

## Electronic Supplementary Information (ESI)

### One-pot Transition-metal Free Transamidation to Sterically Hindered Amides

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## Experimental details and materials

The transamidation reactions were conducted in sealed tube under the protection of a nitrogen atmosphere.

All carboxylic amides and amines were purchased from Energy Chemicals. All dry solvents were purchased from J&K Company. DMAP, Boc<sub>2</sub>O, NaF, KF, CsF, and other bases were purchased from Energy Chemicals. Flash chromatography was performed using 200-300 mesh silica gel.

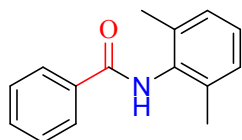
All amides are known compounds. <sup>1</sup>H and <sup>13</sup>C and <sup>19</sup>F NMR data were recorded with Varian (400 MHz) spectrometers in CDCl<sub>3</sub> and DMSO with tetramethylsilane as an internal standard. <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra were recorded at 400 MHz, 101 MHz and 376 MHz at 25 °C in CDCl<sub>3</sub> and DMSO, respectively. Spectral data are reported as follows: chemical shift (δ, ppm); multiplicity (s-singlet, d-doublet, t-triplet, q-quadruplet, m-multiplet); coupling constants (J, Hz) and number of protons. MS were recorded using ESI and HRMS were recorded using EI at 70 eV. <sup>1</sup>H NMR, <sup>13</sup>C NMR, MS and HRMS data are reported for all new compounds.

## Experimental Procedures

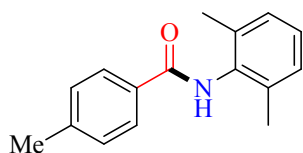
### General transamidation procedure for Amide from Amides

General procedure for the synthesis of 3: benzoic amide (121 mg, 1.0 mmol, 1.0 equiv) was dissolved in CH<sub>3</sub>CN (1.5 mL), then DMAP (12.2 mg, 0.1 mmol, 0.1 equiv) and Boc<sub>2</sub>O (436 mg, 2.0 mmol, 1.0 equiv) were added into the sealed vessel. After stirring at room temperature for 8 h, CsF (30.2 mg, 0.2 mmol, 0.2 equiv) and 2,6-dimethylaniline (121 mg, 1.0 mmol, 1.0 equiv) were added into the sealed vessel. After stirring at 100°C for 10 h, the reaction mixture was concentrated under reduced pressure. The resulting crude residue was purified by flash chromatography (10:1 Petroleum Ether : EtOAc) to yield amine 3aa.

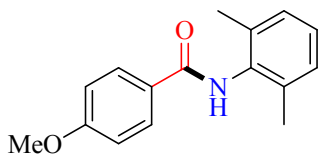
### Characterization Data



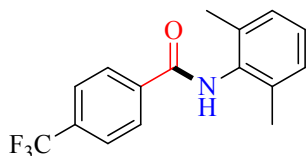
**N-(2,6-dimethylphenyl) benzamide (3a).**<sup>1</sup> Following general procedure, 3a was isolated as a white solid (193mg, 86%), m. p. 162-164 °C. FT-IR (cm<sup>-1</sup>) 3273, 2920, 2856, 2418, 1930, 1643, 1579, 1520, 1473, 1301, 1212, 1155, 1076, 1032, 768, 709. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 7.2 Hz, 2H), 7.64 (s, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.16 – 7.07 (m, 3H), 2.24 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.00, 135.62, 134.38, 133.98, 131.70, 128.66, 128.20, 127.34, 127.27, 18.44.



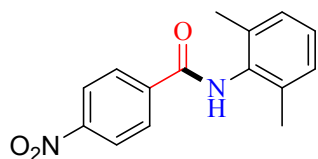
**N-(2,6-dimethylphenyl)-4-methylbenzamide (3b).**<sup>2</sup> Following general procedure, 3b was isolated as a white solid (201mg, 84%), m. p. 162-164 °C. FT-IR (cm<sup>-1</sup>) 3266, 3041, 2966, 2920, 2856, 1639, 1529, 1495, 1295, 1121, 837, 767. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.23 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 6.8 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 2.17 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.18, 141.95, 135.84, 134.48, 131.50, 129.20, 128.10, 127.51, 127.12, 21.54, 18.40.



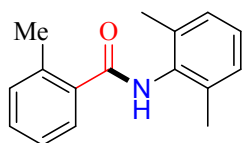
**N-(2,6-dimethylphenyl)-4-methoxybenzamide(3c).**<sup>2</sup> Following general procedure, 3c was isolated as a white solid (222mg, 87%), m. p. 168-170 °C. FT-IR (cm<sup>-1</sup>) 3255, 3012, 2956, 2838, 1639, 1607, 1530, 1499, 1306, 1259, 1178, 1032, 845, 771. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.58 (s, 1H), 7.17 – 6.98 (m, 3H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 2.22 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.51, 162.39, 135.68, 134.23, 129.16, 128.21, 127.24, 126.63, 113.86, 55.48, 18.48.



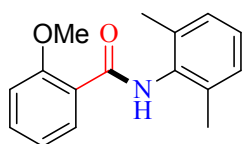
**N-(2,6-dimethylphenyl)-4-(trifluoromethyl) benzamide (3d).**<sup>2</sup> Following general procedure, 3d was isolated as a white solid (237mg, 81%), m. p. 205-207 °C. FT-IR (cm<sup>-1</sup>) 3281, 2994, 2956, 2928, 2858, 2428, 1937, 1651, 1581, 1529, 1500, 1324, 1132, 1066, 858, 775. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.81 (s, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.17 – 7.12 (m, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 2.21 (s, 6H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -63.52. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.11, 137.27, 135.58, 133.74, 133.115 (q, *J*<sub>C-F</sub> = 32.3 Hz), 128.17, 127.84, 127.73, 127.57, 125.44 (q, *J*<sub>C-F</sub> = 3.5 Hz), 119.59 (q, *J*<sub>C-F</sub> = 274.3 Hz), 18.21.



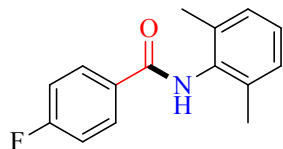
**N-(2,6-dimethylphenyl)-4-nitrobenzamide(3e).**<sup>3</sup> Following general procedure, 3e was isolated as a white solid (221mg, 82%), m. p. 194-196 °C. FT-IR (cm<sup>-1</sup>) 3237, 3046, 2092, 2858, 2449, 1929, 1648, 1601, 1527, 1349, 1308, 1111, 858, 767, 709. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.27 (d, *J* = 8.8 Hz, 2H), 8.01 (d, *J* = 8.8 Hz, 2H), 7.73 (s, 1H), 7.17 (dd, *J* = 8.8, 6.2 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 2H), 2.24 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.12, 149.65, 139.74, 135.46, 133.24, 128.39, 127.91, 123.85, 77.33, 77.01, 76.69, 18.37.



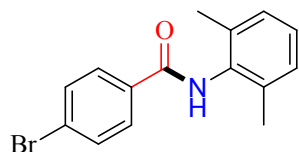
**N-(2,6-dimethylphenyl)-2-methylbenzamide(3f).**<sup>2</sup> Following general procedure, 3f was isolated as a white solid (179mg, 75%), m. p. 138-140 °C. FT-IR (cm<sup>-1</sup>) 3279, 3024, 2963, 2922, 2855, 1937, 1648, 1593, 1510, 1380, 1305, 1101, 775, 742, 673. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.56 (d, *J* = 7.4 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.28 (dd, *J* = 7.4, 3.2 Hz, 2H), 7.17 – 7.10 (m, 3H), 7.07 (s, 1H), 2.54 (s, 3H), 2.33 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.56, 136.46, 136.32, 135.57, 133.74, 131.12, 130.03, 128.23, 127.40, 126.74, 125.74, 19.86, 18.60.



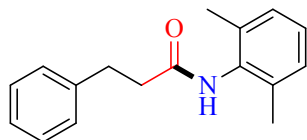
**N-(2,6-dimethylphenyl)-2-methoxybenzamide(3g).**<sup>3</sup> Following general procedure, 3g was isolated as a colorless liquid (191mg, 75%). FT-IR (cm<sup>-1</sup>) 3361, 3018, 2946, 2848, 2029, 1931, 1664, 1598, 1512, 1480, 1297, 1240, 1164, 1019, 760. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.20 (s, 1H), 8.30 (dd, *J* = 7.8, 2.2 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.16 – 7.10 (m, 4H), 7.06 (d, *J* = 8.4 Hz, 1H), 4.02 (s, 3H), 2.32 (s, 6H).



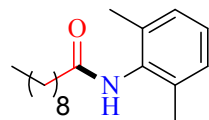
**N-(2,6-dimethylphenyl)-4-fluorobenzamide (3h).**<sup>4</sup> Following general procedure, 3h was isolated as a white solid (194mg, 80%), m. p. 179-181 °C. FT-IR (cm<sup>-1</sup>) 3310, 3069, 2919, 2855, 2420, 1922, 1528, 1494, 1283, 1236, 1158, 849, 766, 627, 532. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.09 (s, 1H), 7.78 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.14 – 7.09 (m, 1H), 7.04 (d, *J* = 7.2 Hz, 2H), 6.98 (t, *J* = 8.6 Hz, 2H), 2.14 (s, 6H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -108.05 – -108.16 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.10, 164.84 (d, *J*<sub>C-F</sub> = 168 Hz), 135.66, 133.98, 130.43, 130.41, 129.69 (d, *J*<sub>C-F</sub> = 6.1 Hz), 129.66, 128.24, 127.46, 115.62 (d, *J*<sub>C-F</sub> = 14.1 Hz), 18.38.



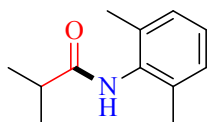
**4-bromo-N-(2,6-dimethylphenyl) benzamide (3i).**<sup>5</sup> Following general procedure, 3i was isolated as a white solid (237mg, 78%), m. p. 190-192 °C. FT-IR (cm<sup>-1</sup>) 3265, 3037, 2972, 2918, 2424, 1643, 1591, 1523, 1480, 1311, 1120, 843, 770, 533. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.77 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.17 – 7.03 (m, 3H), 2.18 (s, 6H).



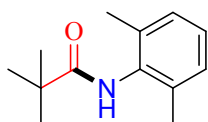
**N-(2,6-dimethylphenyl)-3-phenylpropanamide (3j).**<sup>6</sup> Following general procedure, 3j was isolated as a white solid (192mg, 76%), m. p. 143-145 °C. FT-IR (cm<sup>-1</sup>) 3433, 3227, 3026, 2923, 1649, 1535, 1427, 1139, 702, 526. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.31 – 7.26 (m, 2H), 7.22 (d, *J* = 7.2 Hz, 3H), 7.07 – 7.02 (m, 2H), 6.98 (d, *J* = 7.6 Hz, 2H), 3.02 (t, *J* = 7.4 Hz, 2H), 2.66 (t, *J* = 7.4 Hz, 2H), 2.03 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 171.06, 140.78, 135.41, 134.04, 128.47, 128.46, 127.94, 127.05, 126.19, 37.67, 31.71, 18.21.



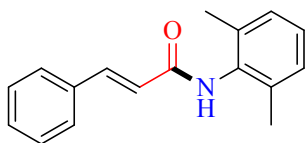
**N-(2,6-dimethylphenyl)decanamide(3k).**<sup>2</sup> Following general procedure, 3k was isolated as a white solid (156mg, 57%), m. p. 84-86 °C. FT-IR (cm<sup>-1</sup>) 3277, 2958, 2921, 2852, 1643, 1596, 1519, 1468, 1223, 964, 765, 714, 530. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.46 (s, 1H), 7.04– 6.90 (m, 3H), 2.26 (t, *J* = 7.6 Hz, 2H), 2.09 (s, 6H), 1.66 – 1.58 (m, 2H), 1.26 (s, 12H), 0.89 (t, *J* = 6.6 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 172.07, 135.36, 134.14, 127.91, 126.93, 36.44, 31.89, 29.52, 29.41, 29.40, 29.30, 26.08, 22.69, 18.34, 14.12.



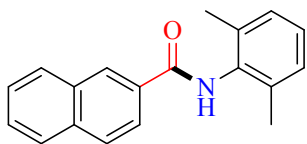
**N-(2,6-dimethylphenyl) isobutyramide(3l).**<sup>7</sup> Following general procedure, 3l was isolated as a white solid (97mg, 51%), m. p. 128-130 °C. FT-IR (cm<sup>-1</sup>) 3269, 2036, 2966, 2926, 2872, 2739, 1655, 1526, 1464, 1378, 1226, 1143, 1100, 763, 700, 534. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.51 (s, 1H), 6.98 (dd, *J* = 8.8, 6.4 Hz, 1H), 6.93 (d, *J* = 6.8 Hz, 2H), 2.57 – 2.44 (m, 1H), 2.05 (s, 6H), 1.24 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 175.66, 135.43, 134.03, 127.86, 126.82, 77.43, 77.11, 76.79, 35.40, 19.74, 18.16.



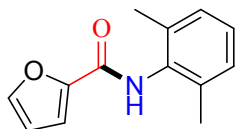
**N-(2,6-dimethylphenyl) pivalamide (3m).**<sup>7</sup> Following general procedure, 3m was isolated as a white solid (88mg, 43%), m. p. 141-143 °C. FT-IR (cm<sup>-1</sup>) 3272, 3023, 2962, 2927, 2871, 2400, 1648, 1514, 1476, 1369, 1294, 1225, 1142, 765, 640, 533. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.14 (s, 1H), 7.05 – 6.95 (m, 3H), 2.09 (s, 6H), 1.25 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.59, 135.46, 134.13, 127.99, 126.92, 39.16, 27.69, 18.18.



**N-(2,6-dimethylphenyl) cinnamamide. (3n)**<sup>8</sup> Following general procedure, 3n was isolated as a white solid (173mg, 69%), m. p. 176-178 °C. FT-IR (cm<sup>-1</sup>) 3244, 3022, 2960, 2920, 2854, 2424, 1938, 1655, 1623, 1525, 1469, 1336, 1222, 1179, 1143, 973, 760, 536. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.75 (dd, *J* = 38.4, 15.6 Hz, 1H), 7.53 – 7.35 (m, 4H), 7.33 – 7.27 (m, 2H), 7.23 – 7.03 (m, 3H), 6.43 (m, 1H), 2.25 (d, *J* = 13.6 Hz, 6H) (cis/trans isomer mixture, cis : trans = 1 : 3.6).

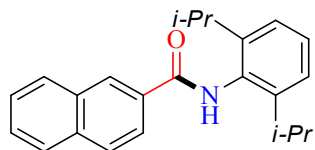


**N-(2,6-dimethylphenyl)-2-naphthamide (3o).**<sup>9</sup> Following general procedure, 3o was isolated as a white solid (225mg, 82%), m. p. 160-162 °C. FT-IR (cm<sup>-1</sup>) 3268, 3054, 3017, 2921, 2855, 1913, 1854, 1641, 1510, 1467, 1298, 1131, 764, 534, 479. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.44 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.90 (dd, *J* = 8.0, 4.0 Hz, 3H), 7.74 (s, 1H), 7.61 – 7.52 (m, 2H), 7.17 – 7.09 (m, 3H), 2.29 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.15, 135.66, 134.89, 134.08, 132.68, 131.68, 129.04, 128.62, 128.29, 127.83, 127.80, 127.42, 126.84, 123.86, 18.54.

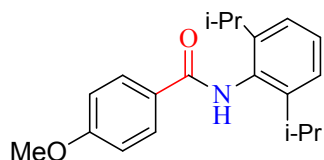


**N-(2,6-dimethylphenyl) furan-2-carboxamide(3p).**<sup>2</sup>Following general procedure, 3p was isolated as a white solid (175mg, 81%), m. p. 125-127 °C. FT-IR (cm<sup>-1</sup>) 3251, 3121, 3019, 2976,

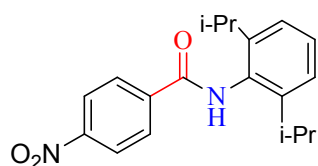
2948, 2920, 2856, 2813, 1930, 1853, 1647, 1587, 1513, 1471, 1304, 765. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.67 (s, 1H), 7.52 (s, 1H), 7.20 (d, *J* = 2.4 Hz, 1H), 7.17 – 7.09 (m, 3H), 6.55 (s, 1H), 2.28 (s, 6H).



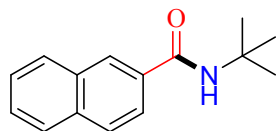
**N-(2,6-diisopropylphenyl)-2-naphthamide(4a).**<sup>9</sup> Following general procedure, 4a was isolated as a white solid (261mg, 79%). FT-IR (cm<sup>-1</sup>) 3344, 2055, 2964, 2931, 2870, 2446, 1943, 1648, 1505, 1468, 1291, 1139, 775, 760, 540. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.45 (s, 1H), 8.00 – 7.86 (m, 4H), 7.64 (s, 1H), 7.61 – 7.52 (m, 2H), 7.38 – 7.33 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 2H), 3.26 – 3.12 (m, 2H), 1.46 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.13, 146.51, 134.89, 132.72, 131.67, 131.44, 129.08, 128.68, 128.55, 127.85, 127.80, 126.86, 123.78, 123.61, 28.99, 23.71. [HRMS] calcd for C<sub>23</sub>H<sub>25</sub>NO [M]=332.20089, found [M<sup>+</sup>] =322.20041



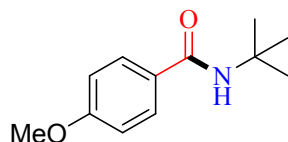
**N-(2,6-diisopropylphenyl)- 4-methoxybenzamide (4b).** Following general procedure, 4a was isolated as a white solid (248mg, 80%). FT-IR (cm<sup>-1</sup>) 3329, 3062, 2962, 2869, 1640, 1606, 1488, 1256, 1177, 1142, 1033, 844, 532. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.45 (s, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H), 3.16 (hept, *J* = 6.9 Hz, 2H), 1.22 (d, *J* = 6.9 Hz, 12H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 166.43, 162.41, 146.49, 131.49, 129.09, 128.35, 126.73, 123.51, 113.94, 77.27, 77.06, 76.85, 55.50, 28.89, 23.66. [HRMS] calcd for C<sub>20</sub>H<sub>25</sub>NO<sub>2</sub> [M]=312.19580, found [M<sup>+</sup>] =312.19543.



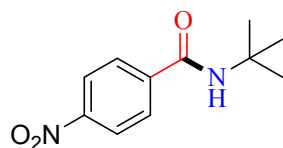
**N-(2,6-diisopropylphenyl)- 4-nitrobenzamide (4c).** Following general procedure, 4a was isolated as a white solid (267mg, 82%). FT-IR (cm<sup>-1</sup>) 3305, 3105, 3078, 2964, 2929, 2870, 1650, 1600, 1522, 1482, 1342, 1286, 1140, 925, 854, 829, 718, 533. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.22 (d, *J* = 8.6 Hz, 2H), 7.99 (d, *J* = 8.6 Hz, 2H), 7.85 (s, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 10.3 Hz, 2H), 3.18 – 2.99 (m, 2H), 1.21 (d, *J* = 6.8 Hz, 12H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 165.10, 149.72, 146.31, 139.70, 130.60, 129.04, 128.43, 123.96, 123.79, 29.01, 23.62. [HRMS] calcd for C<sub>19</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub> [M]=327.17031, found [M] =327.16977.



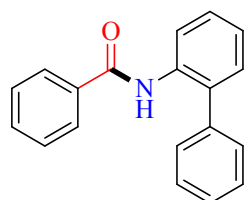
***N*-(*tert*-butyl)-2-naphthamide(4d).** <sup>11</sup>Following general procedure, 4c was isolated as a white solid (136mg, 60%), m. p. 156-158 °C. FT-IR (cm<sup>-1</sup>) 3334, 3054, 2980, 2963, 2932, 1637, 1542, 1454, 1400, 1320, 1222, 901, 834, 780, 632. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.19 (s, 1H), 7.83 (d, *J* = 6.8 Hz, 1H), 7.79 (d, *J* = 9.2 Hz, 3H), 7.52 – 7.42 (m, 2H), 6.26 (s, 1H), 1.50 (s, 9H).



***N*-(*tert*-butyl)- 4-methoxybenzamide (4e).** Following general procedure, 4c was isolated as a white solid (130mg, 62%), m. p. 113-115 °C. FT-IR (cm<sup>-1</sup>) 3329, 3062, 2962, 2869, 1640, 1606, 1488, 1256, 1177, 1142, 1033, 844, 532. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.69 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.94 (s, 1H), 3.83 (s, 1H), 1.47 (s, 9H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 166.47, 161.84, 128.46, 128.19, 113.59, 55.37, 51.45, 28.93. [HRMS] calcd for C<sub>12</sub>H<sub>17</sub>NO<sub>2</sub> [M] = 208.13320, found [M<sup>+</sup>] = 208.13301



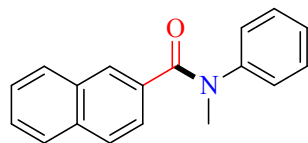
***N*-(*tert*-butyl)- 4-nitrobenzamide (4f).** Following general procedure, 4c was isolated as a white solid (142mg, 64%), m. p. 161-163 °C. FT-IR (cm<sup>-1</sup>) 3305, 3105, 3078, 2964, 2929, 2870, 1650, 1600, 1522, 1482, 1342, 1286, 1140, 925, 854, 829, 718, 533. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.25 (d, *J* = 8.8 Hz, 2H), 7.88 (d, *J* = 8.8 Hz, 2H), 6.08 (s, 1H), 1.50 (s, 9H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 164.90, 149.31, 141.54, 127.96, 123.72, 52.30, 28.74. [HRMS] calcd for C<sub>19</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub> [M] = 223.10771, found [M<sup>+</sup>] = 223.10756



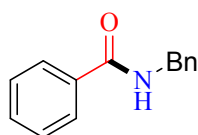
***N*-([1,1'-biphenyl]-2-yl) benzamide (4g).** <sup>12</sup>Following general procedure, 4d was isolated as a white solid (177mg, 65%), m. p. 87-89 °C. FT-IR (cm<sup>-1</sup>) 3423, 3262, 3055, 1951, 1811, 1683, 1644, 1579, 1524, 1487, 1305, 1151, 918, 747, 697. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 165.01, 138.09,



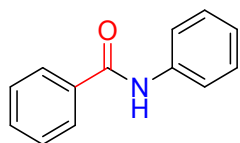
134.95, 134.80, 132.40, 131.76, 130.03, 129.39, 129.26, 128.77, 128.63, 128.22, 126.84, 124.41, 121.20.



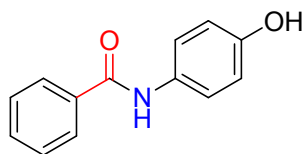
**N-methyl-N-phenyl-2-naphthamide(4h).**<sup>10</sup> Following general procedure, 4b was isolated as a white solid (180mg, 69%), m. p. 108-110 °C. FT-IR (cm<sup>-1</sup>) 3055, 2924, 2855, 1944, 1726, 1635, 1592, 1493, 1471, 1372, 1297, 1129, 827, 762, 696. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89 (s, 1H), 7.71 (t, *J* = 5.8 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.44 (p, *J* = 7.0 Hz, 2H), 7.31 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.12 – 7.05 (m, 3H), 3.55 (s, 3H).



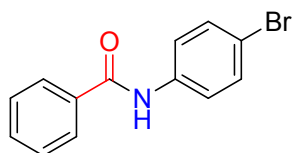
**N-benzylbenzamide(4i).**<sup>13</sup> Following general procedure, 4e was isolated as a white solid (158mg, 75%), m. p. 103-105 °C. FT-IR (cm<sup>-1</sup>) 3290, 3062, 1639, 1604, 1551, 1490, 1415, 1324, 1316, 1058, 1030, 728, 694. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.37 – 7.25 (m, 5H), 6.65 (s, 1H), 7.37 – 7.25 (m, 5H), 6.65 (s, 1H), 4.62 (d, *J* = 5.2 Hz, 2H). <sup>13</sup>C NMR (101 MHz, DMSO) δ 167.50, 138.29, 134.33, 131.49, 128.70, 128.52, 127.81, 127.48, 127.04, 44.01.



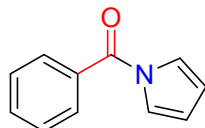
**N-phenylbenzamide(4j).**<sup>14</sup> Following general procedure, 4f was isolated as a white solid (171mg, 87%), m. p. 160-162 °C. FT-IR (cm<sup>-1</sup>) 3345, 3055, 3038, 3027, 1657, 1601, 1579, 1538, 1449, 1440, 1323, 1262, 760, 716, 692. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H).



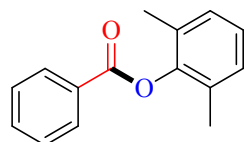
**N-(4-hydroxyphenyl) benzamide(4k).**<sup>15</sup> Following general procedure, 4g was isolated as a white solid (mg, 65%). FT-IR (cm<sup>-1</sup>) 3382, 3324, 3025, 1647, 1542, 1200, 1154, 707, 528. <sup>1</sup>H NMR (400 MHz, DMSO) δ 10.07 (s, 1H), 9.86 (s, 1H), 8.10 (d, *J* = 7.2 Hz, 2H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.61 – 7.52 (m, 4H), 7.21 (d, *J* = 8.8 Hz, 2H).



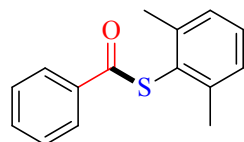
**N-(4-bromophenyl) benzamide. (4l)** <sup>16</sup>Following general procedure, 4h was isolated as a white solid (234mg, 85%), m. p. 204-206 °C. FT-IR (cm<sup>-1</sup>) 3331, 3092, 2979, 1900, 1772, 1647, 1592, 1519, 1492, 1390, 1310, 1143, 820, 716, 652, 507. <sup>1</sup>H NMR (400 MHz, DMSO) δ 10.34 (s, 1H), 7.92 (d, *J* = 7.2 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.60 – 7.43 (m, 5H). <sup>13</sup>C NMR (101 MHz, DMSO) δ 166.14, 139.07, 135.20, 132.17, 131.90, 128.88, 128.17, 122.68, 115.81.



**phenyl(1H-pyrrol-1-yl) methanone (4m).** <sup>17</sup>Following general procedure, 4i was isolated as colorless liquid (128mg, 75%). FT-IR (cm<sup>-1</sup>) 147, 3062, 1697, 1600, 1467, 1401, 1332, 1086, 879, 744, 721. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.72, 133.26, 132.30, 129.52, 128.51, 121.32, 113.19.



**2,6-dimethylphenyl benzoate (5a).** <sup>18</sup> Following general procedure, 5a was isolated as colorless liquid (171mg, 76%). FT-IR (cm<sup>-1</sup>) 3062, 3035, 2926, 2858, 1734, 1599, 1475, 1450, 1264, 1175, 1088, 1064, 1024, 863, 771, 708. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.30 (d, *J* = 7.2 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.21 – 7.10 (m, 3H), 2.25 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.46, 148.51, 133.71, 130.46, 130.28, 129.43, 128.78, 128.75, 126.04, 16.50.



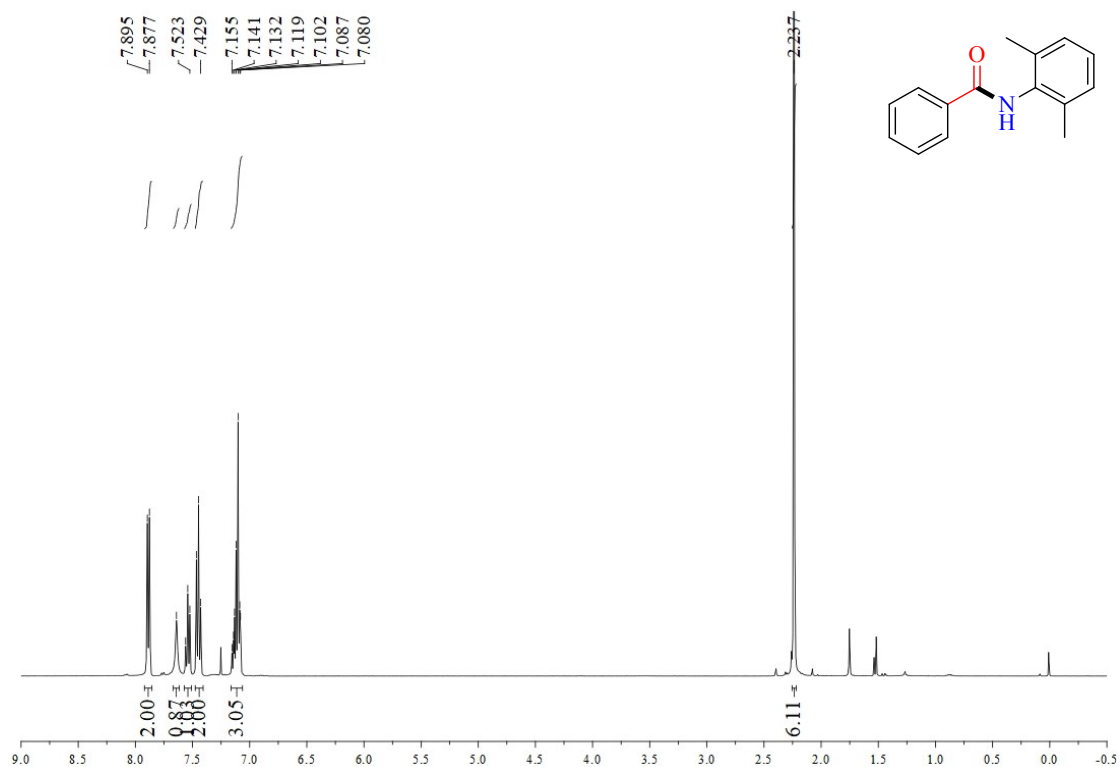
**S-(2,6-dimethylphenyl) benzothioate(5b).** <sup>19</sup> Following general procedure, 5b was isolated as colorless liquid (169mg, 70%). FT-IR (cm<sup>-1</sup>) 3055, 3030, 2920, 2840, 1720, 1620, 1455, 1430, 1262, 1200, 1024, 863. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.11 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.29 (dd, *J* = 8.0, 6.8 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 2H), 2.43 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 189.10, 143.32, 137.09, 133.58, 130.02, 128.81, 128.44, 127.66, 126.75, 21.89.

## Reference

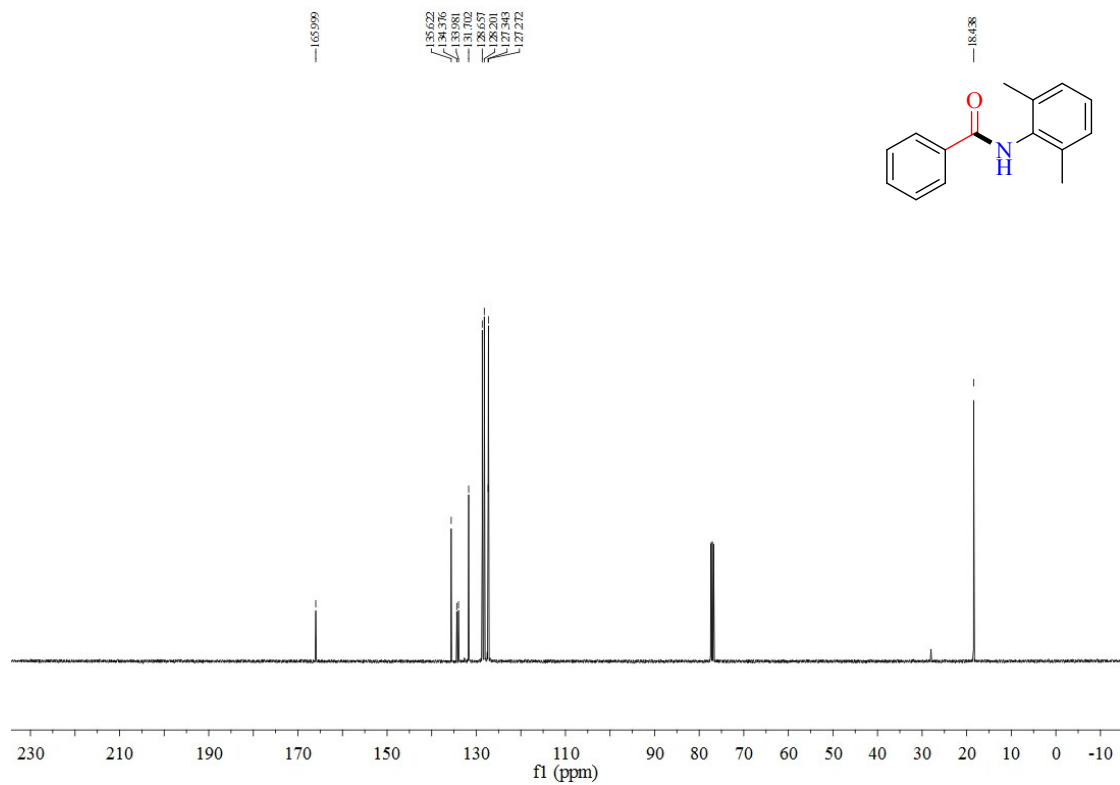
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# $^1\text{H}$ , $^{13}\text{C}$ , $^{19}\text{F}$ NMR Spectra

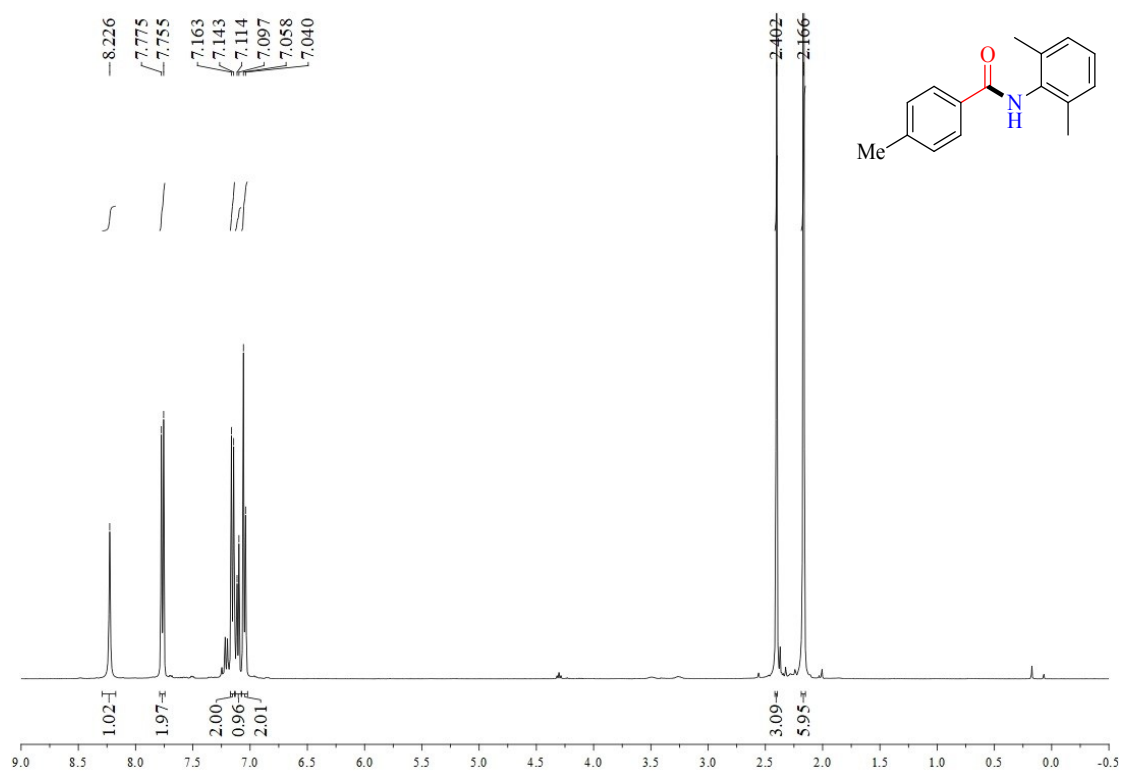
N-(2,6-dimethylphenyl) benzamide (3a).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



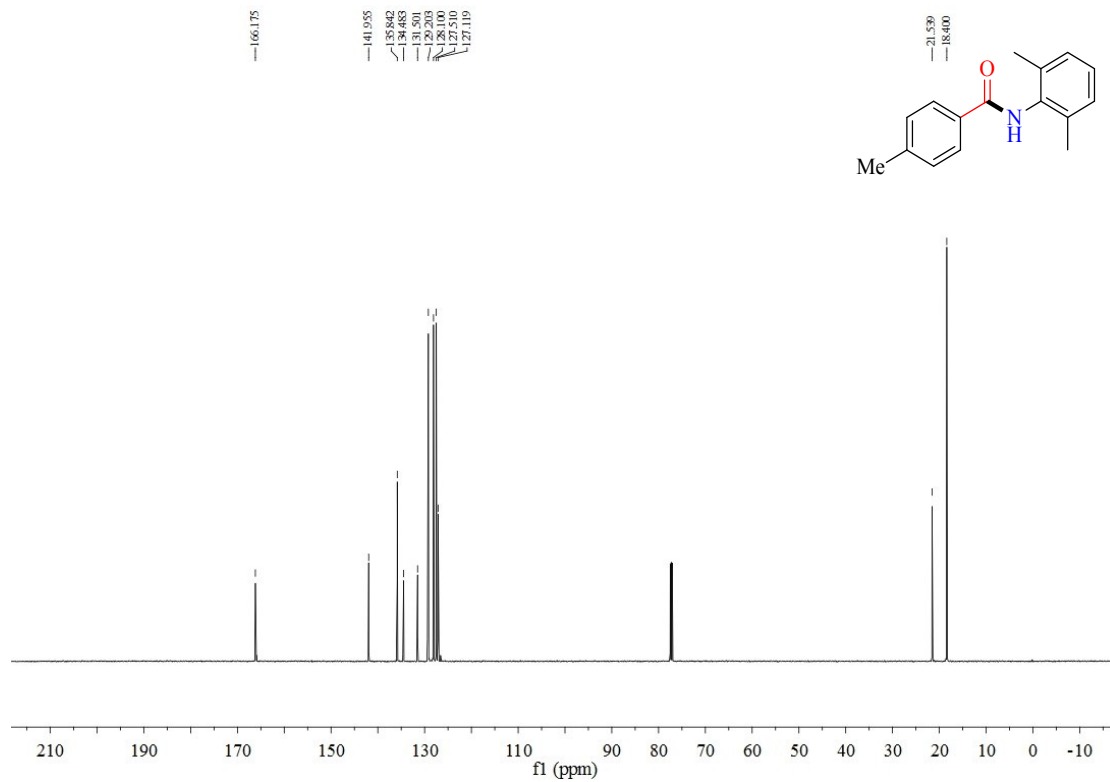
N-(2,6-dimethylphenyl) benzamide (3a).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



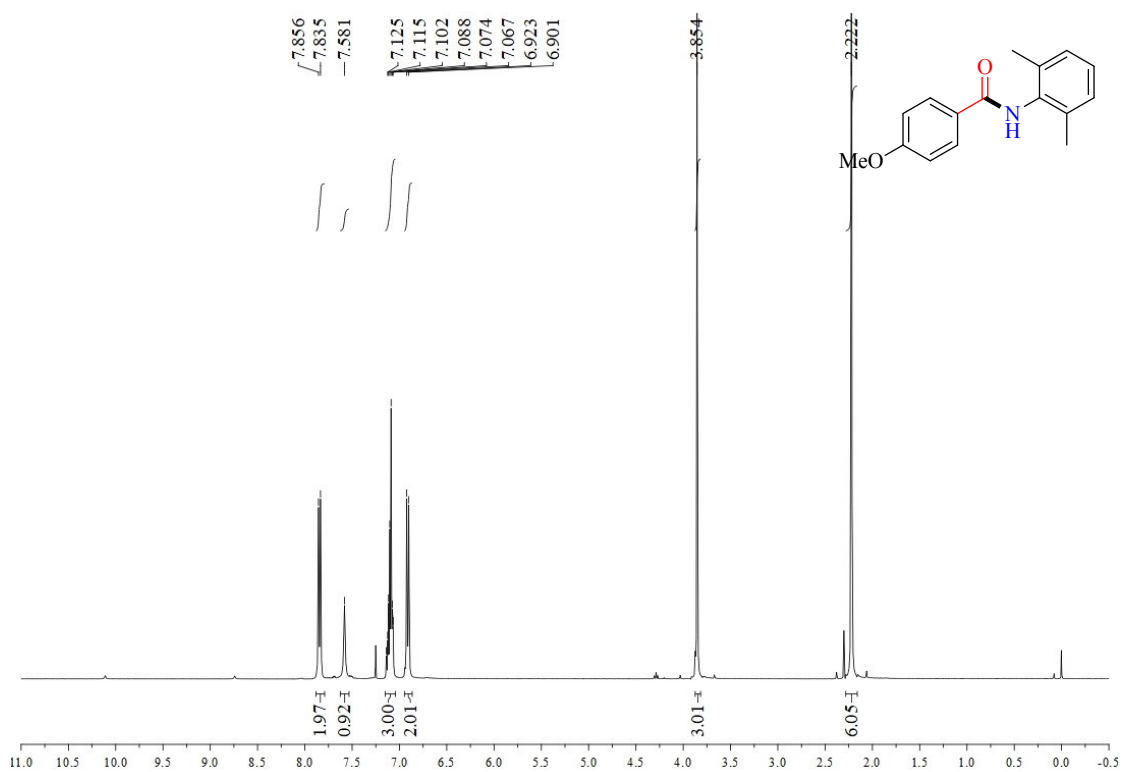
**N-(2,6-dimethylphenyl)-4-methylbenzamide (3b).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



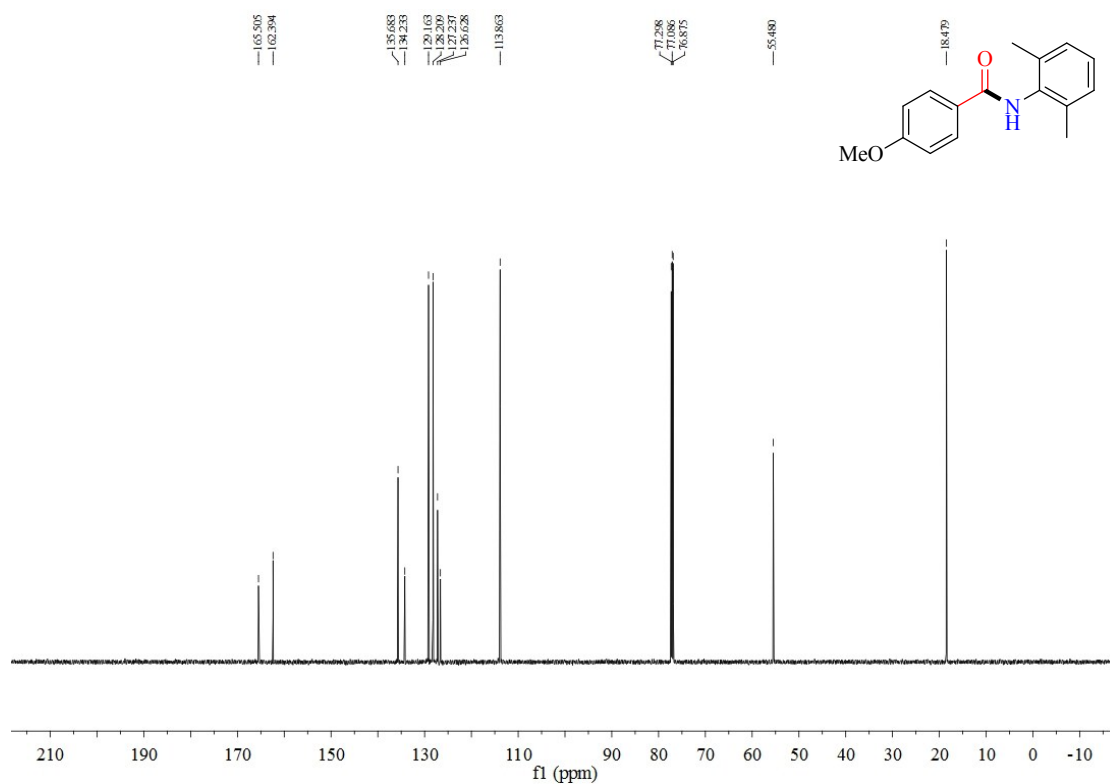
**N-(2,6-dimethylphenyl)-4-methylbenzamide (3b).**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



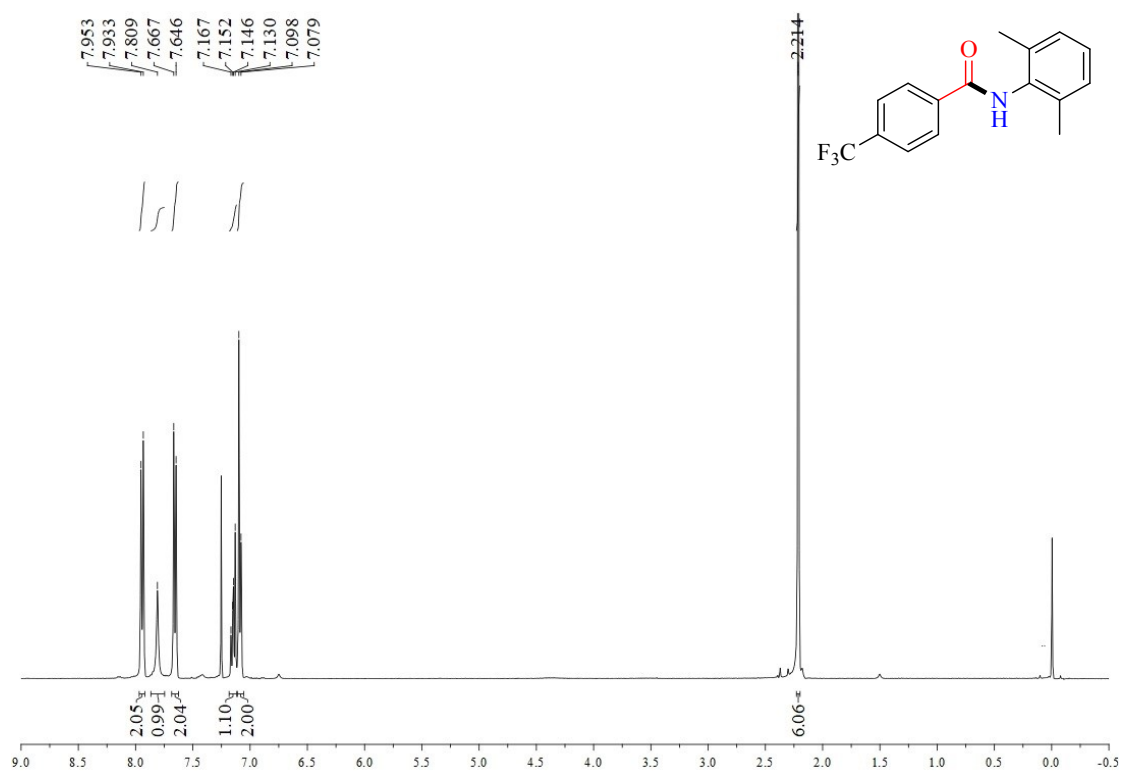
**N-(2,6-dimethylphenyl)-4-methoxybenzamide(3c).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



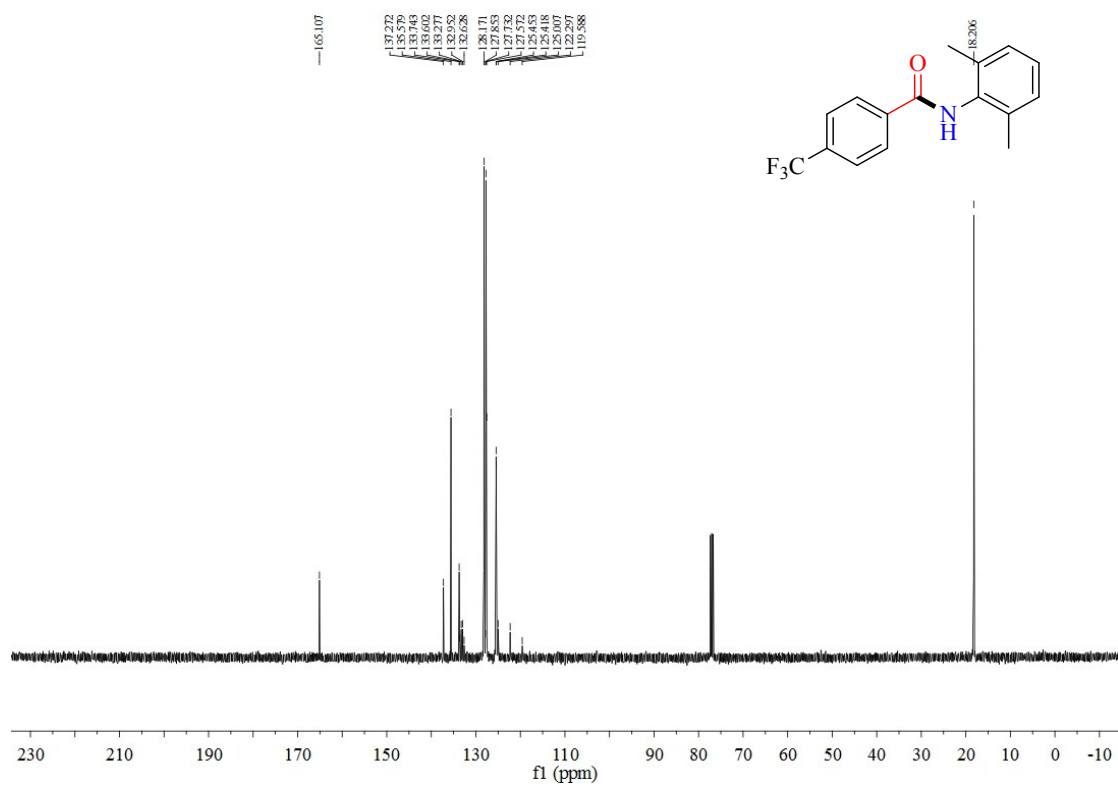
**N-(2,6-dimethylphenyl)-4-methoxybenzamide(3c).**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )



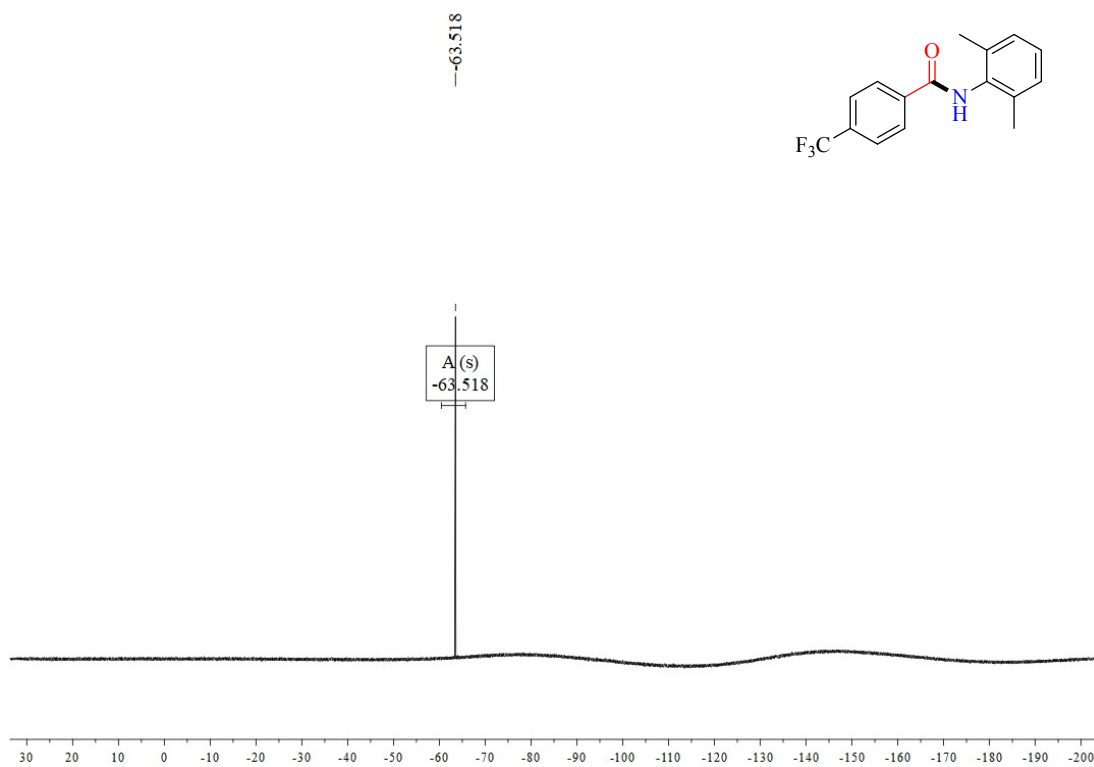
**N-(2,6-dimethylphenyl)-4-(trifluoromethyl) benzamide (3d).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



**N-(2,6-dimethylphenyl)-4-(trifluoromethyl) benzamide (3d).**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

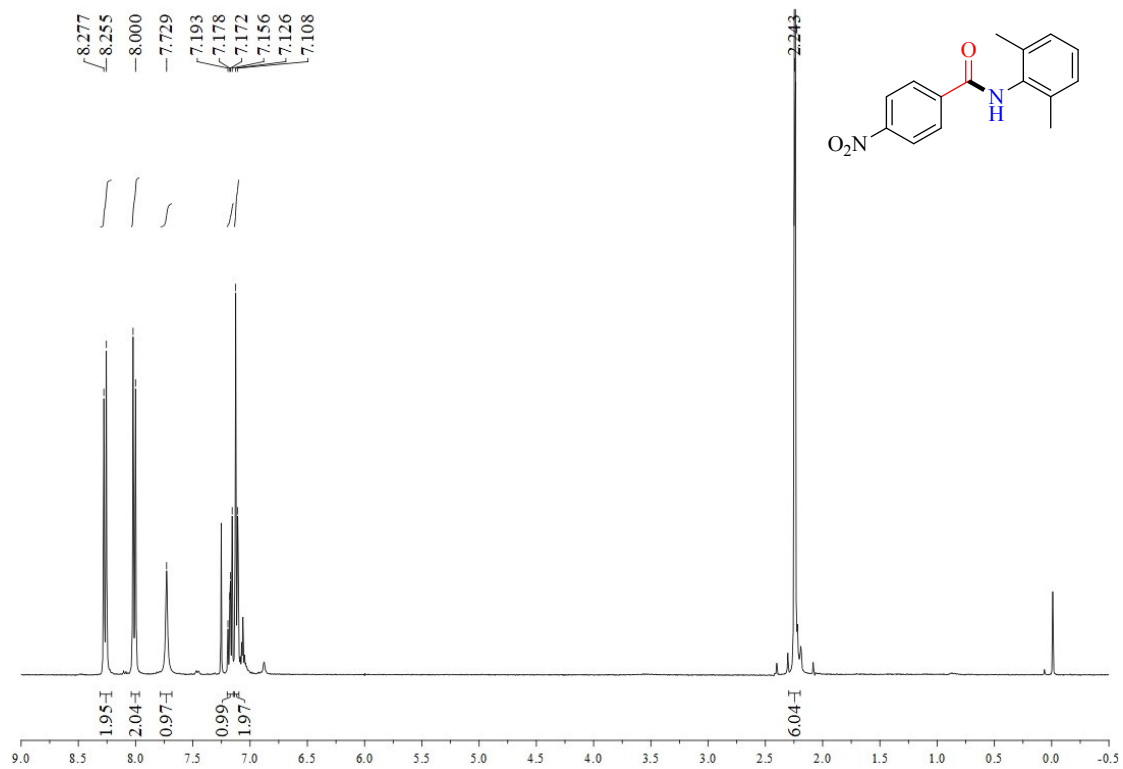


**N-(2,6-dimethylphenyl)-4-(trifluoromethyl) benzamide (3da).**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )

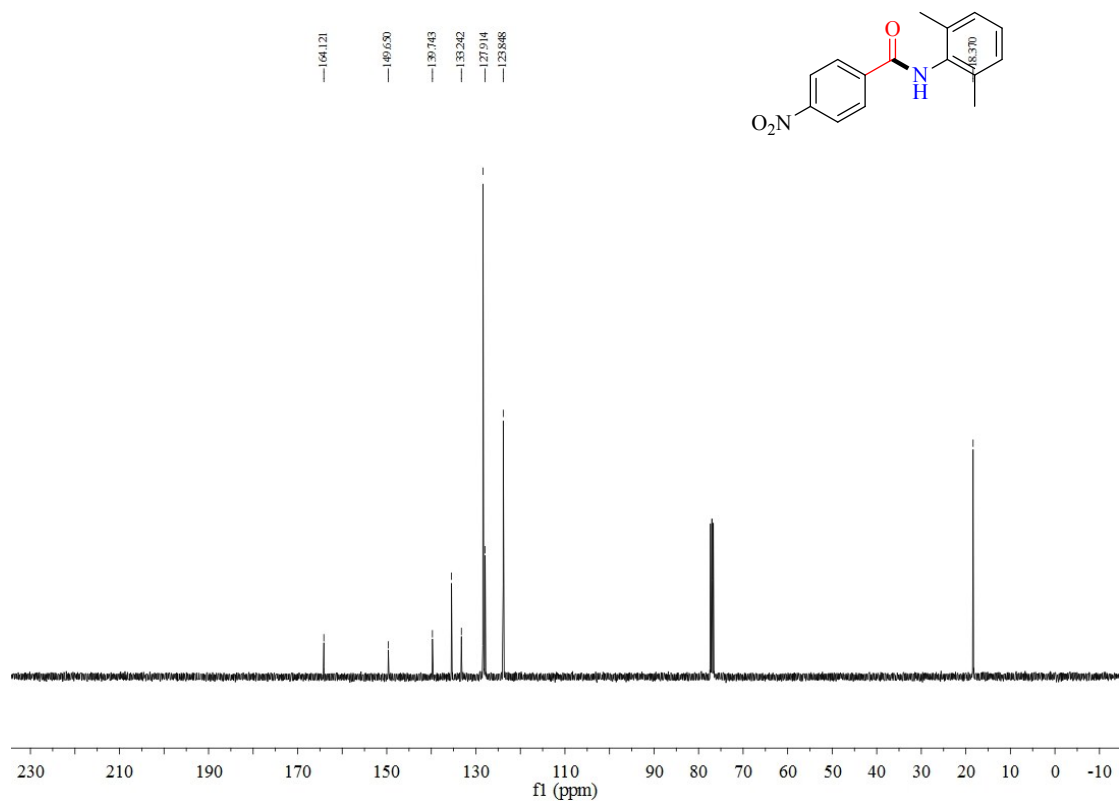




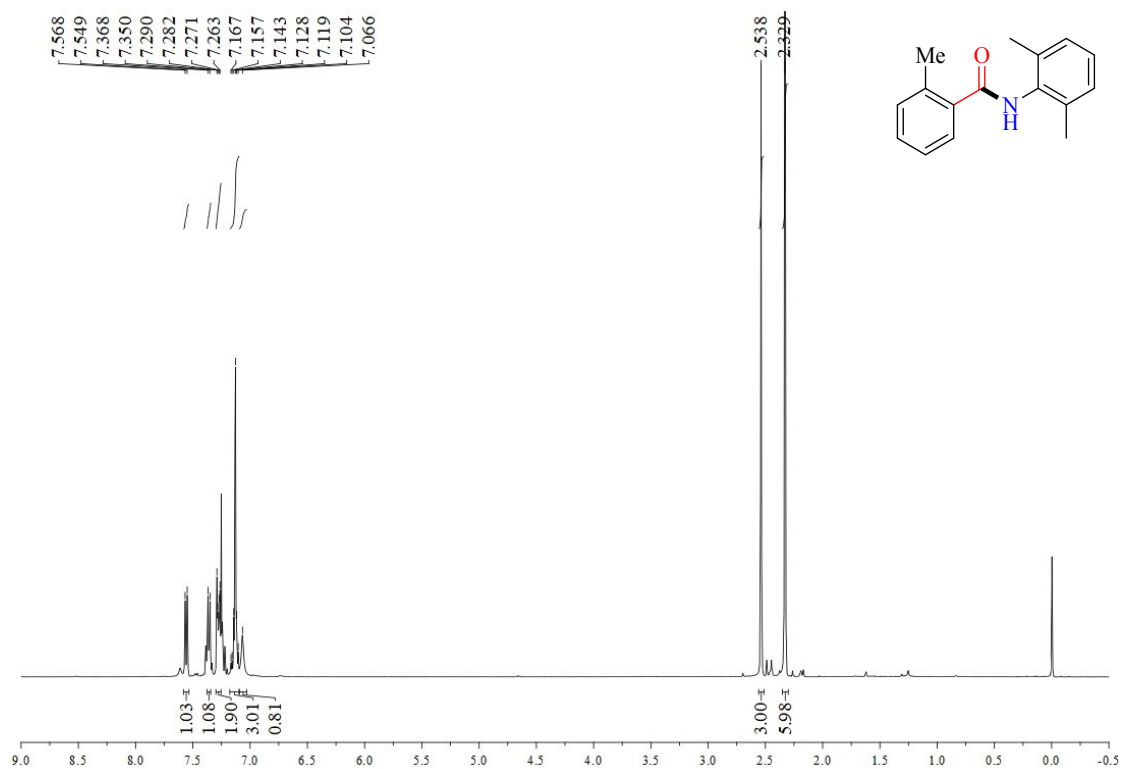
**N-(2,6-dimethylphenyl)-4-nitrobenzamide(3e).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



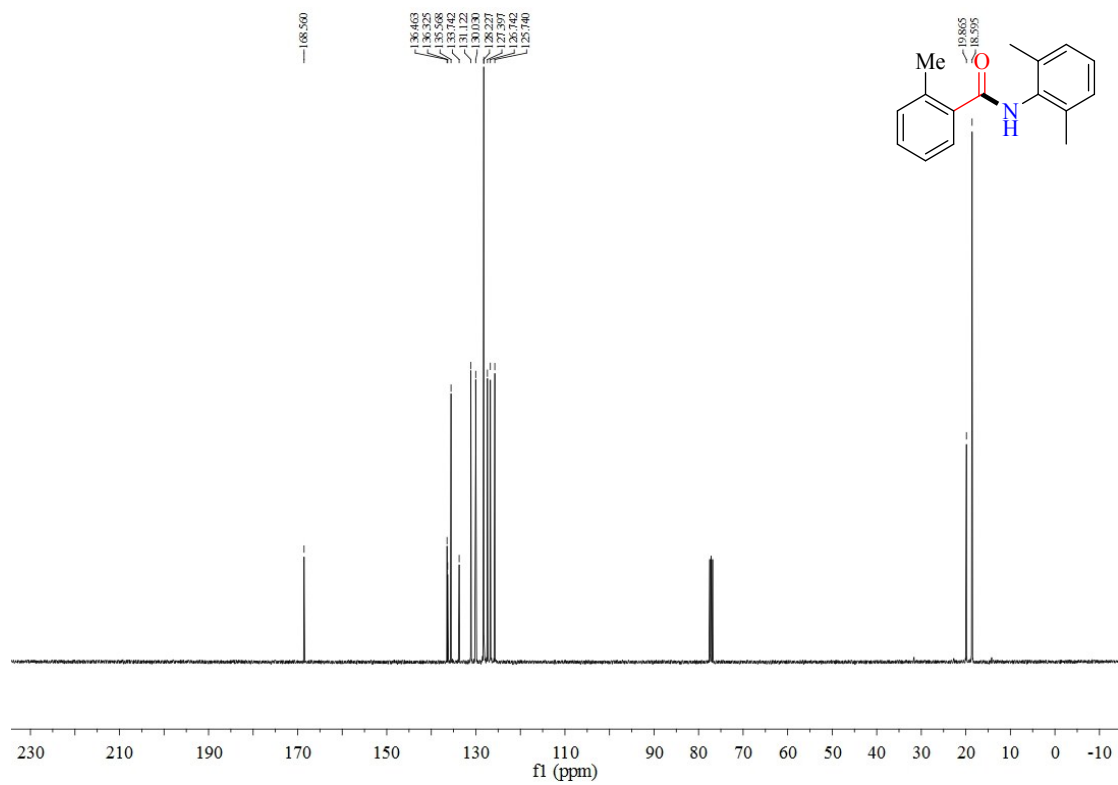
**N-(2,6-dimethylphenyl)-4-nitrobenzamide(3e).**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



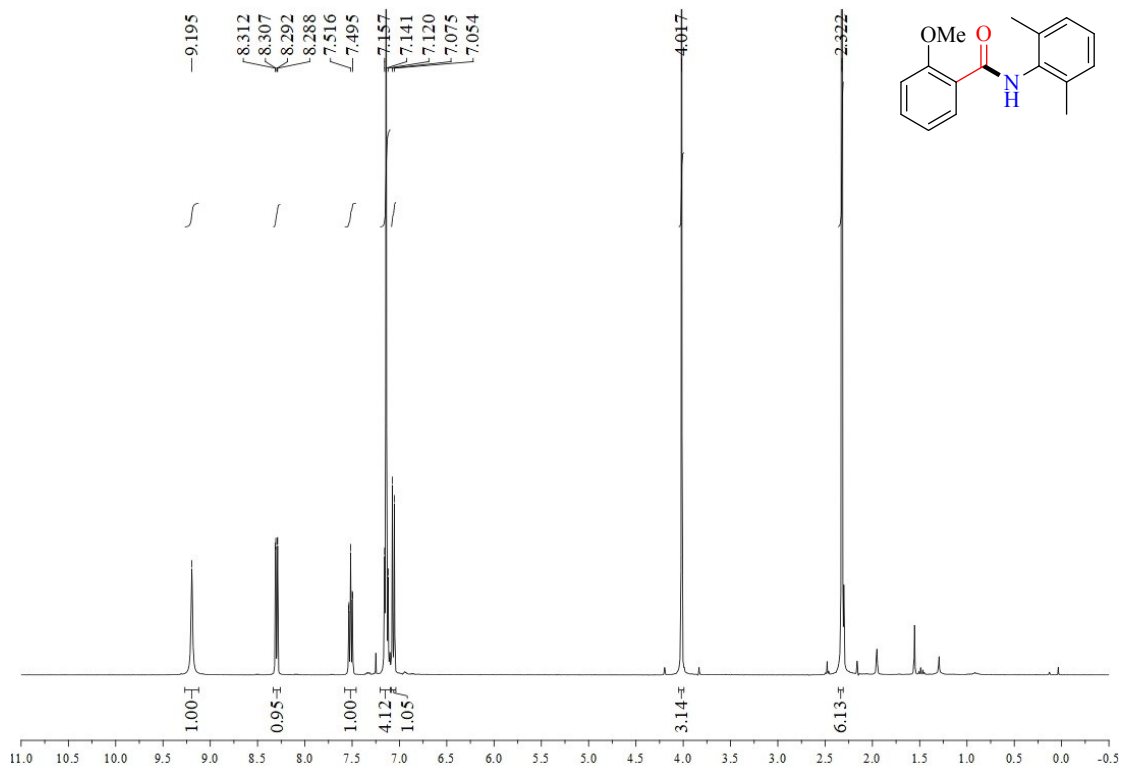
**N-(2,6-dimethylphenyl)-2-methylbenzamide(3f).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



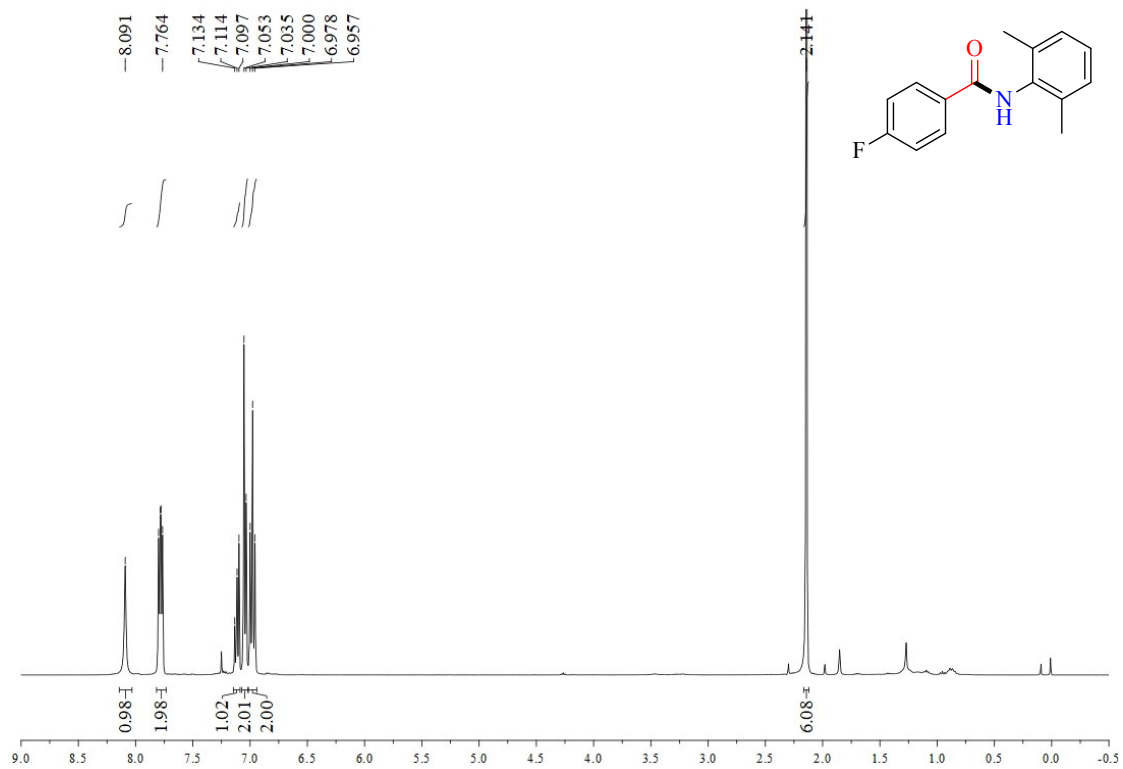
**N-(2,6-dimethylphenyl)-2-methylbenzamide(3f).**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )



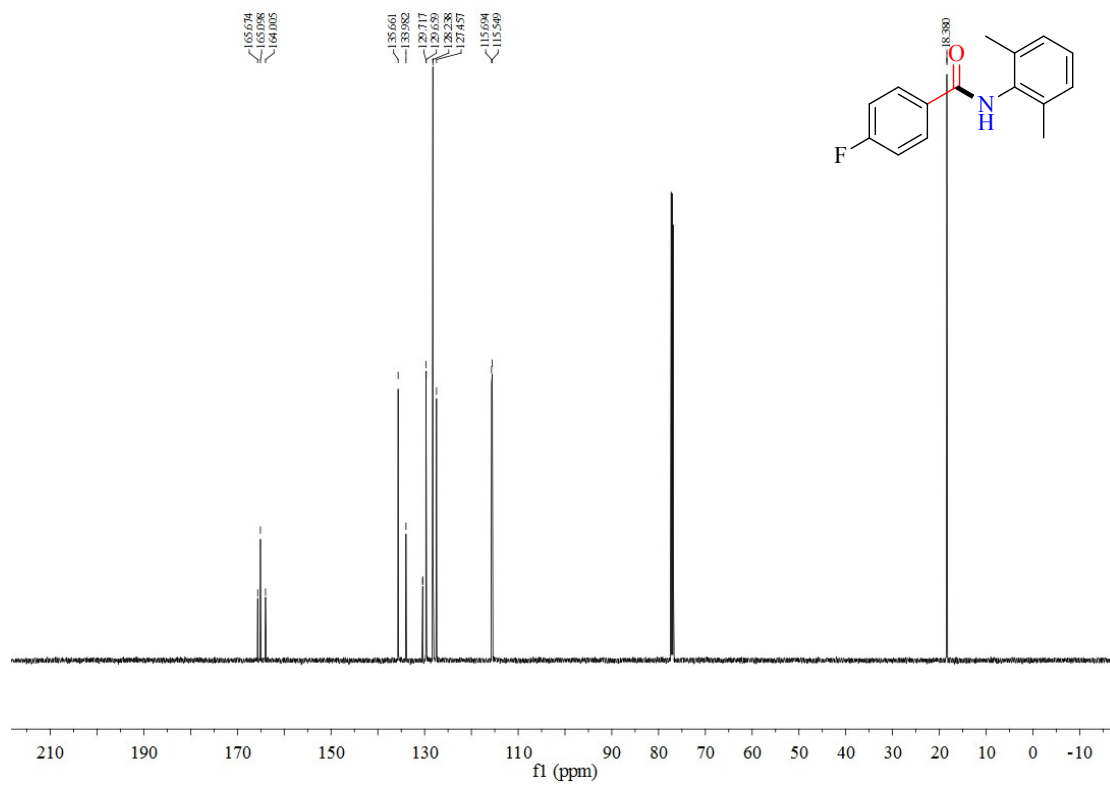
**N-(2,6-dimethylphenyl)-2-methoxybenzamide(3g).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



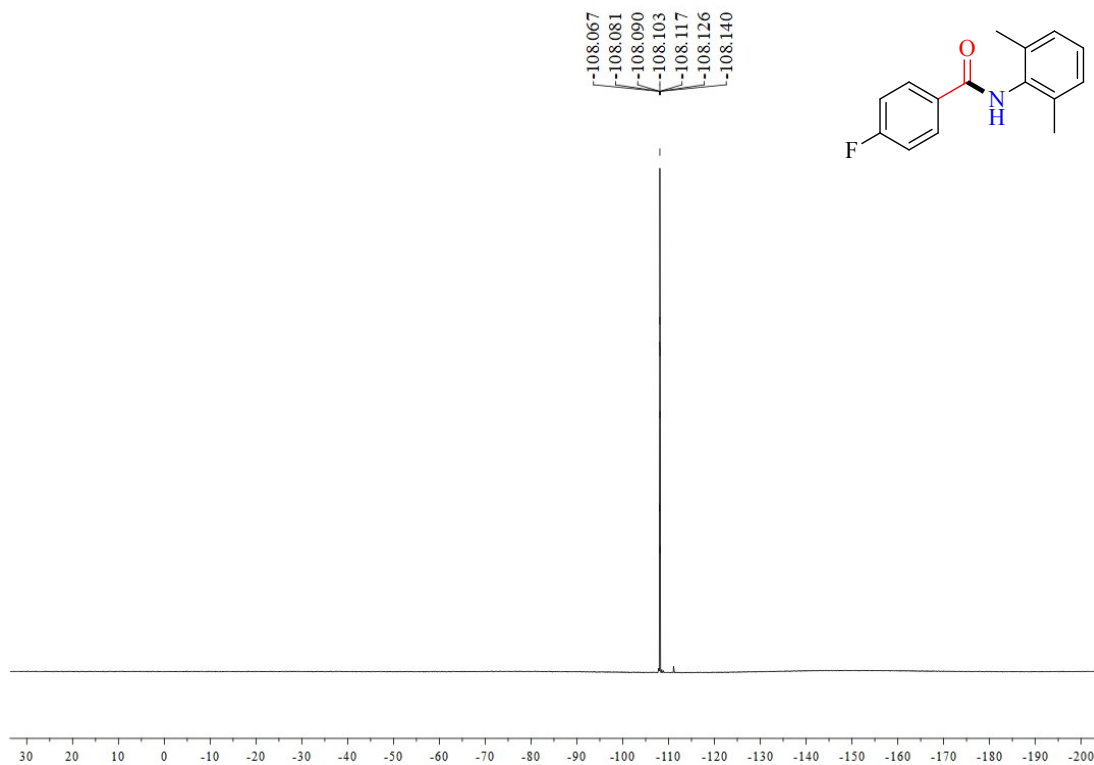
**N-(2,6-dimethylphenyl)-4-fluorobenzamide (3h).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



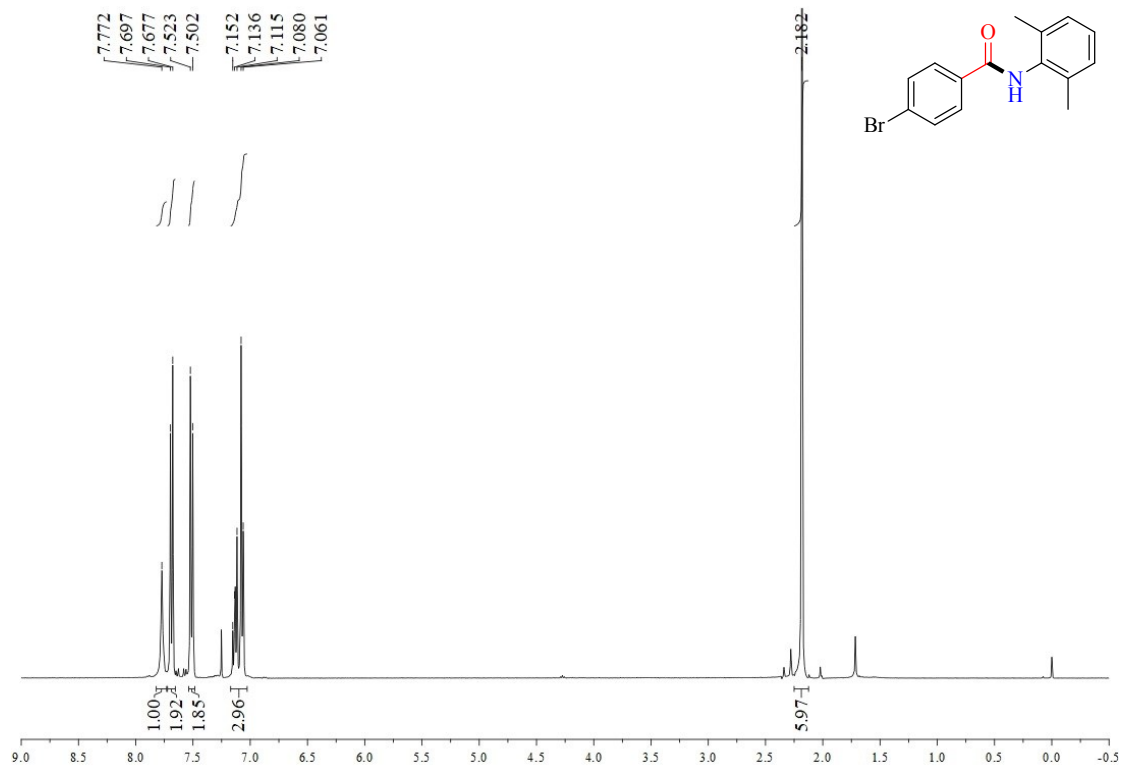
**N-(2,6-dimethylphenyl)-4-fluorobenzamide (3h).**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



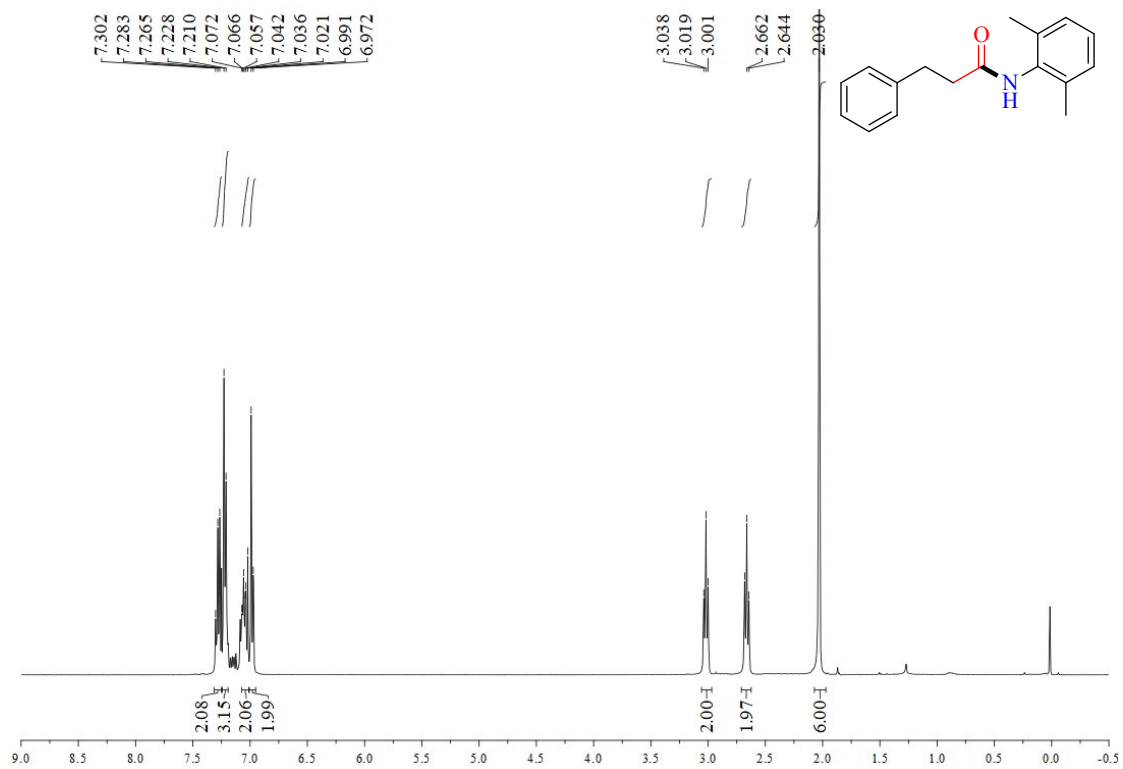
**N-(2,6-dimethylphenyl)-4-fluorobenzamide (3h).**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )



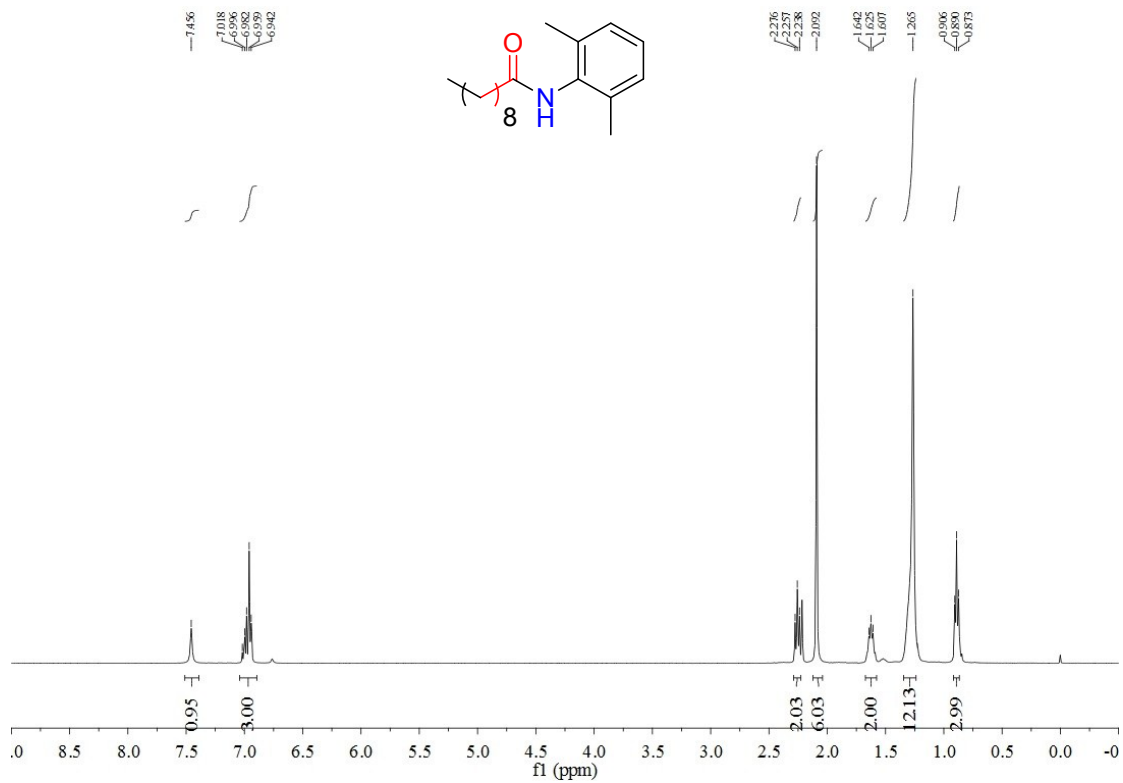
**4-bromo-N-(2,6-dimethylphenyl) benzamide (3i).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



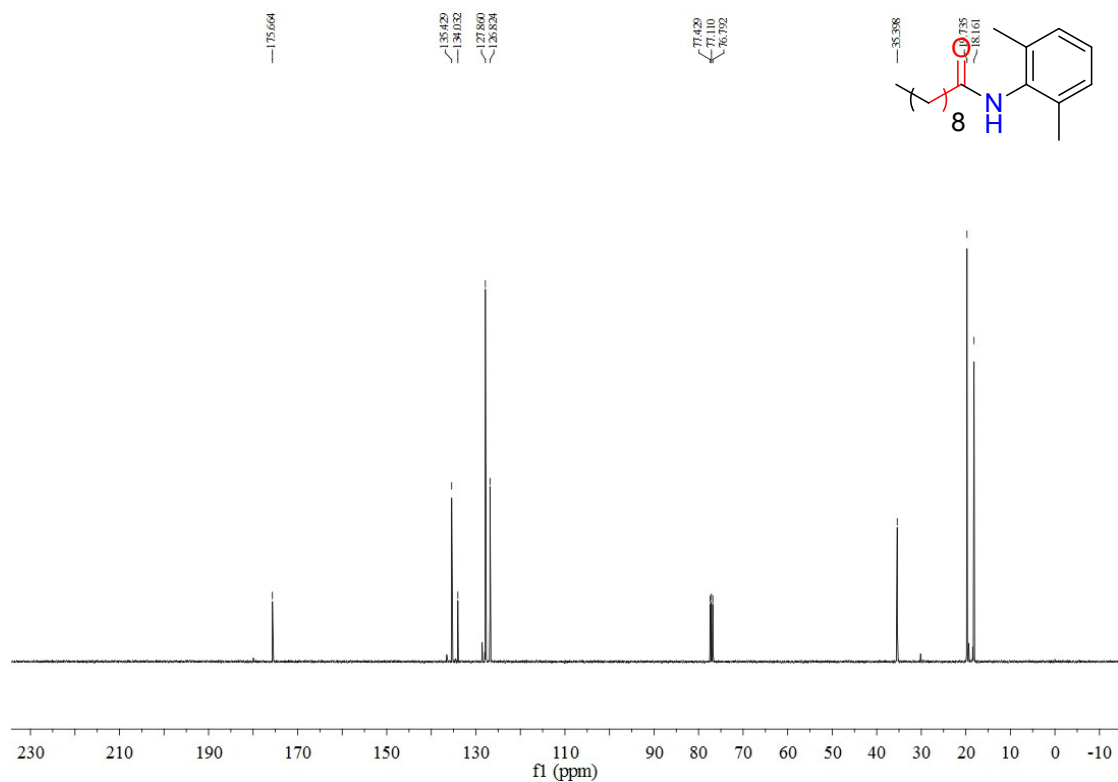
**N-(2,6-dimethylphenyl)-3-phenylpropanamide (3j).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



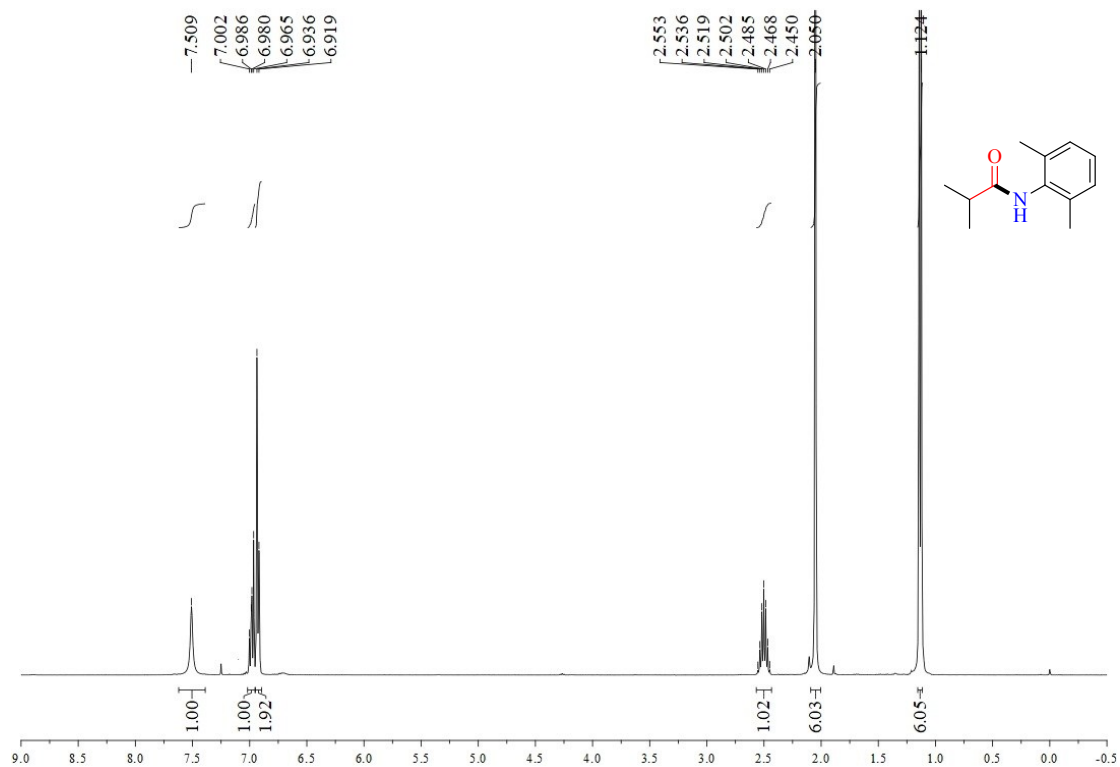
**N-(2,6-dimethylphenyl)decanamide(3k)**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



**N-(2,6-dimethylphenyl)decanamide(3k)**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



**N-(2,6-dimethylphenyl) isobutyramide(31).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

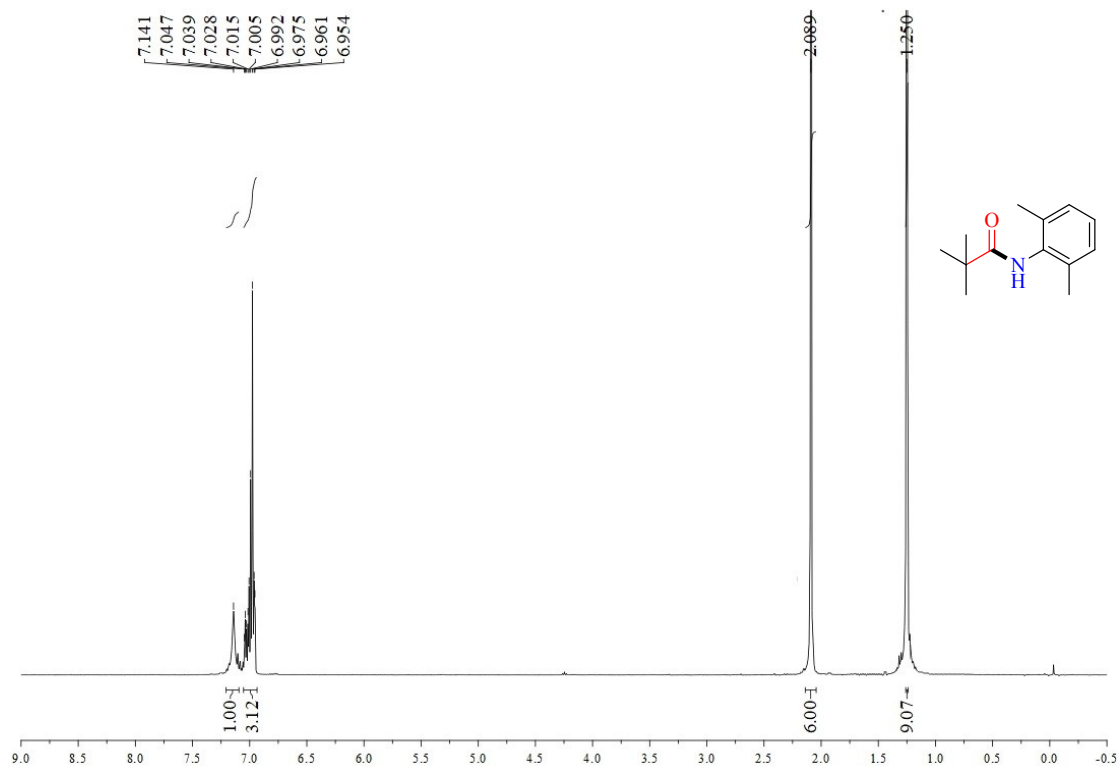


**N-(2,6-dimethylphenyl) isobutyramide(31).**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

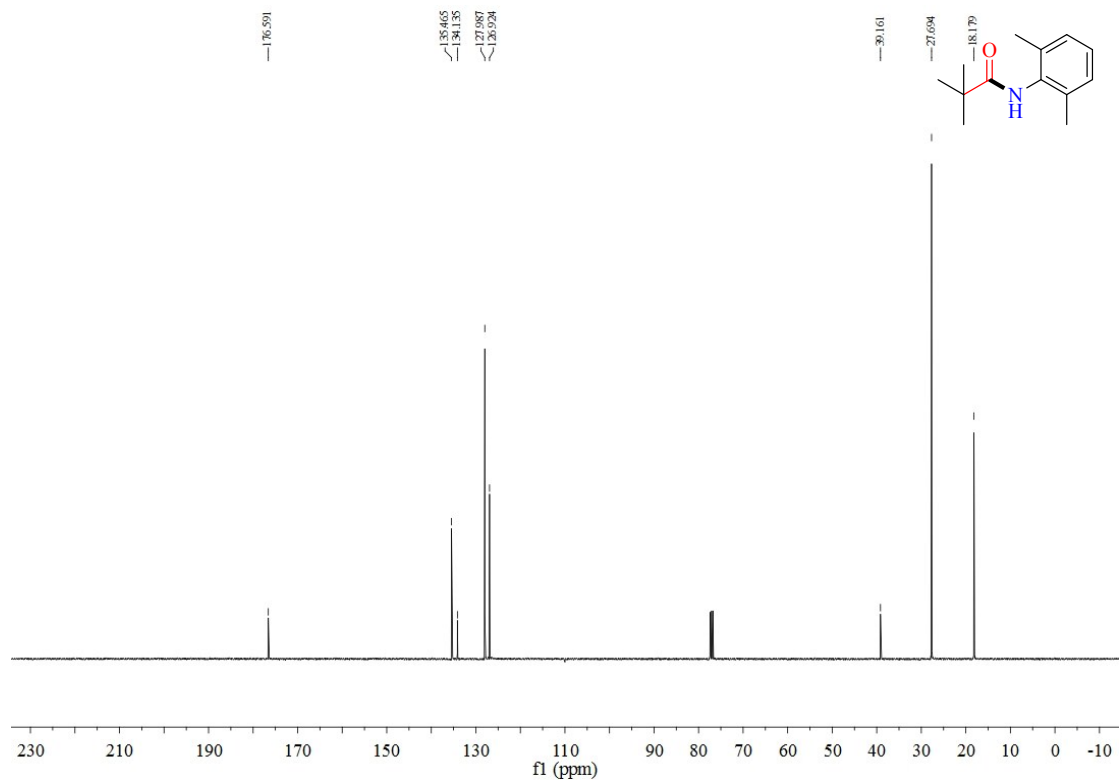




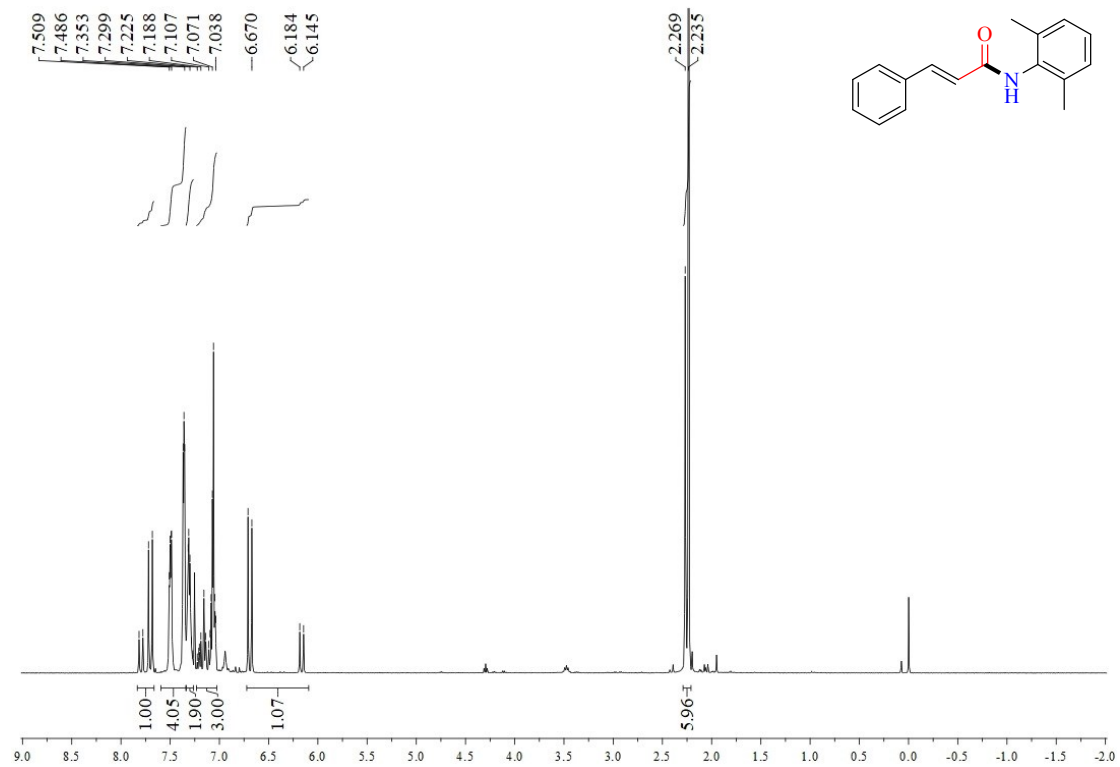
**N-(2,6-dimethylphenyl) pivalamide (3m).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



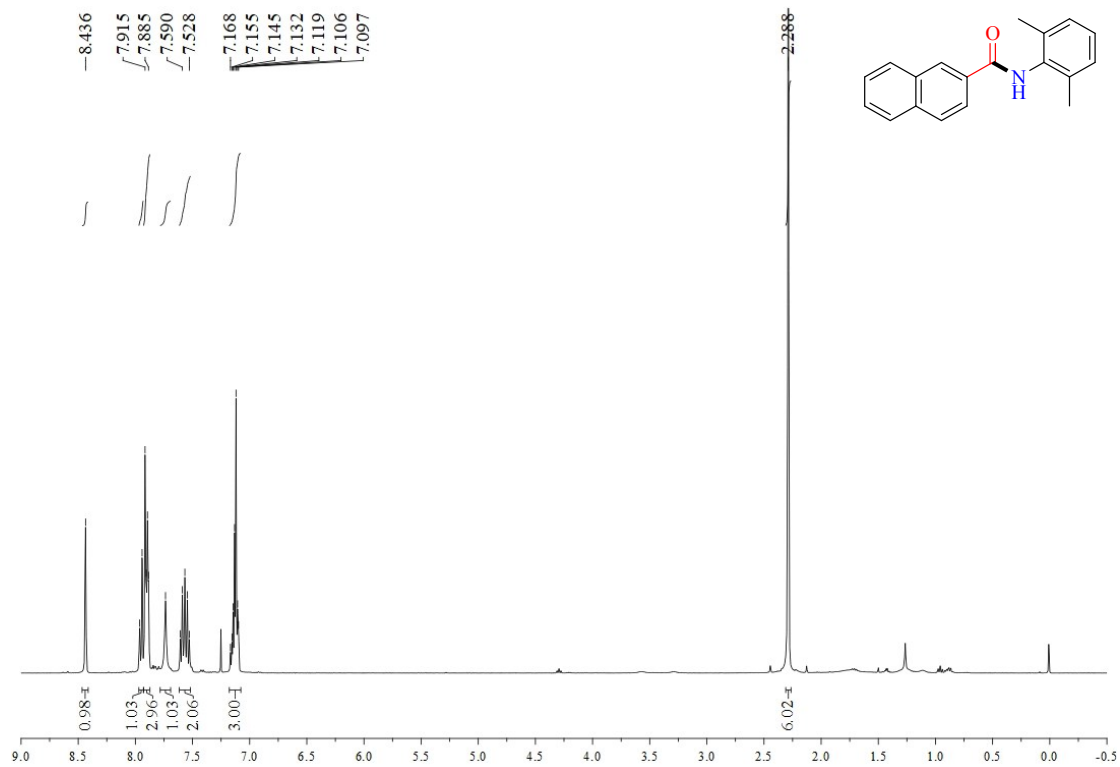
**N-(2,6-dimethylphenyl) pivalamide (3m).**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



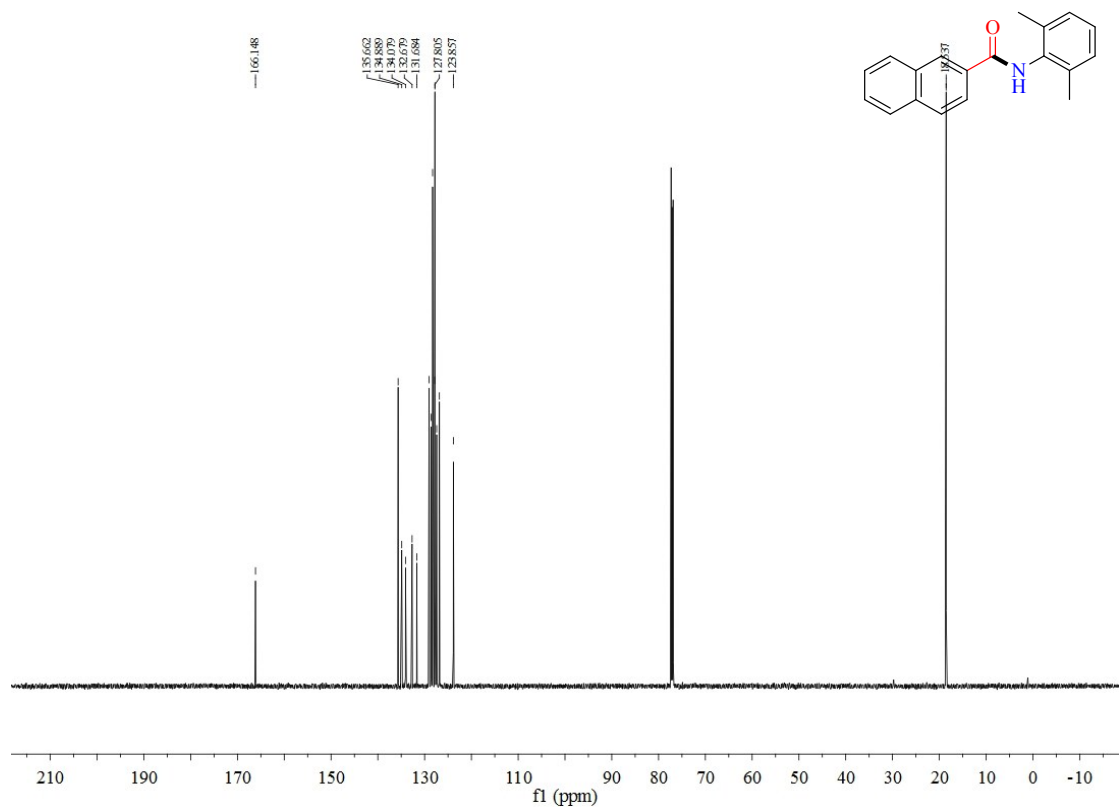
**N-(2,6-dimethylphenyl) cinnamamide. (3n)**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



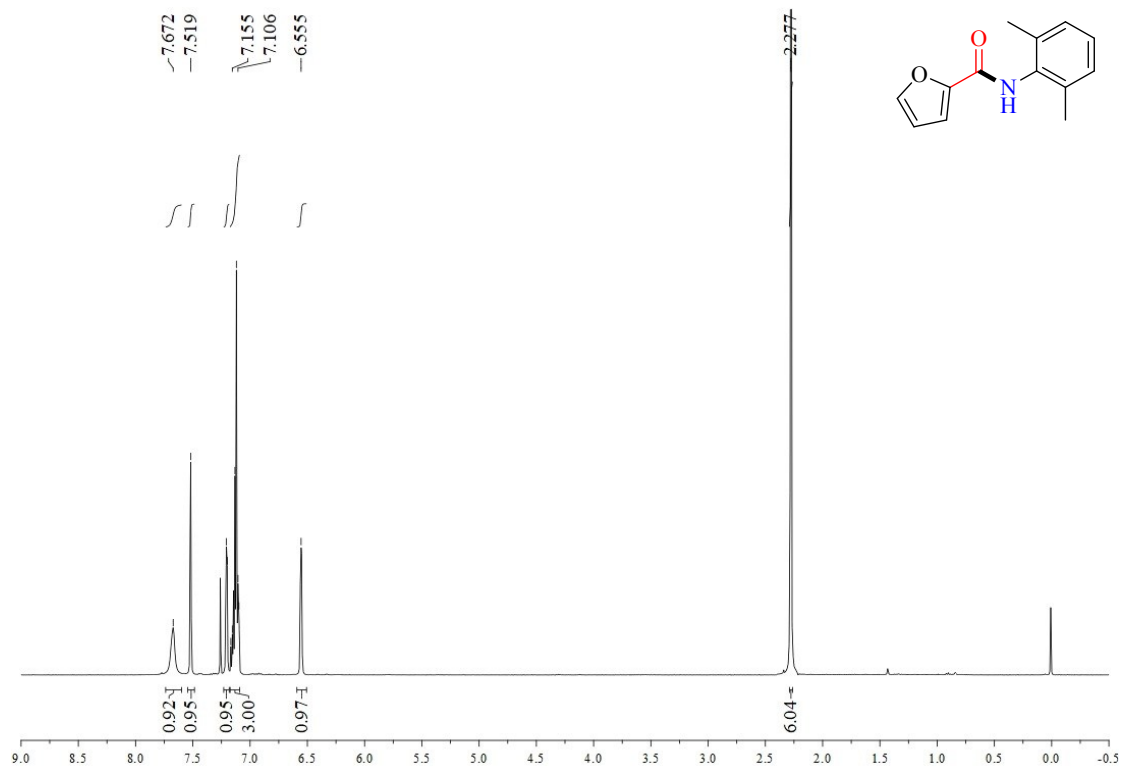
**N-(2,6-dimethylphenyl)-2-naphthamide (3o).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



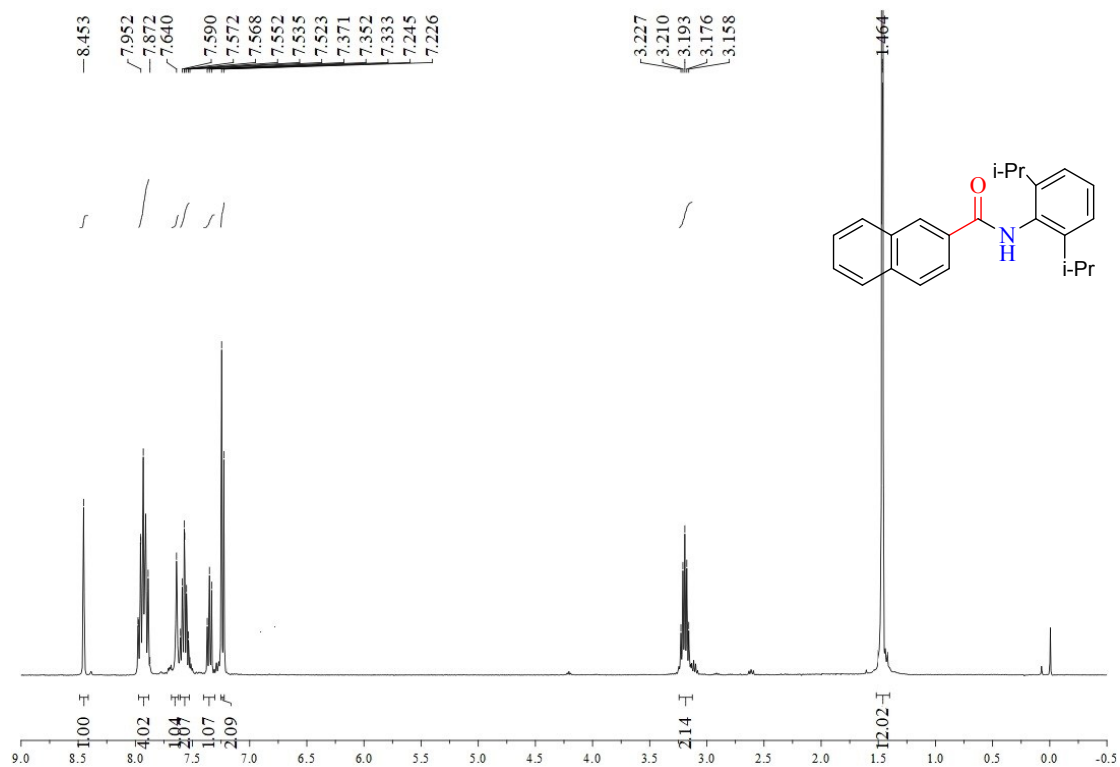
**N-(2,6-dimethylphenyl)-2-naphthamide (3o).**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )



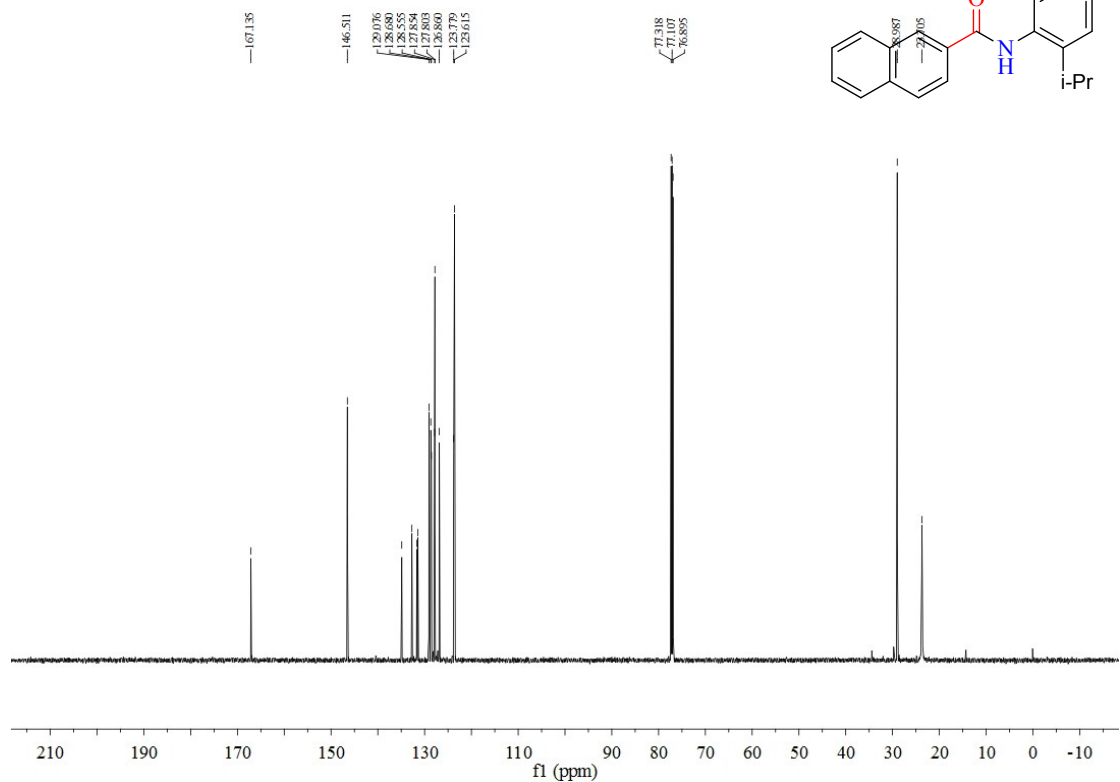
**N-(2,6-dimethylphenyl) furan-2-carboxamide(3p).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



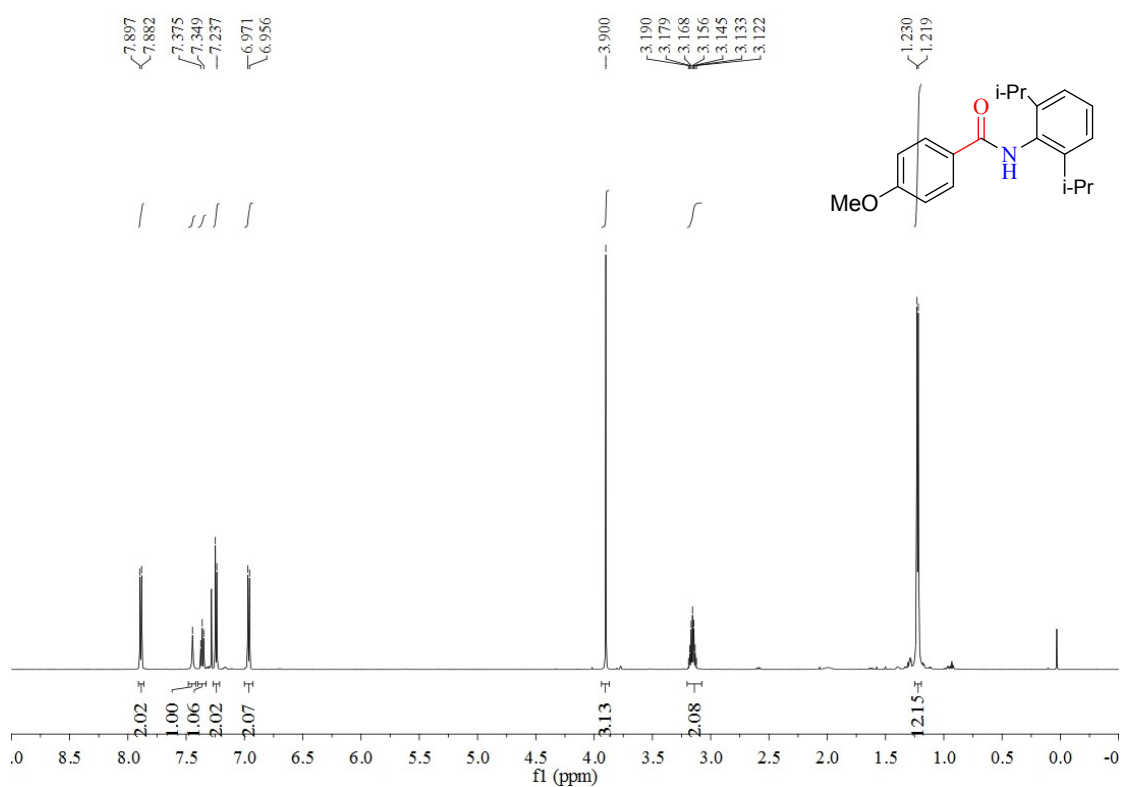
**N-(2,6-diisopropylphenyl)-2-naphthamide(4a).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



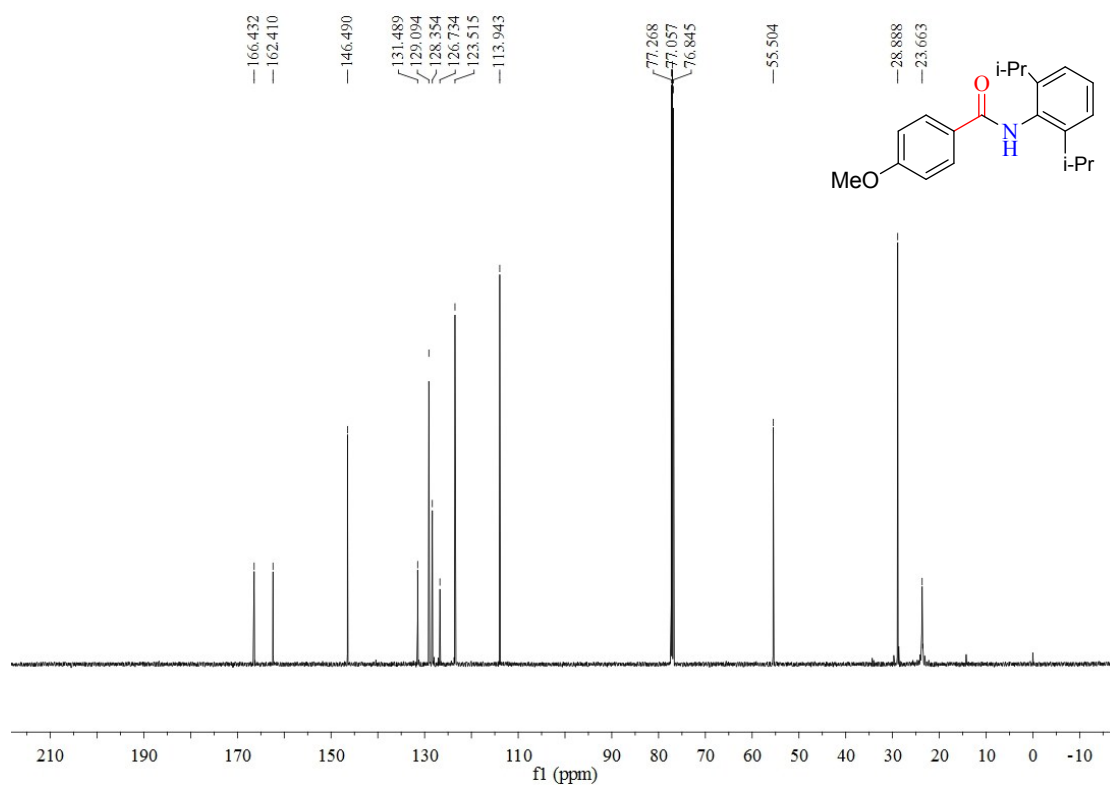
**N-(2,6-diisopropylphenyl)-2-naphthamide(4a).**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



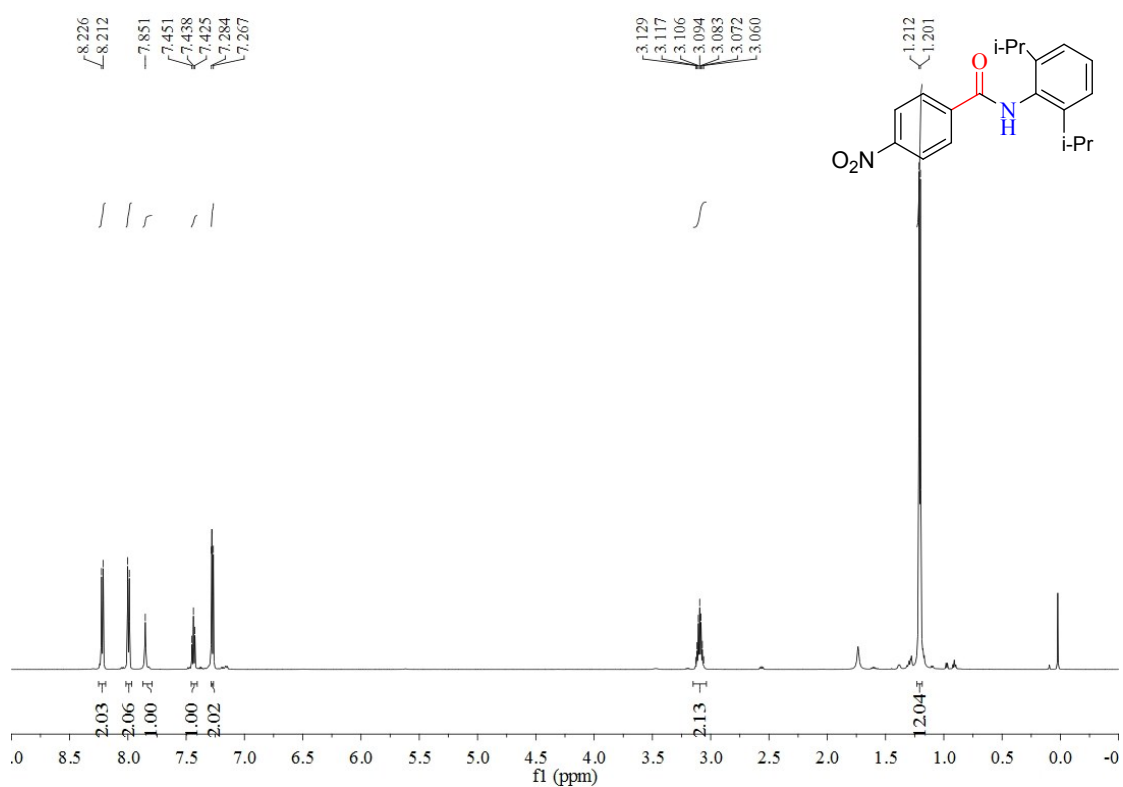
**N-(2,6-diisopropylphenyl)-4-methoxybenzamide(4b).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



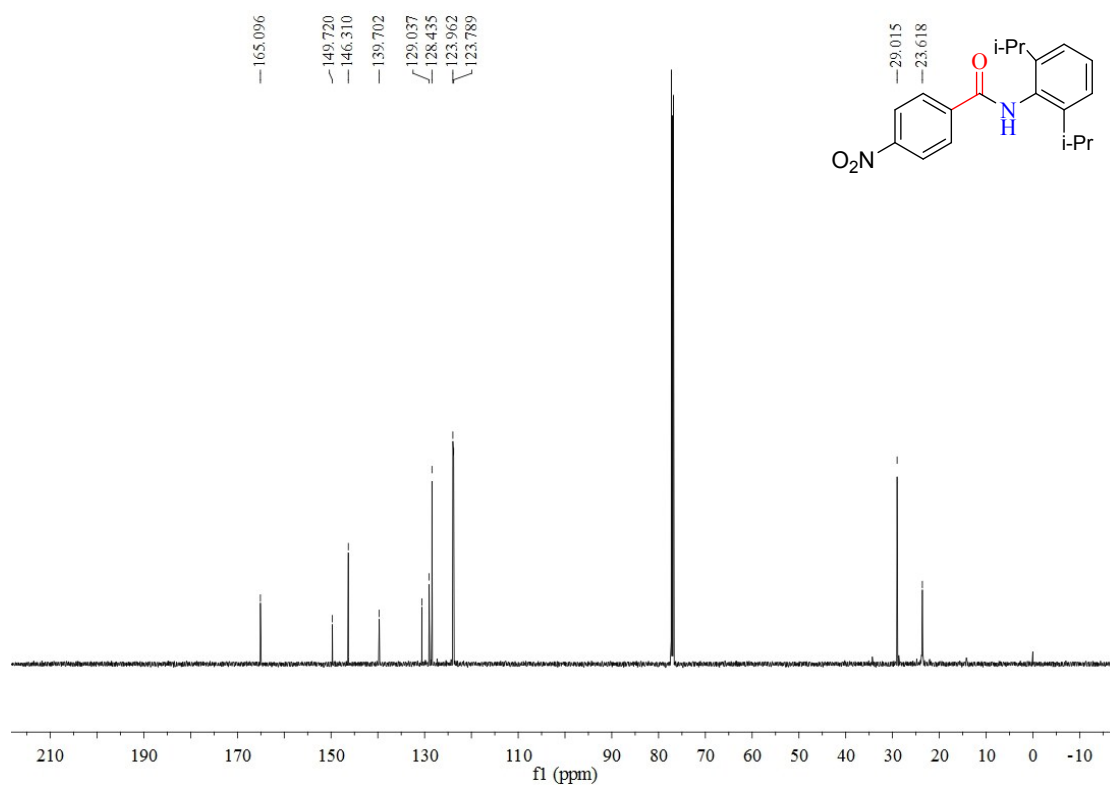
**N-(2,6-diisopropylphenyl)-4-methoxybenzamide(4b).**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )



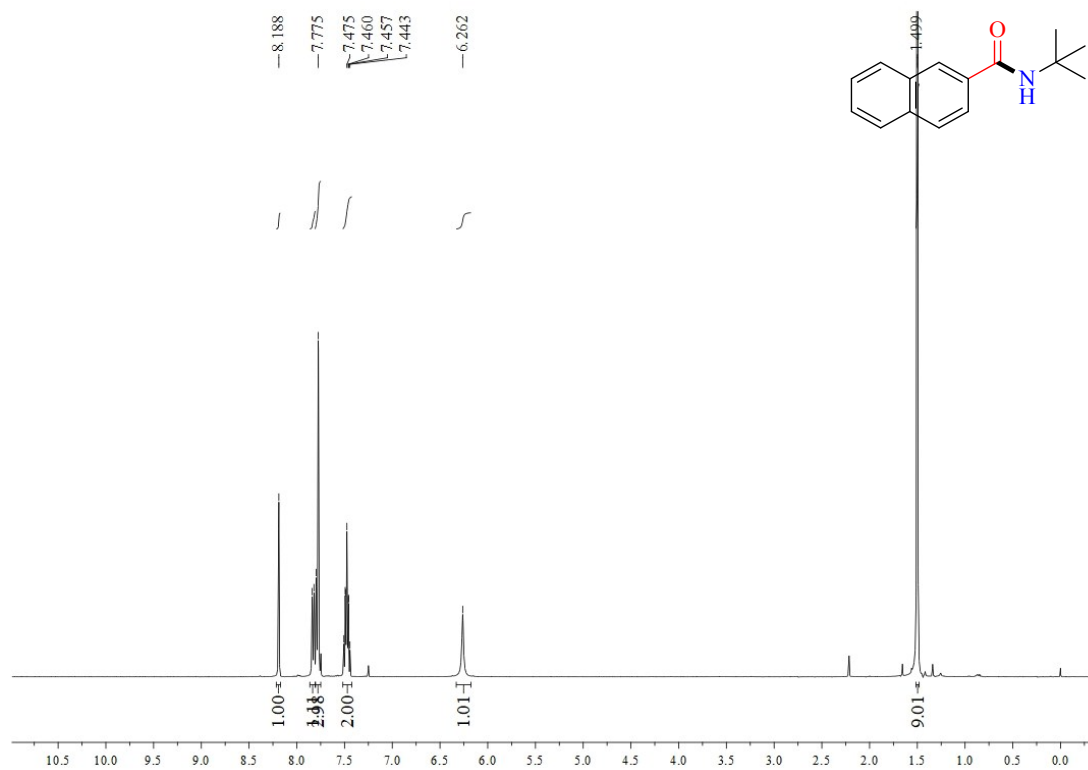
**N-(2,6-diisopropylphenyl)-4-nitrobenzamide (4c).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



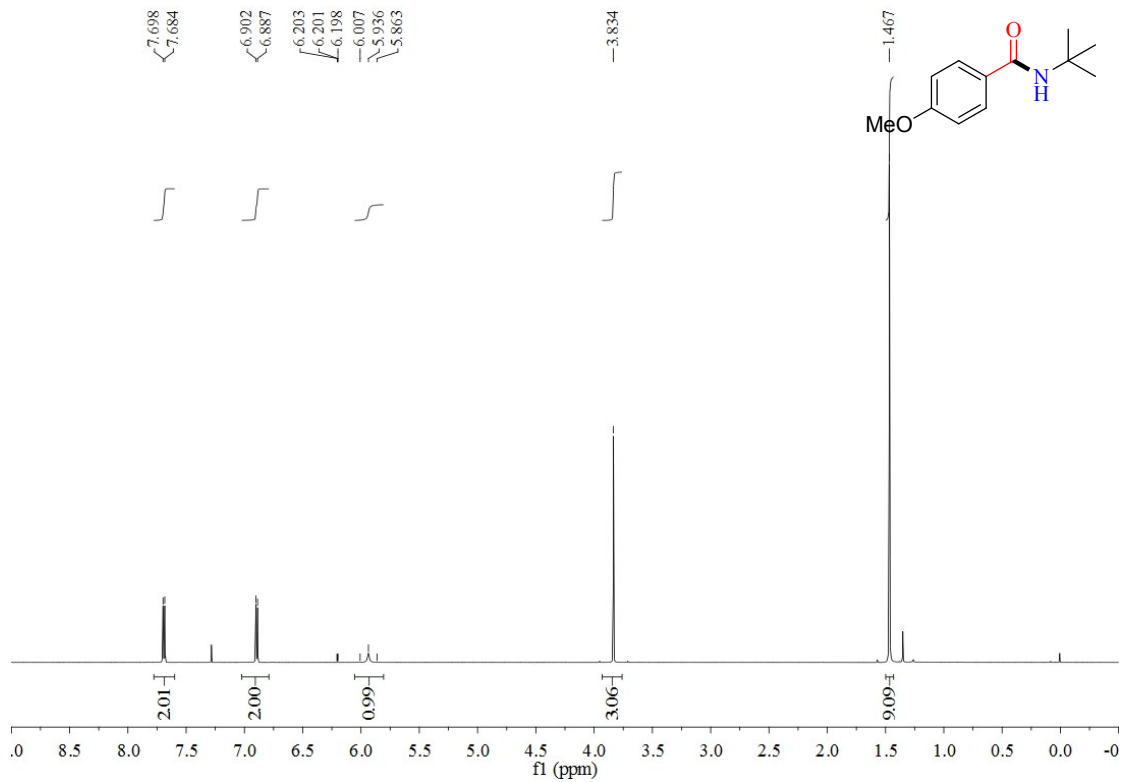
**N-(2,6-diisopropylphenyl)-4-nitrobenzamide (4c).**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )



**N-(tert-butyl)-2-naphthamide(4d).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

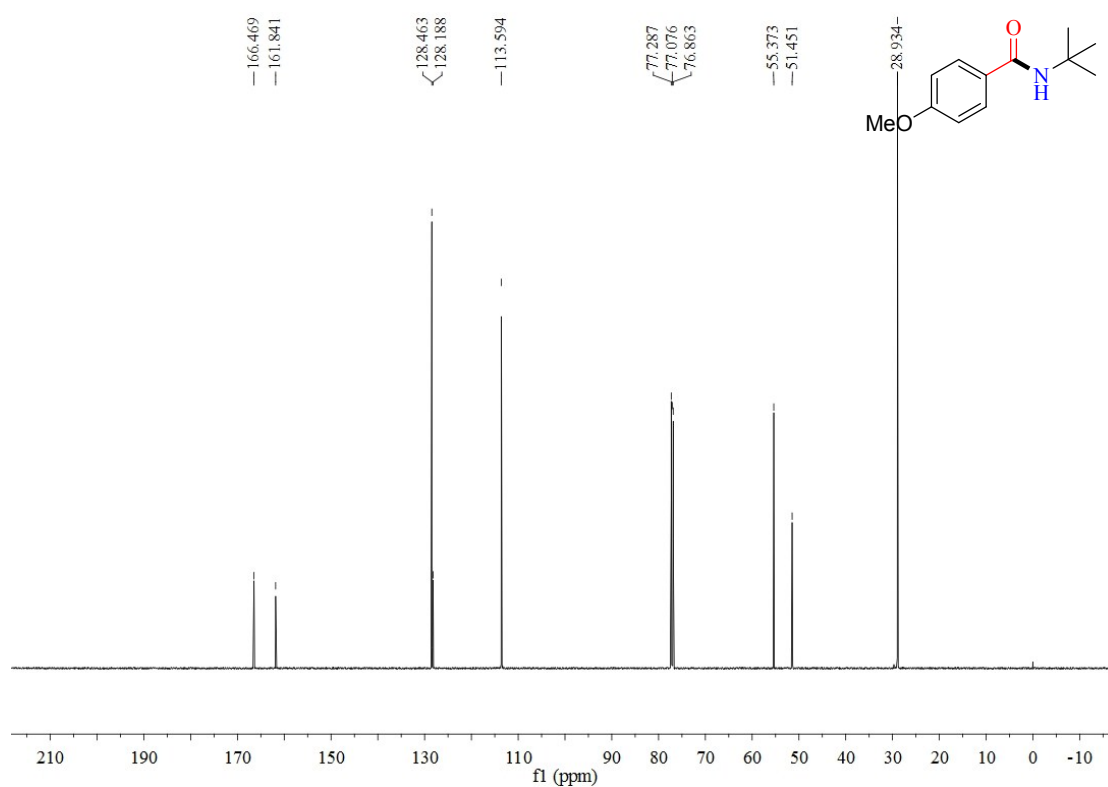


**N-(tert-butyl)-4-methoxybenzamide (4e).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

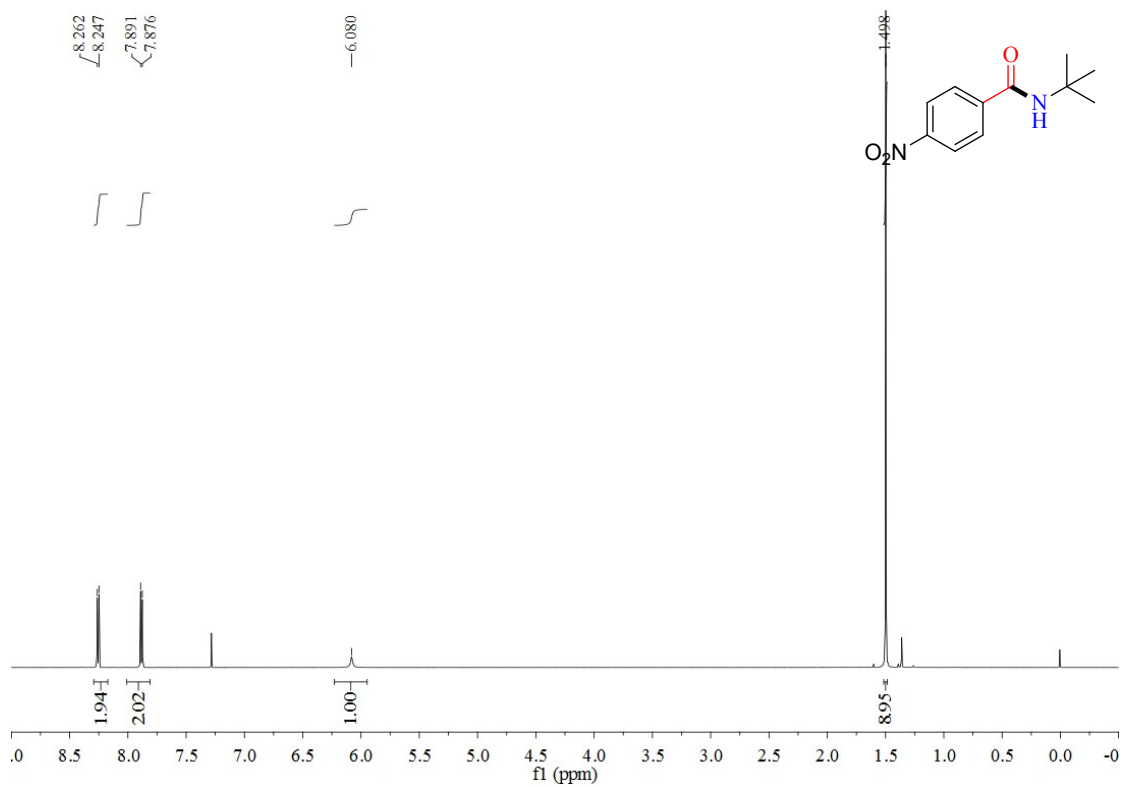




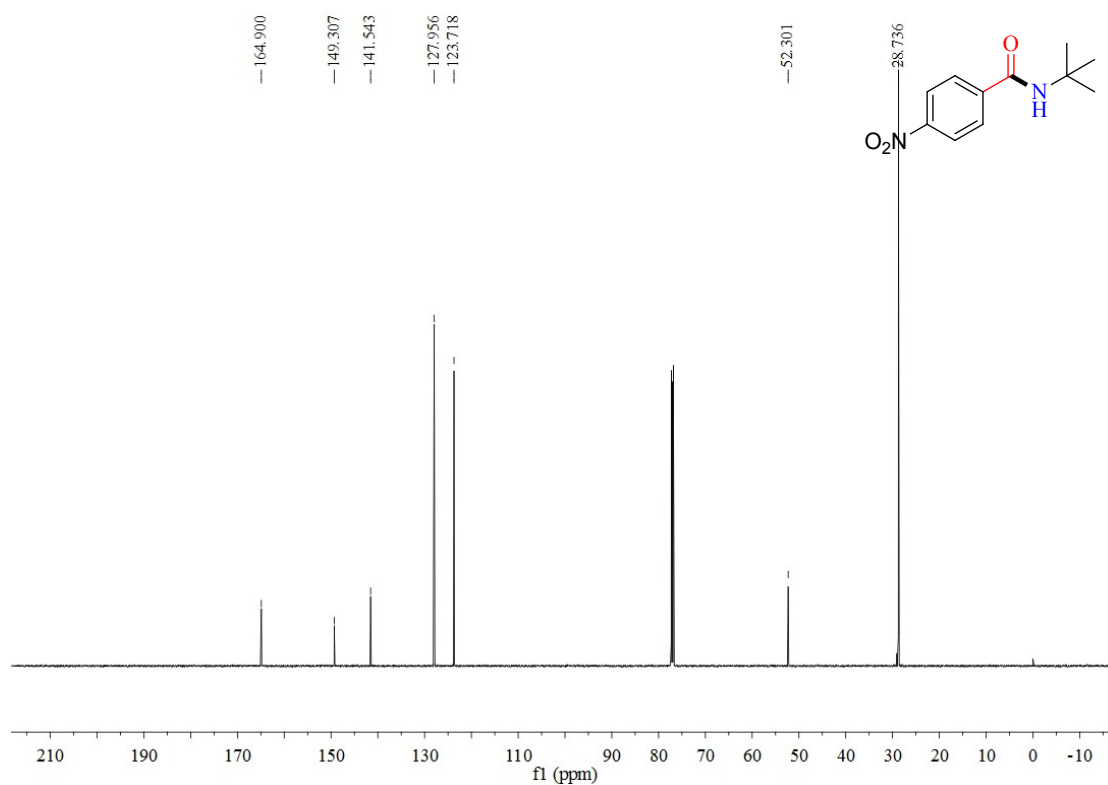
**N-(tert-butyl)-4-methoxybenzamide (4e).**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )



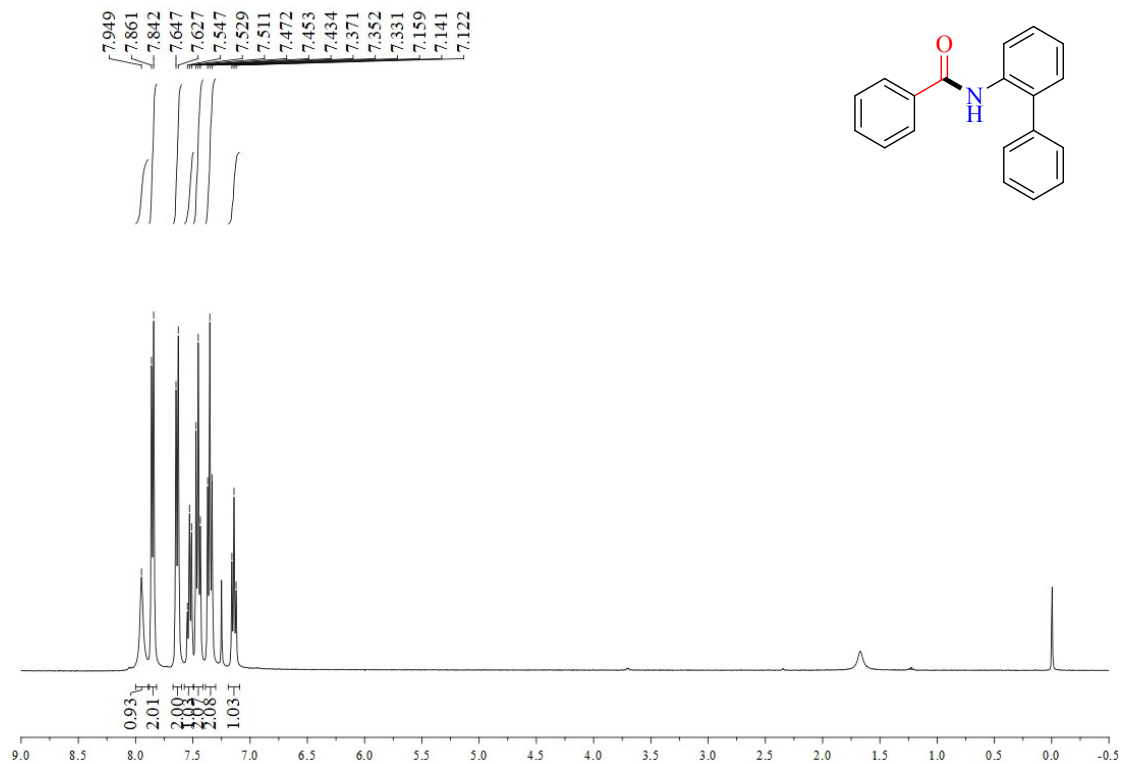
**N-(tert-butyl)-4-nitrobenzamide (4f).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



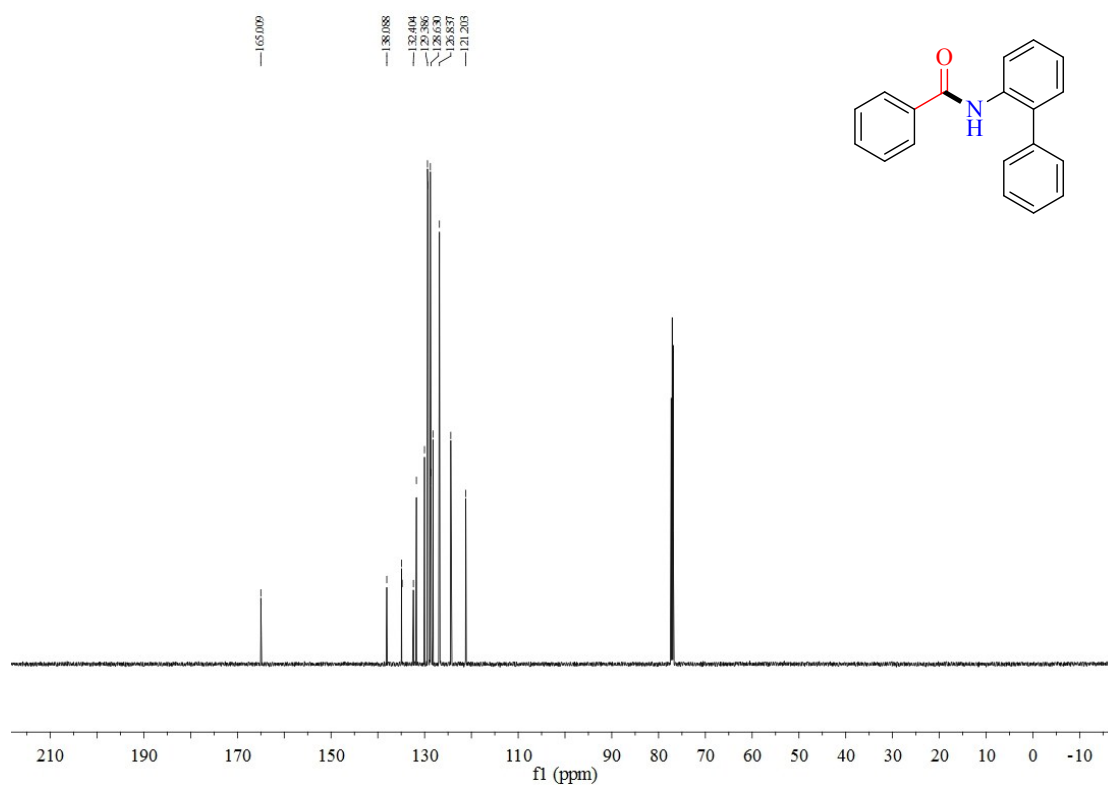
**N-(tert-butyl)-4-nitrobenzamide (4f).**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )



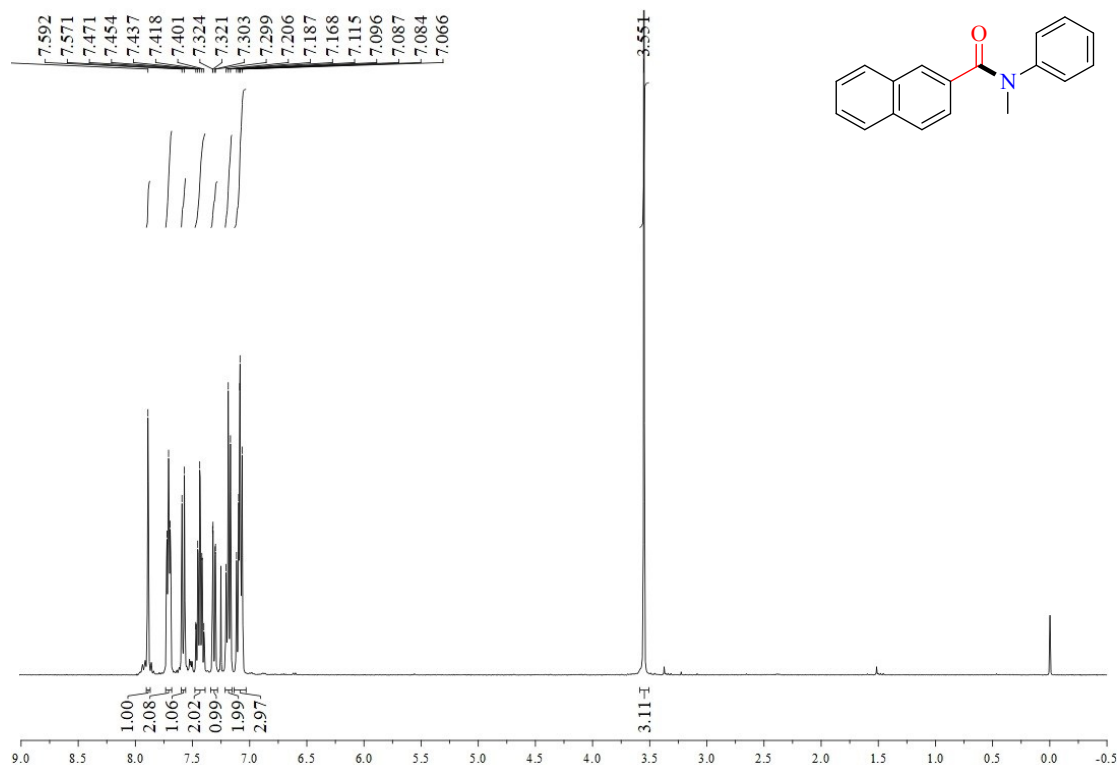
**N-([1,1'-biphenyl]-2-yl) benzamide (4g).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



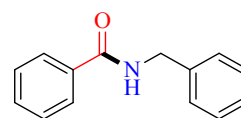
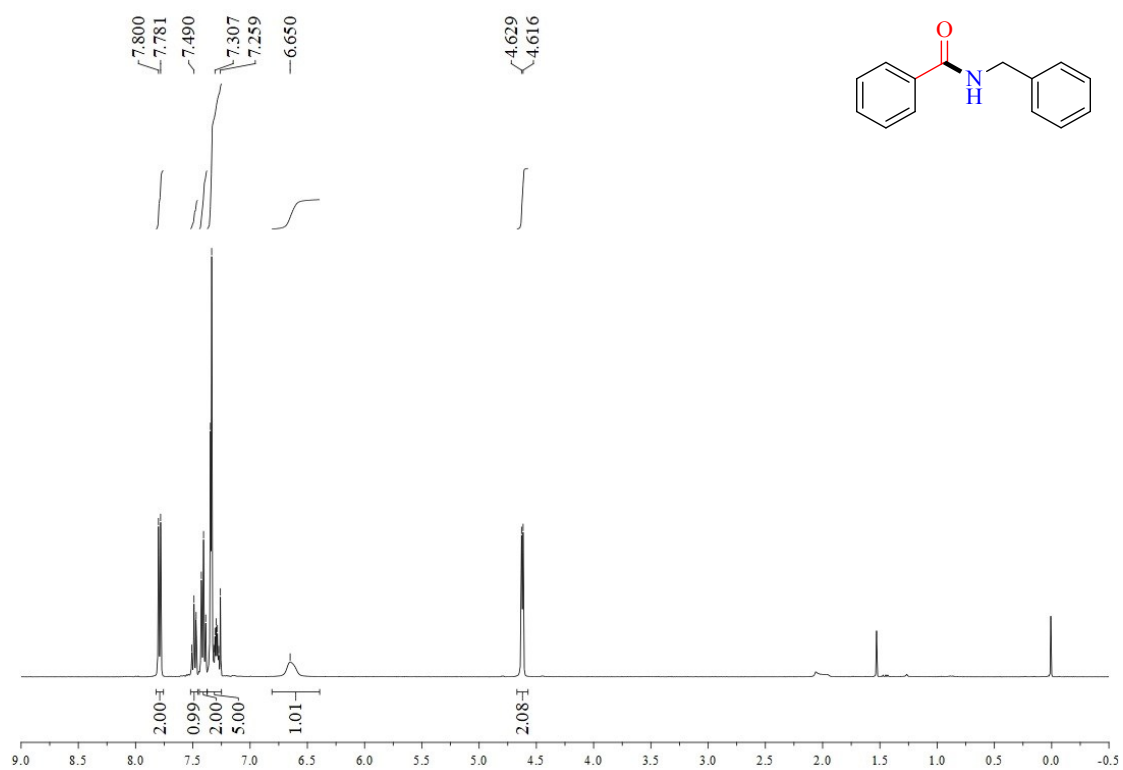
**N-([1,1'-biphenyl]-2-yl) benzamide (4g).**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )



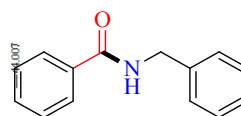
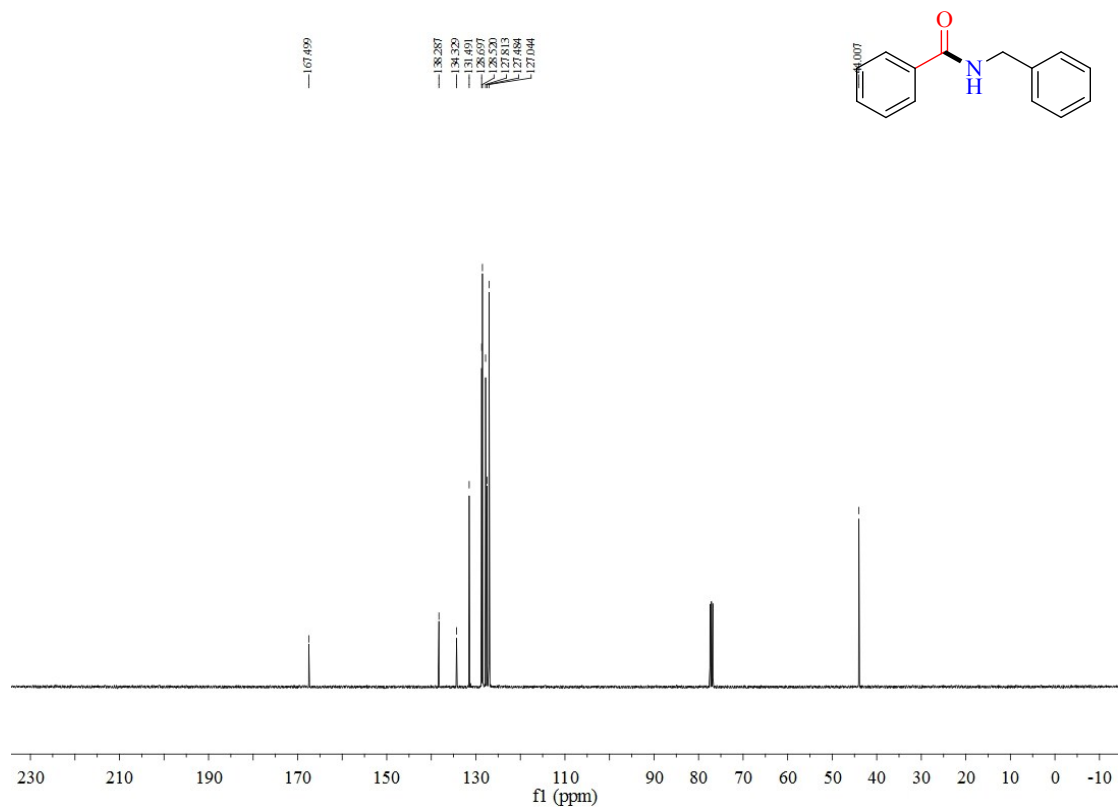
**N-methyl-N-phenyl-2-naphthamide (4h).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



**N-benzylbenzamide(4i).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



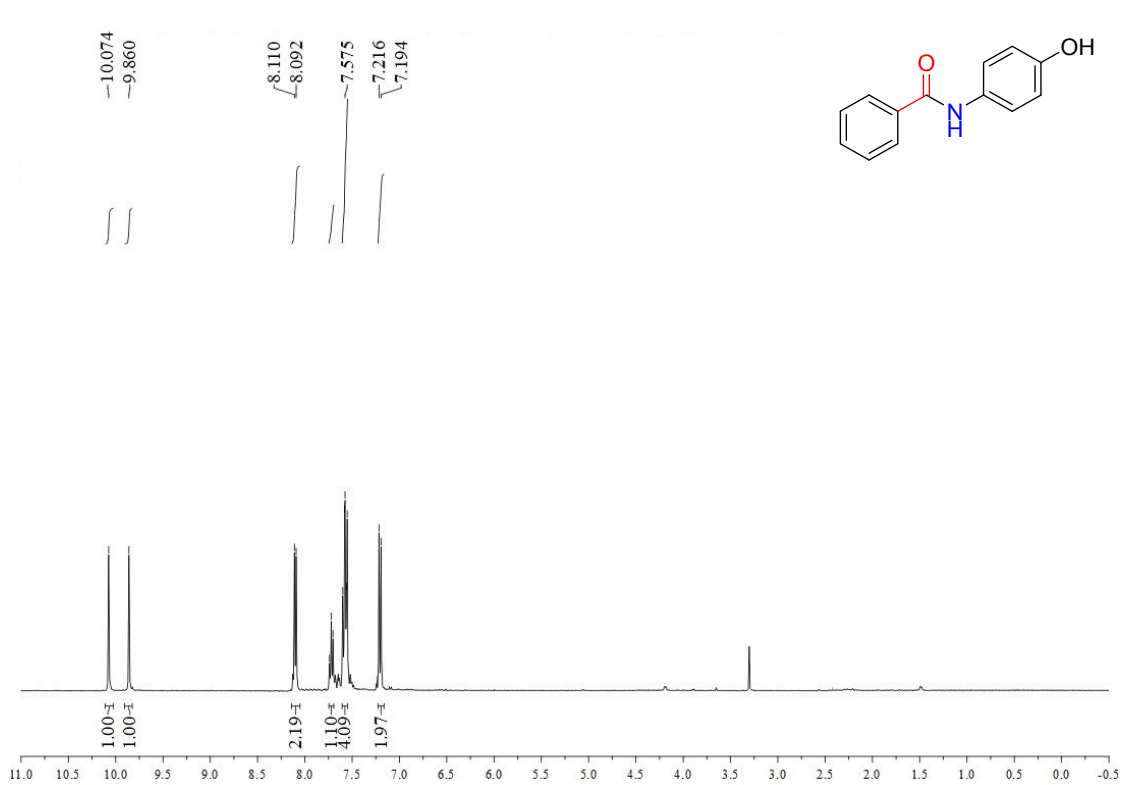
**N-benzylbenzamide(4i).**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )



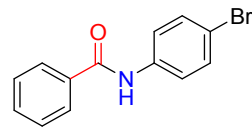
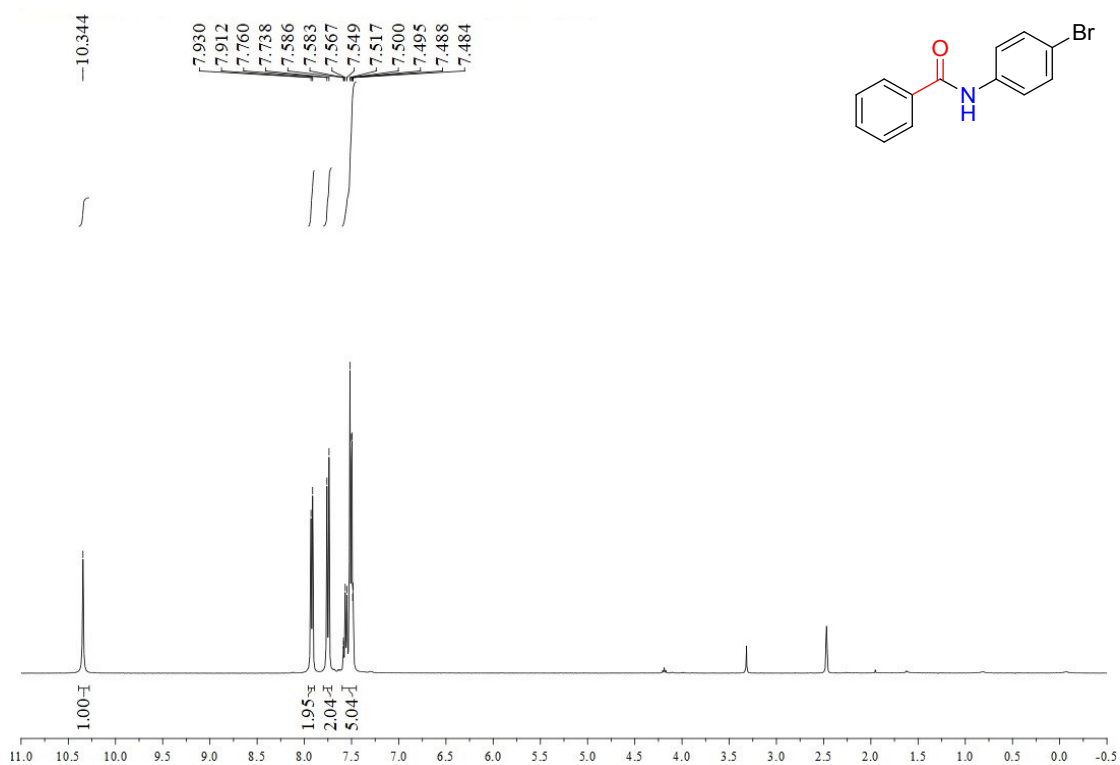
**N-phenylbenzamide(4j).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



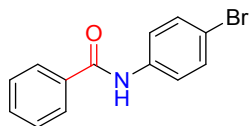
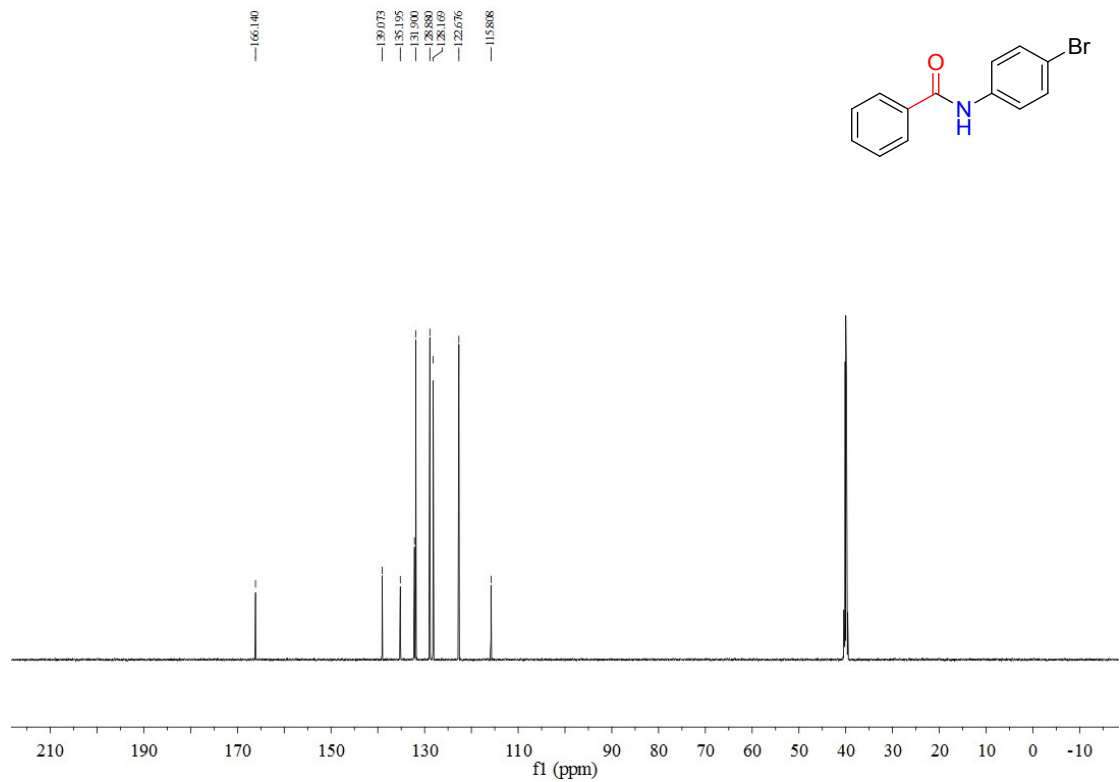
**N-(4-hydroxyphenyl) benzamide(4k).**  $^1\text{H}$  NMR (400 MHz, DMSO)



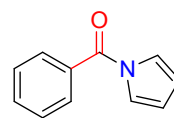
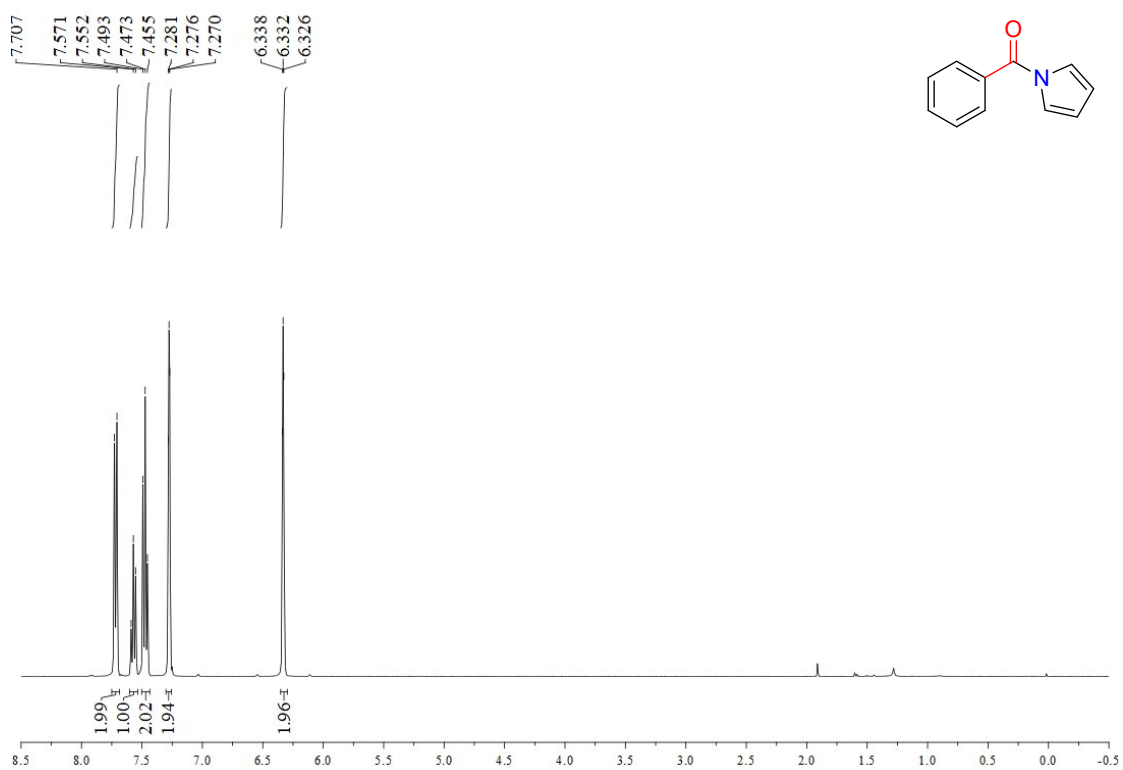
**N-(4-bromophenyl) benzamide. (4k)**  $^1\text{H}$  NMR (400 MHz, DMSO)



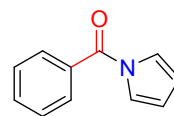
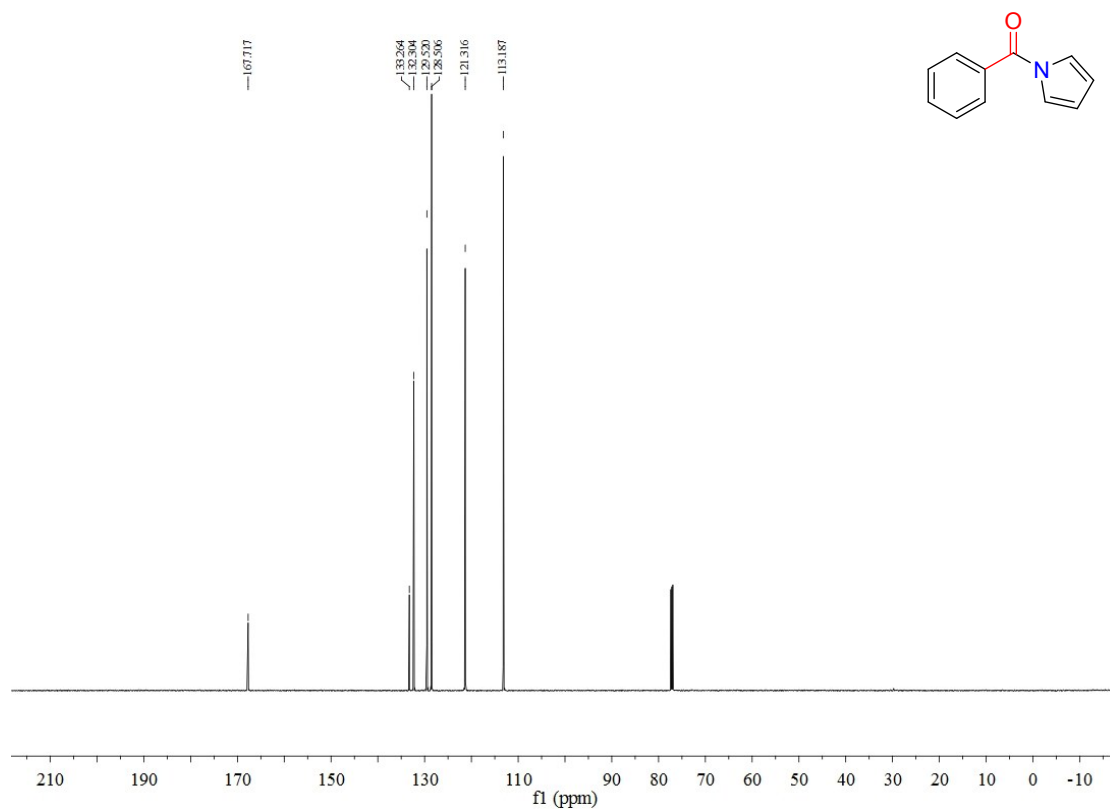
**N-(4-bromophenyl) benzamide. (4l)**  $^{13}\text{C}$  NMR (101 MHz, DMSO)



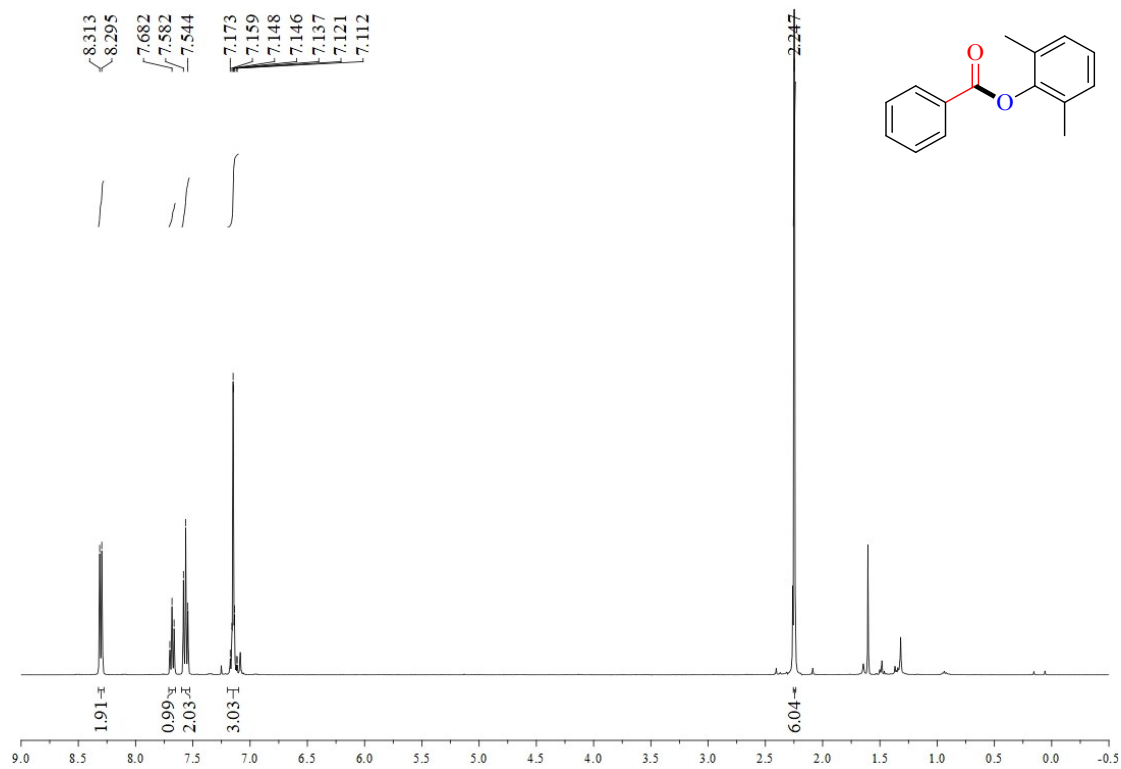
Phenyl (1H-pyrrol-1-yl) methanone (4m). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



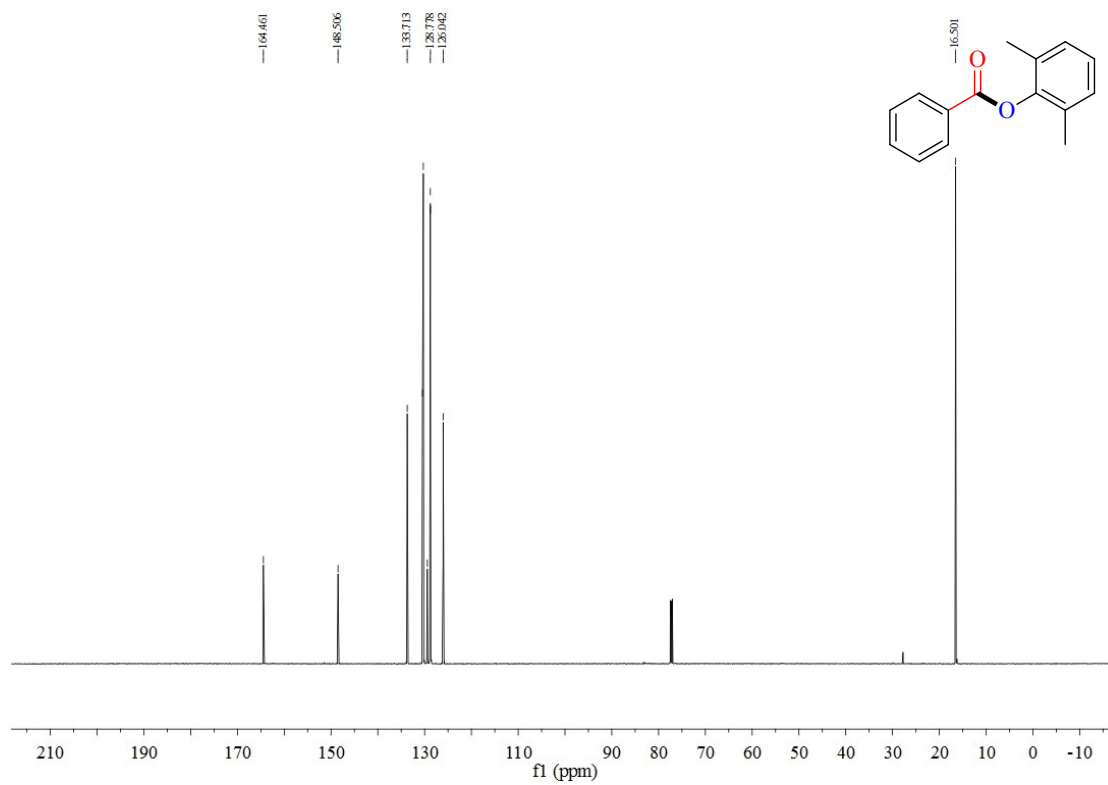
Phenyl (1H-pyrrol-1-yl) methanone (4m). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>)



**2,6-dimethylphenyl benzoate (5a).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

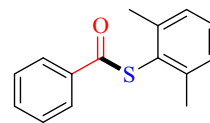
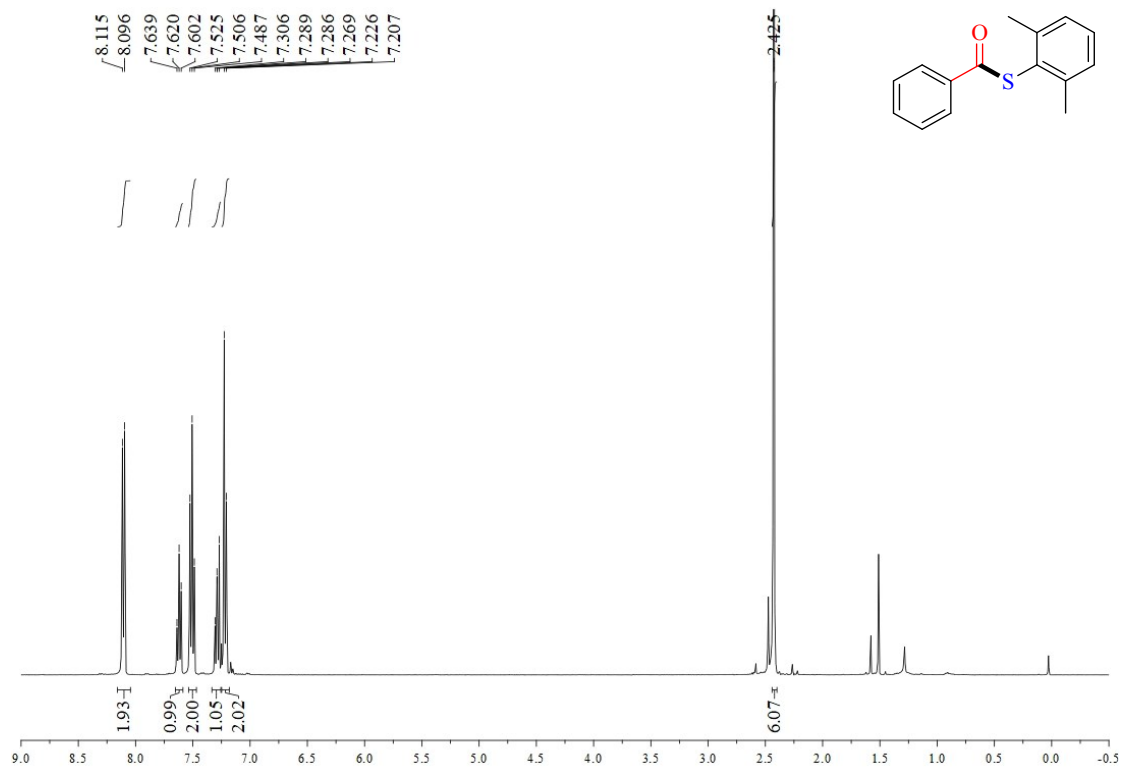


**2,6-dimethylphenyl benzoate (5a).**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )

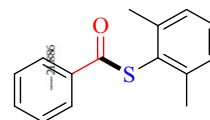
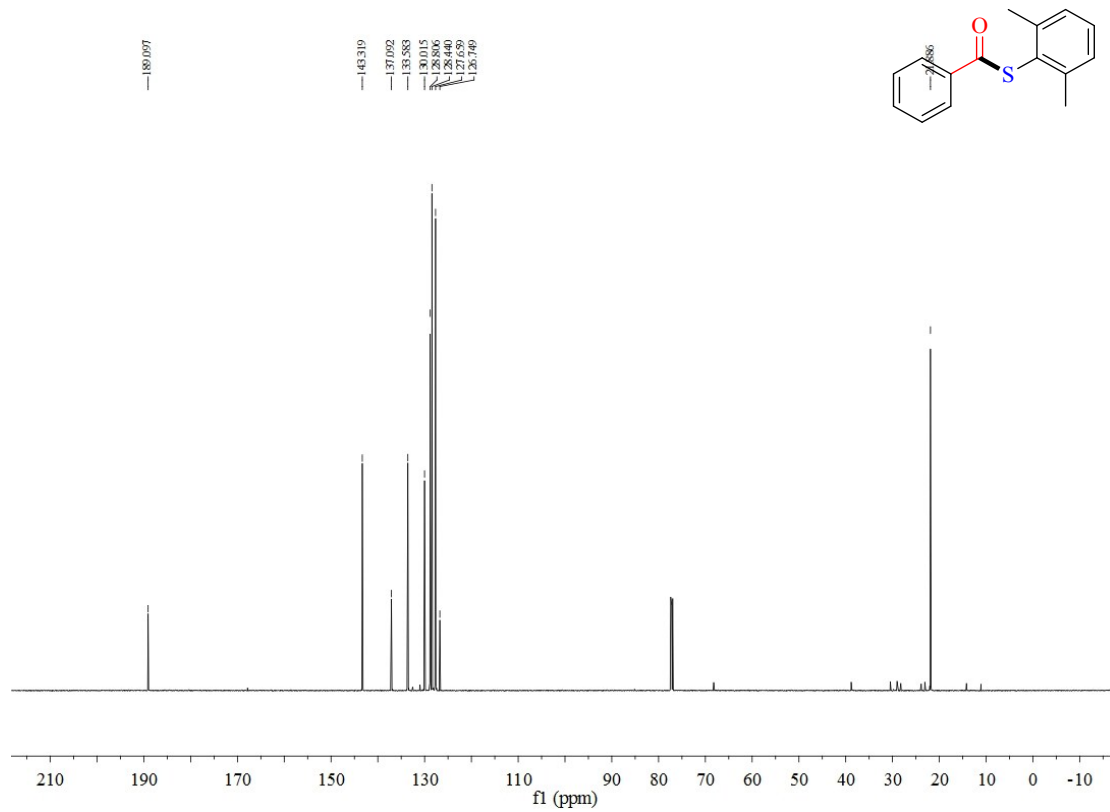




**S-(2,6-dimethylphenyl) benzothioate(5b).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

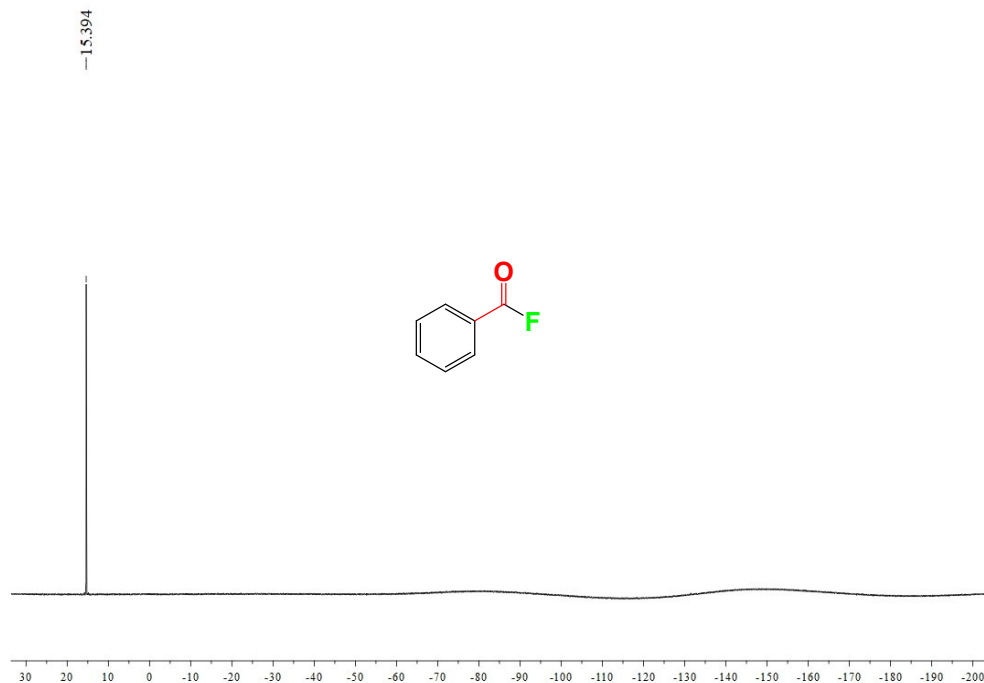


**S-(2,6-dimethylphenyl) benzothioate(5b).**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )



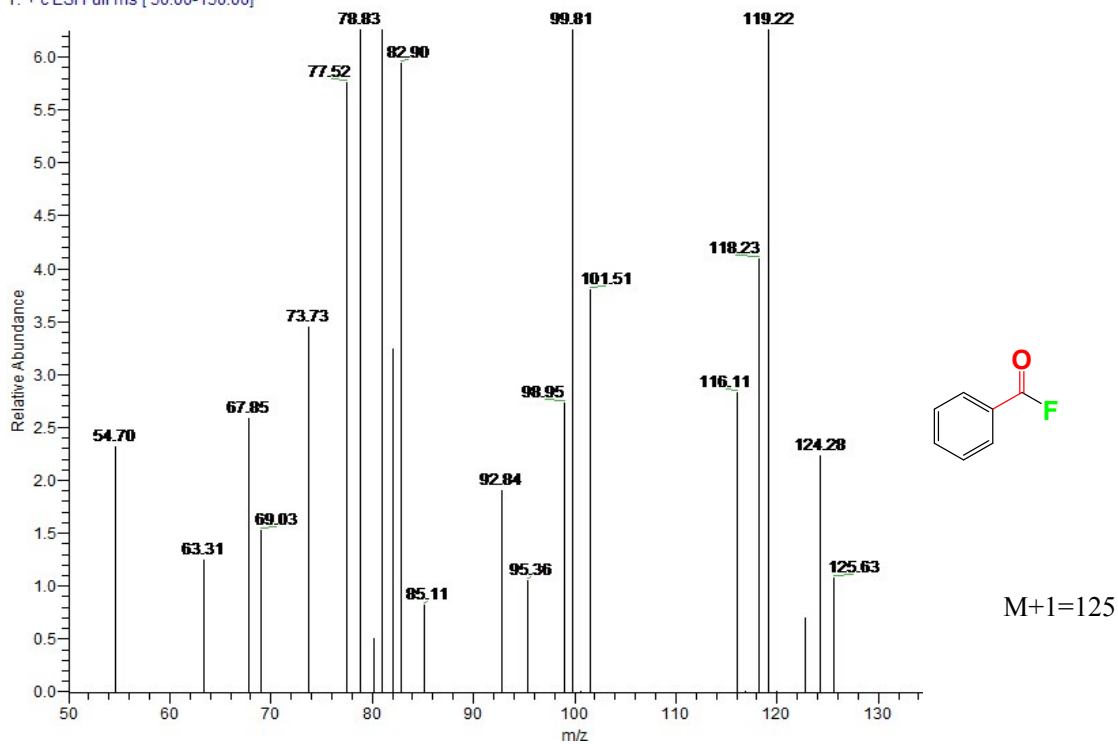
# Acyl fluoride in the reaction mixture analysed by <sup>19</sup>F MR, MS, GC-FID

Acyl fluoride <sup>19</sup>F NMR spectrum of the reaction mixture

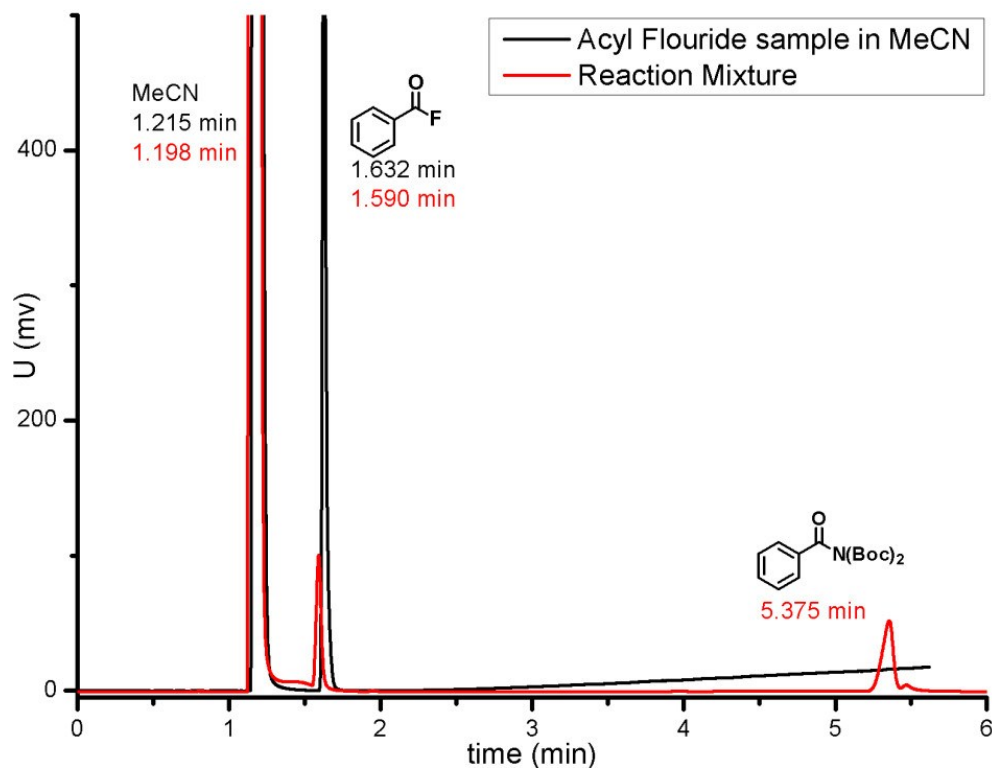


Acyl fluoride MS spectrum of the reaction mixture

jiang-5180322164226\_180324105952 #136 RT: 0.67 AV: 1 NL: 2.37E7  
T: + cESI Full ms [ 50.00-150.00]



GC-FID analysis for Acyl fluoride standard sample in MeCN (black line) and reaction mixture (N-di(t-butoxycarbonyl)-benzamide combined with 5 equivalent cesium fluoride in MeCN at 100 °C for 4 hours)



The gas chromatographic analyses were accomplished using an KeJie Instrument GC5890 (Nanjing, JiangShu, China). The capillary chromatographic column used was a SE-30 column. . The GC analysis was performed in the GC injector maintained at 200 °C. The oven temperature was set at 150 °C. The flame ionization detector temperature was maintained at 250 °C.