Electronic Supplementary Information

Ruthenium pincer-catalyzed synthesis of substituted γ-butyrolactones using hydrogen autotransfer methodology

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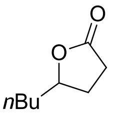
General information: Unless otherwise is stated, all reactions were conducted under an argon atmosphere with exclusion of moisture from reagents and glassware using standard techniques for manipulation air sensitive compounds. Reaction temperatures refer to external bath temperatures. TLC was effected on silica gel 60 F_{254} (layer thickness 0.2 mm) and components were located by observation under UV light and/or by treating the plates with a phosphomolybdic acid, or *p*-anisaldehyde reagent followed by heating. Column chromatography was performed on silica gel (230–400 mesh) using 20% ethyl acetate/heptane as eluent. NMR spectra were performed in a Bruker Avance 400 spectrometer using the residual solvent signal as internal standard [chloroform: 7.26 ppm (^{1}H), 77.0 ppm (^{13}C)]. All measurements were carried out at room temperature unless otherwise stated, and DEPT was used to assign carbon types. Mass spectra were in general recorded on a MAT 95XP or a HP 5973N mass selective detector. Gas chromatography was performed on a HP 6890N chromatograph with a HP5 column. Infrared spectra were taken on a Bruker Alpha with ATR (“attenuated total reflectance”). Unless otherwise statement, commercial reagents were used as received without purification.

General procedure for the ruthenium pincer-catalyzed synthesis of γ-butyrolactones using borrowing-hydrogen methodology: In a glass pressure tube (25 mL) under an argon atmosphere, [Ru-MACHO-BH] (11.8 mg, 0.02 mmol), K_2CO_3 (13.8 mg, 0.10 mmol), 1,2-diol (**1a-i**, 1.0 mmol) and corresponding malonate (**2, 4a-d or 5a-c**, 2.0 mmol) were dissolved in *t*-amyl alcohol (1 mL). Next the pressure tube was closed and the resulting mixture was stirred at 150 °C in an oil bath for 18 h. After cooling down to room temperature, the crude was directly purified by flash chromatography on silica gel eluting with 20% ethyl acetate/heptane to afford, after concentration and high-vacuum drying, the corresponding γ-butyrolactones (**3a-i, 6a-c**) in the reported yields.

Analytical data of all synthesized γ-butyrolactones (3a-i, 6a-c):



5-butyldihydrofuran-2(3H)-one (3a)[1]**:** Following the general procedure, **3a** was obtained as a colorless oil (86.7 mg, 0.61 mmol, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.90-1.97 (t, , J = 7.1 Hz, 3H), 1.29-1.48 (m, 4H), 1.54-1.63 (m, 1H), 1.68-1.76 (m, 1H), 1.79-1.90 (m, 1H), 2.16-2.35 (m, 1H), 2.51 (ddd, J = 1.8, 6.8, 9.1 Hz, 2H), 4.44-4.51 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.0 (CH_3), 22.5 (CH_2), 27.4 (CH_2), 28.1 (CH_2), 29.0 (CH_2), 35.4 (CH_2), 81.1 (CH), 177.4 (C) ppm; IR (ATR): ν = 2956, 2932, 2862, 1767, 1460, 1421, 1350, 1168, 1125, 1012 cm^{-1}; GCMS (EI): *m/z* (%): 142 (4) [M^+], 127 (1) [$M^+ - CH_3$], 85 (100) [$M^+ - C_4H_9$]; HRMS (ESI-TOF): *m/z*: calcd for $C_8H_{14}O_2$: 143.1067 $[M+H]^+$; found: 143.1069.

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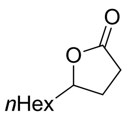
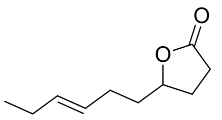
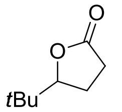
[1] Sigma-Aldrich Co., Ref. W279617. CAS# [104-50-7].



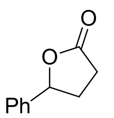
5-hexyldihydrofuran-2(3H)-one (3b)[2]: Following the general procedure, **3b** was obtained as a colorless oil (88.5 mg, 0.52 mmol, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.88 (t, J = 6.8 Hz, 3H), 1.23-1.49 (m, 8H), 1.52-1.64 (m, 1H), 1.69-1.78 (m, 1H), 1.81-1.89 (m, 1H), 2.27-2.36 (m, 1H), 2.50-2.55 (m, 2H), 4.43-4.52 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.2 (CH_3), 22.7 (CH_2), 25.3 (CH_2), 28.1 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 31.8 (CH_2), 35.7 (CH_2), 81.2 (CH), 177.4 (C) ppm; IR (ATR): ν = 2929, 2858, 1771, 1459, 1373, 1351, 1178, 911 cm^{-1}; GCMS (EI): m/z (%): 170 (1) [M^+], 141 (2) [$M^+ – C_2H_5$], 128 (11) [$M^+ – C_3H_6$], 85 (100) [$M^+ – C_6H_{13}$]; HRMS (ESI-TOF): m/z: calcd for $C_{10}H_{18}O_2$: 171.1379 [$M+H]^+$; found: 171.1378.



(E)-5-(hex-3-en-1-yl)dihydrofuran-2(3H)-one (3c)[3]: Following the general procedure, **3c** was obtained as a colorless oil (94.2 mg, 0.56 mmol, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.36-1.65 (m, 6H), 1.68-1.79 (m, 1H), 1.80-1.89 (m, 1H), 1.96-2.17 (m, 2H), 2.26-2.35 (m, 1H), 2.47-2.55 (m, 2H), 4.48 (ddtd, J = 2.9, 5.1, 6.5, 7.9 Hz, 1H), 5.33-5.51 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 18.0 (CH_3), 25.2 (CH_2), 28.1 (CH_2), 29.0 (CH_2), 32.2 (CH_2), 35.1 (CH_2), 81.0 (CH), 125.7 (CH), 130.6 (CH), 177.4 (C) ppm; IR (ATR): ν = 2933, 2859, 1768, 1458, 1350, 1174, 967, 913 cm^{-1}; GCMS (EI): m/z (%): 168 (5) [M^+], 140 (7) [$M^+ – CO$], 85 (42) [$M^+ – C_6H_{11}$], 68 (100); HRMS (ESI-TOF): m/z: calcd for $C_{10}H_{16}O_2$: 169.1223 [$M+H]^+$; found: 169.1220.



5-(tert-butyl)dihydrofuran-2(3H)-one (3d)[4]: Following the general procedure, **3d** was obtained as a colorless oil (76.8 mg, 0.54 mmol, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.95 (s, 9H), 1.94-2.05 (m, 1H), 2.07-2.14 (m, 1H), 2.51-2.55 (m, 2H), 4.19 (dd, J = 6.8, 8.9 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 23.1 (CH_2), 25.0 (3 x CH_3), 29.5 (CH_2), 34.0 (CH_2), 88.4 (CH), 177.6 (C) ppm; IR (ATR): ν = 2958, 2872, 1769, 1479, 1367, 1343, 1177, 1005, 986 cm^{-1}; GCMS (EI): m/z (%): 142 (1) [M^+], 127 (8) [$M^+ – CH_3$], 114 (5) [$M^+ – CO$], 85 (100) [$M^+ – C_4H_9$]; HRMS (ESI-TOF): m/z: calcd for $C_8H_{14}O_2$: 143.1067 [$M+H]^+$; found: 143.1063.



5-phenyldihydrofuran-2(3H)-one (3e)[5]: Following the general procedure, **3e** was obtained as a white solid (35.7 mg, 0.22 mmol, 22%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.13-2.26 (m, 1H), 2.62-2.71 (m, 3H), 5.51 (t, J = 8.0 Hz, 1H), 7.31-7.41 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 29.0 (CH_2), 31.1 (CH_2), 81.3 (CH), 125.4 (2 x CH), 128.5 (CH), 128.9 (2 x CH), 139.5 (C), 177.0 (C) ppm; IR (ATR): ν = 2987, 2959, 2929, 1760, 1495,

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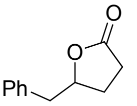
[2] Sigma-Aldrich Co., Ref. W236004. CAS# [706-14-9].

[3] D. J. Gavin and N. W. A. Geraghty, *Synthetic Commun.,* 1994, **24**, 1351.

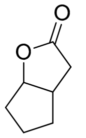
[4] E. O. Martins and J. L. Gleason, *Org. Lett.,* 1999, **1**, 1643.

[5] Sigma-Aldrich Co., Ref. 176451. CAS# [1008-76-0].

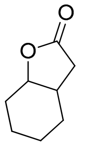
1454, 1417, 1328, 1313, 1297 cm^{-1}; GCMS (EI): *m/z* (%): 162 (100) [M$^+$], 117 (52), 107 (50), 85 (2) [M$^+$–C_6H_5]; HRMS (EI): *m/z*: calcd for $C_{10}H_{10}O_2$: 162.0675 [M$^+$]; found: 162.0671.



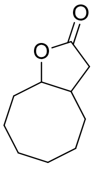
5-benzyldihydrofuran-2(3H)-one (3f)[6]: Following the general procedure, **3f** was obtained as a colorless oil (100.4 mg, 0.57 mmol, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.91-2.02 (m, 1H), 2.21-2.30 (m, 1H), 2.34-2.51 (m, 2H), 2.93 (dd, *J* = 6.3, 14.0 Hz, 1H), 3.07 (dd, *J* = 6.1, 14.0 Hz, 1H), 4.73 (dq, *J* = 6.4, 7.6 Hz, 1H), 7.22-7.34 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 27.3 (CH_2), 28.8 (CH_2), 41.5 (CH_2), 80.9 (CH), 127.1 (CH), 128.8 (2 x CH), 129.6 (2 x CH), 136.0 (C), 177.1 (C) ppm; IR (ATR): ν = 3062, 3028, 2943, 1763, 1497, 1454, 1352, 1285, 1171 cm^{-1}; GCMS (EI): *m/z* (%): 176 (47) [M$^+$], 148 (2) [M$^+$–CO], 85 (100) [M$^+$–C_7H_7]; HRMS (EI): *m/z*: calcd for $C_{11}H_{12}O_2$: 176.0832 [M$^+$]; found: 176.0831.



Hexahydro-2H-cyclopenta[b]furan-2-one (3g)[7]: Following the general procedure, **3g** was obtained as a colorless oil (65.6 mg, 0.52 mmol, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.49-1.56 (m, 1H), 1.61-1.90 (m, 4H), 1.99-2.07 (m, 1H), 2.28 (dd, *J* = 2.0, 17.5 Hz, 1H), 2.82 (dd, *J* = 1.0, 17.7 Hz, 1H), 2.82-2.91 (m, 1H), 4.99 (ddd, *J* = 1.6, 4.9, 6.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 23.6 (CH_2), 33.7 (CH_2), 33.8 (CH_2), 36.2 (CH_2), 38.1 (CH), 86.5 (CH), 177.9 (C) ppm; IR (ATR): ν = 2959, 2872, 1761, 1418, 1355, 1172, 1097, 1026, 982 cm^{-1}; GCMS (EI): *m/z* (%): 126 (11) [M$^+$], 98 (56) [M$^+$–C_2H_4], 84 (12) [M$^+$–C_3H_6], 67 (100); HRMS (ESI-TOF): *m/z*: calcd for $C_7H_{10}O_2$: 127.0754 [M+H]$^+$; found: 127.0753.



Hexahydrobenzofuran-2(3H)-one (3h)[8]: Following the general procedure, **3h** was obtained as a colorless oil (88.3 mg, 0.63 mmol, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.21-1.31 (m, 2H), 1.43-1.51 (m, 2H), 1.58-1.75 (m, 3H), 2.02-2.09 (m, 1H), 2.24 (dd, *J* = 2.7, 16.8 Hz, 1H), 2.33-2.41 (m, 1H), 2.60 (dd, *J* = 6.9, 16.7 Hz, 1H), 4.50 (q, *J* = 4.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 20.0 (CH_2), 22.9 (CH_2), 27.2 (CH_2), 27.9 (CH_2), 35.0 (CH), 37.6 (CH_2), 79.2 (CH), 177.7 (C) ppm; IR (ATR): ν = 2931, 2857, 1769, 1447, 1422, 1347, 1224, 1170, 1140 cm^{-1}; GCMS (EI): *m/z* (%): 140 (6) [M$^+$], 112 (7) [M$^+$–C_2H_4], 96 (27) [M$^+$–CO_2], 81 (100); HRMS (EI): *m/z*: calcd for $C_8H_{12}O_2$: 141.0910 [M$^+$]; found: 141.0909.



Octahydrocycloocta[b]furan-2(3H)-one (3i)[9]: Following the general procedure, **3i** was obtained as a colorless oil (90.8 mg, 0.54 mmol, 54%).^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.19-2.08 (m, 11H), 2.18-2.29 (m, 1H), 2.23 (dd, *J* = 7.3, 16.5 Hz, 1H), 2.52-2.60 (m, 1H), 2.62 (dd, *J* = 8.2, 16.6 Hz, 1H), 4.68 (pd, *J* = 3.1, 7.1 Hz, 1H) ppm; ^{13}C NMR

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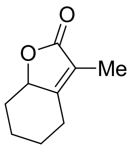
[6] C. Shu, M.-Q. Liu, Y.-Z. Sun and L.-W. Ye, *Org. Lett.,* 2012, **14**, 4958.

[7] J. D. Nguyen, E. M. D'Amato, J. M. R. Narayanam and C. R. J. Stephenson, *Nature Chem*., 2012, **4**, 854.

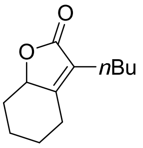
[8] N. Sasakura, K. Nakano, Y. Ichikawa and H. Kotsuki, *RSC. Adv.,* 2012, **2**, 6135.

[9] C. Bolm and G. Schlingloff, *J. Chem. Soc., Chem. Commun.,* 1995, 1247.

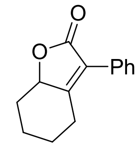
(100 MHz, $CDCl_3$) δ = 25.0 (CH_2), 25.3 (CH_2), 26.0 (CH_2), 27.0 (CH_2), 27.1 (CH_2), 28.5 (CH_2), 36.5 (CH_2), 39.1 (CH), 81.2 (CH), 176.2 (C) ppm; IR (ATR): ν = 2921, 2857, 1796, 1770, 1467, 1447, 1362, 1346, 1175, 1047 cm^{-1}; GCMS (EI): *m/z* (%): 168 (17) [M^+], 98 (100) [$M^+-C_5H_{10}$], 84 (37) [$M^+-C_6H_{12}$]; HRMS (ESI-TOF): *m/z*: calcd for $C_{10}H_{16}O_2$: 169.1223 $[M+H]^+$; found: 169.1221.



3-Methyl-5,6,7,7a-tetrahydrobenzofuran-2(4H)-one (6a)[10]: Following the general procedure, **6a** was obtained as a colorless oil (83.7 mg, 0.55 mmol, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.14-1.32 (m, 2H), 1.39-1.51 (m, 1H), 1.80 (t, J = 1.6 Hz, 3H), 1.86-1.92 (m, 1H), 1.95-2.03 (m, 1H), 2.14 (dddt, J = 1.3, 5.8, 13.0, 14.3 Hz, 1H), 2.49 (ddtd, J = 1.6, 3.2, 6.3, 12.3 Hz, 1H), 2.81 (ddt, J = 2.0, 4.2, 14.1 Hz, 1H), 4.53-4.61 (dd, J = 6.4, 11.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 8.3 (CH_3), 22.9 (CH_2), 26.4 (2 x CH_2), 34.3 (CH_2), 80.3 (CH), 119.6 (C), 162.6 (C), 175.0 (C) ppm; IR (ATR): ν = 3486, 2939, 2862, 1739, 1678, 1448, 1350, 1305, 1090, 1033, 1021 cm^{-1}; GCMS (EI): *m/z* (%): 152 (100) [M^+], 137 (2) [M^+-CH_3], 124 (39) [$M^+-C_2H_4$], 95 (95) [$M^+-C_4H_8$]; HRMS (EI): *m/z*: calcd for $C_9H_{12}O_2$: 152.0832 $[M^+]^+$; found: 152.0829.



3-Butyl-5,6,7,7a-tetrahydrobenzofuran-2(4H)-one (6b): Following the general procedure, **6b** was obtained as a colorless oil (97.1 mg, 0.50 mmol, 50%). A mixture of tautomers was observed by NMR, with the following signals for the major conformation: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.90 (t, J = 6.9 Hz, 3H), 1.24-1.41 (m, 6H), 1.56-1.75 (m, 4H), 1.84-1.95 (m, 1H), 2.00-2.08 (m, 1H), 2.33 (td, J = 4.3, 7.6 Hz, 2H), 4.20 (qdd, J = 1.5, 3.7, 7.2 Hz, 1H) ppm; IR (ATR): ν = 3467, 2934, 2861, 1728, 1450, 1369, 1227, 1173, 1111, 1075, 1017 cm^{-1}; GCMS (EI): *m/z* (%): 194 (86) [M^+], 179 (6) [M^+-CH_3], 165 (41) [$M^+-C_2H_5$], 152 (100), 137 (34) [$M^+-C_4H_9$]; HRMS (EI): *m/z*: calcd for $C_{12}H_{18}O_2$: 194.1301 [M^+]; found: 194.1298.



3-Phenyl-5,6,7,7a-tetrahydrobenzofuran-2(4H)-one (6c)[11]: Following the general procedure, **6c** was obtained as a colorless oil (64.3 mg, 0.30 mmol, 30%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.23-1.42 (m, 2H), 1.48-1.59 (m, 1H), 1.93-2.05 (m, 2H), 2.33 (td, J = 5.6, 13.6 Hz, 1H), 2.60 (ddtd, J = 1.7, 3.0, 6.3, 12.6 Hz, 1H), 3.13 (ddt, J = 2.0, 4.3, 14.4 Hz, 1H), 4.76 (dd, J = 6.2, 11.2 Hz, 1H), 7.30-7.51 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 22.8 (CH_2), 26.6 (CH_2), 27.0 (CH_2), 34.5 (CH_2), 80.0 (CH), 123.7 (C), 128.5 (CH), 128.7 (2 x CH), 129.0 (2 x CH), 130.0 (C), 164.1 (C), 172.7 (C) ppm; IR (ATR): ν = 2960, 2936, 2859,1732, 1659, 1493, 1444, 1260, 1092, 1038 cm^{-1}; GCMS (EI): *m/z* (%): 214 (100)

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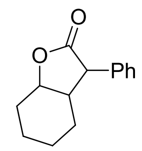
[10] K. Matsuo and M. Shindo, *Org. Lett.,* 2010, **12**, 5346.

[11] J. Barluenga, M. G. Suero, I. Pérez-Sánchez and J. Flórez, *J. Am. Chem.Soc.,* 2008, **130**, 2708.

[M^+], 185 (87) [M^+–C_2H_4], 157 (22) [M^+–C_4H_8]; HRMS (EI): *m/z*: calcd for $C_{14}H_{14}O_2$: 214.0988 [M^+]; found: 214.0985.



3-Phenylhexahydrobenzofuran-2(3H)-one (6c')[12]**:** Following the general procedure, **6c'** was obtained as a colorless oil (121.1 mg, 0.56 mmol, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.32-1.43 (m, 1H), 1.47-1.62 (m, 3H), 1.66-1.77 (m, 3H), 1.94-2.01 (m, 1H), 2.62 (dq, J = 5.8, 8.7 Hz, 1H), 3.66 (d, J = 8.6 Hz, 1H), 4.62 (dt, J = 5.7, 7.6 Hz, 1H), 7.21-7.39 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.3 (CH_2), 21.6 (CH_2), 25.7 (CH_2), 28.7 (CH_2), 43.6 (CH), 50.9 (CH), 77.4 (CH), 127.7 (CH), 128.4 (2 x CH), 129.0 (2 x CH), 135.0 (C), 177.6 (C) ppm; IR (ATR): ν = 2933, 2859, 1763, 1734, 1497, 1451, 1372, 1241, 1157, 1118 cm^{-1}; GCMS (EI): *m/z* (%): 216 (3) [M^+], 188 (1) [M^+–C_2H_4], 172 (100); HRMS (EI): *m/z*: calcd for $C_{14}H_{16}O_2$: 216.1145 [M^+]; found: 216.1144.

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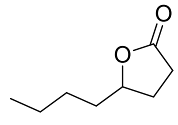
[12] T. H. Black, W. J. DuBay III and P. S. Tully, *J. Org. Chem.,* 1988, **53**, 5922.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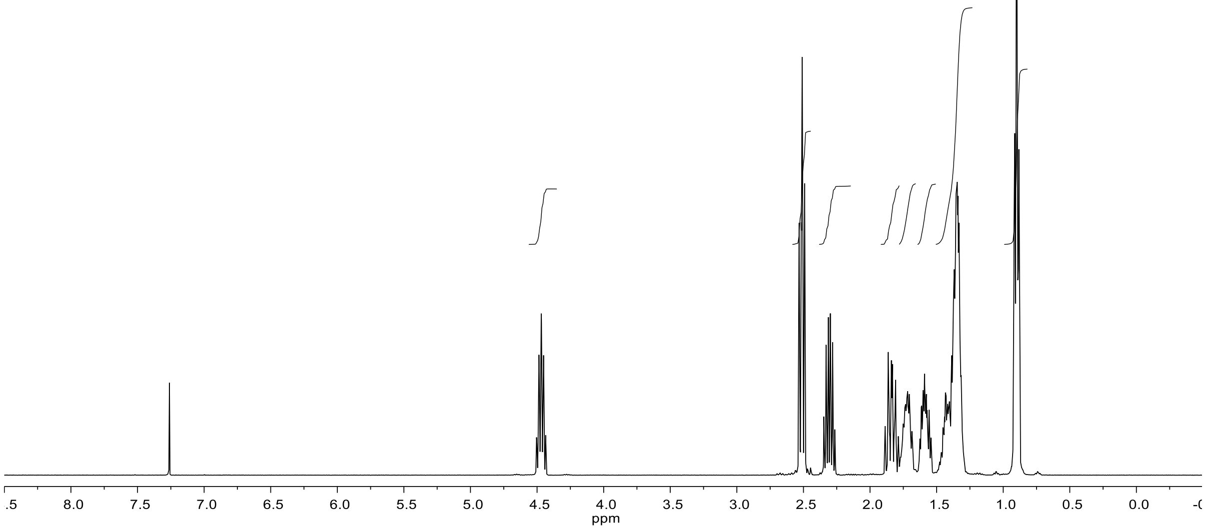
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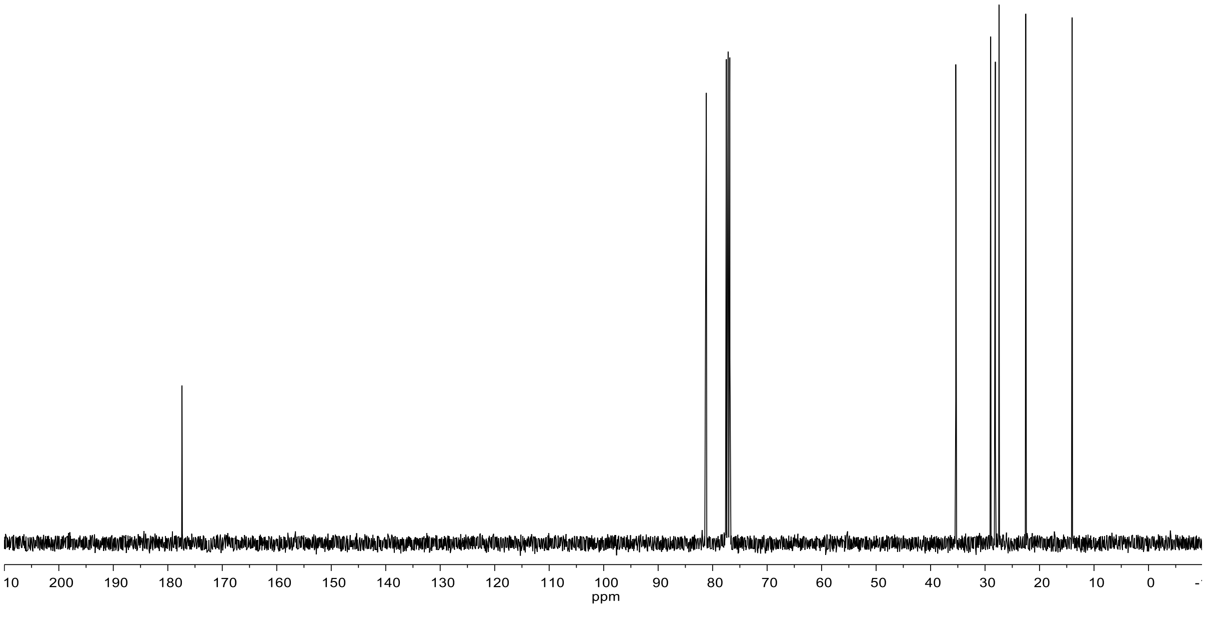
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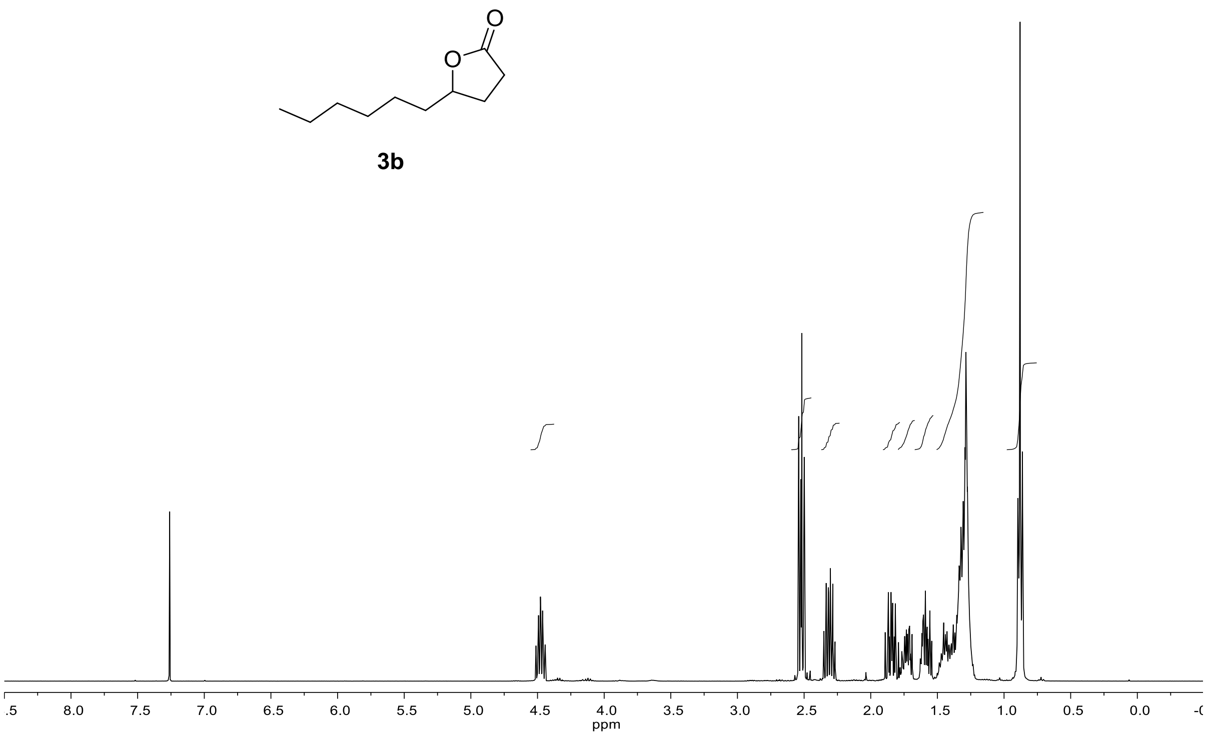
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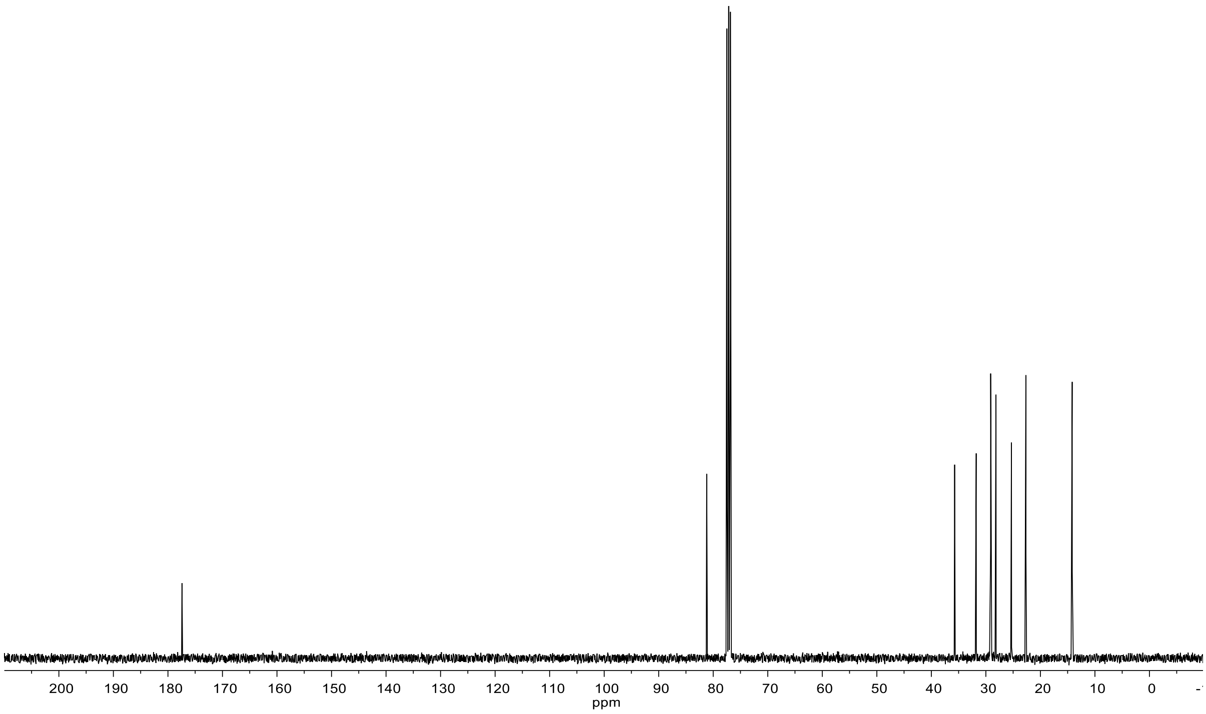
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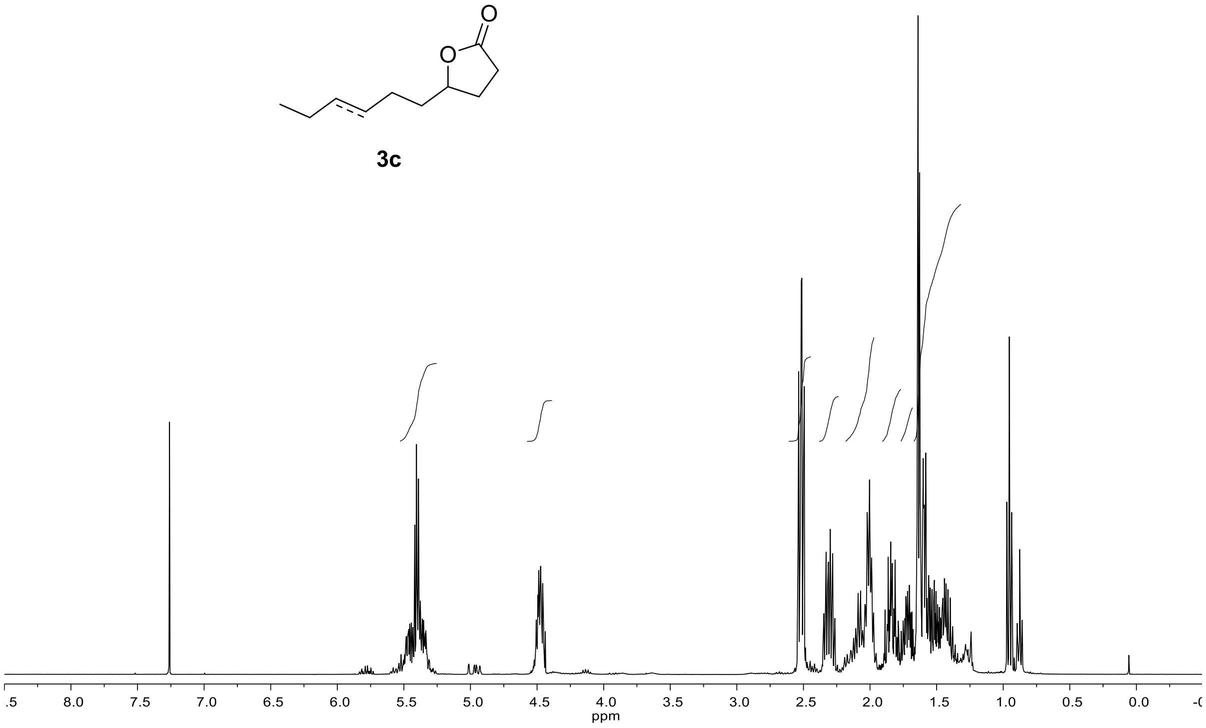

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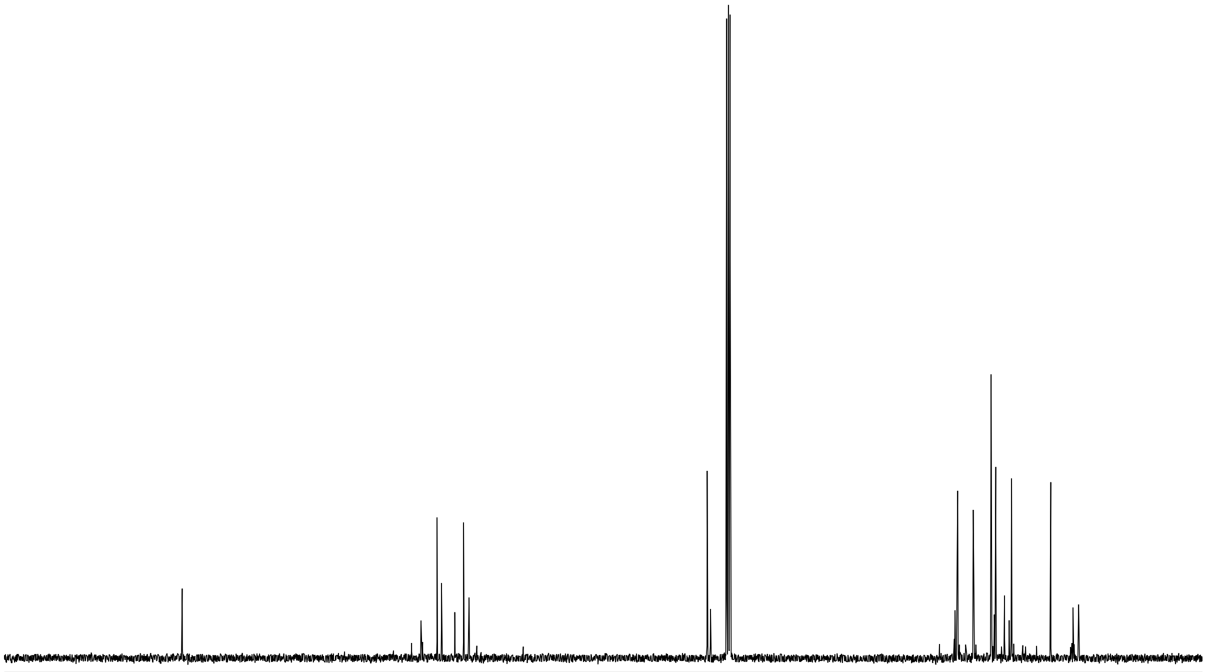

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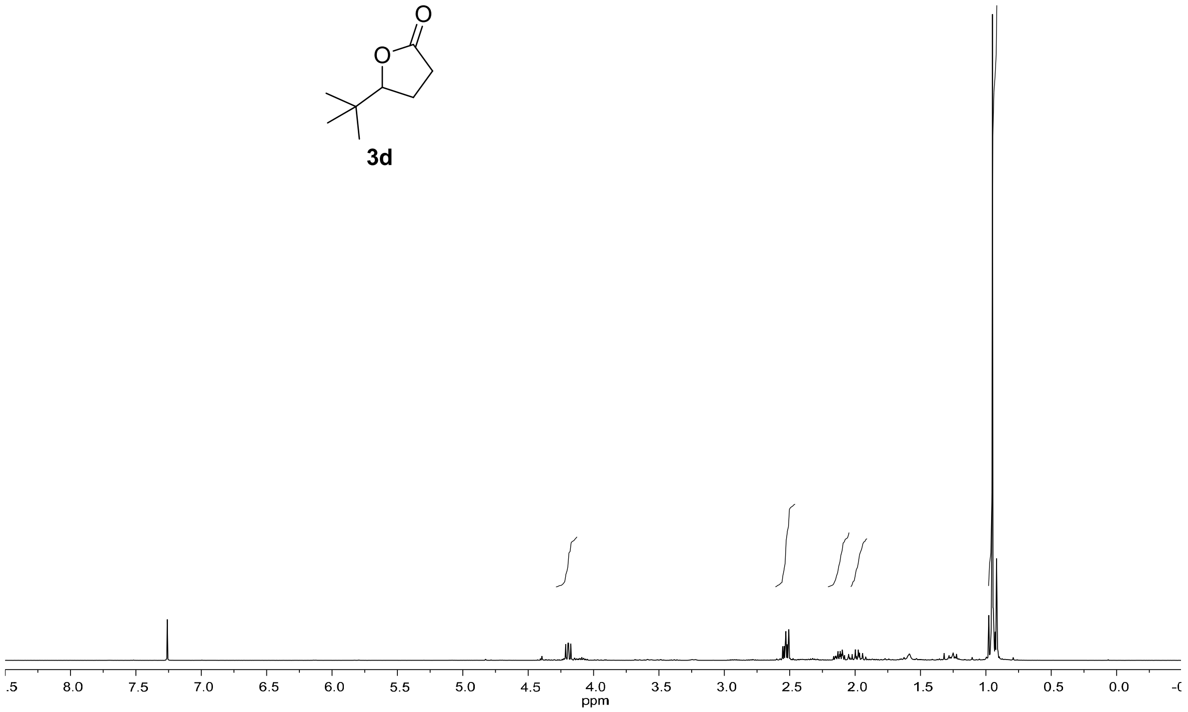
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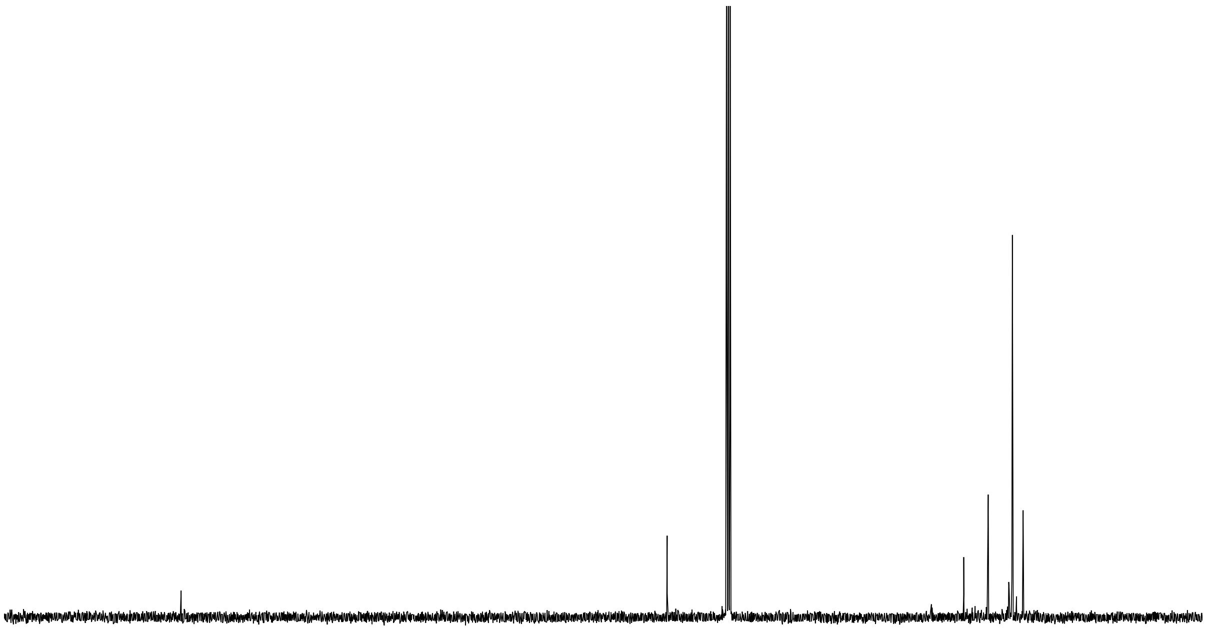
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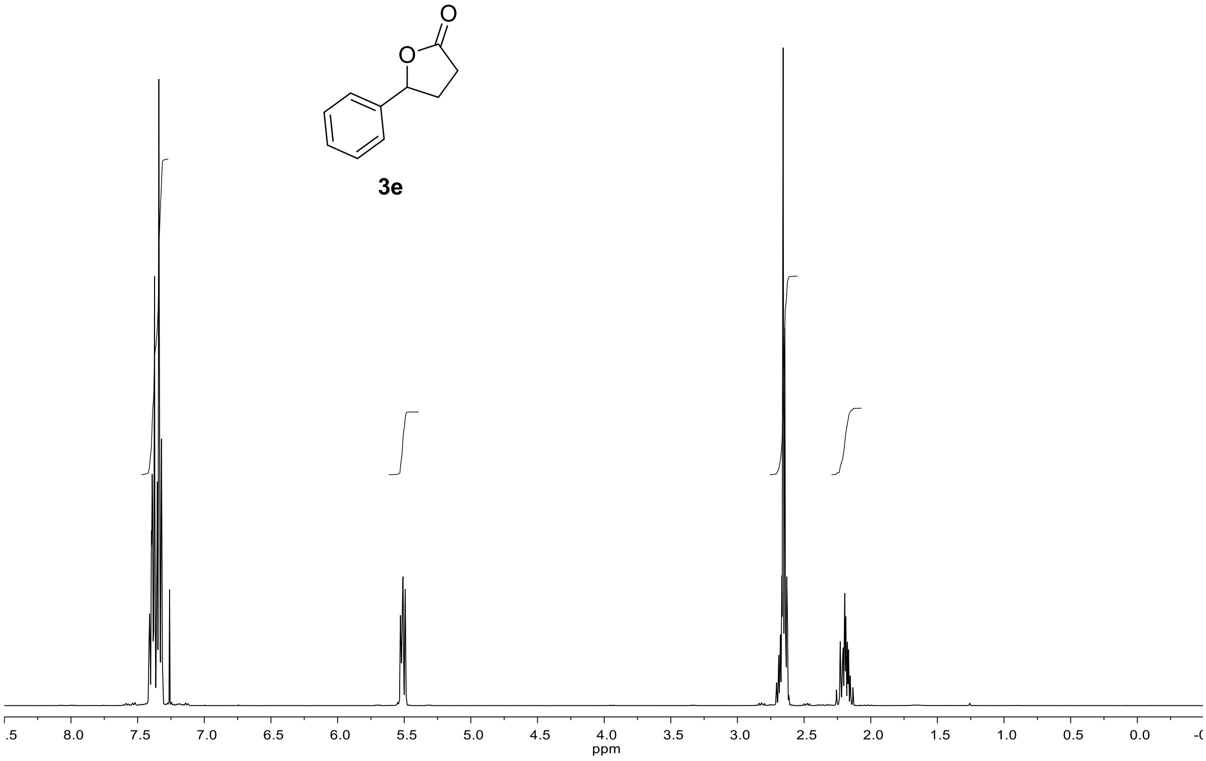
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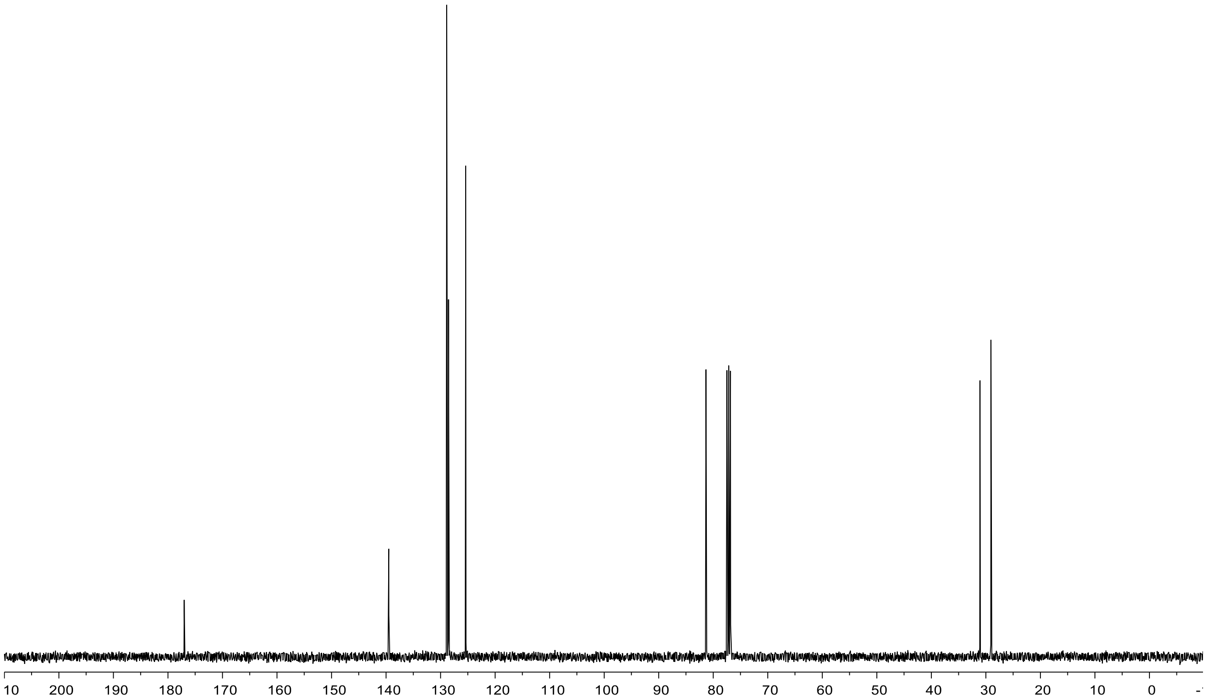
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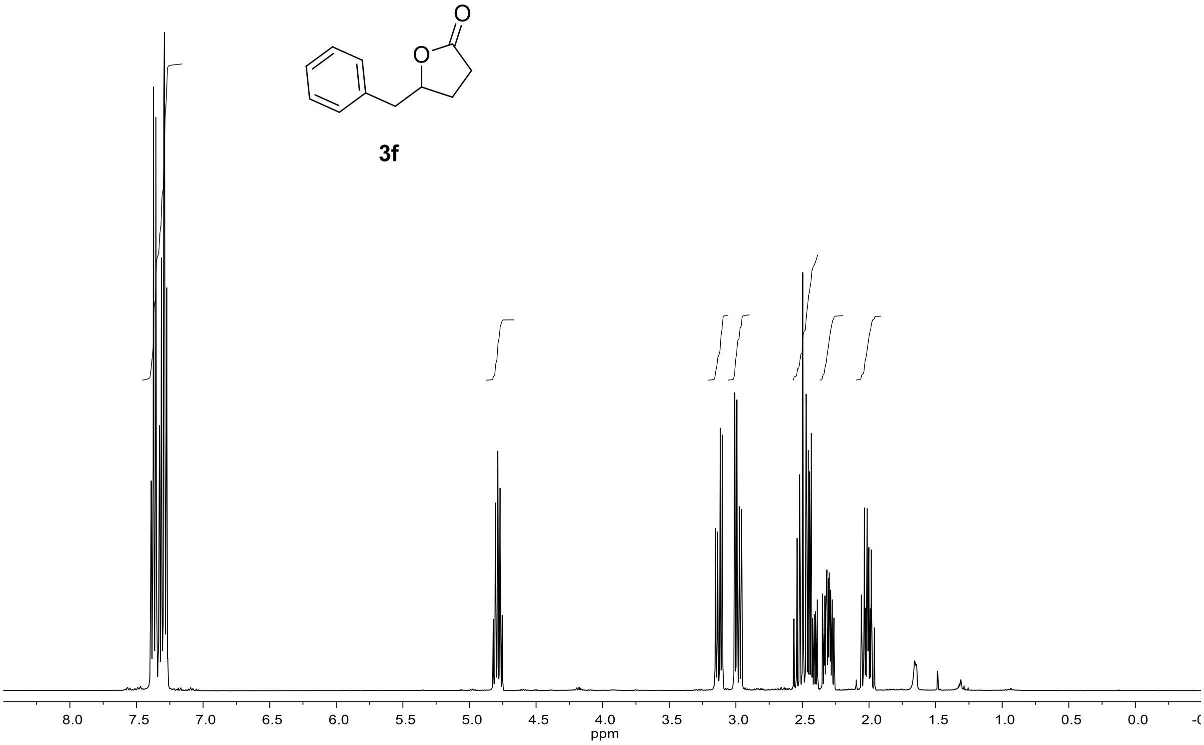
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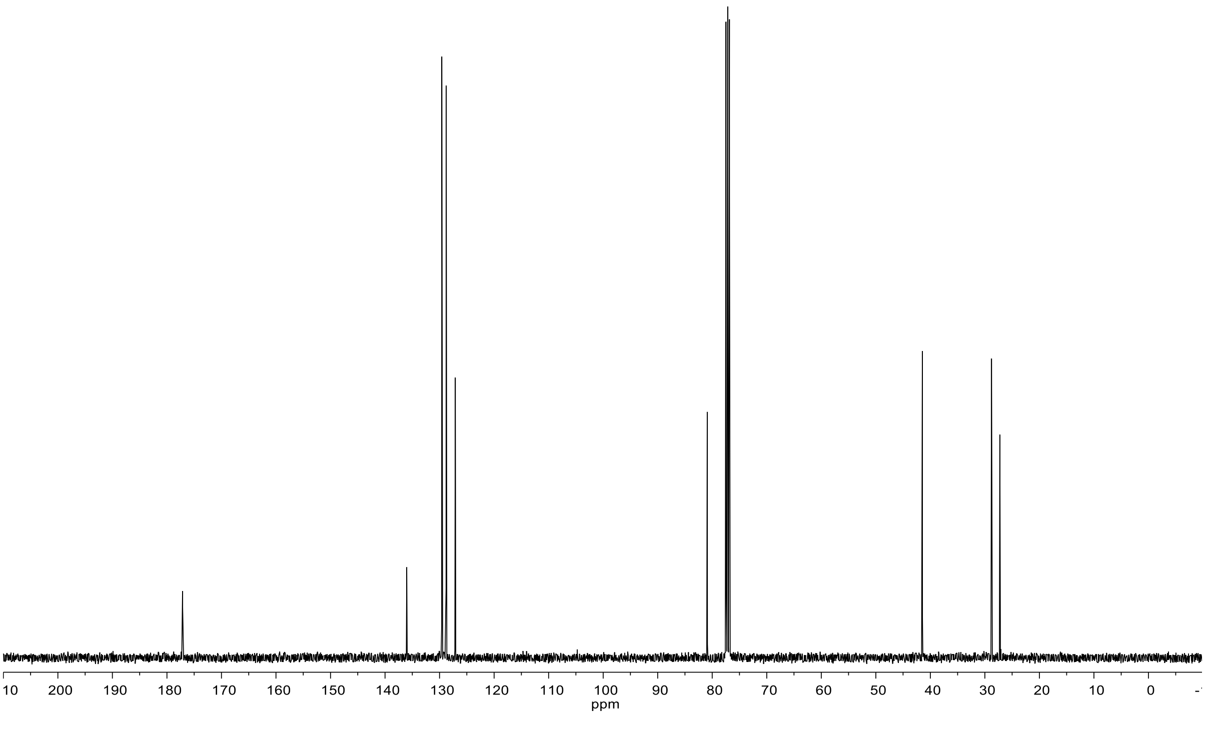
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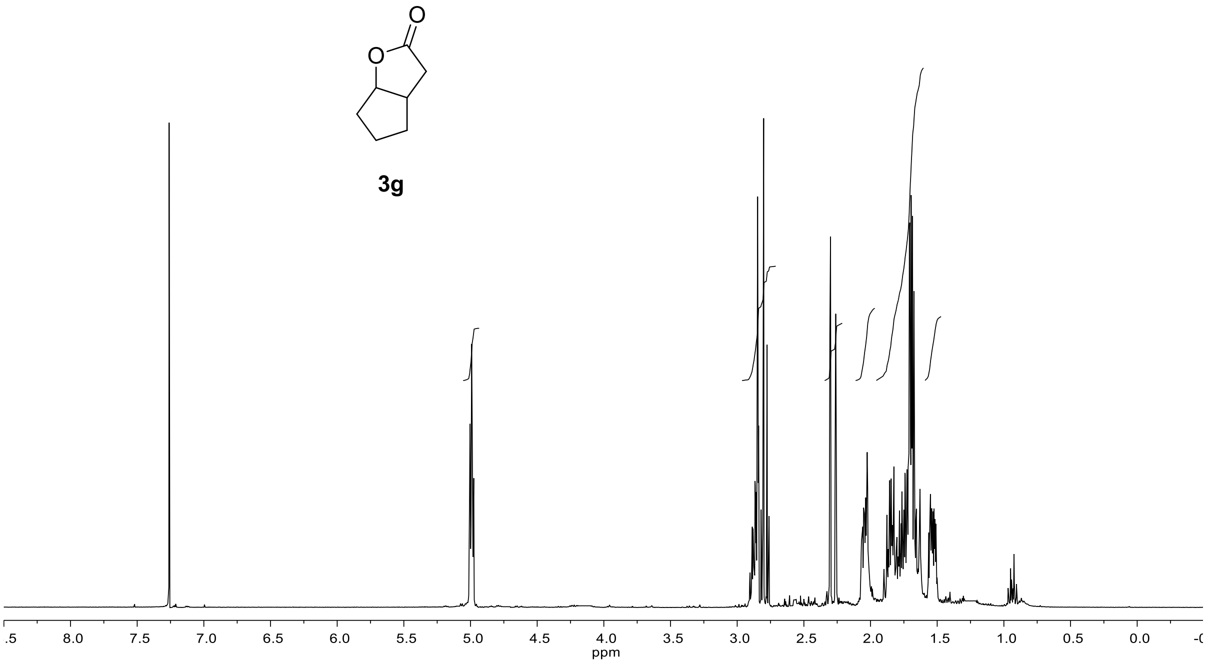
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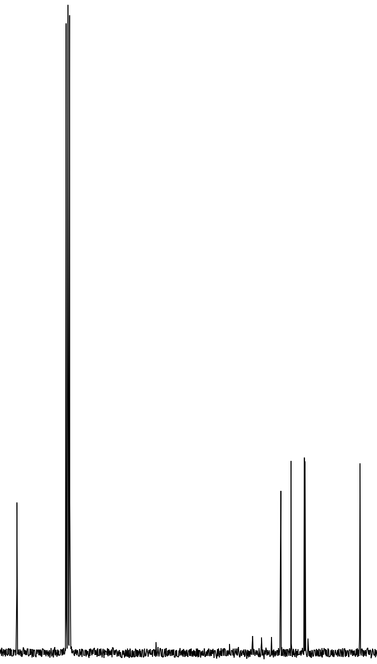
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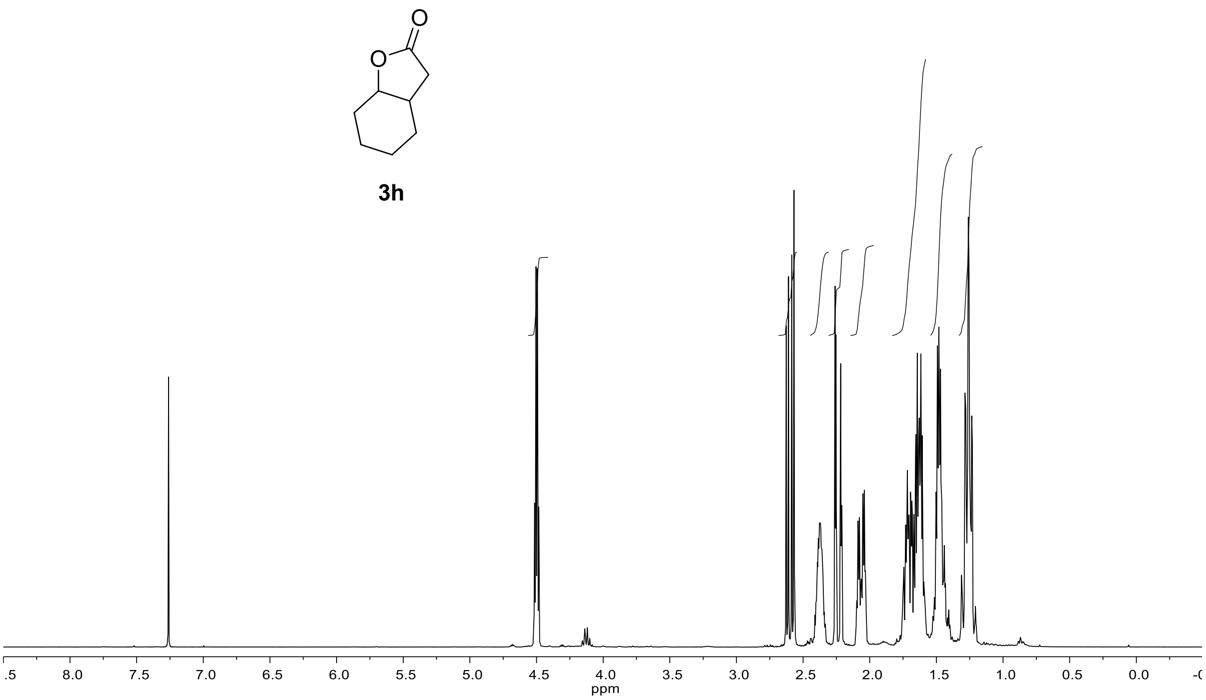

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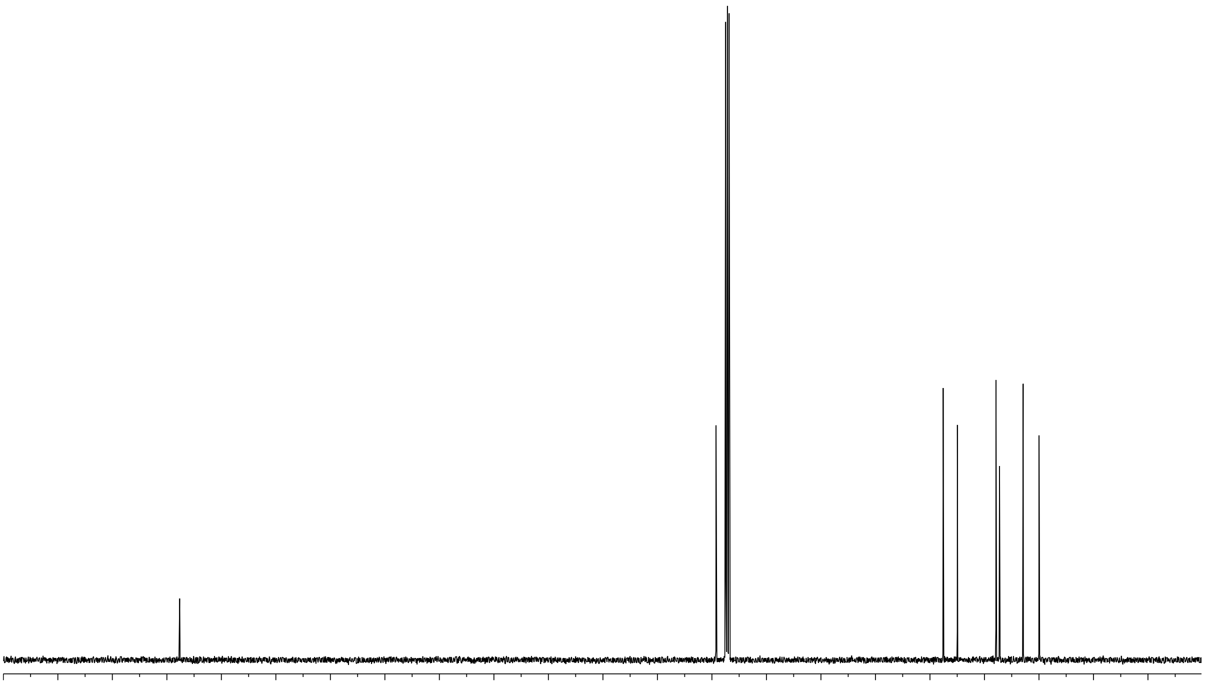

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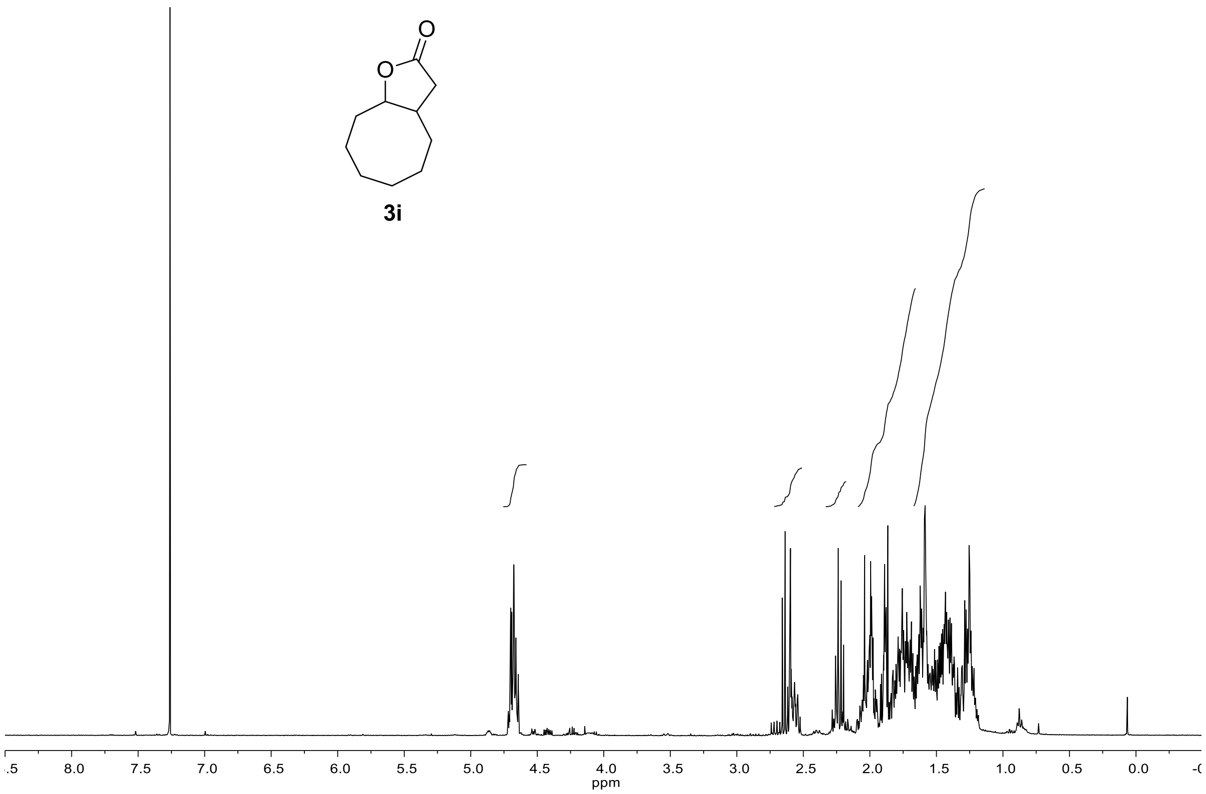
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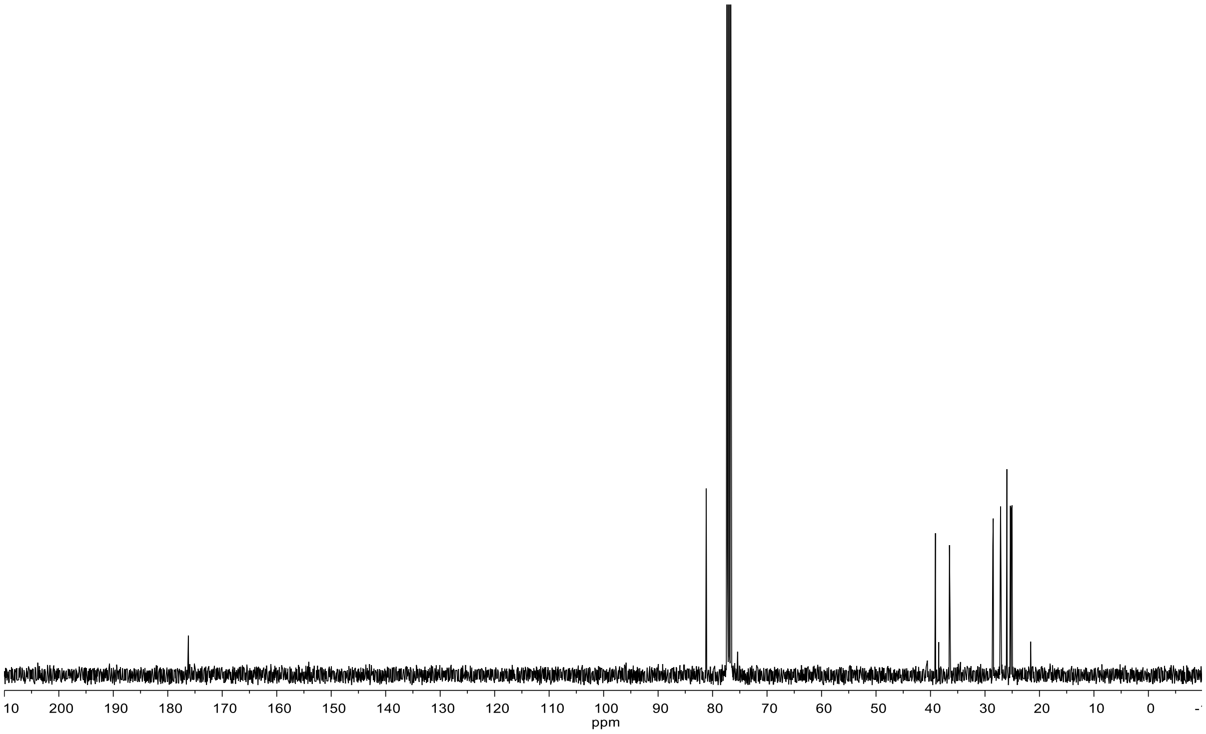
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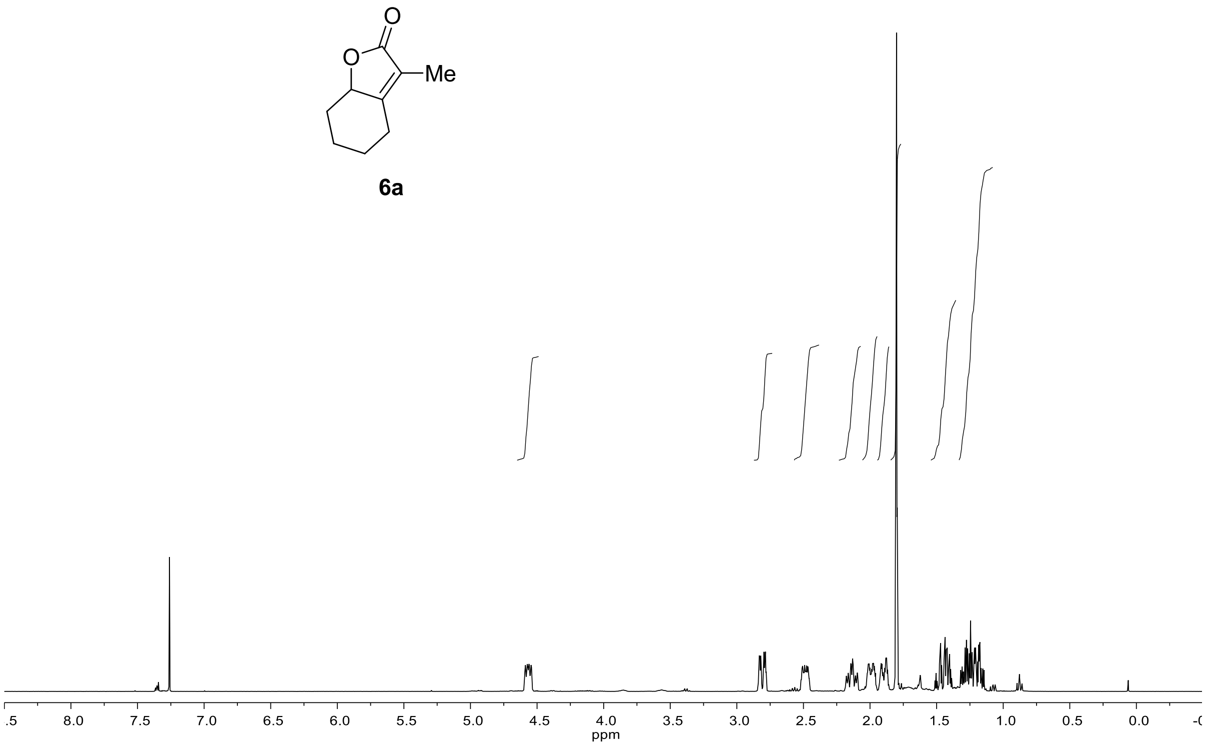
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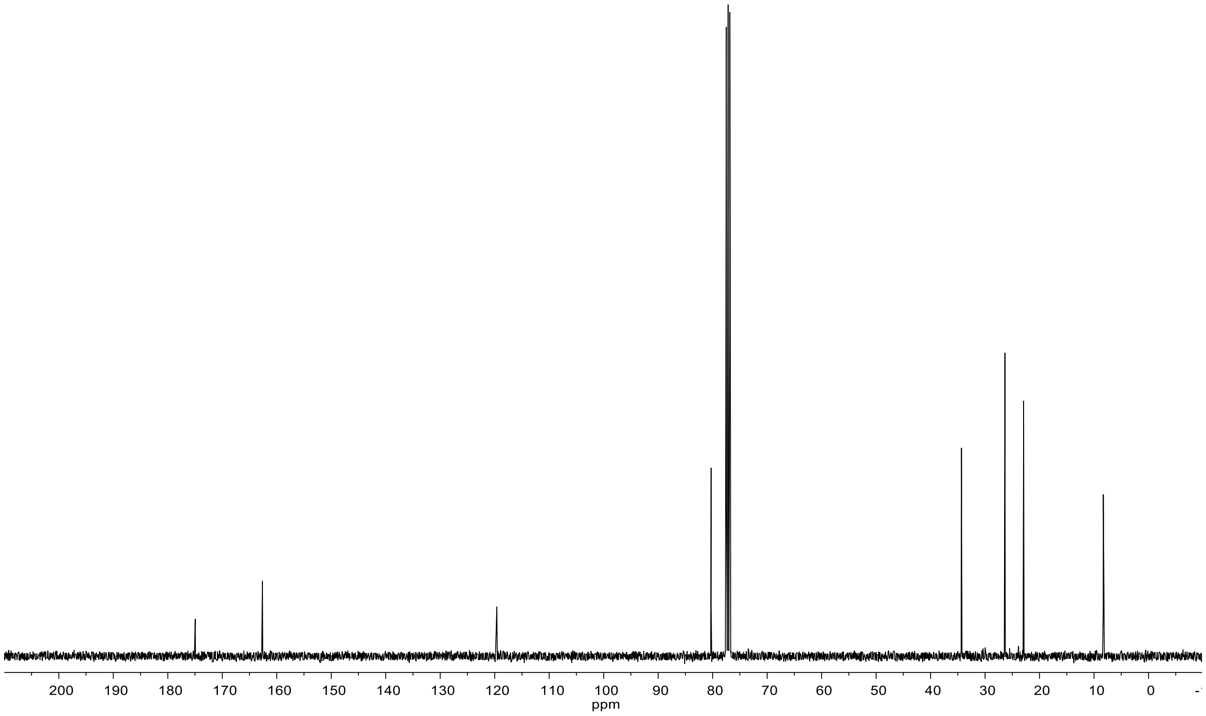
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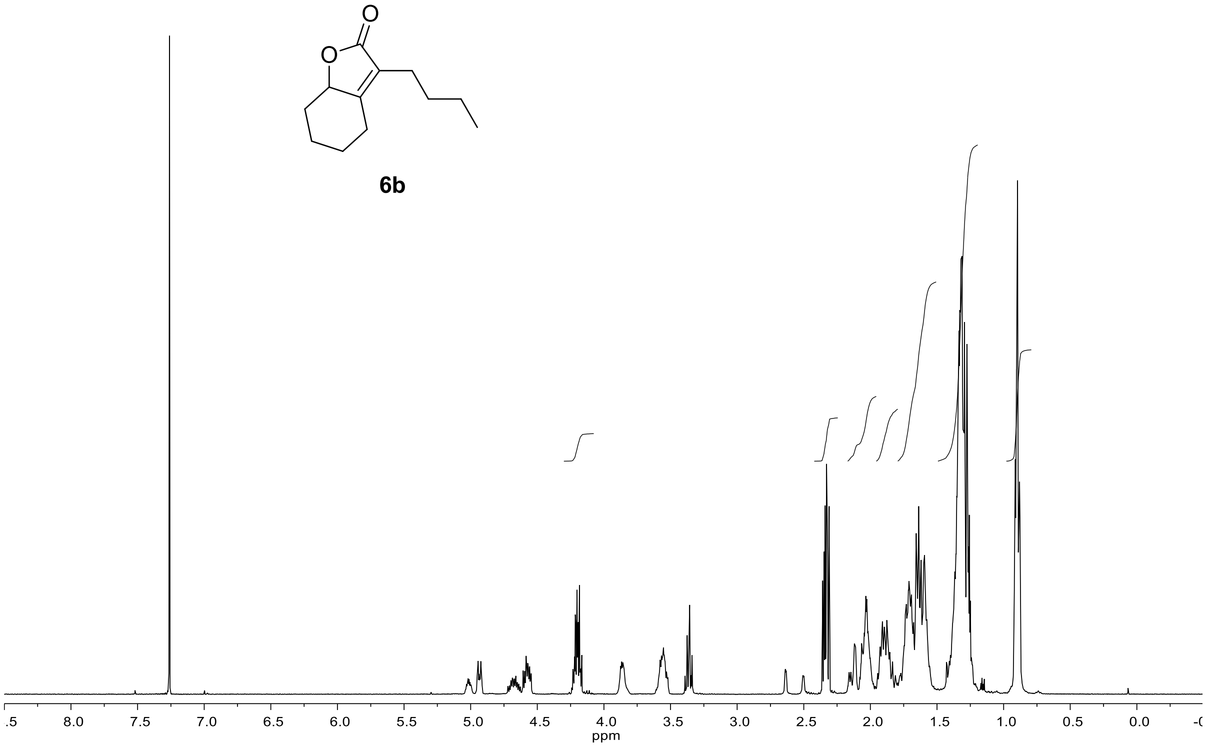
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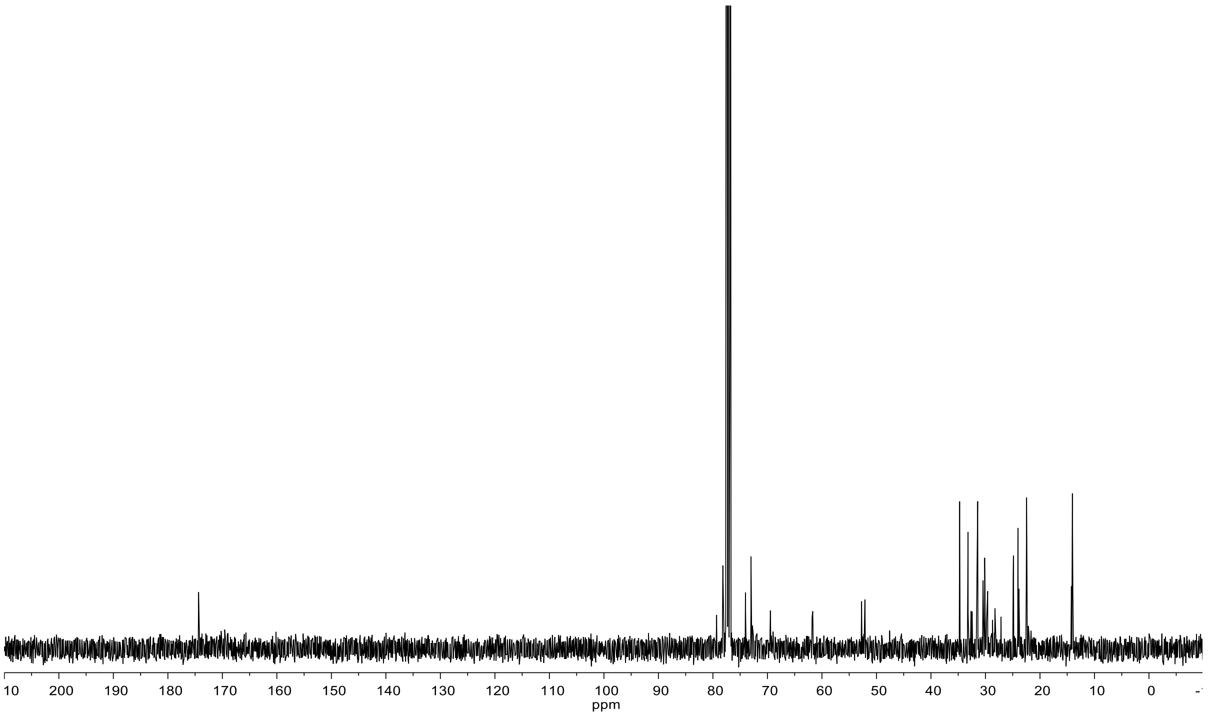
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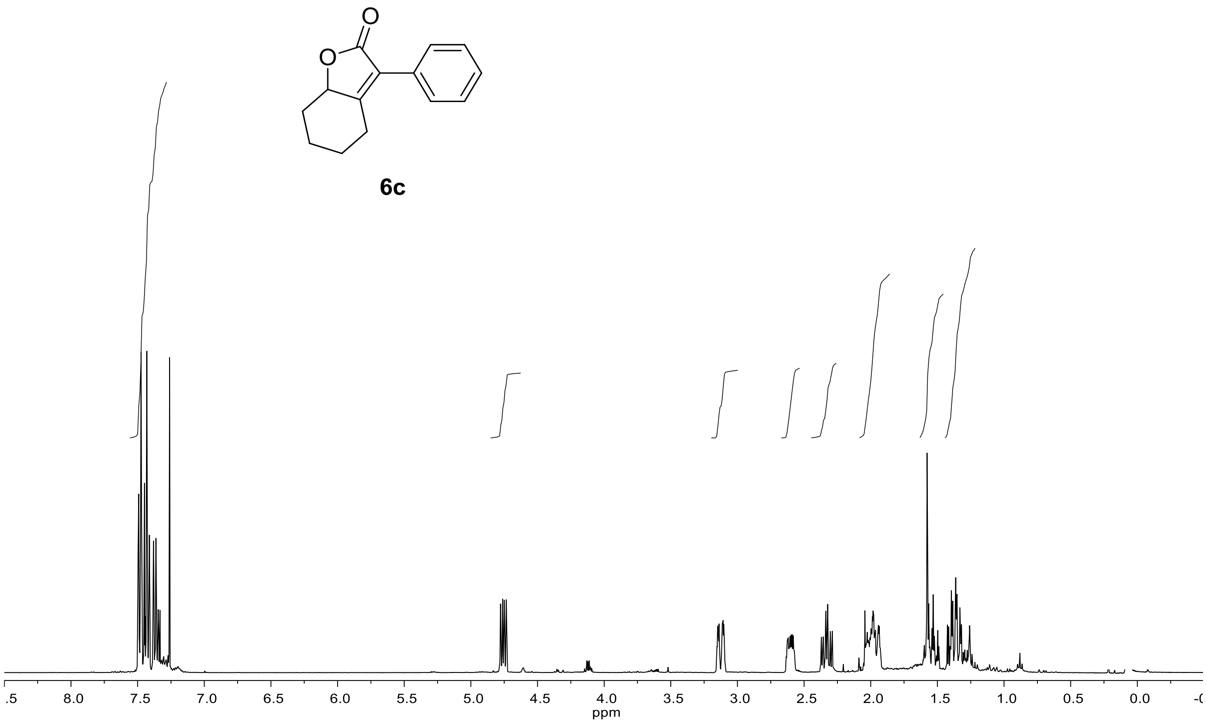

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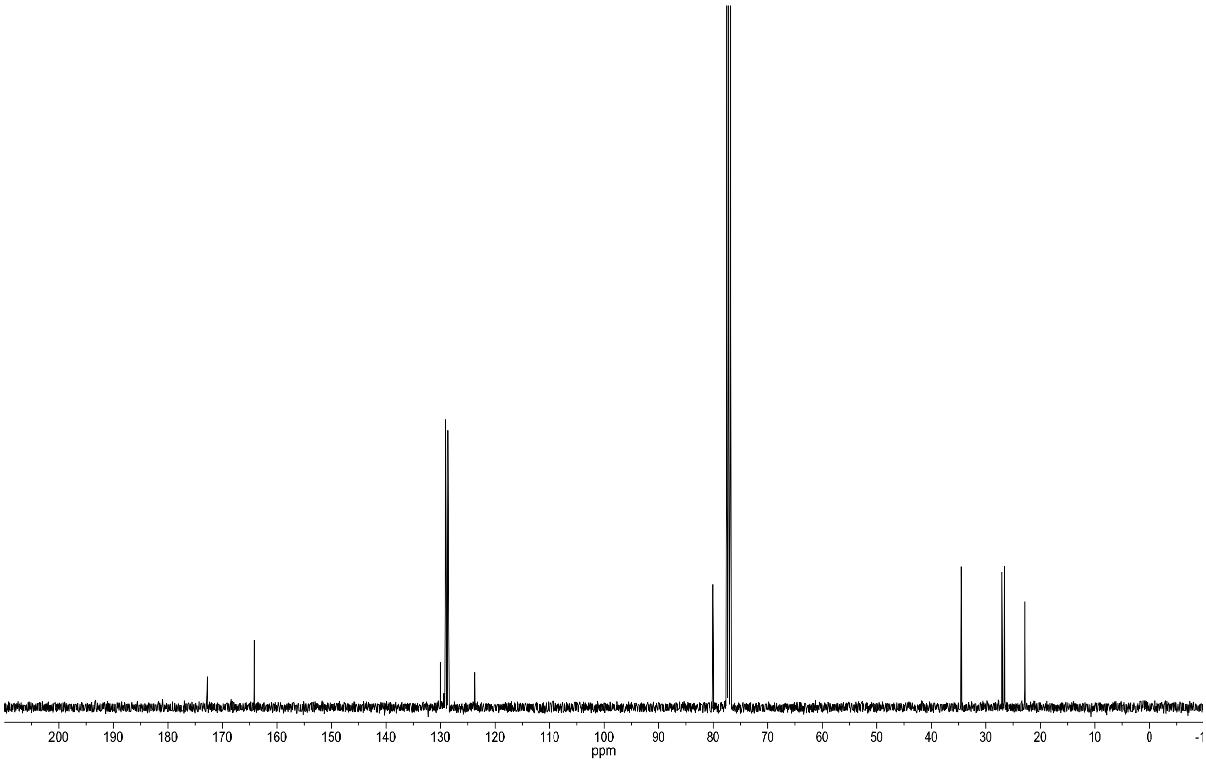

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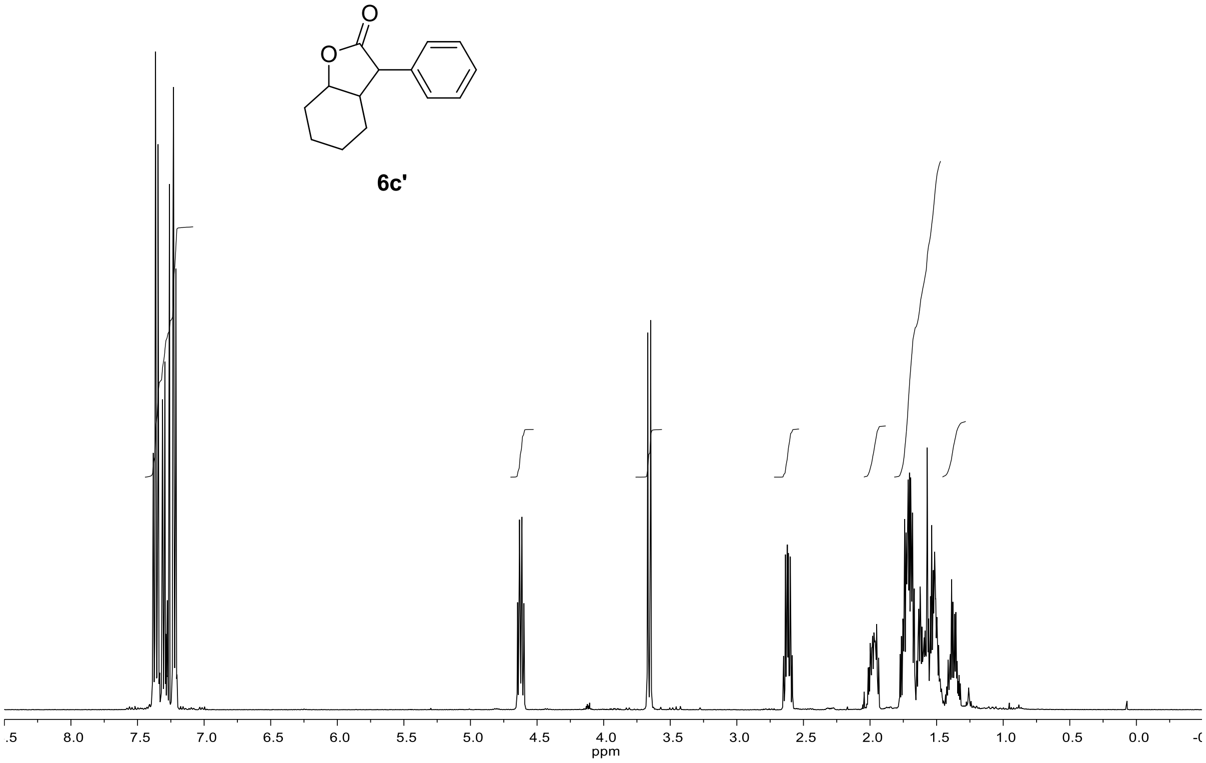
6c'
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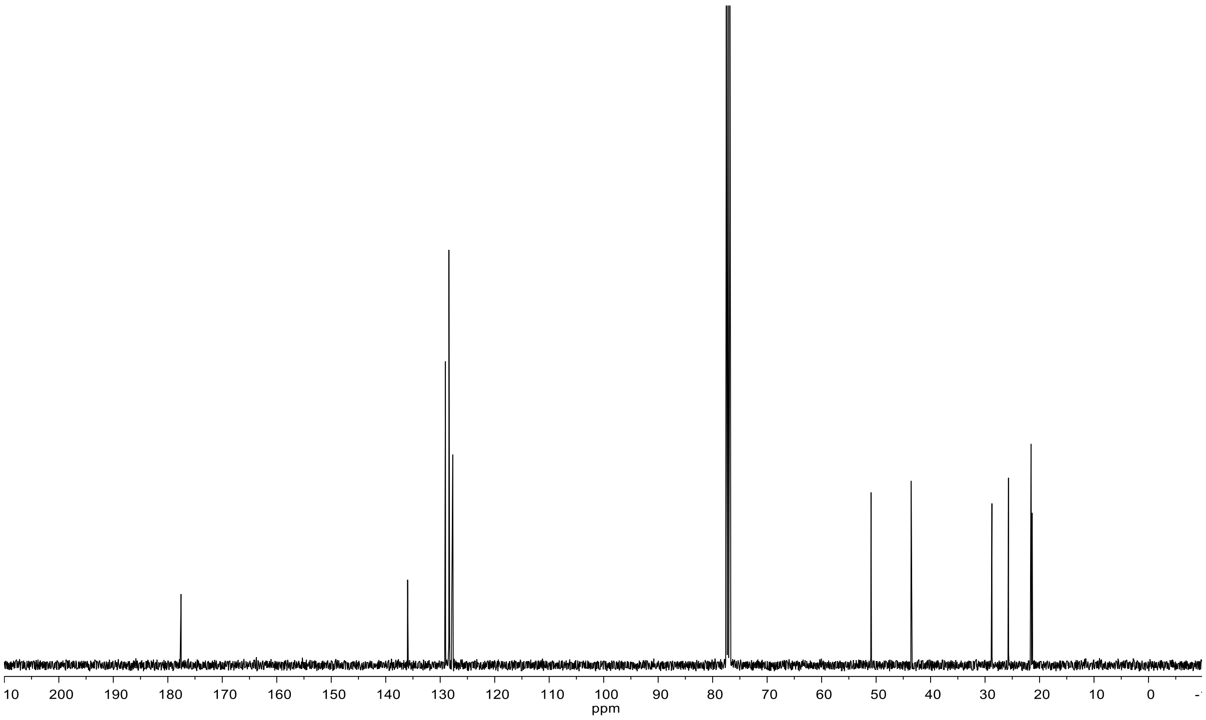
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ppm