Supporting Information for

Difluorodiazoethane as a Masked Acetylene Equivalent in Formal [3+2] Cycloadditions with Ketones to Access 2,3-Functionalized Furans

Xiaolong Zhang,[b] Xin Li,[a] Paramasivam Sivaguru,[b] Jiayi Wu,[b] Giuseppe Zanoni,[b] Jin-Na Song*,[a] and Yongquan Ning*[b]

a. School of Life Science, Jilin University, Changchun 130012, China.

b. Jilin Province Key Laboratory of Organic Functional Molecular Design & Synthesis, Department of Chemistry, Northeast Normal University, Changchun 130024, China.

c. Department of Chemistry, University of Pavia, Viale Taramelli 12, Pavia 27100, Italy.

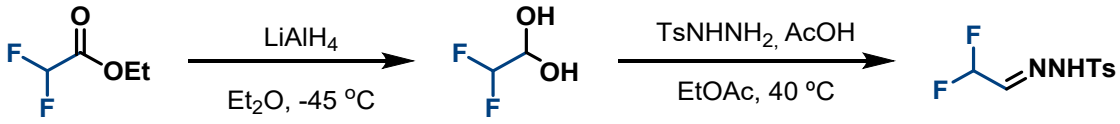
Email: songjn2010@jlu.edu.cn; ningyq508@nenu.edu.cn.

Contents

I. General information.

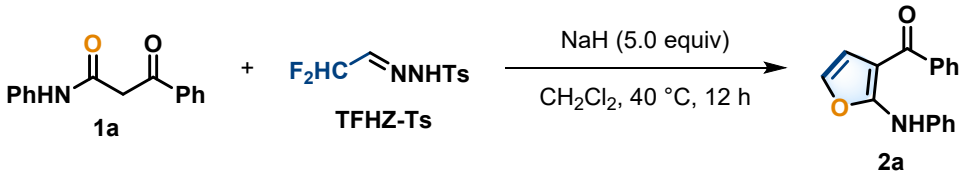
All reagents were purchased from commercial sources and used without purification unless otherwise mentioned. The products were purified by column chromatography over silica gel (300-400). NMR spectra were recorded on a Brüker Advance 600 (^{1}H: 600 MHz, ^{13}C: 150 MHz) and Brüker Advance 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz, ^{19}F: 471 MHz) at ambient temperature. Data were reported as chemical shifts in ppm relative to TMS (0.00 ppm) for ^{1}H and $CDCl_3$ (77.0 ppm) for ^{13}C. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectra were recorded on BRUKER AutoflexIII Smartbeam MS-spectrometer. High-resolution mass spectra (HRMS) were recorded on Bruck microTof by using ESI method.

II. General procedures for the synthesis of difluoroacetaldehyde *N*-tosylhydrazone (DFHZ-Ts).



A 100 mL bottom flask was charged with $LiAlH_4$ (750 mg, 20 mmol), evacuated and filled with argon for three times, followed by addition of dry Et_2O (40 mL) via syringe.under -45°C. Then ethyl difluoroacetate (9.3 g, 75 mmol) was added slowly, and the resulting mixture was allowed to stir overnight. The reaction was quenched by adding water and extracted three times with EA. The combined organic layer was dried with Na_2SO_4. Then 4-methylbenzenesulfonhydrazide ($TsNHNH_2$) (11.16 g, 60 mmol) and acetic acid (1 mL) were added and the mixture was stirred at 40 °C and monitored by TLC. After completion, the reaction mixture was concentrated under reduced pressure and the obtained crude solid was prurified by column chromatography using PE/EA (5:1 to 4:1) as eluent to afford the product DFHZ-Ts as a white solid.

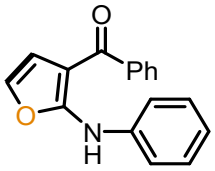
III. General procedures for synthesis of 2,3-Functionalized Furans.



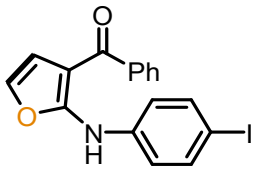
A Shrek reaction tube was charged with **DFHZ-Ts** (248 mg, 1.0 mmol), 3-Oxo-3-phenylpropionanilid

1a (119.5 mg, 0.5 mmol), NaH (60 % in oil, 100 mg, 2.5 mmol), evacuated and filled with argon for three times, followed by addition of dry CH_2Cl_2 (5.0 mL) via syringe. The resulting mixture was allowed to stir at 40 °C until TLC showed complete consumption of **1a**. After the reaction was completed, the reaction mixture was evaporated under reduced pressure to leave a crude mixture, which was purified by column chromatography on silica gel to afford **2a** as a white solid (109 mg, 83% yield).

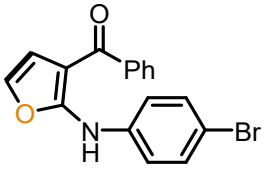
IV. Characterization data of prepared compounds.



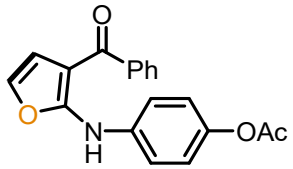
Phenyl(2-(phenylamino)furan-3-yl)methanone (2a): White solid, mp: 64-65°C, **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.62 (s, 1H), 7.79 (d, *J* = 7.6 Hz, 2H), 7.52-7.50 (m, 1H), 7.50-7.44 (m, 4H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.09 (t, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 2.4 Hz, 1H), 6.68 (d, *J* = 2.4 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 188.6, 160.6, 139.8, 137.8, 132.8, 131.28, 129.4, 128.4, 128.1, 123.4, 118.7, 110.6, 99.1. **IR** (Film): 3493, 3057, 1622, 1592, 1247, 1146, 720 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{17}H_{13}NNaO_2^+$ $[M+Na]^+$: 286.0838; Found: 286.0848.



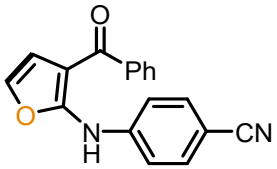
(2-((4-iodophenyl)amino)furan-3-yl)(phenyl)methanone (2b). Yellow solid, mp: 80-81°C, **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.62 (s, 1H), 7.78 (d, *J* = 7.2 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 2.4 Hz, 1H), 6.69 (d, *J* = 2.4 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 188.8, 159.9, 139.6, 138.2, 137.6, 133.1, 131.3, 128.4, 128.0, 120.4, 110.6, 99.4, 86.0. **IR** (Film): 3404, 2958, 1607, 1509, 1248, 828, 698 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{17}H_{12}INNaO_2^+$ $[M+Na]^+$: 411.9805; Found: 411.9811.



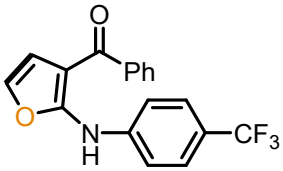
(2-((4-bromophenyl)amino)furan-3-yl)(phenyl)methanone (2c). Dark solid, mp: 77-78℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.55 (s, 1H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.44-7.37 (m, 4H), 7.27 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 2.4 Hz, 1H), 6.62 (d, *J* = 2.4 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 187.8, 159.0, 138.6, 135.9, 132.0, 131.3, 130.3, 127.4, 127.0, 119.1, 114.8, 109.6, 98.4. **IR** (Film): 3358, 2925, 1587, 1563, 1376, 816, 696 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{17}H_{12}BrNNaO_2^+$ $[M+Na]^+$: 363.9949; Found: 363.9942.



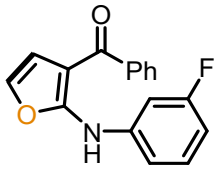
4-((3-benzoylfuran-2-yl)amino)phenyl acetate (2d). Yellow solid, mp: 84-85℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.80 (s, 1H), 7.98 (d, *J* = 9.0 Hz, 2H), 7.80 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.2Hz, 1H), 7.53-7.47 (m, 4H), 7.02 (d, *J* = 2.4 Hz, 1H), 6.73 (d, *J* = 2.4 Hz, 1H), 2.58 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ196.6, 189.3, 159.3, 142.2, 139.43, 133.6, 131.8, 131.6, 130.3, 128.5, 128.1, 117.5, 110.7, 100.2, 26.4. **IR** (Film): 3383, 2927, 2203, 1607, 1172 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{19}H_{15}NNaO_4^+$ $[M+Na]^+$: 344.0898; Found: 344.0901.



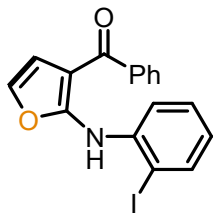
4-((3-benzoylfuran-2-yl)amino)benzonitrile (2e). Yellow solid, mp: 99-100℃. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.80 (s, 1H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.46-7.54 (m, 4H), 7.03 (d, *J* = 2.5 Hz, 1H), 6.74 (d, *J* = 2.5 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 189.5, 158.9, 141.8, 139.2, 133.8, 133.7, 131.7, 128.5, 128.1, 119.1, 118.1, 110.8, 105.6, 100.5. **IR** (Film): 3469, 2986, 1604, 1562, 737, 698 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{18}H_{12}N_2NaO_2^+$ $[M+Na]^+$: 311.0801; Found: 311.0799.



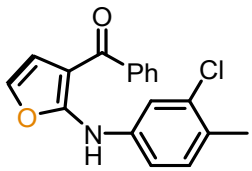
Phenyl(2-((4-(trifluoromethyl)phenyl)amino)furan-3-yl)methanone (2f). Yellow solid, mp: 74-75℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.75 (s, 1H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.56-7.51 (m, 3H), 7.49 (t, *J* = 7.2 Hz, 2H), 6.98 (d, *J* = 2.4 Hz, 1H), 6.71 (d, *J* = 2.4 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 189.2, 159.5, 140.9, 139.5, 133.4, 131.5, 128.5, 128.1, 126.7 (q, *J* = 4.5 Hz), 124.8 (q, *J* = 33.0 Hz), 124.3 (q, *J* = 270.0 Hz), 117.9, 110.7, 100.0. **IR** (Film): 3415, 2958, 1756, 1662, 1376, 1049 cm^{-1}. **^{19}F NMR** (564 MHz, $CDCl_3$) δ -63.29 (s). **HRMS** (ESI) m/z calcd. for $C_{18}H_{12}F_3NNaO_2^+$ $[M+Na]^+$: 354.0718; Found:354.0723.



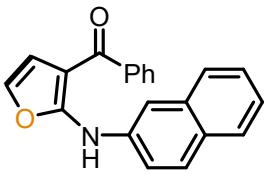
(2-((3-fluorophenyl)amino)furan-3-yl)(phenyl)methanone (2g). Brown solid, mp: 43-44℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.66 (s, 1H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.28-7.34 (m, 2H), 7.15 (dd, *J* = 1.8 Hz, 7.8 Hz, 1H), 6.97 (d, *J* = 2.4 Hz, 1H), 6.78 (dt, *J* = 2.4 Hz, 8.4 Hz, 1H), 6.70 (d, *J* = 2.4 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 189.0, 164.3, 162.6, 159.9, 139.6, 139.4 (d, *J* = 10.5 Hz), 133.2, 131.4, 130.5 (d, *J* = 10.5 Hz), 128.4, 128.1, 114.2, 110.6, 109.9 (d, *J* = 21.0 Hz), 105.7 (d, *J* = 25.5 Hz). **^{19}F NMR** (564 MHz, $CDCl_3$) δ -112.73--112.80 (m). **IR** (Film): 3415, 3029, 1625, 1473, 1185, 1048 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{17}H_{12}FNNaO_2^+$ $[M+Na]^+$: 304.0708; Found: 304.0705.



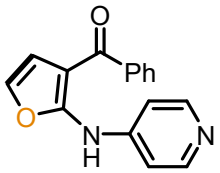
(2-((2-iodophenyl)amino)furan-3-yl)(phenyl)methanone (2h). Yellow solid, mp: 72-73℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.83 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 6.96 (d, *J* = 1.8 Hz, 1H), 6.80 (t, *J* = 7.2 Hz, 1H), 6.71 (d, *J* = 1.8 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 189.0, 159.5, 139.8, 139.6, 139.4, 133.0, 131.3, 129.2, 128.4, 128.2, 124.5, 118.6, 110.9, 100.1, 88.4. **HRMS** (ESI) m/z calcd. for $C_{17}H_{12}INNaO_2^+$ $[M+Na]^+$: 411.9805; Found: 411.9807.



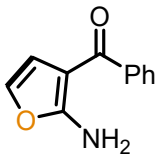
(2-((3-chloro-4-methylphenyl)amino)furan-3-yl)(phenyl)methanone (2i). Brown solid, mp: 87-88℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.57 (s, 1H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.56 (s, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.22-7.16 (m, 1H), 6.94 (d, *J* = 2.4 Hz, 1H), 6.69 (d, *J* = 2.4 Hz, 1H), 2.35 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 188.8, 160.2, 139.7, 136.6, 134.9, 133.1, 131.4, 131.3, 130.8, 128.4, 128.1, 119.0, 117.1, 110.6, 99.2, 19.4. **IR** (Film): 3447, 3152, 3119, 2922, 1628, 1540 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{18}H_{14}ClNNaO_2^+$ $[M+Na]^+$: 334.0611; Found: 334.0611.



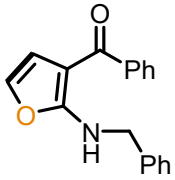
(2-(naphthalen-2-ylamino)furan-3-yl)(phenyl)methanone (2j). White solid, mp: 101-102℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.74 (s, 1H), 7.93 (d, *J* = 1.8 Hz, 1H), 7.77-7.70 (m, 5H), 7.48-7.44 (m, 1H), 7.44-7.40 (m, 4H), 7.32 (t, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 2.4 Hz, 1H), 6.65 (d, *J* = 2.4 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 188.7, 160.5, 139.8, 135.3, 134.2, 133.0, 131.2, 130.1, 129.3, 128.4, 128.1, 127.7, 127.3, 126.8, 124.7, 119.6, 114.3, 110.7, 99.5. **IR** (Film): 3853, 3162, 3055, 1621, 1588, 1543 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{21}H_{15}NNaO_2^+$ $[M+Na]^+$: 336.1000; Found: 336.1001.



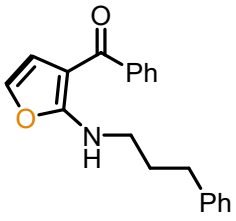
Phenyl(2-(pyridin-4-ylamino)furan-3-yl)methanone (2k). Yellow solid, mp: 69-70℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.53 (s, 1H), 8.67 (d, *J* = 3.0 Hz, 1H), 8.26 (d, *J* = 4.8 Hz, 1H), 7.78-7.75 (m, 1H), 7.74-7.71 (m, 2H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.24-7.21 (m, 1H), 6.90 (d, *J* = 2.4 Hz, 1H), 6.65 (d, *J* = 2.4 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 189.1, 159.9, 144.3, 140.5, 139.4, 134.8, 133.3, 131.5, 128.5, 128.1, 125.0, 123.8, 110.7, 99.8. **IR** (Film): 3568, 2920, 1632, 1458, 736, 698 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{16}H_{12}N_2NaO_2^+$ $[M+Na]^+$: 287.0793; Found: 287.0796.



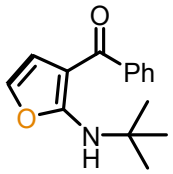
(2-aminofuran-3-yl)(phenyl)methanone (2l). Yellow solid, mp: 69-70℃. **^{1}H NMR** (600 MHz, CDCl3) δ 7.76 (d, *J* = 7.2 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 6.73 (d, *J* = 2.4 Hz, 1H), 6.55 (d, *J* = 2.4 Hz, 1H), 6.45 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 189.0, 164.1, 140.0, 132.1, 131.0, 128.3, 128.0, 110.7, 98.1. **IR** (Film): 3461, 2952, 1758, 1628, 1540, 1187 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{11}H_9NO_2^+$ $[M+Na]^+$: 210.0531; Found: 210.0523.



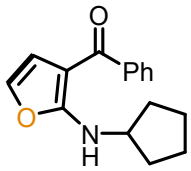
(2-(benzylamino)furan-3-yl)(phenyl)methanone (2m). Yellow solid, mp: 52-53℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.57-7.27 (m, 8H), 6.74 (d, *J* = 2.4 Hz, 1H), 6.58 (d, *J* = 2.4 Hz, 1H), 4.66 (d, *J* = 6.0 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 187.8, 164.6, 140.3, 137.8, 132.2, 130.8, 128.8, 128.3, 128.0, 127.7, 127.4, 110.9, 97.3, 46.0. **IR** (Film): 3420, 3109, 2949, 1643, 752, 697 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{18}H_{15}NNaO_2^+$ $[M+Na]^+$: 300.1000; Found: 300.1007.



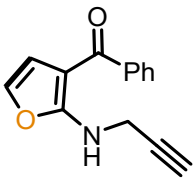
Phenyl(2-((3-phenylpropyl)amino)furan-3-yl)methanone (2n). Yellow solid, mp: 78-79℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.76-7.72 (m, 2H), 7.49-7.42 (m, 3H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.24-7.20 (m, 3H), 6.73 (d, *J* = 2.4 Hz, 1H), 6.56 (d, *J* = 2.4 Hz, 1H), 3.49 (q, *J* = 7.8Hz, 2H), 2.75 (t, *J* = 7.8 Hz, 2H), 2.07-1.99 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 187.6, 165.0, 141.1, 140.4, 132.0, 130.6, 128.5, 128.4, 128.3, 127.9, 126.1, 110.8, 97.1, 41.4, 32.9, 31.6. **IR** (Film): 3502, 2998, 1740, 1667, 1241, 870 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{20}H_{19}NNaO_2^+$ $[M+Na]^+$: 328.1314; Found: 328.1313.



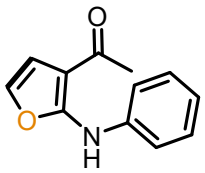
(2-(tert-butylamino)furan-3-yl)(phenyl)methanone (2o). Yellow oil, **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.41-7.33 (m, 3H), 6.67 (d, *J* = 2.4 Hz, 1H), 6.47 (d, *J* = 2.4 Hz, 1H), 1.41 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 187.3, 164.7, 140.5, 132.1, 130.5, 128.2, 127.9, 110.4, 97.6, 52.5, 29.8. **HRMS** (ESI) m/z calcd. for $C_{15}H_{17}NNaO_2^+$ $[M+Na]^+$: 266.1151; Found: 266.1157.



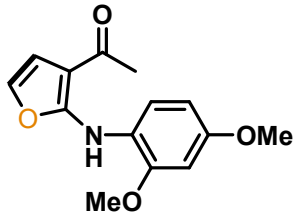
(2-(cyclopentylamino)furan-3-yl)(phenyl)methanone (2p). Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.35 (d, *J* = 6.2 Hz, 1H), 7.75-7.71 (m, 2H), 7.51-7.40 (m, 3H), 6.73 (d, *J* = 2.4 Hz, 1H), 6.55 (d, *J* = 2.4 Hz, 1H), 4.25-4.14 (m, 1H), 2.14-2.03 (m, 2H), 1.84-1.75 (m, 2H), 1.70-1.58 (m, 4H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 187.3, 164.6, 140.4, 132.1, 130.6, 128.2, 127.9, 110.7, 97.0, 53.8, 33.8, 23.7. **IR** (Film): 3362, 2930, 1724, 1598, 1137, 848, 737 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{16}H_{17}NNaO_2^+$ $[M+Na]^+$: 278.1156; Found: 278.1153.



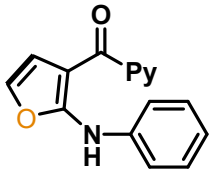
Phenyl(2-(prop-2-yn-1-ylamino)furan-3-yl)methanone (2q). Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 2H), 6.74 (d, *J* = 2.4 Hz, 1H), 6.52 (d, *J* = 2.4 Hz, 1H), 4.20-4.17 (m, 2H), 2.23 (s, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 187.2, 162.6, 139.0, 131.6, 129.9, 127.3, 126.9, 109.9, 96.7, 78.2, 71.0, 30.6. **IR** (Film): 3458, 3192, 2983, 1740, 1624, 1587, 739, 693 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{14}H_{11}NNaO_2^+$ $[M+Na]^+$: 248.0682; Found: 248.0667.



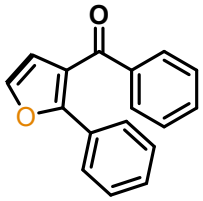
1-(2-(phenylamino)furan-3-yl)ethan-1-one (2r). Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.88 (d, *J* = 2.4 Hz, 1H), 6.56 (d, *J* = 2.4 Hz, 1H), 2.35 (s, 3H).**^{13}C NMR** (150 MHz, $CDCl_3$) δ 192.5, 158.4, 138.0, 132.5, 129.3, 123.1, 118.4, 109.5, 100.1, 27.1. **IR** (Film): 3422, 3181, 2954, 1625, 1473, 1185, 1048 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{12}H_{11}NNaO_2^+$ $[M+Na]^+$: 224.0688; Found: 224.0794.



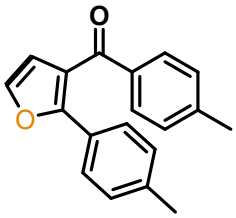
1-(2-((2,4-dimethoxyphenyl)amino)furan-3-yl)ethan-1-one (2s). Brown solid, mp: 72-73℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ10.29 (s, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 6.85 (d, *J* = 2.4 Hz, 1H), 6.55 (d, *J* = 2.4 Hz, 1H), 6.53 (d, *J* = 2.4 Hz, 1H), 6.48 (dd, *J* = 2.4 Hz, *J* = 8.4 Hz, 2H), 3.93 (s, 3H), 3.81 (s, 3H), 2.34 (s, 3H).**^{13}C NMR** (150 MHz, $CDCl_3$) δ 191.7, 158.7, 156.0, 149.3, 132.1, 121.5, 117.9, 109.6, 103.9, 99.9, 99.0, 56.0, 55.6, 26.8. **IR** (Film): 3462, 3126, 3031, 2924, 1590, 1318, 737 cm^{-1}.**HRMS** (ESI) m/z calcd. for $C_{14}H_{15}NNaO_4^+$ $[M+Na]^+$: 284.0893; Found: 284.0902.



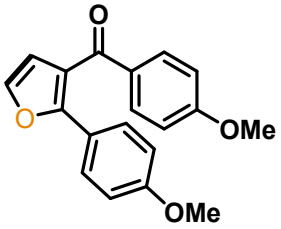
(2-(phenylamino)furan-3-yl)(pyridin-2-yl)methanone (2t). Yellow solid, mp: 86-87℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.59 (s, 1H), 8.78 (d, *J* = 4.2 Hz, 2H), 7.61-7.58 (m, 2H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 8.4 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 2.4 Hz, 1H), 6.60 (d, *J* = 2.4 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 186.0, 161.0, 150.4, 146.4, 137.3, 133.5, 129.5, 124.0, 121.7, 119.0, 109.8, 99.0. **HRMS** (ESI) m/z calcd. for $C_{16}H_{12}N_2NaO_2^+$ $[M+Na]^+$: 287.0793; Found: 287.0796.



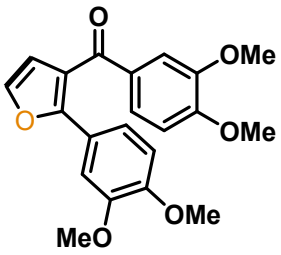
Phenyl(2-phenylfuran-3-yl)methanone (4a). Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 1.2 Hz, 8.4 Hz, 2H), 7.67-7.71 (m, 2H), 7.48-7.52 (m, 2H), 7.37 (t, *J* = 8.4 Hz, 2H), 7.27-7.32 (m, 2H), 7.29 (d, *J* = 1.8 Hz, 1H), 6.70 (d, *J* = 1.8 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 191.8, 156.0, 141.3, 138.0, 132.8, 129.8, 129.8, 129.0, 128.3, 127.5, 120.9, 113.8. **IR** (Film): 2923, 1712, 1628, 1540, 1186 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{17}H_{12}NaO_2^+$ $[M+Na]^+$: 271.0738; Found: 271.0736.



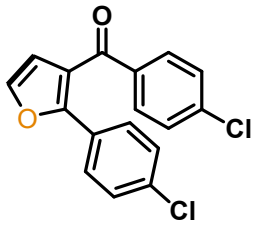
4-tolyl(2-(p-tolyl)furan-3-yl)methanone (4b). Yellow oil, **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 1.8 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.64 (d, *J* = 2.4 Hz, 1H), 2.38 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 191.6, 155.9, 143.6, 140.8, 139.0, 135.6, 130.0, 129.1, 127.3, 120.4, 113.8, 21.7, 21.4. **IR** (Film): 2998, 1762, 1375, 1059, 735, 694 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{19}H_{16}NaO_2^+$ $[M+Na]^+$: 299.1043; Found: 299.1036.



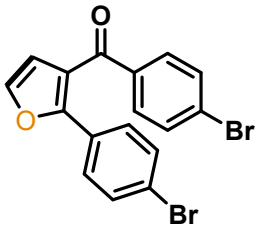
(4-methoxyphenyl)(2-(4-methoxyphenyl)furan-3-yl)methanone (4c). White solid, mp: 68-69℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 1.8 Hz, 8.4 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 4H), 7.37 (t, *J* = 7.8 Hz, 4H), 7.44 (d, *J* = 1.8 Hz, 1H), 6.85 (dd, *J* = 9.0 Hz, 19.8 Hz, 4H), 6.64 (d, *J* = 1.8 Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 190.6, 163.4, 160.1, 155.5, 140.5, 132.1, 131.0, 128.9, 122.7, 113.8, 113.7, 113.6, 55.5, 55.3. **IR** (Film): 3447, 3152, 3119, 2922, 1628, 1540 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{19}H_{16}NaO_4^+$ $[M+Na]^+$: 331.0941; Found: 331.0947.



(3,4-dimethoxyphenyl)(2-(3,4-dimethoxyphenyl)furan-3-yl)methanone (4d). White solid, mp: 85-86°C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43-7.46 (m, 3H), 7.29 (dd, *J* = 1.8 Hz, 8.4 Hz, 1H), 7.24 (d, *J* = 1.8 Hz, 1H), 6.81-6.76 (m, 2H), 6.67 (d, *J* = 1.8 Hz, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 3.82 (s, 3H), 3.76 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 190.5, 155.1, 153.2, 149.7, 148.9, 148.6, 140.6, 131.0, 124.9, 122.9, 120.4, 120.0, 113.9, 111.8, 110.9, 110.8, 110.0, 56.1, 56.0, 55.9, 55.8. **IR** (Film): 2992, 1762, 1649, 1555, 1159 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{19}H_{16}NaO_4^+$ $[M+Na]^+$: 331.0941; Found: 331.0947.

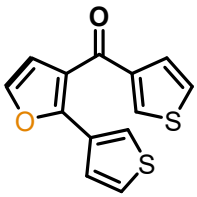


(4-chlorophenyl)(2-(4-chlorophenyl)furan-3-yl)methanone (4e). White solid, mp: 74-75°C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 1.8 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.56 (d, *J* = 1.8 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 190.2, 155.0, 141.5, 139.5, 136.3, 135.3, 131.1, 128.8, 128.7, 128.7, 128.1, 120.8, 113.8. **IR** (Film): 2937, 1711, 1660, 1598, 1427, 1265 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{17}H_{10}Cl_2NaO_2^+$ $[M+Na]^+$: 338.9968; Found: 338.9972.

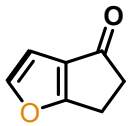


(4-bromophenyl)(2-(4-bromophenyl)furan-3-yl)methanone (4f). White solid, mp: 81-82°C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H),

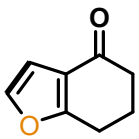
7.44 (d, J = 1.8 Hz, 1H), 7.40 (d, J = 8.4 Hz, 2H), 6.58 (d, J = 1.8 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 190.4, 155.1, 141.6, 136.7, 131.8, 128.9, 128.5, 128.2, 123.6, 120.8, 113.8. **IR** (Film): 2993, 1764, 1377, 1241 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{17}H_{10}Br_2NaO_2^+$ $[M+Na]^+$: 426.8945; Found: 426.8943.



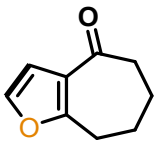
Thiophen-3-yl(2-(thiophen-3-yl)furan-3-yl)methanone (4g). Brown oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.17 (dd, J = 1.2 Hz, 3.0 Hz, 1H), 7.96 (dd, J = 1.2 Hz, 3.0 Hz, 1H), 7.59-7.53 (m, 1H), 7.43 (d, J = 1.8 Hz, 1H), 7.35-7.32 (m, 1H), 7.31-7.29 (m, 1H), 6.76 (d, J = 2.4 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 184.3, 152.9, 142.8, 140.3, 133.4, 130.9, 128.0, 126.7, 126.2, 125.5, 125.5, 120.5, 113.2. **IR** (Film): 2983, 1651, 1432, 1226, 1100, 769 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{13}H_8NaO_2S_2^+$ $[M+Na]^+$: 282.9861; Found: 282.9864.



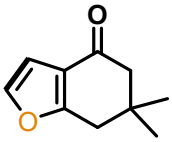
5,6-dihydro-4H-cyclopenta[b]furan-4-one (4h). Colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.52 (d, J = 1.8 Hz, 1H), 6.53 (d, J = 1.8 Hz, 1H), 3.03-2.97 (m, 9.0 Hz, 4H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 195.3, 183.0, 149.6, 128.1, 105.3, 42.1, 22.2. **IR** (Film): 2952, 1763, 1676, 1377, 1055 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_7H_6NaO_2^+$ $[M+Na]^+$: 145.0265; Found: 145.0271.



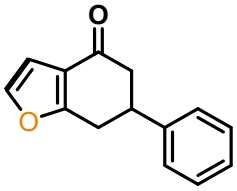
6,7-dihydrobenzofuran-4(5H)-one (4i). colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.30 (d, J = 1.8 Hz, 1H), 6.65 (d, J = 1.8 Hz, 1H), 2.86 (t, J = 6.0 Hz, 2H), 2.48 (t, J = 6.0 Hz, 2H), 2.13-2.19 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 194.5, 167.1, 142.6, 121.1, 106.5, 37.7, 23.4, 22.6. **IR** (Film): 3122, 3028, 2899, 1678, 1448, 1119 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_8H_8NaO_2^+$ $[M+Na]^+$: 159.0422; Found: 159.0421.



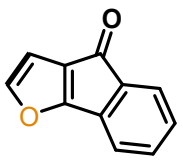
5,6,7,8-tetrahydro-4H-cyclohepta[b]furan-4-one (4j). Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.23 (d, *J* = 1.8 Hz, 1H), 6.71 (d, *J* = 1.8 Hz, 1H), 2.95 (t, *J* = 6.6 Hz, 2H), 2.67 (t, *J* = 6.0 Hz, 2H), 1.99-1.91 (m, 2H), 1.89-1.83 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 196.6, 161.8, 141.1, 123.6, 110.4, 44.5, 29.6, 24.9, 22.9. **IR** (Film): 2984, 1764, 1659, 1598, 1269 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_9H_{10}NaO_2^+$ $[M+Na]^+$: 173.0584; Found: 173.0577.



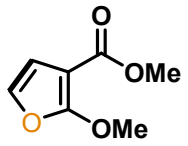
6,6-dimethyl-6,7-dihydrobenzofuran-4 (5H)-one (4k). Colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 1.8 Hz, 1H), 6.65 (d, *J* = 1.8 Hz, 1H), 2.73 (s, 3H), 2.36 (s, 3H), 1.12 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 194.0, 166.3, 142.9, 119.9, 106.3, 52.1, 37.4, 35.3, 28.6. **IR** (Film): 2958, 1756, 1662, 1376, 1049 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{10}H_{12}NaO_2^+$ $[M+Na]^+$: 187.0740; Found: 187.0738.



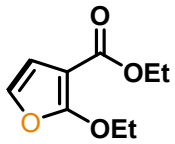
6-phenyl-6,7-dihydrobenzofuran-4(5H)-one (4l). Colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.24-7.30 (m, 2H), 7.18-7.22 (m, 3H), 6.71 (d, *J* = 1.8 Hz, 1H), 3.60-3.50 (m, 1H), 3.22-3.15 (m, 1H), 3.09-3.01 (m, 1H), 2.79-2.74 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 193.0, 166.3, 143.1, 142.5, 128.9, 127.3, 126.8, 121.1, 106.5, 45.0, 41.4, 31.2. **IR** (Film): 2933, 1662, 1508, 1243, 736, 691 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{14}H_{12}NaO_2^+$ $[M+Na]^+$: 235.0745; Found: 235.0756.



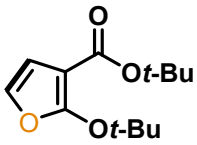
4H-indeno[1,2-b]furan-4-one (4m). White soild, mp: 63-64°C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.2 Hz, 1H), 7.41 (d, *J* = 1.8 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 1.8 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 185.2, 175.4, 148.3, 138.4, 134.1, 133.0, 129.1, 123.8, 123.6, 117.2, 106.9. **IR** (Film): 2957, 1650, 1487, 1376, 1149 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{11}H_6NaO_2^+$ $[M+Na]^+$: 193.0263; Found: 193.0265.



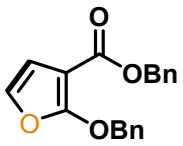
Methyl 2-methoxyfuran-3-carboxylate (4n), colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.84 (d, *J* = 2.4 Hz, 1H), 6.61 (d, *J* = 1.8 Hz, 1H), 4.11 (s, 3H), 3.80 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.5, 162.2, 132.2, 111.8, 91.0, 58.0, 51.3. **IR** (Film): 2933, 1651, 1482, 1444, 1262, 892, 728, 685 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_7H_8NaO_4^+$ $[M+Na]^+$: 179.0320; Found: 179.0319.



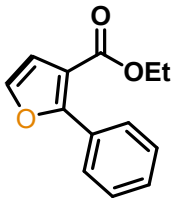
Ethyl 2-ethoxyfuran-3-carboxylate (4o). colorless oil, **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.81 (d, *J* = 1.8 Hz, 1H), 6.58 (d, *J* = 1.8 Hz, 1H), 4.42 (q, *J* = 7.2 Hz, 2H), 4.25 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.1, 162.0, 132.1, 111.6, 92.3, 67.9, 59.8, 15.0, 14.4. **HRMS** (ESI) m/z calcd. for $C_9H_{12}NaO_4^+$ $[M+Na]^+$: 207.0633; Found: 207.0632.



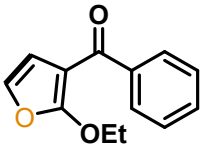
Tert-butyl 2-(tert-butoxy)furan-3-carboxylate (4p). Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.85 (d, *J* = 2.4 Hz, 1H), 6.55 (d, *J* = 2.4 Hz, 1H), 1.53 (s, 9H), 1.46 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 161.7, 158.7, 132.2, 110.2, 99.1, 84.8, 79.1, 27.7, 27.4. **IR** (Film): 3031, 2927, 1651, 1502, 1257, 898, 810, 693 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{13}H_{20}NaO_4^+$ $[M+Na]^+$: 263.1265; Found: 263.1262.



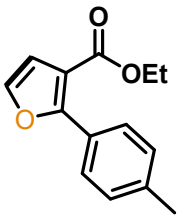
Benzyl 2-(benzyloxy)furan-3-carboxylate (4q). Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39-7.44 (m, 4H), 7.31-7.38 (s, 6H), 6.85 (d, *J* = 2.4 Hz, 1H), 6.66 (d, *J* = 2.4 Hz, 1H), 5.40 (s, 2H), 5.28 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 162.8, 161.8, 136.5, 135.2, 132.7, 128.64, 128.60, 128.5, 128.4, 127.99, 127.95, 111.7, 92.7, 73.2, 65.7. **IR** (Film): 3267, 2985, 1742, 1688, 1266, 1189 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{19}H_{16}NaO_4^+$ $[M+Na]^+$: 331.0942; Found: 331.0946.



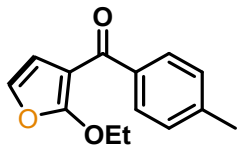
Ethyl 2-phenylfuran-3-carboxylate (4r). Yellow liquid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.38-7.47 (m, 3H), 7.43 (d, *J* = 1.8 Hz, 1H), 6.86 (d, *J* = 1.8 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 162.6, 156.4, 140.2, 128.8, 128.3, 127.4, 127.0, 112.9, 112.0, 59.5, 13.2. **HRMS** (ESI) m/z calcd. for $C_{13}H_{12}NaO_3^+$ $[M+Na]^+$: 239.0684; Found: 239.0687.



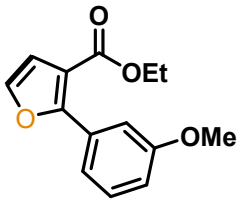
(2-ethoxyfuran-3-yl)(phenyl)methanone (4r'). Yellow liquid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 2H), 6.89 (d, *J* = 2.4 Hz, 1H), 6.69 (d, *J* = 2.4 Hz, 1H), 5.40 (s, 2H), 5.28 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 189.1, 162.0, 139.3, 132.6, 131.6, 128.7, 127.9, 112.5, 100.4, 67.8, 14.8. **HRMS** (ESI) m/z calcd. for $C_{13}H_{13}O_3^+$ $[M+H]^+$: 217.0859; Found: 217.0869.



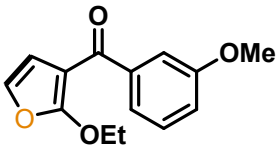
Ethyl 2-(p-tolyl)furan-3-carboxylate (4s). Yellow liquid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 1.2 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.73 (d, *J* = 1.2 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 2.29 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 162.6, 156.8, 139.8, 138.4, 127.7, 127.2, 126.0, 112.3, 111.8, 59.4, 20.4, 13.2. **IR** (Film): 2925, 1632, 1425, 1093, 725, 691 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{14}H_{14}NaO_3^+$ $[M+Na]^+$: 253.0841; Found:253.0841.



(2-ethoxyfuran-3-yl)(p-tolyl)methanone (4s'). Yellow liquid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 2.4 Hz, 1H), 6.68 (d, *J* = 2.4 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.6, 159.3, 157.1, 141.1, 131.0, 129.1, 120.8, 115.5, 114.1, 113.5, 113.1, 60.6, 55.4, 14.3. **HRMS** (ESI) m/z calcd. for $C_{14}H_{14}NaO_3^+$ $[M+Na]^+$: 253.0841; Found:253.0841.

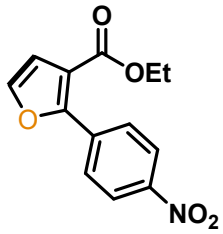


Ethyl 2-(3-methoxyphenyl)furan-3-carboxylate (4t). Yellow solid. mp: 50-52°C, **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.42 (d, *J* = 1.8 Hz, 1H), 7.35 (t, *J* = 8.4 Hz, 1H), 6.96 (dd, *J* = 2.4 Hz, 8.4 Hz, 1H), 6.85 (d, *J* = 1.8 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.6, 159.3, 157.1, 141.1, 131.0, 129.1, 120.8, 115.5, 114.1, 113.5, 113.1, 60.6, 55.4, 14.3. **IR** (Film): 2925, 1651, 1476, 1443, 1093, 885, 725, 691 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{14}H_{14}NaO_4^+$ $[M+Na]^+$: 269.0784; Found: 269.0788.

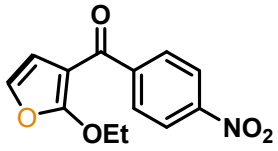


(2-ethoxyfuran-3-yl)(3-methoxyphenyl)methanone (4t'). Yellow solid. mp: 56-58°C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36-7.28 (m, 3H), 7.05 (qd, *J* = 2.4 Hz, 7.8 Hz, 1H), 6.89 (d, *J* = 2.4 Hz, 1H), 6.69 (d, *J* = 2.4 Hz, 1H), 3.39 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz,

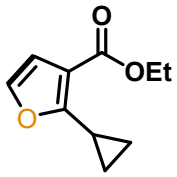
$CDCl_3$) δ 163.6, 159.3, 157.1, 141.1, 131.0, 129.1, 120.8, 115.5, 114.1, 113.5, 113.1, 60.6, 55.4, 14.3. **HRMS** (ESI) m/z calcd. for $C_{14}H_{14}NaO_4^+$ $[M+Na]^+$: 269.0784; Found: 269.0788.



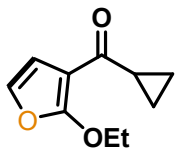
Ethyl 2-(4-nitrophenyl)furan-3-carboxylate (4u). White solid, mp: 104-105℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.26 (q, *J* = 9.0 Hz, 4H), 7.52 (d, *J* = 1.8 Hz, 1H), 6.89 (d, *J* = 2.4 Hz, 1H), 6.91 (d, *J* = 1.8 Hz, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.1, 154.4, 147.7, 142.6, 135.5, 128.9, 123.4, 116.7, 113.8, 61.0, 14.2. **IR** (Film): 2983, 1708, 1430, 1225, 1100, 1031 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{13}H_{11}NNaO_5^+$ $[M+Na]^+$: 284.0533; Found: 284.0539.



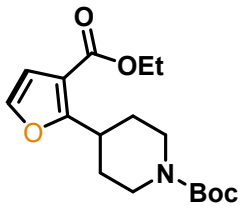
(2-ethoxyfuran-3-yl)(4-nitrophenyl)methanone (4u'). White solid, mp: 96-97℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 9.0 Hz, 2H), 7.85 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 2.4 Hz, 1H), 6.71 (d, *J* = 2.4 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 186.8, 162.4, 149.3, 144.7, 133.4, 129.4, 123.2, 111.8, 99.9, 67.8, 14.8. **HRMS** (ESI) m/z calcd. for $C_{13}H_{11}NNaO_5^+$ $[M+Na]^+$: 284.0533; Found: 284.0539.



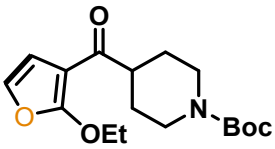
Ethyl 2-cyclopropylfuran-3-carboxylate (4v). Colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.07 (d, *J* = 1.8 Hz, 1H), 6.60 (d, *J* = 1.8 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 2.72-2.80 (m, 1H), 1.34 (t, *J* = 7.2 Hz, 3H), 0.98-1.06 (m, 4H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.38, 162.12, 138.04, 112.05, 109.94, 59.01, 13.38, 8.17, 7.29. **IR** (Film): 3112, 2958, 1651, 1485, 1443, 1263, 1237, 887, 779, 691 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{10}H_{12}NaO_3^+$ $[M+Na]^+$: 203.0684; Found: 203.0685.



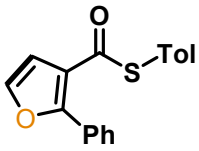
Cyclopropyl(2-ethoxyfuran-3-yl)methanone (4v'). Colorless oil **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.85 (d, *J* = 2.4 Hz, 1H), 6.69 (d, *J* = 2.4 Hz, 1H), 4.48 (q, *J* = 7.2 Hz, 2H), 2.67-2.60 (m, 1H), 1.47 (t, *J* = 7.2 Hz, 3H), 1.10-1.15 (m, *J* = 2H), 0.85-0.90 (m, *J* = 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 194.1, 162.0, 132.7, 110.8, 102.4, 67.5, 18.0, 15.0, 10.5. **HRMS** (ESI) m/z calcd. for $C_{10}H_{12}NaO_3^+$ $[M+Na]^+$: 203.0684; Found: 203.0685.



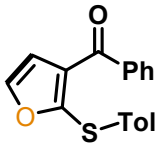
Tert-butyl 4-(3-(ethoxycarbonyl)furan-2-yl)piperidine-1-carboxylate (4w). White solid, mp: 124-125°C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.21 (d, *J* = 1.8 Hz, 1H), 6.59 (d, *J* = 1.8 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 4.15 (s, 1H), 3.56 (tt, *J* = 3.6 Hz, 11.4 Hz, 1H), 2.79 (s, 2H), 1.67-1.82 (m, 4H), 1.43 (s, 9H), 1.30 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.5, 163.8, 154.7, 140.5, 112.4, 110.6, 79.4, 60.1, 44.1, 35.1, 29.7, 28.4, 14.3. **IR** (Film): 3028, 2925, 1668, 1500, 1478, 1045, 935, 808, 745, 682 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{17}H_{25}NNaO_5^+$ $[M+Na]^+$: 346.1628; Found: 346.1635.



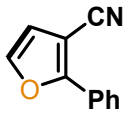
Tert-butyl 4-(2-ethoxyfuran-3-carbonyl)piperidine-1-carboxylate (4w'). White solid, mp: 117-118°C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.84 (d, *J* = 2.4 Hz, 1H), 6.68 (d, *J* = 2.4 Hz, 2H), 4.47 (q, *J* = 7.2 Hz, 2H), 4.13 (s, 1H), 3.09 (tt, *J* = 3.6 Hz, 11.4 Hz, 1H), 2.80 (s, 2H), 1.76 (s, 2H), 1.56-1.67 (m, 2H), 1.43 (s, 9H), 1.47 (t, *J* = 7.2 Hz, 3H), 1.45 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 195.7, 161.2, 154.8, 133.1, 111.0, 100.4, 79.4, 67.4, 45.6, 43.2, 28.5, 15.0. **HRMS** (ESI) m/z calcd. for $C_{17}H_{25}NNaO_5^+$ $[M+Na]^+$: 346.1628; Found: 346.1635.



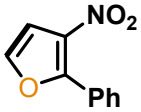
S-(4-tolyl) 2-phenylfuran-3-carbothioate (4x). Brown oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.39 (d, *J* = 1.8 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.73 (d, *J* = 1.8 Hz, 3H), 2.36 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 189.6, 154.0, 143.7, 138.9, 138.4, 133.0, 132.5, 130.0, 129.2, 128.4, 126.9, 124.0, 112.7, 21.3. **IR** (Film): 3031, 2989, 1754, 1672, 1377, 1241, 1055 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{11}H_7NaO_2S^+$ $[M+Na]^+$: 226.0064; Found: 226.0065.



Phenyl(2-(p-tolylthio)furan-3-yl)methanone (4x'). Brown oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85-7.94 (m, 2H), 7.41 (d, *J* = 1.8 Hz, 1H), 7.27-7.34 (m, 5H), 7.18 (d, *J* = 7.2 Hz, 2H), 6.95 (d, *J* = 1.8 Hz, 1H), 2.32 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 185.0, 155.4, 141.5, 139.9, 135.0, 130.1, 129.8, 129.4, 128.2, 1234.0, 120.1, 111.9, 89.70, 21.4. **HRMS** (ESI) m/z calcd. for $C_{11}H_7NaO_2S^+$ $[M+Na]^+$: 226.0064; Found: 226.0065.

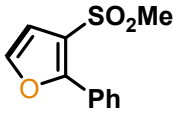


2-phenylfuran-3-carbonitrile (4y). Yellow solid, mp: 68-69°C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.41-7.51 (m, 3H), 7.47 (d, *J* = 1.8 Hz, 1H), 6.68 (d, *J* = 1.8 Hz, 1H), 2.53 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.9, 141.1, 129.1, 128.0, 127.0, 124.4, 113.9, 112.3, 90.6. **IR** (Film): 3196, 3033, 1642, 1599, 1220, 757, 686 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{11}H_7NNaO^+$ $[M+Na]^+$: 192.0424; Found: 192.0425.

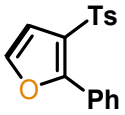


3-nitro-2-phenylfuran (4z). Brown solid, mp: 120-121°C, **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87-7.93 (m, 2H), 7.47-7.53 (m, 3H), 7.43 (d, *J* = 1.8 Hz, 1H), 7.07 (d, *J* = 1.8 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$)

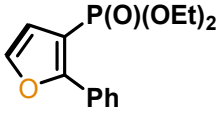
δ 153.1, 141.3, 130.9, 129.0, 128.4, 127.5, 109.1. **HRMS** (ESI) m/z calcd. for $C_{10}H_7NNaO_3^+$ $[M+Na]^+$: 212.0336; Found: 212.0334.



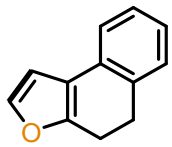
3-(methylsulfonyl)-2-phenylfuran (4aa). Yellow solid, mp: 112-113℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.55-7.52 (m, 4H), 6.90 (d, *J* = 2.4 Hz, 1H), 3.01 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.70, 141.5, 130.3, 128.8, 128.3, 123.4, 112.5, 43.9. **IR** (Film): 3071, 2998, 2942, 1582, 1478, 1408, 1160 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{11}H_{10}NaO_3S^+$ $[M+Na]^+$: 245.0248; Found: 245.0257.



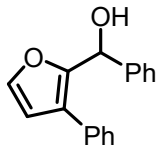
2-phenyl-3-tosylfuran 2-phenyl-3-tosylfuran (4ab). White solid, 120-121℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84-7.88 (m, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 2.4 Hz, 1H), 7.40-7.44 (m, 3H), 7.19 (d, *J* = 7.8 Hz, 2H), 6.84 (d, *J* = 2.4 Hz, 1H), 2.53 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 155.1, 144.2, 141.4, 139.0, 130.0, 129.6, 128.7, 128.3, 127.1, 124.2, 112.7, 21.6. **IR** (Film): 2998, 1428, 1235, 1100, 1031 cm^{-1}. **HRMS** (ESI) m/z calcd. for $C_{17}H_{14}NaO_3S^+$ $[M+Na]^+$: 321.0556; Found: 321.0560.



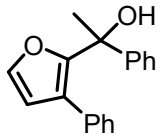
Diethyl (2-phenylfuran-3-yl)phosphonate (4ac). Yellow solid, mp: 97-98℃, **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.50 (t, *J* = 1.8 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 4.01-4.16 (m, 4H), 1.24 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.4(d, *J* = 25.5 Hz), 141.5(d, *J* = 30.0 Hz), 129.6, 129.2, 128.4, 127.5, 115.6(d, *J* = 10.5 Hz), 107.4(d, *J* = 214.5 Hz), 62.2(d, *J* = 4.5 Hz), 16.2(d, *J* = 6.0 Hz). **HRMS** (ESI) m/z calcd. for $C_{14}H_{17}NaO_4P^+$ $[M+Na]^+$: 303.0757; Found: 303.0772.



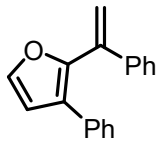
4,5-dihydronaphtho[2,1-b]furan (4ad). White solid, mp: 44-45℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 1.8 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 1.8 Hz, 1H), 3.10 (t, *J* = 7.8 Hz, 2H), 2.92 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.7, 140.8, 132.1, 130.2, 127.0, 125.7, 124.7, 121.1, 117.4, 105.2, 28.4, 20.9. **IR** (Film): 2918, 1678, 1447, 1376, 1241 cm^{-1}. **HRMS** (ESI) m/z calcd. For $C_{12}H_{10}NaO^+$ $[M+Na]^+$: 193.0632; Found: 193.0633.



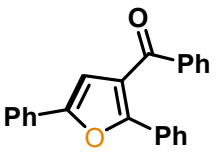
phenyl(3-phenylfuran-2-yl)methanol (5). Colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.67-7.62 (m, 2H), 7.45-7.38 (m, 5H), 7.38-7.31 (m, 3H), 7.30-7.26 (m, 1H), 6.37 (d, *J* = 2.0 Hz, 1H), 6.04 (d, *J* = 2.0 Hz, 1H), 2.29-2.26 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.3, 142.9, 141.7, 130.6, 128.7, 128.5, 127.9, 127.6, 126.5, 126.3, 123.5, 111.4, 68.5. **IR** (Film): 3421, 3060, 3030, 1621, 1486, 769, 695 cm^{-1}.



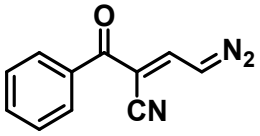
1-phenyl-1-(3-phenylfuran-2-yl)ethan-1-ol (6). Colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46-7.35 (m, 5H), 7.30-7.24 (m, 2H), 7.23-7.17 (m, 4H), 6.54 (d, *J* = 2.0 Hz, 1H), 2.37 (s, 1H), 1.83 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.5, 148.0, 140.7, 131.5, 128.1, 128.0, 127.8, 126.3, 125.4, 112.4, 73.0, 32.7. **IR** (Film): 3447, 3058, 2979, 2359, 1484, 769, 698 cm^{-1}.



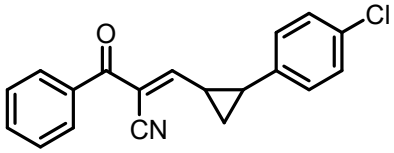
3-phenyl-2-(1-phenylvinyl)furan (7). Colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64-7.58 (m, 2H), 7.47-7.41 (m, 3H), 7.29-7.19 (m, 5H), 7.18-7.12 (m, 1H), 6.38 (d, *J* = 1.5 Hz, 1H), 5.74 (d, *J* = 1.5 Hz, 1H), 5.39 (d, *J* = 1.5 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.6, 141.8, 141.1, 139.6, 130.9, 128.3, 128.2, 127.9, 127.2, 126.8, 125.8, 121.7, 116.1, 114.7. **IR** (Film): 3056, 2359, 2342, 1484, 1059, 769, 692 cm^{-1}.



(2,5-diphenylfuran-3-yl)(phenyl)methanone (10). Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.82-7.77(m, 4H), 7.55-7.53 (m, 1H), 7.45-7.40 (m, 4H), 7.36-7.33 (m, 4H), 6.94 (s, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 191.7, 154.9, 152.4, 138.0, 132.9, 129.7, 129.6, 129.0, 128.8, 128.4, 128.3, 128.1, 127.4, 124.0, 122.8, 108.7. **IR** (Film): 2958, 1650, 1376, 1236, 889, 728, 691 cm^{-1}. **HRMS** (ESI) m/z calcd. For $C_{23}H_{16}NaO_2^+$ $[M+Na]^+$: 347.1126; Found: 347.1125.

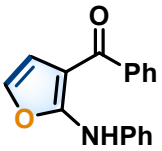


(E)-2-benzoyl-4-diazobut-2-enenitrile (11). Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.19 (d, *J* = 10.8 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 5.77 (d, *J* = 10.8 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 186.0, 150.0, 136.8, 132.6, 128.6, 128.4, 116.7, 98.3, 58.4. **IR** (Film): 3077, 3053, 2923, 2360, 2196, 2158, 2106, 1645, 1541, 711, 688 cm^{-1}.



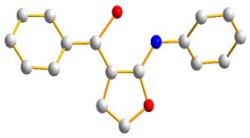
(E)-2-benzoyl-3-(2-(4-chlorophenyl)cyclopropyl)acrylonitrile (13). Yellow solid, mp: 64-65℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50 (t, *J* = 7.2 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.33-7.28 (m, 4H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.51(d, *J* = 10.8 Hz, 1H), 3.02 (m, 1H), 2.66-2.60(m, 1H), 1.86-1.81(m, 1H), 1.64-1.61(m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 187.8, 166.0, 135.5, 134.7, 133.3, 133.0, 130.2, 129.0, 128.9, 128.4, 115.3, 115.0, 28.5, 24.0, 16.4. **HRMS** (ESI) m/z calcd. For $C_{19}H_{14}ClNNaO^+$ $[M+Na]^+$: 330.0662; Found: 330.0658.

V. X-ray single crystal data of 2a and 13.



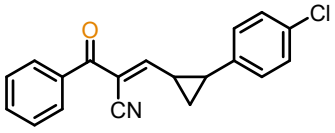
2a

≡



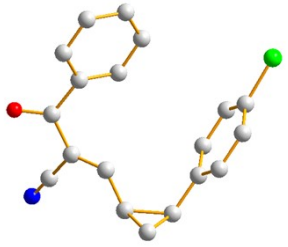
X-ray structure of **2a**

Empirical formula	$C_{17}H_{13}NO_2$
Temperature	273.15K
Wavelength	0.71073Å
Unit cell dimensions	a = 26.498(4) Å alpha = 90° . b = 7.3940(10) Å beta = 90°. c = 6.9959(10) Å gamma =90°.
Volume	1370.7(3) $Å^3$
Z	4
Calculated density	1.276 g/cm^3
Absorption coefficient	0.084mm^{-1}
F(000)	552.0
Crystal size	0.2 × 0.2 × 0.2 mm^3
Theta range for data collection	2.86° to 26.408°.
Reflections collected / unique	7172
Data / restraints / parameters	1408/133/157
Goodness-of-fit on F^2	1.020
Final R indices [I>2sigma(I)]	R1 = 0.0433, wR2 = 0.1111
R indices (all data)	R1 = 0.0722,wR2 = 0.1275



13

≡

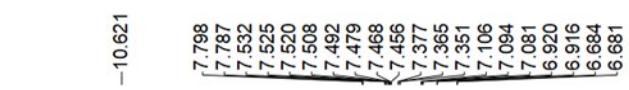


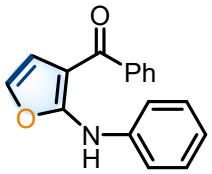
X-ray structure of **13**

Empirical formula	$C_{19}NOClH_{14}$

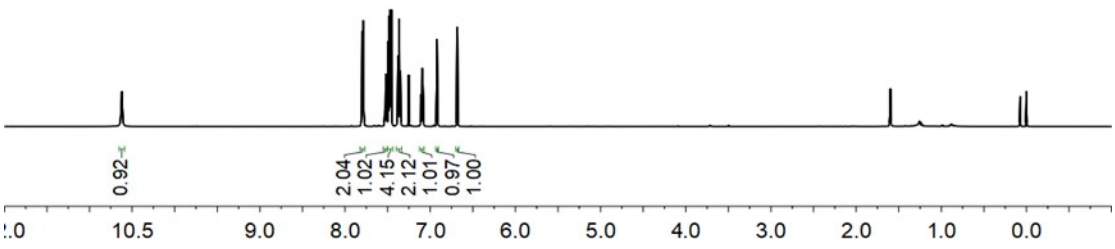
Temperature	293(2)K
Wavelength	0.71069Å
Unit cell dimensions	a = 8.814(5) Å alpha = 90.000(5)° . b = 11.755(5) Å beta = 106.222(5)°. c = 15.281(5) Å gamma = 90.000(5)°.
Volume	1520.2(12) $Å^3$
Z	4
Calculated density	1.345g/cm^3
Absorption coefficient	0.252mm^{-1}
F(000)	640.0
Crystal size	0.04 × 0.03 × 0.02mm^3
Theta range for data collection	2.22° to 26.4°.
Reflections collected / unique	8503
Data / restraints / parameters	3106/0/255
Goodness-of-fit on F^2	1.040
Final R indices [I>2sigma(I)]	R1 =0.0389, wR2 =0.1020
R indices (all data)	R1 = 0.0527,wR2 =0.1108

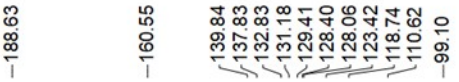
VI. Copies of NMR spectra

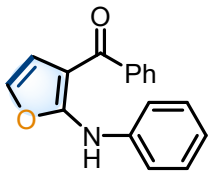




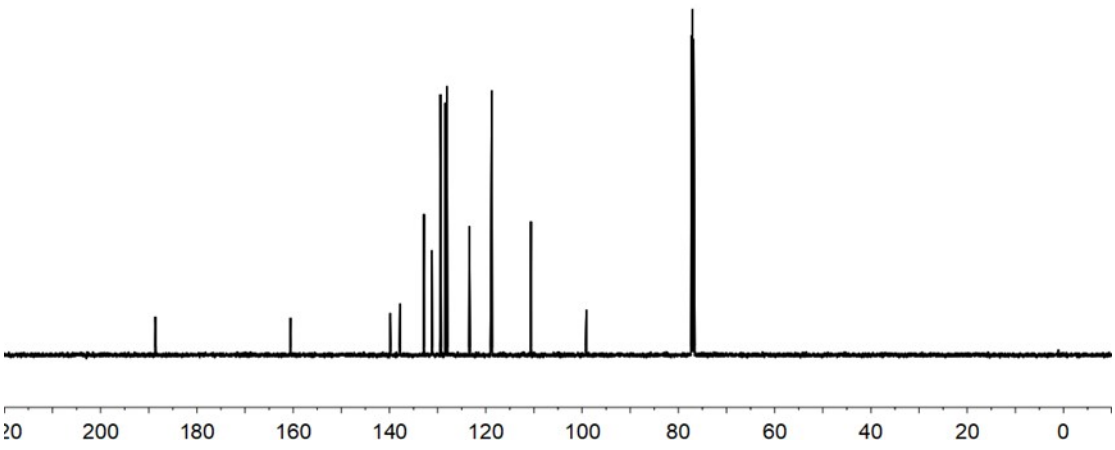
2a

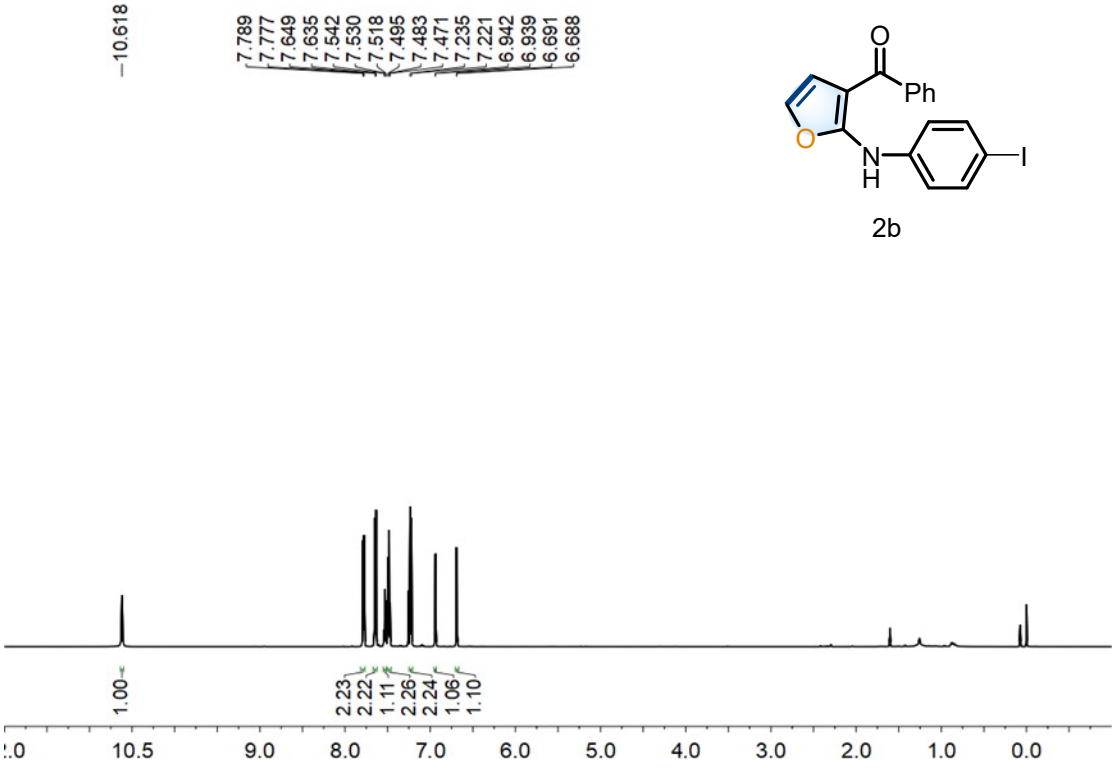






2a

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7.542
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7.518
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7.483
7.471
7.235
7.221
6.942
6.939
6.691
6.688
O
Ph
O
N
H
I
2b
1.00
2.23
2.22
1.11
2.26
2.24
1.06
1.10
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
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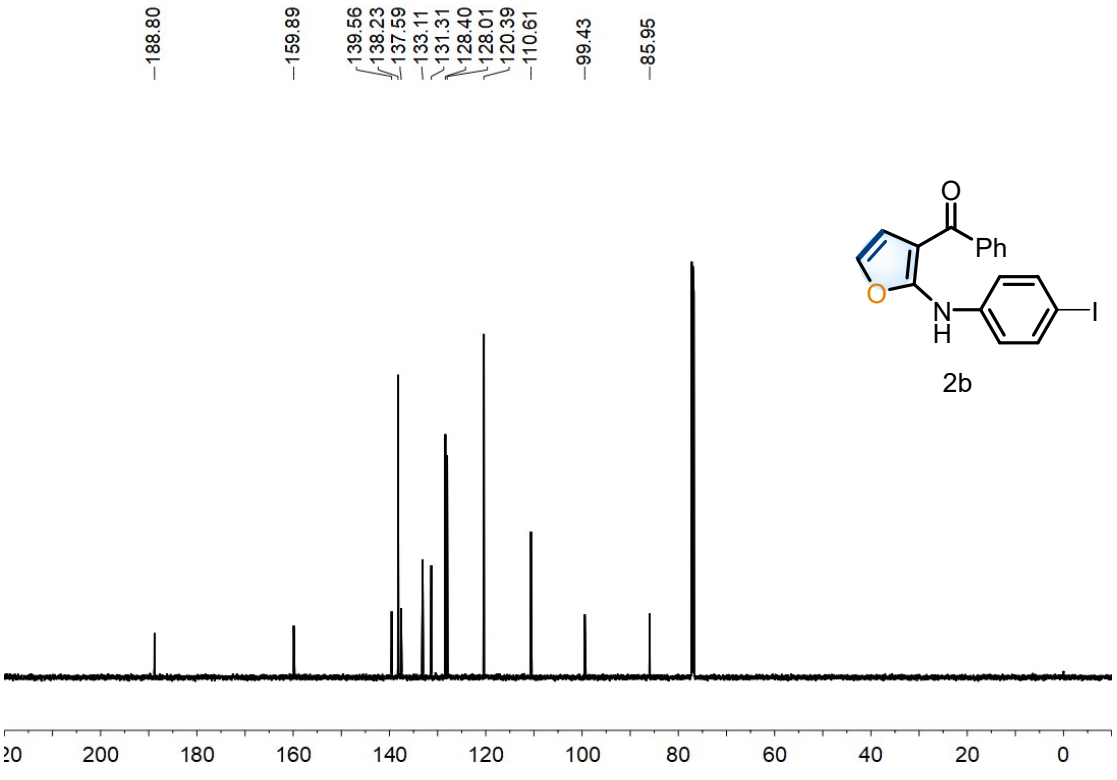
0.0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133.11
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128.40
128.01
120.39
110.61
99.43
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140
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20
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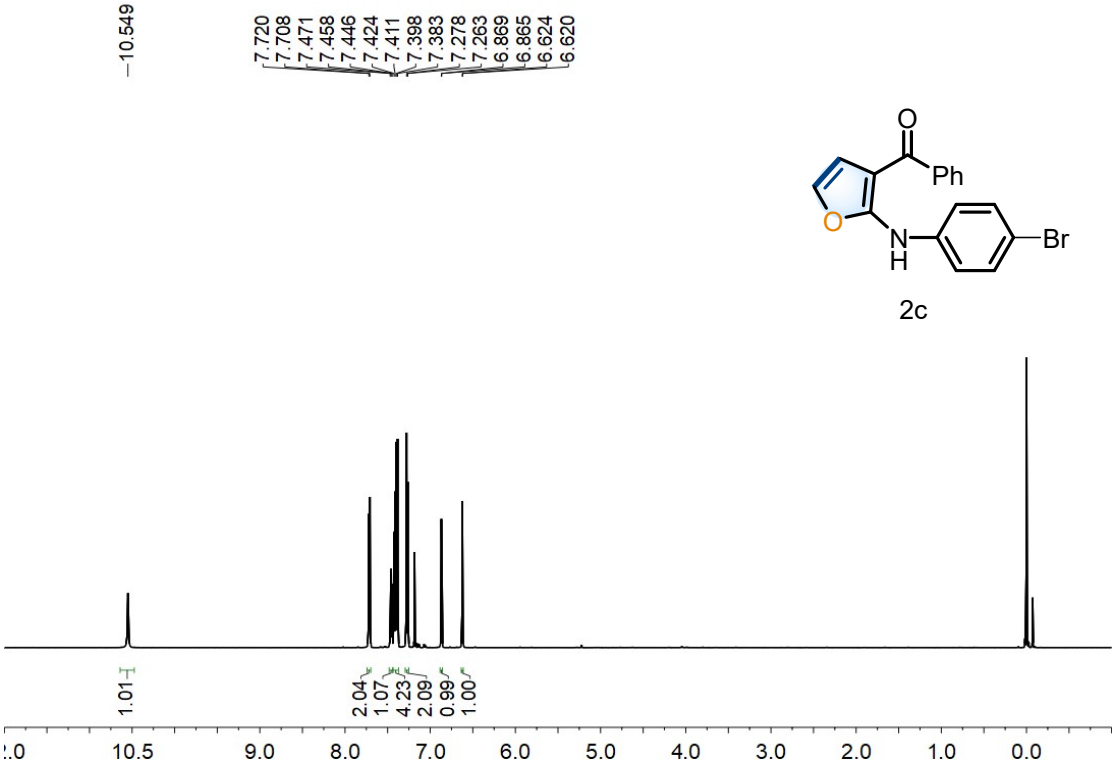
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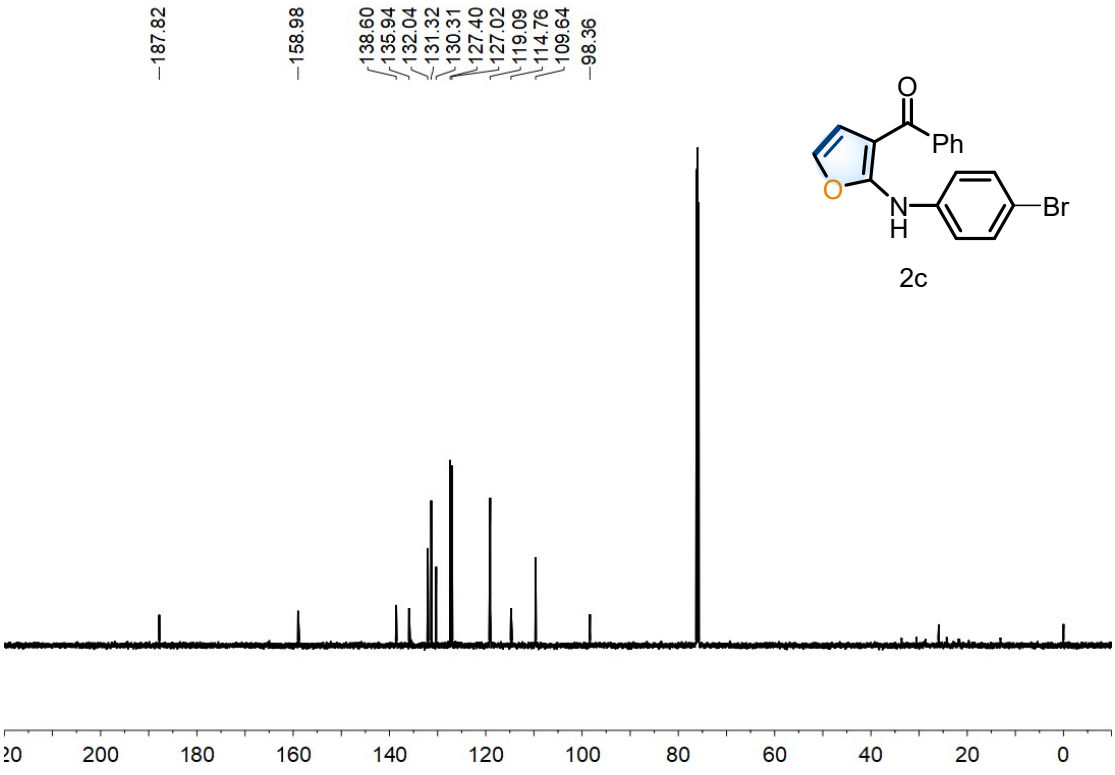
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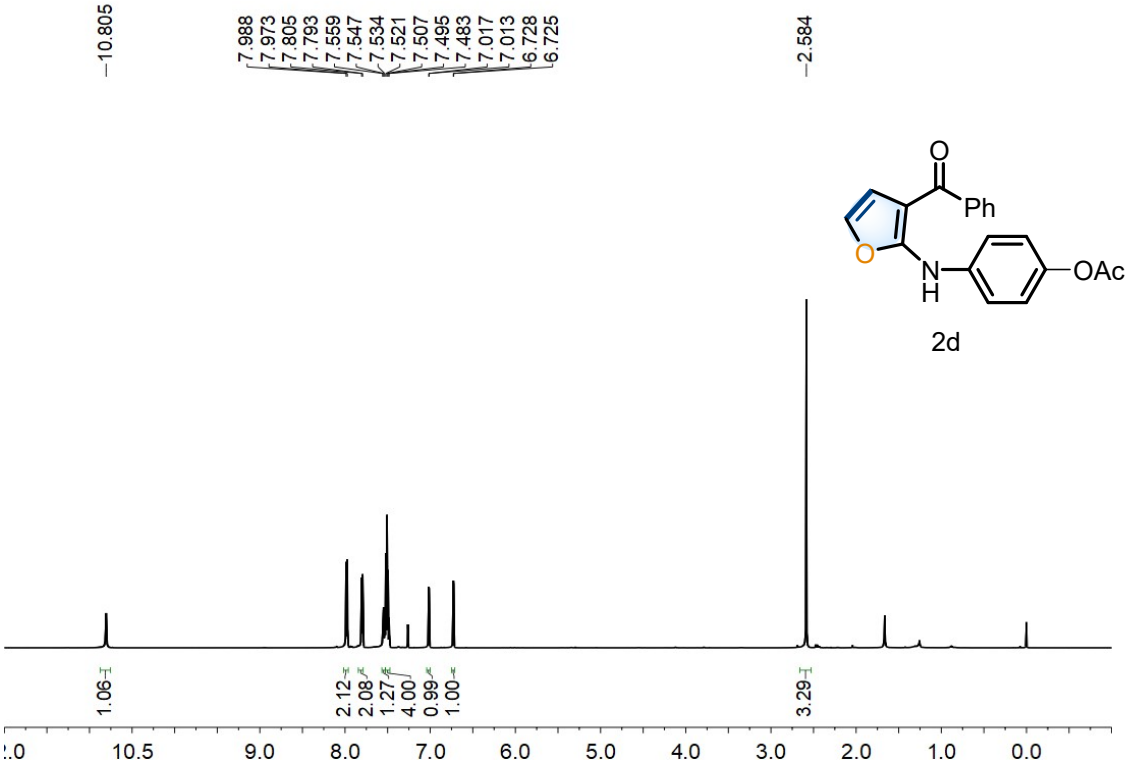
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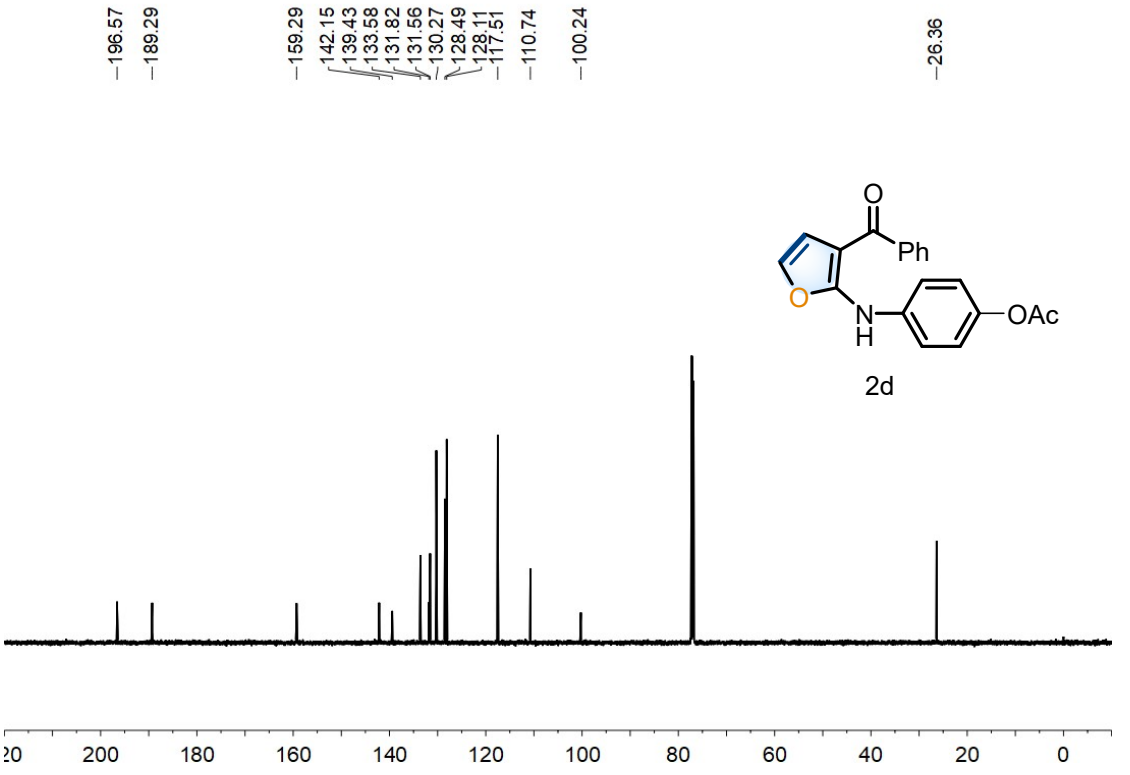
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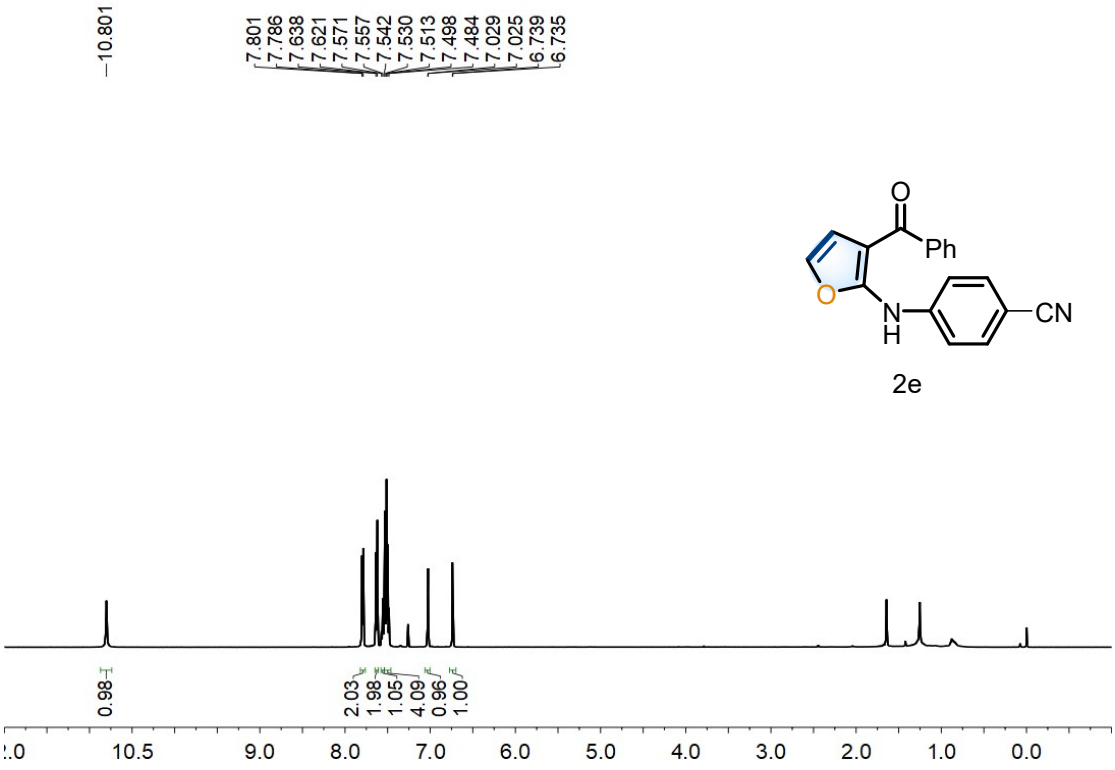
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Ph
O
N
H
CN
2e
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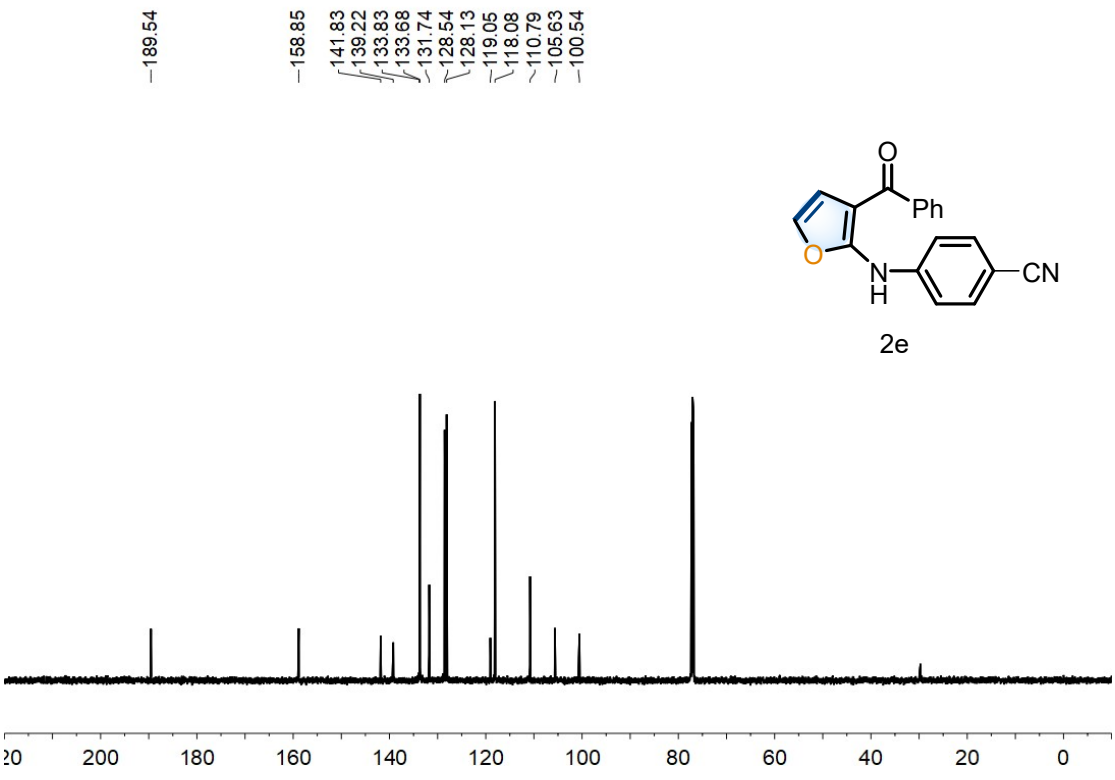
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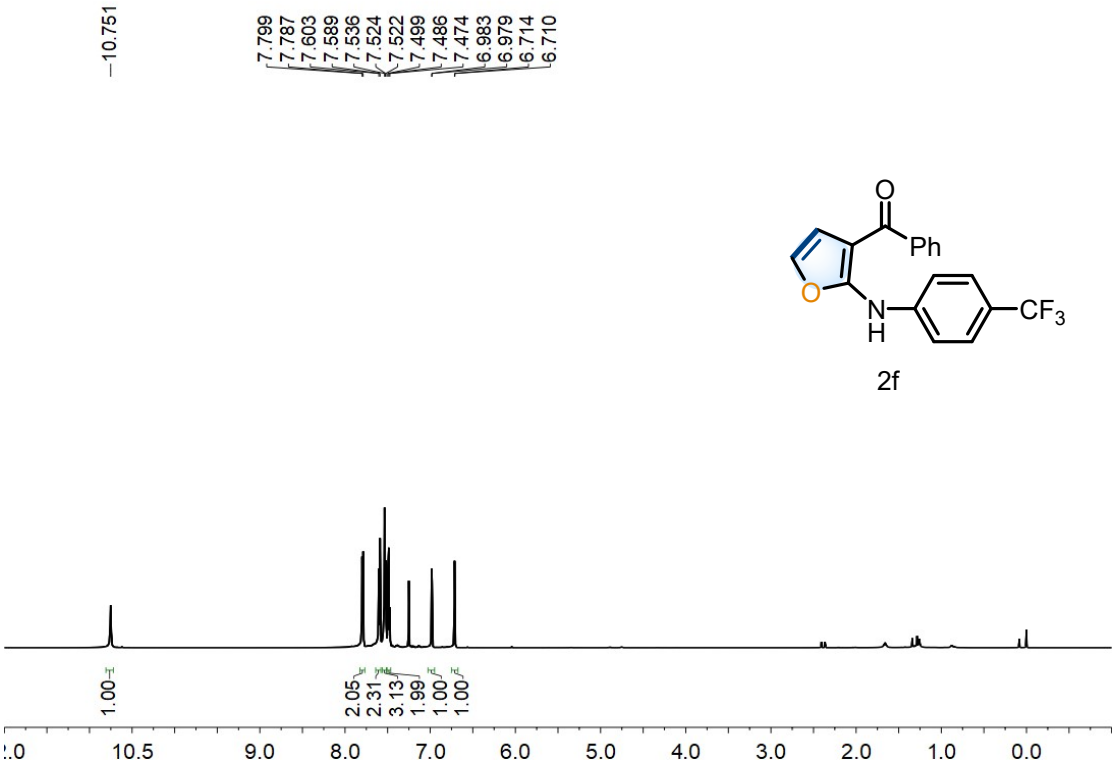
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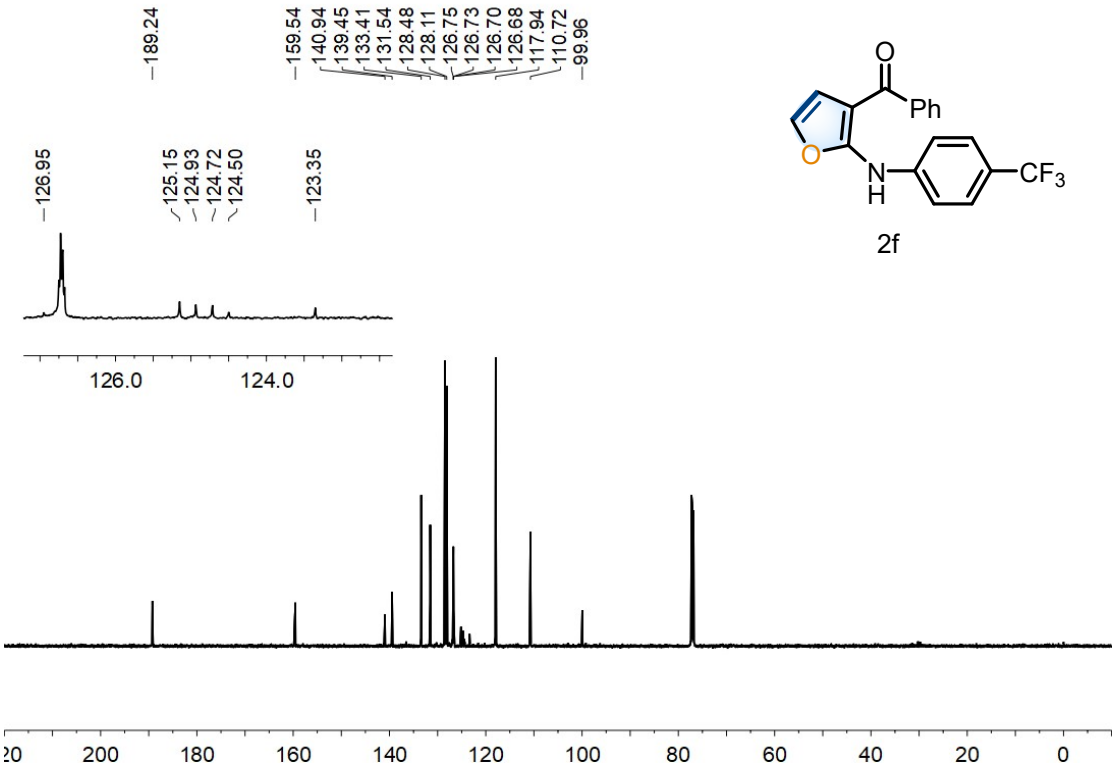
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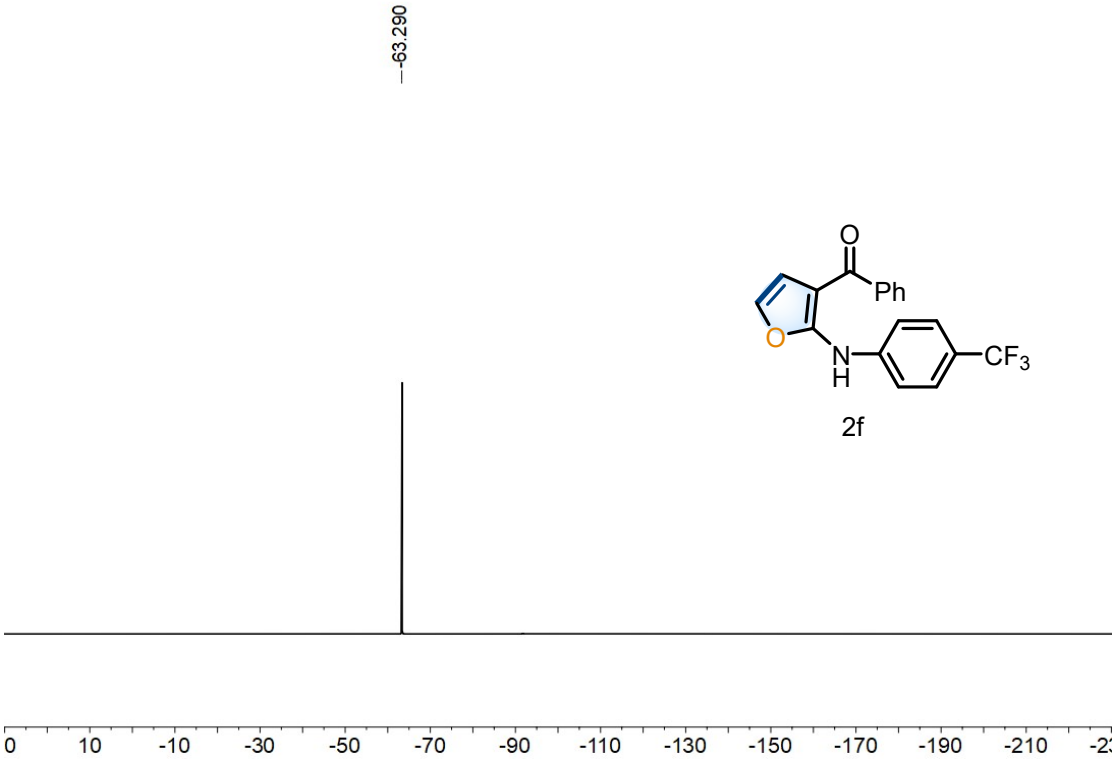
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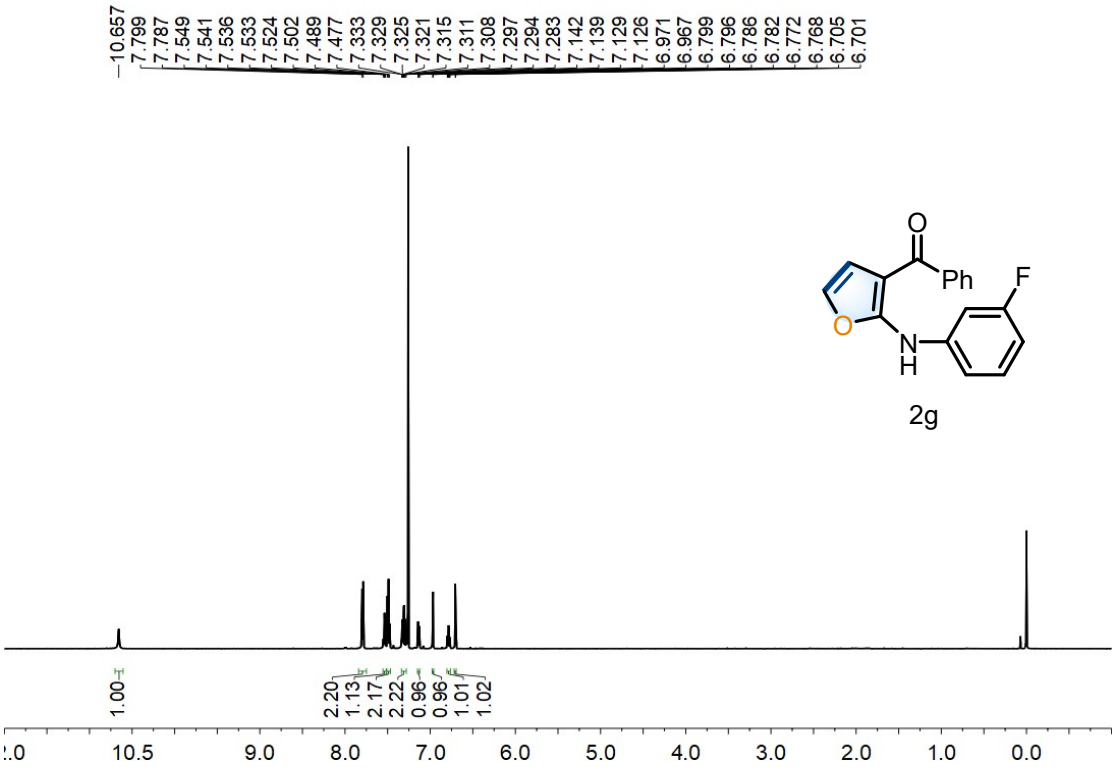
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2.22
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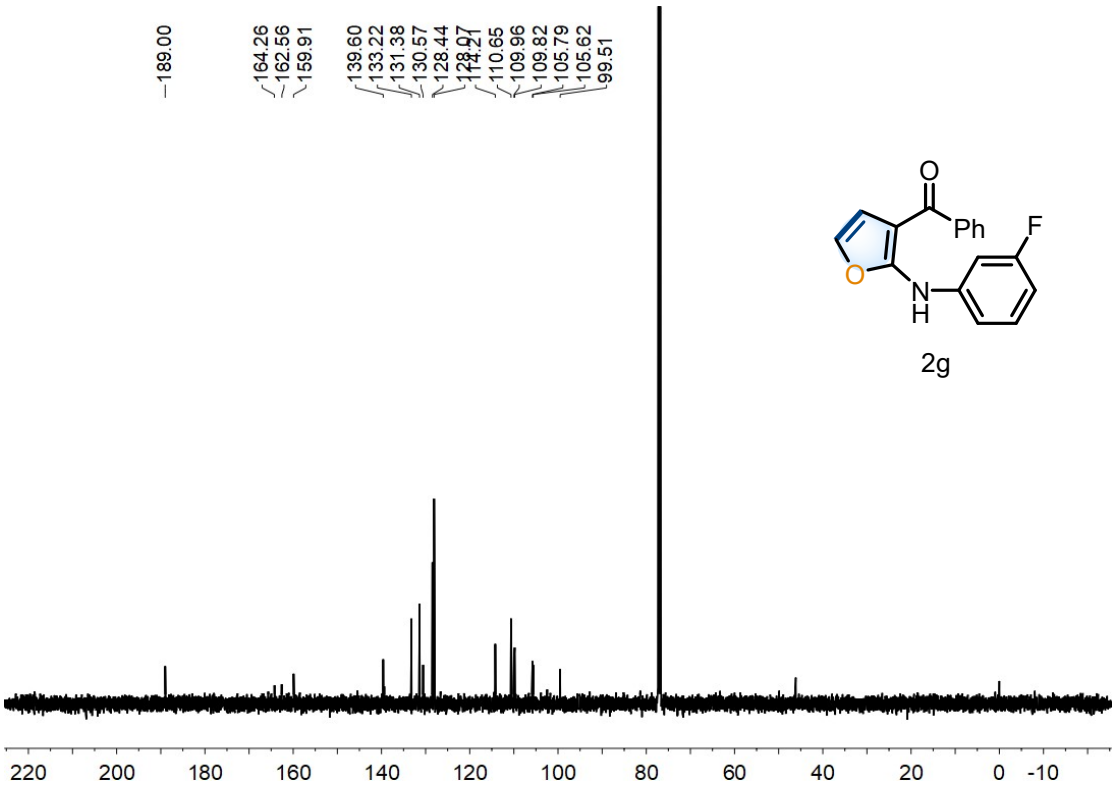
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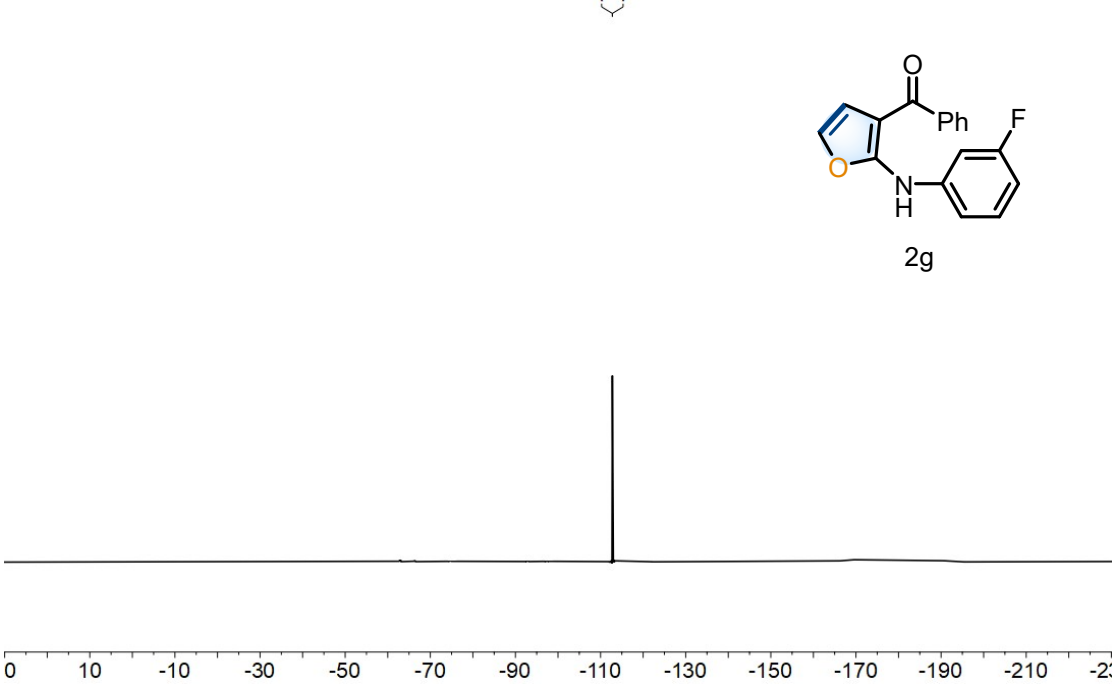
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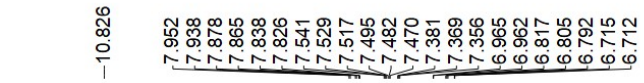
2g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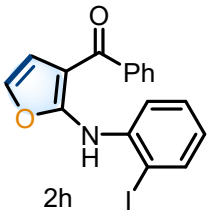
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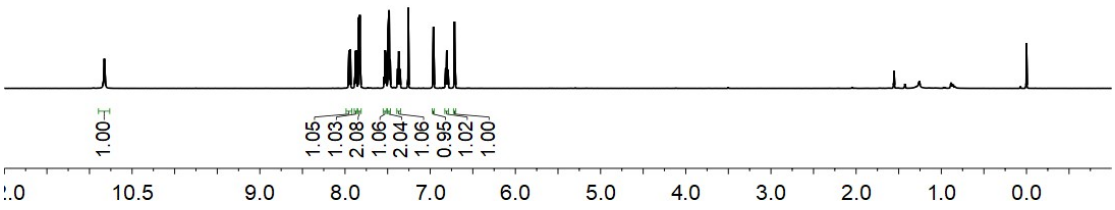
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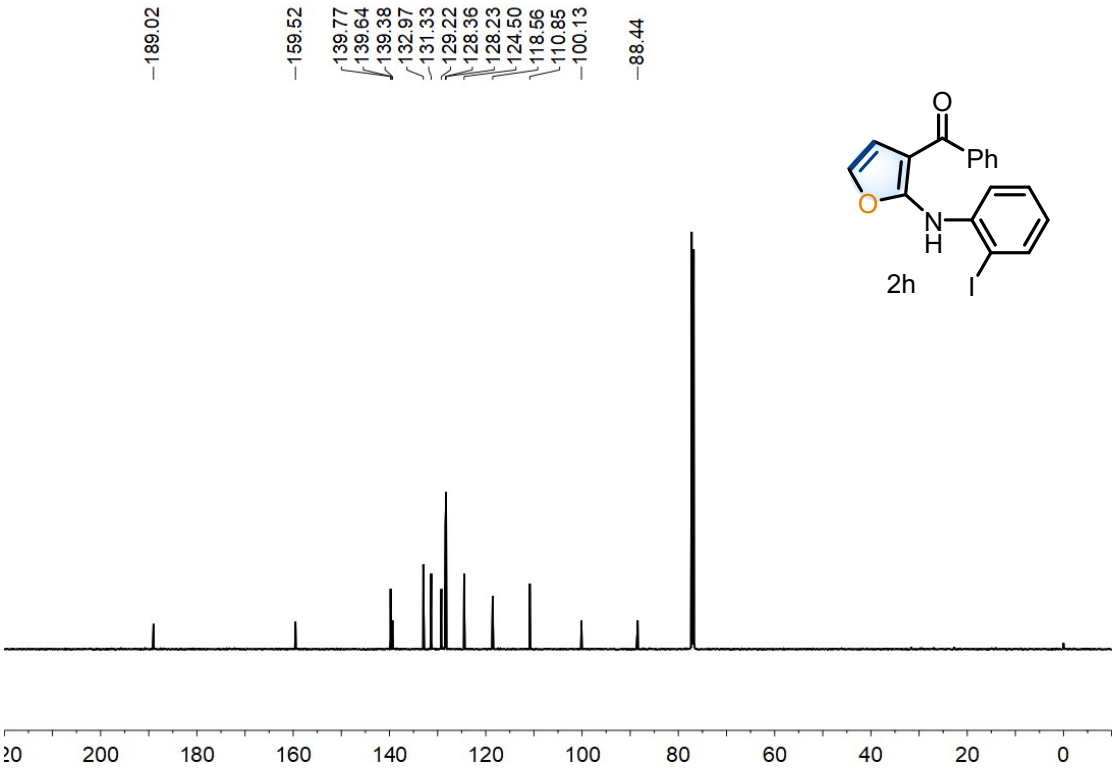
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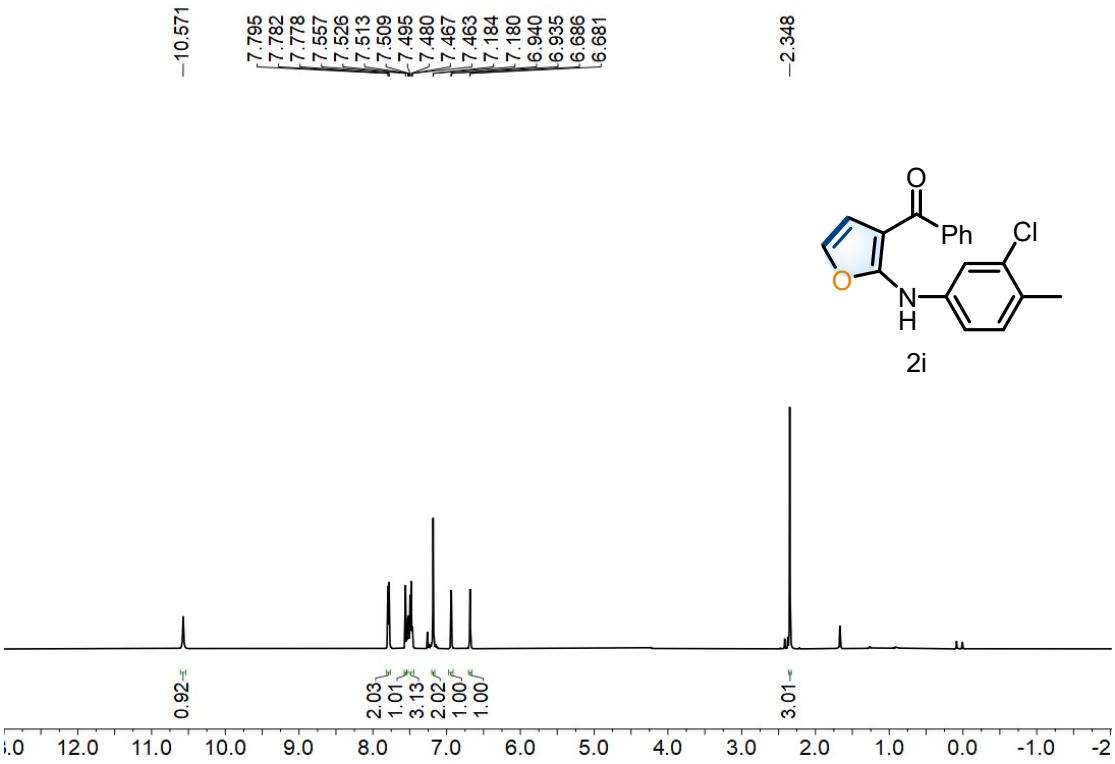
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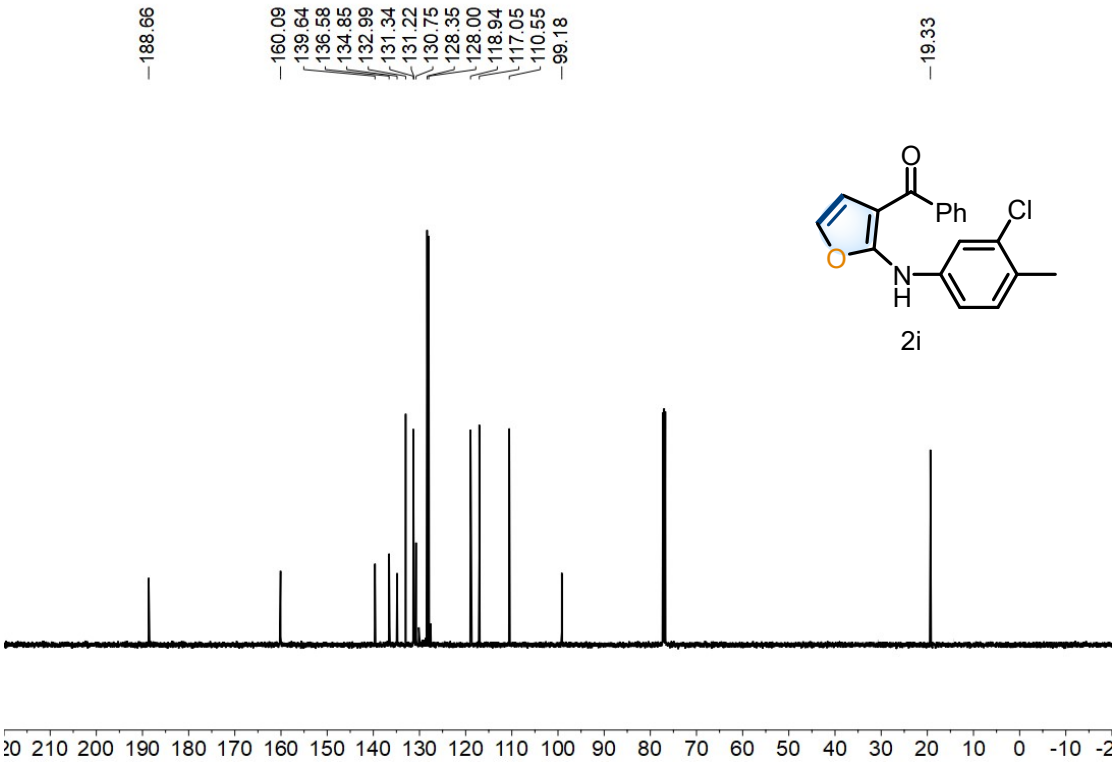
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Cl
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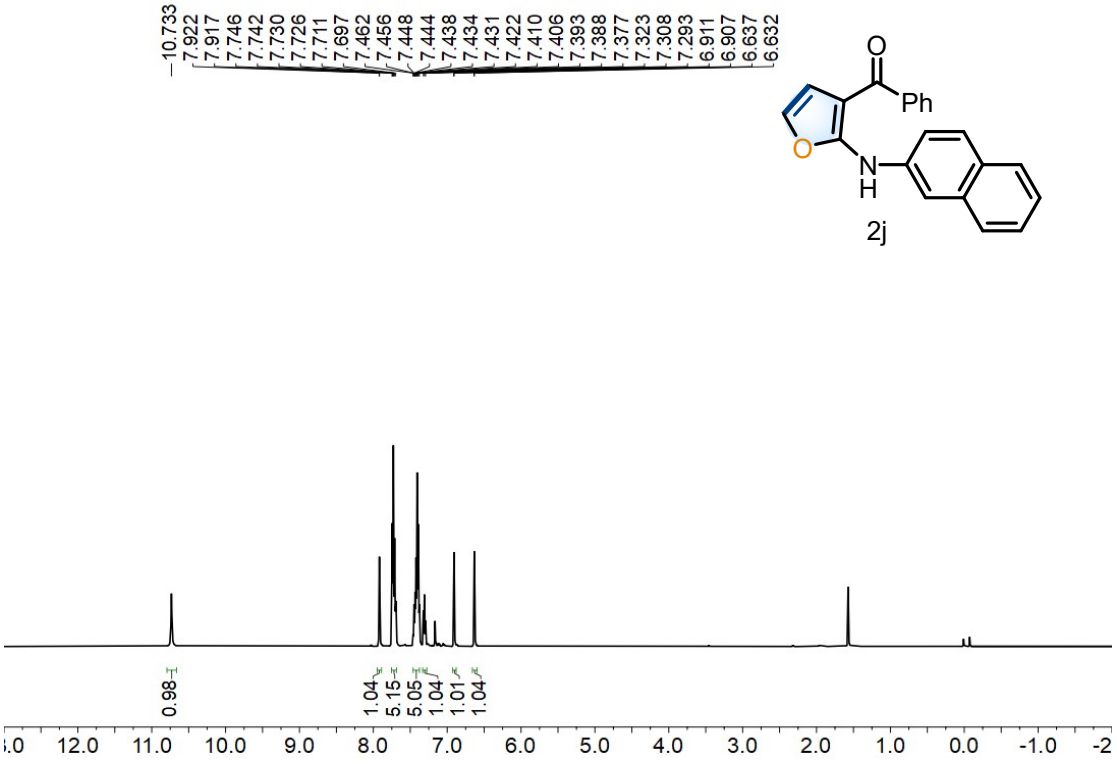
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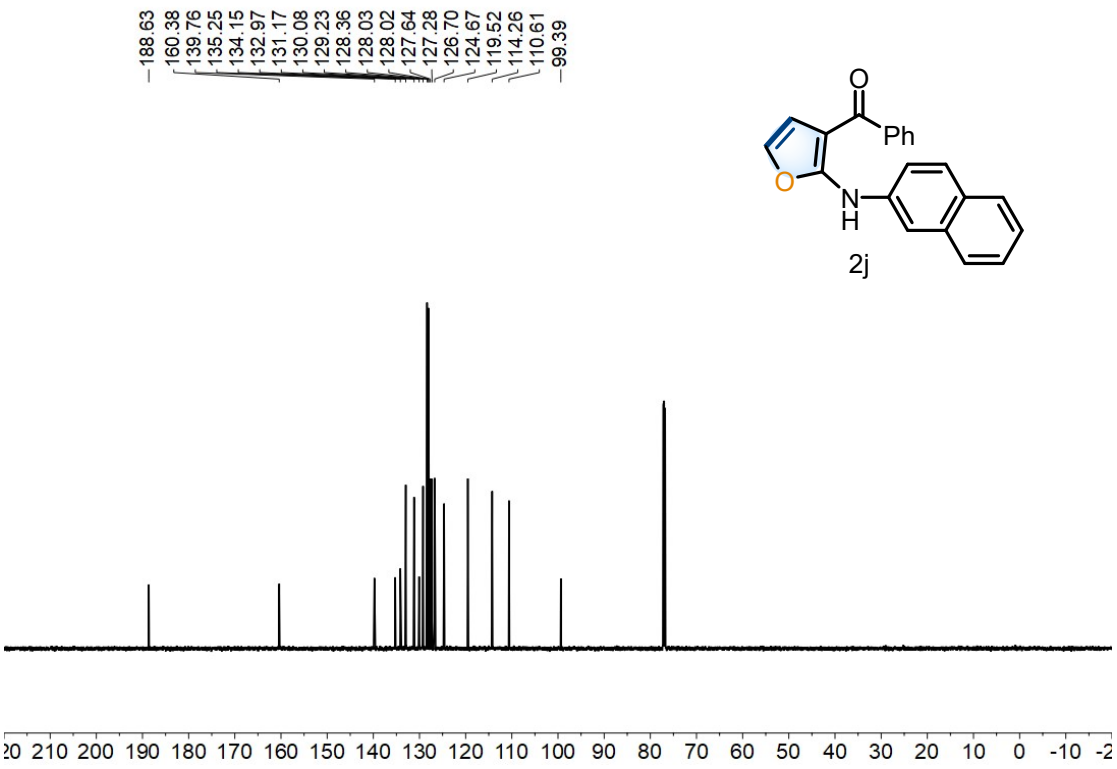
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Ph
O
N
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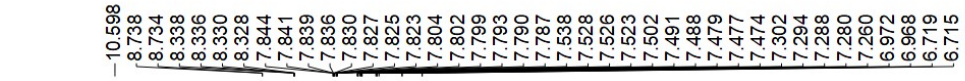
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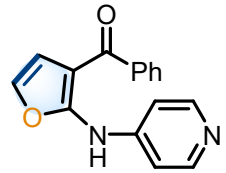
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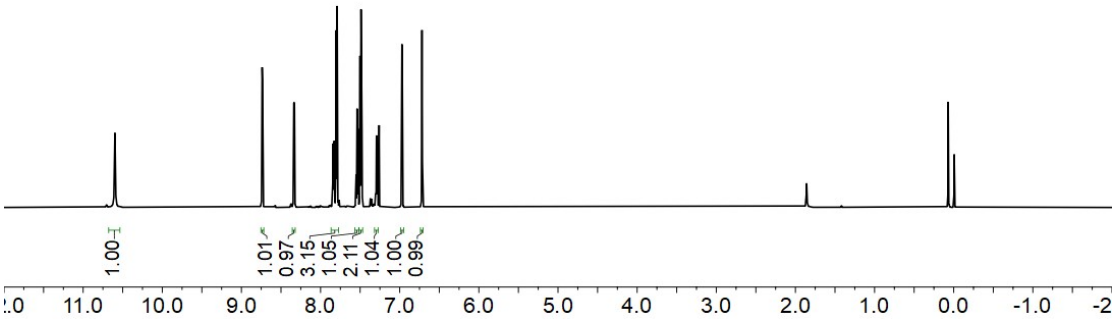
2k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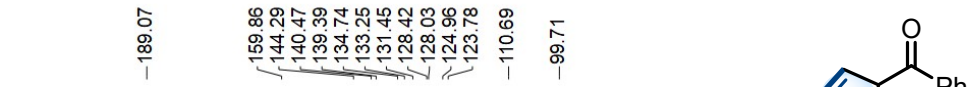
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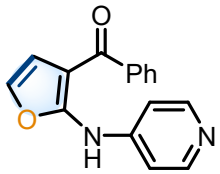
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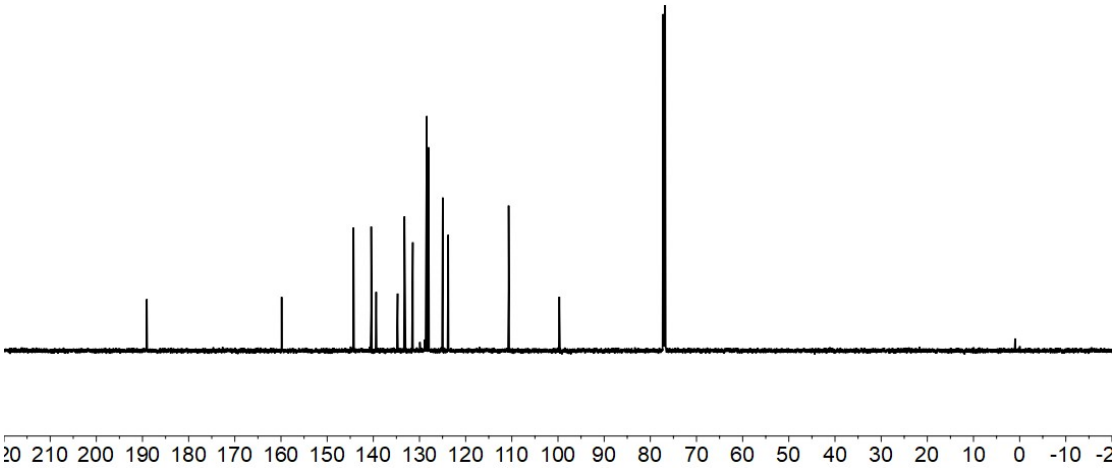
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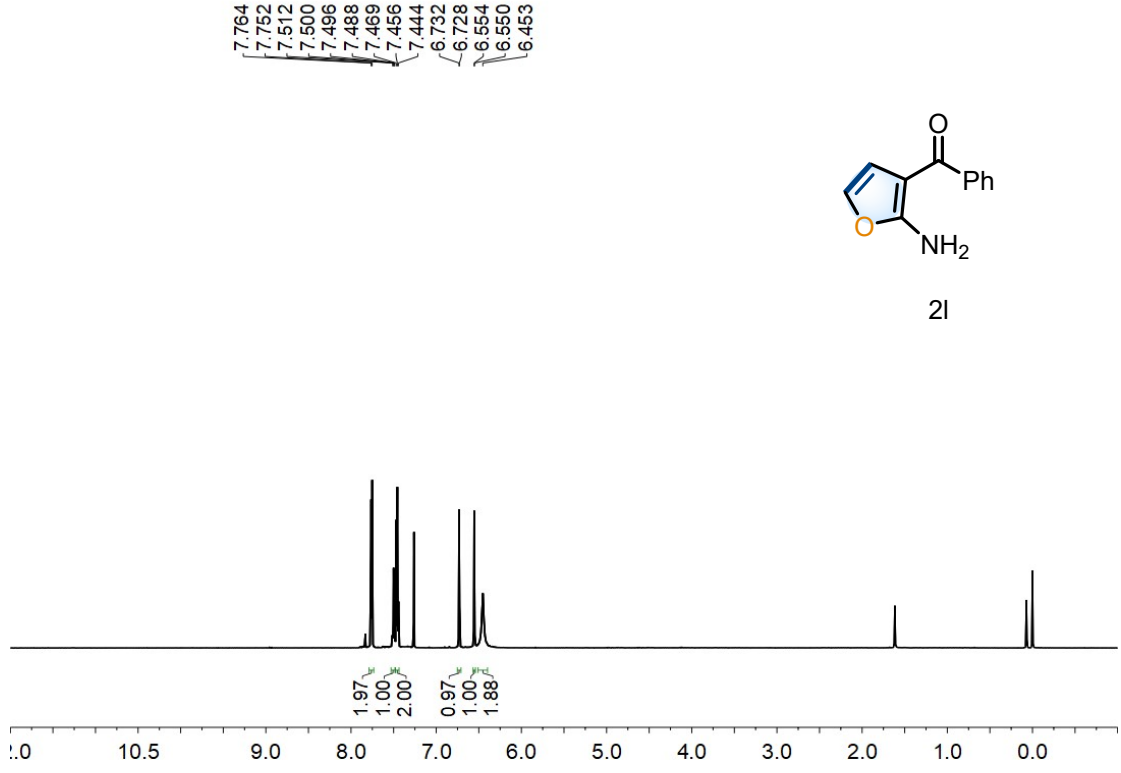
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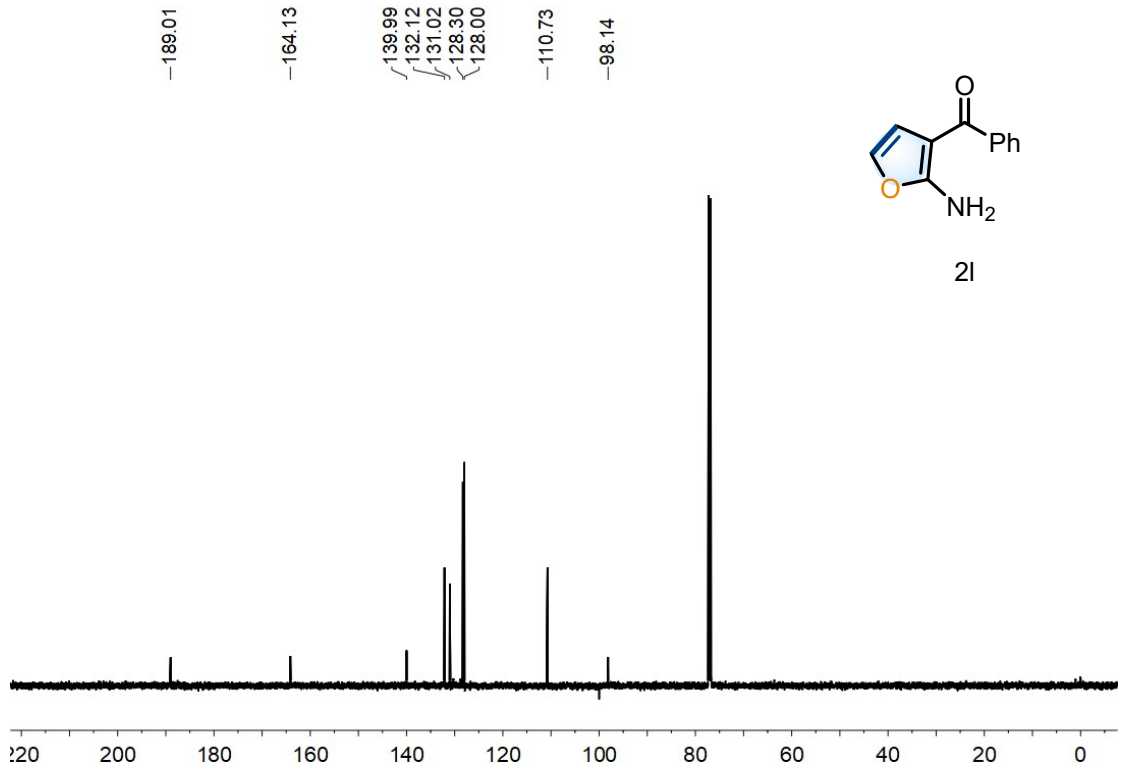
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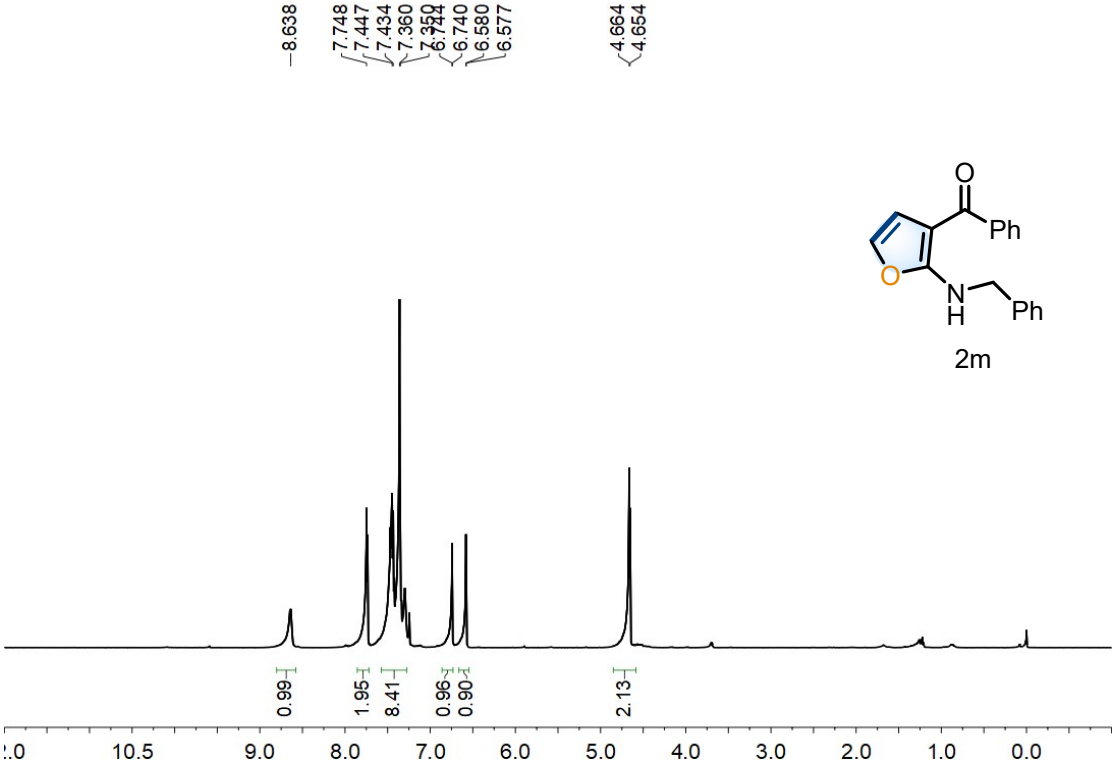
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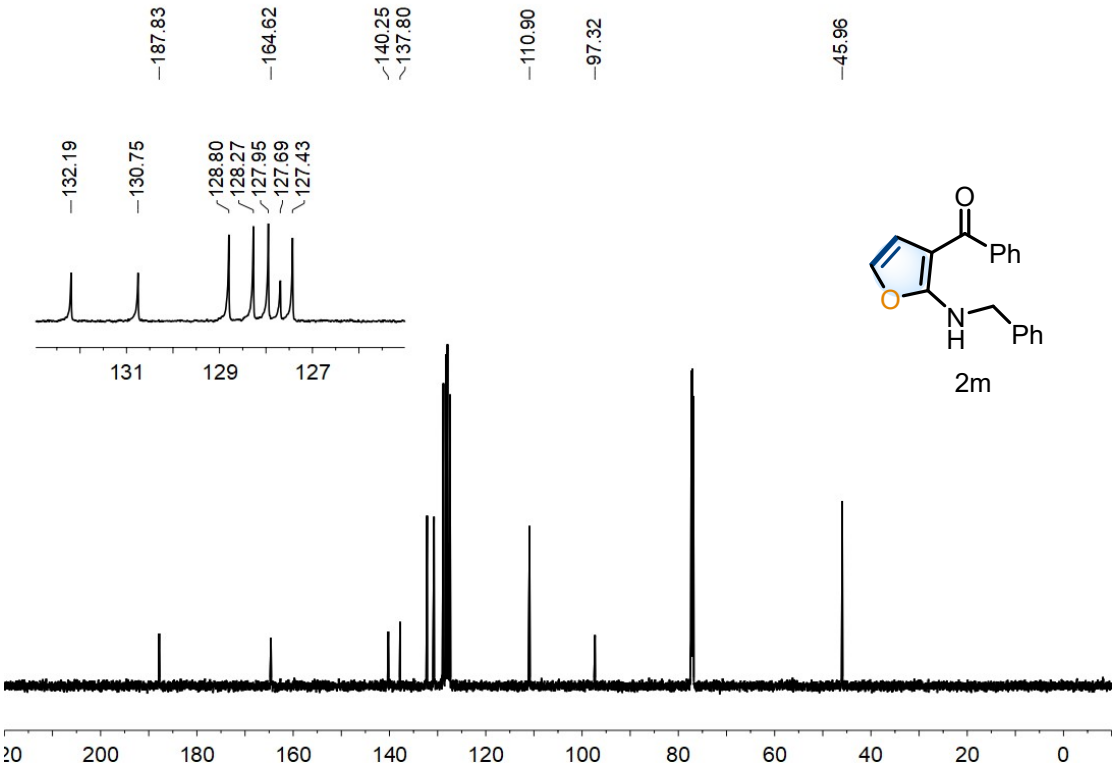
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O
N
H
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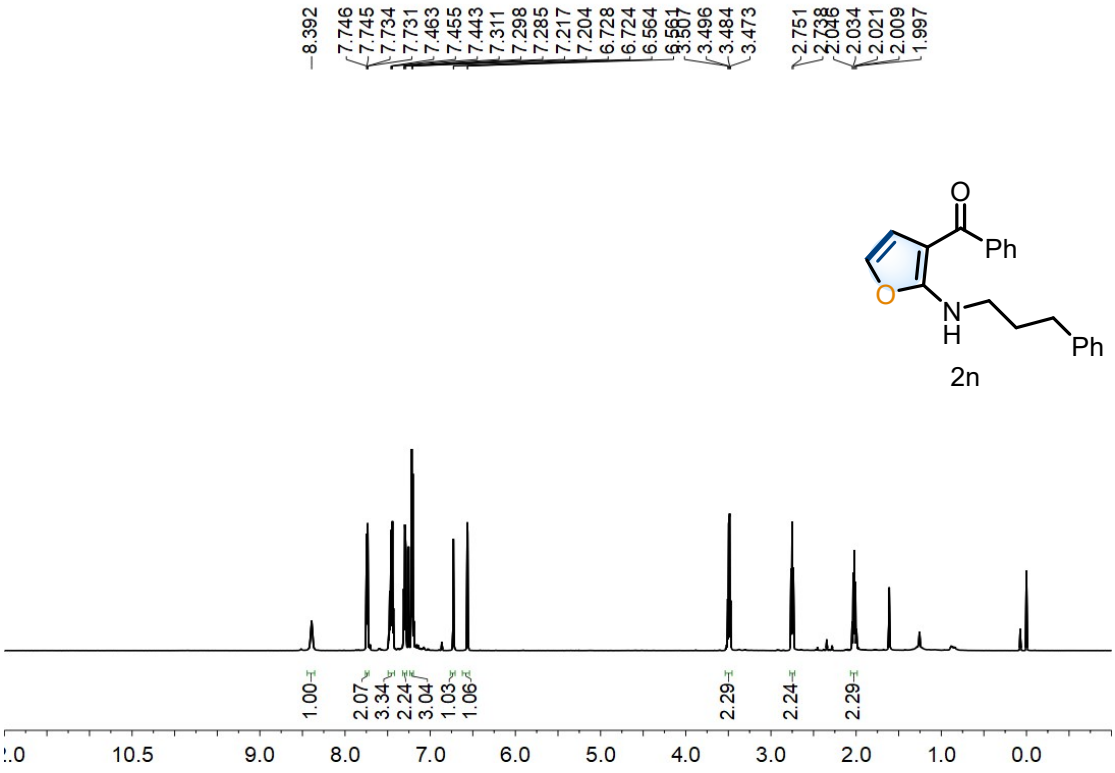
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H
Ph
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1.03
1.06
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2.24
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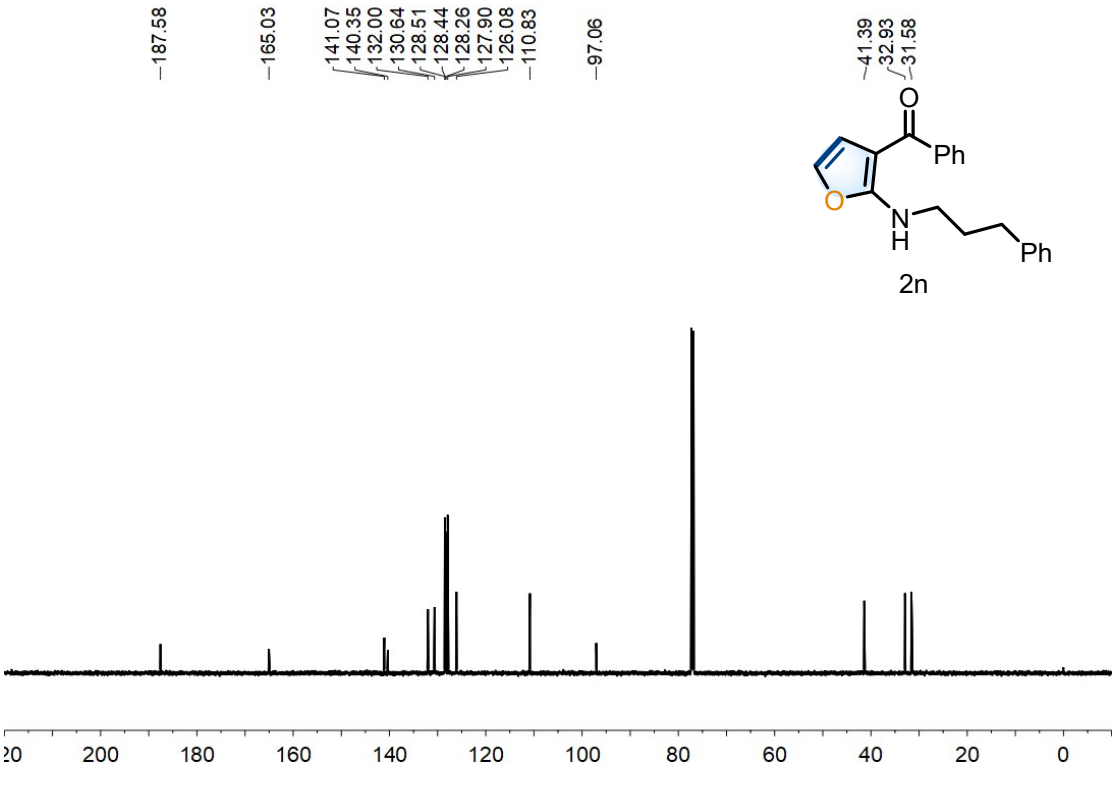
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97.06
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32.93
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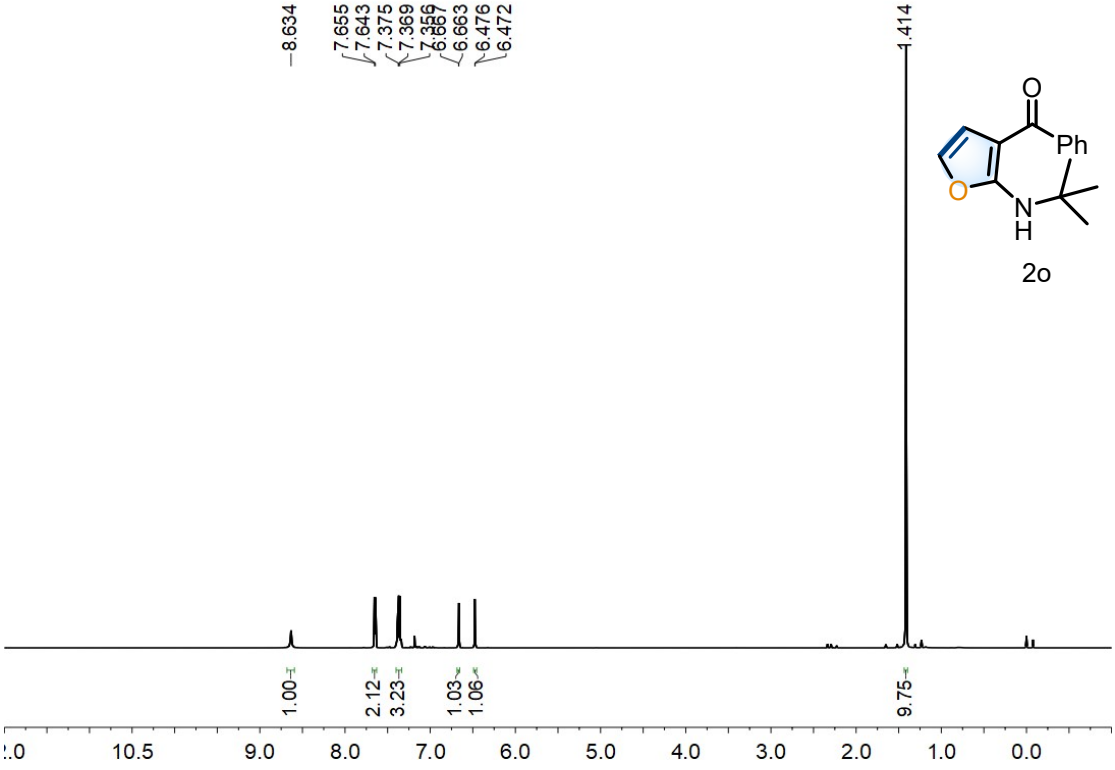
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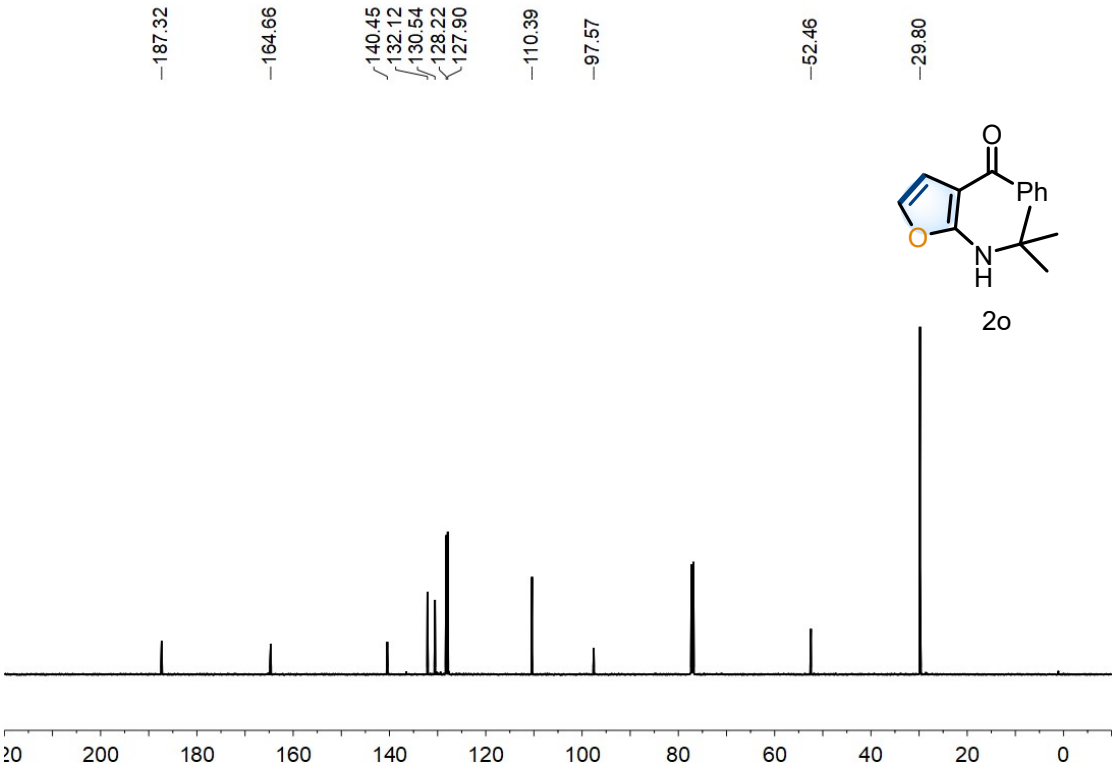
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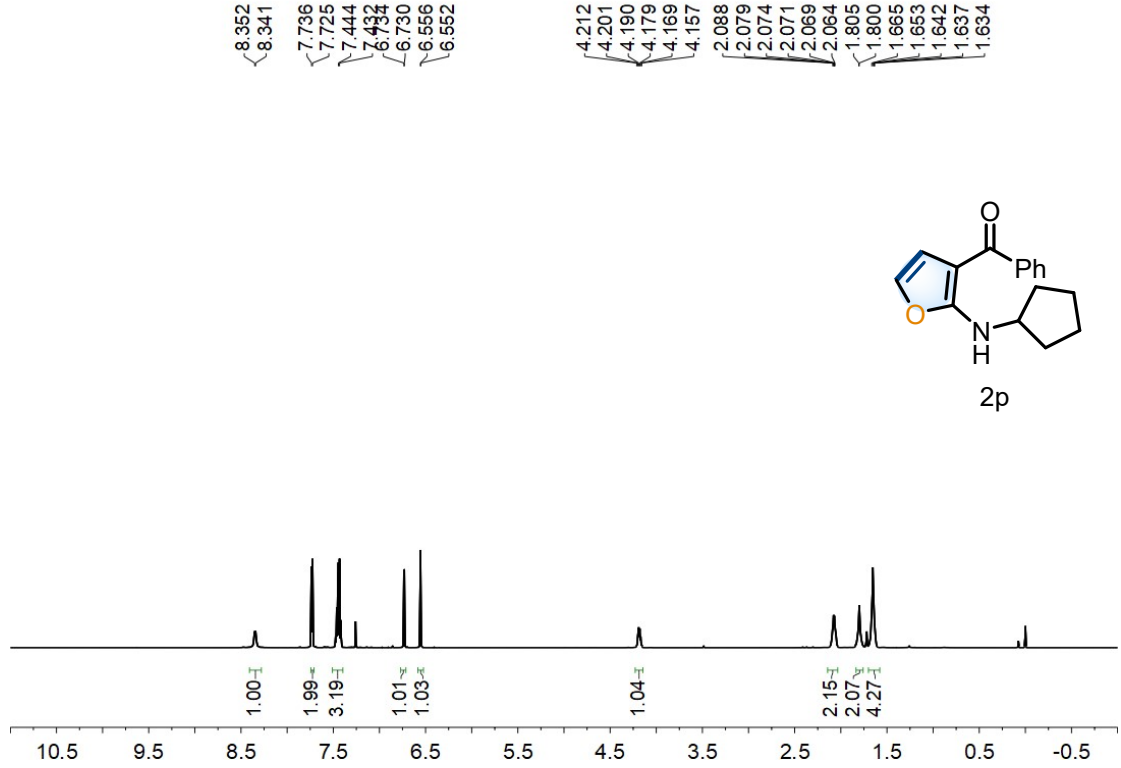
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1.637
1.634
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N
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1.03
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2.15
2.07
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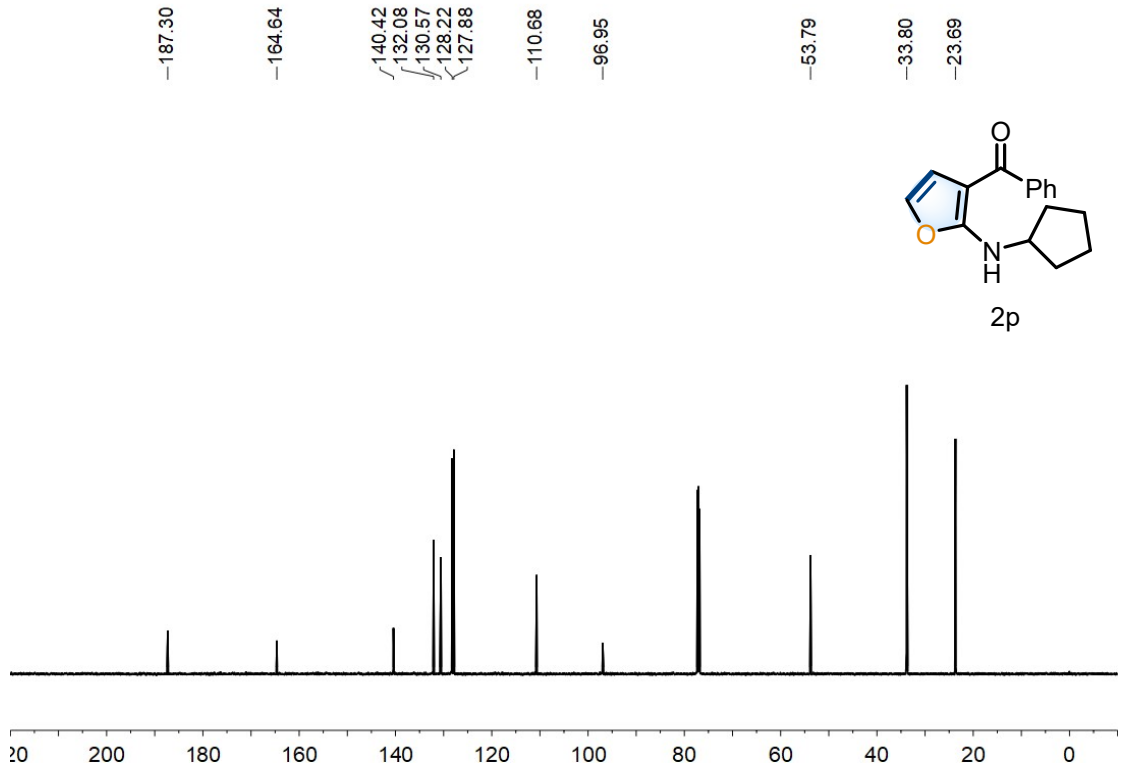
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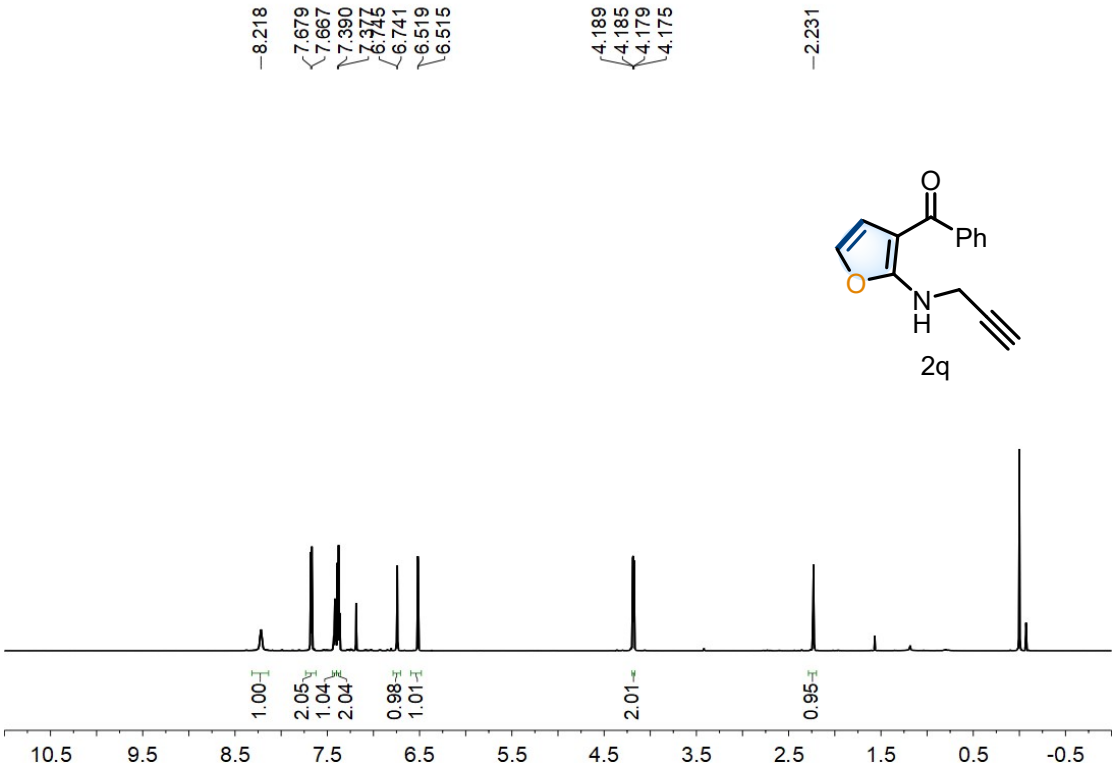
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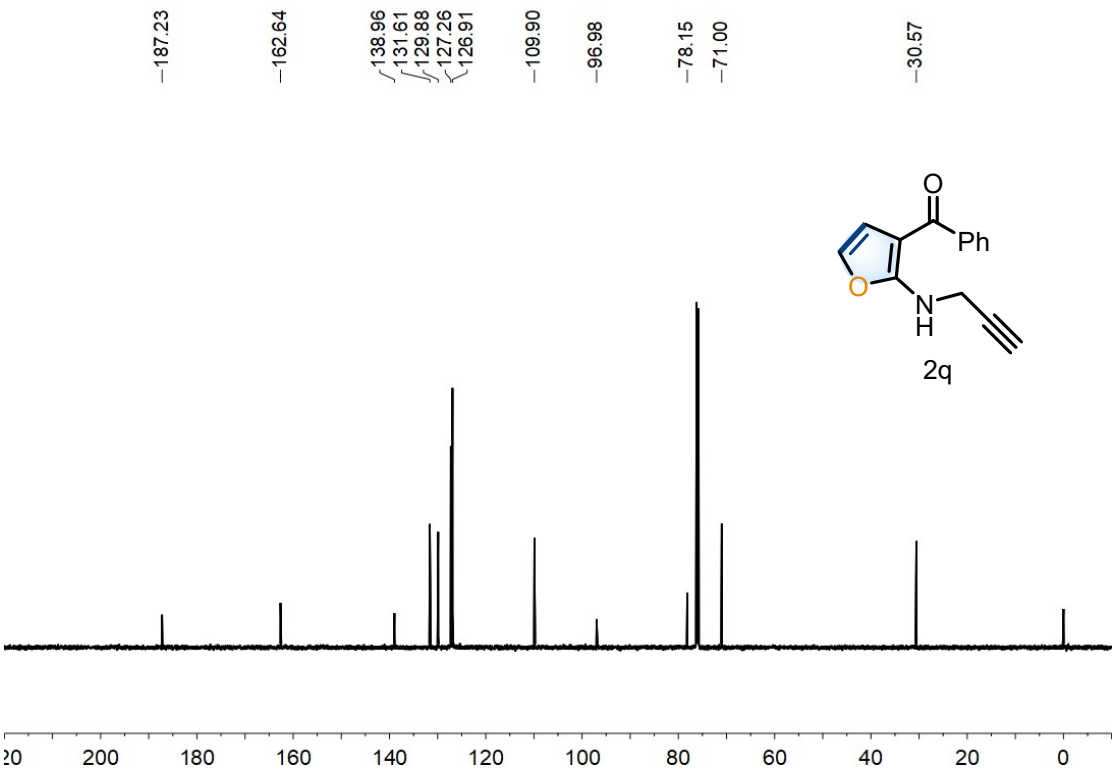
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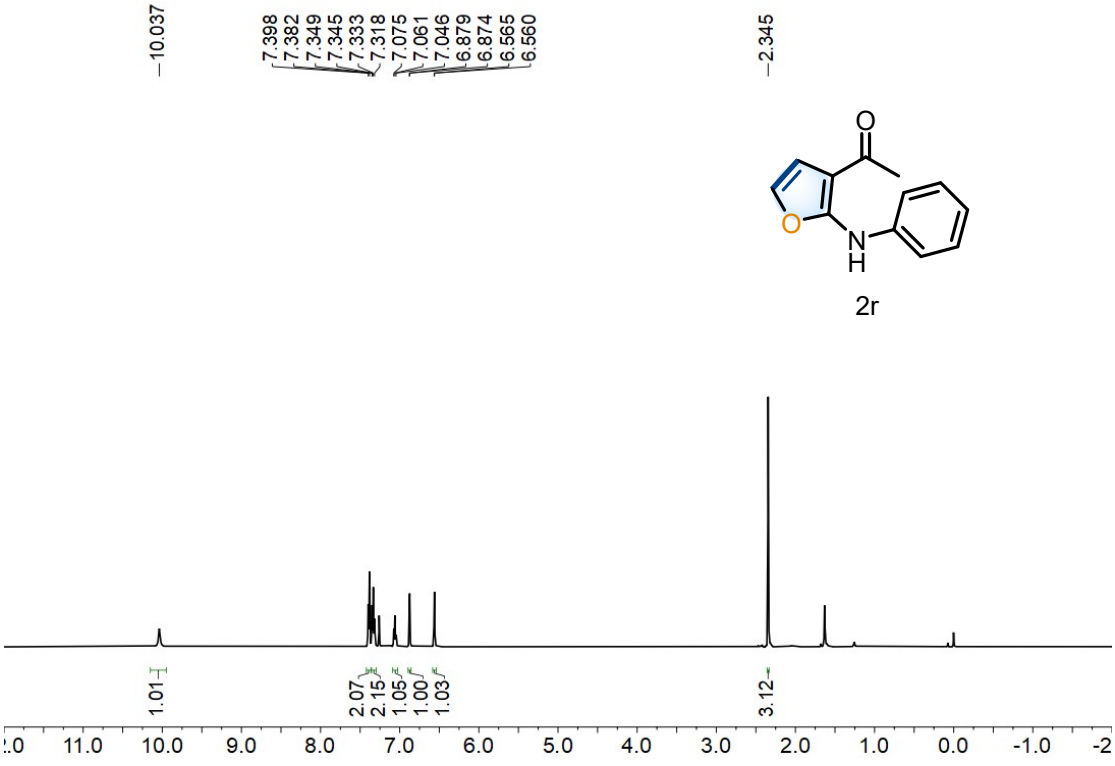
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H
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1.00
1.03
3.12
11.0
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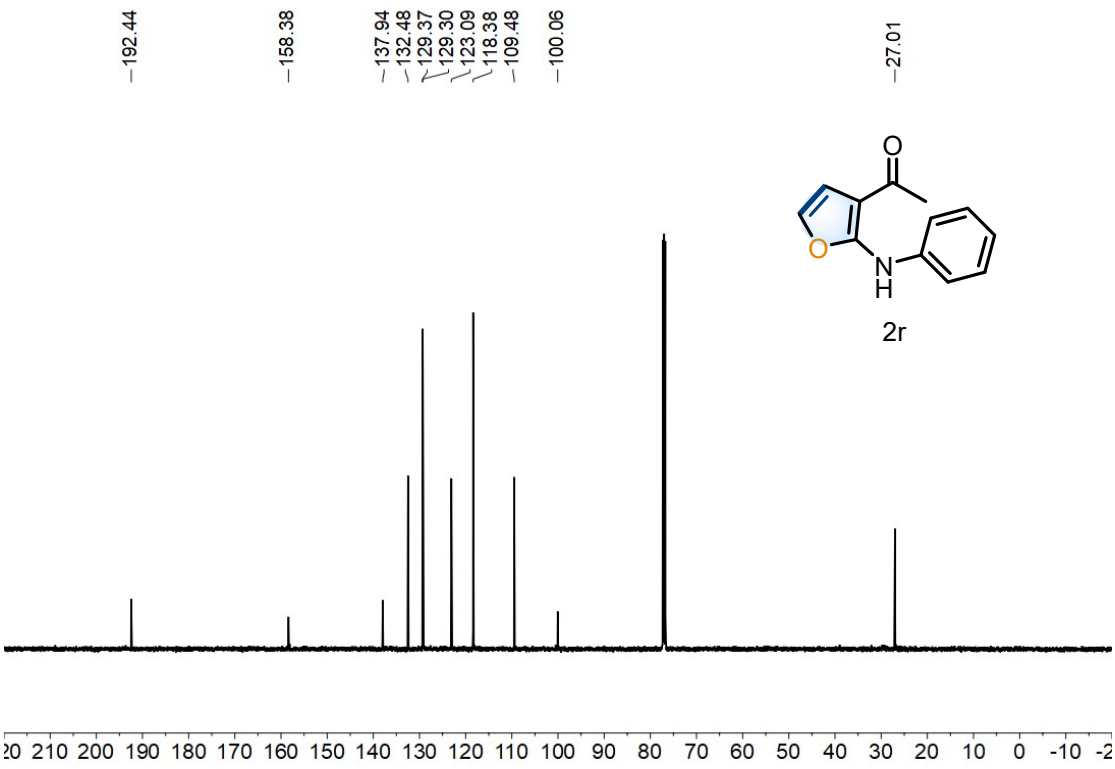
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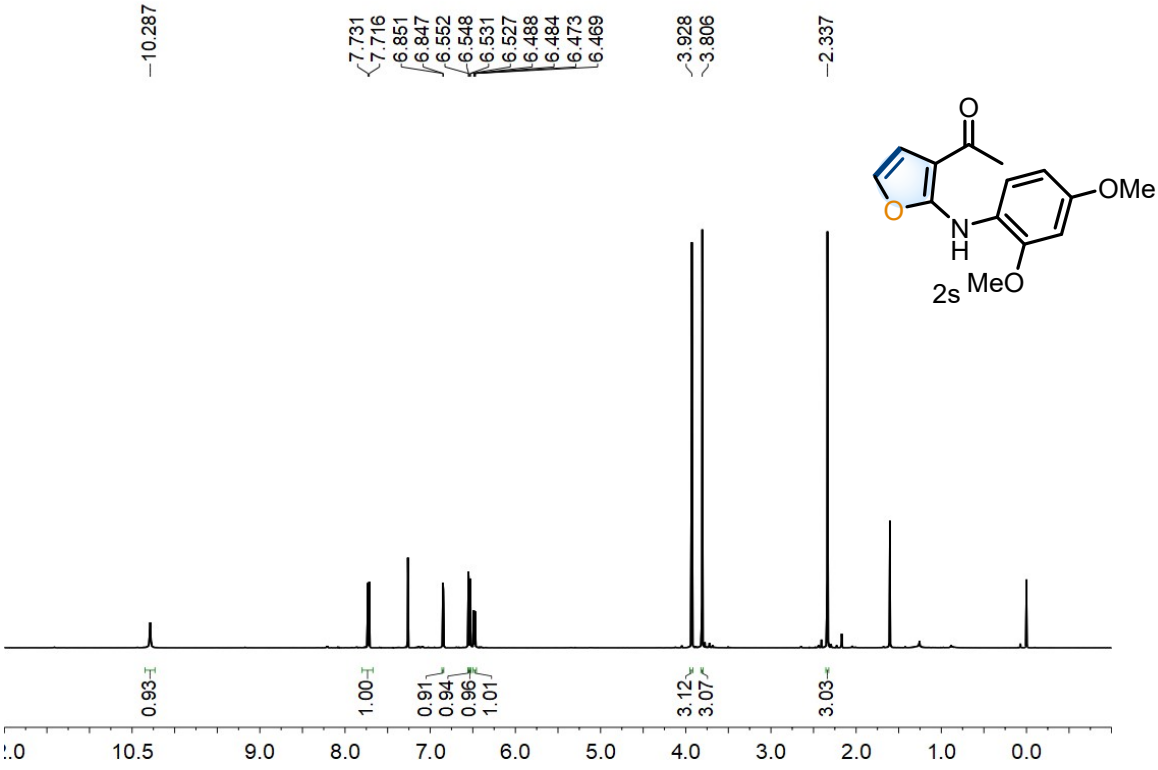
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3.806
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H
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0.91
0.94
0.96
1.01
3.12
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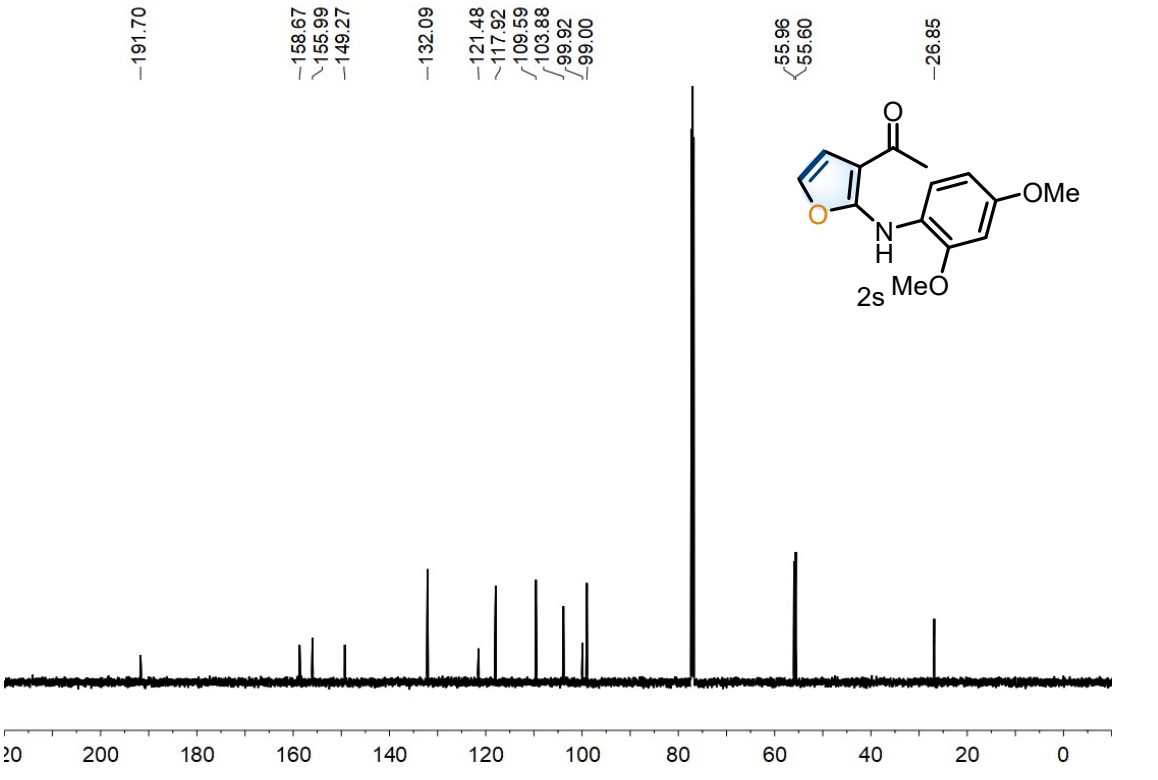
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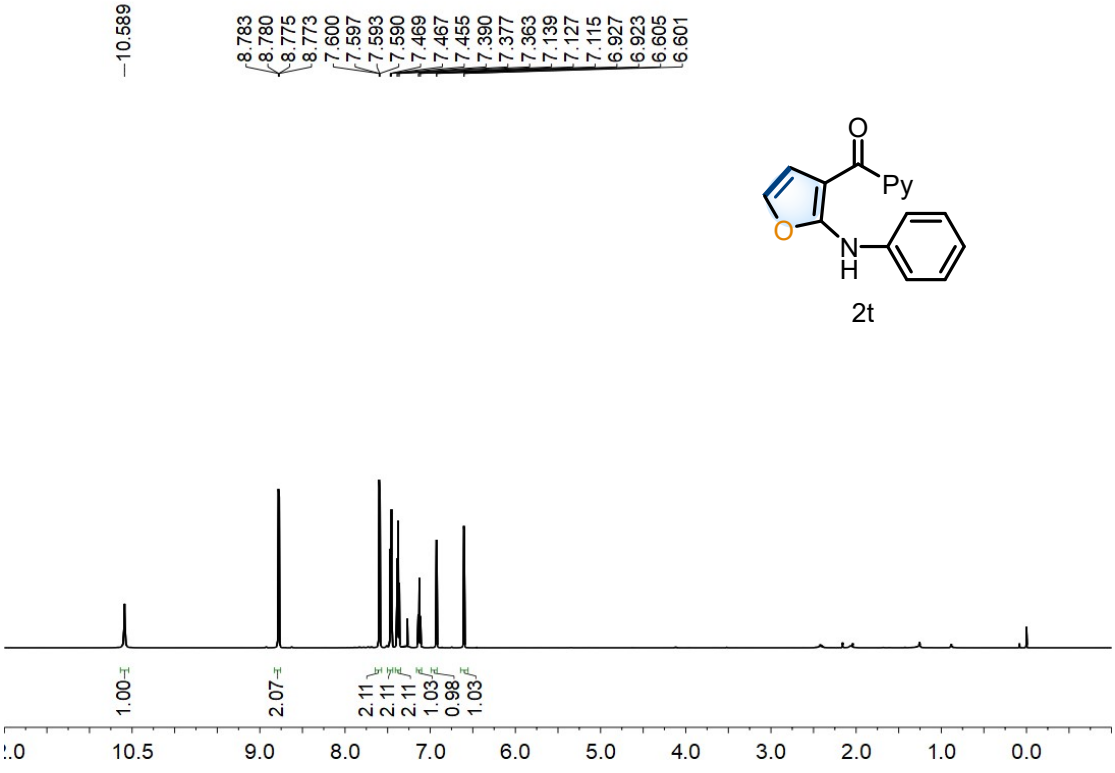
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6.923
6.605
6.601
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Py
O
N
H
2t
1.00
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2.11
1.03
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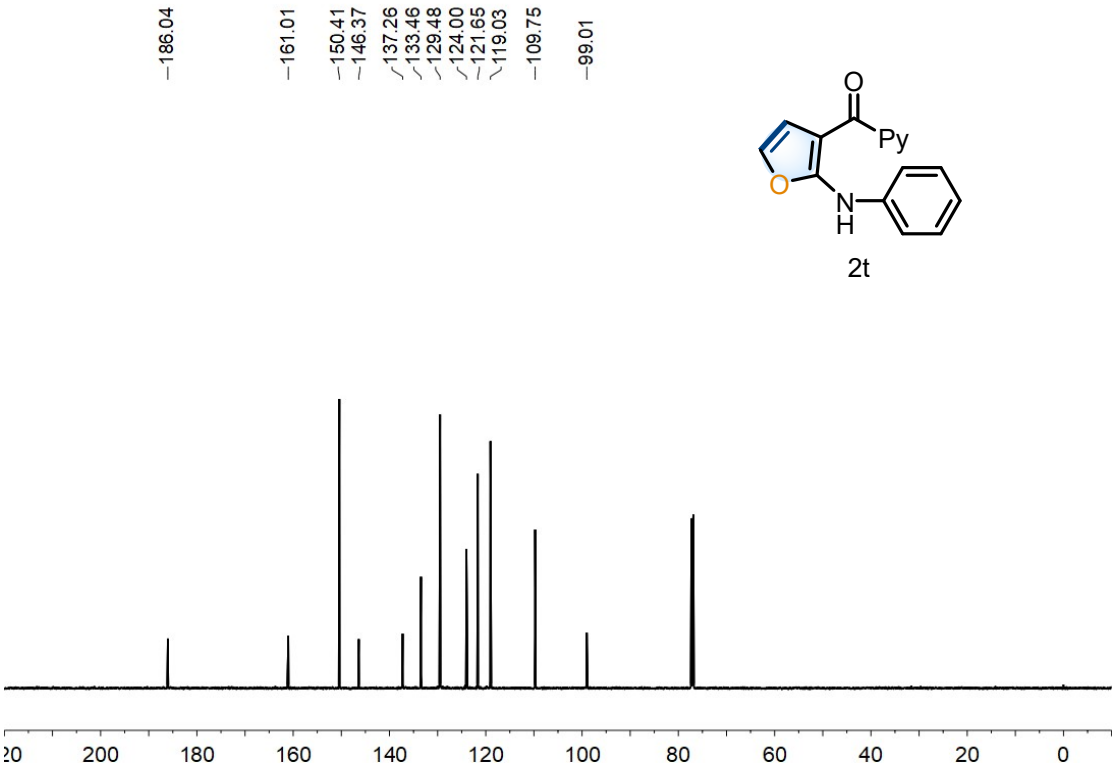
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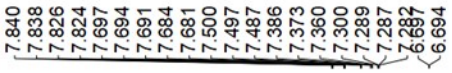
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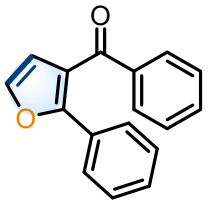
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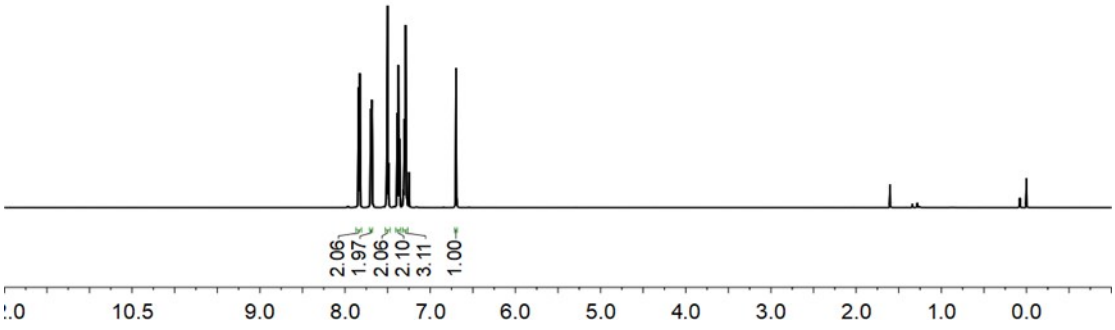
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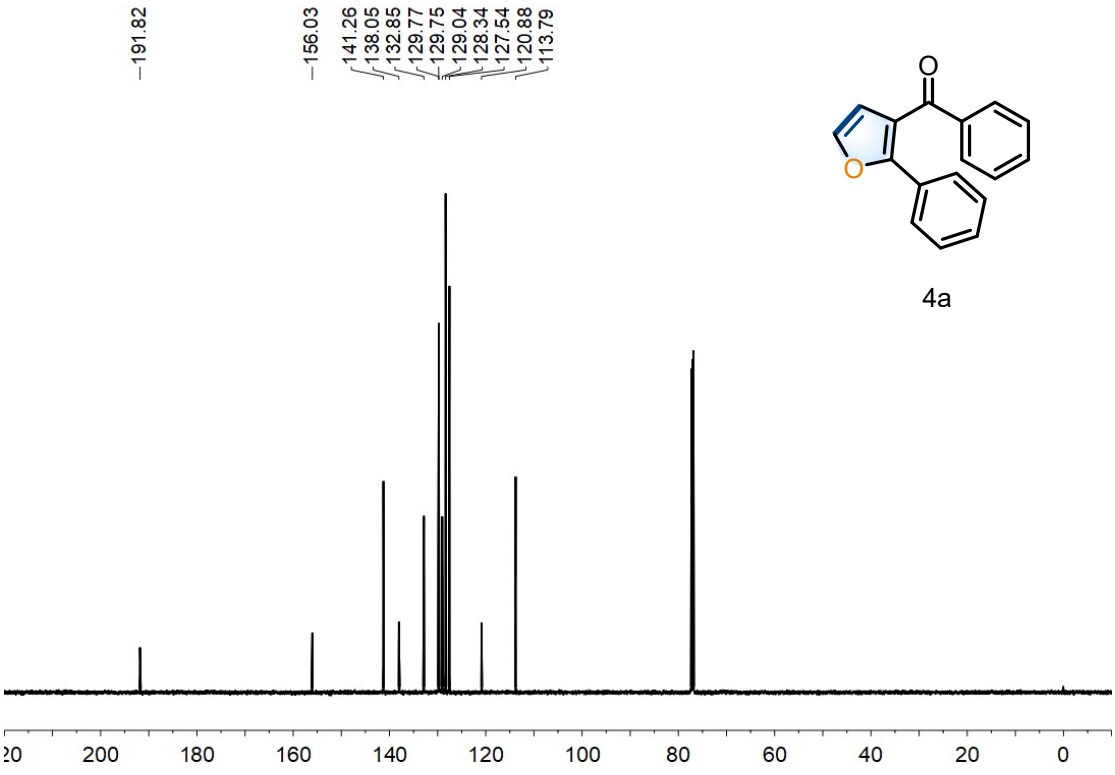
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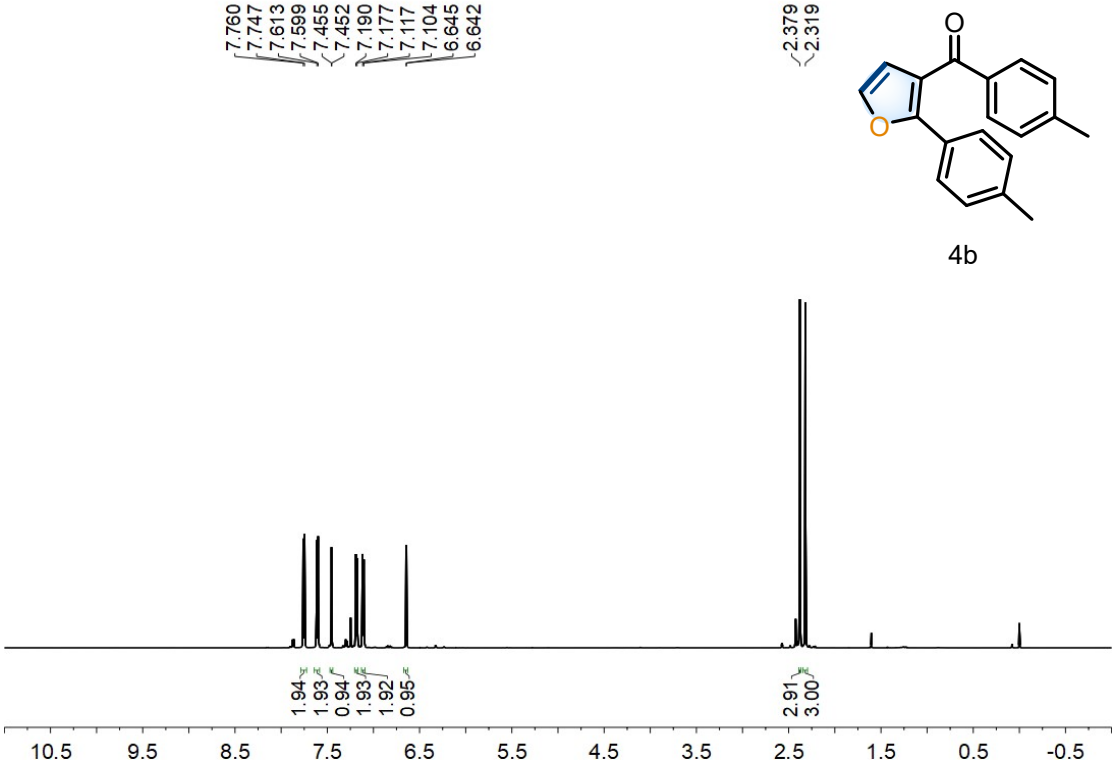
0

O
O

4a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O
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1.93
1.92
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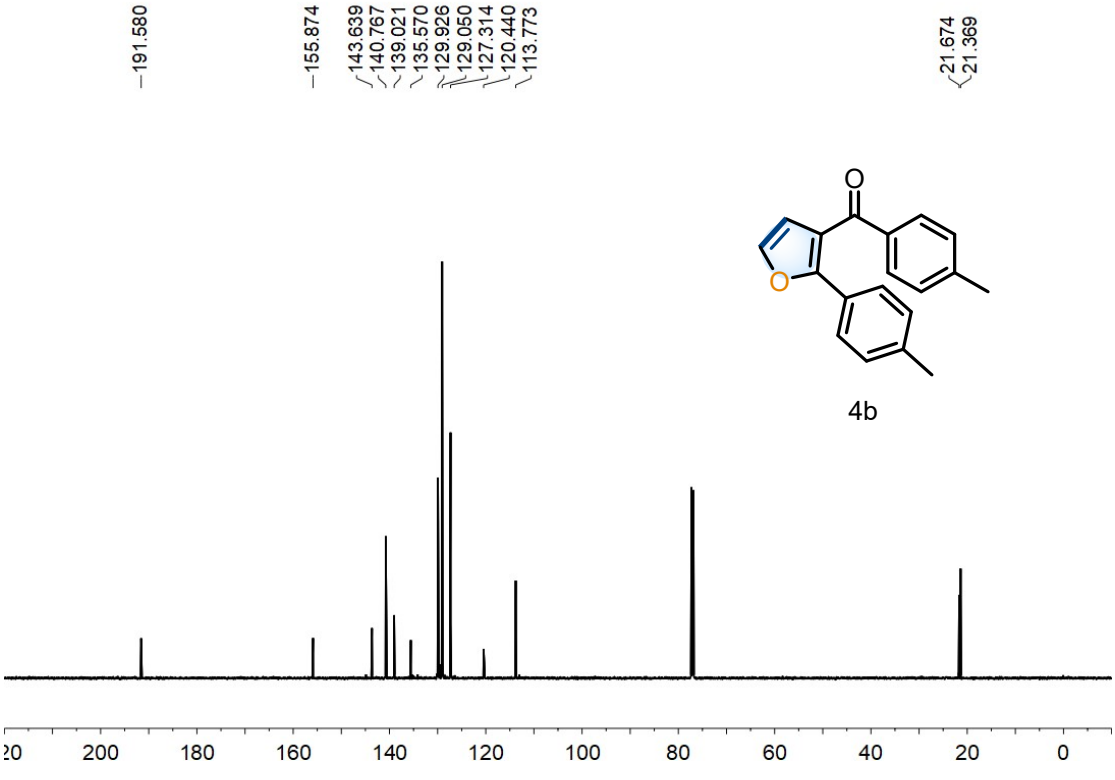
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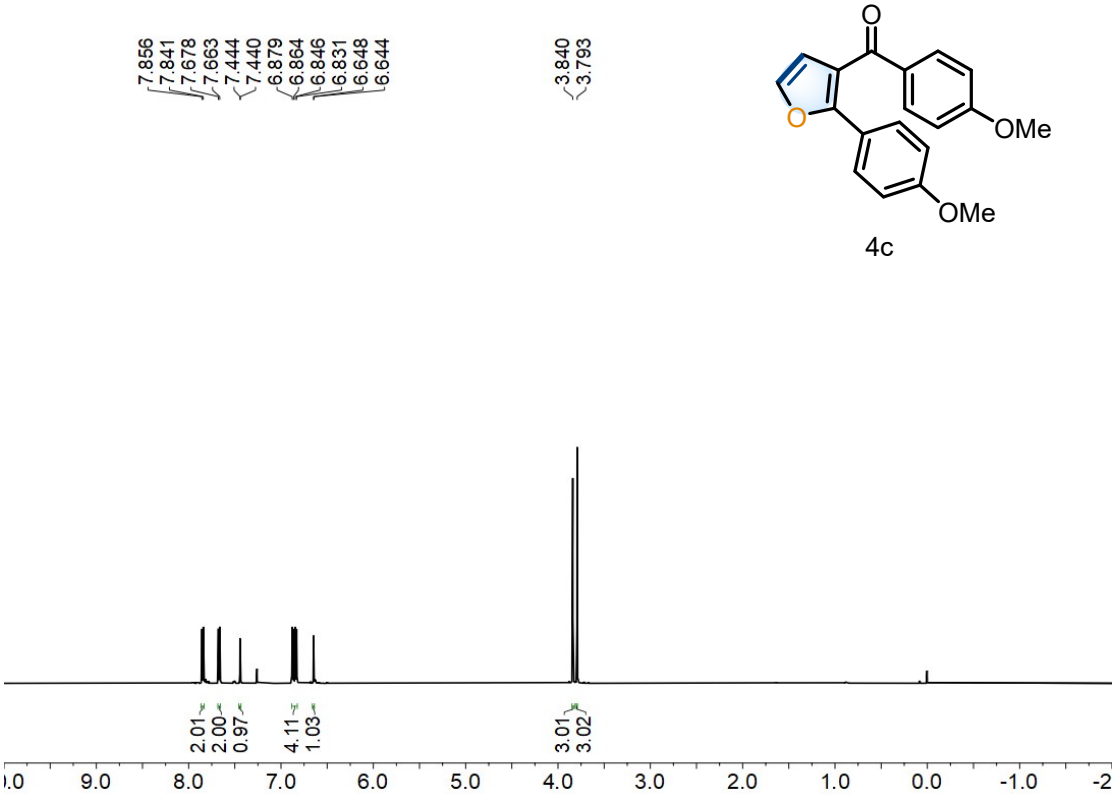
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O
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OMe
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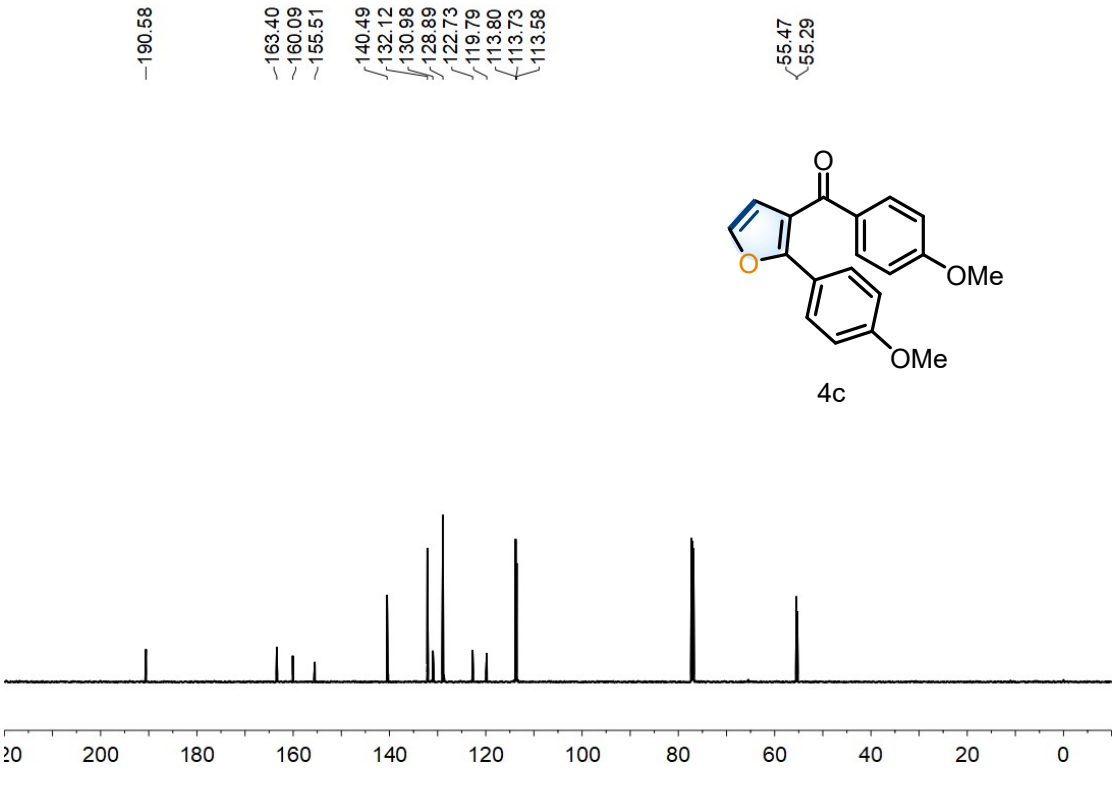
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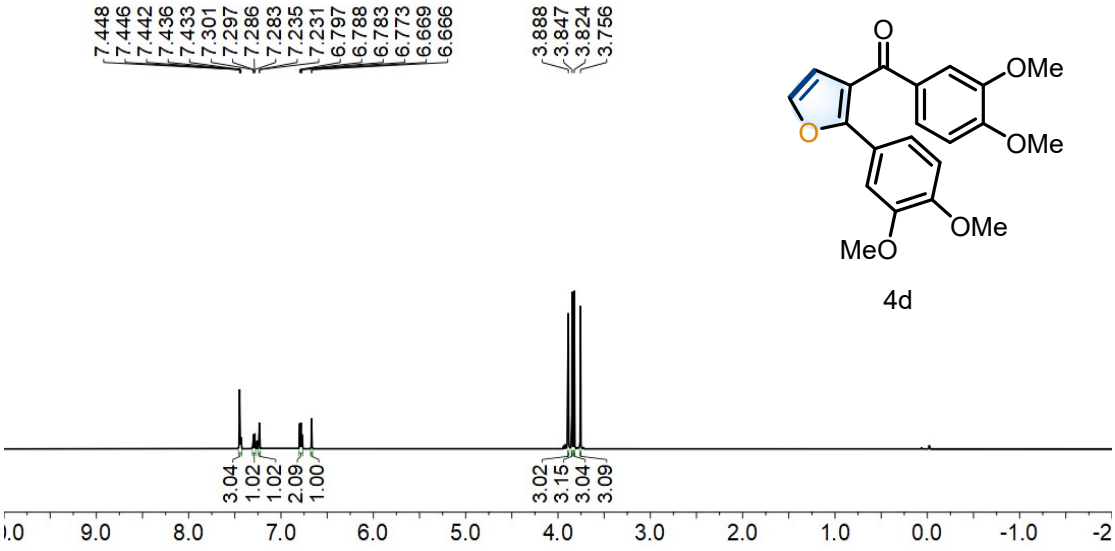
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OMe
OMe
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1.02
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1.00
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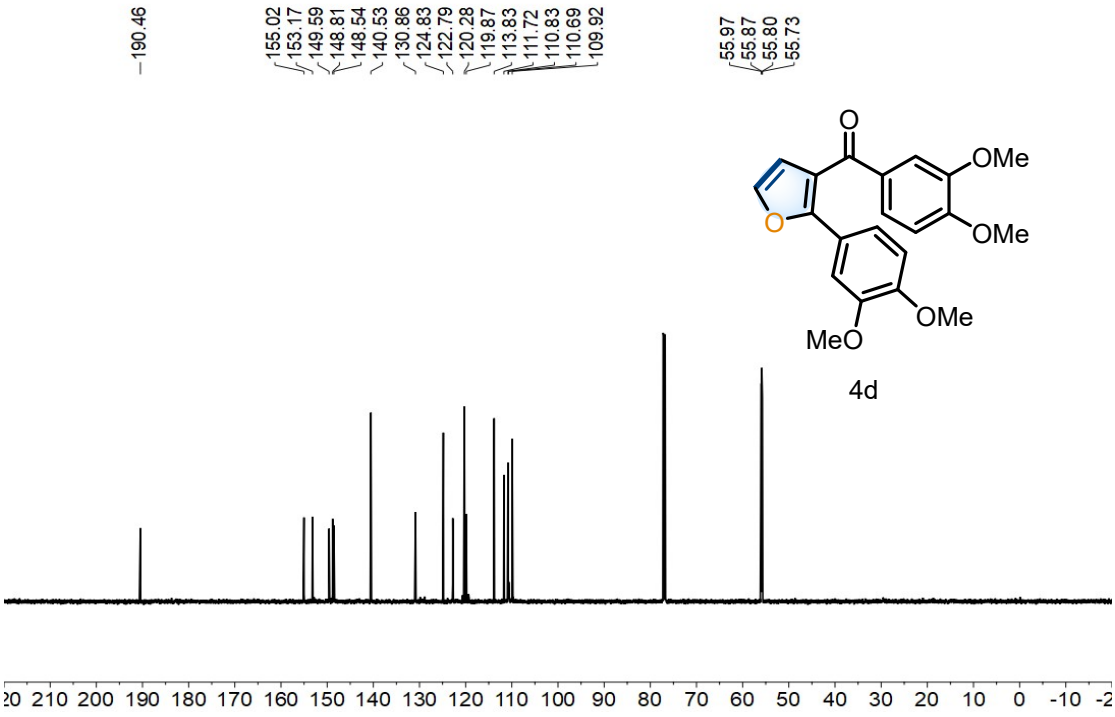
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OMe
OMe
OMe
MeO
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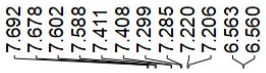
4d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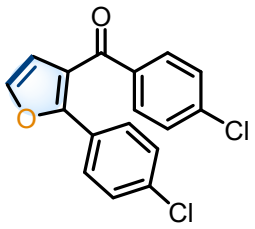
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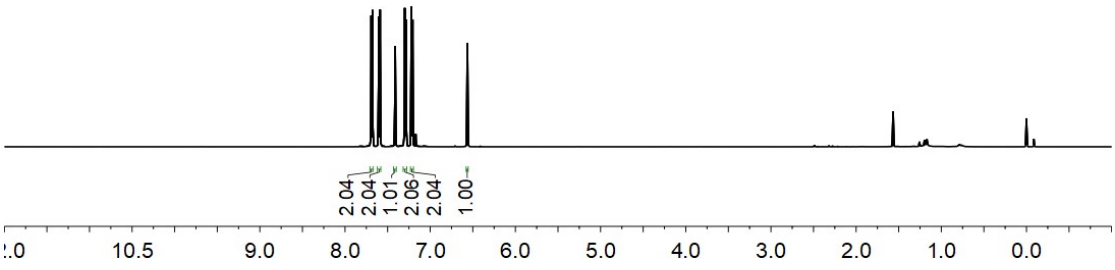
Cl
Cl

4e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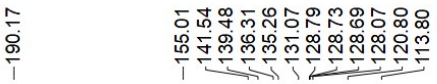
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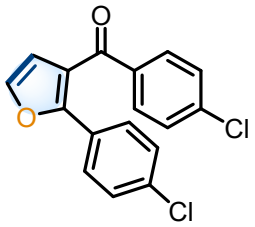
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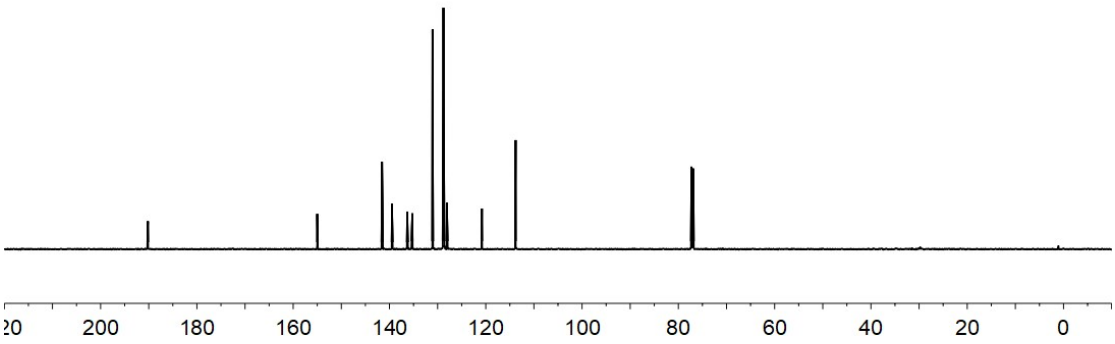
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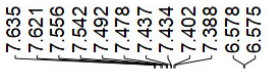
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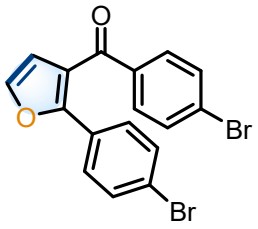
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Br
Br

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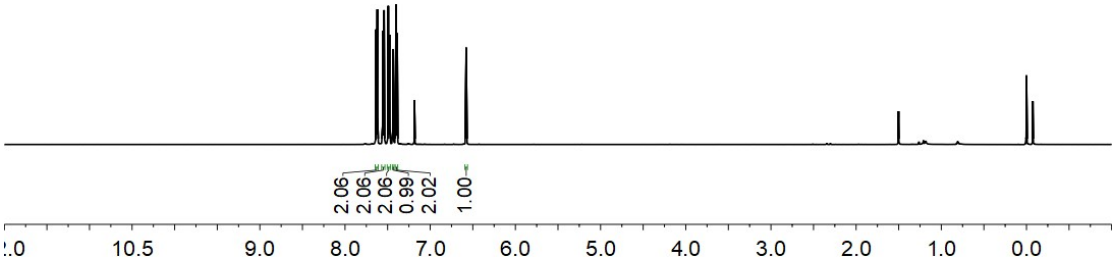
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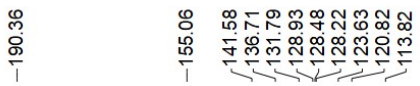
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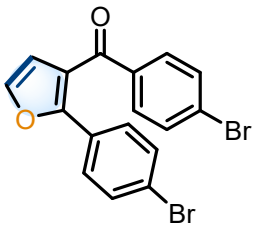
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Br
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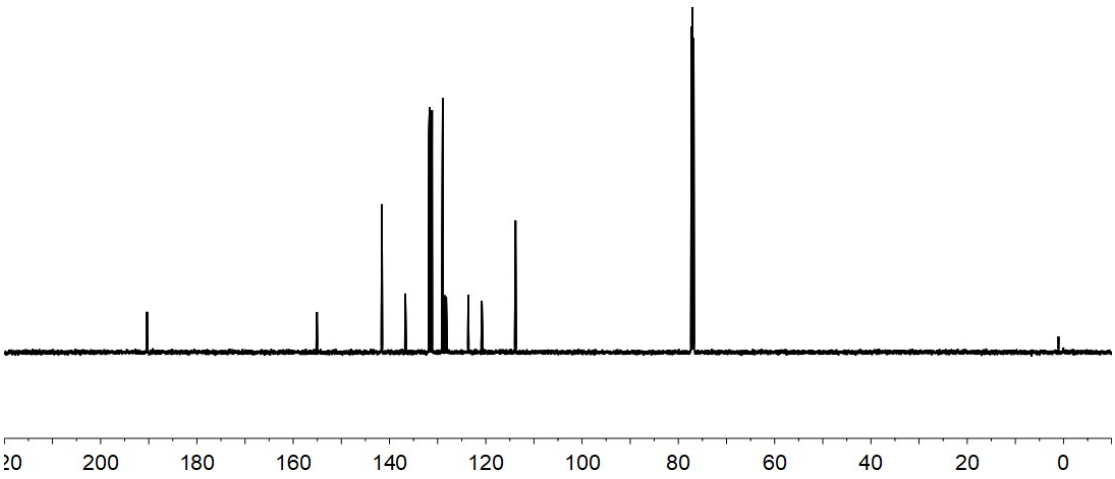
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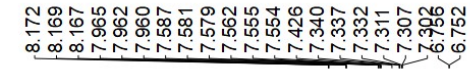
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7.581
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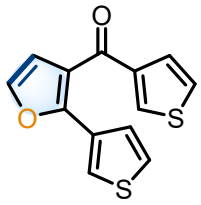
6.752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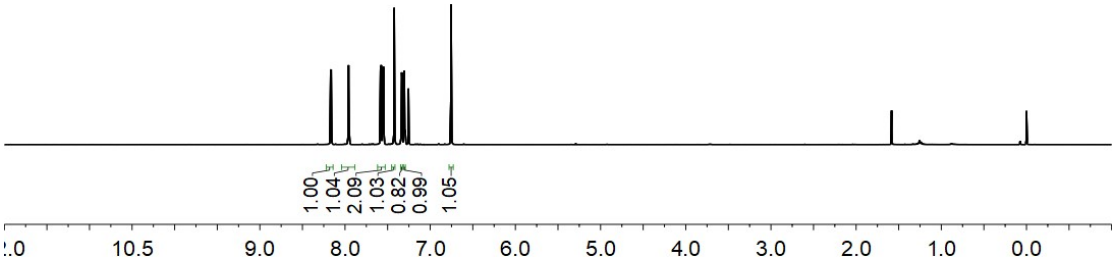
S
S

4g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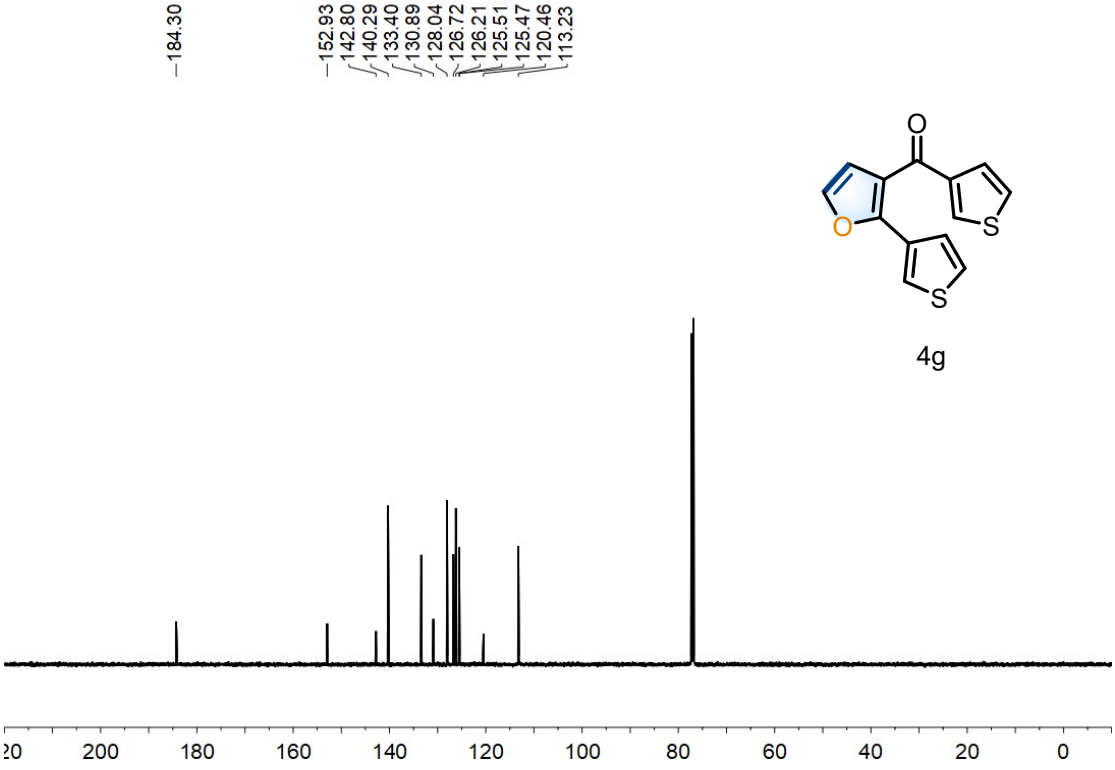
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152.93
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126.72
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125.51
125.47
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200
180
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120
100
80
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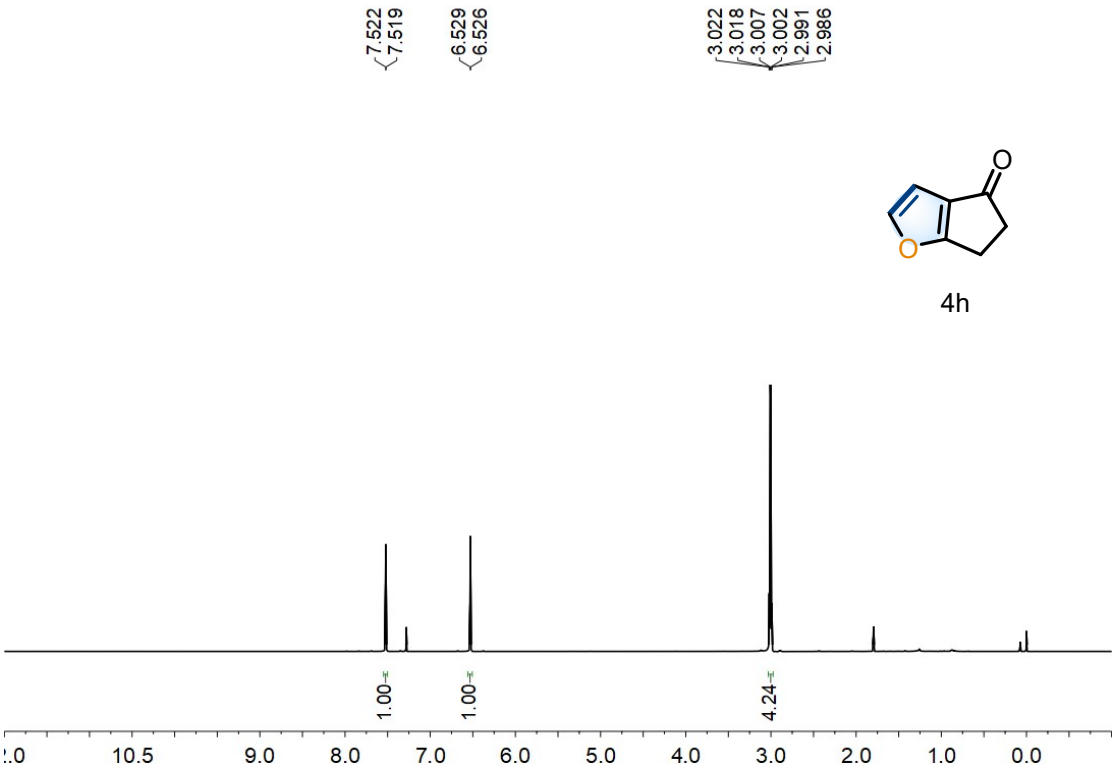
40
20
0

O
O
S
S

4g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3.007
3.002
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2.986
O
O
4h
1.00
1.00
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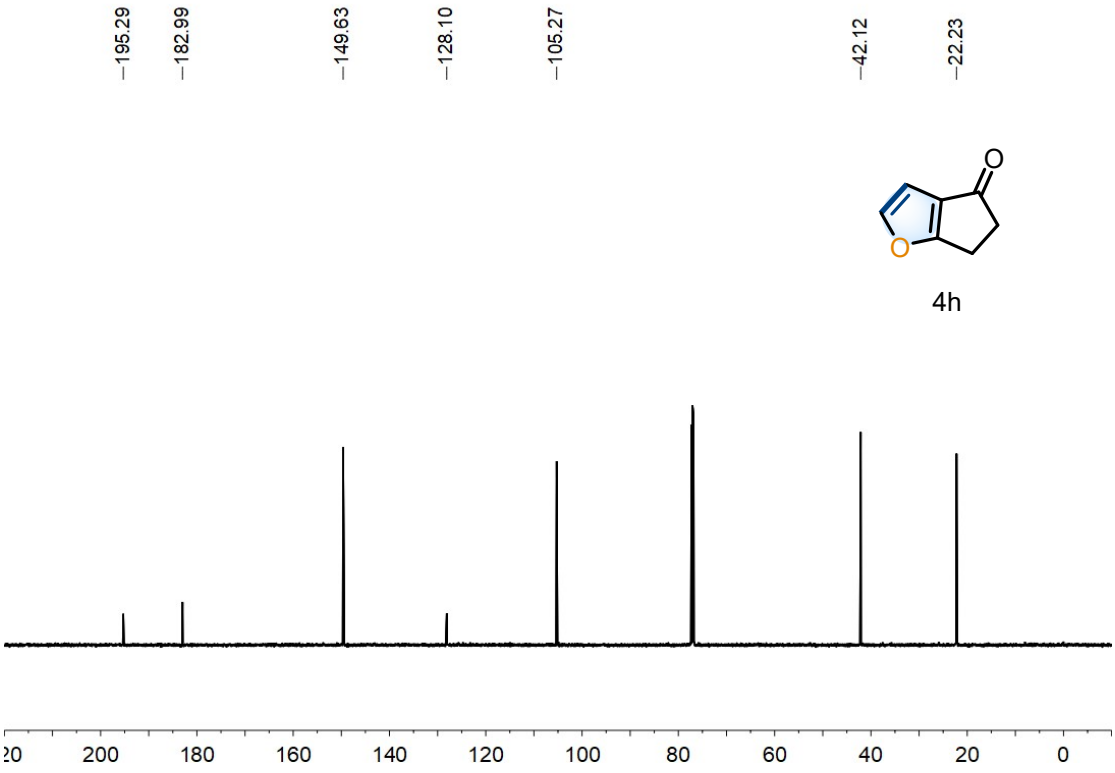
1.0
0.0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22.23
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O
4h
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20
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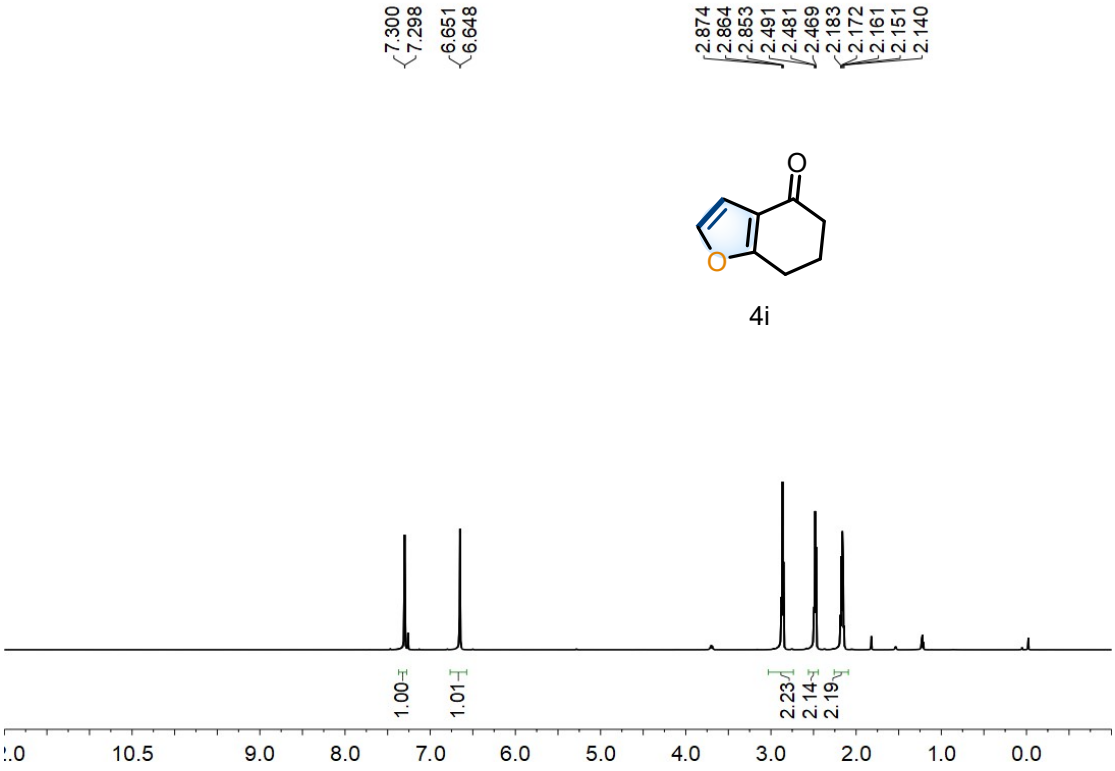
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2.491
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2.172
2.161
2.151
2.140
O
O
4i
1.00
1.01
2.23
2.14
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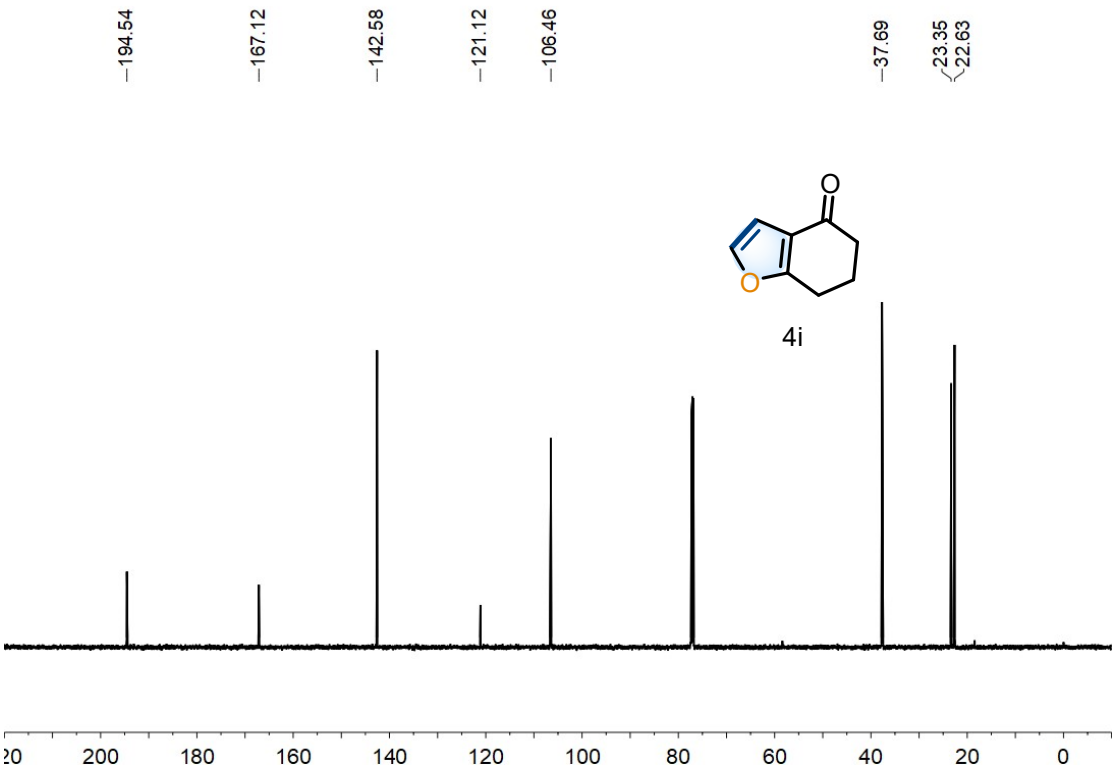
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121.12
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22.63
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O
4i
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140
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60
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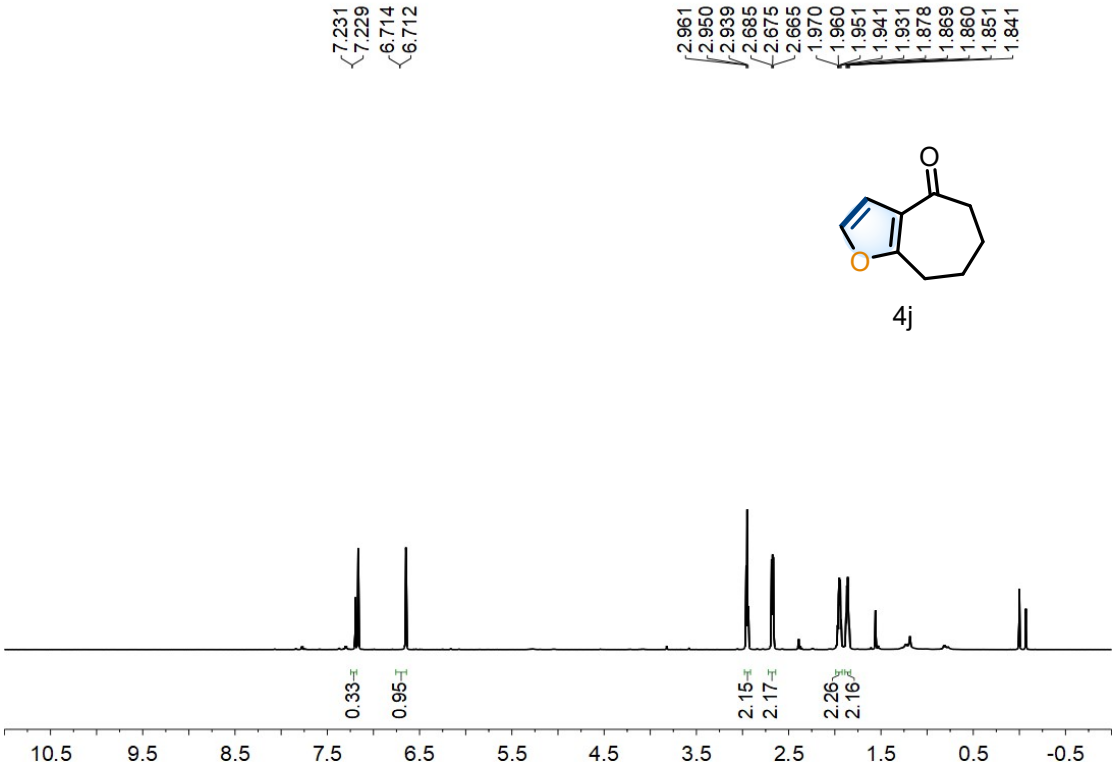
20
0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1.951
1.941
1.931
1.878
1.869
1.860
1.851
1.841
O
O
4j
0.33
0.95
2.15
2.17
2.26
2.16
10.5
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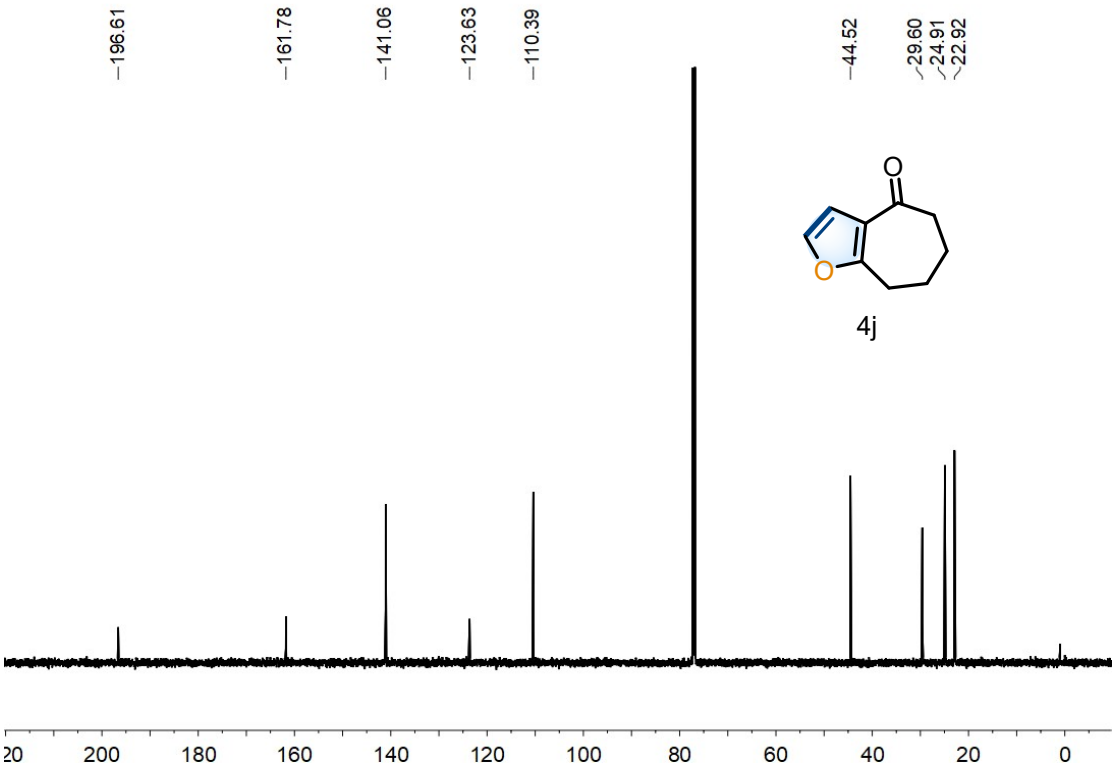
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5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141.06
123.63
110.39
44.52
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24.91
22.92
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O
4j
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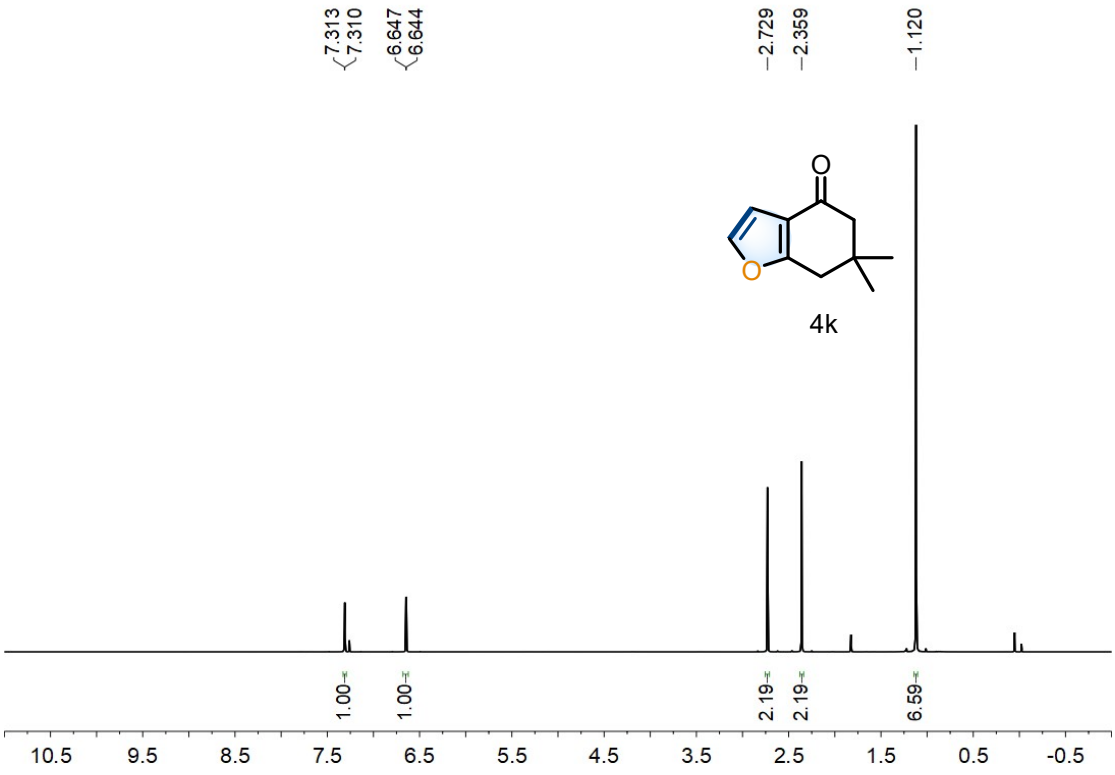
60
40
20
0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6.644
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2.359
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O
O
4k
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1.00
2.19
2.19
6.59
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7.5
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5.5
4.5
3.5
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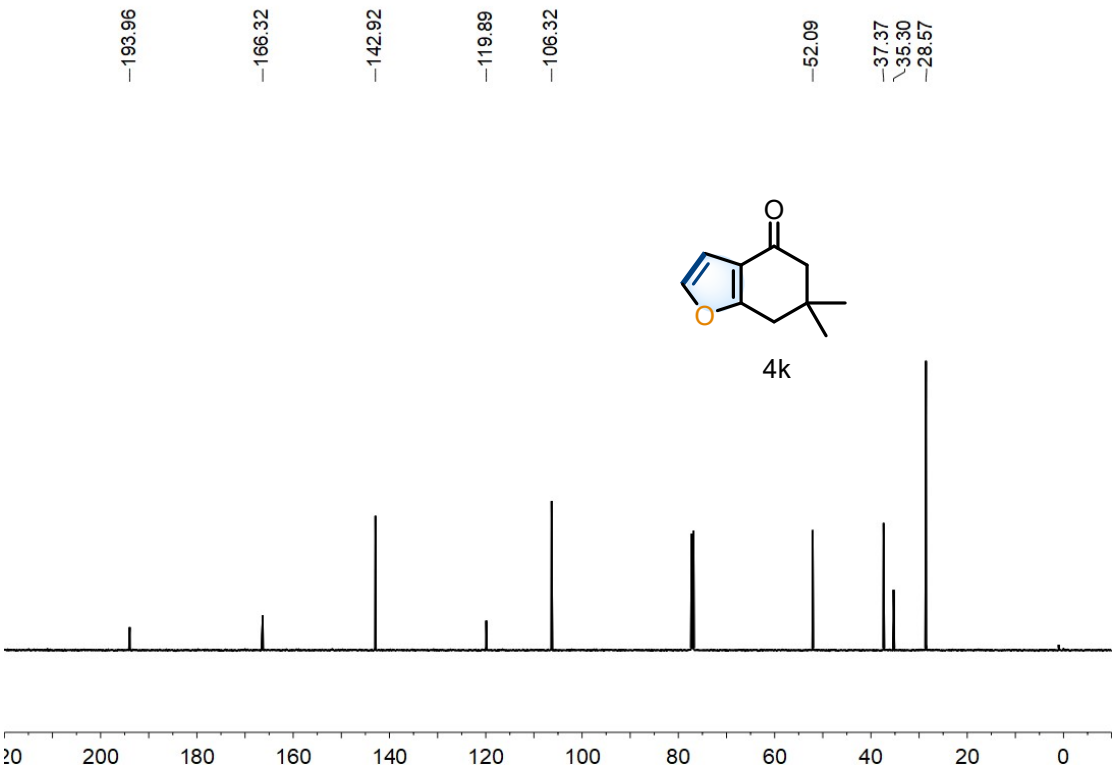
1.5
0.5
-0.5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20
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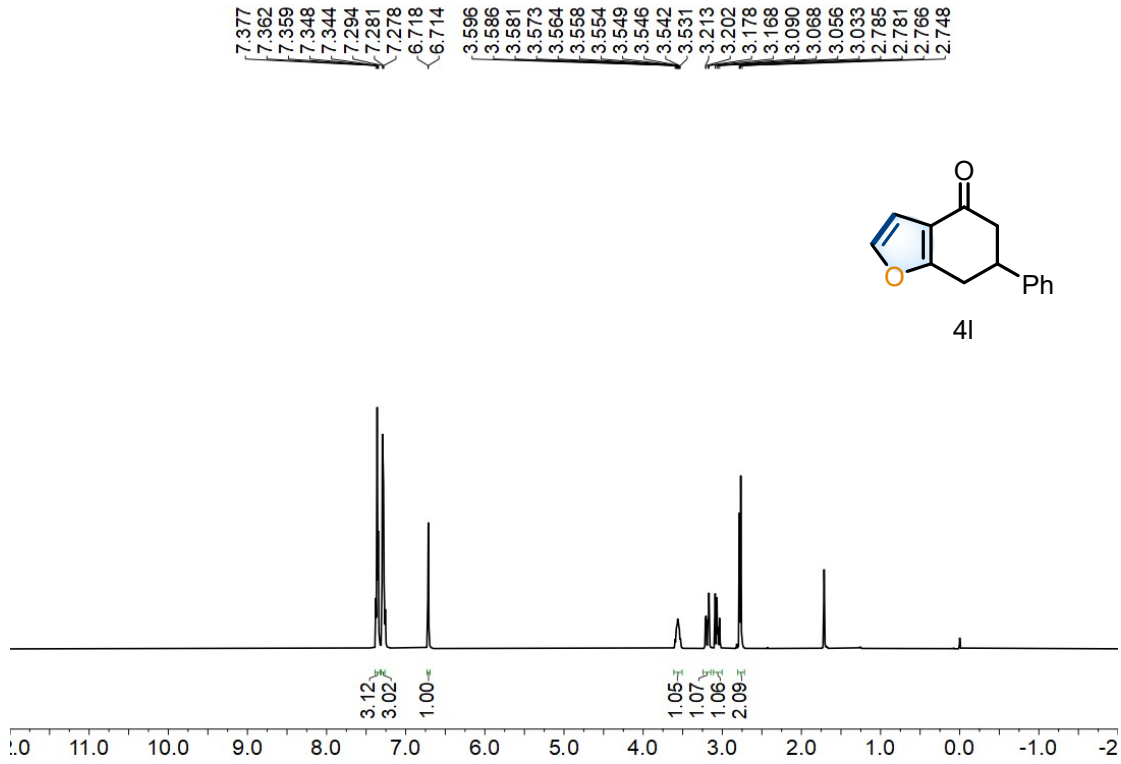
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3.581
3.573
3.564
3.558
3.554
3.549
3.546
3.542
3.531
3.213
3.202
3.178
3.168
3.090
3.068
3.056
3.033
2.785
2.781
2.766
2.748
O
O
Ph
4l
3.12
3.02
1.00
1.05
1.07
1.06
2.09
11.0
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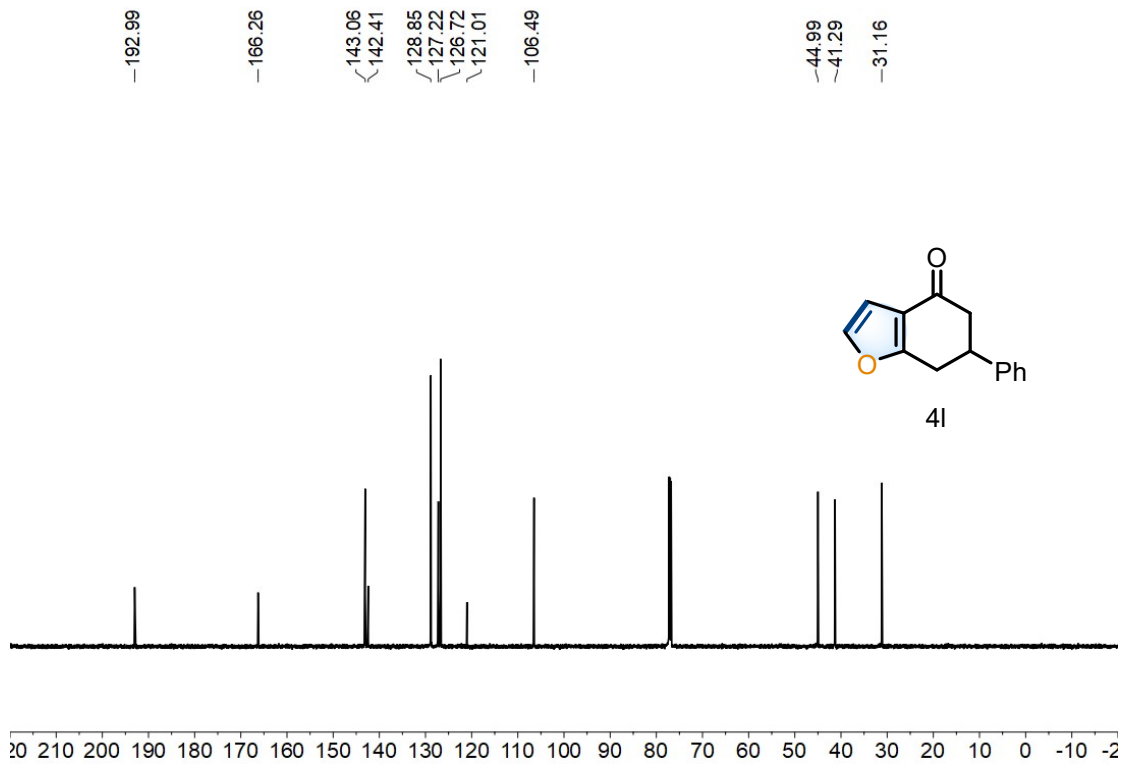
-1.0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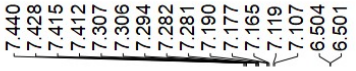
41.29
31.16
O
O
Ph
4l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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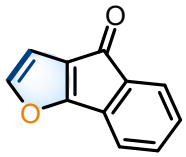
6.501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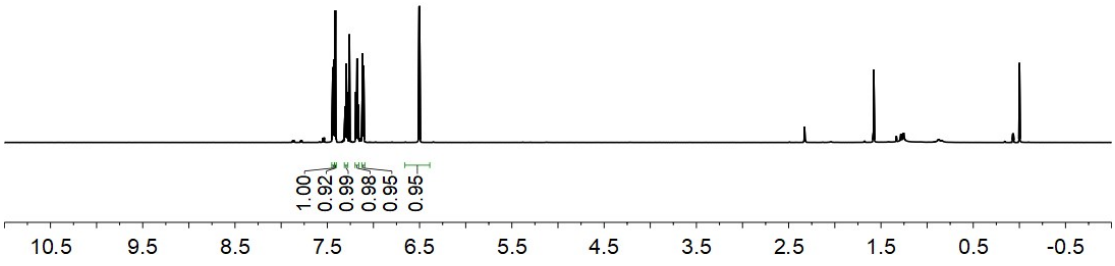
O

4m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0.95
0.95
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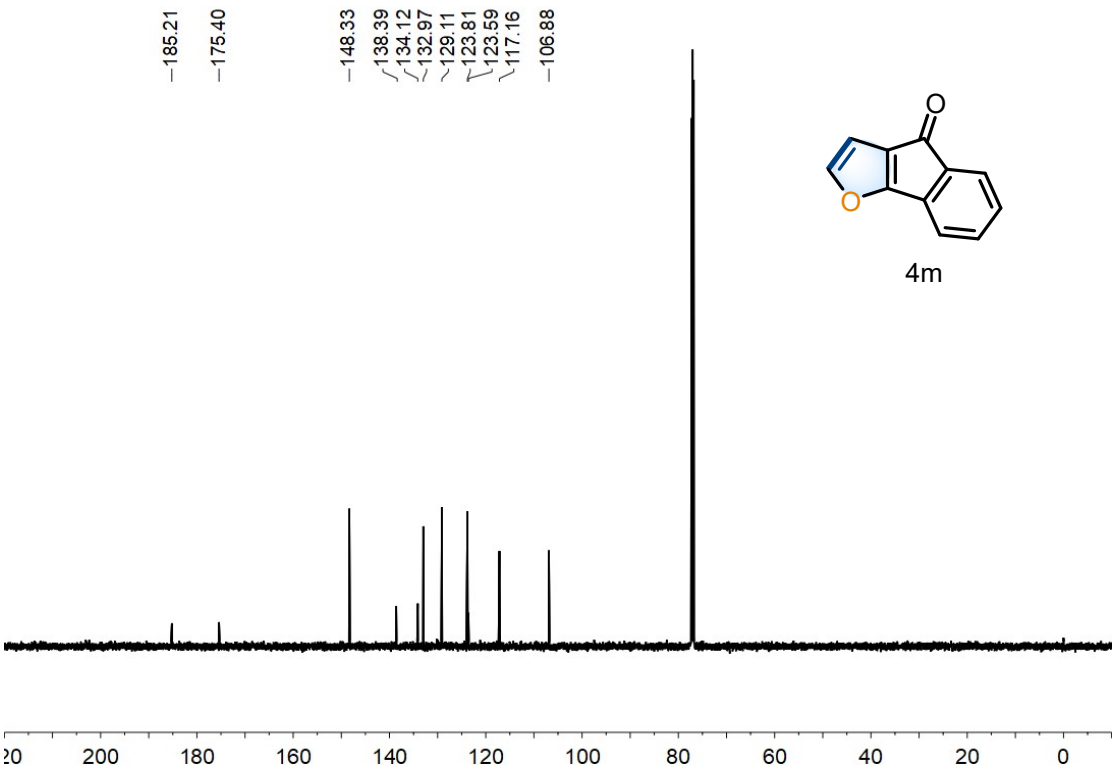
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5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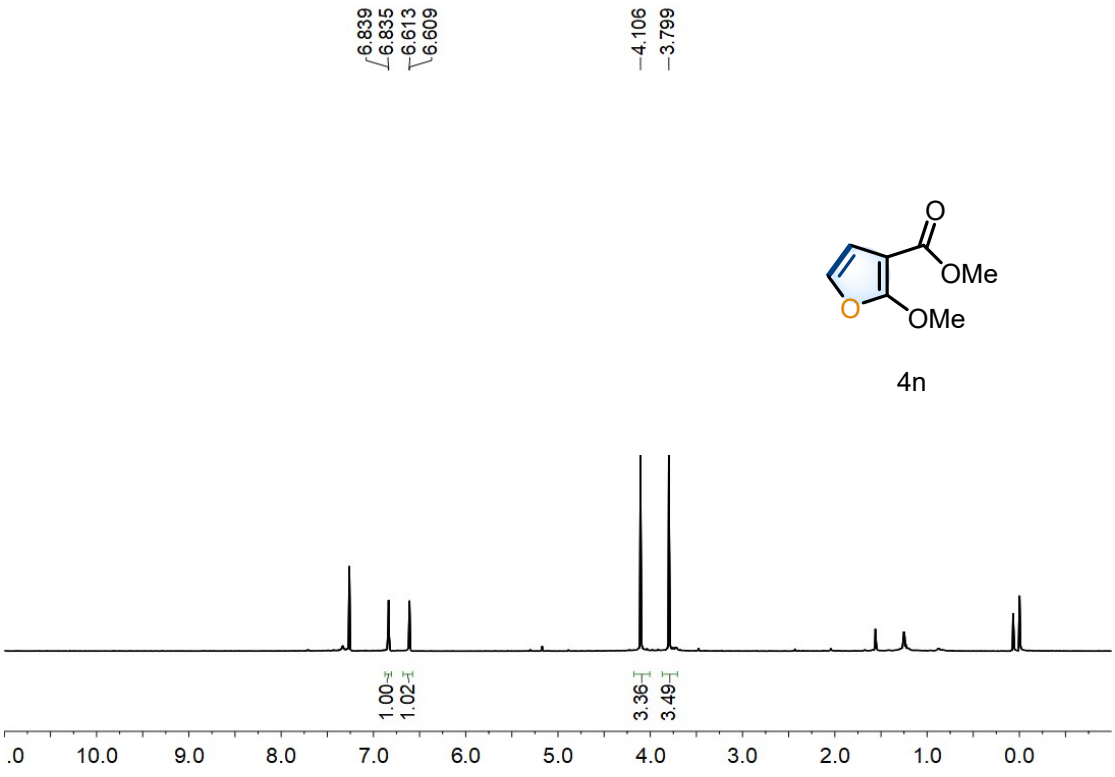
80
60
40
20
0

O
O

4m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OMe
O
OMe
4n
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3.36
3.49
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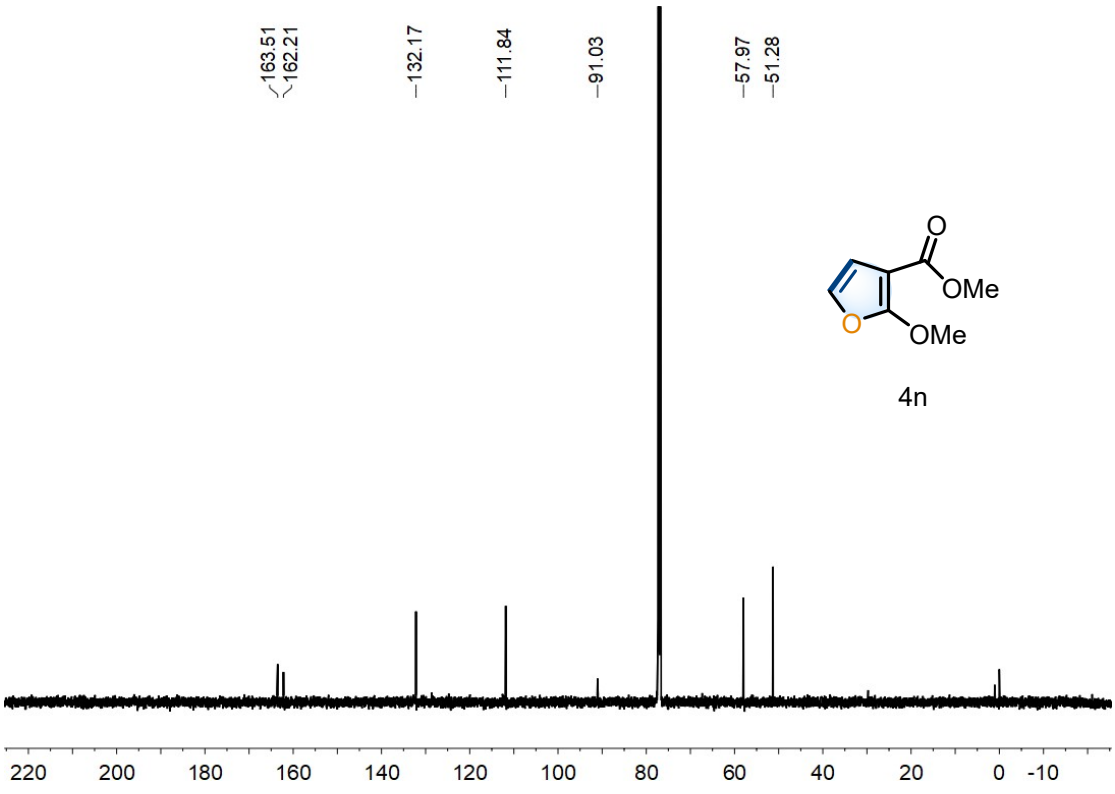
1.0
0.0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OMe
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OMe
4n
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100
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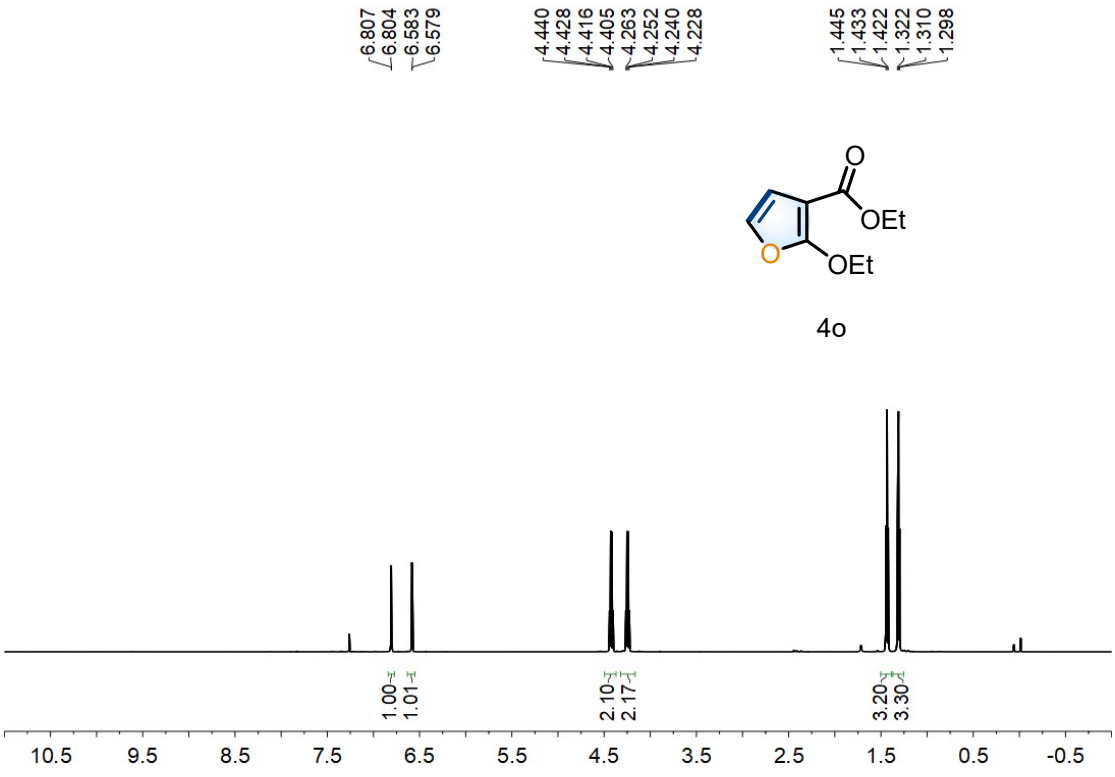
0
-10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1.433
1.422
1.322
1.310
1.298
O
OEt
O
OEt
1.00
1.01
2.10
2.17
3.20
3.30
10.5
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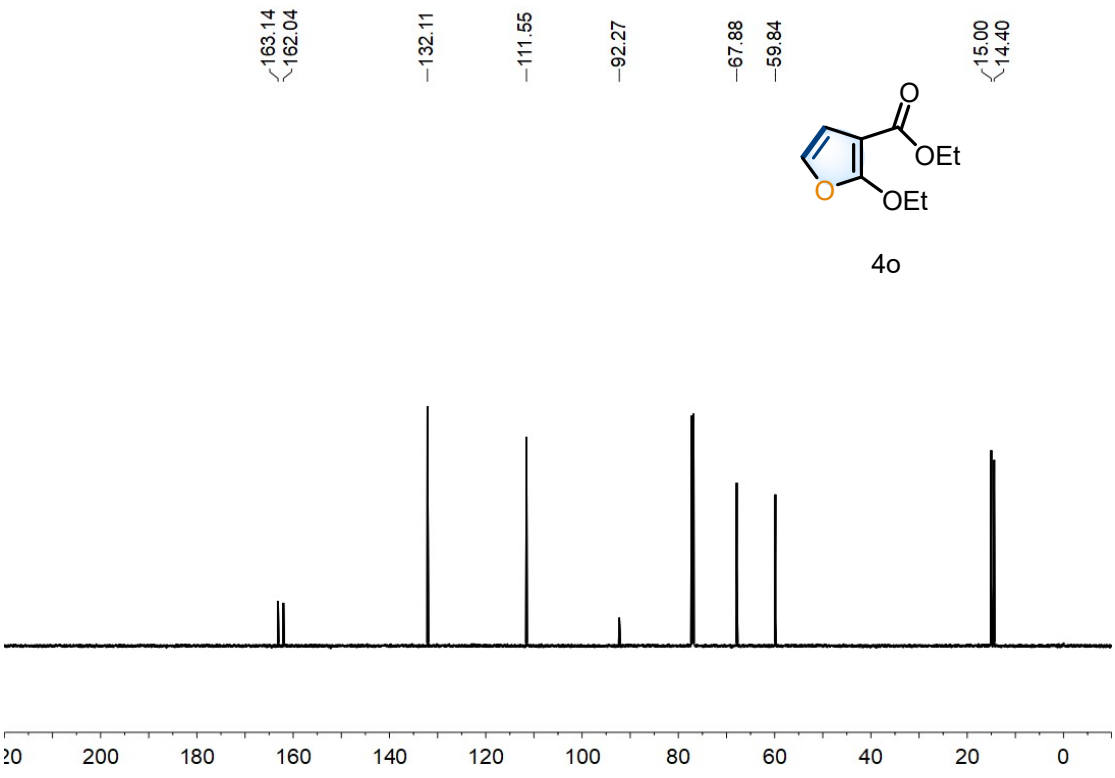
-0.5

4o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OEt
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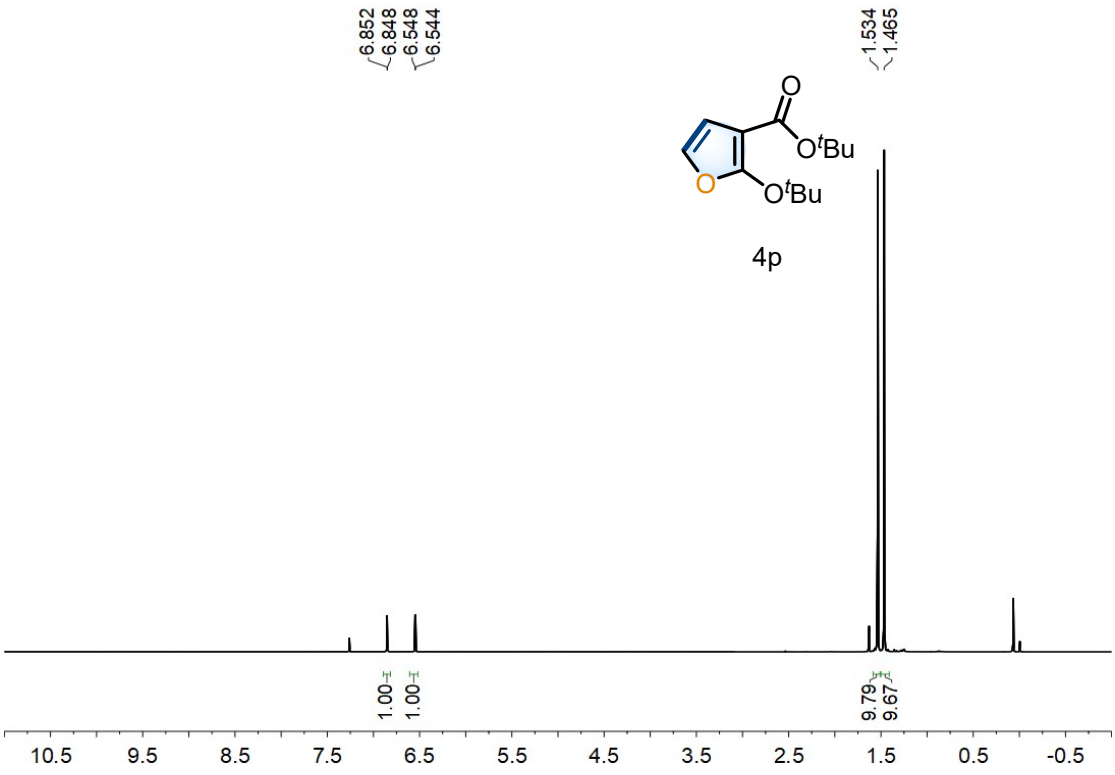
20
0

4o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O^{t}Bu
O
O^{t}Bu
4p
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1.00
9.79
9.67
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5.5
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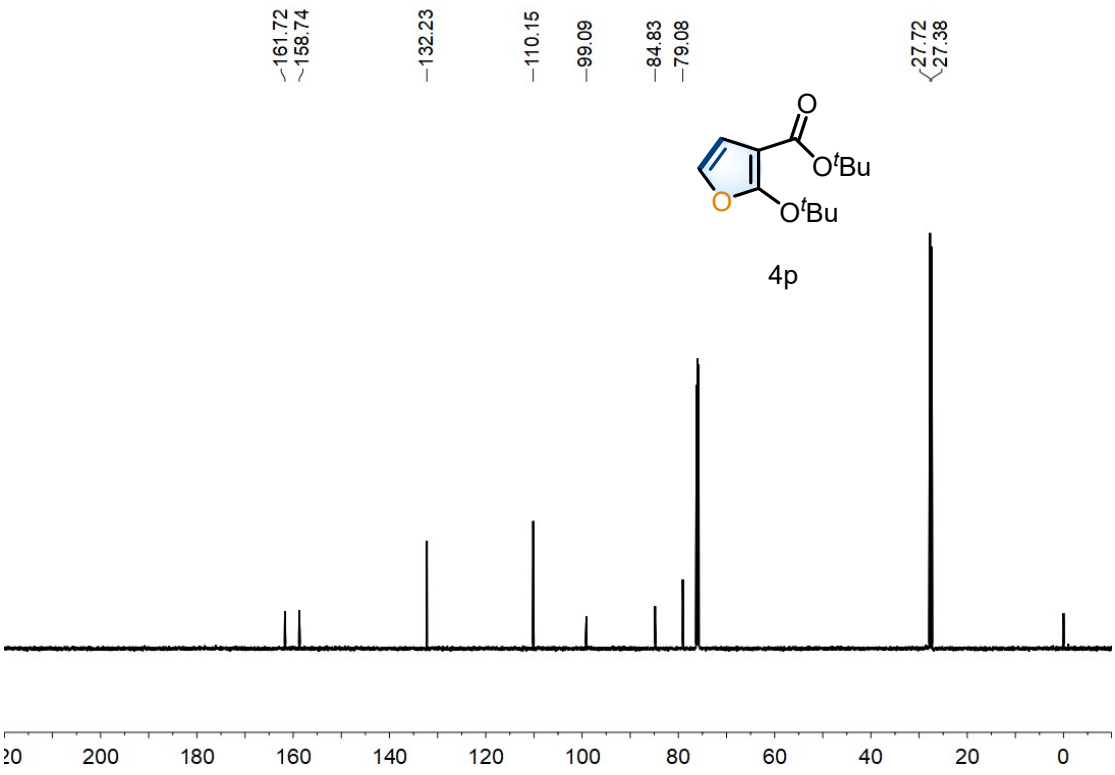
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27.72
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4p
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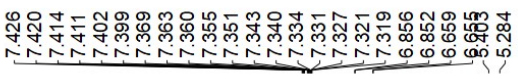
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6.852
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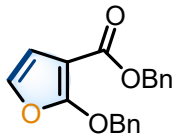
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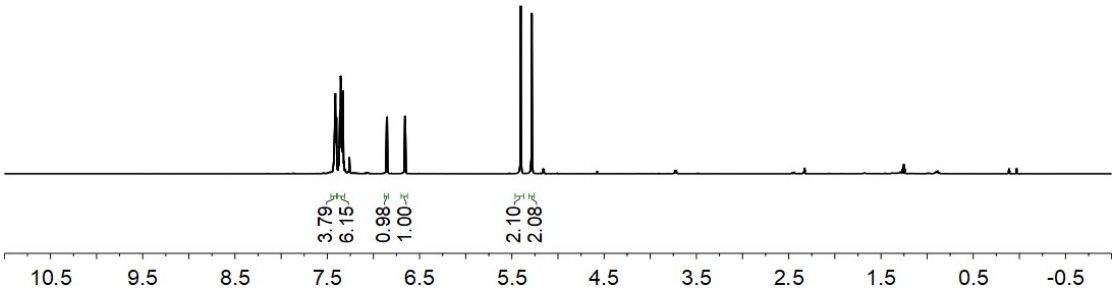
OBn
O
OBn

4q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5.5
4.5
3.5
2.5
1.5
0.5
-0.5


162.83
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136.45
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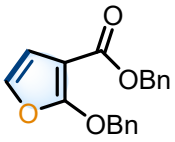
65.66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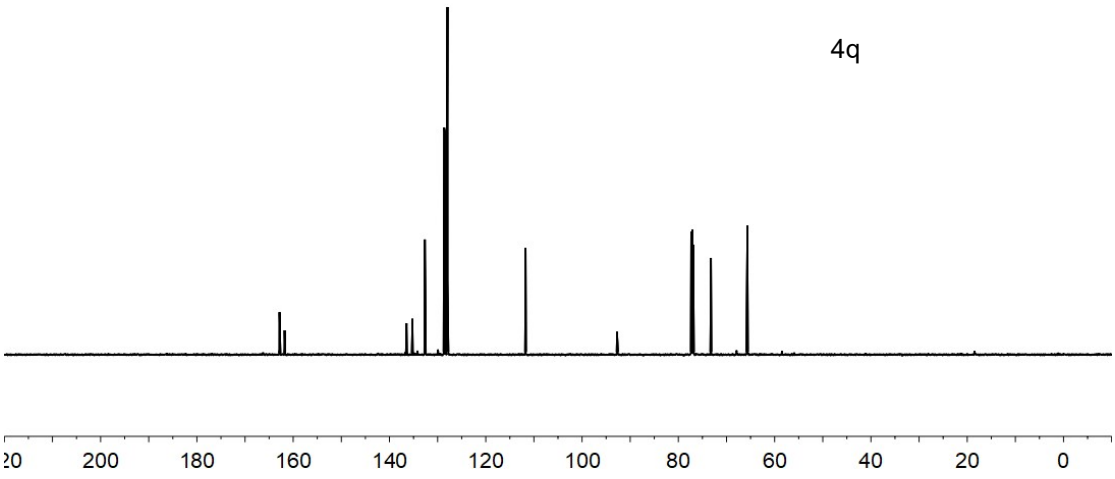
OBn
O
OBn

4q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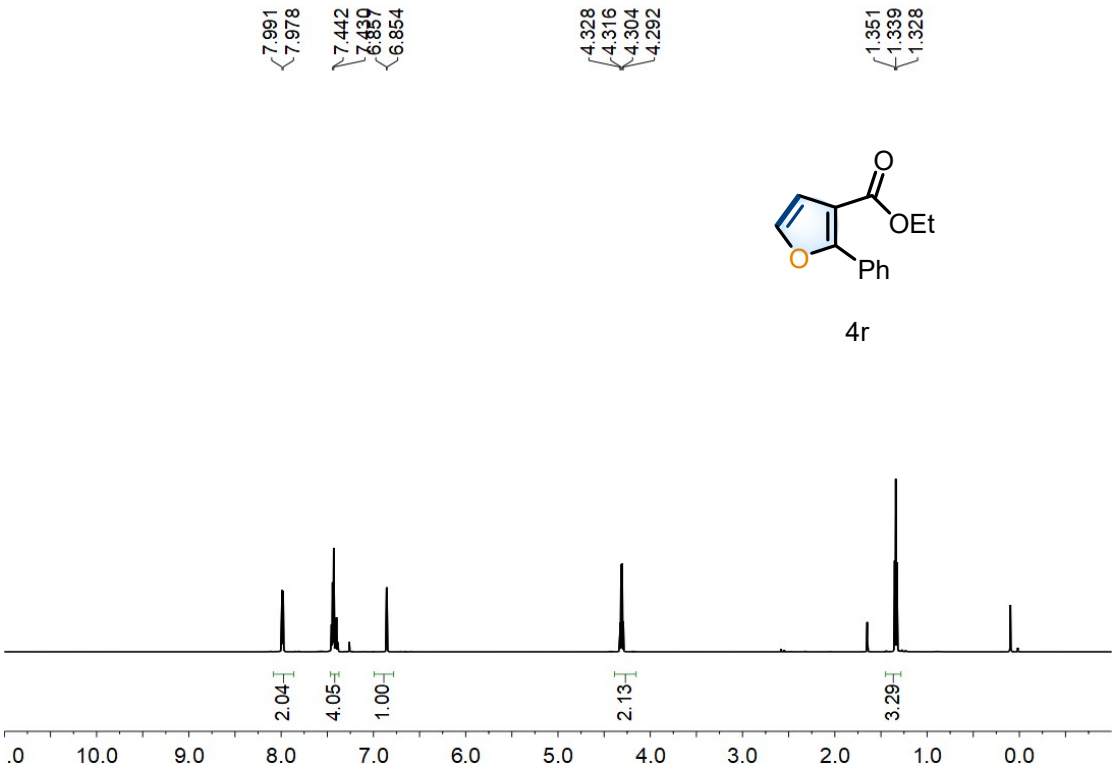
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OEt
O
Ph
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4.05
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2.13
3.29
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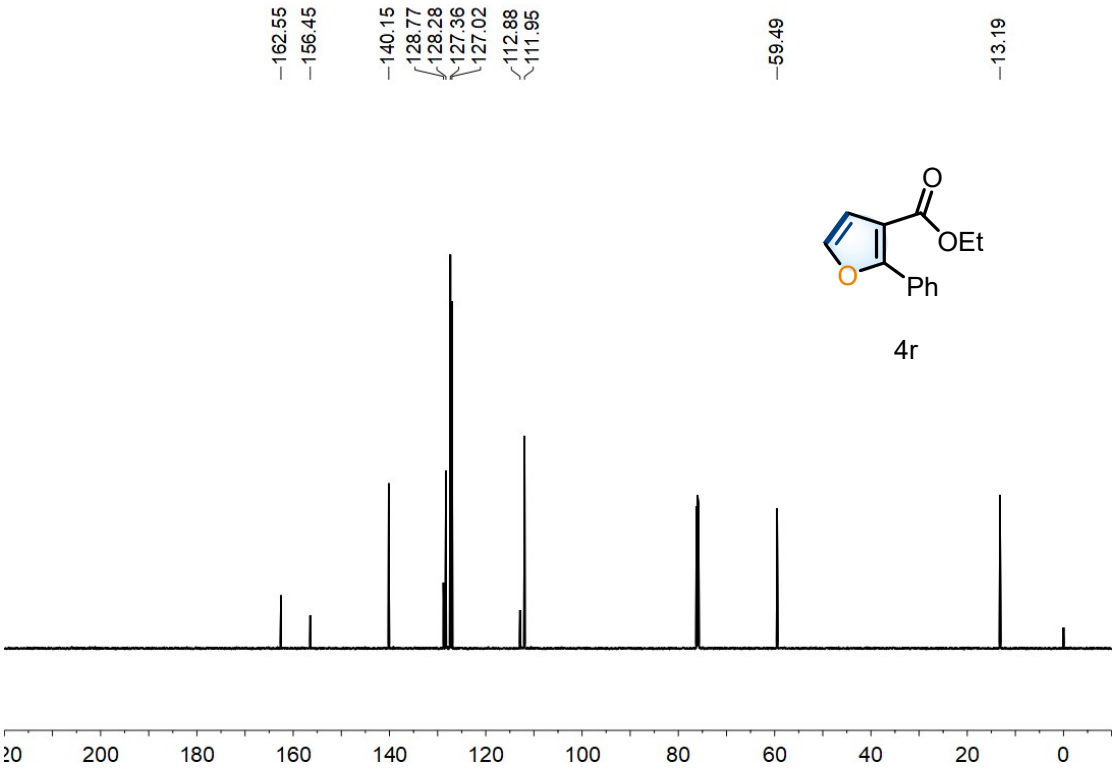
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O
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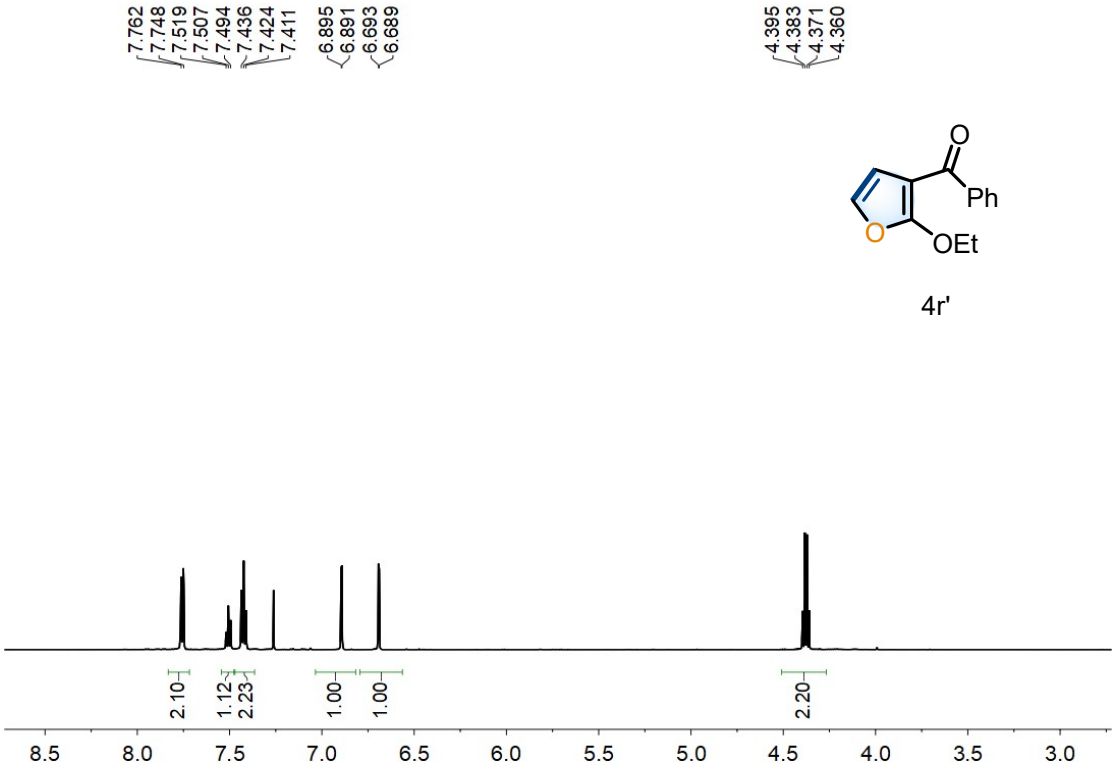
4r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4.383
4.371
4.360
O
Ph
O
OEt
4r'
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2.23
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1.00
2.20
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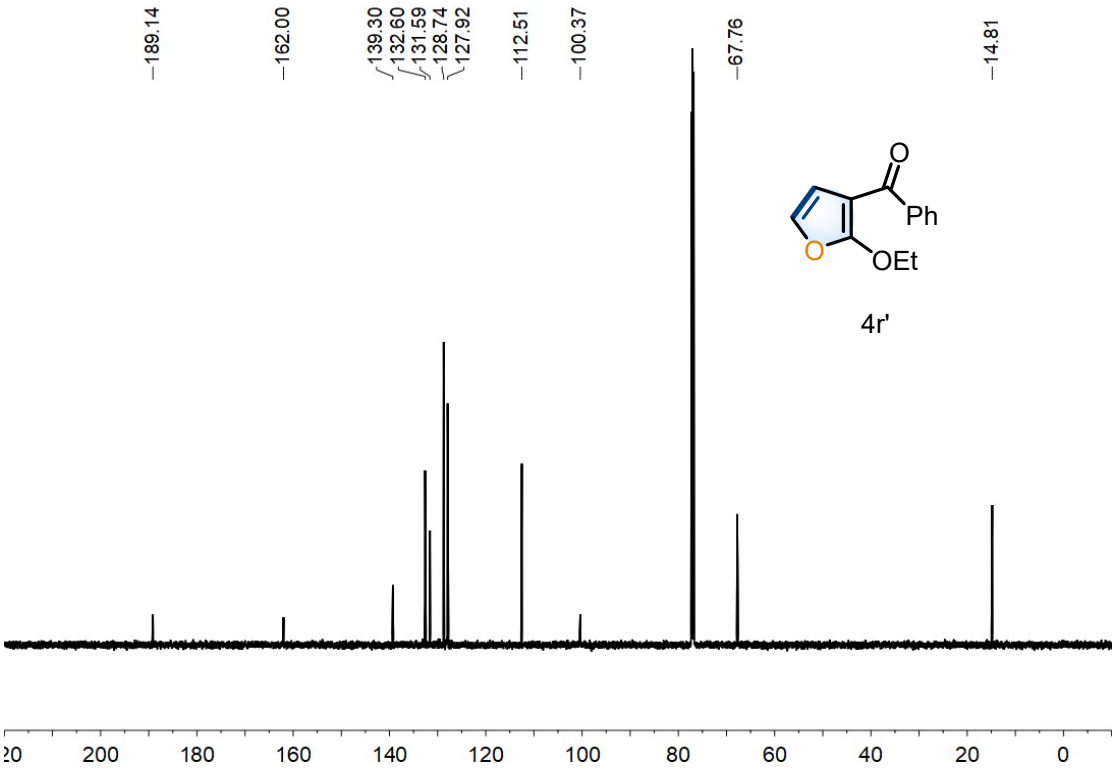
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112.51
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OEt
4r'
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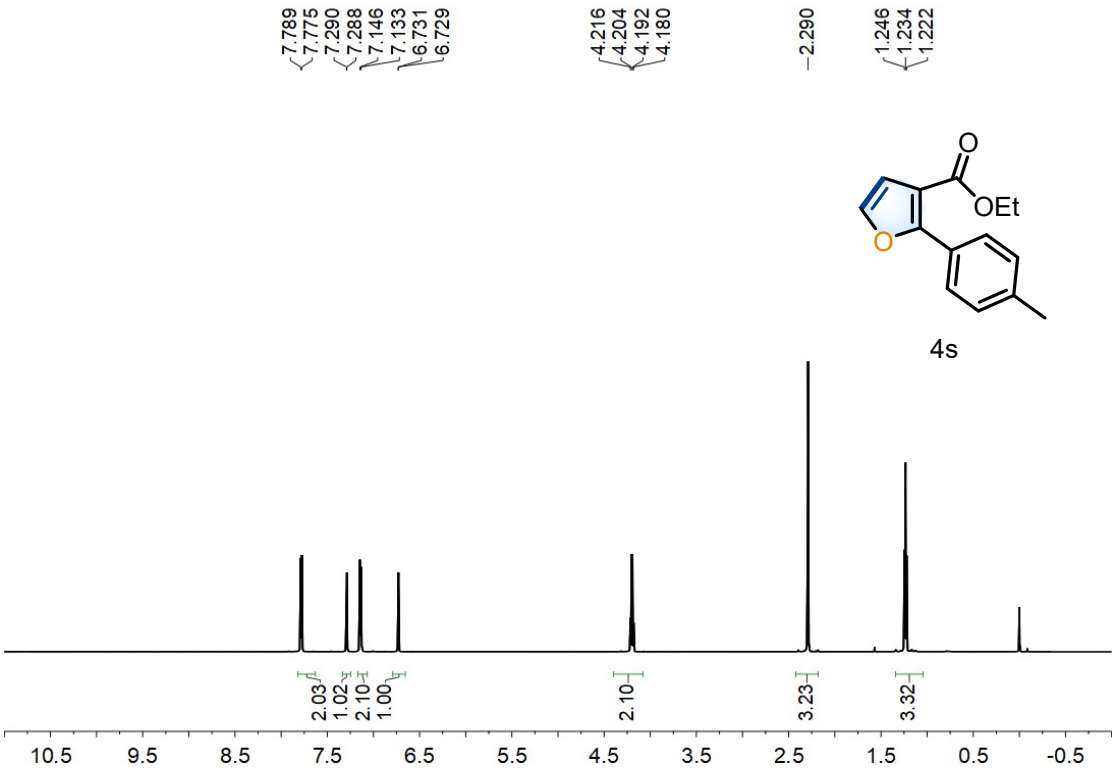
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1.234
1.222
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OEt
O
4s
2.03
1.02
2.10
1.00
2.10
3.23
3.32
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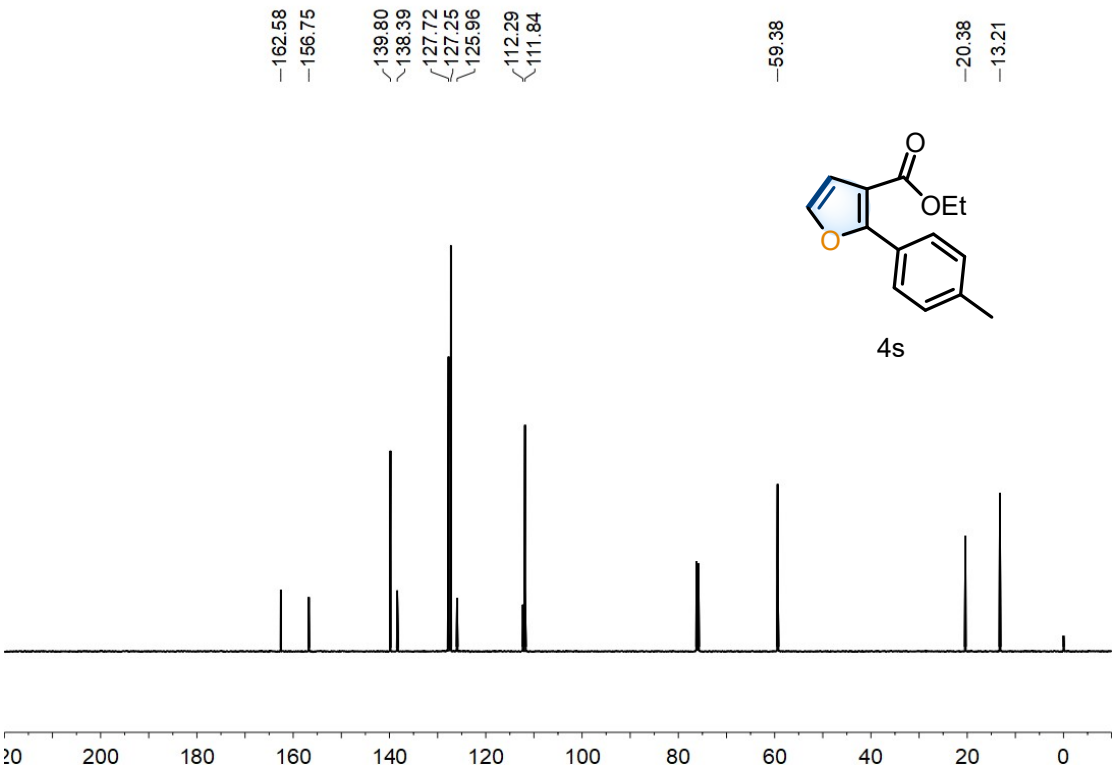
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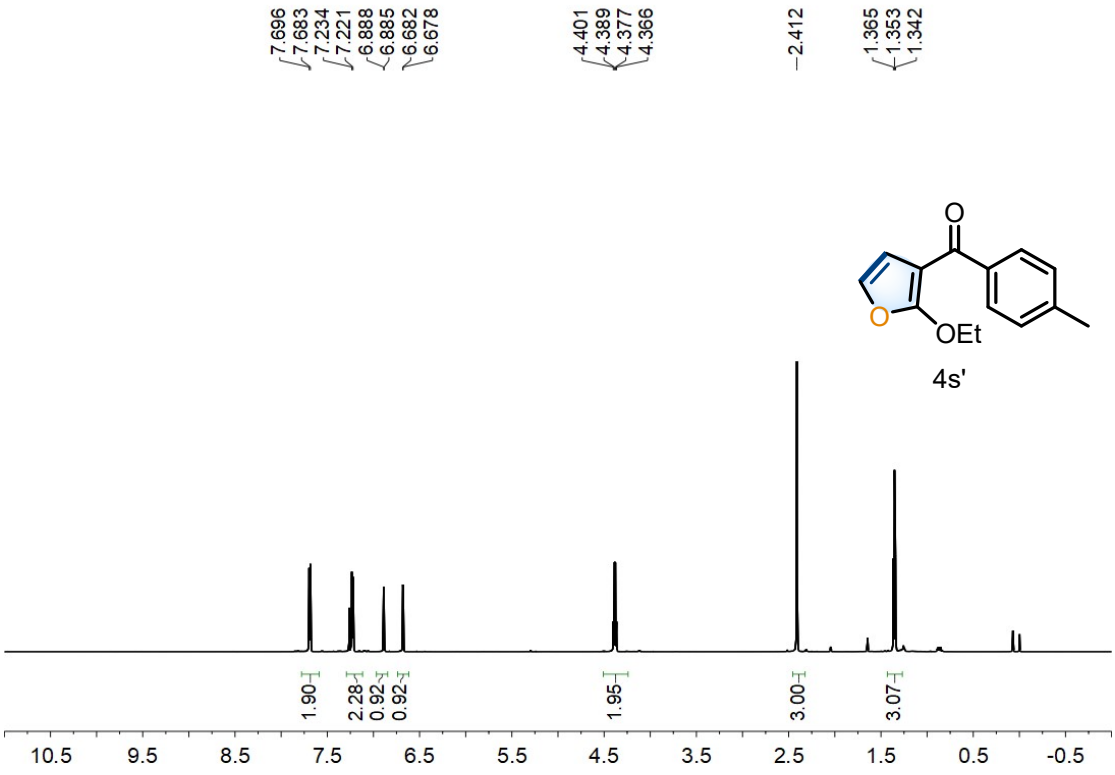
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4.366
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1.365
1.353
1.342
O
O
OEt
4s'
1.90
2.28
0.92
0.92
1.95
3.00
3.07
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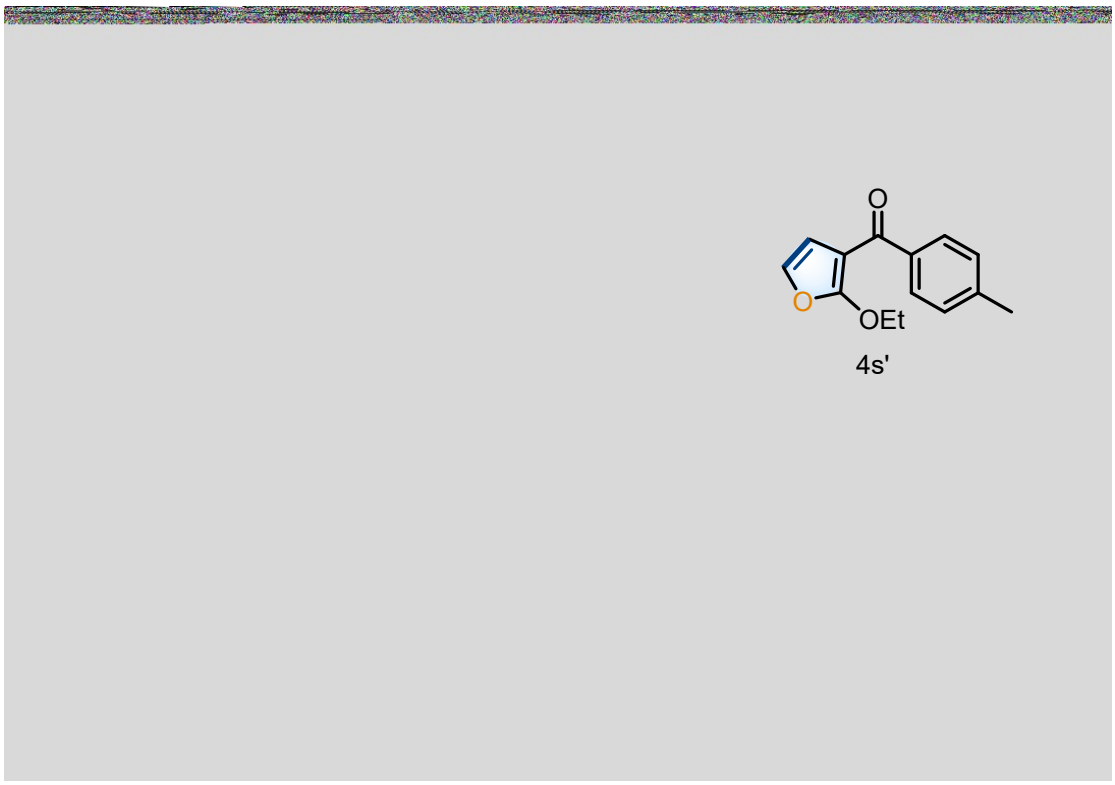
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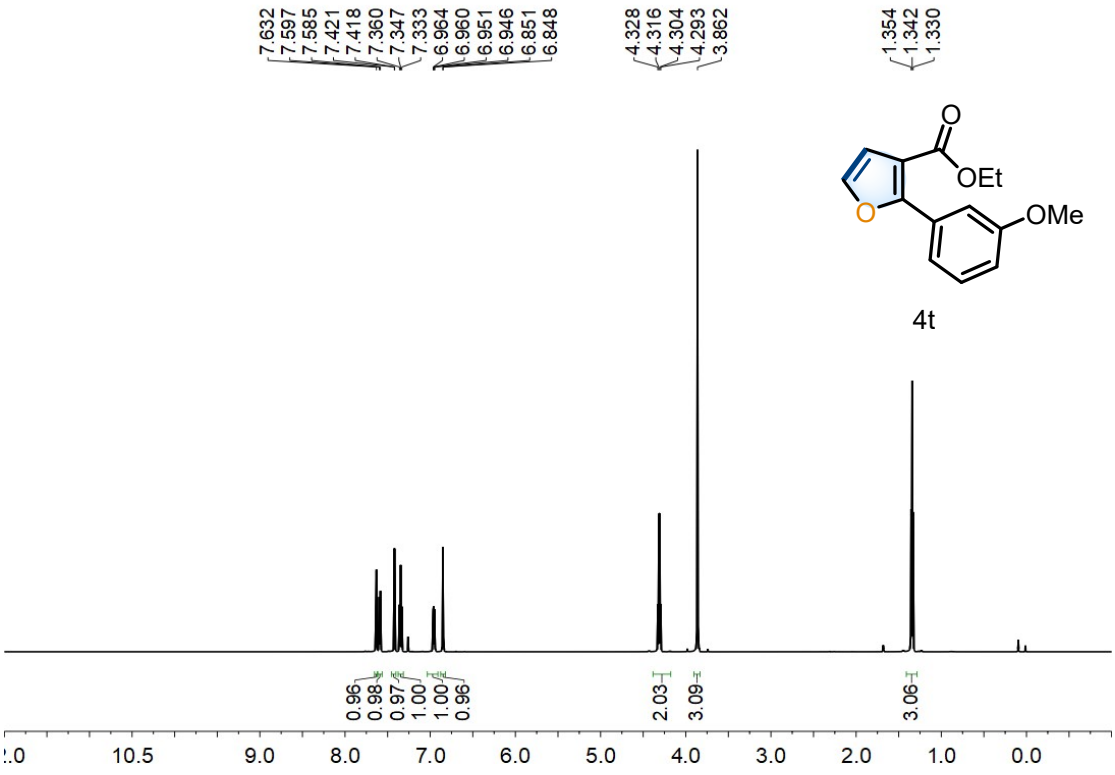
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6.851
6.848
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4.316
4.304
4.293
3.862
1.354
1.342
1.330
O
OEt
O
OMe
4t
0.96
0.98
0.97
1.00
1.00
0.96
2.03
3.09
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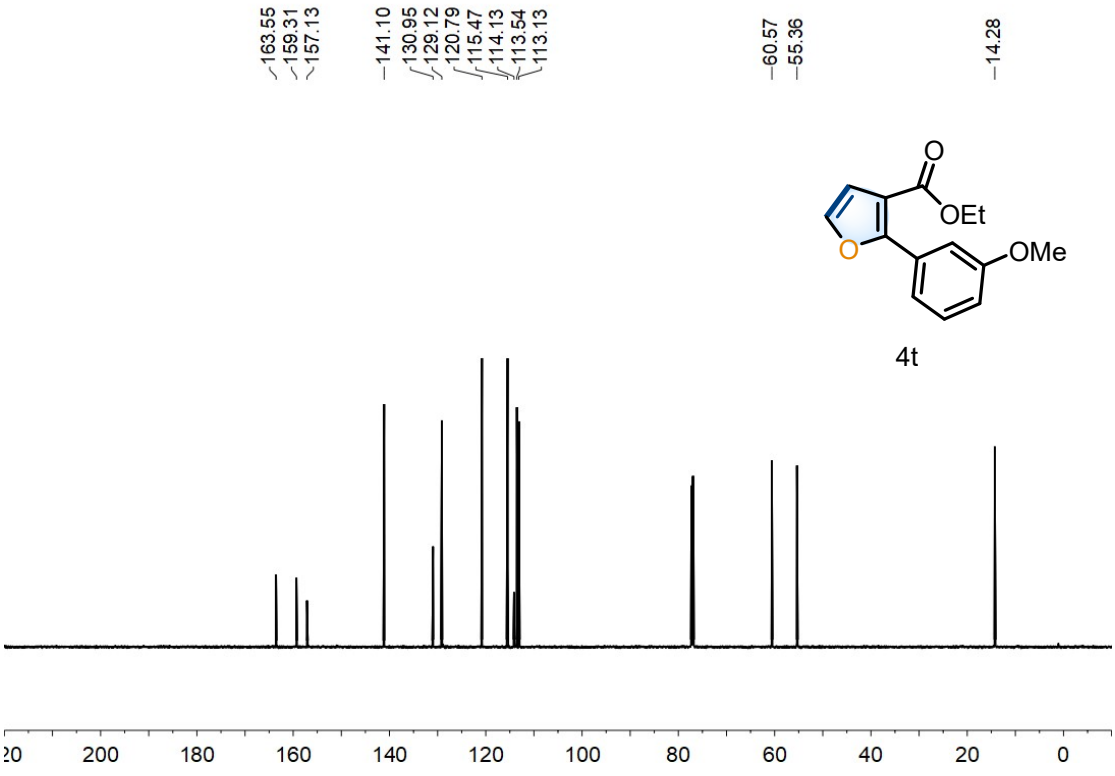
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113.13
60.57
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OEt
O
OMe
4t
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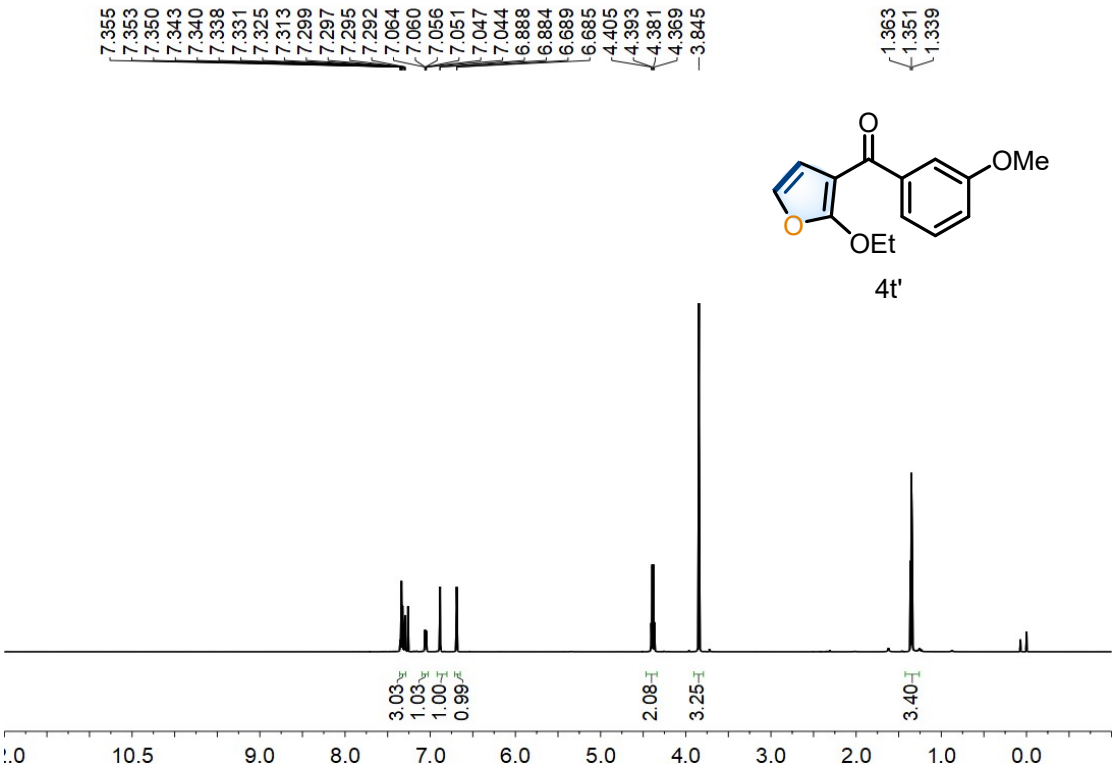
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7.295
7.292
7.064
7.060
7.056
7.051
7.047
7.044
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6.884
6.689
6.685
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4.381
4.369
3.845
1.363
1.351
1.339
O
OMe
O
OEt
4t'
3.03
1.03
1.00
0.99
2.08
3.25
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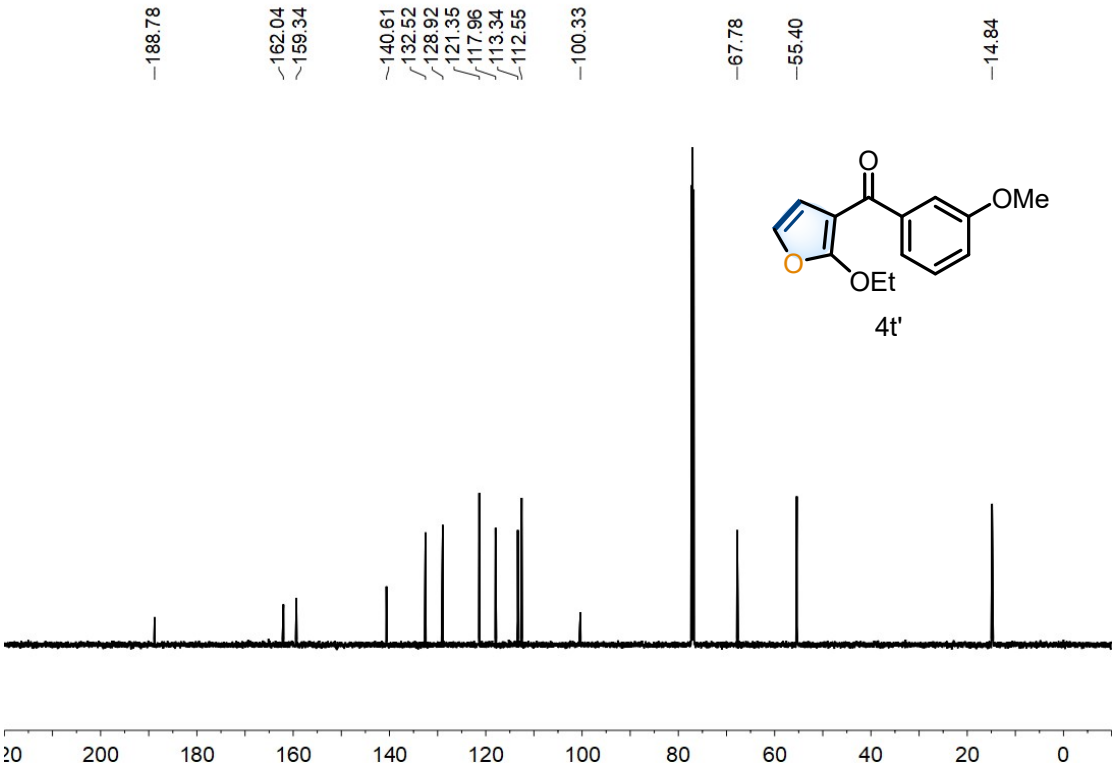
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112.55
100.33
67.78
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OMe
O
OEt
4t'
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180
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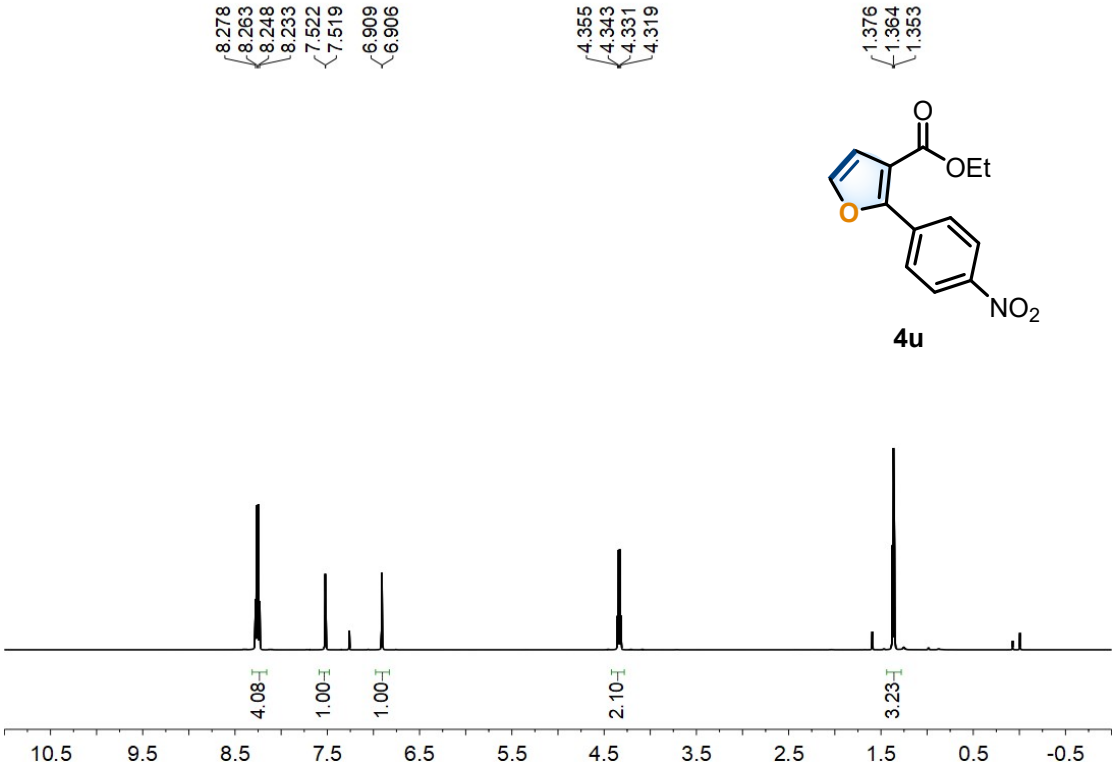
140
120
100
80
60
40
20
0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1.364
1.353
O
OEt
O
NO2
4u
4.08
1.00
1.00
2.10
3.23
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7.5
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5.5
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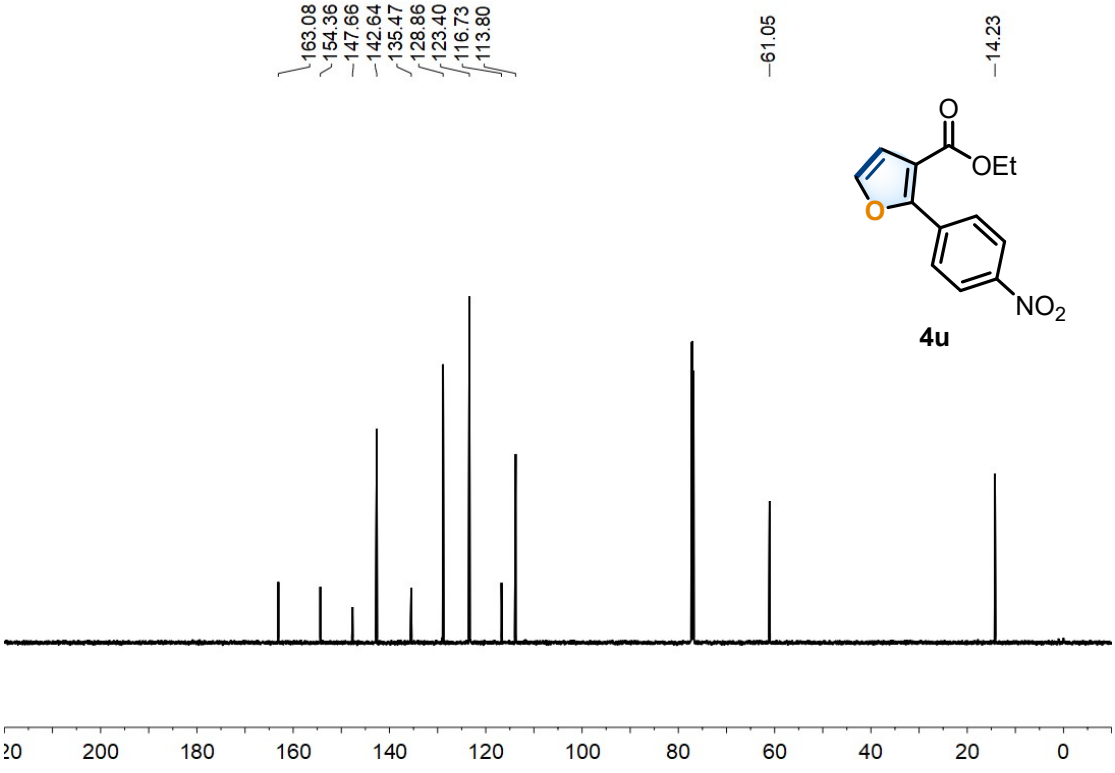
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NO2
4u
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140
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60
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20
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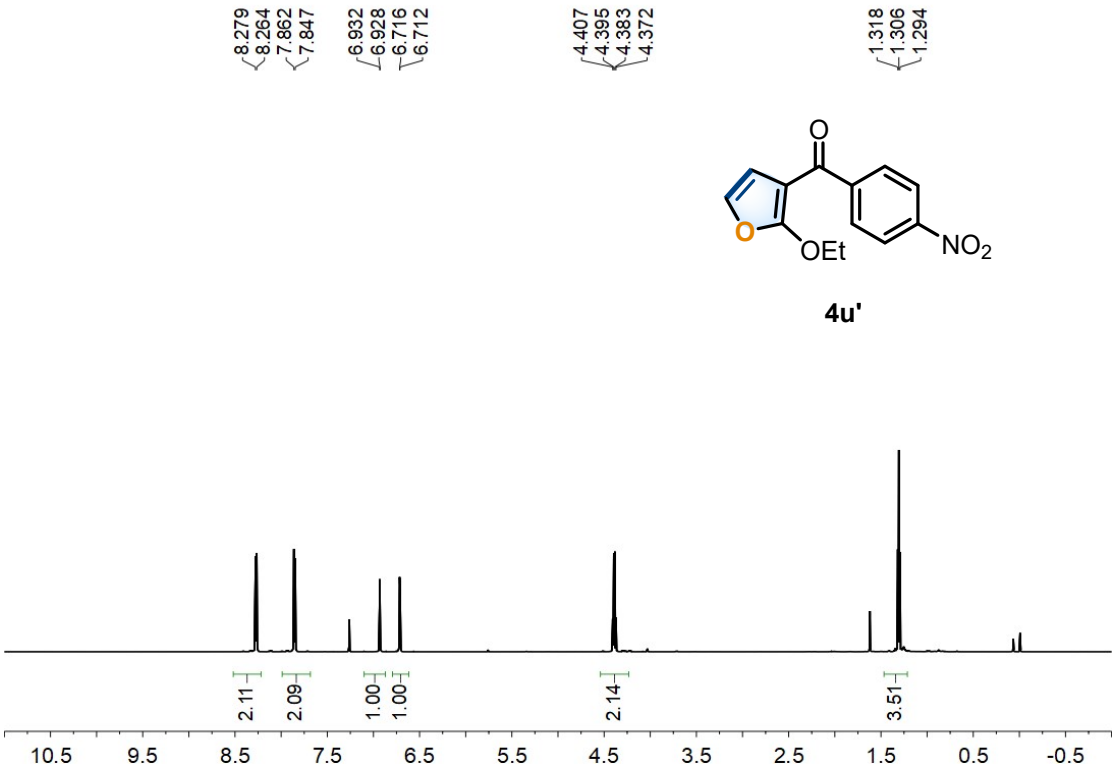
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1.306
1.294
O
O
OEt
NO2
2.11
2.09
1.00
1.00
2.14
3.51
10.5
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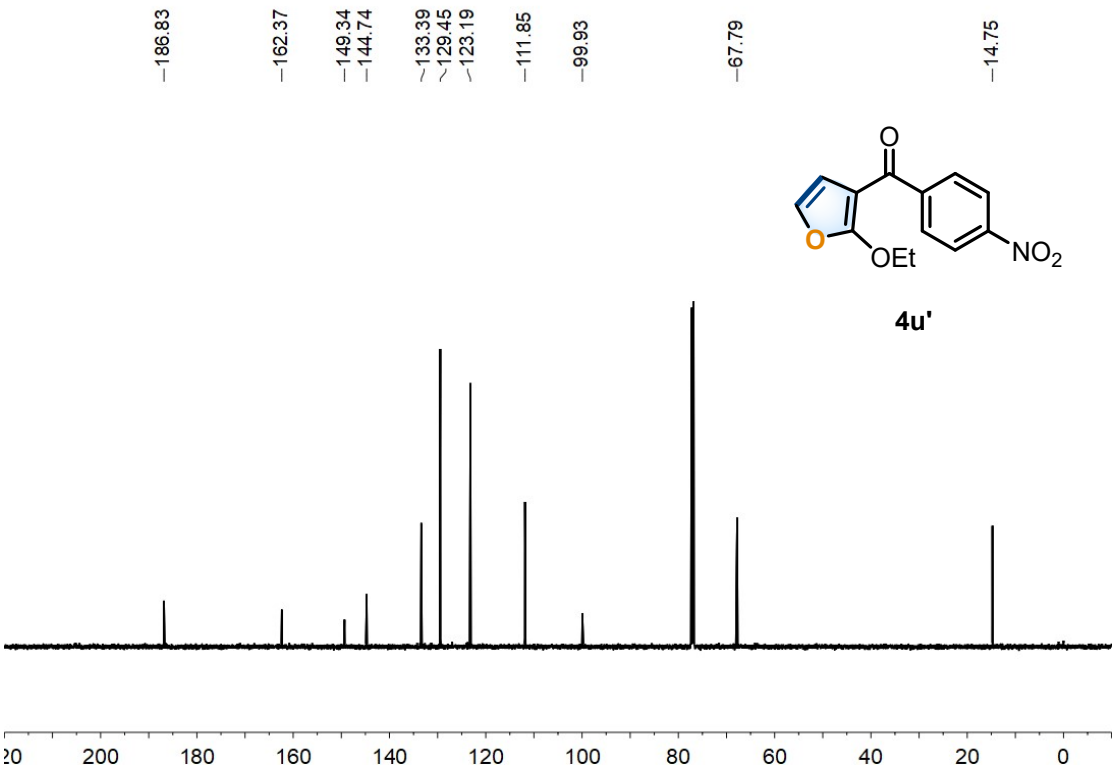
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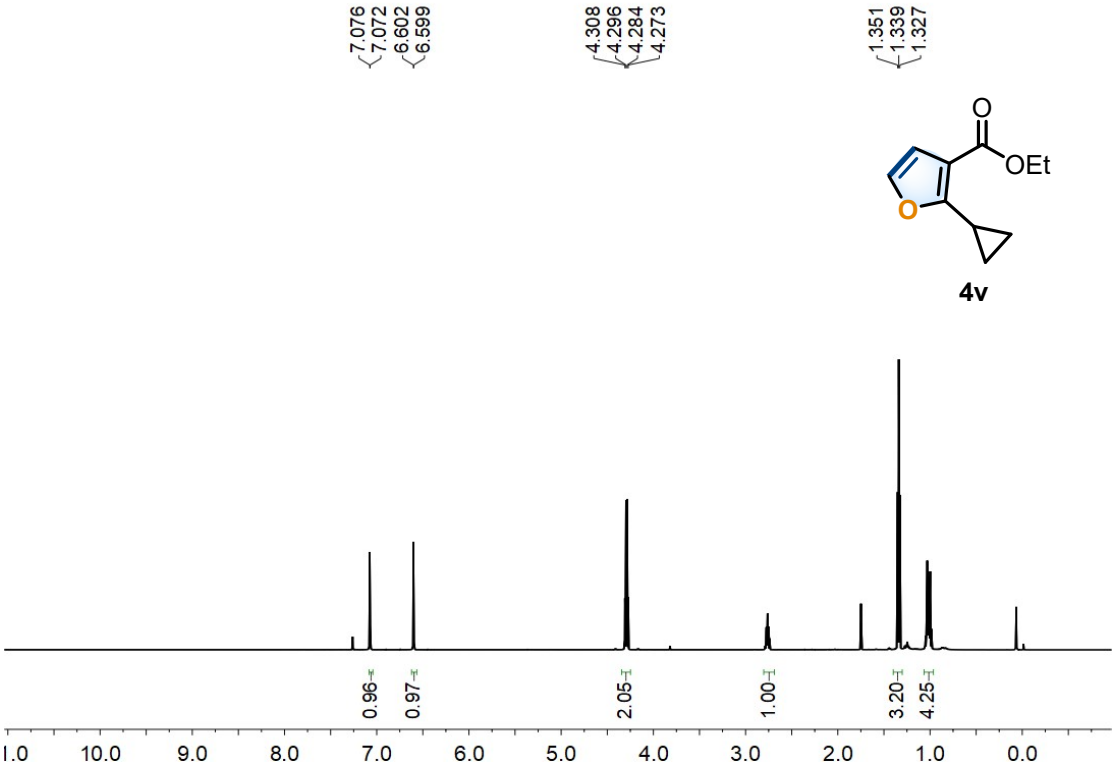
20
0

4u'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1.327
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O
4v
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2.05
1.00
3.20
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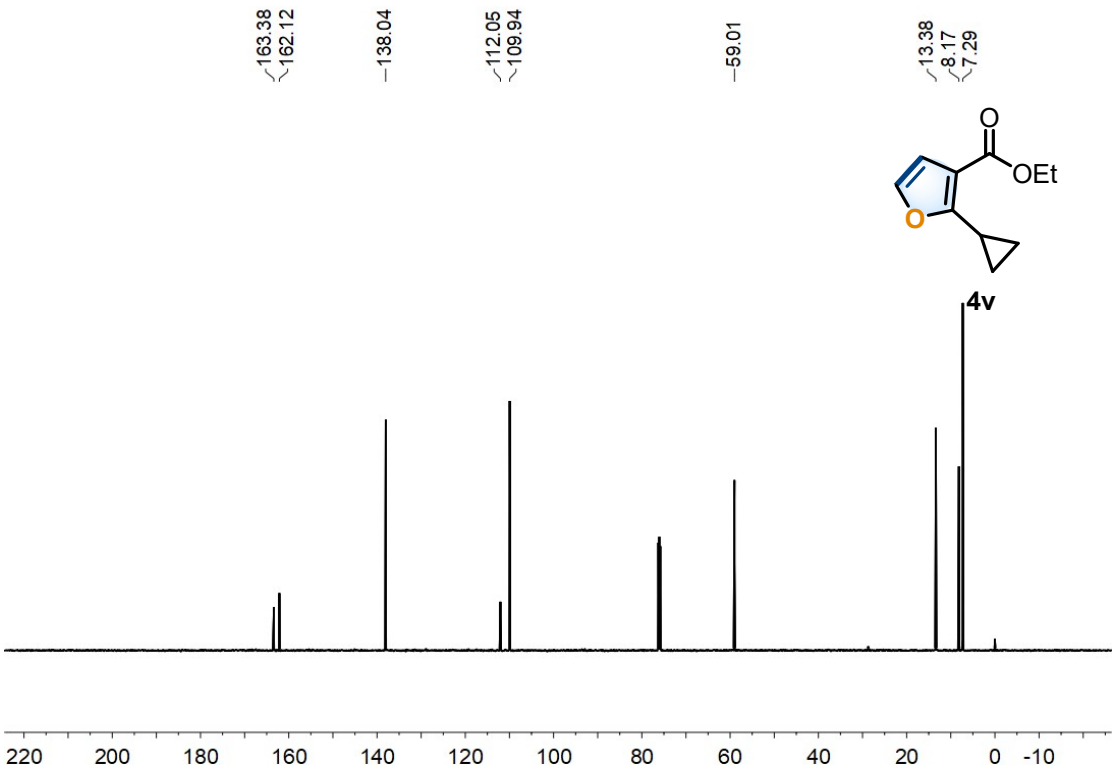
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O
4v
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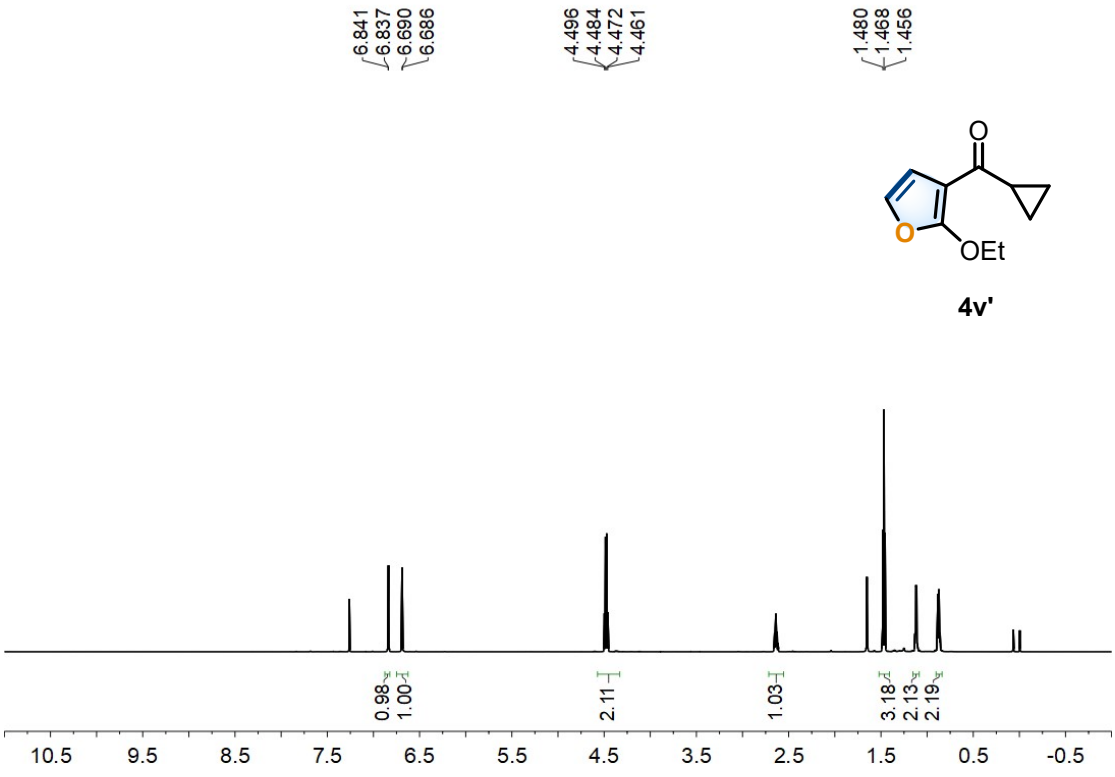
0
-10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O
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1.00
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1.03
3.18
2.13
2.19
10.5
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8.5
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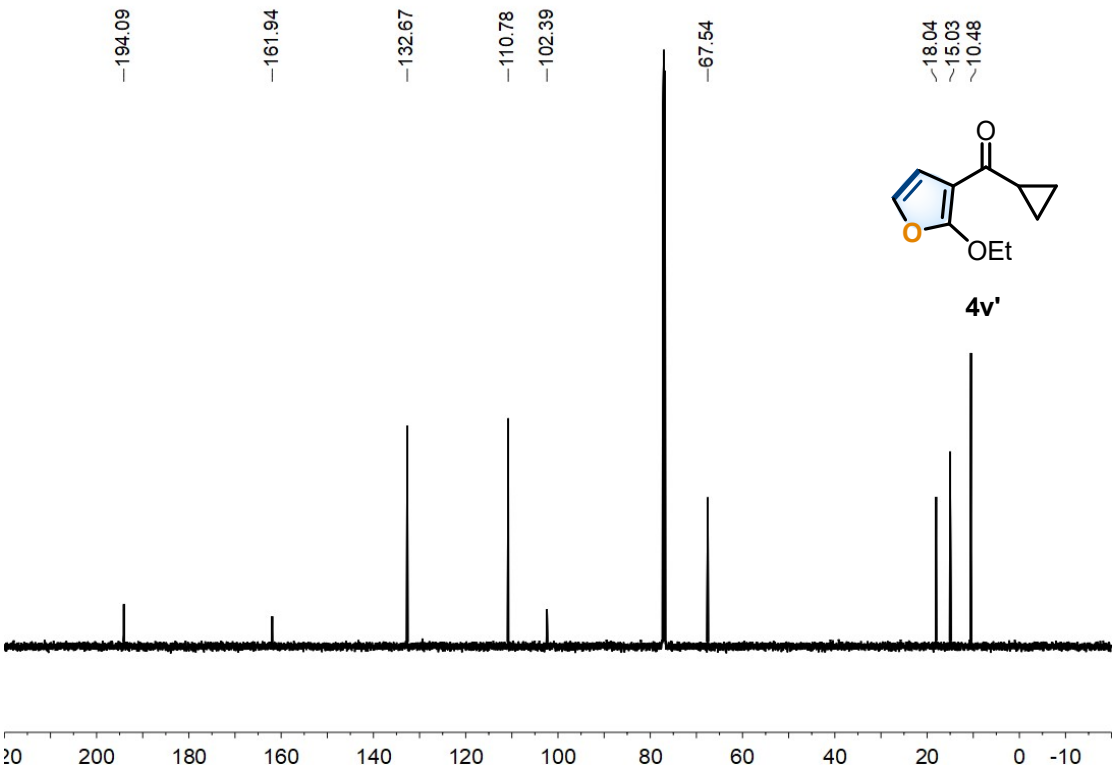
4.5
3.5
2.5
1.5
0.5
-0.5

4v'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O
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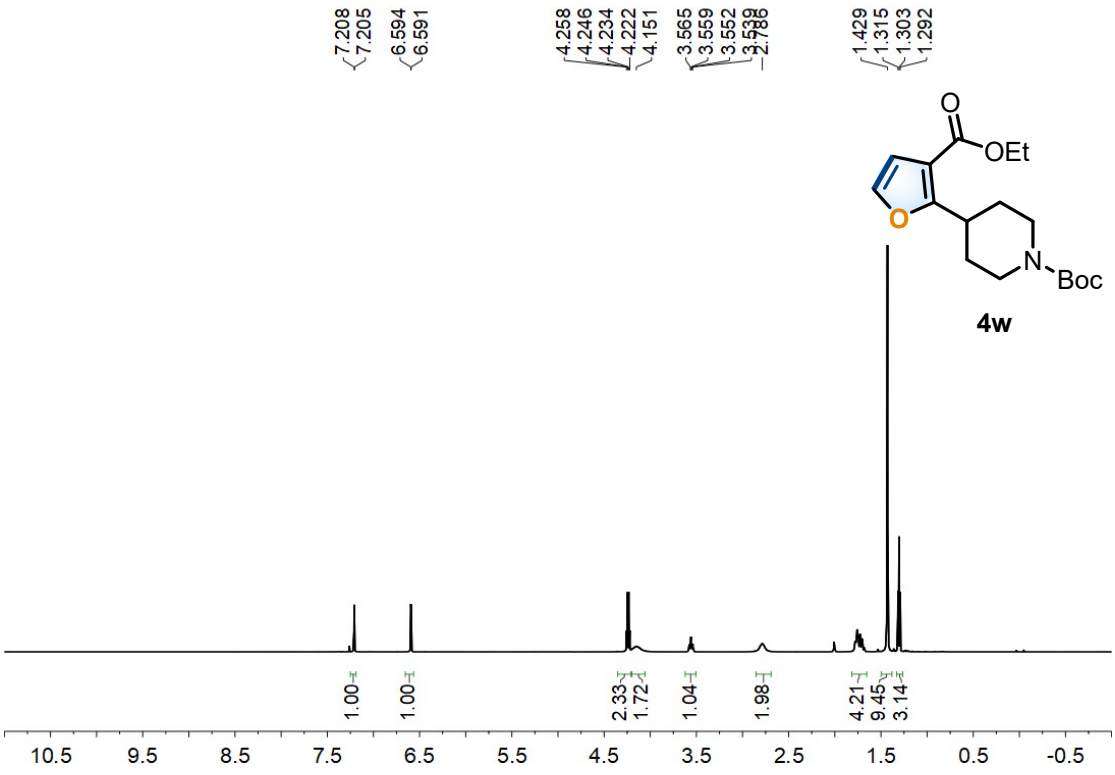
80
60
40
20
0
-10

4v'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1.315
1.303
1.292
OEt
O
N
Boc
4w
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1.00
2.33
1.72
1.04
1.98
4.21
9.45
3.14
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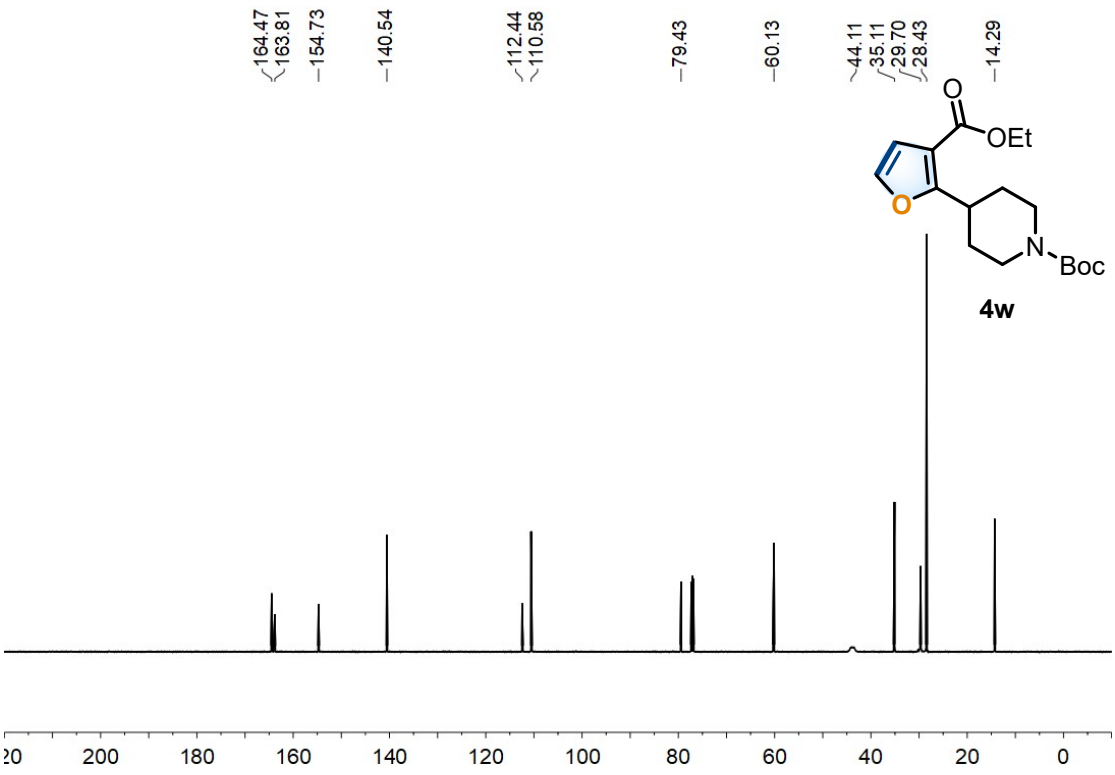
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O
N
Boc
4w
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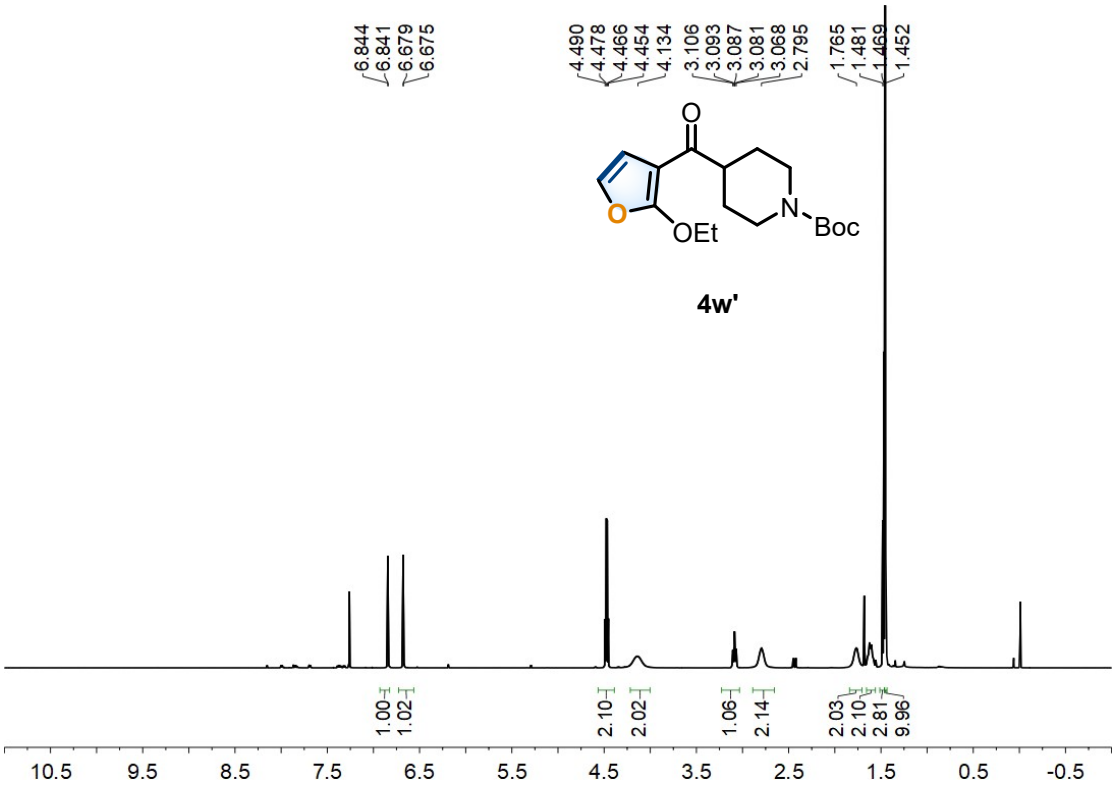
20
0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3.081
3.068
2.795
1.765
1.481
1.469
1.452
O
O
OEt
N
Boc
4w'
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1.02
2.10
2.02
1.06
2.14
2.03
2.10
2.81
9.96
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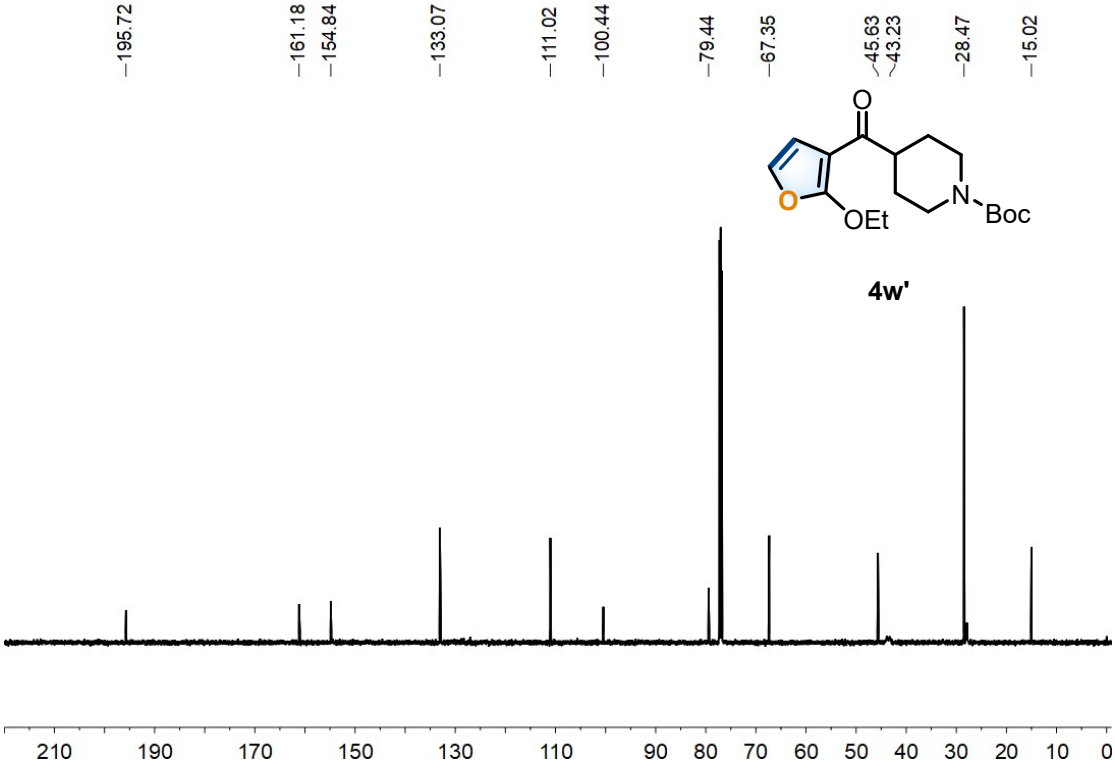
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43.23
28.47
15.02
O
O
OEt
N
Boc
4w'
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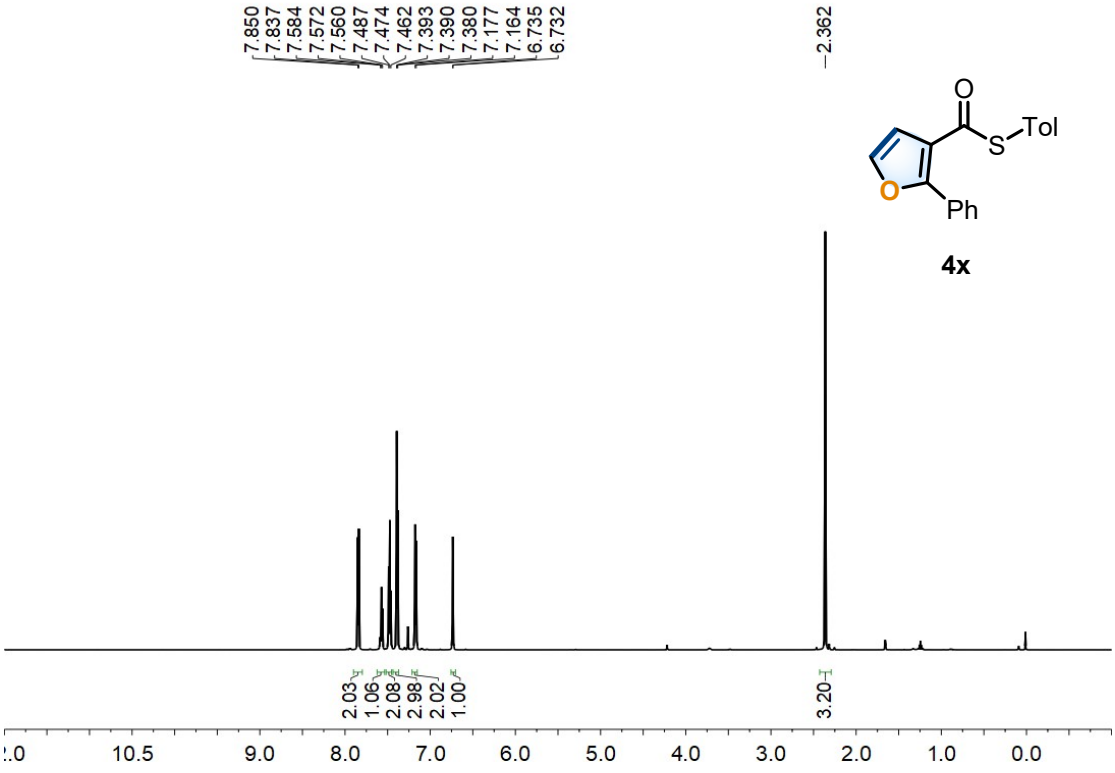
0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7.164
6.735
6.732
2.362
O
S
Tol
O
Ph
4x
2.03
1.06
2.08
2.98
2.02
1.00
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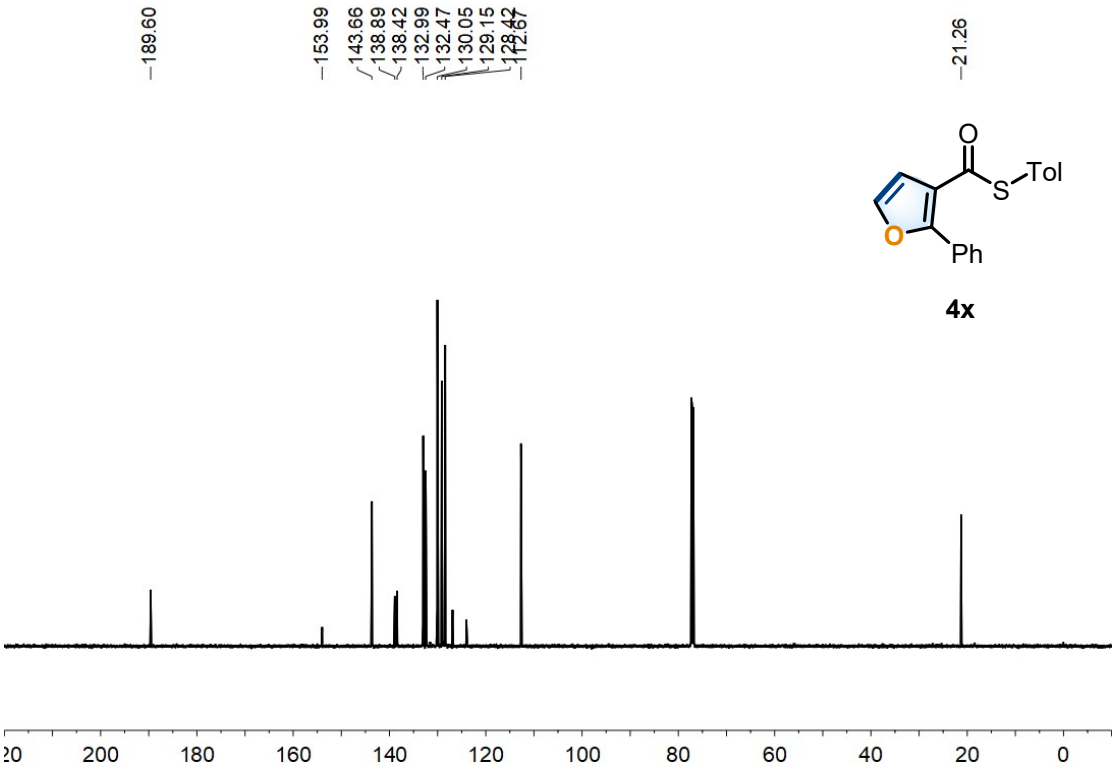
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Tol
O
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20
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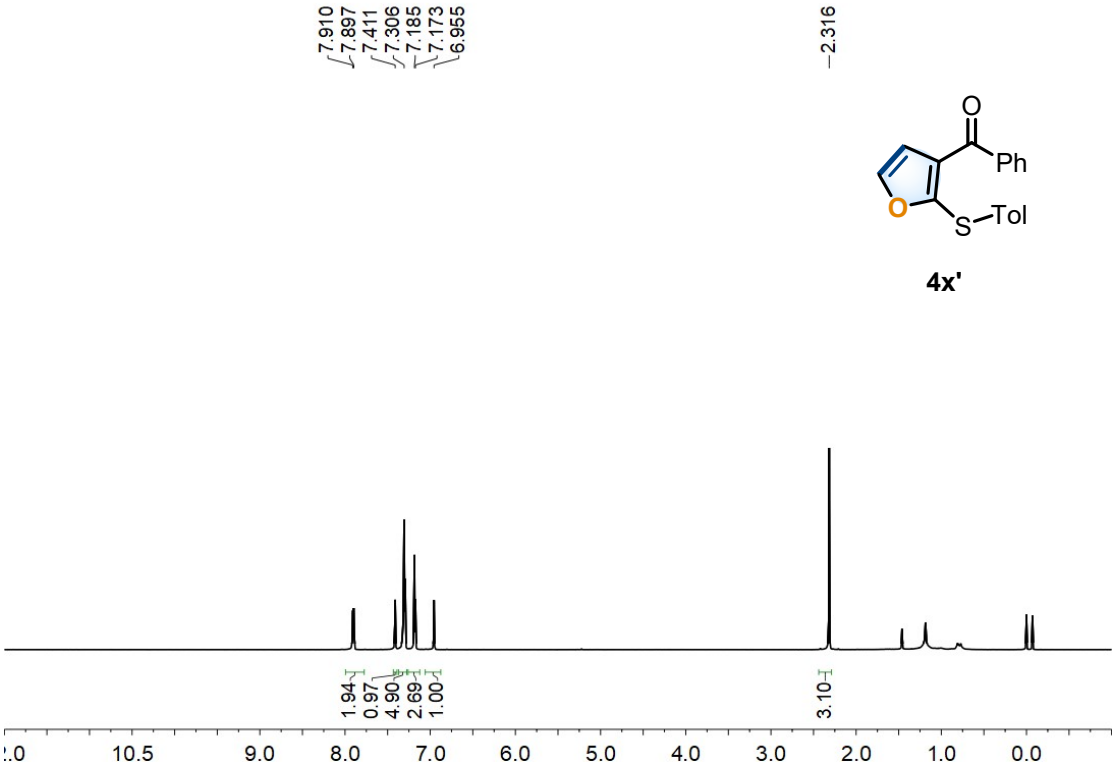
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Ph
O
S
Tol
4x'
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0.97
4.90
2.69
1.00
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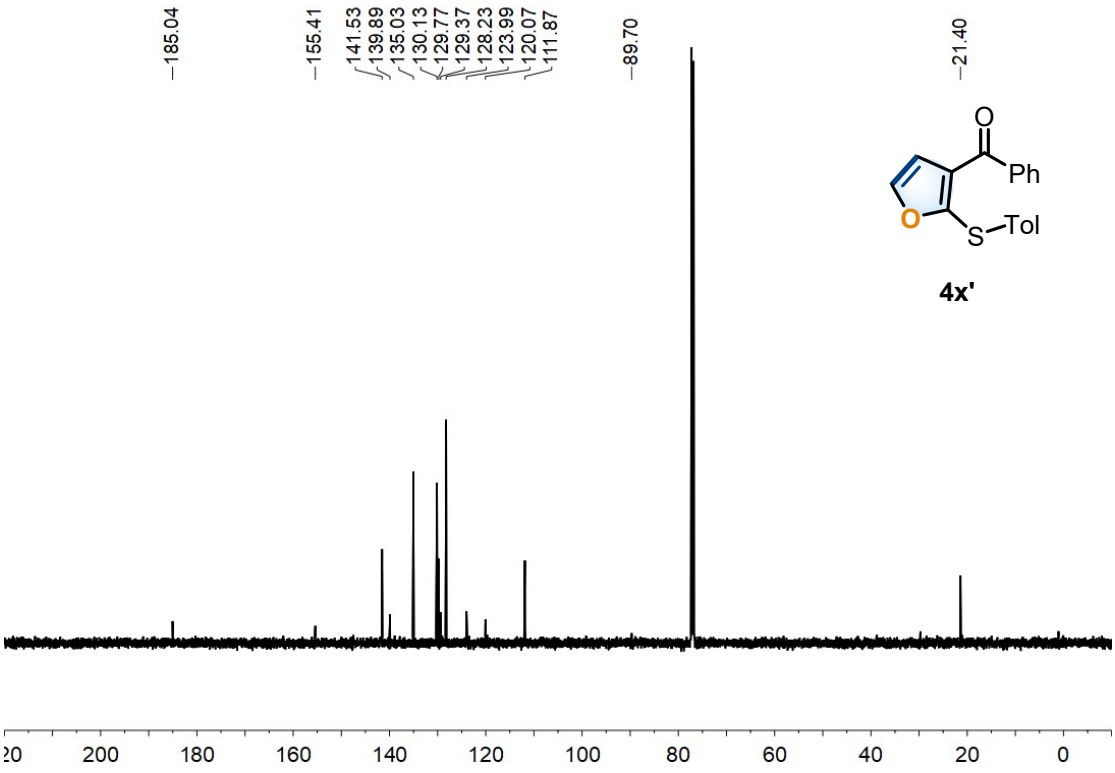
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123.99
120.07
111.87
89.70
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O
S
Tol
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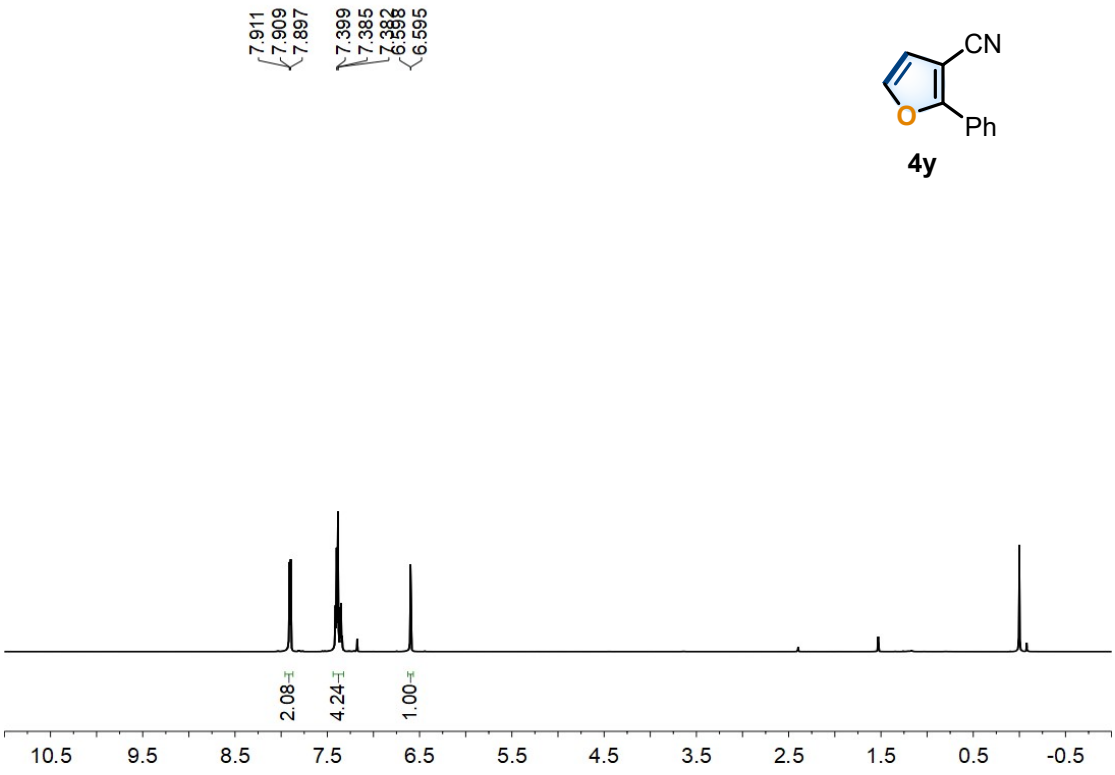
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6.595
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O
Ph
4y
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1.00
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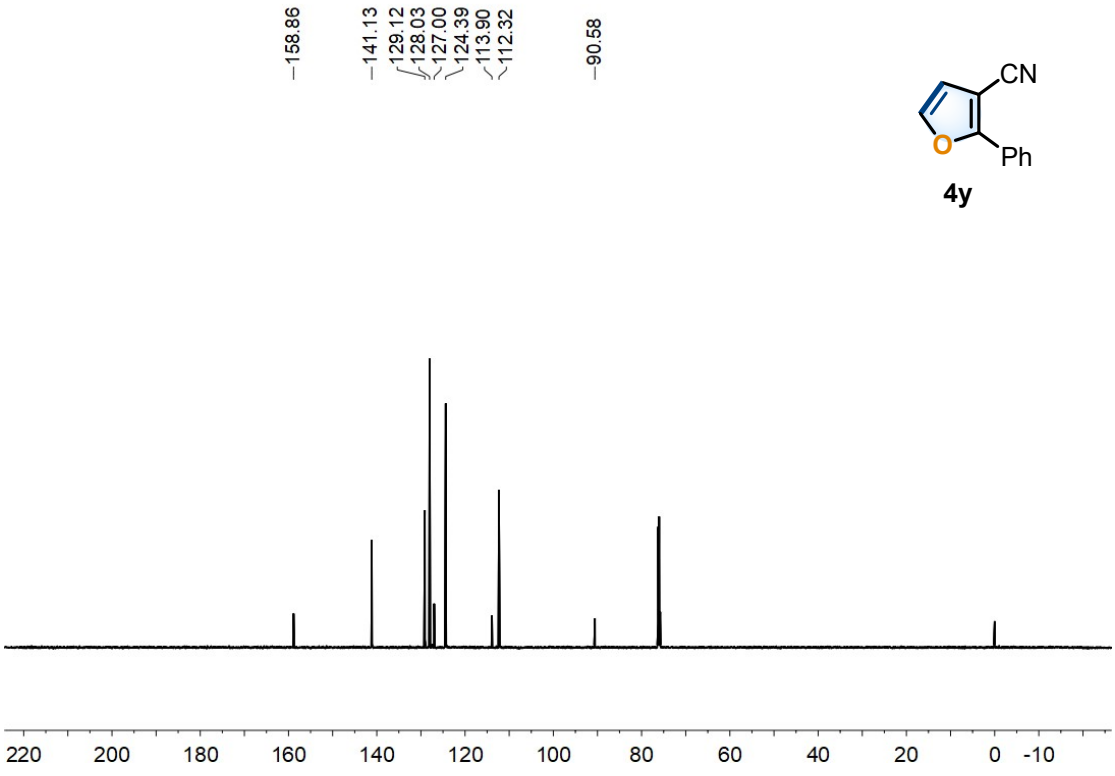
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O
Ph
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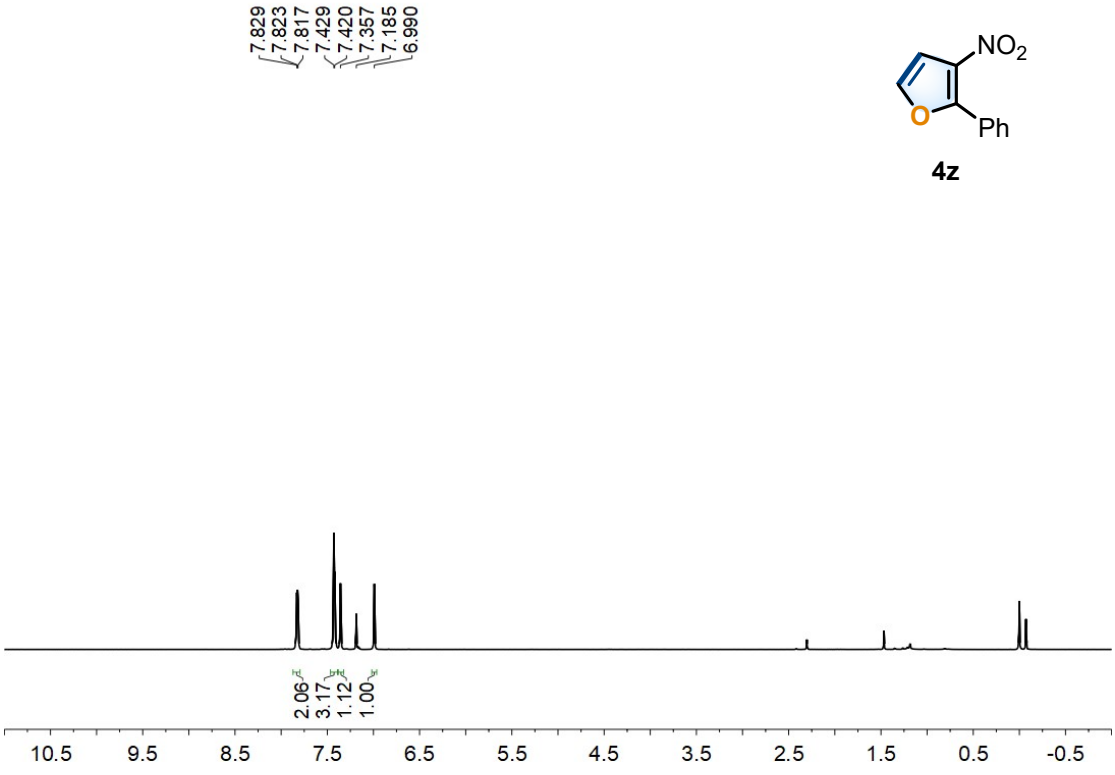
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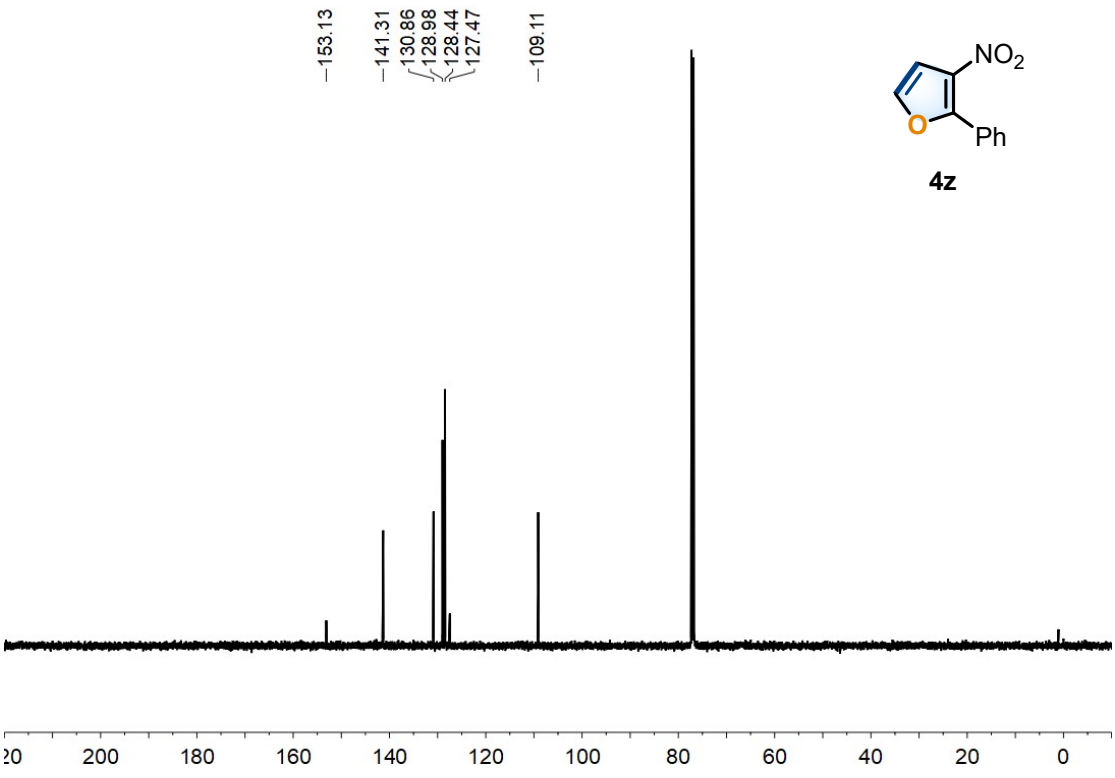
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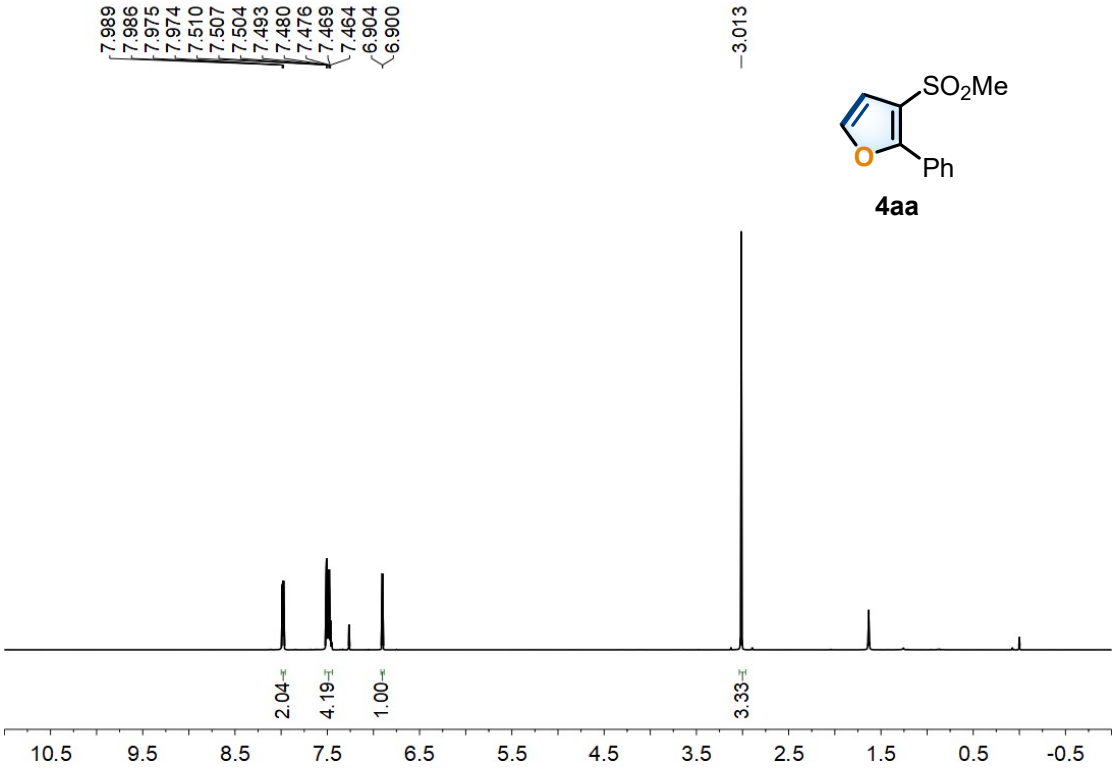
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3.013
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O
Ph
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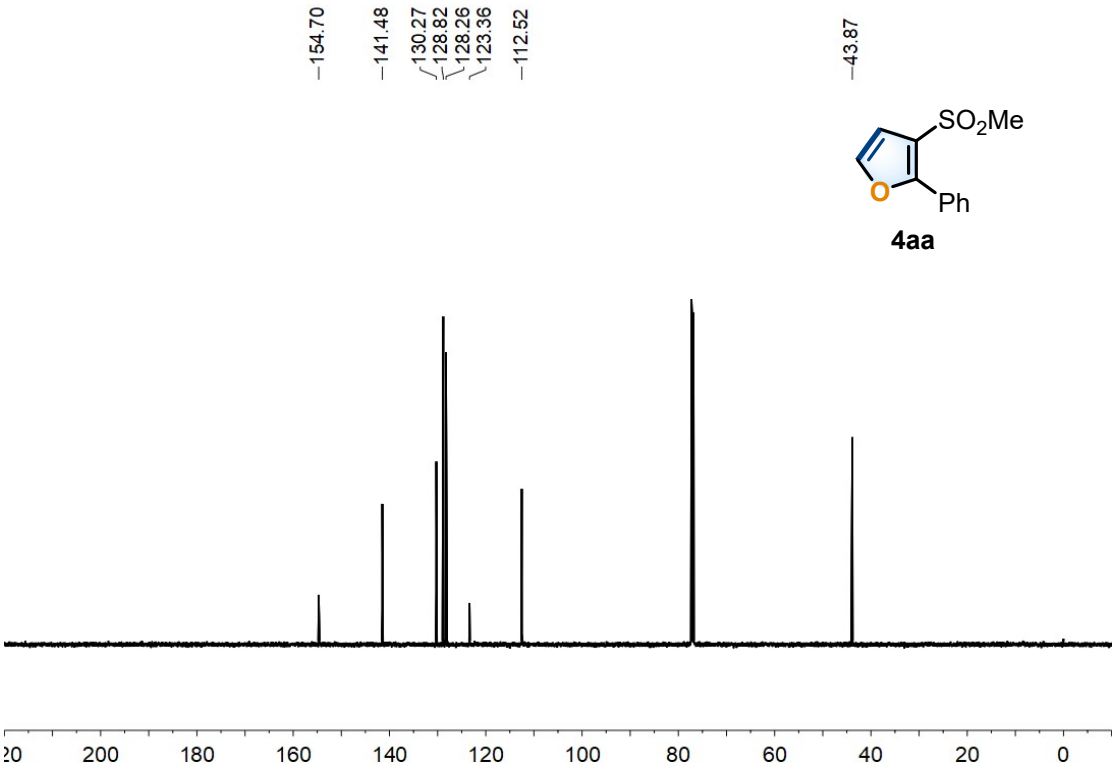
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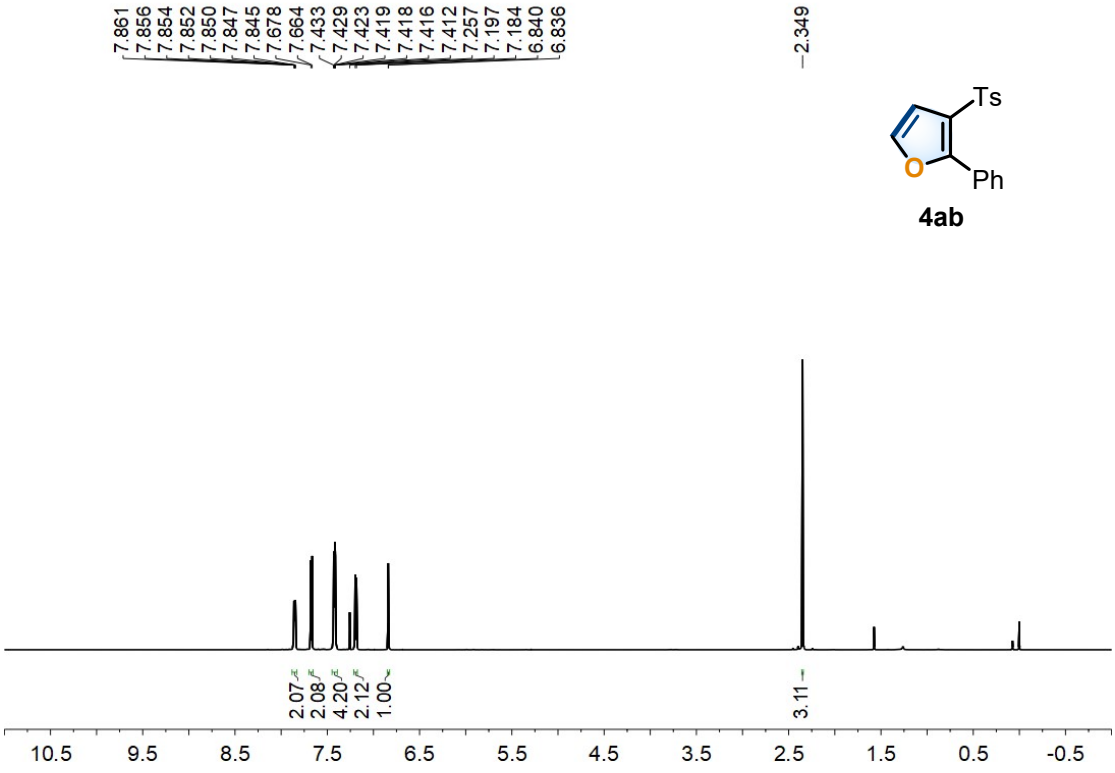
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O
Ph
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2.08
4.20
2.12
1.00
3.11
10.5
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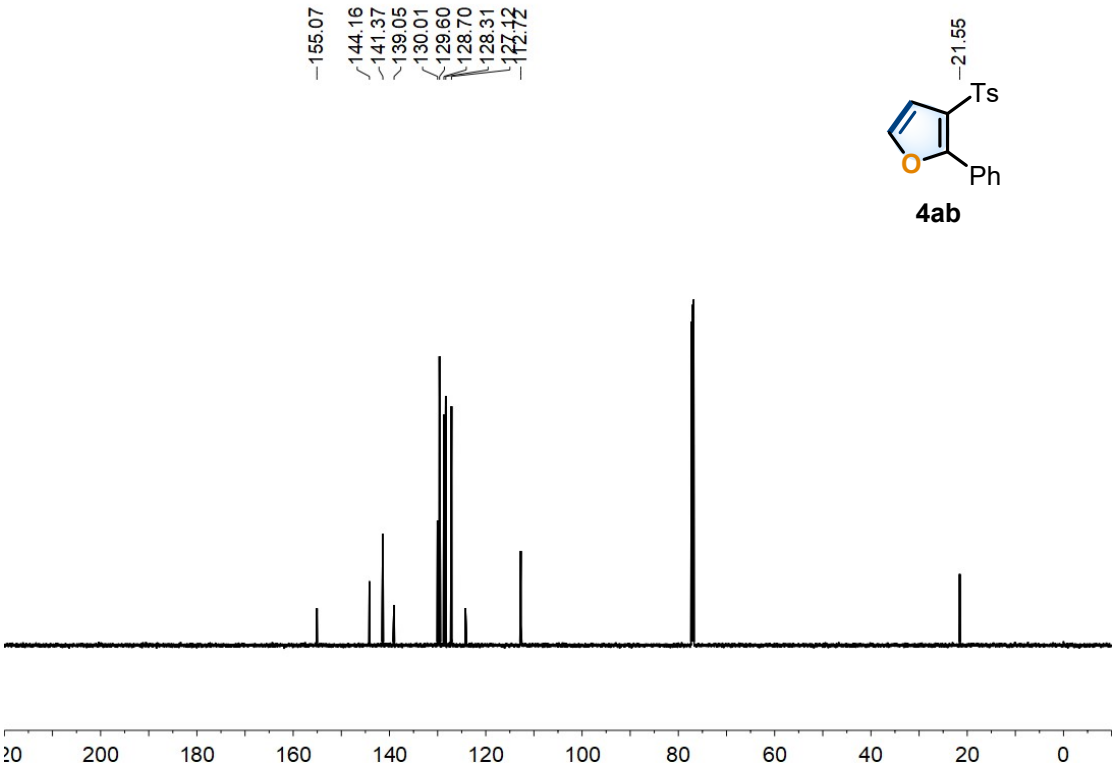
4ab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40
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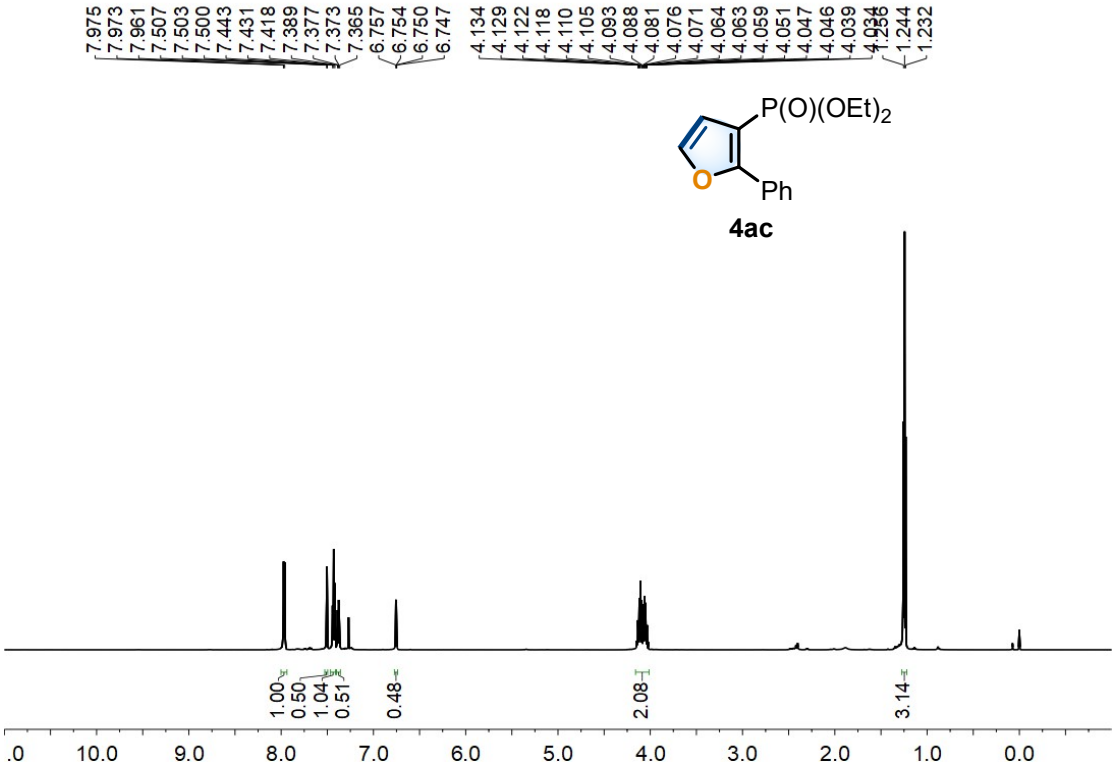
0

4ab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P(O)(OEt)2
O
Ph
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1.04
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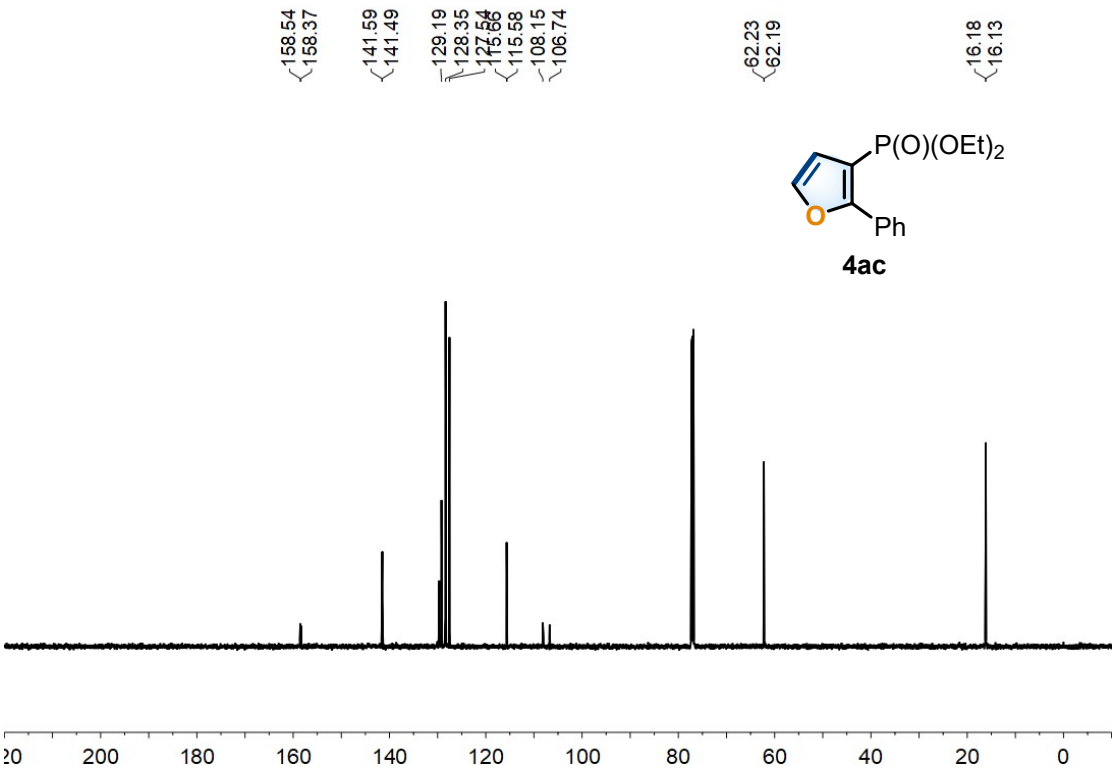
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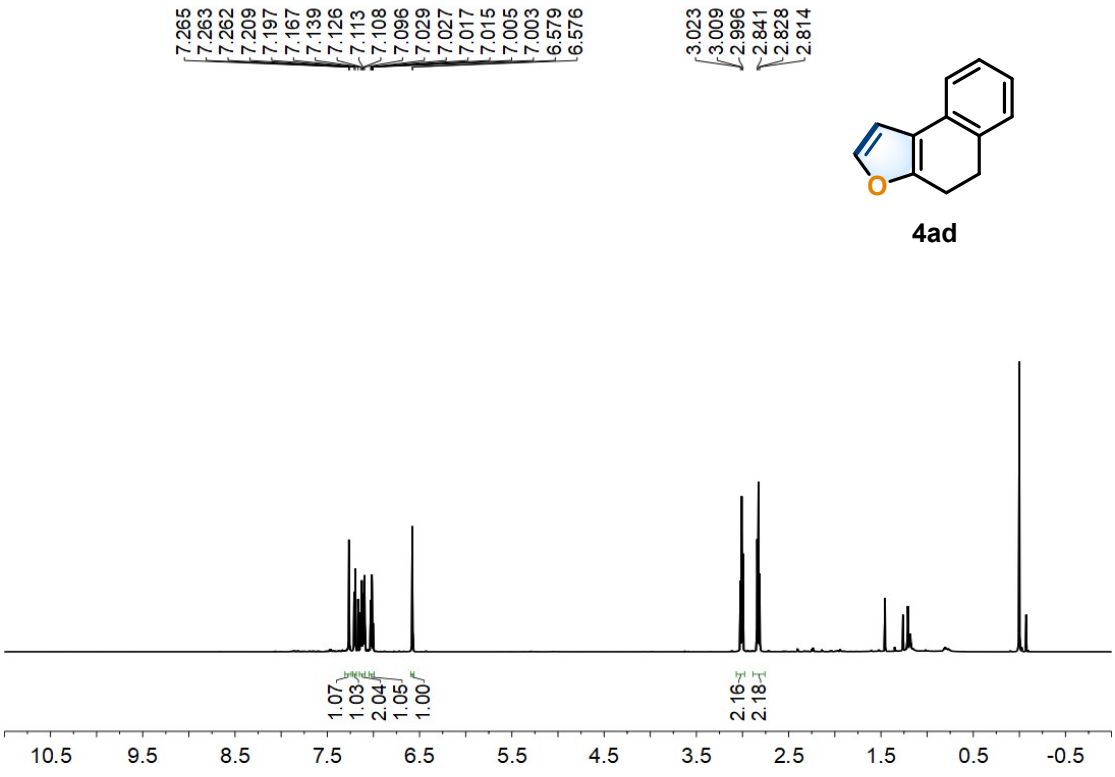
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7.027
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7.015
7.005
7.003
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6.576
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3.009
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2.841
2.828
2.814
O
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1.07
1.03
2.04
1.05
1.00
2.16
2.18
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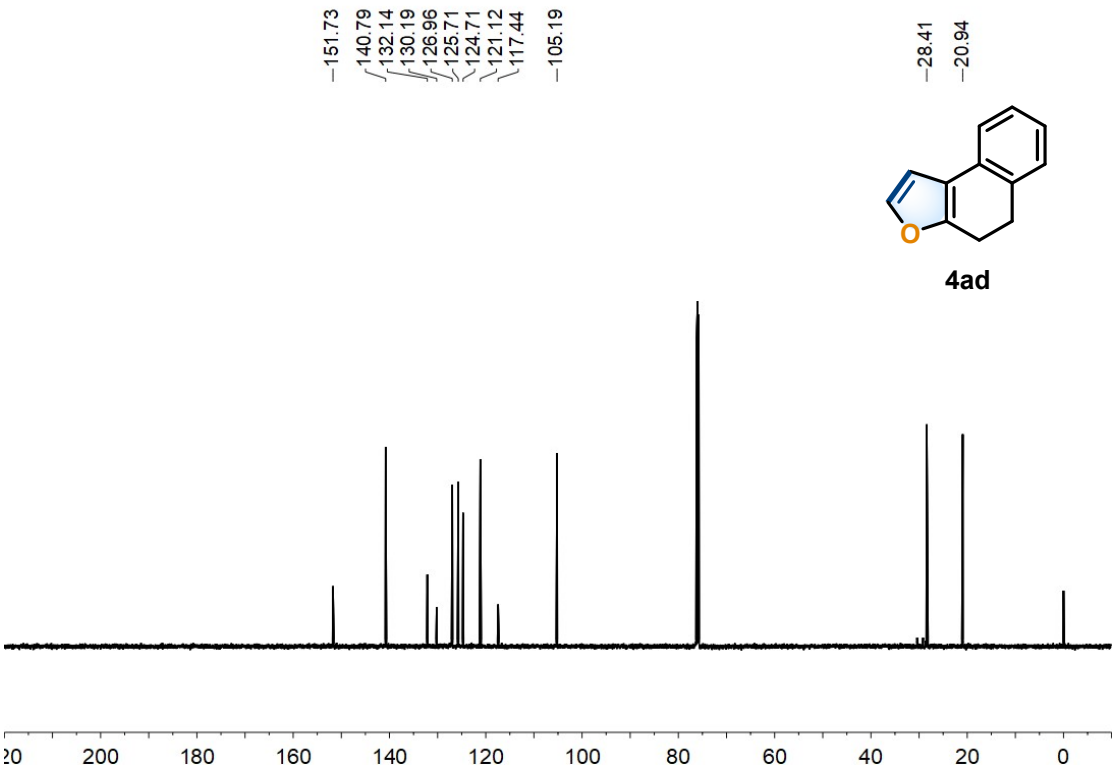
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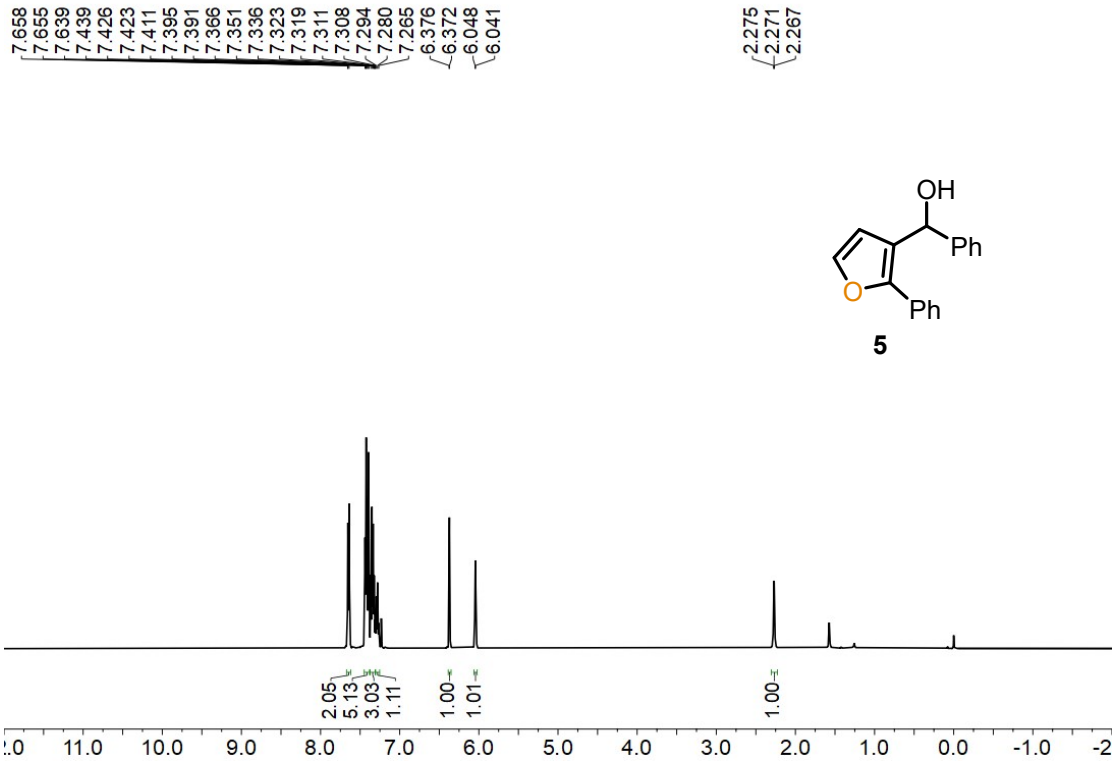
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6.041
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2.271
2.267
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Ph
O
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5.13
3.03
1.11
1.00
1.01
1.00
11.0
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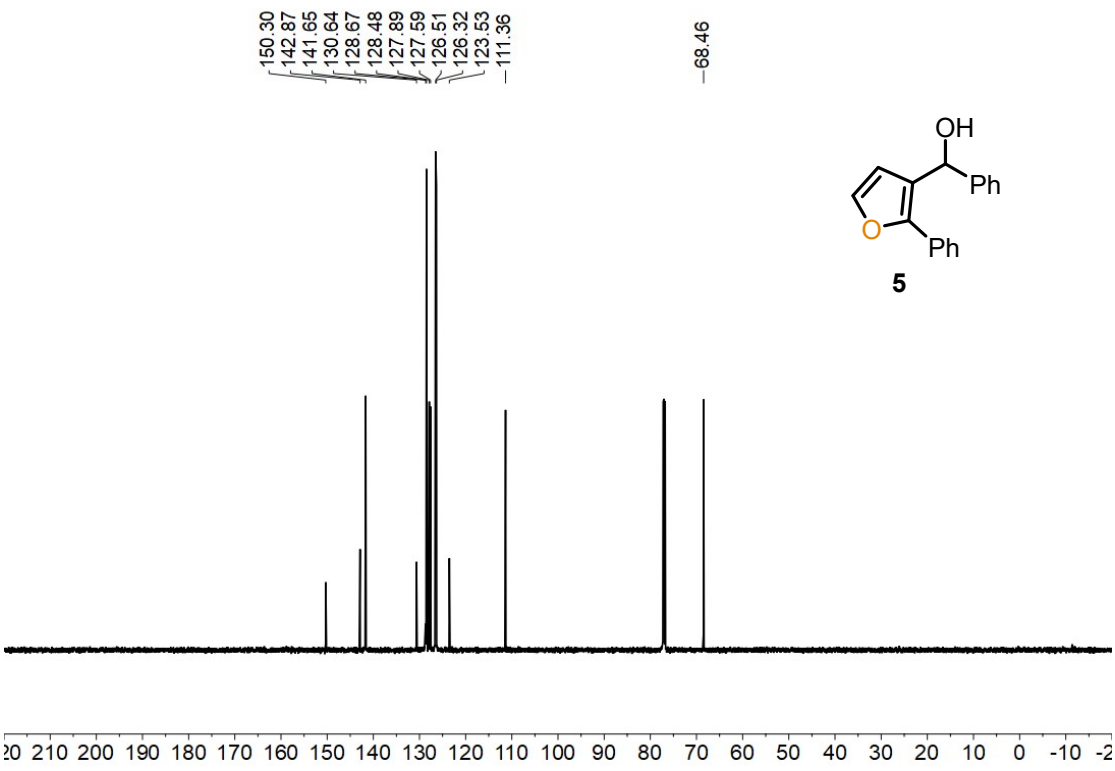
-1.0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Ph
O
Ph
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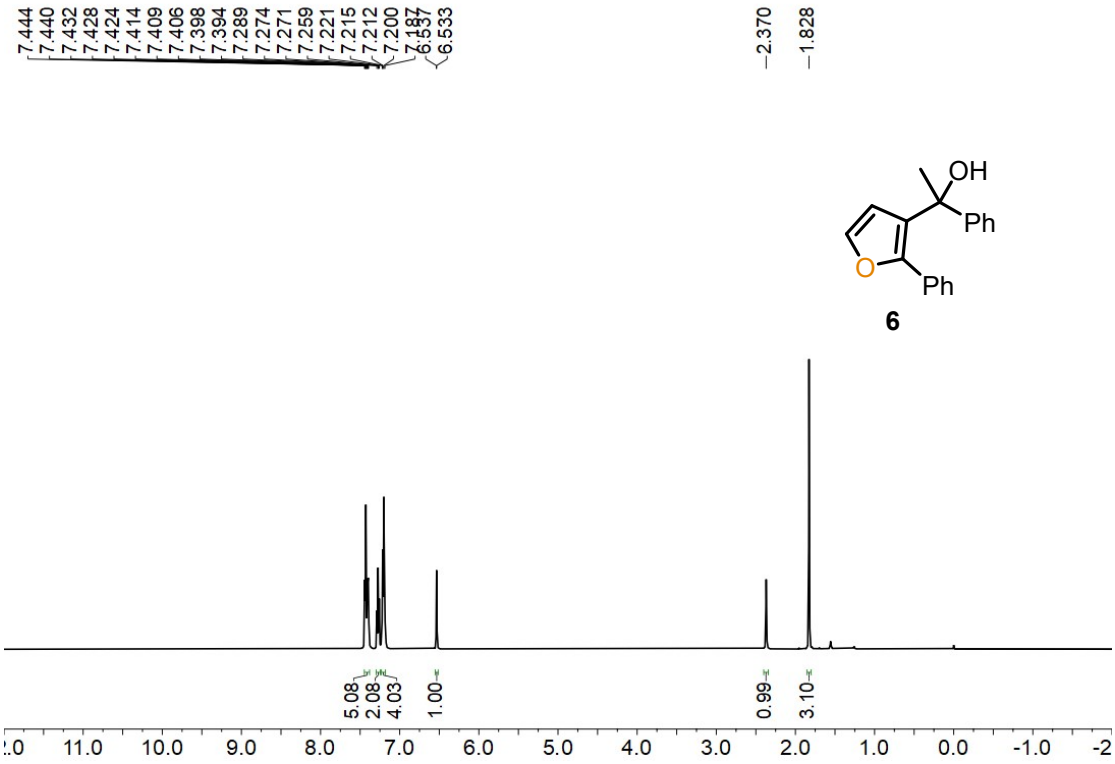
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7.221
7.215
7.212
7.200
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6.533
2.370
1.828
OH
Ph
O
Ph
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5.08
2.08
4.03
1.00
0.99
3.10
11.0
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6.0
5.0
4.0
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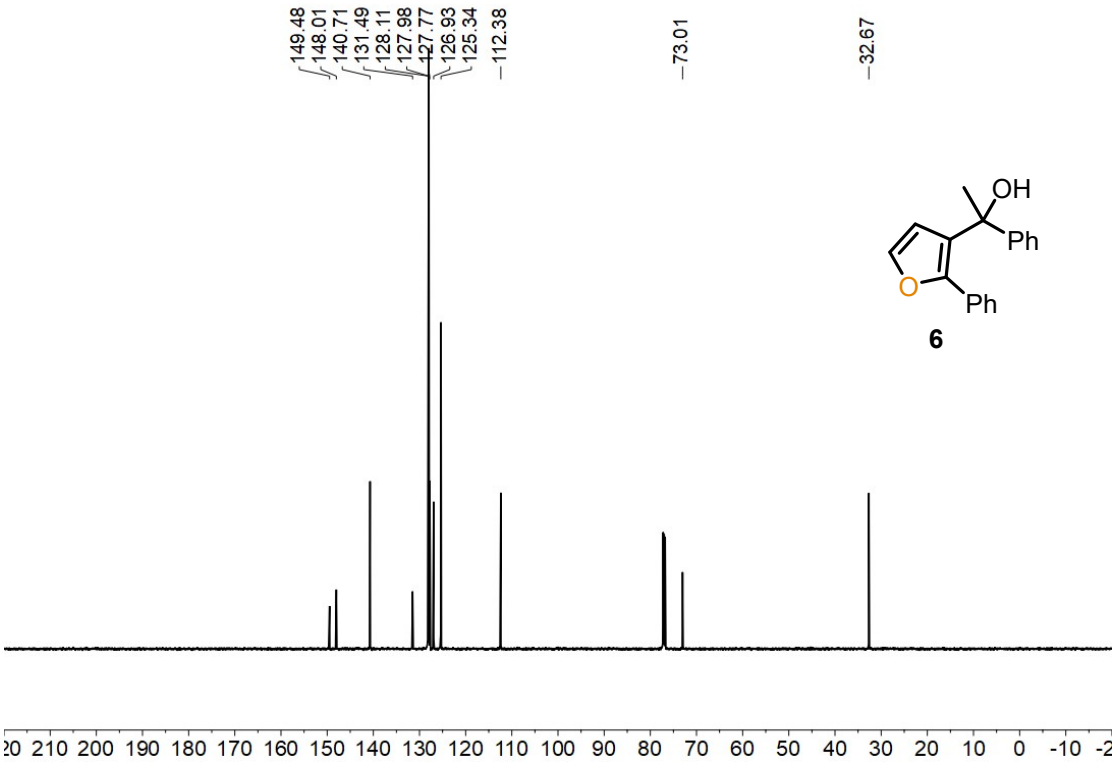
-1.0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Ph
O
Ph
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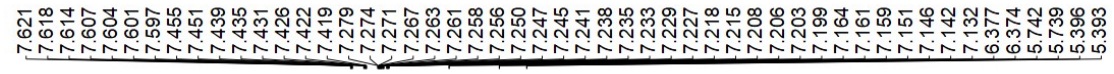
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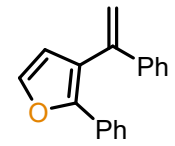
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O
Ph

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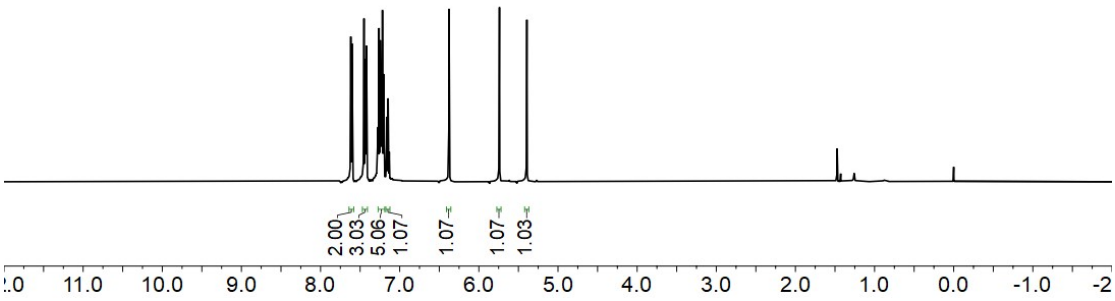
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5.0
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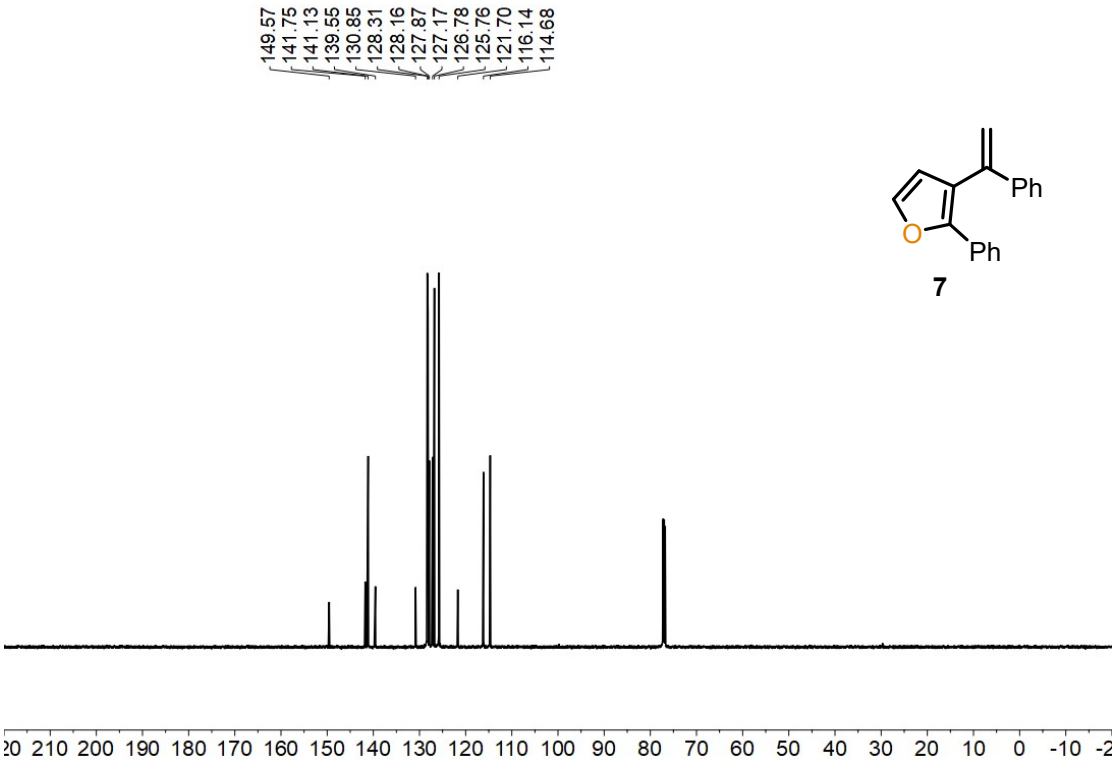
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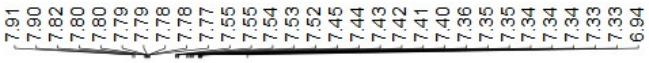
Ph
O
Ph

7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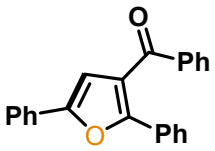
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Ph

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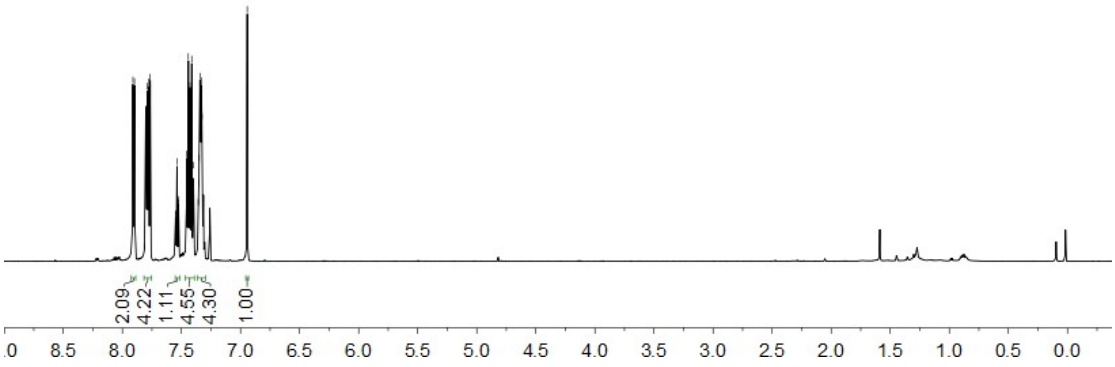
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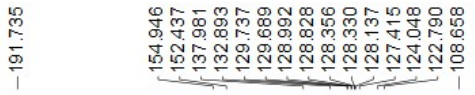
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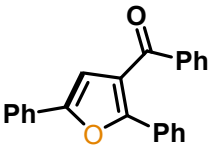
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Ph
Ph

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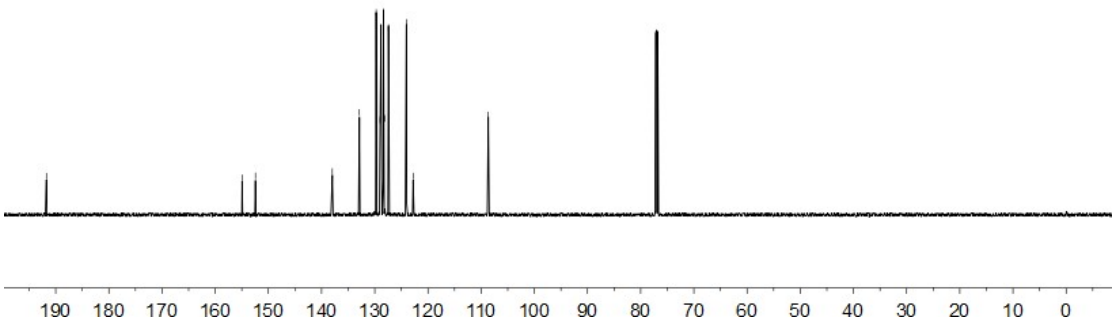
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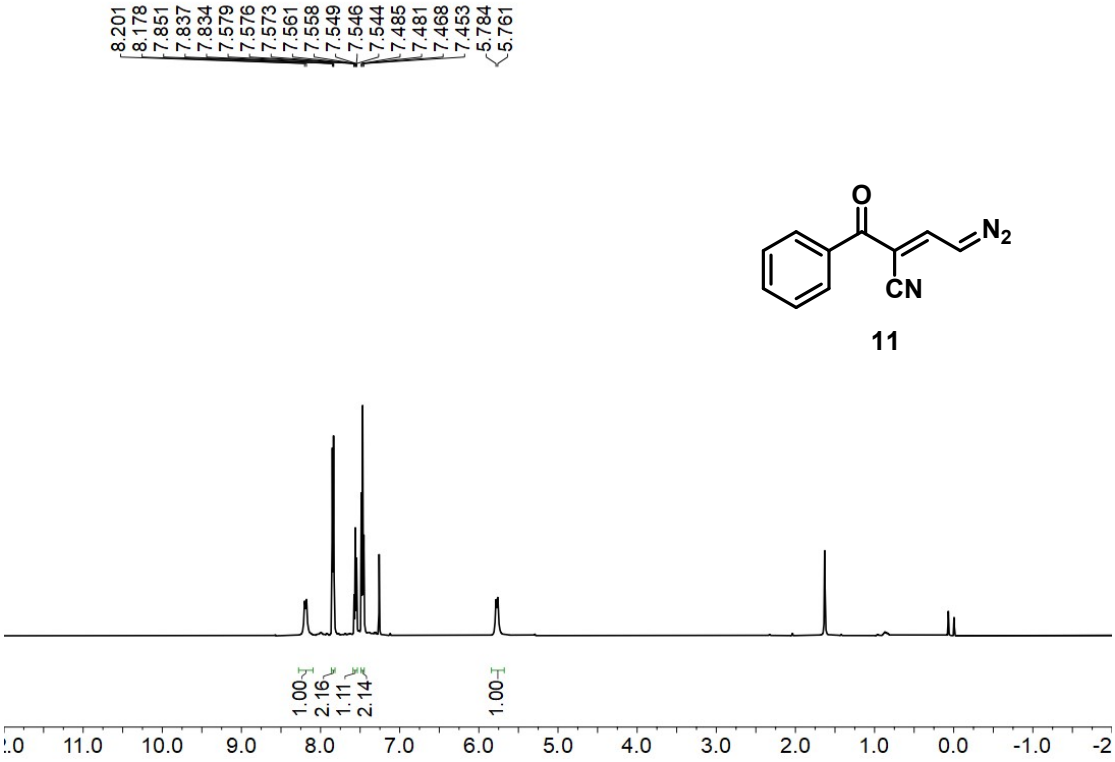
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7.453
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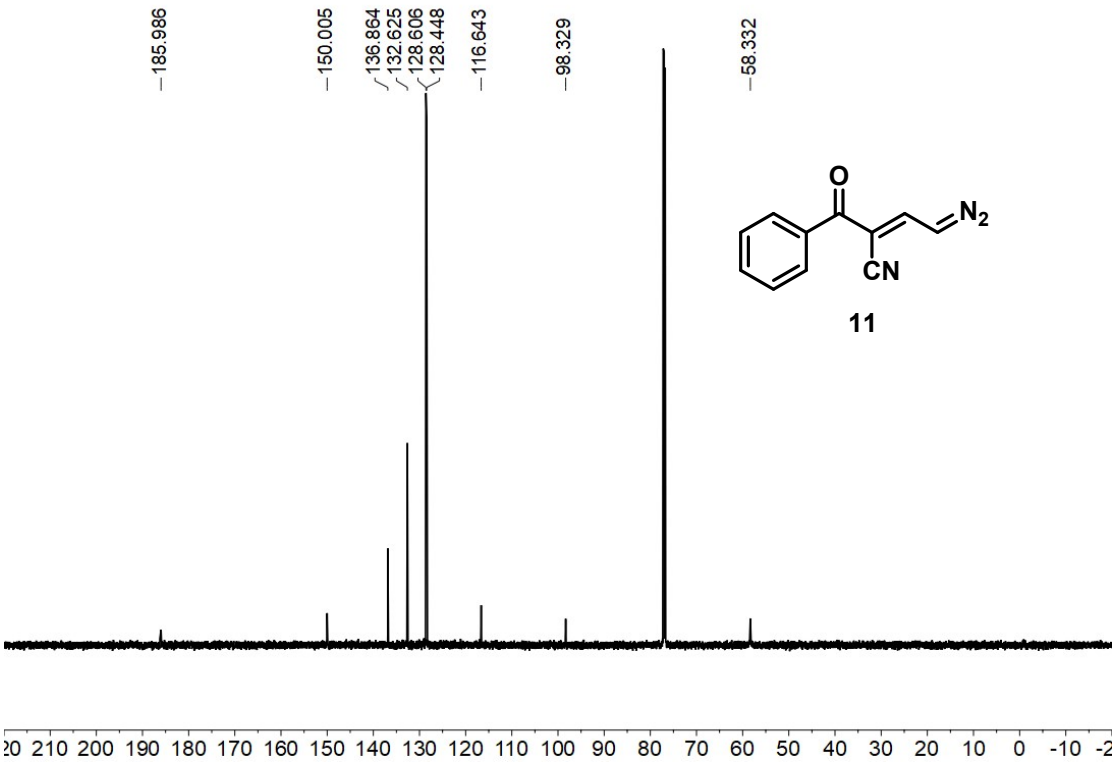
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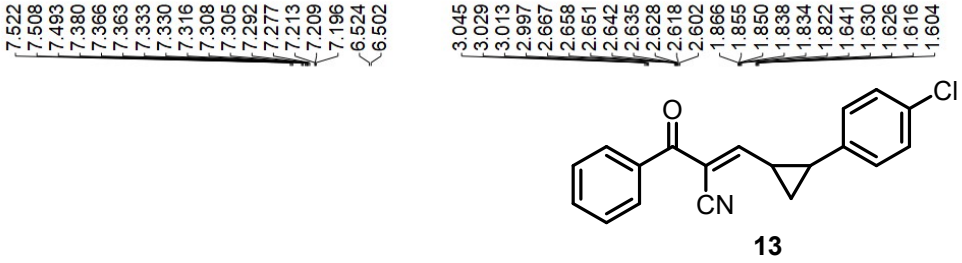
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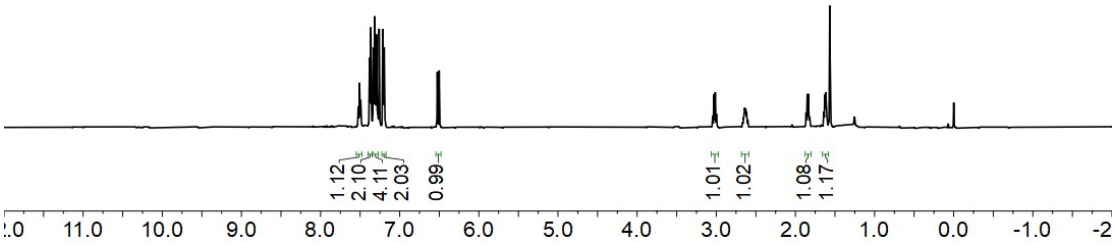
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4.0
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2.0
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-1.0


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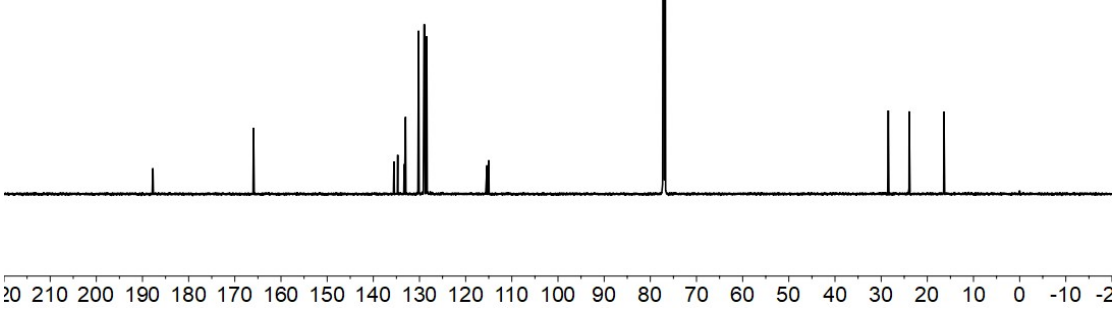
CN

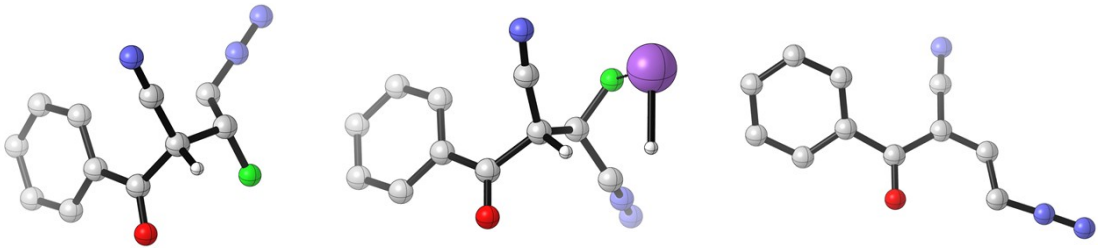
13


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

VII. Computational details

Computational details: All theoretical calculations of this work were performed based on density functional theory (DFT) methods with Gaussian 09 program.[1] All geometry optimizations were performed using the Becke's three-parameter hybrid exchange functional with Lee–Yang–Parr gradient-corrected correlation function (B3LYP)[2-5] and added the D3 version of Grimme's dispersion with Becke-Johnson damping.[6] All the atoms were described with the basis set 6-31G(d,p), double–ζ quality basis set.[7-10] We performed single-point energy calculations for all the optimized structures at the M06-2X/6-311++G(d,p) [11] level with solvent effects simulated by the SMD solvent model[12] (solvent = dichloromethane). The vibrational frequency analysis of reactants, products, intermediates and the transition states were given at the same level. All reactant, intermediate and product configurations having no imaginary frequency and each transition state has only one imaginary frequency, which has been confirmed by the intrinsic reaction coordinate (IRC).[13,14] The key 3D structures were prepared using the CYLview visualization program.[15]

Ball-and-stick models of Int3, Int4, and Int5



Int3 Int4 Int5

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Cartesian coordinates of all optimized structures

3w

Zero-point correction= 0.137634 (Hartree/Particle)
Thermal correction to Energy= 0.147478
Thermal correction to Enthalpy= 0.148469
Thermal correction to Gibbs Free Energy= 0.100533
Sum of electronic and zero-point Energies= -476.942642
Sum of electronic and thermal Energies= -476.932798
Sum of electronic and thermal Enthalpies= -476.931807
Sum of electronic and thermal Free Energies= -476.979743

C	-1.79546500	-1.53231800	0.38281800
C	-0.52703100	-0.96261800	0.46515500
C	-0.33575200	0.38142300	0.11211700
C	-1.43127200	1.14435100	-0.32329900
C	-2.69477900	0.57265700	-0.40535000
C	-2.87836700	-0.76723300	-0.05154800
H	-1.93710400	-2.57334200	0.65390800
H	0.30535300	-1.57519200	0.79136600
H	-1.26143400	2.18131300	-0.58996700
H	-3.53772300	1.16619700	-0.74446000
H	-3.86534700	-1.21477200	-0.11657600
C	0.98566800	1.05664300	0.19095100
O	1.13302700	2.23785200	-0.06175600
C	2.22137200	0.24476300	0.65141600
H	2.05129900	-0.14078900	1.66367100
H	3.05852100	0.94531900	0.68747000
C	2.54963900	-0.87115800	-0.23165400
N	2.79401900	-1.75580200	-0.94214100

Int1

Zero-point correction= 0.140360 (Hartree/Particle)
Thermal correction to Energy= 0.152848
Thermal correction to Enthalpy= 0.153839
Thermal correction to Gibbs Free Energy= 0.098788
Sum of electronic and zero-point Energies= -639.783810
Sum of electronic and thermal Energies= -639.771322

Sum of electronic and thermal Enthalpies= -639.770330
Sum of electronic and thermal Free Energies= -639.825381

C	2.62099600	0.67621600	0.80157700
C	1.25074500	0.77228800	0.57075800
C	0.58877300	-0.23515100	-0.15052300
C	1.32277800	-1.33717200	-0.62776800
C	2.69190500	-1.41660400	-0.41175900
C	3.34359400	-0.40862600	0.30526900
H	3.12350200	1.45362600	1.36731700
H	0.70687500	1.61999600	0.96448900
H	0.79709600	-2.11252400	-1.17297500
H	3.25359300	-2.26156200	-0.79696200
H	4.41366600	-0.47128200	0.47755800
C	-0.86920400	-0.23412600	-0.39357400
O	-1.45606200	-1.29931200	-0.64315600
C	-1.75653000	0.98534900	-0.26025600
H	-2.34461400	0.79531200	0.69712500
H	-2.52094500	0.90485800	-1.03919200
C	-1.18216700	2.31913500	-0.30072200
N	-0.75701800	3.39960400	-0.33095600
Na	-3.19754400	-1.80930700	0.72753100
H	-3.37391400	-0.15663400	1.76372300

TS1

Zero-point correction= 0.138815 (Hartree/Particle)
Thermal correction to Energy= 0.151110
Thermal correction to Enthalpy= 0.152101
Thermal correction to Gibbs Free Energy= 0.097247
Sum of electronic and zero-point Energies= -639.780978
Sum of electronic and thermal Energies= -639.768682
Sum of electronic and thermal Enthalpies= -639.767691
Sum of electronic and thermal Free Energies= -639.822545

C	2.60432100	0.79059800	0.74232200
C	1.23196200	0.83845800	0.50640900
C	0.59679300	-0.21956300	-0.16463100
C	1.36312900	-1.32189800	-0.58638400
C	2.73388100	-1.35497000	-0.36509900
C	3.35801300	-0.29715200	0.30205700
H	3.08406700	1.60917500	1.26879700
H	0.66605400	1.69150900	0.85454700
H	0.85951600	-2.13616200	-1.09426000

H	3.31789100	-2.20310400	-0.70845300
H	4.42901300	-0.32269400	0.47857300
C	-0.86179300	-0.26987900	-0.42328100
O	-1.40283600	-1.37893800	-0.63559400
C	-1.78379900	0.88838800	-0.31138800
H	-2.41516500	0.59757700	0.70761300
H	-2.57858600	0.77265600	-1.05308100
C	-1.30940600	2.25101800	-0.30209300
N	-0.97514500	3.36482500	-0.26981700
Na	-3.06798800	-1.84819800	0.77512800
H	-3.16481300	-0.03104900	1.60585800

Int2

Zero-point correction= 0.174338 (Hartree/Particle)
Thermal correction to Energy= 0.193644
Thermal correction to Enthalpy= 0.194635
Thermal correction to Gibbs Free Energy= 0.122883
Sum of electronic and zero-point Energies= -1025.144961
Sum of electronic and thermal Energies= -1025.125656
Sum of electronic and thermal Enthalpies= -1025.124664
Sum of electronic and thermal Free Energies= -1025.196416

C	3.46098400	-1.44450900	0.65819300
C	2.41044900	-0.63484700	1.08652900
C	1.97503300	0.43604400	0.29376400
C	2.62891400	0.69399600	-0.91995800
C	3.67551600	-0.11600900	-1.34785800
C	4.09209600	-1.19162100	-0.56023900
H	3.79137500	-2.26929500	1.28204900
H	1.94075100	-0.83174500	2.04205100
H	2.29774200	1.54152500	-1.50856900
H	4.16843800	0.08969900	-2.29336500
H	4.90970400	-1.82512200	-0.89143700
C	0.85977400	1.34903800	0.69414000
O	0.79953100	2.49629900	0.12713800
C	-0.14659800	0.95620200	1.60686200
H	-0.72561800	1.75474400	2.07009200
C	-0.45127200	-0.34713500	2.03432700
N	-0.80719100	-1.41901800	2.35019600
Na	-1.29119000	2.18316900	-0.35738300
N	-0.31060600	-0.63751900	-2.03621100
N	-1.22443400	-1.07513800	-1.50673600
C	-2.29459300	-1.53171200	-0.93680400

H	-2.48727100	-2.59318300	-0.98510200
C	-3.06307900	-0.64767700	-0.01881300
H	-2.73332300	-0.63626100	1.02216400
F	-4.37615500	-0.96472200	-0.07384300
F	-2.93969800	0.69533100	-0.48342100

TS2

Zero-point correction= 0.172676 (Hartree/Particle)
Thermal correction to Energy= 0.190696
Thermal correction to Enthalpy= 0.191688
Thermal correction to Gibbs Free Energy= 0.125388
Sum of electronic and zero-point Energies= -1025.116406
Sum of electronic and thermal Energies= -1025.098386
Sum of electronic and thermal Enthalpies= -1025.097394
Sum of electronic and thermal Free Energies= -1025.163694

C	-3.34479800	-0.31633400	0.13224500
C	-2.24275400	-0.70817600	0.89257500
C	-1.02353100	-1.00548900	0.27326700
C	-0.91479000	-0.89539200	-1.12345100
C	-2.01920200	-0.49817100	-1.87828900
C	-3.23666200	-0.21344400	-1.25650400
H	-4.28671300	-0.09152200	0.62314300
H	-2.32380400	-0.78633800	1.97153100
H	0.06149300	-1.01651700	-1.58725500
H	-1.92637300	-0.40385300	-2.95702600
H	-4.09474200	0.09263600	-1.84763900
C	0.16436600	-1.45416800	1.08421300
O	0.74222200	-2.53427100	0.74751900
C	0.60319400	-0.65352800	2.15314700
H	1.39840800	-1.02724000	2.79002700
C	0.14964600	0.65239100	2.36007700
N	-0.14131500	1.79009700	2.43081000
Na	2.37207000	-2.15735100	-0.59569600
N	-1.45456300	2.32578300	-0.21558100
N	-0.41370700	2.06216500	-0.53858300
C	0.82765600	1.83300000	-1.00047300
H	0.92951100	1.69643200	-2.06781500
C	1.82659900	1.59183700	-0.10269000
H	1.66299600	1.55727300	0.96905700
F	3.07090100	1.61968500	-0.48991000
F	2.02659200	-0.42605300	-1.53928200

Int3

Zero-point correction= 0.172978 (Hartree/Particle)
Thermal correction to Energy= 0.188037
Thermal correction to Enthalpy= 0.189029
Thermal correction to Gibbs Free Energy= 0.128264
Sum of electronic and zero-point Energies= -762.973067
Sum of electronic and thermal Energies= -762.958008
Sum of electronic and thermal Enthalpies= -762.957016
Sum of electronic and thermal Free Energies= -763.017781

C	-2.28364300	1.77938700	0.63679700
C	-1.27524000	0.82024500	0.71557600
C	-1.40538200	-0.39632500	0.02563400
C	-2.56433800	-0.63183300	-0.73513000
C	-3.56326700	0.32964000	-0.81541100
C	-3.42461800	1.53898600	-0.12828600
H	-2.17755400	2.71268800	1.18003900
H	-0.40510700	1.02424800	1.32424100
H	-2.65134100	-1.57847400	-1.25553600
H	-4.45018600	0.14027300	-1.41146500
H	-4.20611000	2.29024200	-0.18748000
C	-0.39413400	-1.49072300	0.04725700
O	-0.63558200	-2.58615000	-0.42446700
C	1.04271500	-1.29014100	0.61226100
H	1.42199300	-2.31355500	0.69255300
C	1.13275800	-0.67924000	1.93487800
N	1.23438100	-0.20121600	2.98794200
N	3.45255400	2.50423500	-0.73526700
N	2.61412900	1.72949000	-0.71987500
C	1.65267200	0.85488800	-0.66762000
H	0.67536000	1.19498200	-0.97725000
C	1.98445100	-0.56569700	-0.39446300
H	3.00489700	-0.62969600	-0.00238600
F	1.92815700	-1.33268800	-1.56505900

Int4

Zero-point correction= 0.177053 (Hartree/Particle)
Thermal correction to Energy= 0.194535
Thermal correction to Enthalpy= 0.195527
Thermal correction to Gibbs Free Energy= 0.129588
Sum of electronic and zero-point Energies= -925.817229
Sum of electronic and thermal Energies= -925.799746

Sum of electronic and thermal Enthalpies= -925.798755
Sum of electronic and thermal Free Energies= -925.864693

C	3.04513800	-0.71630900	-1.53148400
C	1.84488300	-0.72385600	-0.82407300
C	1.76901600	-0.12369800	0.44273700
C	2.91440500	0.48170600	0.98634400
C	4.10870900	0.48929900	0.27708900
C	4.17575300	-0.10936900	-0.98435300
H	3.09706700	-1.18791700	-2.50723900
H	0.98465200	-1.21782600	-1.26016300
H	2.83609900	0.93881100	1.96610300
H	4.98872900	0.96018900	0.70316800
H	5.10917900	-0.10408500	-1.53855300
C	0.52440400	-0.07640800	1.25847000
O	0.50253000	0.39769700	2.37741200
C	-0.81797400	-0.57338800	0.65753900
H	-1.56653500	-0.54807100	1.47047600
C	-0.82042700	-1.95261500	0.18053700
N	-0.96721800	-3.04900600	-0.17693600
N	-1.71798200	3.77986300	-0.86931700
N	-1.82122200	2.74945400	-0.39045300
C	-1.92209100	1.58936500	0.19222600
H	-2.60022900	1.49163400	1.03579500
C	-1.31919100	0.40747600	-0.43023100
H	-0.53629000	0.66121700	-1.14551100
F	-2.30201100	-0.31982900	-1.23337900
Na	-3.76470900	-1.56851600	0.03296300
H	-3.67381000	-0.55876600	1.70258200

TS3

Zero-point correction= 0.174097 (Hartree/Particle)
Thermal correction to Energy= 0.191544
Thermal correction to Enthalpy= 0.192536
Thermal correction to Gibbs Free Energy= 0.127062
Sum of electronic and zero-point Energies= -925.821614
Sum of electronic and thermal Energies= -925.804168
Sum of electronic and thermal Enthalpies= -925.803176
Sum of electronic and thermal Free Energies= -925.868650

C	-3.59953000	0.82340900	0.90444300
C	-2.24642000	0.61771900	0.64283200
C	-1.83804500	-0.52469200	-0.06151100

C	-2.79383900	-1.45906000	-0.48872700
C	-4.14280000	-1.24341800	-0.23432900
C	-4.54708200	-0.09978500	0.46121600
H	-3.91277200	1.70326400	1.45713500
H	-1.51659500	1.32931100	1.01471300
H	-2.45172900	-2.34185500	-1.01737800
H	-4.88121000	-1.96282300	-0.57407500
H	-5.60113300	0.06816800	0.66066200
C	-0.40866900	-0.80405600	-0.35190000
O	-0.00892600	-1.91392000	-0.67850500
C	0.58108700	0.33778400	-0.19807200
H	0.58242500	0.81357400	0.92599200
C	0.27490700	1.52308800	-0.96181500
N	0.15004900	2.60856600	-1.37190600
N	3.98365600	-2.81742100	0.36919200
N	3.29443700	-1.92570300	0.54553800
C	2.49494000	-0.92004000	0.74653700
H	2.20485200	-0.70936200	1.76722700
C	2.03315100	-0.11533400	-0.39155600
H	2.20279900	-0.61385600	-1.34564000
F	2.82218700	1.12358500	-0.47021100
Na	1.84933700	2.85592200	0.68969200
H	0.85918900	1.62575200	1.98221700

TS3’

Zero-point correction= 0.166356 (Hartree/Particle)
Thermal correction to Energy= 0.181650
Thermal correction to Enthalpy= 0.182642
Thermal correction to Gibbs Free Energy= 0.121377
Sum of electronic and zero-point Energies= -762.918472
Sum of electronic and thermal Energies= -762.903178
Sum of electronic and thermal Enthalpies= -762.902186
Sum of electronic and thermal Free Energies= -762.963451

C	-3.63996100	0.88022800	0.55693900
C	-2.25317900	0.77781600	0.48077000
C	-1.66064100	-0.40830300	0.02392000
C	-2.47553500	-1.49024800	-0.34318700
C	-3.85953600	-1.37960600	-0.27879200
C	-4.44394600	-0.19290800	0.17131100
H	-4.09163900	1.79858600	0.91730700
H	-1.64194200	1.61662000	0.79056700
H	-2.00012900	-2.40564400	-0.67658600

H	-4.48438800	-2.21592600	-0.57562600
H	-5.52487300	-0.10640400	0.22431000
C	-0.18592200	-0.60637100	-0.04542500
O	0.28809500	-1.73922400	-0.03016900
C	0.70297500	0.61192000	-0.06720200
H	0.95437700	0.98573100	1.12774600
C	0.26078900	1.73106700	-0.86501000
N	-0.07285900	2.64887100	-1.49664900
N	5.29445200	-0.81413600	-0.25556100
N	4.16663300	-0.77914400	-0.18274100
C	2.84487500	-0.77770300	-0.11615100
H	2.34842200	-1.73362100	-0.01678700
C	2.18095300	0.45621900	-0.08297400
H	2.74062600	1.33768500	-0.37100600
F	2.09466300	1.07055100	1.75121000

Int5

Zero-point correction= 0.157629 (Hartree/Particle)
Thermal correction to Energy= 0.171069
Thermal correction to Enthalpy= 0.172060
Thermal correction to Gibbs Free Energy= 0.115716
Sum of electronic and zero-point Energies= -662.546193
Sum of electronic and thermal Energies= -662.532753
Sum of electronic and thermal Enthalpies= -662.531761
Sum of electronic and thermal Free Energies= -662.588106

C	-3.46487300	0.77697100	0.72916800
C	-2.07506400	0.73150100	0.63726800
C	-1.44687000	-0.36148800	0.02328000
C	-2.23168800	-1.41141600	-0.48005100
C	-3.61807900	-1.35380100	-0.40298200
C	-4.23786400	-0.25733800	0.20221200
H	-3.94229800	1.62311700	1.21257900
H	-1.49065900	1.53923900	1.05854200
H	-1.73058000	-2.26187700	-0.92806000
H	-4.21724000	-2.16250200	-0.80948000
H	-5.32079200	-0.21226800	0.26598600
C	0.03442400	-0.52214700	-0.06517200
O	0.51976600	-1.65627300	-0.07711800
C	0.92827800	0.66319800	-0.15694000
C	0.41505200	1.97119200	-0.40794600
N	0.03525800	3.05137100	-0.62386500
N	5.49043500	-0.51948900	0.28734600

N	4.35721100	-0.55297600	0.20654600
C	3.04481500	-0.62817300	0.11240000
H	2.60219600	-1.61323400	0.16938900
C	2.30018700	0.55902200	-0.07238400
H	2.87101200	1.48023700	-0.15532700

TS4

Zero-point correction= 0.154823 (Hartree/Particle)
Thermal correction to Energy= 0.168184
Thermal correction to Enthalpy= 0.169175
Thermal correction to Gibbs Free Energy= 0.113108
Sum of electronic and zero-point Energies= -662.503950
Sum of electronic and thermal Energies= -662.490589
Sum of electronic and thermal Enthalpies= -662.489598
Sum of electronic and thermal Free Energies= -662.545665

C	-3.62174600	0.69407500	0.22856400
C	-2.23513400	0.79915900	0.31277200
C	-1.43022500	-0.32324700	0.06388600
C	-2.03797000	-1.54862000	-0.25759200
C	-3.42118700	-1.64495400	-0.34917800
C	-4.21687900	-0.52227800	-0.10651400
H	-4.23695800	1.56595200	0.42606300
H	-1.79111800	1.74883300	0.58038900
H	-1.40351300	-2.40950100	-0.43347100
H	-3.88143600	-2.59336800	-0.60780800
H	-5.29780000	-0.59681000	-0.17643500
C	0.04731000	-0.29822100	0.15732600
O	0.68322300	-1.37690200	0.27479700
C	0.87929900	0.88039000	0.08270000
C	0.45194900	2.21163200	-0.16260700
N	0.12359300	3.31424700	-0.35076900
N	5.37617800	-0.88111200	-0.41694400
N	4.41141200	-0.59594400	0.06955900
C	2.69744600	-0.73283400	0.22267600
H	2.70044200	-1.50173800	0.97582000
C	2.23920100	0.57905300	0.13413500
H	2.95392700	1.37657500	-0.03287000

4w

Zero-point correction= 0.150461 (Hartree/Particle)
Thermal correction to Energy= 0.160968

Thermal correction to Enthalpy= 0.161960
Thermal correction to Gibbs Free Energy= 0.112495
Sum of electronic and zero-point Energies= -553.116364
Sum of electronic and thermal Energies= -553.105857
Sum of electronic and thermal Enthalpies= -553.104865
Sum of electronic and thermal Free Energies= -553.154330

C	2.60875100	1.30875000	0.00008000
C	1.23388300	1.09636100	0.00005000
C	0.72164000	-0.21340900	-0.00003600
C	1.61812300	-1.29755000	-0.00009100
C	2.99059300	-1.07412900	-0.00004800
C	3.49251400	0.22844400	0.00004000
H	2.98998700	2.32486100	0.00015000
H	0.56262000	1.94617000	0.00009300
H	1.22950700	-2.30896900	-0.00015200
H	3.67071400	-1.92013100	-0.00008000
H	4.56424000	0.40016400	0.00007000
C	-0.71214800	-0.46124500	-0.00003100
O	-1.11807600	-1.76222100	0.00001100
C	-1.84042200	0.34424500	-0.00005400
C	-1.89117300	1.75977300	-0.00010800
N	-1.94826000	2.92294100	-0.00000300
C	-2.48515500	-1.79235900	0.00016500
H	-2.93339900	-2.77244800	0.00000300
C	-2.98350800	-0.53229200	-0.00002000
H	-4.01982500	-0.23200500	0.00016700