

Iron-catalyzed reductive cyclization reaction of 1,6-enynes for the
synthesis of 3-acylbenzofurans and thiophenes

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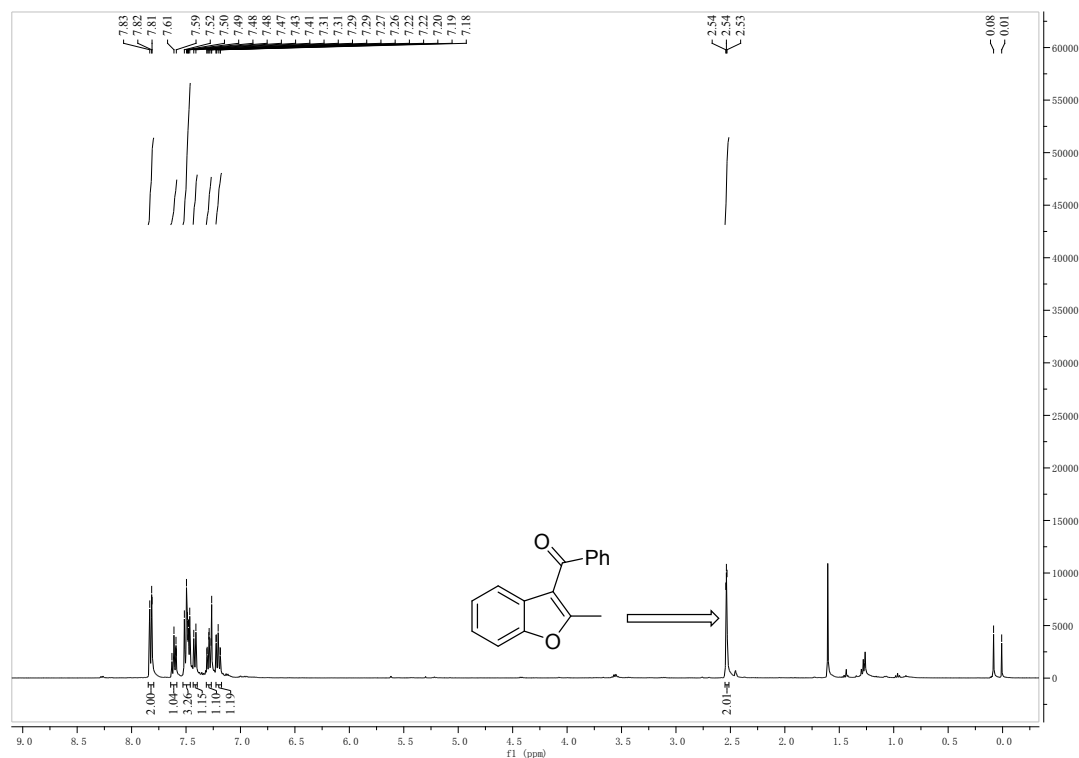
General Remarks: Column chromatography was carried out on silica gel. Unless noted ^1H NMR spectra were recorded on 400 MHz in CDCl_3 , ^{13}C NMR spectra were recorded on 100 MHz in CDCl_3 , ^{19}F NMR spectra were recorded on 376 MHz in CDCl_3 . IR spectra were recorded on an FT-IR spectrometer and only major peaks are reported in cm^{-1} . Melting points were determined on a microscopic apparatus and were uncorrected. All new products were further characterized by HRMS (high resolution mass spectra), high resolution mass spectrometry (HRMS) spectra was obtained on a microTOF-Q instrument equipped with an ESI source; copies of their ^1H NMR and ^{13}C NMR spectra are provided. Products **2a**, **2b**, **2c**, **2i**, **2q**, **2u**, **2z**, **4a** and **4c** are known (see: Y. Liu, J. Qian, S. Lou, and Z. Xu, *J. Org. Chem.*, 2010, **75**, 6300-6303; F. Gao, J.-T. Wang, L.-L. Liu, N. Ma, C. Yang, Y. Gao and W. Xia, *Chem. Commun.*, 2017, **53**, 8533-8536).

General Procedure

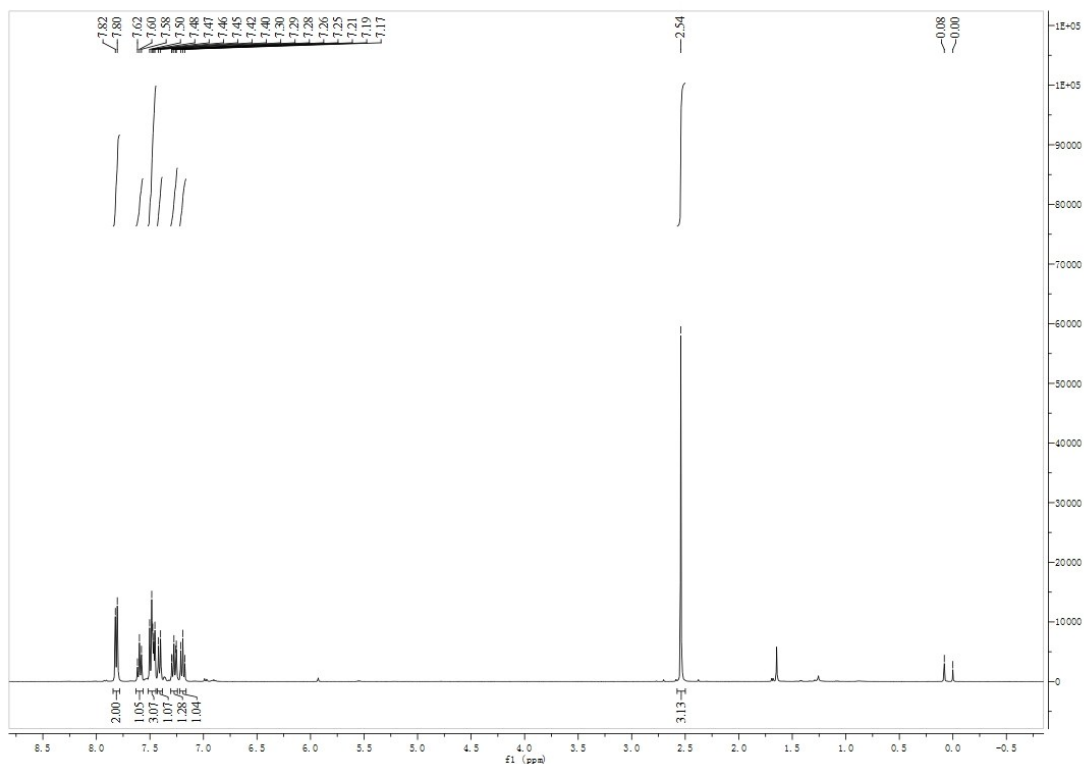
The mixture of 1,6-enynes **1** (0.20 mmol) and PMHS (0.60 mmol), FeCl_2 (0.040mmol), Phen (0.04 mmol) were combined in EtOH (2.0mL) at 60°C for 12 h under 1 atm dioxygen atmosphere. After the reaction, 6 mL water was added to quench the reaction, and the resulting mixture was extracted twice with DCM. The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. Purification of the crude product by flash column chromatography afforded the product (petroleum ether/ethyl acetate as eluent (30:1-20:1)).

Deuterium labeling experiments:

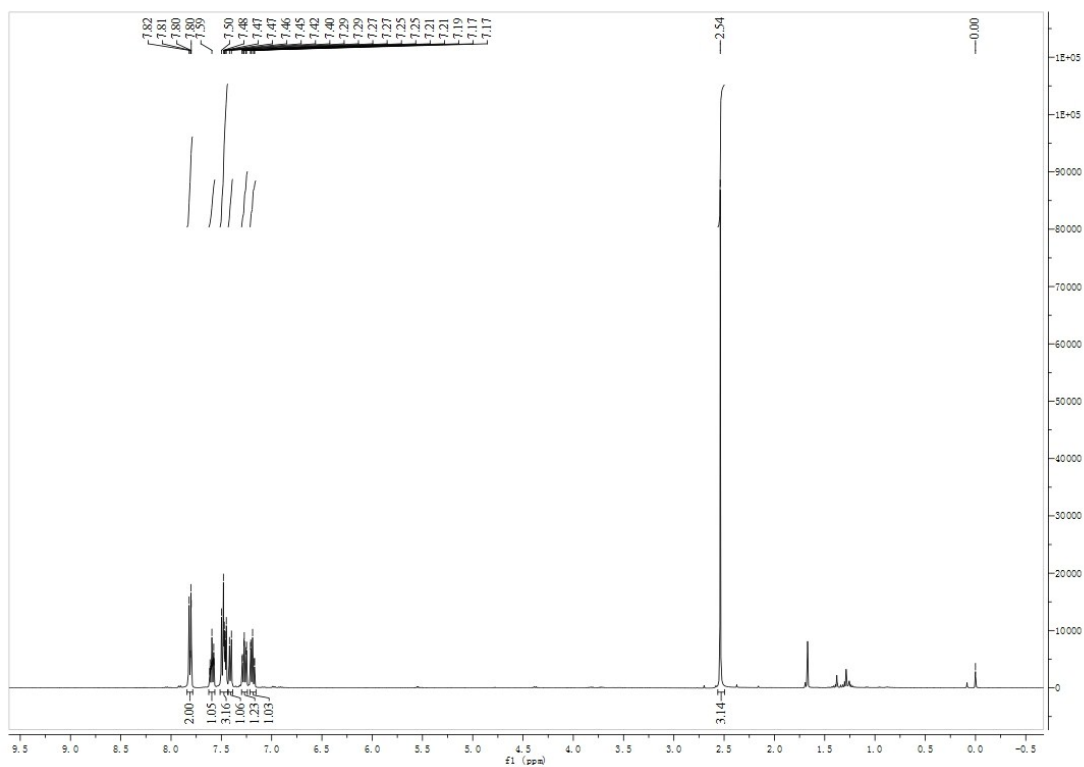
3.0 eq. PhSiD_3 was added in the standard conditions.



Using $\text{CD}_3\text{CD}_2\text{OD}$ as the solvent in standard reaction conditions.



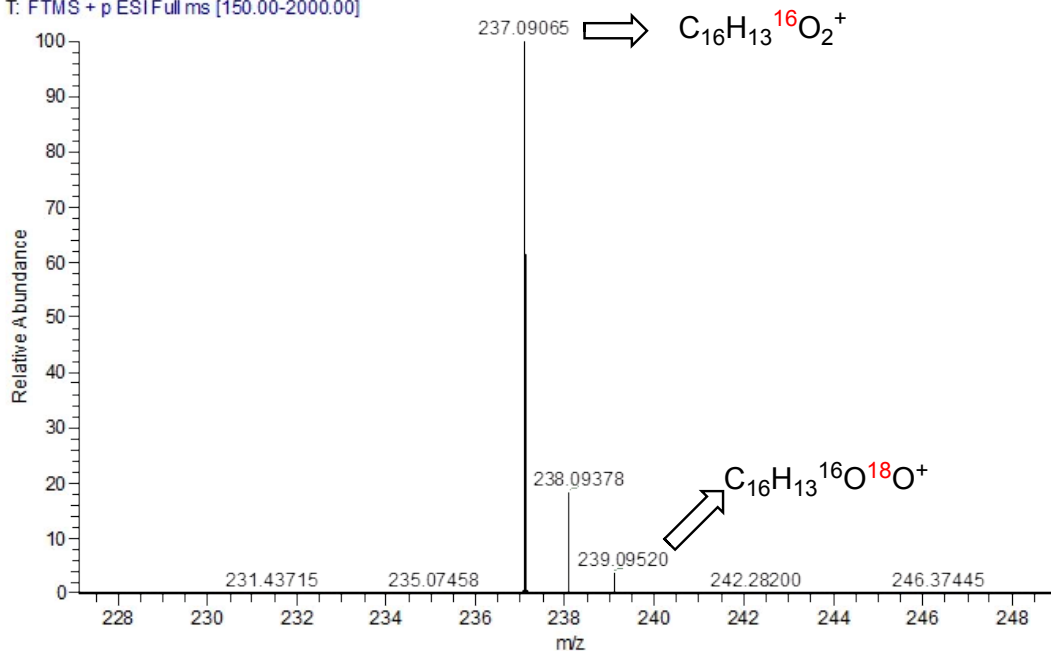
Add 4 eq. D₂O to the standard reaction conditions



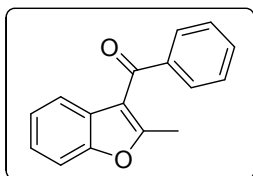
Add 2.0 eq. H₂¹⁸O to the standard reaction conditions.

HRMS (ESI) m/z calcd for C₁₆H₁₃¹⁶O¹⁸O⁺ (M+H)⁺ 239.09525, found 239.09520,
calcd for C₁₆H₁₃¹⁶O₂⁺ (M+H)⁺ 237.09101, found 237.09065. 239 : 237 = 6.37E6 :
1.64E8 = 0.03884.

38 #18 RT: 0.25 AV: 1 NL: 1.64E8
T: FTMS + p ESI Full ms [150.00-2000.00]

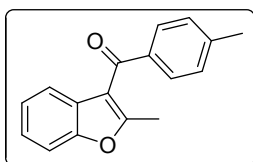


Date of products 2 and 3, 4



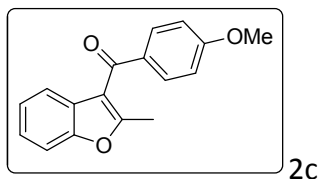
2a

(2-methylbenzofuran-3-yl)(phenyl)methanone, 60%, CAS 18703-72-5, Liquid;
 ^1H NMR (400 MHz, CDCl_3) δ 7.85 (d, $J = 7.4$ Hz, 2H), 7.63 (t, $J = 7.3$ Hz, 1H), 7.55-7.47 (m, 3H), 7.44 (d, $J = 7.7$ Hz, 1H), 7.30 (d, $J = 9.2$ Hz, 1H), 7.22 (t, $J = 7.5$ Hz, 1H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 191.9, 161.9, 153.6, 139.3, 132.6, 129.0, 128.4, 126.9, 124.3, 123.5, 121.3, 116.9, 110.8, 14.6; IR(cm^{-1}): 3064, 2960, 2921, 2852, 1648, 1579, 1474, 1456, 1386, 1267, 1240, 1174, 1124, 1066, 939, 877, 846, 792, 745, 719, 696; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{13}\text{O}_2^+$ ($\text{M}+\text{H}$) $^+$ 237.09101, found 237.09065.



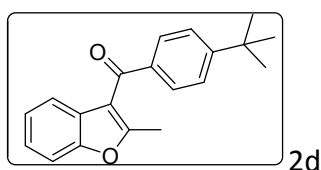
2b

(2-methylbenzofuran-3-yl)(p-tolyl)methanone, 64%, CAS 18703-74-7, Liquid;
 ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 8.1$ Hz, 2H), 7.41-7.47 (m, 2H), 7.25-7.29 (m, 3H), 7.17-7.21 (t, $J = 7.5$ Hz, 1H), 2.54 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 191.6, 161.4, 153.6, 143.4, 136.6, 129.1, 127.0, 124.3, 123.4, 121.3, 117.0, 110.8, 21.7, 14.6; IR(cm^{-1}): 3058, 3031, 2961, 2921, 1638, 1607, 1579, 1473, 1450, 1383, 1352, 1282, 1176, 1098, 1023, 937, 902, 874, 793, 746, 605.



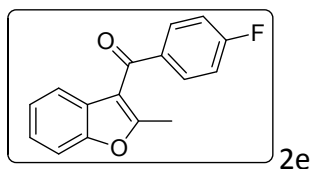
(4-methoxyphenyl)(2-methylbenzofuran-3-yl)methanone, 71%, CAS 94541-06-7, m. p. = 67-70°C

^1H NMR (400 MHz, CDCl_3) δ 7.82-7.86 (m, 2H), 7.41 (dd, J = 13.4, 8.0 Hz, 2H), 7.17-7.31 (m, 2H), 6.94-6.98 (m, 2H), 3.88 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 190.4, 163.4, 160.8, 153.6, 131.8, 131.6, 124.2, 123.9, 121.2, 117.1, 113.7, 110.8, 55.4, 14.4; IR(cm^{-1}): 3072, 3006, 2960, 2937, 2837, 2362, 2049, 1919, 1745, 1649, 1602, 1505, 1451, 1421, 1390, 1370, 1347, 1309, 1255, 1166, 1120, 1027, 939, 904, 880, 836, 776, 746.



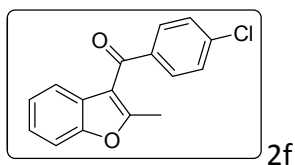
(4-(tert-butyl)phenyl)(2-methylbenzofuran-3-yl)methanone, 60%, Liquid;

^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, J = 8.5 Hz, 2H), 7.45-7.51 (m, 4H), 7.26-7.30 (m, 1H), 7.18-7.22 (m, 1H), 2.54 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.5, 161.4, 156.5, 153.6, 136.4, 129.1, 127.1, 125.4, 124.3, 123.5, 121.3, 117.1, 110.8, 35.1, 31.1, 14.6; IR(cm^{-1}): 3059, 2963, 2907, 2869, 1712, 1645, 1596, 1472, 1449, 1403, 1387, 1367, 1277, 1242, 1176, 1105, 1011, 937, 906, 879, 840, 777, 746, 710; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{21}\text{O}_2^+$ ($\text{M}+\text{H}$) $^+$ 293.15361, found 293.15378.



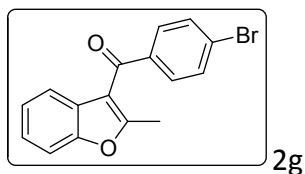
(4-fluorophenyl)(2-methylbenzofuran-3-yl)methanone, 62%, Liquid;

^1H NMR (400 MHz, CDCl_3) δ 7.89 (dd, J = 8.8, 5.4 Hz, 2H), 7.50 (d, J = 8.2 Hz, 1H), 7.39 (d, J = 7.8 Hz, 1H), 7.31 (t, J = 7.7 Hz, 1H), 7.25-7.12 (m, 3H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.4, 166.8, 164.2, 161.7, 135.5, 131.8, 126.8, 124.5, 123.6, 121.0, 116.8, 115.5 (d, J = 22 Hz), 110.9, 14.4; ^{19}F NMR (376 MHz, CDCl_3) δ ppm -105.59; IR(cm^{-1}): 3072, 2964, 2929, 2875, 1649, 1594, 1502, 1456, 1406, 1382, 1352, 1286, 1269, 934, 904, 842, 807, 773, 746, 603; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{12}\text{FO}_2^+$ ($\text{M}+\text{H}$) $^+$ 255.08158, found 255.08144.



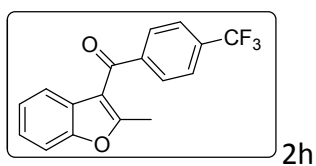
(4-chlorophenyl)(2-methylbenzofuran-3-yl)methanone, 79%, Liquid;

^1H NMR (400 MHz, CDCl_3) δ 7.75-7.78 (m, 2H), 7.45-7.48 (m, 3H), 7.35-7.37 (m, 1H), 7.27-7.31 (m, 1H), 7.18-7.22 (m, 1H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.3, 162.1, 153.6, 139.0, 137.5, 130.6, 128.8, 126.6, 124.5, 123.7, 121.1, 116.7, 110.9, 14.7; IR(cm^{-1}): 3064, 2964, 2922, 2354, 1649, 1594, 1456, 1401, 1351, 1286, 1240, 1178, 1089, 1012, 938, 900, 873, 834, 769, 750; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{12}\text{ClO}_2^+$ ($\text{M}+\text{H}$) $^+$ 271.05203, found 271.05252.



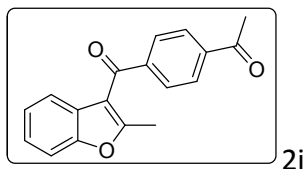
(4-bromophenyl)(2-methylbenzofuran-3-yl)methanone, 66%, Liquid;

^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, $J = 8.4$ Hz, 2H), 7.63 (d, $J = 8.4$ Hz, 2H), 7.47 (d, $J = 8.2$ Hz, 1H), 7.37 (d, $J = 7.7$ Hz, 1H), 7.27-7.31 (m, 1H), 7.21 (t, $J = 7.5$ Hz, 1H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.7, 162.2, 153.6, 138.0, 131.8, 130.7, 127.6, 126.6, 124.5, 123.5, 121.1, 116.5, 111.0, 14.7; IR(cm^{-1}): 3060, 2956, 2925, 2362, 1645, 1583, 1459, 1394, 1278, 1235, 1174, 1096, 1066, 1008, 939, 896, 877, 831, 769, 750, 673, 623; HRMS(ESI) m/z calcd for $\text{C}_{16}\text{H}_{12}\text{BrO}_2^+$ ($\text{M}+\text{H}$) $^+$ 315.00152, found 315.00189.



(2-methylbenzofuran-3-yl)(4-(trifluoromethyl)phenyl)methanone, 45%, m.p. = 69-71°C

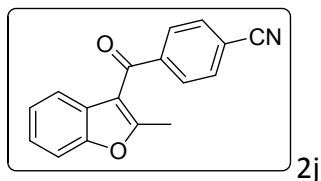
^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 8.0$ Hz, 2H), 7.76 (d, $J = 8.0$ Hz, 2H), 7.49 (d, $J = 8.0$ Hz, 1H), 7.26-7.35 (m, 2H), 7.19-7.23 (m, 1H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.7, 162.9, 153.7, 142.4, 134.1, 133.8, 129.3, 126.4, 125.6, 125.0, 124.7, 123.8, 121.1, 116.5, 111.0, 14.8; ^{19}F NMR (376 MHz, CDCl_3) δ ppm -62.94; IR(cm^{-1}): 3063, 2961, 2922, 2850, 1728, 1650, 1573, 1510, 1476, 1452, 1409, 1385, 1321, 1288, 1237, 1167, 1133, 1108, 1065, 1017, 939, 905, 881, 838, 780, 746, 692, 668, 625; HRMS(ESI) m/z calcd for $\text{C}_{17}\text{H}_{12}\text{F}_3\text{O}_2^+$ ($\text{M}+\text{H}$) $^+$ 305.07839, found 305.07849.



1-(4-(2-methylbenzofuran-3-carbonyl)phenyl)ethanone, 60%, CAS 28222-83-5, Liquid;

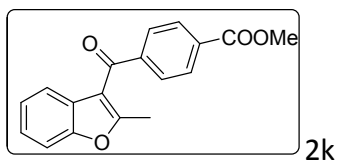
^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 8.0$ Hz, 2H), 7.86 (d, $J = 8.0$ Hz, 2H), 7.47 (d, $J = 8.0$ Hz, 1H), 7.34-7.36 (m, 1H), 7.27-7.31 (m, 1H), 7.18-7.21 (m, 1H), 2.68 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.4, 191.1, 162.7, 153.6, 143.0,

139.7, 129.1, 128.4, 126.4, 124.6, 123.7, 121.1, 116.6, 110.9, 26.8, 14.8; IR(cm^{-1}): 3066, 3003, 2961, 2921, 2362, 2338, 1689, 1649, 1571, 1473, 1450, 1406, 1352, 1258, 1106, 1011, 941, 906, 883, 836, 773, 749, 706, 667.



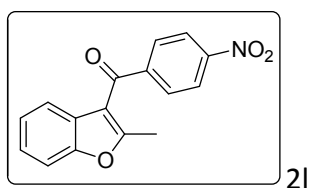
4-(2-methylbenzofuran-3-carbonyl)benzonitrile, 50%, m. p. = 98-101°C

^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 8.3 Hz, 2H), 7.80 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 8.2 Hz, 1H), 7.27-7.31 (m, 2H), 7.21-7.23 (m, 1H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.1, 163.2, 153.6, 142.8, 132.4, 124.7, 123.9, 120.9, 117.9, 116.2, 115.8, 111.1, 14.8; IR(cm^{-1}): 3065, 2960, 2923, 2360, 2341, 2230, 1650, 1605, 1572, 1476, 1453, 1434, 1402, 1389, 1355, 1285, 1241, 1176, 1128, 1015, 942, 906, 884, 842, 774, 752; HRMS(ESI) m/z calcd for $\text{C}_{17}\text{H}_{12}\text{NO}_2^+$ ($\text{M}+\text{H}$) $^+$ 262.08626, found 262.08612.



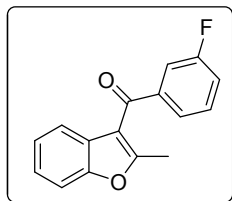
methyl 4-(2-methylbenzofuran-3-carbonyl)benzoate, 48%, Liquid;

^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, J = 8.3 Hz, 2H), 7.84 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.2 Hz, 1H), 7.26-7.30 (m, 2H), 7.17-7.21 (m, 1H), 3.97 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.2, 166.2, 162.7, 153.6, 143.0, 133.3, 129.7, 128.8, 126.5, 124.5, 123.7, 121.2, 116.7, 110.9, 52.4, 14.8; IR(cm^{-1}): 3060, 2956, 2848, 2358, 1721, 1649, 1571, 1475, 1456, 1436, 1405, 1382, 1282, 1232, 1178, 1105, 1016, 939, 904, 866, 827, 750, 715; HRMS(ESI) m/z calcd for $\text{C}_{18}\text{H}_{15}\text{O}_4^+$ ($\text{M}+\text{H}$) $^+$ 295.09649, found 295.09641.



(2-methylbenzofuran-3-yl)(4-nitrophenyl)methanone, 54%, m. p. = 107-110°C

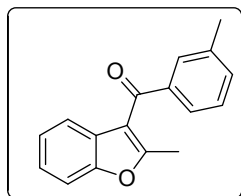
^1H NMR (400 MHz, CDCl_3) δ 8.35 (d, J = 8.2 Hz, 2H), 7.95 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.2 Hz, 1H), 7.27-7.34 (m, 2H), 7.20-7.24 (m, 1H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 189.9, 163.4, 153.6, 149.9, 144.5, 129.8, 128.6, 126.1, 124.8, 124.0, 120.9, 116.3, 111.1, 14.9; IR(cm^{-1}): 3111, 3075, 2921, 2856, 2354, 1652, 1602, 1575, 1521, 1475, 1456, 1405, 1386, 1339, 1285, 1231, 1178, 1127, 1097, 1012, 943, 904, 850, 823, 780, 750, 715, 623; HRMS(ESI) m/z calcd for $\text{C}_{16}\text{H}_{12}\text{NO}_4^+$ ($\text{M}+\text{H}$) $^+$ 282.07608, found 282.07623.



2m

(3-fluorophenyl)(2-methylbenzofuran-3-yl)methanone, 79%, Liquid;

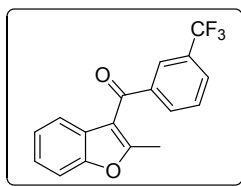
^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, J = 7.6 Hz, 1H), 7.57-7.45 (m, 3H), 7.42 (d, J = 7.8 Hz, 1H), 7.28 (dt, J = 15.9, 5.6 Hz, 3H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.5, 163.9, 162.4, 161.4, 153.7, 141.4 (d, J = 6 Hz), 130.2 (d, J = 7 Hz), 126.6, 124.6, 123.7, 121.1, 119.6, 116.7, 115.9, 110.9, 14.7; ^{19}F NMR (376 MHz, CDCl_3) δ ppm -111.80; IR(cm^{-1}): 3076, 2960, 2933, 2867, 2362, 1656, 1580, 1478, 1451, 1436, 1370, 1262, 1249, 1201, 1174, 1112, 1070, 842, 819, 796, 769; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{12}\text{FO}_2^+$ ($\text{M}+\text{H}$) $^+$ 255.08158, found 255.08183.



2n

(2-methylbenzofuran-3-yl)(m-tolyl)methanone, 64%, Liquid;

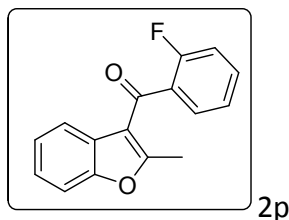
^1H NMR (400 MHz, CDCl_3) δ 7.64 (s, 1H), 7.58-7.59 (m, 1H), 7.42-7.47 (m, 3H), 7.33-7.39 (m, 1H), 7.25-7.29 (m, 1H), 7.17-7.21 (m, 1H), 2.53 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 192.1, 161.7, 153.6, 139.4, 138.3, 133.3, 129.4, 128.3, 126.2, 124.3, 123.6, 121.3, 117.0, 110.8, 21.3, 14.7; IR(cm^{-1}): 3512, 3061, 3023, 2963, 2923, 2362, 1599, 1574, 1492, 1479, 1461, 1378, 1344, 1289, 1261, 1239, 1202, 1144, 1108, 1091, 1031, 940, 867, 817, 752, 714; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{15}\text{O}_2^+$ ($\text{M}+\text{H}$) $^+$ 251.10666, found 251.10625.



2o

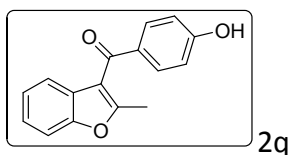
(2-methylbenzofuran-3-yl)(3-(trifluoromethyl)phenyl)methanone, 62%, Liquid;

^1H NMR (400 MHz, CDCl_3) δ 8.09 (s, 1H), 7.99-8.00 (m, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.61-7.65 (m, 1H), 7.47-7.49 (m, 1H), 7.19-7.37 (m, 3H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.2, 162.8, 153.7, 139.9, 132.1, 129.2, 128.9, 126.4, 126.0, 125.3, 124.7, 123.8, 121.0, 116.4, 111.0, 14.8; ^{19}F NMR (376 MHz, CDCl_3) δ ppm -62.78; IR(cm^{-1}): 3074, 2964, 2918, 2366, 2166, 1649, 1610, 1575, 1477, 1454, 1435, 1387, 1328, 1285, 1234, 1176, 1129, 1070, 945, 910, 816, 781, 750, 690, 655; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{12}\text{F}_3\text{O}_2^+$ ($\text{M}+\text{H}$) $^+$ 305.07839, found 305.07855.



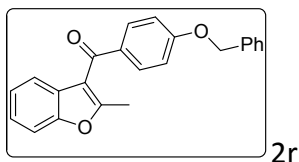
(2-fluorophenyl)(2-methylbenzofuran-3-yl)methanone, 61%, Liquid;

^1H NMR (400 MHz, CDCl_3) δ 7.50-7.58 (m, 2H), 7.43-7.49 (m, 2H), 7.25-7.29 (m, 2H), 7.14-7.23 (m, 2H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 188.0, 163.6, 160.9, 158.4, 153.6, 133.0, 129.8, 126.2, 124.6, 124.5, 123.9, 121.1, 117.8, 116.5 (d, J = 21 Hz), 116.2, 110.8, 14.6; ^{19}F NMR (376 MHz, CDCl_3) δ ppm -114.51; IR(cm^{-1}): 3070, 2964, 2925, 1645, 1610, 1575, 1477, 1450, 1391, 1356, 1282, 1234, 1215, 1180, 1101, 1015, 941, 906, 882, 746, 659, 620; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{12}\text{FO}_2^+$ ($\text{M}+\text{H}$) $^+$ 255.08158, found 255.08180.



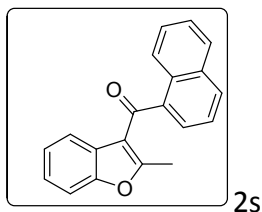
(4-hydroxyphenyl)(2-methylbenzofuran-3-yl)methanone, 53%, CAS 52490-47-8, m. p. = 133-135°C

^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, J = 8.7 Hz, 2H), 7.47 (dd, J = 14.8, 8.0 Hz, 2H), 7.18-7.29 (m, 2H), 6.90-6.94 (m, 2H), 4.72 (s, 1 H, OH), 2.56 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.1, 161.2, 160.5, 153.6, 132.1, 131.5, 127.2, 124.3, 123.5, 121.1, 117.0, 115.3, 110.8, 14.5; IR(cm^{-1}): 2972, 2967, 2167, 1597, 1583, 1513, 1476, 1453, 1389, 1356, 1270, 1245, 1167, 1125, 1098, 1078, 1046, 903, 803, 776, 753.



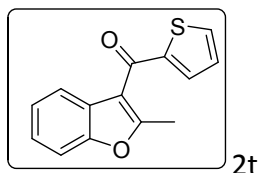
(4-(benzyloxy)phenyl)(2-methylbenzofuran-3-yl)methanone, 40%, m. p. = 93-96°C

^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, J = 8.8 Hz, 2H), 7.36-7.43 (m, 7H), 7.17-7.29 (m, 2H), 7.03-7.06 (m, 2H), 5.15 (s, 2H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.4, 162.6, 160.9, 153.6, 136.2, 132.0, 131.7, 128.7, 128.2, 127.5, 127.2, 124.2, 123.4, 121.1, 117.1, 114.6, 110.8, 70.2, 14.5; IR(cm^{-1}): 3068, 3033, 2921, 2362, 1641, 1598, 1506, 1456, 1382, 1305, 1240, 1167, 1124, 1012, 939, 904, 839, 750, 696; HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{19}\text{O}_3^+$ ($\text{M}+\text{H}$) $^+$ 343.13287, found 343.13297.



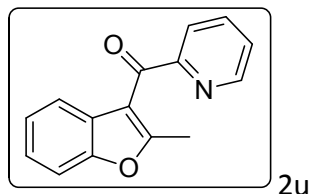
(2-methylbenzofuran-3-yl)(naphthalen-1-yl)methanone, 31%, Liquid;

^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 8.0$ Hz, 1H), 8.02 (d, $J = 8.0$ Hz, 1H), 7.92-7.94 (m, 1H), 7.56-7.58 (m, 1H), 7.44-7.52 (m, 5H), 7.25-7.29 (m, 1H), 7.16-7.20 (m, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.2, 163.8, 153.7, 138.2, 133.8, 131.2, 130.1, 128.4, 127.4, 126.5, 125.2, 124.8, 124.5, 123.9, 121.7, 118.4, 110.7, 14.8; IR(cm^{-1}): 3059, 2961, 2921, 2358, 2338, 2170, 1712, 1637, 1575, 1509, 1473, 1454, 1383, 1364, 1239, 1172, 1102, 1047, 933, 894, 843, 792, 749, 612; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{15}\text{O}_2^+$ ($\text{M}+\text{H}$) $^+$ 287.10666, found 287.10638.



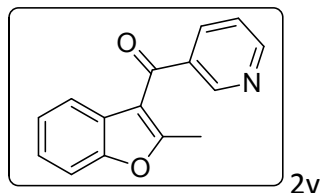
(2-methylbenzofuran-3-yl)(thiophen-2-yl)methanone, 30%, Liquid;

^1H NMR (400 MHz, CDCl_3) δ 7.72-7.74 (m, 1H), 7.66-7.68 (m, 1H), 7.58-7.60 (m, 1H), 7.46-7.48 (m, 1H), 7.21-7.31 (m, 2H), 7.13-7.15 (m, 1H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 183.1, 160.4, 153.7, 144.9, 134.1, 133.9, 127.8, 126.8, 124.4, 123.4, 120.9, 117.1, 110.9, 14.4; IR(cm^{-1}): 3059, 2960, 2921, 2358, 2338, 2170, 1712, 1638, 1575, 1509, 1473, 1454, 1383, 1364, 1278, 1239, 1172, 1102, 1047, 933, 894, 843, 792, 749, 667, 612; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{11}\text{O}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 243.04743, found 243.04733.



(2-methylbenzofuran-3-yl)(pyridin-2-yl)methanone, 37%, CAS 17571-03-8, Liquid;

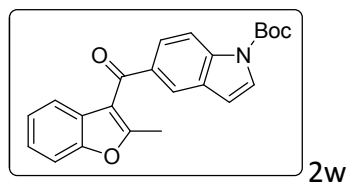
^1H NMR (400 MHz, CDCl_3) δ 8.70-8.72 (m, 1H), 7.92-7.98 (m, 2H), 7.44-7.52 (m, 3H), 7.19-7.29 (m, 2H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.8, 163.6, 156.0, 153.7, 148.9, 137.2, 126.9, 126.5, 124.4, 123.6, 123.5, 121.7, 116.5, 110.8, 15.3; IR (cm^{-1}): 3053, 3010, 2968, 2920, 2852, 2166, 1728, 1651, 1574, 1475, 1454, 1435, 1390, 1282, 1248, 1178, 1101, 1090, 1047, 1020, 993, 941, 908, 879, 852, 810, 746, 702, 669, 615.



(2-methylbenzofuran-3-yl)(pyridin-3-yl)methanone, 30%, Liquid;

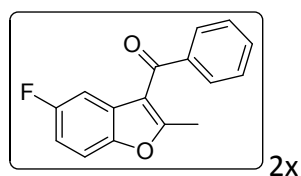
^1H NMR (400 MHz, CDCl_3) δ 9.01 (s, 1H), 8.83 (d, $J = 4.8$ Hz, 1H), 8.11 (t, $J = 4.0$ Hz, 1H), 7.45-7.50 (m, 2H), 7.37-7.39 (m, 1H), 7.27-7.33 (m, 1H), 7.20-7.24 (m, 1H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 189.9, 162.8, 153.7, 153.0, 150.2, 136.3, 134.8, 126.4, 124.7, 124.0, 123.5, 121.0, 116.6, 111.1, 14.8; IR(cm^{-1}): 3074, 2964,

2925, 2361, 2170, 1650, 1610, 1575, 1454, 1387, 1328, 1281, 1234, 1172, 1129, 1066, 945, 906, 816, 780, 746, 699, 675; HRMS (ESI) m/z calcd for $C_{15}H_{12}NO_2^+$ (M+H) $^+$ 238.08626, found 238.08652.



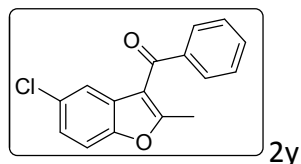
tert-butyl 5-(2-methylbenzofuran-3-carbonyl)-1H-indole-1-carboxylate, 32%, m. p. = 133-135°C

1H NMR (400 MHz, $CDCl_3$) δ 8.22-8.25 (m, 1H), 8.08 (s, 1H), 7.81-7.84 (m, 1H), 7.67-7.68 (m, 1H), 7.47-7.49 (m, 1H), 7.39-7.41 (m, 1H), 7.26-7.29 (m, 1H), 7.16-7.20 (m, 1H), 6.64-6.65 (m, 1H), 2.56 (s, 3H), 1.69 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 161.3, 153.6, 149.4, 137.8, 134.0, 130.3, 127.3, 125.5, 124.2, 123.5, 121.3, 117.3, 114.9, 110.8, 107.8, 84.4, 28.1, 14.6; IR(cm^{-1}): 2981, 2927, 1737, 1641, 1604, 1575, 1535, 1473, 1454, 1437, 1367, 1348, 1334, 1282, 1250, 1230, 1157, 1136, 1109, 1082, 1039, 1022, 954, 922, 876, 854, 833, 787, 768, 748, 723, 673, 606, 590; HRMS (ESI) m/z calcd for $C_{23}H_{22}NO_4^+$ (M+H) $^+$ 376.15433, found 376.15454.



(5-fluoro-2-methylbenzofuran-3-yl)(phenyl)methanone, 60%, m. p. = 60-63°C

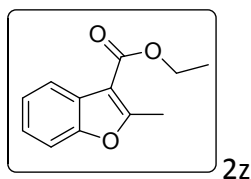
1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.0 Hz, 2H), 7.59-7.61 (m, 1H), 7.47-7.51 (m, 2H), 7.36-7.40 (m, 1H), 7.09-7.12 (m, 1H), 6.96-7.01 (m, 1H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 163.6, 160.8, 158.4, 149.8, 139.1, 132.7, 128.9, 128.6, 127.8, 117.2, 111.4, 107.4 (d, J = 26 Hz), 107.1, 14.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -119.23; IR(cm^{-1}): 3066, 2964, 2921, 2361, 1649, 1599, 1470, 1454, 1387, 1363, 1344, 1262, 1246, 1168, 1117, 1027, 957, 922, 898, 862, 800, 745, 718, 698, 655; HRMS (ESI) m/z calcd for $C_{16}H_{12}FO_2^+$ (M+H) $^+$ 255.08158, found 255.08124.



(5-chloro-2-methylbenzofuran-3-yl)(phenyl)methanone, 61%, Liquid;

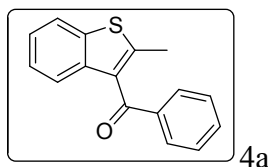
1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.1 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.48-7.52 (m, 2H), 7.44 (s, 1H), 7.36-7.38 (m, 1H), 7.22-7.26 (m, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 163.1, 152.0, 139.0, 132.8, 129.4, 129.0, 128.6, 128.3, 124.7, 121.0, 116.6, 111.8, 14.8; IR(cm^{-1}): 3074, 2964, 2918, 2366, 2166, 1649, 1610, 1575, 1477, 1454, 1435, 1386, 1356, 1285, 1234, 1176, 1129, 1070, 945, 910,

851, 816, 781, 750, 698, 675, 655; HRMS (ESI) m/z calcd for $C_{16}H_{12}ClO_2^+$ ($M+H$)⁺ 271.05203, found 271.05215.



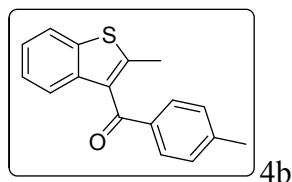
ethyl 2-methylbenzofuran-3-carboxylate, 36%, CAS 40484-97-7, Liquid;

¹H NMR (400 MHz, CDCl₃) δ 7.95-7.97 (m, 1H), 7.42-7.44 (m, 1H), 7.26-7.30 (m, 2H), 4.39-4.44 (q, J = 7.1 Hz, 2H), 2.77 (s, 3H), 1.45 (t, J = 8.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.5, 163.6, 153.6, 126.2, 124.2, 123.7, 121.7, 110.7, 109.0, 60.2, 14.4; IR(cm⁻¹): 2958, 2925, 2850, 1711, 1595, 1479, 1454, 1410, 1383, 1338, 1286, 1234, 1178, 1105, 1084, 1032, 1007, 930, 852, 785, 750, 673, 627.



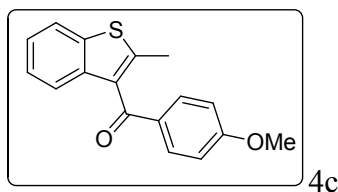
(2-methylbenzo[b]thiophen-3-yl)(phenyl)methanone, 45%, CAS 65628-46-8

m. p. = 75-77°C; ¹H NMR (400 MHz, CDCl₃) δ 7.87-7.82 (m, 2H), 7.77 (td, J = 7.0, 1.4 Hz, 1H), 7.62-7.58 (m, 1H), 7.52-7.44 (m, 3H), 7.27 (dt, J = 5.8, 2.4 Hz, 2H), 2.50 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 193.4, 145.7, 139.0, 138.6, 137.9, 133.2, 132.3, 129.6, 128.6, 124.7, 124.3, 123.2, 121.7, 15.7; IR(cm⁻¹): 3062, 1650, 1596, 1577, 1558, 1527, 1492, 1457, 1448, 1432, 1400, 1378, 1351, 1272, 1230, 1176, 1153, 1064, 1024, 910, 873, 806, 755, 734, 725, 694, 676, 655, 632, 605.



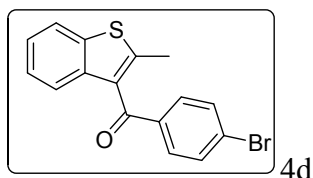
(2-methylbenzo[b]thiophen-3-yl)(p-tolyl)methanone, 40%, Liquid;

¹H NMR (400 MHz, CDCl₃) δ 7.79-7.73 (m, 3H), 7.50 (dd, J = 5.7, 3.1 Hz, 1H), 7.28-7.22 (m, 4H), 2.49 (s, 3H), 2.43 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 193.1, 144.9, 144.2, 139.1, 132.6, 129.9, 129.7, 129.0, 125.4, 124.6, 123.2, 121.7, 21.7, 15.6; IR(cm⁻¹): 3057, 2919, 2359, 2194, 1650, 1604, 1569, 1526, 1509, 1493, 1433, 1407, 1378, 1350, 1312, 1272, 1234, 1208, 1178, 1153, 1134, 1114, 1083, 1063, 1049, 1019, 972, 911, 877, 835, 817, 772, 727, 710, 669, 650, 609; HRMS (ESI) m/z calcd for $C_{17}H_{15}OS^+$ ($M+H$)⁺ 267.08381, found 267.08336.



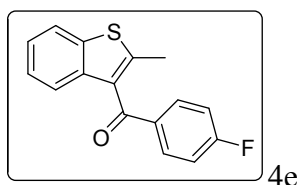
(4-methoxyphenyl)(2-methylbenzo[*b*]thiophen-3-yl)methanone, 36%, CAS 39620-23-0, Liquid;

^1H NMR (400 MHz, CDCl_3) δ 7.86-7.81 (m, 2H), 7.80-7.72 (m, 1H), 7.52- 7.48 (m, 1H), 7.30-7.24 (m, 2H), 6.95-6.91 (m, 2H), 3.87 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 192.1, 163.8, 144.1, 139.1, 137.9, 132.6, 132.1, 131.2, 124.5, 124.1, 123.1, 121.7, 113.8, 55.4, 15.5; IR(cm^{-1}): 3058, 3003, 2959, 2931, 2838, 1911, 1650, 1598, 1573, 1507, 1456, 1433, 1350, 1312, 1259, 1241, 1166, 1134, 1110, 1082, 1064, 1025, 991, 911, 879, 844, 781, 730, 716, 672, 638, 610.



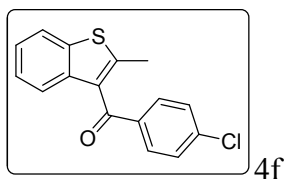
(4-bromophenyl)(2-methylbenzo[*b*]thiophen-3-yl)methanone, 43%, Liquid;

^1H NMR (400 MHz, CDCl_3) δ 7.78 (dd, J = 6.9, 1.5 Hz, 1H), 7.72-7.68 (m, 2H), 7.63-7.59 (m, 2H), 7.47 (dd, J = 7.2, 1.8 Hz, 1H), 7.32-7.26 (m, 2H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 192.1, 146.2, 138.8, 137.9, 137.3, 132.0, 131.8, 131.1, 128.4, 124.8, 124.4, 123.1, 121.8, 15.7; IR(cm^{-1}): 3059, 2956, 2921, 2852, 1914, 1698, 1652, 1587, 1525, 1480, 1457, 1432, 1395, 1349, 1271, 1228, 1174, 1153, 1068, 1010, 992, 910, 875, 789, 731, 686, 640, 625, 601; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{12}\text{BrOS}^+$ ($\text{M}+\text{H}$) $^+$ 330.97867, found 330.97880.



(4-fluorophenyl)(2-methylbenzo[*b*]thiophen-3-yl)methanone, 46%, Liquid;

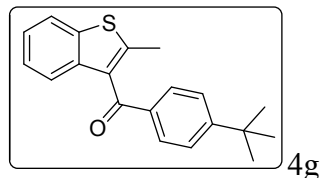
^1H NMR (400 MHz, CDCl_3) δ 7.87 (dp, J = 4.6, 2.5 Hz, 2H), 7.80-7.76 (m, 1H), 7.48-7.45 (m, 1H), 7.32-7.26 (m, 2H), 7.16-7.11 (m, 2H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.7, 165.9 (d, J = 254 Hz), 145.6, 138.9, 137.9, 134.9, 132.0, 121.8, 115.9, 115.8 (d, J = 22 Hz), 115.7, 115.4, 15.6; ^{19}F NMR (376 MHz, CDCl_3) δ -93.75; IR(cm^{-1}): 3061, 2960, 2922, 2853, 1911, 1650, 1588, 1558, 1457, 1433, 1408, 1351, 1294, 1272, 1175, 1153, 1095, 1063, 1013, 993, 912, 879, 849, 815, 752, 730, 713, 672, 632, 605; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{12}\text{FOS}^+$ ($\text{M}+\text{H}$) $^+$ 271.05874, found 271.05884.



(4-chlorophenyl)(2-methylbenzo[*b*]thiophen-3-yl)methanone, 44%, Liquid;

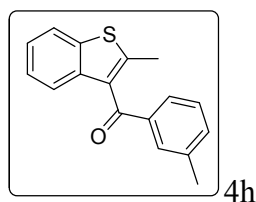
^1H NMR (400 MHz, CDCl_3) δ 7.81-7.76 (m, 3H), 7.45 (ddd, J = 11.0, 6.8, 1.6 Hz, 3H), 7.29 (td, J = 7.3, 1.4 Hz, 2H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 192.0,

146.2, 139.7, 138.8, 137.9, 136.9, 131.8, 131.0, 129.0, 124.8, 124.4, 123.1, 121.8, 15.7; IR(cm^{-1}): 3059, 2957, 2922, 2853, 1914, 1705, 1650, 1586, 1524, 1485, 1457, 1432, 1398, 1349, 1271, 1228, 1172, 1153, 1090, 1063, 1013, 993, 910, 877, 842, 780, 747, 733, 693, 642, 627, 602; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{12}\text{ClOS}^+$ ($\text{M}+\text{H}$) $^+$ 287.02919, found 287.02936.



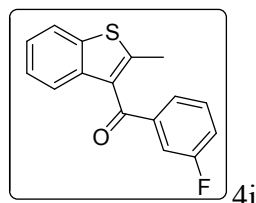
(4-(tert-butyl)phenyl)(2-methylbenzo[b]thiophen-3-yl)methanone, 31%, m. p. = 130-133°C;

^1H NMR (400 MHz, CDCl_3) δ 7.80-7.75 (m, 3H), 7.52 (dd, $J = 6.6, 2.3$ Hz, 1H), 7.49-7.45 (m, 2H), 7.27 (ddd, $J = 8.4, 5.1, 2.8$ Hz, 2H), 2.49 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.1, 157.2, 144.7, 139.1, 137.9, 135.8, 132.6, 129.7, 125.6, 124.6, 124.2, 123.2, 121.7, 35.1, 31.0, 15.6; IR(cm^{-1}): 3059, 2962, 2867, 1707, 1651, 1603, 1562, 1530, 1458, 1433, 1406, 1345, 1313, 1270, 1235, 1188, 1173, 1154, 1110, 1064, 1023, 992, 912, 880, 849, 835, 788, 777, 752, 708, 644, 608; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{21}\text{OS}^+$ ($\text{M}+\text{H}$) $^+$ 309.13076, found 309.13086.



(2-methylbenzo[b]thiophen-3-yl)(m-tolyl)methanone, 35%, Liquid;

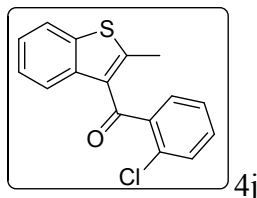
^1H NMR (400 MHz, CDCl_3) δ 7.79-7.75 (m, 1H), 7.69 (s, 1H), 7.59 (d, $J = 7.6$ Hz, 1H), 7.54-7.50 (m, 1H), 7.40 (d, $J = 7.5$ Hz, 1H), 7.33 (t, $J = 6.3$ Hz, 1H), 7.30-7.24 (m, 2H), 2.48 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.6, 145.4, 139.1, 138.6, 138.5, 137.9, 134.0, 132.4, 129.8, 128.4, 127.1, 124.6, 124.2, 123.2, 121.6, 21.2, 15.7; IR(cm^{-1}): 3058, 3025, 2952, 2919, 2859, 1947, 1907, 1874, 1650, 1600, 1583, 1558, 1525, 1482, 1455, 1432, 1378, 1349, 1272, 1251, 1186, 1164, 1153, 1091, 1064, 1025, 1000, 935, 910, 894, 852, 831, 808, 767, 744, 727, 688, 674, 657, 636, 611; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{15}\text{OS}^+$ ($\text{M}+\text{H}$) $^+$ 267.08381, found 267.08368.



(3-fluorophenyl)(2-methylbenzo[b]thiophen-3-yl)methanone, 38%, Liquid;

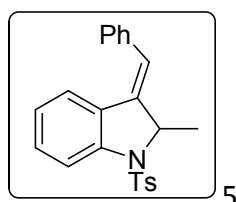
^1H NMR (400 MHz, CDCl_3) δ 7.78 (dd, $J = 6.8, 1.7$ Hz, 1H), 7.60-7.53 (m, 2H), 7.50 (dd, $J = 6.9, 1.8$ Hz, 1H), 7.43 (dt, $J = 6.7, 3.4$ Hz, 1H), 7.29 (ddd, $J = 8.1, 5.0, 1.6$ Hz, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.9, 162.8 (d, $J = 247$ Hz), 146.5,

140.8, 140.7, 138.7, 137.8, 130.3, 124.4, 123.1, 121.7, 120.2(d, $J = 22$ Hz), 116.1 (d, $J = 22$ Hz), 15.8; ^{19}F NMR (376 MHz, CDCl_3) δ ppm -111.68; IR(cm^{-1}): 3065, 2958, 2923, 2854, 1650, 1607, 1585, 1523, 1480, 1457, 1434, 1351, 1309, 1270, 1251, 1205, 1184, 1154, 1081, 1063, 1025, 1001, 972, 942, 888, 842, 829, 801, 772, 749, 727, 708, 681, 654, 637, 616; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{12}\text{FOS}^+$ ($\text{M}+\text{H}$) $^+$ 271.05874, found 271.05856.



(2-chlorophenyl)(2-methylbenzo[*b*]thiophen-3-yl)methanone, 33%, m. p. = 107-109°C;

^1H NMR (400 MHz, CDCl_3) δ 7.85-7.80 (m, 1H), 7.77-7.71 (m, 1H), 7.47-7.42 (m, 3H), 7.39-7.35 (m, 1H), 7.31 (ddd, $J = 7.0, 4.0, 1.7$ Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.6, 151.6, 140.4, 138.6, 137.1, 131.7, 131.6, 131.5, 130.5, 129.4, 127.2, 125.2, 124.5, 123.6, 121.5, 16.0; IR(cm^{-1}): 3063, 2961, 2924, 1958, 1922, 1867, 1828, 1791, 1747, 1729, 1688, 1681, 1636, 1589, 1567, 1557, 1506, 1489, 1456, 1430, 1353, 1266, 1223, 1171, 1151, 1100, 1067, 1053, 1026, 998, 949, 878, 859, 804, 781, 761, 748, 730, 703, 658, 629; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{12}\text{ClOS}^+$ ($\text{M}+\text{H}$) $^+$ 287.02919, found 287.02905.



(*E*)-3-benzylidene-2-methyl-1-tosylindoline, 72%, Liquid;

^1H NMR (400 MHz, CDCl_3) δ 7.71-7.73 (m, 1H), 7.59-7.61 (m, 2H), 7.25-7.32 (m, 4H), 7.18-7.22 (m, 4H), 7.05-7.07 (m, 1H), 6.76-6.80 (m, 1H), 6.36 (s, 1H), 4.69-4.75 (m, 1H), 2.35 (s, 3H), 1.66 (d, $J = 8.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.4, 143.9, 139.8, 136.6, 134.6, 128.5, 128.1, 127.2, 124.2, 123.8, 121.8, 116.9, 63.7, 24.7, 21.5; IR(cm^{-1}): 3061, 3027, 2973, 2927, 1917, 1720, 1643, 1596, 1493, 1473, 1455, 1355, 1305, 1270, 1236, 1168, 1090, 967, 921, 843, 812, 762, 735, 700, 667, 634, 618; HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{22}\text{NO}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 376.13658, found 376.13638.

