

Supporting Information

Phosphazene Base-Catalyzed Intramolecular Cyclization for Efficient Synthesis of Benzofurans via Carbon-Carbon Bond Formation

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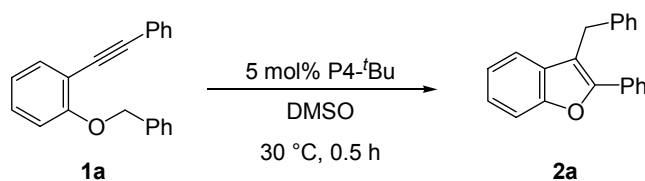
General Information: Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer. ^1H NMR spectra were recorded on JEOL AL300 (300 MHz) and JEOL JNM-A500 (500 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance as the internal standard (CDCl_3 : 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broadened) and coupling constants (Hz). ^{13}C NMR spectra were recorded on JEOL AL300 (75 MHz) and JEOL JNM-A500 (126 MHz) spectrometer with complete proton decoupling. Column chromatography was performed on silica gel 60N (spherical, neutral, 100-210 μm ; Kanto Chemical Co., Inc.). Mass spectra analysis was performed on a Bruker Daltonics APEX III FT-ICR-MS spectrometer at the Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University.

All reactions were carried out under an argon (Ar) atmosphere in dried glassware. DMSO was dried over activated $\text{MS3\AA}$ and used under Ar atmosphere. The other simple chemicals were purchased and used.

Experimental procedure

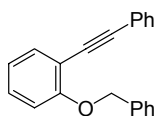
o-Alkynylphenyl ethers **1a** - **1p**, **3** and **5** were synthesized from *o*-iodophenol following reference.¹

General Procedure for the Phosphazene Base-Catalyzed Synthesis of **2**



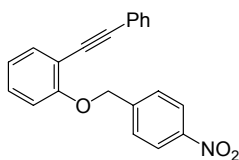
A DMSO solution (0.2 mL) of benzyl 2-(2'-phenylethynyl)phenyl ether (**1a**) (56.9 mg, 0.2 mmol) was added phosphazene base $\text{P4-}^t\text{Bu}$ (1 M solution in hexane, 10 μL , 10 μmol) under an Ar atmosphere. The solution was stirred at 30 °C for 0.5 h. After the consumption of **1a**, a few drops of diluted aqueous HCl were added. The reaction mixture was filtered through a short silica gel pad with ether and concentrated. The residue was purified by silica gel column chromatography (*n*-hexane/AcOEt 50/1-10/1 as eluent) to give 3-benzyl-2-phenylbenzofuran **2a** in 96% yield as colorless oil.

Analytical data



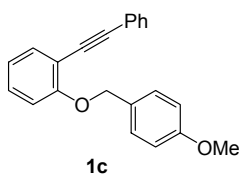
1a

Benzyl 2-(2'-phenylethynyl)phenyl ether (1a): light yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 5.21 (2H, s), 6.95-6.98 (2H, m), 7.26-7.41 (7H, m), 7.51-7.56 (5H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 70.40, 85.90, 93.72, 112.84, 113.41, 120.90, 123.68, 126.86, 127.70, 128.03, 128.24, 128.42, 129.60, 131.53, 133.25, 137.05, 159.23; IR (neat) 3062, 3032, 2866, 2217, 1593, 1497, 1482, 1444, 1278, 1240, 1226, 1105, 1023, 913, 859 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{16}\text{NaO}$ ($\text{M}^+ + \text{Na}$) 307.1093. Found 307.1092.



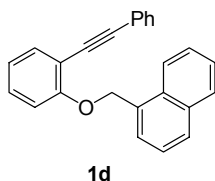
1b

***p*-Nitrophenylmethyl 2-(2'-phenylethynyl)phenyl ether (1b):** yellow solid; ^1H NMR (500 MHz, CDCl_3) δ 5.29 (2H, s), 6.93 (1H, d, $J = 8.0\text{ Hz}$), 7.00-7.03 (1H, m), 7.28-7.32 (1H, m), 7.35-7.39 (3H, m), 7.51-7.56 (3H, m), 7.72-7.75 (2H, m), 8.23-8.26 (2H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 69.15, 85.44, 94.00, 108.81, 112.62, 113.47, 121.55, 123.72, 127.21, 128.33, 128.42, 129.69, 131.43, 133.49, 144.46, 147.46, 158.48; IR (neat) 3081, 3065, 2849, 2450, 2215, 1511, 1498, 1442, 1349, 1241, 1105, 1052, 758, 742, 731, 686 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{15}\text{NNaO}_3$ ($\text{M}^+ + \text{Na}$) 352.0944. Found 352.0943.

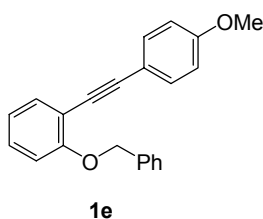


1c

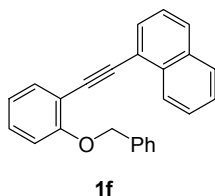
***p*-Methoxyphenylmethyl 2-(2'-phenylethynyl)phenyl ether (1c):** white solid; ^1H NMR (500 MHz, CDCl_3) δ 3.82 (3H, s), 5.14 (2H, s), 6.89-6.97 (4H, m), 7.25-7.35 (5H, m), 7.44-7.46 (2H, m), 7.49-7.53 (2H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 55.26, 70.37, 85.95, 93.64, 113.08, 113.47, 113.83, 120.87, 123.71, 128.01, 128.24, 128.57, 129.11, 129.58, 131.54, 133.25, 159.23, 159.30; IR (neat) 2933, 2835, 2217, 1513, 1496, 1444, 1278, 1239, 1173, 1032, 749, 689 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{18}\text{NaO}_2$ ($\text{M}^+ + \text{Na}$) 337.1199. Found 337.1199.



α-Naphthylmethyl 2-(2'-phenylethynyl)phenyl ether (1d): light yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 5.66 (2H, s), 6.98 (1H, td, $J = 8.0, 1.0$ Hz), 7.09 (1H, d, $J = 8.0$ Hz), 7.26-7.32 (4H, m), 7.35-7.38 (2H, m), 7.45-7.54 (4H, m), 7.76 (1H, dd, $J = 7.0, 1.0$ Hz), 7.85 (1H, d, $J = 8.0$ Hz), 7.89-7.92 (1H, m), 8.17-8.20 (1H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 69.25, 85.87, 93.75, 108.80, 113.11, 113.63, 121.07, 123.59, 123.66, 125.29, 125.78, 125.84, 126.33, 127.96, 128.15, 128.61, 128.66, 129.59, 131.18, 131.51, 132.29, 133.28, 133.66, 159.28; IR (neat) 3053, 2216, 1593, 1496, 1482, 1444, 1279, 1226, 1104, 1000, 793, 748, 688 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{25}\text{H}_{18}\text{NaO}$ ($\text{M}^+ + \text{Na}$) 357.1250. Found 357.1248.

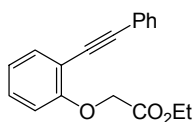


Benzyl 2-[2'-(*p*-methoxyphenyl)ethynyl]phenyl ether (1e): white solid; ^1H NMR (500 MHz, CDCl_3) δ 3.83 (3H, s), 5.21 (2H, s), 6.86-6.89 (2H, m), 6.93-6.97 (2H, m), 7.23-7.27 (1H, m), 7.30-7.33 (1H, m), 7.37-7.40 (2H, m), 7.45-7.48 (2H, m), 7.49-7.51 (1H, m), 7.53-7.55 (2H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 55.28, 70.44, 84.51, 93.73, 112.89, 113.78, 113.92, 115.85, 120.93, 126.89, 127.70, 128.43, 129.24, 132.99, 133.08, 137.14, 159.07, 159.47; IR (neat) 3066, 2901, 2837, 2216, 1511, 1442, 1247, 1025, 829 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{18}\text{NaO}_2$ ($\text{M}^+ + \text{Na}$) 337.1199. Found 337.1197.



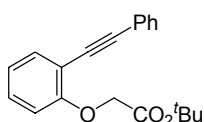
Benzyl 2-(2'-α-naphthylethynyl)phenyl ether (1f): white solid; ^1H NMR (500 MHz, CDCl_3) δ 5.25 (2H, s), 6.99-7.04 (2H, m), 7.27-7.49 (7H, m), 7.58-7.60 (2H, m), 7.63 (1H, dd, $J = 7.5, 1.5$ Hz), 7.75 (1H, dd, $J = 7.5, 1.5$ Hz), 7.82 (2H, t, $J = 8.0$ Hz), 8.45

(1H, d, $J = 8.0$ Hz); ^{13}C NMR (126 MHz, CDCl_3) δ 70.56, 90.88, 91.95, 112.39, 113.42, 120.88, 121.39, 125.19, 126.26, 126.62, 126.67, 127.51, 127.90, 128.03, 128.48, 128.57, 129.69, 130.02, 133.13, 133.26, 133.34, 136.82, 159.35; IR (neat) 3056, 3033, 2207, 1491, 1441, 1380, 1280, 1237, 1112, 1010, 933, 916, 856 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{25}\text{H}_{18}\text{NaO}$ ($\text{M}^+ + \text{Na}$) 357.1250. Found 357.1248.



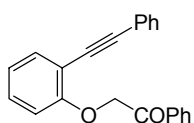
1h

Ethoxycarbonylmethyl 2-(2'-phenylethynyl)phenyl ether (1h): light yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 1.30 (3H, t, $J = 7.5$ Hz), 4.28 (2H, q, $J = 7.5$ Hz), 4.75 (2H, s), 6.84 (1H, d, $J = 8.0$ Hz), 6.98-7.02 (1H, m), 7.26-7.36 (4H, m), 7.52 (1H, dd, $J = 7.5, 2.0$ Hz), 7.56-7.58 (2H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 14.11, 61.31, 66.36, 85.30, 93.93, 113.01, 113.50, 121.77, 123.44, 128.15, 128.21, 129.50, 131.61, 133.62, 158.38, 168.66; IR (neat) 3061, 2982, 2926, 2219, 1756, 1735, 1497, 1194, 1112, 1070, 751, 690 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{16}\text{NaO}_3$ ($\text{M}^+ + \text{Na}$) 303.0992. Found 303.0990.



1i

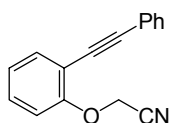
t-Butoxycarbonylmethyl 2-(2'-phenylethynyl)phenyl ether (1i): light yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 1.48 (9H, s), 4.63 (2H, s), 6.81 (1H, d, $J = 7.5$ Hz), 6.98 (1H, t, $J = 7.5$ Hz), 7.25-7.36 (4H, m), 7.51 (1H, dd, $J = 7.5, 1.5$ Hz), 7.57 (2H, dd, $J = 7.5, 1.5$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 28.01, 66.49, 82.31, 85.43, 93.75, 112.56, 113.26, 121.47, 123.48, 128.10, 128.19, 129.44, 131.64, 133.65, 158.38, 167.70; IR (neat) 2979, 2219, 1751, 1497, 1483, 1451, 1368, 1217, 1149, 1112, 749, 690 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{20}\text{NaO}_3$ ($\text{M}^+ + \text{Na}$) 331.1305. Found 331.1304.



1j

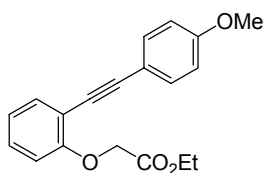
1-Phenyl-2-[2'-(2''-phenylethynyl)phenoxy]ethanone (1j): light yellow liquid; ^1H

NMR (500 MHz, CDCl₃) δ 5.35 (2H, s), 6.87 (1H, d, J = 8.0 Hz), 6.99 (1H, td, J = 8.0, 1.0 Hz), 7.25-7.32 (4H, m), 7.44-7.48 (4H, m), 7.51 (1H, dd, J = 7.5, 1.5 Hz), 7.58 (1H, td, J = 7.5, 1.5 Hz), 8.06-8.09 (2H, m); ¹³C NMR (126 MHz, CDCl₃) δ 71.99, 85.46, 93.95, 112.88, 113.40, 121.65, 123.41, 128.11, 128.19, 128.45, 128.71, 129.58, 131.57, 133.55, 133.76, 134.59, 158.46, 194.56; IR (neat) 3060, 2217, 1701, 1595, 1496, 1482, 1448, 1216, 1112, 966 cm⁻¹; HRMS (ESI) Calcd for C₂₂H₁₆NaO₂ (M⁺+Na) 335.1043. Found 335.1041.



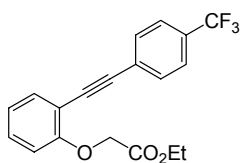
1k

Cyanomethyl 2-(2'-phenylethynyl)phenyl ether (1k): yellow liquid; ¹H NMR (300 MHz, CDCl₃) δ 4.91 (2H, s), 7.04-7.15 (2H, m), 7.34-7.40 (4H, m), 7.54-7.58 (3H, m); ¹³C NMR (126 MHz, CDCl₃) δ 54.79, 84.30, 94.63, 114.33, 114.39, 114.98, 122.92, 123.53, 128.37, 128.54, 129.81, 131.62, 134.01, 156.83; IR (neat) 3062, 2929, 2253, 2219, 1496, 1482, 1444, 1218, 1107, 1051, 1036, 905 cm⁻¹; HRMS (ESI) Calcd for C₁₆H₁₁NNaO (M⁺+Na) 256.0733. Found 256.0731.



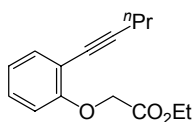
1l

Ethoxycarbonylmethyl 2-[2'-(*p*-methoxyphenyl)ethynyl]phenyl ether (1l): light yellow liquid; ¹H NMR (300 MHz, CDCl₃) δ 1.30 (3H, t, J = 7.5 Hz), 3.83 (3H, s), 4.28 (2H, q, J = 7.5 Hz), 4.74 (2H, s), 6.81-6.90 (3H, m), 6.96-7.02 (1H, m), 7.23-7.29 (1H, m), 7.48-7.53 (3H, m); ¹³C NMR (75 MHz, CDCl₃) δ 14.11, 55.22, 61.28, 66.34, 83.93, 93.96, 113.00, 113.80, 113.84, 115.55, 121.75, 129.13, 133.05, 133.43, 158.19, 159.50, 168.70; IR (neat) 2980, 2936, 2838, 2216, 1756, 1606, 1510, 1488, 1286, 1246, 1193, 1111, 1026, 831, 749 cm⁻¹; HRMS (ESI) Calcd for C₁₉H₁₉NaO₄ (M⁺+Na) 333.1097. Found 333.1096.



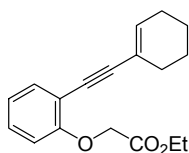
1m

Ethoxycarbonylmethyl 2-[2'-(*p*-trifluoromethylphenyl)ethynyl]phenyl ether (1m): light yellow liquid; ^1H NMR (300 MHz, CDCl_3) δ 1.30 (3H, t, $J = 7.5$ Hz), 4.29 (2H, q, $J = 7.5$ Hz), 4.74 (2H, s), 6.82 (1H, d, $J = 7.5$ Hz), 7.01 (1H, td, $J = 7.5, 1.0$ Hz), 7.29-7.35 (1H, m), 7.53 (1H, dd, $J = 7.5, 1.5$ Hz), 7.63-7.69 (4H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 14.14, 61.40, 66.14, 87.83, 92.45, 112.59, 112.73, 121.75, 122.88, 123.55, 125.12, 125.15, 125.18, 125.21, 127.34, 127.36, 129.62, 130.14, 131.81, 133.73, 158.53, 168.49; IR (neat) 2984, 2221, 1758, 1320, 1197, 1164, 1114, 1105, 1064, 1015, 842 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{15}\text{F}_3\text{NaO}_3$ ($\text{M}^+ + \text{Na}$) 371.0866. Found 371.0865.



1n

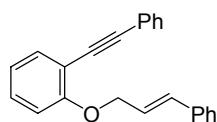
Ethoxycarbonylmethyl 2-(1'-pentynyl)phenyl ether (1n): yellow liquid; ^1H NMR (300 MHz, CDCl_3) δ 1.06 (3H, t, $J = 7.5$ Hz), 1.29 (3H, t, $J = 7.5$ Hz), 1.66 (2H, sextet, $J = 7.5$ Hz), 2.45 (2H, t, $J = 7.5$ Hz), 4.27 (2H, q, $J = 7.5$ Hz), 4.70 (2H, s), 6.77 (1H, d, $J = 8.0$ Hz), 6.91-6.96 (1H, m), 7.18-7.23 (1H, m), 7.40 (1H, dd, $J = 7.5, 1.5$ Hz); ^{13}C NMR (126 MHz, CDCl_3) δ 13.53, 14.12, 21.72, 22.20, 61.25, 66.39, 76.39, 95.03, 113.05, 114.26, 121.70, 128.61, 133.80, 158.31, 168.80; IR (neat) 2963, 2934, 2235, 1758, 1735, 1491, 1449, 1190, 1123, 1074, 1028 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{15}\text{H}_{18}\text{NaO}_3$ ($\text{M}^+ + \text{Na}$) 269.1148. Found 269.1146.



1o

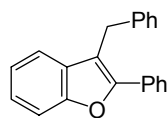
Ethoxycarbonylmethyl 2-(2'-cyclohexenyl)phenyl ether (1o): yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 1.30 (3H, t, $J = 7.5$ Hz), 1.59-1.64 (2H, m), 1.65-1.71 (2H, m), 2.12-2.17 (2H, m), 2.24-2.28 (2H, m), 4.27 (2H, q, $J = 7.5$ Hz), 4.70 (2H, s), 6.24 (1H, septet, $J = 2.0$ Hz), 6.79 (1H, d, $J = 8.0$ Hz), 6.95 (1H, td, $J = 7.5, 1.0$ Hz), 7.19-7.23

(1H, m), 7.40 (1H, dd, $J = 7.5, 1.5$ Hz); ^{13}C NMR (126 MHz, CDCl_3) δ 14.10, 21.48, 22.29, 25.71, 29.12, 61.22, 66.39, 82.50, 95.88, 113.16, 114.02, 120.83, 121.72, 128.89, 133.43, 135.09, 158.12, 168.71; IR (neat) 2930, 2859, 2202, 1758, 1736, 1491, 1449, 1190, 1098, 1070, 918, 842 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{20}\text{NaO}_3$ ($\text{M}^+ + \text{Na}$) 307.1305. Found 307.1304.



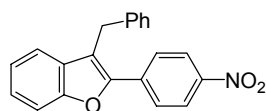
1p

2-(2'-Phenylethynyl)phenyl *E*-3-phenyl-2-propenyl ether (1p): white solid; ^1H NMR (300 MHz, CDCl_3) δ 4.82 (2H, dd, $J = 5.4, 1.8$ Hz), 6.47 (1H, dt, $J = 16.0, 5.4$ Hz), 6.87 (1H, dt, $J = 16.0, 1.8$ Hz), 6.94-6.99 (2H, m), 7.25-7.42 (9H, m), 7.51-7.59 (3H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 69.20, 85.84, 93.63, 112.72, 113.23, 120.86, 123.65, 124.36, 126.55, 127.76, 128.08, 128.27, 128.57, 129.64, 131.62, 132.34, 133.44, 136.57, 159.14; IR (neat) 3022, 2851, 2218, 1496, 1443, 1237, 1108, 965 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{23}\text{H}_{18}\text{NaO}$ ($\text{M}^+ + \text{Na}$) 333.1250. Found 333.1248.



2a

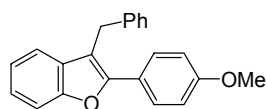
3-Benzyl-2-phenylbenzofuran (2a): colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 4.32 (2H, s), 7.16-7.19 (1H, m), 7.20-7.24 (1H, m), 7.26-7.31 (5H, m), 7.35-7.39 (2H, m), 7.42-7.46 (2H, m), 7.52-7.54 (1H, m), 7.75-7.78 (2H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 30.07, 111.05, 113.73, 119.93, 122.54, 124.42, 126.29, 126.91, 128.15, 128.34, 128.60, 128.69, 130.47, 130.86, 139.25, 152.08, 154.10; IR (neat) 2954, 2923, 2853, 1493, 1454, 1261, 1226, 1100, 1059, 740, 724, 695 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{16}\text{NaO}$ ($\text{M}^+ + \text{Na}$) 307.1093. Found 307.1092.



2b

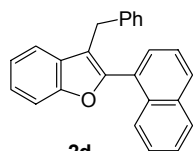
3-Benzyl-2-(*p*-nitrophenyl)benzofuran (2b): yellow solid; ^1H NMR (500 MHz, CDCl_3) δ 4.37 (2H, s), 7.23-7.26 (4H, m), 7.29-7.32 (2H, m), 7.36-7.40 (1H, m),

7.44-7.46 (1H, m), 7.56-7.58 (1H, m), 7.91-7.93 (2H, m), 8.27-8.29 (2H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 30.13, 108.84, 111.38, 117.58, 120.42, 123.17, 124.08, 125.92, 126.71, 126.96, 128.01, 128.87, 130.23, 136.85, 138.22, 146.93, 149.41, 154.45; IR (neat) 2924, 2853, 2440, 1594, 1507, 1334, 1110, 1093, 850, 740, 724, 693 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{15}\text{NNaO}_3$ ($\text{M}^+ + \text{Na}$) 352.0944. Found 352.0942.



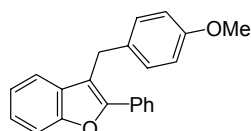
2c

3-Benzyl-2-(p-methoxyphenyl)benzofuran (2c): colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 3.85 (3H, s), 4.28 (2H, s), 6.95-6.98 (2H, m), 7.14-7.17 (1H, m), 7.20-7.31 (6H, m), 7.32-7.34 (1H, m), 7.49-7.51 (1H, m), 7.67-7.70 (2H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 30.02, 55.25, 110.87, 112.25, 114.16, 119.62, 122.44, 123.50, 123.98, 126.23, 128.12, 128.31, 128.57, 130.63, 139.41, 152.21, 153.90, 159.70; IR (neat) 3060, 3027, 2931, 2836, 1507, 1452, 1249, 1175, 1029, 832 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{18}\text{NaO}_2$ ($\text{M}^+ + \text{Na}$) 337.1199. Found 337.1199.



2d

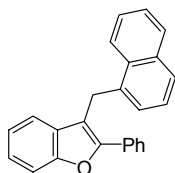
3-Benzyl-2-(α -naphthyl)benzofuran (2d): colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 4.09 (2H, s), 7.15-7.24 (6H, m), 7.30-7.39 (2H, m), 7.49-7.64 (5H, m), 7.92-8.02 (3H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 30.27, 111.24, 116.48, 120.37, 122.53, 124.28, 125.05, 126.02, 126.09, 126.19, 126.72, 127.86, 128.30, 128.33, 128.38, 128.78, 129.39, 129.84, 132.29, 133.77, 139.51, 152.43, 154.73; IR (neat) 3059, 3028, 1494, 1452, 1266, 1225, 1108, 1092, 801, 775, 744, 715, 694 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{25}\text{H}_{18}\text{NaO}$ ($\text{M}^+ + \text{Na}$) 357.1250. Found 357.1248.



2e

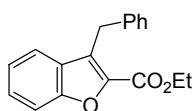
3-(4-methoxybenzyl)-2-phenylbenzofuran (2e): colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 3.78 (3H, s), 4.25 (2H, s), 6.81-6.84 (2H, m), 7.15-7.19 (3H, m), 7.27-7.31

(1H, m), 7.34-7.38 (2H, m), 7.42-7.46 (2H, m), 7.51-7.53 (1H, m), 7.75-7.77 (2H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 29.20, 55.21, 111.03, 114.01, 114.13, 119.96, 122.52, 124.38, 126.91, 128.31, 128.69, 129.07, 130.48, 130.90, 131.23, 151.92, 154.10, 158.10; IR (neat) 2957, 2928, 1508, 1242, 1175, 1036, 818, 749, 701 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{18}\text{NaO}_2$ ($\text{M}^+ + \text{Na}$) 337.1199. Found 337.1199.



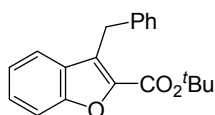
2f

3-(α -naphthylmethyl)-2-phenylbenzofuran (2f): colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 4.73 (2H, s), 7.13-7.20 (2H, m), 7.28-7.40 (6H, m), 7.56-7.63 (3H, m), 7.69-7.72 (2H, m), 7.76-7.79 (1H, m), 7.93-7.95 (1H, m), 8.19-8.21 (1H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 27.32, 111.11, 112.97, 119.88, 122.59, 123.21, 124.49, 125.07, 125.70, 125.76, 126.14, 126.79, 127.10, 128.34, 128.73, 128.85, 130.62, 130.74, 132.04, 133.78, 134.28, 152.51, 154.19; IR (neat) 3054, 2920, 1455, 1442, 1261, 1059, 793, 766, 743, 692 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{25}\text{H}_{18}\text{NaO}$ ($\text{M}^+ + \text{Na}$) 357.1250. Found 357.1250.



2h

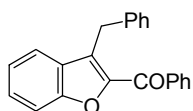
3-Benzyl-2-ethoxycarbonylbenzofuran (2h): colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 1.43 (3H, t, $J = 7.0$ Hz), 4.47 (2H, q, $J = 7.0$ Hz), 4.49 (2H, s), 7.17-7.31 (6H, m), 7.40-7.43 (1H, m), 7.49-7.51 (1H, m), 7.55-7.57 (1H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 14.32, 30.14, 61.27, 112.23, 121.70, 123.27, 126.34, 127.68, 128.03, 128.27, 128.47, 128.48, 138.89, 141.07, 154.54, 160.33; IR (neat) 2958, 2925, 1704, 1295, 1266, 1156, 1092, 747, 726 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{16}\text{NaO}_3$ ($\text{M}^+ + \text{Na}$) 303.0992. Found 303.0992.



2i

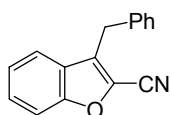
3-Benzyl-2- t -butoxycarbonylbenzofuran (2i): white solid; ^1H NMR (500 MHz, CDCl_3)

δ 1.61 (9H, s), 4.46 (2H, s), 7.17-7.21 (2H, m), 7.24-7.29 (4H, m), 7.37-7.40 (1H, m), 7.45-7.47 (1H, m), 7.53-7.55 (1H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 28.24, 30.16, 82.66, 112.14, 121.57, 123.07, 126.25, 126.37, 127.31, 128.36, 128.41, 138.97, 142.21, 154.38, 159.62; IR (neat) 3727, 3625, 2974, 1709, 1303, 1154, 1144, 748 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{20}\text{NaO}_3$ ($\text{M}^+ + \text{Na}$) 331.1305. Found 331.1303.



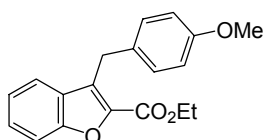
2j

(3-Benzylbenzofuran-2-yl)(phenyl)methanone (2j): colorless liquid; ^1H NMR (500 MHz, CDCl_3) δ 4.46 (2H, s), 7.19 (1H, tt, $J = 7.5, 1.5$ Hz), 7.24-7.29 (3H, m), 7.36-7.38 (2H, m), 7.44-7.48 (1H, m), 7.51-7.58 (4H, m), 7.62 (1H, tt, $J = 7.5, 1.5$ Hz), 8.10-8.13 (2H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 30.45, 112.25, 122.08, 123.45, 126.33, 128.05, 128.27, 128.39, 128.46, 128.68, 129.11, 129.81, 132.68, 137.67, 139.07, 148.30, 154.37, 185.80; IR (neat) 3060, 3028, 1642, 1555, 1287, 1263, 747, 714, 691, 677 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{16}\text{NaO}_2$ ($\text{M}^+ + \text{Na}$) 335.1043. Found 335.1041.



2k

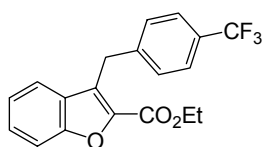
3-Benzyl-2-cyanobenzofuran (2k): white solid; ^1H NMR (500 MHz, CDCl_3) δ 4.21 (2H, s), 7.24-7.34 (6H, m), 7.44-7.52 (3H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 30.37, 111.79, 112.18, 121.50, 124.08, 125.13, 126.01, 127.09, 128.39, 128.58, 128.85, 132.56, 137.03, 155.71; IR (neat) 2959, 2925, 2854, 2220, 1443, 1260, 1093, 1031, 817 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{11}\text{NNaO}$ ($\text{M}^+ + \text{Na}$) 256.0733. Found 256.0732.



2l

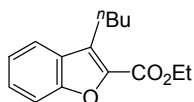
2-Ethoxycarbonyl-3-(p-methoxybenzyl)benzofuran (2l): colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 1.44 (3H, t, $J = 7.0$ Hz), 3.76 (3H, s), 4.43 (2H, s), 4.47 (2H, q, $J = 7.0$ Hz), 6.78-6.83 (2H, m), 7.20-7.25 (3H, m), 7.38-7.44 (1H, m), 7.49-7.57 (2H, m); ^{13}C

NMR (75 MHz, CDCl₃) δ 14.33, 29.26, 55.13, 61.24, 112.20, 113.84, 121.71, 123.22, 127.65, 128.22, 128.50, 129.43, 130.95, 140.84, 154.51, 158.07, 160.35; IR (neat) 2980, 2936, 2906, 2835, 1706, 1510, 1292, 1245, 1141, 1091, 1030, 744 cm⁻¹; HRMS (ESI) Calcd for C₁₉H₁₈NaO₄ (M⁺+Na) 333.1097. Found 333.1097.



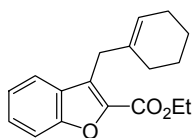
2m

2-Ethoxycarbonyl-3-(*p*-trifluoromethylbenzyl)benzofuran (2m): colorless liquid; ¹H NMR (500 MHz, CDCl₃) δ 1.43 (3H, t, *J* = 7.0 Hz), 4.47 (2H, q, *J* = 7.0 Hz), 4.55 (2H, s), 7.24-7.27 (1H, m), 7.39-7.53 (6H, m), 7.57-7.59 (1H, m); ¹³C NMR (126 MHz, CDCl₃) δ 14.31, 29.90, 61.43, 112.42, 121.31, 123.53, 125.39, 125.42, 125.45, 125.48, 126.98, 127.97, 128.75, 141.33, 143.00, 154.54, 160.18; IR (neat) 2983, 1708, 1323, 1294, 1118, 1106, 1065, 745 cm⁻¹; HRMS (ESI) Calcd for C₁₉H₁₅F₃NaO₃ (M⁺+Na) 371.0866. Found 371.0864.



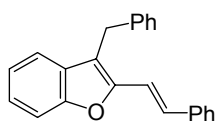
2n

3-*n*-Butyl-2-ethoxycarbonylbenzofuran (2n): colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 0.97 (3H, t, *J* = 7.5 Hz), 1.43 (2H, sextet, *J* = 7.5 Hz), 1.44 (3H, t, *J* = 7.5 Hz), 1.65-1.72 (2H, m), 3.08 (2H, t, *J* = 7.5 Hz), 4.45 (2H, q, *J* = 7.5 Hz), 7.27-7.31 (1H, m), 7.42-7.45 (1H, m), 7.54-7.56 (1H, m), 7.64-7.67 (1H, m); ¹³C NMR (126 MHz, CDCl₃) δ 13.90, 14.36, 22.71, 23.90, 32.02, 61.07, 112.26, 121.28, 123.03, 127.59, 128.56, 130.47, 140.62, 154.45, 160.43; IR (neat) 2957, 2930, 2861, 1709, 1293, 1266, 1142, 1092, 1021, 855 cm⁻¹; HRMS (ESI) Calcd for C₁₅H₁₈NaO₃ (M⁺+Na) 269.1148. Found 269.1147.



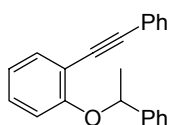
2o

3-Cyclohexenylmethyl-2-ethoxycarbonylbenzofuran (2o): colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 1.44 (3H, t, $J = 7.0$ Hz), 1.49-1.61 (4H, m), 1.92-2.01 (4H, m), 3.78 (2H, s), 4.45 (2H, q, $J = 7.0$ Hz), 5.54 (1H, br s), 7.25-7.28 (1H, m), 7.41-7.44 (1H, m), 7.54-7.56 (1H, m), 7.67-7.69 (1H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 14.35, 22.22, 22.78, 25.20, 28.22, 32.63, 61.07, 112.11, 121.96, 122.98, 123.01, 127.46, 127.56, 128.73, 134.90, 141.17, 154.40, 160.41; IR (neat) 2925, 2835, 1710, 1292, 1267, 1140, 1090, 856 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{20}\text{NaO}_3$ ($\text{M}^+ + \text{Na}$) 307.1305. Found 307.1304.



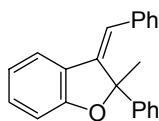
2p

(E)-3-benzyl-2-styrylbenzofuran (2p): white solid; ^1H NMR (500 MHz, CDCl_3) δ 4.14 (2H, s), 7.06 (1H, d, $J = 16$ Hz), 7.12 (1H, td, $J = 7.5, 1.0$ Hz), 7.17-7.22 (1H, m), 7.23-7.37 (10H, m), 7.43-7.45 (1H, m), 7.49-7.51 (2H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 29.65, 110.74, 114.28, 116.55, 119.75, 122.52, 124.80, 126.34, 126.63, 128.00, 128.38, 128.56, 128.72, 129.72, 129.75, 136.79, 139.28, 151.28, 154.34; IR (neat) 3021, 2925, 1493, 1450, 1177, 965, 752, 740, 723, 690 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{23}\text{H}_{18}\text{NaO}$ ($\text{M}^+ + \text{Na}$) 333.1250. Found 333.1249.



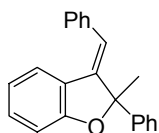
3a

1-(1'-Phenylethoxy)-2-(2'-phenylethynyl)benzene (3a): colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 1.71 (3H, t, $J = 6.5$ Hz), 5.42 (1H, q, $J = 6.5$ Hz), 6.77 (1H, d, $J = 8.5$ Hz), 6.87-6.90 (1H, m), 7.11-7.15 (1H, m), 7.24-7.27 (1H, m), 7.32-7.38 (5H, m), 7.44-7.48 (3H, m), 7.55-7.58 (2H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 24.29, 77.11, 86.24, 93.48, 114.04, 114.87, 120.78, 123.84, 125.62, 127.45, 128.00, 128.28, 128.51, 129.35, 131.51, 133.17, 143.01, 158.59; IR (neat) 3060, 3031, 2978, 1593, 1495, 1480, 1445, 1275, 1238, 1066, 933, 915 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{18}\text{NaO}$ ($\text{M}^+ + \text{Na}$) 321.1250. Found 321.1249.



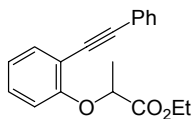
Z-4a

(Z)-3-Benzylidene-2-methyl-2-phenyl-2,3-dihydrobenzofuran (Z-4a): light yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 1.95 (3H, d, $J = 3.5$ Hz), 6.82 (1H, dd, $J = 7.0, 2.0$ Hz), 6.92-6.99 (3H, m), 7.06 (1H, d, $J = 2.0$ Hz), 7.08-7.11 (3H, m), 7.22-7.26 (1H, m), 7.31-7.34 (3H, m), 7.46-7.50 (2H, m), 7.54-7.57 (1H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 22.22, 91.26, 110.60, 118.98, 120.17, 120.66, 126.21, 126.78, 127.62, 127.91, 128.36, 128.63, 129.02, 130.47, 135.61, 142.19, 144.25, 160.01; IR (neat) 3057, 3025, 2979, 1594, 1464, 1260, 1056, 881 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{18}\text{NaO}$ ($\text{M}^+ + \text{Na}$) 321.1250. Found 321.1249.



E-4a

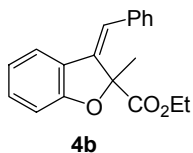
(E)-3-Benzylidene-2-methyl-2-phenyl-2,3-dihydrobenzofuran (E-4a): white solid; ^1H NMR (500 MHz, CDCl_3) δ 1.97 (3H, s), 6.31 (1H, s), 6.70 (1H, t, $J = 7.5$ Hz), 6.93 (1H, d, $J = 7.5$ Hz), 7.18-7.22 (1H, m), 7.27-7.31 (3H, m), 7.33-7.40 (6H, m), 7.53-7.55 (2H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 27.56, 91.23, 110.63, 120.25, 121.53, 123.80, 124.14, 125.37, 127.25, 127.70, 128.38, 128.46, 130.75, 136.85, 144.13, 145.23, 161.77; IR (neat) 3057, 3024, 2979, 1587, 1459, 1444, 1253, 1059, 895 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{18}\text{NaO}$ ($\text{M}^+ + \text{Na}$) 321.1250. Found 321.1250.



3b

Ethyl 2-[2'-(2''-phenylethynyl)phenoxy]propanoate (3b): light yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 1.25 (3H, t, $J = 7.0$ Hz), 1.70 (3H, d, $J = 7.0$ Hz), 4.18-4.25 (2H, m), 4.86 (1H, q, $J = 7.0$ Hz), 6.86 (1H, d, $J = 8.0$ Hz), 6.98-7.01 (1H, m), 7.23-7.26 (1H, m), 7.32-7.37 (3H, m), 7.50 (1H, dd, $J = 8.0, 1.8$ Hz), 7.53-7.55 (2H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 14.10, 18.61, 61.22, 74.45, 85.59, 93.79, 114.31, 115.19, 121.97, 123.62, 128.12, 128.27, 129.45, 131.55, 133.51, 158.41, 171.97; IR (neat) 2985, 2219,

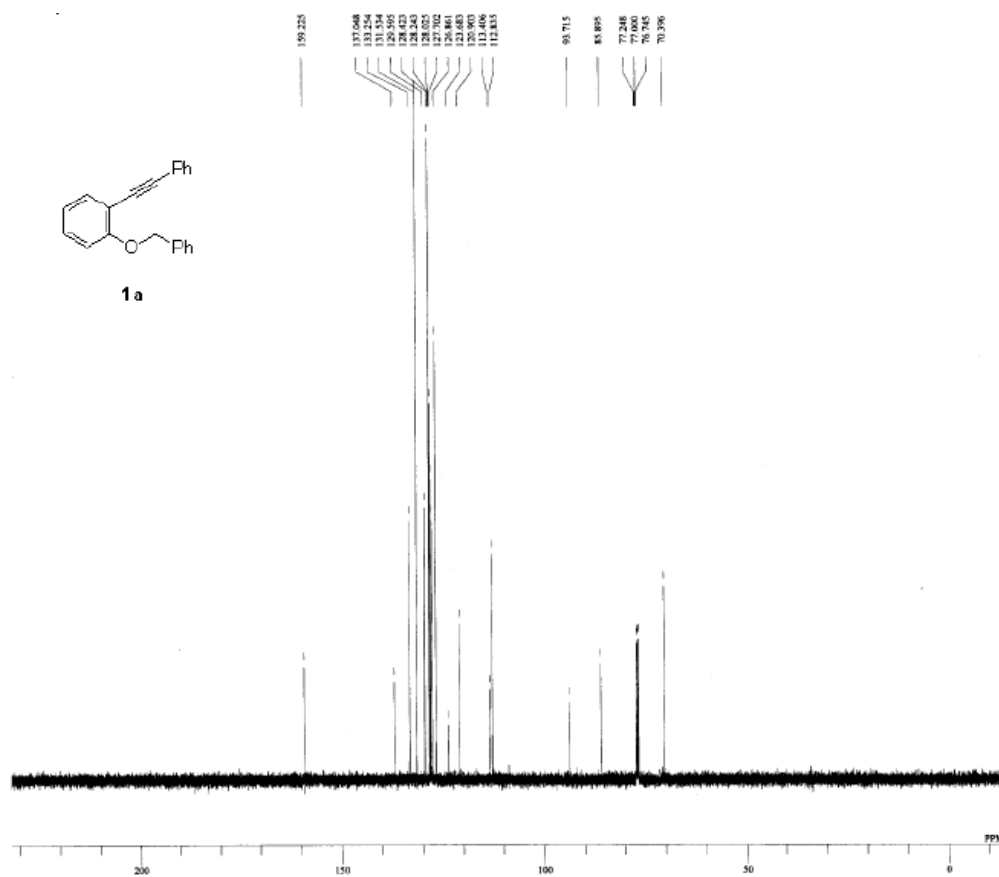
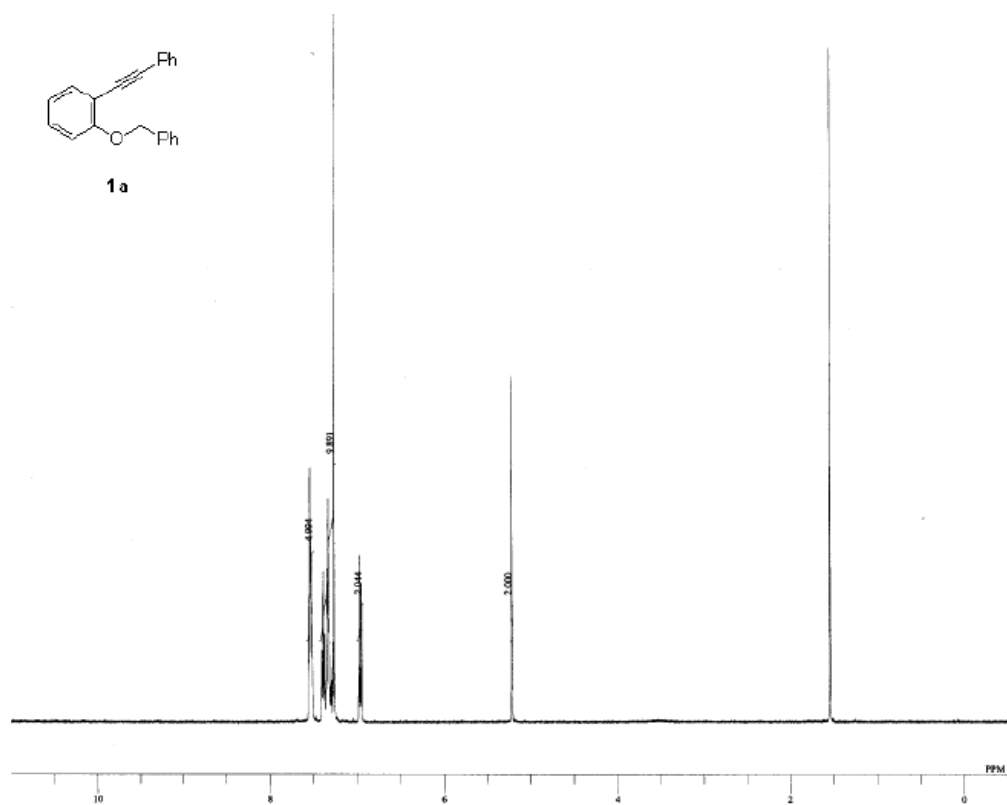
1750, 1733, 1496, 1445, 1276, 1237, 1194, 1131, 1093, 1046, 947, 859 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{18}\text{NaO}_3$ ($\text{M}^+ + \text{Na}$) 317.1148. Found 317.1147.

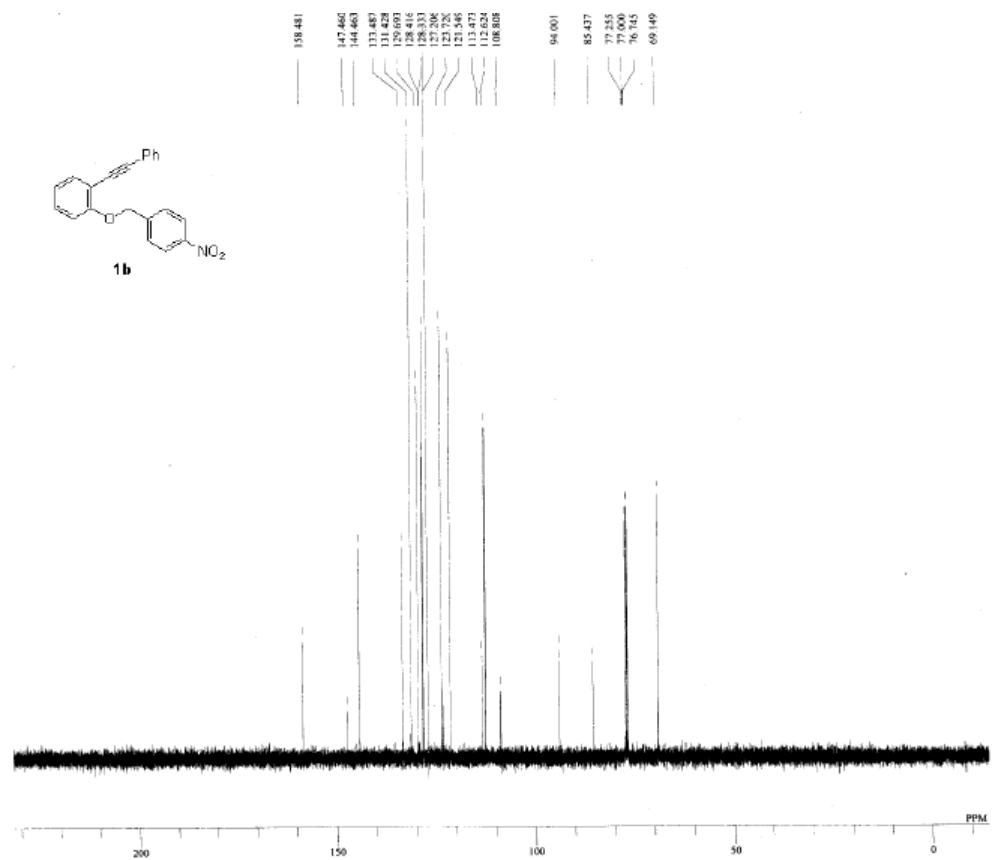
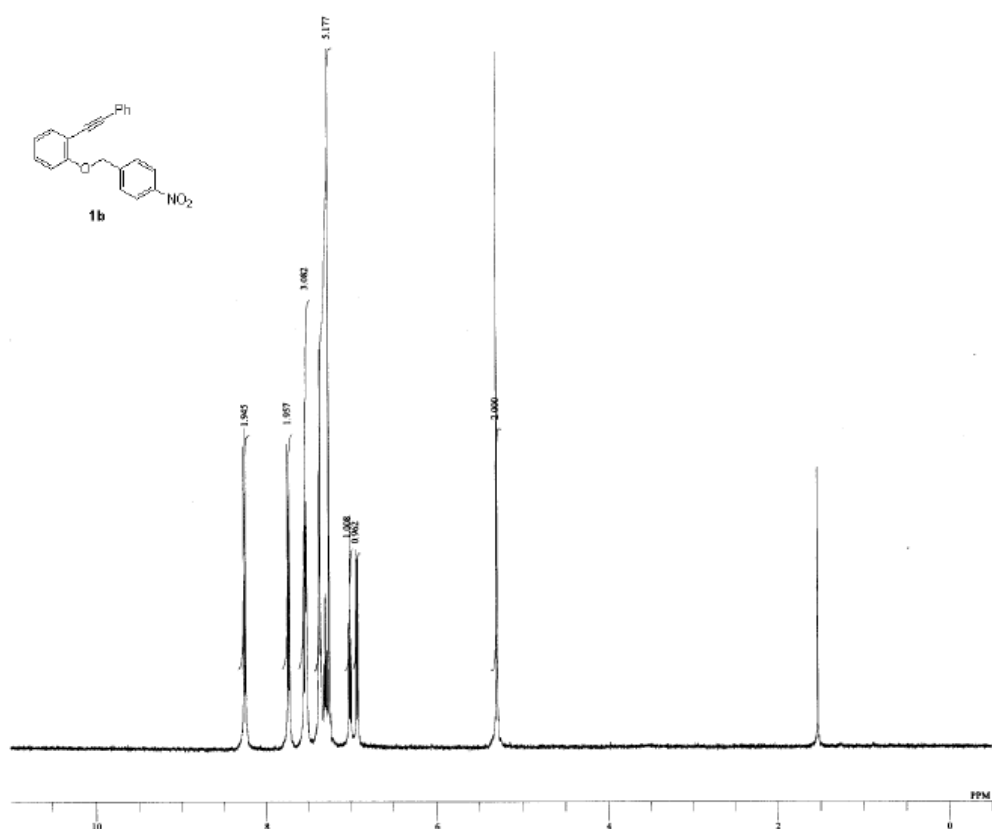


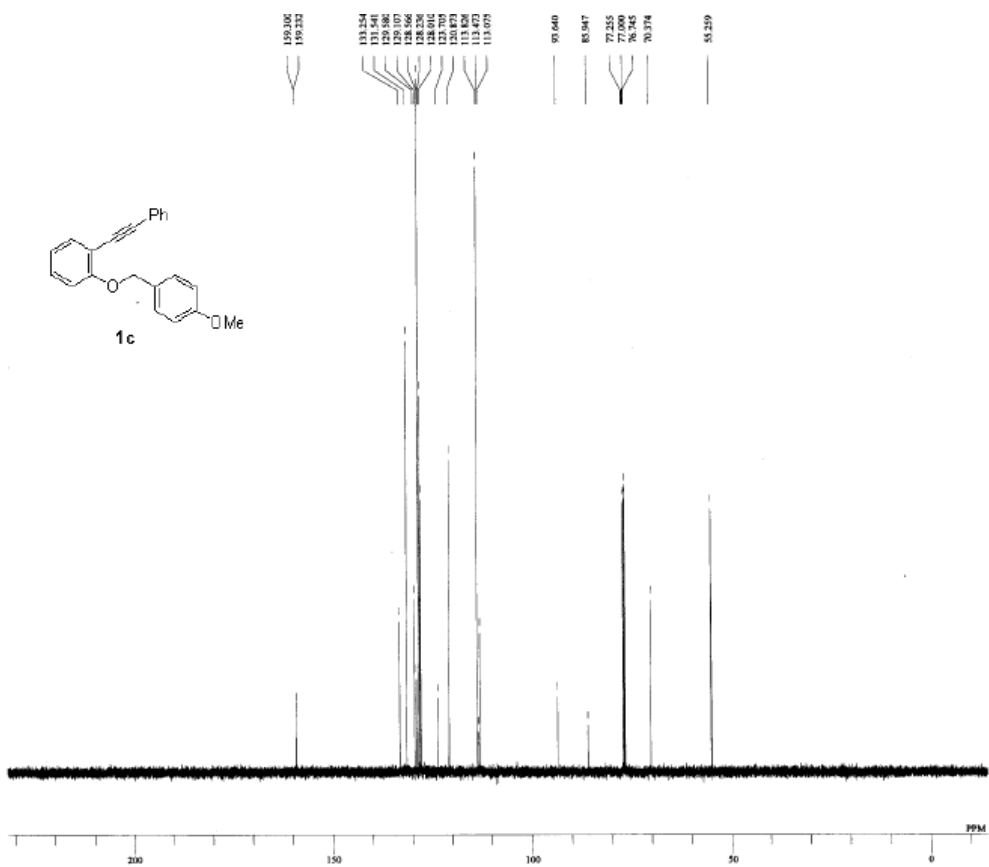
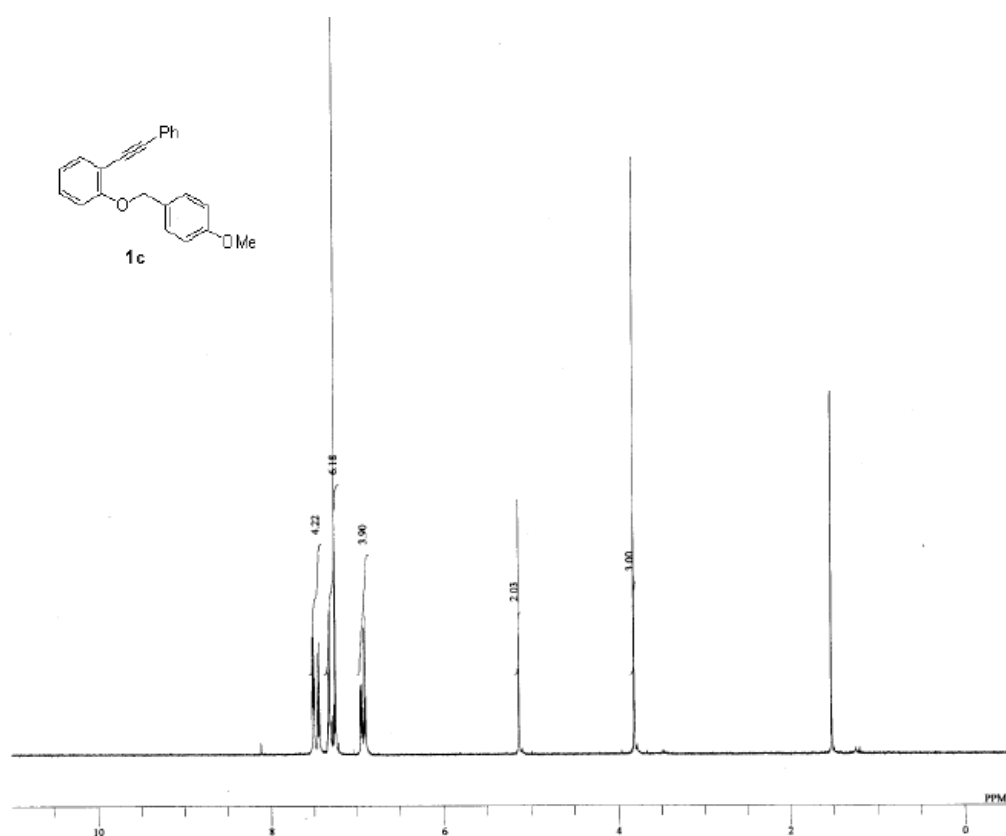
(Z)-Ethyl 3-benzylidene-2-methyl-2,3-dihydrobenzofuran-2-carboxylate (4b): colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 1.15 (3H, t, $J = 7.0$ Hz), 1.70 (3H, s), 4.08-4.25 (2H, m), 6.87 (1H, d, $J = 7.0$ Hz), 6.95-7.00 (2H, m), 7.21-7.36 (6H, m), 7.46-7.50 (1H, m); ^{13}C NMR (126 MHz, CDCl_3) δ 13.78, 20.68, 61.92, 89.28, 110.43, 119.79, 120.31, 121.27, 127.09, 127.33, 128.35, 128.55, 130.30, 135.40, 140.38, 160.20, 169.75; IR (neat) 3457, 2983, 1737, 1595, 1465, 1253, 1127, 1017, 911, 858 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{18}\text{NaO}_3$ ($\text{M}^+ + \text{Na}$) 317.1148. Found 317.1147.

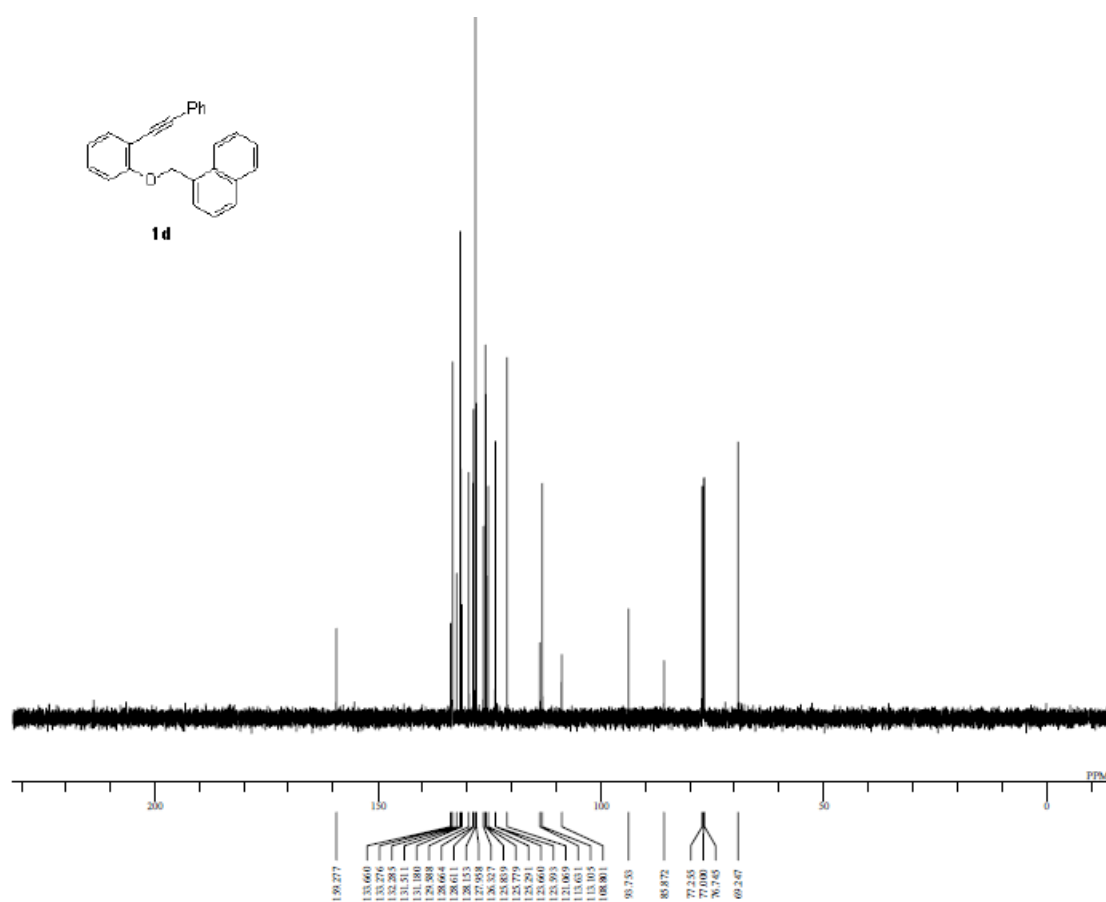
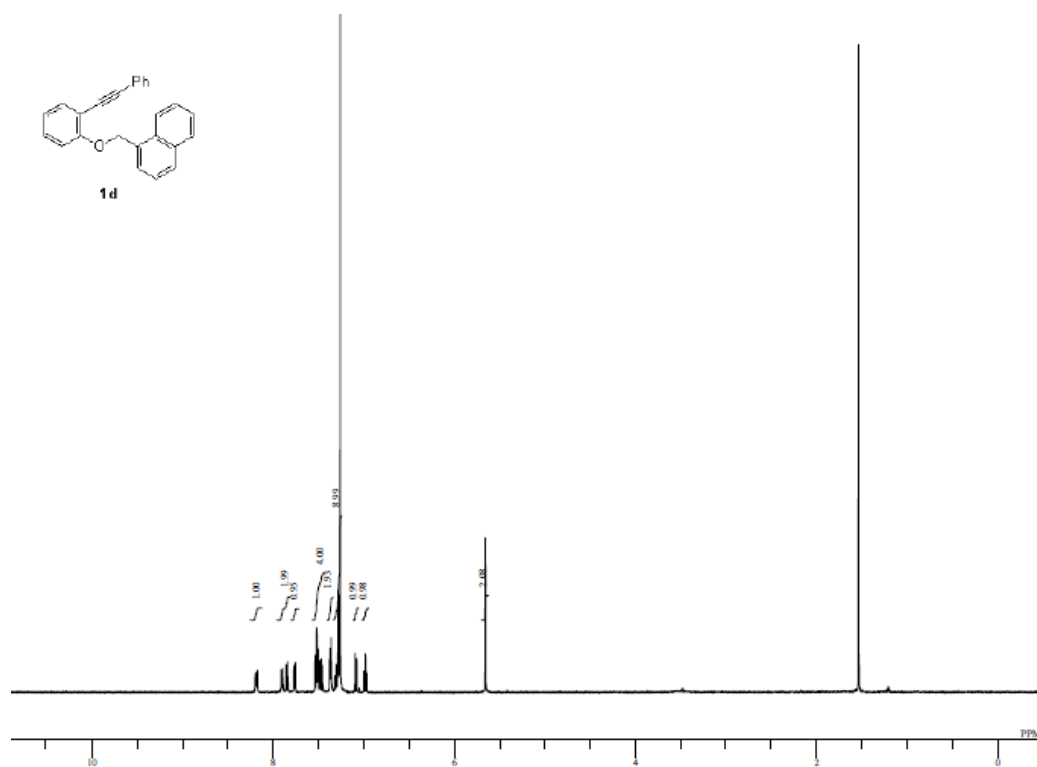
Reference

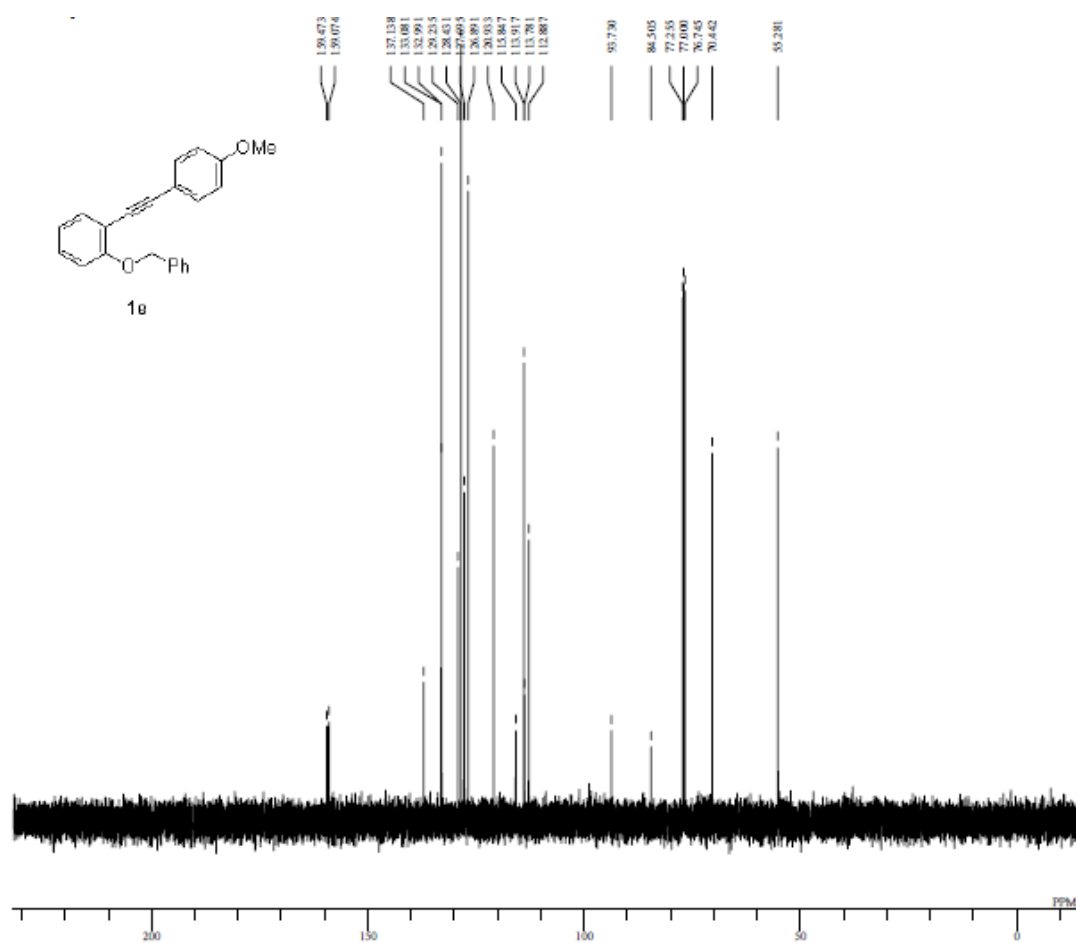
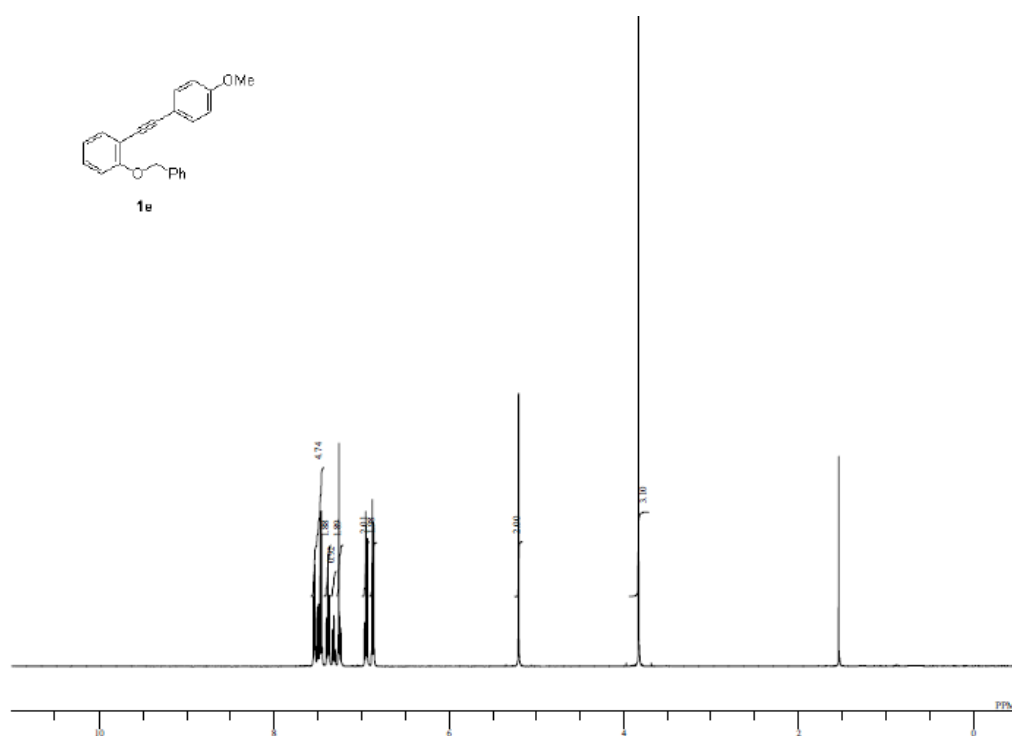
(1) Fürstner, A.; Davies, P. W. *J. Am. Chem. Soc.* **2005**, *127*, 15024-15025.

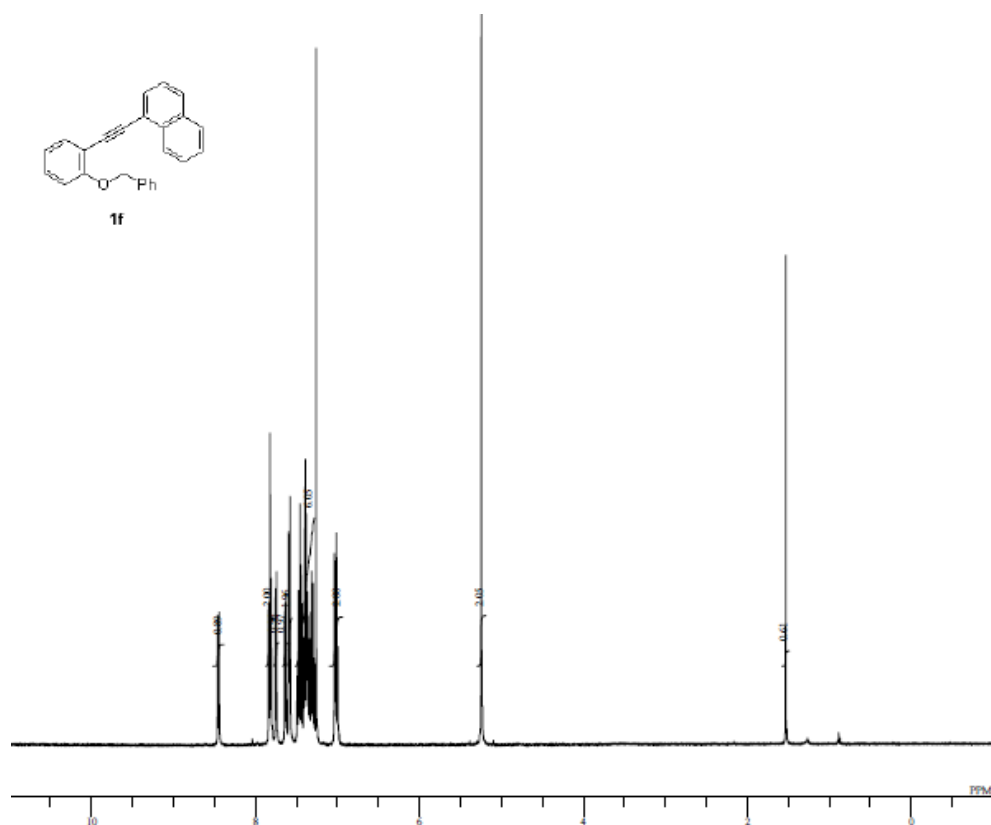


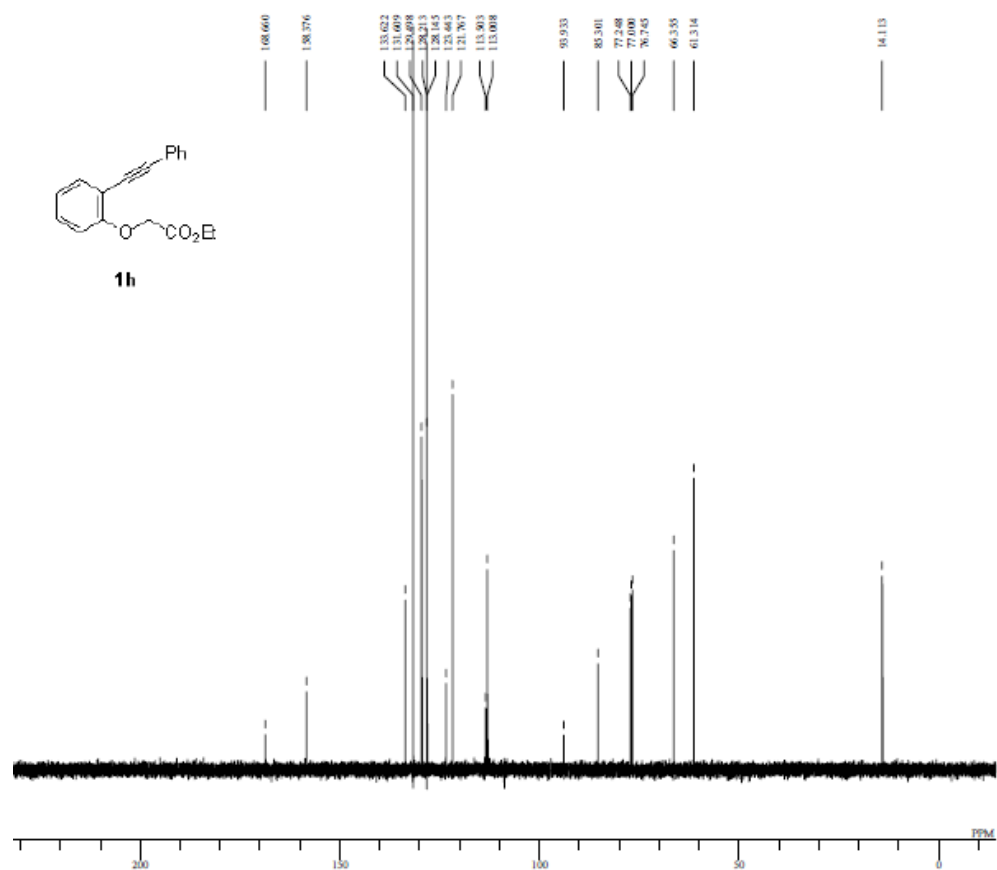
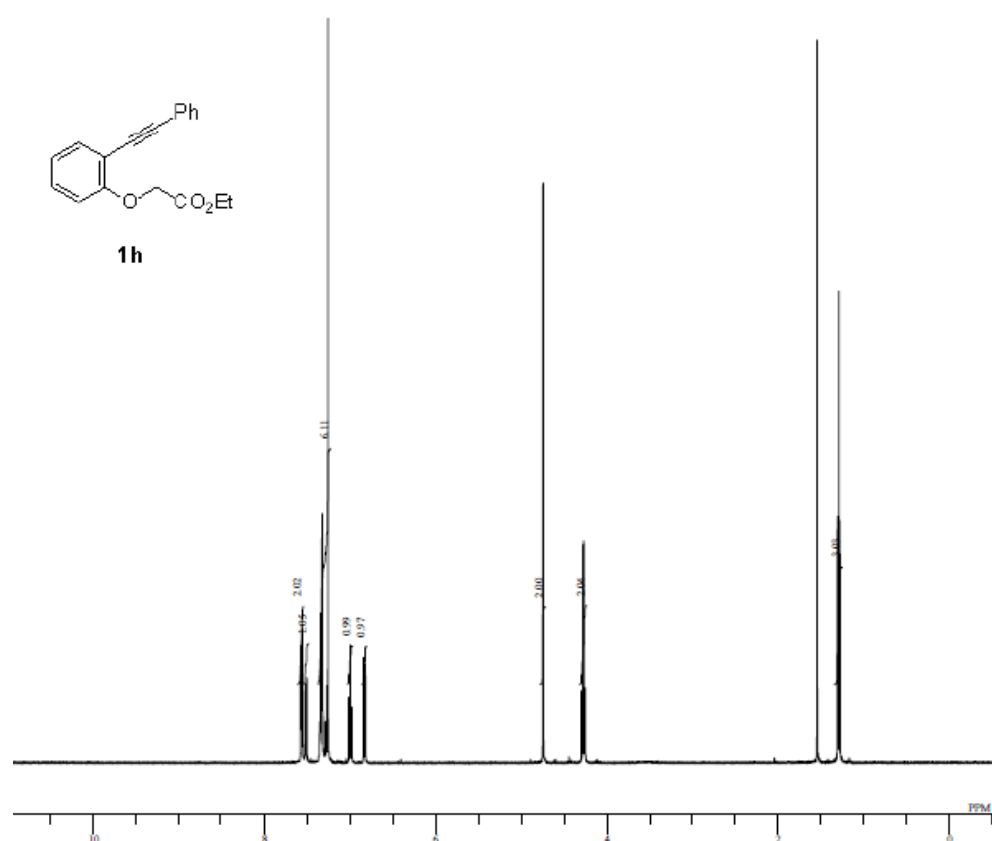


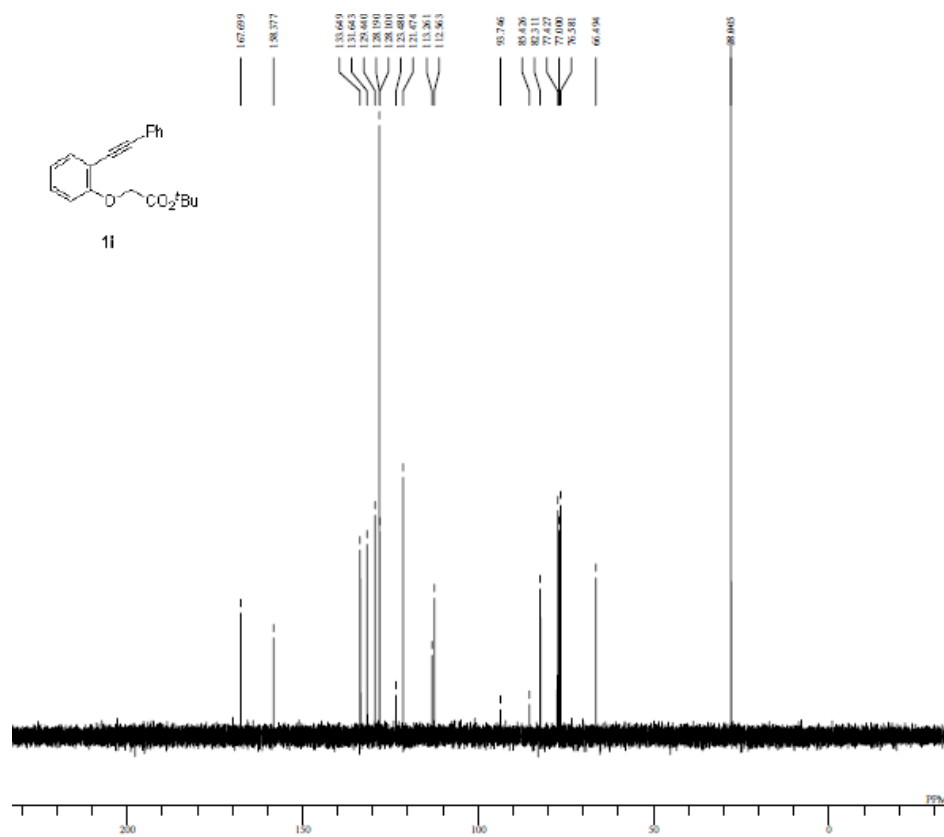
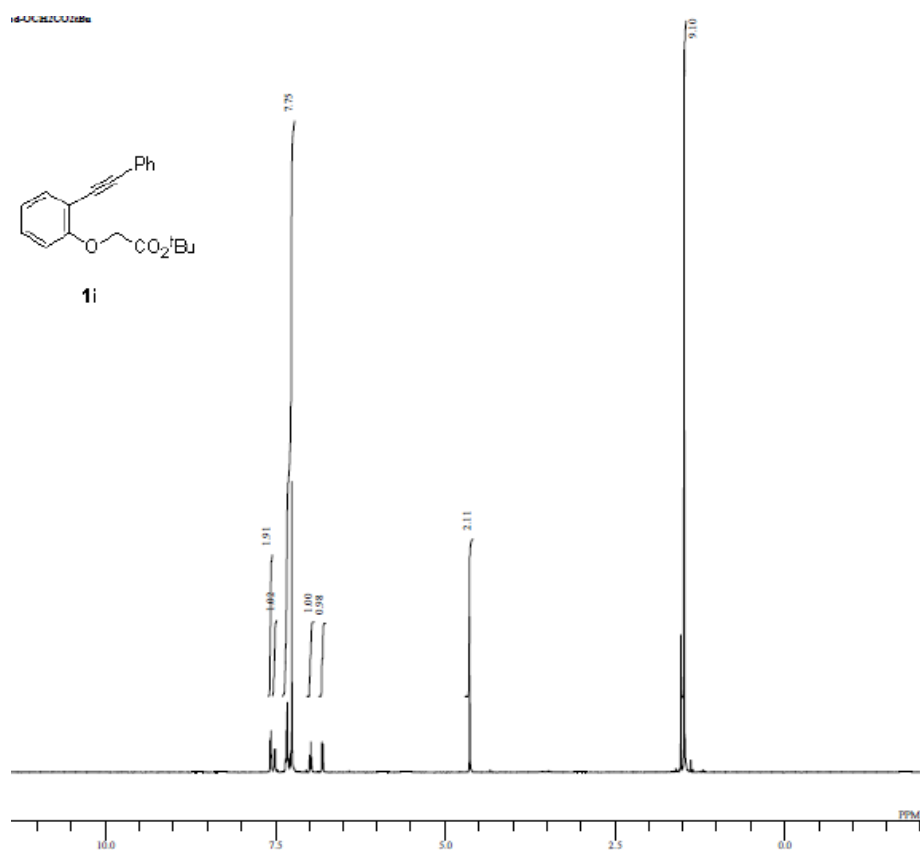


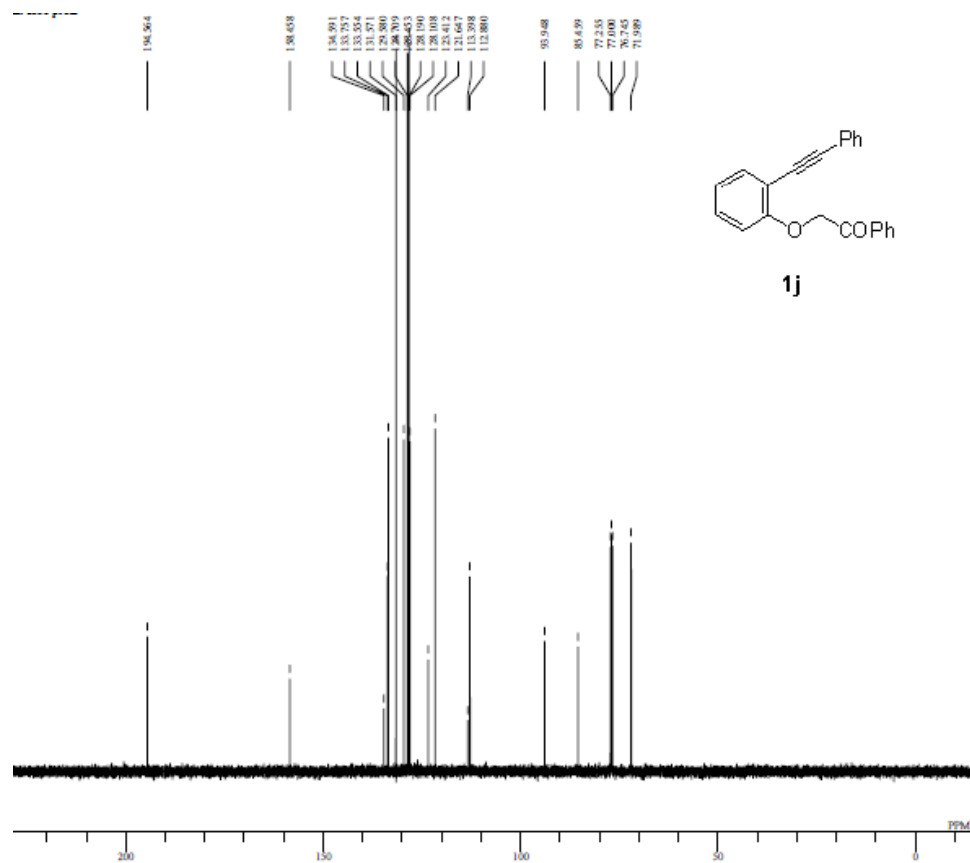
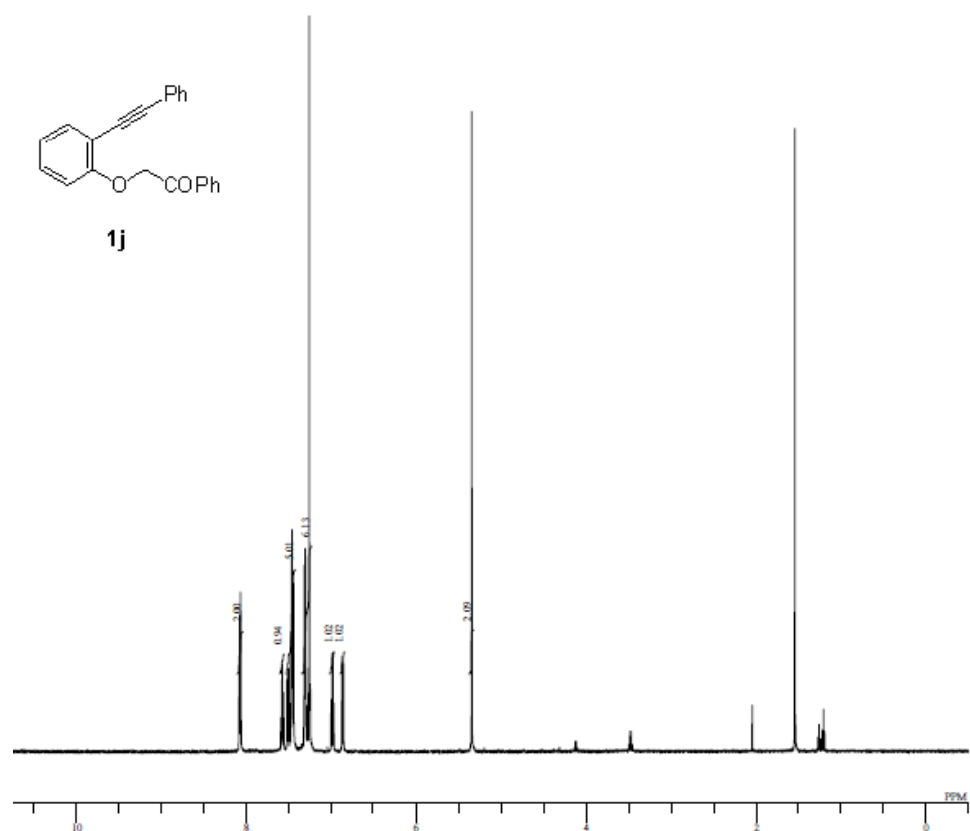


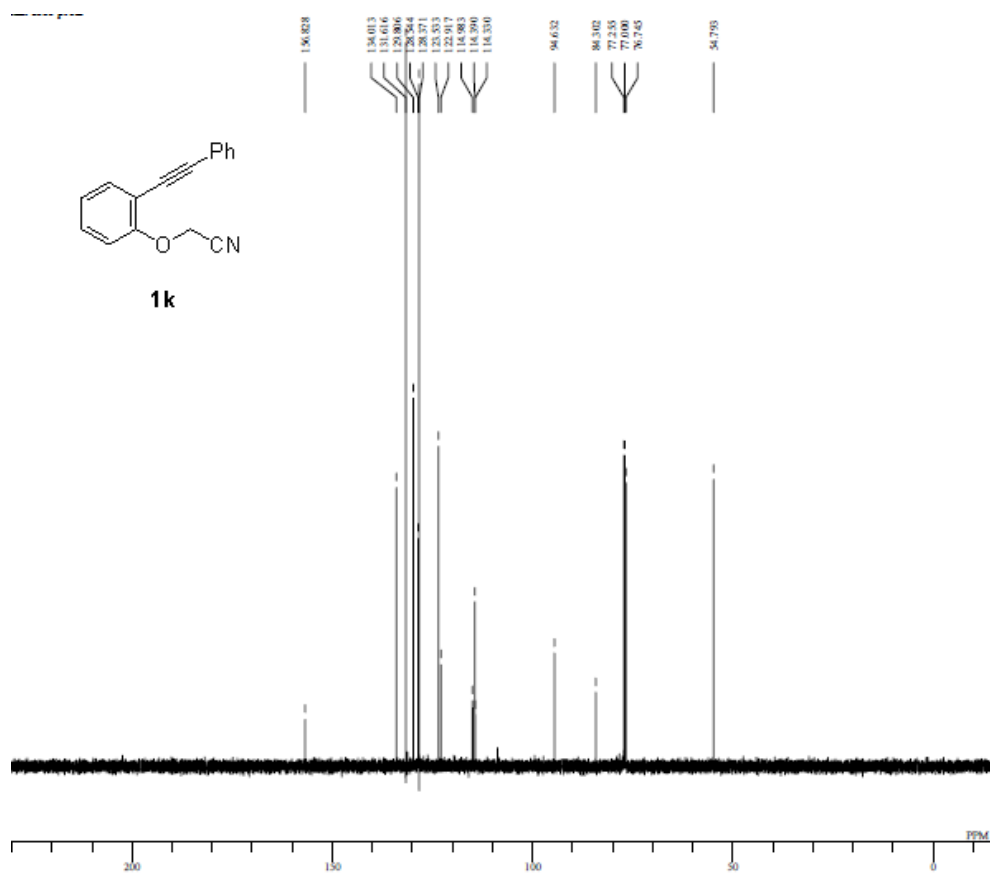
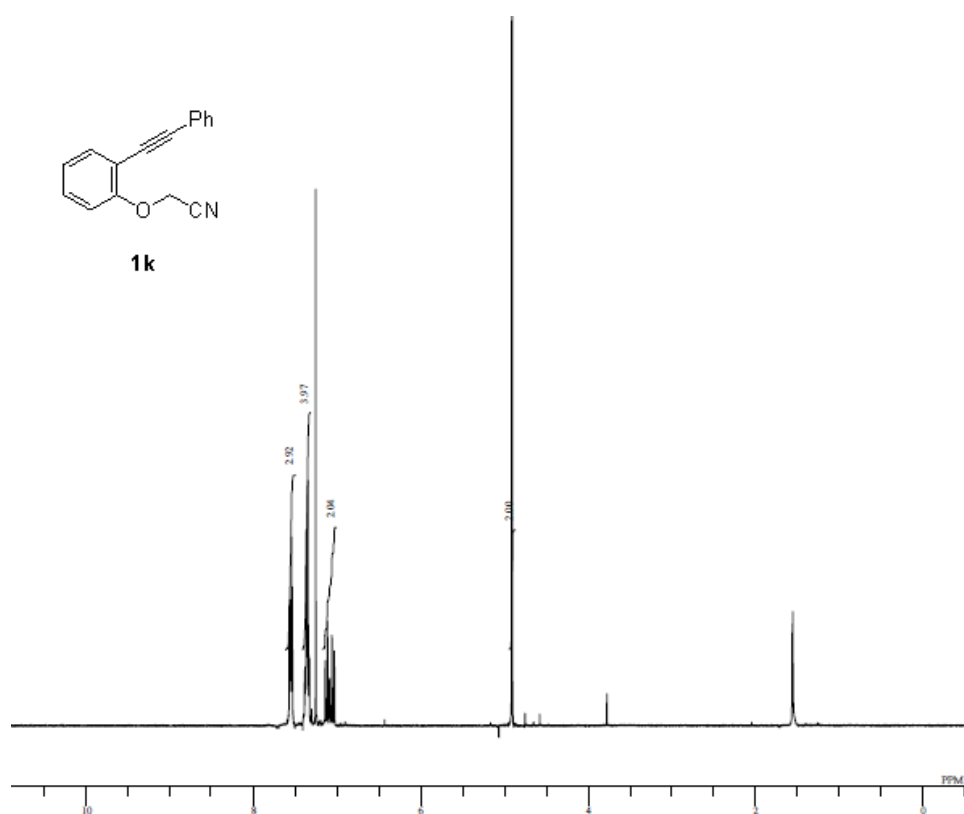


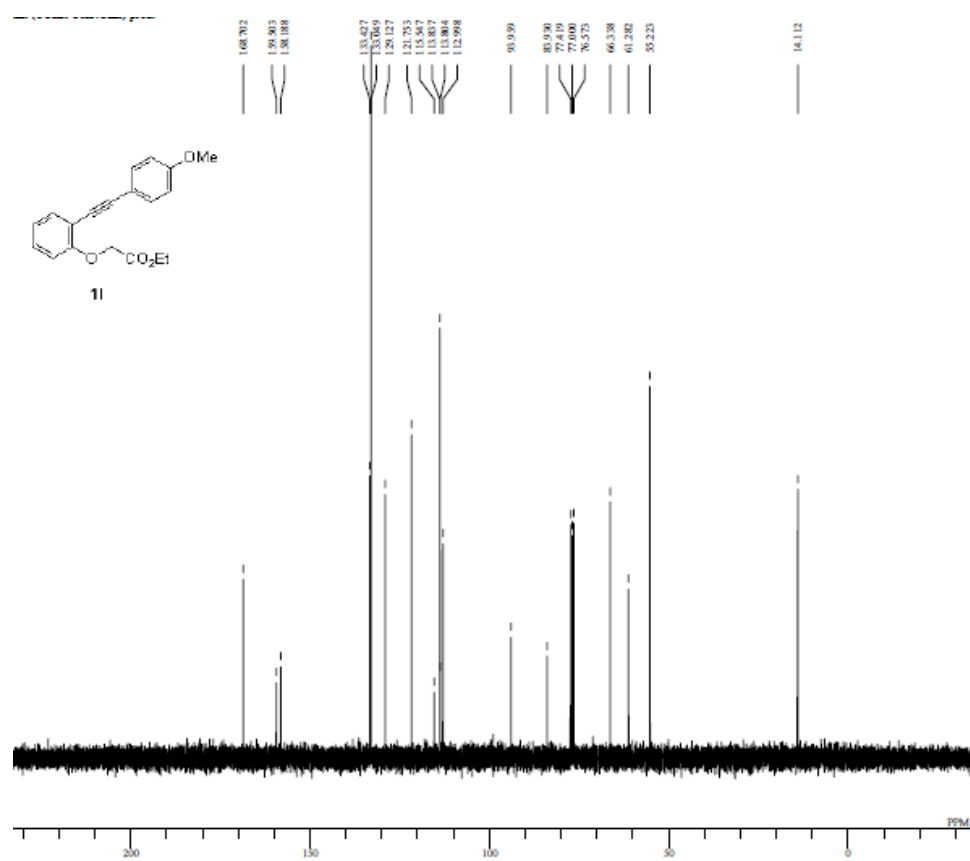
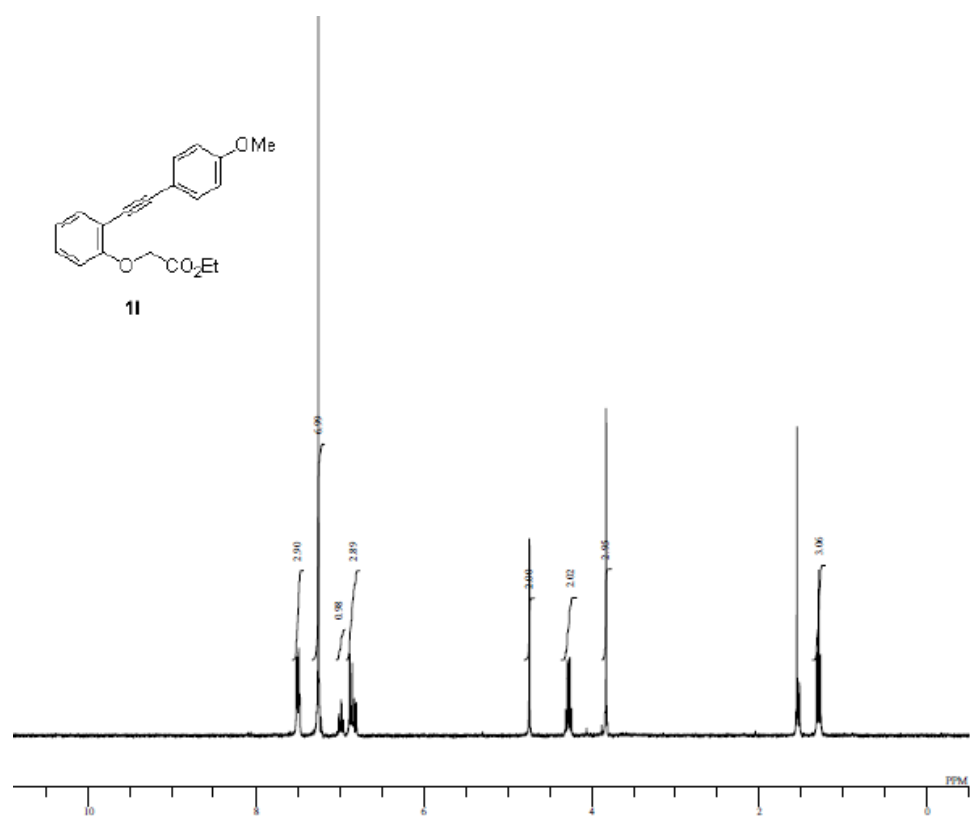


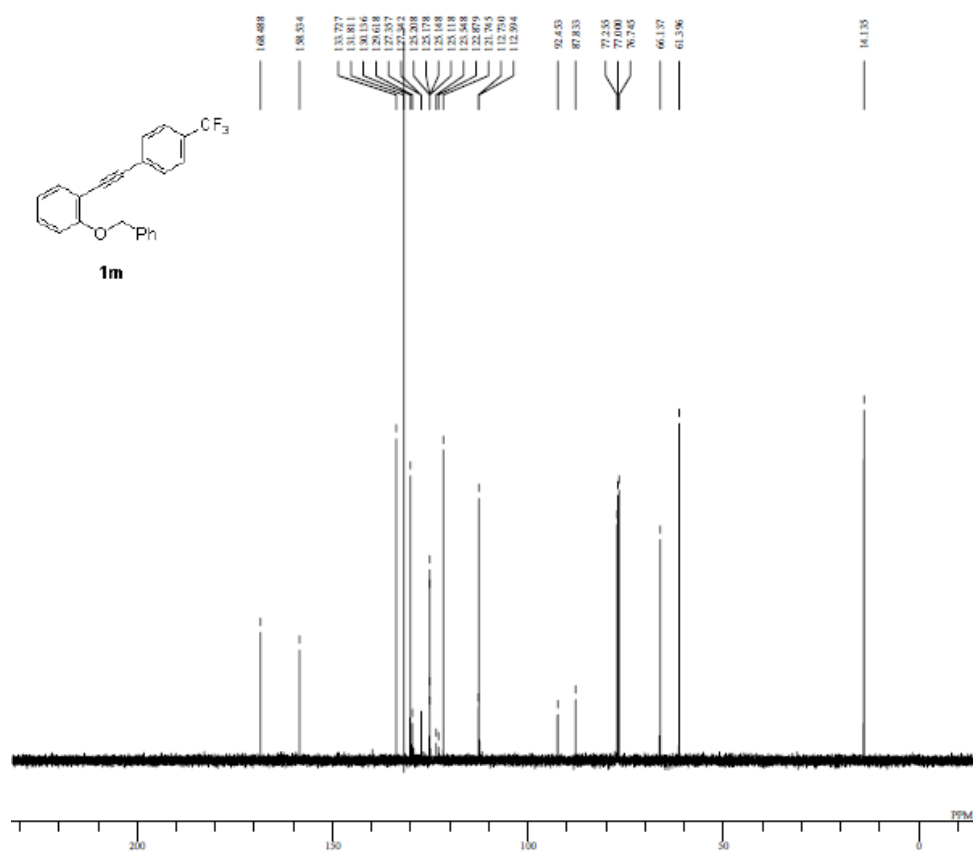
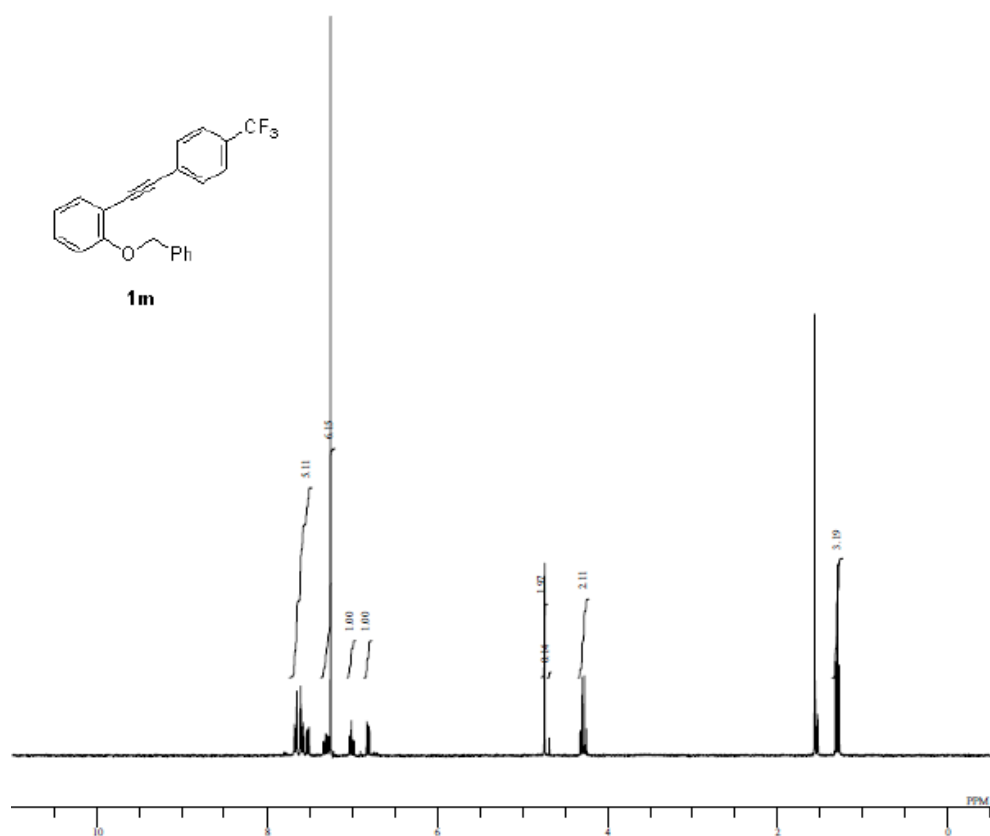


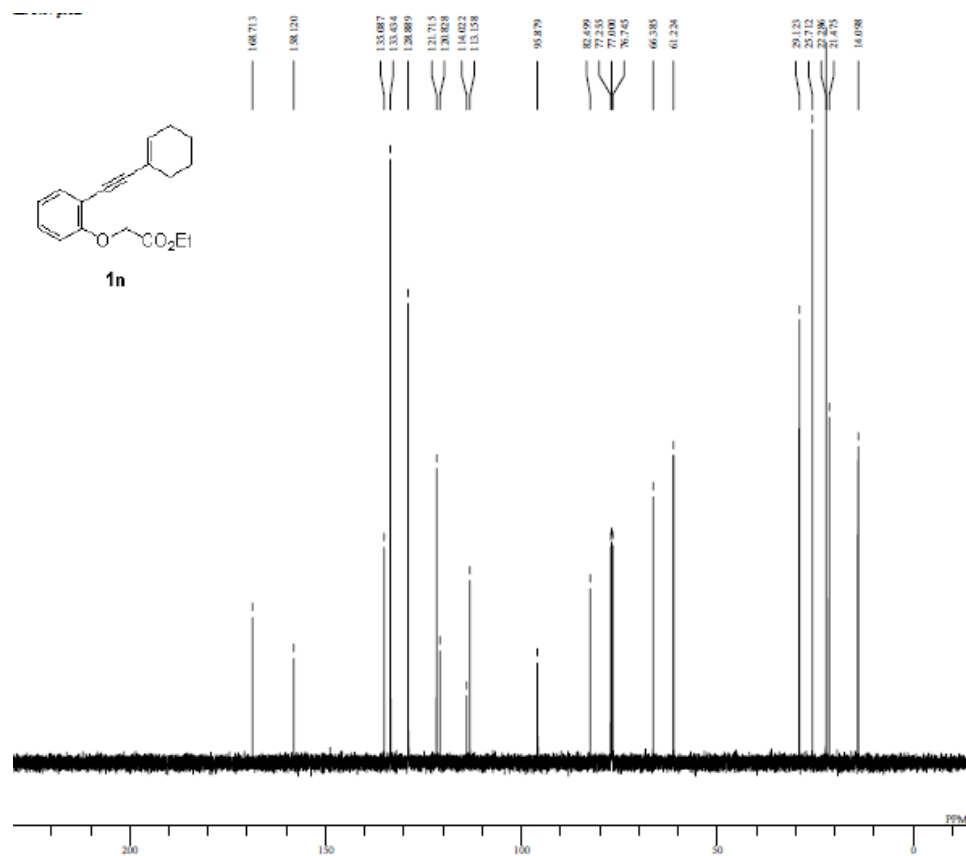
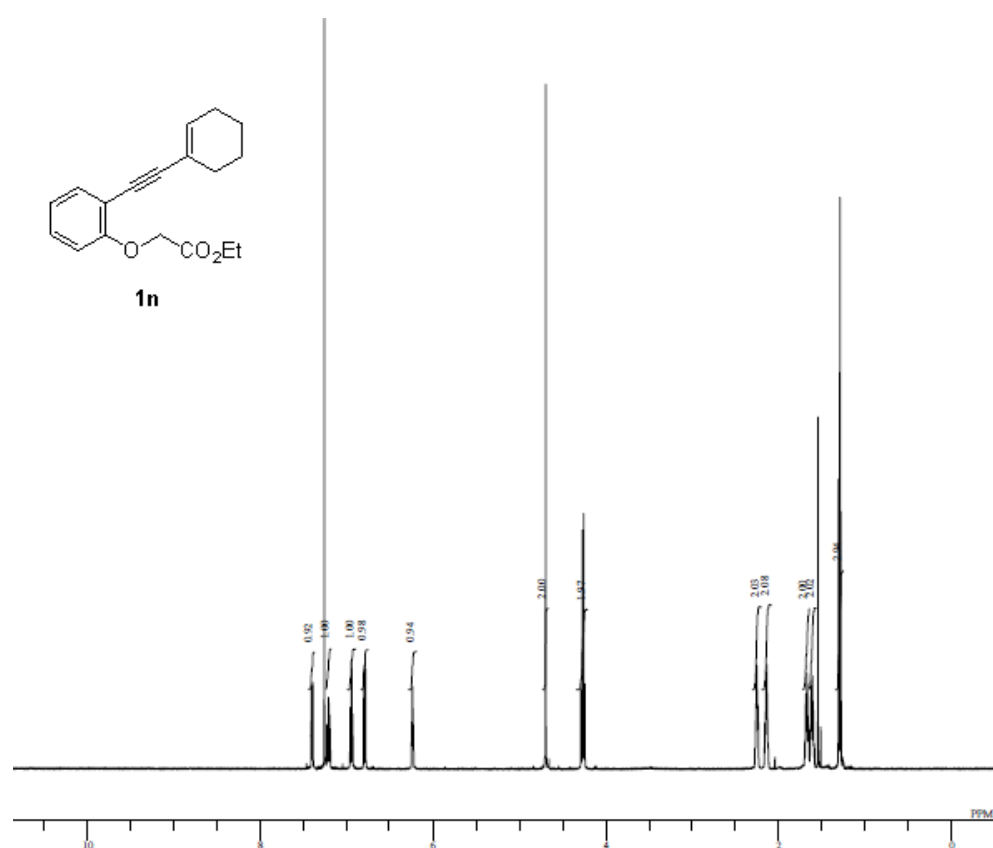


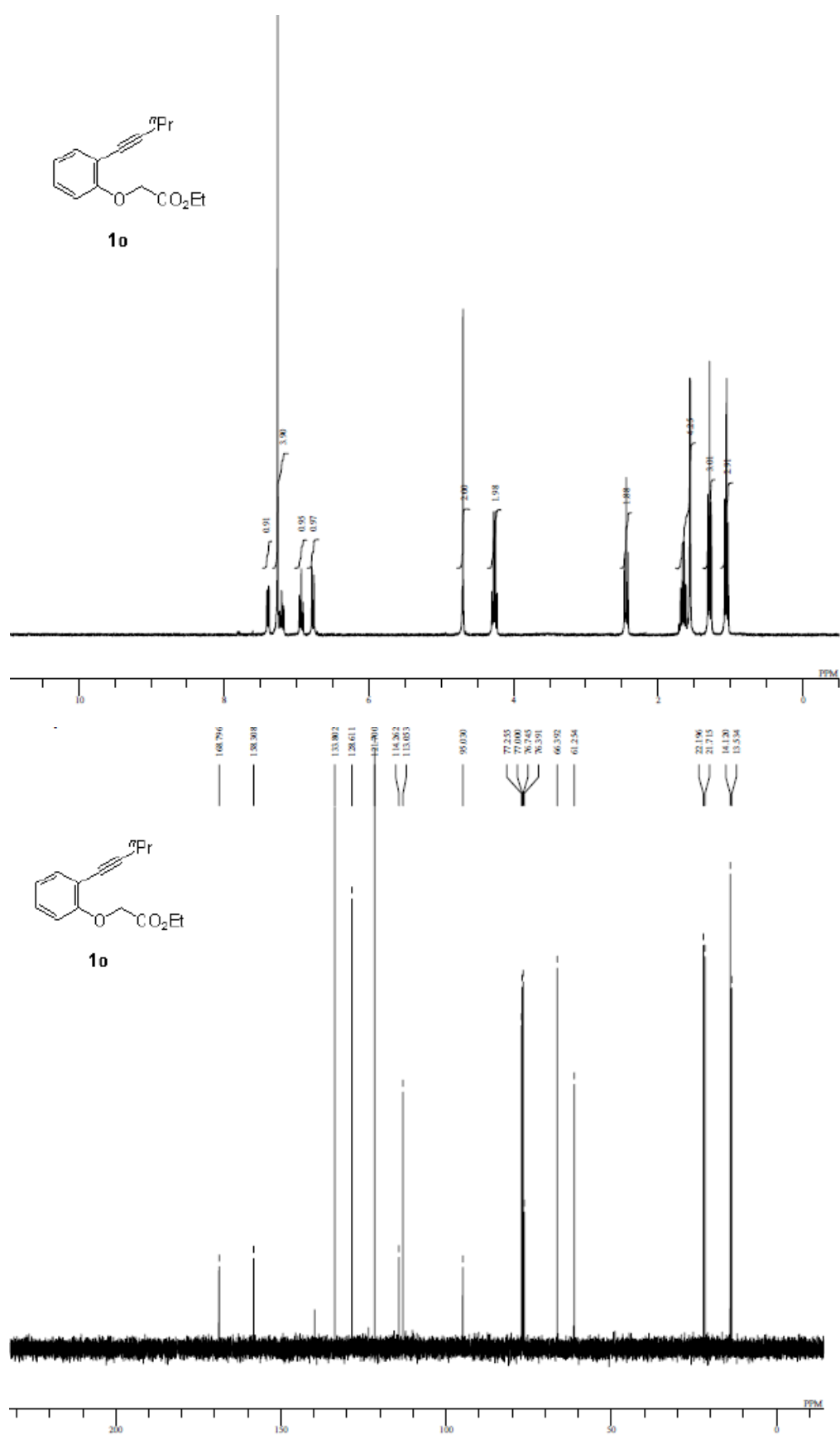


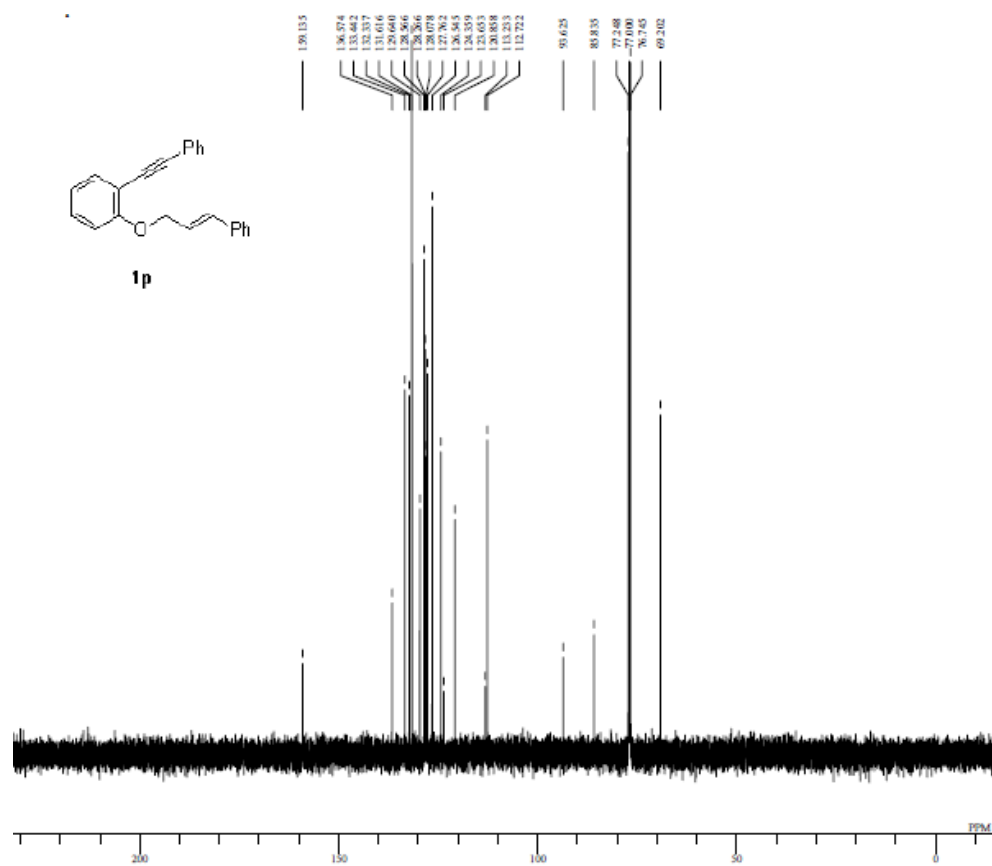
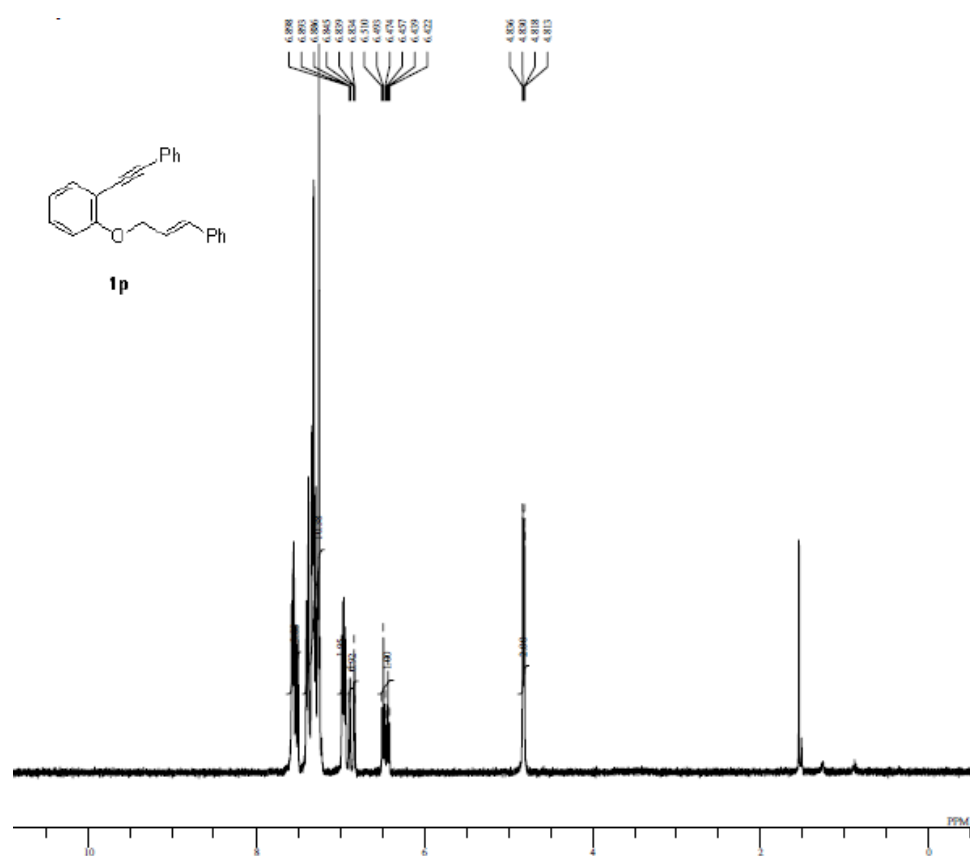


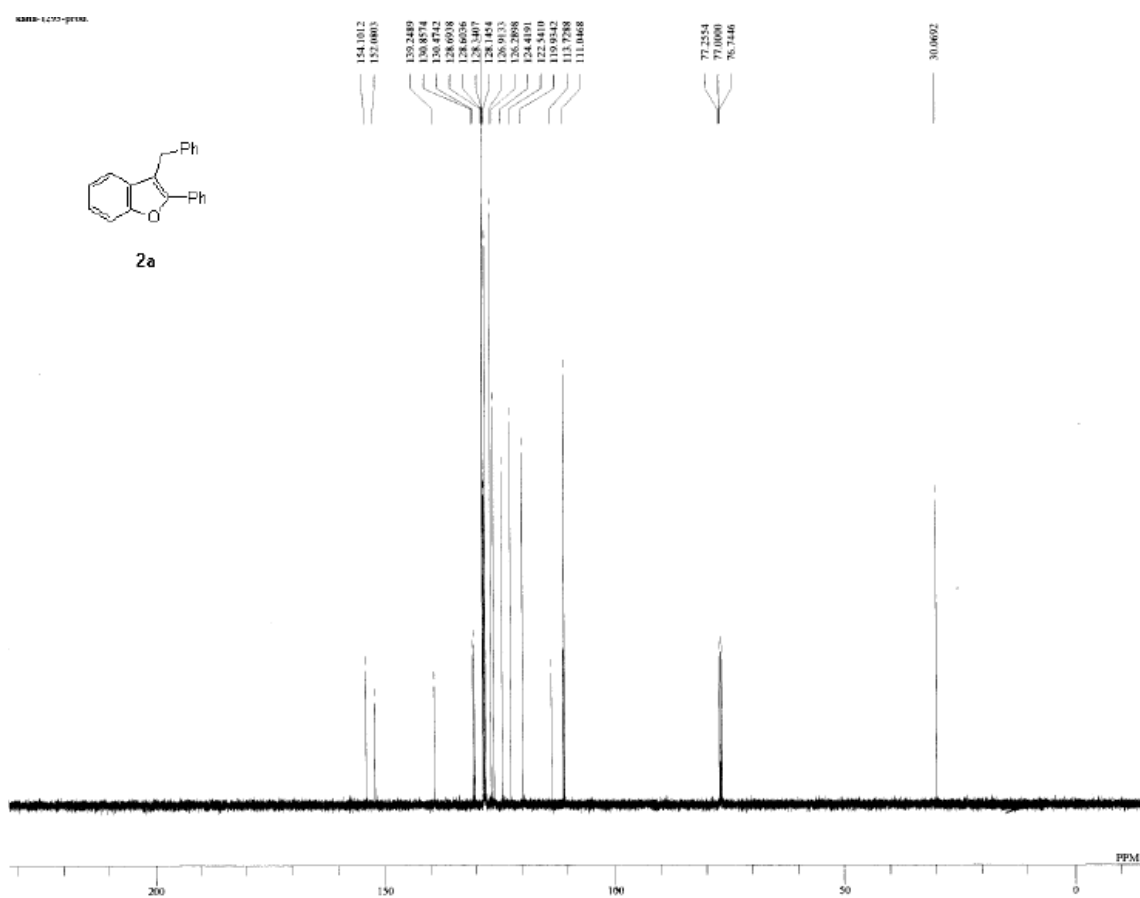
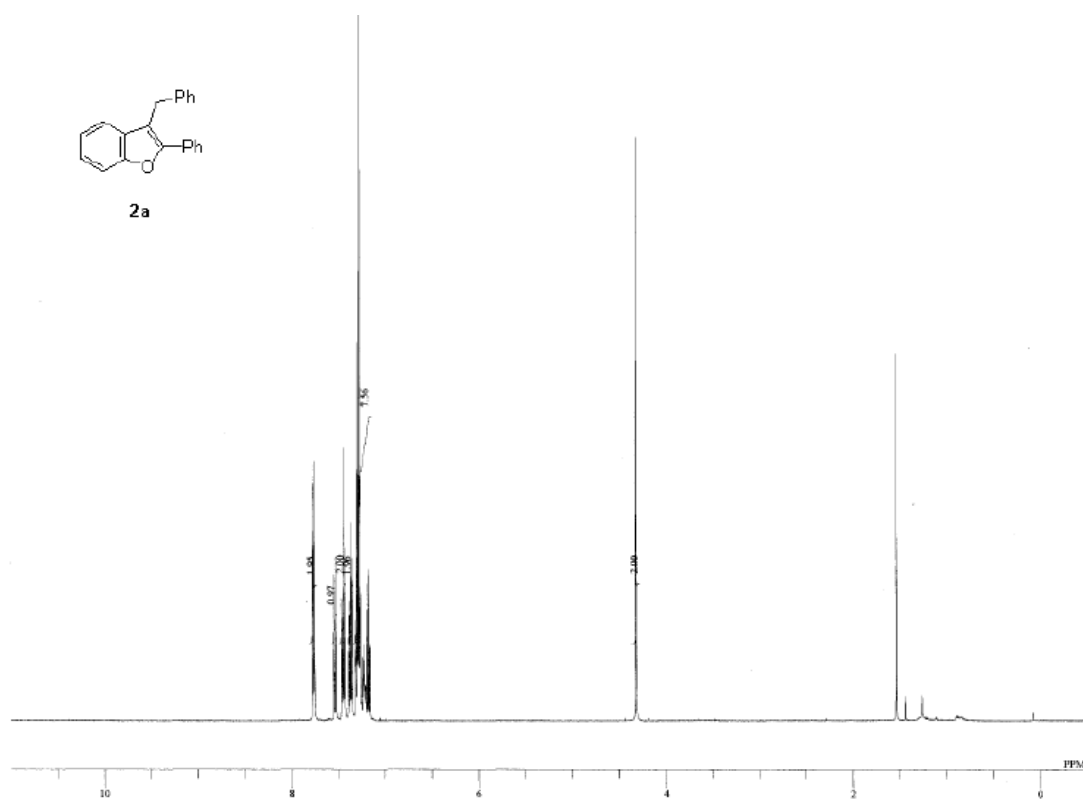


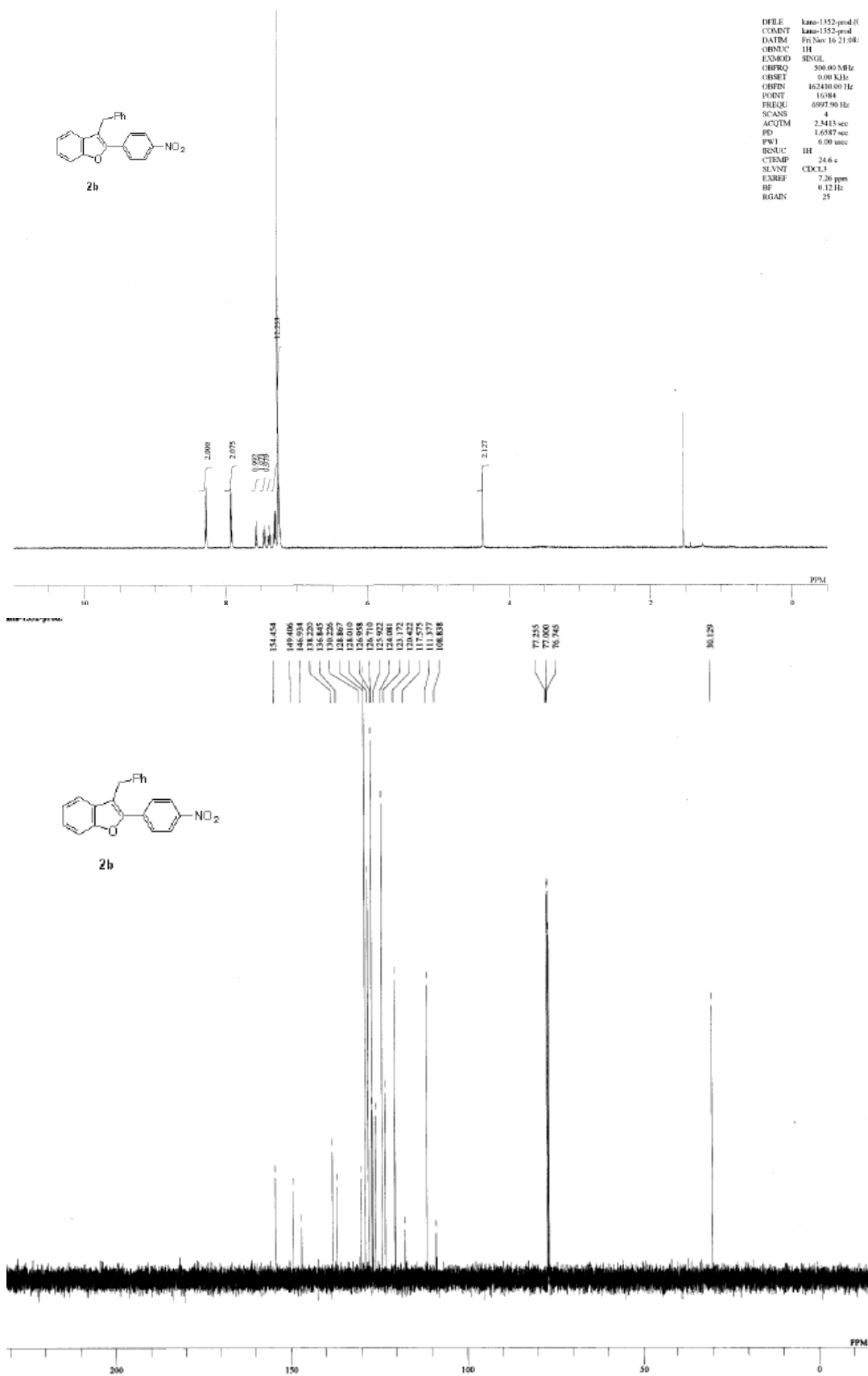


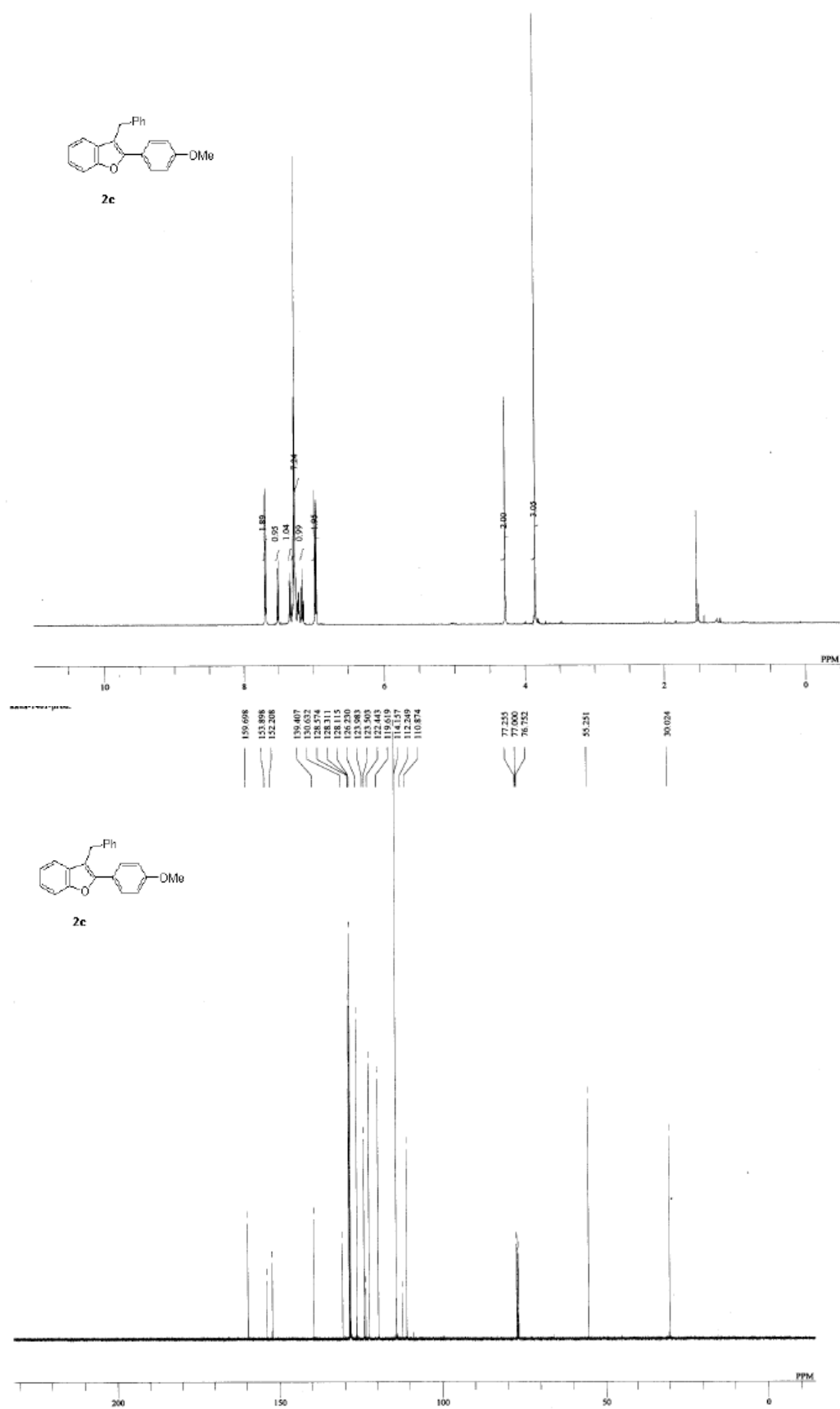


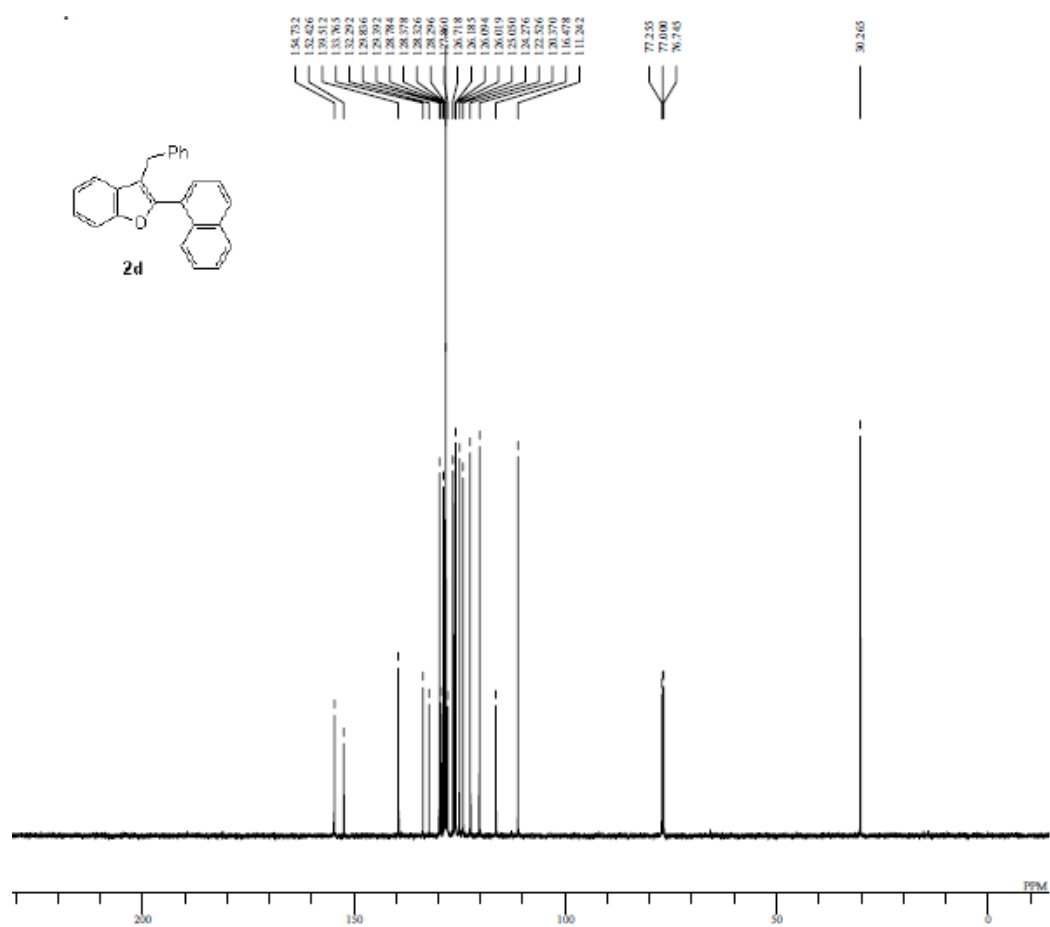
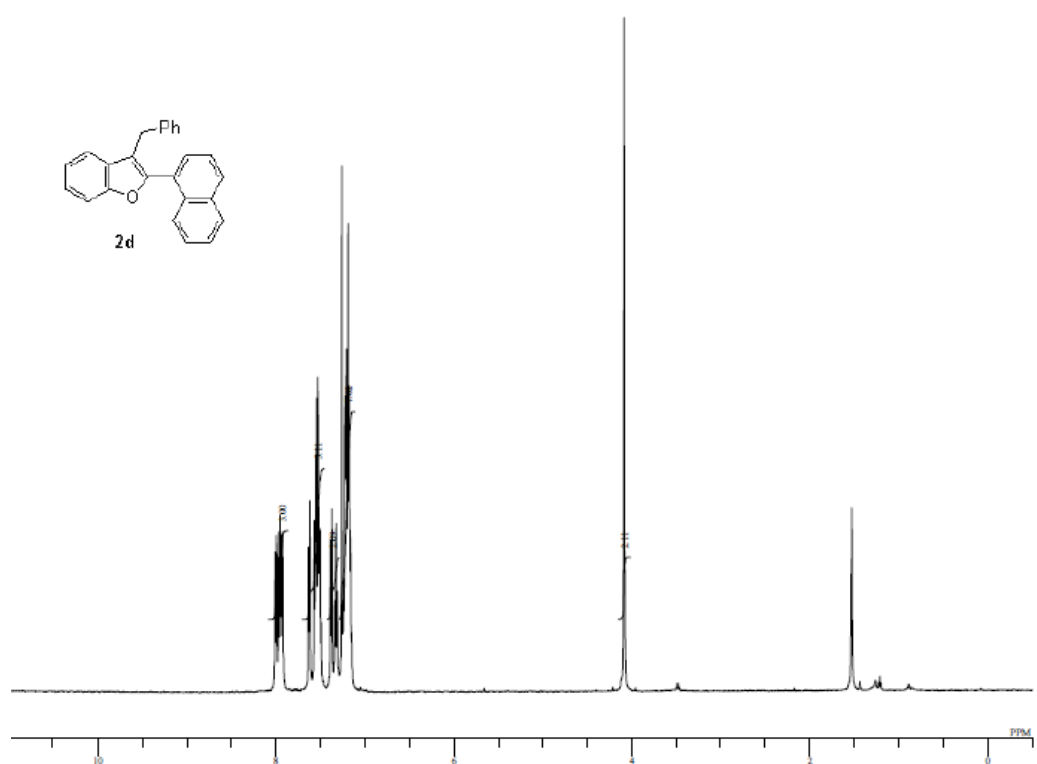


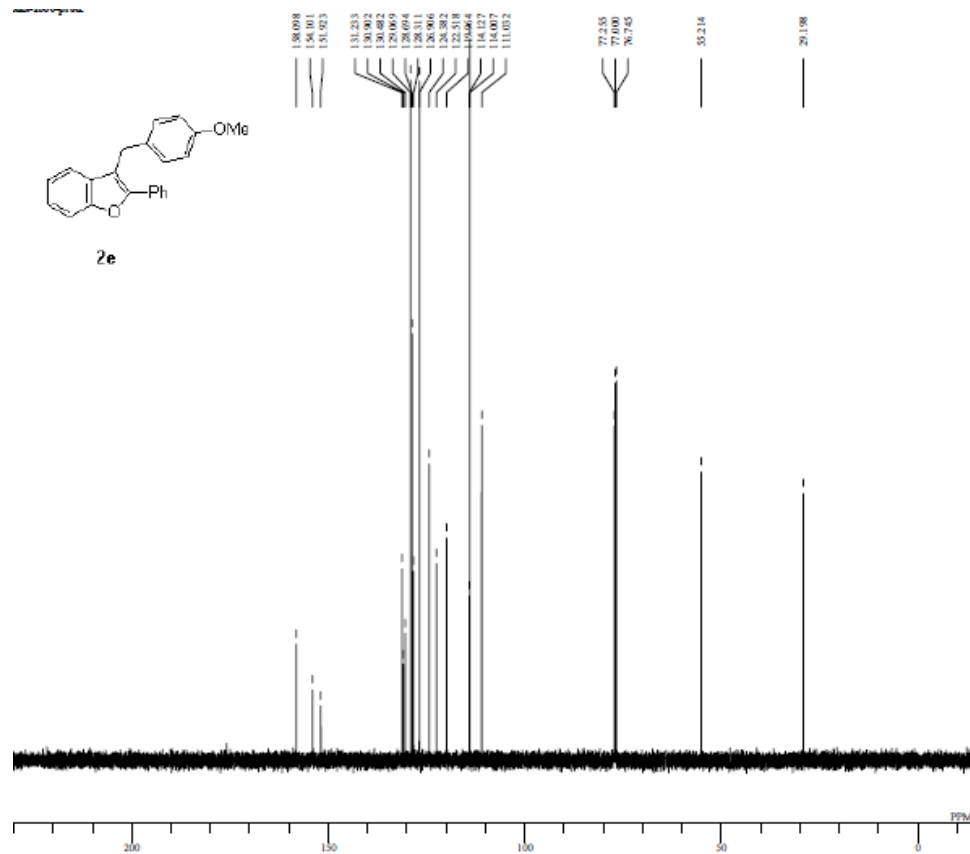
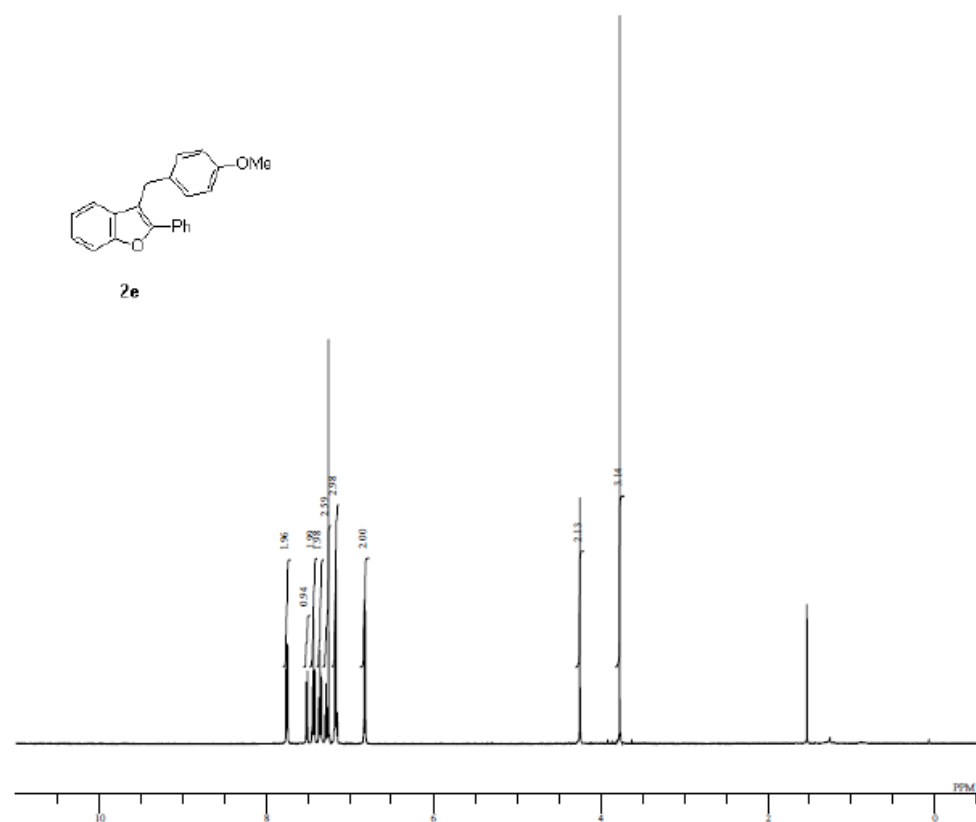


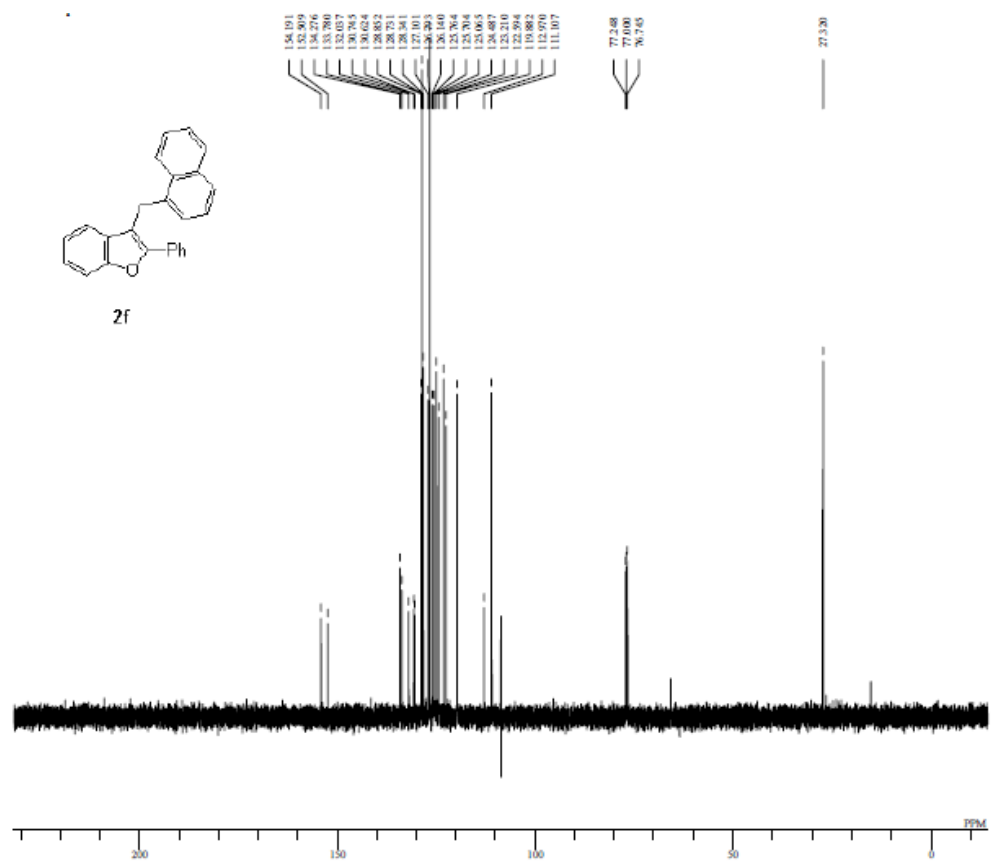


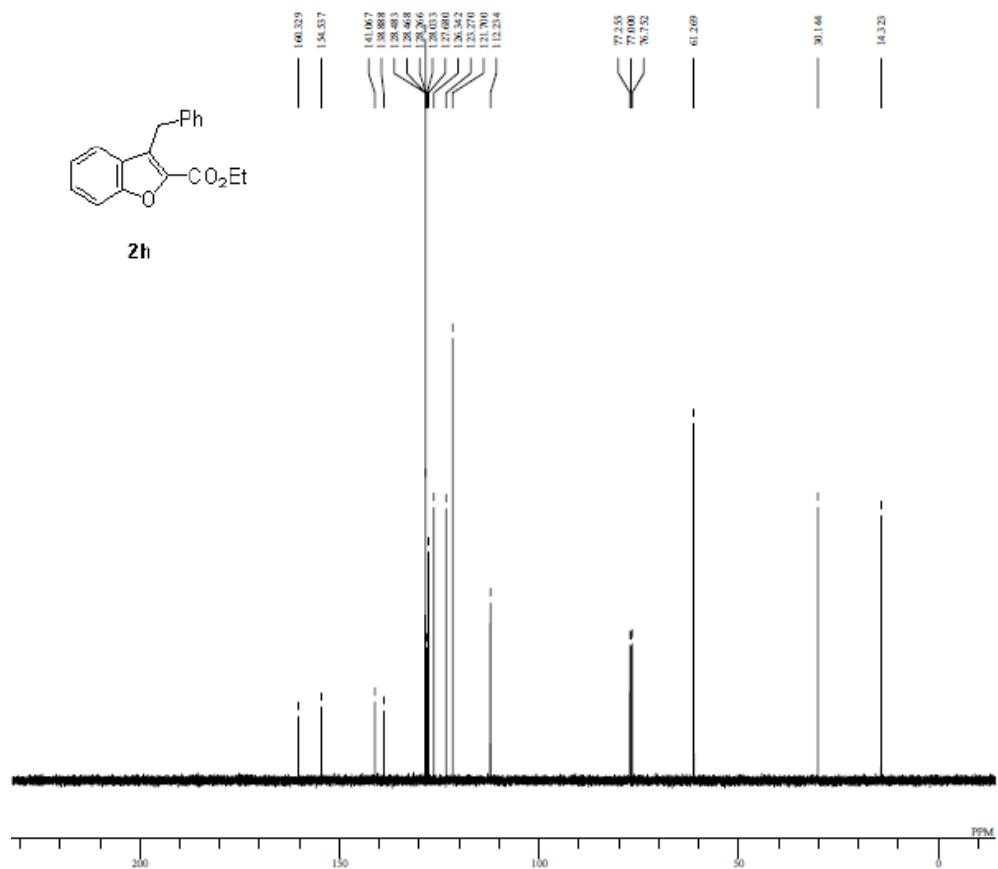
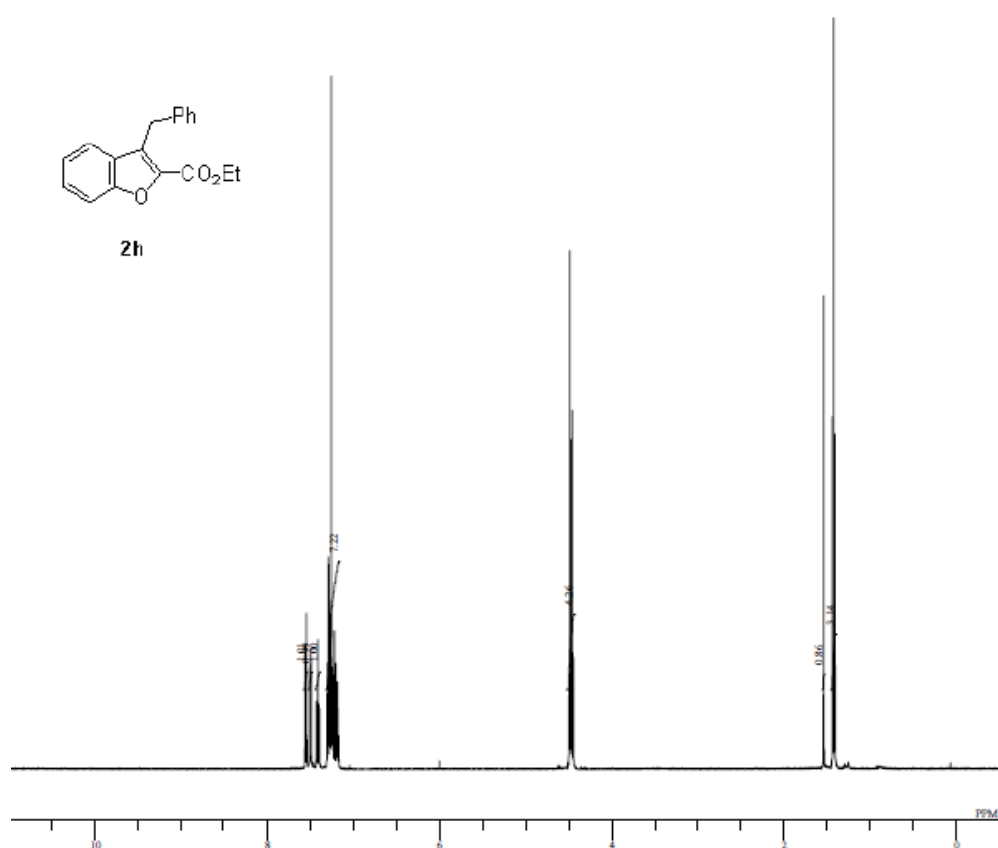


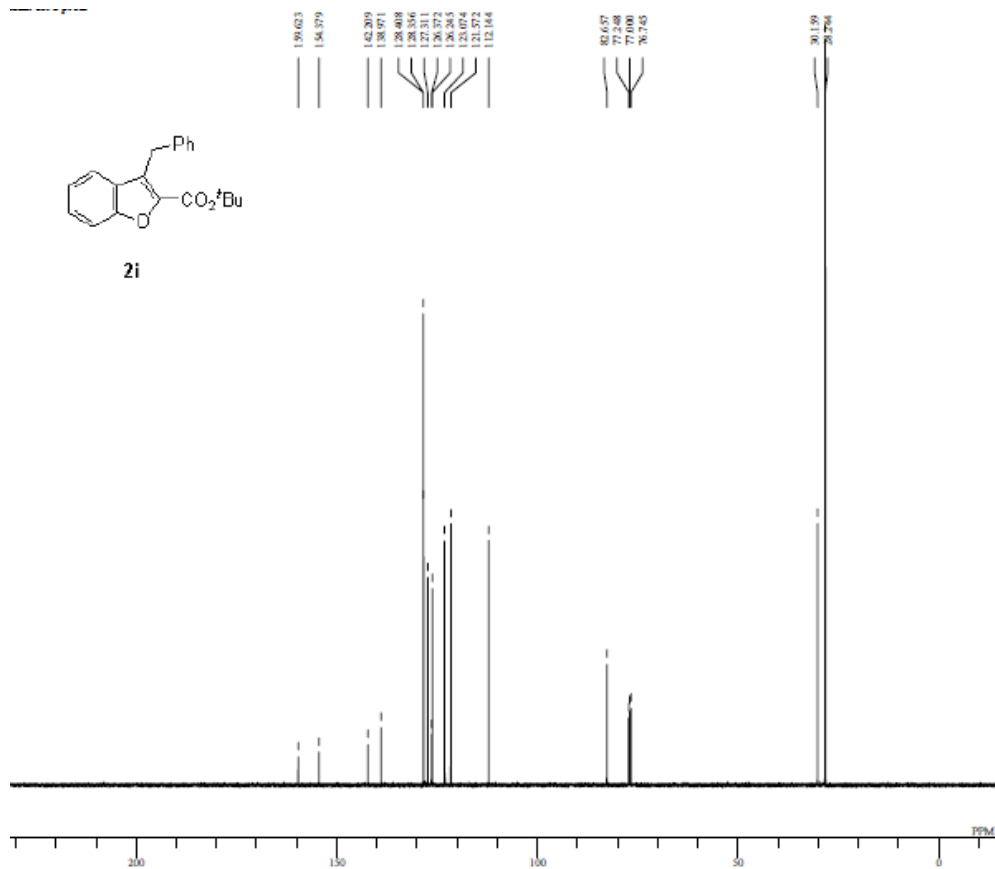
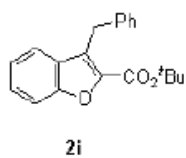
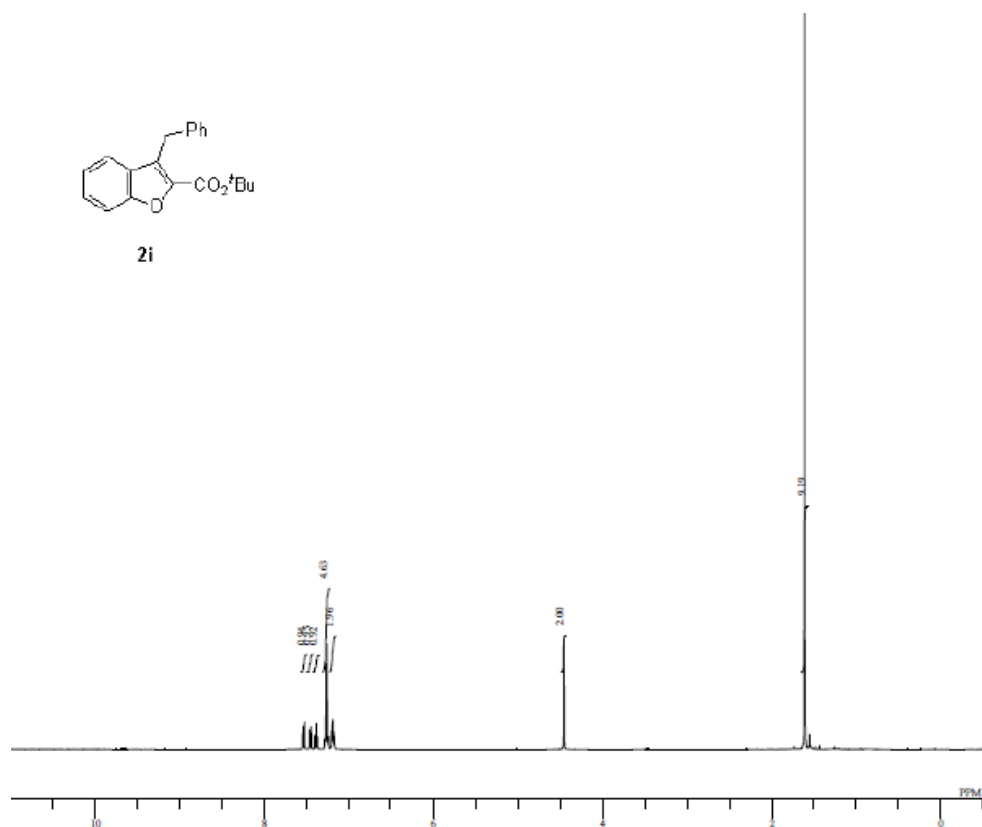
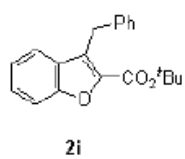


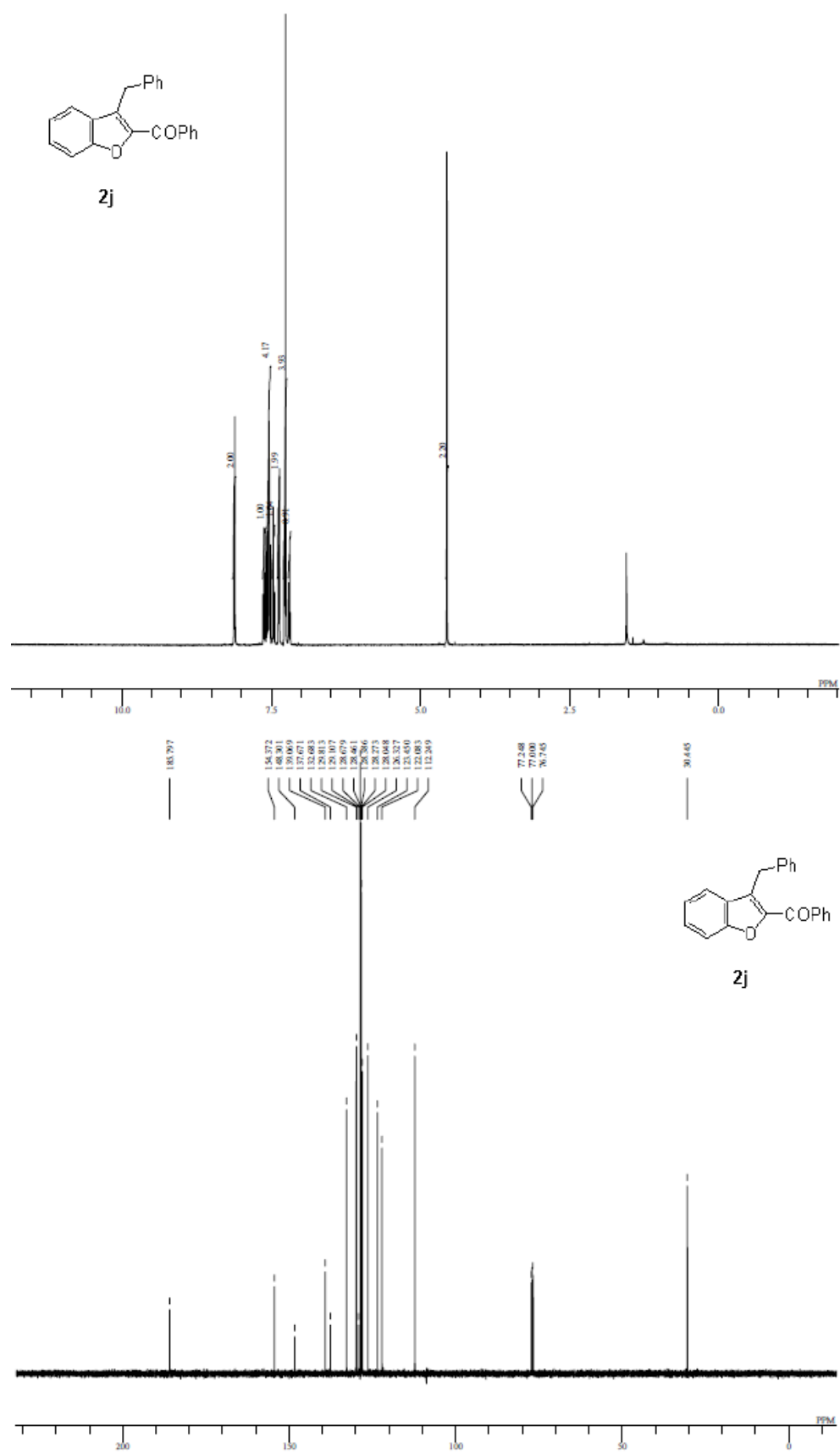


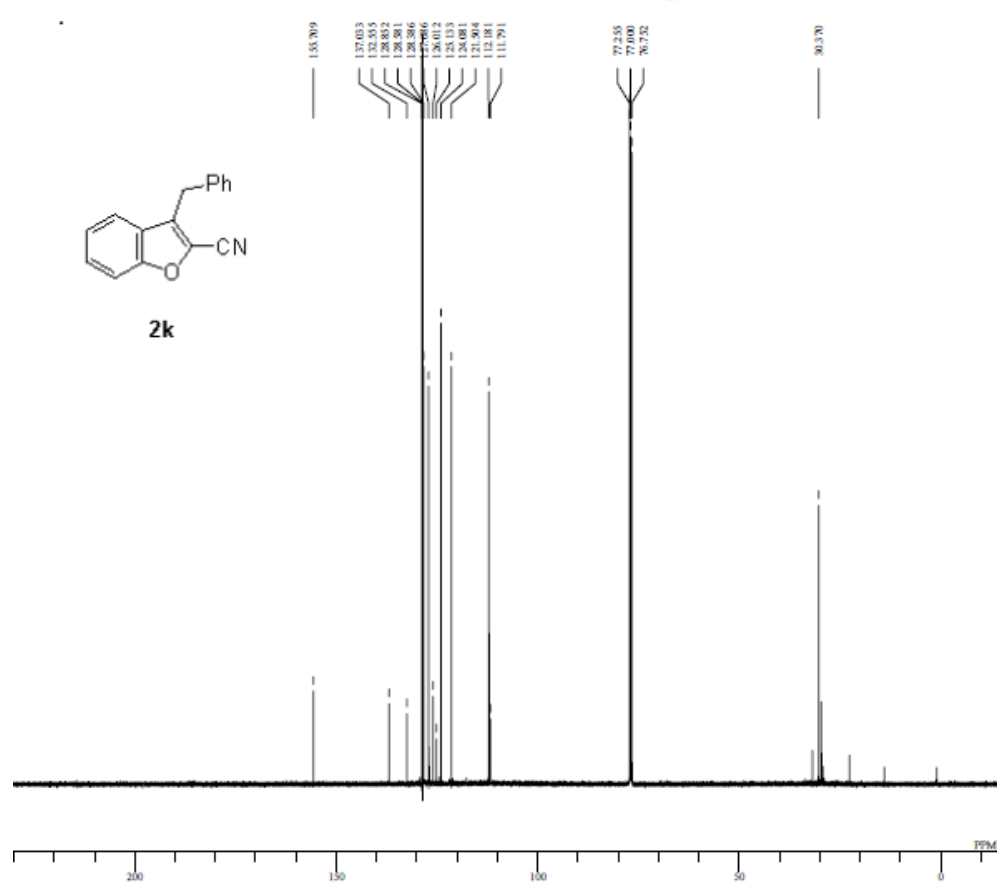
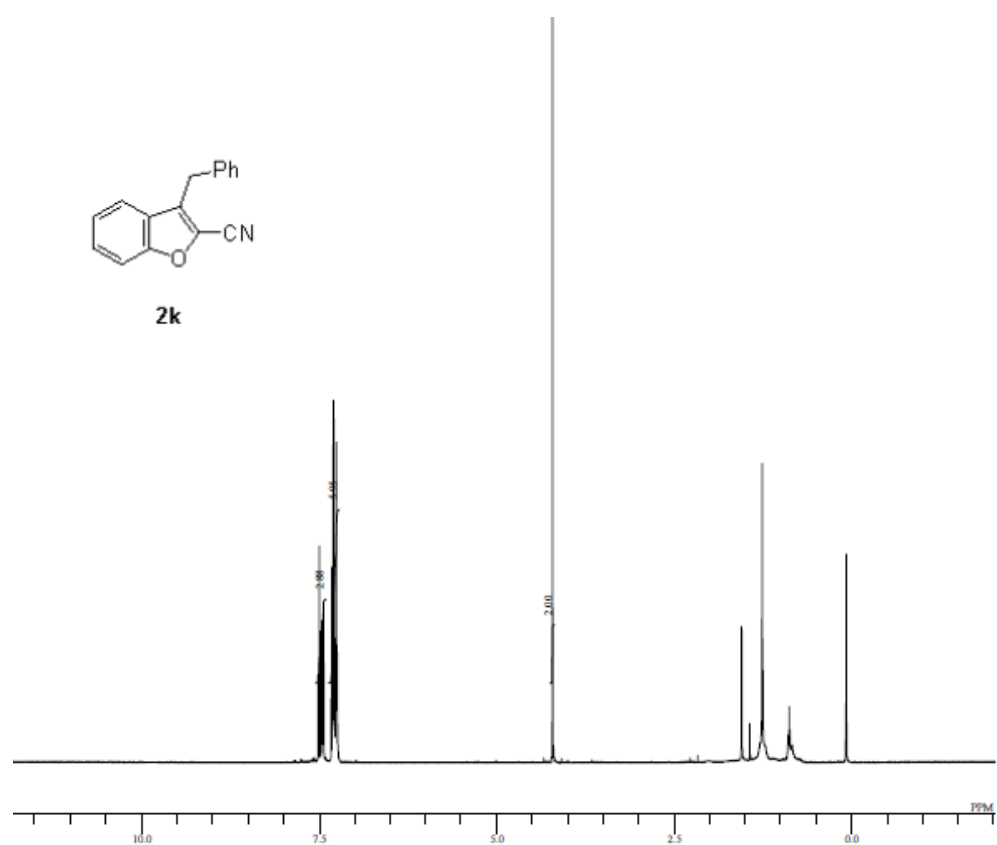


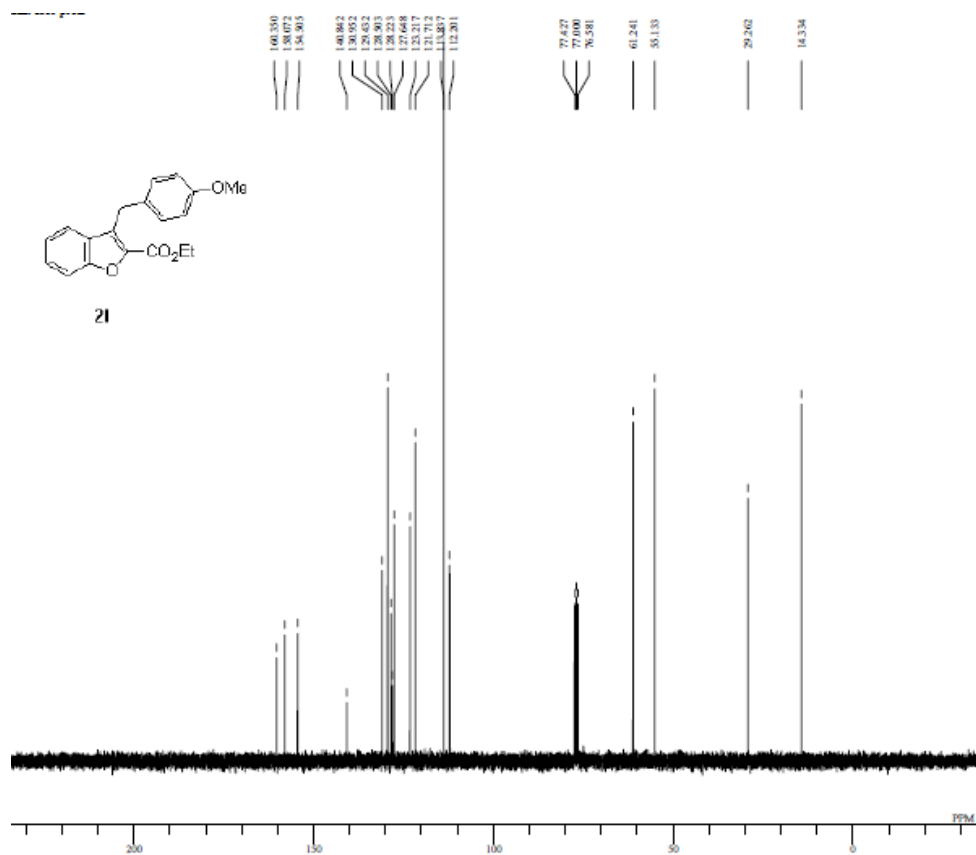
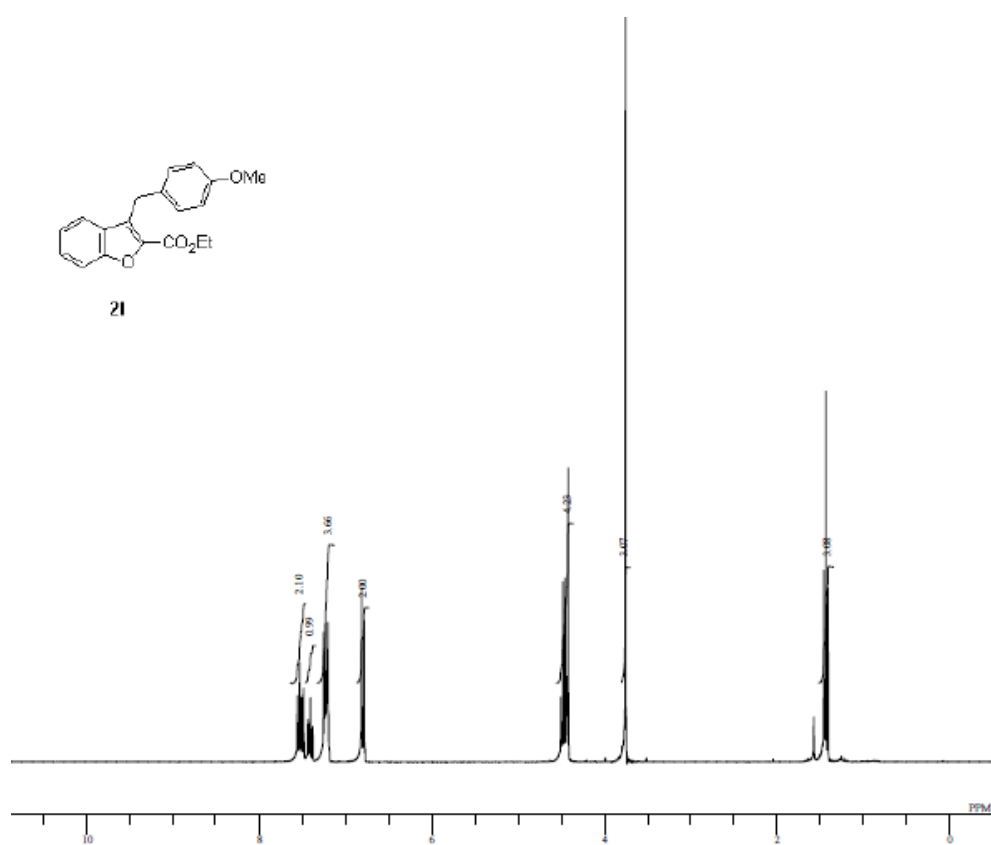


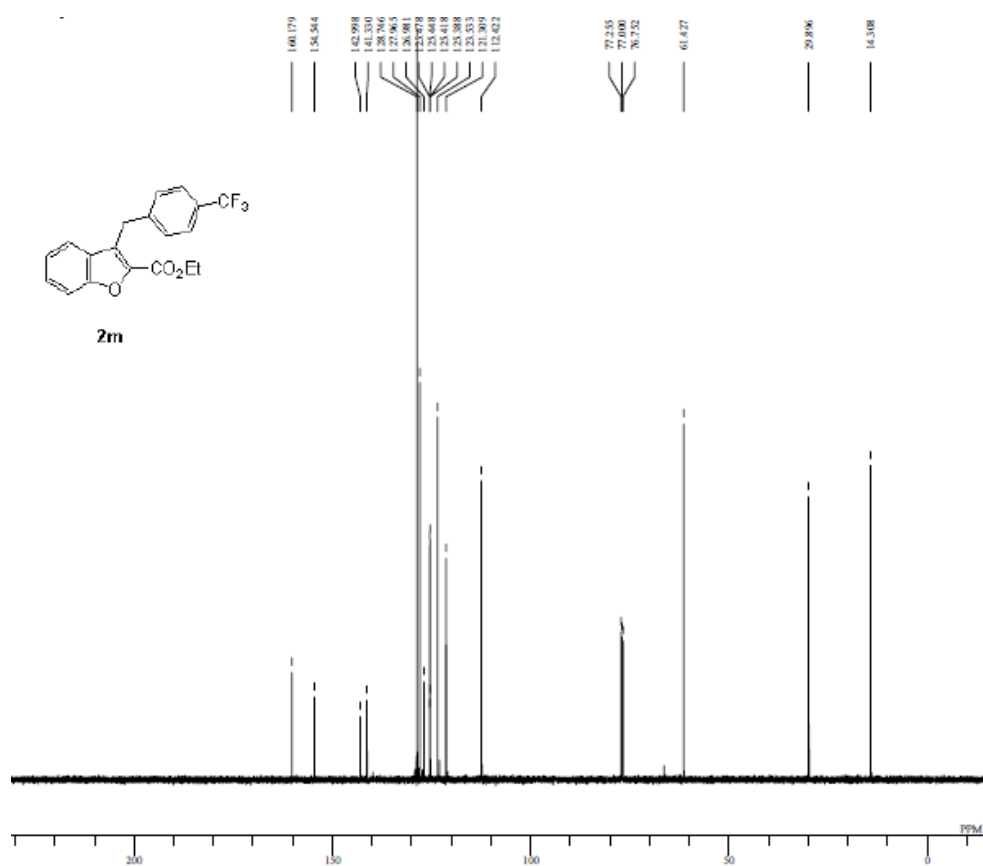
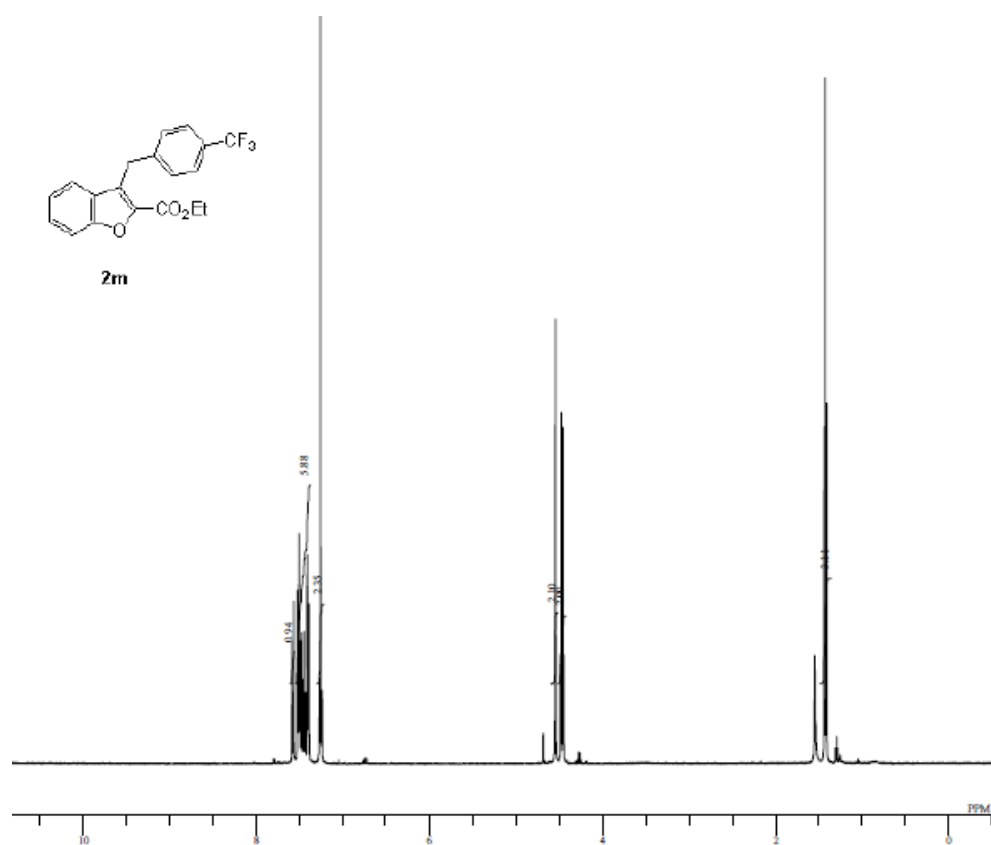


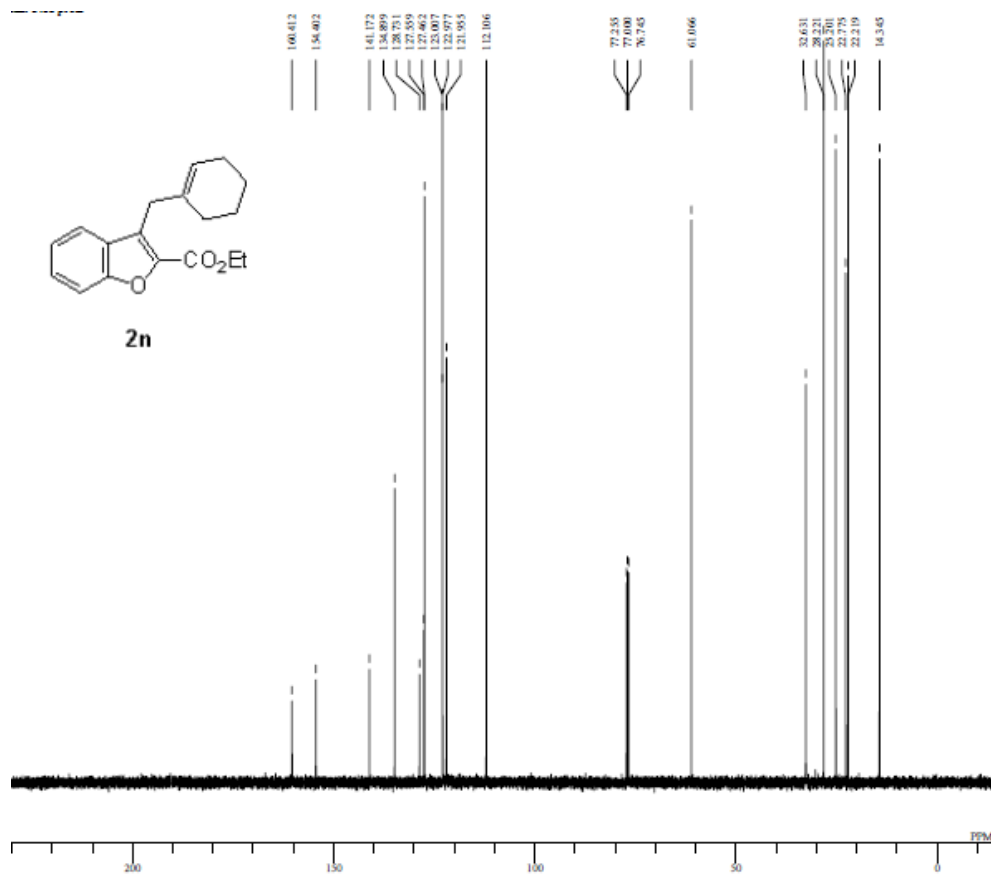
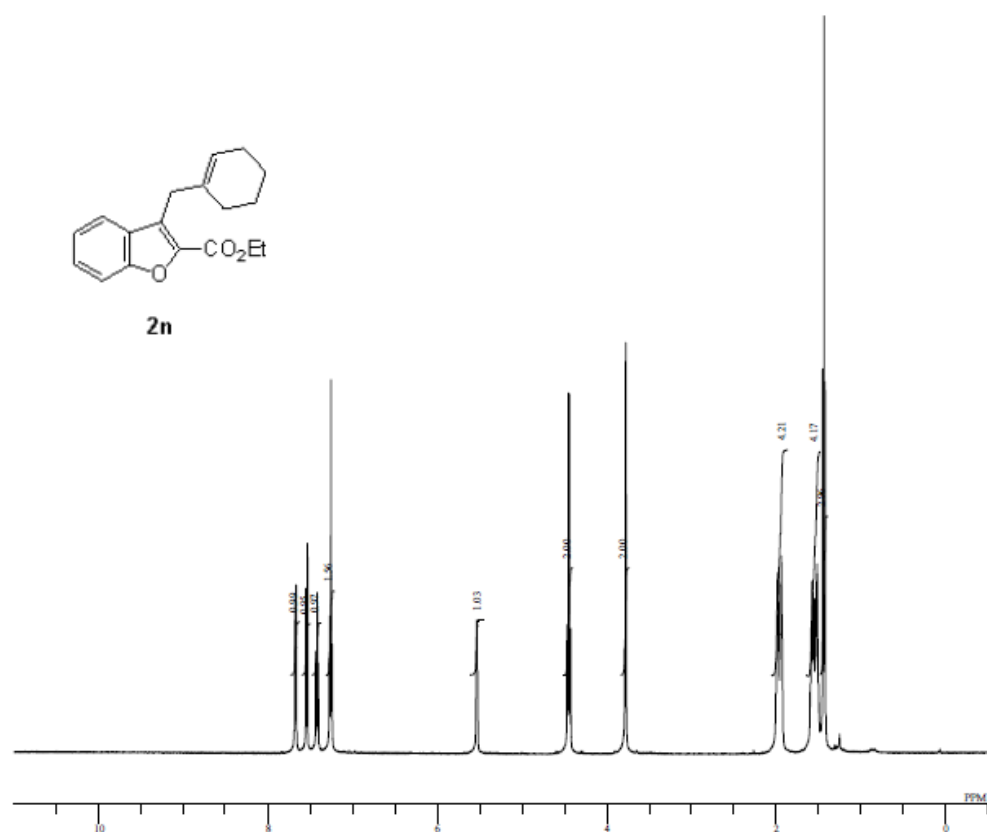


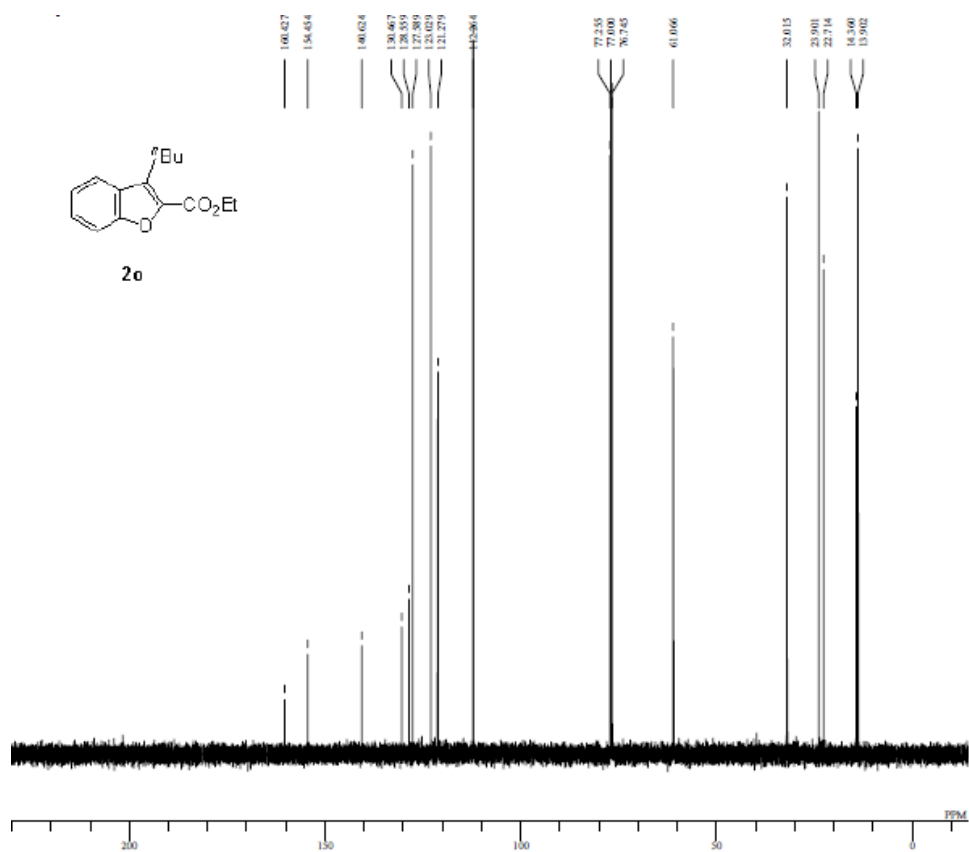
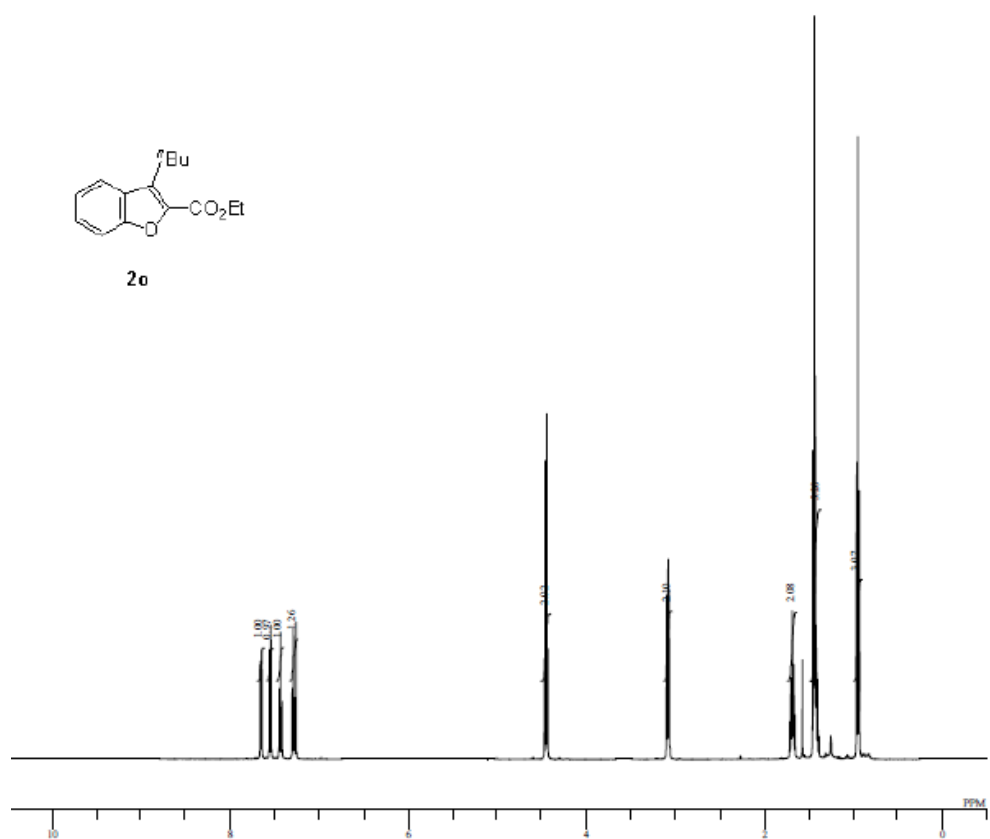
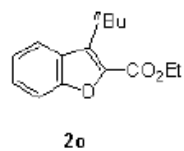


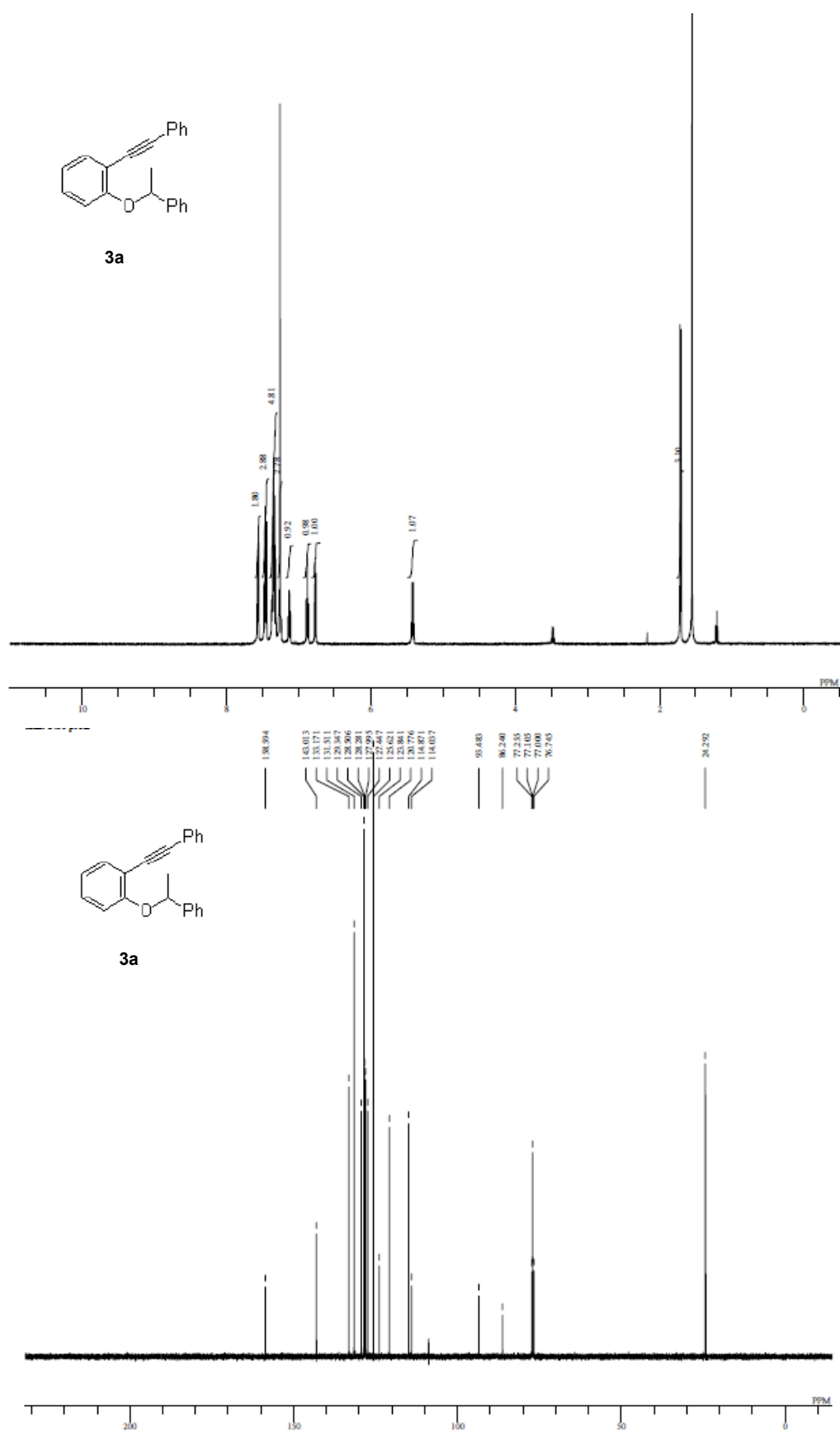


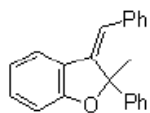




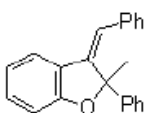
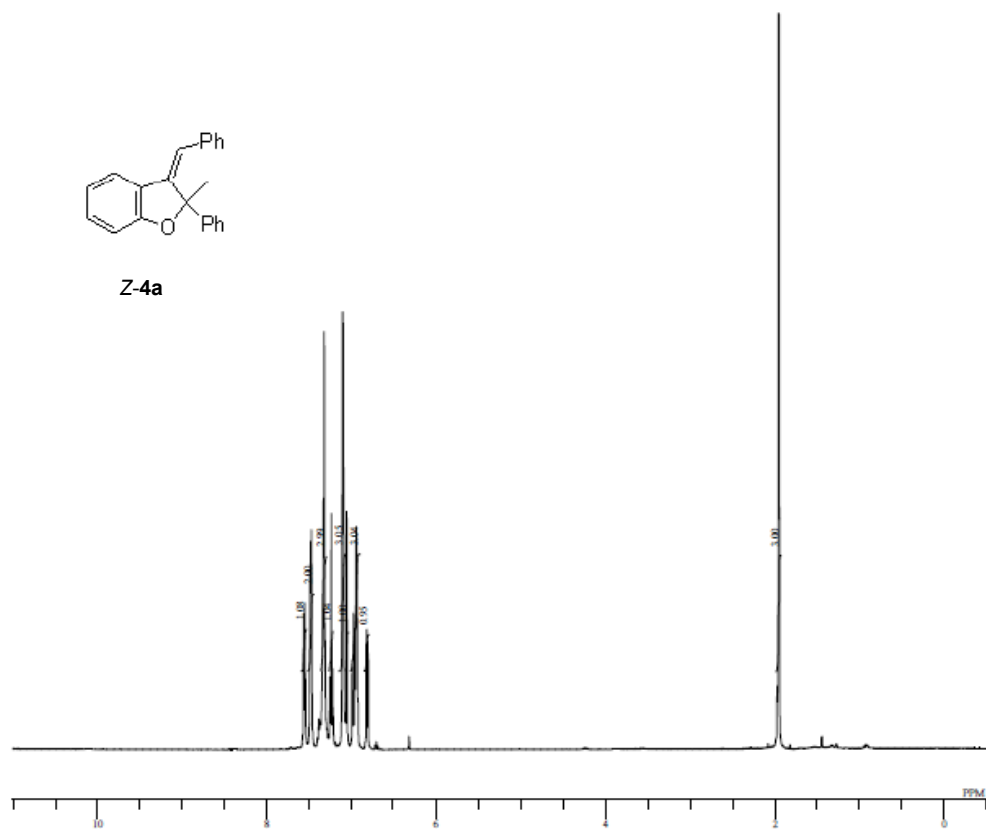




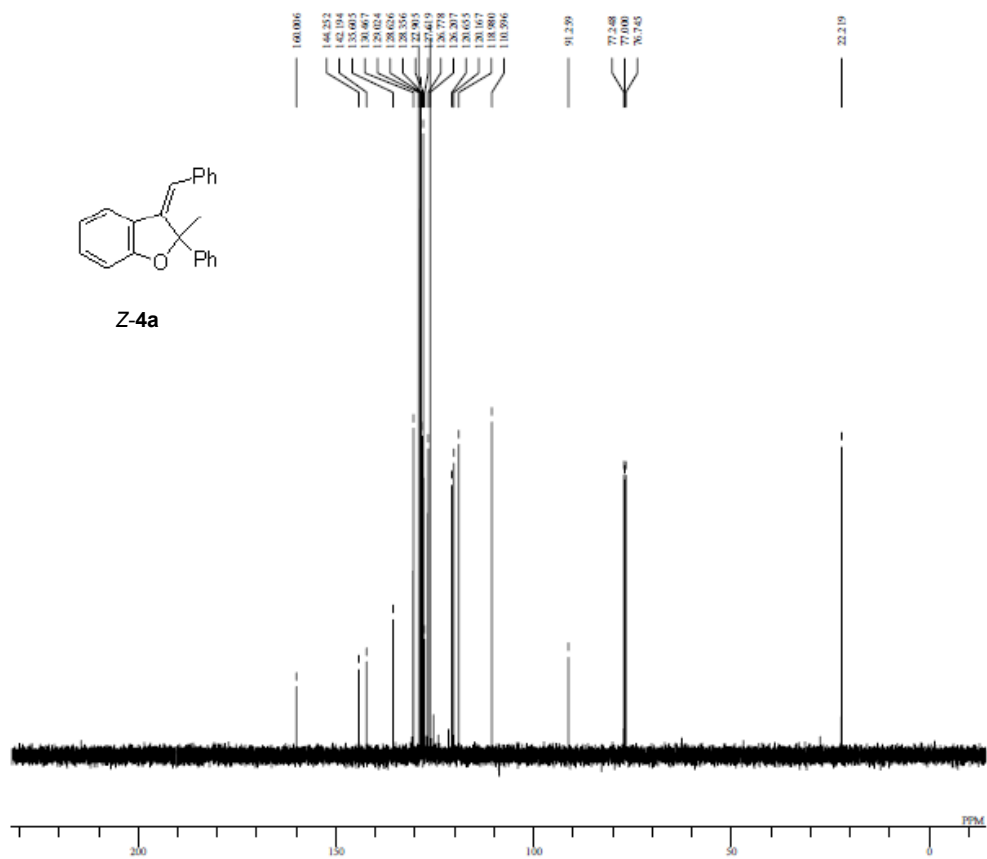


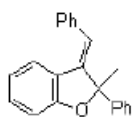


Z-4a

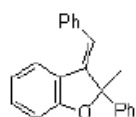
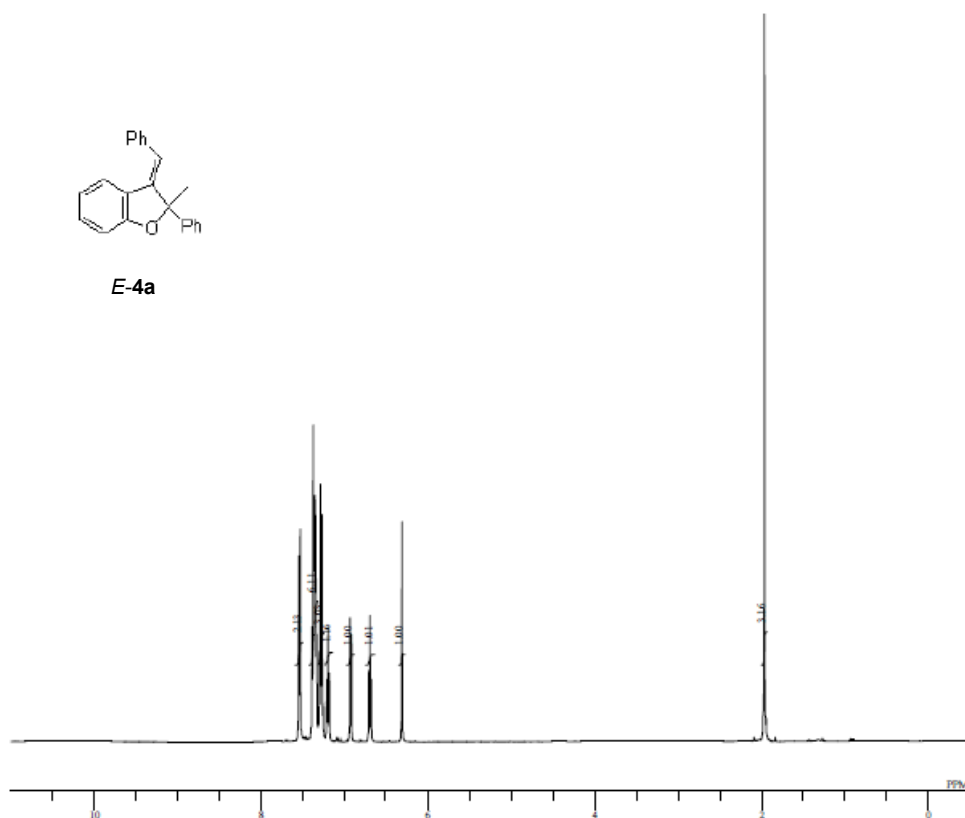


Z-4a





***E*-4a**



***E*-4a**

