SUPPORTING INFORMATION

Functionalized 3(2*H*)-furanones via photooxygenation of (β-keto)-2-substituted furans: Application to the biomimetic synthesis of merrekentrone C

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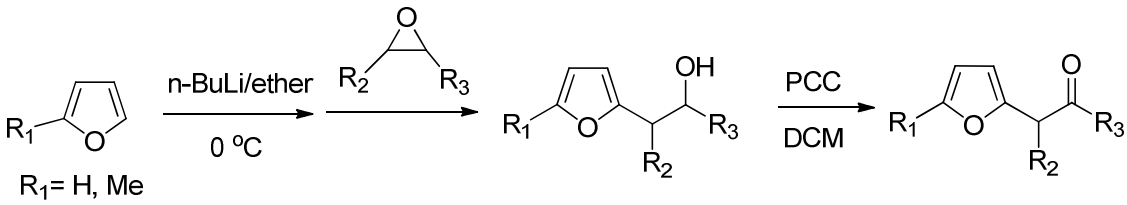
Experimental Section

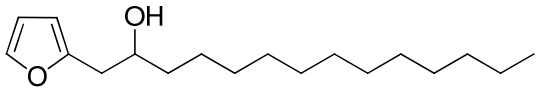
Synthesis of β-keto-2-substituted furans

Method A: Addition of furyl lithium to epoxides[1] followed by PCC oxidation of the resulting alcohols



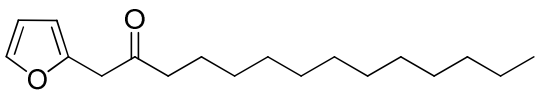
In a two necked flask were placed under an inert atmosphere furan or 2-methylfuran (20 mmol) in dry diethyl ether (50 mL). At 0 °C were added n-BuLi (15 mmol, 1.6 M in hexanes) and the reaction was let at room temperature for 2 hours. Then the appropriate epoxide (10 mmol) was added at 0 °C and the reaction mixture was left for an additional 16 h at room temperature. After quenching with H_2O, and extraction with ether, the solvent were evaporated and the residue was chromatographed using hexane/ethyl acetate~5-10/1. The β-hydroalkyl-2-substituted furans were isolated in 55-80% yields (based on the epoxide). The purified furans were subsequently oxidized with 1.5 equiv of PCC in dichloromethane (4 h, room temperature) to produce the desired β-keto-2-substituted furans in 42-78% yield after column chromatography (hexane/ethyl acetate~10-15/1).

1-(Furan-2-yl)tetradecan-2-ol



1-(Furan-2-yl)tetradecan-2-ol was prepared in 77% yield by the reaction of 2-furyl lithium with commercially available 1,2-epoxytetradecane. ^{1}H NMR (300 MHz, $CDCl_3$): 7.35 (br s, 1H), 6.30 (m, 1H), 6.10 (br s, 1H), 3.88 (m, 1H), 2.84 (dd, J_1 = 15.0 Hz, J_2 = 5.0 Hz, 1H), 2.71 (dd, J_1 = 15.0 Hz, J_2 = 8.0 Hz, 1H), 1.72 (br s, 1H -OH), 1.43-1.52 (m, 2H), 1.20-1.40 (m, 18H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 153.0, 141.6, 110.3, 106.9, 70.5, 36.7, 36.1, 31.9, 29.6, 29.6, 29.6, 29.6, 29.6, 29.6, 29.3, 25.6, 22.7, 14.1; MS (EI): 280 (M^+, 1%), 262 (M^+-H_2O, 4%), 197 (3%), 121 (9%), 107 (12%), 94 (20%), 82 (100%).

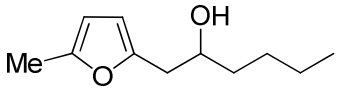
1-(Furan-2-yl)tetradecan-2-one (1)



1

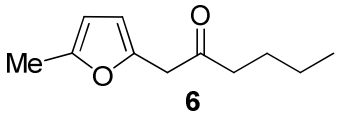
It was isolated in 78% yield after the oxidation of 1-(furan-2-yl)tetradecan-2-ol with PCC. ^{1}H NMR (300 MHz, $CDCl_3$): 7.36 (br s, 1H), 6.34 (m, 1H), 6.18 (br s, 1H), 3.69 (s, 2H), 2.44 (t, J = 7.5 Hz, 2H), 1.50-1.62 (m, 2H), 1.20-1.40 (m, 18H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 206.3, 148.4, 142.0, 110.6, 108.1, 42.4, 41.9, 31.9, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3, 29.3, 29.3, 29.1, 23.6; MS (EI): 278 (M^+, 8%), 197 (100%), 179 (1%), 137 (3%), 123 (12%), 109 (20%), 95 (37%), 81 (75%), 57 (82%); HRMS: calcd for $C_{18}H_{30}O_2$+H, 279.232; found 279.231.

1-(5-Methylfuran-2-yl)hexan-2-ol[1]



1-(5-Methylfuran-2-yl)hexan-2-ol was prepared in 74% yield by the reaction of 5-methyl-2-furyl lithium with commercially available 1,2-epoxyhexane. ^{1}H NMR (300 MHz, $CDCl_3$): 5.97 (d, J = 3.0 Hz, 1H), 5.88 (d, J = 3.0 Hz, 1H), 3.84 (m, 1H), 2.79 (dd, J_1 = 15.0 Hz, J_2 = 4.0 Hz, 1H), 2.63 (dd, J_1 = 15.0 Hz, J_2 = 8.0 Hz, 1H), 2.26 (s, 3H), 1.78 (br s, 1H - OH), 1.32-1.52 (m, 4H), 0.91 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 151.1, 151.0, 107.7, 106.0, 70.4, 36.3, 36.2, 27.8, 22.7, 14.0, 13.5.

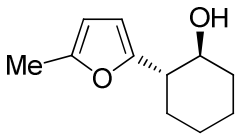
1-(5-Methylfuran-2-yl)hexan-2-one (6)[2]



6

It was isolated in 63% yield after oxidation of 1-(5-methylfuran-2-yl)hexan-2-ol with PCC. ^{1}H NMR (300 MHz, $CDCl_3$): 6.05 (d, J = 3.0 Hz, 1H), 5.91 (d, J = 3.0 Hz, 1H), 3.63 (s, 2H), 2.45 (t, J = 7.5 Hz, 2H), 2.26 (s, 3H), 1.49-1.59 (m, 2H), 1.23-1.35 (m, 2H), 0.88 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 206.8, 151.7, 146.5, 108.8, 106.4, 42.6, 41.4, 25.7, 22.2, 13.8, 13.5; MS (EI): 180 (M^+, 42%), 95 (100%), 85 (40%), 79 (9%), 65 (19%), 57 (41%).

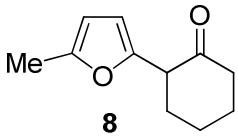
***trans*-2-(5-Methylfuran-2-yl)cyclohexanol**[2]



trans-2-(5-Methylfuran-2-yl)cyclohexanol was prepared in 61% yield by the reaction of 5-methyl-2-furyl lithium with commercially available 1,2-epoxycyclohexane. ^{1}H NMR (300 MHz, $CDCl_3$): 5.97 (d, J = 3.0 Hz, 1H), 5.88 (d, J_1 = 3.0 Hz, 1H), 3.57 (m, 1H), 2.48 (dt, J_1 = 11.0 Hz, J_2 = 3.0 Hz, 1H), 2.26 (s, 3H), 1.71-2.10 (m, 5H), 1.54 (m, 1H), 1.30 (m, 2H);

^{13}C NMR (75 MHz, $CDCl_3$): 155.4, 151.0, 106.1, 105.9, 73.0, 45.9, 34.0, 30.1, 25.4, 24.6, 13.5.

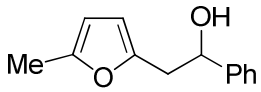
2-(5-Methylfuran-2-yl)cyclohexanone (8)[3]



8

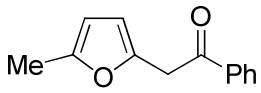
It was isolated in 60% yield after oxidation of *trans*-2-(5-methylfuran-2-yl)cyclohexanol with PCC. ^{1}H NMR (300 MHz, $CDCl_3$): 6.02 (d, J = 3.0 Hz, 1H), 5.91 (d, J = 3.0 Hz, 1H), 3.64 (dd, J_1 = 10.5 Hz, J_2 = 5.5 Hz, 1H), 2.45-2.54 (m, 1H), 2.36-2.43 (m, 1H), 2.26 (s, 3H), 2.22-2.29 (m, 1H), 1.92-2.11 (m, 3H), 1.72-1.89 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 208.9, 151.3, 150.6, 107.3, 106.1, 50.7, 41.5, 32.2, 27.6, 24.3, 13.5; MS (EI): 178 (M^+, 32%), 150 (19%), 121 (100%), 107 (27%), 95 (23%), 79 (19%).

2-(5-Methylfuran-2-yl)-1-phenylethanol[2]



2-(5-Methylfuran-2-yl)-1-phenylethanol was prepared in 80% yield by the reaction of 5-methyl-2-furyl lithium with commercially available epoxystyrene. ^{1}H NMR (300 MHz, $CDCl_3$): 7.29-7.38 (m, 5H), 5.98 (d, J = 3.0 Hz), 5.89 (d, J = 3.0 Hz), 4.97 (dd, J_1 = 8.0 Hz, J_2 = 5.0 Hz, 1H), 3.02 (dd, J_1 = 5.0 Hz, J_2 = 3.0 Hz, 1H) 2.95 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 1H), 2.29 (s, 3H), 2.23 (br s, 1H, -OH); ^{13}C NMR (75 MHz, $CDCl_3$): 151.3, 150.4, 143.4, 128.4, 127.6, 125.7, 108.1, 106.1, 72.9, 38.6, 13.5.

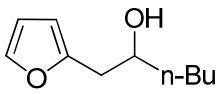
2-(5-Methylfuran-2-yl)-1-phenylethanone (10)[4]



10

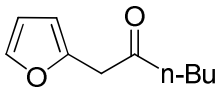
It was isolated in 42% yield after oxidation of 2-(5-methylfuran-2-yl)-1-phenylethanol with PCC. ^{1}H NMR (300 MHz, $CDCl_3$): 8.00 (d, J = 7.0 Hz, 2H), 7.57 (t, J = 7.0 Hz, 1H), 7.47 (t, J = 7.0 Hz, 2H), 6.10 (d, J = 3.0 Hz, 1H), 5.91 (d, J = 3.0 Hz, 1H), 4.25 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 195.3, 151.7, 146.3, 136.3, 133.3, 128.6, 109.0, 106.5, 38.5, 13.5; MS (EI): 200 (M^+, 30%), 171 (2%), 157 (1%), 128 (3%), 115 (2%), 105 (100%), 95 (85%), 77 (49%), 65 (5%), 51 (18%).

1-(Furan-2-yl)hexan-2-ol[2]



1-(Furan-2-yl)hexan-2-ol was prepared in 71% yield by reaction of 2-furyl lithium with commercially available 1,2-epoxyhexane. ^{1}H NMR (300 MHz, $CDCl_3$): 7.34 (br s, 1H), 6.31 (br s, 1H), 6.10 (br s, 1H), 3.88 (m, 1H), 2.86-2.82 (dd, J = 2.0 Hz, J = 9.0 Hz, 1H), 2.74-2.69 (dd, J_1 = 4.5 Hz, J_2 = 9.0 Hz, 1H), 1.83 (br s, 1H), 1.53-1.27 (m, 6H), 0.91 (t, J = 4.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 153.0, 141.5, 110.3, 107.0, 70.5, 36.4, 36.2, 27.8, 22.7, 14.1.

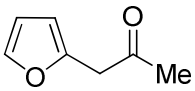
1-(Furan-2-yl)hexan-2-one (16)[3]



16

It was isolated in 78% yield after oxidation of 1-(furan-2-yl)hexan-2-ol with PCC. ^{1}H NMR (300 MHz, $CDCl_3$): 7.35 (d, J = 2.0 Hz, 1H), 6.33 (dd, J_1 = 2.0 Hz, J_2 = 3.5 Hz, 1H), 6.18 (d, J = 3.5 Hz, 1H), 3.69 (s, 2H), 2.44 (t, J = 7.0 Hz, 2H), 1.54 (m, 2H), 1.27 (m, 2H), 0.87 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 206.5, 148.4, 142.1, 110.7, 108.2, 42.5, 41.6, 25.7, 22.2, 13.8; MS (EI): 166 (M^+, 68%), 85 (95%), 81 (89%), 57 (100%), 53 (65%). HRMS: calcd for $C_{10}H_{14}O_2$+H, 167.107; found 167.106.

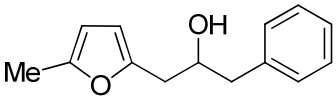
1-(Furan-2-yl)propan-2-one (18)



18

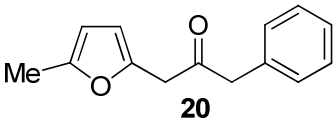
Ketone **18** is commercially available by ALFA Chem.

1-(5-Methylfuran-2-yl)-3-phenylpropan-2-ol



1-(5-Methylfuran-2-yl)-3-phenylpropan-2-ol was prepared in 68% yield by reaction of 5-methyl-2-furyl lithium with commercially available (2,3-epoxypropyl)benzene. ^{1}H NMR (300 MHz, $CDCl_3$): 7.22-7.32 (m, 5H), 6.00 (d, J = 3.0 Hz, 1H), 5.88 (d, J = 3.0 Hz, 1H), 4.11 (m, 1H), 2.68-2.88 (m, 4H), 2.26 (s, 3H), 1.91 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): 151.2, 150.6, 138.3, 129.5, 128.5, 126.5, 107.9, 106.1, 71.5, 43.1, 35.5, 13.5. HRMS: calcd for $C_{14}H_{16}O_2$+H, 217.123; found 217.121.

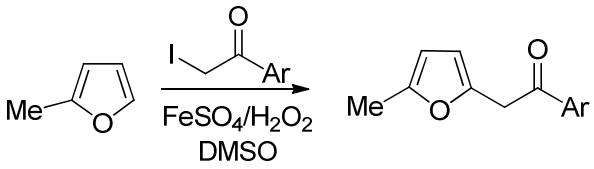
1-(5-methylfuran-2-yl)-3-phenylpropan-2-one (20)



20

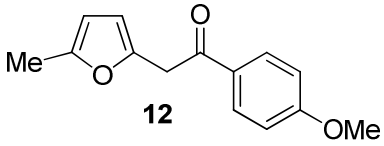
It was isolated in 55% yield after oxidation of 1-(5-methylfuran-2-yl)-3-phenylpropan-2-ol with PCC. ^{1}H NMR (300 MHz, $CDCl_3$): 7.23-7.35 (m, 3H), 7.17 (dd, J_1 = 7.0 Hz, J_2 = 1.5 Hz, 2H), 6.05 (d, J = 3.0 Hz, 1H), 5.92 (d, J = 3.0 Hz, 1H), 3.74 (s, 2H), 3.68 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 203.8, 151.8, 146.0, 133.8, 129.5, 128.7, 127.0, 109.2, 106.5, 48.7, 41.9, 13.5; MS (EI): 214 (M^+, 15%), 95 (100%), 91 (52%), 79 (5%), 65 (12%); HRMS: calcd for $C_{14}H_{14}O_2$+H, 215.107; found 215.106.

Method B: Cross coupling of α-iodo ketones with 2-methylfuran[1,5]



In a one-neck flask were placed 2-methylfuran (50 mmol, 10 equiv), the appropriate α-iodo ketone (5.0 mmol, 1 equiv), $FeSO_4.7H_2O$ (2.5 mmol, 0.5 equiv) and DMSO (20 mL). Subsequently, H_2O_2 (0.75 mL, 35% in H_2O, 8.6 mmol, 1.9 equiv) were added at 0 ^{o}C. The α-iodo ketones were prepared by iodination of the corresponding ketone with I_2/selectfluor® in methanol).[6] After 1-2 h the reaction was complete (TLC). Diethyl ether was added and the organic layer was washed with brine. The β-keto-2-substituted furans were isolated in 52-71% yield after column chromatography using hexane/ethyl acetate~10-15/1.

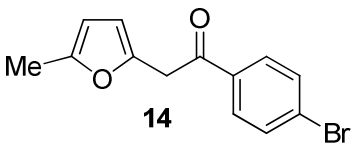
1-(4-Methoxyphenyl)-2-(5-methylfuran-2-yl)ethanone (12)[7]



12

Ketone **12** was prepared in 69% yield by coupling 2-methylfuran with α-iodo *p*-methoxyacetophenone. ^{1}H NMR (300 MHz, $CDCl_3$): 8.00 (d, J = 7.0 Hz, 2H), 6.94 (d, J = 7.0 Hz, 2H), 6.08 (d, J = 3.0 Hz, 1H), 5.90 (d, J = 3.0 Hz, 1H), 4.20 (s, 2H), 3.88 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 193.9, 163.6, 146.7, 131.0, 129.3, 113.8, 108.8, 106.5, 55.5, 38.4, 13.6; MS (EI): 230 (M^+, 6%), 135 (100%), 107 (8%), 95 (8%), 77 (12%), 64 (5%).

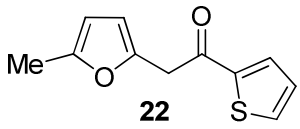
1-(4-Bromophenyl)-2-(5-methylfuran-2-yl)ethanone (14)[7]



14

Ketone **14** was prepared in 71% yield by coupling 2-methylfuran with α-iodo *p*-bromoacetophenone. ^{1}H NMR (300 MHz, $CDCl_3$): 7.84 (d, J = 7.0 Hz, 2H), 7.60 (d, J = 7.0 Hz, 2H), 6.08 (d, J = 3.0 Hz, 1H), 5.90 (d, J = 3.0 Hz, 1H), 4.21 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 194.3, 151.8, 145.8, 134.9, 131.9, 130.1, 128.5, 109.1, 106.6, 38.6, 13.5; MS (EI): 278 (M^+, 10%), 280 (11%), 183 (43%), 185 (41%), 155 (20%), 157 (16%), 95 (100%), 76 (9%), 75 (8%).

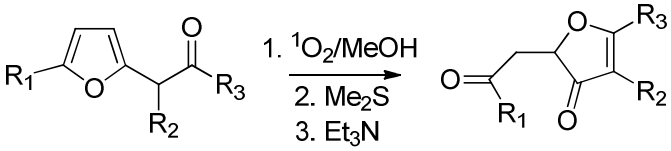
2-(5-Methylfuran-2-yl)-1-(thiophen-2-yl)ethanone (22)[4]



22

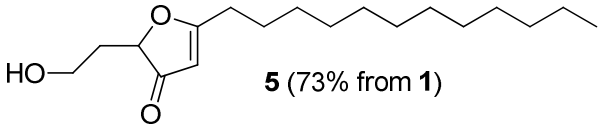
Ketone **22** was prepared in 52% yield by coupling 2-methylfuran with α-iodo 2-acetylthiophene. ^{1}H NMR (300 MHz, $CDCl_3$): 7.78 (d, J = 1.5 Hz, 1H), 7.69 (d, J = 1.5 Hz, 1H), 7.13 (t, J = 1.5 Hz, 1H), 6.12 (d, J = 2.5 Hz, 1H), 5.91 (d, J = 2.5 Hz, 1H), 4.17 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 188.1, 151.8, 146.0, 143.4, 134.2, 132.9, 128.1, 109.1, 106.6, 39.4, 13.5; MS (EI): 206 (M^+, 24%), 111 (99%), 95 (100%), 83 (7%), 67 (5%), 51 (5%).

General procedure for the synthesis of 3(2*H*)-furanones via photooxygenation of β-keto-2-substituted furans



In a vial was dissolved the appropriate β-keto-2-substituted furan (0.2 mmol) in MeOH (1 mL). Methylene blue was added (concentration ~10^{-4} M) and the tube was irradiated with visible light using a 300 W Xenon lamp, under a constant flow (bubbling) of oxygen gas. After the disappearance of the starting material (TLC) the solvent was evaporated, and replaced by CH_2Cl_2 or $CDCl_3$. Then Me_2S were added (0.8 mmol, 4 equiv) and stirring continued for 16 h at 25 ^{o}C, followed by Et_3N (0.2 mmol, 1 equiv). After 10 h the solvent was evaporated and the residue was chromatographed to provide the 3(2*H*)-furanones in 53-83% yield. For the case of the chromatographically unstable 3(2*H*)-furanone-substituted aldehydes formed in the photooxygenation process of monosubstituted furans **1**, **16** and **18**, direct reduction of the crude reaction mixture with $NaBH_4$ (1.2 equiv) in moistened THF provided the corresponding alcohols (**5**, **17** and **19**, respectively).

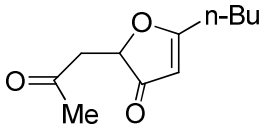
5-Dodecyl-2-(2-hydroxyethyl)furan-3(2*H*)-one (5)



5 (73% from **1**)

^{1}H NMR (300 MHz, $CDCl_3$): 5.45 (s, 1H), 4.60 (t, J = 7.0 Hz, 1H), 3.86 (m, 2H), 2.50 (t, J = 7.0 Hz, 2H), 2.40 (br s, -OH), 1.92-2.14 (m, 2H), 1.60-1.69 (m, 2H), 1.22-1.40 (m, 18H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 205.5, 194.5, 103.2, 84.4, 59.1, 33.9, 31.9, 30.8, 29.6, 29.5, 29.5, 29.4, 29.3, 29.2, 29.1, 26.0, 22.6, 14.0; MS (EI): 296 (M^+, 3%), 252 (49%), 209 (14%), 167 (19%), 139 (16%), 111 (100%), 81 (10%), 55 (15%); HRMS: calcd for $C_{18}H_{32}O_3$+H, 297.243; found 297.242.

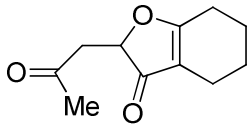
5-Butyl-2-(2-oxopropyl)furan-3(2*H*)-one (7)



7 (65% from **6**)

^{1}H NMR (300 MHz, $CDCl_3$): 5.46 (s, 1H), 4.86 (dd, J_1 = 9.5 Hz, J_2 = 3.0 Hz, 1H), 3.03 (dd, J_1 = 18.0 Hz, J_2 = 3.0 Hz, 1H), 2.70 (dd, J_1 = 18.0 Hz, J_2 = 9.5 Hz, 1H), 2.49 (t, J = 8.0 Hz, 2H), 2.23 (s, 3H), 1.56-1.87 (m, 2H), 1.32-1.44 (m, 2H), 0.93 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 203.9, 203.7, 194.5, 103.1, 81.0, 44.4, 30.5, 30.1, 28.0, 22.2, 13.6; MS (EI): 196 (M^+, 13%), 179 (4%), 153 (100%), 136 (12%), 97 (41%), 71 (38%), 55 (19%); HRMS: calcd for $C_{11}H_{16}O_3$, 196.1099; found 196.1101.

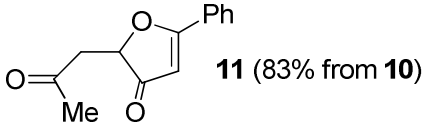
2-(2-Oxopropyl)-4,5,6,7-tetrahydrobenzofuran-3(2*H*)-one (9)



9 (57% from **8**)

^{1}H NMR (300 MHz, $CDCl_3$): 4.83 (dd, J_1 = 9.5 Hz, J_2 = 2.5 Hz, 1H), 3.06 (dd, J_1 = 18.0 Hz, J_2 = 3.5 Hz, 1H), 2.68 (dd, J_1 = 18.0 Hz, J_2 = 10.0 Hz, 1H), 2.40-2.46 (m, 2H), 2.23 (s, 3H), 2.15-2.22 (m, 2H), 1.78-1.87 (m, 2H), 1.63-1.71 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 204.1, 202.2, 188.6, 112.9, 80.3, 44.5, 30.1, 25.8, 21.7, 21.6, 18.1; HRMS: calcd for $C_{11}H_{14}O_3$, 194.0943; found 194.0944.

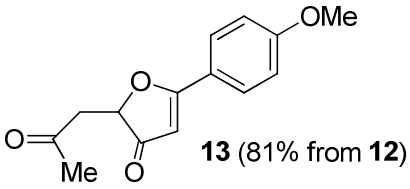
2-(2-Oxopropyl)-5-phenylfuran-3(2*H*)-one (11)[8]



11 (83% from **10**)

^{1}H NMR (300 MHz, $CDCl_3$): 7.80 (d, J = 7.0 Hz, 2H), 7.54 (t, J = 7.0 Hz, 1H), 7.48 (d, J = 7.0 Hz, 2H), 6.07 (s, 1H), 5.10 (dd, J_1 = 9.5 Hz, J_2 = 3.0 Hz, 1H), 3.12 (dd, J_1 = 18.0 Hz, J_2 = 3.0 Hz, 1H), 2.85 (dd, J_1 = 18.0 Hz, J_2 = 9.5 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 203.6, 203.3, 185.7, 132.9, 128.9, 128.6, 127.2, 100.7, 81.4, 44.6, 30.2; MS (EI): 216 (M^+, 12%), 173 (100%), 129 (10%), 115 (3%), 102 (78%), 71 (18%), 63 (2%), 51 (7%); HRMS: calcd for $C_{13}H_{12}O_3$, 216.0786; found 216.0785.

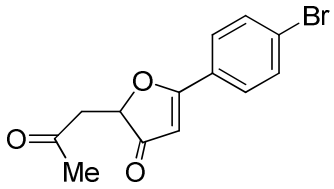
5-(4-Methoxyphenyl)-2-(2-oxopropyl)furan-3(2*H*)-one (13)



13 (81% from **12**)

^{1}H NMR (300 MHz, $CDCl_3$): 7.75 (d, J = 7.5 Hz, 2H), 6.96 (d, J = 7.5 Hz, 2H), 5.95 (s, 1H), 5.08 (dd, J_1 = 9.5 Hz, J_2 = 3.0 Hz, 1H), 3.88 (s, 3H), 3.12 (dd, J_1 = 18.0 Hz, J_2 = 3.0 Hz, 1H), 2.82 (dd, J_1 = 18.0 Hz, J_2 = 9.5 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 203.6, 202.9, 185.5, 163.4, 129.6, 121.0, 114.3, 99.0, 81.3, 55.5, 44.7, 30.2; MS (EI): 246 (M^+, 1%), 228 (55%), 213 (43%), 200 (60%), 185 (8%), 129 (31%), 115 (100%), 105 (24%), 89 (12%), 69 (78%), 51 (10%); HRMS: calcd for $C_{14}H_{14}O_4$+H, 247.097; found 247.096.

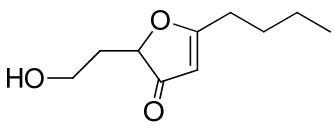
5-(4-Bromoxyphenyl)-2-(2-oxopropyl)furan-3(2*H*)-one (15)



15 (77% from **14**)

^{1}H NMR (300 MHz, $CDCl_3$): 7.63 (d, J = 7.5 Hz, 2H), 7.60 (d, J = 7.5 Hz, 2H), 6.06 (s, 1H), 5.08 (dd, J_1 = 9.5 Hz, J_2 = 3.0 Hz, 1H), 3.13 (dd, J_1 = 18.0 Hz, J_2 = 3.0 Hz, 1H), 2.86 (dd, J_1 = 18.0 Hz, J_2 = 9.5 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 203.5, 203.1, 184.3, 132.2, 128.5, 127.7, 127.5, 101.0, 81.5, 44.5, 30.1; MS (EI): 294 (M^+, 10%), 296 (11%), 251 (100%), 253 (100%), 180 (89%), 182 (90%), 155 (16%), 157 (15%), 101 (50%), 71 (45%), 51 (11%); HRMS: calcd for $C_{13}H_{11}O_3Br$+H, 294.997; found 294.996.

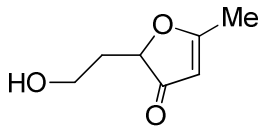
5-Butyl-2-(2-hydroxyethyl)furan-3(2*H*)-one (17)



17 (74% from **16**)

^{1}H NMR (300 MHz, $CDCl_3$): 5.46 (s, 1H), 4.61 (t, J = 7.0 Hz, 1H), 3.86 (m, 2H), 2.51 (t, J = 7.0 Hz, 2H), 2.40 (br s, -OH), 1.92-2.14 (m, 2H), 1.58-1.70 (m, 2H), 1.37-1.46 (m, 2H), 0.92 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 205.5, 194.4, 103.2, 84.4, 59.2, 33.9, 30.5, 28.0, 22.2, 13.6; MS (EI): 184 (M^+, 1%), 140 (100%), 111 (27%), 97 (89%), 81 (15%), 67 (18%), 55 (13%); HRMS: calcd for $C_{10}H_{16}O_3$+H, 185.118; found 185.117.

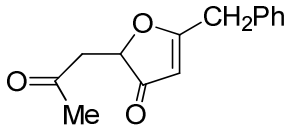
2-(2-Hydroxyethyl)-5-methylfuran-3(2*H*)-one (19)



19 (70% from **18**)

^{1}H NMR (300 MHz, $CDCl_3$): 5.48 (s, 1H), 4.62 (t, J = 7.0 Hz, 1H), 3.87 (m, 2H), 2.36 (br s, -OH), 2.25 (s, 3H), 1.94-2.16 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 205.5, 190.4, 104.2, 84.8, 59.1, 33.8, 16.9; MS (EI): 142 (M^+, 1%), 111 (9%), 98 (100%), 85 (8%), 68 (15%), 55 (8%); HRMS: calcd for $C_7H_{10}O_3$+H, 143.071; found 143.070.

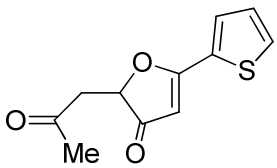
5-Benzyl-2-(2-oxopropyl)furan-3(2*H*)-one (21)



21 (57% from **20**)

^{1}H NMR (300 MHz, $CDCl_3$): 7.22-7.36 (m, 5H), 5.36 (s, 1H), 4.89 (dd, J_1 = 9.5 Hz, J_2 = 2.5 Hz, 1H), 3.78 (s, 2H), 3.03 (dd, J_1 = 18.0 Hz, J_2 = 3.0 Hz, 1H), 2.73 (dd, J_1 = 18.0 Hz, J_2 = 10.0 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 203.6, 203.5, 192.4, 134.2, 129.1, 128.9, 127.5, 104.3, 81.5, 44.2, 37.3, 30.2; MS (EI): 230 (M^+, 9%), 187 (100%), 144 (14%), 115 (49%), 105 (8%), 91 (29%), 69 (13%), 55 (4%); HRMS: calcd for $C_{14}H_{14}O_3$+H, 231.102; found 231.101.

2-(2-Oxopropyl)-5-(thiophen-2-yl)furan-3(2*H*)-one (23)



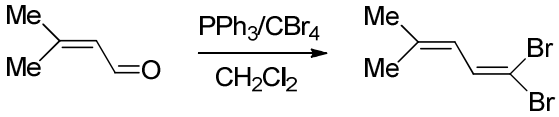
23 (77% from **22**)

^{1}H NMR (300 MHz, $CDCl_3$): 7.68 (d, J = 1.5 Hz, 1H), 7.64 (t, J = 1.5 Hz, 1H), 7.16 (d, J = 1.5 Hz, 1H), 5.90 (s, 1H), 5.08 (dd, J_1 = 9.0 Hz, J_2 = 2.0 Hz, 1H), 3.11 (dd, J_1 = 18.0 Hz, J_2 = 2.0 Hz, 1H), 2.86 (dd, J_1 = 18.0 Hz, J_2 = 10.0 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 203.6, 202.3, 179.9, 132.1, 131.6, 130.9, 128.5, 99.6, 81.5, 44.5, 30.2; MS (EI):

222 (M^+, 28%), 179 (80%), 137 (14%), 108 (100%), 69 (19%); HRMS: calcd for $C_{11}H_{10}O_3S$+H, 223.043; found 223.042.

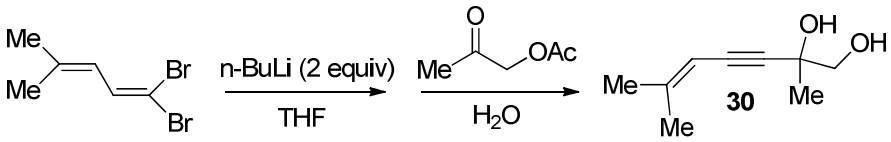
Synthesis of merrekentrone C

1,1-Dibromo-4-methylpenta-1,3-diene[9]



In a dry flask were placed under an inert atmosphere CBr_4 (5.5 g, 16.5 mmol) and dry CH_2Cl_2 (12 mL). At -78 ^oC were added PPh_3 (8.5 g, 32.5 mmol) dissolved in CH_2Cl_2 (20 mL), and immediately after Et_3N (1.35 mL, 9.5 mmol). After 40 min were added at the same temperature 3,3-dimethylacrolein (1.0 mL, 10.5 mmol) and the reaction temperature was increased gradually to 25 ^oC over a period of 6 hours. Most of the solvent was evaporated under vacuum and then hexane (150 mL) was added to precipitate Ph_3PO and inorganic salts. The supernatant was evaporated and the residue was chromatographed with hexane to provide 1.11 g of 1,1-dibromo-4-methylpenta-1,3-diene (46% yield). ^1H NMR (300 MHz, $CDCl_3$): 7.11 (d, J = 10.5 Hz, 1H), 5.85 (d, J = 10.5 Hz, 3H), 1.80 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 140.8, 133.6, 122.2, 88.5, 26.3, 19.3.

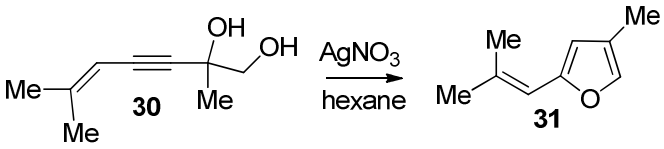
2,6-Dimethylhept-5-yn-1,2-diol (30)[10]



In a dry flask were placed under an inert atmosphere 1,1-dibromo-4-methylpenta-1,3-diene (1.1 g, 4.7 mmol) and dry THF (7 mL). At -78 ^oC was added *n*-BuLi (6.8 mL, 1.6M in hexanes, 10.8 mmol). After 1.5 h were syringed at the same temperature hydroxyacetone acetate (0.61 g, 5.2 mmol) dissolved in THF (6 mL). The reaction was complete after 2 h (TLC), and 1 mL of H_2O was added. The mixture was left stirring at room temperature for an additional 3 h. At that time the initially formed acetate **29** had completely hydrolyzed to diol **30** (GC-MS). After extractive workup, and chromatographic purification (hexane/ethyl acetate=3/1) diol **30** was isolated as a white solid (0.55 g, 75% yield). ^1H NMR (300 MHz, $CDCl_3$): 5.26 (s, 1H), 3.65 (d, J = 11.0 Hz, 1H), 3.51 (m, 1H), 2.63 (br s, 1H) 2.14 (br s, 1H), 1.87 (s, 3H), 1.79 (s, 3H), 1.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 149.7, 104.2,

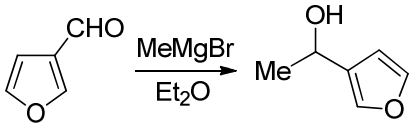
92.3, 82.6, 70.9, 69.1, 25.5, 24.8, 21.0; MS (EI): 154 (M^+, 3%), 136 (2%), 123 (99%), 107 (4%), 91 (5%), 43 (100%); HRMS: calcd for $C_9H_{14}O_2$, 154.0994; found 154.1002.

4-Methyl-2(2-methylprop-1-enyl)furan (31)



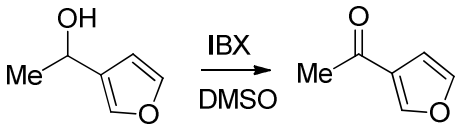
In a vial containing diol **30** (0.55 g, 3.55 mmol) and hexane (7 mL), were added a catalytic amount of $AgNO_3$[11] (68 mg, 0.36 mmol). After 1 h the reaction was complete and pure furan **31** (0.47 g, 95% yield) was isolated after evaporation of the supernatant hexane solution. ^{1}H NMR (300 MHz, $CDCl_3$): 7.09 (br s, 1H), 6.04 (s, 1H), 6.01 (br s, 1H), 2.01 (d, J = 1.5 Hz, 3H), 1.96 (d, J = 1.5 Hz, 3H), 1.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 153.6, 137.1, 134.8, 121.2, 114.5, 109.8, 26.9, 20.0, 9.8; MS (EI): 136 (M^+, 100%), 121 (37%), 107 (14%), 91 (51%), 77 (30%), 65 (12%), 39 (21%); HRMS: calcd for $C_9H_{12}O$, 136.0888; found 136.0890.

1-(Furan-3-yl)ethanol



In a dry flask containing MeMgBr (3.4 mL, 3M in Et_2O, 10.1 mmol) was added dropwise at 0 ^{o}C 3-furaldehyde (0.65 mL, 7.8 mmol) dissolved in dry Et_2O (7 mL). After 30 min, H_2O (300 μL) was added and the supernatant organic layer was decanted, the solvent was evaporated to leave 0.79 g (96% yield) of pure 1-(furan-3-yl)ethanol. ^{1}H NMR (300 MHz, $CDCl_3$): 7.39 (s, 1H), 7.38 (d, J = 1.5 Hz, 1H), 6.43 (d, J = 1.5 Hz, 1H), 4.86 (q, J = 7.0 Hz, 1H), 1.71 (br s, 1H -OH), 1.49 (d, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 143.0, 138.4, 130.3, 108.6, 62.7, 23.8; MS (EI): 112 (M^+, 43%), 97 (100%), 94 (84%), 69 (51%), 65 (59%).

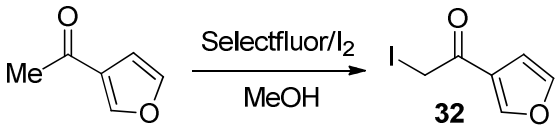
1-(Furan-3-yl)ethanone[12]



In a flask were placed 1-(furan-3-yl)ethanol (0.78 g, 6.5 mmol), DMSO (8 mL) and IBX (2.15 g, 7.7 mmol). The reaction was complete at room temperature after 30 min. Diethyl

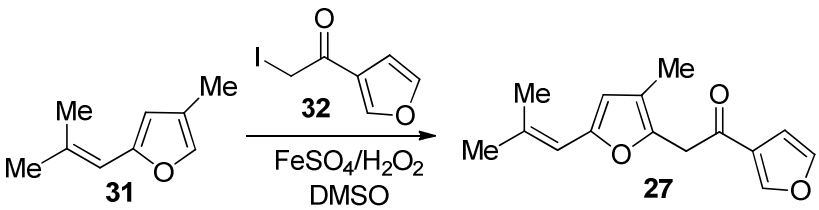
ether was added and the resulting solution was extracted with saturated solution of $NaHCO_3$. The solvents were evaporated and the residue was chromatographed (hexane/ethyl acetate=10/1). The desired 1-(furan-3-yl)ethanone was isolated (0.56 g, 72% yield) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): 8.02 (d, J = 1.5 Hz, 1H), 7.44 (br s, 1H), 6.77 (d, J = 1.5 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 192.4, 147.5, 144.3, 128.1, 108.6, 27.8; MS (EI): 110 (M^+, 34%), 96 (5%), 95 (100%), 67 (9%), 53 (2%), 50 (5%).

1-(Furan-3-yl)-2-iodoethanone (32)[13]



In flask were placed MeOH (7 mL), 1-(furan-3-yl)ethanone (0.51 g, 4.65 mmol), elemental I_2 (0.83 g, 3.25 mmol) and Selectfluor®[6] (0.98 g, 2.77 mmol). After 15 h GC analysis revealed the complete iodination of the ketone. Most of methanol was evaporated under vacuum and CH_2Cl_2 was added. The organic layer was washed with 1M $Na_2S_2O_3$ solution. After solvent evaporation, 0.79 g of the α-iodo ketone **32** were isolated (78% yield). ^{1}H NMR (300 MHz, $CDCl_3$): 8.13 (d, J = 1.5 Hz, 1H), 7.46 (t, J = 1.5 Hz, 1H), 6.79 (dd, J_1 = 1.5 Hz, J_2 = 1.5 Hz, 1H), 4.13 (d, J=1.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 187.6, 148.2, 144.6, 124.3, 109.2, 2.5; MS (EI): 236 (M^+, 30%), 141 (1%), 127 (3%), 109 (8%), 95 (100%), 81 (7%), 67 (5%), 53 (23%).

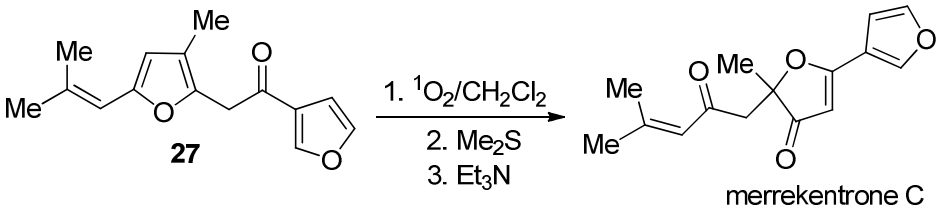
1-(Furan-3-yl)-2-(3-methyl-5-(2-methylprop-1-en-1-yl)furan-2-yl)ethanone (27)



In a flask were placed 0.32 g of alkenyl furan **31** (2.35 mmol, 5.0 equiv), 0.11 g of iodide **32** (0.46 mmol, 1.0 equiv), 65 mg $FeSO_4.7H_2O$ (0.23 mmol, 0.5 equiv) and DMSO (2 mL). Subsequently H_2O_2 (0.07 mL, 35% in H_2O, 0.86 mmol, 1.9 equiv) were added at 0 ^{o}C. After 30 min 0.09 g of iodide **32** and 41 mg of $FeSO_4.7H_2O$ were added, accompanied by the addition of 0.06 mL solution of H_2O_2. This kind of addition sequence was re-iterated three additional times every 30 minutes with the quantities of reactants (iodide **32**, $FeSO_4.7H_2O$, H_2O_2) as follows: 3rd: 0.085 g, 0.05 g, 0.06 mL, respectively; 4^{rth}: 0.065 g,

0.04 g and 0.045 mL, respectively; last: 0.045 g, 0.025 g and 0.03 mL, respectively. After this multiple additions sequence, diethyl ether was added and the solution was washed with brine. The residue after the evaporation of organic solvents was chromatographed with hexane/ethyl acetate=15/1 to provide 0.15 g of difuran **27** (46% yield). ^{1}H NMR (300 MHz, $CDCl_3$): 7.95 (br s, 1H), 7.40 (t, J = 1.5 Hz, 1H), 6.77 (t, J = 1.5 Hz, 1H), 6.01 (s, 1H), 5.97 (br s, 1H) 3.95 (s, 2H), 1.99 (s, 3H), 1.92 (br s, 3H), 1.87 (br s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 190.0, 152.2, 147.9, 143.9, 141.2, 134.8, 126.8, 118.8, 114.2, 110.9, 109.0, 39.3, 27.0, 20.1, 9.9; MS (EI): 244 (M^+, 12%), 149 (100%), 105 (8%), 95 (17%), 77 (8%), 65 (6%), 55 (5%). HRMS: calcd for $C_{15}H_{16}O_3$+Na, 267.0992; found 267.0991.

5-Methyl-5-(4-methyl-2-oxopent-3-en-1-yl)-[2,3'-bifuran]-4(5*H*)-one (merrekentrone C)



In vial were placed keto difuran **27** (5 mg) CH_2Cl_2 (0.5 mL) and methylene blue as sensitizer. The mixture was irradiated at 0 ^{o}C with visible light using a 300 W Xenon lamp, under a constant flow (bubbling) of oxygen gas. After the disappearance of the starting material (3 min, TLC), 4 equiv of dimethyl sulfide were added (30 min) and then 1 equiv of Et_3N (3 hours). The solvent was evaporated under vacuum and the residue was chromatographed (hexane/ethyl acetate=3/1) to provide 2.4 mg of merrekentrone C (48% yield), whose spectroscopic data are in agreement to those reported in the literature.[14] ^{1}H NMR (300 MHz, $CDCl_3$): 7.97 (br s, 1H), 7.50 (d, J = 2.0 Hz, 1H), 6.04 (d, J = 2.0 Hz, 1H), 5.77 (s, 1H), 2.97 (d, J = 15.0 Hz, 1H), 2.94 (d, J = 15.0 Hz, 1H), 2.07 (s, 3H), 1.86 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 205.1, 195.0, 178.1, 156.9, 144.4, 144.2, 123.6, 117.7, 108.5, 99.8, 87.7, 49.6, 27.7, 22.6, 20.9; MS (EI): 260 (M^+, 9%), 164 (36%), 80 (100%).

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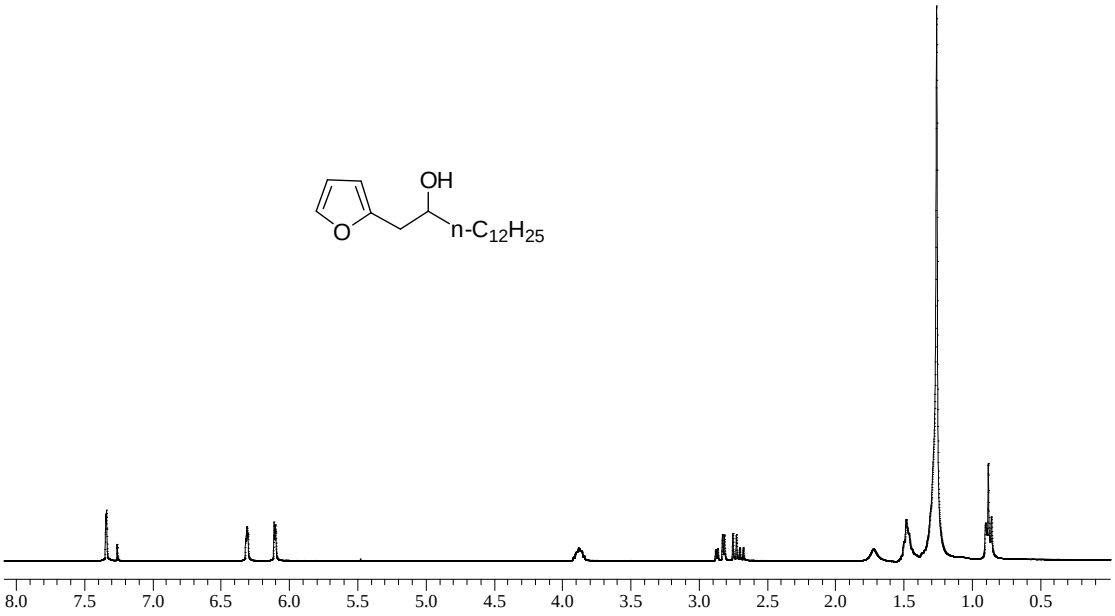
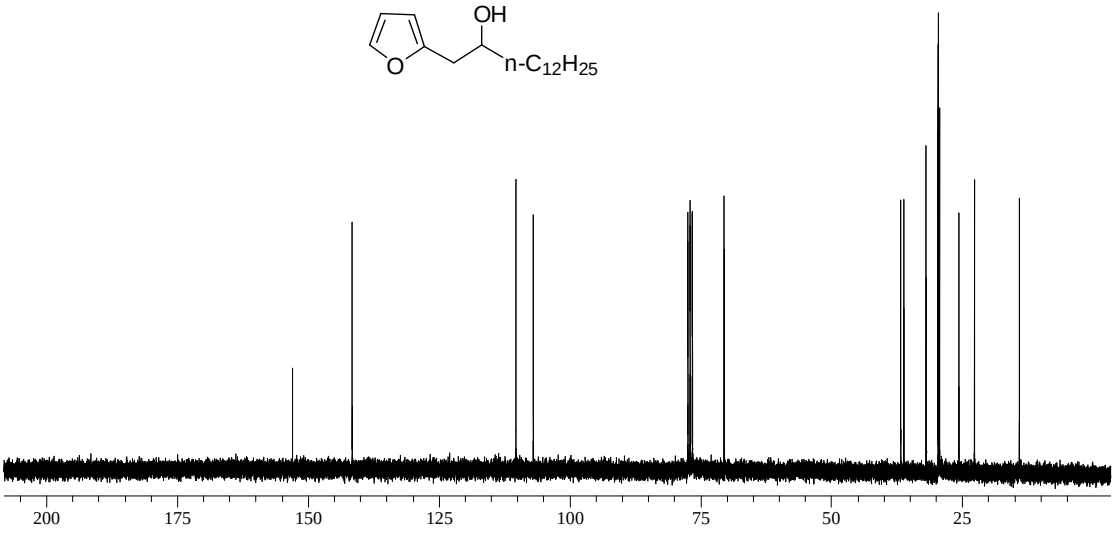
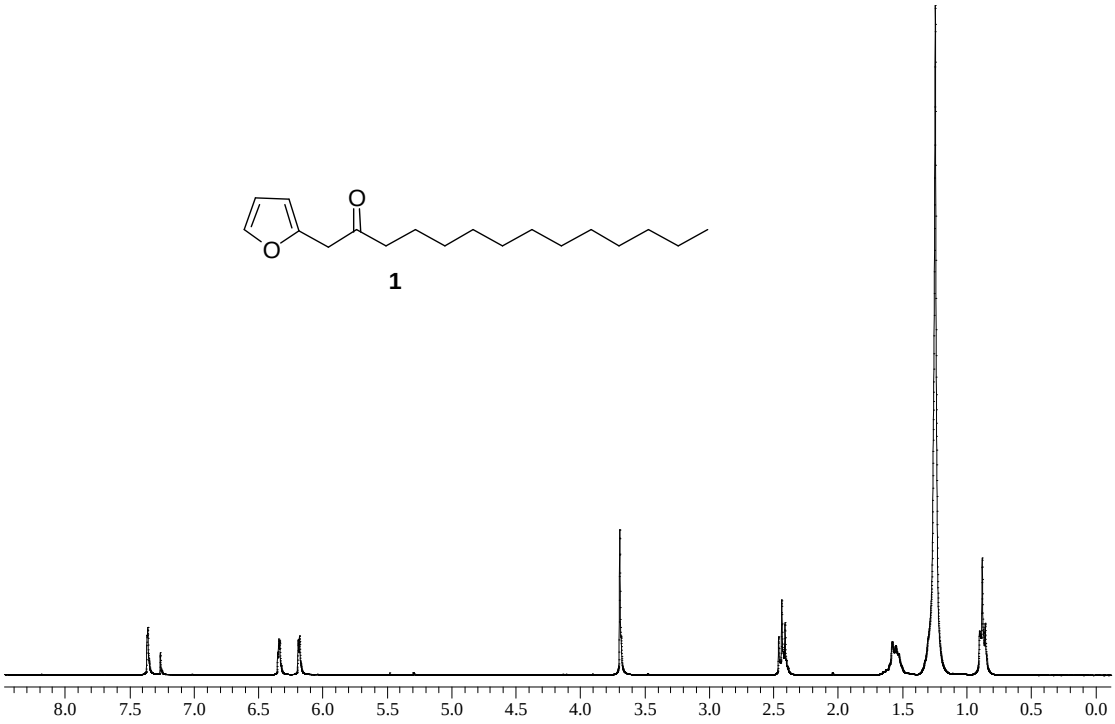
^{1}H and ^{13}C NMR spectra



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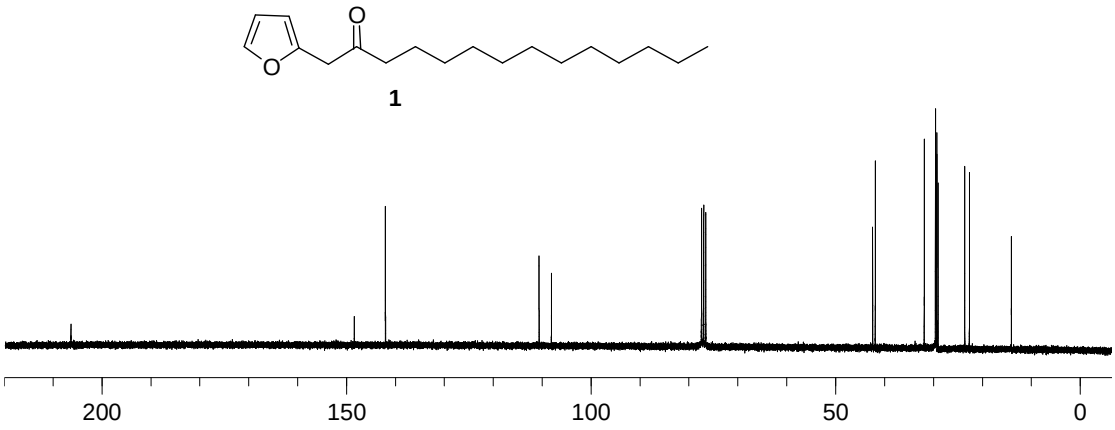
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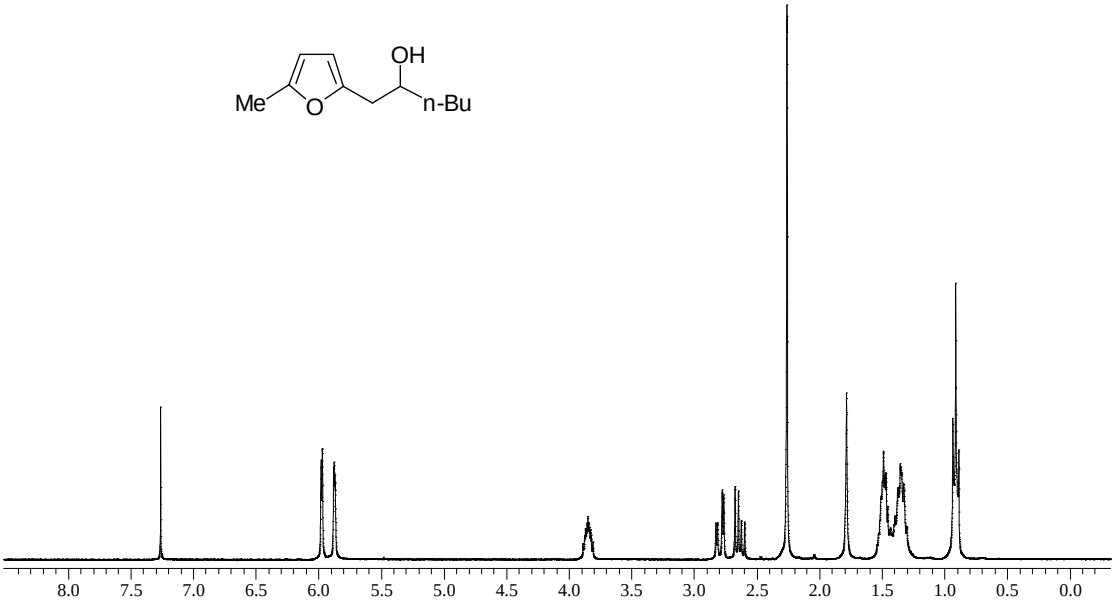

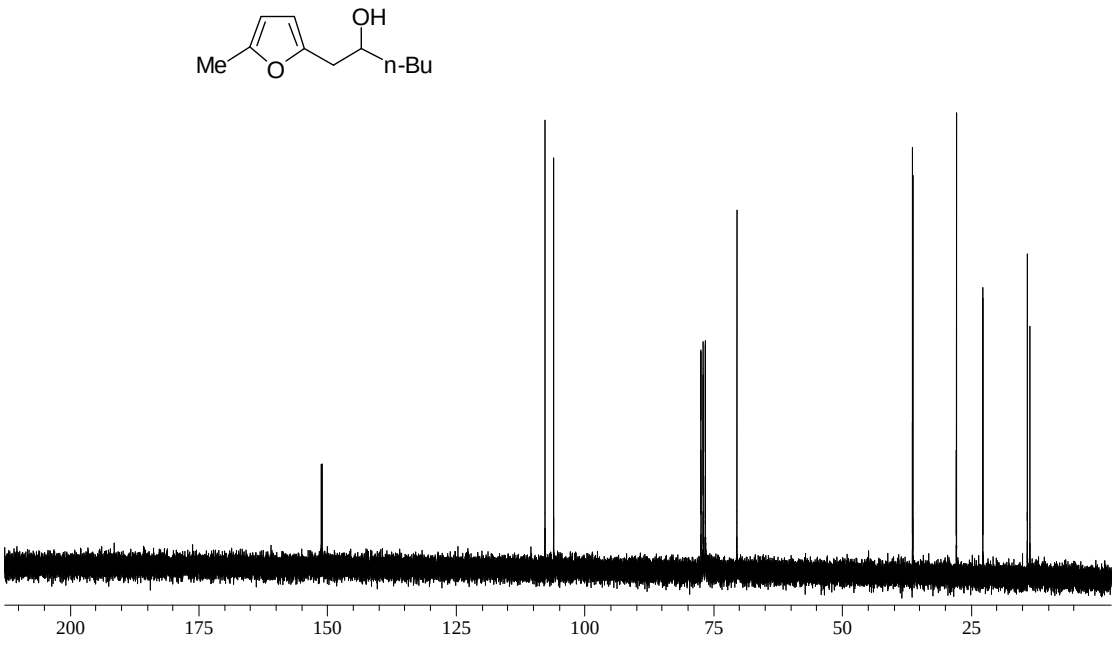

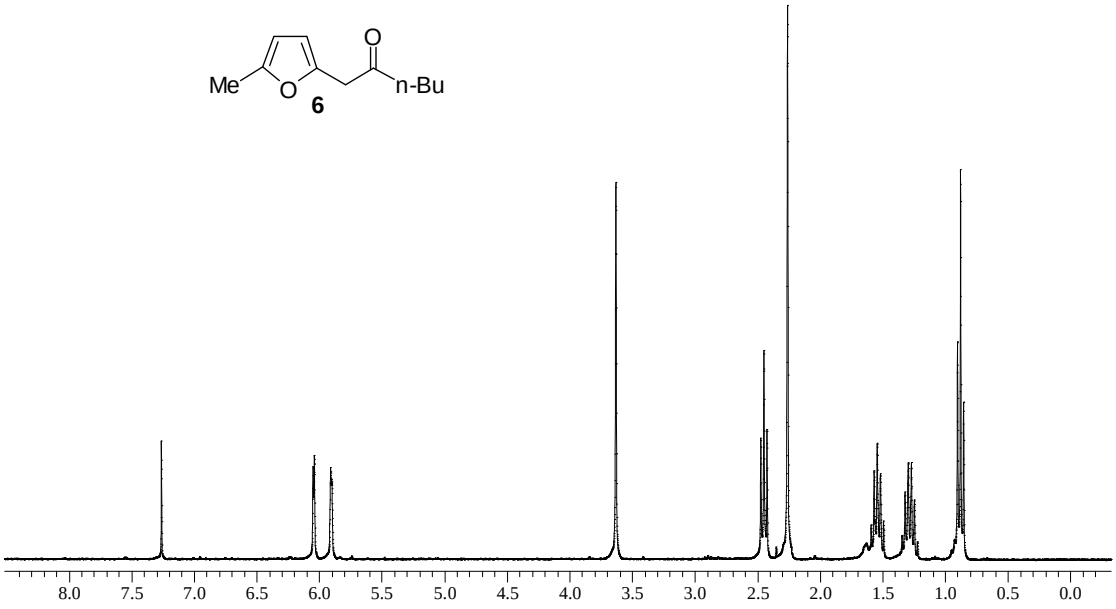
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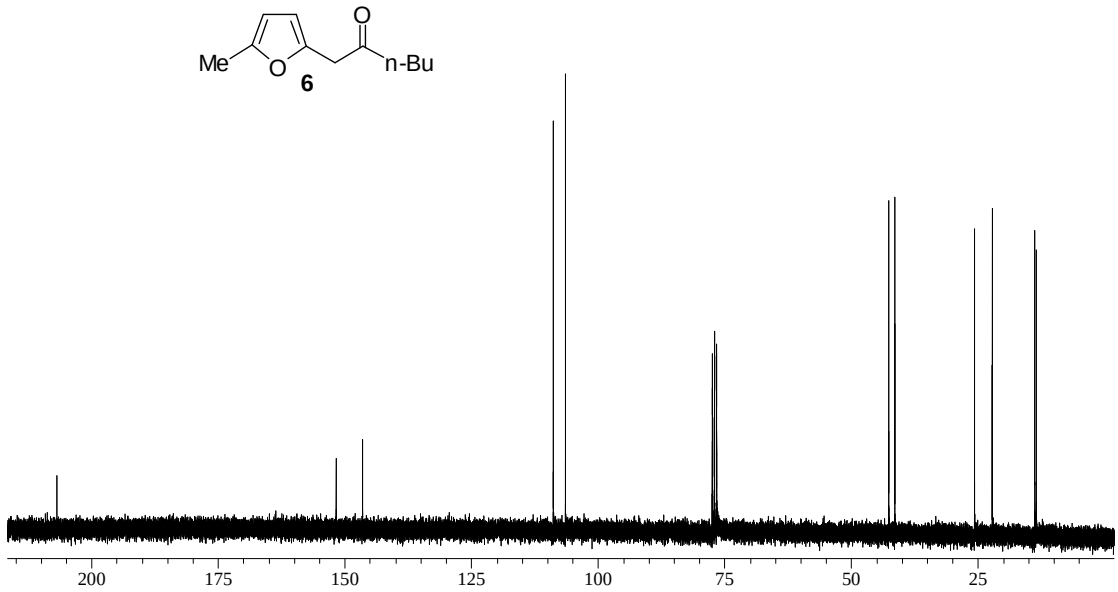
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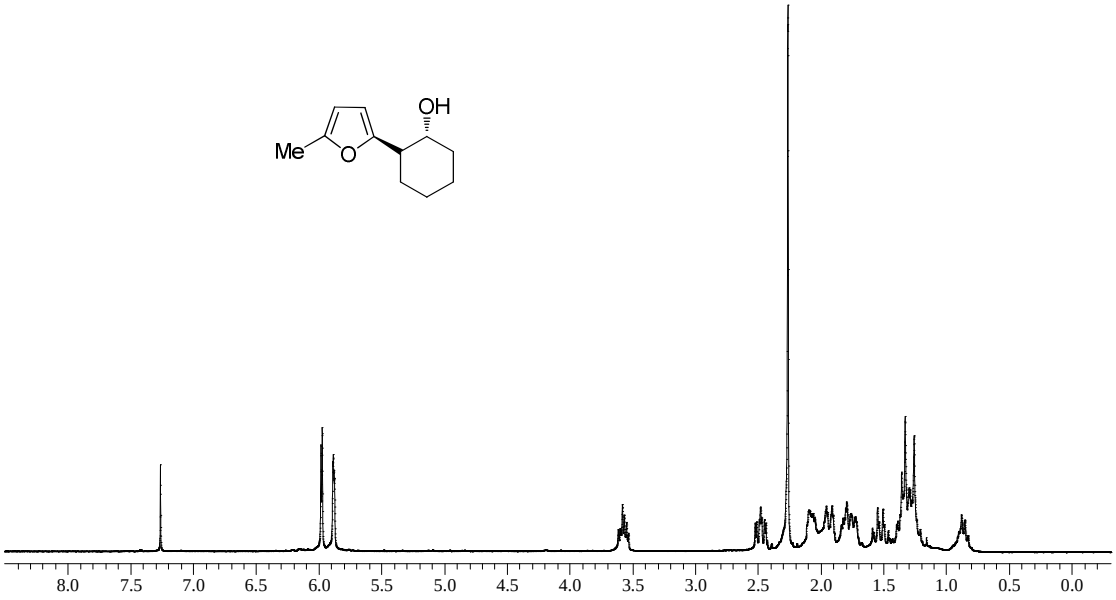
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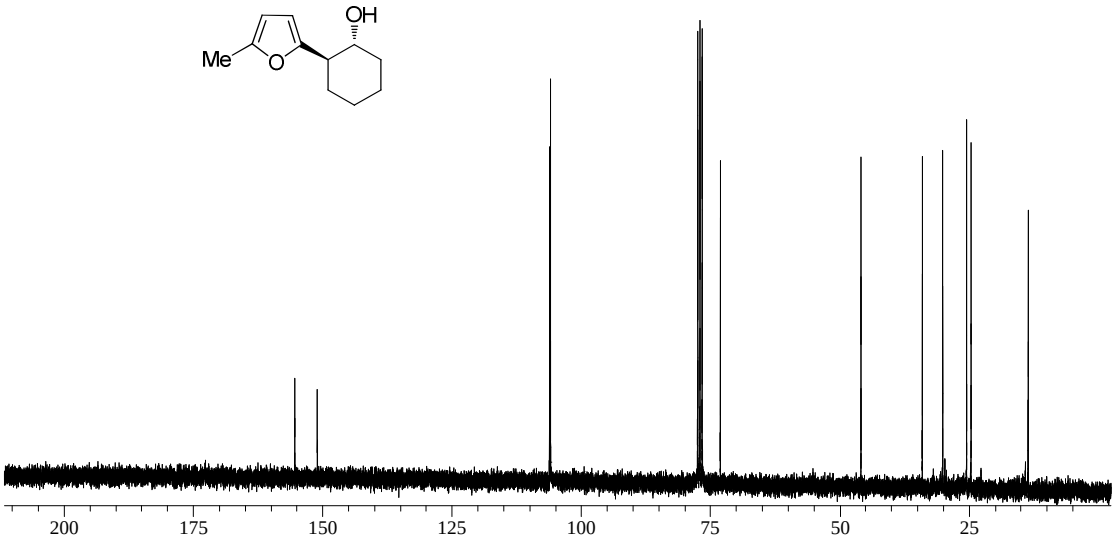
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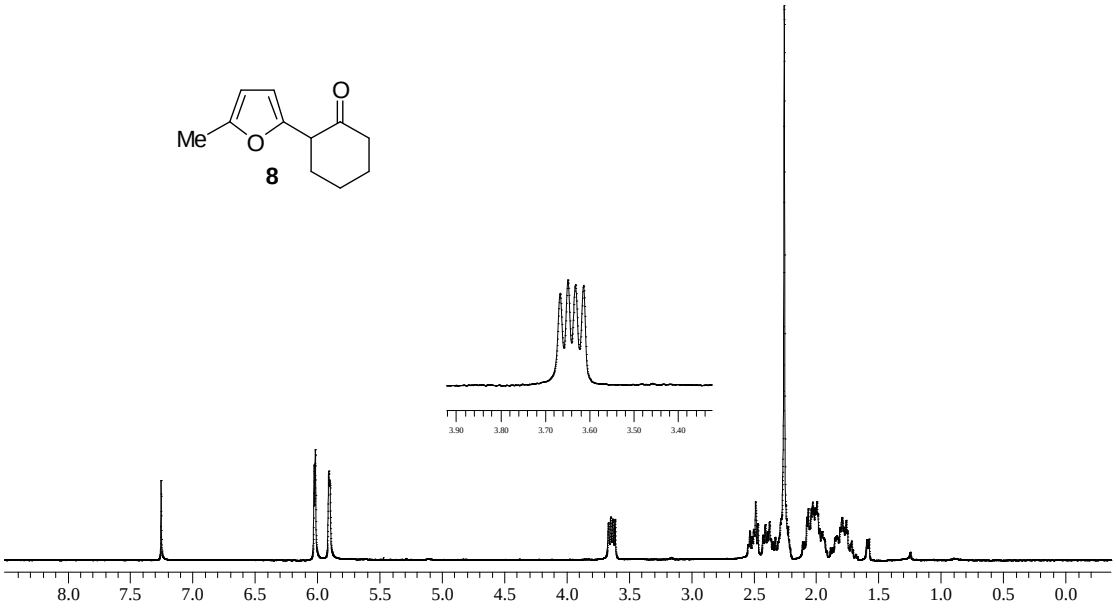
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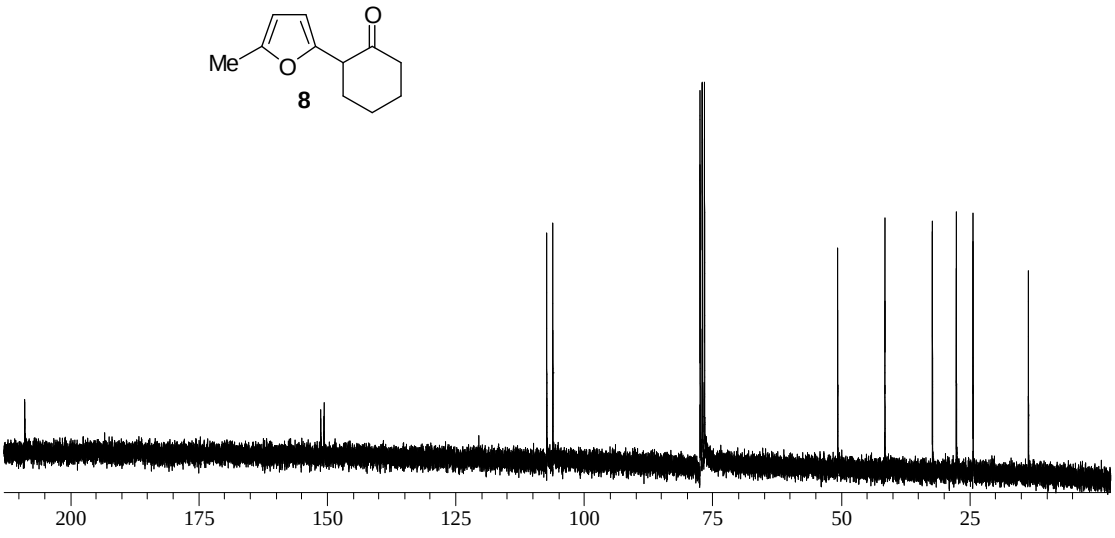
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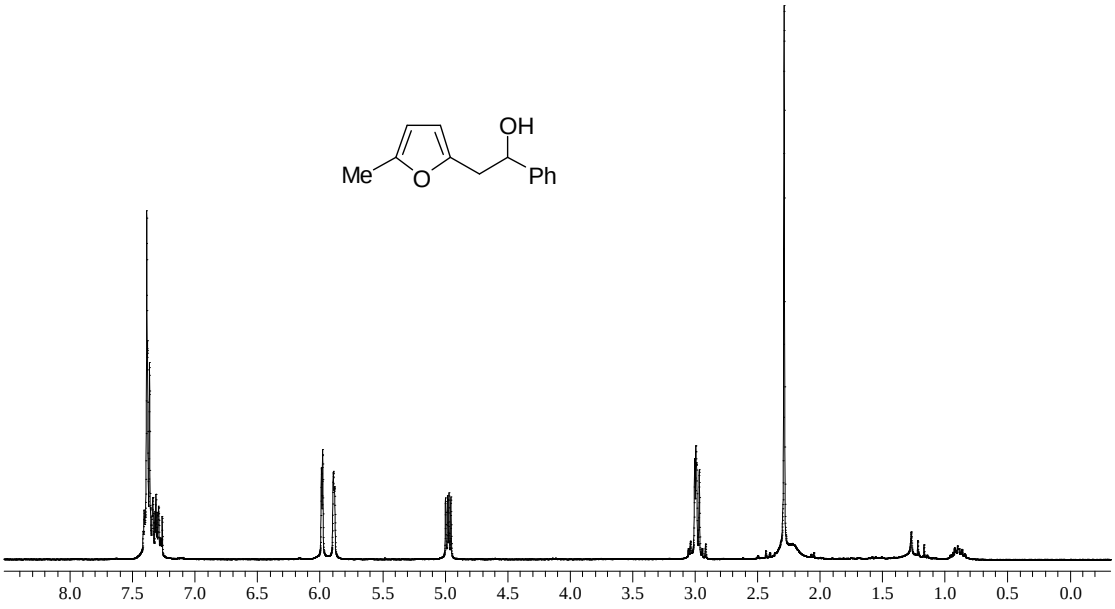
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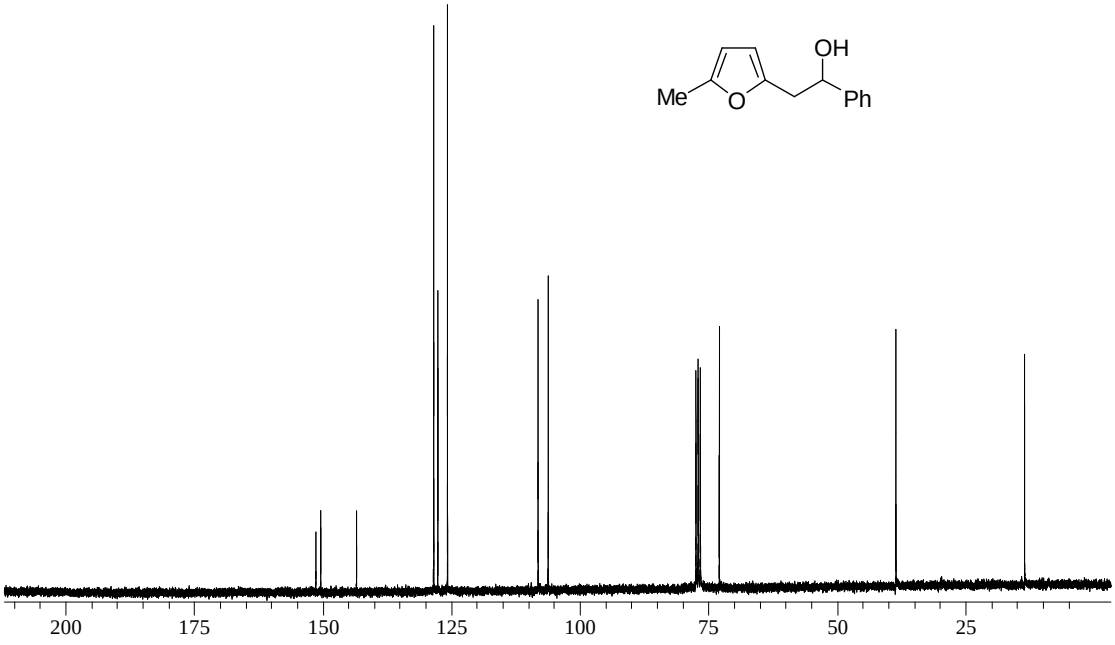
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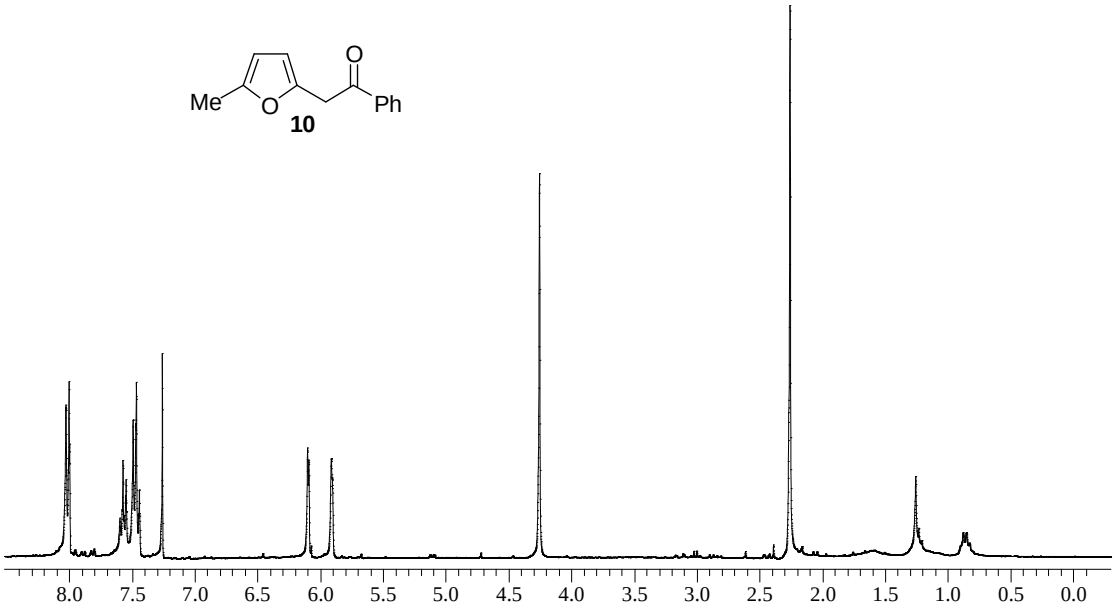

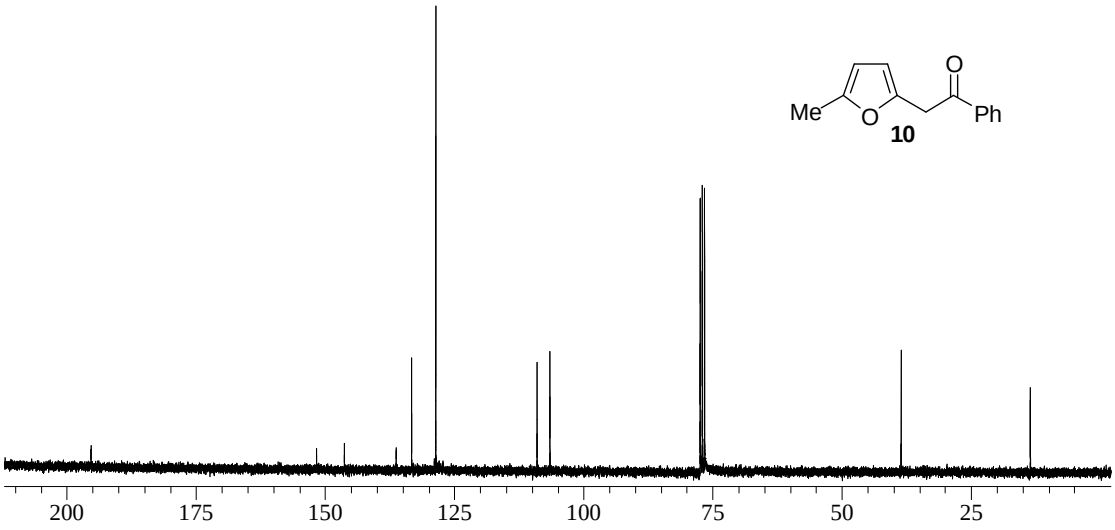

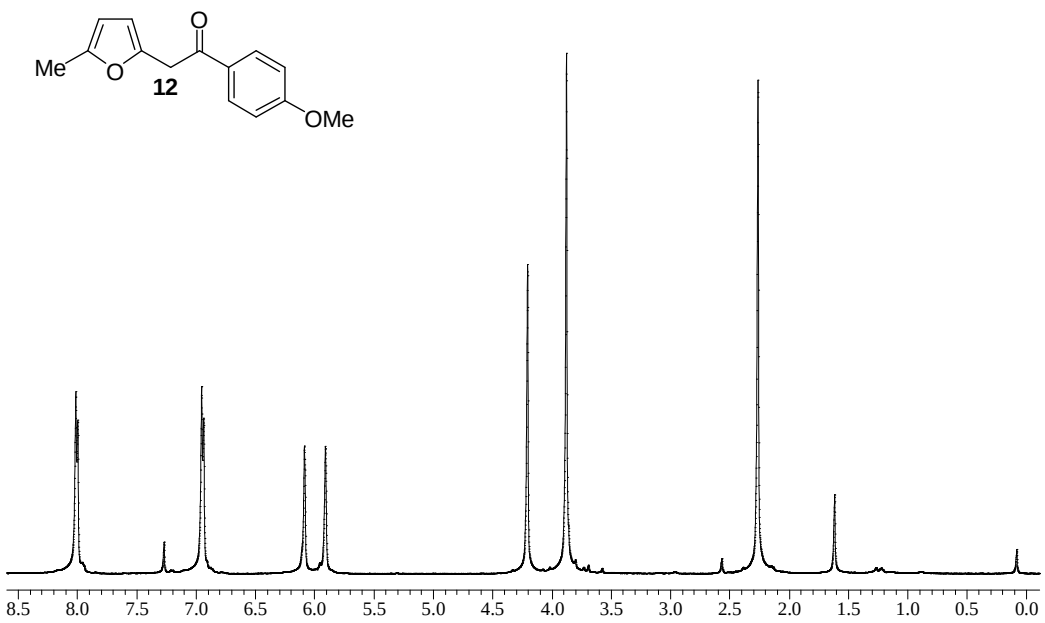

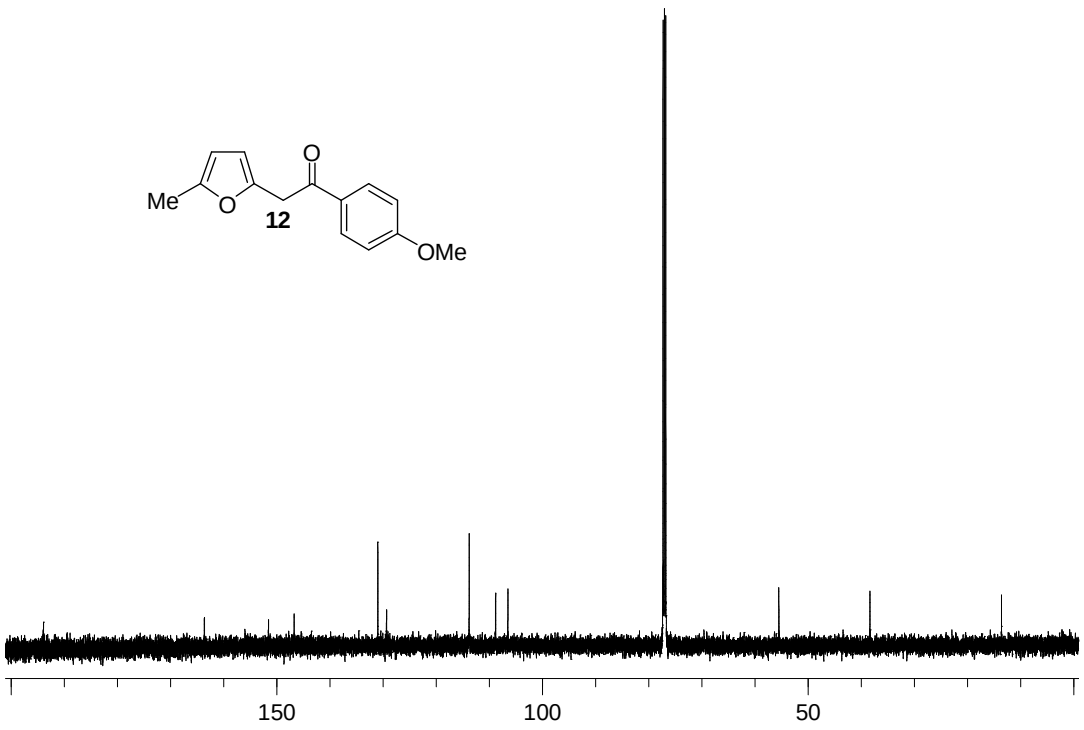

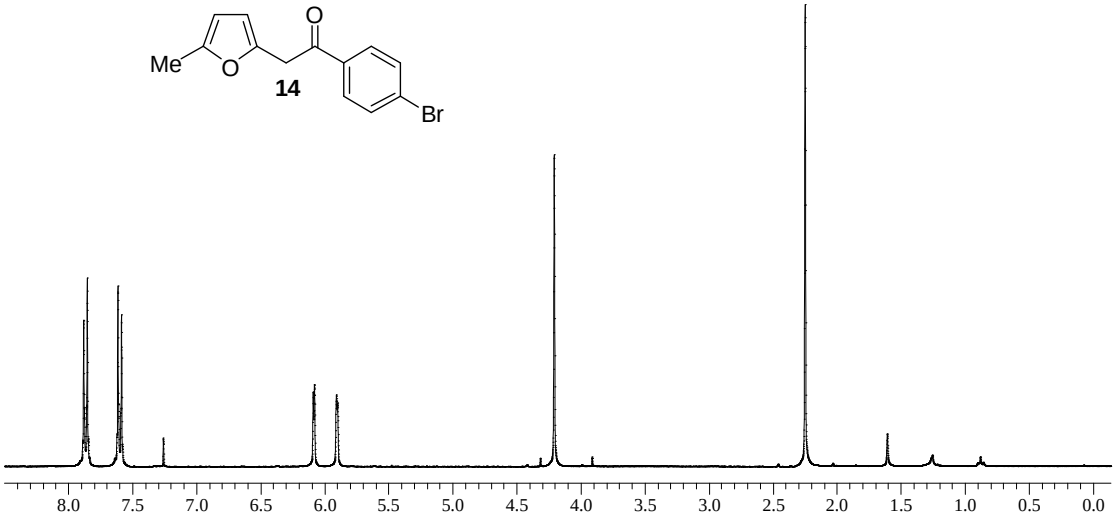
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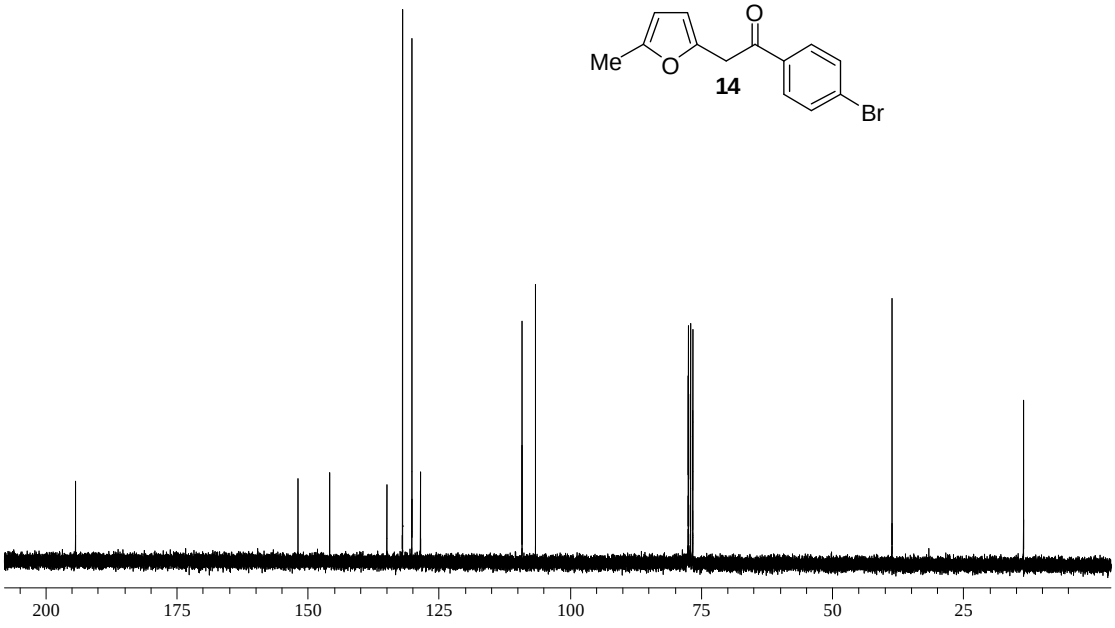
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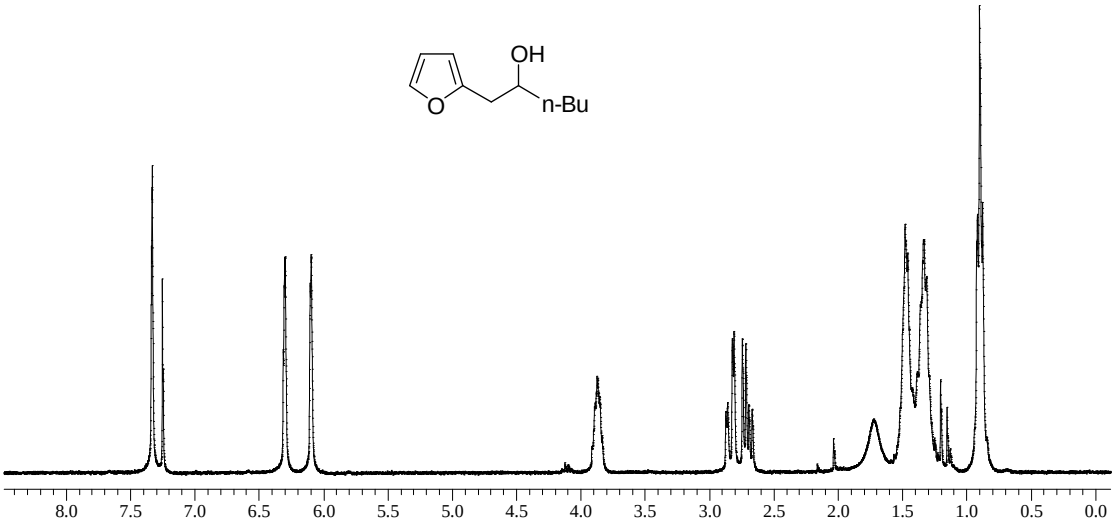

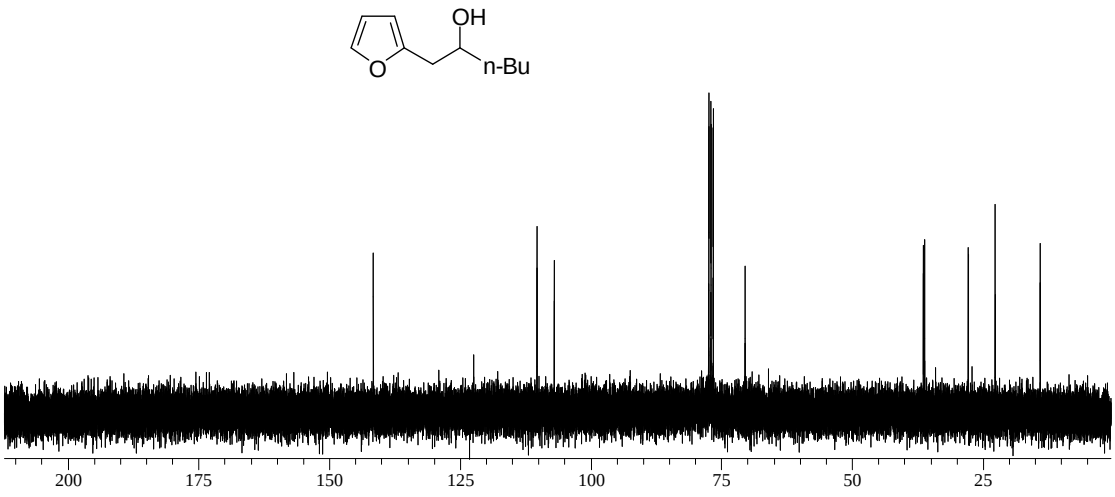

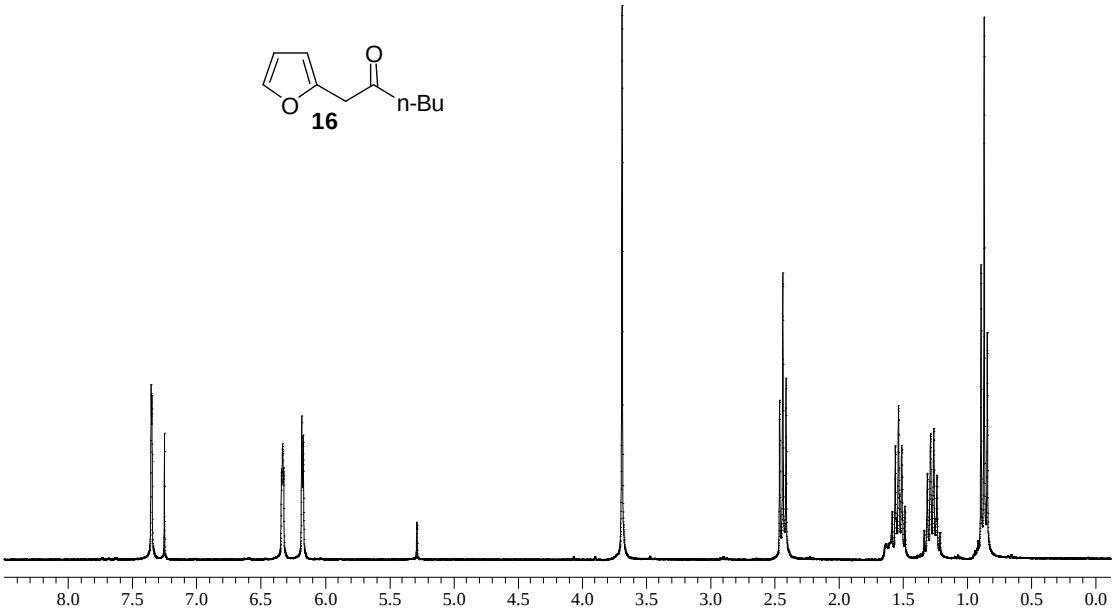
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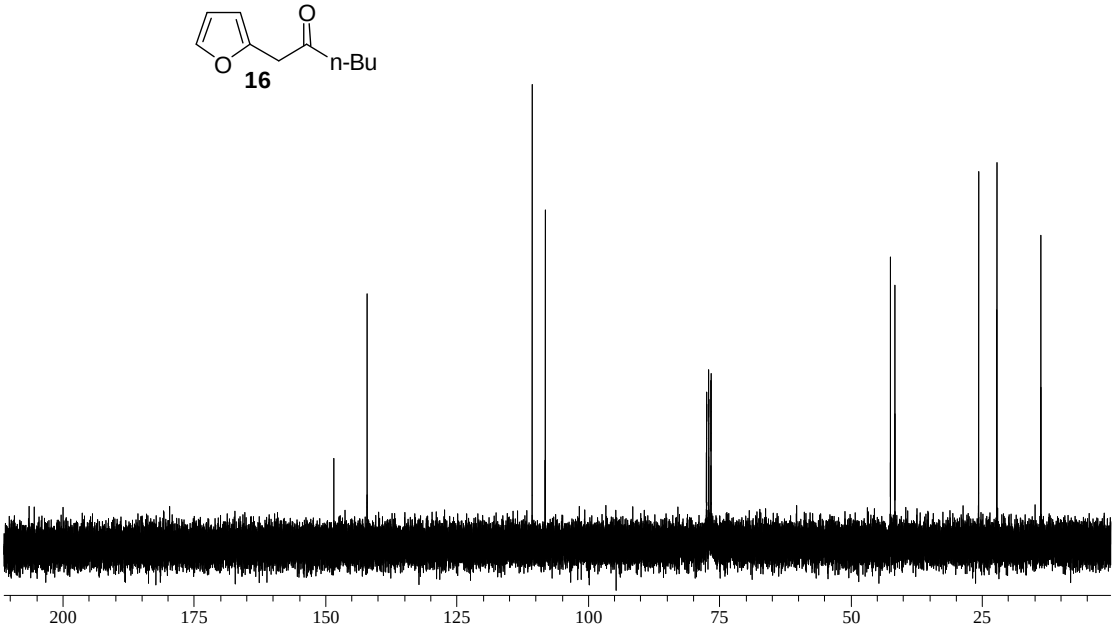
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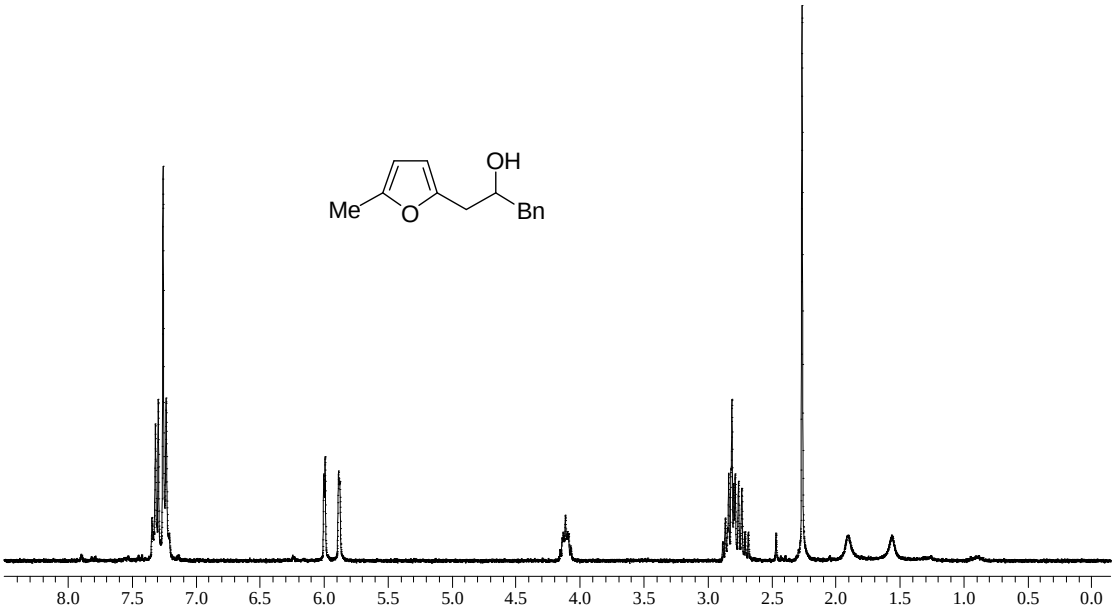
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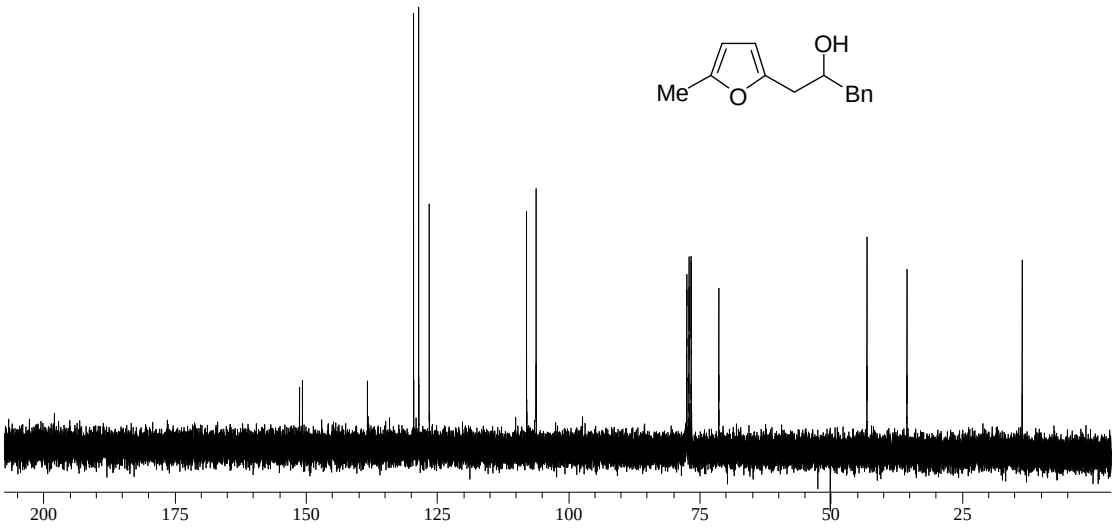
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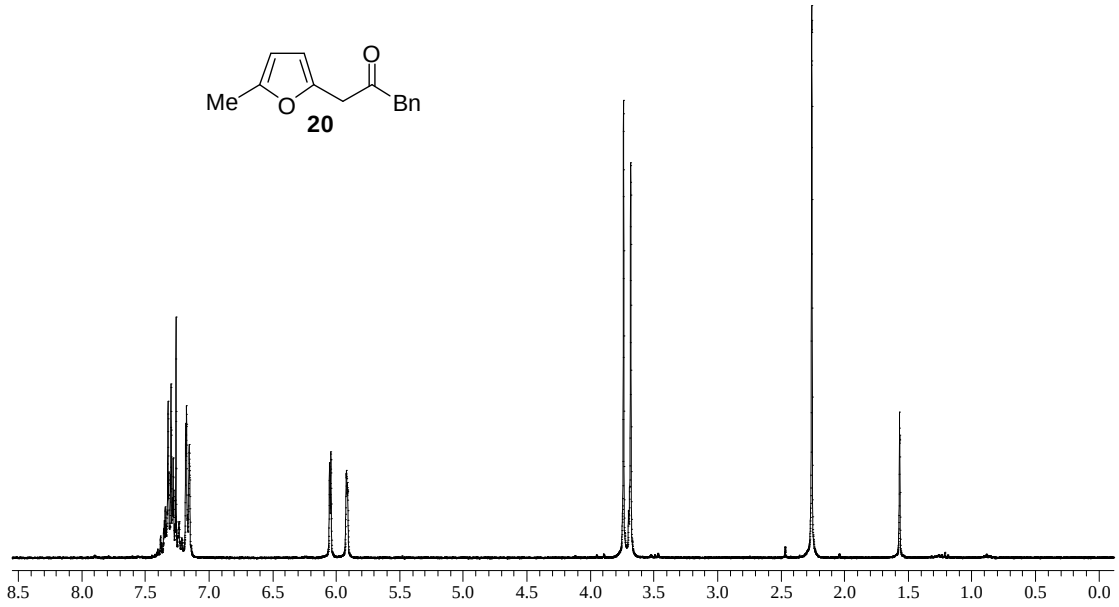
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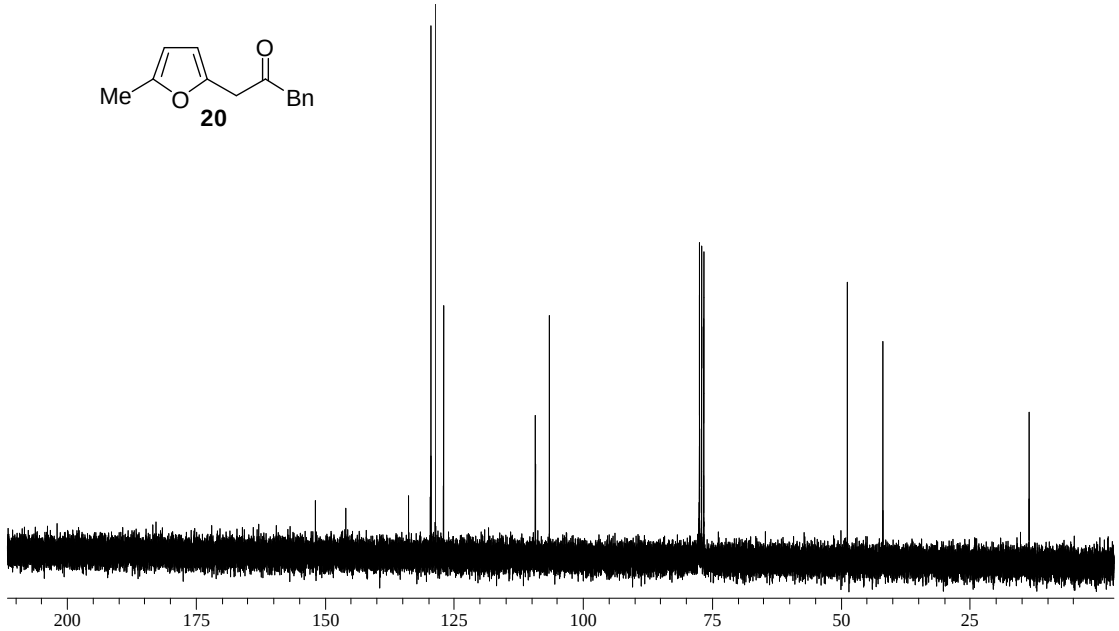
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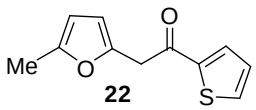
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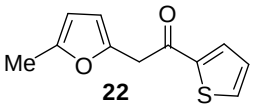
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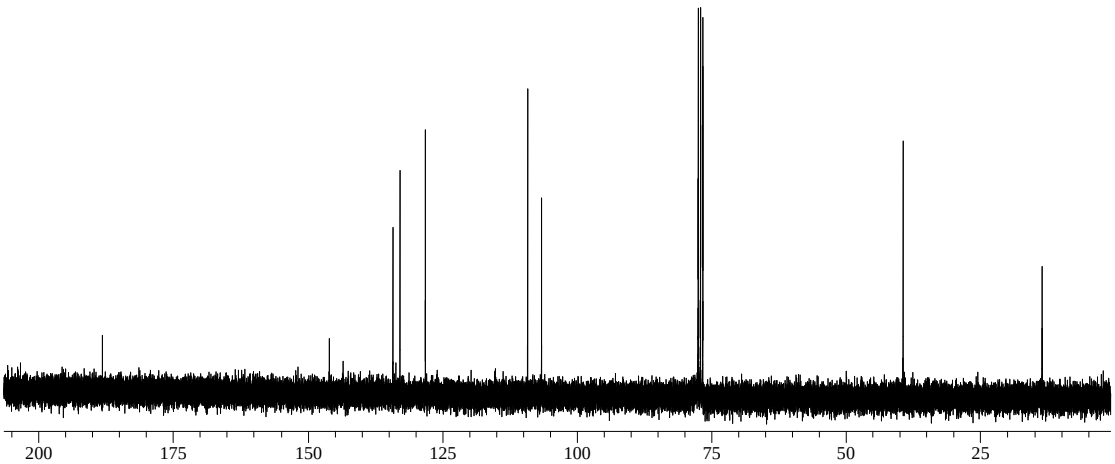
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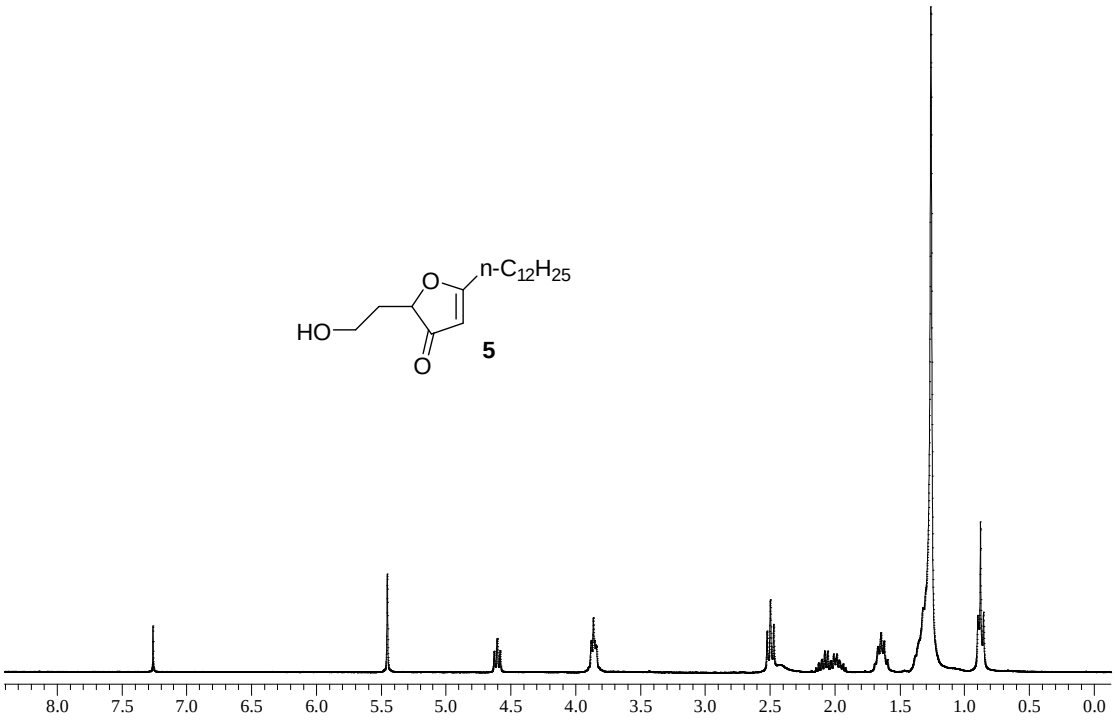
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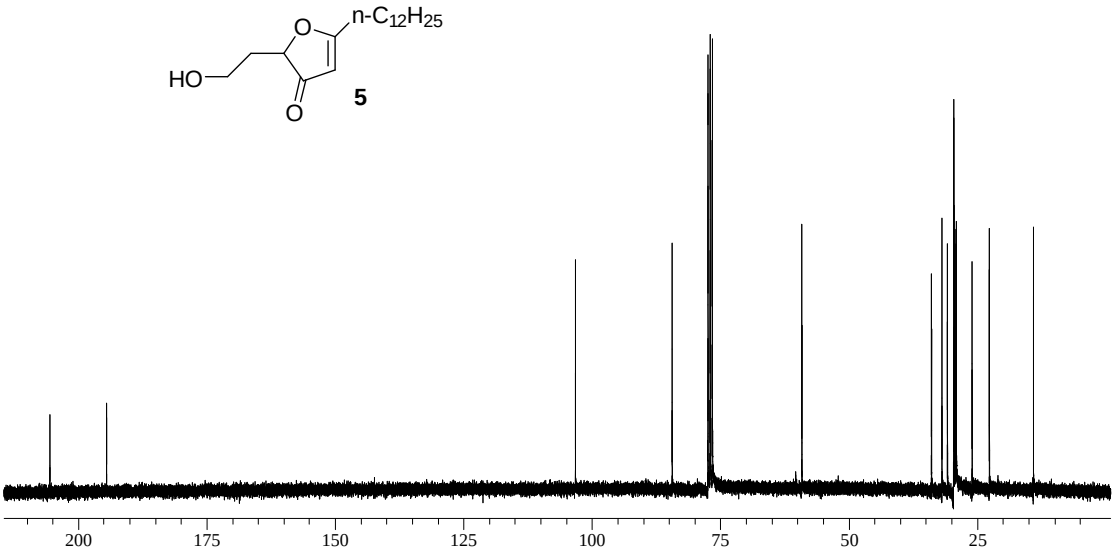
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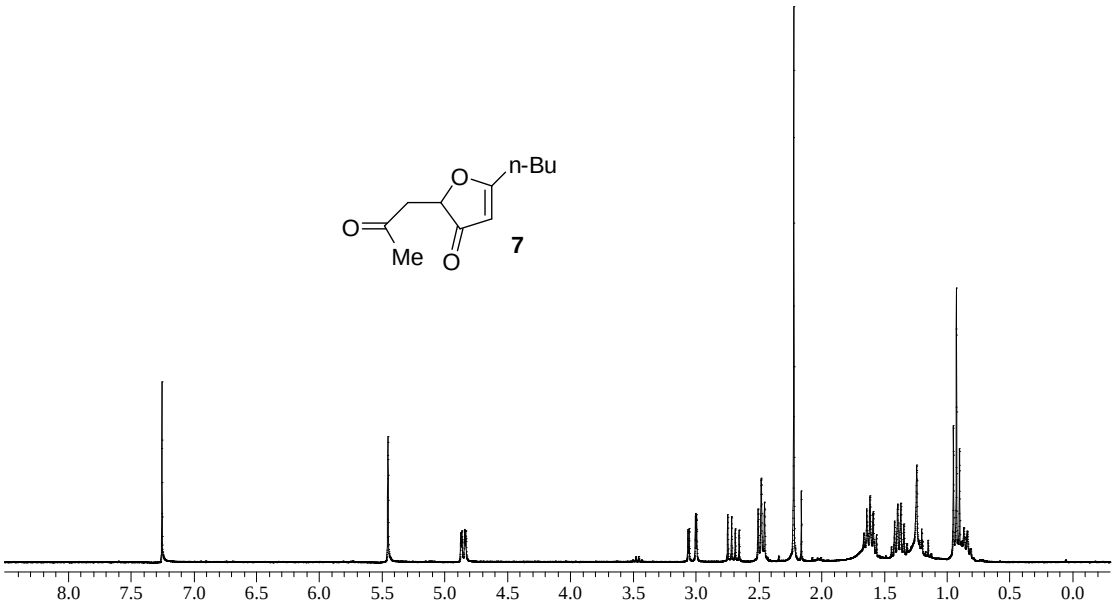
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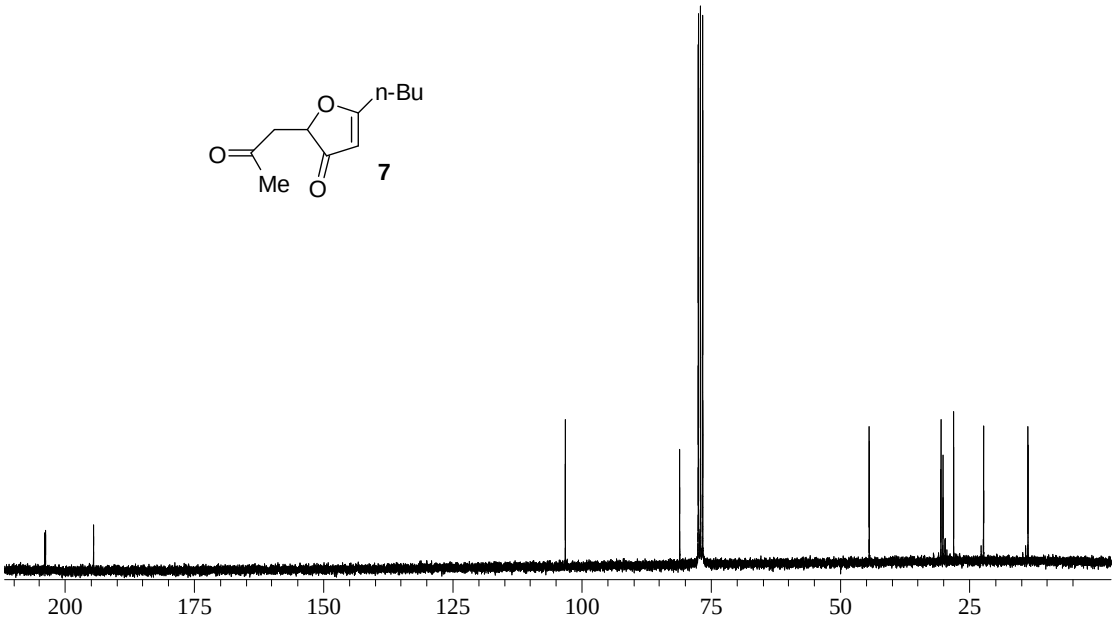
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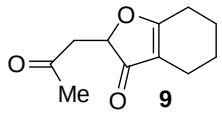
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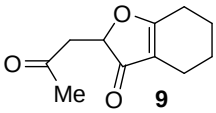
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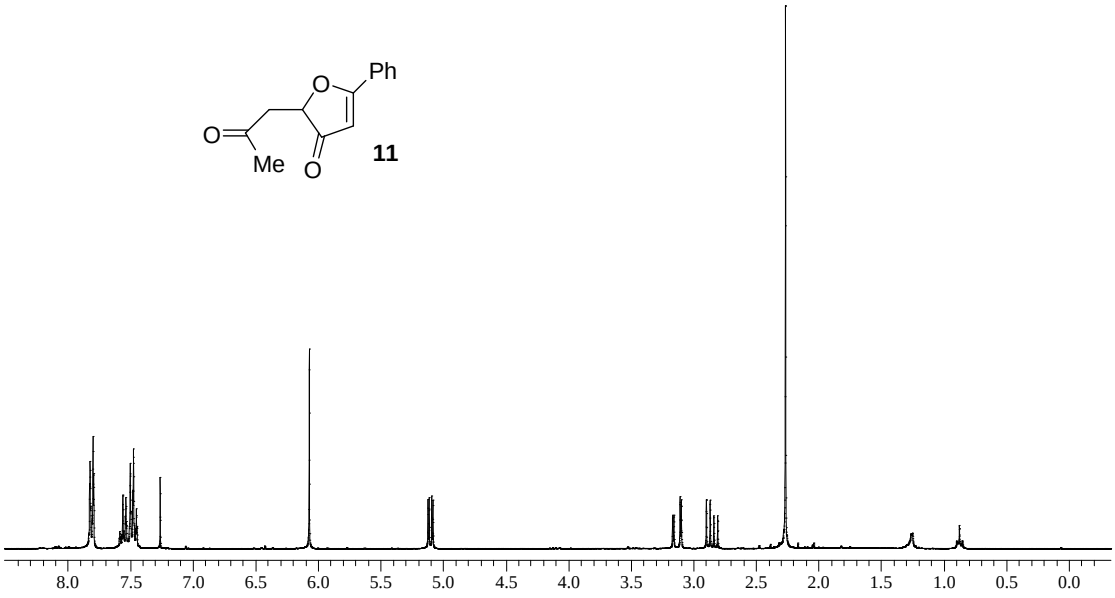
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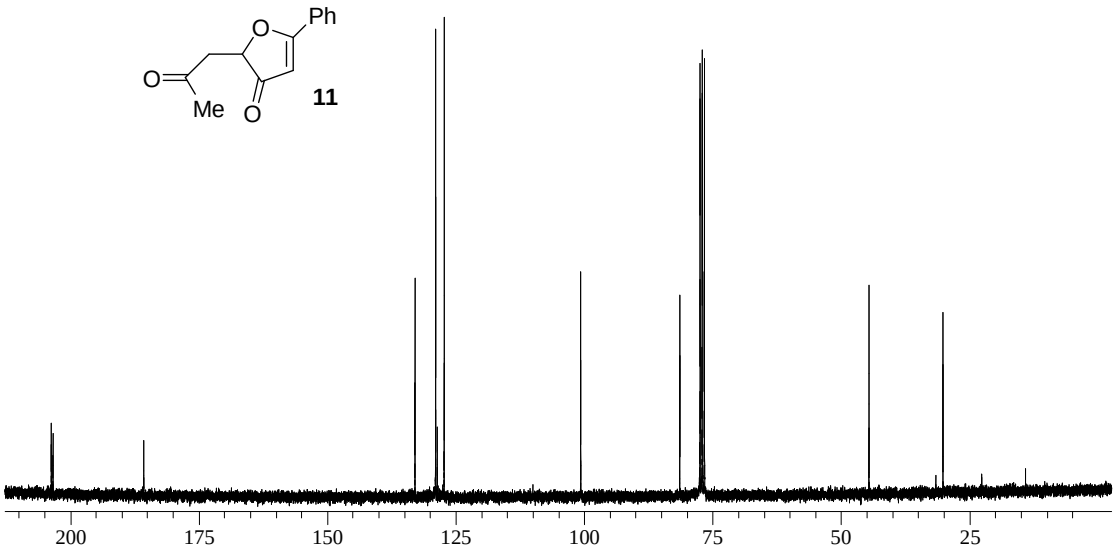
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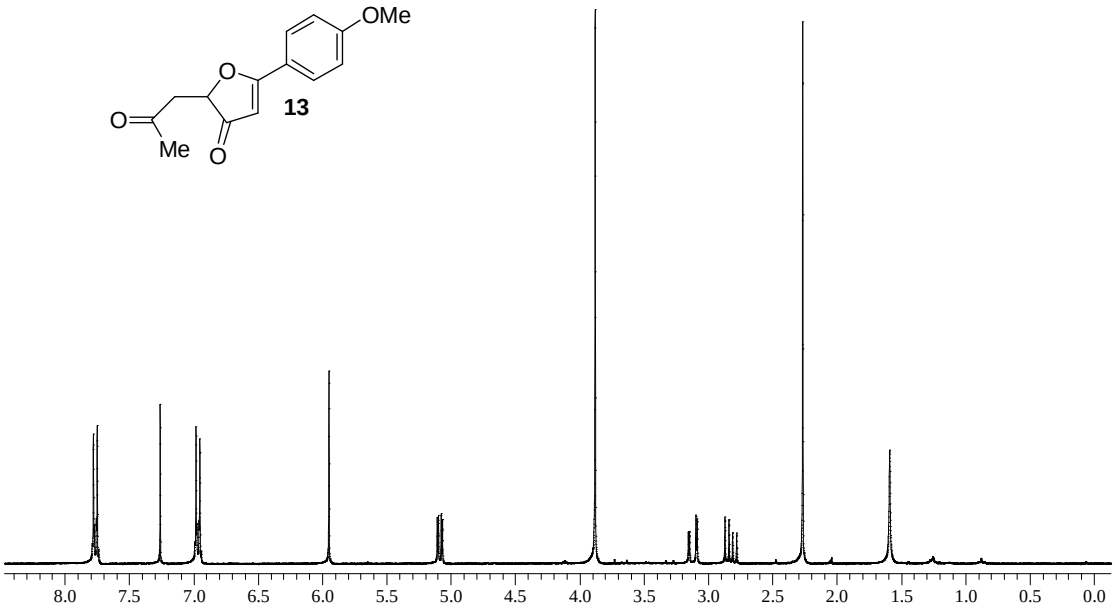
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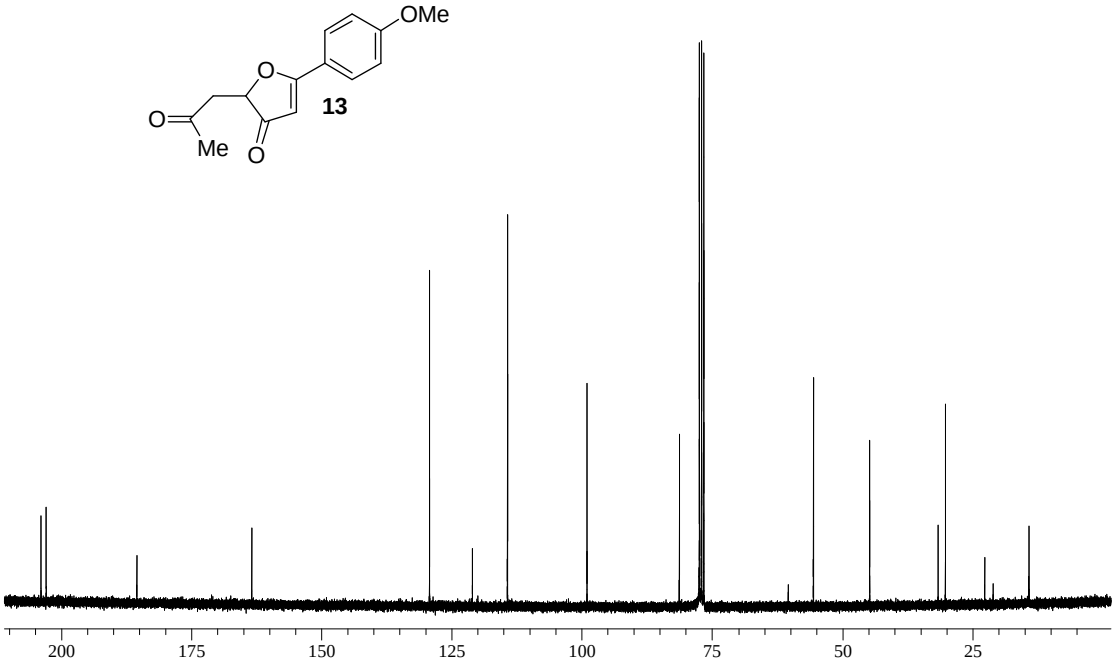
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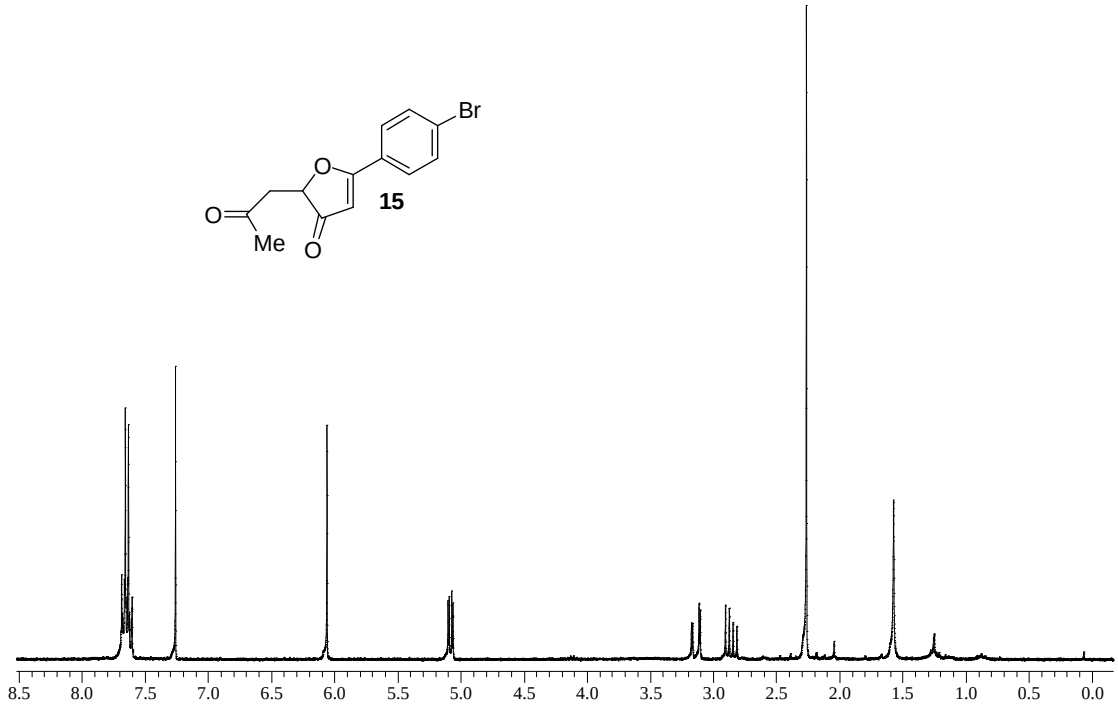
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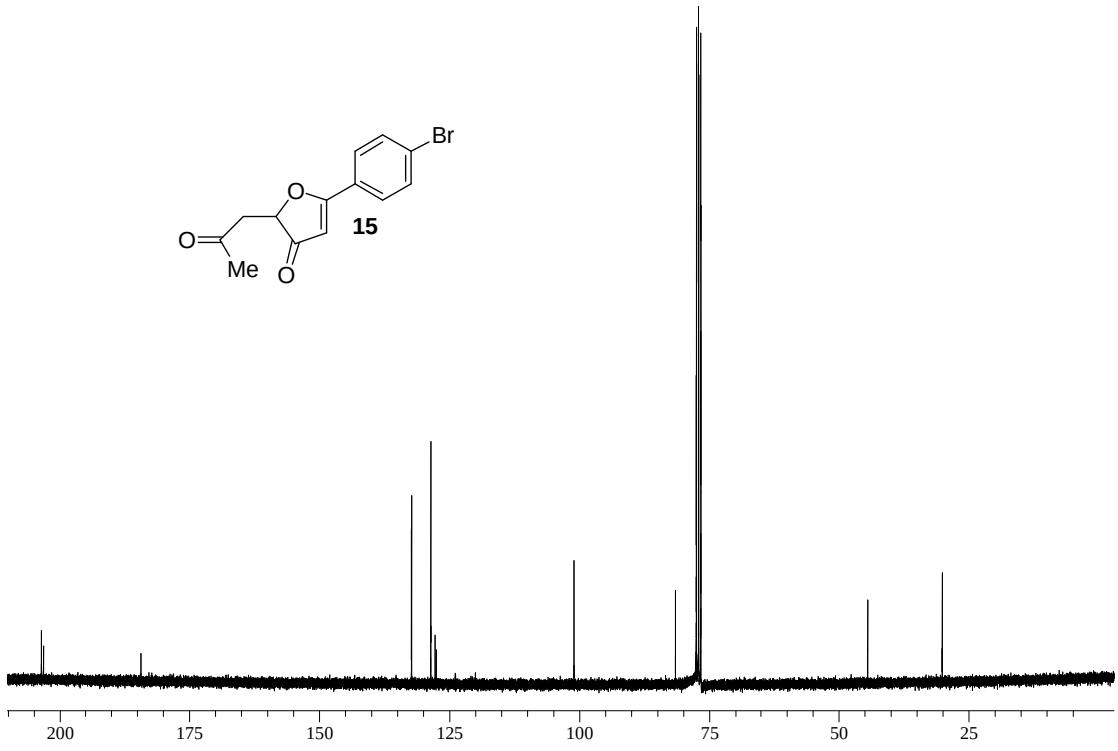
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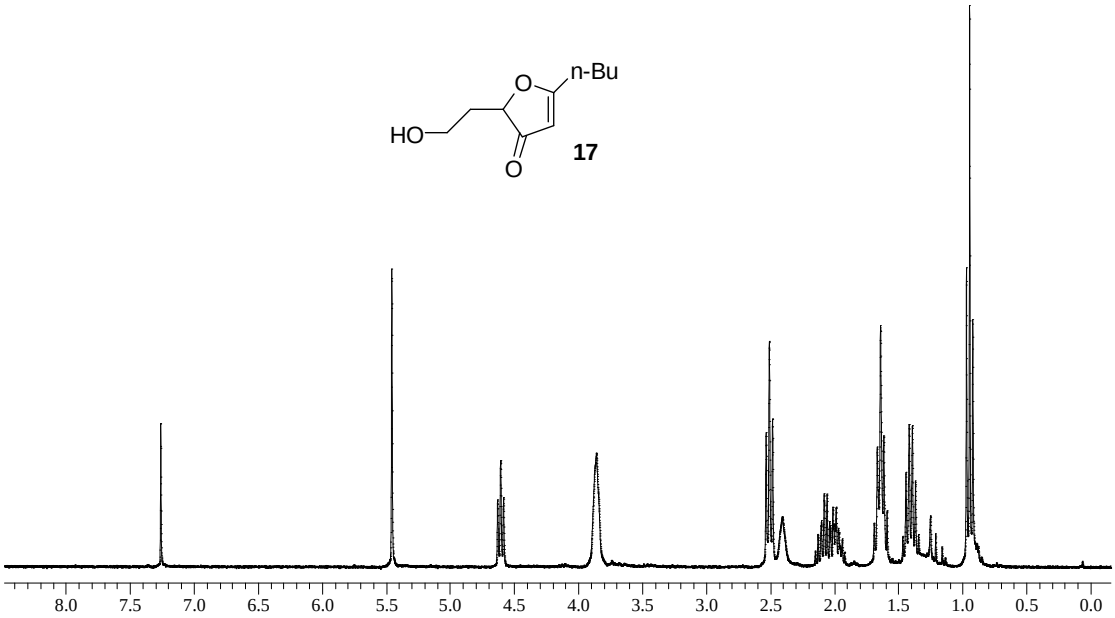
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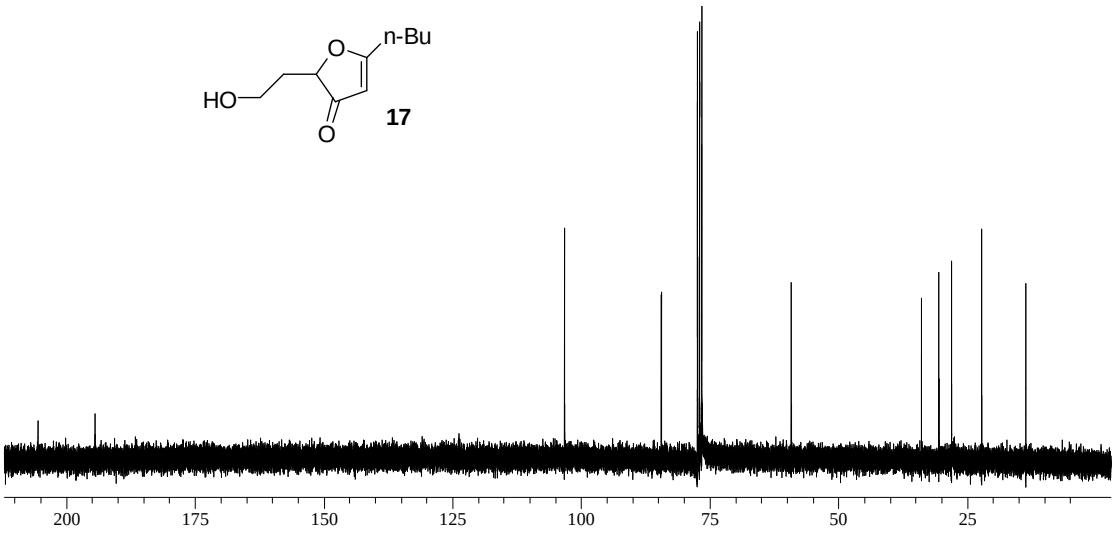
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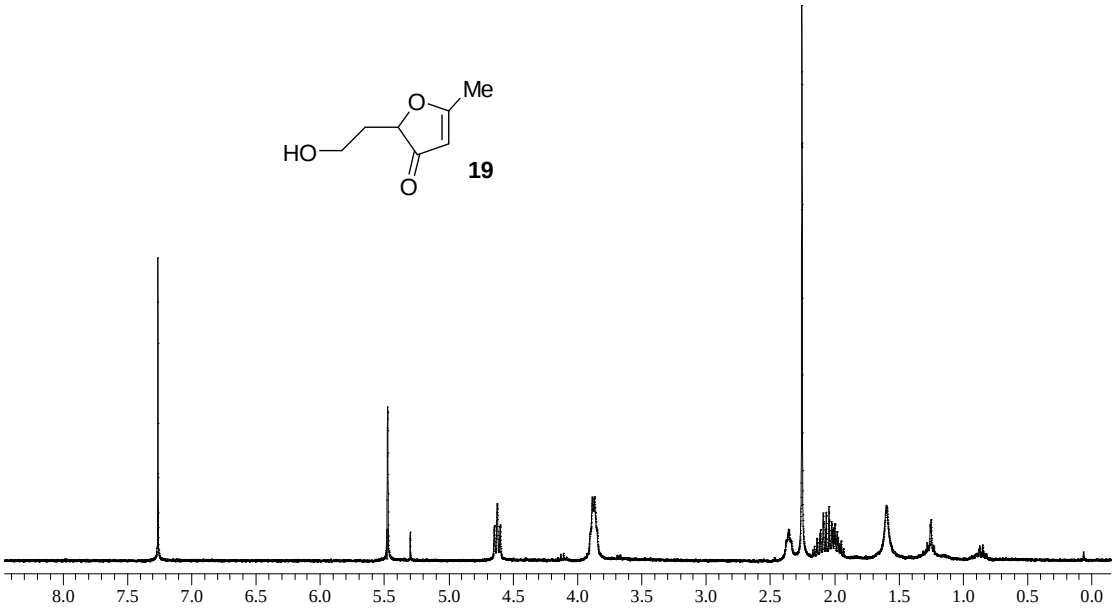

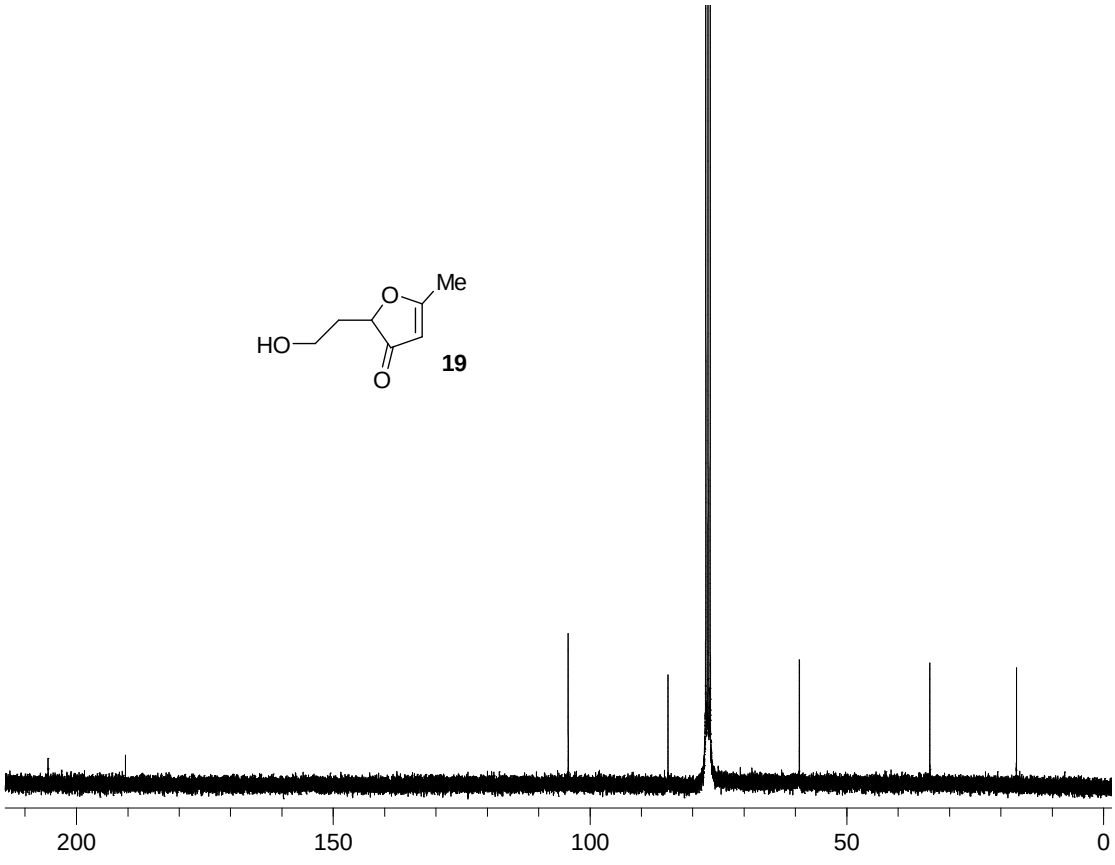

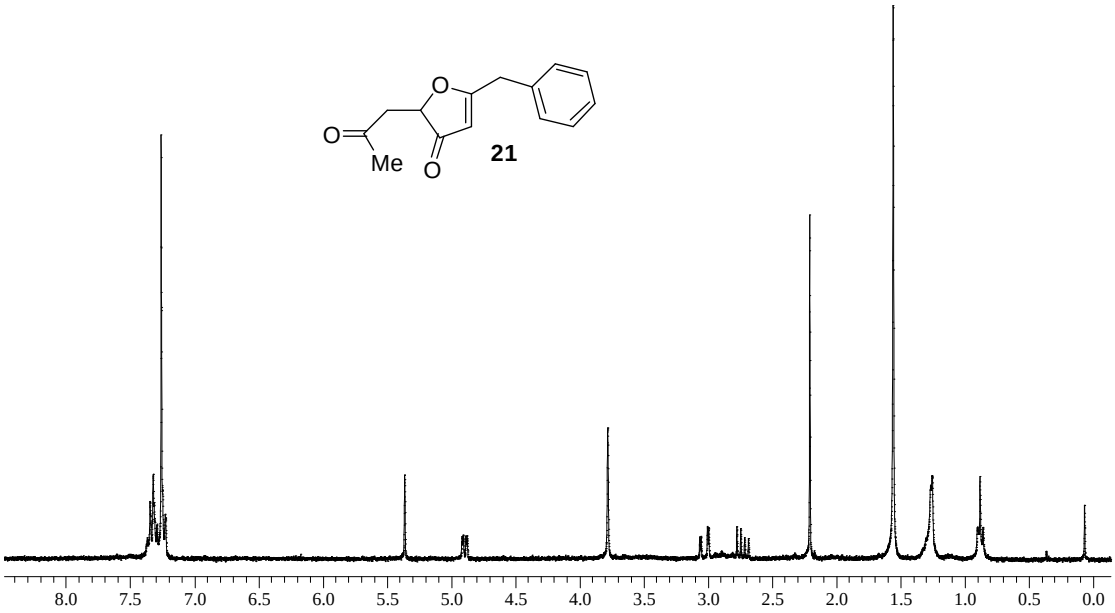
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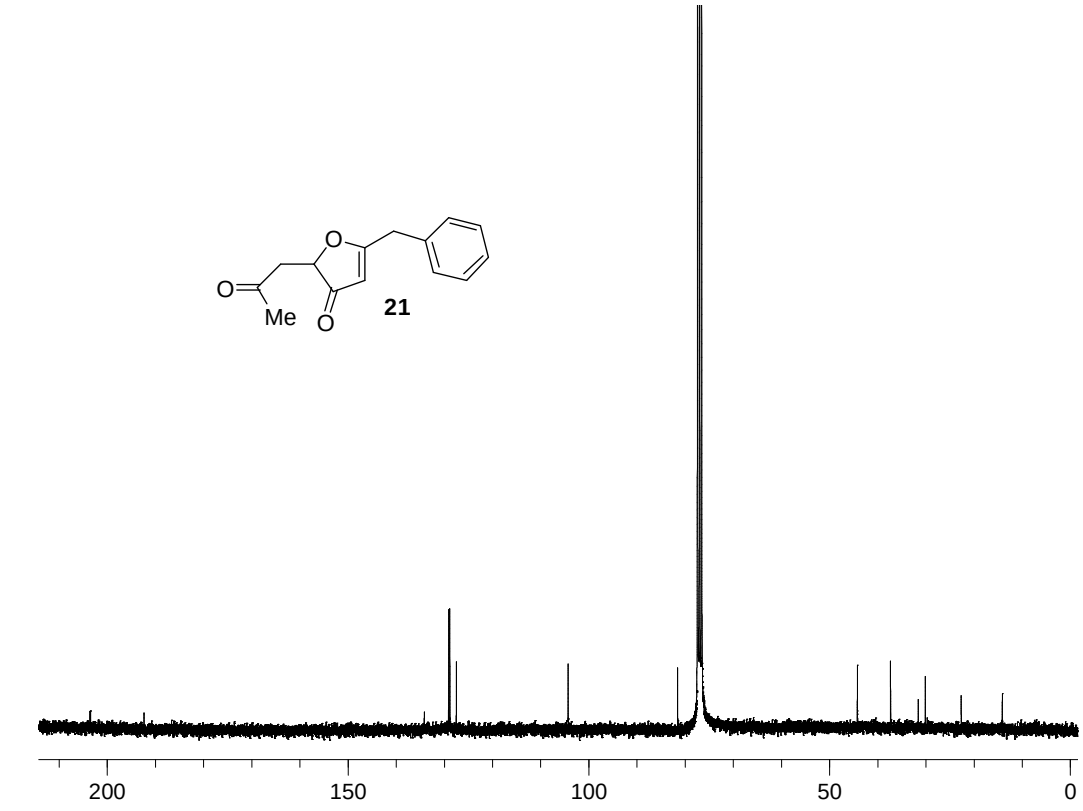
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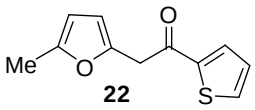
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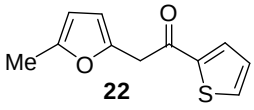
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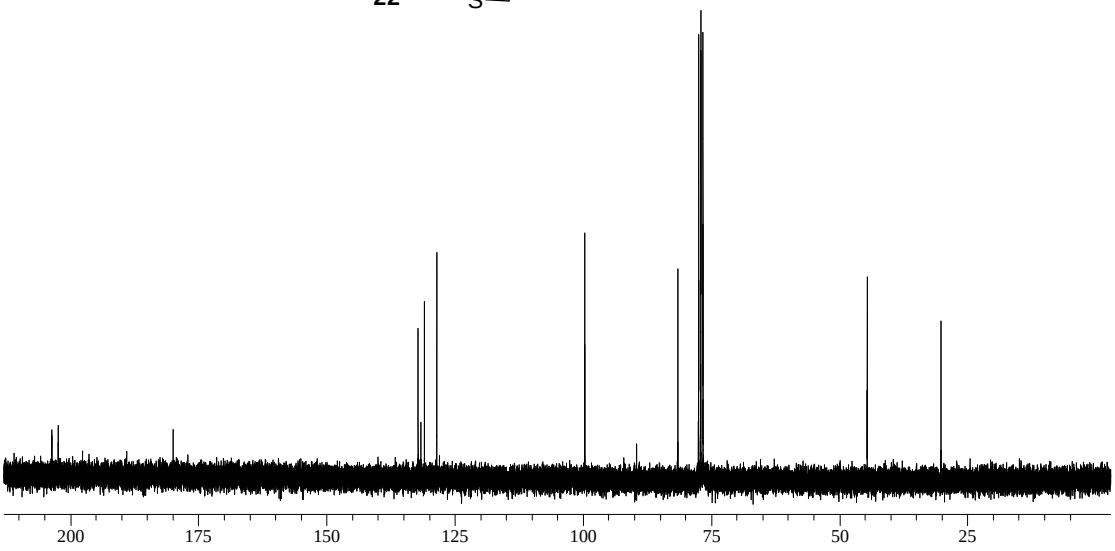
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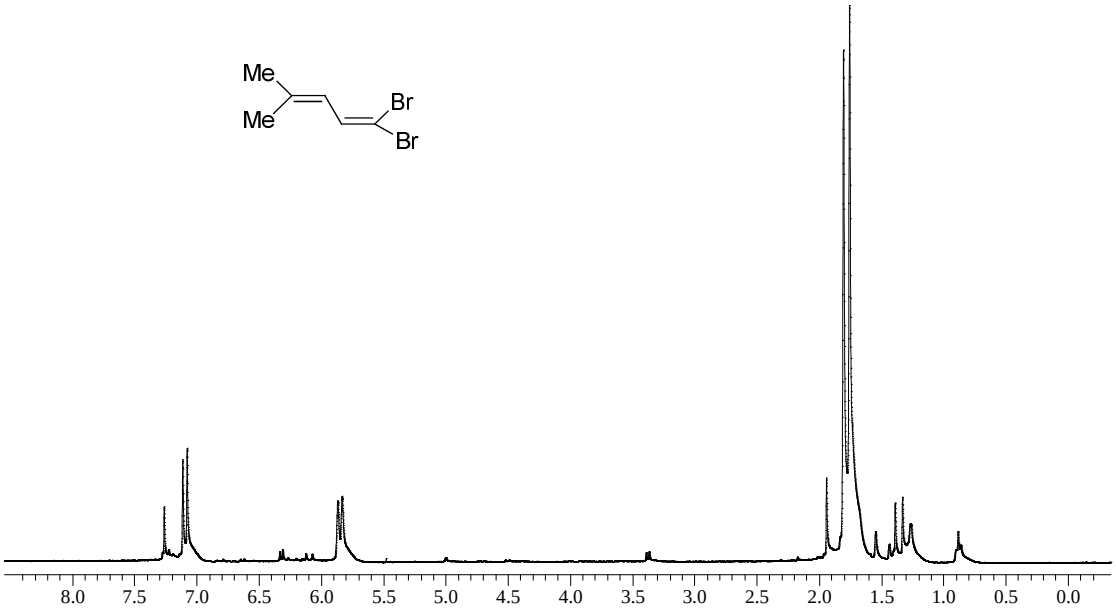
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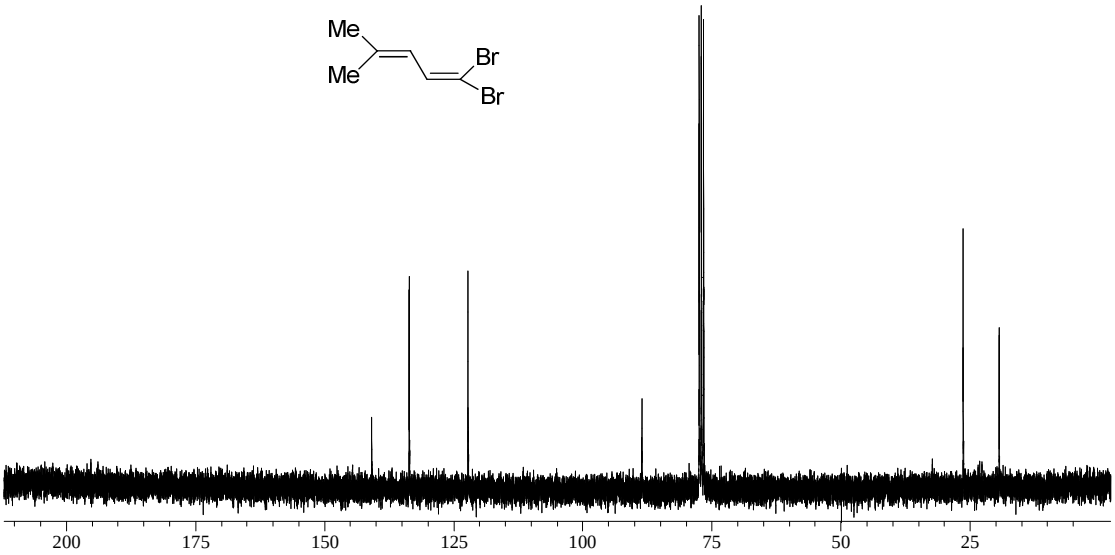
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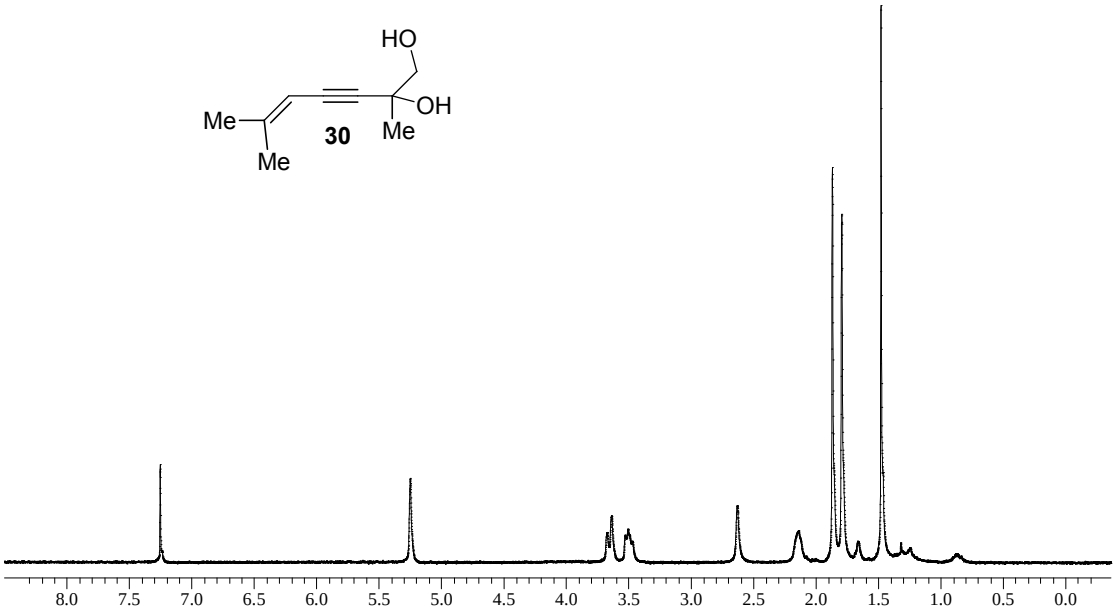

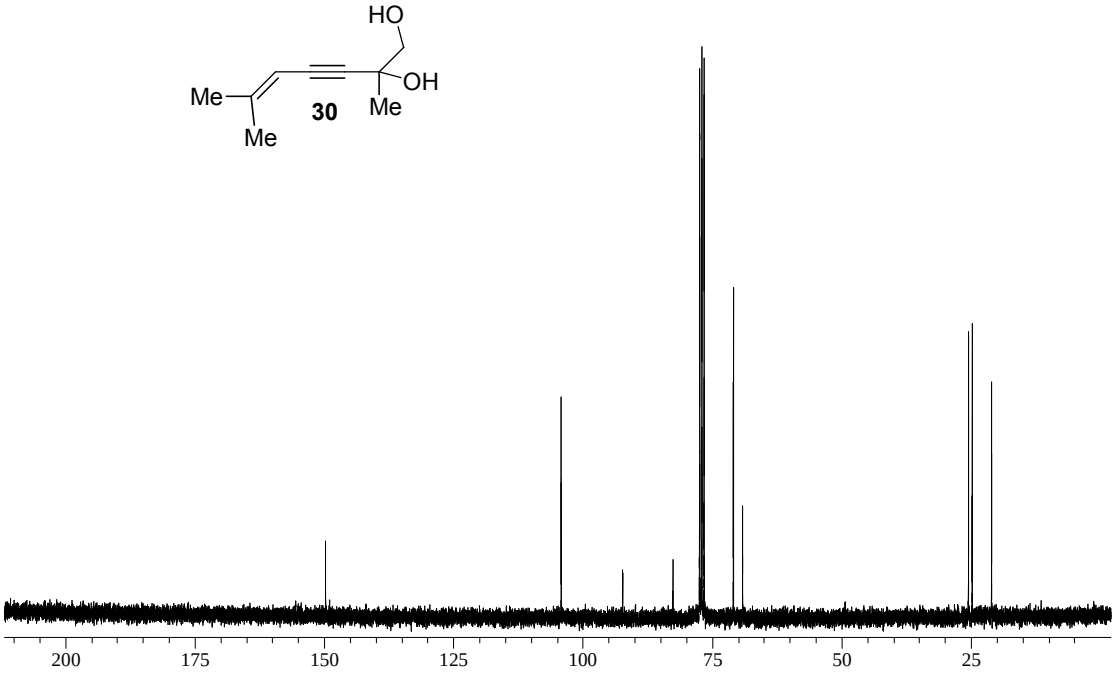

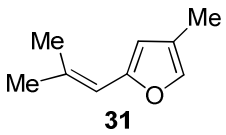
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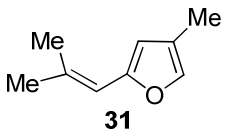
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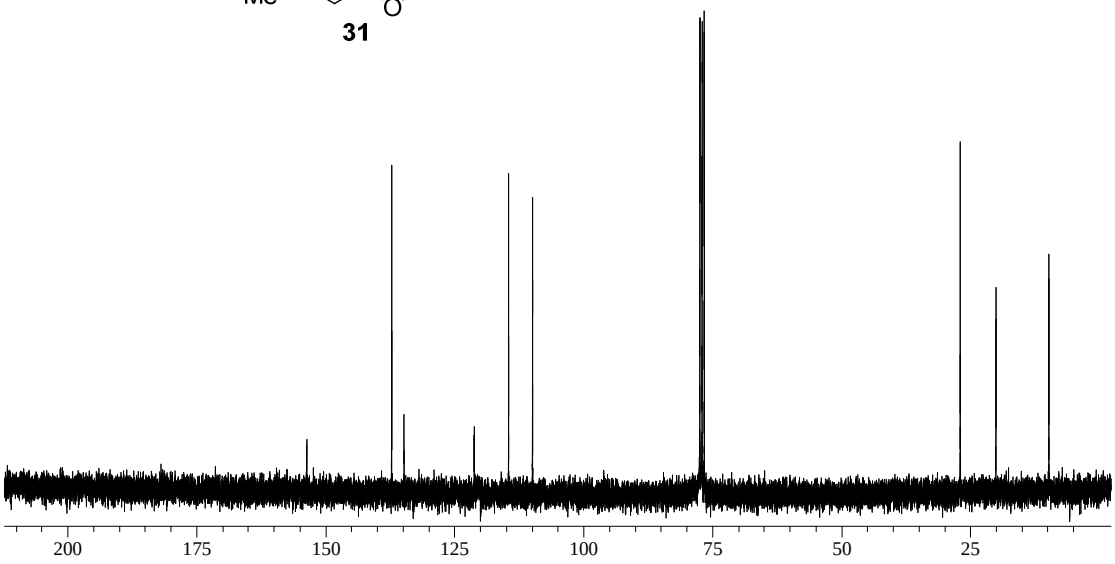
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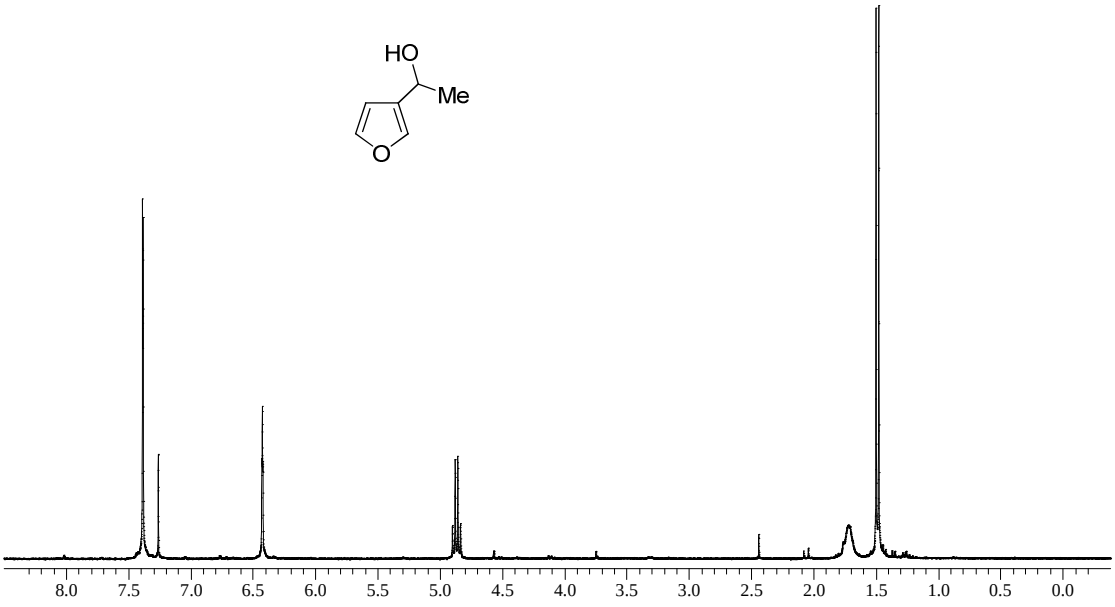
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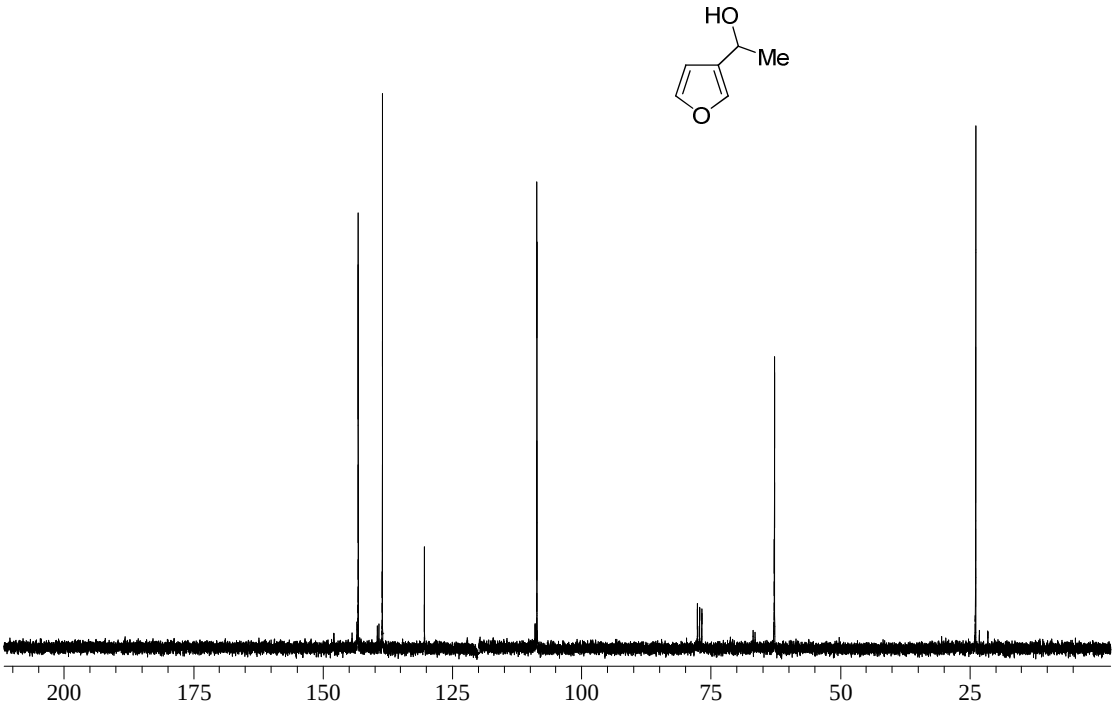
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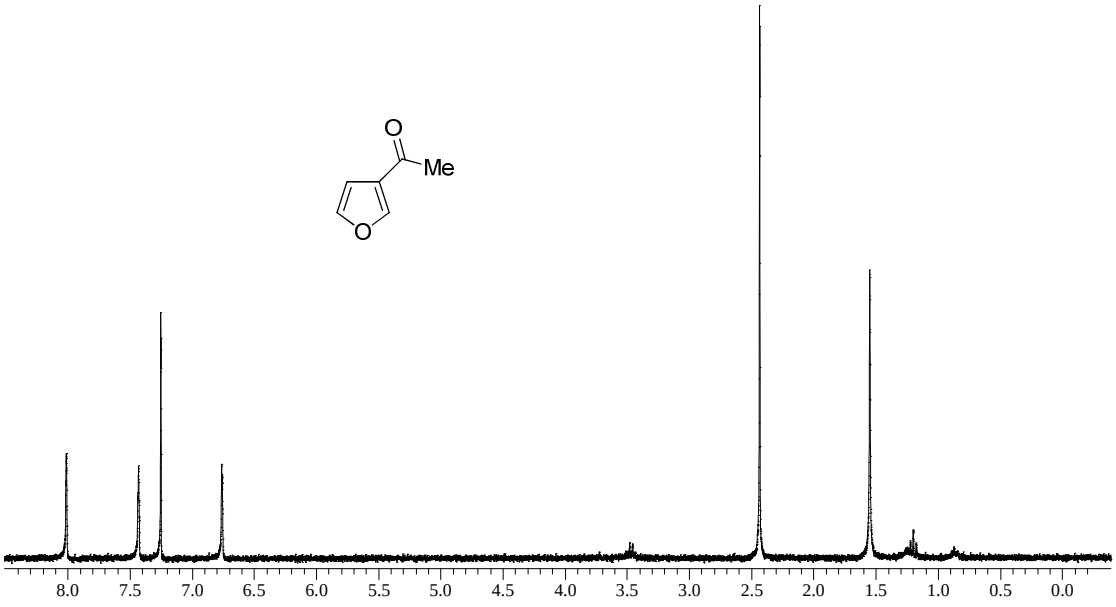
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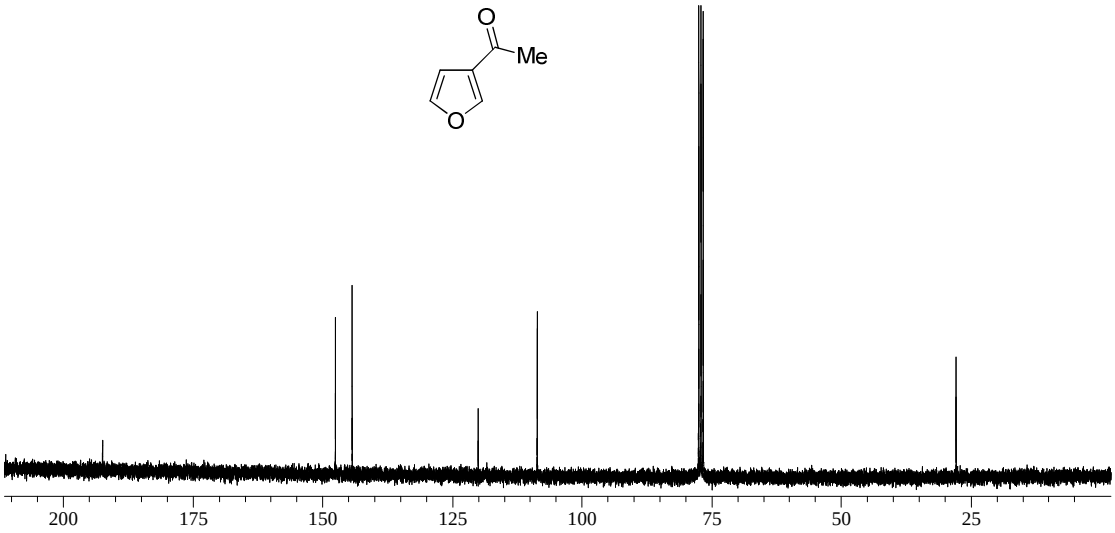
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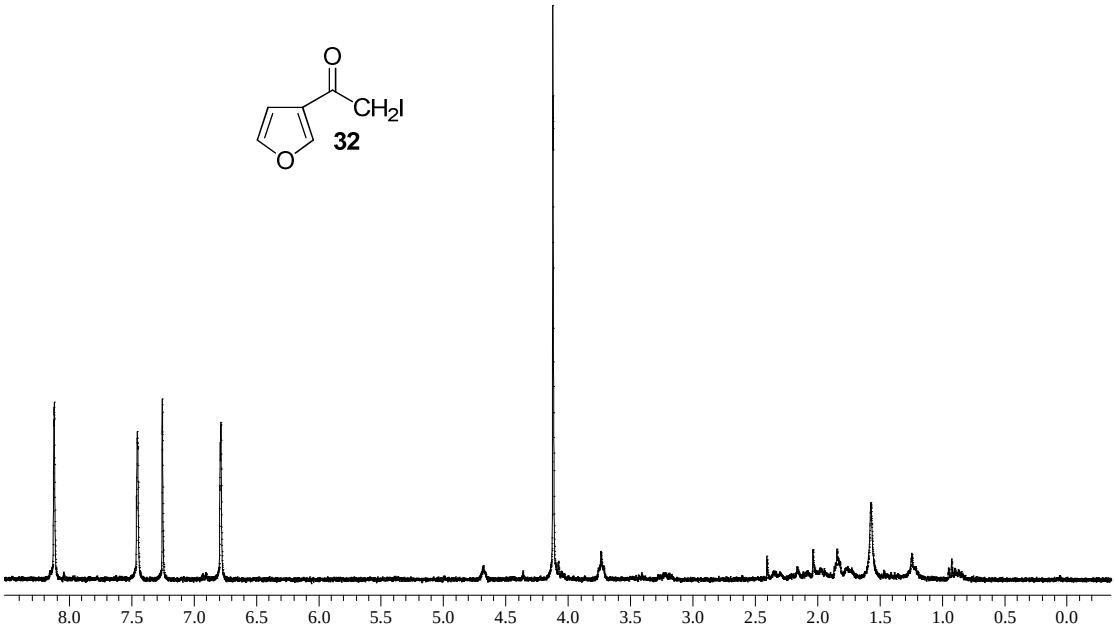
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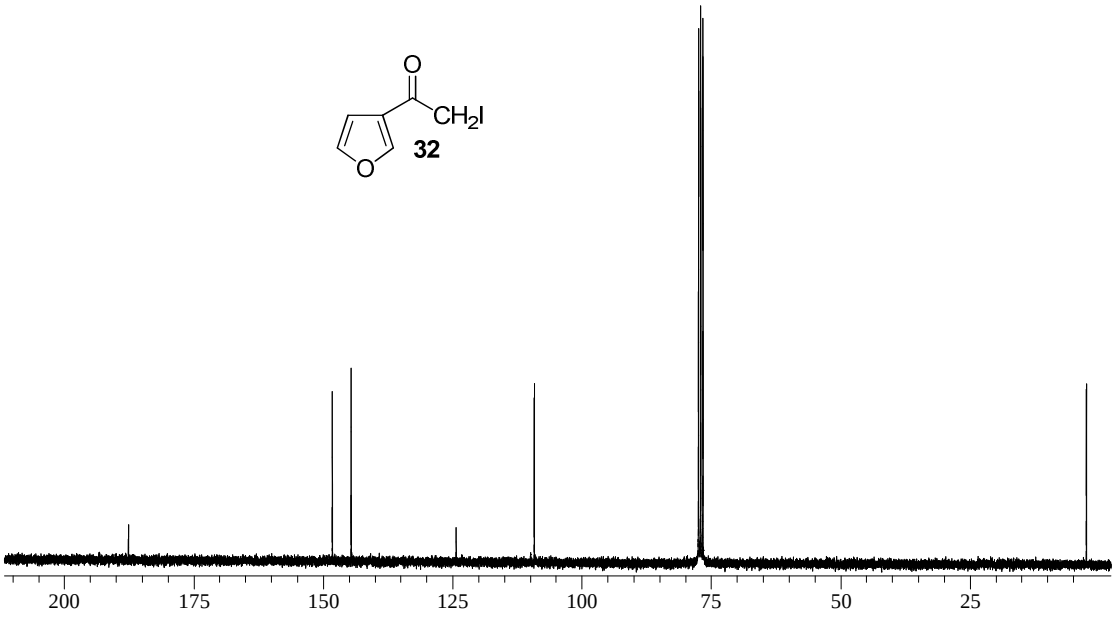
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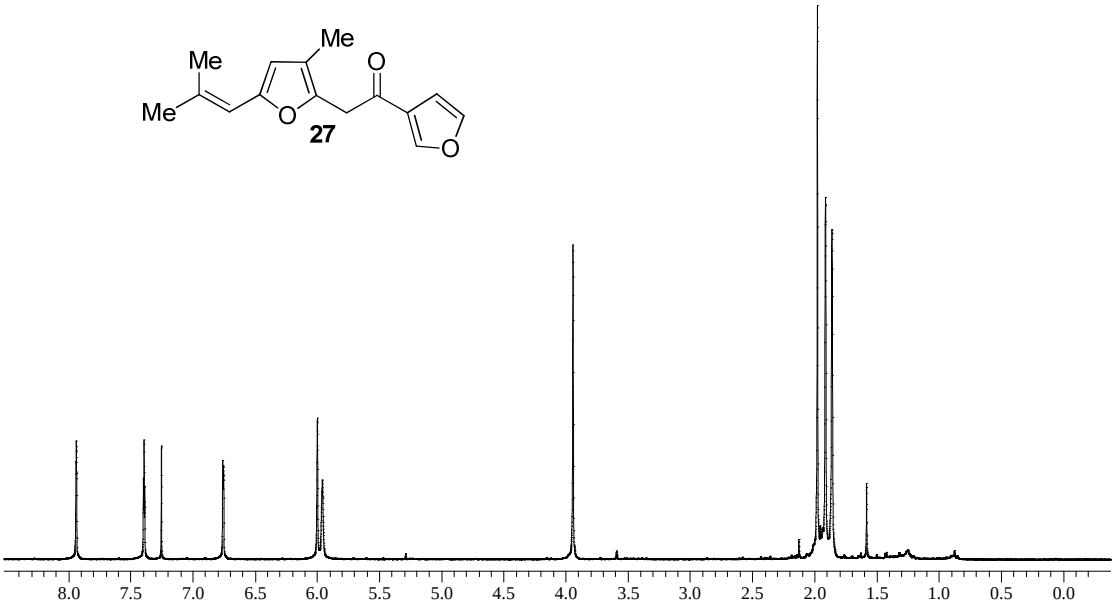
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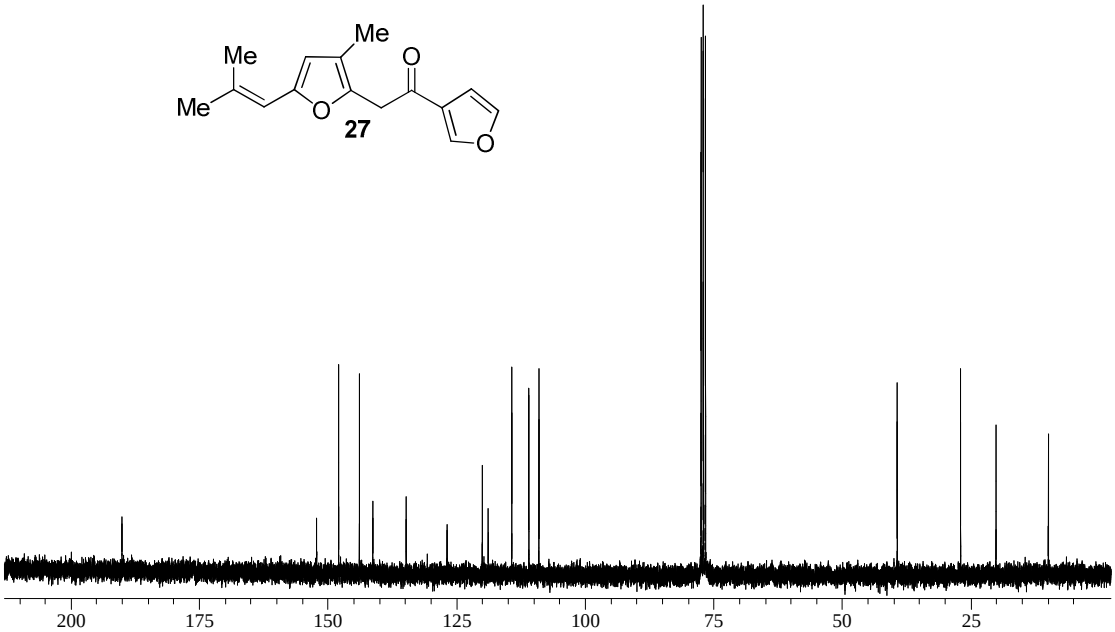
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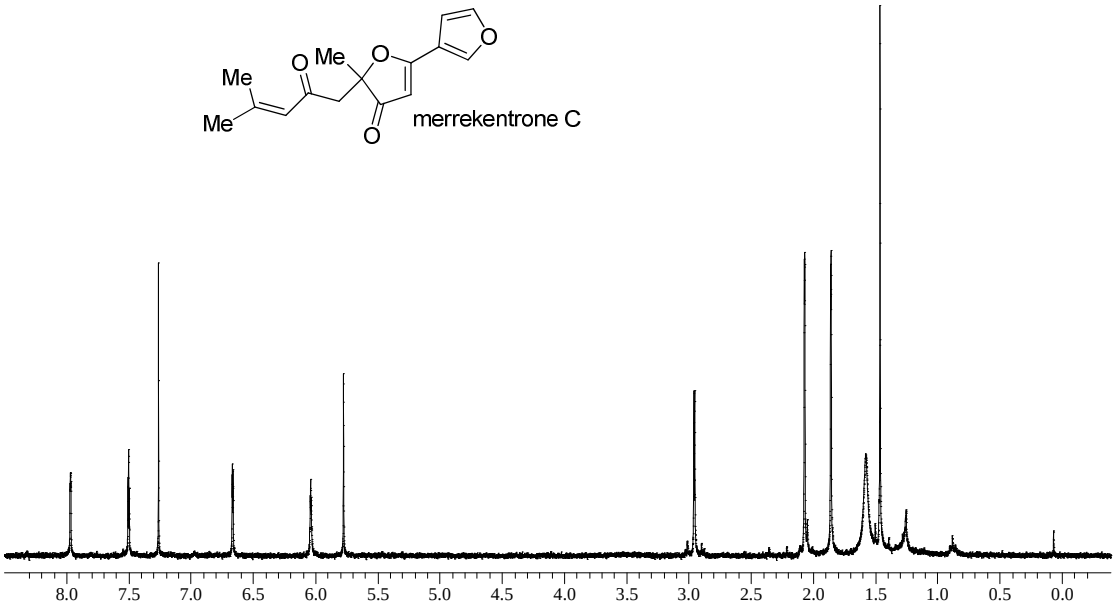
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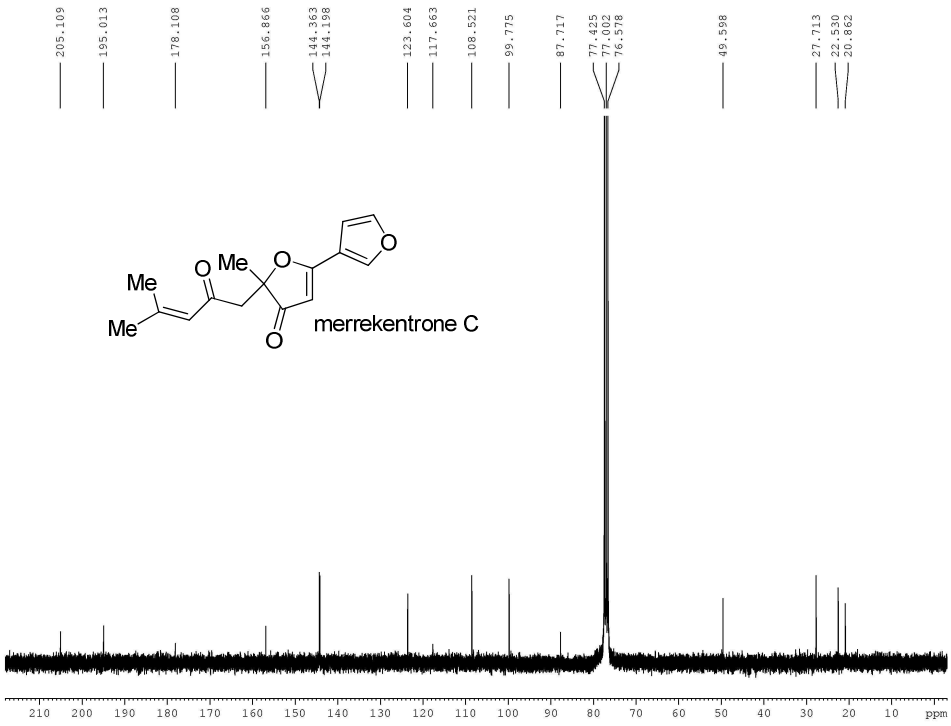
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