Gold-catalyzed cycloisomerization of alk-4-yn-1-ones

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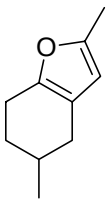
Supporting Information

General remarks: Gold precatalysts were purchased from commercial sources (Acros, Sigma-Aldrich, Chempur) and used without further purification. Column chromatography was carried out with Acros silica gel 60. ^{1}H-NMR and ^{13}C-NMR spectra were recorded with Bruker DRX 400 or DRX500 spectrometers in $CDCl_3$ as solvent. Chemical shifts were determined relative to the residual solvent peaks ($CHCl_3$: $\delta = 7.26$ for protons, $\delta = 77.1$ for carbon atoms). The signals of the major component of a product mixture are marked with an asterisk (*). Decomposition can be observed for the cyclic acetals **4la-4ta** in chloroform.

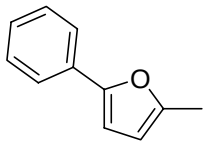
General procedure for gold-catalyzed cycloisomerization of alk-4-yn-1-ones 1 to substituted furans 2: To the solution of the alk-4-yn-1-one **1** (0.4 mmol) in 4 mL of dry toluene under argon was added 2 mol% of Ph_3PAuCl, 2 mol% of AgOTf, and 5 mol% of *p*-TsOH · H_2O. The mixture was stirred at room temperature, and the reaction was monitored by TLC. After completion, the reaction mixture was filtered through Celite® and the solvent was removed under vacuum. The crude product was purified by flash column chromatography.

4,5,6,7-Tetrahydro-2,5-dimethylbenzofuran (2a)



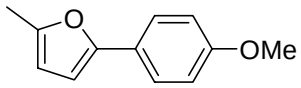
^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 5.77$ (s, 1 H), 2.60-2.58 (m, 2 H), 2.48-2.43 (m, 1 H), 2.26 (s, 3 H), 2.05-1.98 (m, 1 H), 1.90-1.81 (m, 2 H), 1.52-1.48 (m, 1 H), 1.05 (d, J = 6.8 Hz, 3 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 149.9, 148.7, 117.4, 106.4, 31.6, 30.6, 29.7, 22.7, 21.5, 13.7.
MS (ESI): m/z (%): 149 (100) [M–H$^+$], 131 (10), 91 (10).
HRMS: m/z: calcd. for $C_{10}H_{15}O$: 151.1117 [M+H]$^+$; found: 151.1115.
IR: ν = 2950, 2922, 2846, 1580, 1456, 1247, 1223, 1131, 948, 790 cm^{-1}.

2-Methyl-5-phenylfuran (2b)



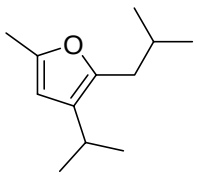
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.63-7.61 (m, 2 H), 7.36-7.32 (m, 2 H), 7.22-7.18 (m, 1 H), 6.53 (d, J = 3.0 Hz, 1 H), 6.04-6.03 (m, 1 H), 2.35 (s, 3 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 152.4, 152.1, 131.3, 128.7, 126.8, 123.4, 107.8, 106.0, 13.8.

2-(4-Methoxyphenyl)-5-methylfuran (2c)



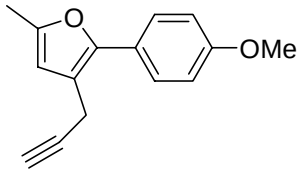
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, J = 8.3 Hz, 2 H), 6.90 (d, J = 8.3 Hz), 6.40 (d, J = 3.0 Hz, 1 H), 6.03 (d, J = 3.0 Hz, 1 H), 3.81 (s, 3 H), 2.36 (s, 3 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 158.7, 152.4, 151.3, 128.8, 114.1, 107.6, 104.3, 55.3, 13.8.
MS (EI): m/z (%): 188 (94) [M^+], 173 (100).
HRMS: m/z: calcd. for $C_{12}H_{12}O_2$: 188.0837 [M^+]; found: 188.0832.
IR: ν = 2962, 2837, 1500, 1292, 1251, 1181, 1030, 1020, 831, 787 cm^{-1}.

2-Isobutyl-3-isopropyl-5-methylfuran (2d)



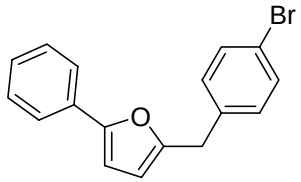
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.84 (s, 1 H), 2.75-2.69 (m, 1 H), 2.39 (d, J = 7.0 Hz, 2 H), 2.23 (s, 3 H), 1.95-1.92 (m, 1 H), 1.13 (d, J = 6.8 Hz, 6 H), 0.92 (d, J = 6.8 Hz, 6 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 149.4, 147.3, 127.1, 104.5, 35.3, 28.5, 24.7, 24.1, 22.6, 13.8.
MS (EI): m/z (%): 180 (20) [M^+], 137 (100).
HRMS: m/z: calcd. for $C_{12}H_{20}O$: 180.1509 [M^+]; found: 180.1506.
IR: ν = 2958, 2927, 1580, 1465, 1383, 1269, 1042, 963, 797 cm^{-1}.

2-(4-Methoxyphenyl)-5-methyl-3-(prop-2-ynyl)furan (2e)



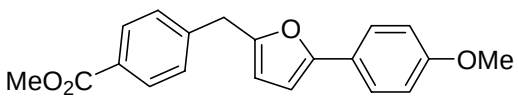
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, J = 8.5 Hz, 2 H), 6.95 (d, J = 8.5 Hz, 2 H), 6.14 (s, 1 H), 3.82 (s, 3 H), 3.48 (d, J = 2.5 Hz, 2 H), 2.32 (s, 3 H), 2.11 (d, J = 2.5 Hz, 1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 158.7, 150.6, 147.5, 127.1, 124.1, 115.1, 114.1, 109.4, 82.2, 69.0, 55.3, 16.2 ,13.7.
MS (EI): m/z (%): 226 (100) [M^+], 211 (70), 211 (28), 183 (21).
HRMS: m/z: calcd. for $C_{15}H_{14}O_2$: 226.0994 [M^+]; found: 226.0996.
IR: ν = 3054, 1608, 1506, 1265, 1179, 1037, 835, 739, 704 cm^{-1}.

2-(4-Bromobenzyl)-5-phenylfuran (2f)



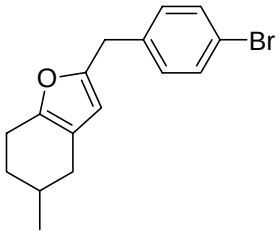
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.62-7.60 (m, 2 H), 7.43-7.41 (m, 2 H), 7.36-7.32 (m, 2 H), 7.23-7.13 (m, 3 H), 6.54 (d, J = 3.3 Hz, 1 H), 6.05 (d, J = 3.3 Hz, 1 H), 3.96 (s, 2 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.6, 153.2, 131.7, 130.6, 128.7, 127.2, 123.5, 120.5, 108.8, 105.9, 34.2.
MS (EI): m/z (%): 312 (100) [M^+], 233 (60), 157 (48), 128 (38), 77 (10).
HRMS: m/z: calcd. for $C_{17}H_{13}OBr$: 312.0150 [$M]^+$; found: 312.0152.
IR: ν = 3120, 2922, 1595, 1546, 1487, 1447, 1265, 1072, 1021, 967, 794, 761 cm^{-1}.

Methyl 4-((5-(4-methoxyphenyl)furan-2-yl)methyl)benzoate (2g)



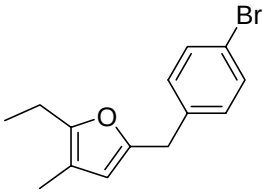
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, J = 8.3 Hz, 2 H), 7.55 (d, J = 8.8 Hz, 2 H), 7.35 (d, J = 8.3 Hz, 2 H), 6.89 (d, J = 8.8 Hz, 2 H), 6.43(d, J = 3.0 Hz, 2 H), 6.07 (d, J = 3.0 Hz, 2 H), 4.07 (s, 2 H), 3.91 (s, 3 H), 3.82 (s, 3 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 176.1, 158.9, 153.4, 152.5, 143.7, 130.0, 128.9, 125.0, 124.1, 114.2, 108.8, 104.3, 55.40, 52.2, 34.7.
MS (EI): m/z (%): 322 (100) [M^+], 263 (14), 187 (24).
HRMS: m/z: calcd. for $C_{20}H_{18}O_4$: 322.1200[M^+]; found: 322.1201.
IR: ν = 2952, 2916, 1716, 1613, 1501, 1433, 1283, 1254, 1110, 1024, 832, 787 cm^{-1}.

2-(4-Bromobenzyl)-4,5,6,7-tetrahydro-5-methylbenzofuran (2h)



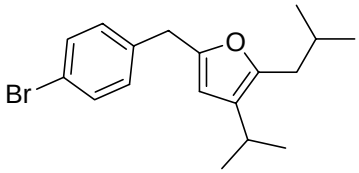
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 8.3 Hz, 2 H), 7.13 (d, J = 8.3 Hz, 2 H), 5.77 (s, 1 H), 3.86 (s, 2 H), 2.58-2.57 (m, 2 H), 2.46-2.41 (m, 1 H), 2.03-1.97 (m, 1 H), 1.88-1.79 (m, 2 H), 1.48-1.43 (m, 1 H), 1.04 (d, J = 6.5 Hz, 3 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 151.8, 149.7, 137.7, 131.6, 130.6, 120.3, 117.4, 107.5, 34.3, 31.4, 30.5, 29.7, 22.8, 21.5.
MS (EI): m/z (%): 304 (100) [M^+].
HRMS: m/z: calcd. for $C_{16}H_{17}BrO$: 304.0463 [M^+]; found: 304.0457.
IR: ν = 2949, 2924, 2844, 1568, 1487, 1455, 1403, 1222, 1126, 1071, 1012, 965, 795, 779 cm^{-1}.

5-(4-Bromobenzyl)-2-ethyl-3-methylfuran (2i)



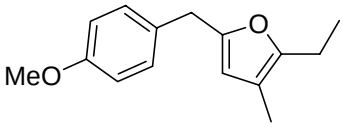
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.3 Hz, 2 H), 7.10 (d, J = 8.3 Hz, 2 H), 5.74 (s, 1 H), 3.83 (s, 2 H), 2.54 (q, J = 7.5 Hz, 2 H), 1.90 (s, 3 H), 1.17 (t, J = 7.5 Hz, 3 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 151.7, 150.8, 131.7, 131.6, 120.3, 113.7, 109.8, 34.1, 19.4, 13.3, 9.9.
MS (EI): m/z (%): 278 (88) [M^+], 263 (100), 249 (30), 184 (60).
HRMS: m/z: calcd. for $C_{14}H_{15}OBr$: 278.0306 [M^+]; found: 278.0297.
IR: ν = 3054, 2986, 2305, 1488, 1265, 986, 738, 705 cm^{-1}.

5-(4-Bromobenzyl)-2-isobutyl-3-isopropylfuran (2j)



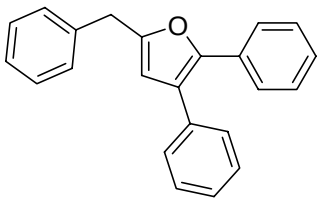
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 8.3 Hz, 2 H), 7.11 (d, J = 8.3 Hz, 2 H), 5.83 (s, 1 H), 3.85 (s, 2 H), 2.75-2.68 (m, 1 H), 2.39 (d, J = 7.0 Hz, 2 H), 1.94-1.90 (m, 1 H), 1.11 (d, J = 6.8 Hz, 6 H), 0.90 (d, J = 6.5 Hz, 6 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 151.1, 148.3, 137.8, 131.6, 130.6, 127.1, 120.2, 105.6, 35.2, 34.2, 28.5, 24.63, 24.1, 22.5.
MS (EI): m/z (%): 334 (25) [M^+], 291 (100).
HRMS: m/z: calcd. for $C_{18}H_{23}BrO$: 334.0927 [M^+]; found: 334.0935.
IR: ν = 3054, 2986, 1422, 1265, 896, 738, 705 cm^{-1}.

5-(4-Methoxybenzyl)-2-ethyl-3-methylfuran (2k)



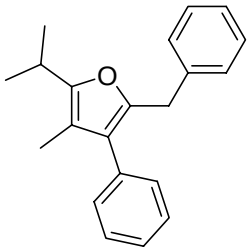
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.16 (d, J = 8.6 Hz, 2 H), 6.85 (d, J = 8. 6 Hz, 2 H), 5.70 (s, 1 H), 3.84 (s, 2 H), 3.80 (s, 3 H), 2.54 (q, J = 7.5 Hz, 2 H), 1.90 (s, 3 H), 1.18 (t, J = 7.5 Hz, 3 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 158.2, 152.1, 151.4, 130.8, 129.8, 113.9, 113.6, 109.4, 55.4, 33.8, 19.5, 13.3, 9.9.
MS (EI): m/z (%): 230 (100) [M^+], 215 (70), 199 (40), 135 (52).
HRMS: m/z: calcd. for $C_{15}H_{18}O_2$: 230.1301 [M^+]; found: 230.1296.
IR: ν = 2968, 2935, 1613, 1585, 1512, 1463, 1246, 1176, 1036, 979 cm^{-1}.

5-Benzyl-2,3-diphenylfuran (2l)



^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.71-7.69 (m, 2 H), 7.47-7.24 (m, 13 H), 6.85 (s, 1 H), 4.23 (s, 2 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 152.4, 148.9, 138.5, 133.7, 128.6, 128.6, 128.6, 128.3, 127.6, 127.2, 126.8, 126.4, 124.4, 123.5, 106.6, 32.9.
MS (EI): m/z (%): 310 (100) [M^+], 233 (40), 105 (20).
HRMS: m/z: calcd. for $C_{23}H_{18}O$: 310.1352 [M^+]; found: 310.1350.
IR: ν = 3060, 3028, 1596, 1533, 1494, 1452, 1122, 1073, 984, 758, 728, 694 cm^{-1}.

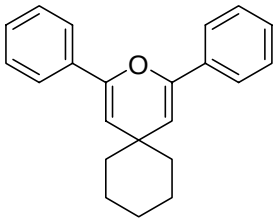
2-Benzyl-5-isopropyl-4-methyl-3-phenylfuran (2m)



^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.38- 7.18 (m, 10 H), 3.96 (s, 2 H), 3.08-3.00 (m, 1 H), 1.94 (s, 3 H), 1.27 (d, J = 7.0 Hz, 6 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 154.4, 146.7, 139.6, 134.2, 129.5, 128.5, 128.4, 127.6, 126.6, 126.1, 112.0, 132.6, 26.4, 21.5, 9.0.
MS (EI): m/z (%): 290 (50) [M^+], 275 (100).
HRMS: m/z: calcd. for $C_{21}H_{22}O$: 290.1160 [M^+]; found: 290.1165.
IR: ν = 2967, 2929, 1707, 1675, 1605, 1495, 1454, 1074, 1054, 990, 767, 702 cm^{-1}.

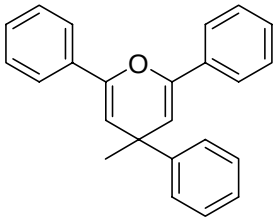
General procedure for gold-catalyzed cycloisomerization of alk-4-yn-1-ones 1 to 4*H*-pyrans 3: To the solution of the alk-4-yn-1-one **1** (0.4 mmol) in 4 mL of dry toluene under argon was added 2 mol% of Ph_3PAuCl and 2 mol% of AgOTf. The mixture was stirred at room temperature, and the reaction was monitored by TLC. After completion, the reaction mixture was filtered through Celite® and the solvent was removed under vacuum. The crude product was purified by flash column chromatography.

2,4-Diphenyl-3-oxaspiro[5.5]undec-1,4-dien (3n)



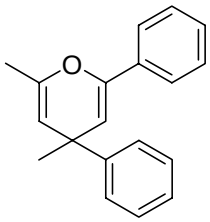
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.76-7.73 (m, 4 H), 7.43-7.32 (m, 6 H), 5.52 (s, 2 H), 1.66-1.60 (m, 8 H), 1.56-1.51 (m, 2 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 147.1, 134.9, 128.4, 128.3, 124.7, 105.5, 41.4, 26.1, 21.1.
MS (EI): m/z (%): 302 (22) [M^+], 259 (100).
HRMS: m/z: calcd. for $C_{22}H_{22}O$: 302.1671 [M^+]; found: 302.1659.
IR: ν = 2926, 2856, 1724, 1682, 1599, 1495, 1448, 1285, 1105, 1065, 1028, 960, 761, 691 cm^{-1}.

4-Methyl-2,4,6-triphenyl-4*H*-pyran (3o)



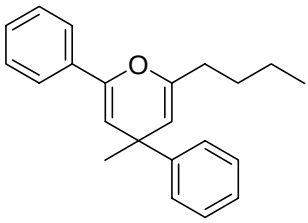
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.76-7.74 (m, 4 H), 7.51-7.32 (m, 11 H), 5.48 (s, 2 H), 1.70 (s, 3 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 150.0, 146.7, 134.6, 128.5, 128.1, 126.9, 126.3, 126.5, 126.3, 125.4, 105.9, 38.0, 30.5.
MS (EI): m/z (%): 324 (12) [M^+], 309 (100)
HRMS: m/z: calcd. for $C_{24}H_{20}O$: 324.1514 [M^+]; found: 324.1509.
IR: ν = 3085, 3057, 3027, 2970, 1684, 1599, 1494, 1447, 1313, 1286, 1179, 1065, 1027, 932, 916, 757, 693 cm^{-1}.

2,4-Dimethyl-4,6-diphenyl-4*H*-pyran (3p)



^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.66-7.64 (m, 2 H), 7.46-7.44 (m, 2 H), 7.38-7.29 (m, 5 H), 7.24-7.19 (m, 1 H), 5.38 (d, J = 2.5 Hz, 1 H), 4.68 (m, 1 H), 1.98 (s, 3 H), 1.59 (s, 3 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 150.3, 146.6, 145.6, 134.4, 128.2, 128.1, 126.5, 125.8, 124.5, 105.5, 105.4, 37.5, 30.5, 19.2.
MS (EI): m/z (%): 262 (6) [M^+], 247 (100)
HRMS: m/z: calcd. for $C_{19}H_{18}O$: 262.1358 [M^+]; found: 262.1352.
IR: ν = 3084, 3056, 3026, 2962, 2921, 1702, 1493, 1445, 1294, 1176, 1064, 1028, 910, 759, 696 cm^{-1}.

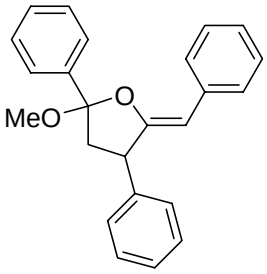
2-Butyl-4-methyl-4,6-diphenyl-4*H*-pyran (3q)



^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.68-7.66 (m, 2 H), 7.49-7.47 (m, 2 H), 7.40-7.34 (m, 5 H), 7.24-7.21 (m, 1 H), 5.40 (d, J = 2.5 Hz, 1 H), 4.70 (d, J = 2.3 Hz, 1 H), 2.23 (t, J = 7.5 Hz, 2 H), 1.70-1.43 (m, 11 H), 1.00 (t, J = 7.3 Hz, 3 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 150.6, 149.3, 146.6, 134.7, 128.3, 128.2, 126.8, 126.0, 124.6, 105.8, 105.0, 37.6, 33.1, 30.8, 29.2, 27.1, 22.4, 14.1.
MS (EI): m/z (%): 304(4) [M^+], 289 (100).
HRMS: m/z: calcd. for $C_{22}H_{24}O$: 304.1827[M^+]; found: 304.1813.
IR: ν = 2958, 2927, 2870, 1699, 1645, 1598, 1493, 1446, 1384, 1298, 1269, 1170, 1028, 760 cm^{-1}.

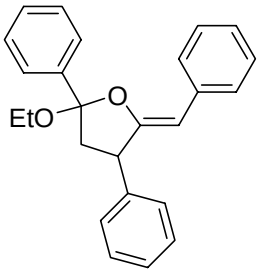
General procedure for gold-catalyzed cycloisomerization of alk-4-yn-1-ones 1 to tetrahydrofuranyl ethers 4: To the solution of the alk-4-yn-1-one 1 (0.4 mmol) in 4 mL of the corresponding dry alcohol under argon was added 2 mol% of Ph_3PAuCl and 2 mol% of AgOTf. The mixture was stirred at room temperature, and the reaction was monitored by TLC. After completion, the reaction mixture was filtrated through Celite® and the solvent was removed under vacuum. The crude product was purified by flash column chromatography.

(*Z*)-5-Benzylidenetetrahydro-2-methoxy-2,4-diphenylfuran (4la)



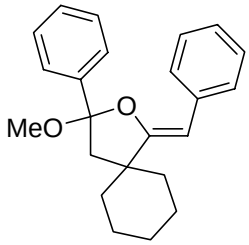
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.83-7.72 (m, 4 H), 7.40-7.11 (m, 11 H), 5.30/5.27* (d, J = 2.8 Hz, 1H), 4.63-4.58*/4.01-3.95 (m, 1H), 3.22/3.21* (s, 3 H), 2.72*/2.68 (dd, J = 12.5 Hz, 7.8 Hz), 2.45/2.13 (dd, J = 12.5 Hz, 7.8 Hz).
^{13}C-NMR (400 MHz, C_6D_6): δ = 160.2*/159.5, 142.0/139.5*, 141.0/136.9*, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.0, 127.8, 127.0, 126.2, 126.1, 125.3, 112.2/110.7*, 101.9*/101.8, 50.9/50.3*, 48.8*/48.2, 48.4*/47.3.

(*Z*)-5-Benzylidene-2-ethoxytetrahydro-2,4-diphenylfuran (4lb)



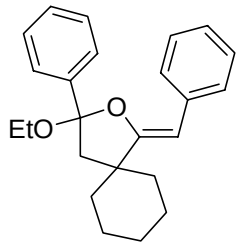
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.86-7.63 (m, 4 H), 7.34-7.10 (m, 11 H), 5.30/5.28*(d, J = 2.0 Hz, 1 H), 4.70-4.62*/4.01-3.95 (m, 1 H), 3.80/3.74* (dq, J = 9.5 Hz, 7.0 Hz, 1 H), 3.39*/3.37 (dq, J = 9.5 Hz, 7.0 Hz, 1 H), 2.75*/2.70 (dd, J = 12.5 Hz, 7.5 Hz, 1 H), 2.47/2.13* (dd, J = 12.5 Hz, 9.5 Hz), 1.11*/1.08 (t, J = 7.0 Hz, 3 H).
^{13}C-NMR (400 MHz, C_6D_6): δ =160.4*/159.6, 141.9*/140.3, 136.9*/136.9, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 127.8, 127.0, 126.8, 126.0, 126.0, 125.3, 112.0/110.6*, 101.7*/101.5, 59.5/58.9*, 48.9*/48.2, 48.7*/47.5, 15.3*/15.1.

(*Z*)-1-Benzylidenetetrahydro-3-methoxy-2-oxa-3-phenylspiro[5.4]decan (4na)



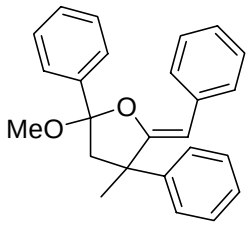
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.69-7.68 (m, 2 H), 7.56-7.55 (m, 2 H), 7.46-7.28 (m, 5 H), 7.13-7.09 (m, 1 H), 5.30 (s, 1 H), 3.13 (s, 3 H), 2.61 (d, J = 13.1 Hz, 1 H), 1.87 (d, J = 13.1 Hz, 1 H), 1.59-1.20 (s, 10 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.3, 140.7, 137.1, 128.6, 128.5, 128.3, 127.7, 126.1, 125.0, 111.2, 98.3, 50.8, 48.3, 47.5, 39.8, 37.7, 25.8, 23.7, 23.6.
MS (EI): m/z (%): 334 (24) [M^+], 207 (100).
HRMS: m/z: calcd. for $C_{23}H_{26}O_2$: 334.1933 [M^+]; found: 334.1927.
IR: ν = 2931, 2854, 1705, 1673, 1597, 1448, 1323, 1310, 1264, 1176, 1127, 1022, 987, 938, 751, 696 cm^{-1}.

(*Z*)-1-Benzylidene-3-ethoxytetrahydro-2-oxa-3-phenylspiro[5.4]decan (4nb)



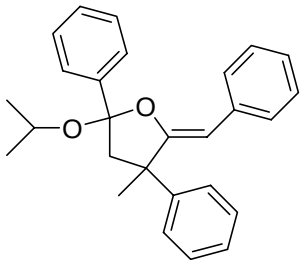
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.71-7.69 (m, 2 H), 7.60-7.58 (m, 2 H), 7.43-7.30 (m, 5 H), 7.15-7.12 (m, 1 H), 5.32 (s, 1 H), 3.59 (dq, J = 9.5 Hz, 7.0 Hz, 1 H), 3.28 (dq, J = 9.5 Hz, 7.0 Hz, 1 H), 2.64 (d, J = 13.3 Hz, 1 H), 2.29-2.27 (m, 1 H), 1.87 (d, J = 13.3 Hz, 1 H), 1.76-1.48 (m, 7 H), 1.28-1.24 (m, 2 H), 1.10 (t, J = 7.0 Hz, 3 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ =166.3, 141.3, 137.0, 128.3, 128.3, 128.0, 127.4, 125.8, 124.7, 110.8, 97.8, 58.8, 48.3, 47.4, 39.6, 37.4, 25.6, 23.4, 23.4, 15.4.
MS (EI): m/z (%): 348 (40) [M^+], 105 (100)
HRMS: m/z: calcd. for $C_{24}H_{28}O_2$: 348.2089 [M^+]; found: 348.2097.
IR: ν = 2929, 2854, 1668, 1598, 1448, 1310, 1264, 1175, 1062, 986, 750, 696 cm^{-1}.

(*Z*)-5-Benzylidenetetrahydro-2-methoxy-4-methyl-2,4-diphenylfuran (4oa)



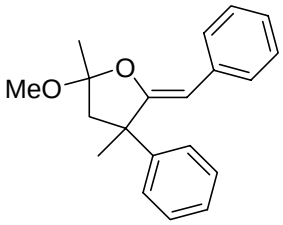
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.79-7.19 (m, 15 H), 5.33/5.13* (s, 1 H), 3.26*/3.10 (s, 3 H), 2.94*/2.72 (d, J = 13.5 Hz, 1 H), 2.52*/2.37 (d, J = 13.5 Hz, 1 H), 1.96*/1.69 (s, 3 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 165.6/163.6, 147.9/147.6, 140.5/140.2, 136.8/136.7, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 127.9, 127.3, 126.7, 126.6, 126.4, 126.3, 126.2, 126.1, 125.5, 125.4, 125.3, 124.8, 111.3/111.1, 101.4/101.2, 56.5/55.5, 51.2/51.1, 51.0/50.5, 29.9/27.9.
MS (EI): m/z (%): 356 (24) [M^+], 309 (100).
HRMS: m/z: calcd. for $C_{25}H_{24}O_2$: 356.1771 [M^+]; found: 356.1776.
IR: ν = 3058, 3025, 2968, 2936, 1716, 1673, 1598, 1493, 1447, 1353, 1312, 1172, 1076, 986 cm^{-1}.

(*Z*)-5-Benzylidenetetrahydro-2-isopropoxy-4-methyl-2,4-diphenylfuran (4ob)



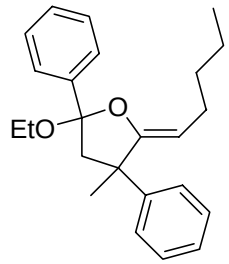
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.82-7.16 (m, 15 H), 5.33/5.09* (s, 1 H), 4.01-3.82 (m, 1 H), 3.04/2.74* (d, J = 13.3 Hz, 1 H), 2.46*/2.34 (d, J = 13.3 Hz, 1 H), 2.02*/1.64 (s, 3 H), 1.19*/1.01 (d, J = 6.3 Hz, 3 H), 1.03*/0.83 (d, J = 6.3 Hz, 3 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.1/163.4, 148.1/147.3, 142.2/141.8, 137.0/136.8, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 127.8, 127.7, 127.0, 126.7, 126.3, 126.2, 126.2, 125.3, 125.1, 111.7/111.3, 101.0/100.9, 67.4/67.3, 56.9/55.4, 51.1, 30.5/27.5, 24.3/24.3, 23.8/23.6.
MS (EI): m/z (%): 384 (30) [M^+], 309 (60), 105 (100).
HRMS: m/z: calcd. for $C_{12}H_{12}O_2$: 388.2084 [M^+]; found: 388.2079.
IR: ν = 3086, 3058, 2971, 2932, 1671, 1598, 1493, 1447, 1382, 1317, 1169, 1107, 981, 909, 756, 734, 699 cm^{-1}.

(*Z*)-5-Benzylidenetetrahydro-2-methoxy-2,4-dimethyl-4-phenylfuran (4pa)



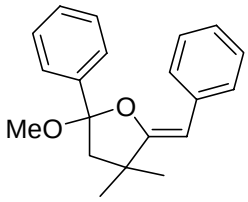
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.69-7.13 (m, 10 H), 5.19/5.12* (s, 1 H), 3.43*/3.25 (s, 3 H), 2.43-2.42 (m, 2 H), 1.81*/1.73 (s, 3 H), 1.67/1.55* (s, 3 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 164.2/163.4, 148.2, 136.8/136.7, 128.4, 128.4, 128.4, 128.1, 127.7, 127.6, 126.6, 126.4, 125.2, 125.2, 110.0/109.6, 100.3, 53.1/53.0, 51.3/51.2, 49.8/49.4, 30.2/28.0, 22.8/22.8.
MS (EI): m/z (%): 294 (12) [M^+], 247 (100)
HRMS: m/z: calcd. for $C_{20}H_{22}O_2$: 294.1620 [M^+]; found: 294.1614.
IR: ν = 3085, 3056, 3022, 2989, 2831, 1713, 1668, 1598, 1494, 1445, 1382, 1357, 1323, 1217, 1125, 1030, 954, 817, 696 cm^{-1}.

(*Z*)-2-Ethoxytetrahydro-4-methyl-5-pentylidene-2,4-diphenylfuran (4qa)



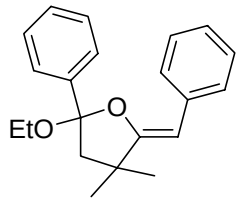
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.59-7.16 (m, 10 H), 4.36/4.20* (t, J = 7.3 Hz, 1 H), 3.63*/3.46 (dq, J = 9.5 Hz, 7.3 Hz, 1 H), 3.25*/3.07 (dq, J = 9.5 Hz, 7.3 Hz, 1 H), 2.91/2.66* (d, J = 13.3 Hz, 1 H), 2.42*/2.24 (d, J = 13.3 Hz, 1 H), 2.40-2.30 (m, 2 H), 1.85/1.55 (s, 3 H), 1.50-1.40 (m, 4 H), 1.21/1.03 (t, J = 7.3 Hz, 3 H), 0.97/0.87 (t, J = 7.0 Hz, 3 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.3/161.1, 148.9/148.0, 141.9/141.5, 128.4, 128.3, 128.1, 128.0, 128.0, 127.9, 126.7, 126.4, 126.0, 126.0, 125.8, 125.3, 108.6/108.2, 100.6/100.3, 58.5/57.9, 57.5/56.2, 49.2/48.9, 32.5/32.4, 29.9/28.3, 25.2/25.1, 22.6/22.4, 15.7/15.2, 14.2/14.2.
MS (EI): m/z (%): 350 (20) [M^+], 289 (100), 207 (50), 105 (80).
HRMS: m/z: calcd. for $C_{24}H_{30}O_2$: 350.2240 [M^+]; found: 350.2244.
IR: ν = 2928, 2871, 1694, 1600, 1494, 1447, 1376, 1315, 1245, 1175, 1043, 994, 947, 758, 699 cm^{-1}.

(*Z*)-5-Benzylidenetetrahydro-2-methoxy-4,4-dimethyl-2-phenylfuran (4ra)



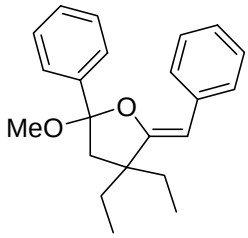
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.56-7.36 (m, 10 H), 5.22 (s, 1 H), 3.16 (s, 3 H), 2.41 (d, J = 13.1 Hz, 1 H), 2.04 (d, J = 13.1 Hz, 1 H), 1.49 (s, 3 H), 1.27 (s, 3 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.6, 140.3, 136.0, 131.5, 129.1, 128.6, 128.5, 128.2, 126.0, 111.1, 96.4, 52.9, 50.9, 42.8, 30.2, 29.9.
MS (CI): 294 (90) [M^+], 263 (60), 161 (44), 71 (50), 56 (100).
IR: ν = 2961, 1709, 1487, 1448, 1350, 1322, 1222, 1168, 1094, 1040, 983, 924, 841, 753, 701 cm^{-1}.

(*Z*)-5-Benzylidene-2-ethoxytetrahydro-4,4-dimethyl-2-phenylfuran (4rb)



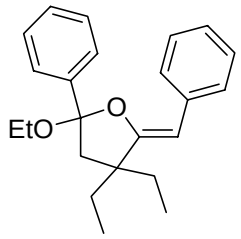
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.55-7.35 (m, 10 H), 5.21 (s, 1 H), 3.58 (dq, J = 9.5 Hz, 7.3 Hz, 1 H), 3.28 (dq, J = 9.5 Hz, 7.3 Hz, 1 H), 2.41 (d, J = 13.0 Hz, 1 H), 2.01 (d, J = 13.0 Hz, 1 H), 1.52 (s, 3 H), 1.27 (s, 3 H), 1.12 (t, J = 7.0 Hz, 3 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.6, 140.9, 135.8, 131.2, 131.2, 128.9, 128.4, 128.1, 125.7, 111.8, 95.9, 58.9, 52.9, 42.7, 30.0, 29.6, 15.4.
MS (CI): m/z (%): 308 (100) [M^+].
HRMS: m/z: calcd. for $C_{21}H_{24}O_2$: 308.1771 [M^+]; found: 308.1758.
IR: ν = 2972, 2931, 1668, 1487, 1448, 1268, 1221, 1007, 927, 840, 701 cm^{-1}.

(*Z*)-5-Benzylidene-4,4-diethyltetrahydro-2-methoxy-2-phenylfuran (4sa)



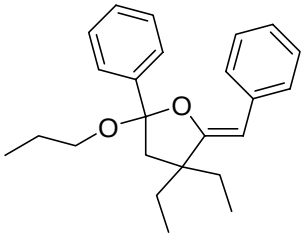
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.74-7.73 (m, 2 H), 7.59-7.57 (m, 2 H), 7.44-7.35 (m, 6 H), 5.22 (s, 1 H), 3.18 (s, 3 H), 2.41 (d, J = 13.3 Hz, 1 H), 2.06 (d, J = 13.3 Hz, 1 H), 1.85 (q, J = 7.5 Hz, 2 H), 1.68-1.62 (m, 1 H), 1.51-1.42 (m, 1 H), 1.03(t, J = 7.5 Hz, 3 H), 0.85 (t, J = 7.5 Hz, 3 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 162.9, 140.9, 136.9, 128.4, 128.3, 128.1, 127.5, 125.9, 124.8, 110.7, 98.9, 50.7, 50.2, 47.6, 32.1, 31.2, 9.0, 8.8.
MS (CI): m/z (%): 323 (100) [M+H]$^+$, 322 (50) [M^+].
HRMS: m/z: calcd. for $C_{22}H_{26}O_2$: 322.1933 [M^+]; found: 322.1926.
IR: ν = 2965, 2936, 2877, 1670, 1596, 1492, 1448, 1320, 1180, 1094, 990, 909, 733, 695 cm^{-1}.

(*Z*)-5-Benzylidene-2-ethoxy-4,4-diethyltetrahydro-2-phenylfuran (4sb)



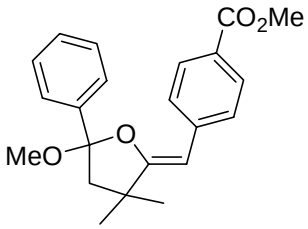
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.75- 7.70 (m, 2 H), 7.60-7.56 (m, 2 H), 7.41-7.31 (m, 5 H), 7.16-7.12 (m, 1 H), 5.18 (s, 1 H), 3.61 (dq, J = 9.3 Hz, 7.3 Hz, 1 H), 3.27 (dq, J = 9.3 Hz, 7.3 Hz, 1 H), 2.39 (d, J = 13.5 Hz, 1 H), 2.01 (d, J = 13.5 Hz, 1 H), 1.85 (q, J = 7.5 Hz, 2 H), 1.86-1.60 (m, 1 H), 1.50-1.40 (m, 1 H), 1.12 (t, J = 7.0 Hz, 3 H), 1.02 (t, J = 7.5 Hz, 3 H), 0.83 (t, J = 7.3 Hz, 3 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.2, 141.9, 137.2, 128.5, 128.4, 128.1, 127.6, 125.9, 124.9, 110.8, 98.8, 59.0, 50.5, 48.0, 32.3, 31.5, 15.6, 9.2, 8.9.
MS (EI): m/z (%): 336 (24) [M^+], 261 (100)
HRMS: m/z: calcd. for $C_{23}H_{28}O_2$: 336.2089 [M^+]; found: 336.2072.

(*Z*)-5-Benzylidene-4,4-diethyltetrahydro-2-phenyl-2-propoxyfuran (4sc)



^{1}H-NMR (400 MHz, $CDCl_3$): δ =7.71– 7.69 (m, 2 H), 7.56-7.54 (m, 2 H), 7.43-7.30 (m, 5 H), 7.14-7.10 (m, 1 H), 5.17 (s, 1 H), 3.48 (dt, J = 9.3 Hz, 6.8 Hz, 1 H), 3.16 (dt, J = 9.3 Hz, 6.8 Hz, 1 H), 2.39 (d, J = 13.3 Hz, 1 H), 2.00 (d, J = 13.3 Hz, 1 H), 1.85-1.82 (m, 2 H), 1.66-1.46 (m, 4 H), 1.01 (t, J = 7.3 Hz, 3 H), 0.86 (t, J = 7.3 Hz, 3 H), 0.83 (t, J = 7.3 Hz, 3 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ =163.3, 141.9, 137.2, 128.6, 128.5, 128.4, 127.7, 126.0, 124.8, 110.7, 103.9, 98.8, 65.1, 50.5, 47.9, 32.2, 31.5, 23.3, 9.5, 9.2, 8.9.
MS (EI): m/z (%): 350 (14) [M^+], 261 (100).
HRMS: m/z: calcd. for $C_{24}H_{30}O_2$: 350.2246 [M^+]; found: 350.2238.
IR: ν = 2964, 2935, 2876, 1668, 1597, 1448, 1320, 1281, 1181, 1090, 1019, 940, 909, 750, 694 cm^{-1}.

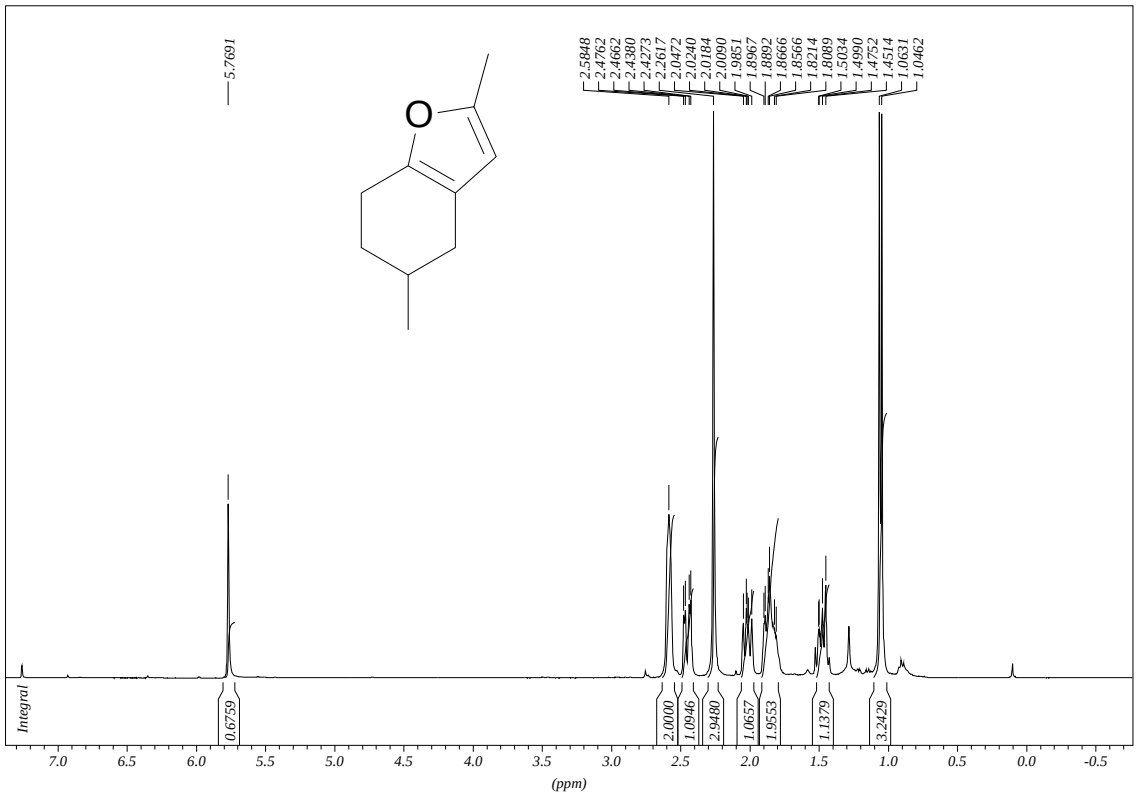
Methyl 4-((Z)-(Dihydro-5-methoxy-3,3-dimethyl-5-phenylfuran-2(3H)-ylidene)methyl)-benzoate (4ta)

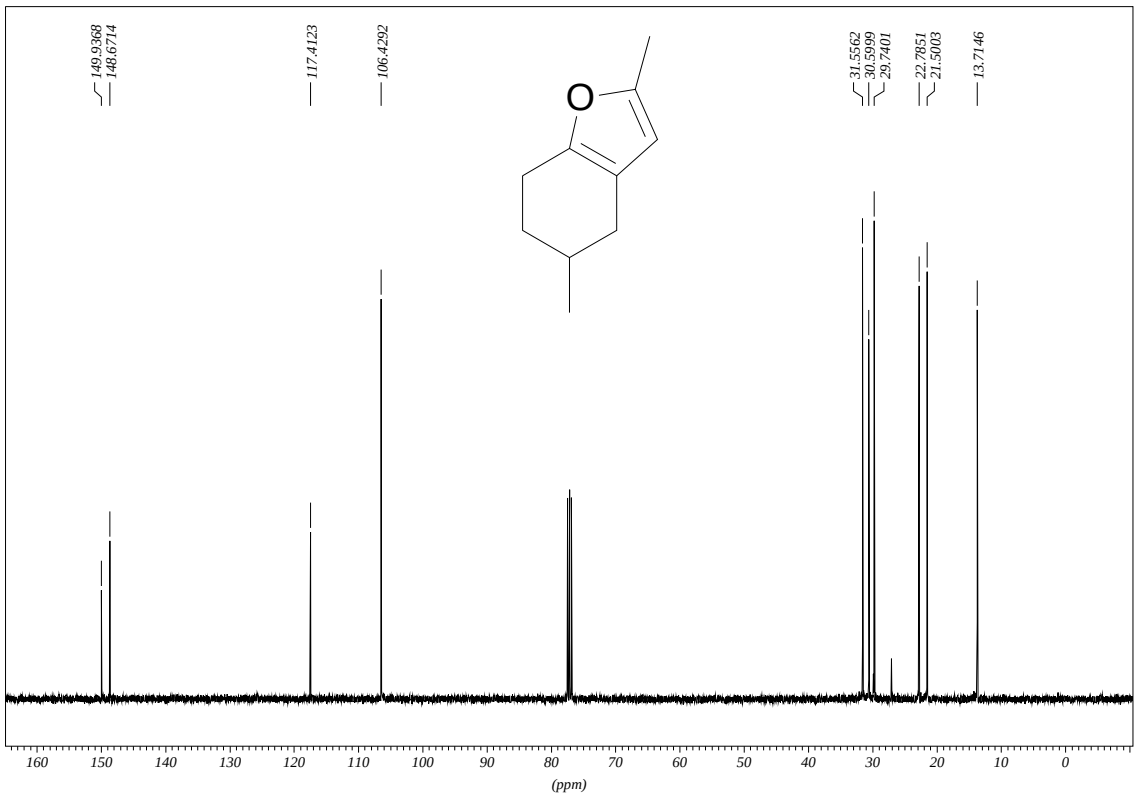


^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.98–7.96 (m, 2 H), 7.71-7.69 (m, 2 H), 7.42-7.28 (m, 5 H), 5.31 (s, 1 H), 3.88 (s, 3 H), 3.15 (s, 3 H), 2.39 (d, J = 13.1 Hz, 1 H), 2.03 (d, J = 13.1 Hz, 1 H), 1.49 (s, 3 H), 1.26 (s, 3 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.5, 167.4, 142.0, 140.2, 129.9, 128.7, 128.5, 127.3, 126.1, 126.3, 111.5, 96.9, 52.8, 52.0, 43.1, 30.2, 29.8.
MS (EI): m/z (%): 352 (50) [M^+], 305 (100), 175 (70), 105 (40).
HRMS: m/z: calcd. for $C_{22}H_{24}O_4$: 352.1669 [M^+]; found: 352.1665.
IR: ν = 2962, 2869, 2280, 1716, 1669, 1601, 1448, 1352, 1312, 1286, 1222, 1177, 1038, 985, 764, 701 cm^{-1}.

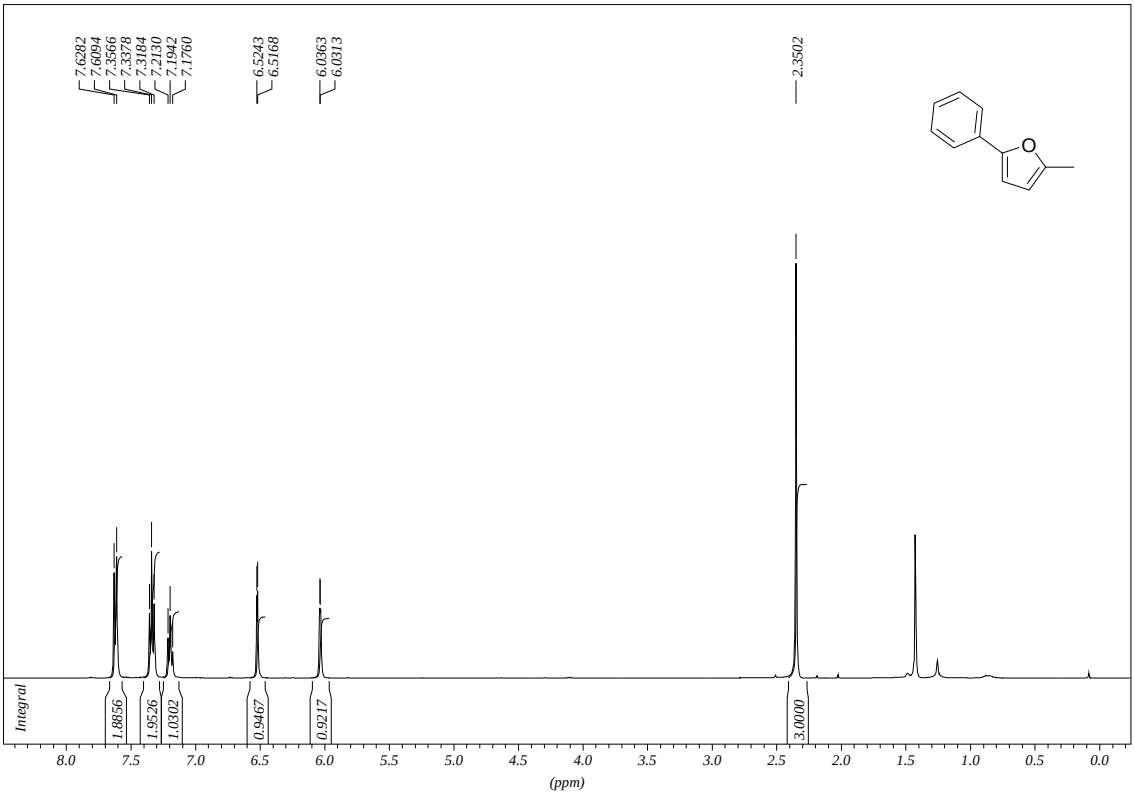
4,5,6,7-Tetrahydro-2,5-dimethylbenzofuran (2a)

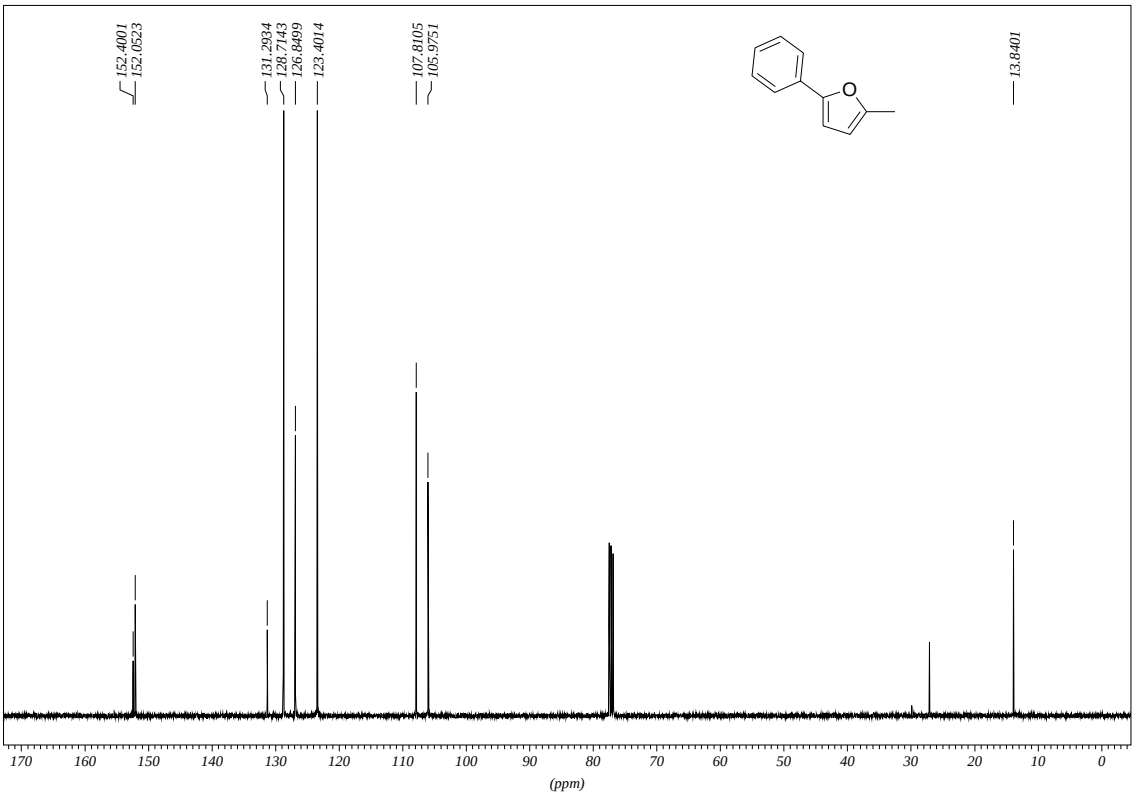
2a



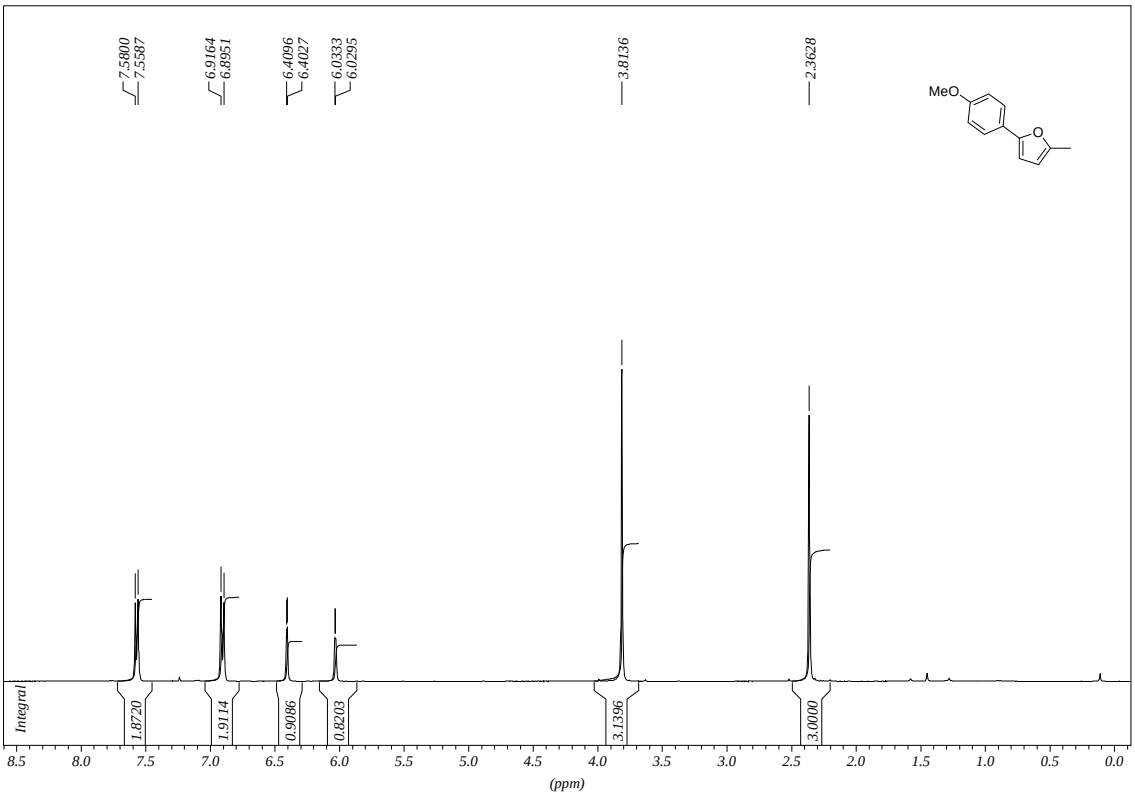


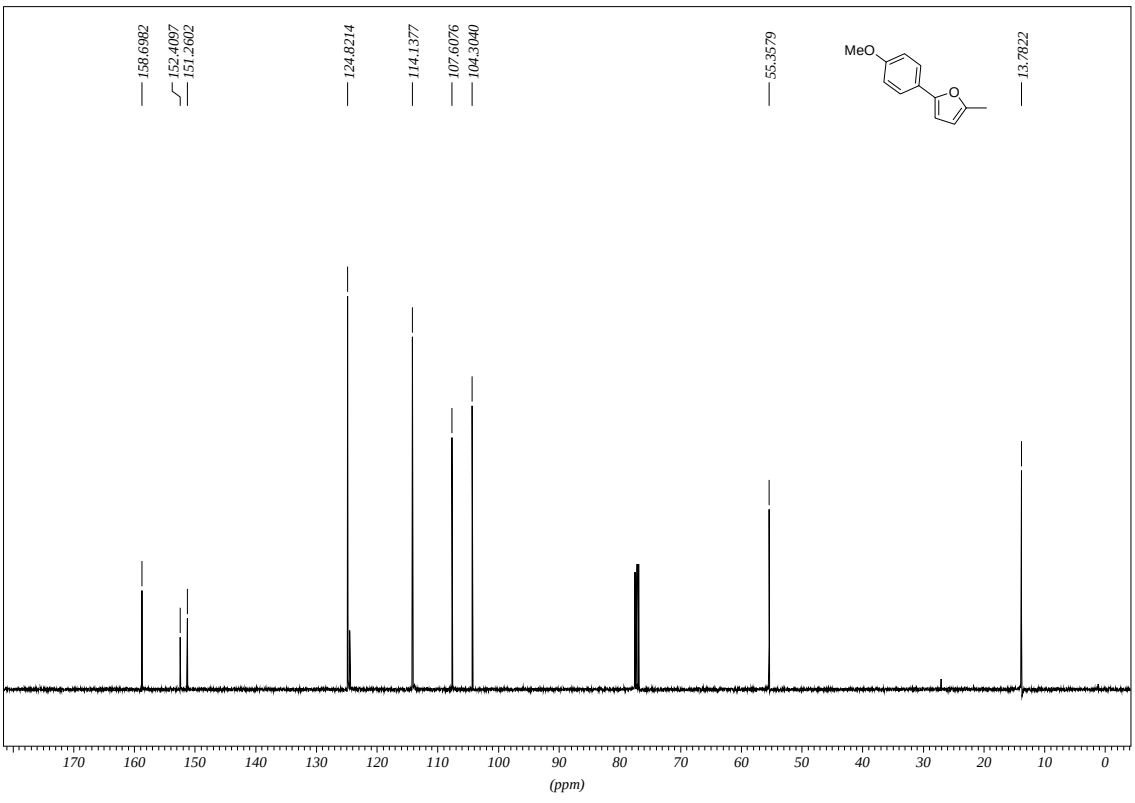
2-Methyl-5-phenylfuran (2b)



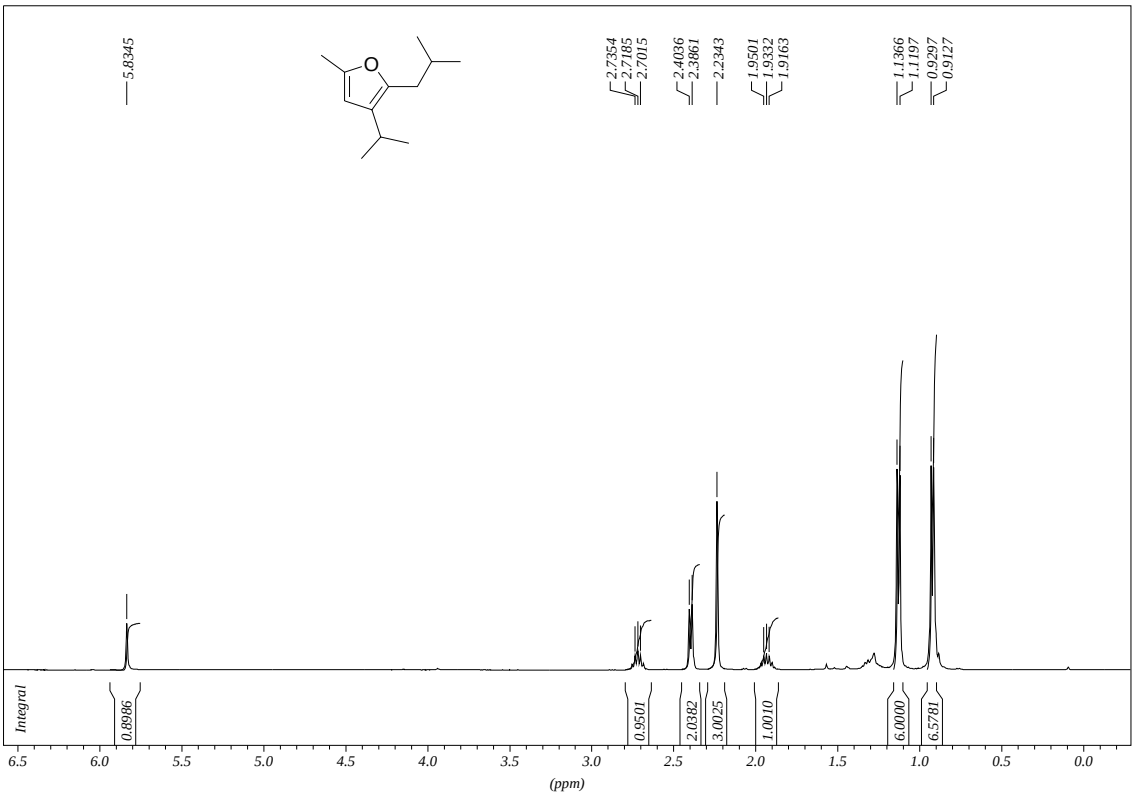


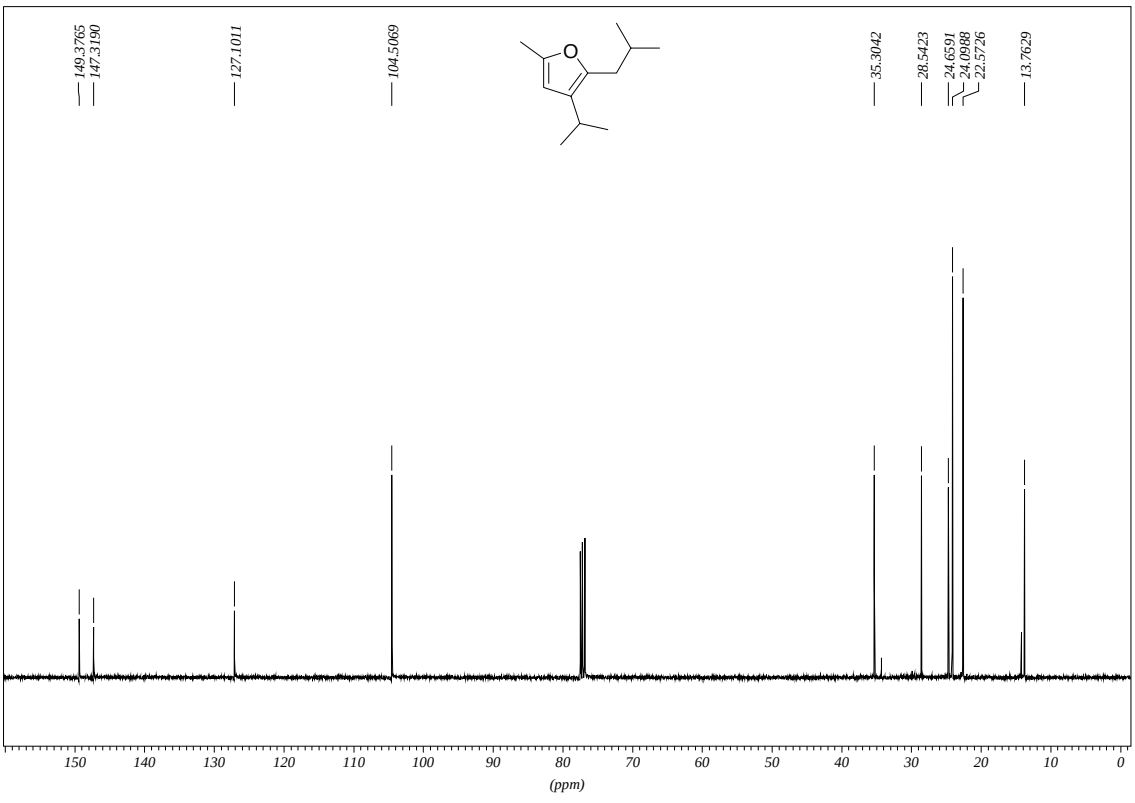
2-(4-Methoxyphenyl)-5-methylfuran (2c)



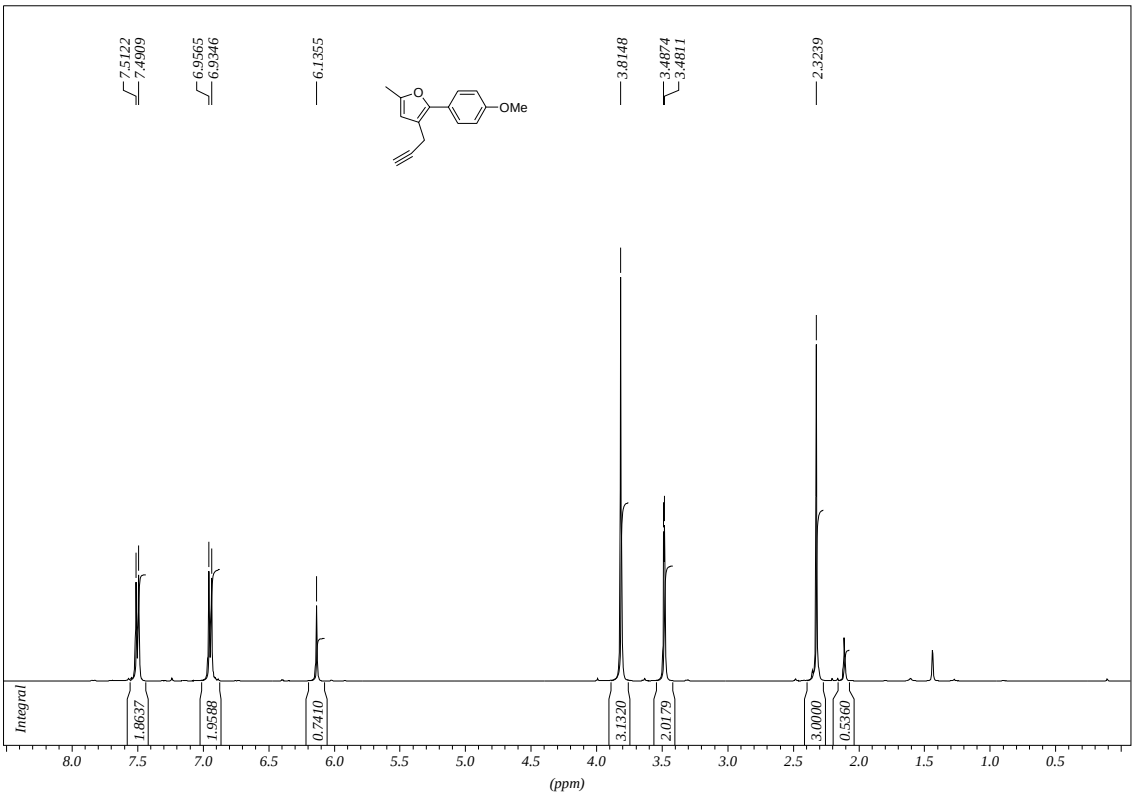


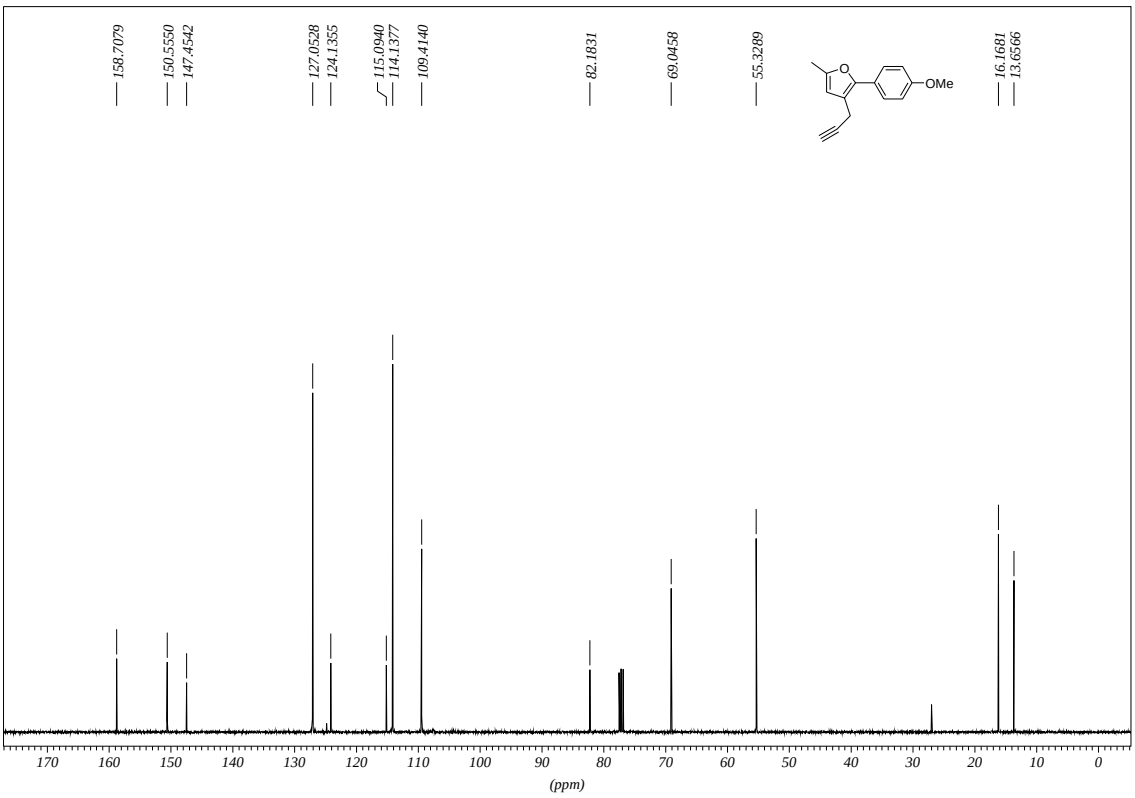
2-Isobutyl-3-isopropyl-5-methylfuran (2d)



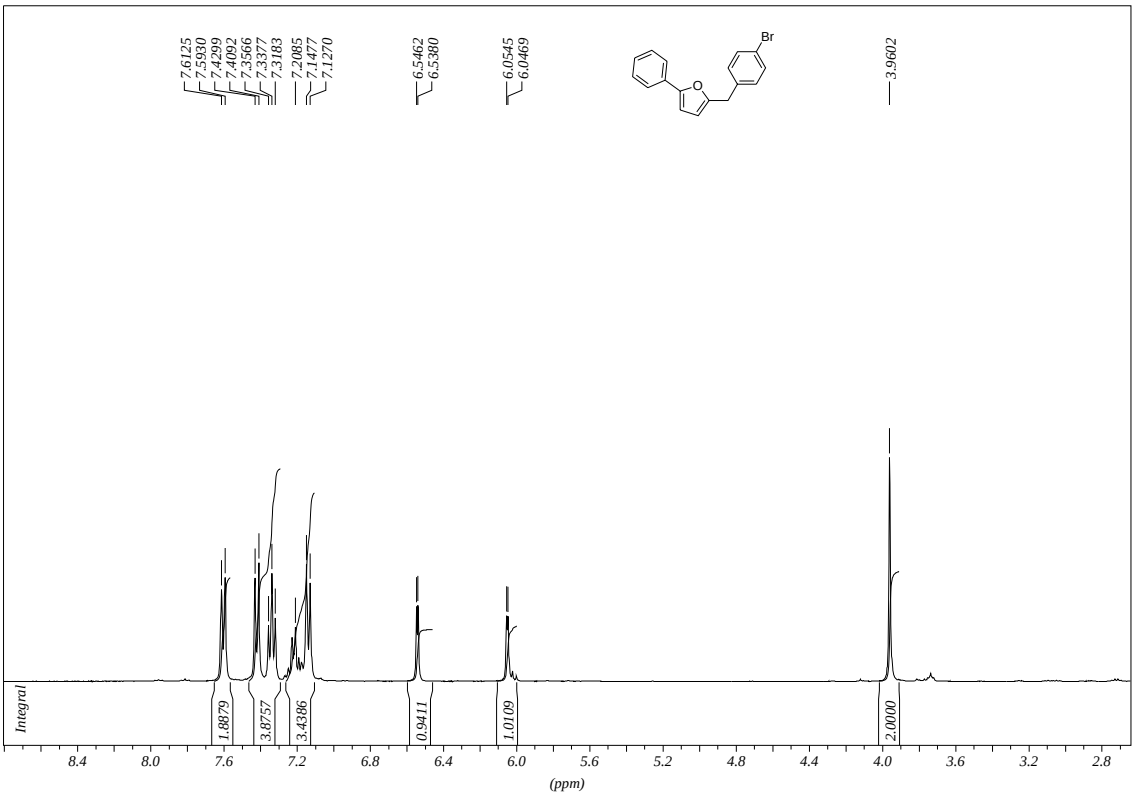


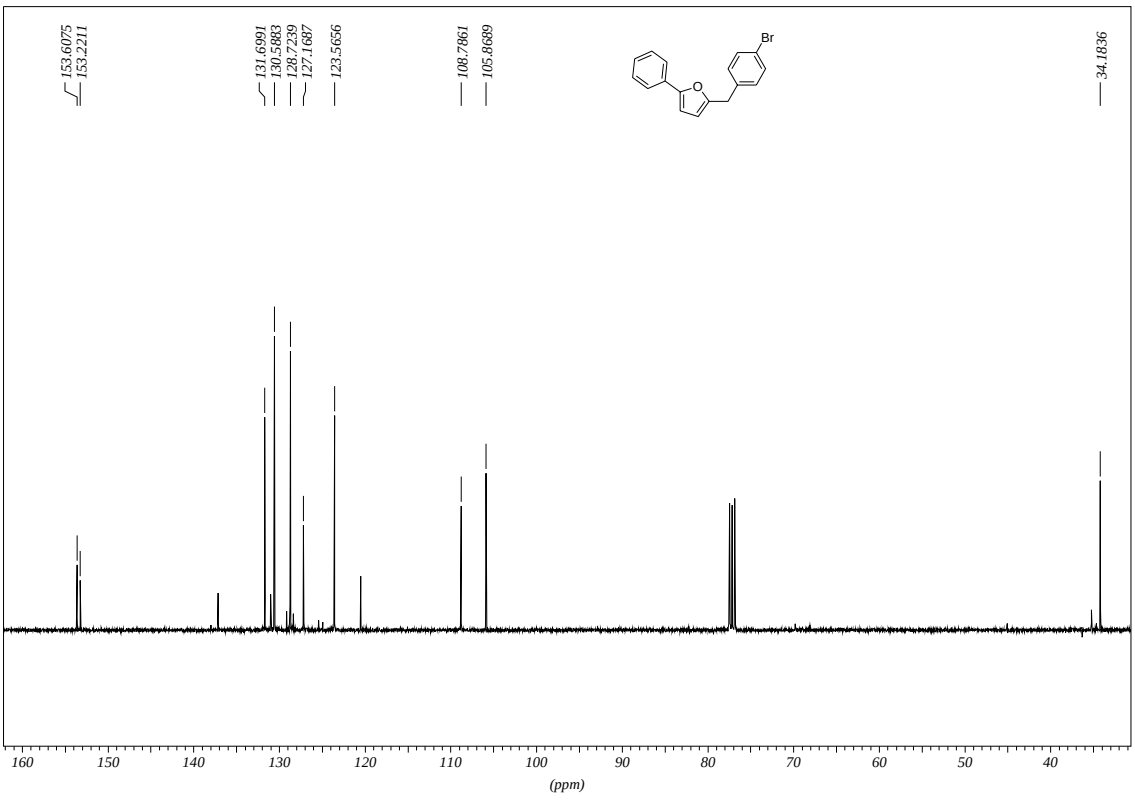
2-(4-Methoxyphenyl)-5-methyl-3-(prop-2-ynyl)furan (2e)



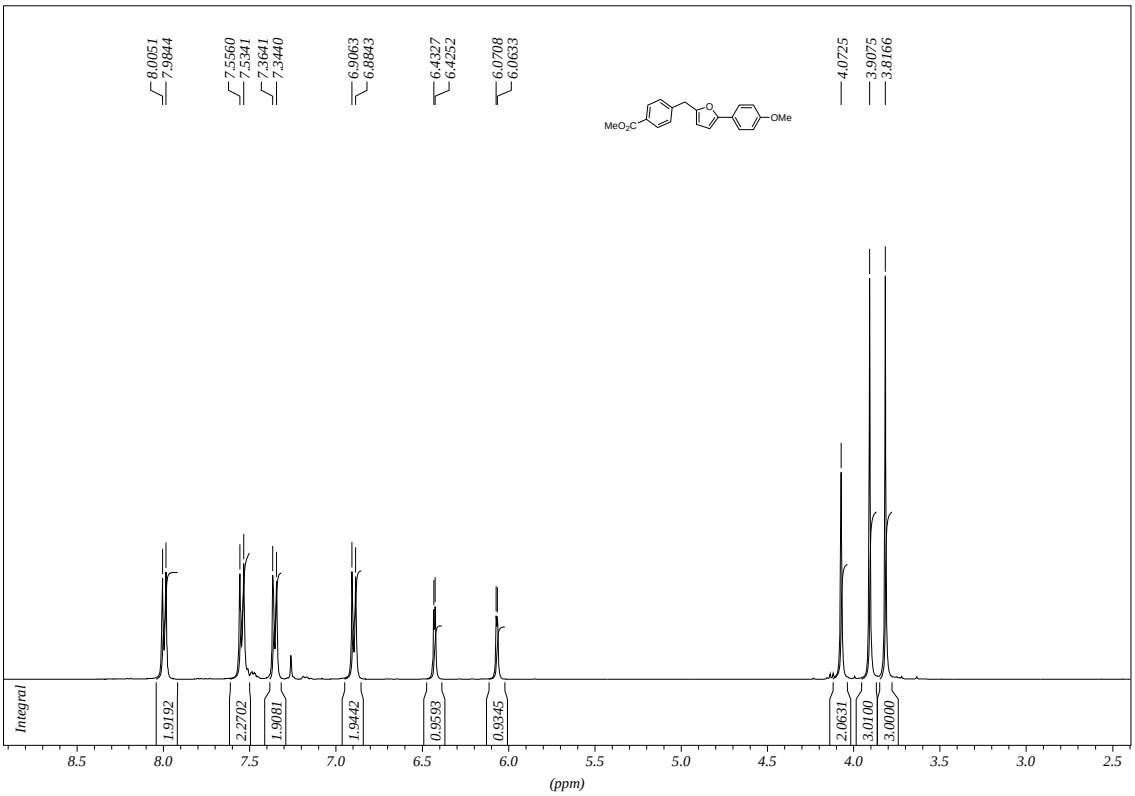


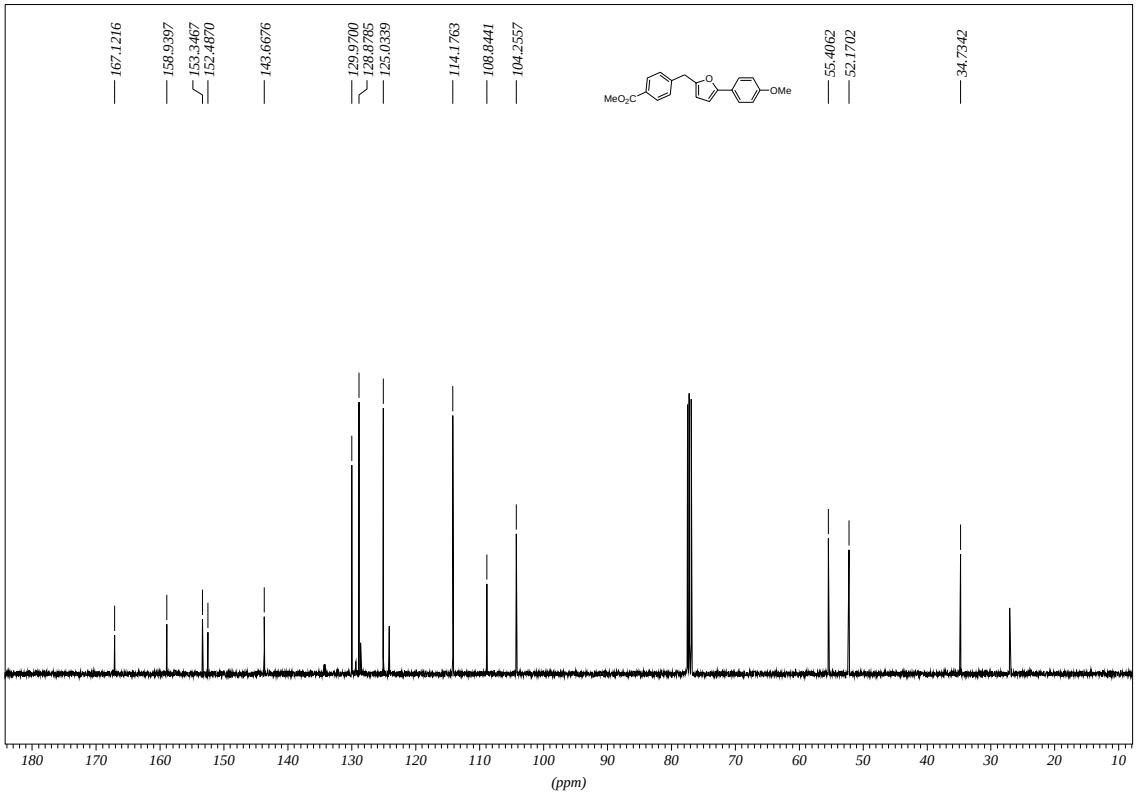
2-(4-Bromobenzyl)-5-phenylfuran (2f)



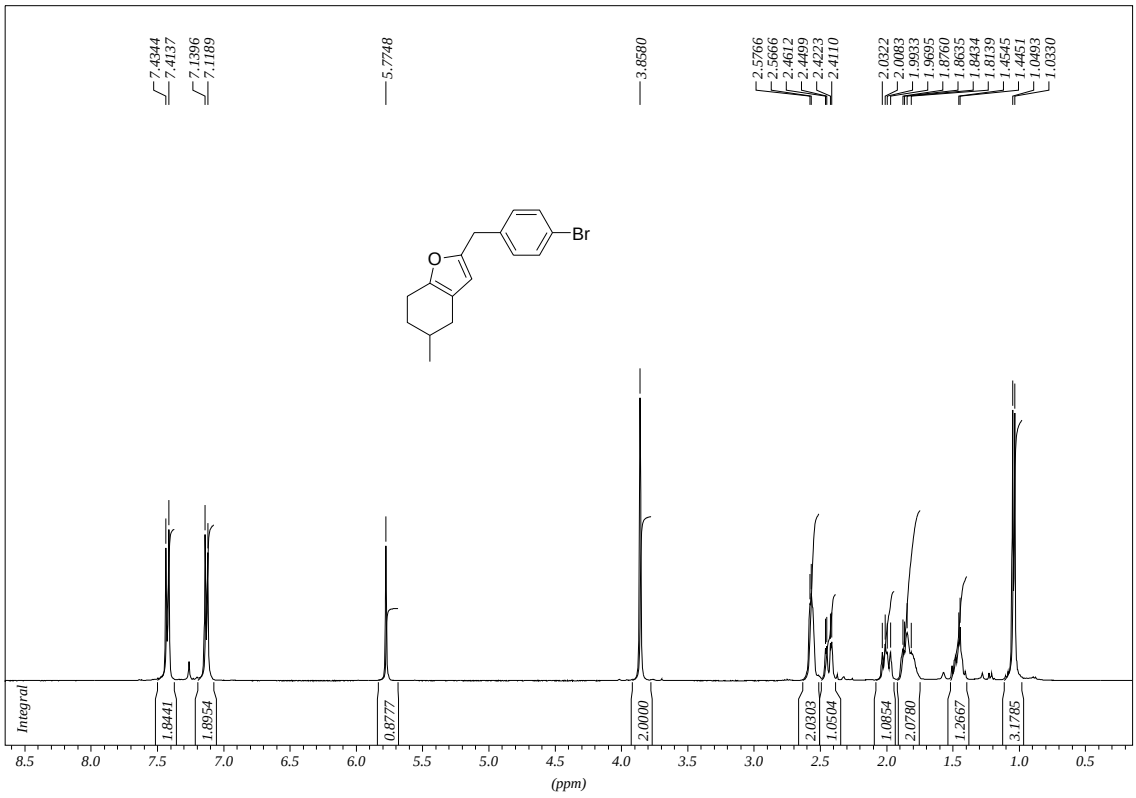


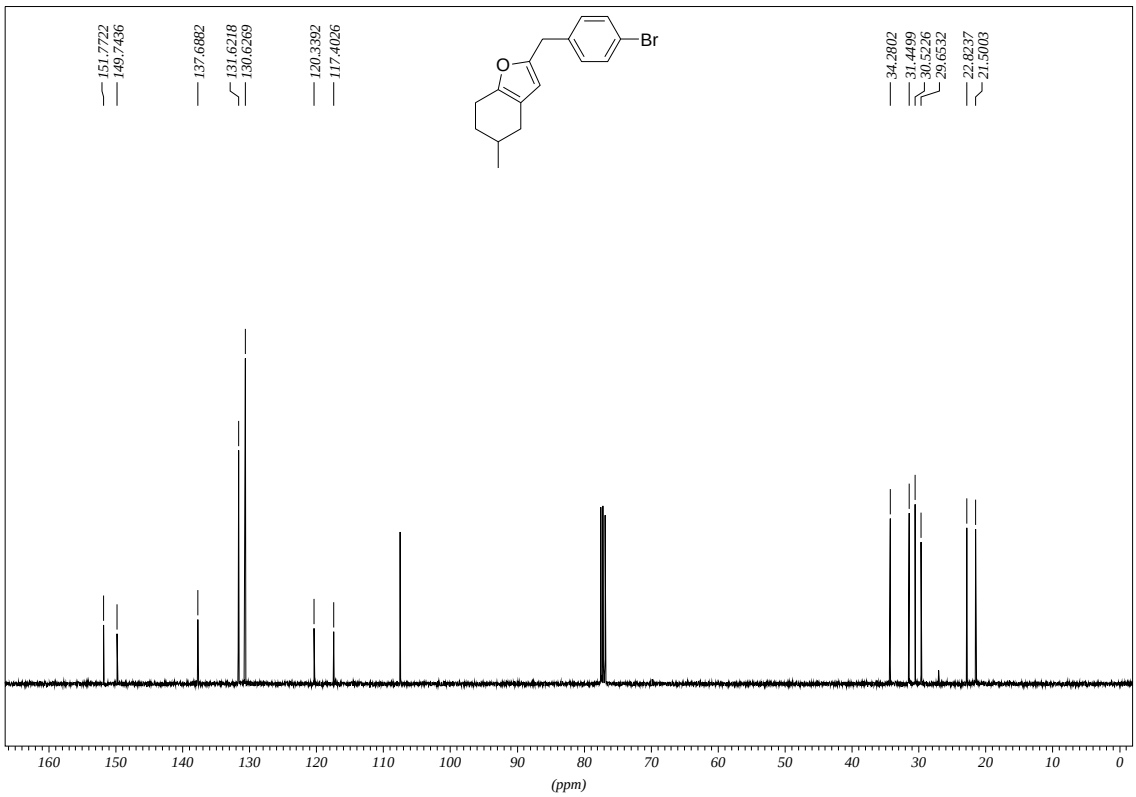
Methyl 4-((5-(4-methoxyphenyl)furan-2-yl)methyl)benzoate (2g)



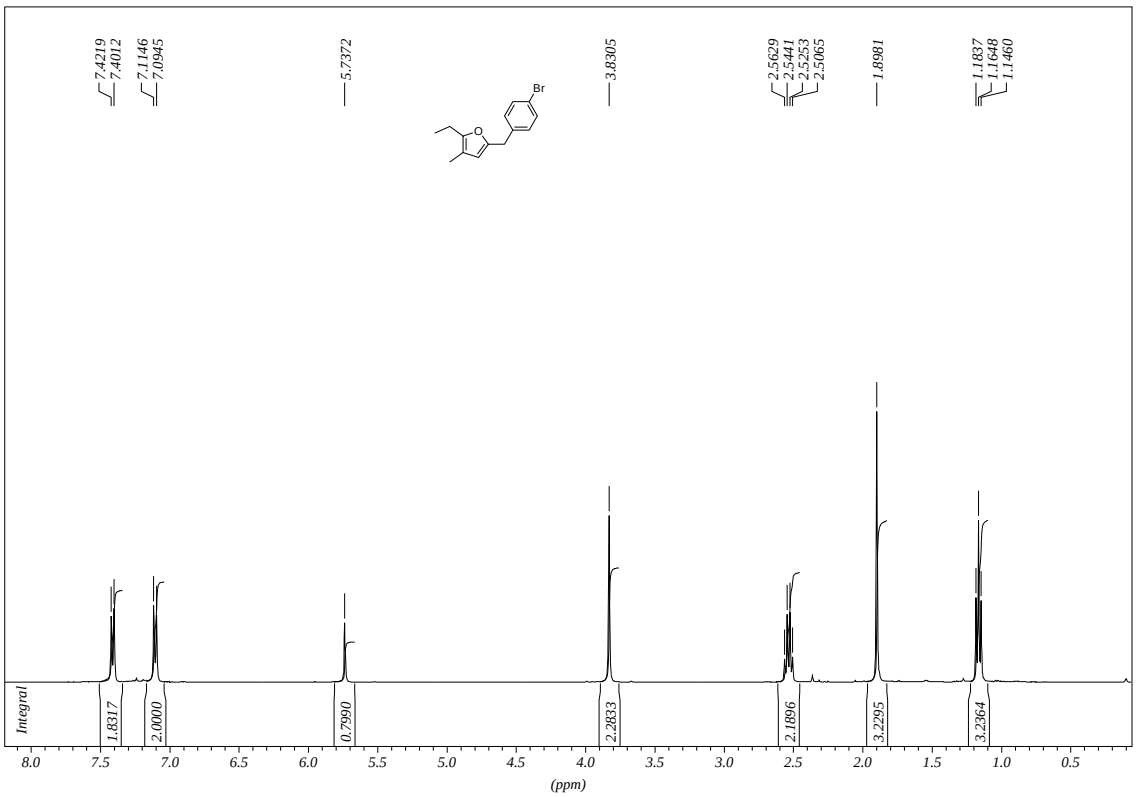


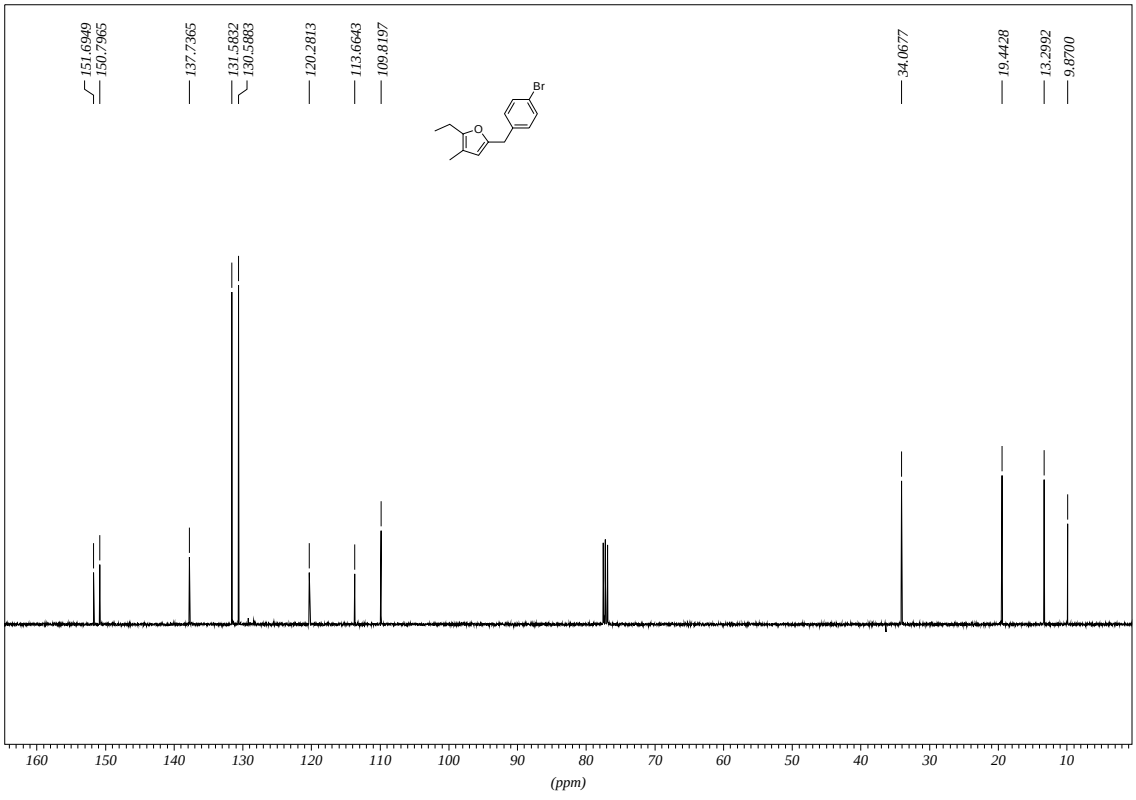
2-(4-Bromobenzyl)-4,5,6,7-tetrahydro-5-methylbenzofuran (2h)



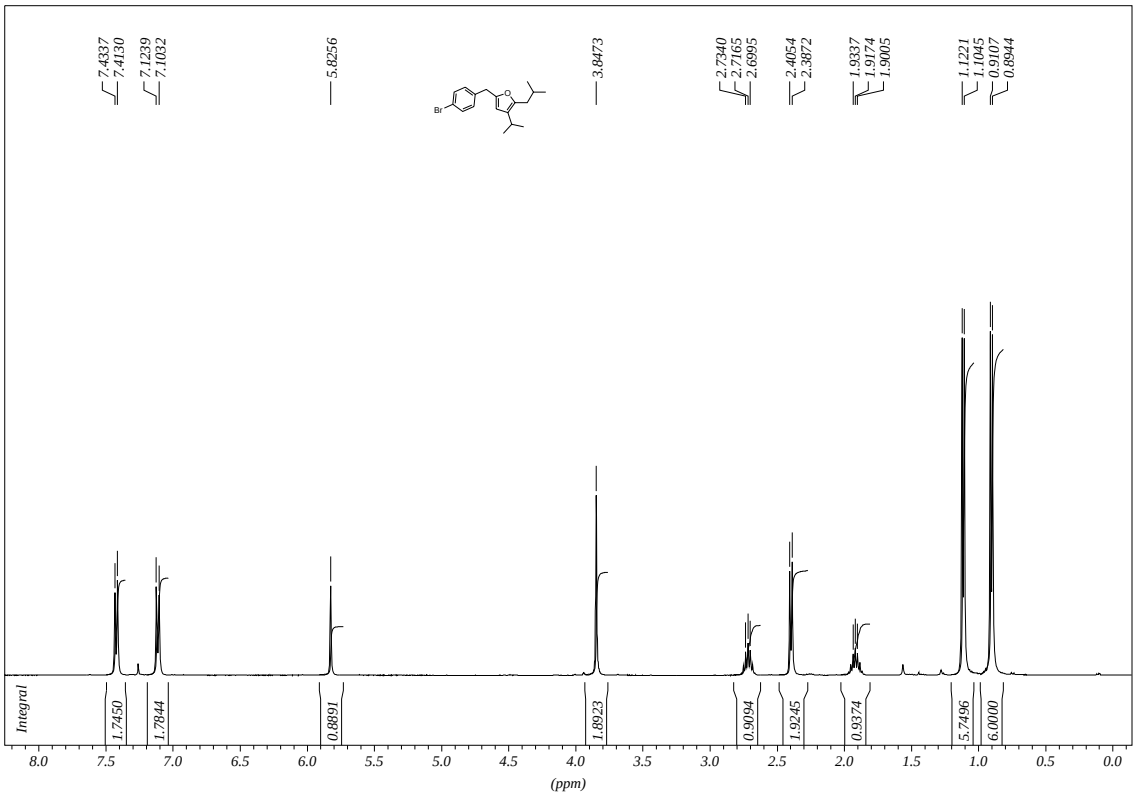


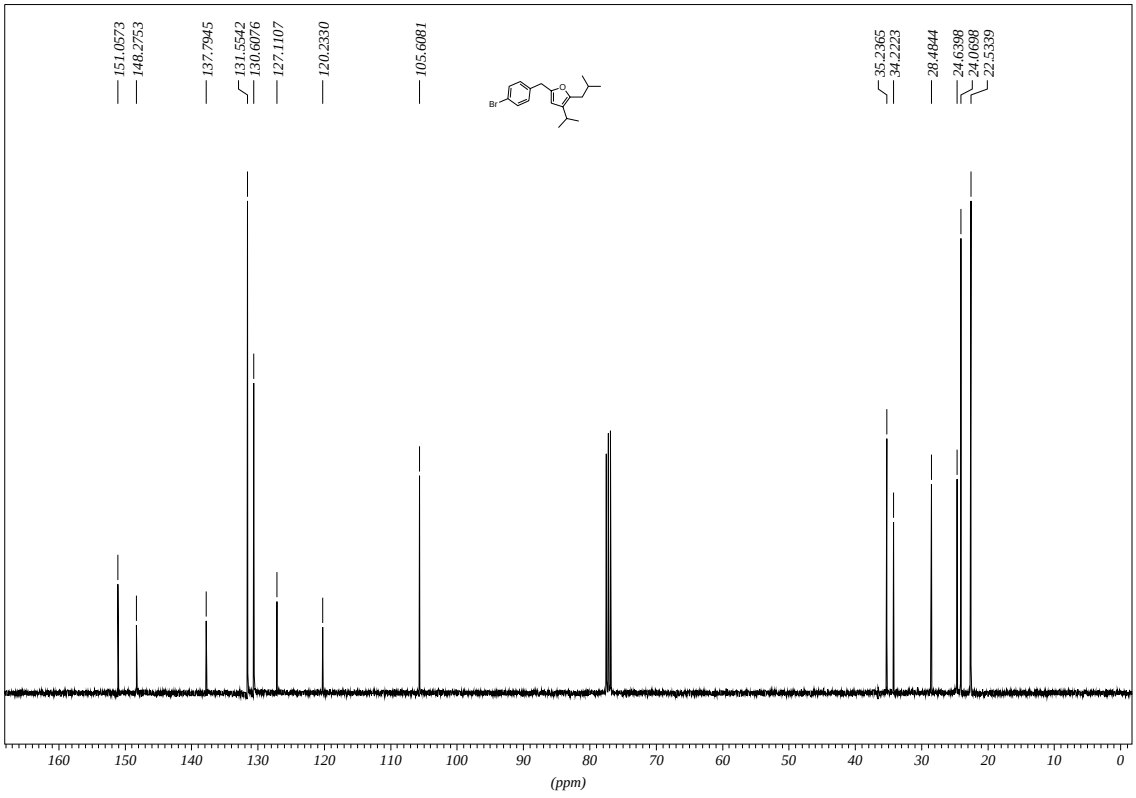
5-(4-Bromobenzyl)-2-ethyl-3-methylfuran (2i)



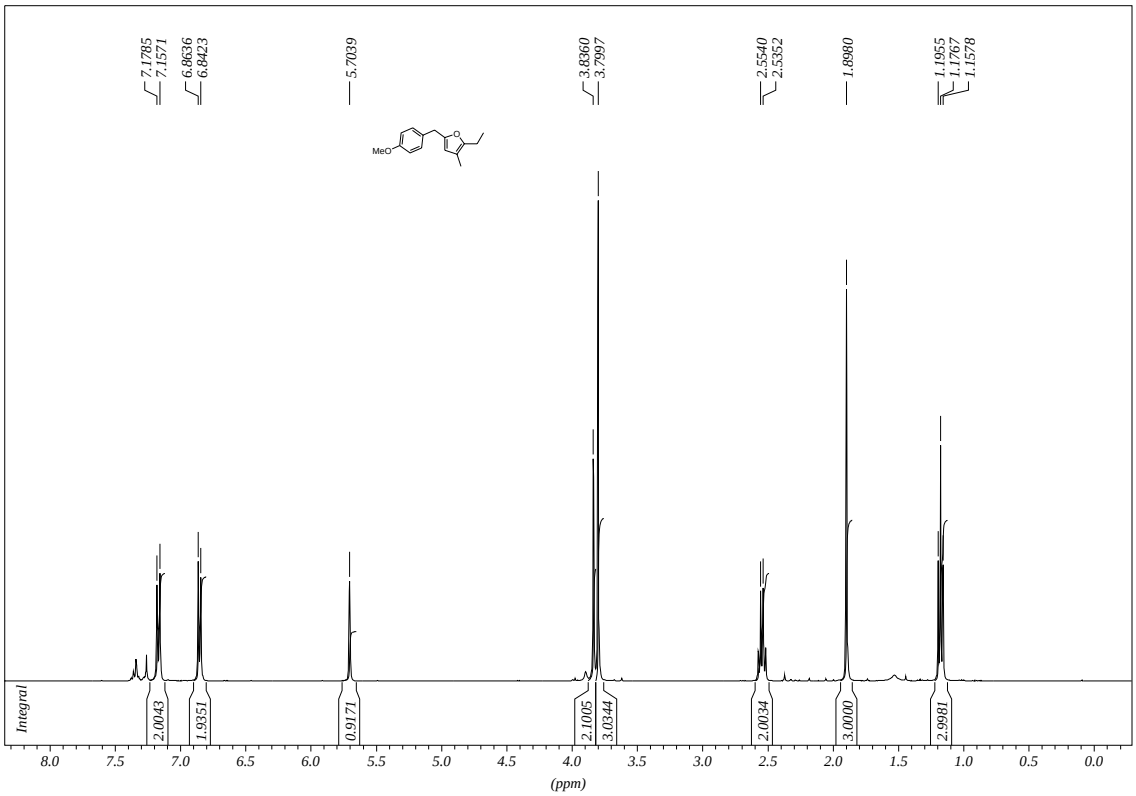


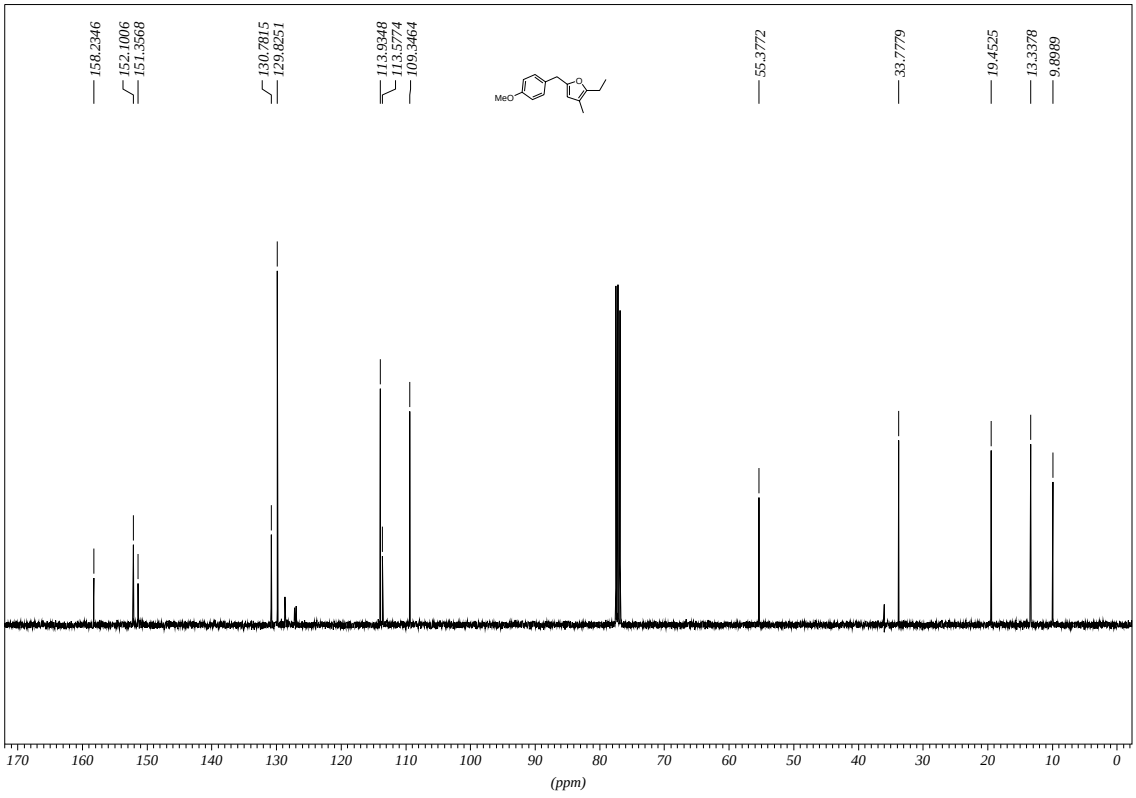
5-(4-Bromobenzyl)-2-isobutyl-3-isopropylfuran (2j)



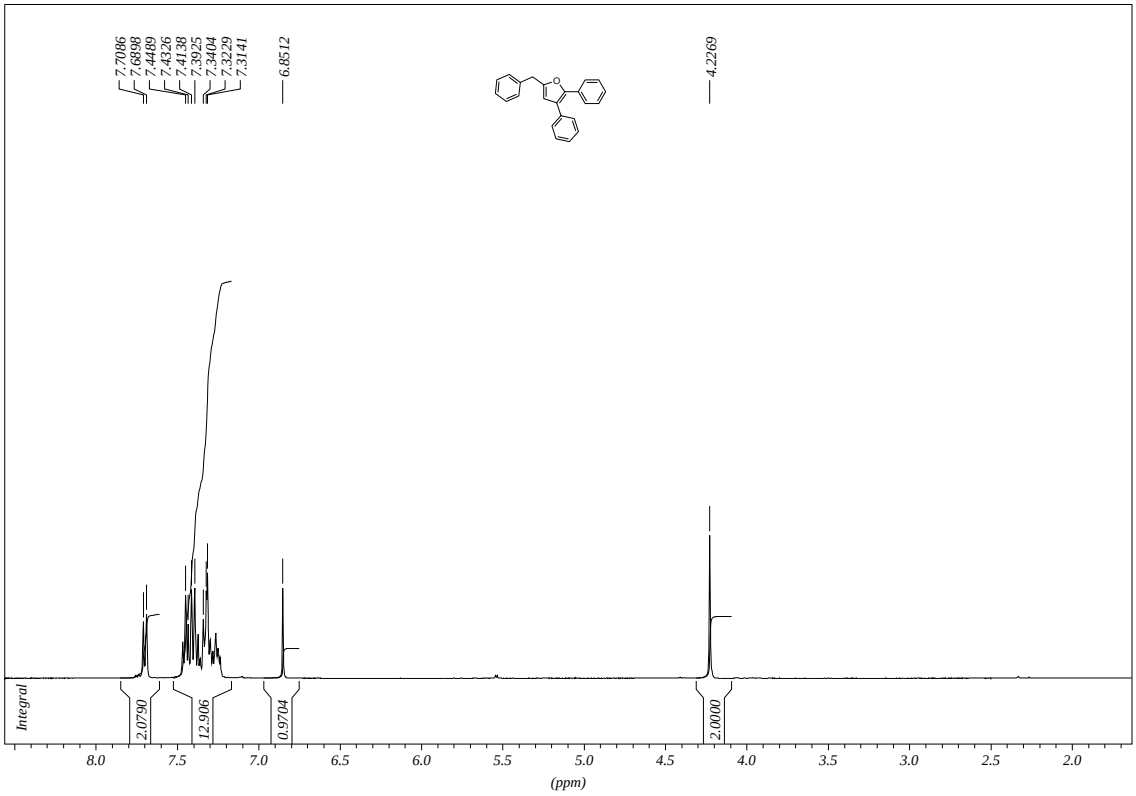


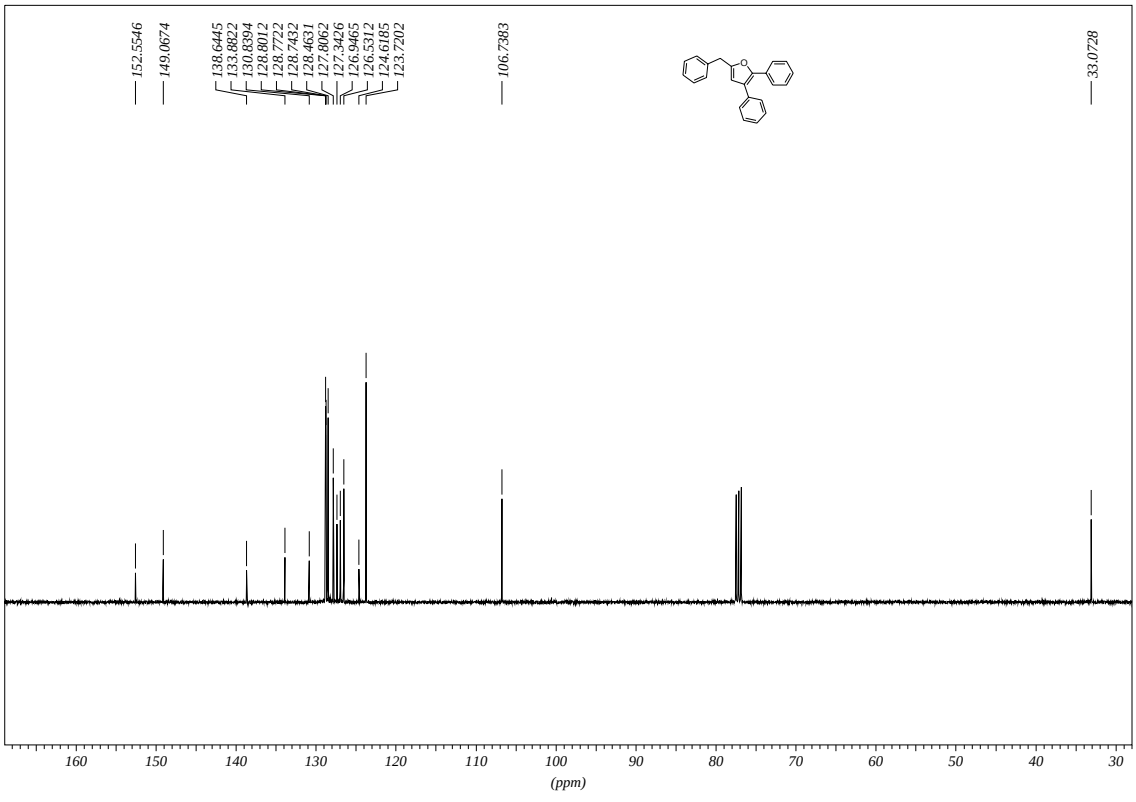
5-(4-Methoxybenzyl)-2-ethyl-3-methylfuran (2k)



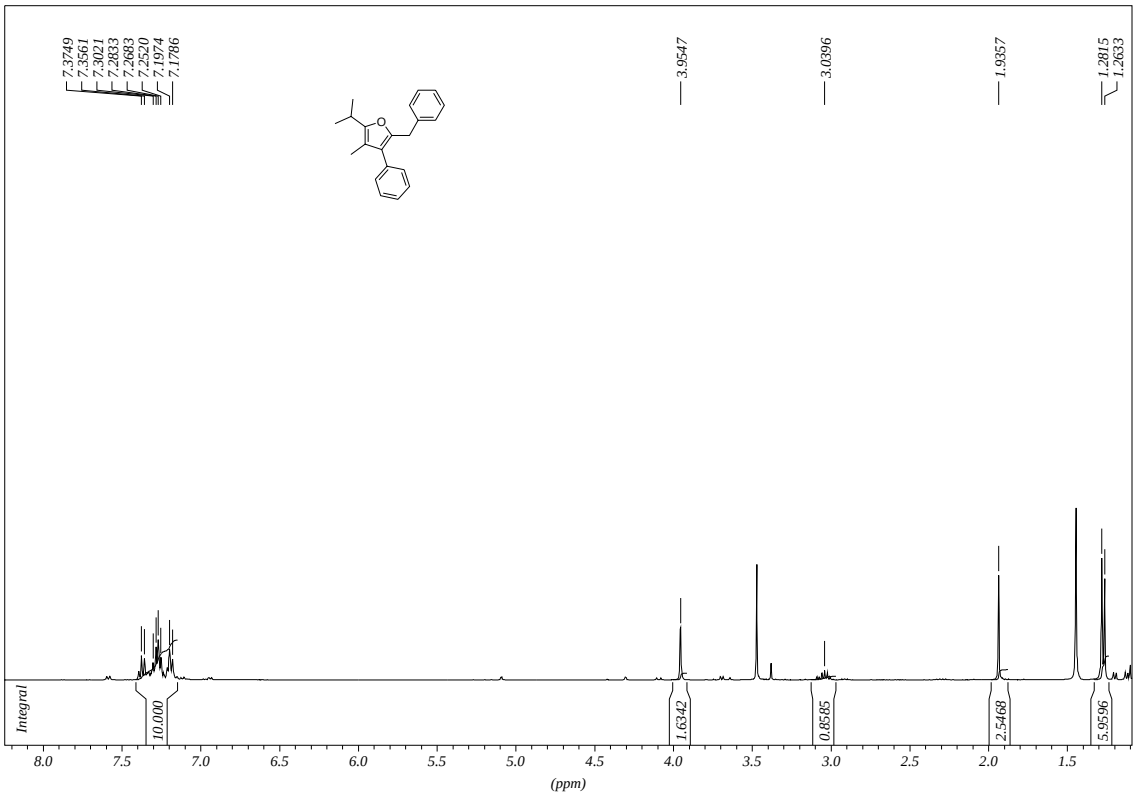


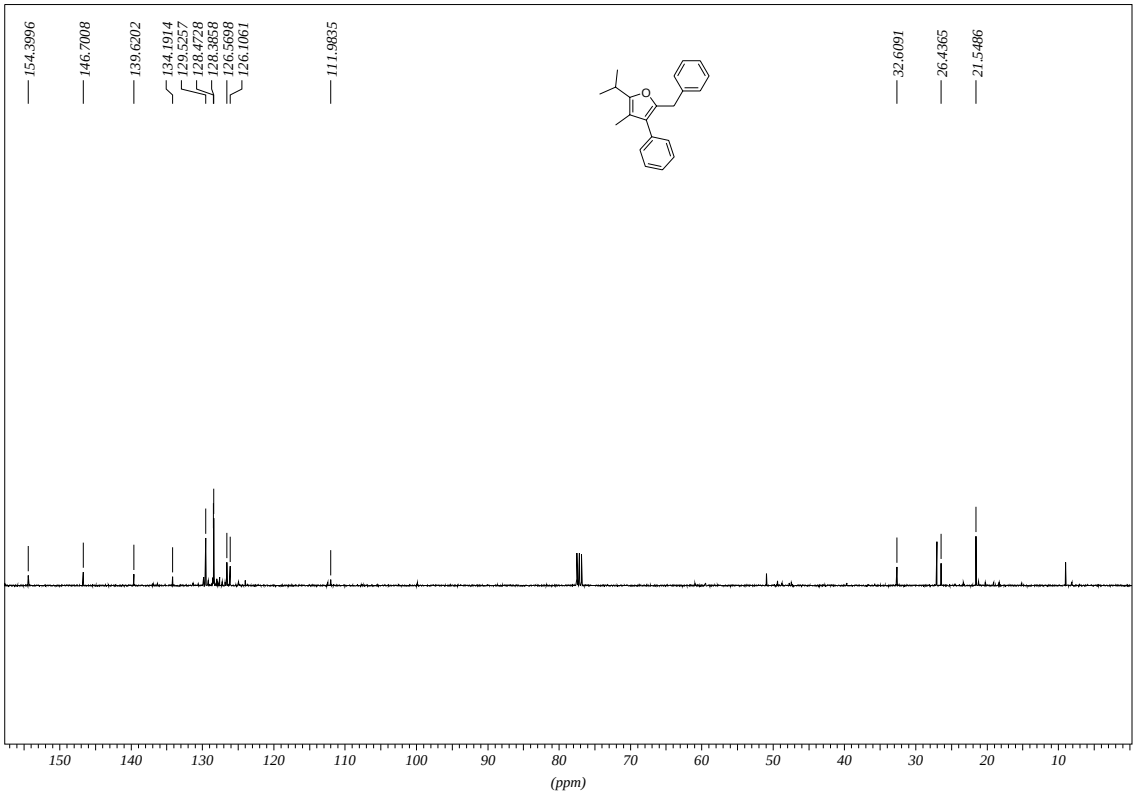
5-Benzyl-2,3-diphenylfuran (2l)



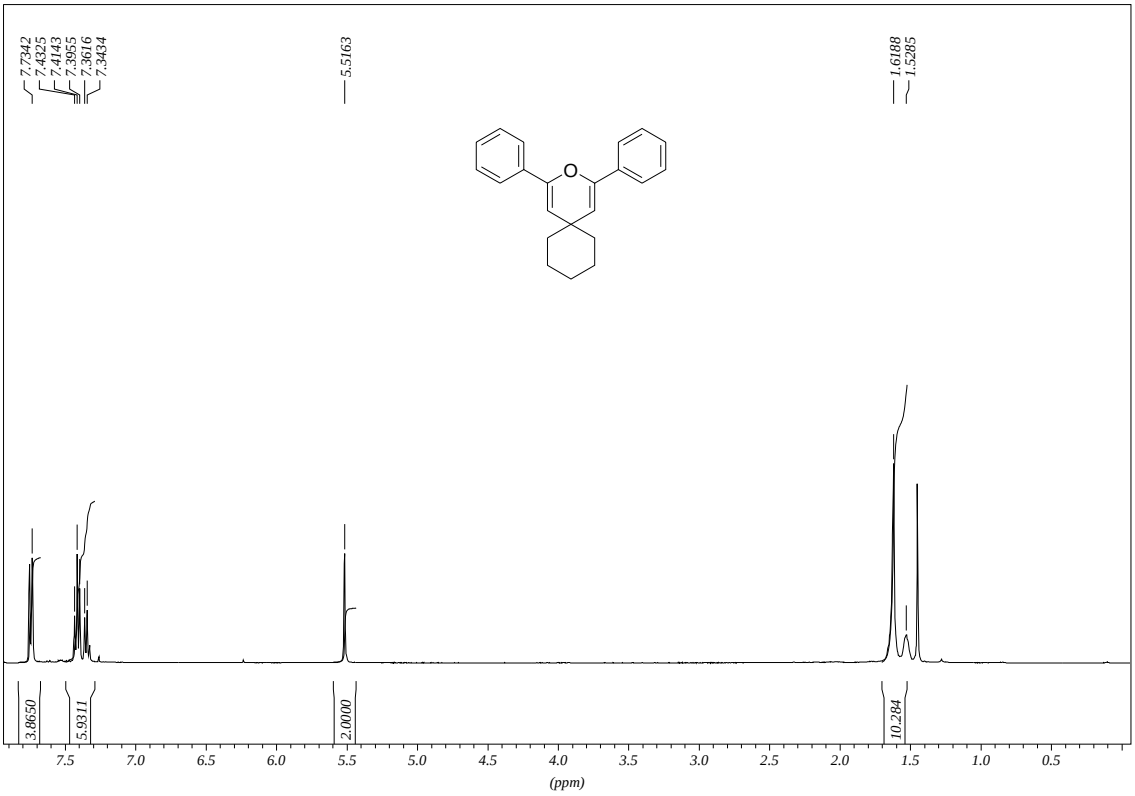


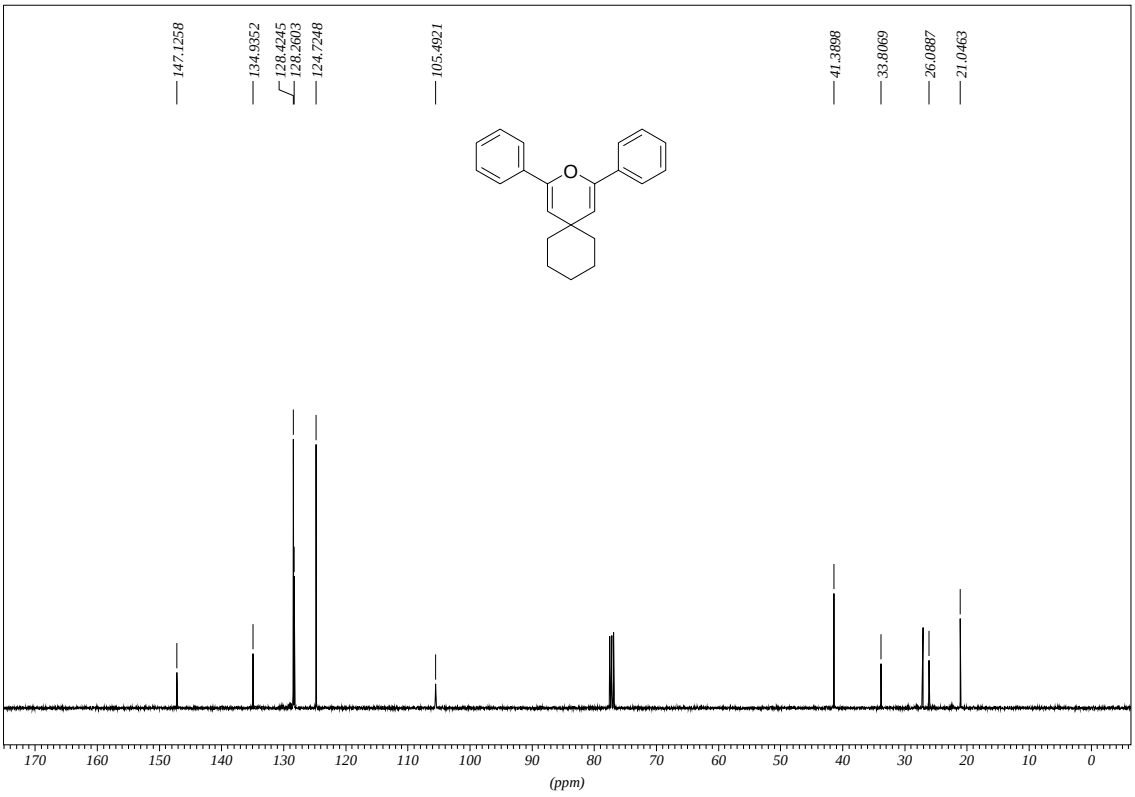
2-Benzyl-5-isopropyl-4-methyl-3-phenylfuran (2m)



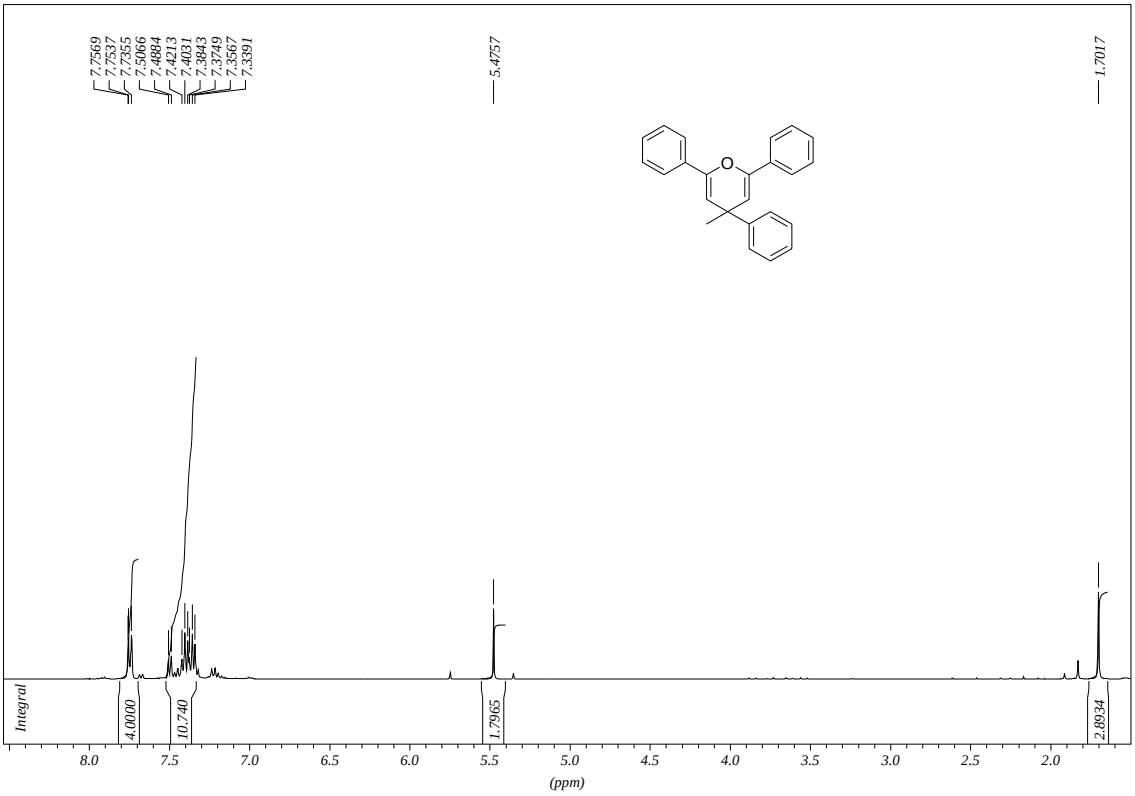


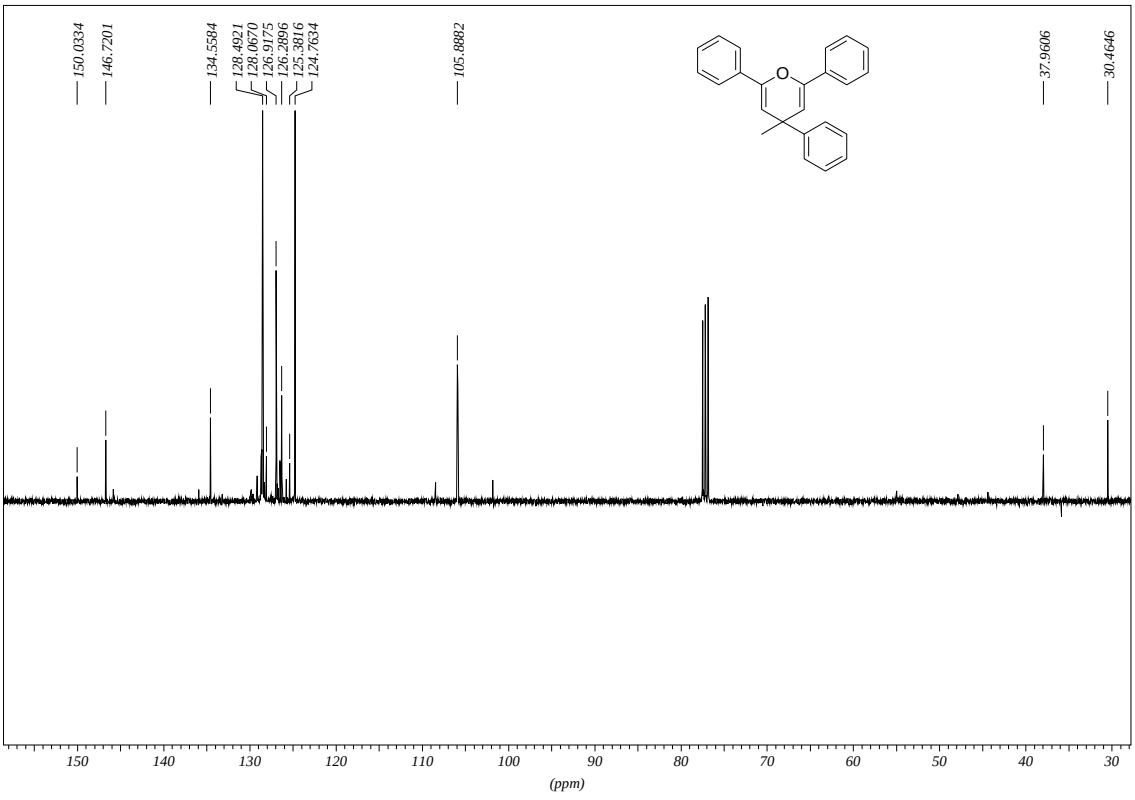
2,4-Diphenyl-3-oxaspiro[5.5]undec-1,4-dien (3n)



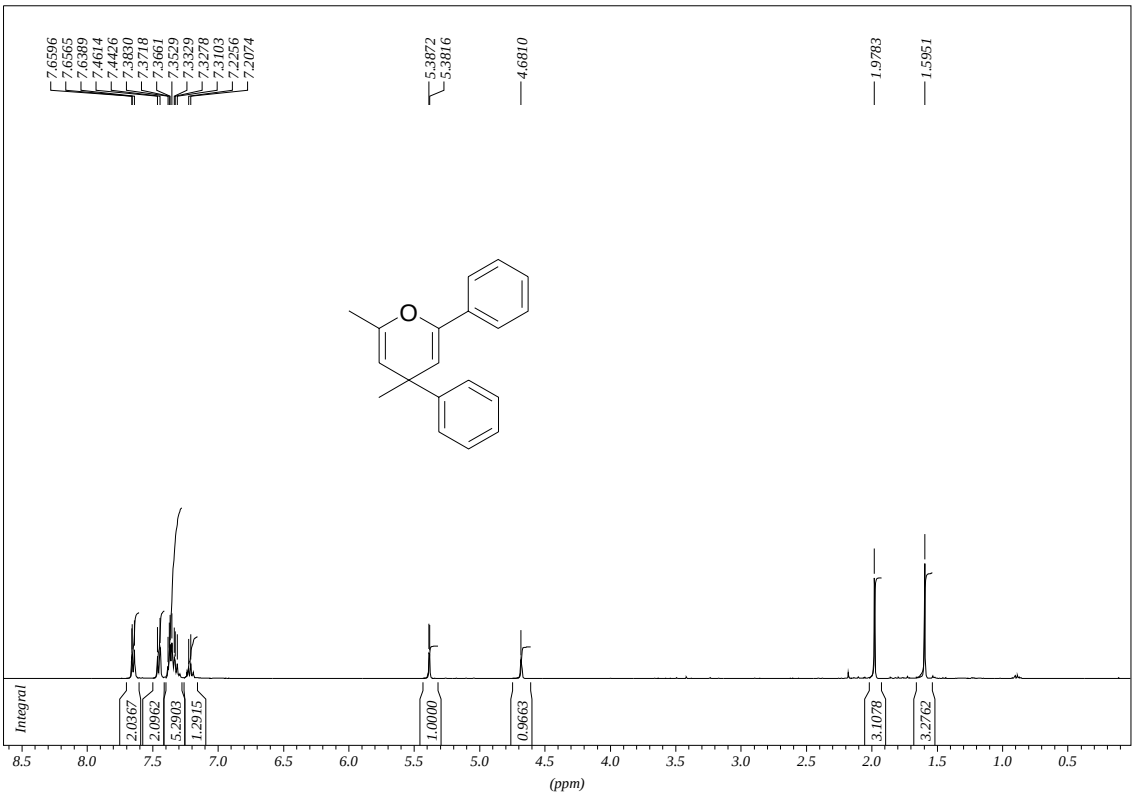


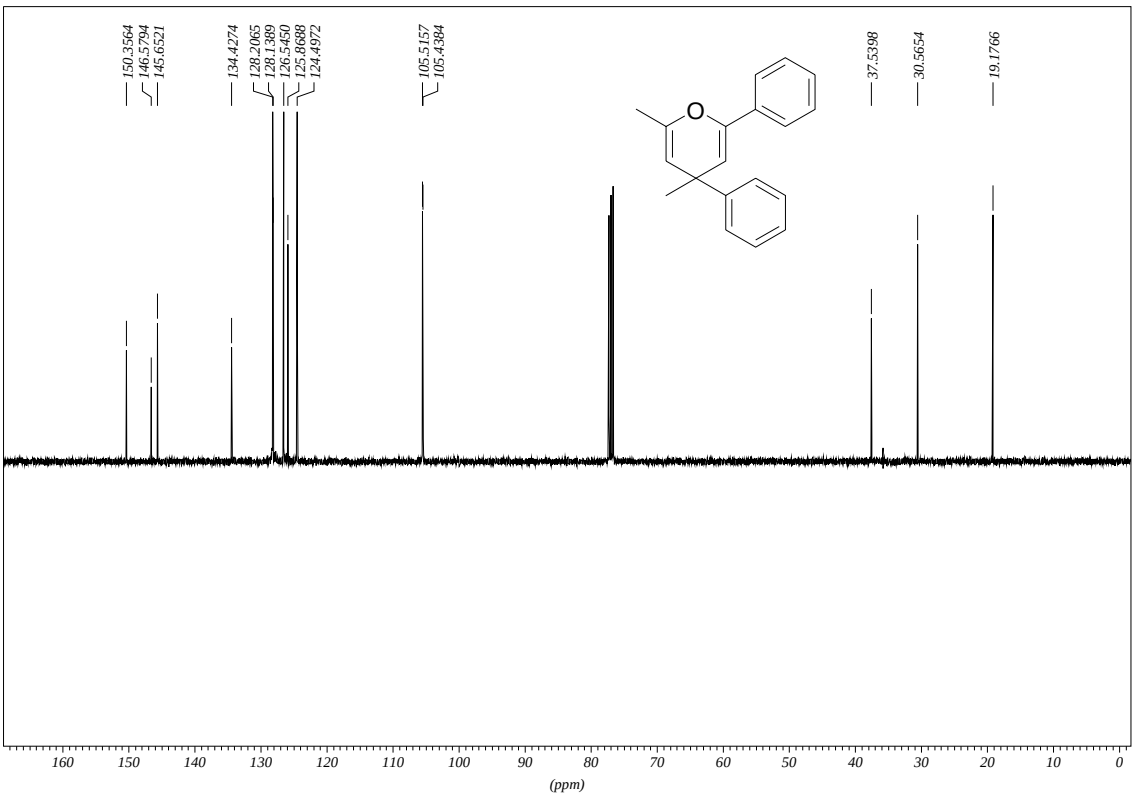
4-Methyl-2,4,6-triphenyl-4*H*-pyran (3o)



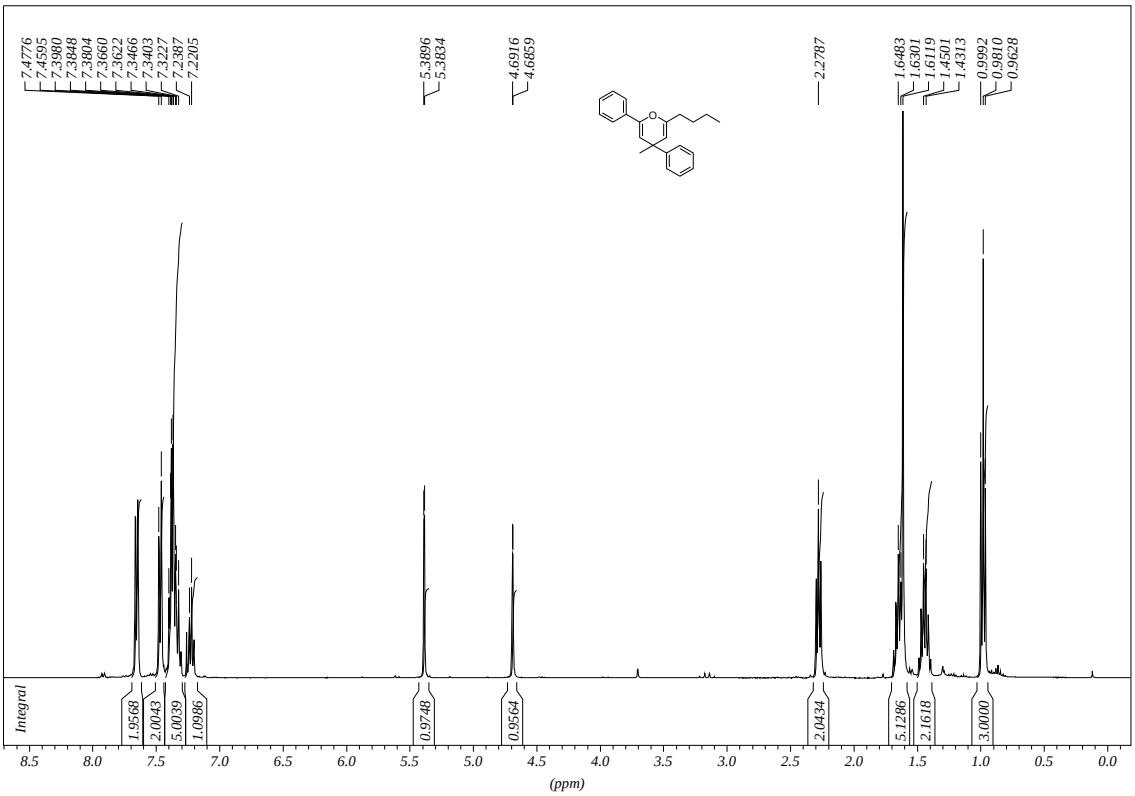


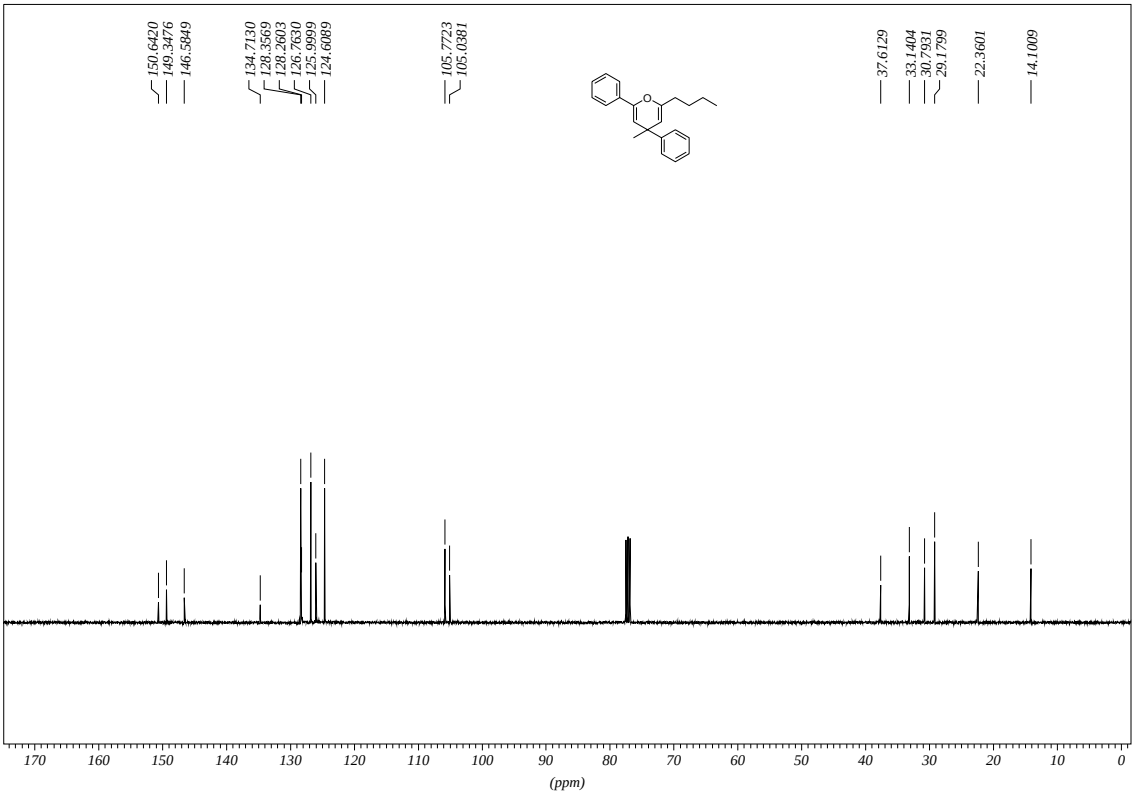
2,4-Dimethyl-4,6-diphenyl-4*H*-pyran (3p)



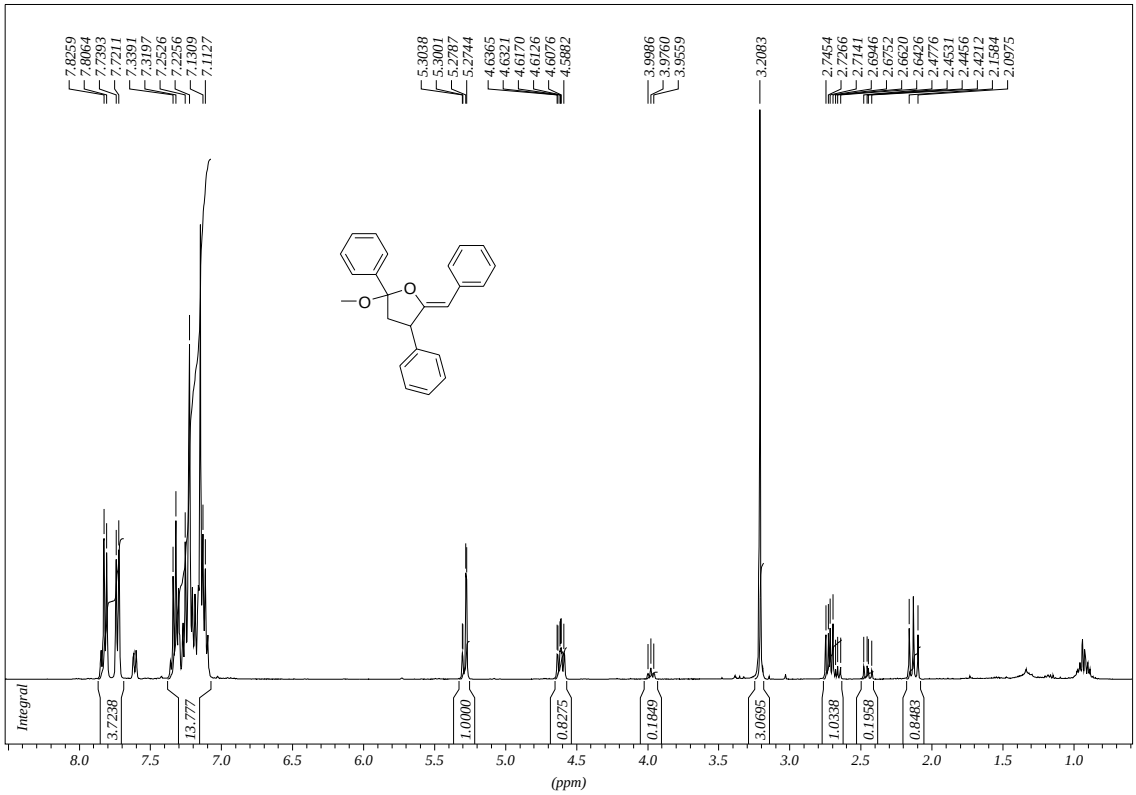


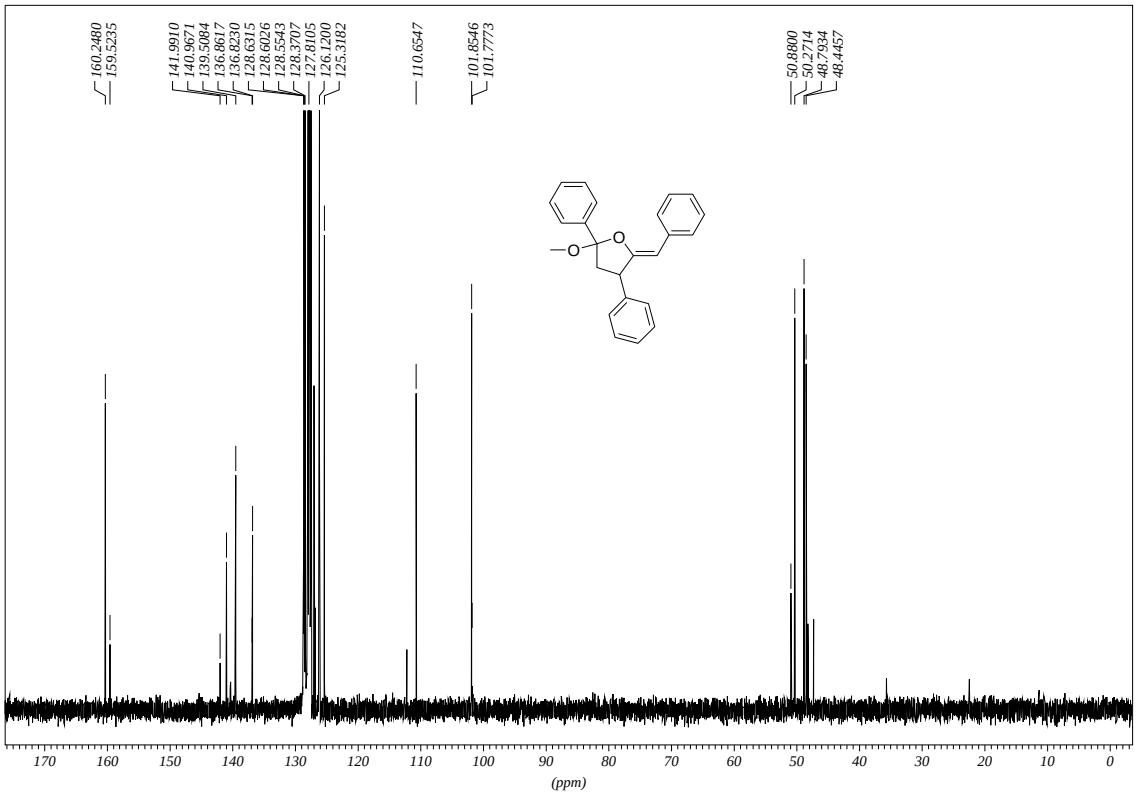
2-Butyl-4-methyl-4,6-diphenyl-4*H*-pyran (3q)



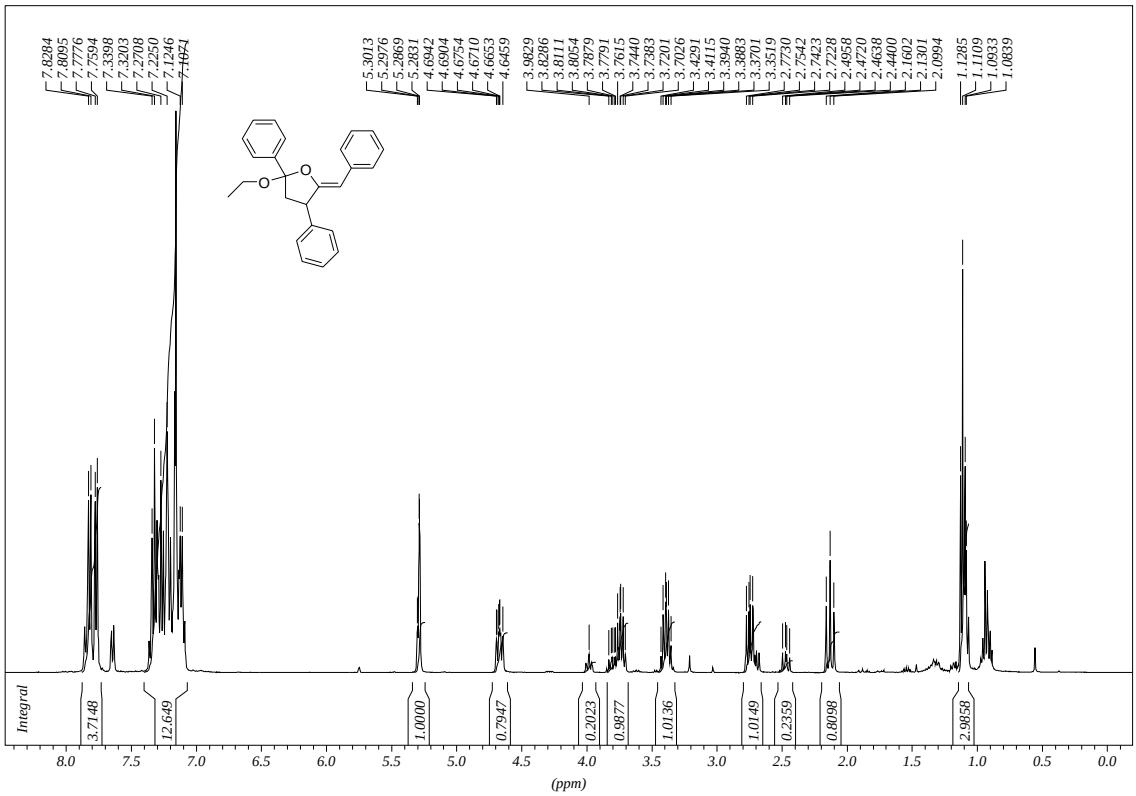


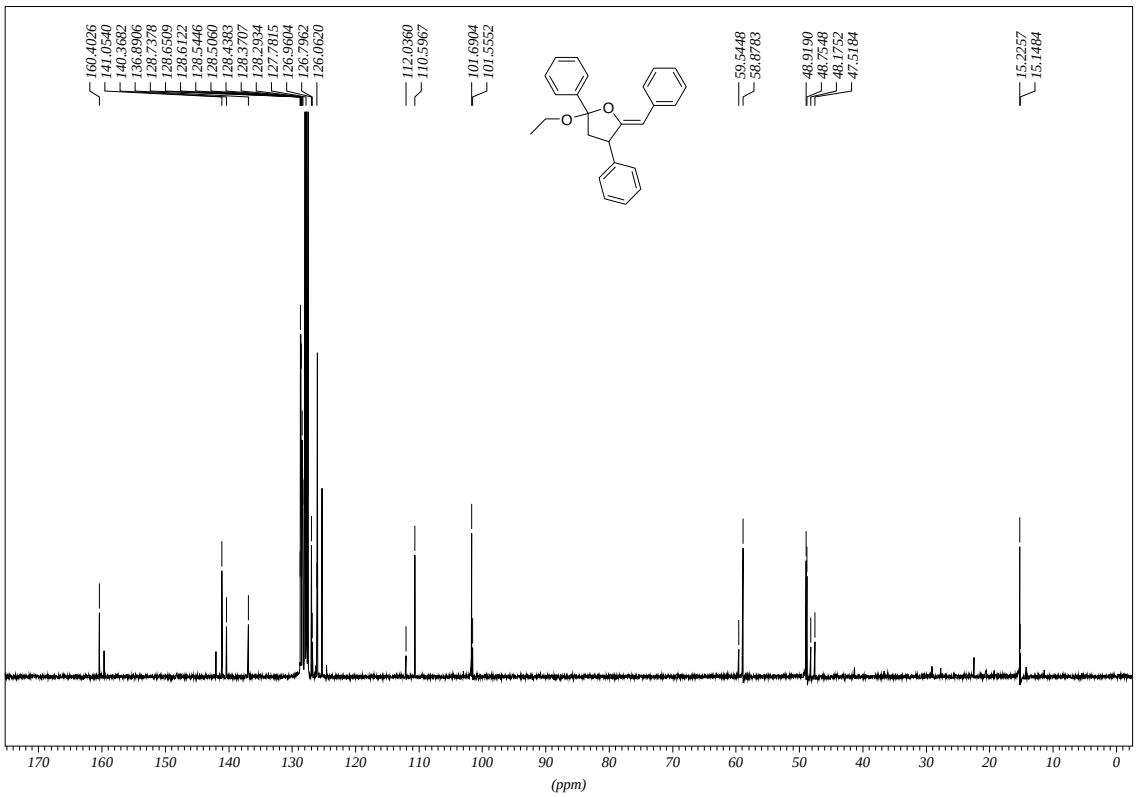
(*Z*)-5-Benzylidenetetrahydro-2-methoxy-2,4-diphenylfuran (4la)



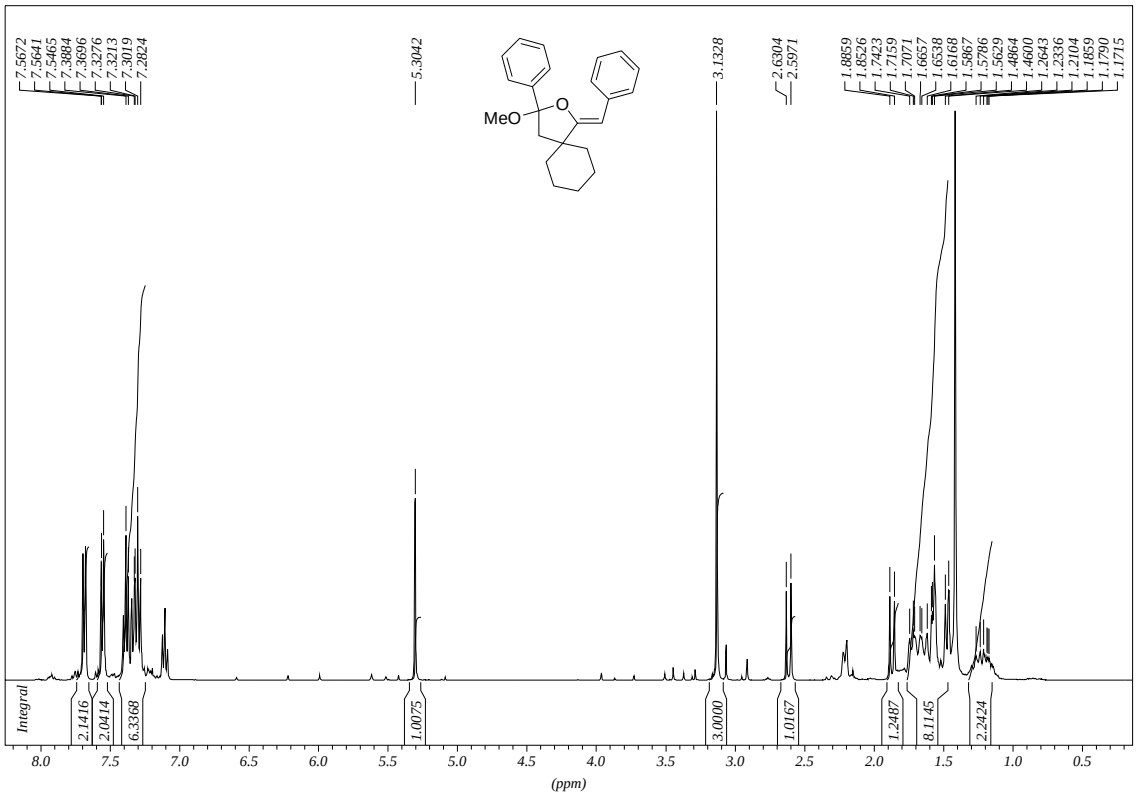


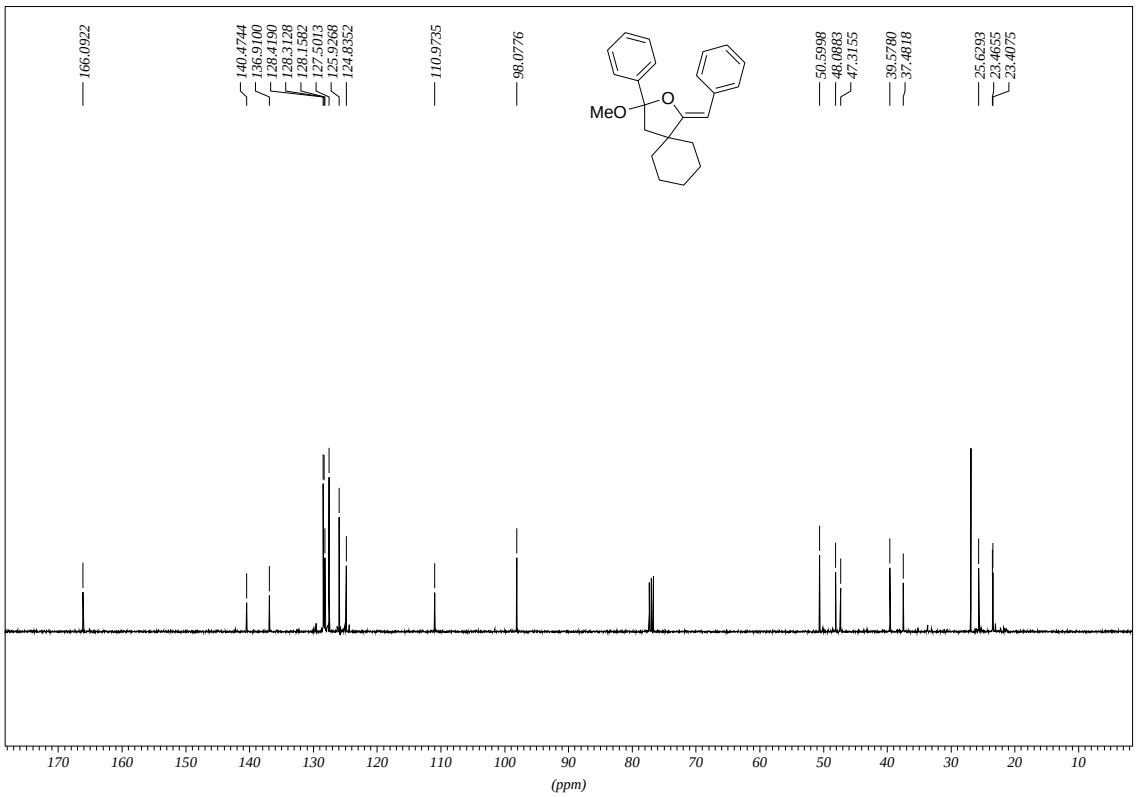
(*Z*)-5-Benzylidene-2-ethoxytetrahydro-2,4-diphenylfuran (4lb)



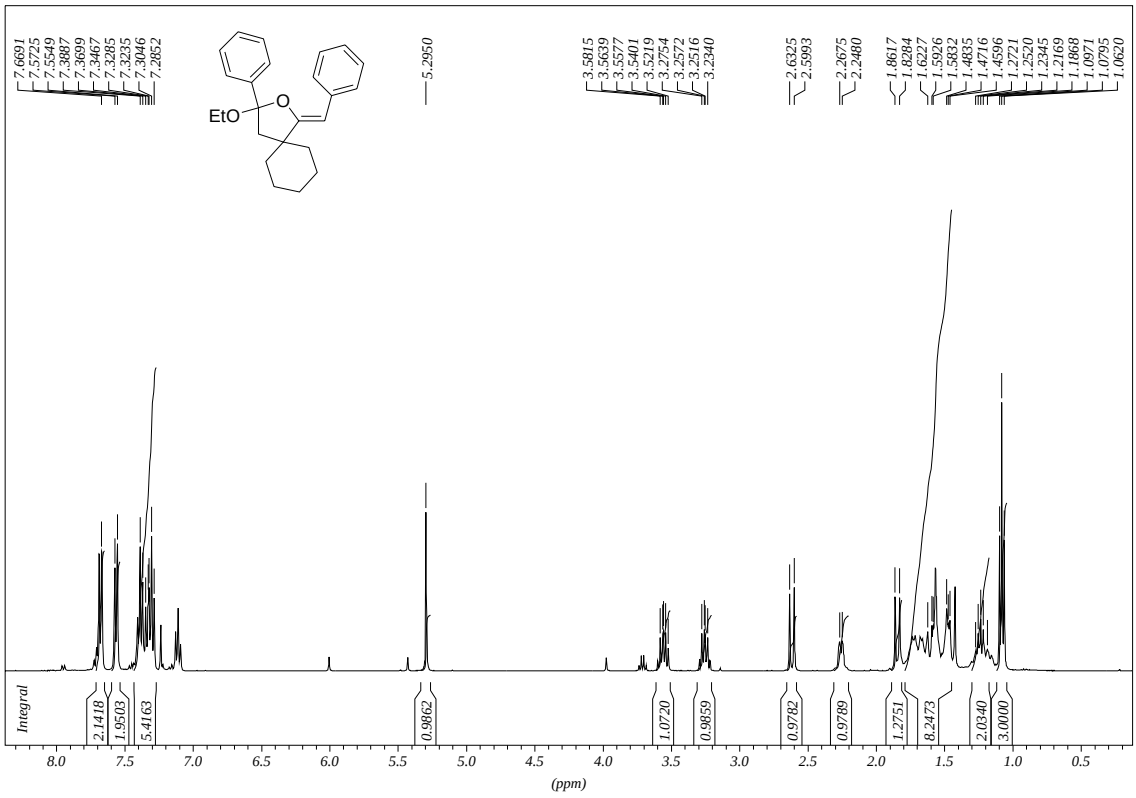


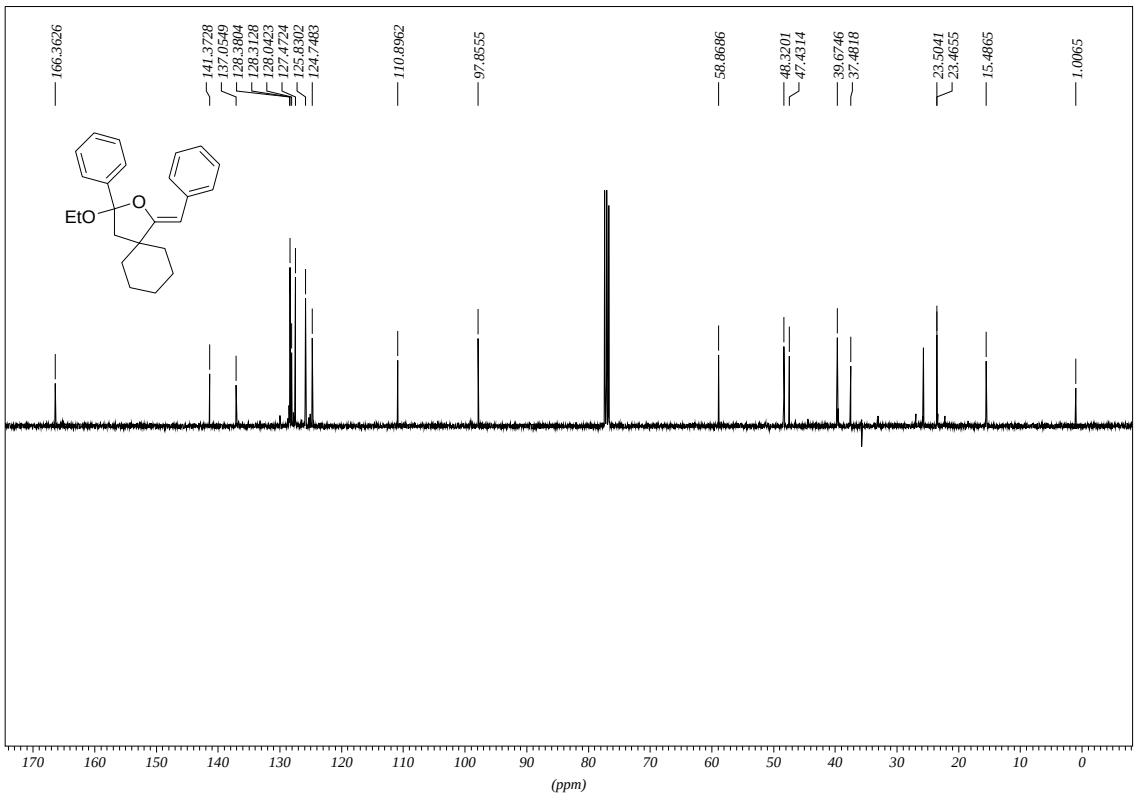
(*Z*)-1-Benzylidenetetrahydro-3-methoxy-2-oxa-3-phenylspiro[5.4]decan (4na)



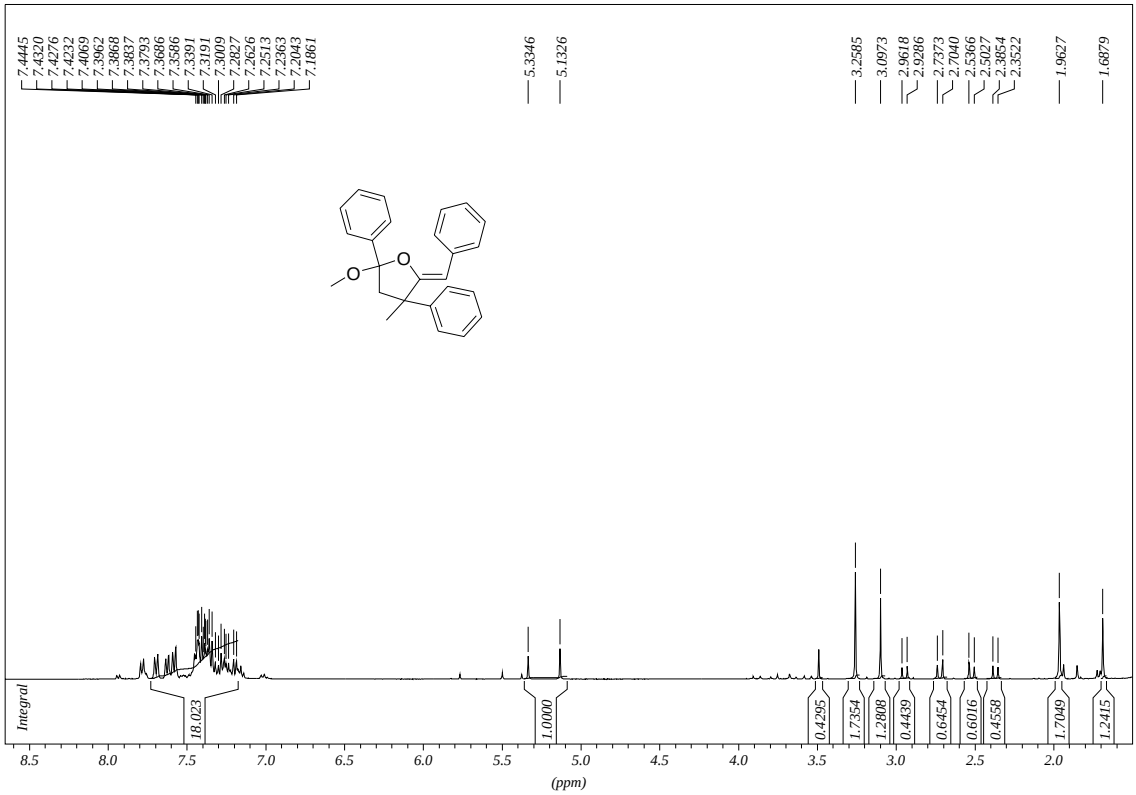


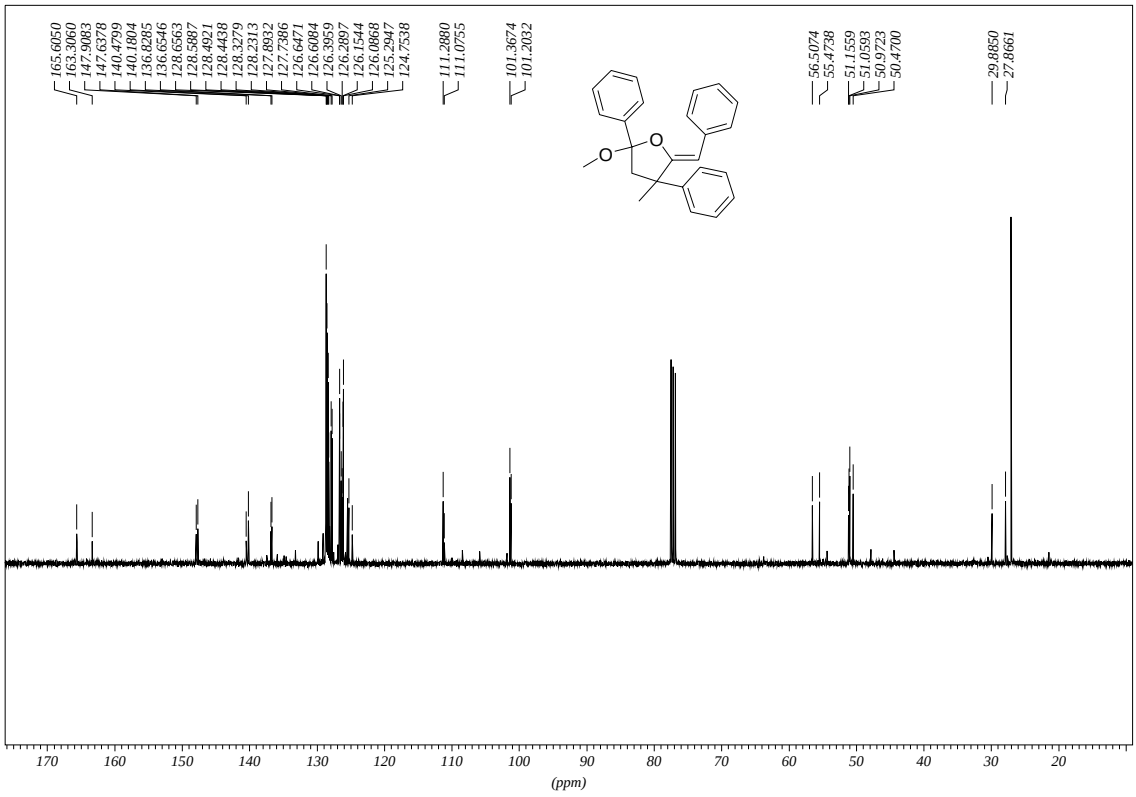
(*Z*)-1-Benzylidene-3-ethoxytetrahydro-2-oxa-3-phenylspiro[5.4]decan (4nb)



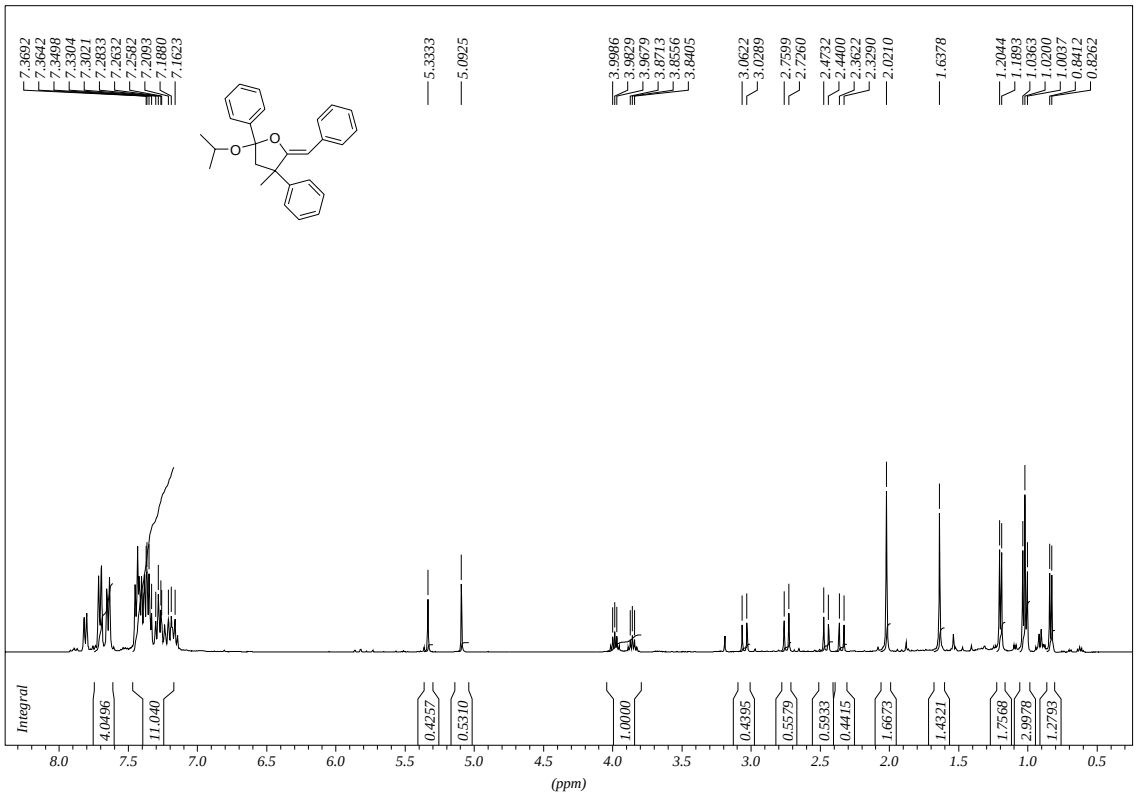


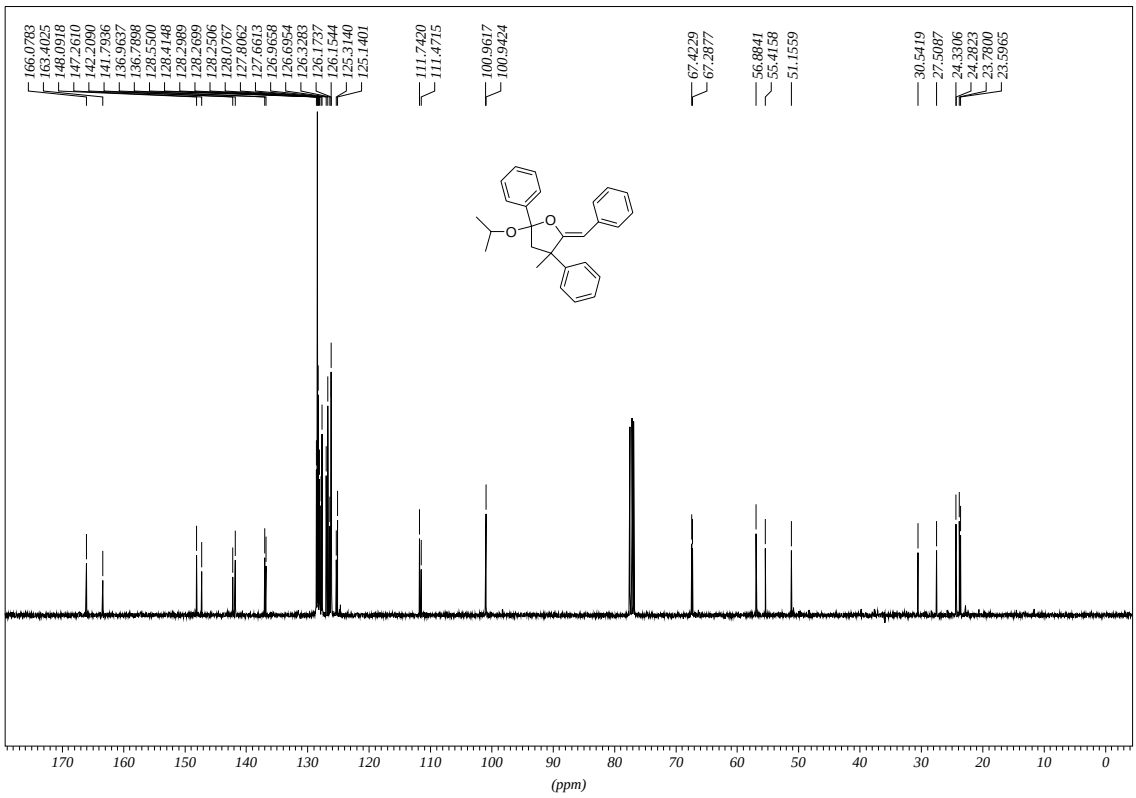
(*Z*)-5-Benzylidenetetrahydro-2-methoxy-4-methyl-2,4-diphenylfuran (4oa)



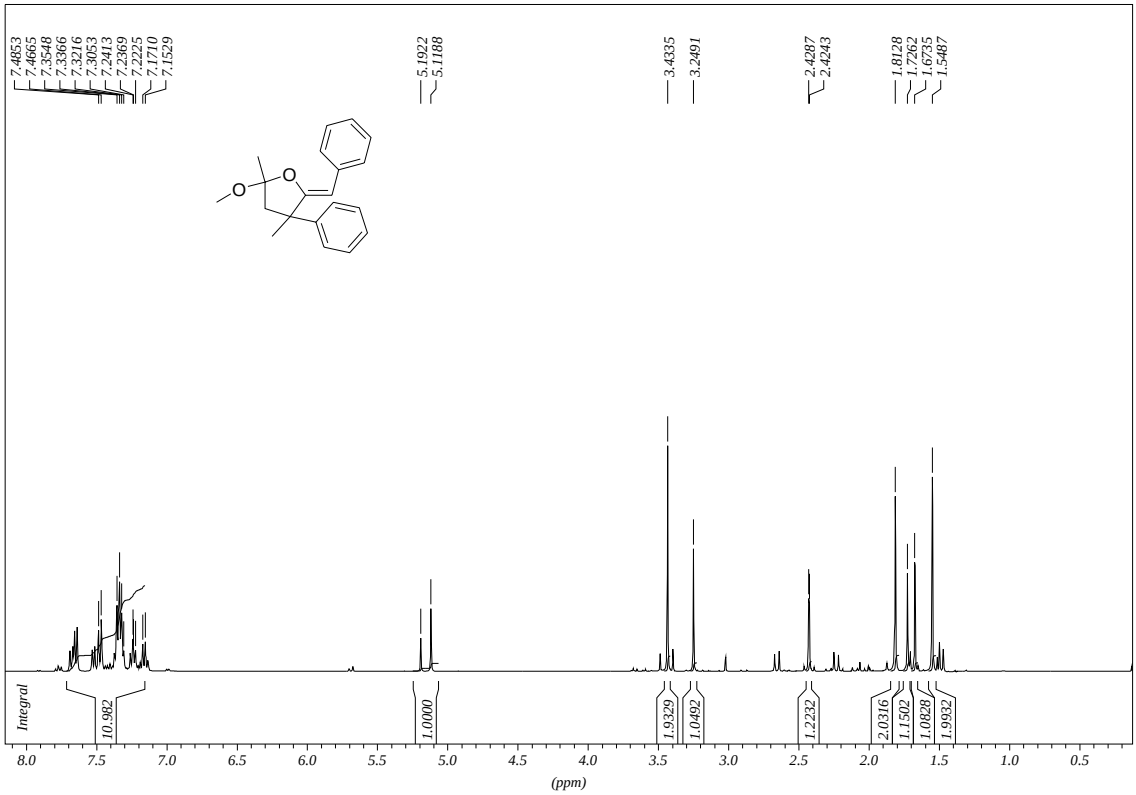


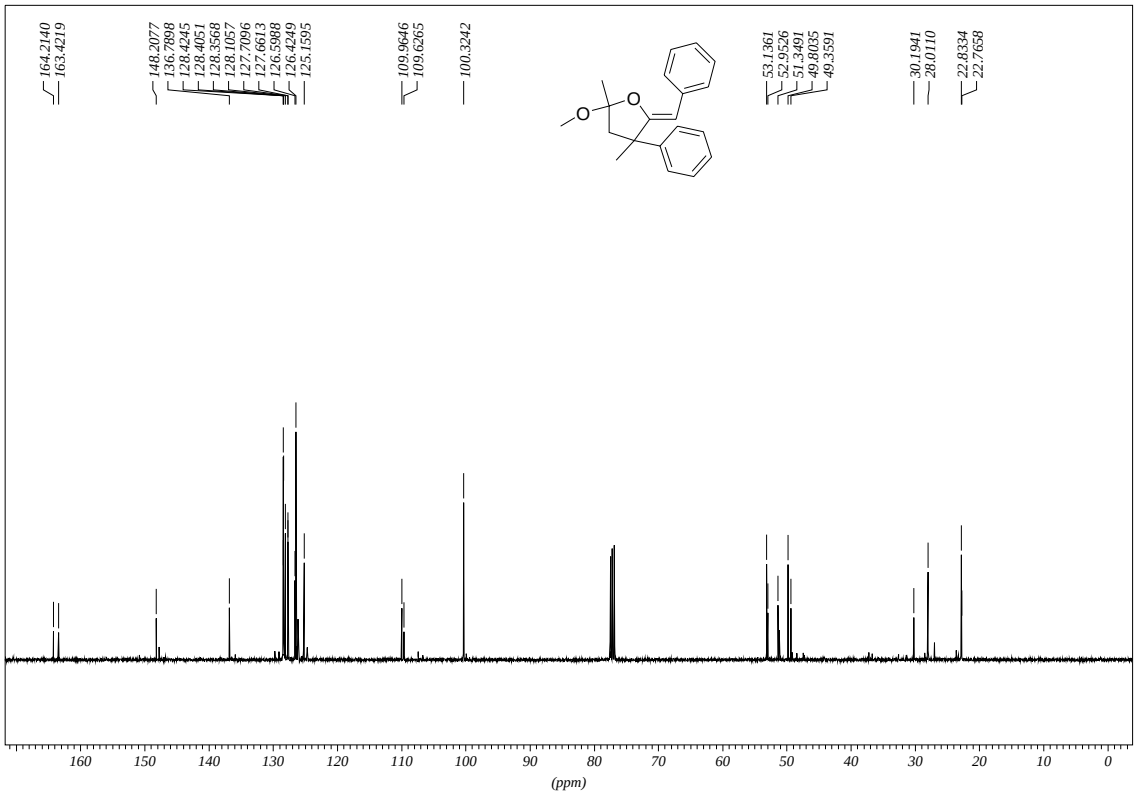
(*Z*)-5-Benzylidenetetrahydro-2-isopropoxy-4-methyl-2,4-diphenylfuran (4ob)



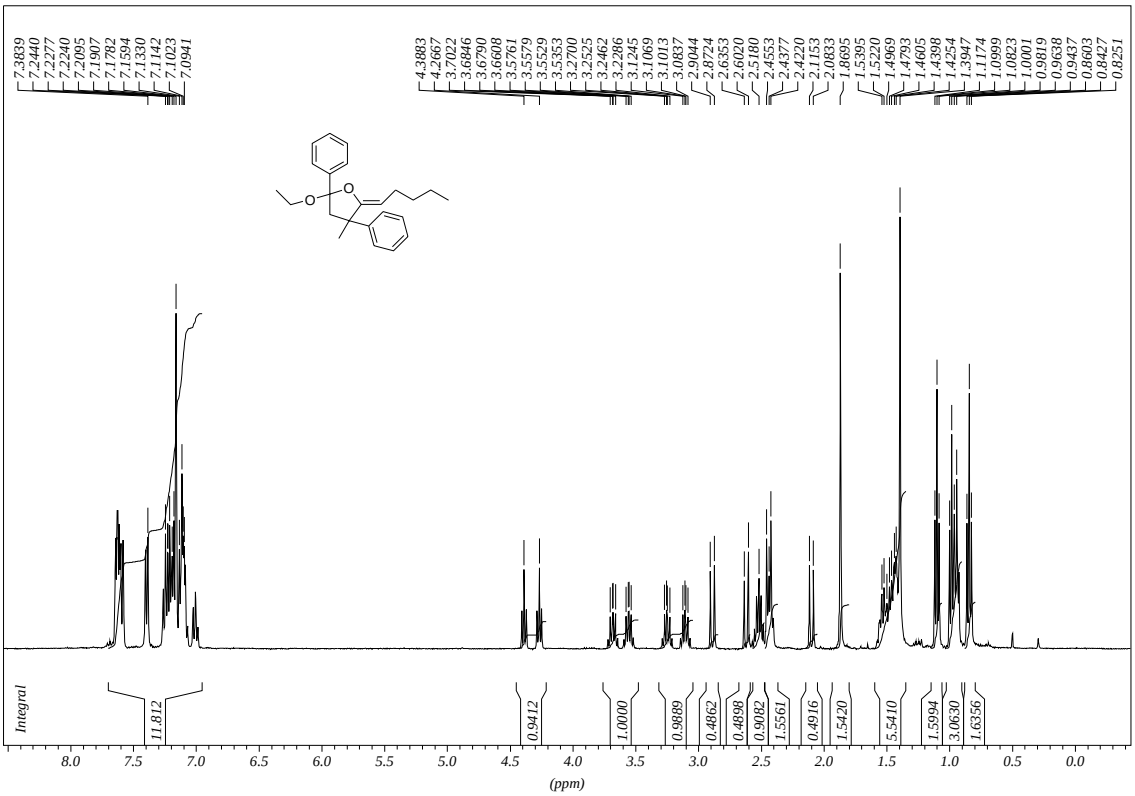


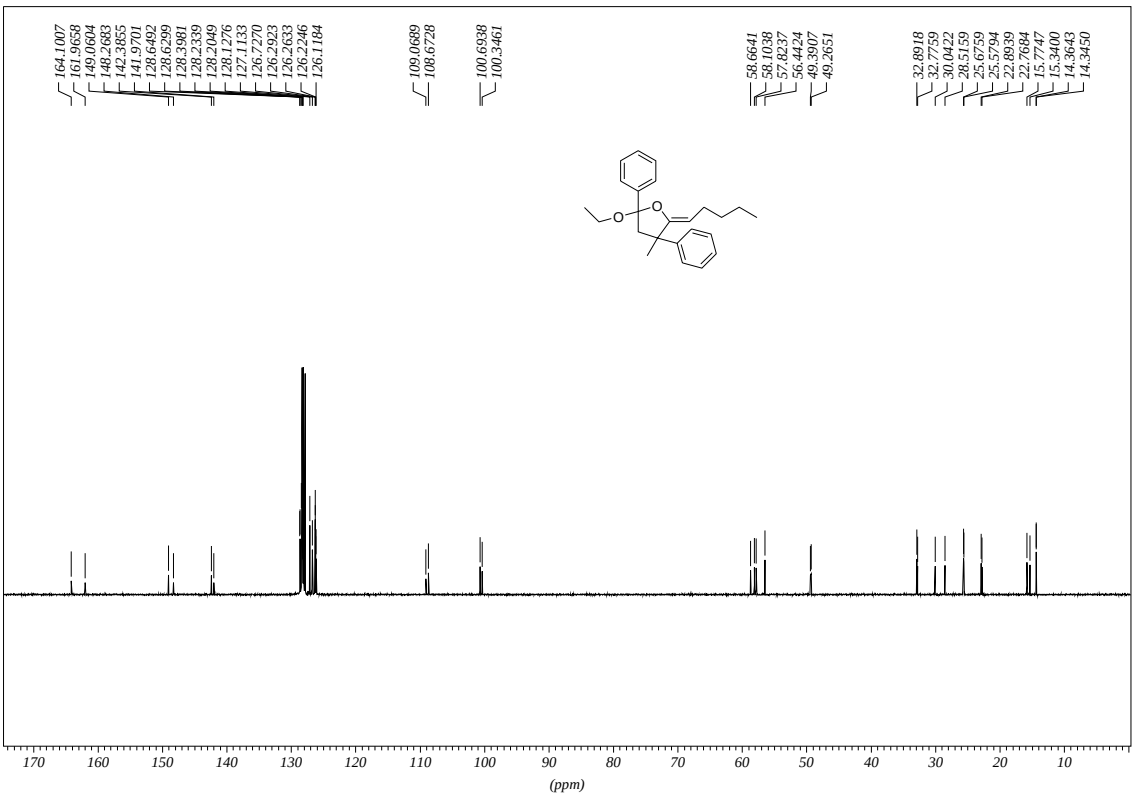
(*Z*)-5-Benzylidenetetrahydro-2-methoxy-2,4-dimethyl-4-phenylfuran (4pa)



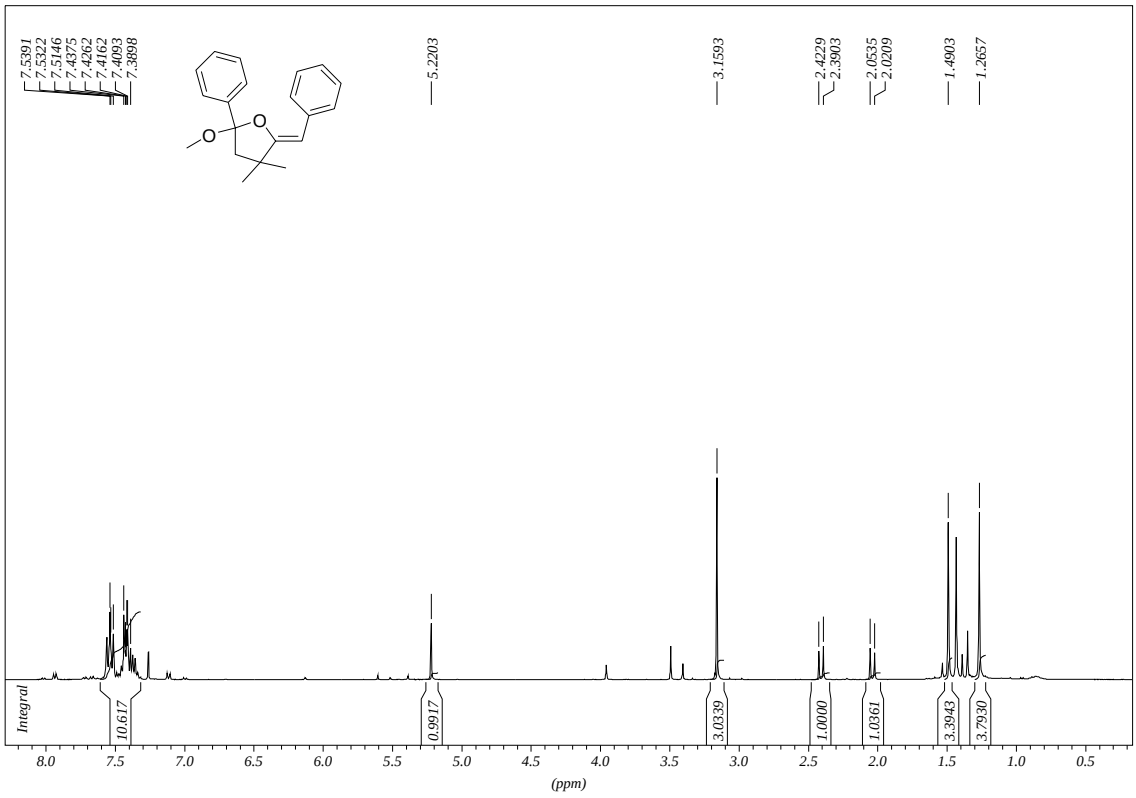


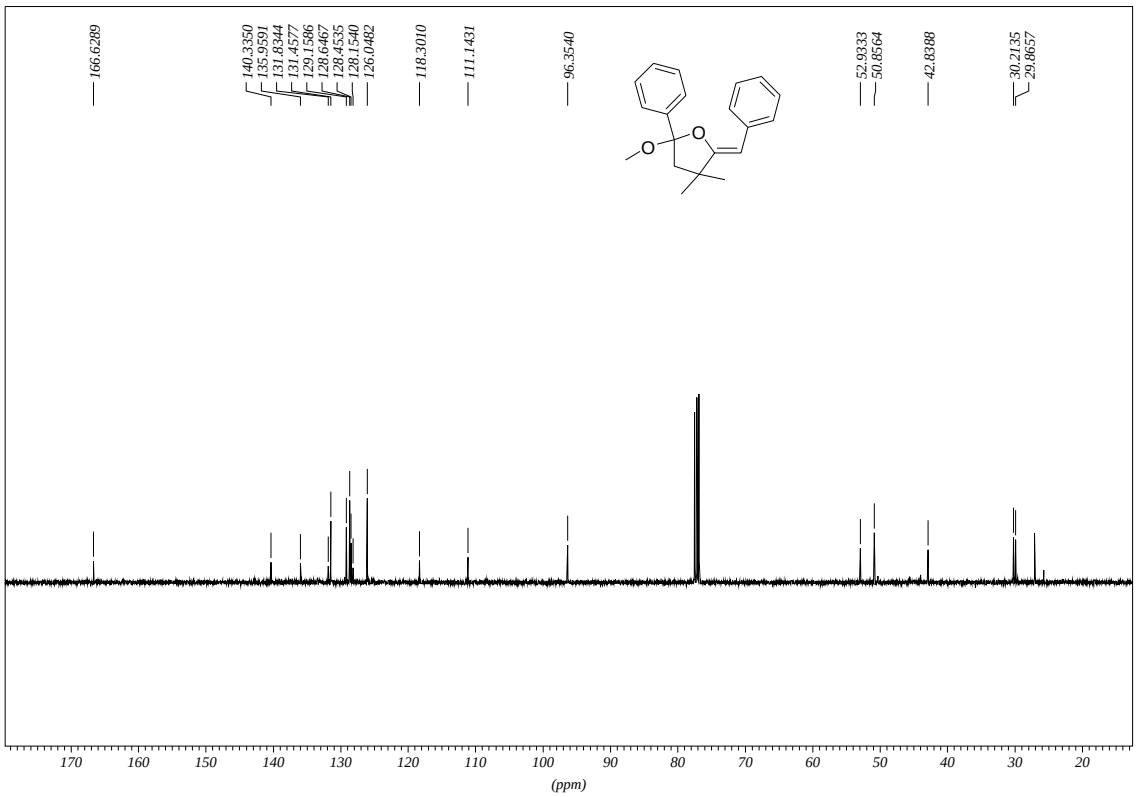
(*Z*)-2-Ethoxytetrahydro-4-methyl-5-pentylidene-2,4-diphenylfuran (4qa)



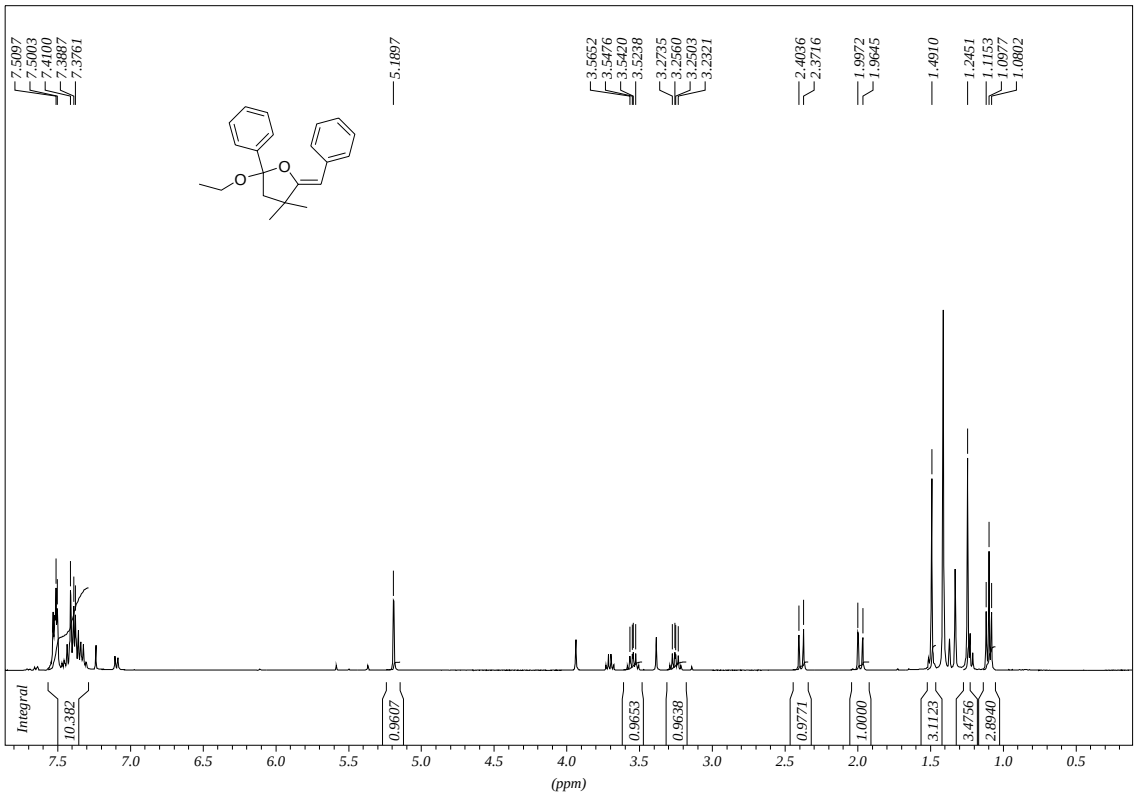


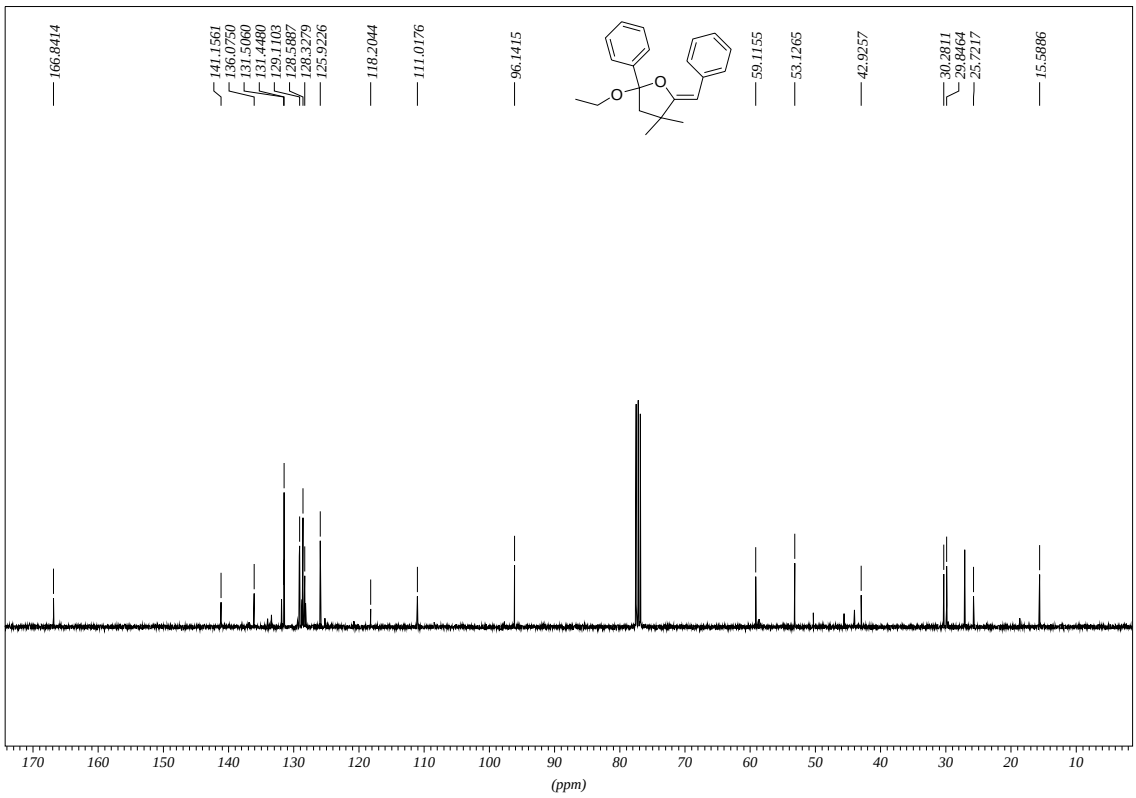
(*Z*)-5-Benzylidenetetrahydro-2-methoxy-4,4-dimethyl-2-phenylfuran (4ra)



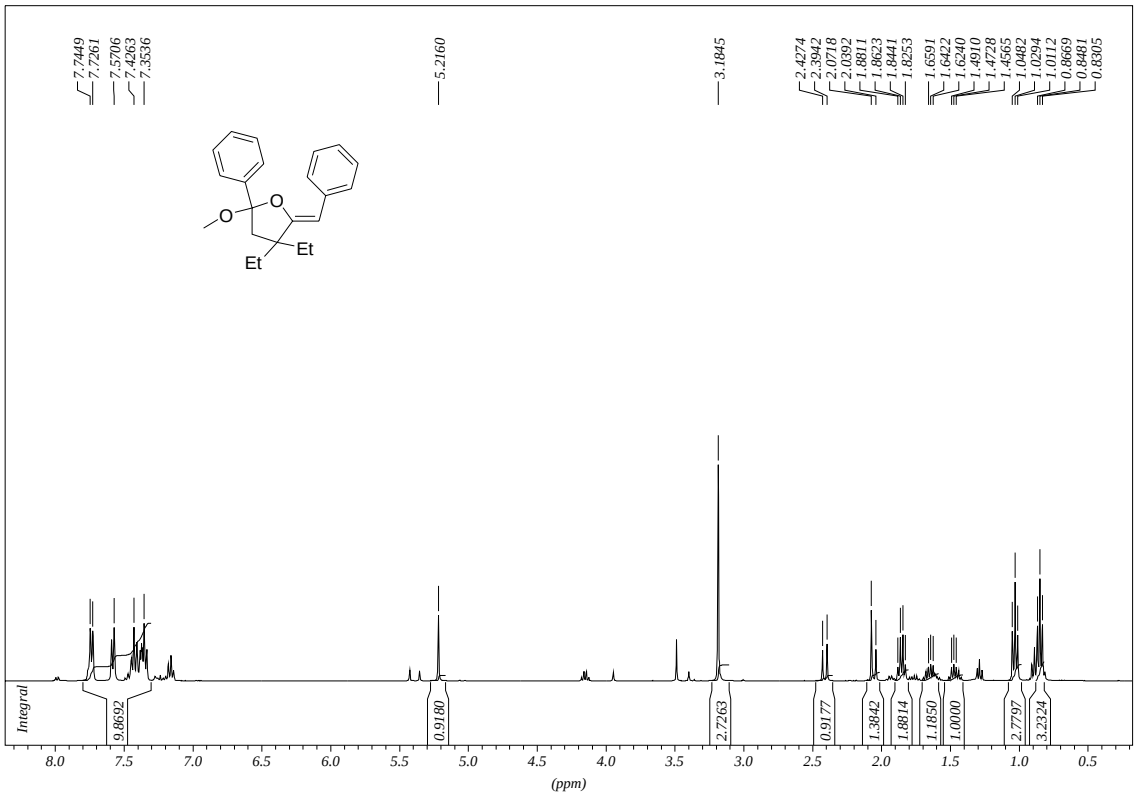


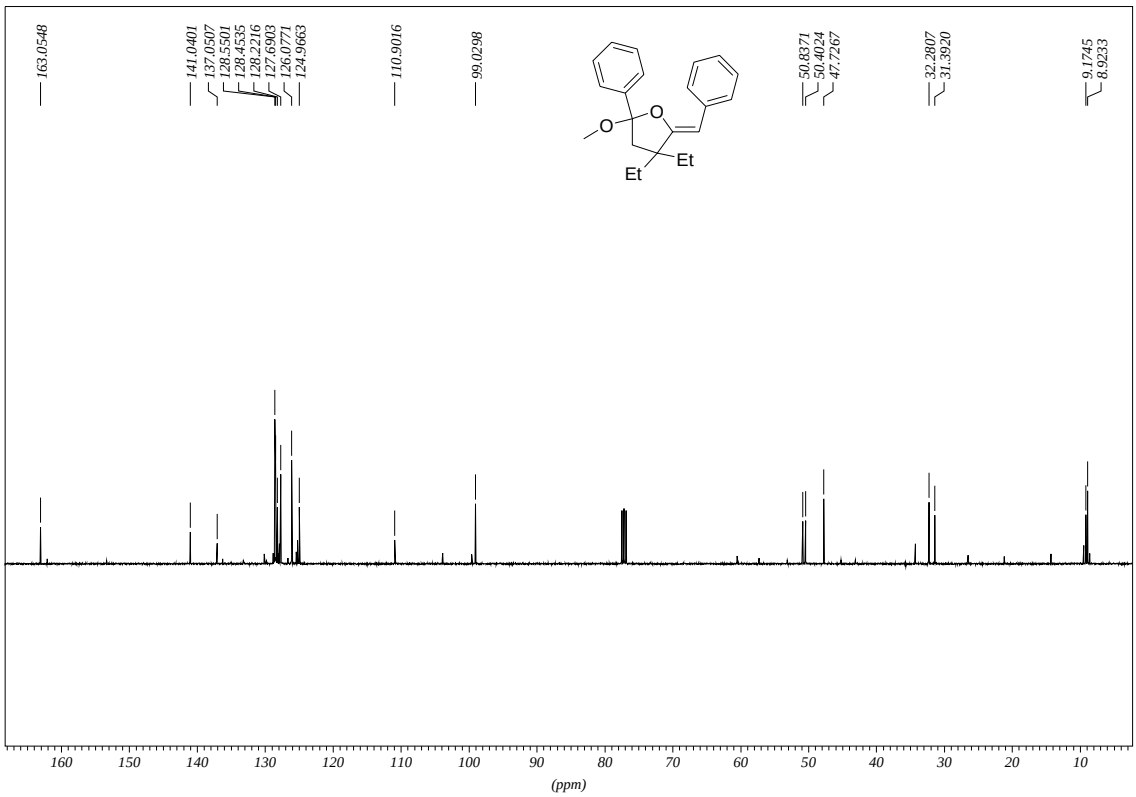
(*Z*)-5-Benzylidene-2-ethoxytetrahydro-4,4-dimethyl-2-phenylfuran (4rb)



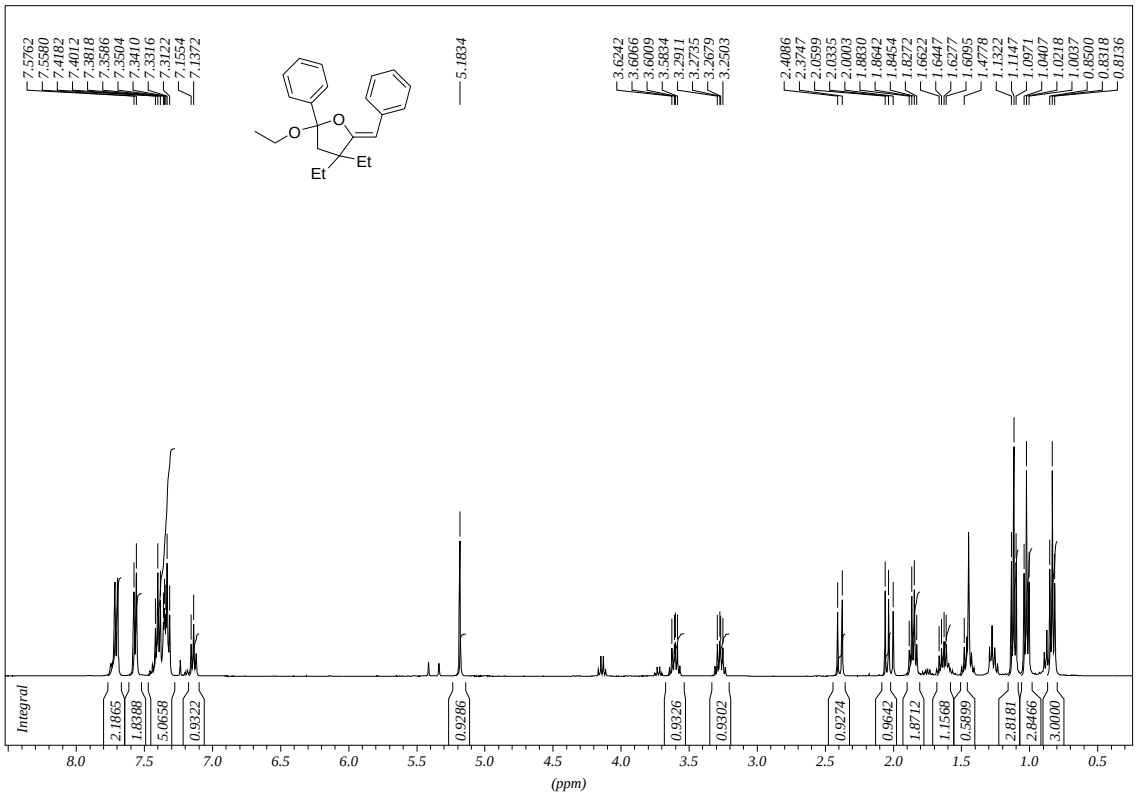


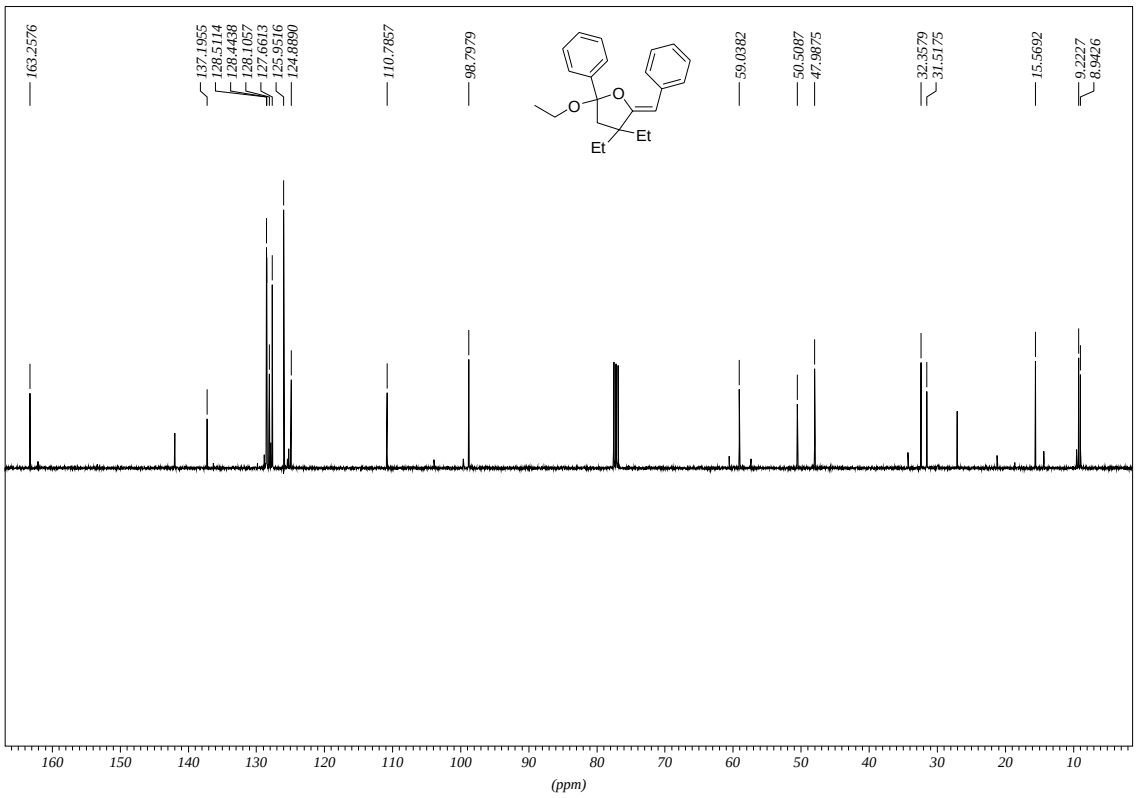
(*Z*)-5-Benzylidene-4,4-diethyltetrahydro-2-methoxy-2-phenylfuran (4sa)



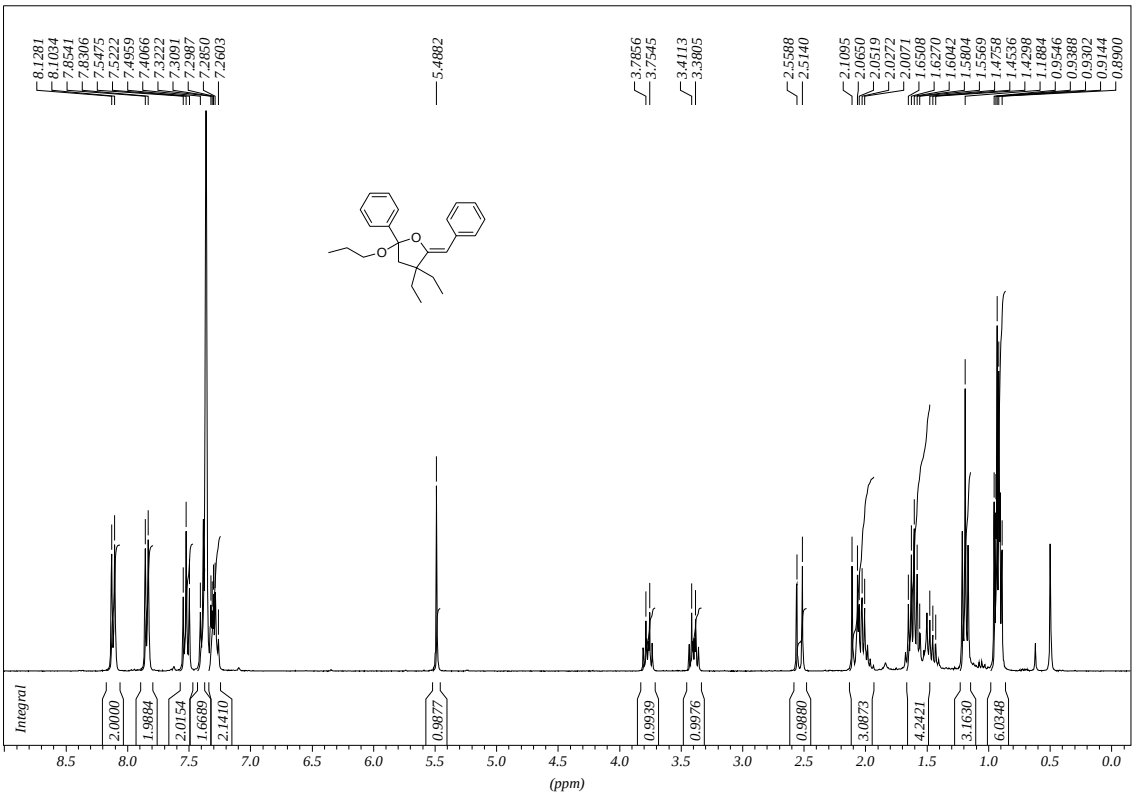


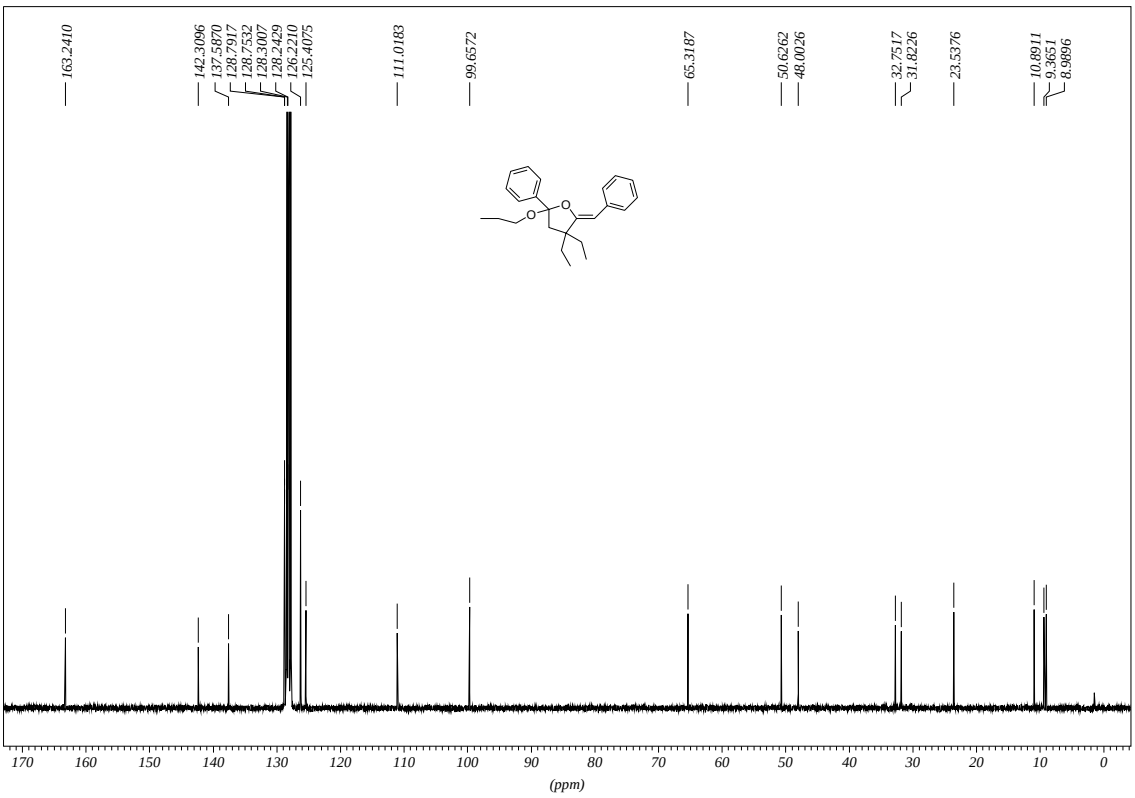
(*Z*)-5-Benzylidene-2-ethoxy-4,4-diethyltetrahydro-2-phenylfuran (4sb)





(*Z*)-5-Benzylidene-4,4-diethyltetrahydro-2-phenyl-2-propoxyfuran (4sc)





Methyl 4-((Z)-(Dihydro-5-methoxy-3,3-dimethyl-5-phenylfuran-2(3H)-ylidene)methyl)-benzoate (4ta)