Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

$TiCl_4$-Mediated Deoxygenative Reduction of Aromatic Ketones to Alkylarenes with Ammonia Borane

Yongjun Zang,[a] Yunfeng Ma,[b] Qilin Xu,[a] Guosi Li,[a] Naidong Chen[a], Xing Li,*[c] and Fucheng Zhu*[a]

[a]Anhui Province Key Laboratory for Quality Evaluation and Improvement of Traditional Chinese Medicine, Department of Biological and Pharmaceutical Engineering, West Anhui University, Lu'an, 237012, Anhui, P.R. China. E-mail address: fucheng323@163.com.

[b]Anhui Anlito Biological Technology Co., LTD，Anhui Huoshan Economic and Technological Development Zone P.R. China. 237200.

[c]College of Pharmacy and Chemistry & Chemical Engineering, Taizhou University, Taizhou, Jiangsu 225300, P.R. China. E-mail: lixingluck@126.com

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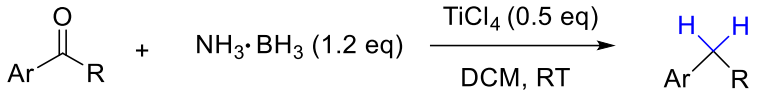
1. General Information

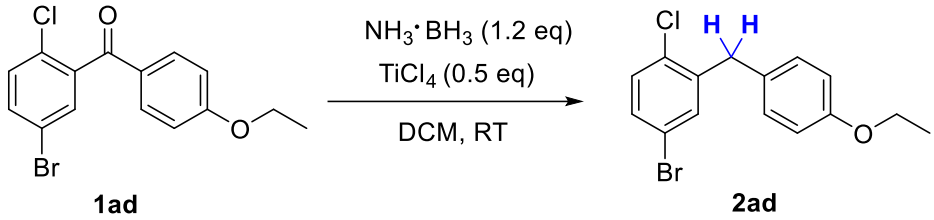
All the reagents and solvents were obtained via commercial sources and used without further purification. Ammonia Borane (purity, 98.6%) was purchased from Shanghai Haohong Scientific Co.,Ltd. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F254 plates (Qingdao Ocean Chemical Company, China). Column chromatography was carried out on silica gel (200-300 mesh, Qingdao Ocean Chemical Company, China). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker 600 MHz and 151 MHz respectively, using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Data are reported in chemical shifts, integration, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplets, dd = doublet of doublet), and coupling constants (*J*) in Hz.

2. The typical reaction procedures



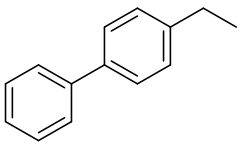
A 10 mL dried round-bottom flask was charged with ketones (1 mmol, 1 equiv), DCM (2 mL) was added, and the solution was stirred at room temperature. Subsequently, titanium tetrachloride ($TiCl_4$) (0.5 mmol, 0.5 eq) was added dropwise to the solution slowly. Then solid ammonia borane (NH_3BH_3) (1.2 mmol, 1.2 eq) was added to the reaction mixture. Upon complete addition, the reaction was stirred at room temperature for 1 h, and monitored by TLC. On completion of the reaction, the mixture was quenched with 1N HCl (2.0 mL). Then the mixture was extracted with CH_2Cl_2 (3 ×□2 mL). The combined organic phases were dried over Na_2SO_4, then filtered and evaporated under reduced pressure. The crude product was purified by a silica gel-packed flash chromatography column with pure hexane as the eluent to give the pure desired products.

3. Gram scale synthesis

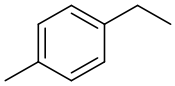


A 100 mL dried round-bottom flask was charged with **1ad** (1.94g, 6.0 mmol), DCM (10 mL) was added, and the solution was stirred in an ice-water bath. Subsequently, titanium tetrachloride ($TiCl_4$) (330 uL, 3.0 mmol) was added dropwise to the solution slowly. Then solid ammonia borane (NH_3BH_3) (223 mg, 7.2 mmol) was added to the reaction mixture. Upon complete addition, the reaction was stirred at room temperature for 1 h, and monitored by TLC. On completion of the reaction, the mixture was quenched with 1N HCl (10 mL). Then the mixture was extracted with CH_2Cl_2 (3 ×□6 mL). The combined organic phases were dried over Na_2SO_4, then filtered and evaporated under reduced pressure. The crude product was purified by a silica gel-packed flash chromatography column with pure hexane as the eluent to give the pure desired **2ad** (1.91g, 98% yield).

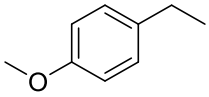
4. Characterization data for the compounds



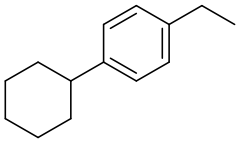
4-ethyl-1,1'-biphenyl (2a)[1]: White solid (178 mg, 99%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 2H), 2.69 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.42, 141.23, 138.65, 128.74, 128.32, 127.12, 127.05, 127.00, 28.55, 15.62.



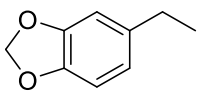
1-ethyl-4-methylbenzene (2b)[2]: colorless oil (108 mg, 90%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (s, 4H), 2.61 (q, *J* = 7.6 Hz, 2H), 2.32 (s, 3H), 1.22 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.67, 136.65, 128.74, 113.77, 55.28, 28.01, 15.80.



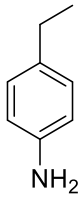
1-ethyl-4-methoxybenzene (2c)[2]: colorless oil (121 mg, 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.5 Hz, 1H), 6.83 (d, *J* = 8.6 Hz, 1H), 3.79 (s, 3H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 128.58, 113.78, 54.52, 27.83, 16.09.



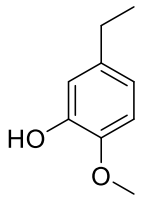
1-cyclohexyl-4-ethylbenzene (2d)[1]: colorless oil (160 mg, 86%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 (s, 4H), 2.62 (q, *J* = 7.6 Hz, 2H), 2.51 – 2.42 (m, 1H), 1.92 – 1.79 (m, 4H), 1.77 – 1.71 (m, 1H), 1.45 – 1.33 (m, 4H), 1.23 (t, *J* = 7.6 Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.39, 141.57, 127.75, 126.74, 44.20, 34.59, 28.43, 27.00, 26.24, 15.58.



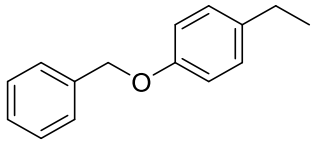
5-ethylbenzo[d][1,3]dioxole (2e)[3]: colorless oil (102 mg, 68%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.72 (d, *J* = 7.9 Hz, 1H), 6.69 (s, 1H), 6.64 (d, *J* = 8.5 Hz, 1H), 5.90 (s, 2H), 2.56 (q, *J* = 7.6 Hz, 2H), 1.19 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.52, 145.41, 138.24, 120.42, 108.43, 108.11, 100.70, 28.35, 15.81.



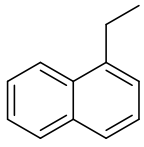
4-ethylaniline (2f)[4]: yellow oil (94 mg, 78%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.98 (d, *J* = 8.2 Hz, 2H), 6.61 (d, *J* = 8.3 Hz, 2H), 3.39 (s, 2H), 2.53 (q, *J* = 7.6 Hz, 2H), 1.18 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.11, 134.50, 128.53 (d, *J* = 31.7 Hz), 115.34, 28.03, 16.00.



5-ethyl-2-methoxyphenol (2g)[5]: colorless oil (115 mg, 76%).^{1}H NMR (600 MHz, $CDCl_3$) δ 6.79 (s, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 6.67 (d, *J* = 8.1 Hz, 1H), 5.59 (s, 1H), 3.85 (s, 3H), 2.55 (q, *J* = 7.6 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.46, 144.60, 137.76, 119.05, 114.19, 110.66, 56.05, 28.26, 15.77.

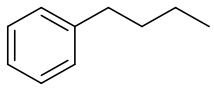


1-(benzyloxy)-4-ethylbenzene (2h)[6]: White solid (150 mg, 71%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 5.04 (s, 2H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H) ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.89, 137.31, 136.72, 128.75, 128.57 , 127.89, 127.49, 114.74, 70.10, 28.01, 15.87.

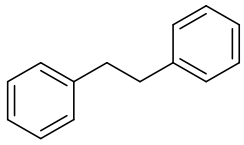


1-ethylnaphthalene (2i)[1]: White solid (140 mg, 90%). ^{1}H NMR (600 MHz, $CDCl_3$) δ

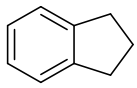
8.05 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 6.9 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.33 (d, *J* = 7.0 Hz, 1H), 3.11 (q, *J* = 7.5 Hz, 2H), 1.38 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.30, 133.84, 131.80, 128.76, 126.40, 125.69, 125.41, 124.87, 123.76, 25.91, 15.06.



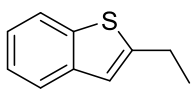
Butylbenzene (2j)[2]: colorless oil (114 mg, 85%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.21 – 7.13 (m, 3H), 2.66 – 2.57 (m, 2H), 1.64 – 1.57 (m, 2H), 1.40 – 1.32 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.52 , 139.38, 128.56, 128.43, 127.53, 100.42, 34.17, 14.56.



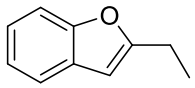
1,2-diphenylethane (2k)[7]: White solid (142 mg, 78%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.5 Hz, 4H), 7.19 (t, *J* = 7.8 Hz, 6H), 2.92 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.81, 128.47, 128.35, 125.93, 37.96.



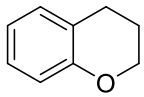
2,3-dihydro-1H-indene (2l)[2]: colorless oil (73 mg, 62%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 5.0, 3.5 Hz, 2H), 7.13 (dd, *J* = 5.4, 3.2 Hz, 2H), 2.91 (t, *J* = 7.4 Hz, 4H), 2.13 – 1.99 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.96, 125.97, 124.37, 32.87, 25.34 .



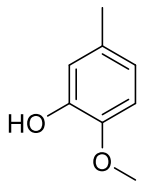
2-ethylbenzo[b]thiophene (2m)[8]: colorless oil (130 mg, 80%).^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 7.0 Hz, 1H), 7.00 (s, 1H), 2.94 (q, *J* = 7.5 Hz, 2H), 1.38 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.33, 140.26, 139.21, 124.04, 123.36, 122.69, 122.13, 119.66.



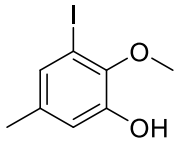
2-ethylbenzofuran (2n)[9]: colorless oil (108 mg, 76%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.3 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.14 (m, 2H), 2.80 (q, *J* = 7.5 Hz, 2H), 1.33 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.02, 154.64, 129.01, 123.06, 122.36, 120.19, 110.68, 100.99, 21.80, 11.90.



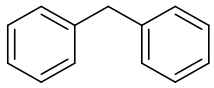
Chromane (2o)[2]: Colorless oil (100 mg, 75%).^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (t, *J* = 7.7 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 4.18 (t, *J* = 6.0 Hz, 2H), 2.78 (t, *J* = 6.5 Hz, 2H), 2.05 – 1.95 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.92, 129.83, 127.21, 122.24, 120.11, 116.71, 66.44, 24.89, 22.40.



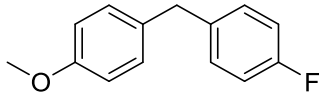
2-methoxy-5-methylphenol (2p)[10]: White solid (89 mg, 65%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.77 – 6.72 (m, 2H), 6.64 (d, *J* = 8.1 Hz, 1H), 5.55 (s, 1H), 3.85 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.37, 144.45, 131.16, 120.26, 115.36, 110.64, 56.07, 20.78.



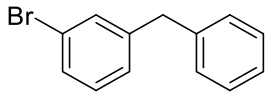
3-iodo-2-methoxy-5-methylphenol (2q): White solid (158 mg, 60%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (s, 1H), 6.64 (s, 1H), 5.91 (s, 1H), 3.86 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.77, 143.47, 131.39, 130.46, 111.88, 81.07, 56.18, 20.62. HRMS (ESI) calcd for $C_8H_9IO_2$: $[M - H]^-$ = 262.9574, found m/z = 262.9572.



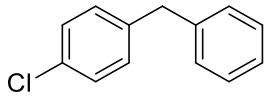
Diphenylmethane (2r)[1]: White solid (137 mg, 83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.7 Hz, 4H), 7.19 (t, *J* = 7.1 Hz, 6H), 3.98 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.15, 128.97, 128.49, 126.10, 41.98.



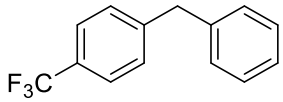
1-fluoro-4-(4-methoxybenzyl)benzene (2s)[11]: Colorless oil (210 mg, 98%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.95 (t, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.88 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.39 (d, *J* = 243.4 Hz), 158.08, 137.26 (d, *J* = 3.2 Hz), 133.09, 130.1, 130.14, 129.80, 115.18 (d, *J* = 20.9 Hz), 113.97 , 55.27, 40.20.



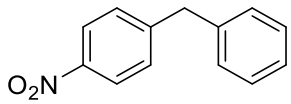
1-benzyl-3-bromobenzene (2t)[12]: Colorless oil (242 mg, 98%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 4H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.19 – 7.15 (m, 2H), 7.13 (d, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 3.94 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.48, 140.19, 131.94, 130.03, 129.26, 128.95, 128.64, 127.60, 126.41, 122.58, 41.56.



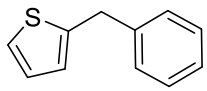
1-benzyl-4-chlorobenzene (2u)[7]: Colorless oil (187 mg, 93%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.22 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 3.94 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.58 , 139.61, 131.92, 130.28, 128.89, 128.60, 126.32, 41.27.



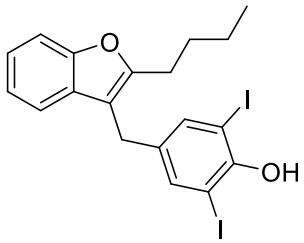
1-benzyl-4-(trifluoromethyl)benzene (2v)[13]: Colorless oil (233 mg, 100%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 4H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 2H), 4.03 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.22, 139.99, 129.20, 128.95, 128.68, 126.48, 125.41 (dd, *J* = 7.3, 3.4 Hz), 41.72.



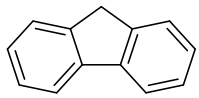
1-benzyl-4-nitrobenzene (2w)[14]: Colorless oil (188 mg, 89%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.7 Hz, 2H), 7.32 (dd, *J* = 12.7, 8.2 Hz, 4H), 7.27 – 7.23 (m, 1H), 7.17 (d, *J* = 7.2 Hz, 2H), 4.07 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.89, 146.54 , 139.21, 129.67, 128.98, 128.84, 126.78, 123.77, 41.74.



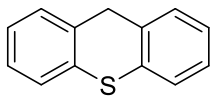
2-benzylthiophene (2x)[11]: Colorless oil (135 mg, 78%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.19 (m, 3H), 7.13 (d, *J* = 5.1 Hz, 1H), 6.94 – 6.89 (m, 1H), 6.79 (d, *J* = 3.3 Hz, 1H), 4.15 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.07, 140.44, 128.62, 128.57, 126.84, 126.51, 125.18, 123.96.



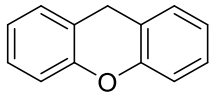
4-((2-butylbenzofuran-3-yl)methyl)-2,6-diiodophenol (2y): White solid (507 mg, 95%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (s, 2H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 5.61 (s, 1H), 3.84 (s, 2H), 2.74 (t, *J* = 7.5 Hz, 2H), 1.76 – 1.65 (m, 2H), 1.43 – 1.32 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.84, 154.06, 151.99 , 138.84, 135.98, 129.08, 123.40, 122.33, 118.98, 111.83, 110.81, 82.25, 30.46, 27.72 , 26.20, 22.46, 13.88. HRMS (ESI) calcd for $C_{19}H_{18}I_2O_2$: $[M - H]^-$ = 530.9323, found m/z = 530.9314.



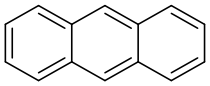
9H-fluorene (2z)[11]: White solid (172 mg, 100%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 – 7.14 (m, 4H), 7.09 – 6.99 (m, 4H), 4.04 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.99, 128.93, 127.65, 122.97, 120.60, 116.48, 27.90.



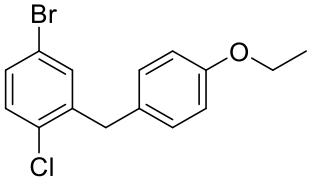
9H-thioxanthene (2aa)[11]: White solid (162 mg, 82%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.1 Hz, 2H), 7.30 (d, *J* = 7.0 Hz, 2H), 7.22 – 7.14 (m, 4H), 3.84 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.23, 133.88, 127.96, 126.89, 126.63, 126.55, 39.23.



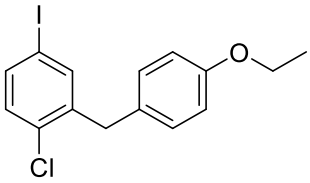
9H-xanthene (2ab)[11]: Colorless oil (186 mg, 100%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 – 7.13 (m, 4H), 7.08 – 6.96 (m, 4H), 4.04 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.99, 128.93, 127.66, 122.97, 120.60, 116.49, 27.90.



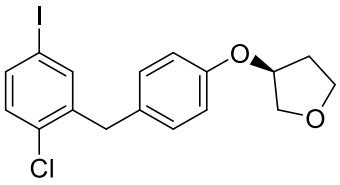
Anthracene (2ac)[15]: White solid (166 mg, 93%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (s, 2H), 7.99 (dd, *J* = 6.3, 3.1 Hz, 4H), 7.45 (dd, *J* = 6.5, 3.1 Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 131.71, 128.19, 126.24, 125.36.



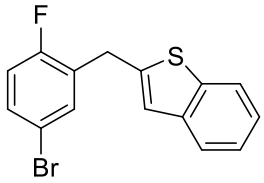
4-bromo-1-chloro-2-(4-ethoxybenzyl)benzene (2ad)[16]: White solid (309 mg, 96%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 6.7 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 4.04 – 3.99 (m, 2H), 3.98 (s, 2H), 1.40 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.69 141.39, 133.58, 133.11, 130.89, 130.56, 130.41, 129.98, 120.49, 114.65, 63.43, 38.24, 14.91.



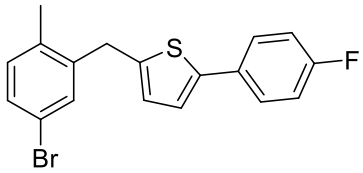
1-chloro-2-(4-ethoxybenzyl)-4-iodobenzene (2ae)[17]: White solid (369 mg, 98%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.07 (dd, *J* = 8.3, 3.2 Hz, 3H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.01 (q, *J* = 7.0 Hz, 2H), 3.96 (s, 2H), 1.40 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.64, 141.57, 139.54, 136.55, 134.22, 131.19, 130.47, 129.91 , 114.62, 91.67, 63.43, 38.08, 14.90.



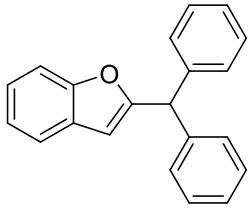
(S)-3-(4-(2-chloro-5-iodobenzyl)phenoxy)tetrahydrofuran (2af)[18]: White solid (351 mg, 85%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.08 (dd, *J* = 8.4, 2.8 Hz, 3H), 6.80 (s, 1H), 6.79 (s, 1H), 4.91 – 4.88 (m, 1H), 4.01 – 3.94 (m, 5H), 3.91 – 3.87 (m, 1H), 2.22 – 2.11 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.09, 141.40, 139.55, 136.62, 134.22, 131.22, 130.99, 130.01 , 115.50, 91.68, 73.15, 67.22, 38.04, 33.03.



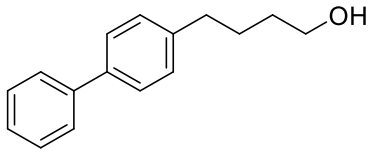
2-(5-bromo-2-fluorobenzyl)benzo[b]thiophene (2ag)[19]: White solid (303 mg, 95%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.36 – 7.29 (m, 2H), 7.29 – 7.25 (m, 1H), 7.03 (s, 1H), 6.96 (t, *J* = 9.0 Hz, 1H), 4.20 (s, 2H). ^{3}C NMR (151 MHz, $CDCl_3$) δ 159.82 (d, *J* = 247.0 Hz), 142.21 (s), 139.87 (d, *J* = 17.6 Hz), 133.53 (d, *J* = 4.0 Hz), 131.55, 131.49, 128.93 (d, *J* = 17.4 Hz), 124.33, 123.98, 123.1 122.31, 122.22, 117.28 (d, *J* = 23.9 Hz), 116.71 (d, *J* = 3.5 Hz), 29.66 (d, *J* = 3.2 Hz).



2-(5-bromo-2-methylbenzyl)-5-(4-fluorophenyl)thiophene (2ah)[16]: White solid (207 mg, 87%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.3, 5.4 Hz, 2H), 7.34 (s, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.12 – 6.99 (m, 4H), 6.67 (d, *J* = 3.1 Hz, 1H), 4.07 (s, 2H), 2.27 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.17 (d, *J* = 246.8 Hz), 142.21, 141.88, 140.36, 135.32, 132.13 (d, *J* = 17.3 Hz), 130.74 (d, *J* = 3.2 Hz), 129.93, 127.21, 127.16, 126.28, 122.75, 119.68, 115.76 (d, *J* = 21.8 Hz), 33.84, 19.04.



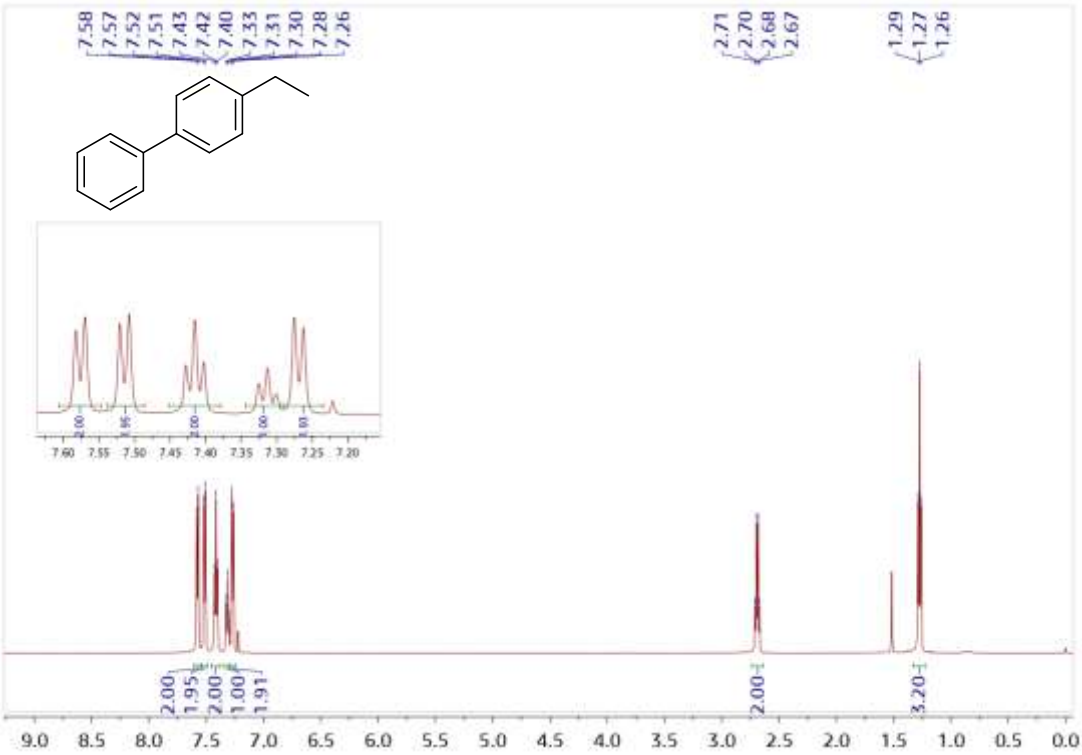
2-benzhydrylbenzofuran[20]: White solid (242 mg, 85%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.4 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 4H), 7.26 (d, *J* = 7.2 Hz, 2H), 7.25 – 7.20 (m, 5H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.27 (s, 1H), 5.58 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.94, 155.15, 141.05, 128.93, 128.61, 128.50, 127.03, 123.77, 122.65, 120.68, 111.20, 105.69, 51.36.

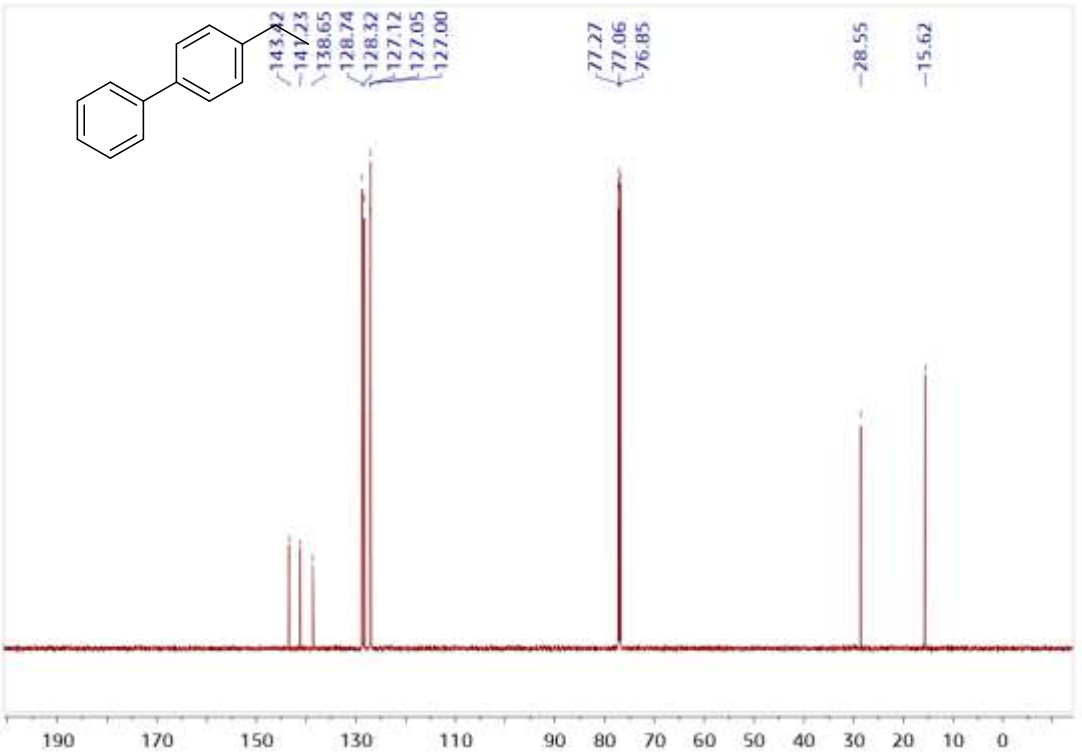


4-([1,1'-biphenyl]-4-yl)butan-1-ol[21]: White solid (181 mg, 80%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.4 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.26 (d, *J* = 6.8 Hz, 2H), 3.68 (t, *J* = 6.5 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 1.79 – 1.70 (m, 2H), 1.68 – 1.60 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.47, 141.12, 138.77, 128.85, 128.73, 127.08, 127.02, 127.01, 62.85 35.28, 32.37, 27.54.

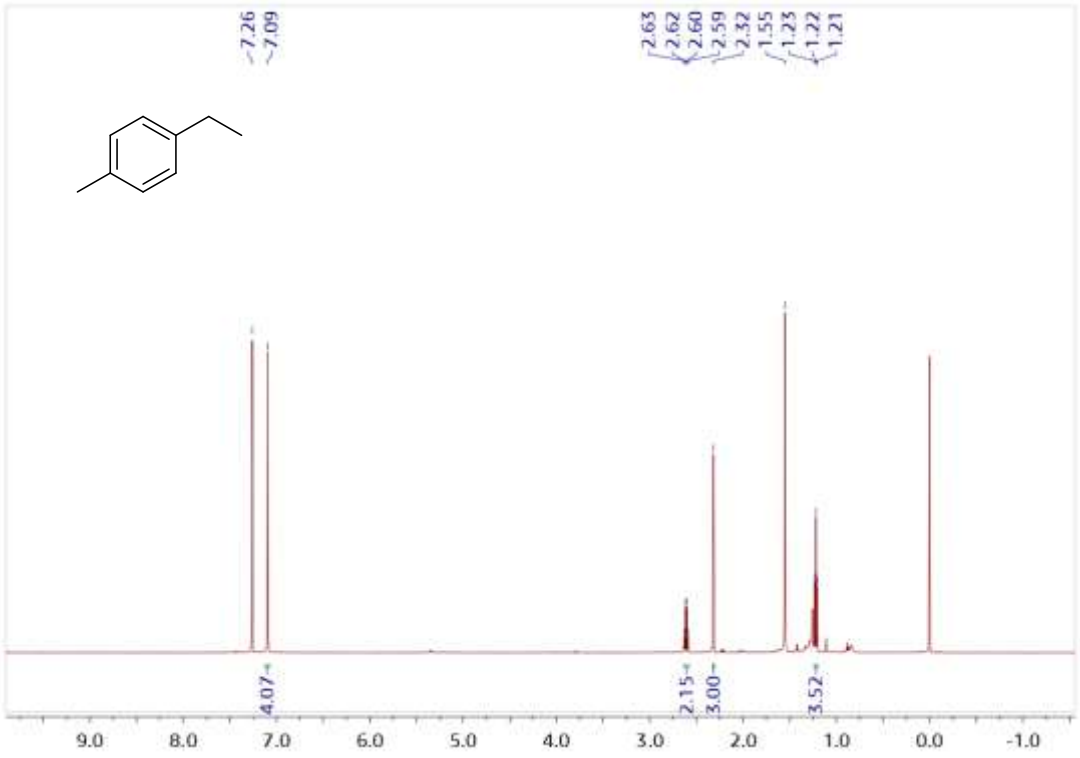
5. Copies of ^{1}H and ^{13}C NMR spectra of all products

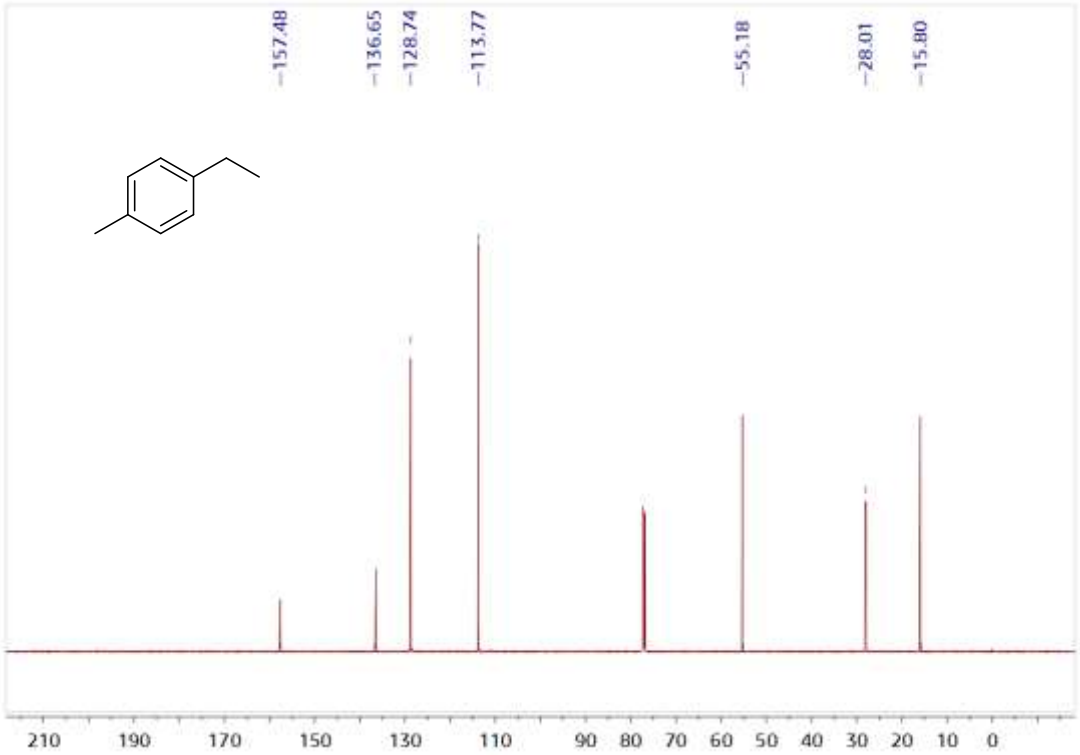
4-ethyl-1,1'-biphenyl (2a)



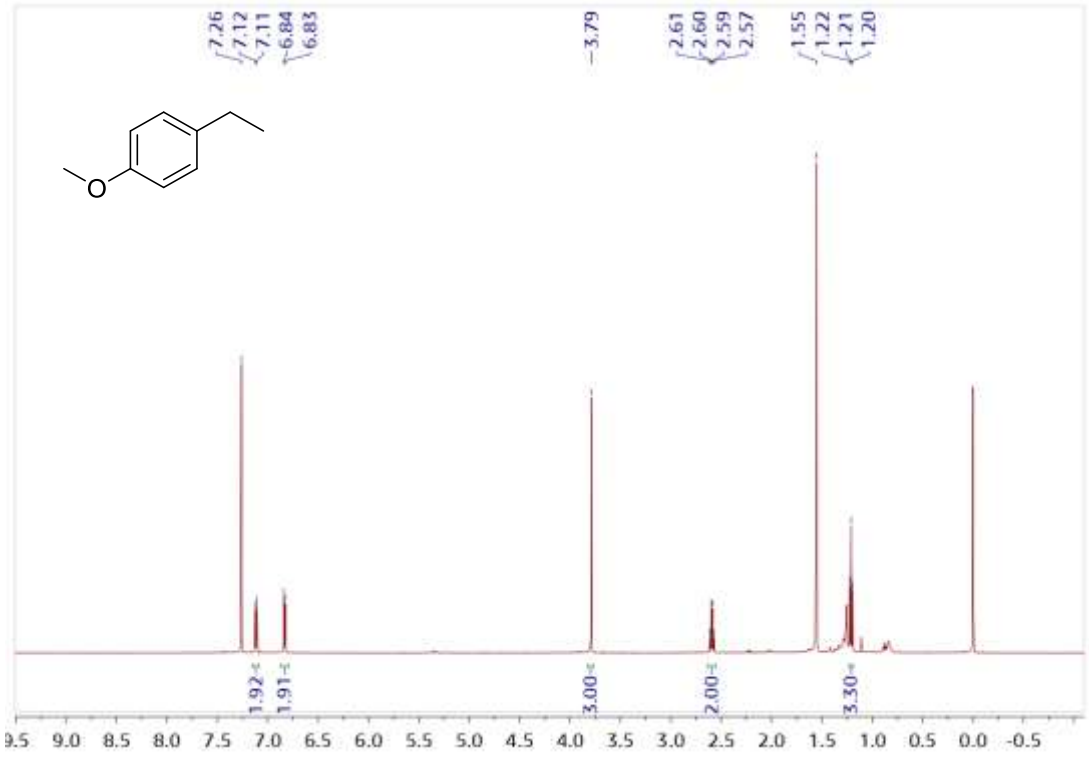


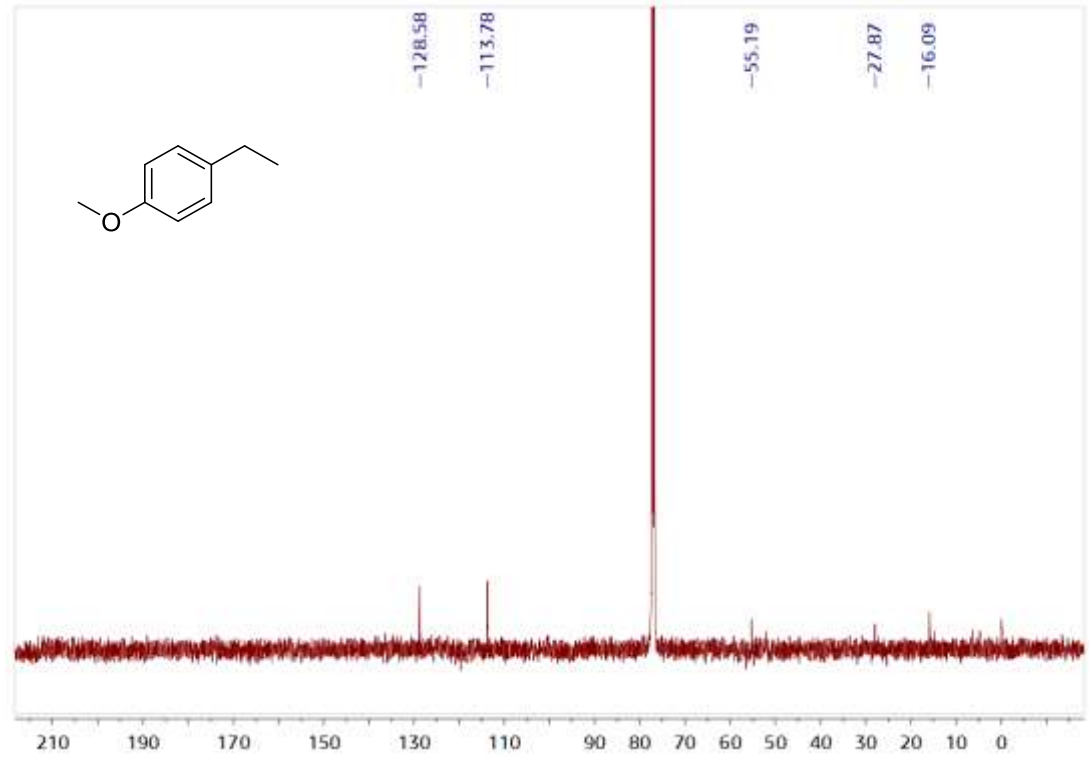
1-ethyl-4-methylbenzene (2b)



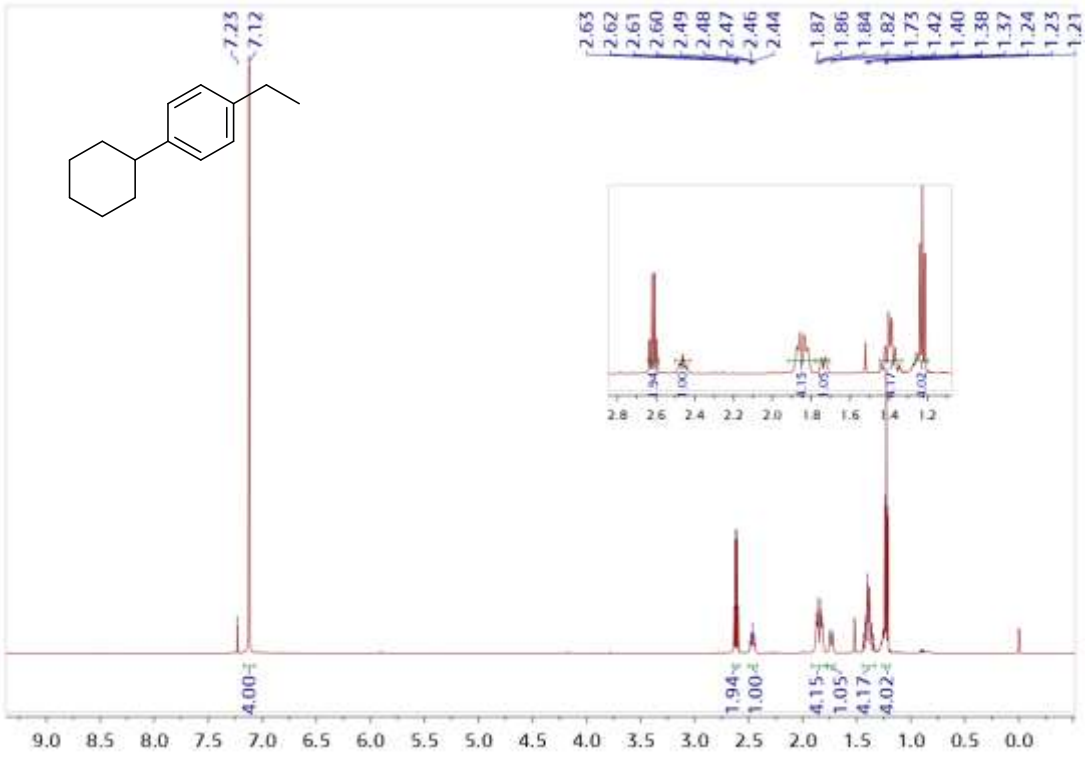


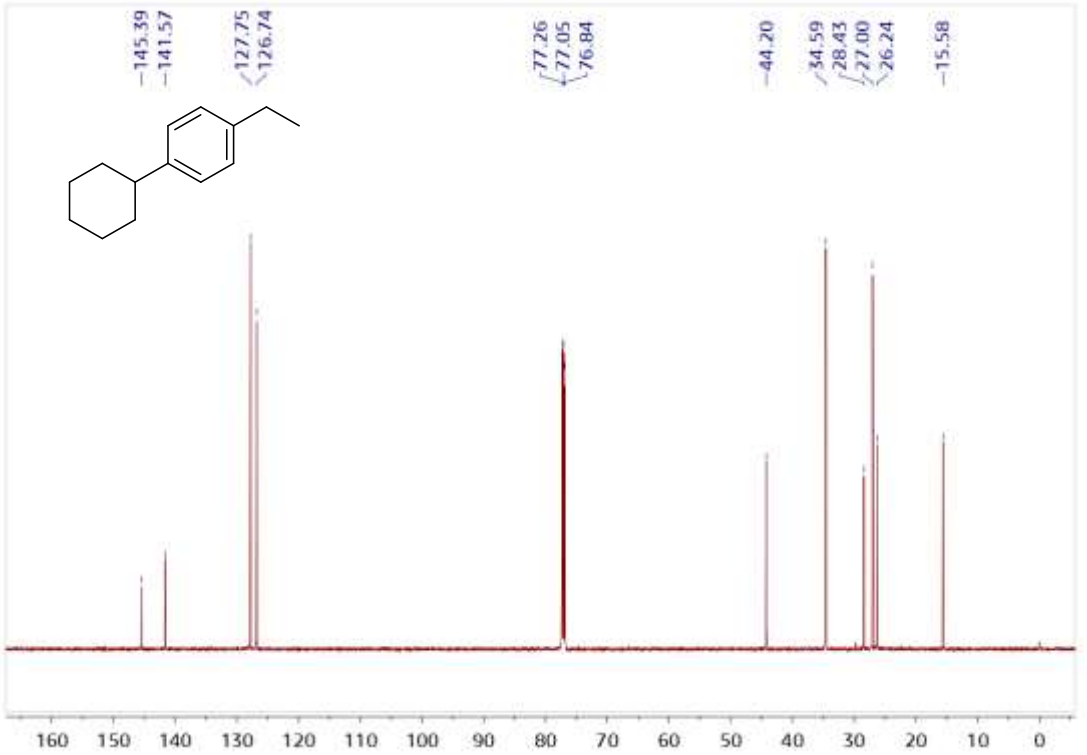
1-ethyl-4-methoxybenzene (2c)



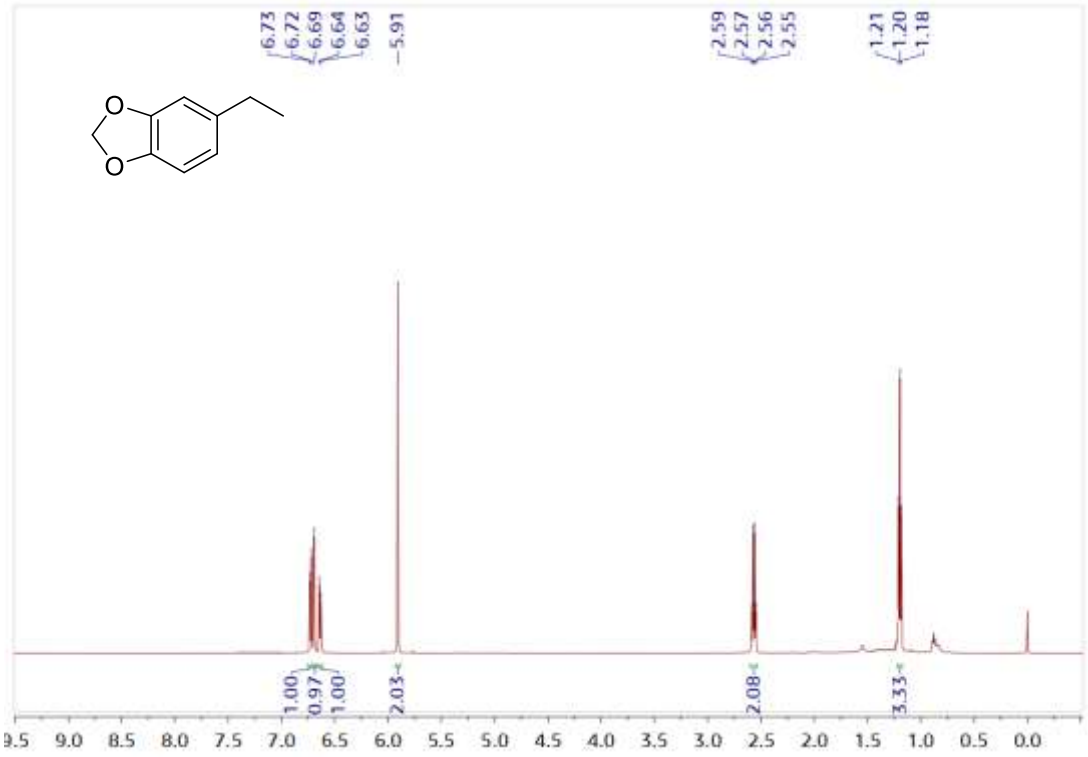


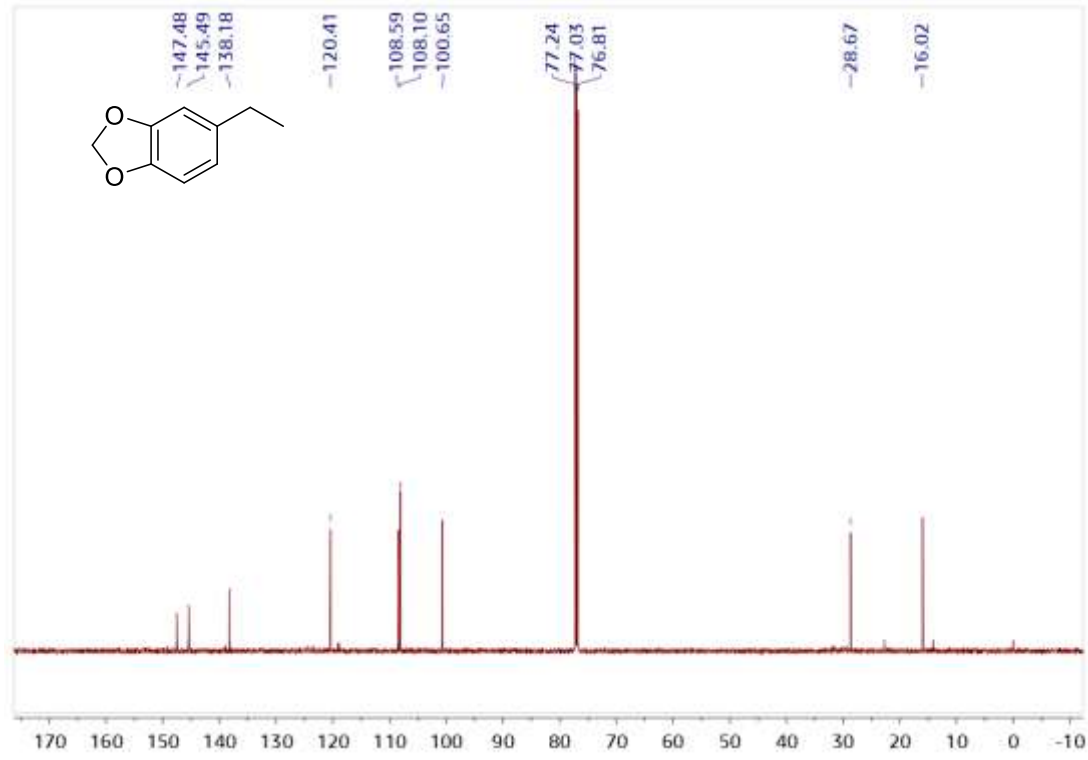
1-cyclohexyl-4-ethylbenzene (2d)



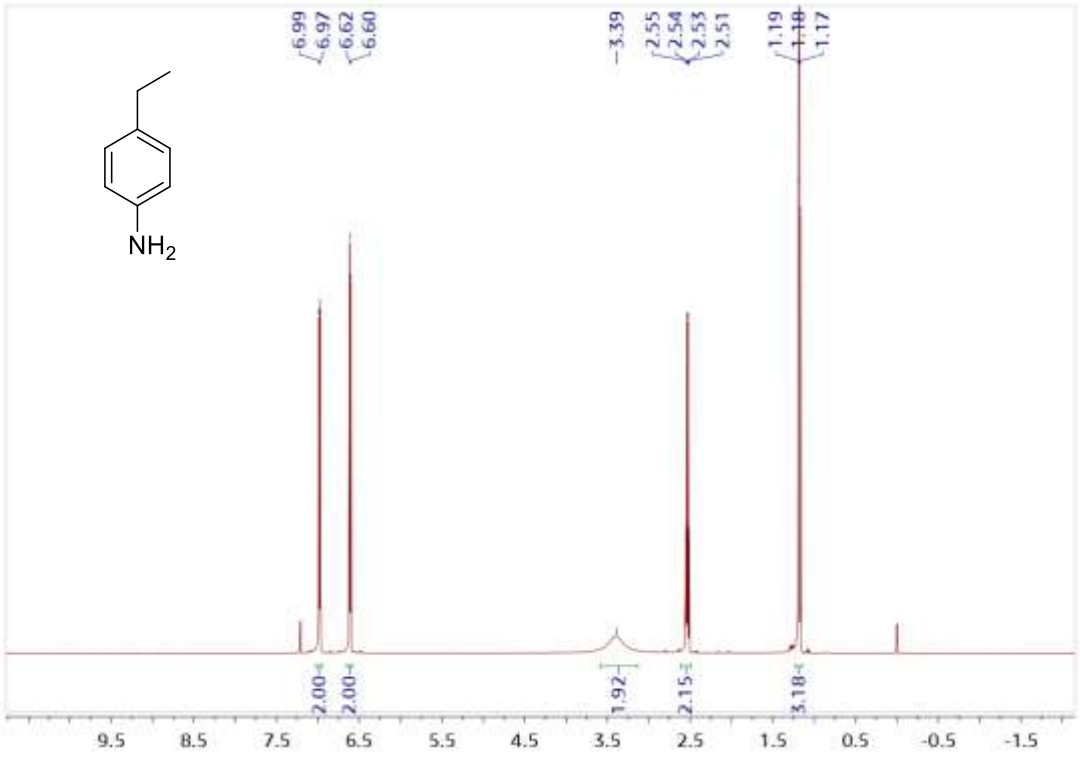


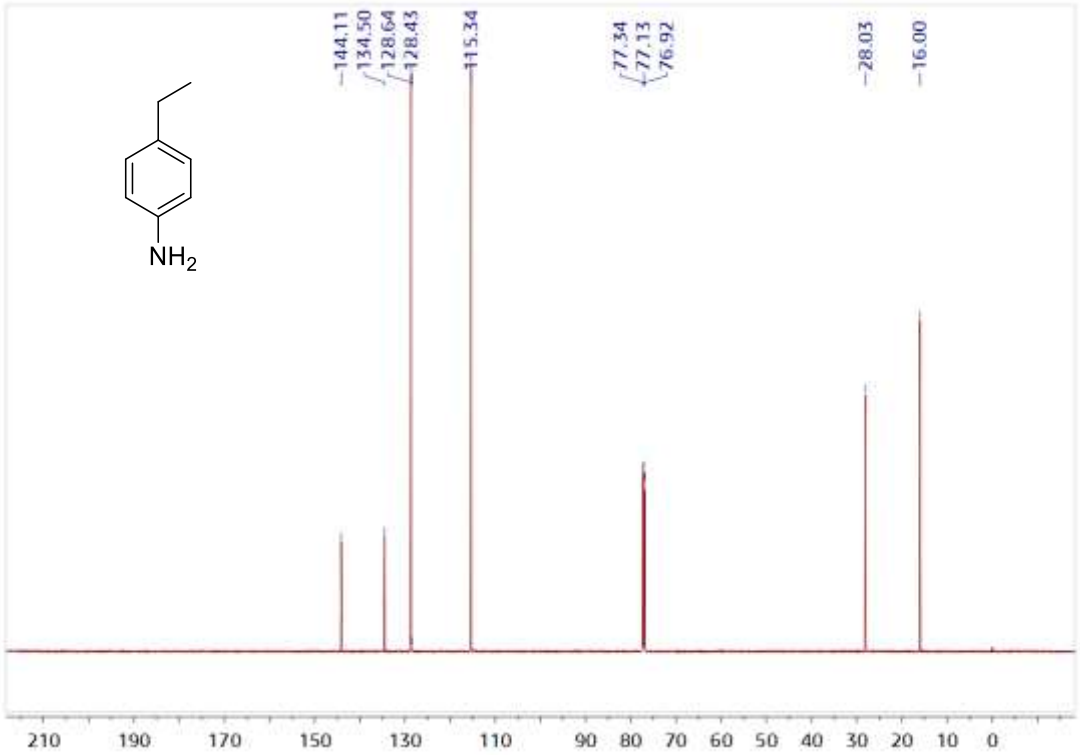
5-ethylbenzo[d][1,3]dioxole (2e)



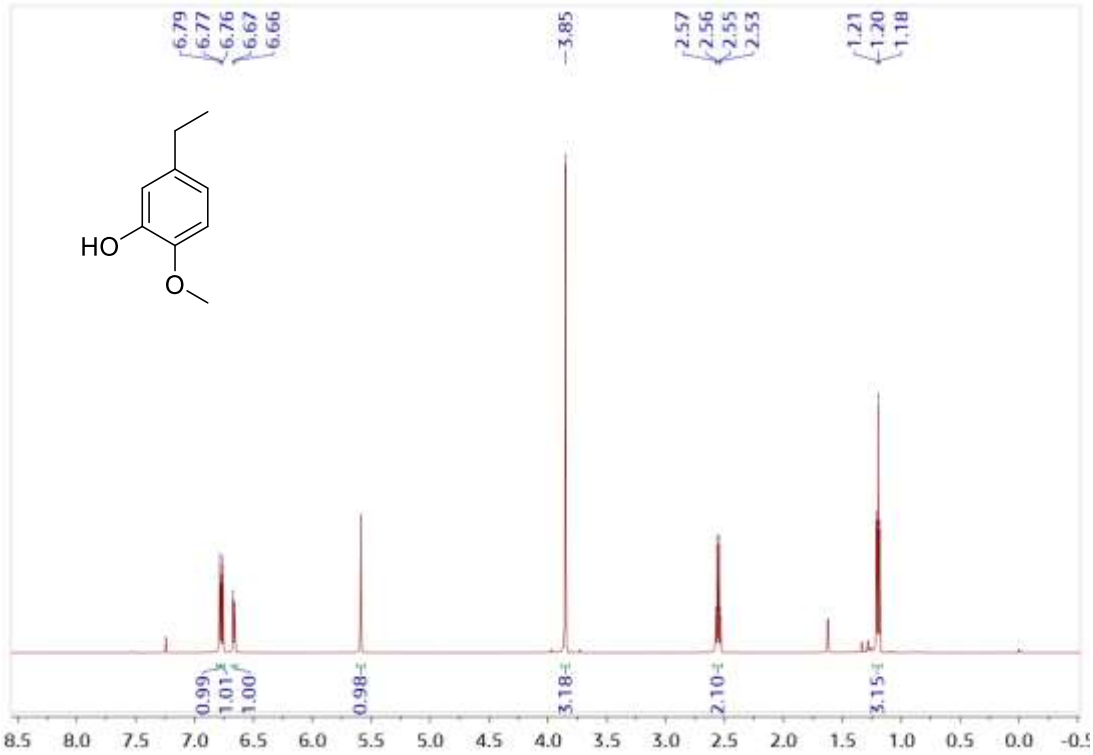


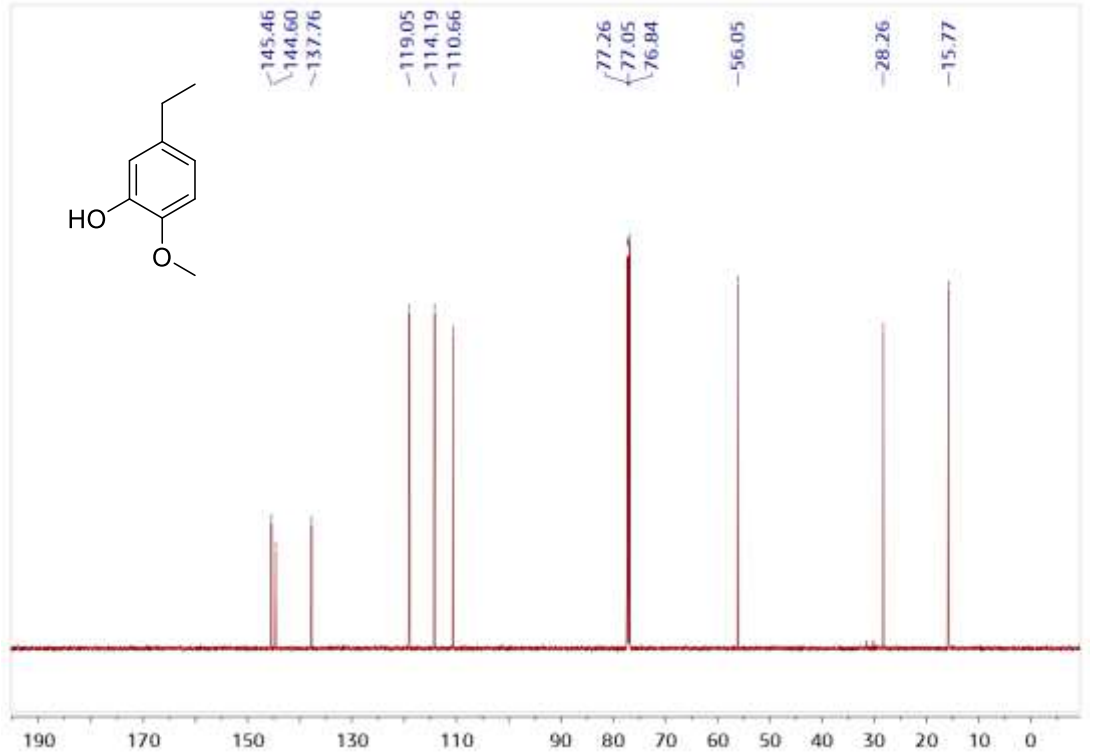
4-ethylaniline (2f)



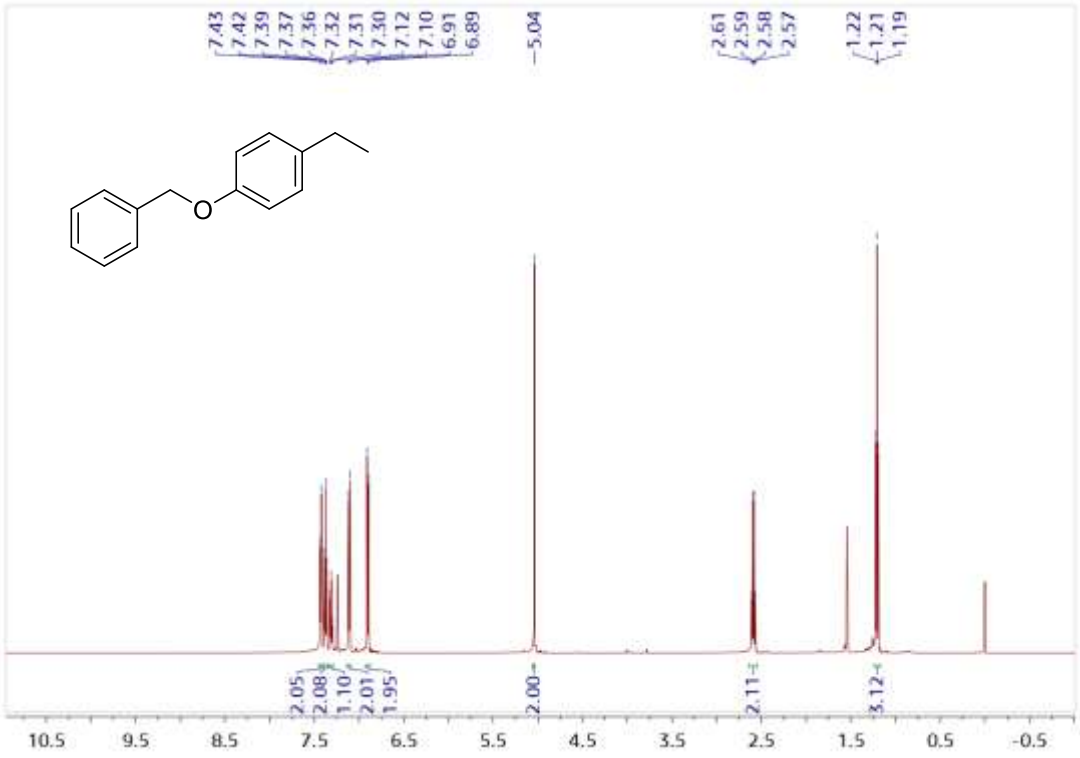


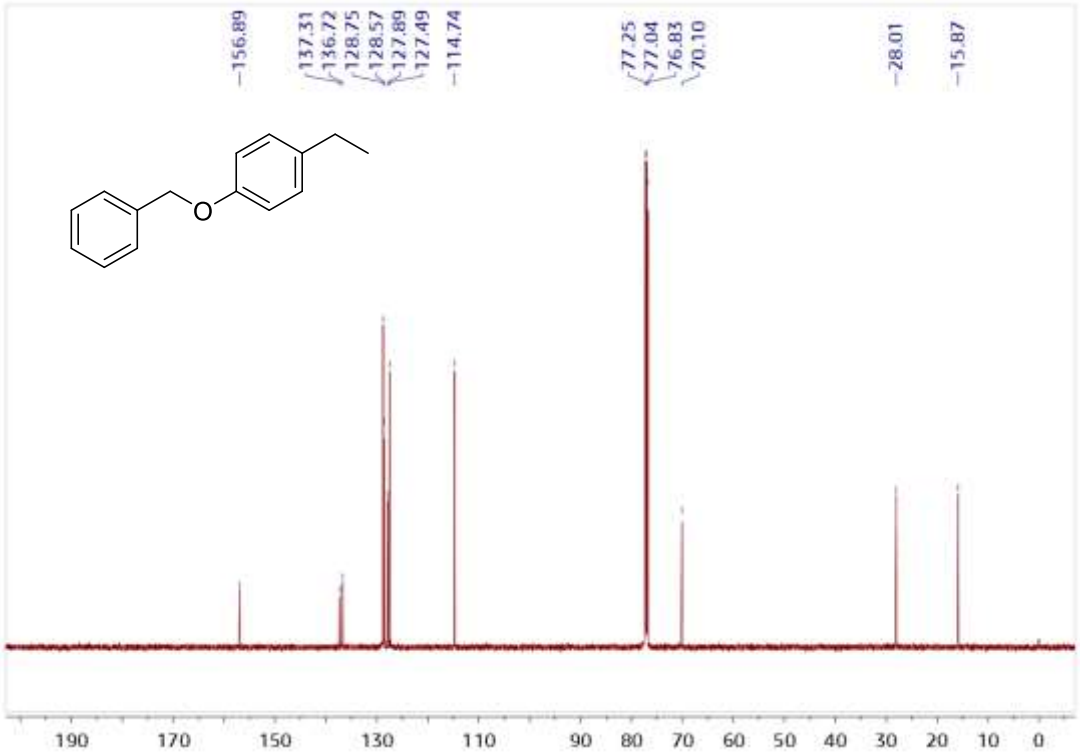
5-ethyl-2-methoxyphenol (2g)



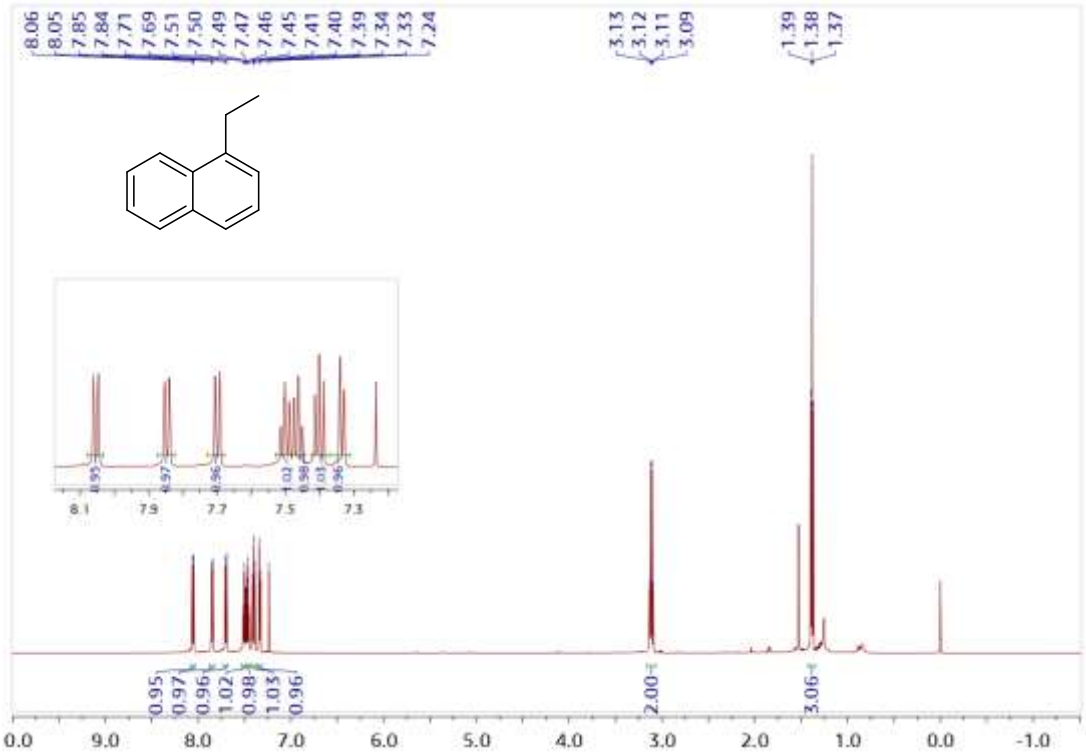


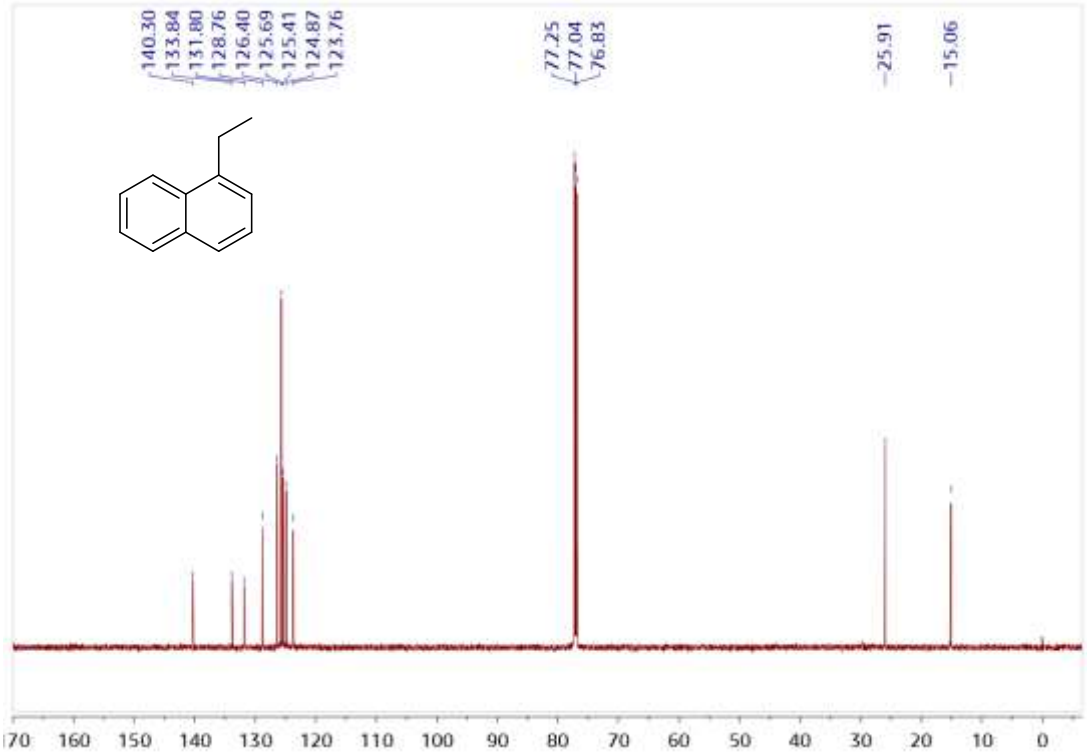
1-(benzyloxy)-4-ethylbenzene (2h)



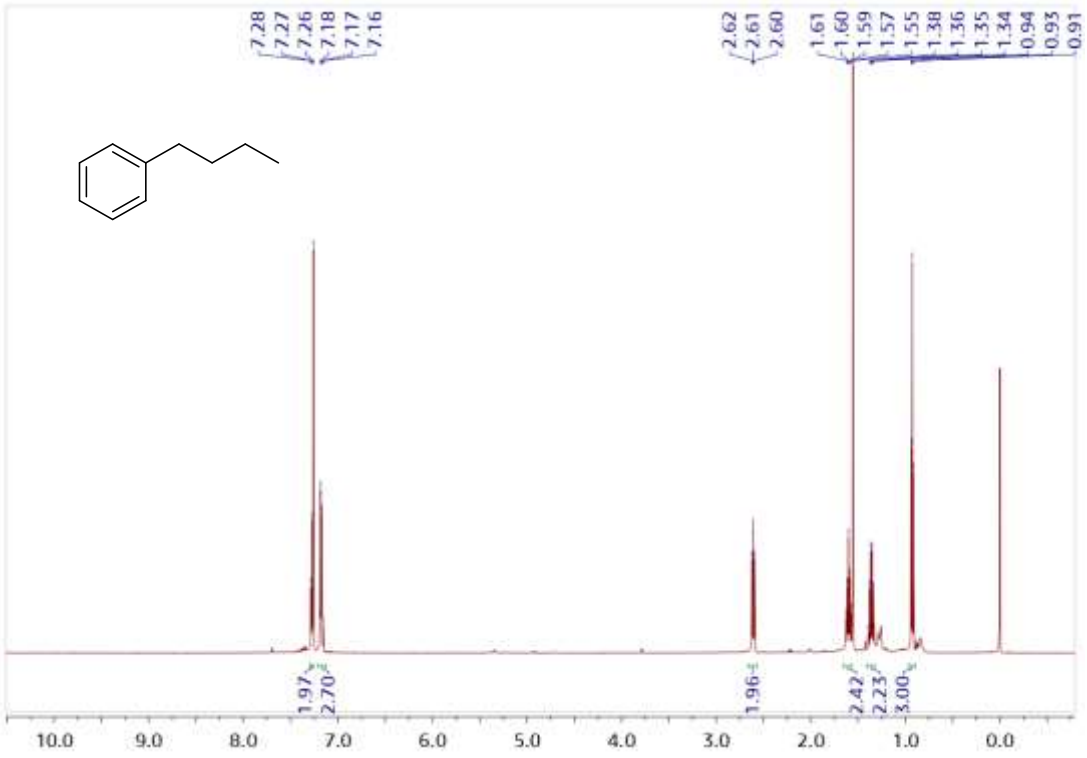


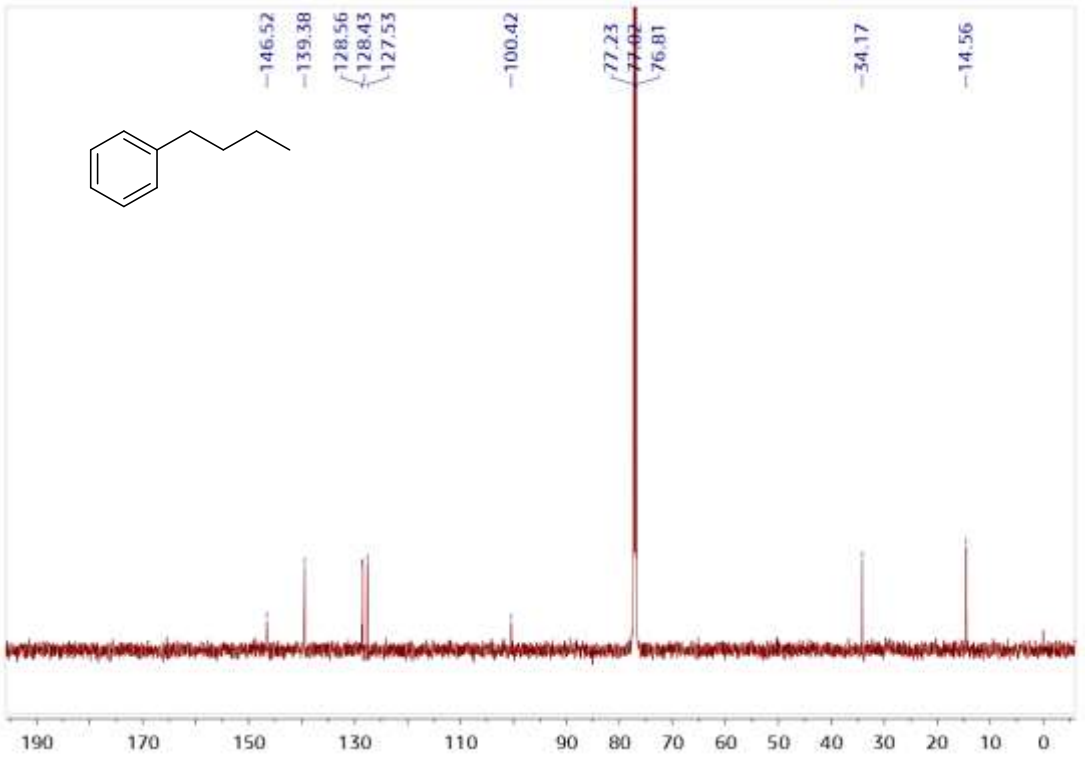
1-ethylnaphthalene (2i)



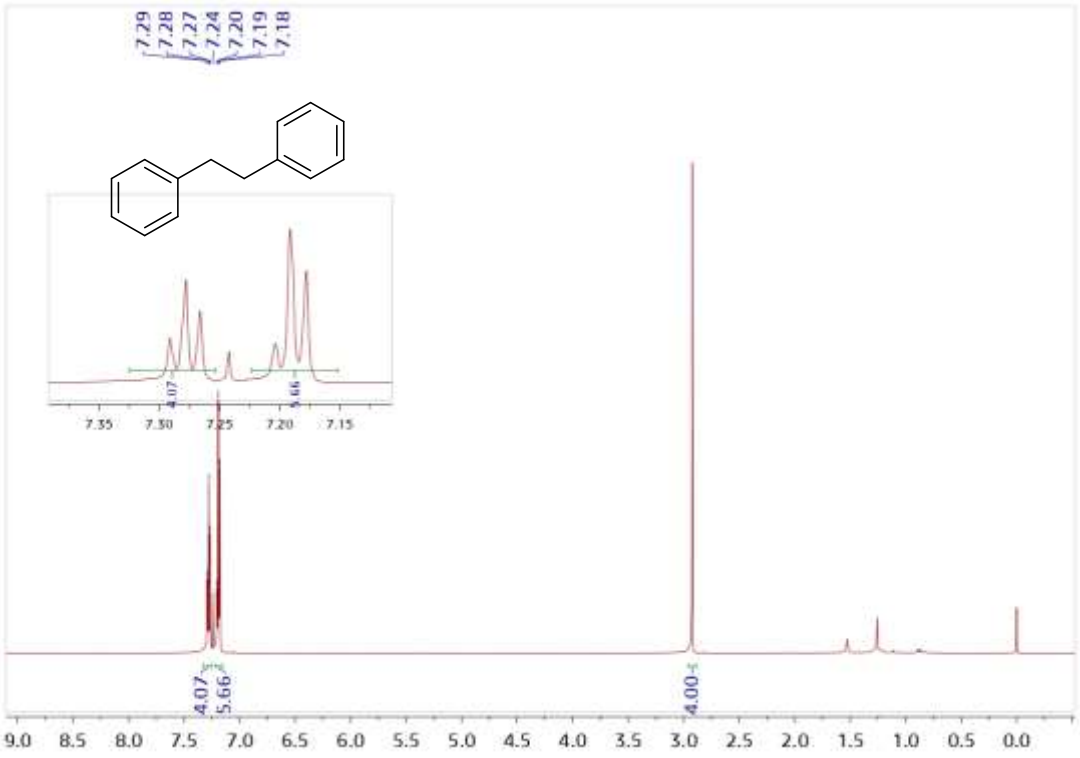


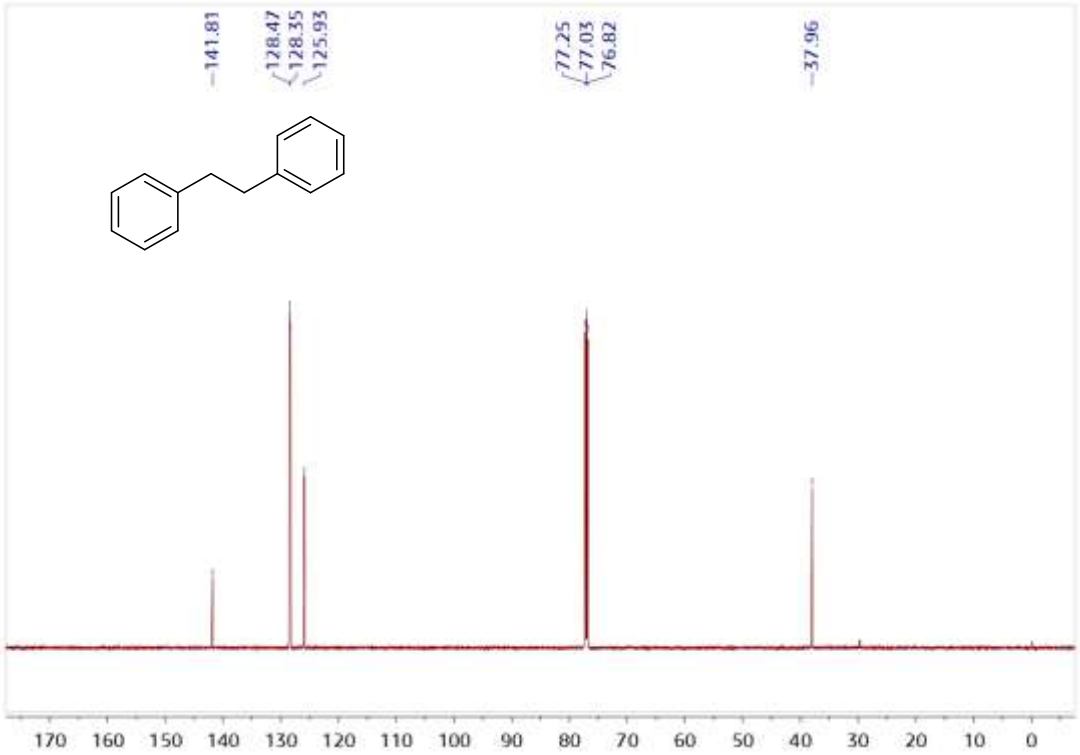
Butylbenzene (2j)



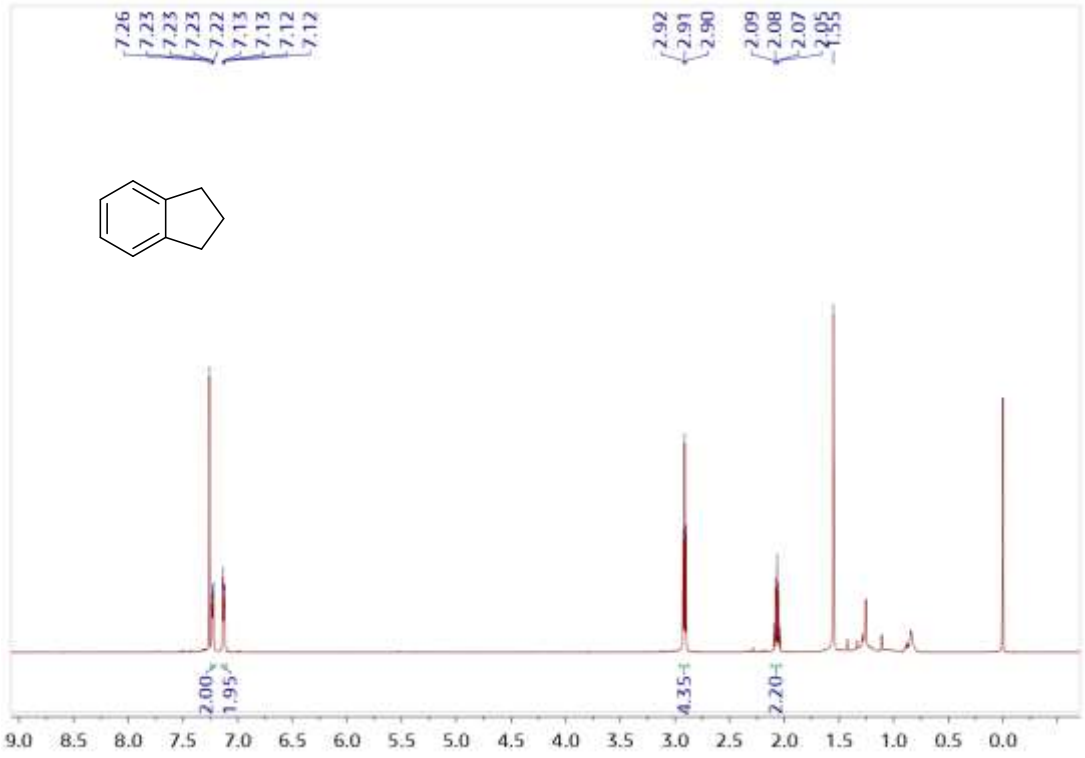


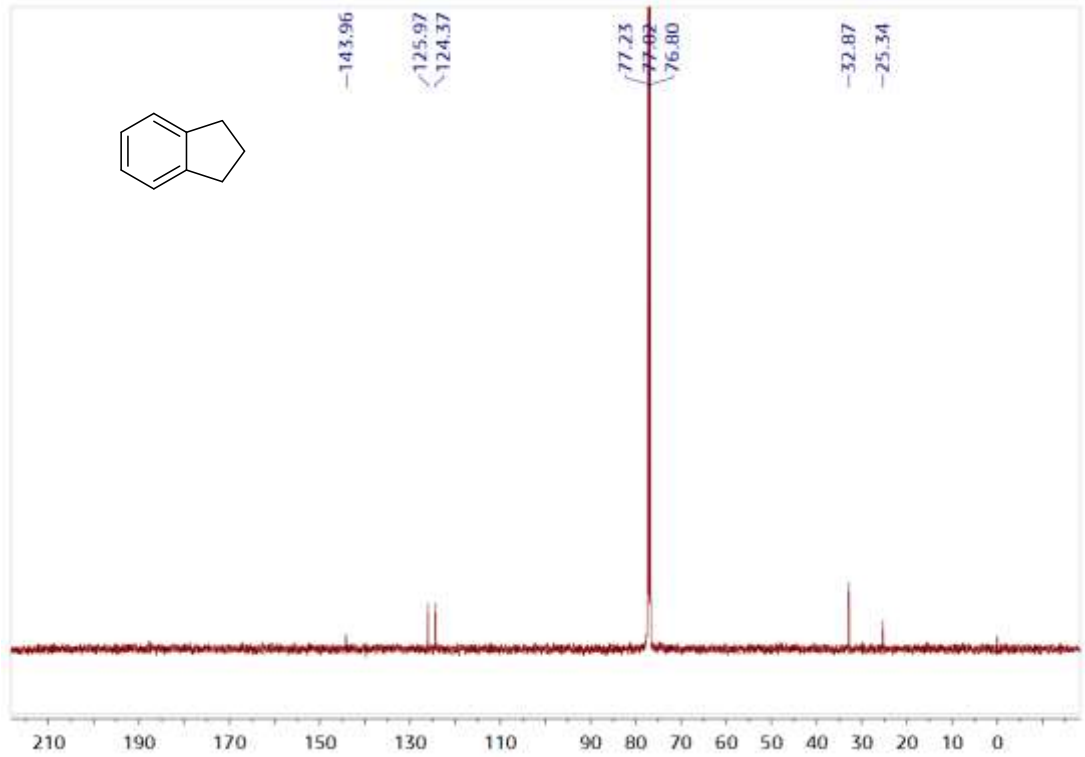
1,2-diphenylethane (2k)



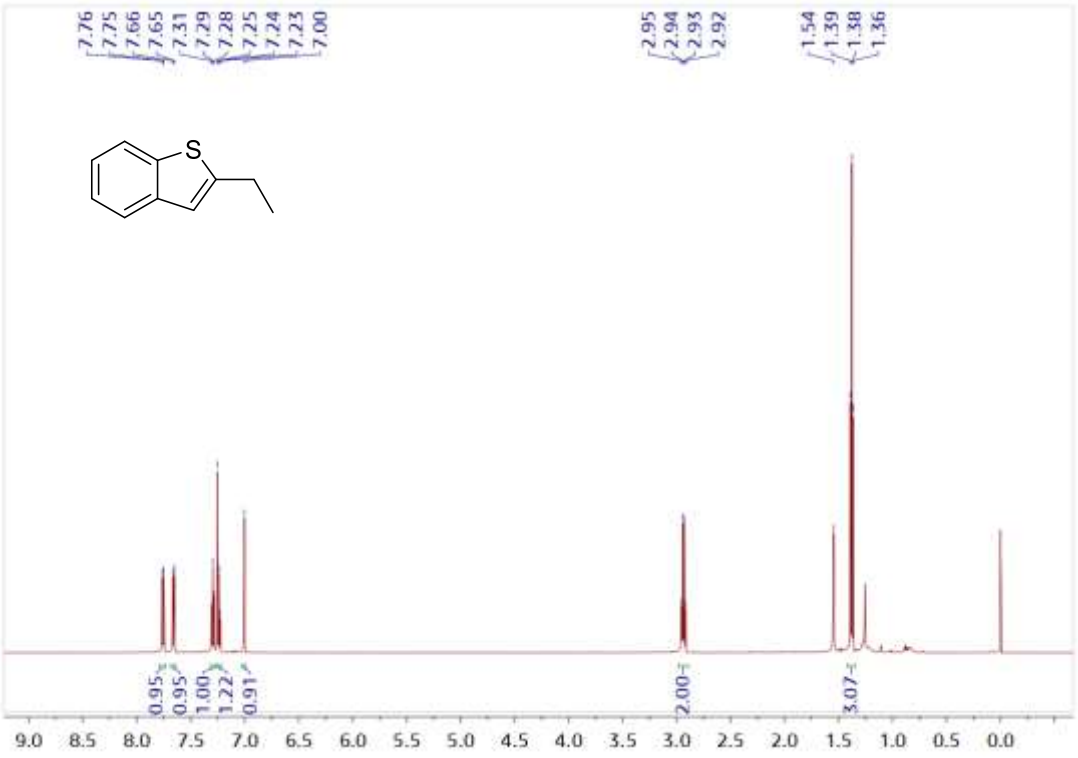


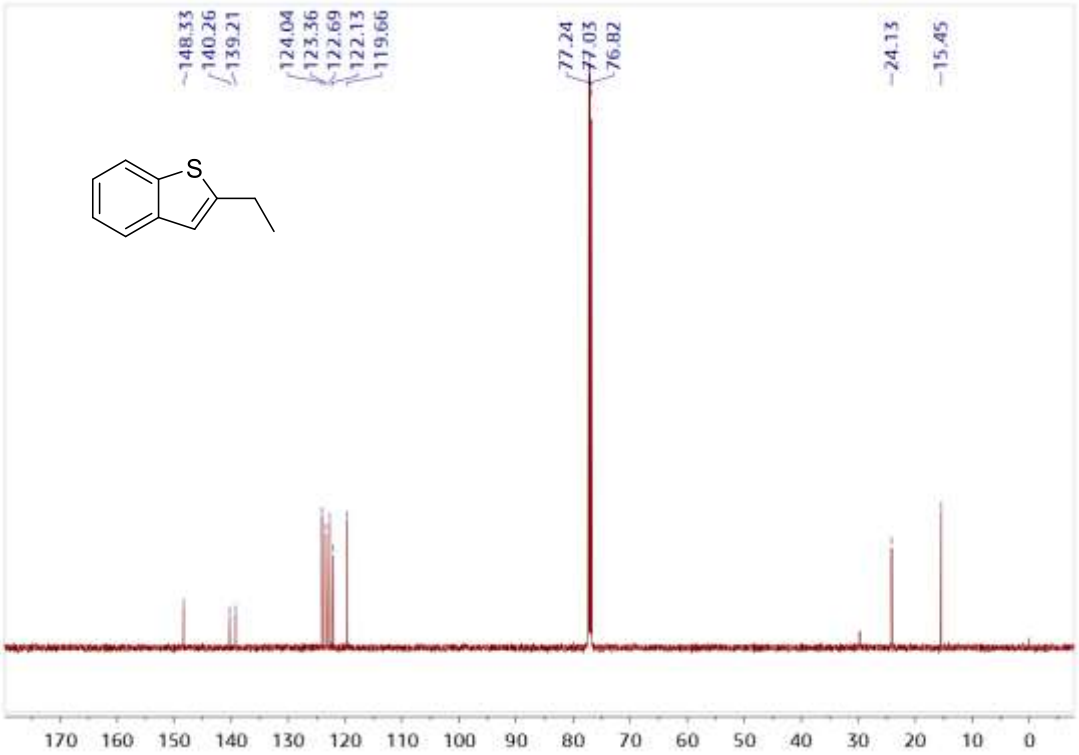
2,3-dihydro-1H-indene (2l)



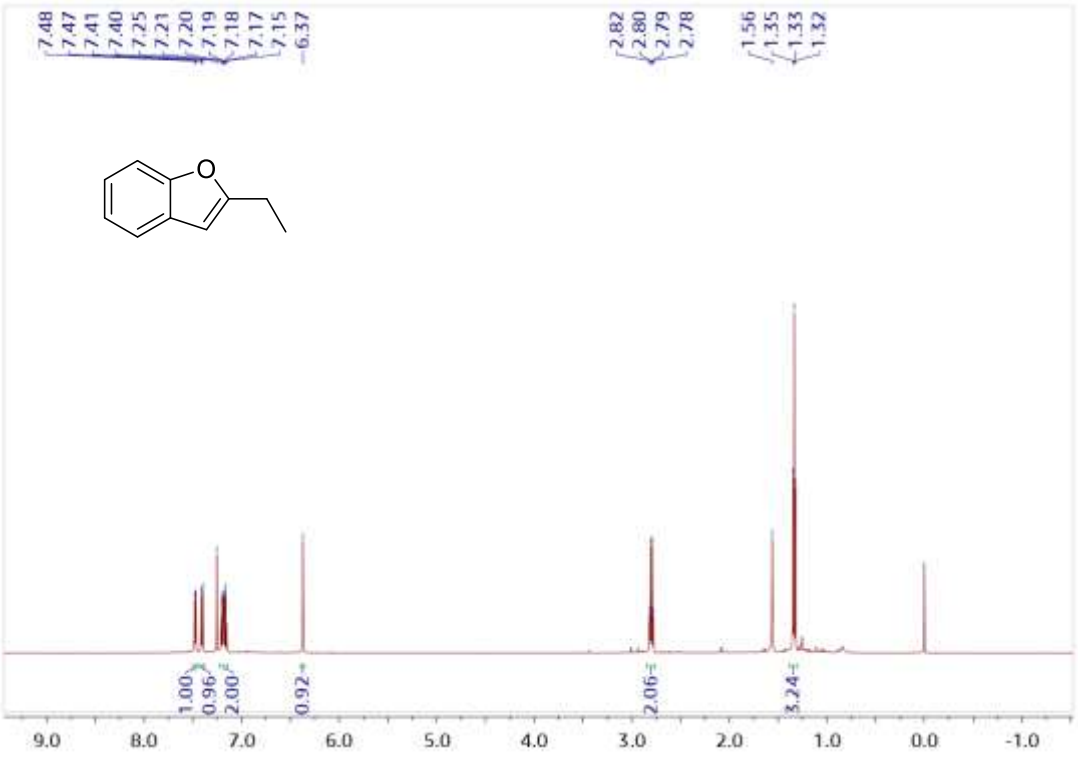


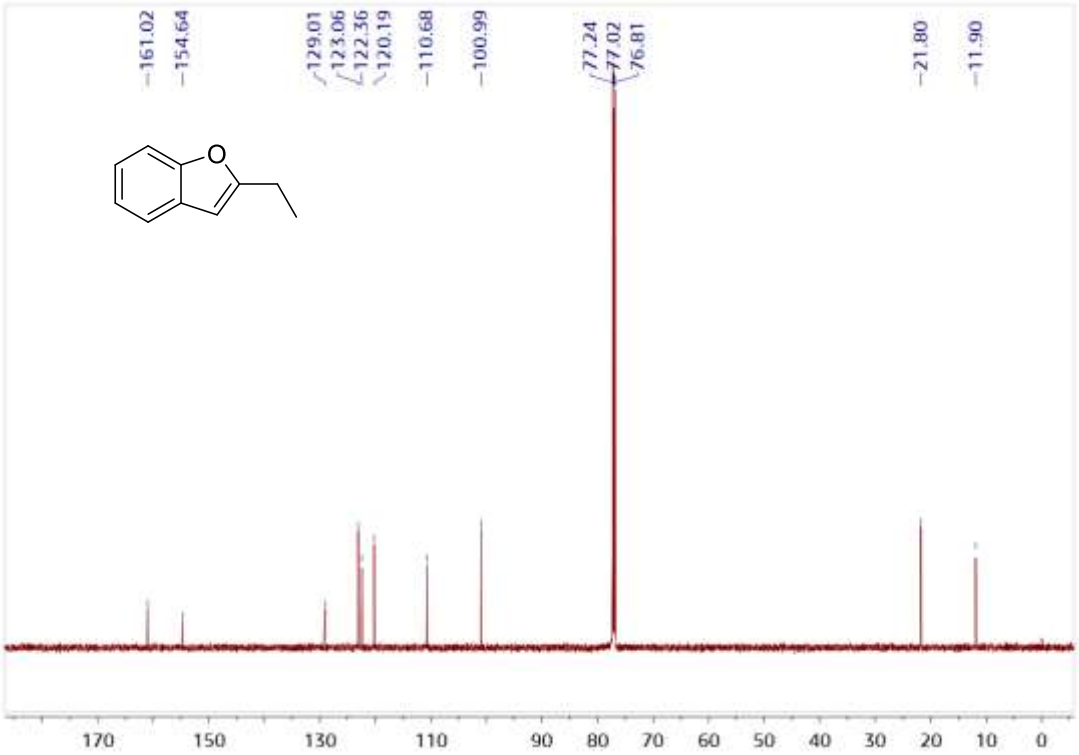
2-ethylbenzo[b]thiophene (2m)



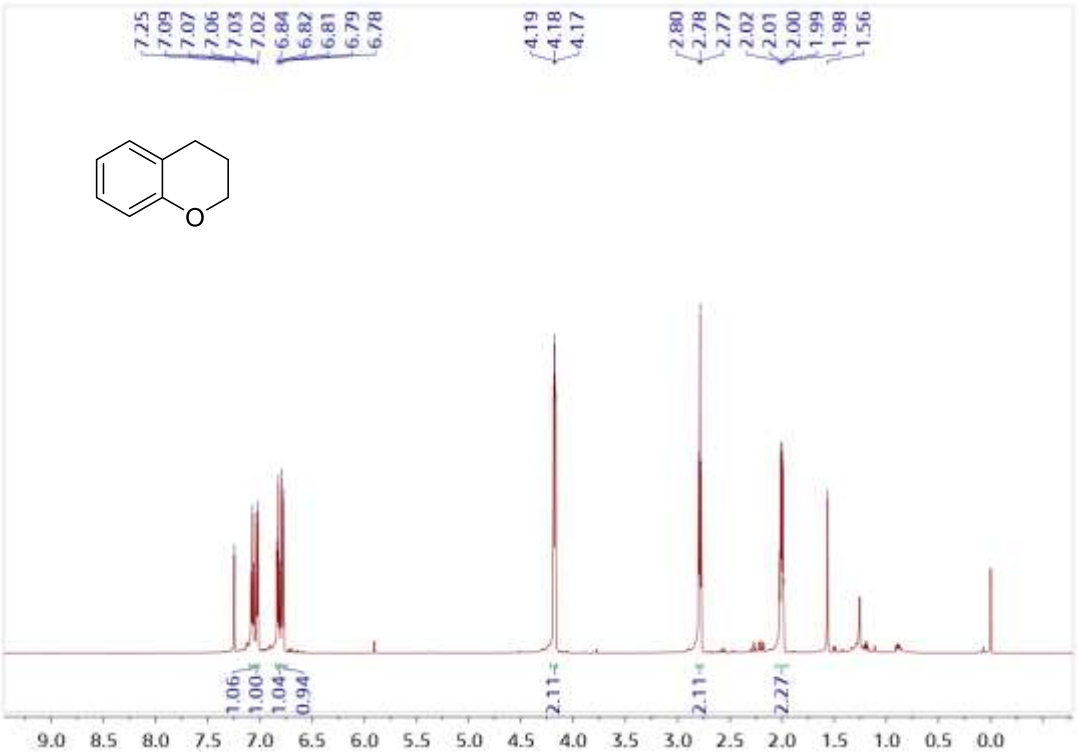


2-ethylbenzofuran (2n)





Chromane (2o)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6.82
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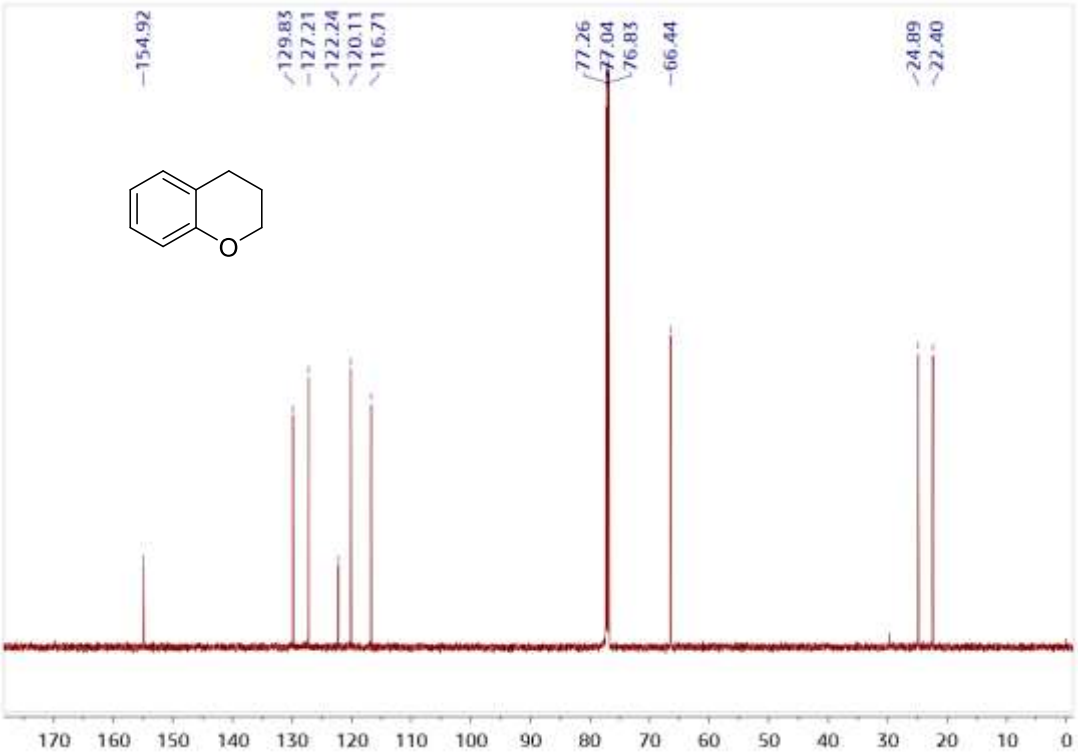
6.79
6.78
4.19
4.18
4.17
2.80
2.78
2.77
2.02
2.01
2.00
1.99
1.98
1.56
O
1.06
1.00
1.04
0.94
2.11
2.11
2.27
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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77.26
77.04
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22.40
O
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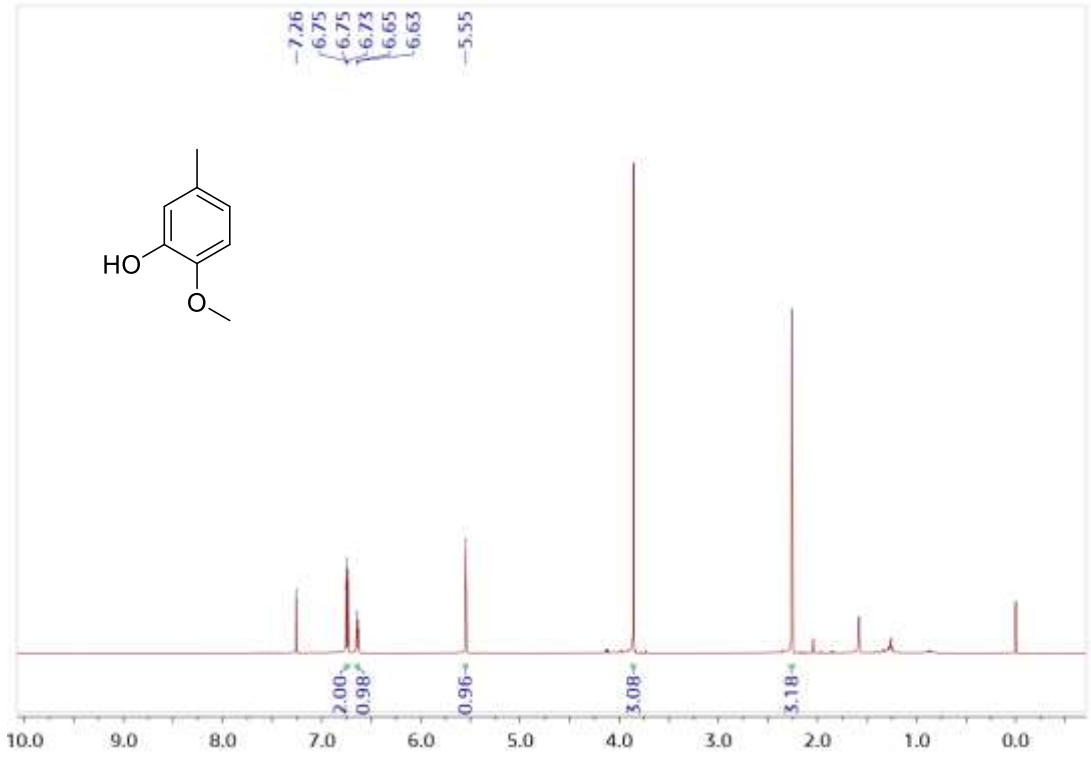
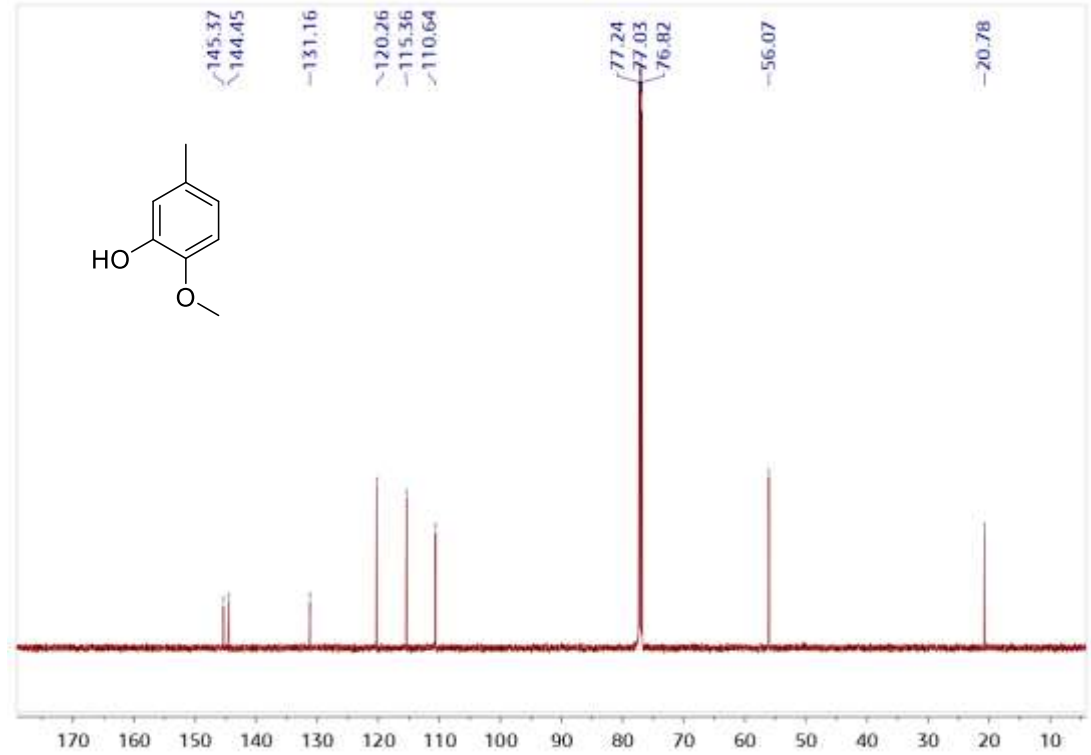
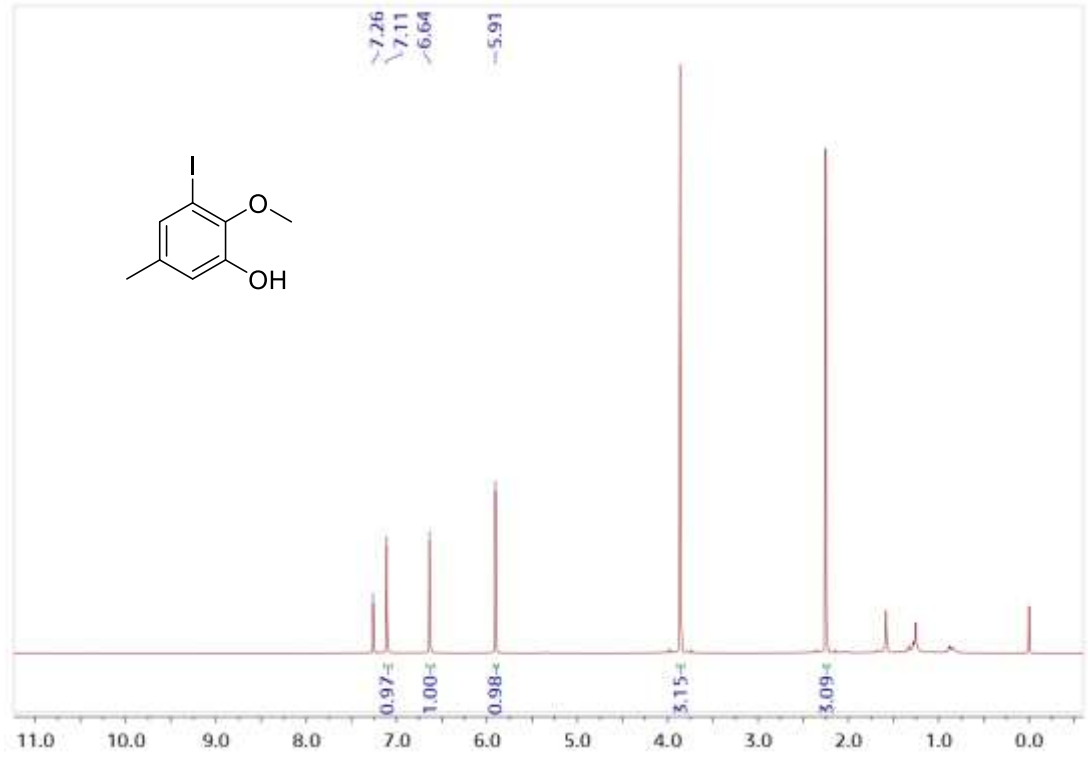
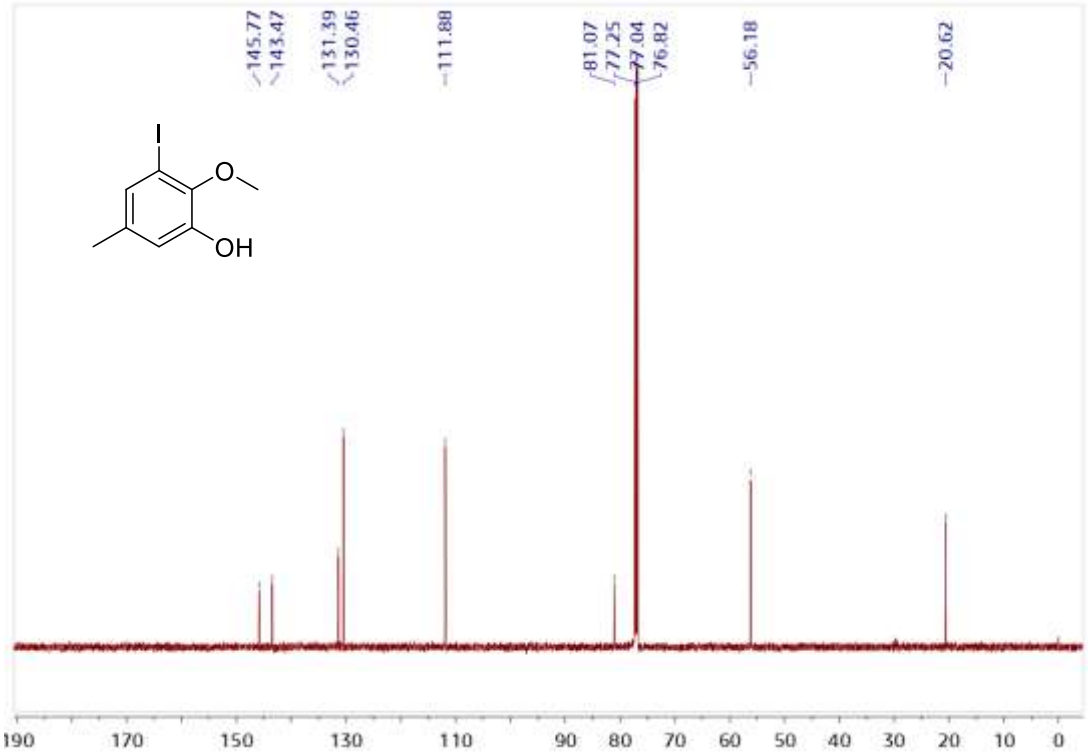
2-methoxy-5-methylphenol (2p)



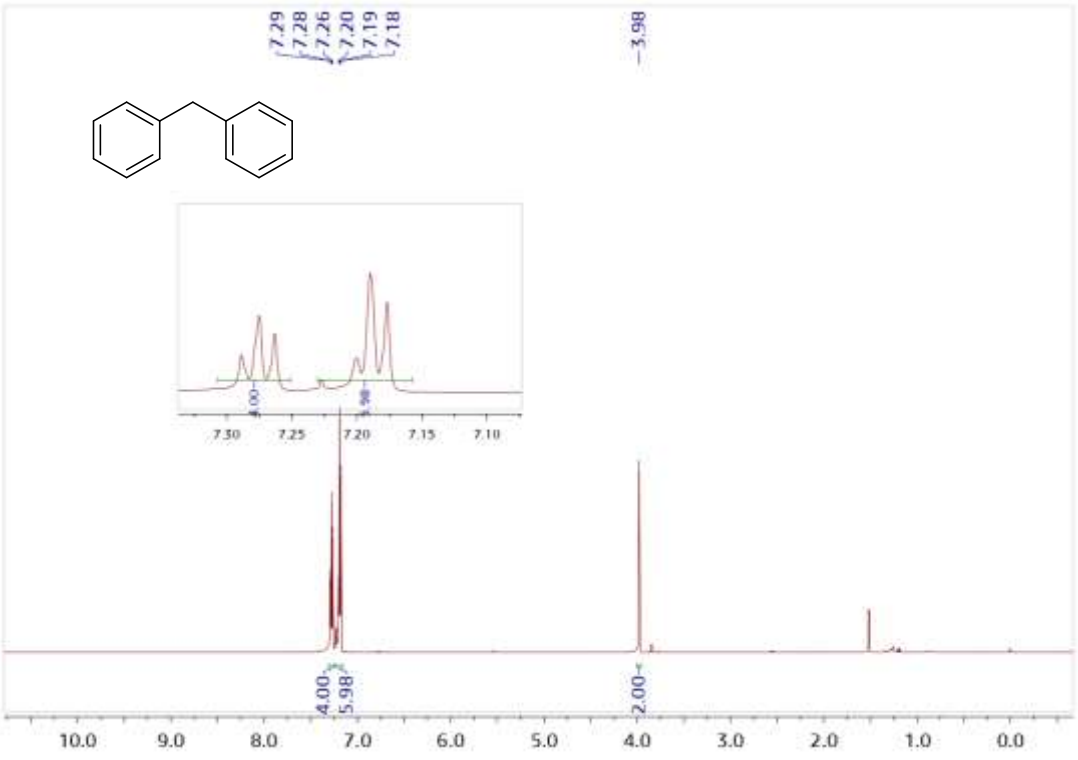


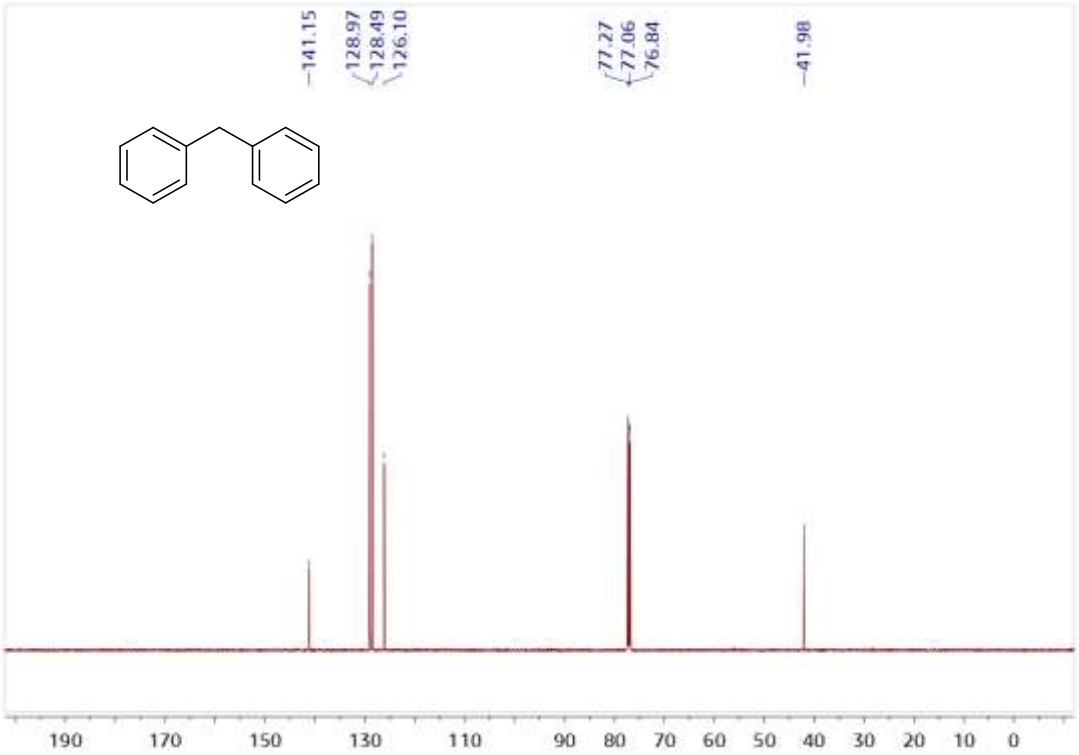
3-iodo-2-methoxy-5-methylphenol (2q)



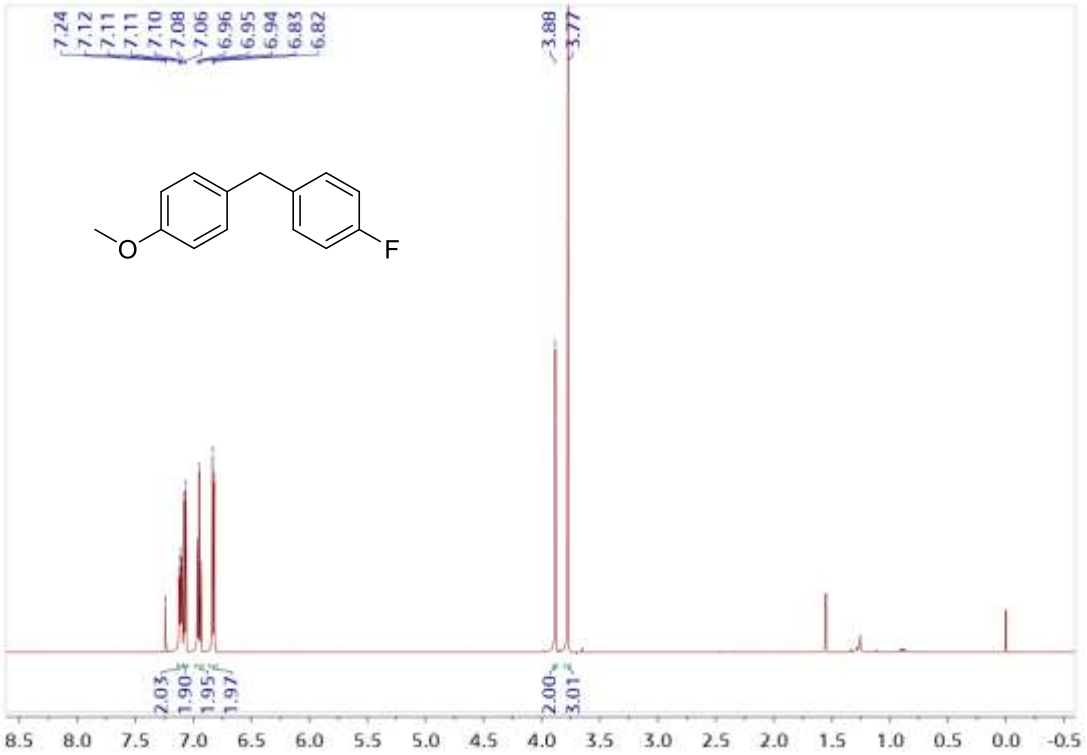


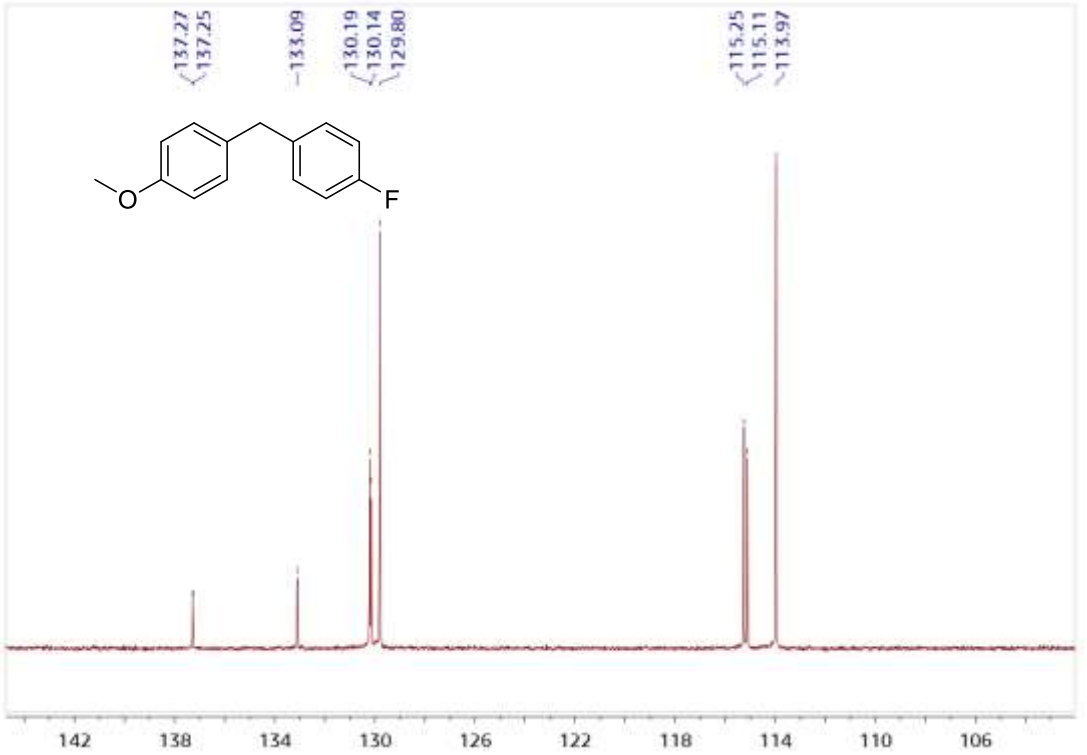
Diphenylmethane (2r)



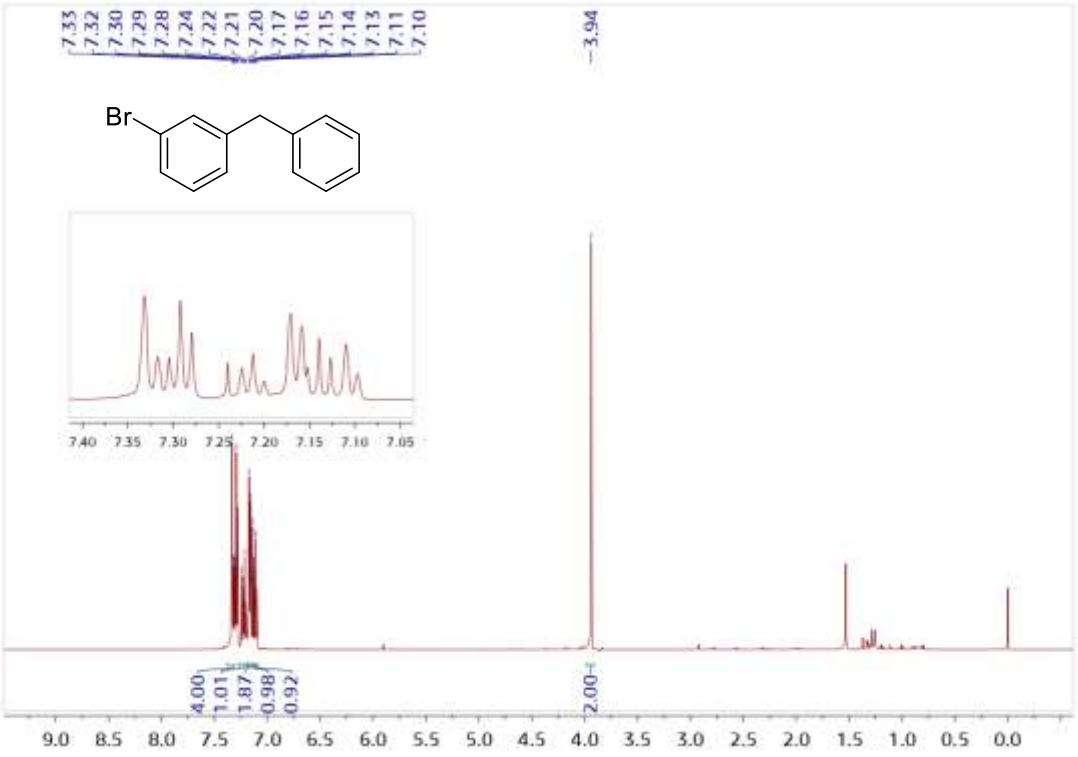


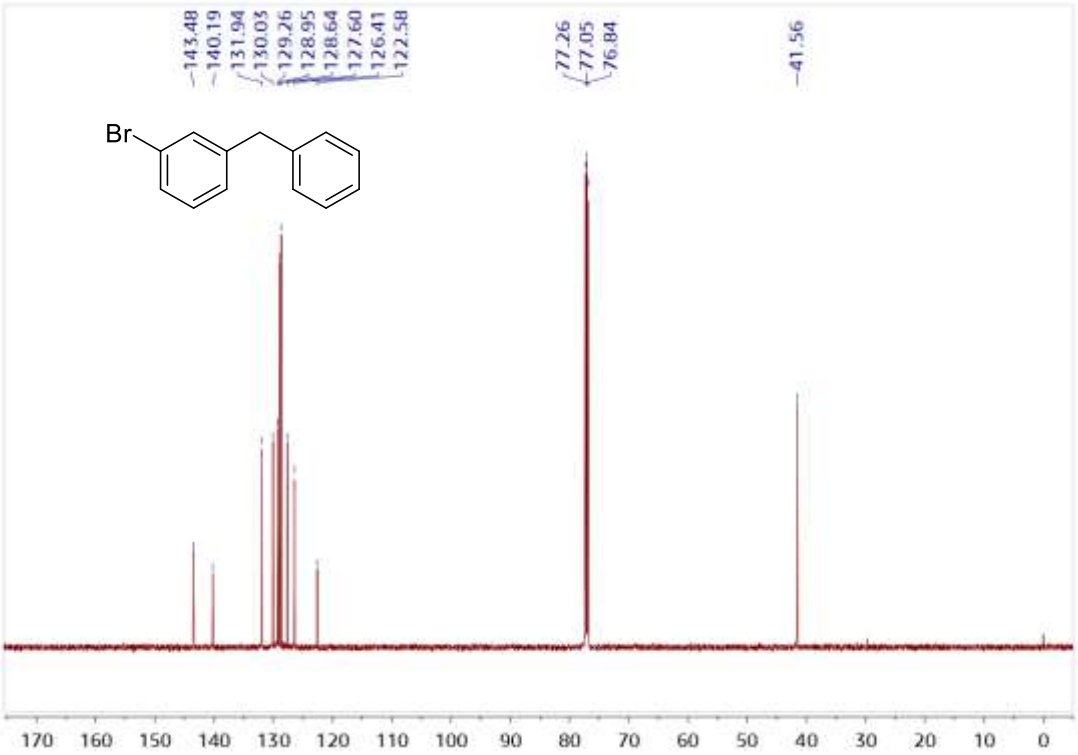
1-fluoro-4-(4-methoxybenzyl)benzene (2s)



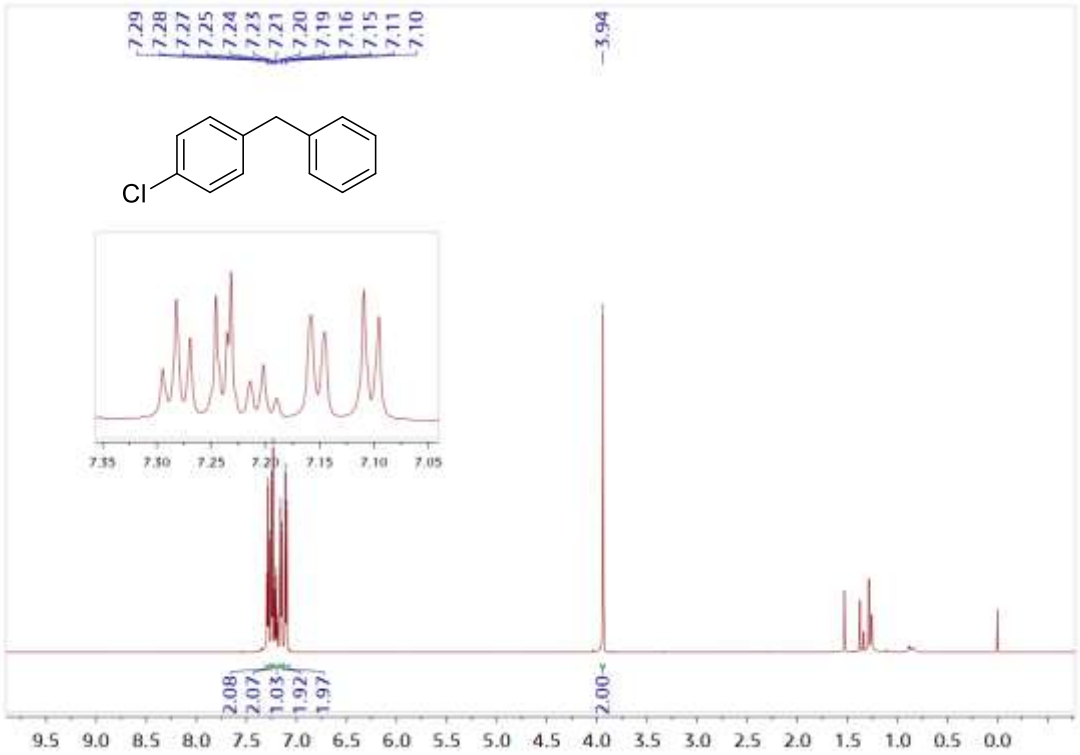


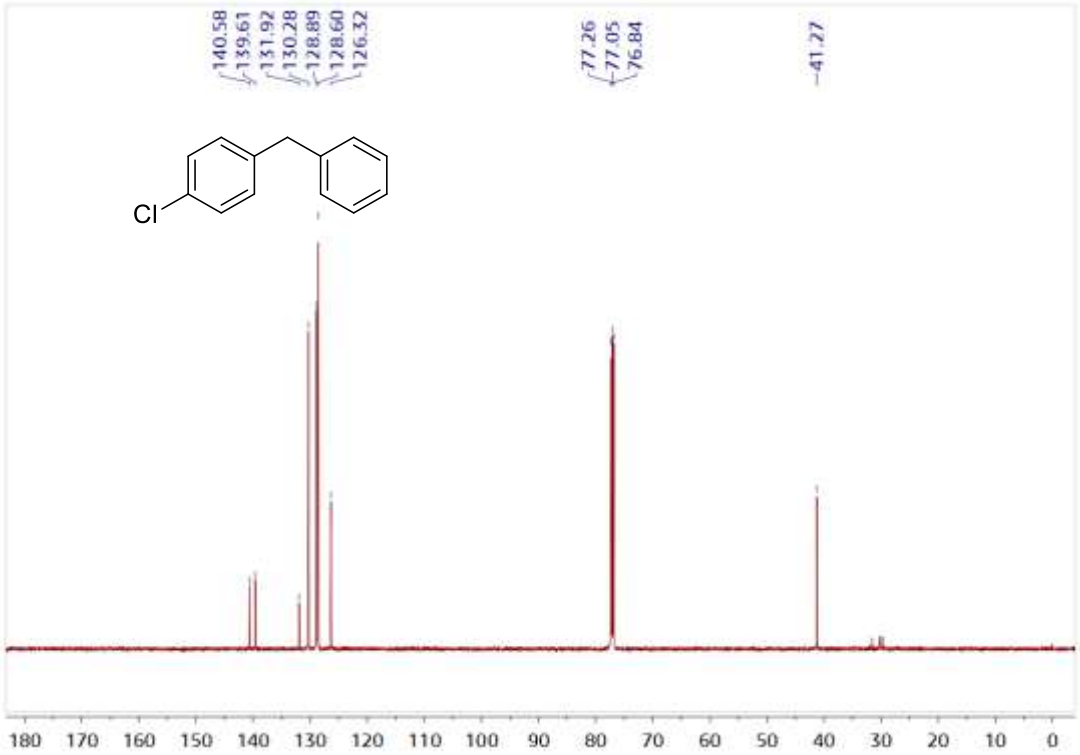
1-benzyl-3-bromobenzene (2t)



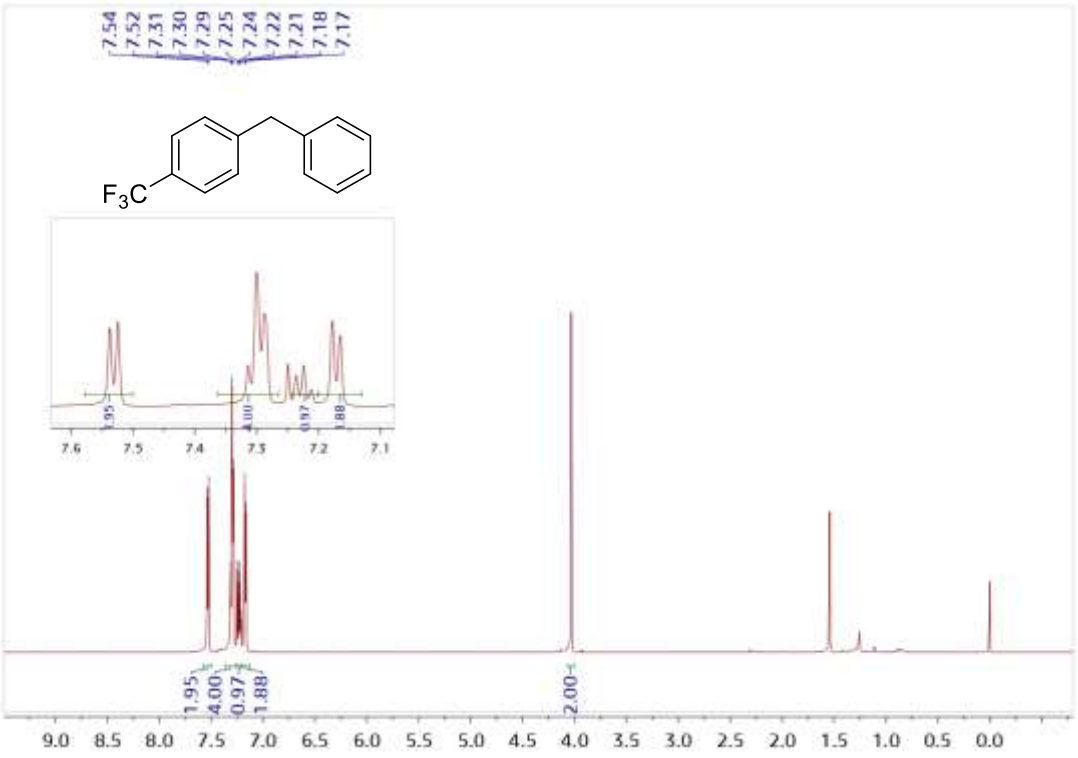


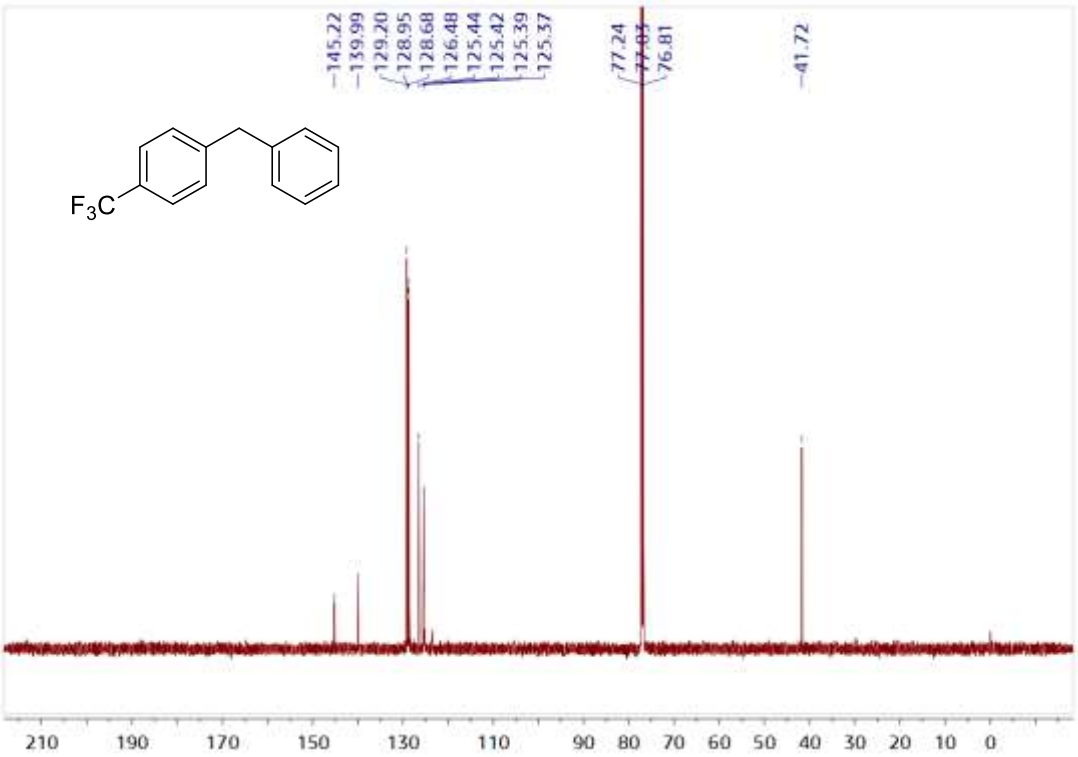
1-benzyl-4-chlorobenzene (2u)



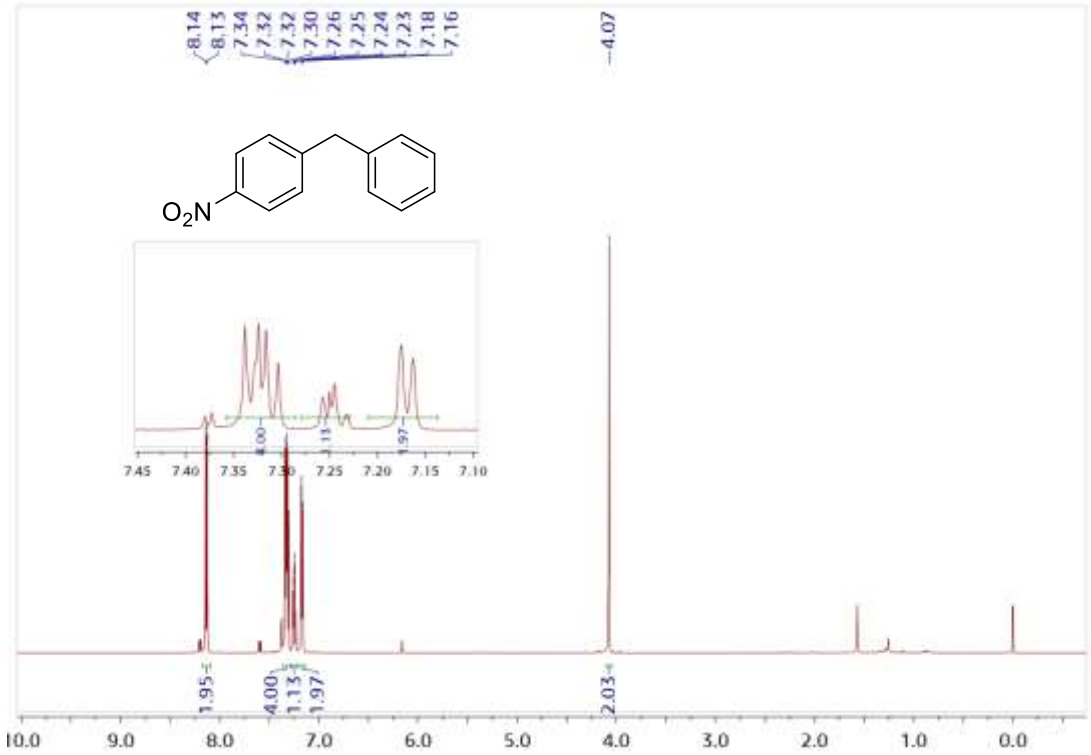


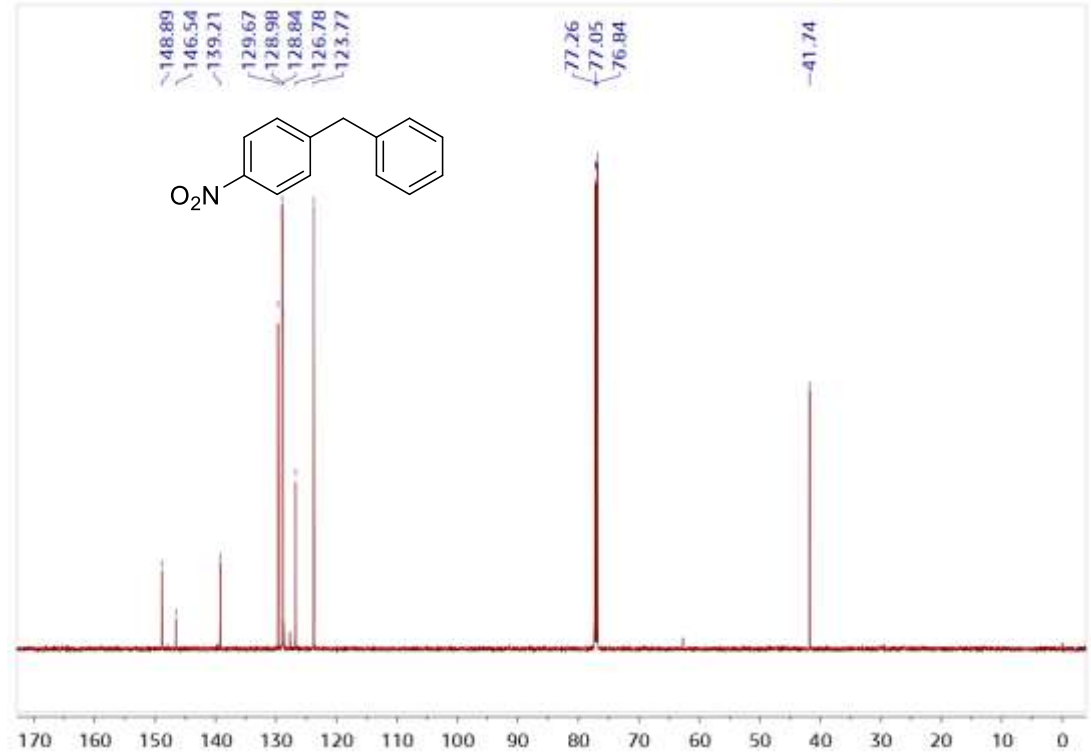
1-benzyl-4-(trifluoromethyl)benzene (2v)



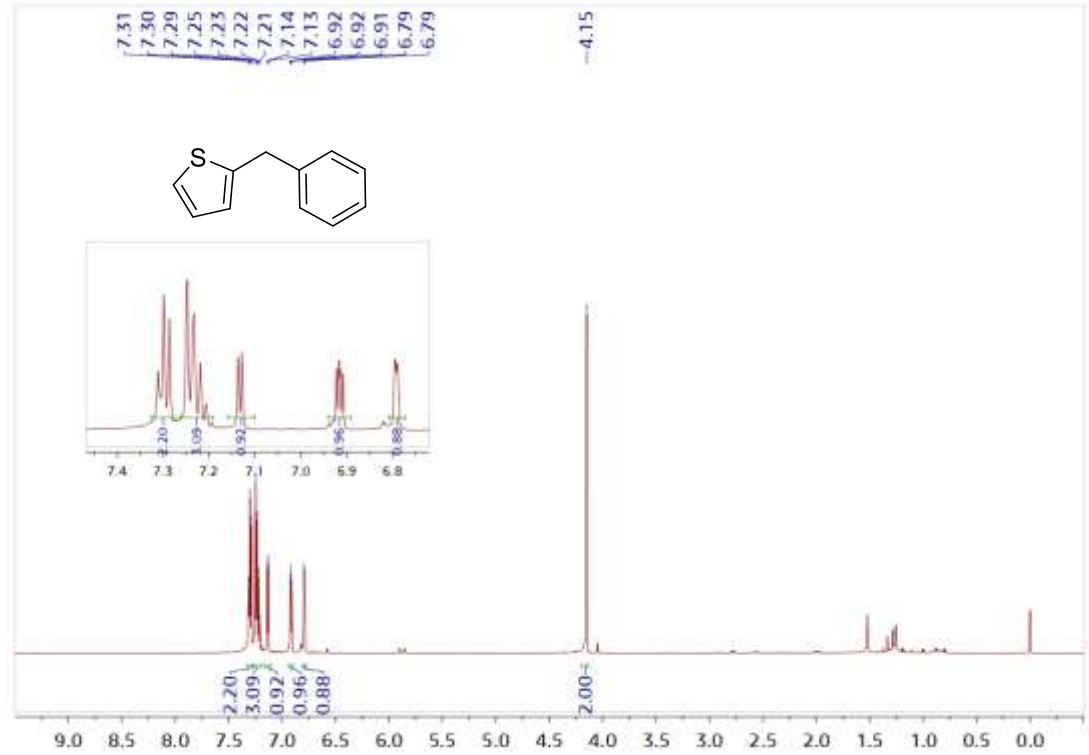


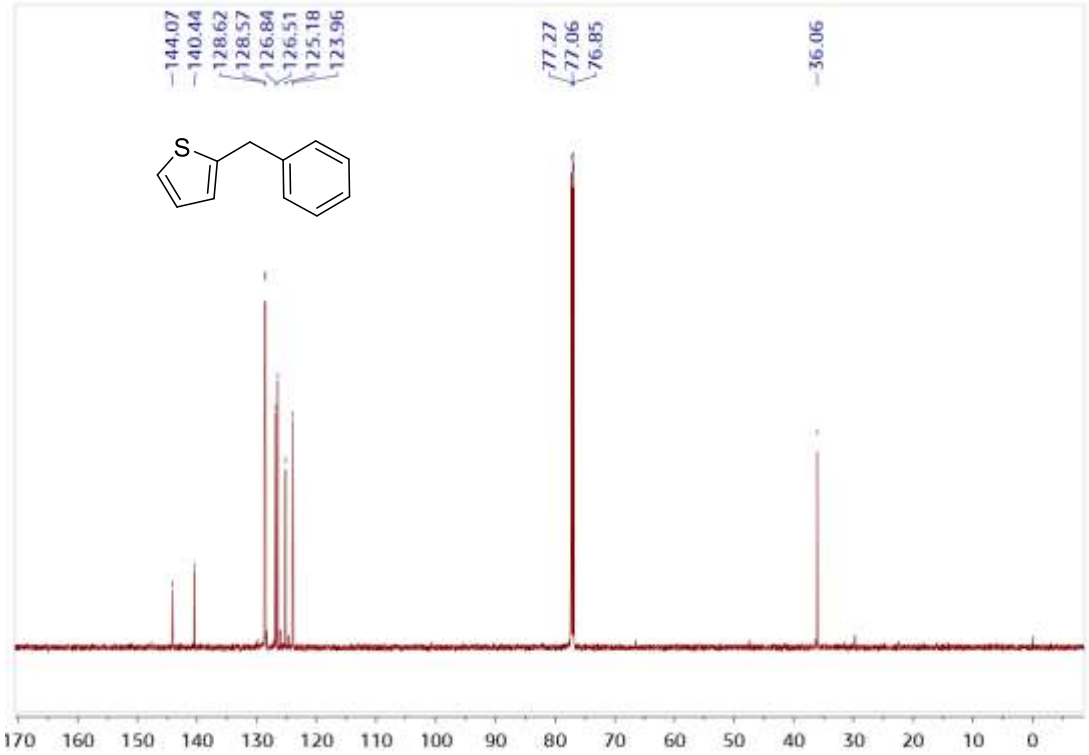
1-benzyl-4-nitrobenzene (2w)



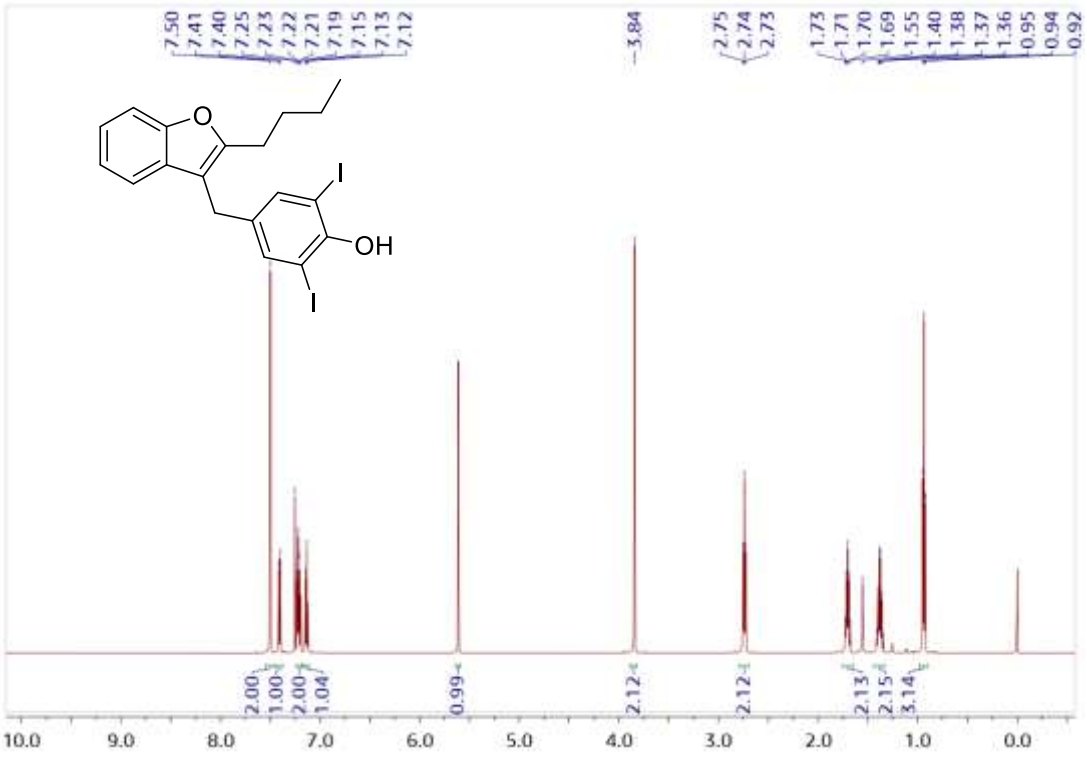


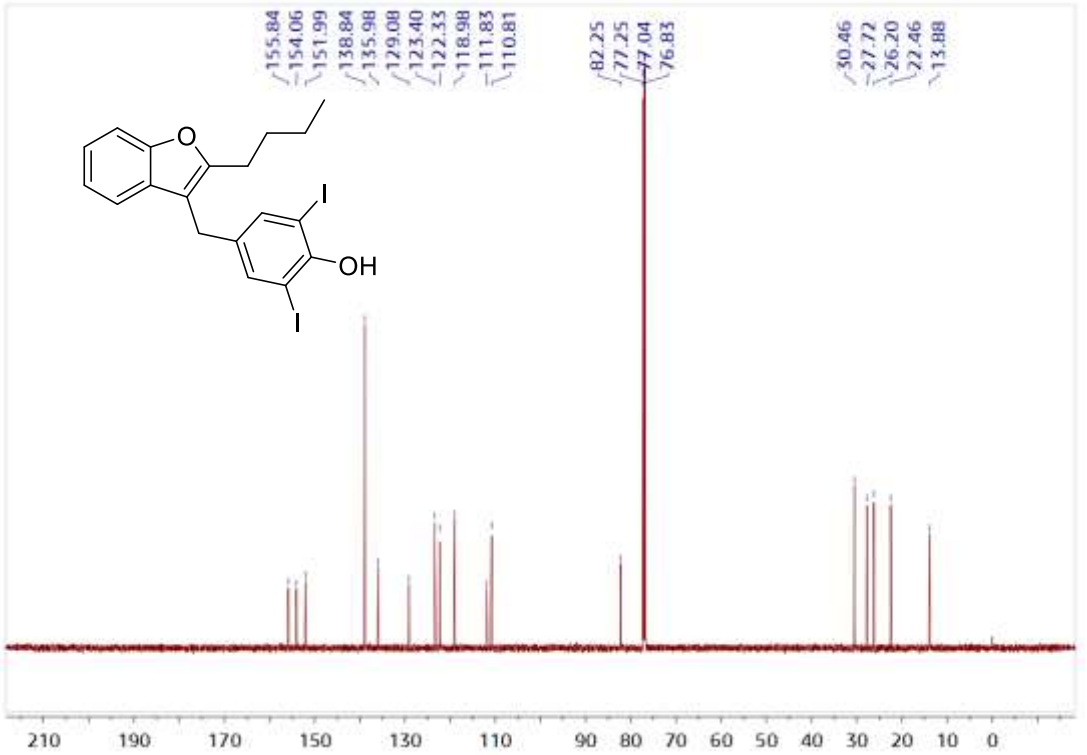
2-benzylthiophene (2x)



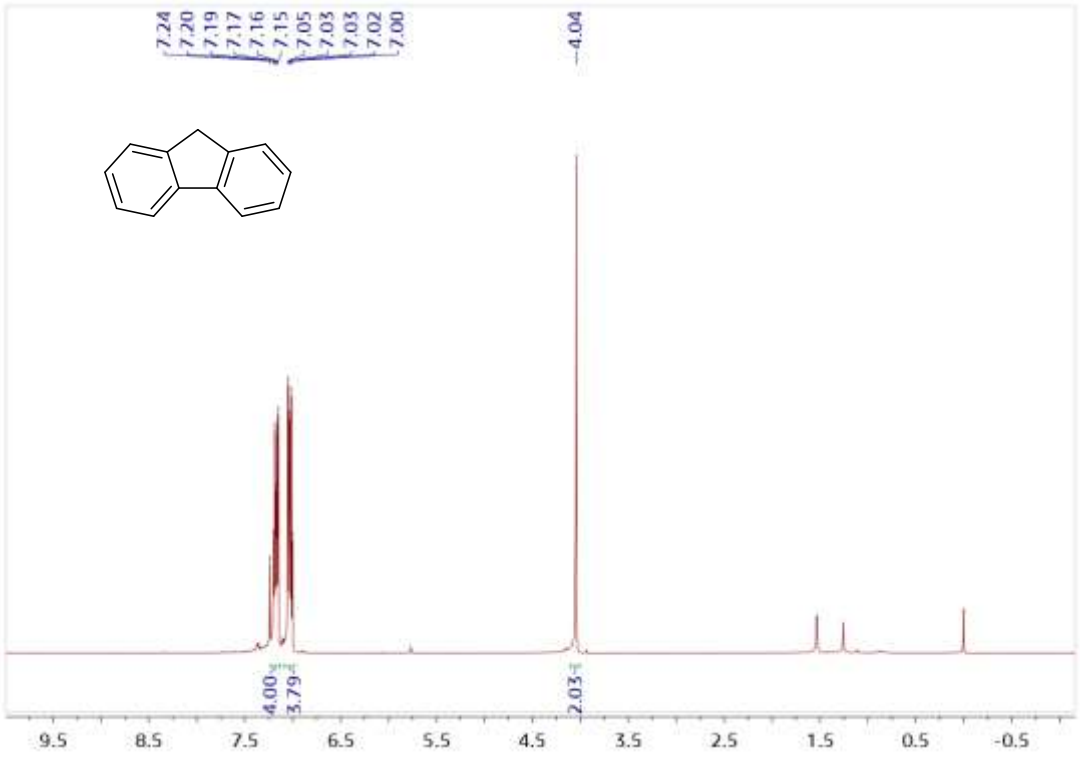


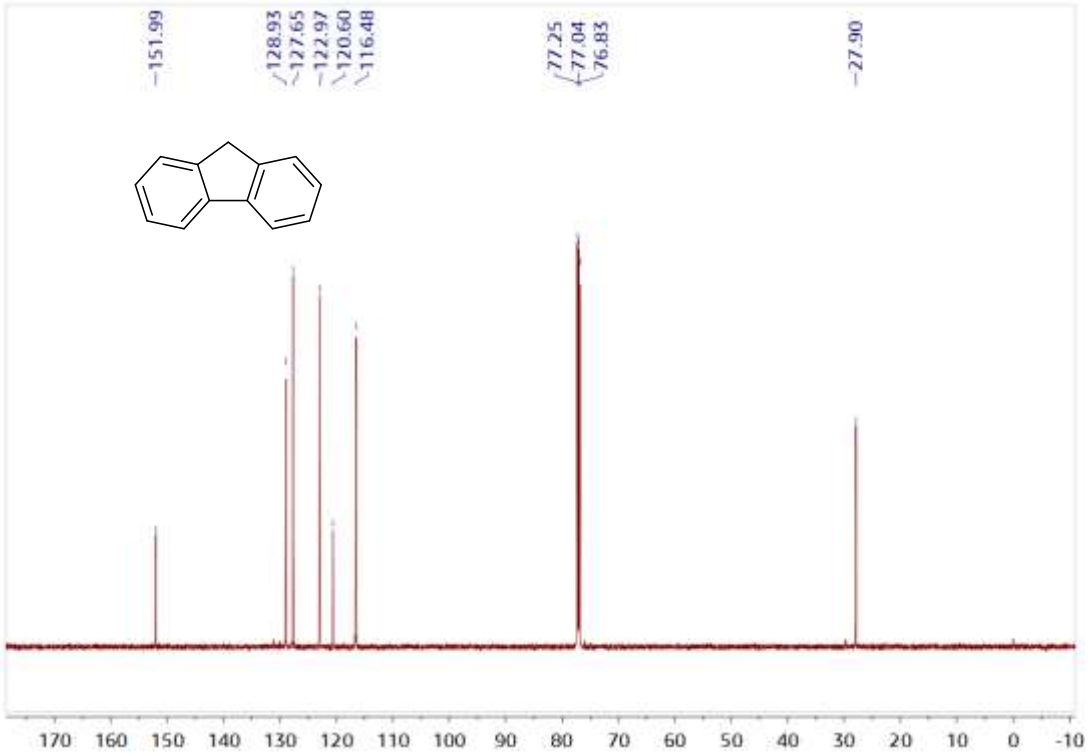
4-((2-butylbenzofuran-3-yl)methyl)-2,6-diiodophenol (2y)



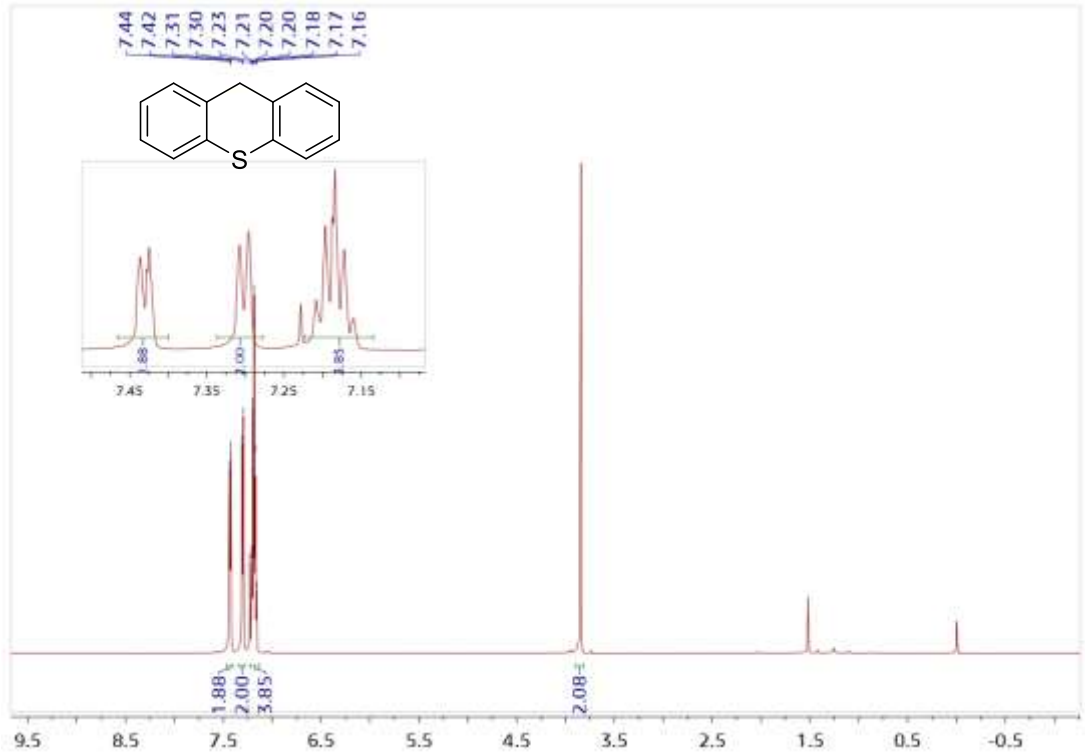


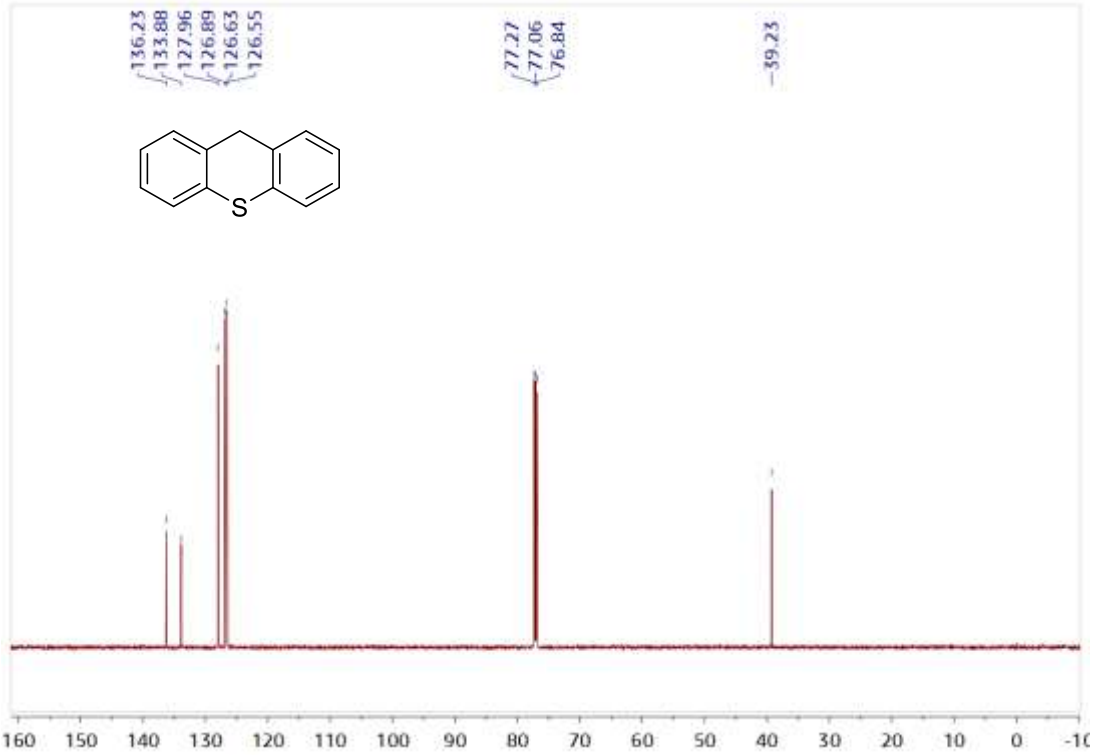
9H-fluorene (2z)



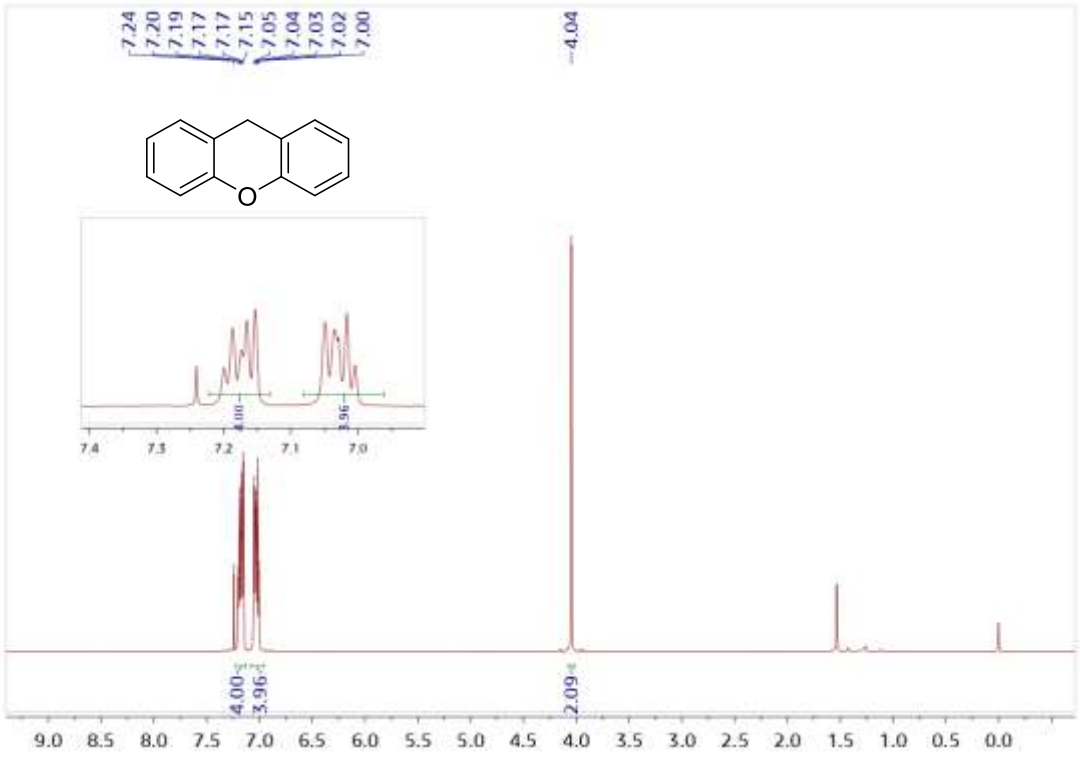


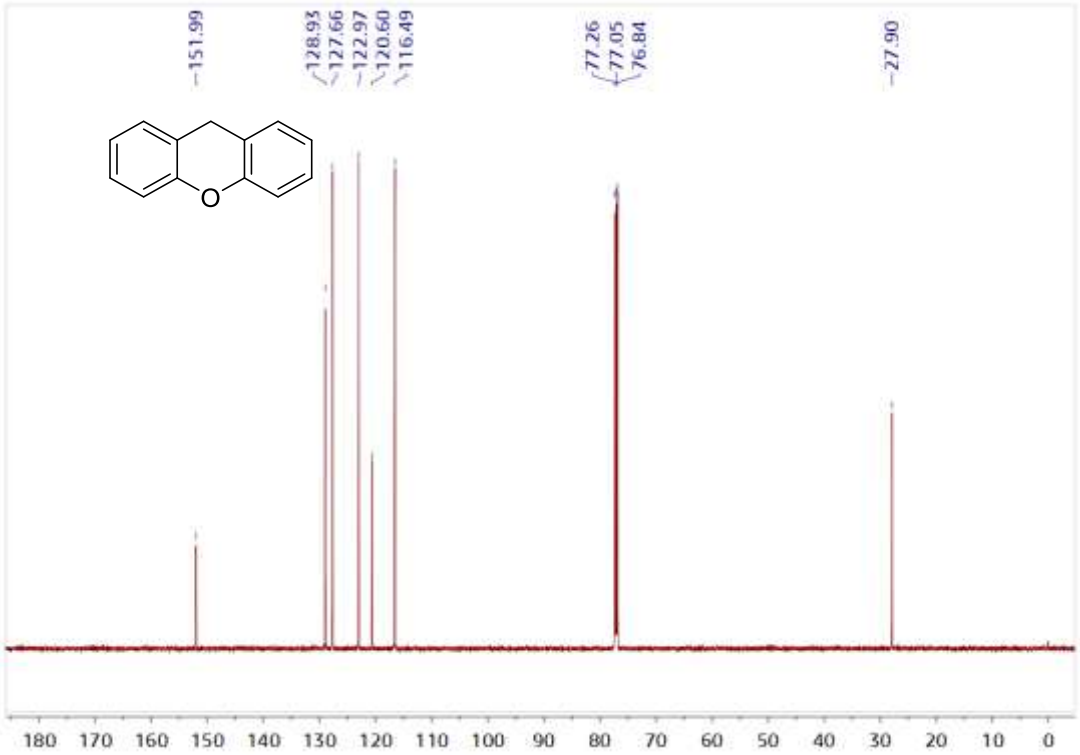
9H-thioxanthene (2aa)



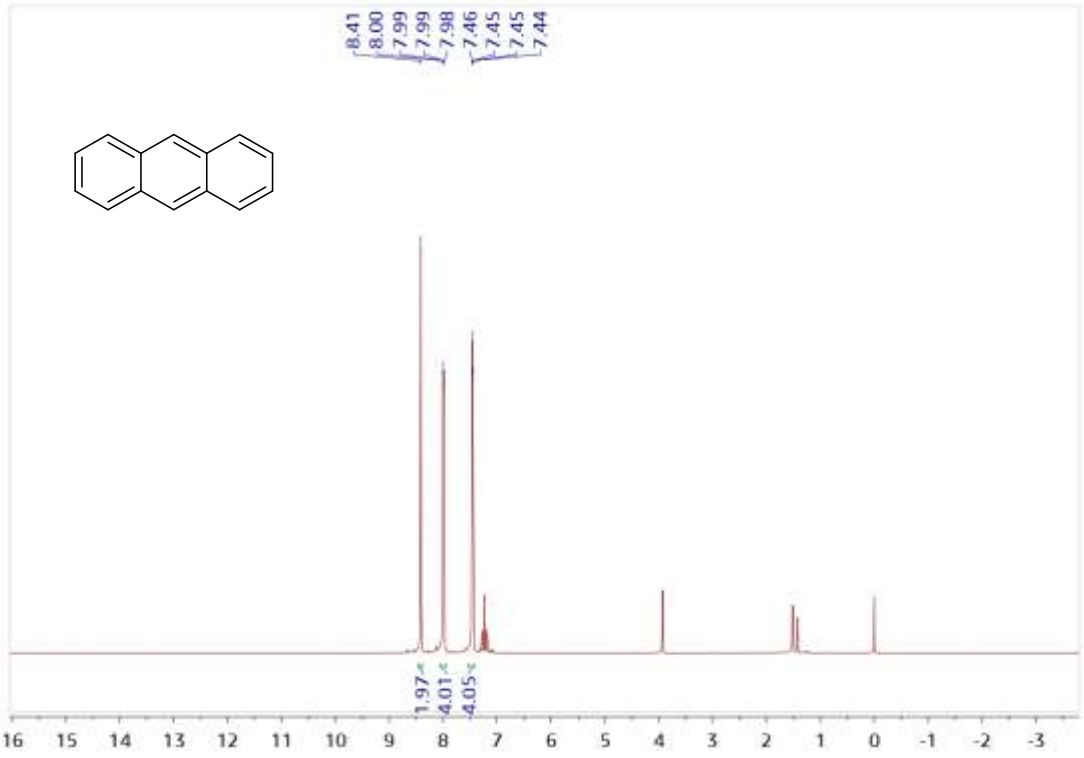


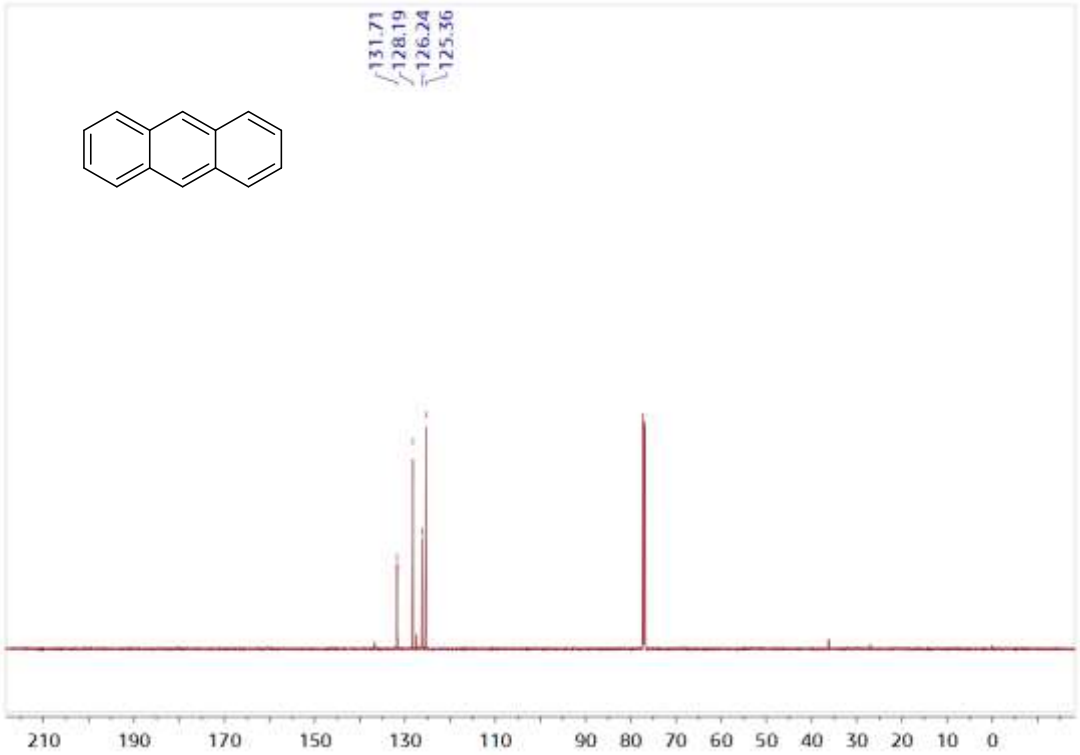
9H-xanthene (2ab)



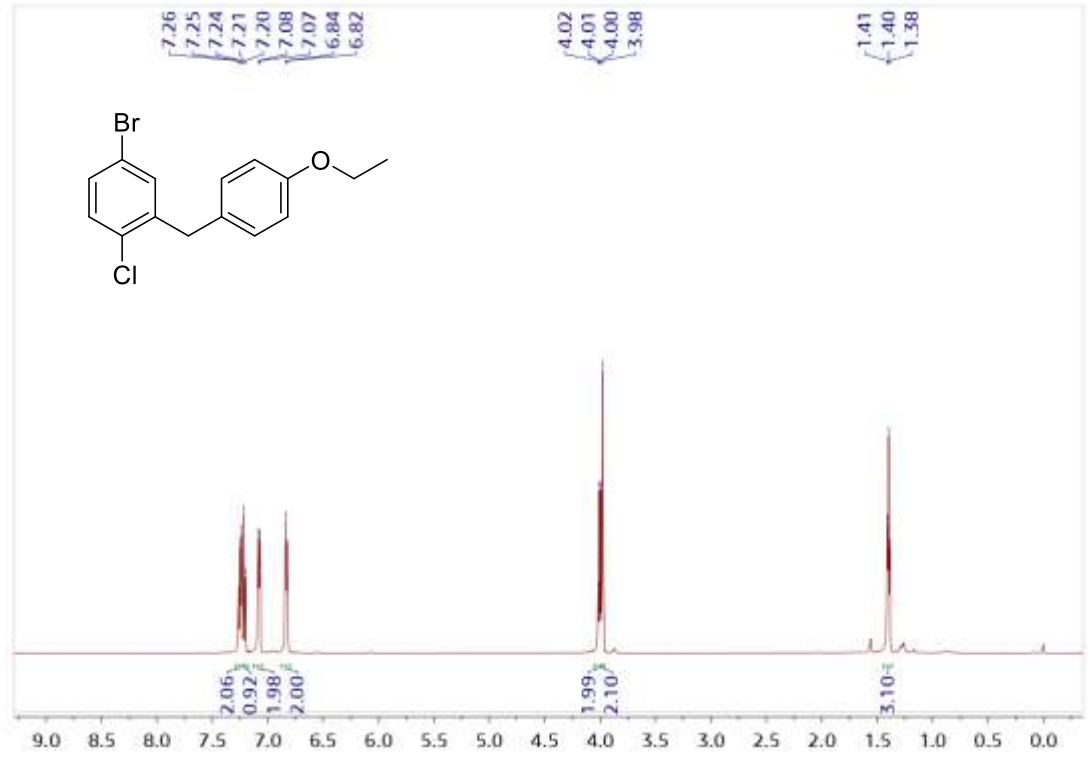


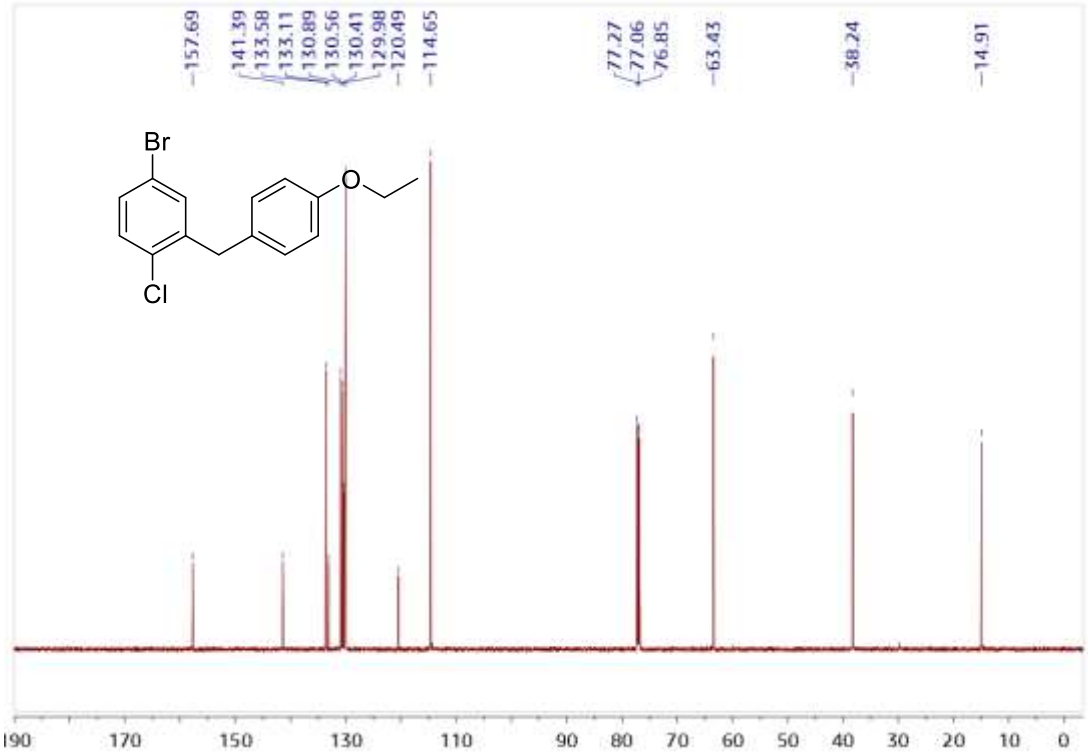
Anthracene (2ac)



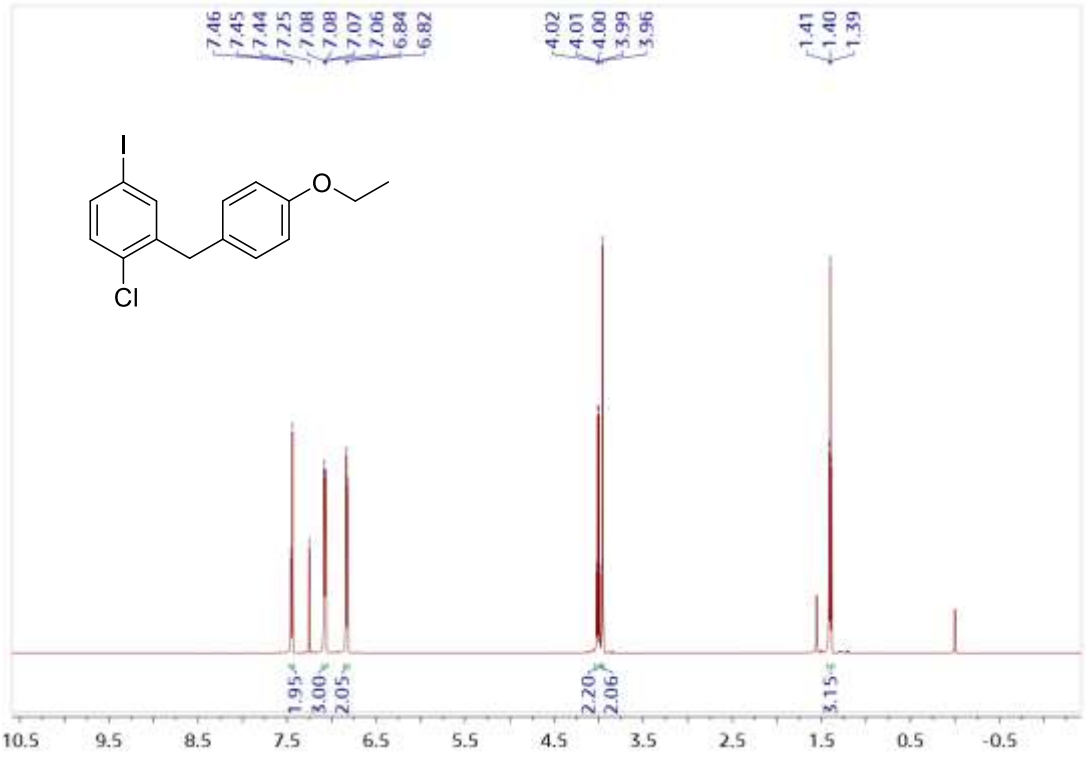


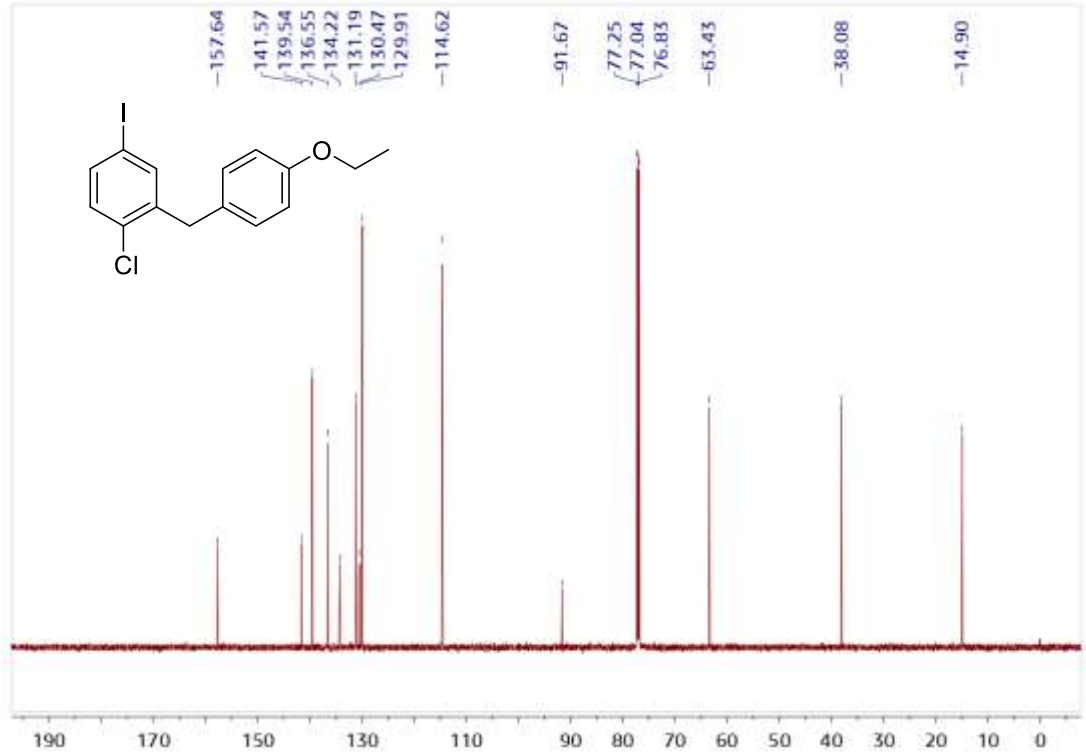
4-bromo-1-chloro-2-(4-ethoxybenzyl)benzene (2ad)



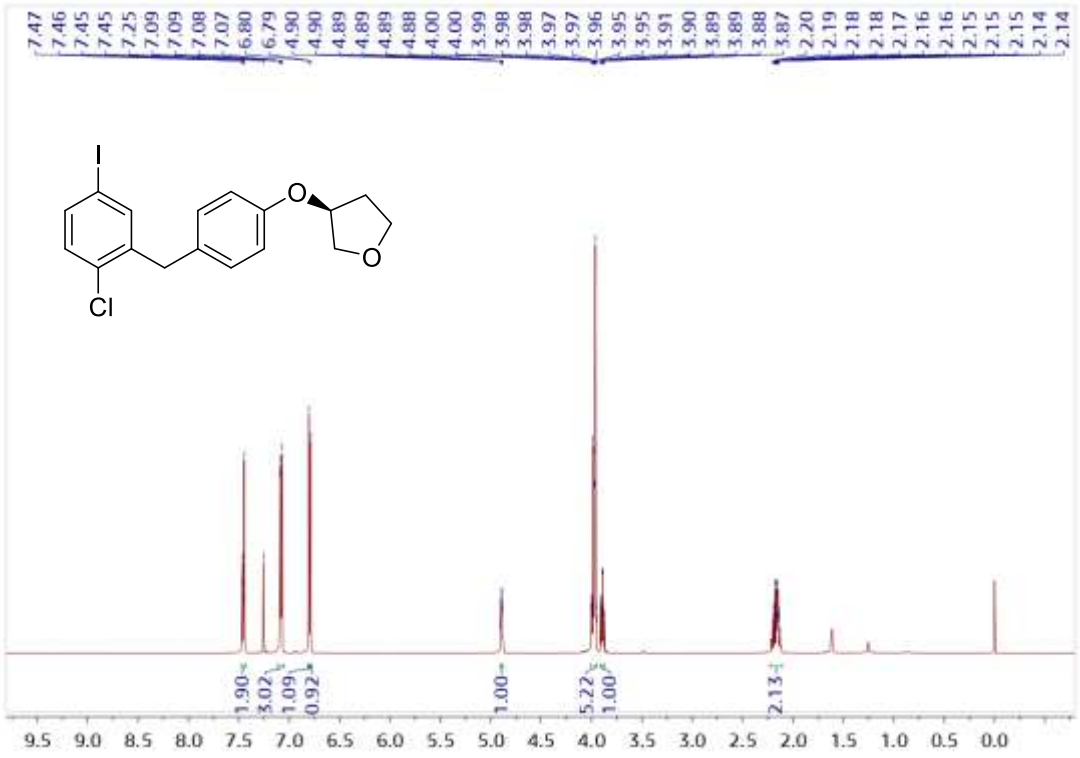


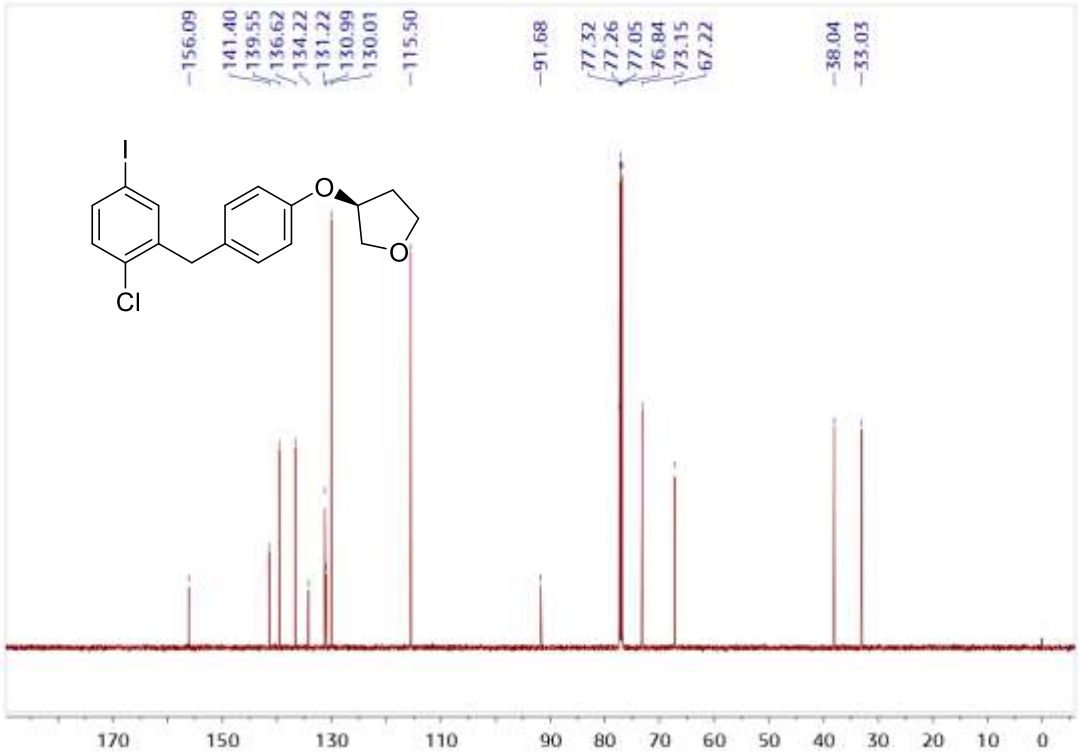
1-chloro-2-(4-ethoxybenzyl)-4-iodobenzene (2ae)



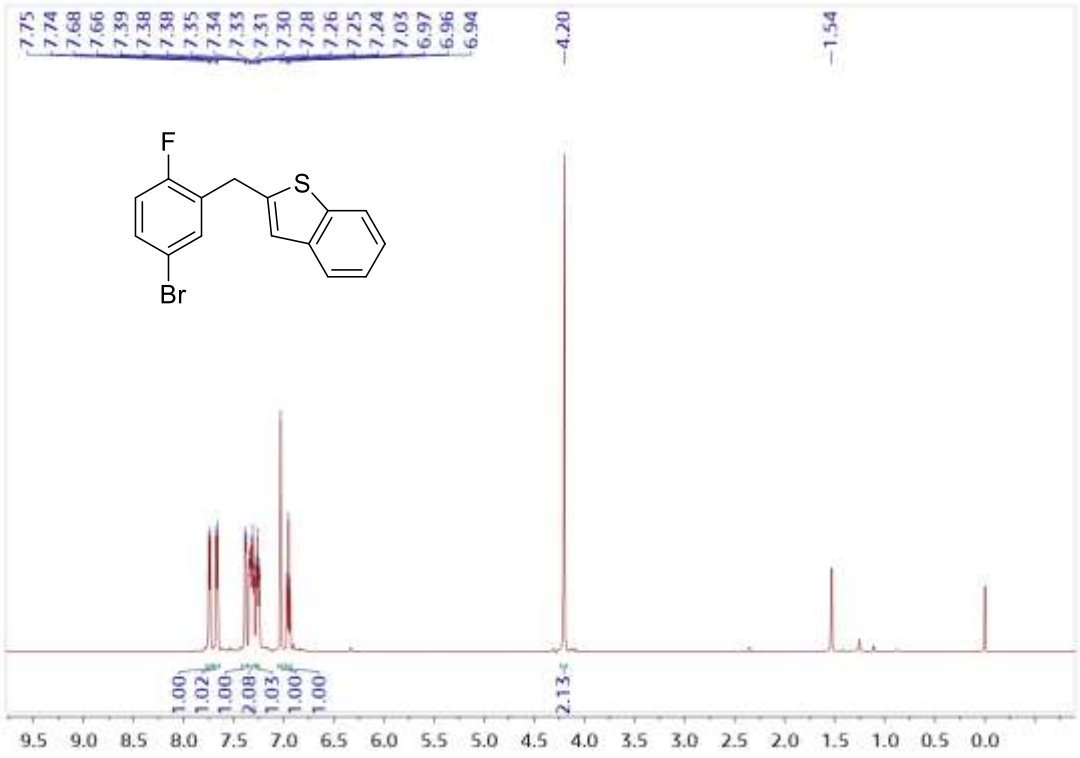


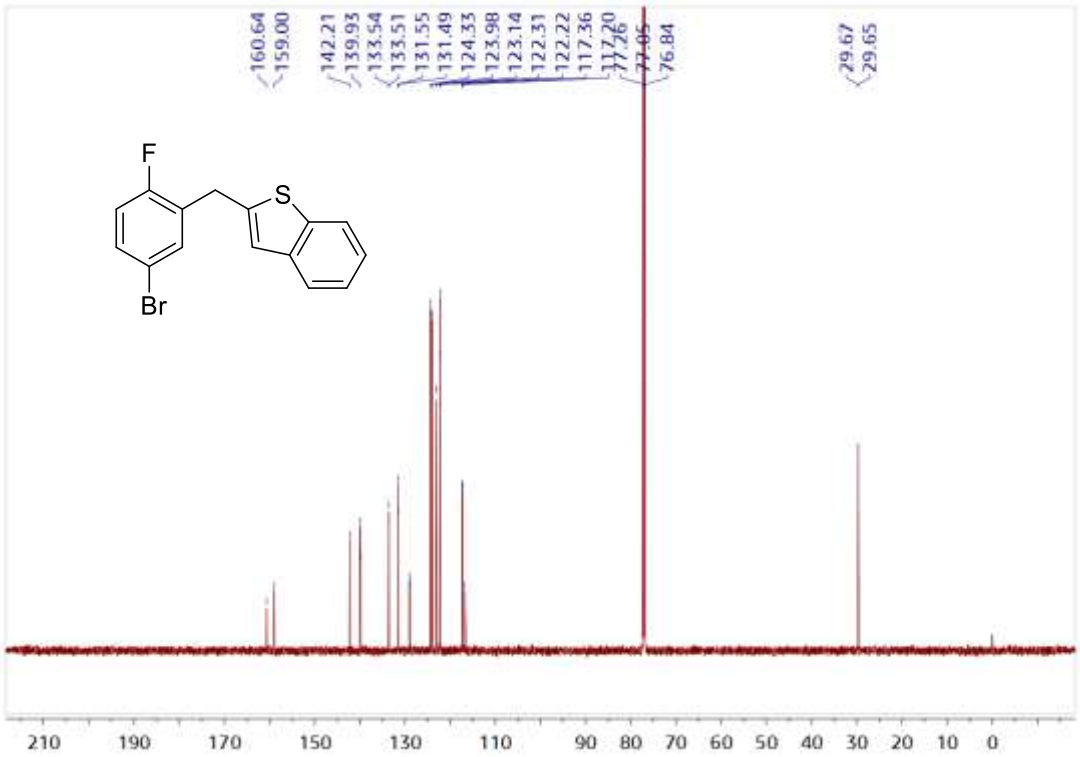
(S)-3-(4-(2-chloro-5-iodobenzyl)phenoxy)tetrahydrofuran (2af)



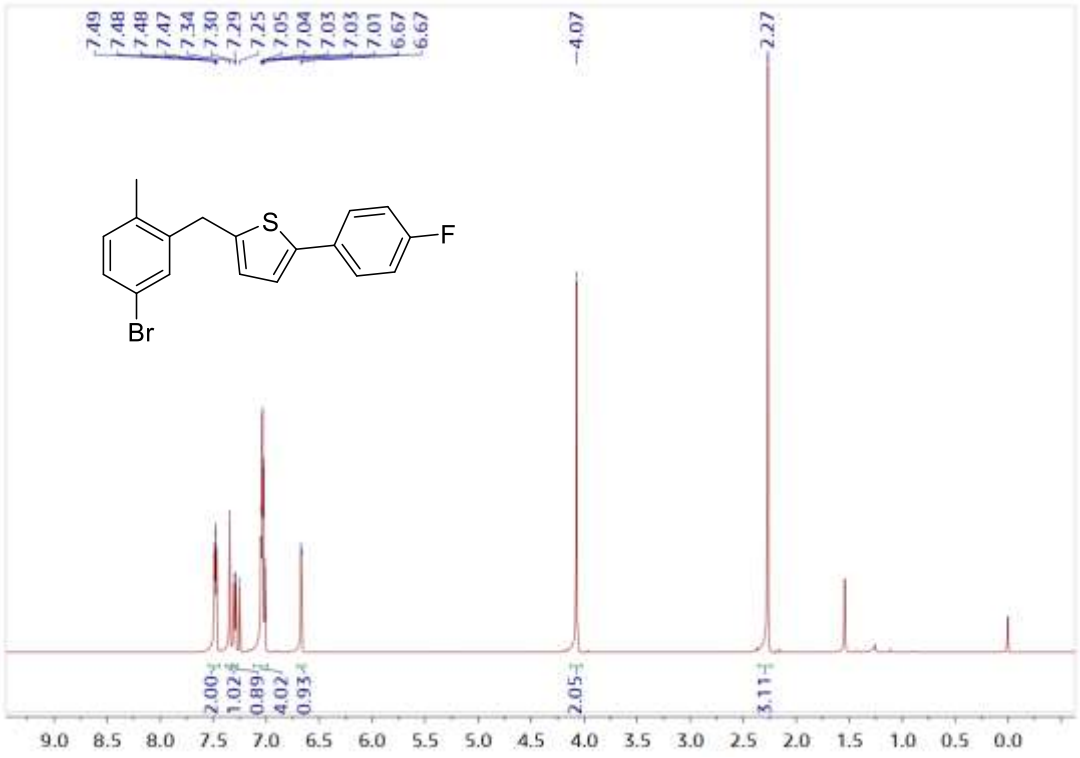


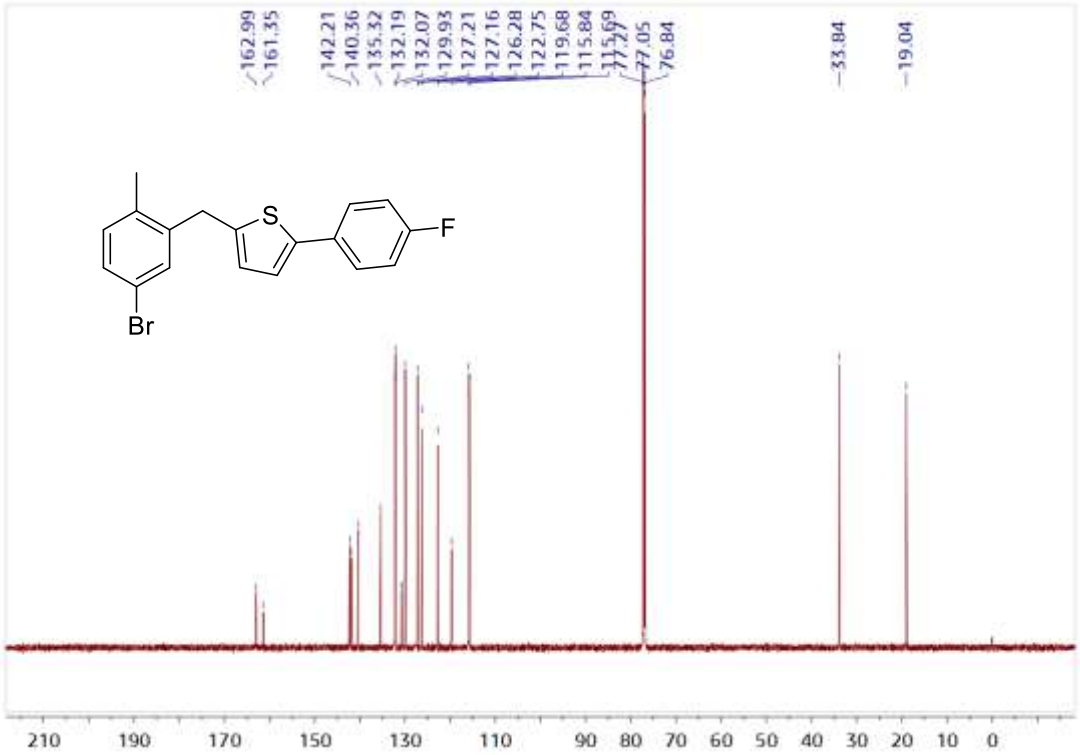
2-(5-bromo-2-fluorobenzyl)benzo[b]thiophene (2ag)



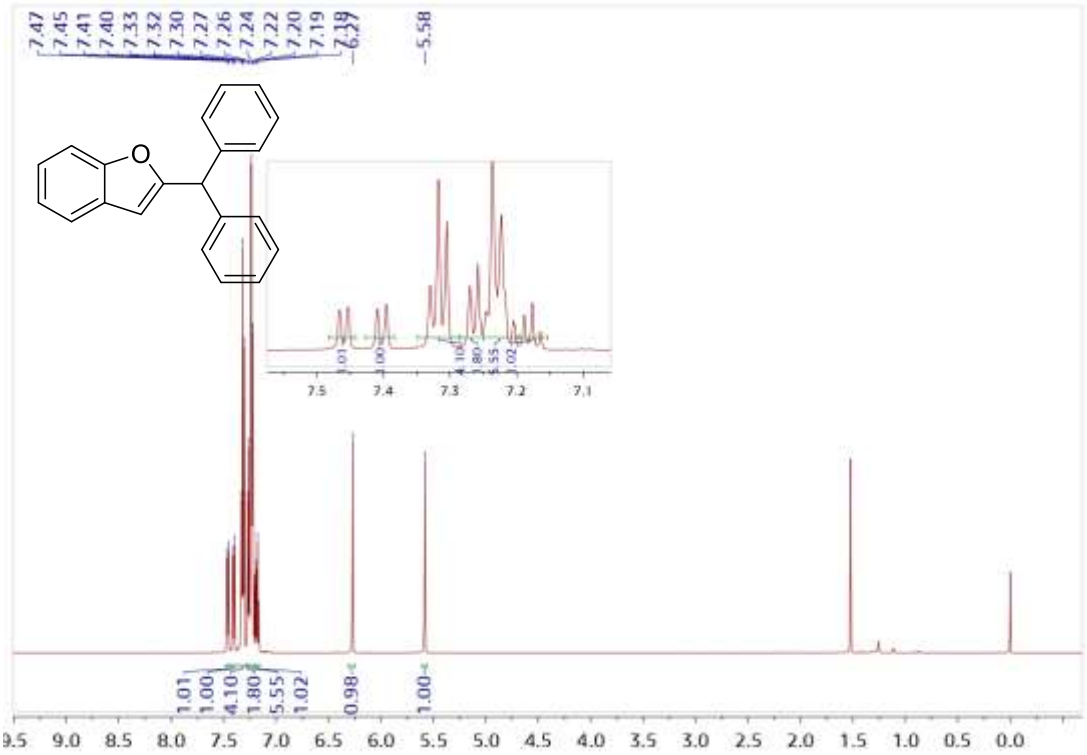


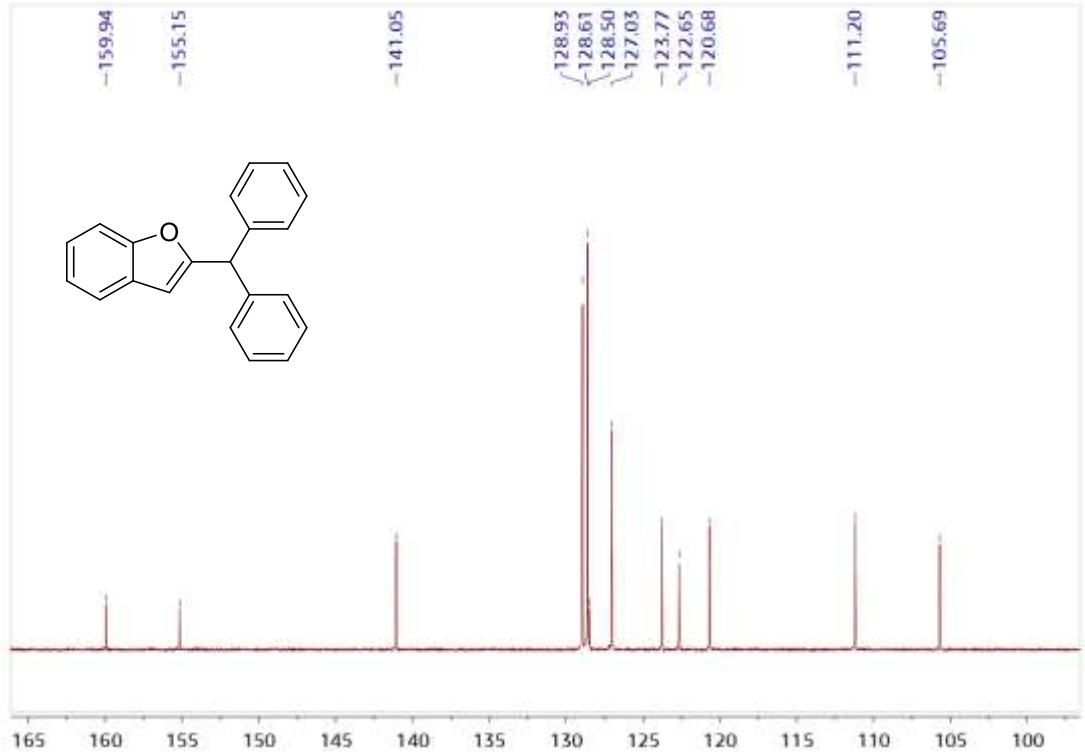
2-(5-bromo-2-methylbenzyl)-5-(4-fluorophenyl)thiophene (2ah)



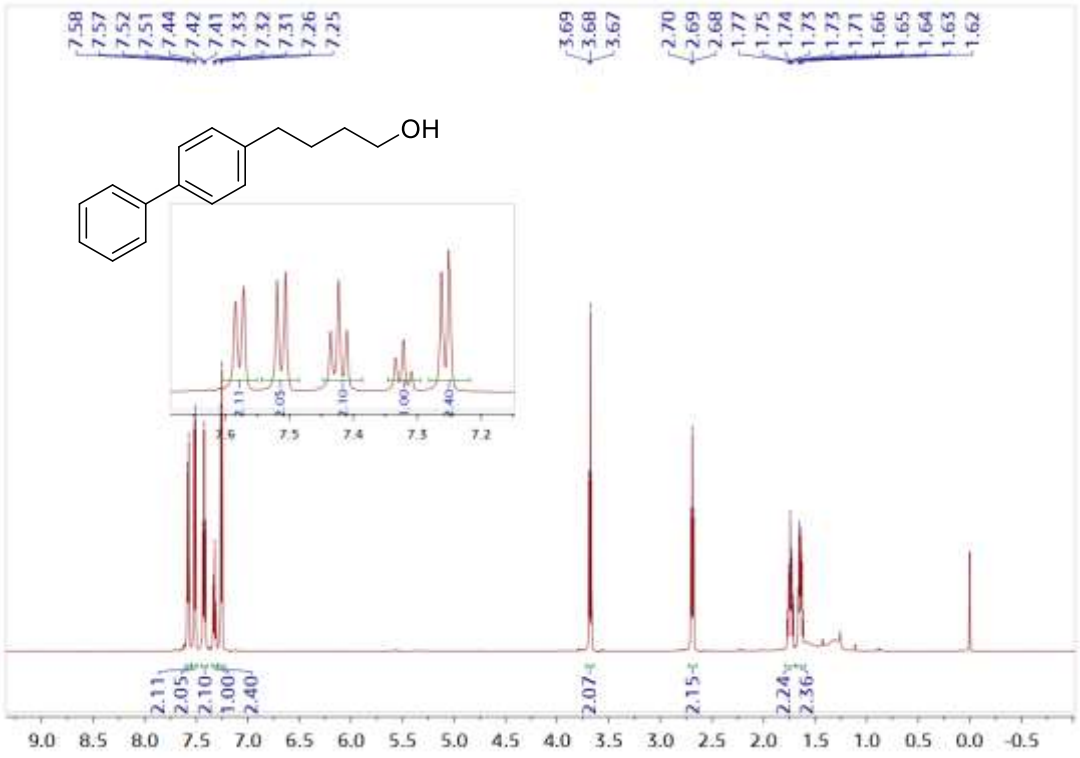


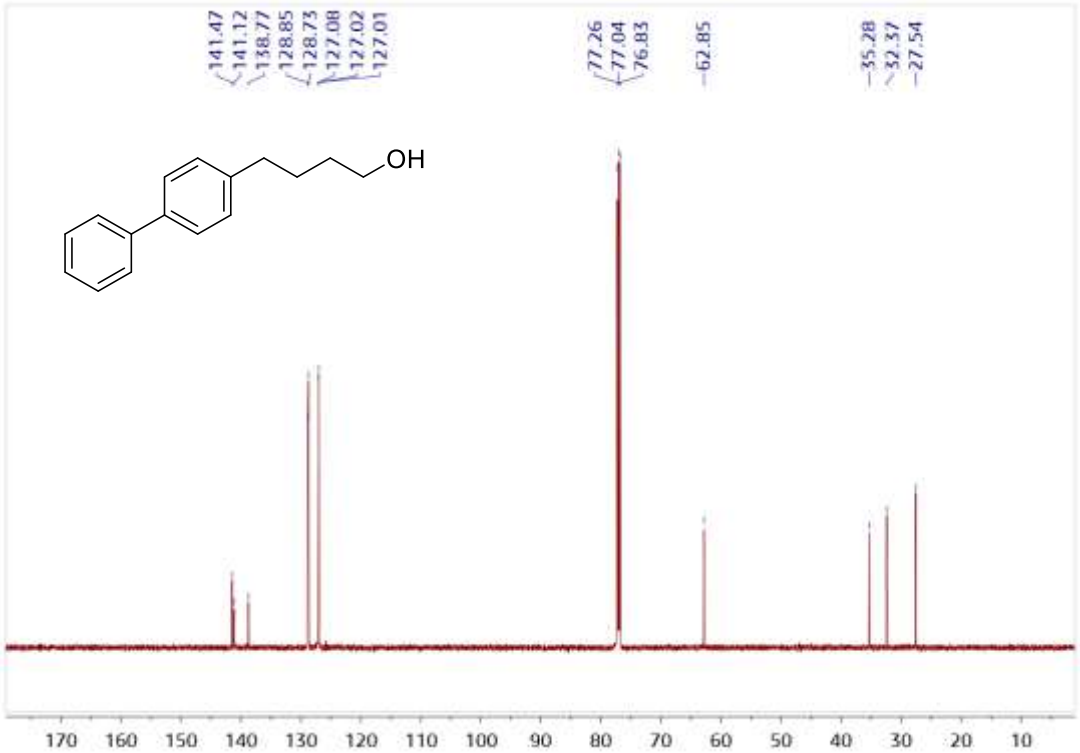
2-benzhydrylbenzofuran





4-([1,1'-biphenyl]-4-yl)butan-1-ol





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