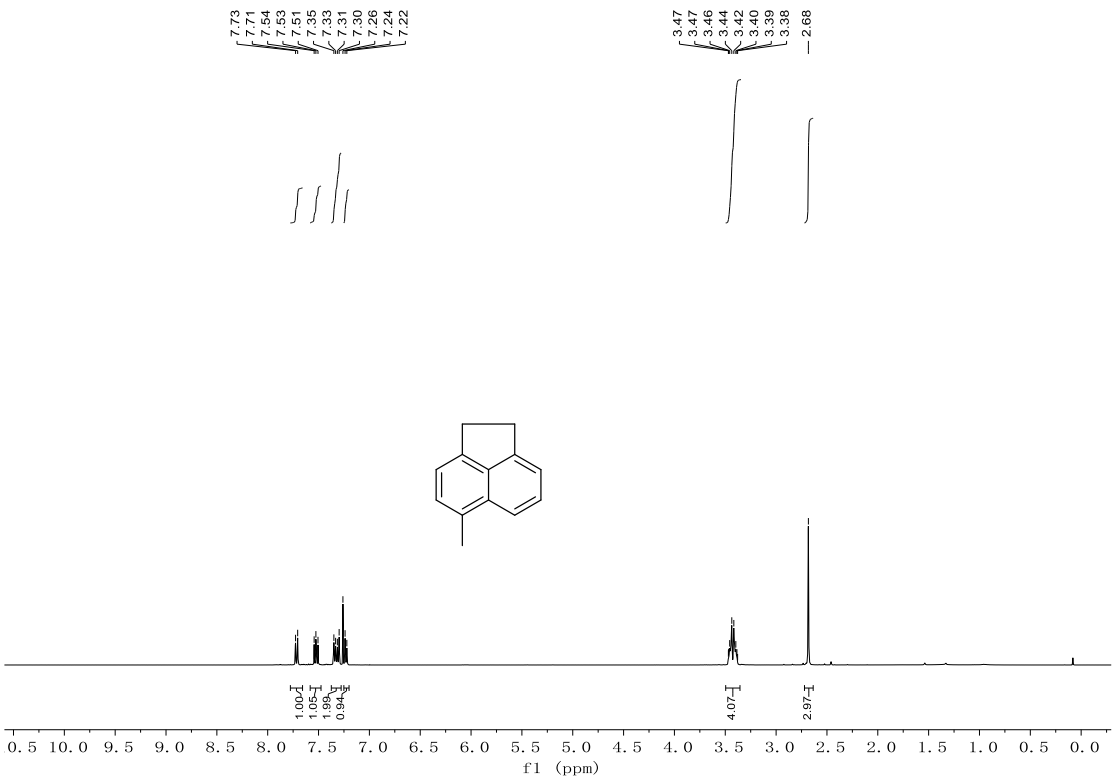


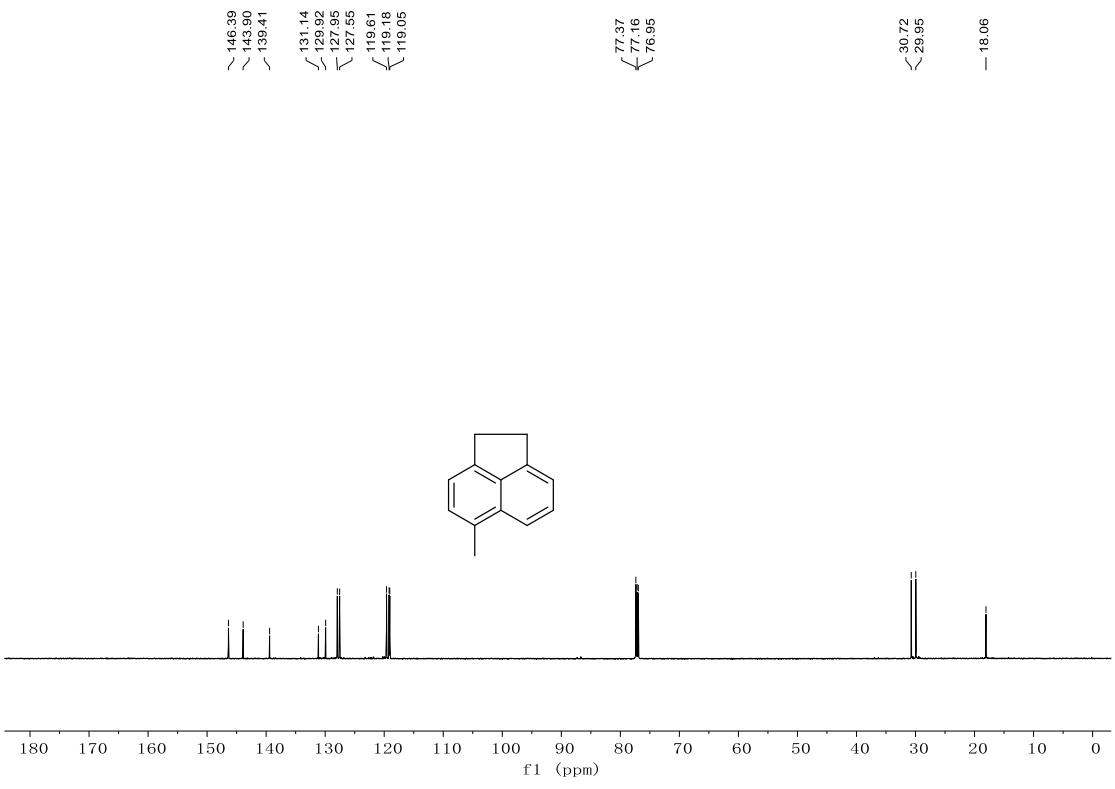
1,4-dimethylnaphthalene (13a)



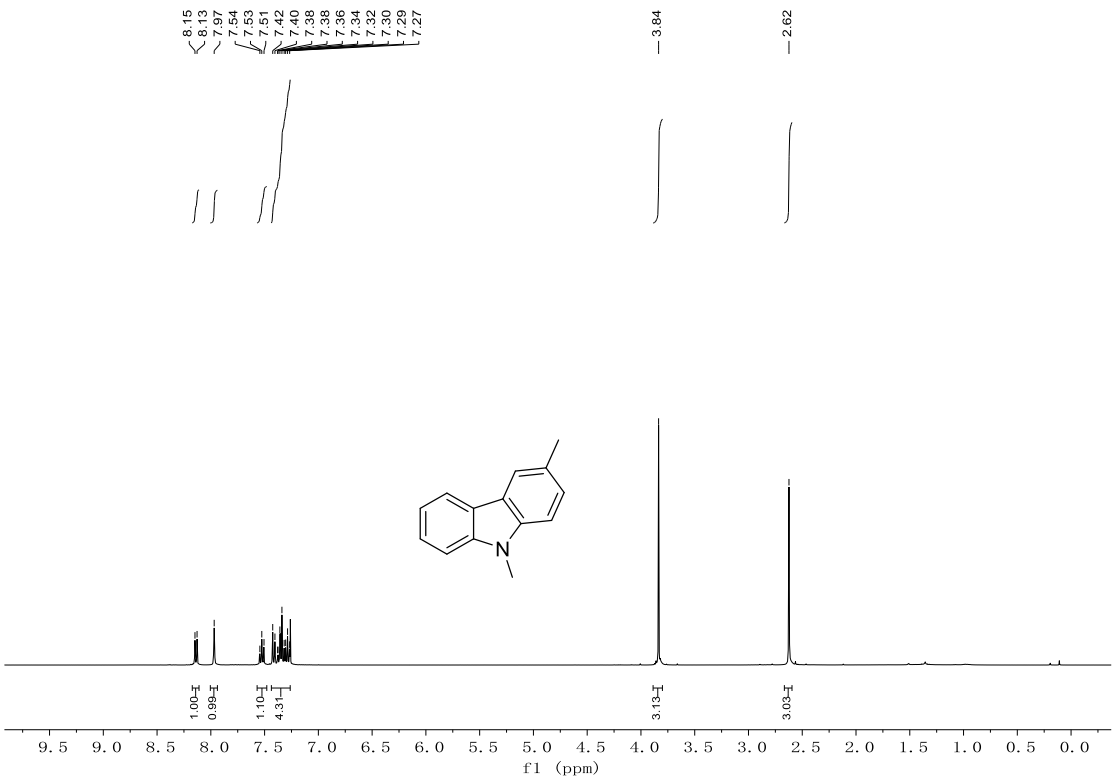


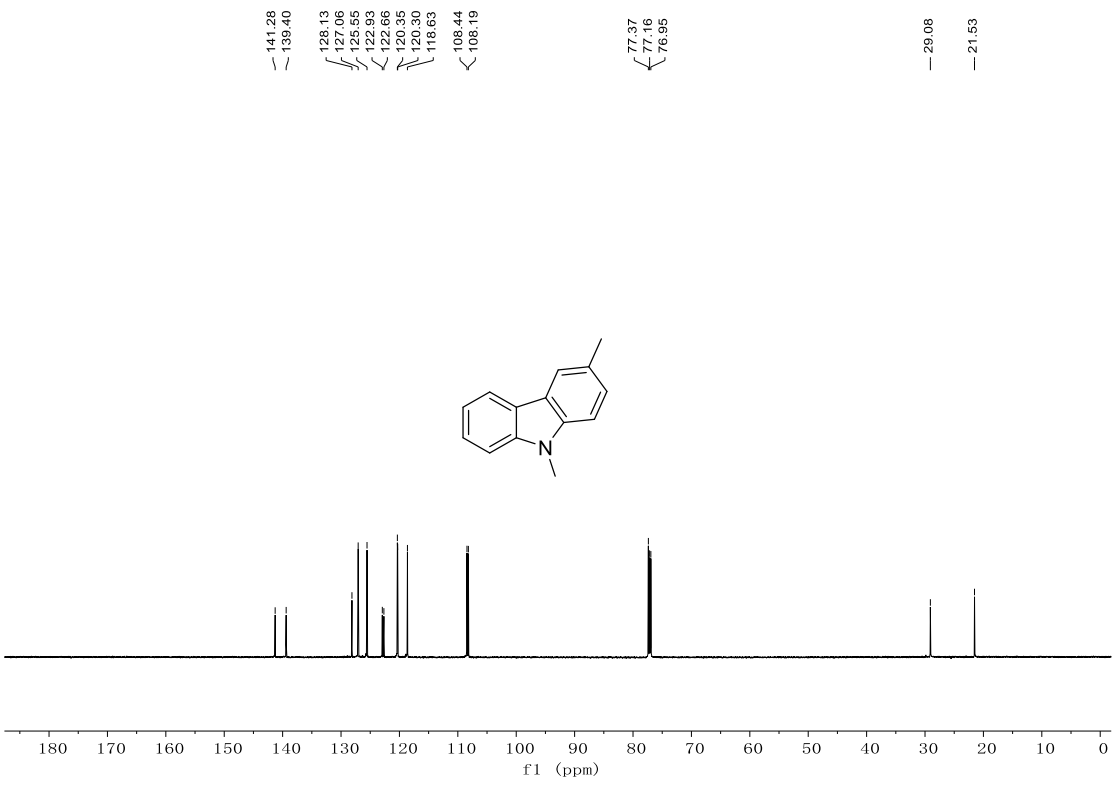
5-methyl-1,2-dihydroacenaphthylene (14a)



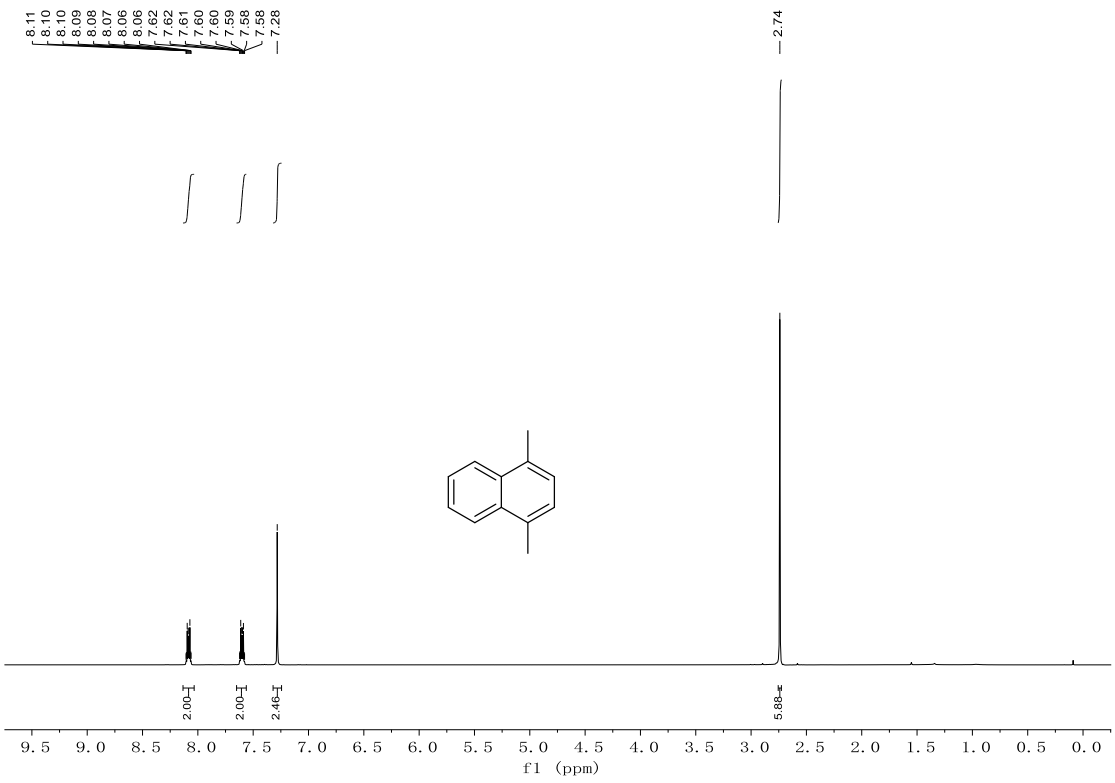


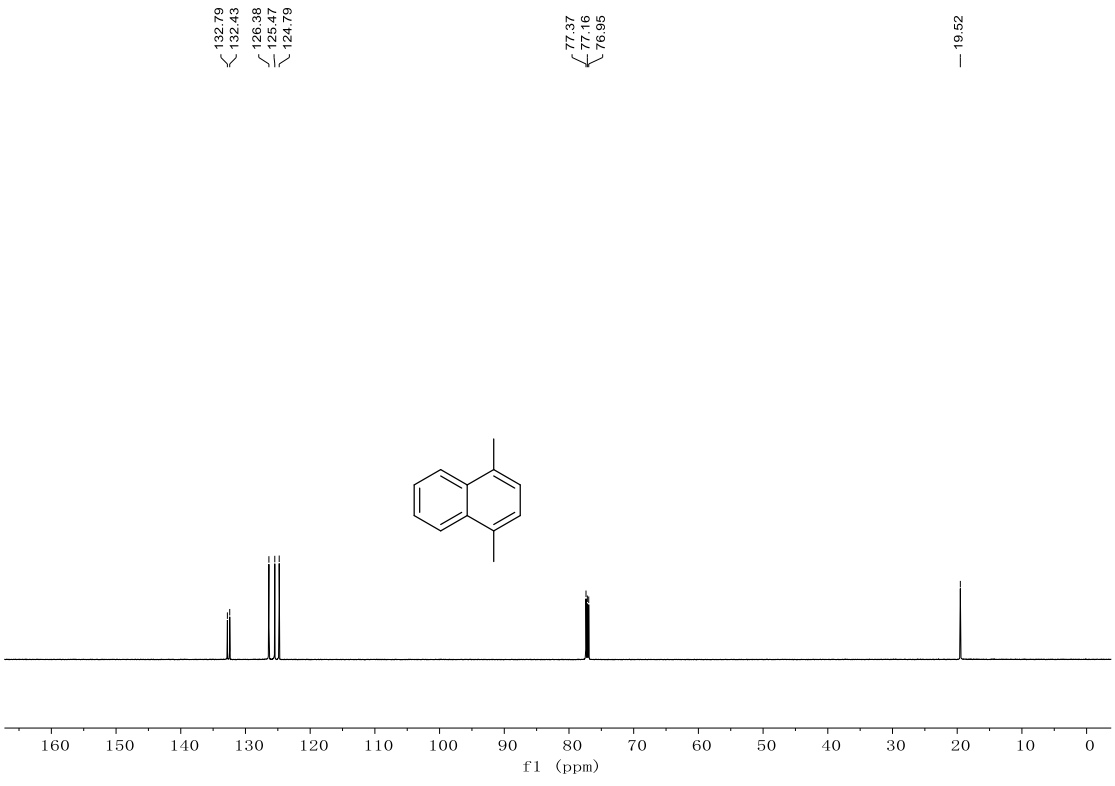
3,9-dimethyl-9*H*-carbazole (15a)



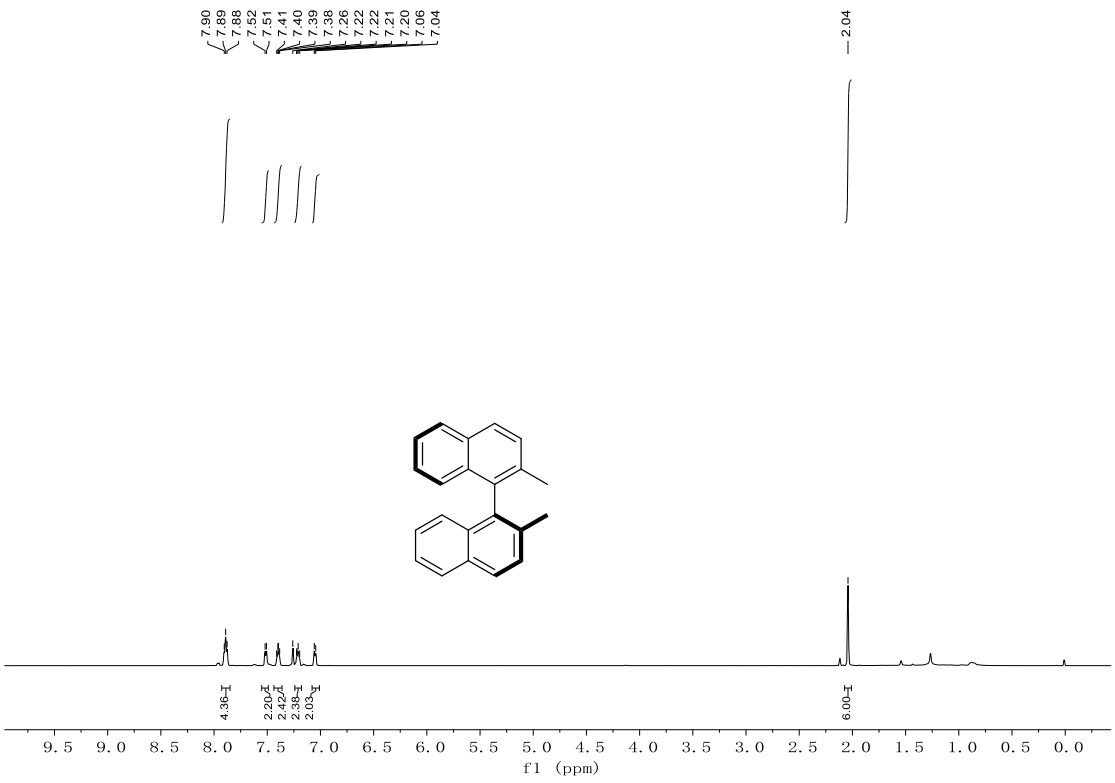


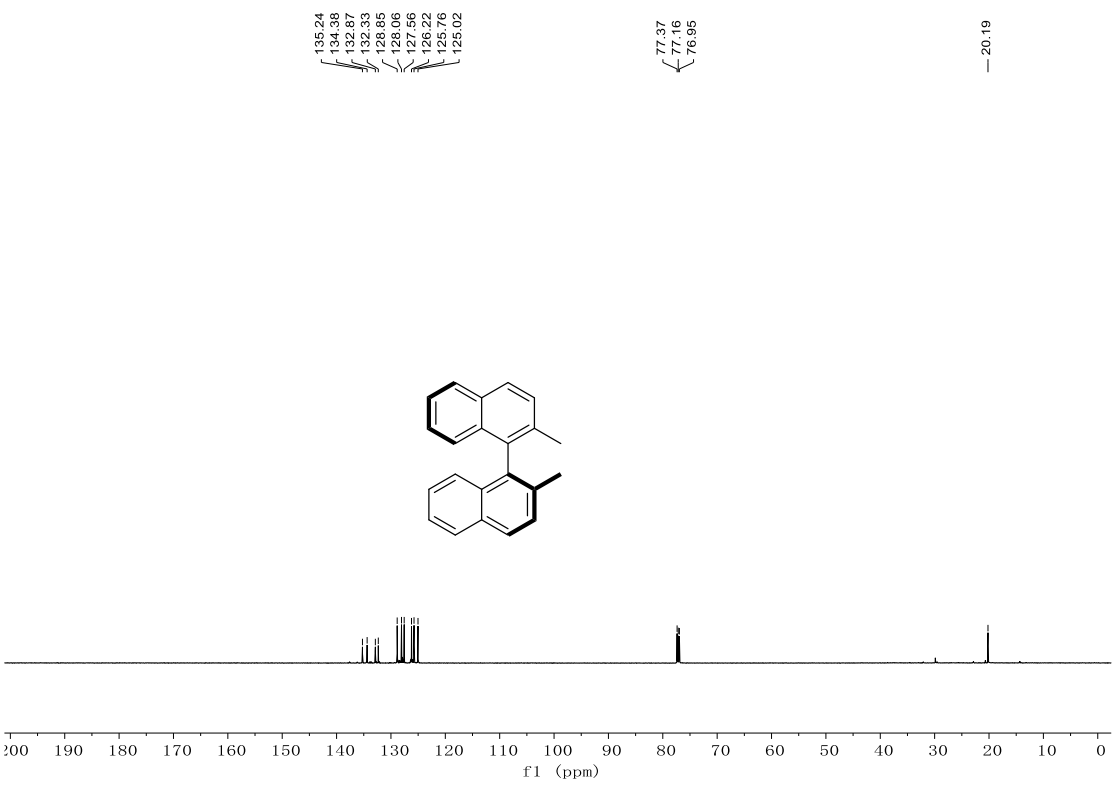
1,4-dimethylnaphthalene (16a)



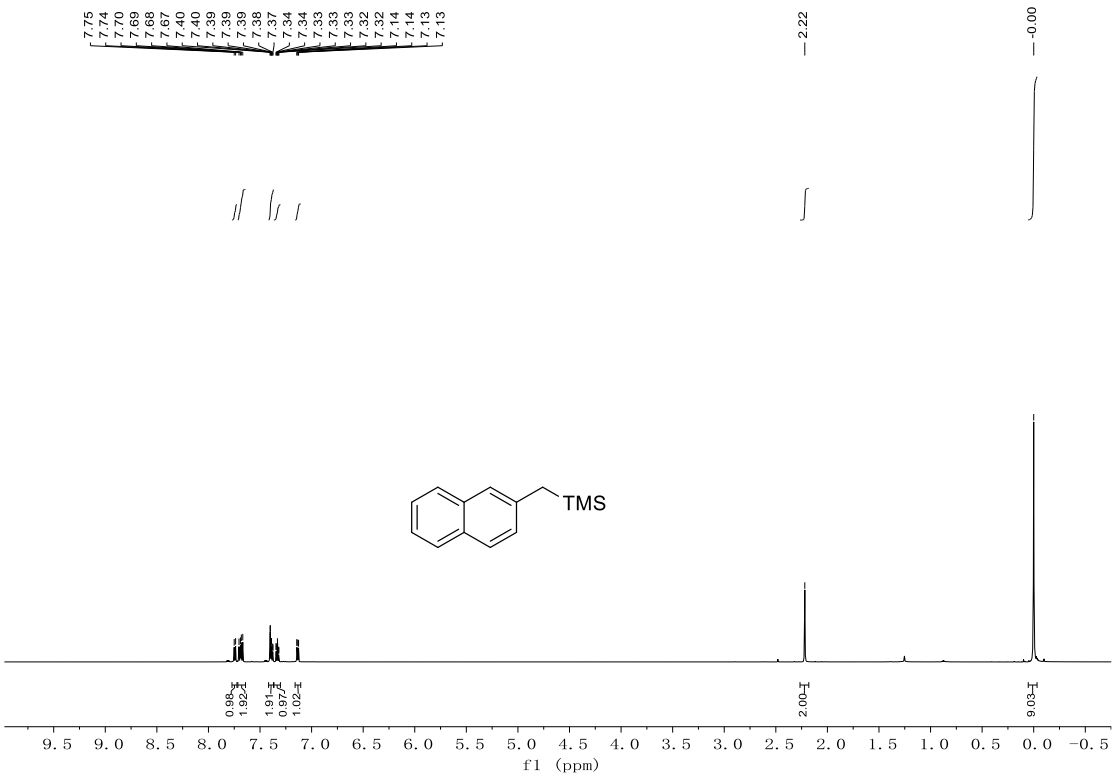


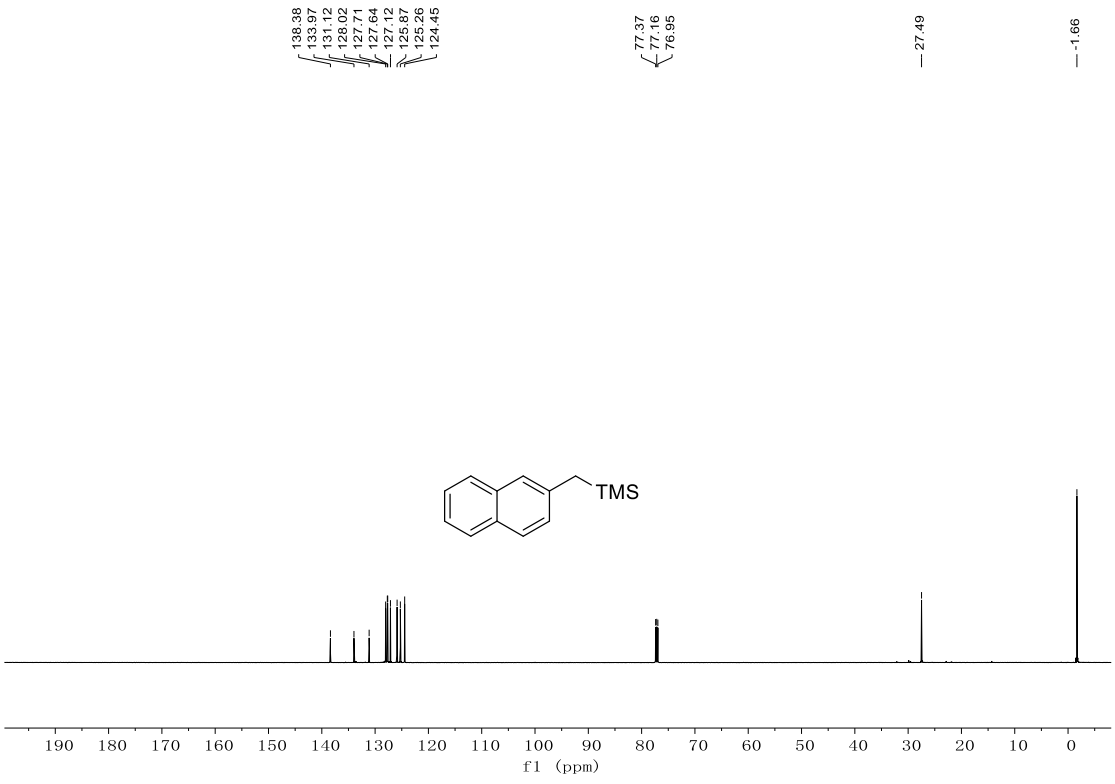
(*S*)-2,2'-dimethyl-1,1'-binaphthalene (17a)



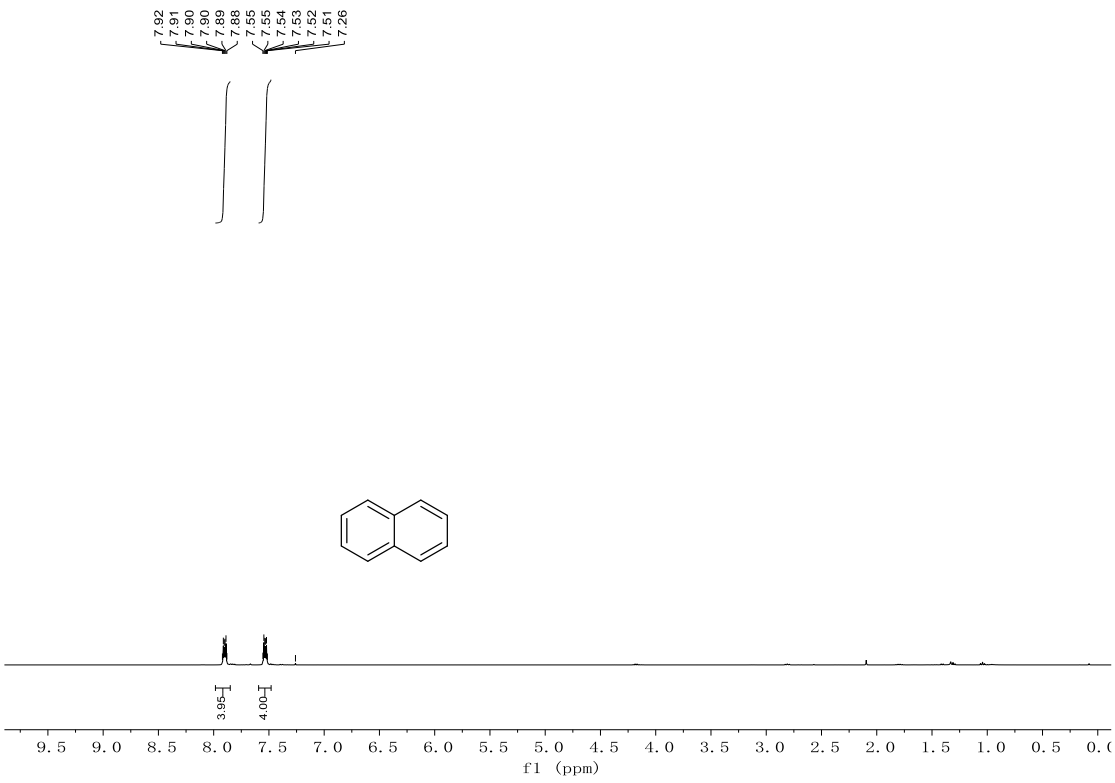


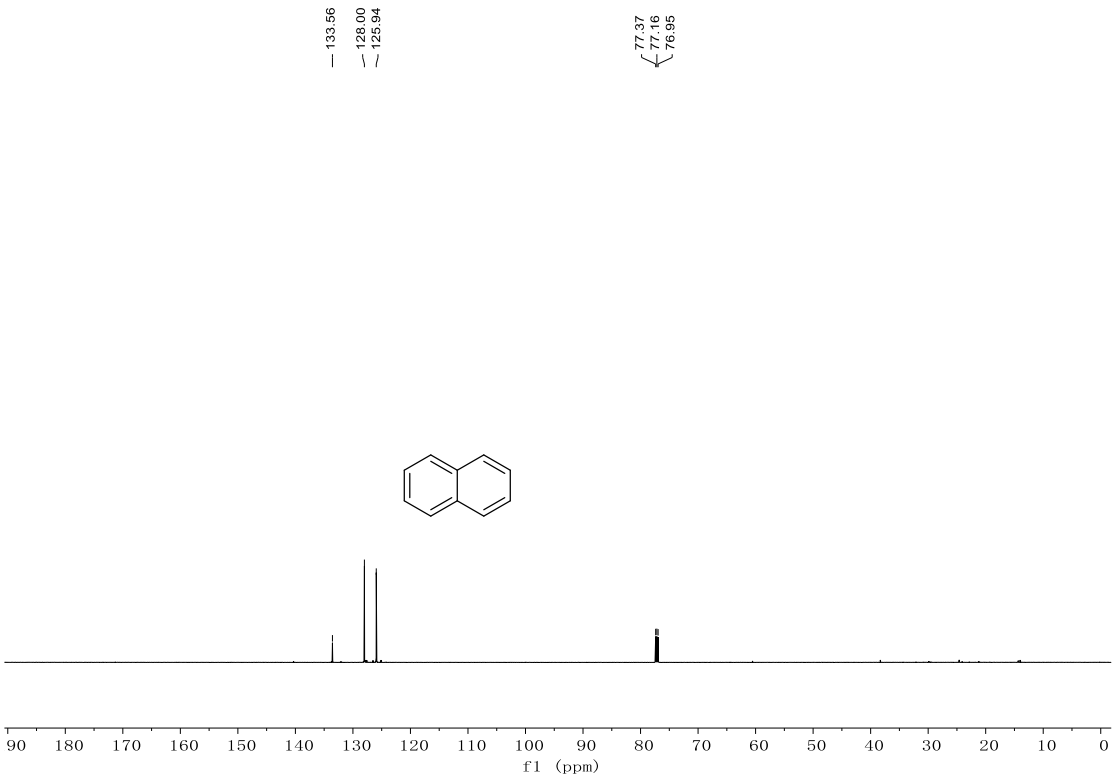
trimethyl(naphthalen-2-ylmethyl)silane (1b)



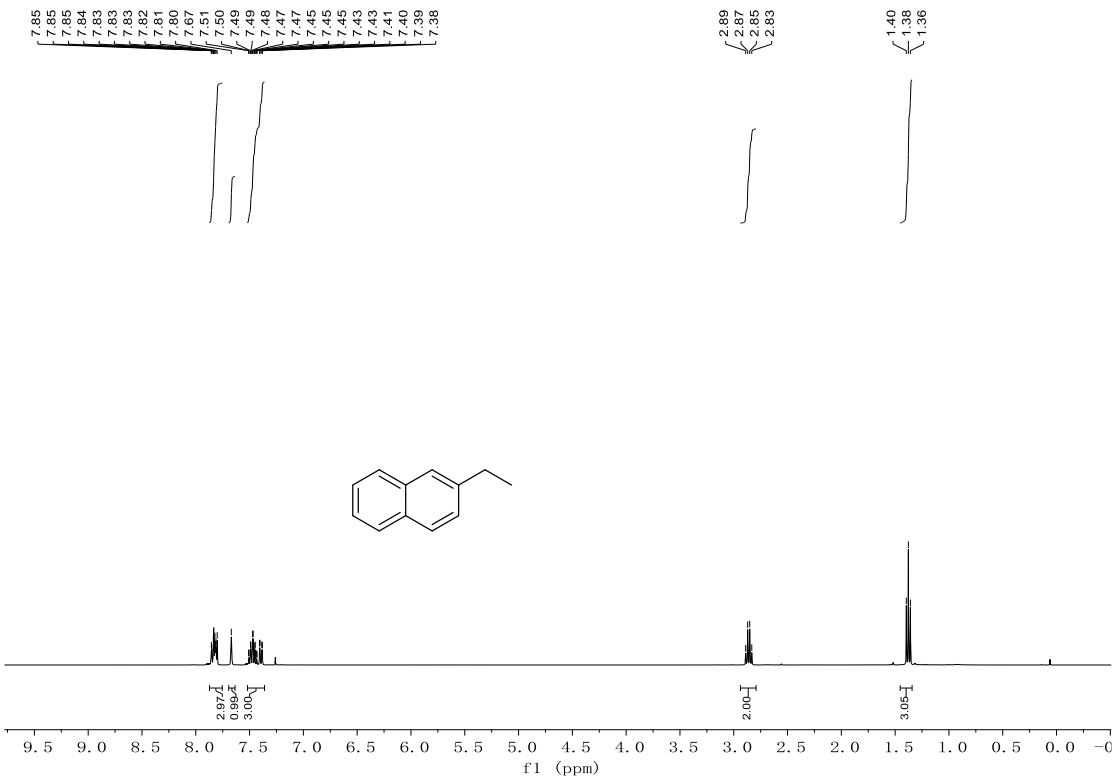


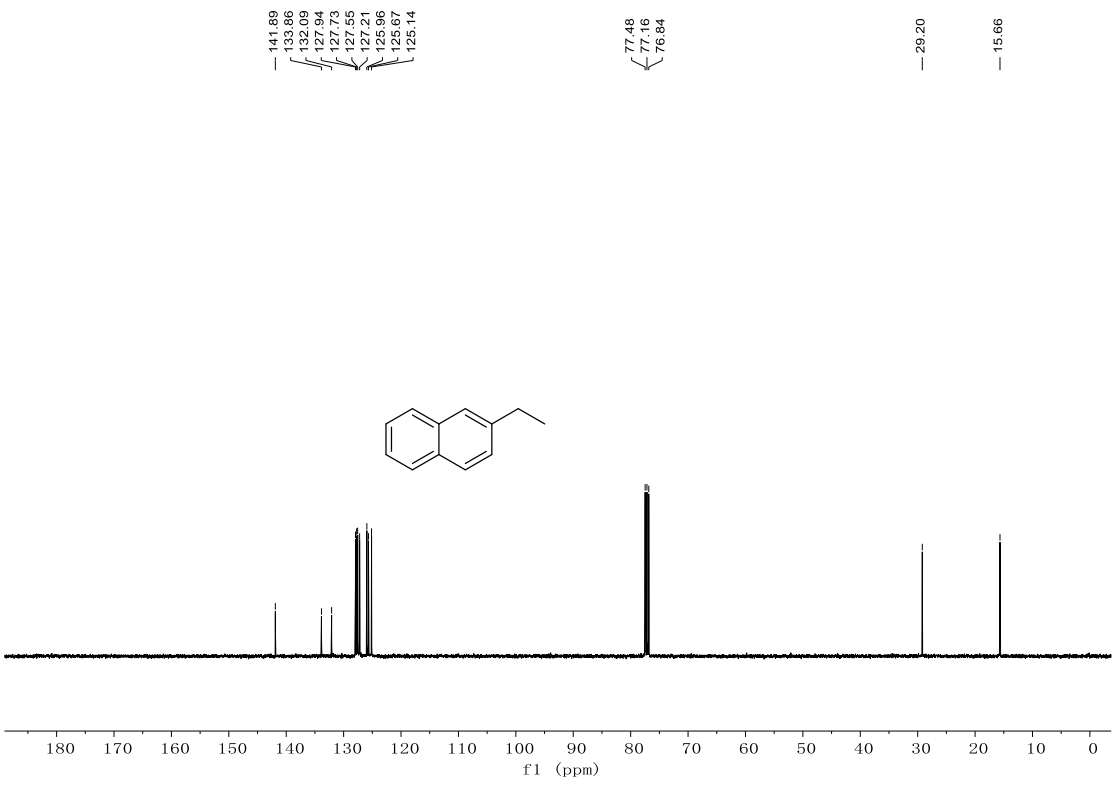
naphthalene (1c)



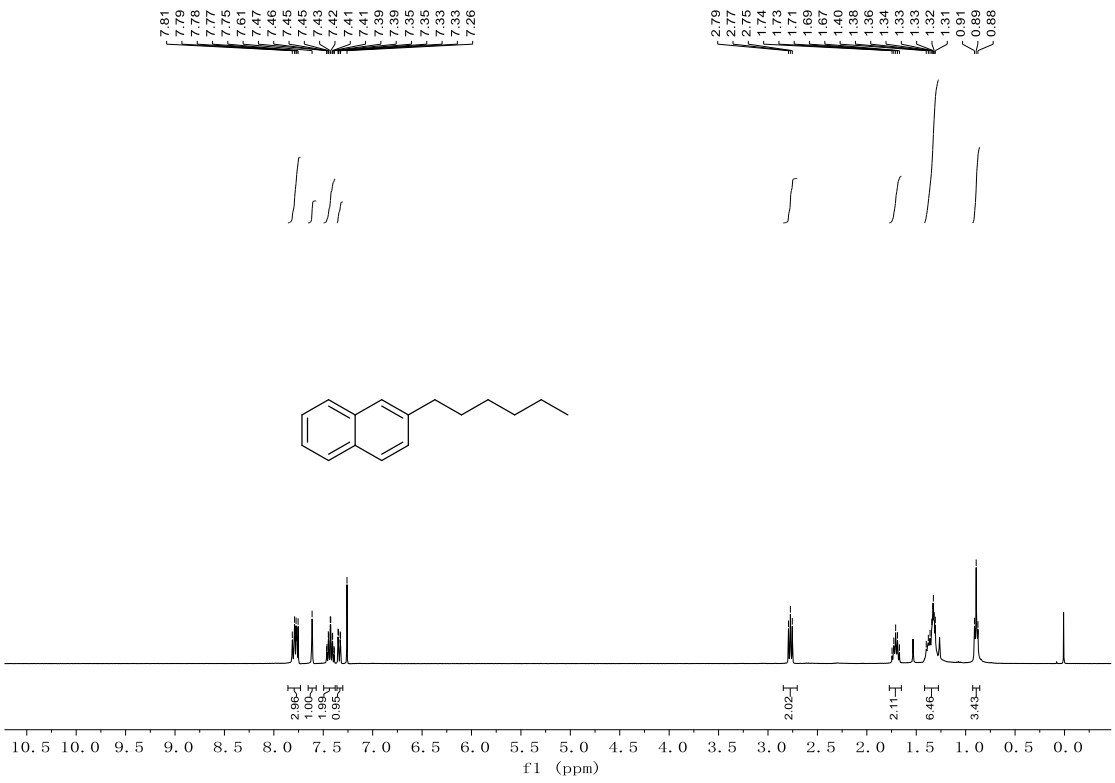


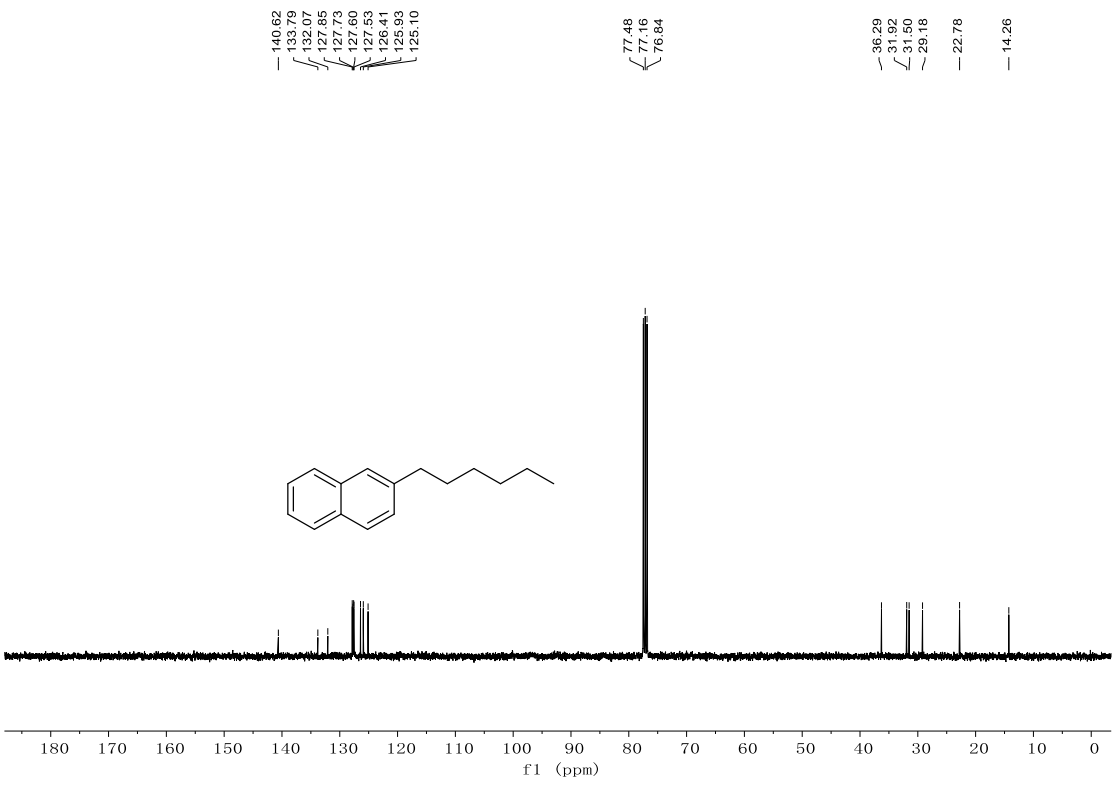
2-ethylnaphthalene (1d)



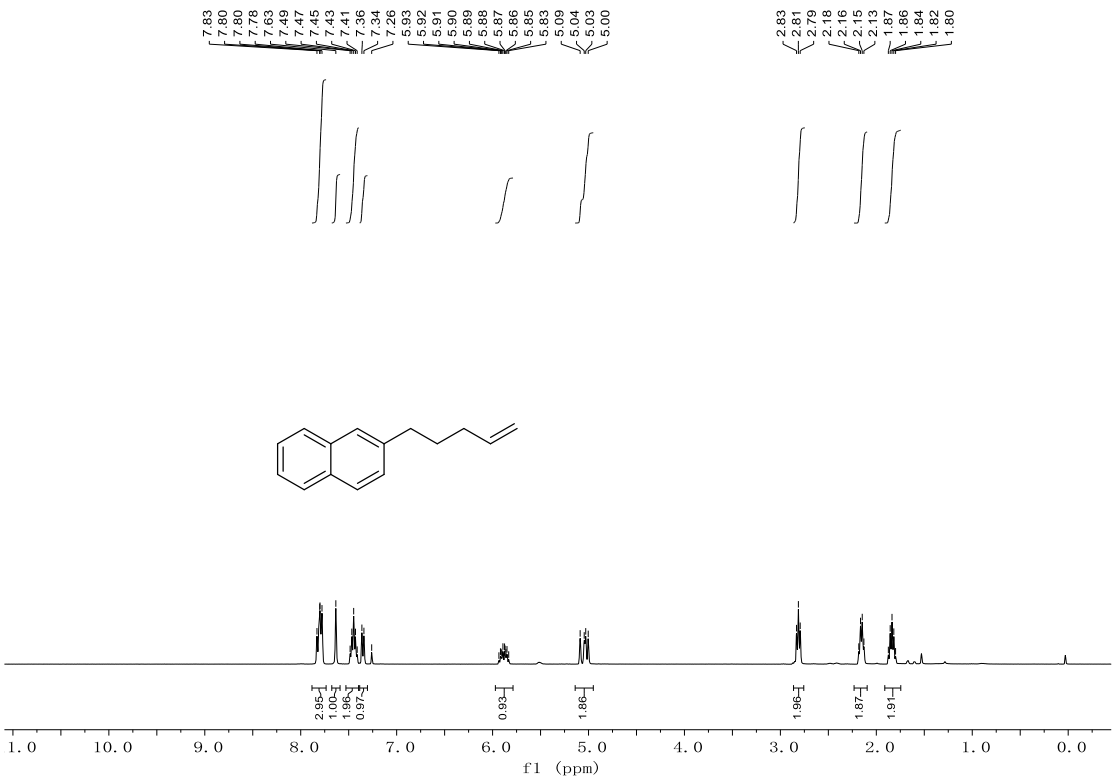


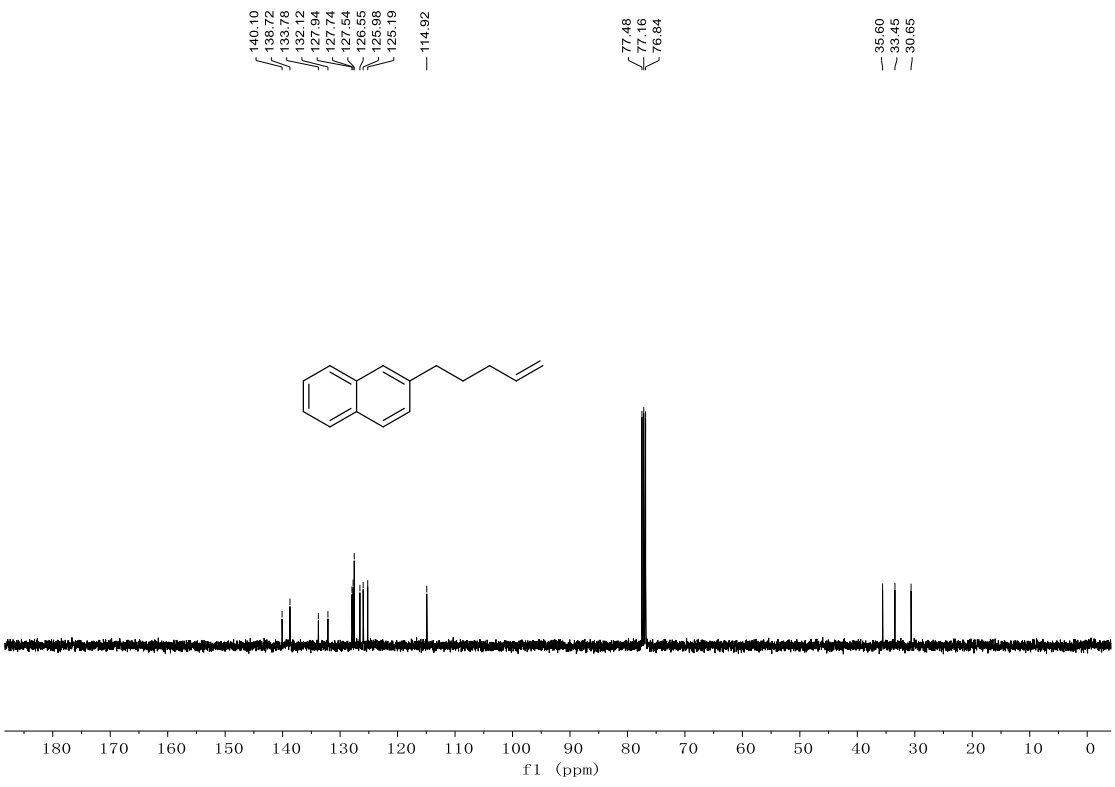
2-hexylnaphthalene (1e)



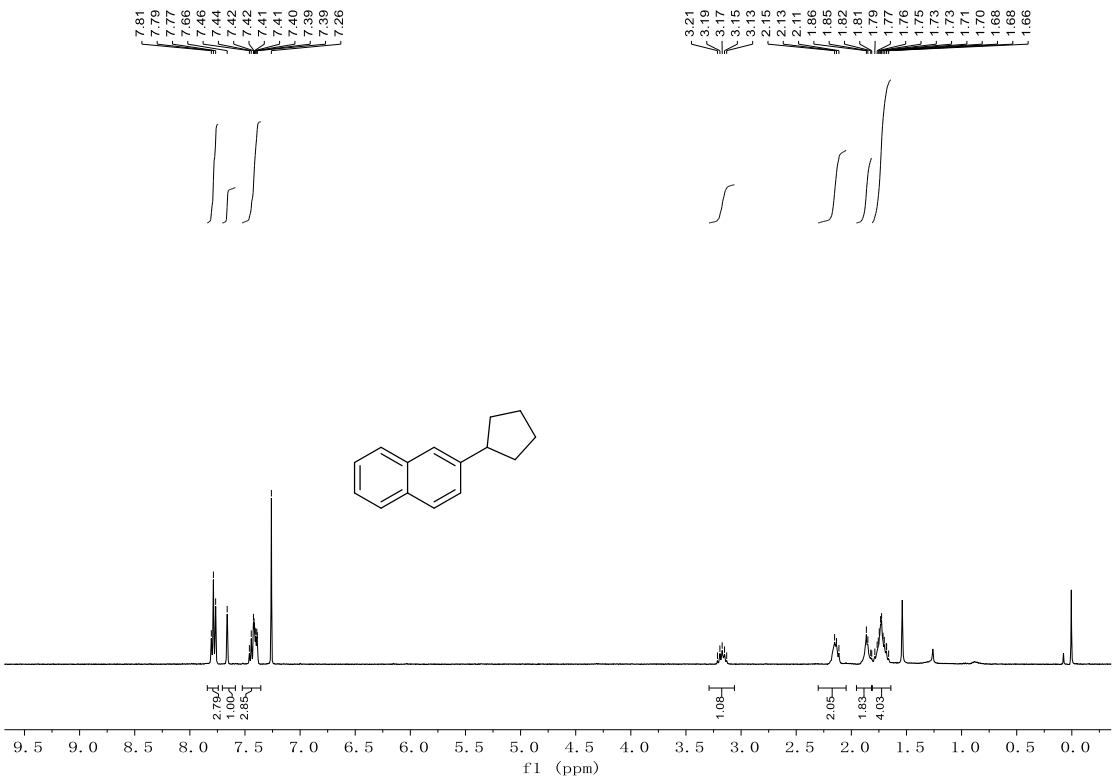


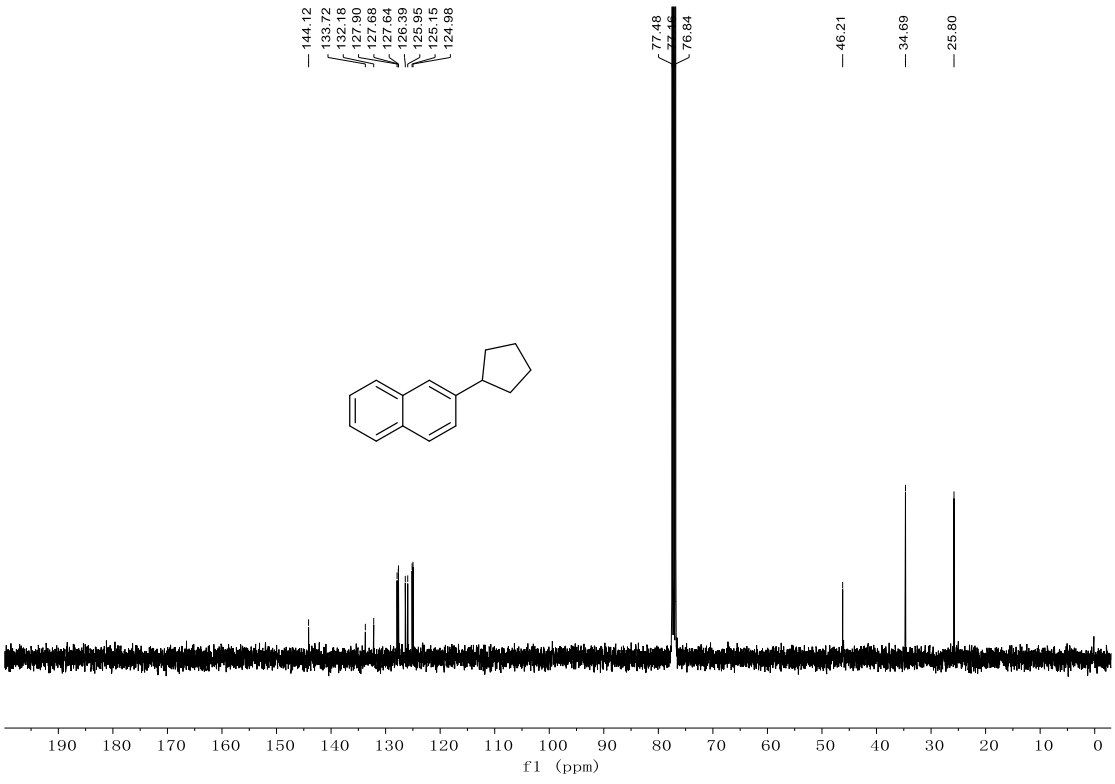
2-(pent-4-en-1-yl)naphthalene (1f)





2-cyclopentylnaphthalene (1g)





2-cyclohexylnaphthalene (1h)