Electronic Supplementary Material (ESI) for Chemical Communications

Gold Catalysed Synthesis of 3-Alkoxy Furans at Room Temperature

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All reactions were carried out under an atmosphere of air unless otherwise indicated. Tetrahydrofuran was used following purification from a zeolite drying apparatus. All other chemicals were used as supplied unless otherwise indicated. Column chromatography was carried out using silica gel (40-60 µm) and analytical thin layer chromatography was carried out using aluminium-backed plates coated with silica gel. Components were visualised using combinations of ultra-violet lights, iodine, ceric ammonium molybdate, phosphomolybdic acid and potassium permanganate. ^{1}H NMR spectra were recorded at 400 MHz, 500 MHz or at 600 MHz on a spectrometer in $CDCl_3$ using residual protic solvent $CHCl_3$ (δ = 7.26 ppm, s) as the internal standard. Chemical shifts are quoted in ppm using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; qn, quintet; m, multiplet; br, broad or a combination of these. The coupling constants (*J*) are measured in Hertz. ^{13}C NMR spectra were recorded at 100 MHz, 125 MHz or at 150 MHz on a spectrometer in $CDCl_3$ using the central reference of $CHCl_3$ (δ = 77.0 ppm, t) as the internal standard.

1. Propargylic Alcohol Synthesis

General Procedure: *n*-Butyllithium (1.6M in hexanes, 1.2 eq.) was added dropwise to a stirred solution of 3,3-diethoxypropyne (1 eq.) in dry THF (1 mLmmol^{-1}) at -78 ˚C under an argon atmosphere. After 30 min the aldehyde (1 eq.) was added and the resulting solution was allowed to warm to rt and stirred overnight. The reaction was quenched with sat. aq. $NaHCO_3$ and the organic phase extracted with diethyl ether. The combined organic extracts were washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography to give the propargylic alcohol. Reactions were performed on scales using up to 9.3 g of 3,3-diethoxypropyne.

4,4-Diethoxy-1-(4-(trifluoromethyl)phenyl)but-2-yn-1-ol 1a
99% yield; IR (film) ν = 3404, 2980, 2936, 2888, 2246 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.66-7.59 (m, 4H), 5.56 (d, *J* = 5.7 Hz, 1H), 5.33 (s, 1H), 3.77-3.68 (m, 2H), 3.63-3.54 (m, 2H), 3.41 (br s, 1H), 1.21 (t, *J* = 7.1 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.9, 130.5 (q, *J* = 32.3 Hz), 126.9, 125.5 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 272.0 Hz), 91.2, 84.5, 82.3, 65.8, 63.5, 61.1, 15.0 ppm; Found (ES): [M-H]$^{+}$ 301.1051, $C_{15}H_{16}O_3F_3$ requires 301.1052.

6,6-Diethoxy-1-phenylhex-4-yn-3-ol 1b
75% yield; IR (film) ν = 3418, 2977, 2930, 2885, 2248 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28-7.15 (m, 5H), 5.30 (s, 1H), 4.40 (br s, 1H), 3.77-3.70 (m, 2H), 3.62-3.54 (m, 2H), 2.89 (br s, 1H), 2.78 (t, *J* = 7.9 Hz, 2H), 2.07-1.98 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.2, 128.51, 128.46, 126.0, 91.3, 86.5, 80.3, 61.3, 60.99, 60.91, 39.0, 31.4, 15.1 ppm; Found (CI): [M-OEt]$^{+}$ 217.12276, $C_{14}H_{17}O_2$ requires 217.12231.

4,4-Diethoxy-1-(4-methoxyphenyl)but-2-yn-1-ol 1c
96% yield; IR (film) ν = 3412, 2976, 2933, 2889, 2243 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 5.46 (d, *J* = 6.0 Hz, 1H), 5.34 (s, 1H), 3.80 (s, 3H), 3.79-3.70 (m, 2H), 3.65-3.55 (m, 2H), 2.53 (br s, 1H), 1.23 (t, *J* = 7.1 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.8, 132.4, 128.1,

114.0, 91.4, 85.3, 81.7, 64.0, 61.03, 60.96, 55.3, 15.1 ppm; Found (EI): $[M]^+$ 264.135933, $C_{15}H_{20}O_4$ requires 264.13561.

1-Cyclopropyl-4,4-diethoxybut-2-yn-1-ol 1d
86% yield; IR (film) ν = 3410, 2978, 2932, 2890, 2248 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 5.26 (s, 1H), 4.18 (t, *J* = 6.0 Hz, 1H), 3.72-3.65 (m, 2H), 3.57-3.52 (m, 2H), 2.46 (d, *J* = 6.0 Hz, 1H), 1.25-1.20 (m, 1H), 1.19 (t, *J* = 7.2 Hz, 6H), 0.56-0.47 (m, 2H), 0.45-0.38 (m, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 91.3, 84.6, 80.2, 65.5, 61.0, 60.9, 17.0, 15.1, 3.34, 1.76 ppm; Found (CI): $[M\text{-}OEt]^+$ 153.10159, $C_9H_{13}O_2$ requires 153.09101.

4,4-Diethoxy-1-phenylbut-2-yn-1-ol 1e
95% yield; IR (film) ν = 3317, 2977, 1493, 1455 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.57–7.54 (m, 2H), 7.43–7.33 (m, 3H), 5.55 (d, *J* = 6.2 Hz, 1H), 5.83 (s, 1H), 3.81–3.73 (m, 2H), 3.67–3.58 (m, 2H), 2.43 (d, *J* = 6.2 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.1, 128.7, 128.5, 126.7, 91.4, 85.2, 82.0, 64.5, 61.1, 61.0, 15.1 ppm; data in accordance with the literature.[1]

1-(2,6-Dimethylphenyl)-4,4-diethoxybut-2-yn-1-ol 1f
97% yield; IR (film) ν = 3424, 2976, 2930, 2890, 2248 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.10-7.05 (m, 1H), 7.01-6.97 (m, 2H), 5.94 (s, 1H), 5.26 (s, 1H), 3.75-3.65 (m, 2H), 3.60-3.50 (m, 2H), 2.60 (br s, 1H), 2.49 (s, 6H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.4, 143.0, 110.4, 107.9, 91.2, 82.9, 80.9, 61.08, 61.01, 57.8, 15.0 ppm; Found (CI): $[M]^+$ 261.148379, $C_{16}H_{22}O_3$ requires 261.14852.

(6*R*)-1,1-Diethoxy-6,10-dimethylundec-9-en-2-yn-4-ol 1g
88% yield; IR (film) ν = 3388, 2974, 2913, 2236, 1480 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 5.26 (s, 1H), 5.04 (t, *J* = 5.7 Hz, 1H), 4.46-4.42 (m, 1H), 3.72-3.66 (m, 2H), 3.57-3.51 (m, 2H), 2.54 (d, *J* = 5.3 Hz, 0.6H), 2.46 (d, *J* = 5.7 Hz, 0.4H), 2.01-1.88 (m, 2H), 1.77-1.70 (m, 0.5H), 1.69-1.64 (m, 1H), 1.63 (s, 3H), 1.56 (s, 3H), 1.56-1.50 (m, 1H), 1.47-1.42 (m, 0.5H), 1.37-1.27 (m, 1H), 1.19 (t, *J* = 7.2 Hz, 6H), 1.17-1.10 (m, 1H), 0.88 (dd, *J* = 6.4, 4.5 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 131.4, 131.3, 124.7, 124.6, 91.3, 87.2, 86.9, 80.0, 79.7, 61.0, 60.9, 60.3, 44.9, 44.8, 37.2, 37.1, 29.4, 29.0, 25.8, 25.41, 25.38, 19.7, 19.2, 17.7, 15.1 ppm; Found (CI): $[M\text{-}OEt]^+$ 237.184928, $C_{15}H_{25}O_2$ requires 237.18491. $[\alpha]_D^{20}$ -1.7 (c 0.71 in $CHCl_3$)

4-(4,4-Diethoxy-1-hydroxybut-2-yn-1-yl)benzonitrile 1h
43% yield; IR (film) ν = 3423, 2977, 2932, 2888, 2230 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.67-7.64 (m, 4H), 5.57 (d, *J* = 5.8 Hz, 1H), 5.32 (s, 1H), 3.78-3.68 (m, 2H), 3.64-3.54 (m, 2H), 3.47 (br s, 1H), 1.22 (t, *J* = 7.1 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.2, 132.4, 127.2, 118.6, 112.0, 91.2, 84.1, 82.6, 65.8, 63.3, 61.2, 15.0 ppm; Found (ES): $[M\text{-}H]^+$ 258.1130, $C_{15}H_{16}NO_3$ requires 258.1130.

4,4-Diethoxy-1-(thiophen-2-yl)but-2-yn-1-ol 1i
51% yield; IR (film) ν = 3395, 2976, 2930, 2888, 2243 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.29-7.26 (m, 1H), 7.16-7.13 (m, 1H), 6.97-6.93 (m, 1H), 5.69 (d, *J* = 6.7 Hz, 1H), 5.33 (s, 1H), 3.80-3.70 (m, 2H), 3.65-3.55 (m, 2H), 3.44 (br s, 1H), 1.22 (t, *J* = 7.1 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.1, 126.7, 126.0, 125.7, 91.2,

84.7, 81.1, 61.1, 61.0, 60.0, 15.0 ppm; Found (CI): $[M\text{-}OH]^+$ 223.078664, $C_{12}H_{15}O_2S$ requires 223.07873.

4,4-Diethoxy-1-(furan-2-yl)but-2-yn-1-ol 1j
94% yield; IR (film) ν = 3404, 2977, 2933, 2890, 2240 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.41-7.39 (m, 1H), 6.44 (d, *J* = 3.3 Hz, 1H), 6.35-6.32 (m, 1H), 5.51 (d, *J* = 6.8 Hz, 1H), 5.34 (s, 1H), 3.80-3.70 (m, 2H), 3.65-3.55 (m, 2H), 3.27 (br s, 1H), 1.23 (t, *J* = 7.1 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.5, 143.0, 110.4, 107.9, 91.2, 82.9, 80.9, 61.08, 61.01, 57.8, 15.0 ppm; Found (EI): $[M]^+$ 224.104178, $C_{12}H_{16}O_4$ requires 224.10431.

1-Cyclohexyl-4,4-diethoxybut-2-yn-1-ol 1k
84% yield; IR (film) ν = 3416, 2925, 1450 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 5.29 (s, 1H), 4.19 (br d, *J* = 6.6 Hz, 1H), 3.75-3.68 (m, 2H), 3.61-3.53 (m, 2H), 2.07 (br s, 1H), 1.87-1.79 (m, 2H), 1.78-1.71 (m, 2H), 1.68-1.60 (m, 1H), 1.58-1.50 (m, 1H), 1.27-0.96 (m, 5H), 1.21 (t, *J* = 7.1 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 91.4, 85.6, 81.0, 67.1, 61.0, 60.9, 43.9, 28.6, 28.3, 26.4, 25.94, 25.91, 15.2 ppm; Found (EI): $[M\text{-}H]^+$ 239.16446, $C_{14}H_{23}O_3$ requires 239.16417. Data in accordance with the literature.[2]

1-(4-Bromophenyl)-4,4-diethoxybut-2-yn-1-ol 1l
48% yield; IR (film) ν = 3397, 2976, 2930, 2887, 2242 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.49 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 5.47 (br s, 1H), 5.33 (s, 1H), 3.77-3.68 (m, 2H), 3.63-3.55 (m, 2H), 2.76 (br s, 1H), 1.22 (t, *J* = 7.1 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.0, 131.7, 128.4, 122.5, 91.3, 84.6, 82.2, 63.7, 61.11, 61.06, 15.1 ppm; Found (EI): $[M\text{-}OEt]^+$ 267.000941, $C_{12}H_{12}O_2Br$ requires 267.00152.

Methyl 3-(4,4-diethoxy-1-hydroxybut-2-yn-1-yl)benzoate 1m
67% yield; IR (film) ν = 3429, 2977, 2934, 2888, 2240, 1722 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.18 (s, 1H), 8.00-7.94 (m, 1H), 7.75-7.70 (m, 1H), 7.39-7.35 (m, 1H), 5.56 (br s, 1H), 5.32 (s, 1H), 3.90 (s, 3H), 3.79-3.68 (m, 2H), 3.63-3.55 (m, 2H), 2.40 (br s, 1H), 1.21 (t, *J* = 7.1 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.8, 140.8, 131.2, 130.3, 129.5, 128.7, 127.8, 91.2, 84.9, 81.9, 63.7, 61.1, 61.0, 52.2, 15.0 ppm; Found (CI): $[M\text{-}OEt]^+$ 247.095983, $C_{14}H_{15}O_4$ requires 247.09649.

2-(4,4-Diethoxy-1-hydroxybut-2-yn-1-yl)phenol 1n
22% yield; IR (film) ν = 3326, 2977, 2931, 2892, 2246 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.70 (s, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 6.88-6.82 (m, 2H), 5.70 (s, 1H), 5.32 (s, 1H), 4.32 (br s, 1H), 3.78-3.69 (m, 2H), 3.63-3.54 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.9, 130.0, 127.7, 124.6, 120.2, 116.9, 91.3, 84.1, 82.3, 62.9, 61.27, 61.25, 15.0 ppm; Found (ES): $[M\text{-}H]^+$ 249.1125, $C_{14}H_{17}O_4$ requires 249.1127.

2-Bromo-3-(4,4-diethoxy-1-hydroxybut-2-yn-1-yl)benzaldehyde 1o
Obtained in 15% yield as a byproduct during the synthesis of **1p**; IR (film) ν = 3408, 2975, 2925, 2248, 1690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 10.24 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 5.78 (d, *J* = 4.8 Hz, 1H), 5.13 (s, 1H), 3.60-3.49 (m, 2H), 3.45-3.35 (m, 2H), 2.98 (br d, *J* = 4.8 Hz, 1H), 1.03 (t, *J* = 7.1 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 191.9, 140.7, 134.1,

133.9, 130.1, 128.1, 127.1, 91.2, 83.7, 82.3, 63.2, 61.2, 61.1, 14.1 ppm; Found (CI): $[M+H]^+$ 341.07010, $C_{15}H_{18}O_4Br$ requires 341.03102.

1,1'-(2-Bromo-1,3-phenylene)bis(4,4-diethoxybut-2-yn-1-ol) 1p

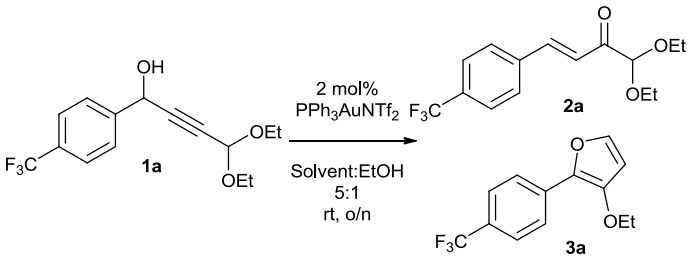
51% yield; IR (film) ν = 3409, 2977, 2931, 2887, 2248 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.73 (d, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 5.90 (d, *J* = 5.5 Hz, 2H), 5.32 (s, 2H), 3.77-3.68 (m, 4H), 3.63-3.54 (m, 4H), 3.02 (br d, *J* = 5.5 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.9, 128.6, 128.1, 123.0, 91.3, 84.2, 81.9, 64.1, 61.1, 61.0, 15.0 ppm; Found (ES): $[M+H]^+$ 467.1075, $C_{22}H_{28}O_6Br$ requires 467.1069.

1,1-Diethoxy-5,5-dimethyloct-7-en-2-yn-4-ol 1q

78% yield; IR (film) ν = 3466, 2977, 2932, 2892, 2249 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 5.75 (m, 1H), 5.25 (s, 1H), 5.02-4.97 (m, 2H), 4.06 (d, *J* = 5.7 Hz, 1H), 3.70-3.64 (m, 2H), 3.55-3.50 (m, 2H), 2.66 (br s, 1H), 2.10 (dd, *J* = 13.6, 7.5 Hz, 1H), 2.03 (dd, *J* = 13.6, 7.2 Hz, 1H), 1.16 (t, *J* = 7.2 Hz, 6H), 0.91 (s, 3H), 0.89 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 134.8, 117.8, 91.3, 85.2, 81.4, 69.7, 61.0, 60.8, 42.7, 38.6, 22.7, 22.5, 15.1 ppm; Found (CI): $[M-OEt]^+$ 195.16034, $C_{12}H_{19}O_2$ requires 195.13796.

2. Furan Synthesis:

Reaction Optimisation



Entry	Solvent[a]	Yield of **2a**[b]	Yield of **3a**[b]
1	PhMe:EtOH	35%	65%
2	Petrol:EtOH	12%	18%
3	CH_2Cl_2:EtOH	35%	47%
4	THF:EtOH	18%	71%
5	Et_2O:EtOH	24%	65%
6	1,4-Dioxane:EtOH	35%	65%
7	EtOAc:EtOH	24%	53%
8	MeCN:EtOH	18%	35%
9	**EtOH only**	**0%**	**94% (89%[c])**
10	CH_2Cl_2 only	45% (40%[c])	55%

[a]5:1 ratio solvent:EtOH unless otherwise stated. [b]Yield calculated by ^{1}H NMR using HC_6Cl_5 as an internal standard. [c]Isolated yield.

General procedure for furan synthesis: $[Ph_3PAuNTf_2]_2$.PhMe (2 mol%) was added to a solution of propargylic alcohol in alcohol (8-10 mL/g) and the solution stirred magnetically at room temperature until starting material had disappeared (TLC). The solvent was removed *in vacuo* (cold water bath – heating during solvent evaporation can promote aerobic oxidation of the 3-alkoxyfuran) and the crude product purified by column chromatography. The product was then stored at 0-5 ˚C to avoid decomposition.

(*E*)-1,1-Diethoxy-4-(4-(trifluoromethyl)phenyl)but-3-en-2-one 2a
Procedure: $[Ph_3PAuNTf_2]_2$.PhMe (2 mol%) was added to a solution of propargylic alcohol in CH_2Cl_2 (10 mL/g) and the solution stirred magnetically at room temperature until starting material had disappeared (TLC). The solvent was removed *in vacuo* and the crude product purified by column chromatography.
IR (film) ν = 2980, 2933, 2884, 1702, 1615, 1321 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 16.2 Hz, 1H), 7.70 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.17 (d, *J* = 16.2 Hz, 1H), 4.80 (s, 1H), 3.75 (q, *J* = 7.2 Hz, 2H), 3.63 (q, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 6H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 194.0, 142.9, 138.1, 132.1 (q, *J* = 32.1 Hz), 128.8, 125.9 (q, *J* = 4.0 Hz), 123.8 (q, *J* = 271.7 Hz), 122.9, 102.7, 63.5, 15.3 ppm; Found (CI): $[M\text{-}OEt]^+$ 257.09021, $C_{13}H_{12}F_3O_2$ requires 257.07839.

3-Ethoxy-2-(4-(trifluoromethyl)phenyl)furan 3a
IR (film) ν = 2979, 2929, 1615, 1322 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.88 (d, *J* = 7.9 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 2.3 Hz, 1H), 6.42 (d, *J* = 2.3 Hz, 1H), 4.12 (q, *J* = 6.8 Hz, 2H), 1.45 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (150 MHz,

$CDCl_3$) δ = 146.3, 141.4, 135.5, 134.2, 127.0 (q, *J* = 32.1 Hz), 125.5 (q, *J* = 4.0 Hz), 124.5 (q, *J* = 271 Hz), 122.8, 103.9, 67.3, 15.3 ppm; Found (CI): $[M]^+$ 256.070568, $C_{13}H_{11}O_2F_3$ requires 256.07057.

3-Ethoxy-2-phenethylfuran 3b
IR (film) ν = 2979, 2930, 1636, 1275 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 7.29-7.23 (m, 2H), 7.20-7.15 (m, 3H), 7.12 (d, *J* = 2.1 Hz, 1H), 6.21 (d, *J* = 2.1 Hz, 1H), 3.78 (q, *J* = 7.0 Hz, 2H), 2.97-2.85 (m, 4H), 1.23 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 142.2, 141.6, 139.9, 139.1, 128.5, 128.3, 125.9, 104.1, 67.9, 34.3, 27.1,15.1 ppm; Found (CI): $[M+H]^+$ 217.121850, $C_{14}H_{17}O_2$ requires 217.12285.

3-Ethoxy-2-(4-methoxyphenyl)furan 3c
IR (film) ν = 2976, 2936, 2895, 1600, 1254 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 8.9 Hz, 2H), 7.22 (d, *J* = 2.1 Hz, 1H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.38 (d, *J* = 2.1 Hz, 1H), 4.07 (q, *J* = 7.0 Hz, 2H), 3.38 (s, 3H), 1.42 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 157.8, 142.9, 139.4, 137.2, 124.5, 124.3, 114.0,104.3, 67.3, 55.4, 15.4 ppm; Found (EI): $[M]^+$ 218.09347, $C_{13}H_{14}O_3$ requires 218.09429.

2-Cyclopropyl-3-ethoxyfuran 3d
IR (film) ν = 2958, 2927, 2870, 1667, 1219 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 7.02 (d, *J* = 1.8 Hz, 1H), 6.22 (d, *J* = 1.8 Hz, 1H), 3.95 (q, *J* = 7.2 Hz, 2H), 1.89-1.83 (m, 1H), 1.33 (t, *J* = 7.2 Hz, 3H), 0.85-0.81 (m, 4H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 142.3, 140.7, 138.3, 104.5, 67.9, 15.3, 6.6, 5.6 ppm; Found (CI): $[M]^+$ 152.083284, $C_9H_{12}O_2$ requires 152.08318.

3-Ethoxy-2-phenylfuran 3e
IR (film) ν = 2980, 1612, 1510, 1391, 1291, 1259 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 1.6 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 6.40 (d, *J* = 1.6 Hz, 1H), 4.10 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.4, 140.2, 136.9, 131.1, 128.5, 125.8, 123.1, 104.1, 67.3, 15.4 ppm; Found (CI): $[M+H]^+$ 188.0831; $C_{12}H_{12}O_2$ requires 188.0831.

2-(2,6-Dimethylphenyl)-3-ethoxyfuran 3f
IR (film) ν = 2979, 2925, 1623, 1283 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 7.35 (br s, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 2H), 6.40 (br s,1H), 3.92 (q, *J* = 7.2 Hz, 2H), 2.23 (s, 6H), 1.27 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 143.6, 140.6, 139.2, 136.5, 129.6, 128.8, 127.4,103.8, 67.0, 20.4, 15.3 ppm; Found (CI): $[M]^+$ 216.113848, $C_{14}H_{16}O_2$ requires 216.11448.

(*R*)-2-(2,6-Dimethylhept-5-en-1-yl)-3-ethoxyfuran 3g
IR (film) ν = 2966, 2914, 1634, 1278 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 7.11 (d, *J* = 1.9 Hz, 1H), 6.24 (d, *J* = 1.9 Hz, 1H), 5.09 (m, 1H), 3.92 (q, *J* = 7.2 Hz, 2H), 2.56 (dd, *J* = 14.7, 6.0 Hz, 1H), 2.42 (dd, *J* 14.7, 7.9 Hz, 1H), 2.08-1.93 (m, 2H), 1.86-1.77 (m, 1H), 1.68 (s, 3H), 1.60 (s, 3H), 1.41-1.32 (m, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.23-1.13 (m,1H), 0.88 (d, *J* = 6.4 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 142.7, 140.2, 139.0, 131.2, 124.9, 103.8, 67.8, 36.8, 32.4, 32.3, 25.9, 25.7, 19.7, 17.8, 15.3 ppm; Found (CI): $[M]^+$ 236.177040, $C_{15}H_{24}O_2$ requires 236.17708; $[\alpha]_D^{20}$ -1.0 (c 0.71 in $CHCl_3$).

4-(3-Ethoxyfuran-2-yl)benzonitrile 3h
IR (film) ν = 2986, 2971, 2899, 2219 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.84 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 1.9 Hz, 1H), 6.42 (d, *J* = 1.9 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 1.46 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 147.4, 142.2, 135.0, 134.9, 132.4, 122.9, 119.7, 108.0, 103.8, 67.4, 15.3 ppm; Found (CI): $[M+H]^+$ 214.085614, $C_{13}H_{12}NO_2$ requires 214.08626.

3-Methoxy-2-(4-(trifluoromethyl)phenyl)furan 4a
IR (film) ν = 2944, 1677, 1270 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.85 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 2.1 Hz, 1H), 6.45 (d, *J* = 2.1 Hz, 1H), 3.91 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 147.4, 141.4, 135.2, 134.1, 127.1 (q, *J* = 32.1 Hz), 125.5 (q, *J* = 4.0 Hz), 124.4 (q, *J* = 270 Hz), 122.8, 103.2, 58.7 ppm; Found (EI): $[M]^+$ 242.055390, $C_{12}H_9O_2F_3$ requires 242.05546.

3-Methoxy-2-phenethylfuran 4b
IR (film) ν = 2980, 2931, 1638, 1277 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.32-7.28 (m, 2H), 7.24-7.18 (m, 3H), 7.17 (d, *J* = 2.1 Hz, 1H), 6.29 (d, *J* = 2.1 Hz, 1H), 3.64 (s, 3H), 2.98-2.90 (m, 4H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 141.5, 139.21, 139.18 128.6, 128.4, 128.3, 125.9, 103.2, 59.5, 34.3, 27.1 ppm; Found (EI): $[M]^+$ 202.099153, $C_{13}H_{14}O_2$ requires 202.09938.

3-Methoxy-2-(4-methoxyphenyl)furan 4c
IR (film) ν = 2979, 2935, 2838, 1672, 1247 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 8.9 Hz, 2H), 7.23 (d, *J* = 2.1 Hz, 1H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.41 (d, *J* = 2.1 Hz, 1H), 3.86 (s, 3H), 3.82 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 157.9, 144.1, 139.4, 136.8, 124.6, 124.2, 114.1, 103.5, 58.9, 55.4 ppm; Found (EI): $[M]^+$ 204.077876, $C_{12}H_{12}O_3$ requires 204.07864.

2-Cyclopropyl-3-methoxyfuran 4d
IR (film) ν = 2957, 2924, 2855, 1667, 1230 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.03 (br s, 1H), 6.25 (br s, 1H), 3.75 (s, 3H), 1.85 (qn, *J* = 7.2 Hz, 1H), 0.85-0.82 (m, 4H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 143.7, 139.9, 138.3, 103.5, 59.5, 6.4, 5.5 ppm; Found (CI): $[M]^+$ 138.07201, $C_8H_{10}O_2$ requires 138.06808.

2-(2,6-Dimethylphenyl)-3-methoxyfuran 4f
IR (film) ν = 2979, 2942, 1626, 1282 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.33 (d, *J* = 2.1 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 2H), 6.40 (d, *J* = 2.1 Hz, 1H), 3.70 (s, 3H), 2.19 (s, 6H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.7, 140.7, 139.3, 136.0, 129.4, 128.9, 127.4, 103.0, 58.8, 20.3 ppm; Found (EI): $[M]^+$ 202.098693, $C_{13}H_{14}O_2$ requires 202.09938.

(*R*)-2-(2,6-Dimethylhept-5-en-1-yl)-3-methoxyfuran 4g
IR (film) ν = 2958, 2913, 1635, 1279 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.12 (d, *J* = 2.1 Hz, 1H), 6.28 (d, *J* = 2.1 Hz, 1H), 5.09 (m, 1H), 3.73 (s, 3H), 2.56 (dd, *J* = 14.8, 6.1 Hz, 1H), 2.42 (dd, *J* = 14.8, 7.8 Hz, 1H), 2.08-1.93 (m, 2H), 1.86-1.77 (m, 1H), 1.68 (s, 3H), 1.60 (s, 3H), 1.41-1.31 (m, 1H), 1.23-1.14 (m, 1H), 0.88 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.0, 139.4, 139.0, 131.3, 124.9, 102.9, 59.5, 36.8, 32.4, 32.3, 25.9, 25.7, 19.6, 17.7 ppm; Found (CI): $[M]^+$ 222.161292, $C_{14}H_{22}O_2$ requires 222.16143.

4-(3-Methoxyfuran-2-yl)benzonitrile 4h
IR (film) ν = 2944, 2232, 1601, 1225 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 2.1 Hz, 1H), 6.46 (d, *J* = 2.1 Hz, 1H), 3.92 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 148.4, 142.2, 134.8, 134.7, 132.4, 122.9, 119.7, 108.1, 103.3, 58.8 ppm; Found (CI): $[M+H]^+$ 200.069819, $C_{12}H_{10}NO_2$ requires 200.07061.

3-Methoxy-2-(thiophen-2-yl)furan 4i
IR (film) ν = 2937, 1624, 1283 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.27-7.24 (m, 1H), 7.22 (d, *J* = 2.1 Hz, 1H), 7.18 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.04 (dd, *J* = 4.9, 3.6 Hz, 1H), 6.40 (d, *J* = 2.1 Hz, 1H), 3.88 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 143.9, 140.0, 134.4, 132.5, 127.4, 122.7, 120.8, 103.3, 59.0 ppm; Found (EI): $[M]^+$ 180.24207, $C_9H_8O_2S$ requires 180.22362.

3-Methoxy-2,2'-bifuran 4j
IR (film) ν = 2972, 1741, 1370 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 (br s, 1H), 7.26 (d, *J* = 2.1 Hz, 1H), 6.48-6.45 (m, 2H), 6.40 (d, *J* = 2.1 Hz, 1H), 3.87 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.5, 144.3, 141.1, 140.5, 130.8, 111.2,104.4, 103.1, 59.0 ppm; Found (EI): $[M]^+$ 164.04811, $C_9H_8O_3$ requires 164.04734.

2-Cyclohexyl-3-methoxyfuran 4k
IR (film) ν = 2927, 2852, 1629, 1274 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.09 (d, *J* = 1.9 Hz, 1H), 6.26 (d, *J* = 1.9 Hz, 1H), 3.72 (s, 3H), 2.73-2.66 (m, 1H),1.85-1.65 (m, 5H), 1.38-1.20 (m, 5H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.1, 142.1, 138.6, 103.2, 59.7, 35.4, 31.3, 26.5, 26.1 ppm; Found (CI): $[M]^+$ 180.114359, $C_{11}H_{16}O_2$ requires 180.1144857.

2-(4-Bromophenyl)-3-methoxyfuran 4l
IR (film) ν = 2939, 2850, 1672, 1217 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.64 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 2.1 Hz, 1H), 6.42 (d, *J* = 2.1 Hz, 1H), 3.88 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 145.9, 140.5, 135.6, 131.5, 129.8, 124.5, 119.1, 103.3, 58.7 ppm; Found (EI): $[M]^+$ 251.977808, $C_{11}H_9O_2Br$ requires 251.97859.

Methyl 3-(3-methoxyfuran-2-yl)benzoate 4m
IR (film) ν = 2953, 2846, 1721, 1673, 1206 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.42 (br s, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 2.1 Hz, 1H), 6.45 (d, *J* = 2.1 Hz, 1H), 3.93 (s, 3H), 3.90 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 167.3, 146.2, 140.6, 135.5, 131.2, 130.4, 128.5, 127.2, 126.6, 124.0, 103.2, 58.7, 52.1 ppm; Found (EI): $[M+H]^+$ 233.08138, $C_{13}H_{13}O_4$ requires 233.08084.

2-(3-Methoxyfuran-2-yl)phenol 4n
IR (film) ν = 3333, 2968, 2944, 1606, 1287 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.99 (s, 1H), 7.37 (d, *J* = 2.1 Hz, 1H), 7.26 (s, 1H), 7.21-7.16 (m, 1H), 6.98-6.92 (m, 2H), 6.46 (d, *J* = 2.1 Hz, 1H), 3.94 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 152.1, 142.7, 141.5, 136.1, 128.9, 126.2, 120.4, 117.9, 117.3, 103.5, 60.2 ppm; Found (EI): $[M+H]^+$ 190.062865, $C_{11}H_{10}O_3$ requires 190.06299.

2-(2-Bromo-3-(dimethoxymethyl)phenyl)-3-methoxyfuran 4o

IR (film) ν = 2935, 2832, 1668, 1235 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.58 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.45 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.39-7.33 (m, 2H), 6.43 (d, *J* = 2.1 Hz, 1H), 5.66 (s, 1H), 3.77 (s, 3H), 3.41 (s, 6H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 145.5, 141.0, 138.1, 136.1, 132.3, 131.9, 127.8, 126.8, 123.7, 103.5, 103.1, 58.8, 54.1 ppm; Found (CI): $[M]^+$ 326.014436, $C_{14}H_{15}BrO_4$ requires 326.01482

2,2'-(2-Bromo-1,3-phenylene)bis(3-methoxyfuran) 4p
IR (film) ν = 2960, 2932, 1245 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 (d, *J* = 7.2 Hz, 2H), 7.37-7.33 (m, 1H), 7.36 (d, *J* = 2.1 Hz, 2H), 6.43 (d, *J* = 2.1 Hz, 2H), 3.78 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.5, 140.9, 136.4, 132.9, 131.1, 126.7, 123.5, 103.2, 58.9 ppm; Found (CI): $[M]^+$ 347.999242, $C_{16}H_{13}BrO_4$ requires 347.99917.

3-Phenethoxy-2-phenethylfuran 5b
IR (film) ν = 2979, 2869, 1636, 1275 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.32-7.12 (m, 10H), 7.13 (d, *J* = 1.9 Hz, 1H), 6.20 (d, *J* = 1.9 Hz, 1H), 3.92 (t, *J* = 7.5 Hz, 2H), 2.92-2.82 (m, 4H), 2.91 (t, *J* = 7.5 Hz, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 142.4, 141.6, 140.0, 139.3, 138.4, 129.0, 128.6, 128.5, 128.4, 126.5, 126.0, 104.1, 73.1, 36.2, 34.4, 27.2 ppm; Found (CI): $[M+H]^+$ 293.153275, $C_{20}H_{21}O_2$ requires 293.15415.

3-(Allyloxy)-2-phenethylfuran 6b
IR (film) ν = 2926, 2858, 1636, 1276 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29-7.23 (m, 2H), 7.20-7.15 (m, 3H), 7.13 (d, *J* = 2.1 Hz, 1H), 6.22 (d, *J* = 2.1 Hz, 1H), 5.90 (ddd, *J* = 17.4, 10.6, 1.5 Hz, 1H), 5.28 (dd, *J* = 17.4, 1.5 Hz, 1H), 5.19 (dd, *J* = 10.6, 1.5 Hz, 1H), 4.23 (dt, *J* = 5.5, 1.5 Hz, 2H), 2.96-2.86 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 142.3, 141.5, 140.0, 139.1, 133.9, 128.5, 128.3, 125.9, 117.5, 104.2, 73.1, 34.3, 27.1 ppm; Found (CI): $[M+H]^+$ 229.12213, $C_{15}H_{17}O_2$ requires 229.12285.

2-((2-Phenethylfuran-3-yl)oxy)ethanol 7b
IR (film) ν = 3420, 2928, 2871, 1660, 1275 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.30-7.24 (m, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 1.9 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 2H), 6.22 (d, *J* = 1.9 Hz, 1H), 3.78-3.69 (m, 4H), 2.96-2.88 (m, 4H), 1.79 (br s, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 142.4, 141.5, 139.9, 139.4, 128.6, 128.4, 126.1, 104.0, 73.6, 61.7, 34.4, 27.2 ppm; Found (CI): $[M+H]^+$ 233.116954, $C_{14}H_{17}O_3$ requires 233.11722.

3-(*tert*-Butoxy)-2-phenethylfuran 8b
IR (film) ν = 2977, 2933, 1624, 1273 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31-7.24 (m, 2H), 7.22-7.17 (m, 3H), 7.15 (d, *J* = 2.1 Hz, 1H), 6.15 (d, *J* = 2.1 Hz, 1H), 2.96-2.83 (m, 4H),1.25 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.8, 141.7, 138.7, 137.1, 128.4, 128.3, 126.0, 109.3, 78.5, 34.1, 28.4, 27.3 ppm; Found (CI): $[M+H]^+$ 245.15352, $C_{16}H_{21}O_2$ requires 245.15415.

3-Isopropoxy-2-phenethylfuran 9b
IR (film) ν = 2975, 2933, 1634, 1274 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30-7.23 (m, 2H), 7.20-7.15 (m, 3H), 7.14 (d, *J* = 2.1 Hz, 1H), 6.19 (d, *J* = 2.1 Hz, 1H), 3.98 (septet, *J* = 6.2 Hz, 1H), 2.95-2.84 (m, 4H), 1.18 (d, *J* = 6.2 Hz, 6H) ppm; ^{13}C NMR

(100 MHz, $CDCl_3$) δ = 141.6, 141.2, 140.9, 139.1, 128.4, 128.3, 125.9, 105.3, 74.4, 34.4, 27.0, 22.2 ppm; Found (CI): $[M+H]^+$ 231.136913, $C_{15}H_{19}O_2$ requires 231.13850.

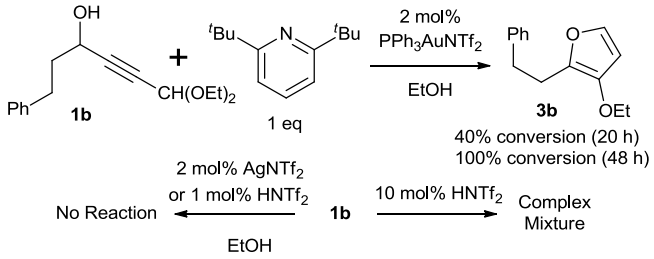
5-Methoxy-7,7-dimethyl-4,5,6,7-tetrahydrobenzofuran 10a

IR (film) ν = 2964, 2928, 2863, 1161 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 7.24 (d, *J* = 1.9 Hz, 1H), 6.14 (d, *J* = 1.9 Hz, 1H), 3.69-3.62 (m, 1H), 3.40 (s, 3H), 2.86 (dd, *J* = 14.8, 5.4 Hz, 1H), 2.32 (dd, *J* = 14.8, 9.1 Hz, 1H), 1.94 (br d, *J* = 12.0 Hz, 1H), 1.67 (app t, *J* = 12.0 Hz, 1H), 1.30 (s, 3H), 1.26 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 156.5, 141.2, 112.5, 110.2, 75.2, 56.2, 44.4, 32.8, 28.9, 28.4, 28.3 ppm; Found (CI): $[M]^+$ 180.114054, $C_{11}H_{16}O_2$ requires 180.11448.

5-Ethoxy-7,7-dimethyl-4,5,6,7-tetrahydrobenzofuran 10b

IR (film) ν = 2967, 2929, 2867, 1161 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 7.23 (d, *J* = 1.9 Hz, 1H), 6.13 (d, *J* = 1.9 Hz, 1H), 3.78-3.72 (m, 1H), 3.63-3.53 (m, 2H), 2.85 (dd, *J* = 15.1, 5.3 Hz, 1H), 2.33 (dd, *J* = 15.1, 9.0 Hz, 1H), 1.93 (br d, *J* = 12.0 Hz, 1H), 1.69 (app t, *J* = 12.0 Hz, 1H), 1.29 (s, 3H), 1.25 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 156.6, 141.2, 112.8, 110.3, 73.5, 63.9, 45.1, 32.9, 29.5, 28.5, 28.3, 15.9 ppm; Found (CI): $[M]^+$ 194.130165, $C_{12}H_{18}O_2$ requires 194.13013.

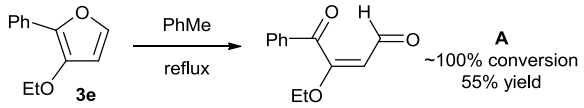
Control Experiments



Reaction of alcohol **1b** with gold catalyst and ethanol in the presence of one equivalent of the hindered base 2,6-di-tert-butylpyridine led to the formation of furan **3b**, although a longer reaction time was required to achieve full conversion. Treatment of alcohol **1b** with 1 mol% Tf_2NH did not lead to furan formation, however. With larger quantities of acid catalyst, complete decomposition of the starting alcohol was observed. Taken together, these experiments suggest that the furan formation is not a simple acid-catalysed process. Treatment of alcohol **1b** with catalytic $AgNTf_2$ in EtOH also did not lead to furan formation, demonstrating that this reaction is not likely to be mediated by silver impurities in the gold catalyst.

3. Reactions of Furan Products

(*E*)-3-Ethoxy-4-oxo-4-phenylbut-2-enal A

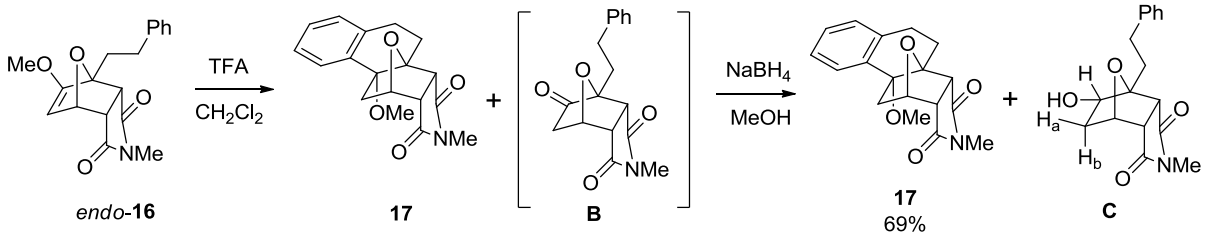


Procedure: Toluene (2.0 mL) was added to 3-ethoxy-2-phenylfuran (103 mg, 0.548 mmol) and the solution heated at reflux under an atmosphere of air for 24 h. The reaction was then allowed to cool before it was concentrated *in vacuo* to give the crude product. This was purified by column chromatography to give 3-cyclohexyl-2-phenylfuran **16** as a white crystalline solid (61 mg, 0.30 mmol, 55%); m.p. 52–54 °C; IR (film) ν = 2981, 1665, 1594, 1447 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.51 (d, *J* = 7.8 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 5.73 (d, *J* = 7.8 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 1H), 1.44 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.1, 66.3, 107.8, 129.1, 130.1, 134.7, 134.9, 172.0, 189.6, 189.8 ppm; Found (CI): $[M+H]^+$ 205.0859, $C_{12}H_{13}O_3$ requires 205.0859.

(3a*S*,4*R*,7*R*,7a*R*)-5-methoxy-2-methyl-4-phenethyl-3a,4,7,7a-tetrahydro-1*H*-4,7-epoxyisoindole-1,3(2*H*)-dione 16

3-methoxy furan **4b** and *N*-methylmaleimide were dissolved in CH_2Cl_2 and stirred overnight at rt. The product was purified by column chromatography.
endo:*exo* crude ratio 2:1. Single distereoisomers isolated: 63% *endo*, 31% *exo*.
***endo*-16:** IR (film) ν = 2931, 1774, 1699, 1625, 1433 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.29 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 5.20 (dd, *J* = 5.3, 1.9 Hz, 1H), 5.02 (br s, 1H), 3.70 (dd, *J* = 7.5, 5.3 Hz, 1H), 3.53 (s, 3H), 3.21 (d, *J* = 7.5 Hz, 1H), 2.85 (s, 3H), 2.80 (t, *J* = 8.5 Hz, 2H), 2.62-2.55 (m, 1H), 2.29-2.22 (m, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 175.6, 174.3, 165.4, 141.6, 128.52, 128.49, 126.1, 96.9, 89.7, 78.2, 58.2, 51.3, 49.8, 31.9, 30.5, 24.6 ppm;
***exo*-16:** IR (film) ν = 2922, 1764, 1698, 1633, 1440 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.28 (t, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 5.19 (d, *J* = 1.9 Hz, 1H), 5.16 (br s, 1H), 3.66 (s, 3H), 3.14 (d, *J* = 6.4 Hz, 1H), 2.96 (s, 3H), 2.93 (d, *J* = 6.4 Hz, 1H), 2.83-2.73 (m, 2H), 2.39-2.33 (m, 1H), 2.29-2.20 (m, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 176.4, 174.9, 168.4, 141.9, 128.5, 128.4, 126.0, 99.6, 89.3, 79.9, 58.3, 54.4, 49.2, 30.8, 29.4, 25.0 ppm;
Found (CI): $[M]^+$ 313.132190, $C_{18}H_{19}NO_4$ requires 313.13086.

(3a*S*,3b*R*,9b*S*,11*R*,11a*R*)-9b-Methoxy-2-methyl-4,5,9b,10,11,11a-hexahydro-3b,11-epoxynaphtho[2,1-*e*]isoindole-1,3(2*H*,3a*H*)-dione 17



Trifluoroacetic acid (0.5 mL) was added to a stirring solution of *endo*-**16** (46 mg, 0.15 mmol) in CH_2Cl_2 (1.0 mL) at -78°C. The reaction was allowed to reach room

temperature and stirred for 16 h before the reaction was quenched with aq. sat. $NaHCO_3$ (10 mL) and diluted with CH_2Cl_2 (10 mL). The aqueous extract was washed with CH_2Cl_2 (3 × 10 mL) and the combined organic extracts washed with brine (20 mL), dried ($MgSO_4$) and the solvent removed *in vacuo* to give the crude product. This was partially purified by column chromatography to give a mixture of **17** and **B** (3:1). The mixture of products was then dissolved in hot methanol (2 mL), cooled to 0 °C and treated with sodium borohydride (10 mg, 0.31 mmol). The resulting suspension was stirred at 0 °C for 4 h before the reaction was diluted with CH_2Cl_2 (10 mL) and treated with Amberlyte IRA743 boron scavenger resin. The mixture was filtered and the solution concentrated *in vacuo* to give the crude product, which was purified by column chromatography to give **17** as a white crystalline solid (32 mg, 0.10 mmol, 69% yield) and side product **C**.

17: m.p. 174–176 °C; IR (film) ν = 2934, 1771, 1693, 1434 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 7.27–7.22 (m, 2H), 7.19 (t, *J* = 7.1 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 4.77 (t, *J* = 6.2 Hz, 1H), 3.71 (1H, dd, *J* = 9.8, 6.2 Hz, 1H), 3.16 (d, *J* = 9.8 Hz, 1H), 3.02–2.96 (m, 4H), 2.85 (dd, *J* = 16.6, 5.7 Hz, 1H), 2.76 (s, 3H), 2.53 (dd, *J* = 13.8, 6.2 Hz, 1H), 2.43 (td, *J* = 14.2, 6.0 Hz, 1H), 2.34 (dd, *J* = 14.2, 6.0 Hz, 1H), 2.25 (d, *J* = 13.8 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 175.5, 174.7, 138.3, 135.8, 128.5, 127.6, 127.5, 91.2, 82.7, 76.9, 54.6, 54.3, 53.1, 46.7, 28.4, 26.0, 25.0 ppm; Found (CI): $[M+H]^+$ 314.1382; $C_{18}H_{20}NO_4$ requires 314.1387.

(3a*S*,4*R*,7*R*,7a*R*)-2-Methyl-4-phenethyltetrahydro-1*H*-4,7-epoxyisoindole-1,3,5(2*H*,6*H*)-trione B

^1H NMR (600 MHz, $CDCl_3$) δ = 7.31–7.28 (m, 2H), 7.23–7.18 (m, 3H), 5.17 (t, *J* = 6.2 Hz, 1H), 3.79 (dd, *J* = 9.3, 6.2 Hz, 1H), 3.33 (d, *J* = 9.3 Hz, 1H), 2.92 (s, 3H), 2.81–2.75 (m, 1H), 2.73–2.65 (m, 2H), 2.51–2.45 (m, 1H), 2.31–2.25 (m, 1H), 2.21 (d, *J* = 18.3 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 207.2, 174.3, 172.3, 140.9, 128.6, 128.5, 126.4, 90.1, 75.2, 51.8, 51.0, 42.2, 30.8, 30.0, 21.2 ppm;

3aS,4R,5R,7R,7aR)-5-Hydroxy-2-methyl-4-phenethylhexahydro-1H-4,7-epoxyisoindole-1,3(2H)-dione C

IR (film) ν = 3445, 2927, 1771, 1691, 1434 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) 7.31 (t, *J* = 7.4 Hz, 2H), 7.27 (d, *J* = 7.4 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 4.77 (t, *J* = 6.1 Hz, 1H), 4.23 (m, 1H), 3.64 (dd, *J* = 9.7, 6.1 Hz, 1H), 3.20 (d, J = 9.7, 1H), 3.00–2.88 (m, 4H), 2.42–2.27 (m, 3H), 1.98–1.95 (m, 1H), 1.49 (dd, J = 13.8, 3.0, 1H), 1.25 (m, 1H) ppm; ^{13}C NMR (150 MHz, CDCl3) 175.8, 175.7, 141.2, 128.8, 128.4, 126.4, 90.8, 77.7, 75.5, 52.8, 51.9, 36.8, 35.0, 30.0, 24.9 ppm; Found (CI): $[M+H]^+$ 302.1385; $C_{17}H_{20}NO_4$ requires 302.1387.

1-(5-Ethoxy-7,7-dimethyl-4,5,6,7-tetrahydrobenzofuran-2-yl)-*N*,*N*-dimethylmethanamine 18

Procedure: *N*-Methyl-*N*-methylenemethanaminium iodide (Eschenmoser's salt, 2 eq.) was added to a solution of **10b** (20 mg, 0.103 mmol) in DMF (1 mL). The resulting solution was stirred at rt for 12h. The reaction was then concentrated *in vacuo* to give the crude product. This was purified by column chromatography to give **18** (24 mg, 0.095 mmol 92%).

IR (film) ν = 2964, 2926, 2866, 1456, 1362 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 5.97 (s, 1H), 3.77-3.70 (m, 1H), 3.62-3.53 (m, 2H), 3.47 (d, *J* = 14.0 Hz, 1H), 3.43 (d, *J* = 14.0 Hz, 1H), 2.80 (dd, *J* = 15.1, 4.9 Hz, 1H), 2.29 (dd, *J* = 15.1, 9.4, 1H), 2.27 (s, 6H), 1.91 (br d, *J* = 12.0 Hz, 1H), 1.66 (t, *J* = 12.1 Hz, 1H), 1.28 (s, 3H), 1.24 (s, 3H),

1.22 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 156.5, 150.1, 113.4, 109.9, 73.4, 63.9, 55.9, 45.1, 44.9, 32.9, 29.5, 28.5, 28.3, 15.8 ppm; Found (CI): $[M]^+$ 251.187845, $C_{15}H_{25}NO_2$ requires 251.18798.

2-Allyl-2-phenethylfuran-3(2H)-one 19

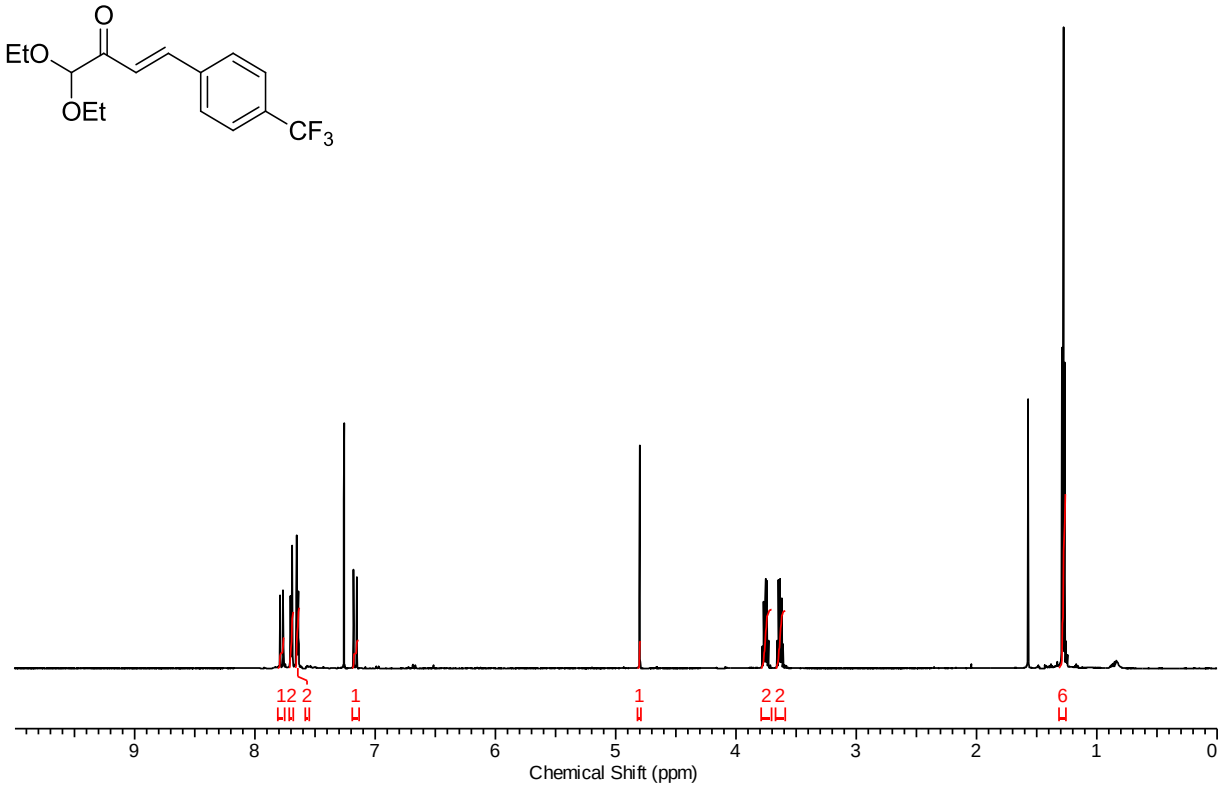
Furan **6b** (50 mg, 0.219 mmol) was dissolved in toluene (2 mL) and heated to reflux for 6 h. The reaction was then allowed to cool before it was concentrated *in vacuo* to give the crude product. This was purified by column chromatography to give **19** as a colourless oil (40 mg, 0.176 mmol 80%);
IR (film) ν = 3064, 3028, 2920, 1697, 1559 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.25 (d, *J* = 2.3 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 2H), 5.70 (d, *J* = 2.3 Hz, 1H), 5.69-5.63 (m, 1H), 5.13 (d, *J* = 18.8 Hz, 1H), 5.11 (d, *J* = 11.3 Hz, 1H), 2.58-2.44 (m, 2H), 2.50 (d, *J* = 7.2 Hz, 1H), 2.10-2.05 (m, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 206.4, 177.3, 141.0, 130.4, 128.6, 128.4, 126.2, 119.9, 107.7, 91.5, 40.4, 37.2, 29.1 ppm; Found (CI): $[M]^+$ 229.122392, $C_{15}H_{17}O_2$ requires 229.12231.

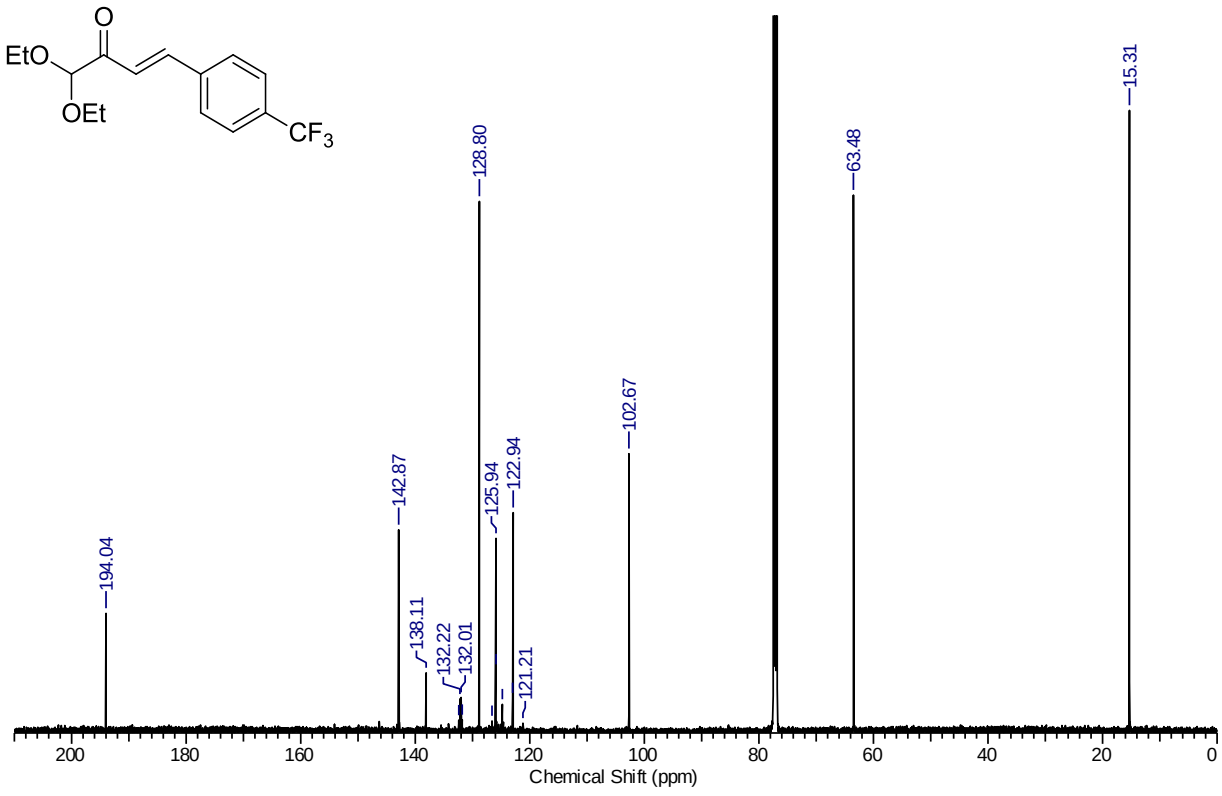
5-Bromo-2-(2,6-dimethylphenyl)-3-ethoxyfuran 20

N-Bromo-succinimide (2 eq.) was added to a solution of **3e** (20 mg, 0.09 mmol) in DMF (1 mL). The solution was stirred at rt for 6 h. The reaction was then concentrated in *vacuo* to give the crude product. This was purified by flash column chromatography to give **20** (18 mg, 0.061 mmol, 68%);
IR (film) ν = 2954, 2924, 2853, 1626 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.20 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 2H), 6.27 (s, 1H), 3.80 (q, *J* = 7.2 Hz, 2H), 2.27 (s, 6H), 1.16 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.7, 139.3, 139.0, 129.2, 128.5, 127.5, 119.7, 105.6, 67.3, 20.4, 15.2 ppm; Found (EI): $[M]^+$ 294.024760, $C_{14}H_{15}BrO_2$ requires 294.02499.

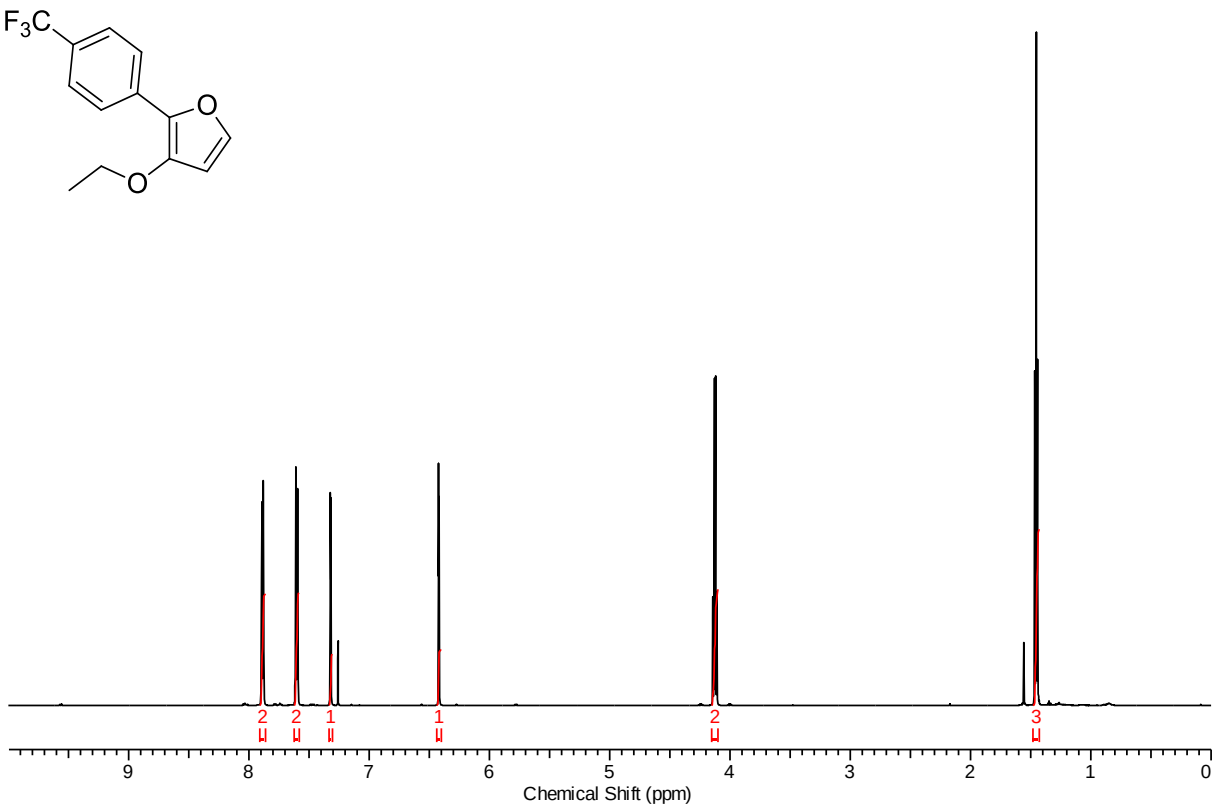
4. ^{1}H and ^{13}C NMR Spectra

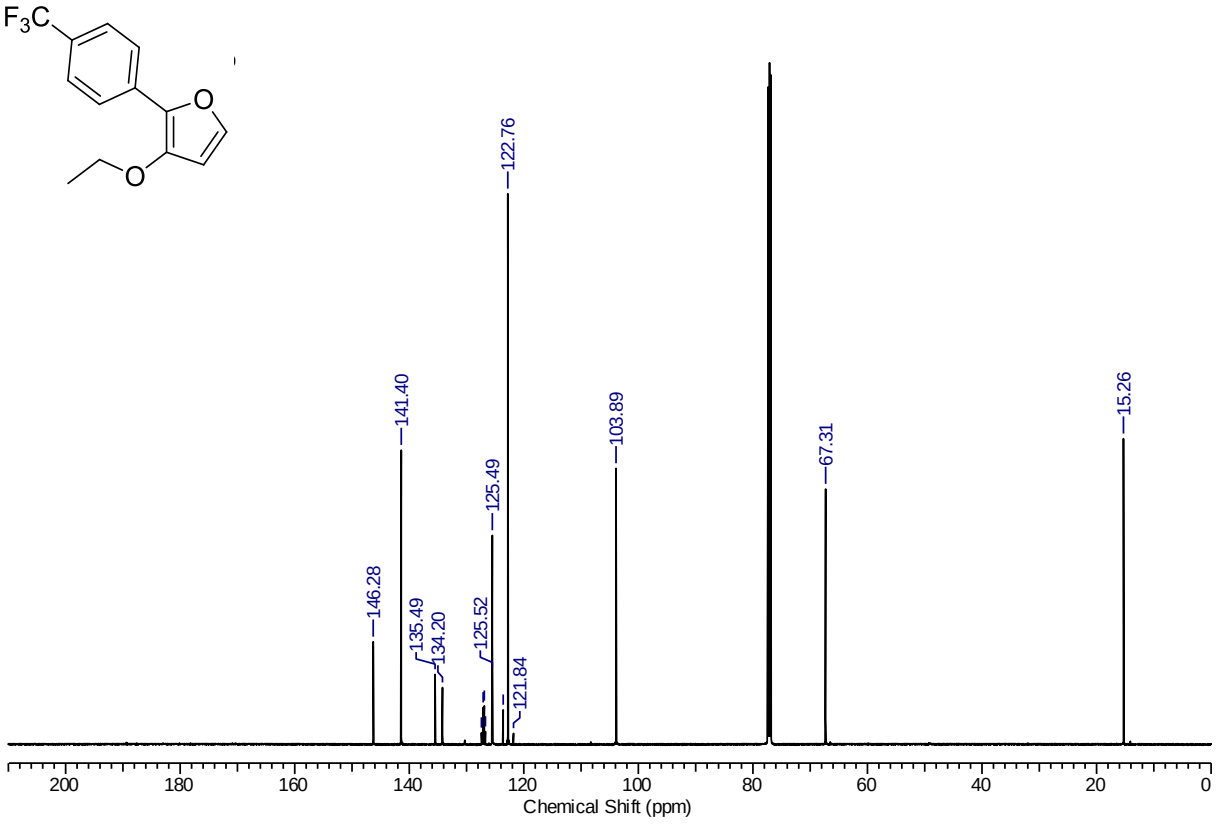
(*E*)-1,1-Diethoxy-4-(4-(trifluoromethyl)phenyl)but-3-en-2-one 2a



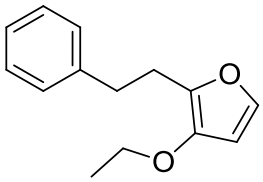


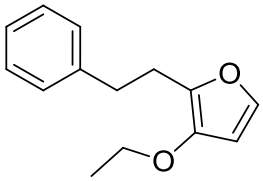
3-Ethoxy-2-(4-(trifluoromethyl)phenyl)furan 3a

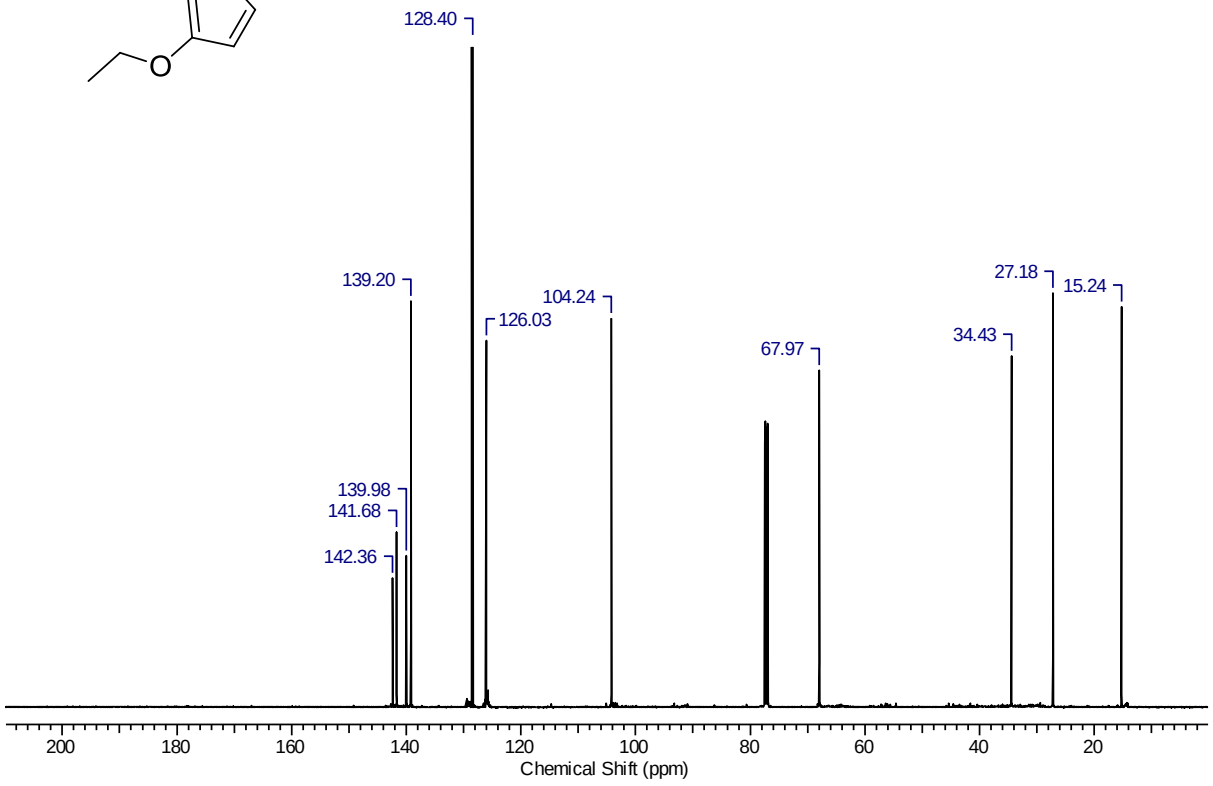




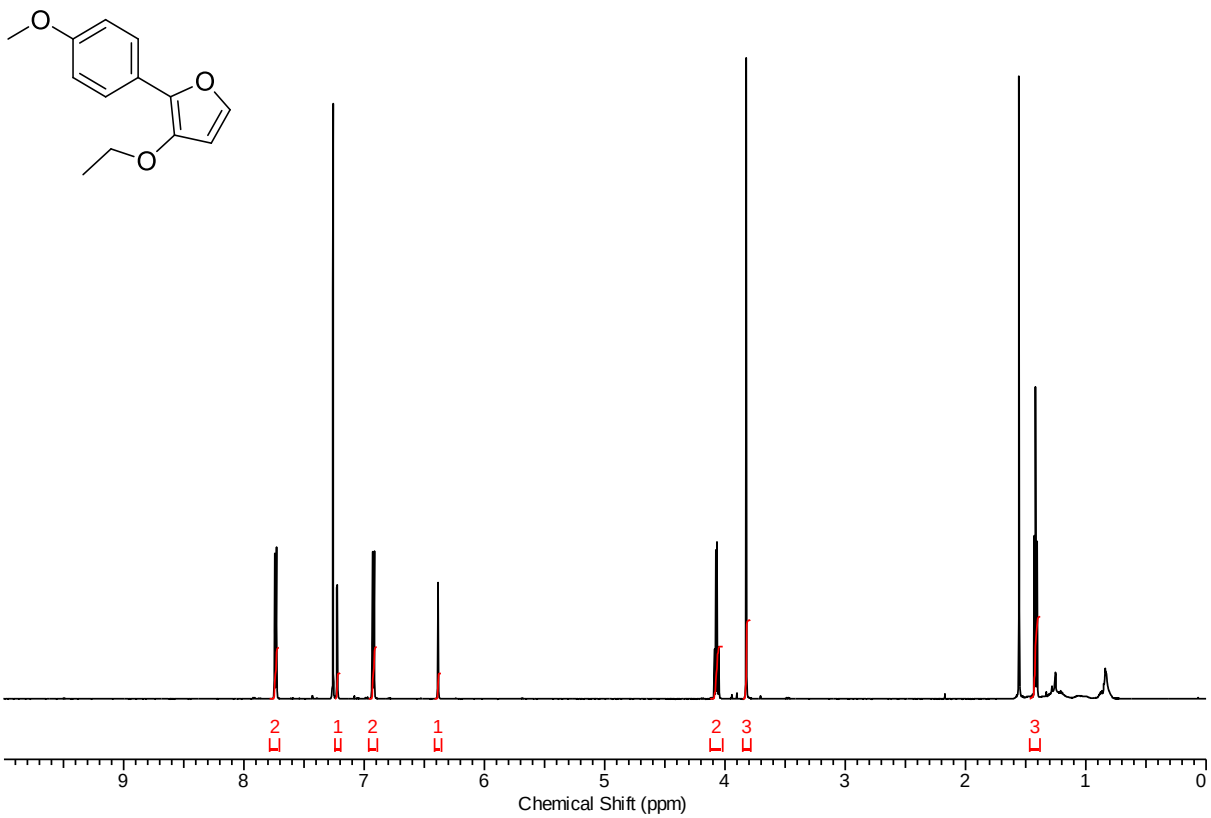
3-Ethoxy-2-phenethylfuran 3b

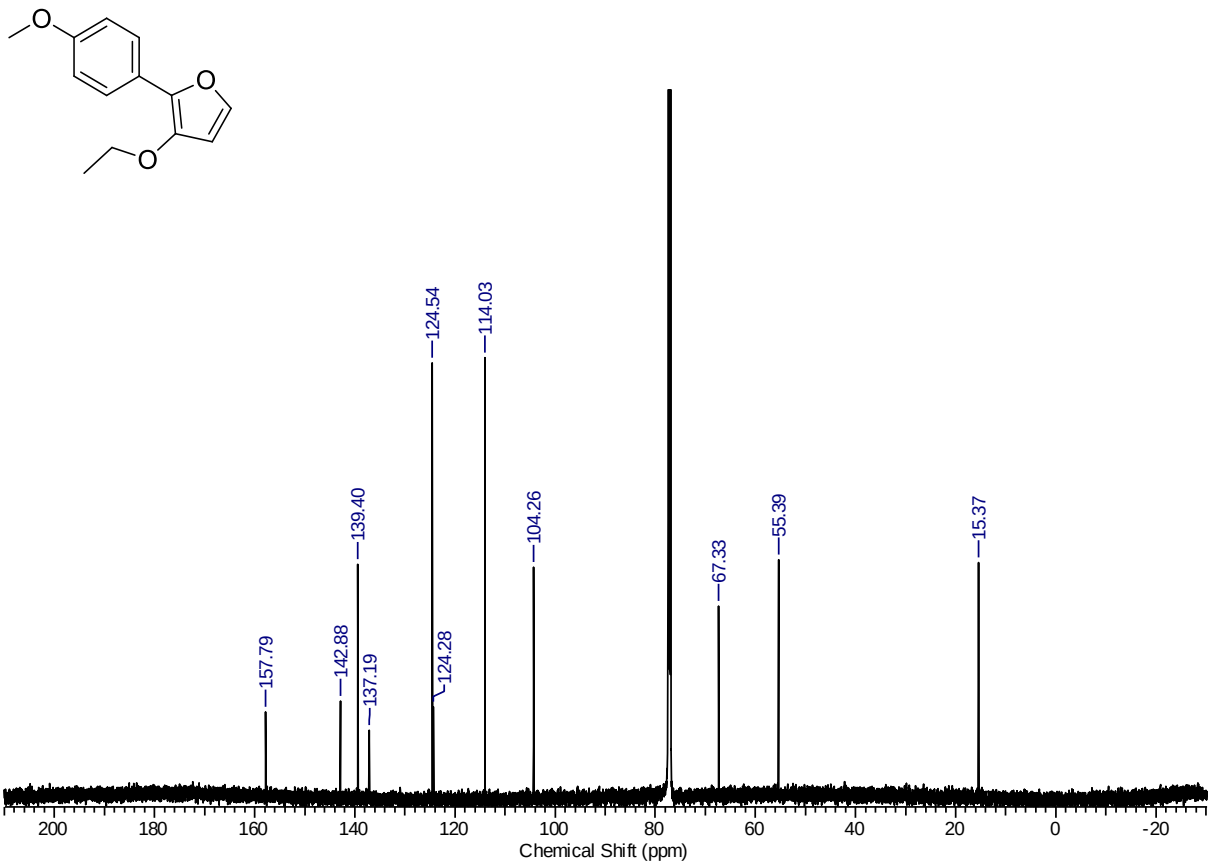




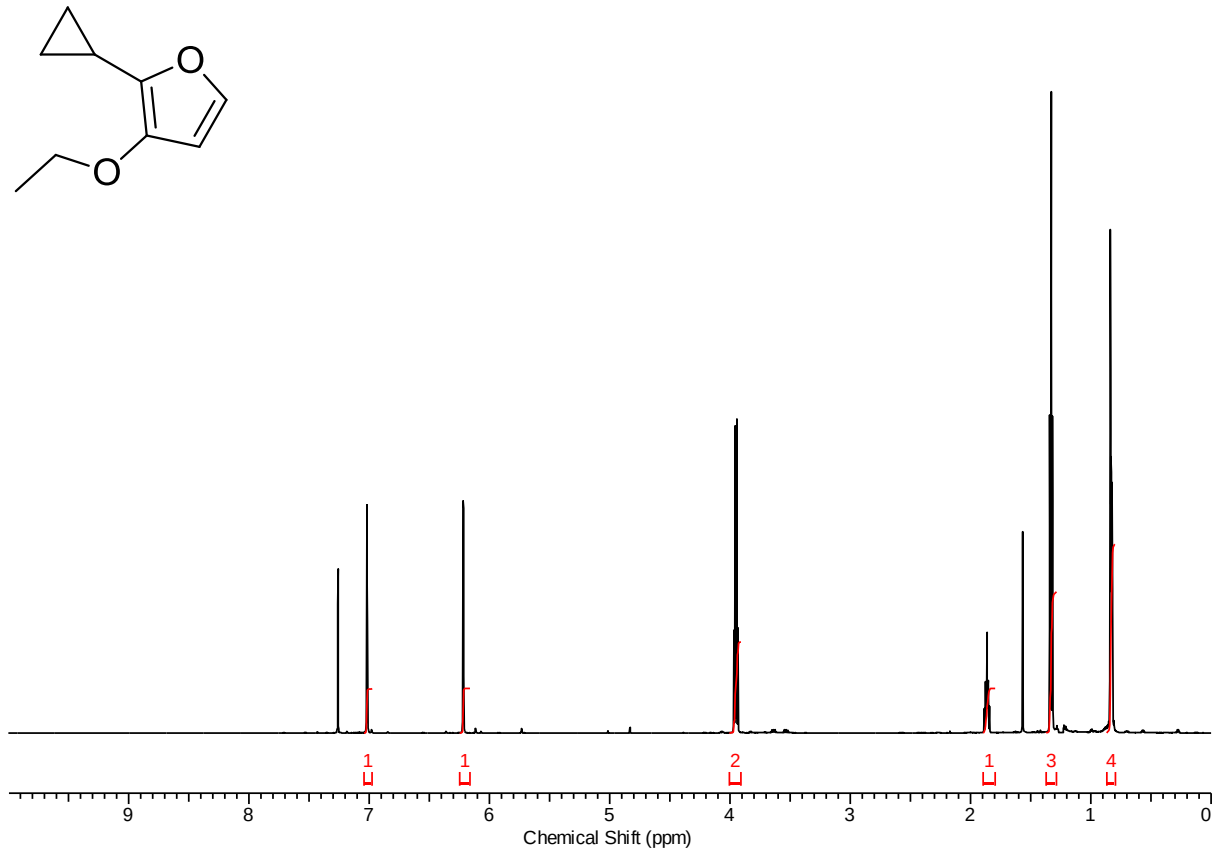


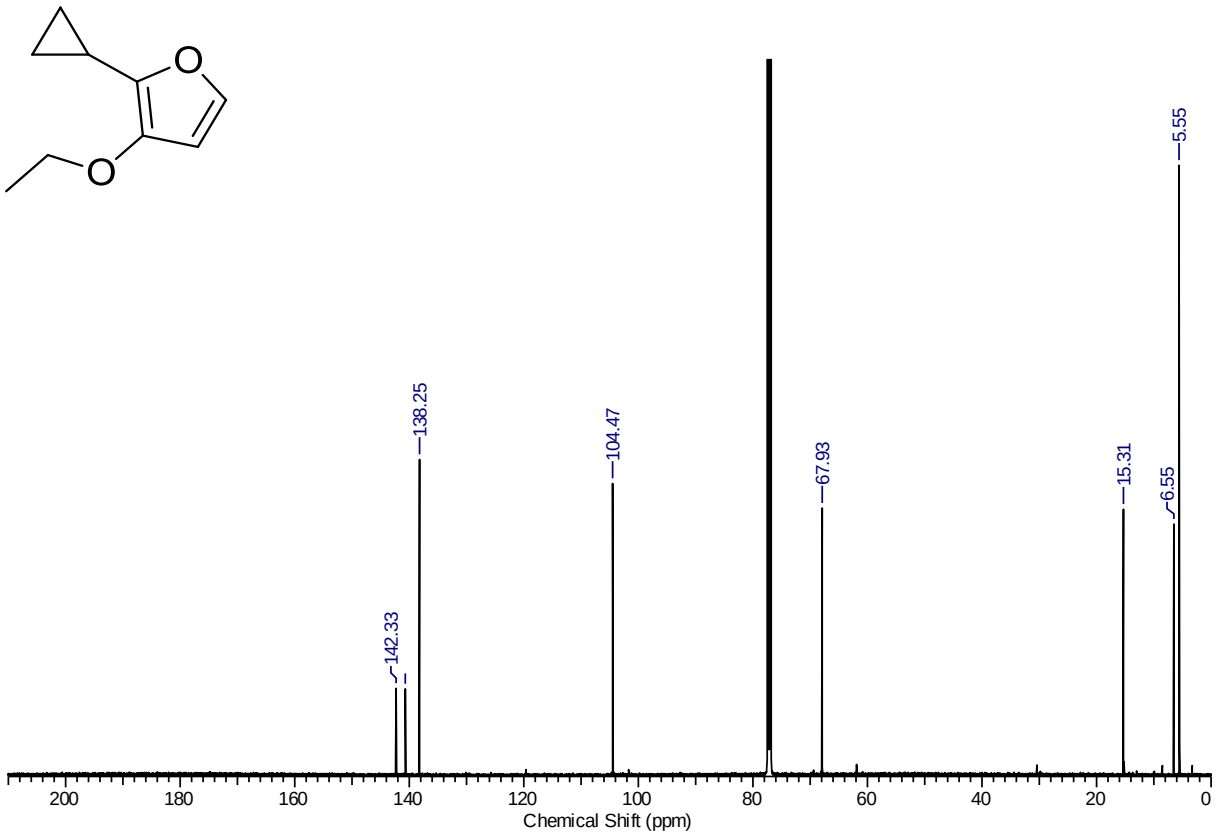
3-Ethoxy-2-(4-methoxyphenyl)furan 3c



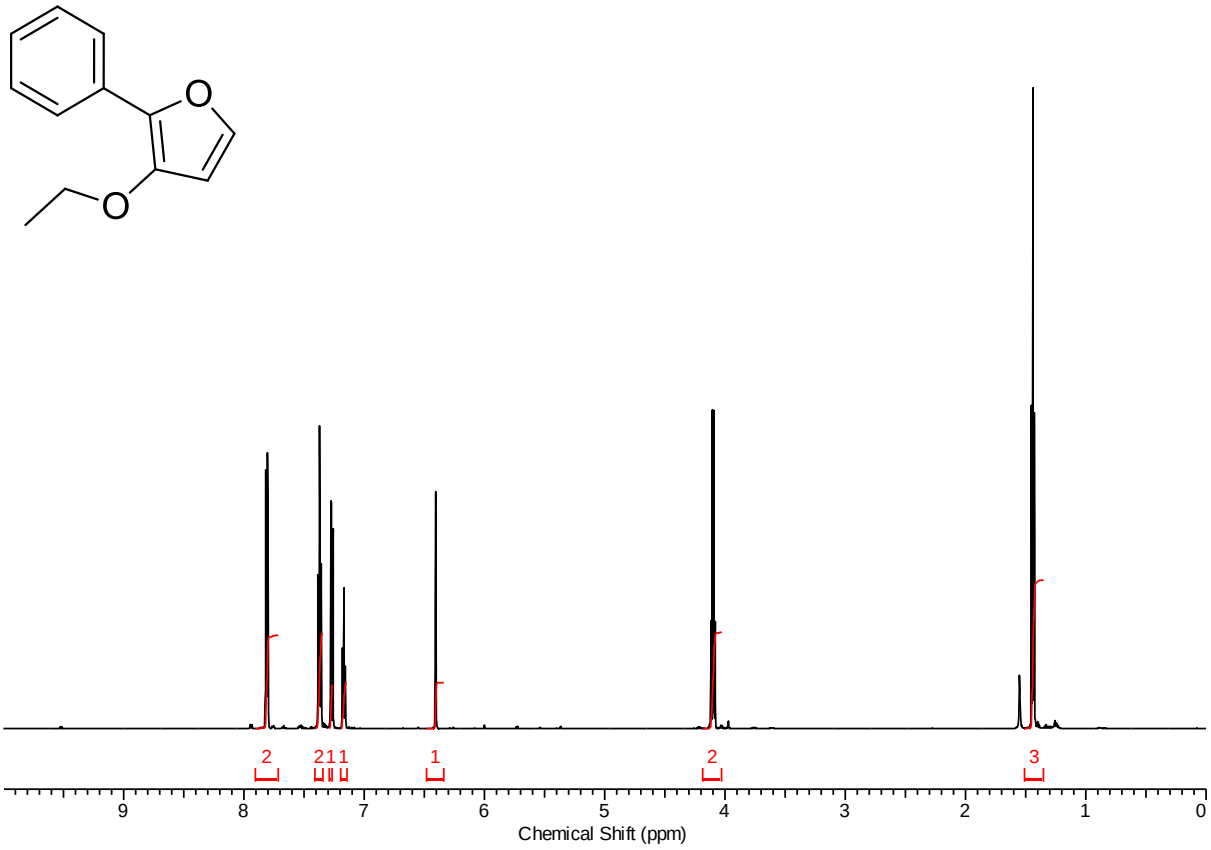


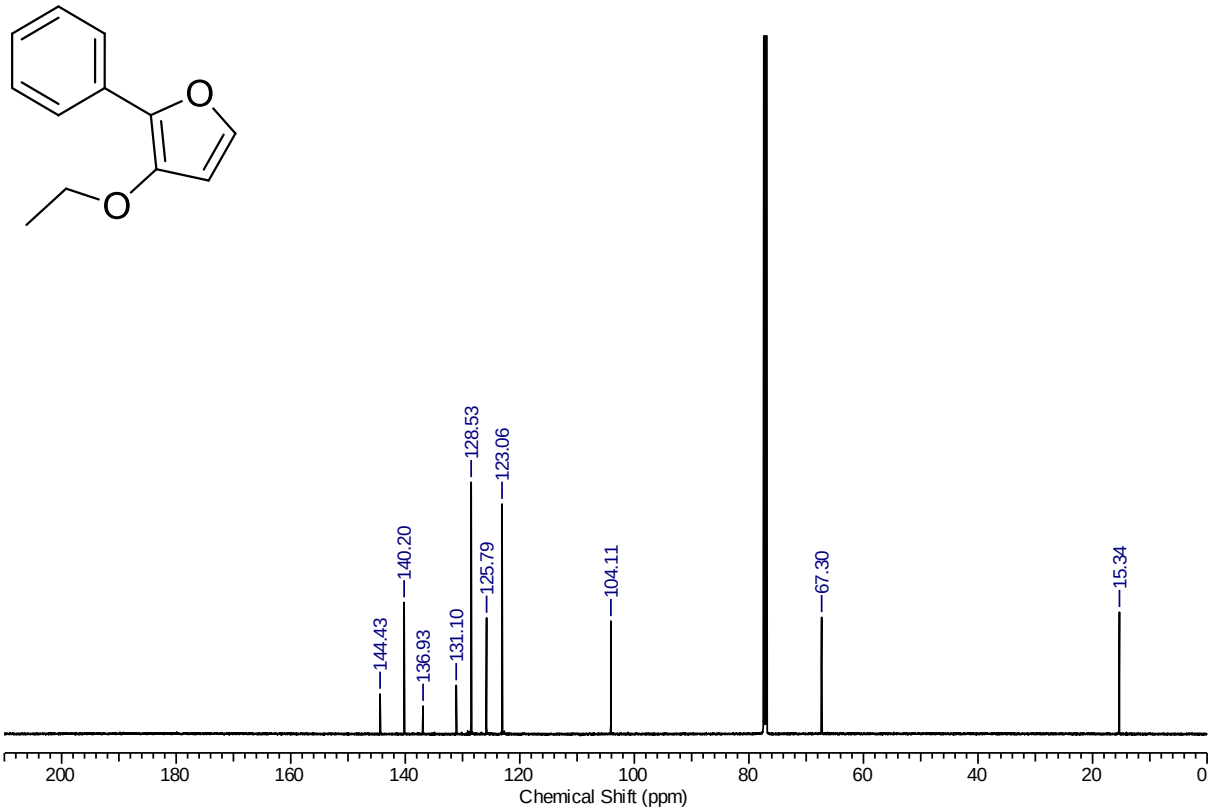
2-Cyclopropyl-3-ethoxyfuran 3d



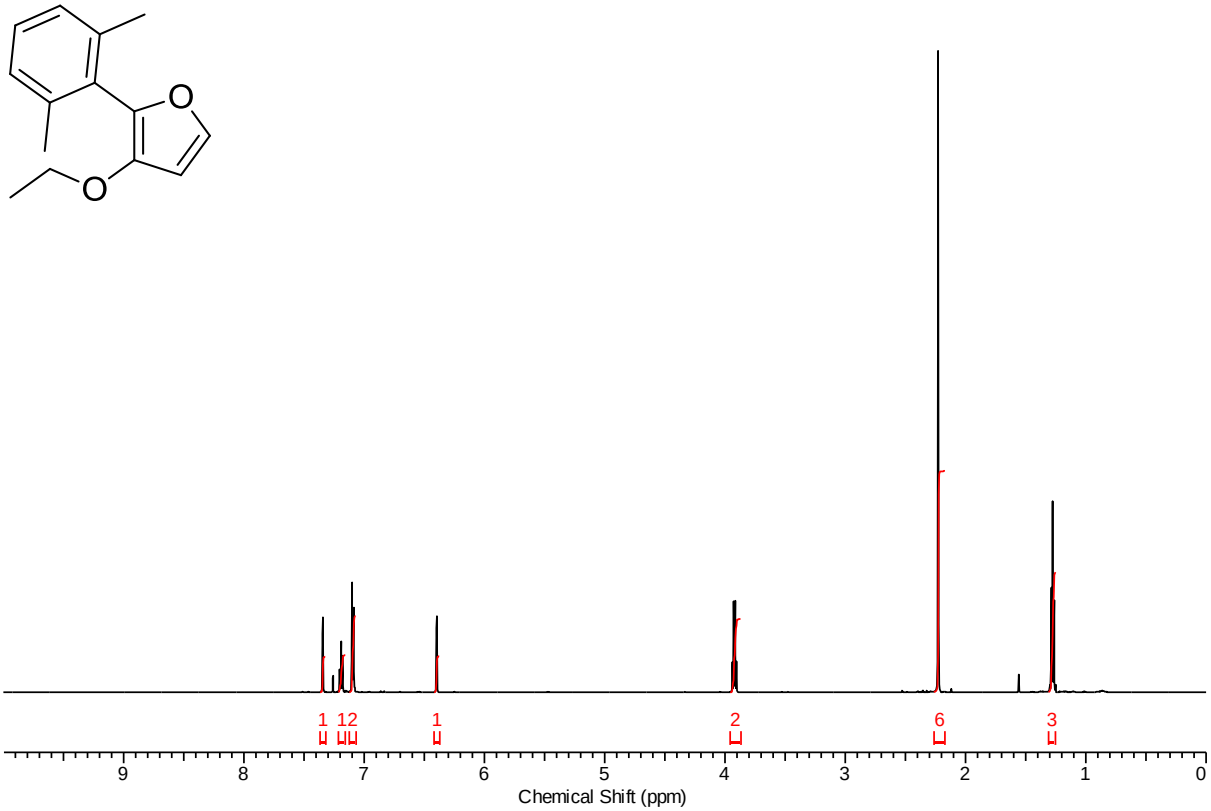


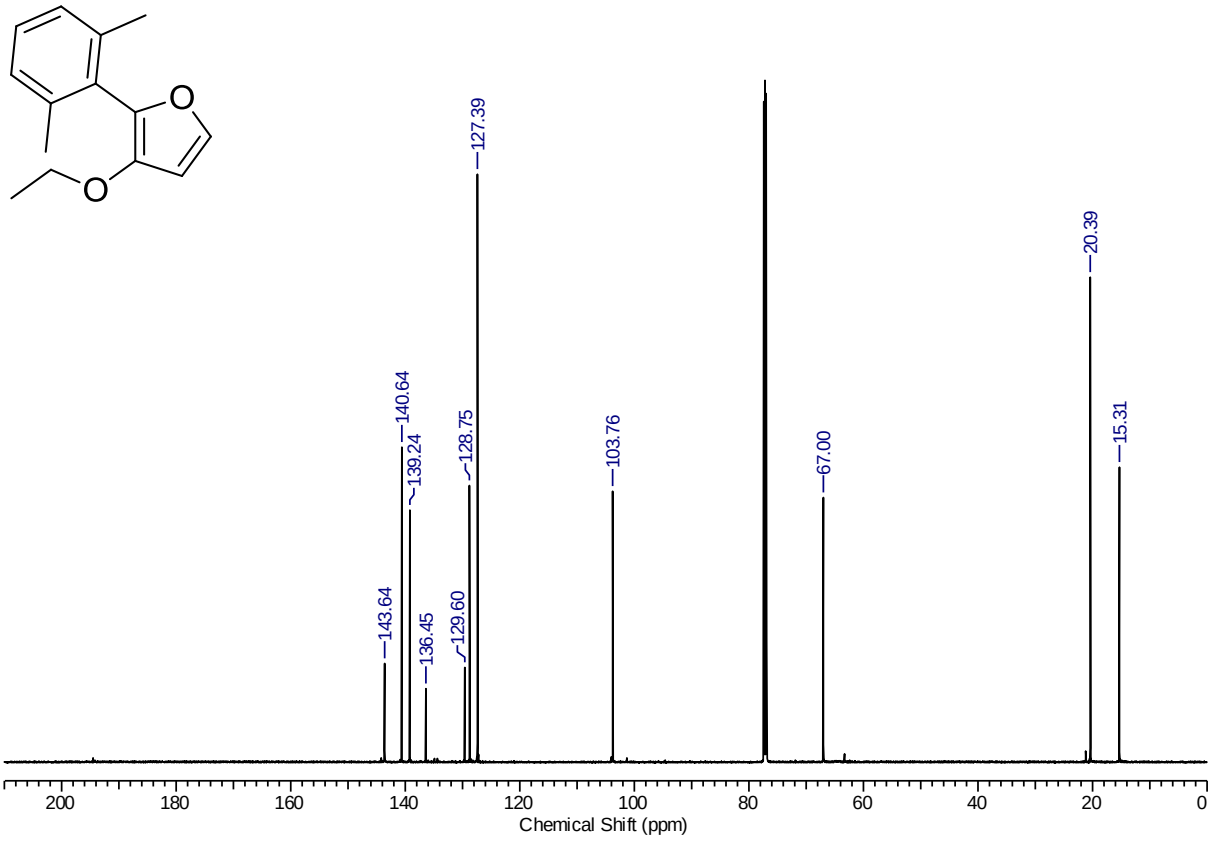
3-Ethoxy-2-phenylfuran 3e



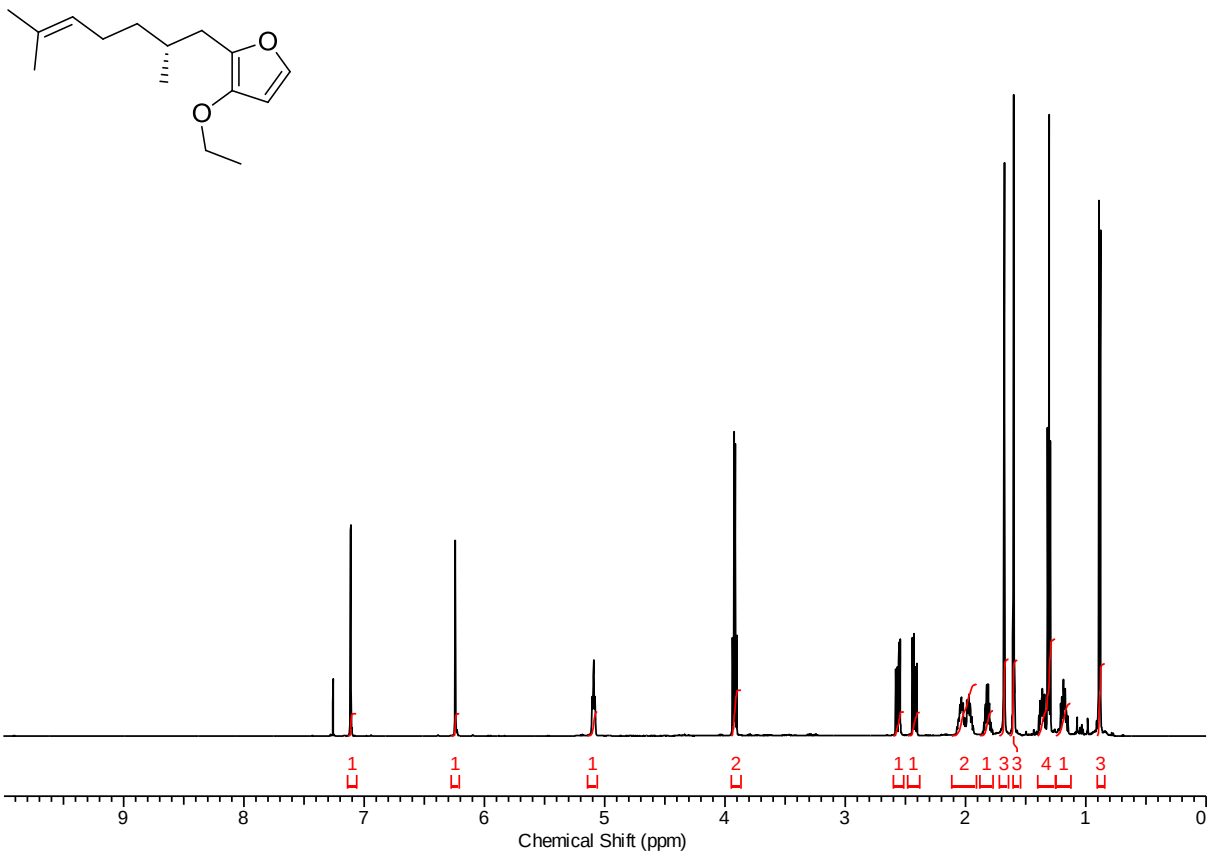


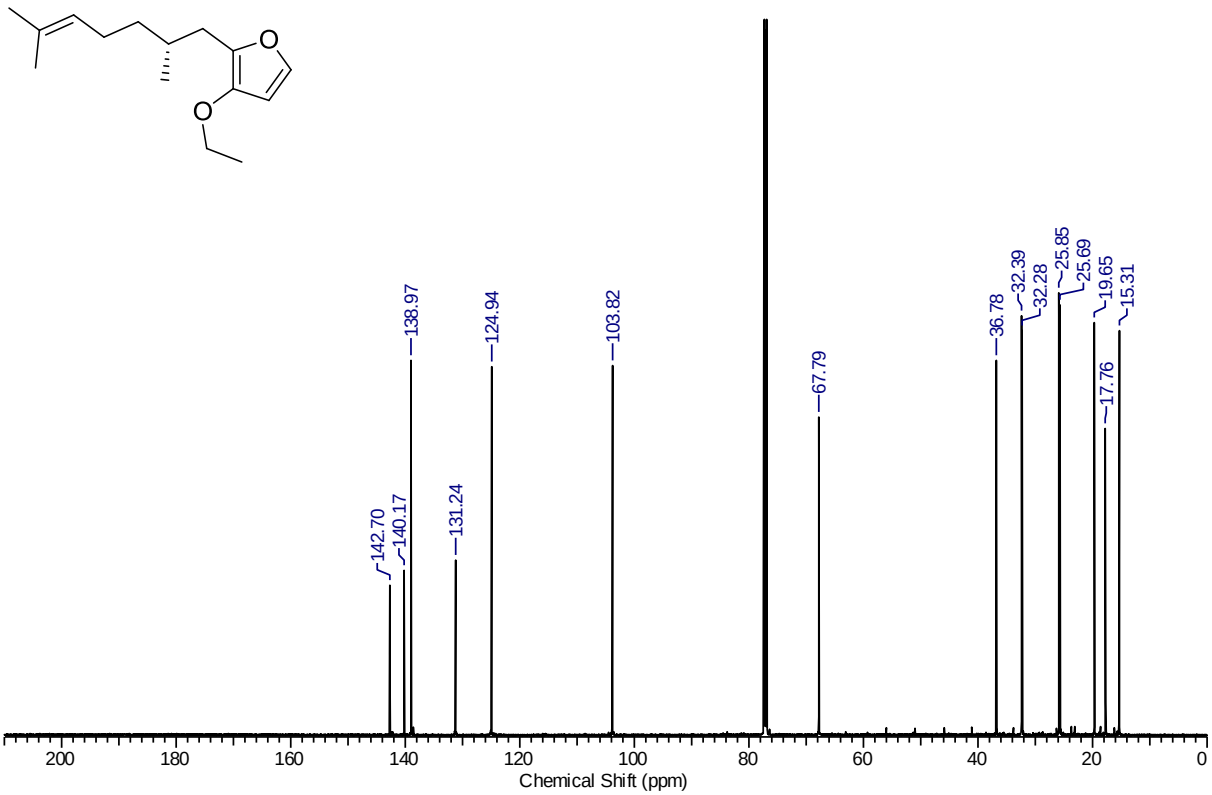
2-(2,6-Dimethylphenyl)-3-ethoxyfuran 3f



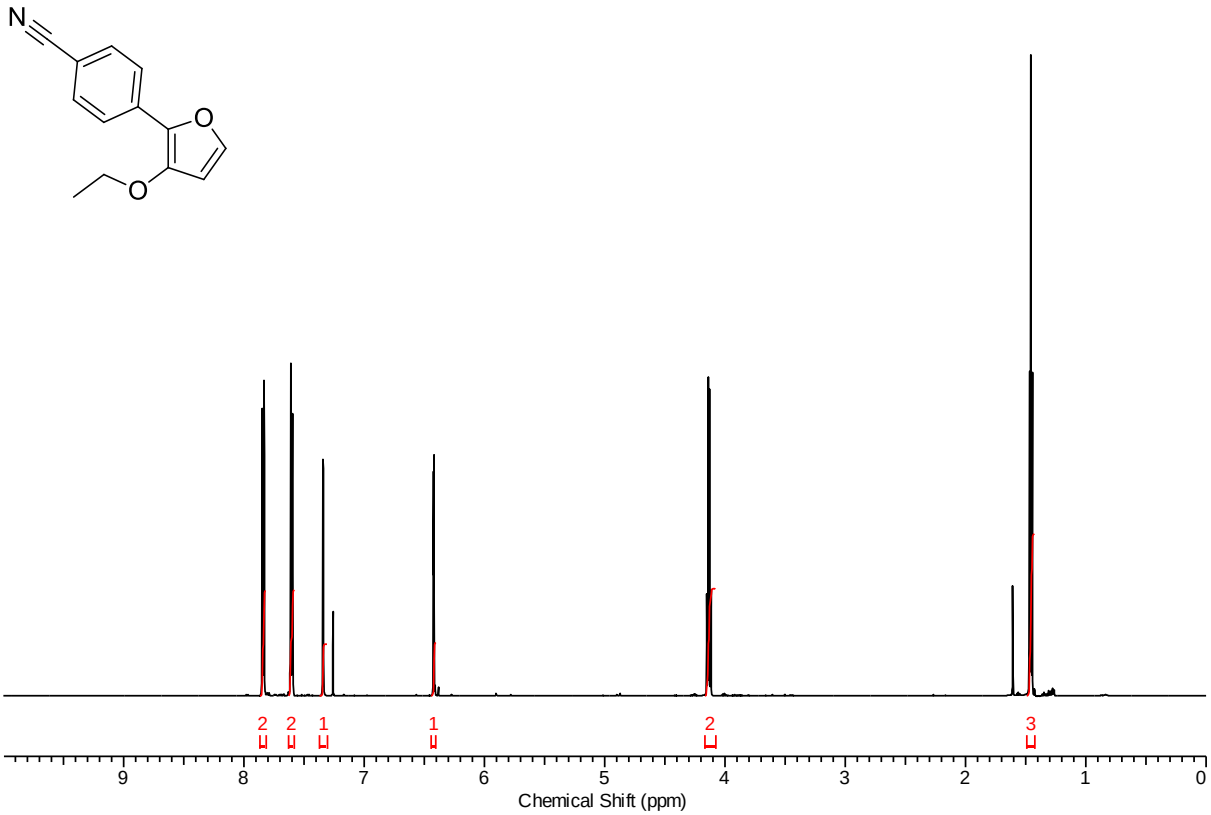


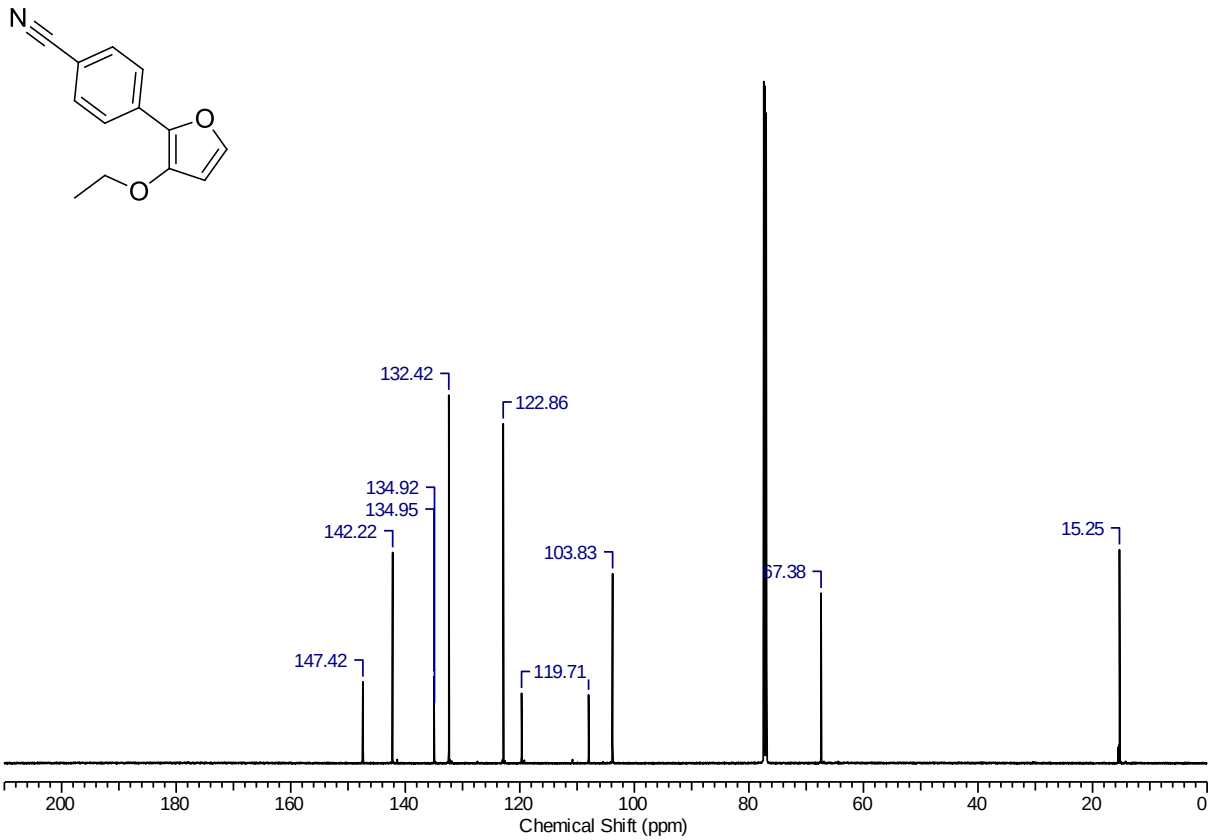
(*R*)-2-(2,6-Dimethylhept-5-en-1-yl)-3-ethoxyfuran 3g



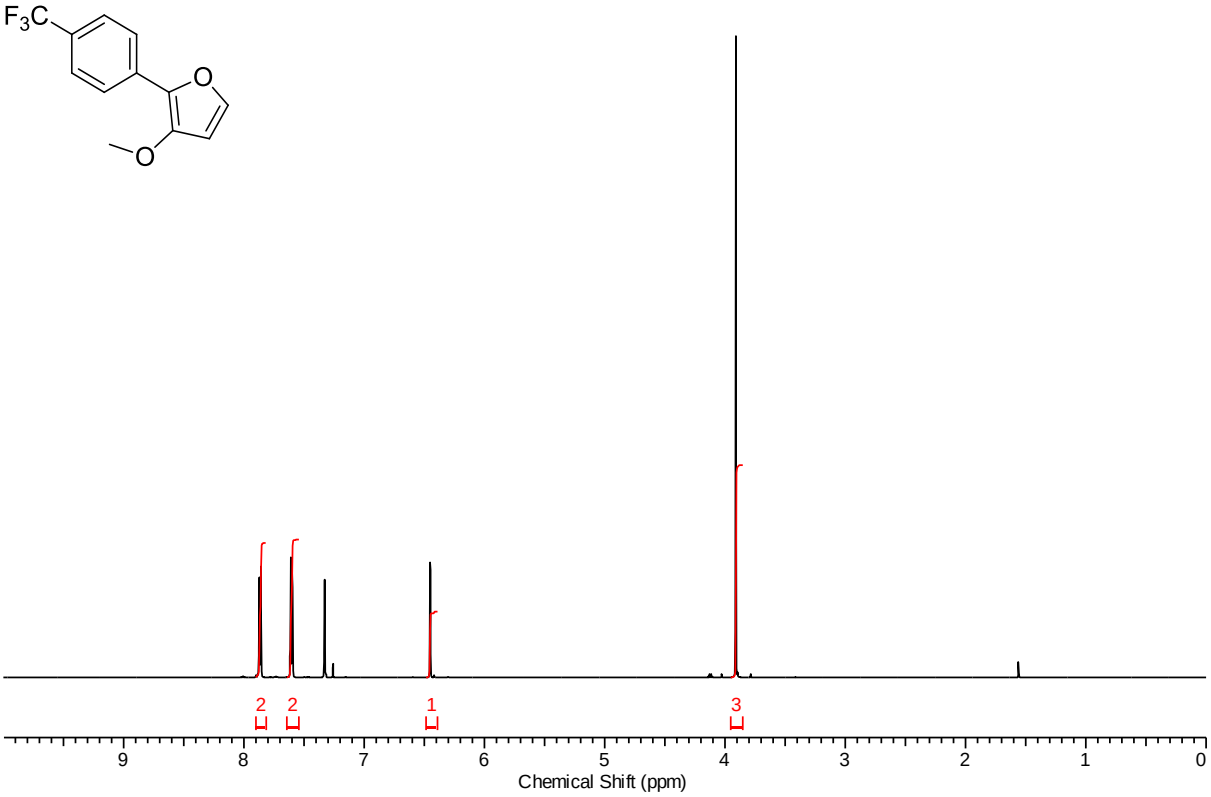


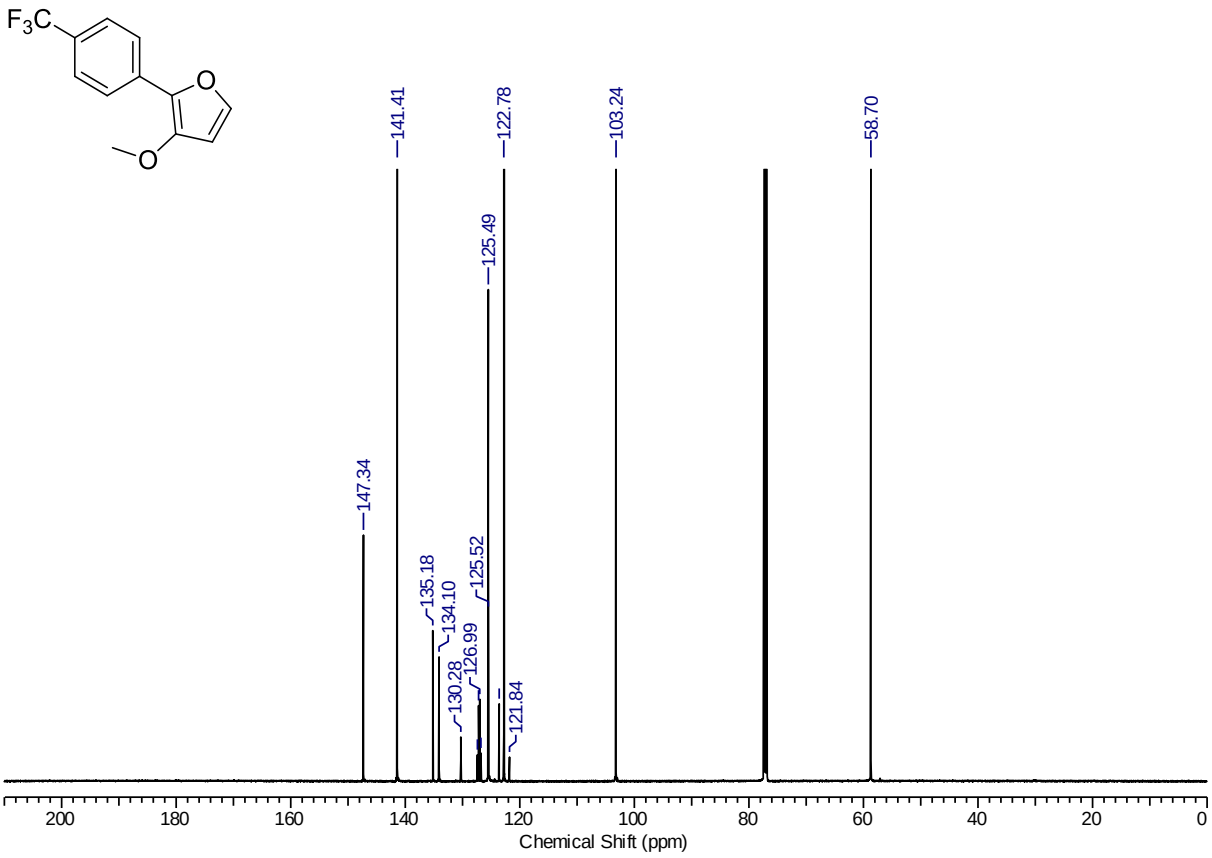
4-(3-Ethoxyfuran-2-yl)benzonitrile 3h



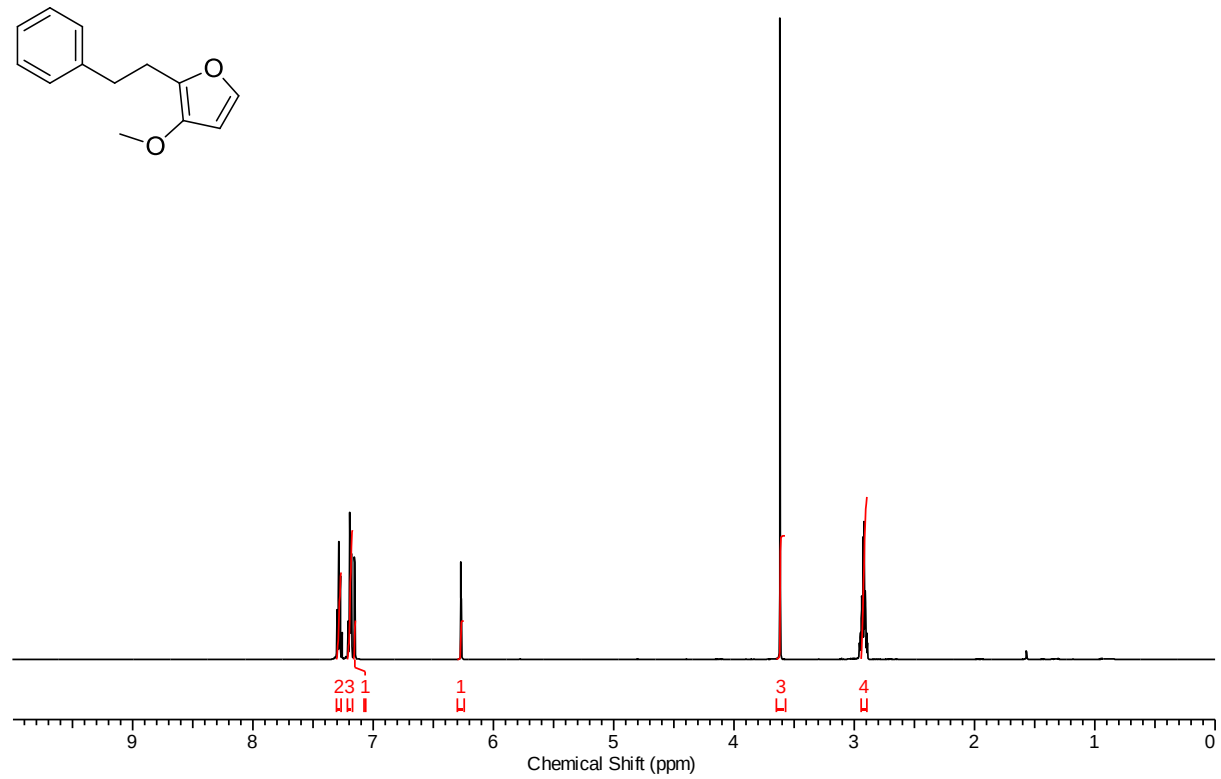


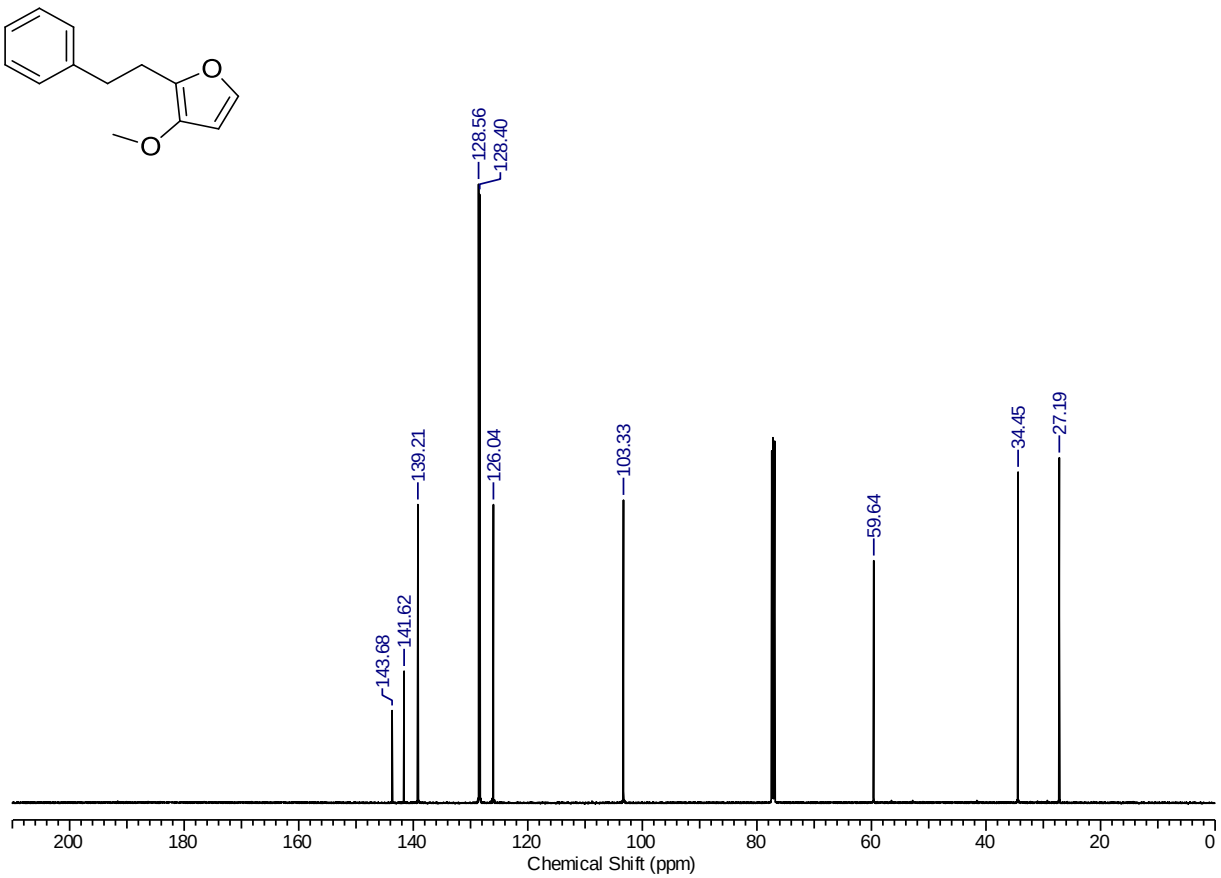
3-Methoxy-2-(4-(trifluoromethyl)phenyl)furan 4a



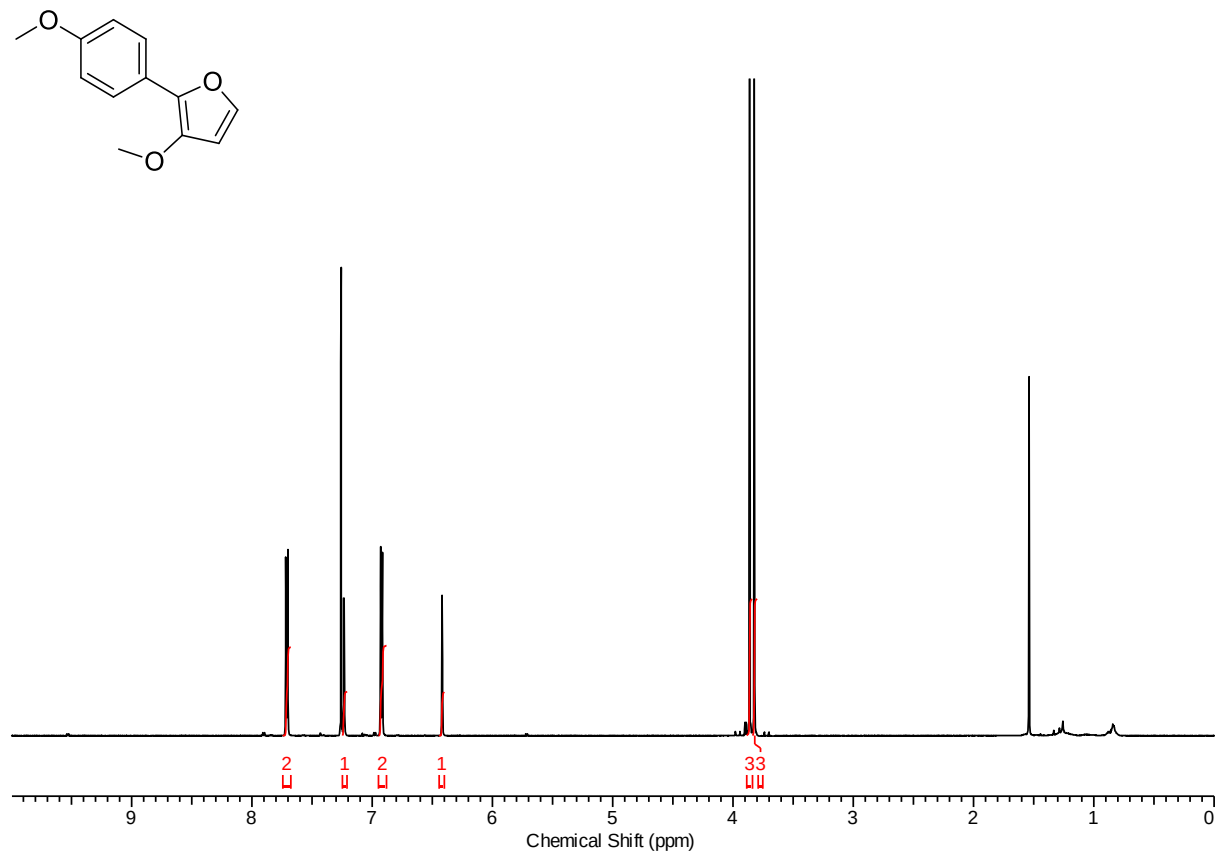


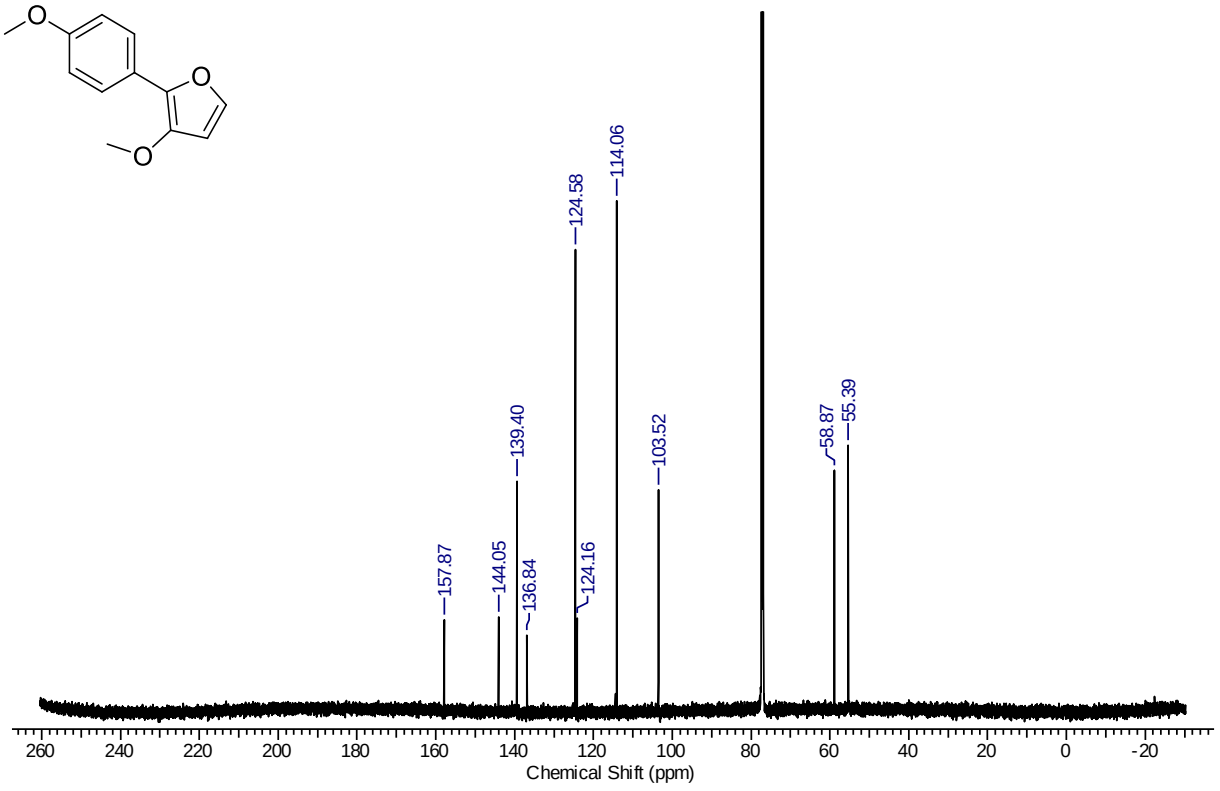
3-Methoxy-2-phenethylfuran 4b



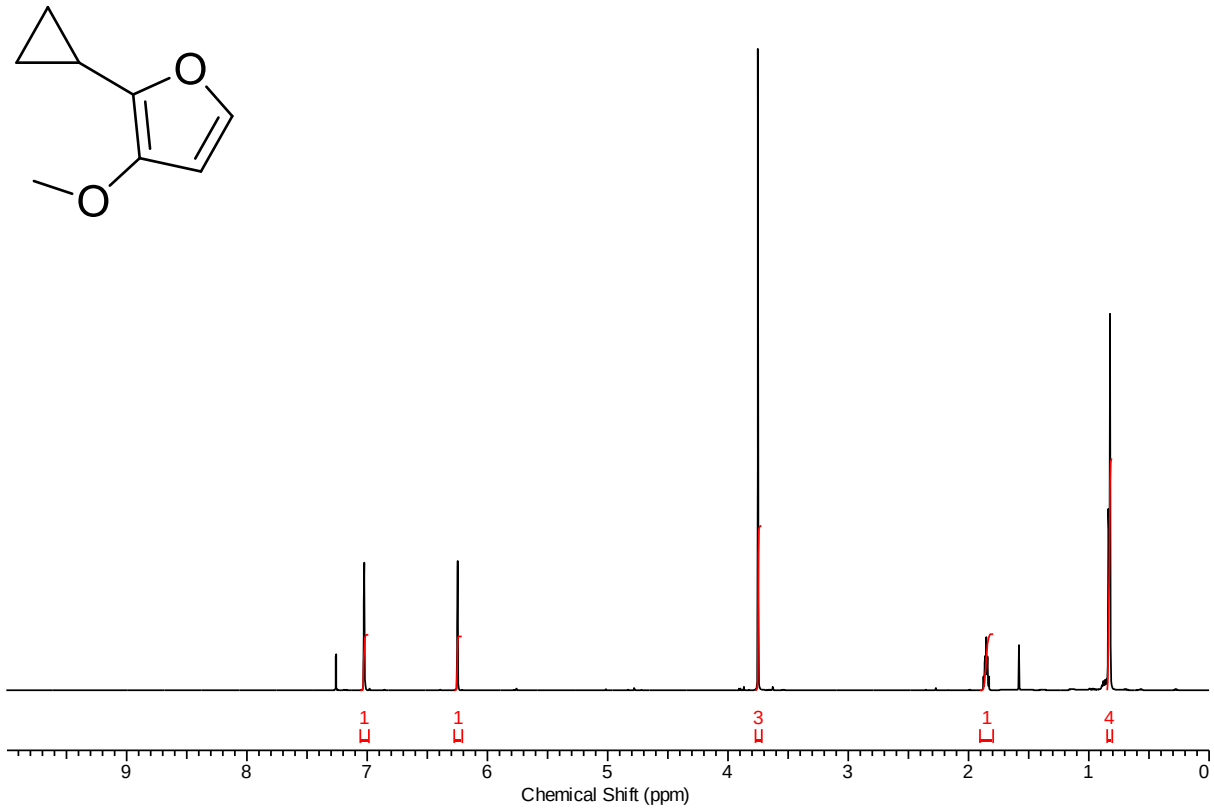


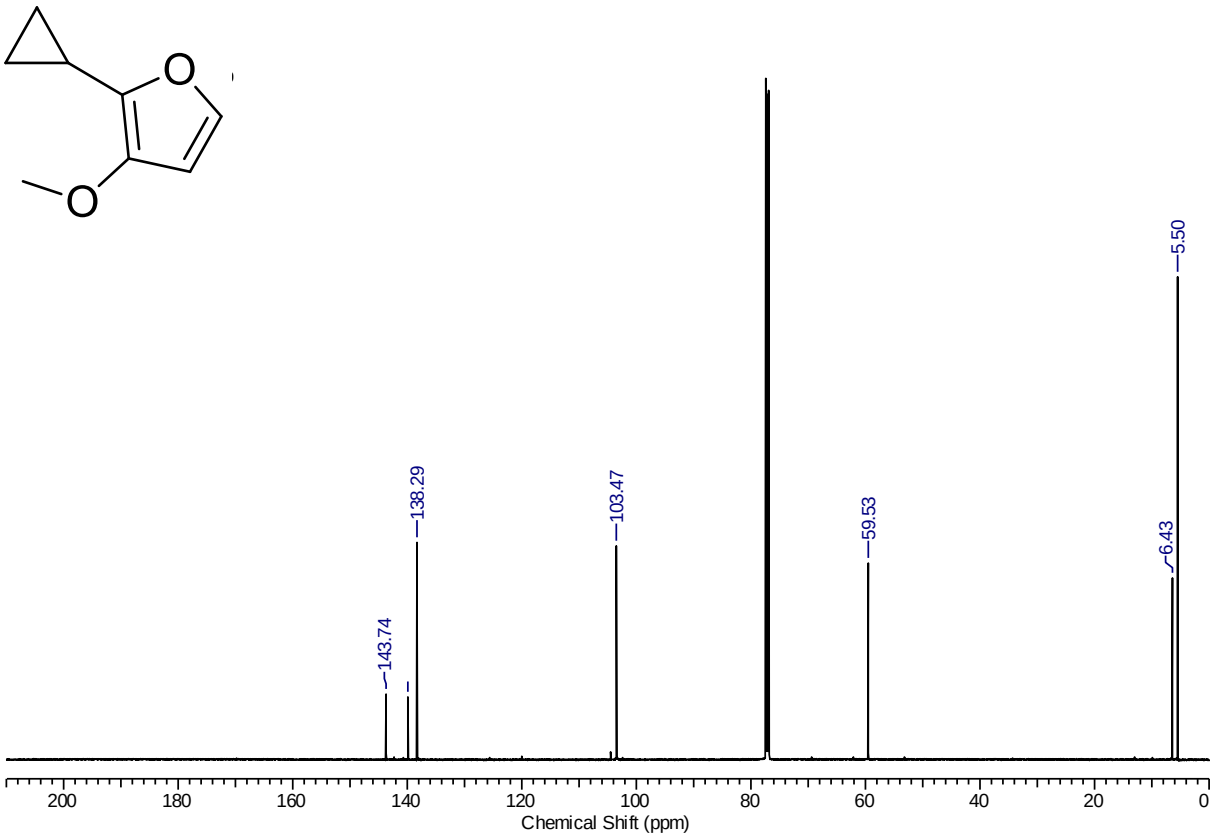
3-Methoxy-2-(4-methoxyphenyl)furan 4c



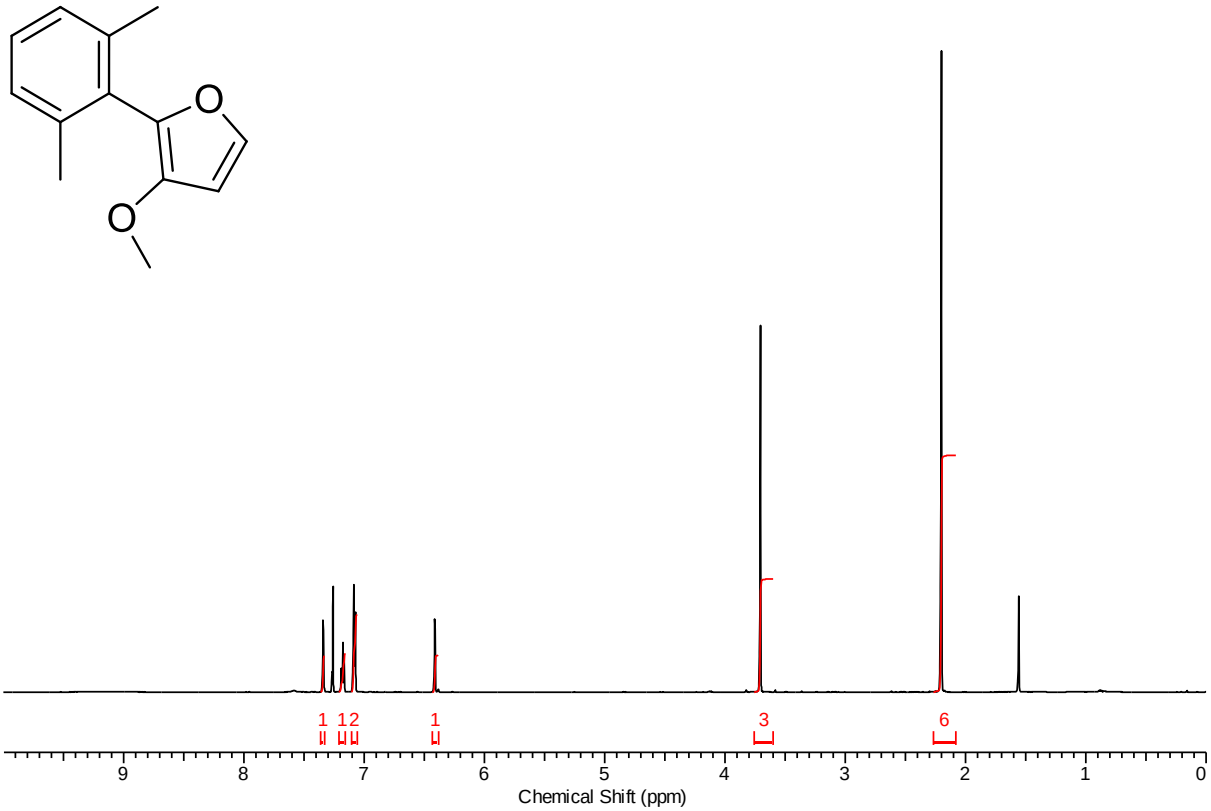


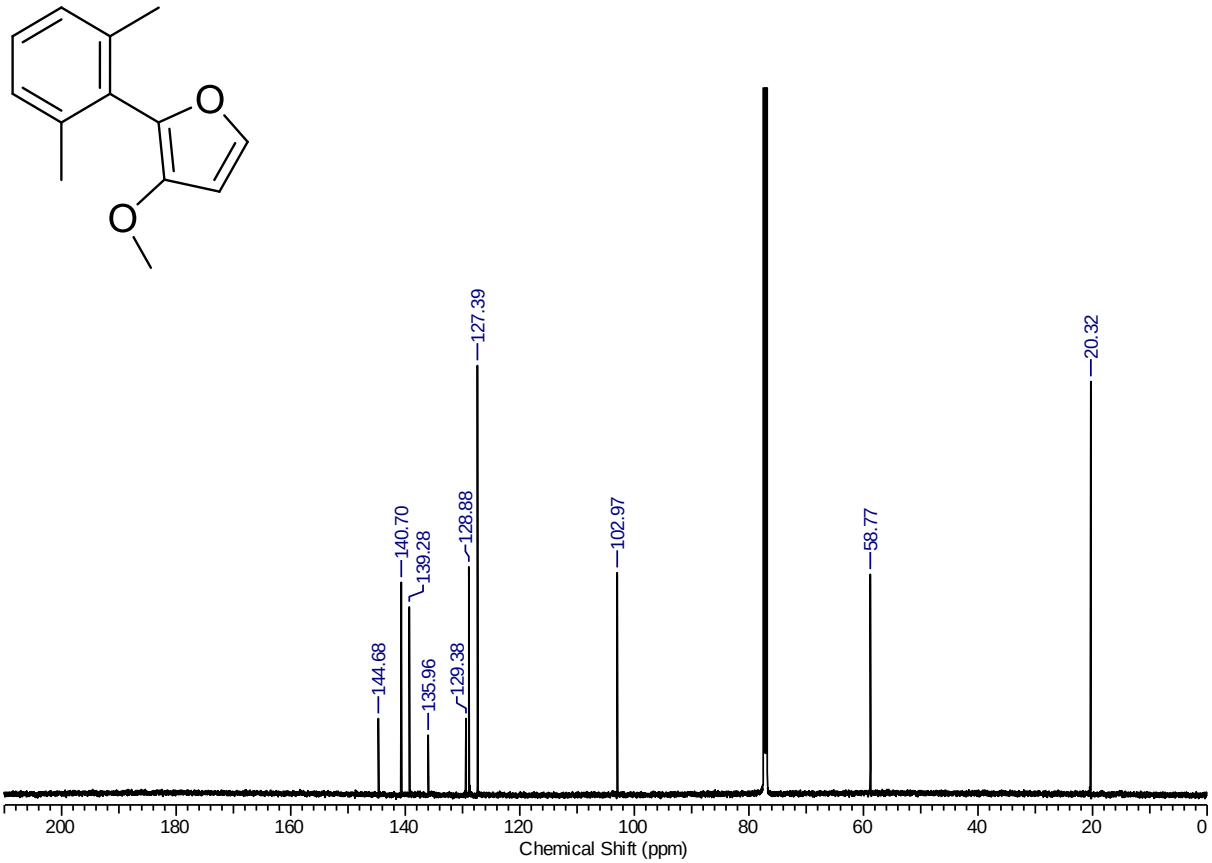
2-Cyclopropyl-3-methoxyfuran 4d



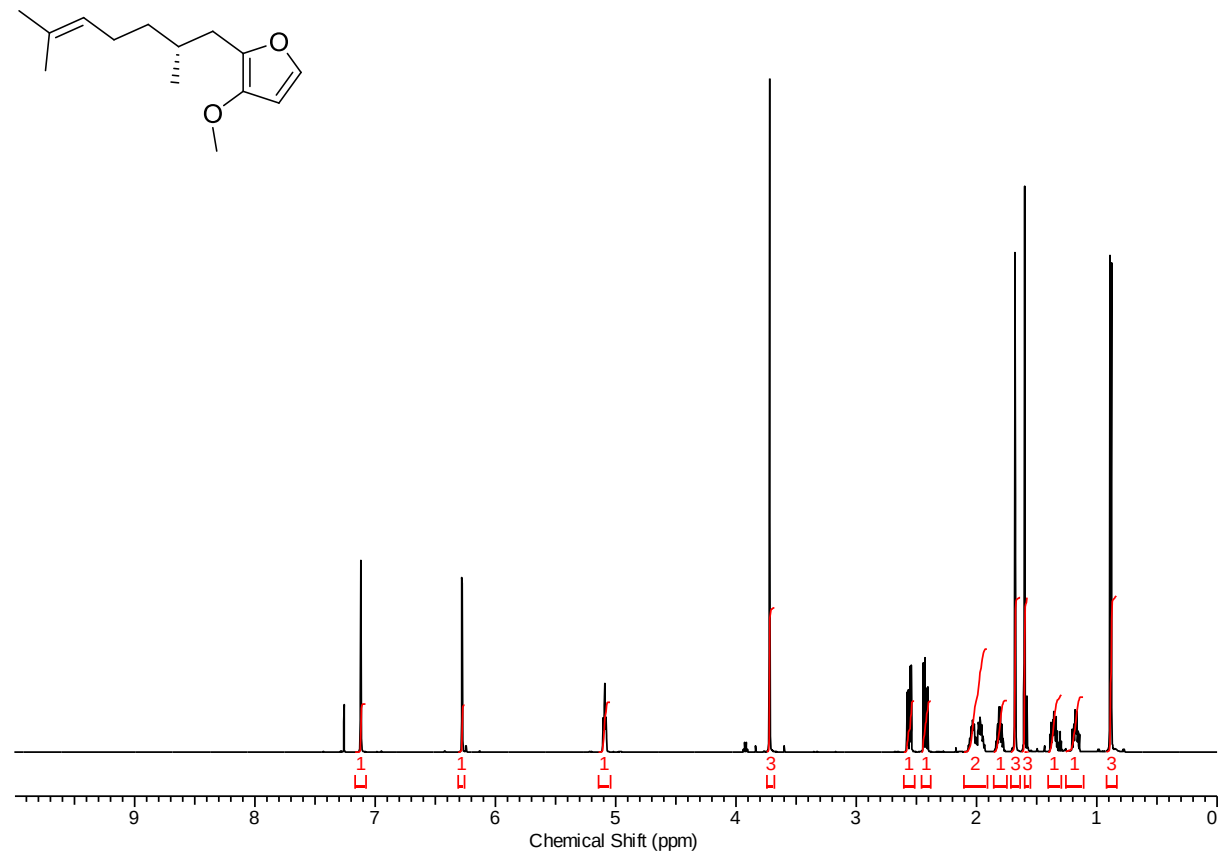


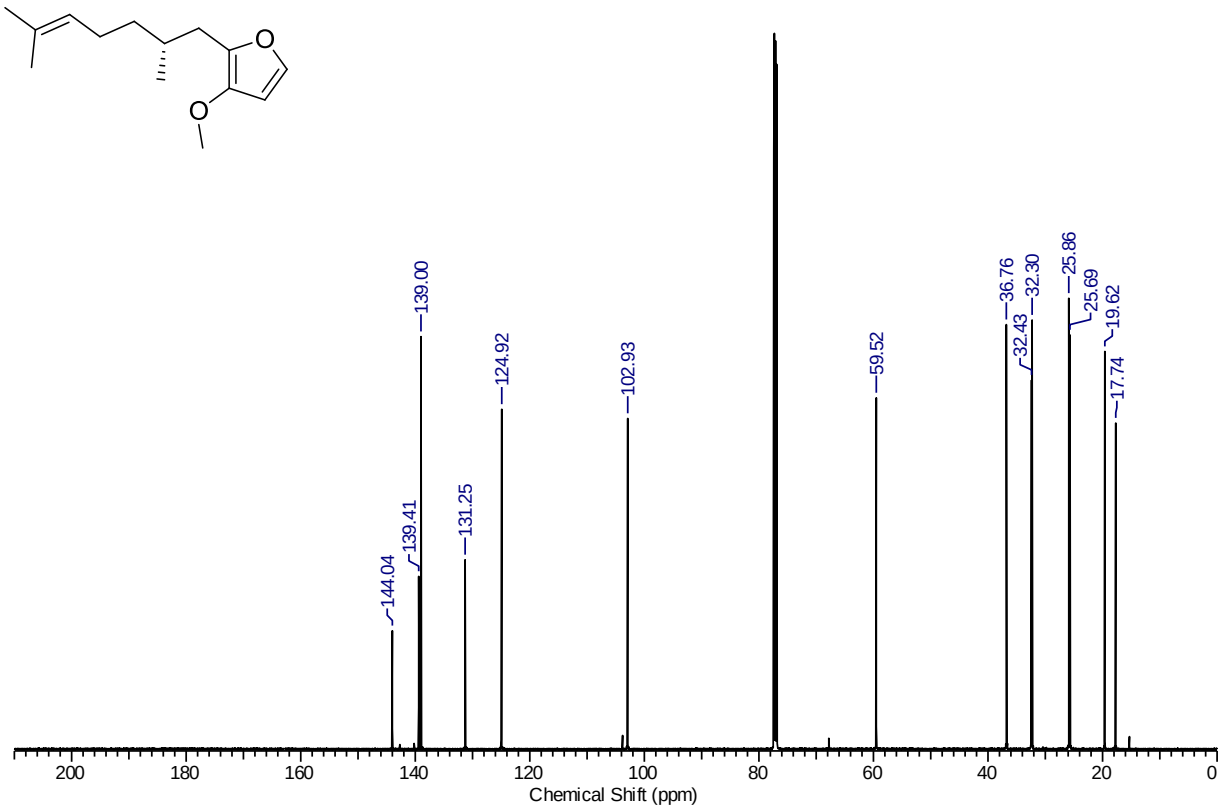
2-(2,6-Dimethylphenyl)-3-methoxyfuran 4f



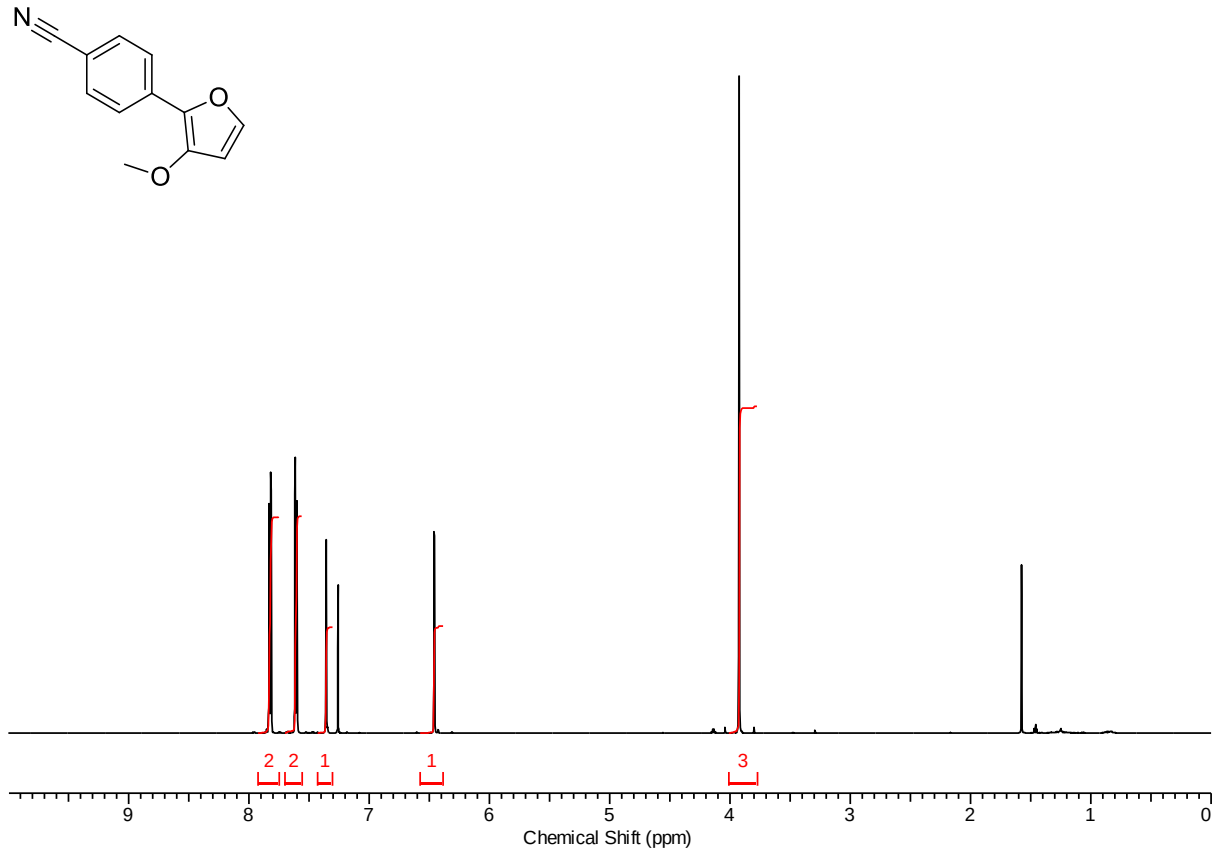


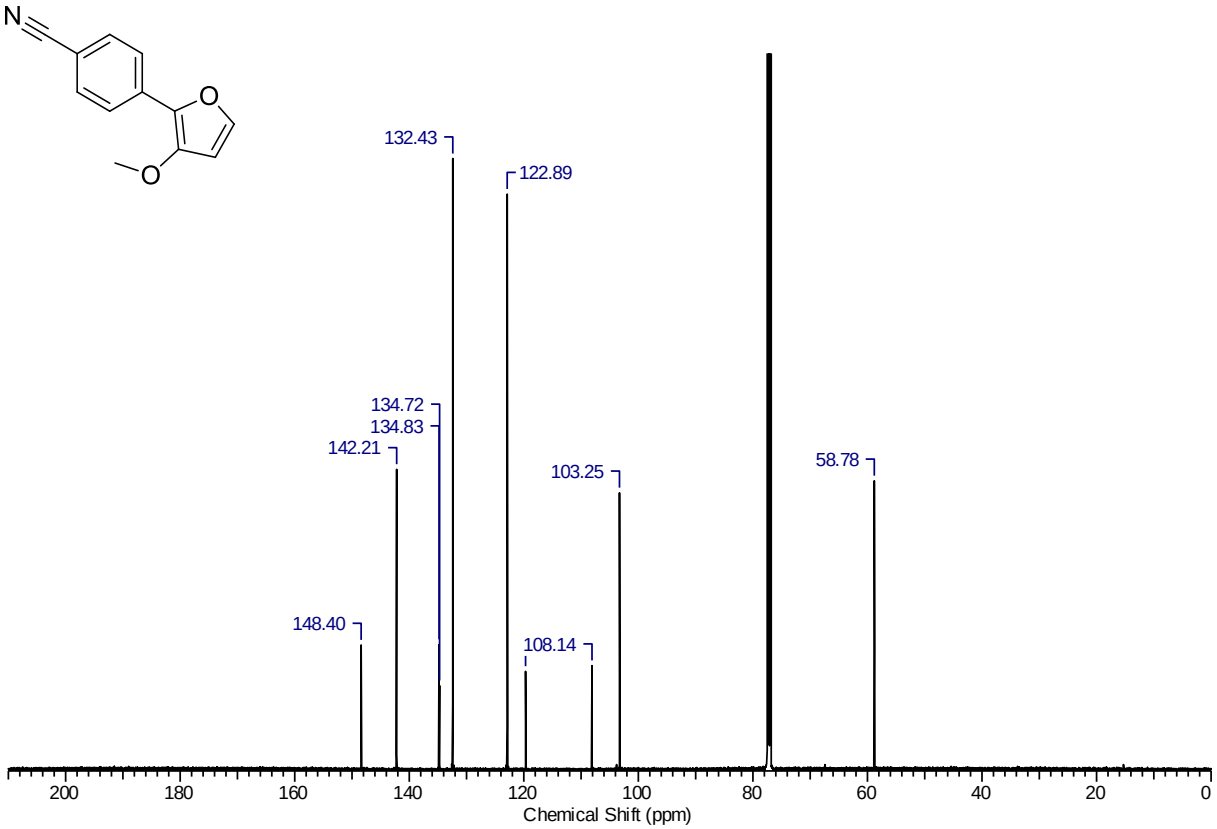
(*R*)-2-(2,6-Dimethylhept-5-en-1-yl)-3-methoxyfuran 4g



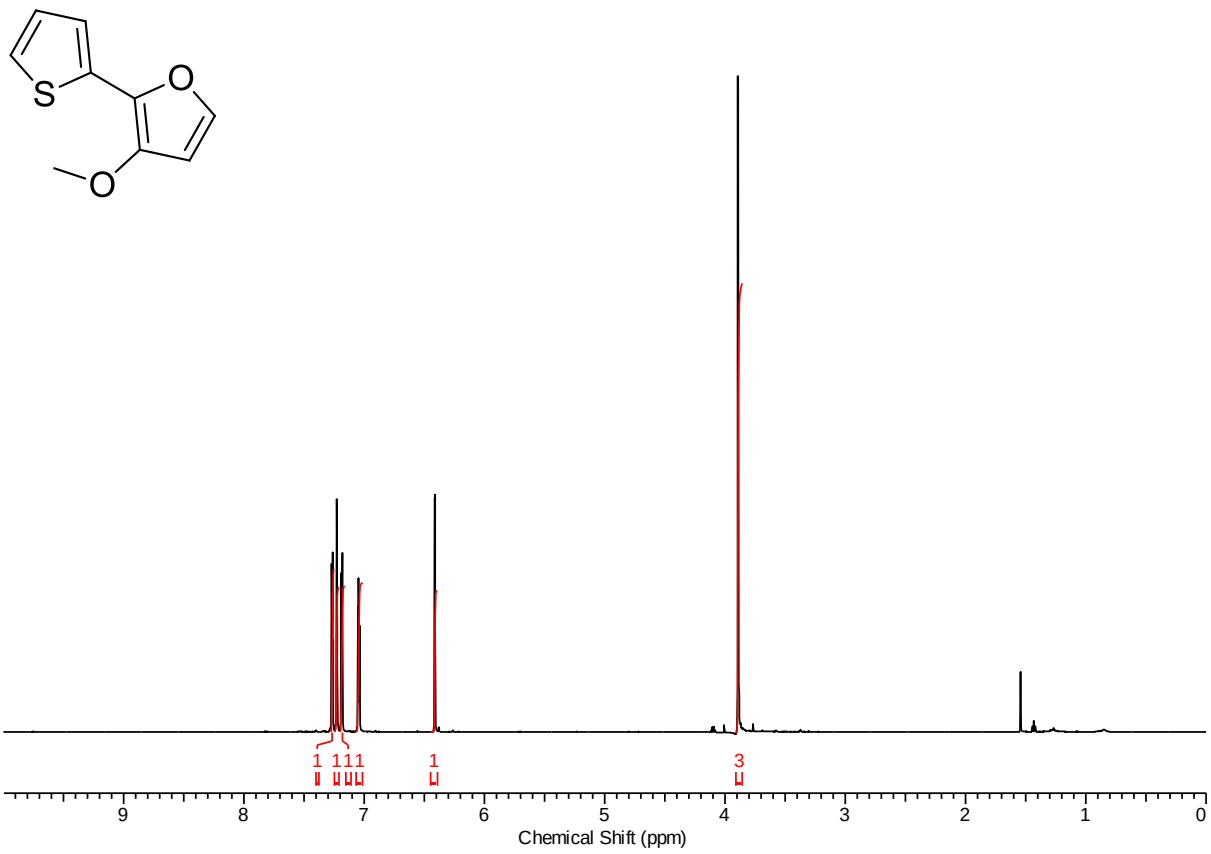


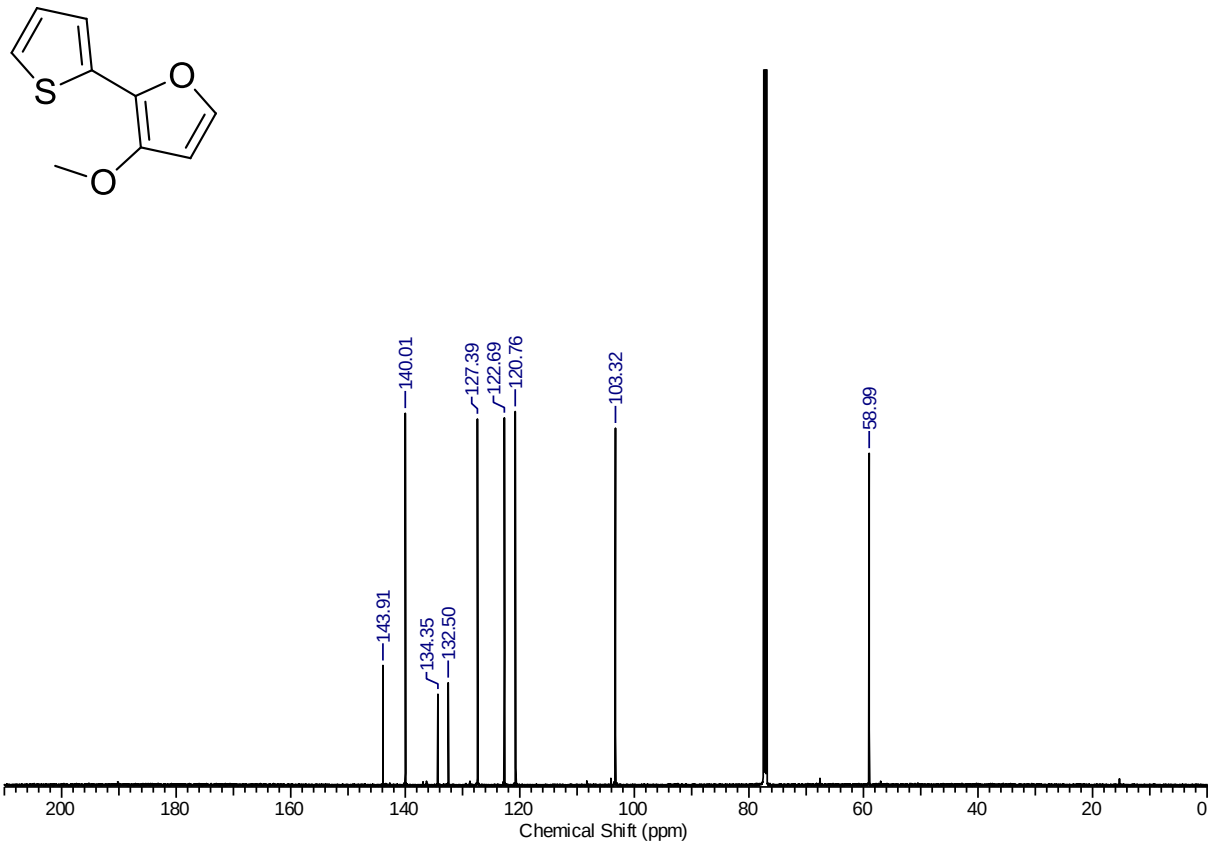
4-(3-Methoxyfuran-2-yl)benzonitrile 4h



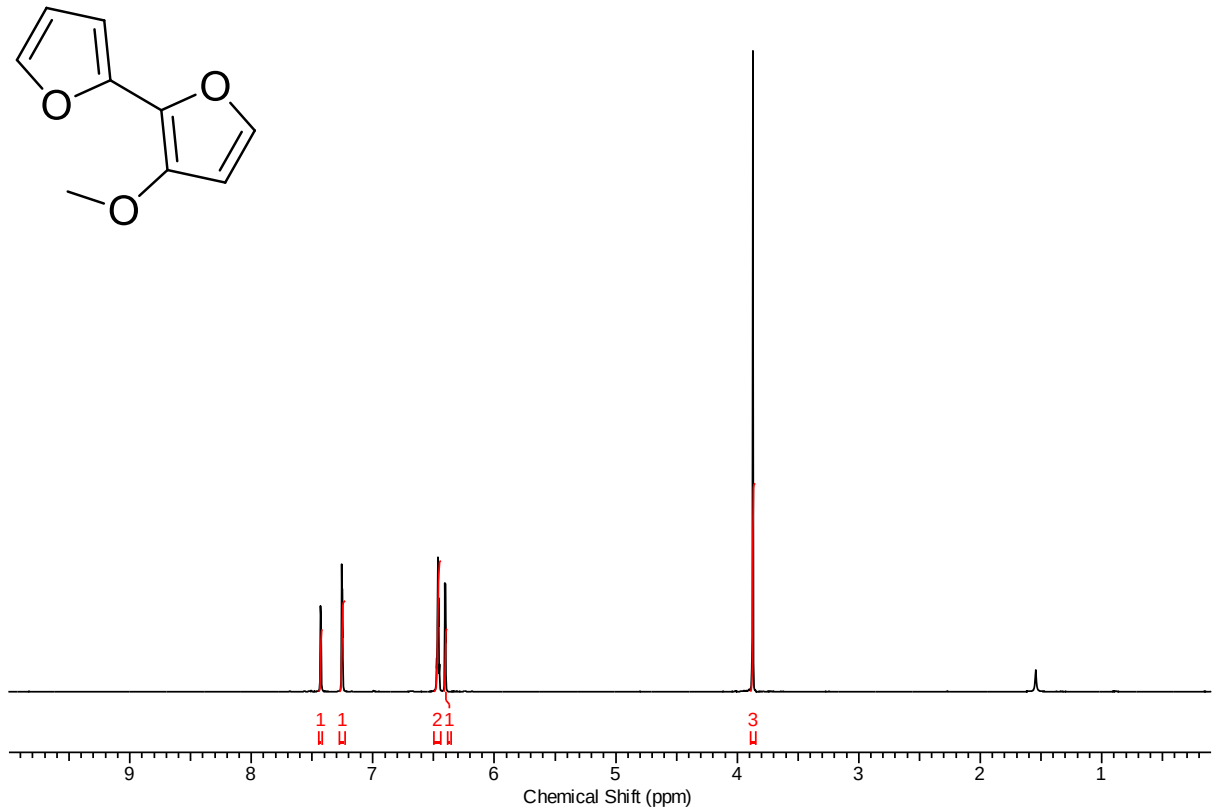


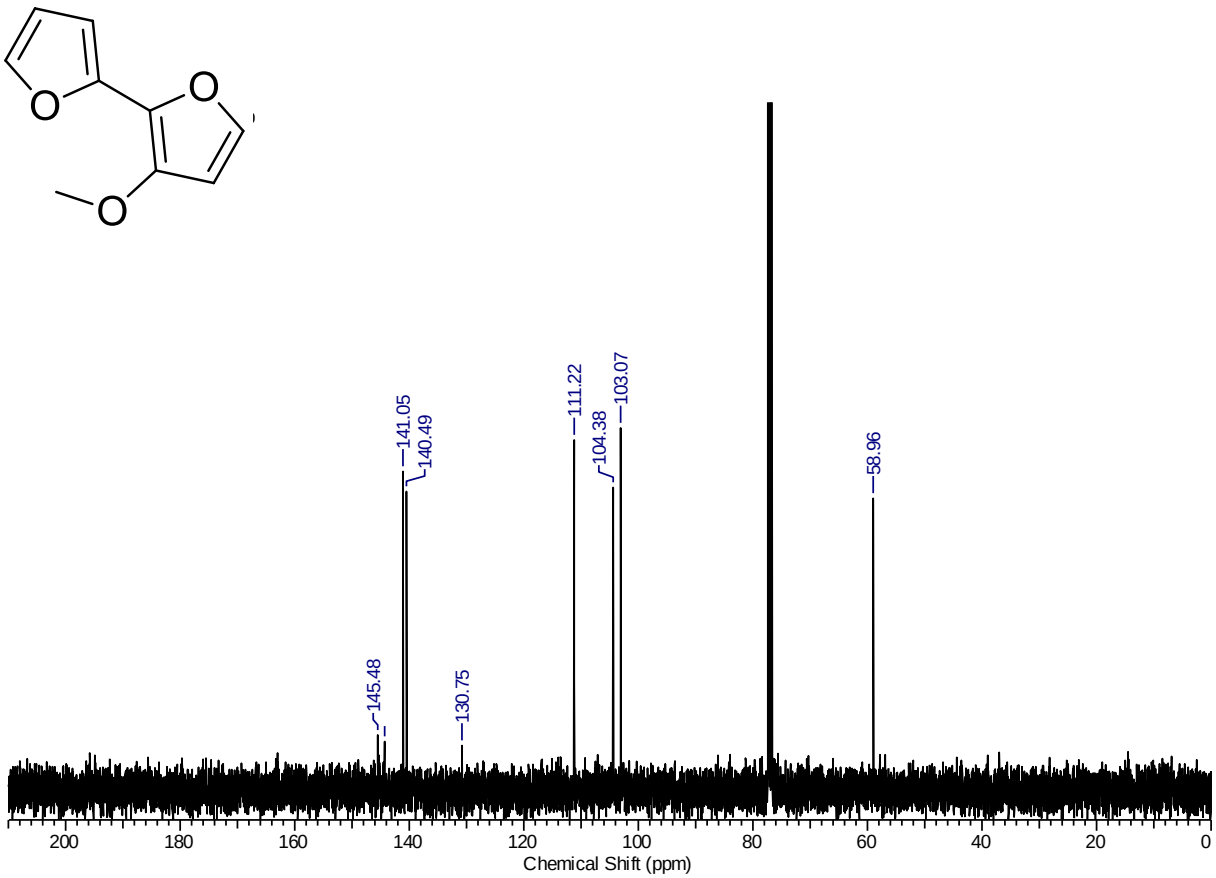
3-Methoxy-2-(thiophen-2-yl)furan 4i



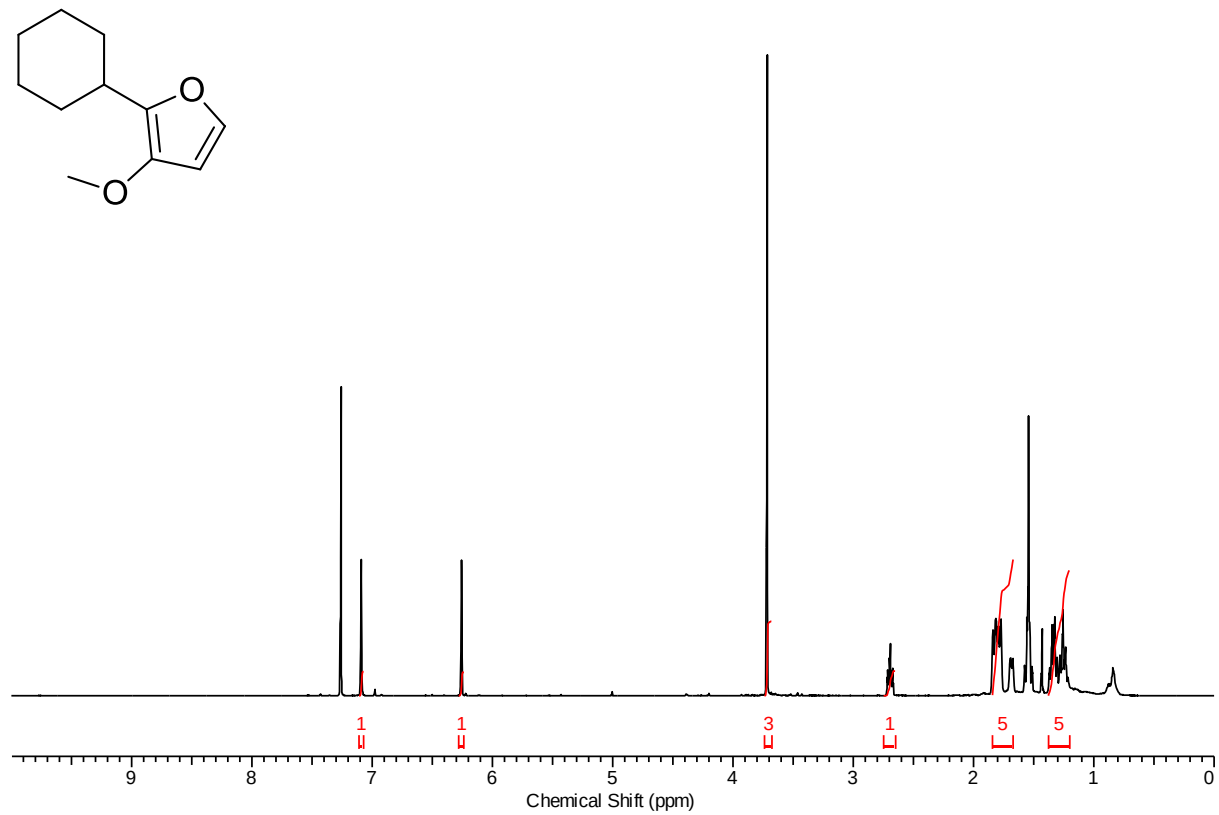


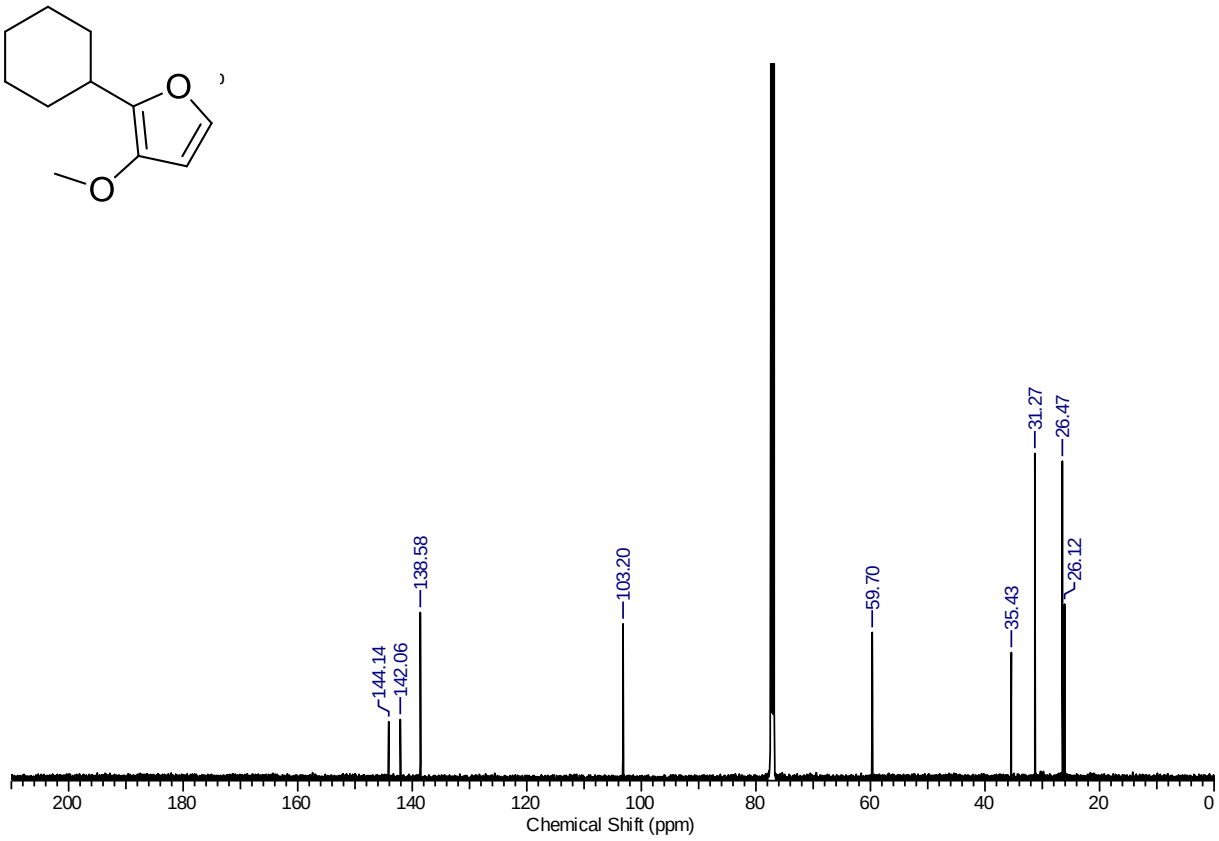
3-Methoxy-2,2'-bifuran 4j



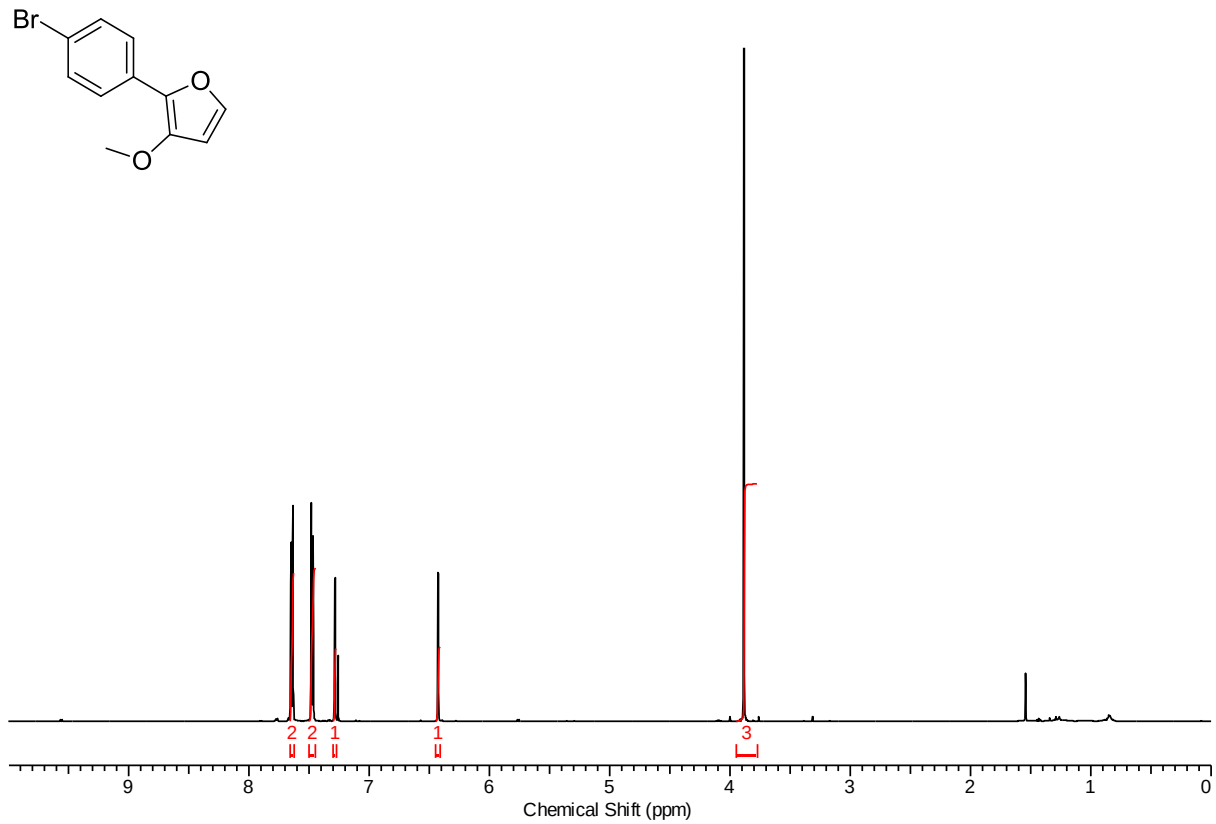


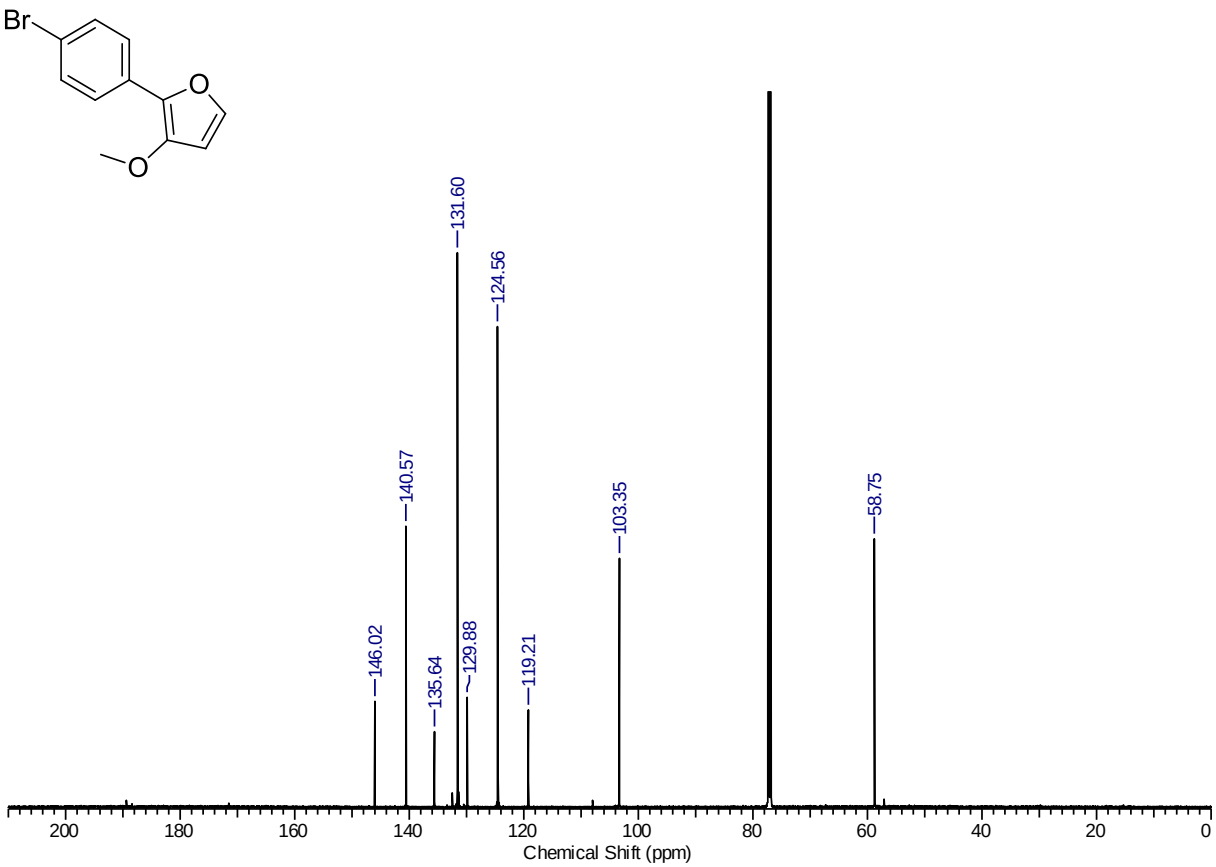
2-Cyclohexyl-3-methoxyfuran 4k



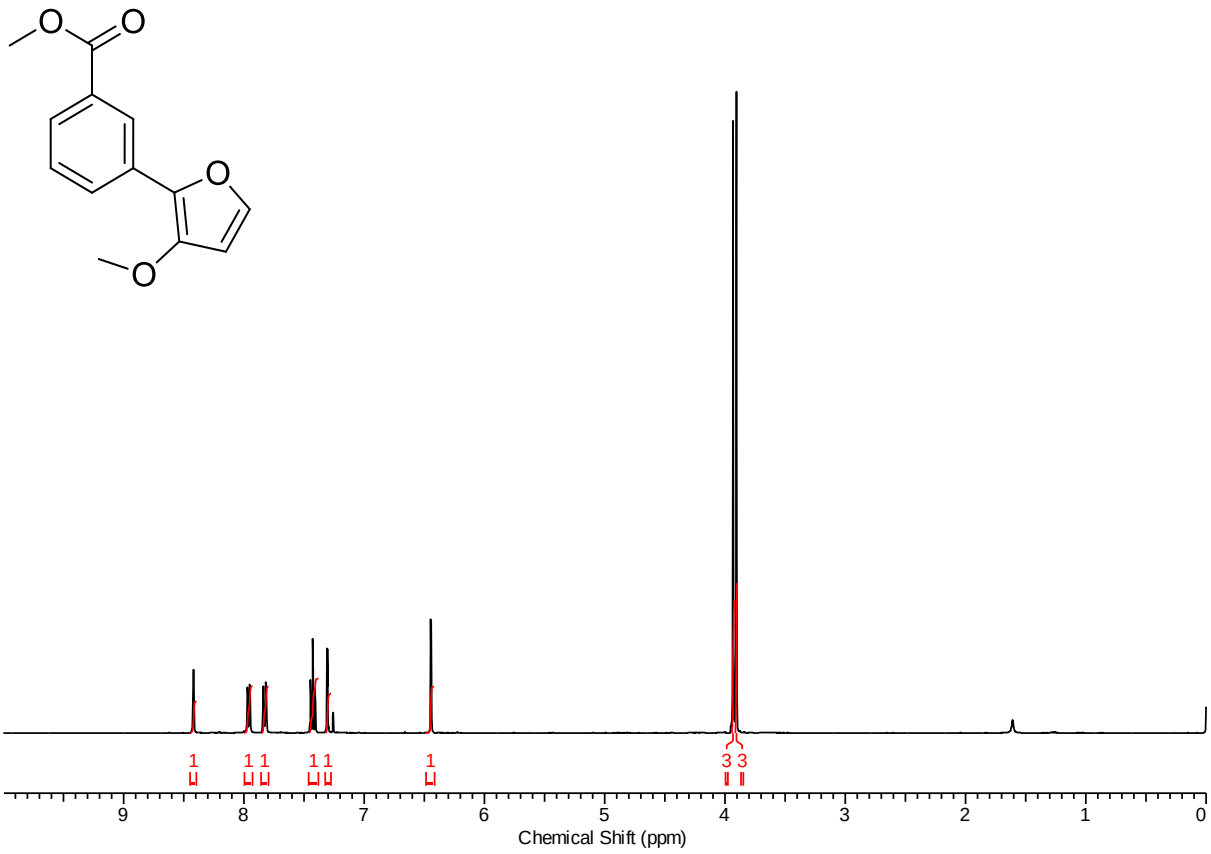


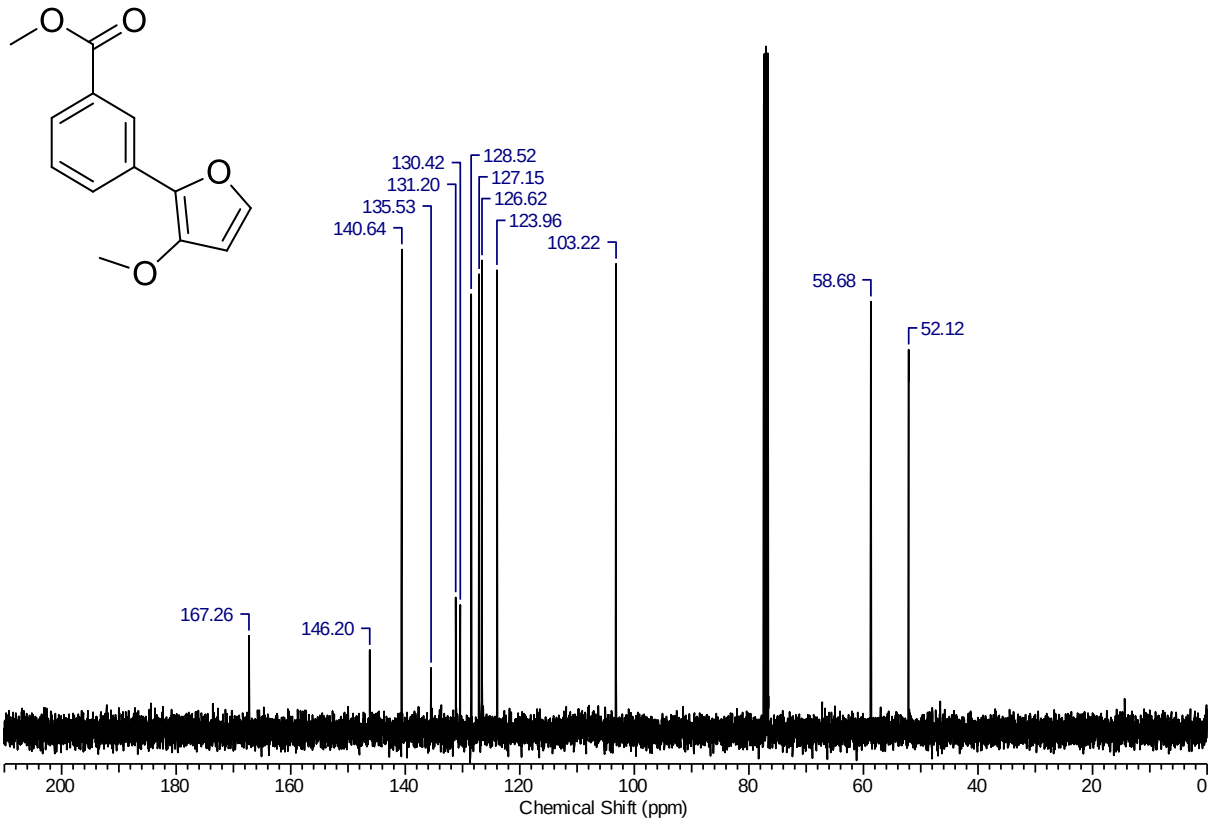
2-(4-Bromophenyl)-3-methoxyfuran 4l



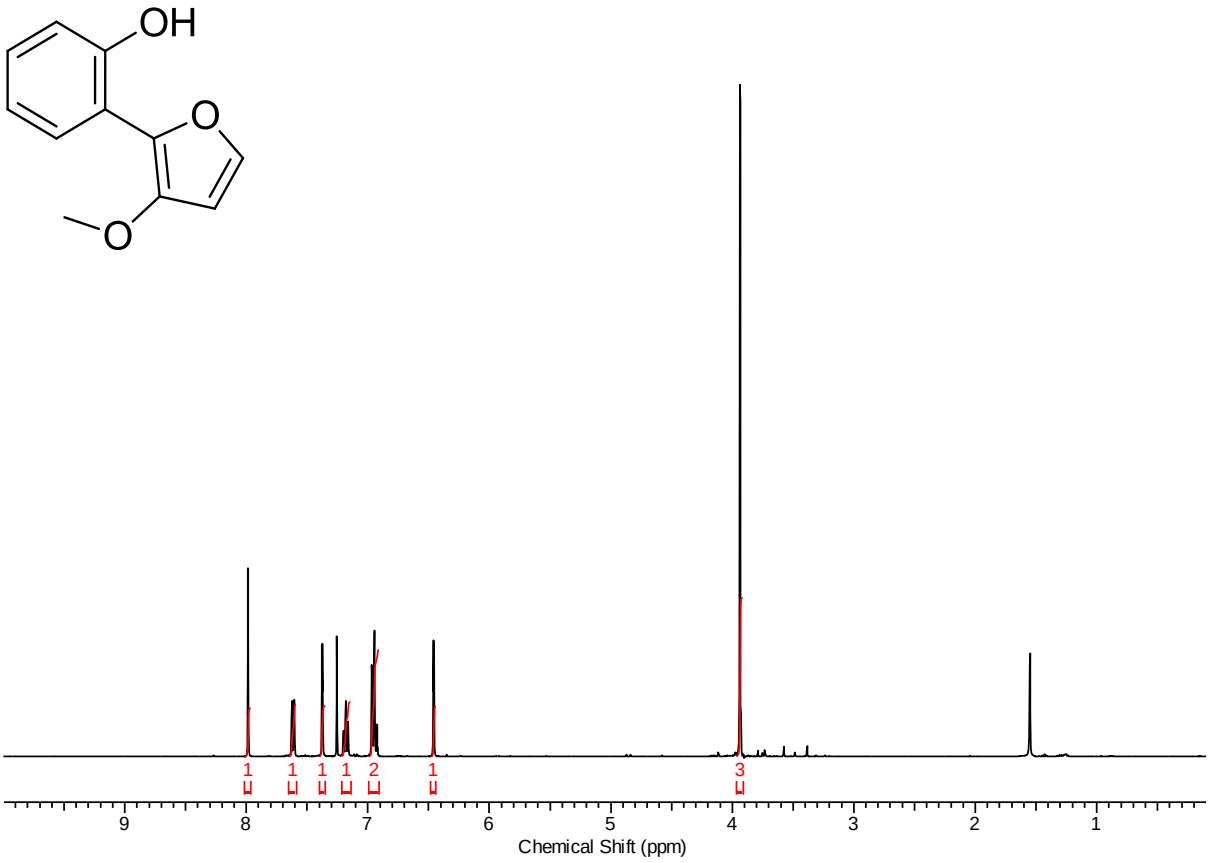


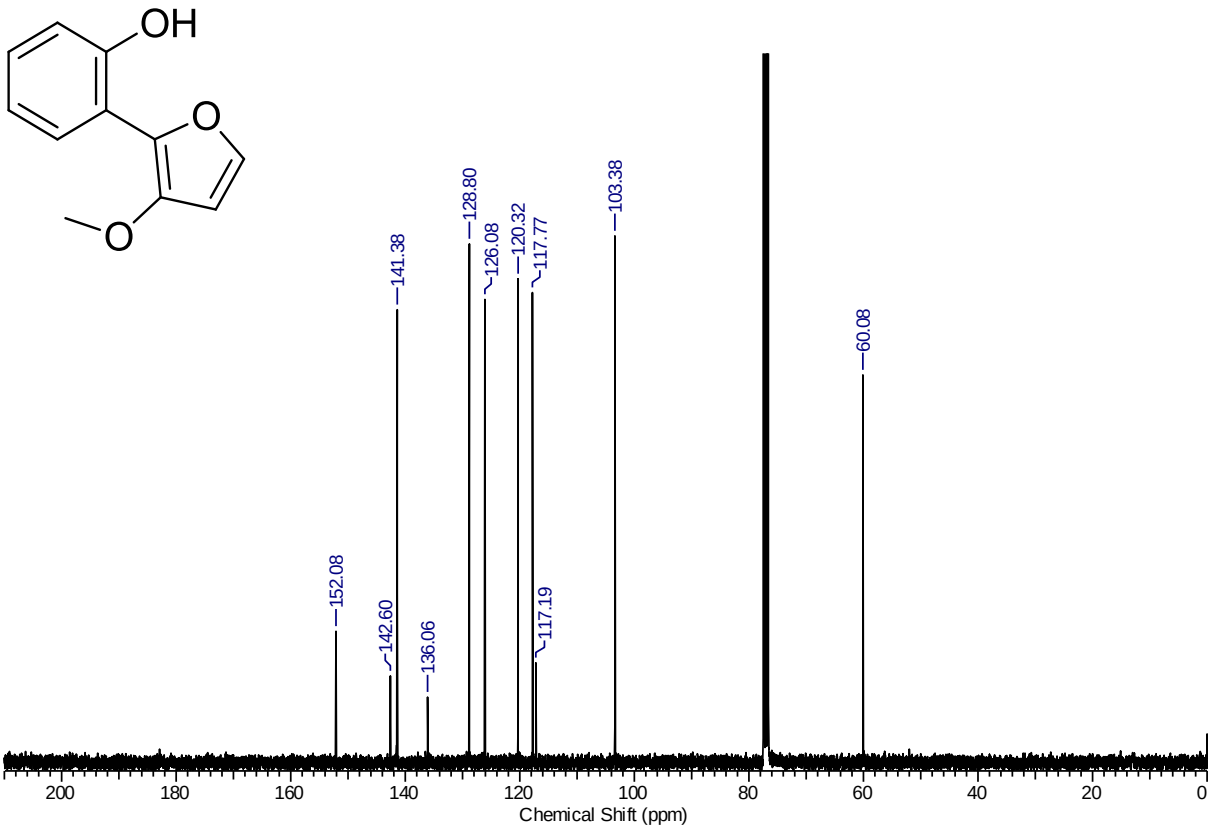
Methyl 3-(3-methoxyfuran-2-yl)benzoate 4m



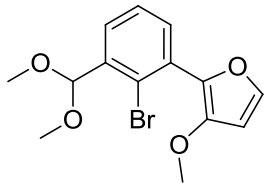


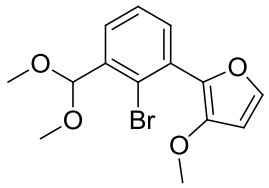
2-(3-methoxyfuran-2-yl)phenol 4n



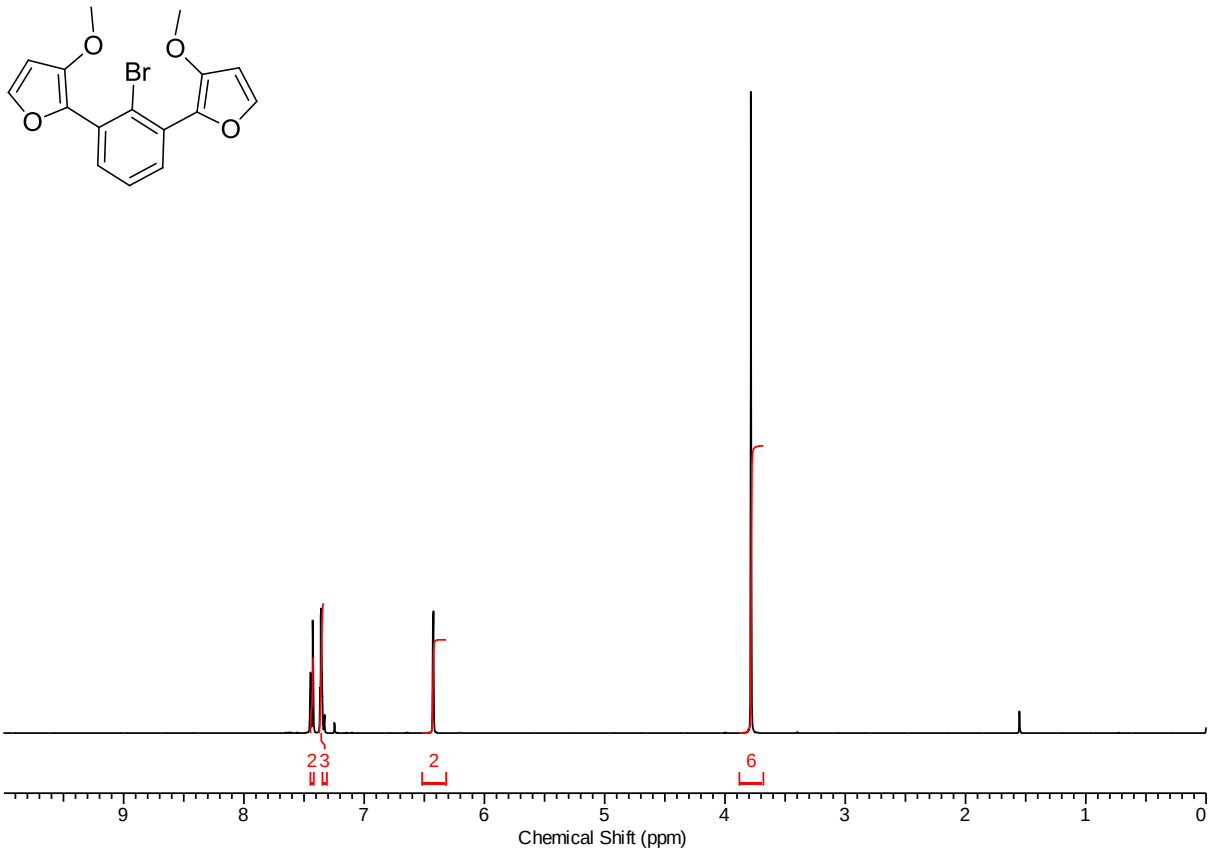


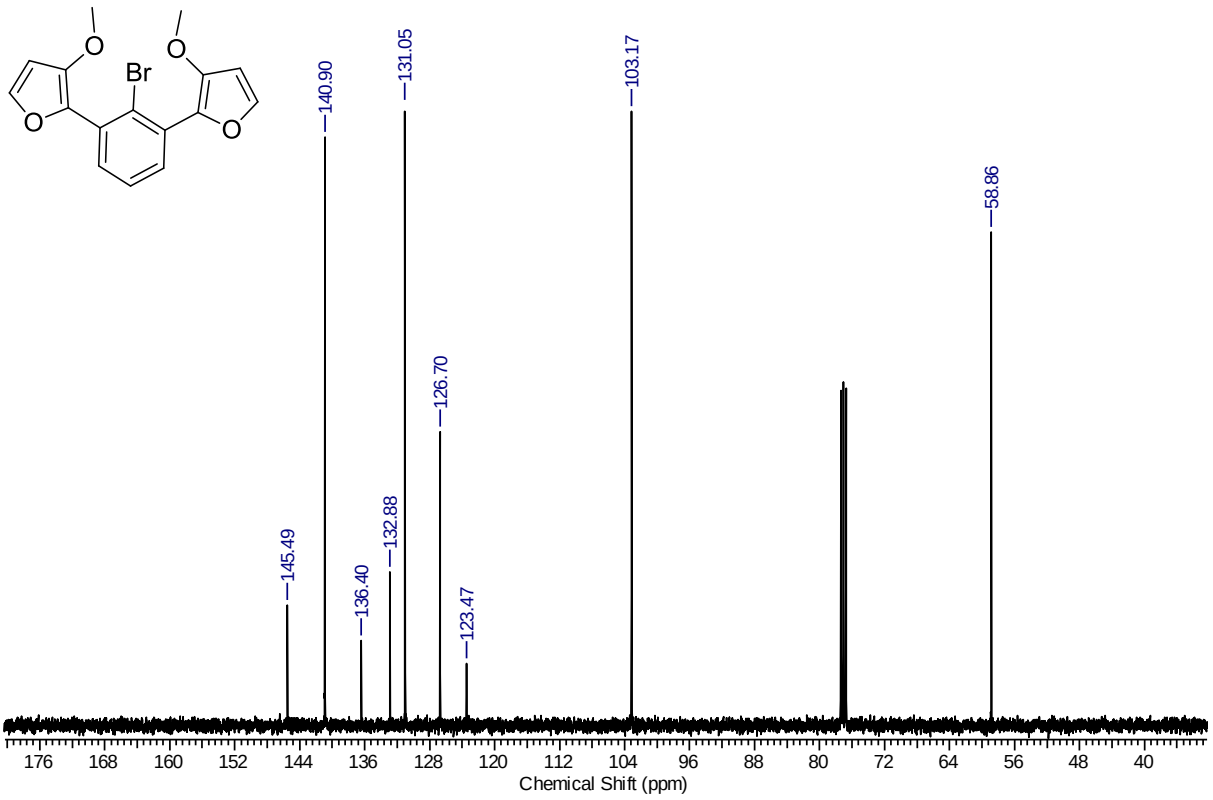
2-(2-Bromo-3-(dimethoxymethyl)phenyl)-3-methoxyfuran 4o



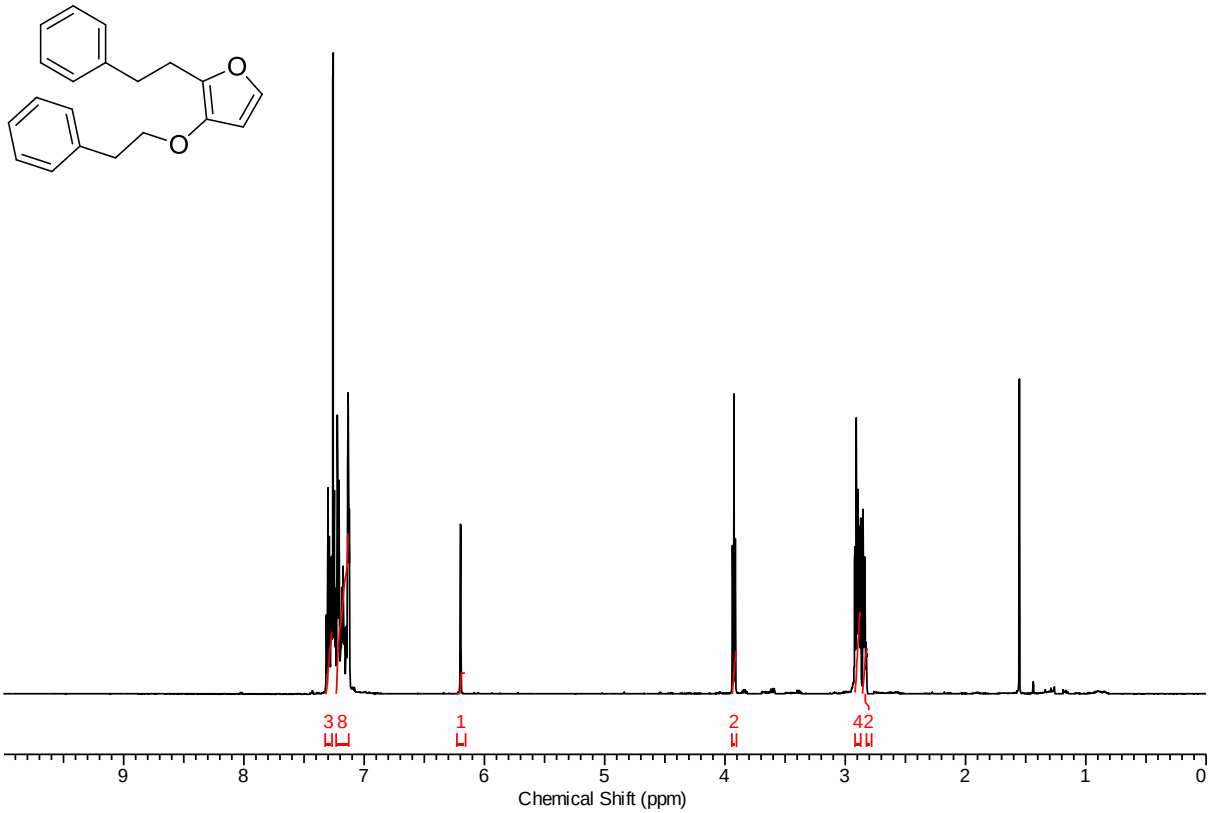


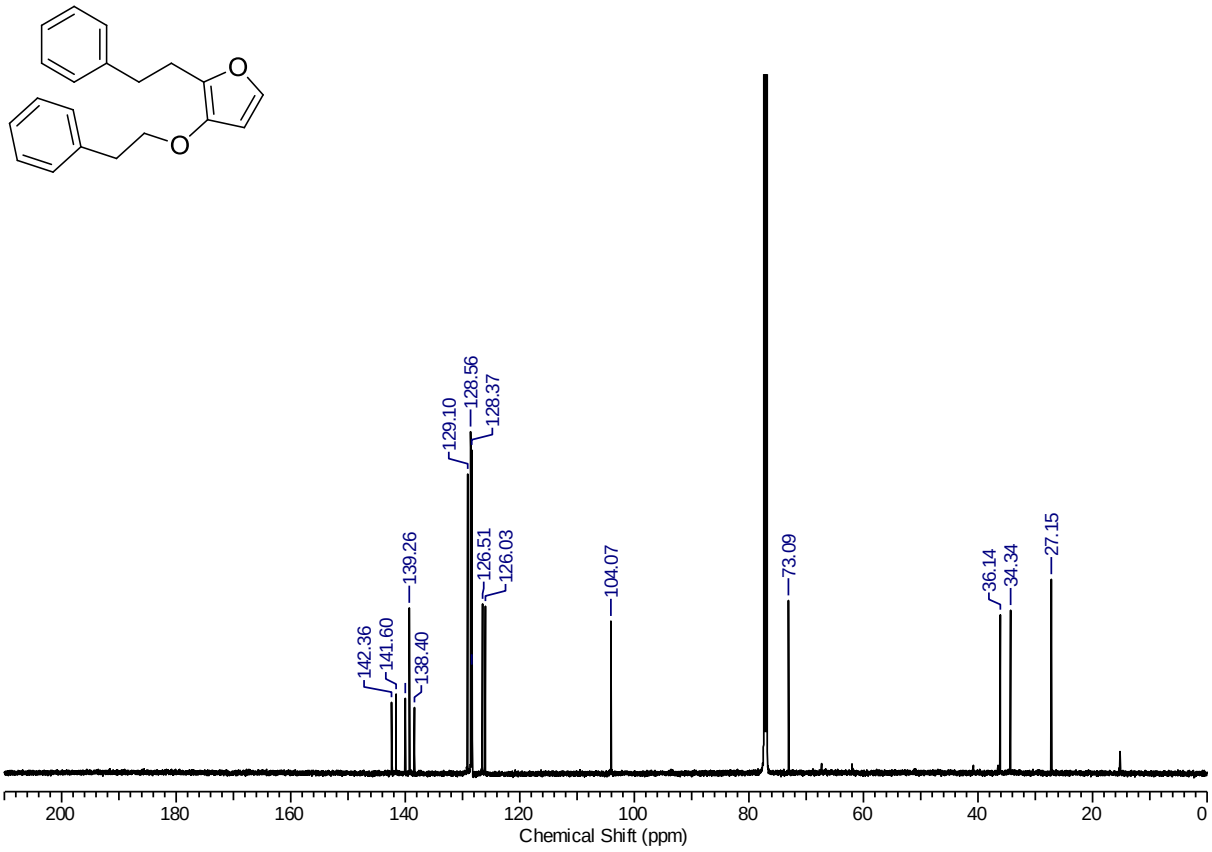
2,2'-(2-Bromo-1,3-phenylene)bis(3-methoxyfuran) 4p



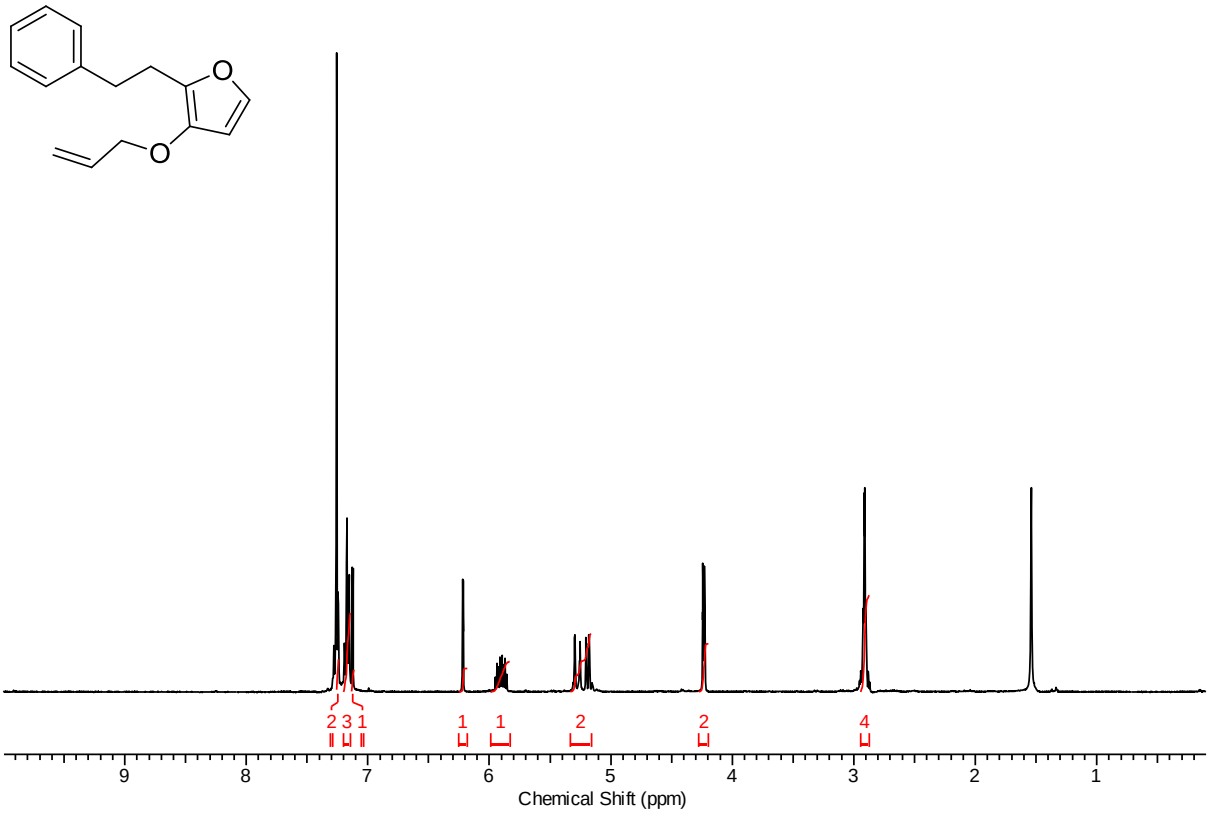


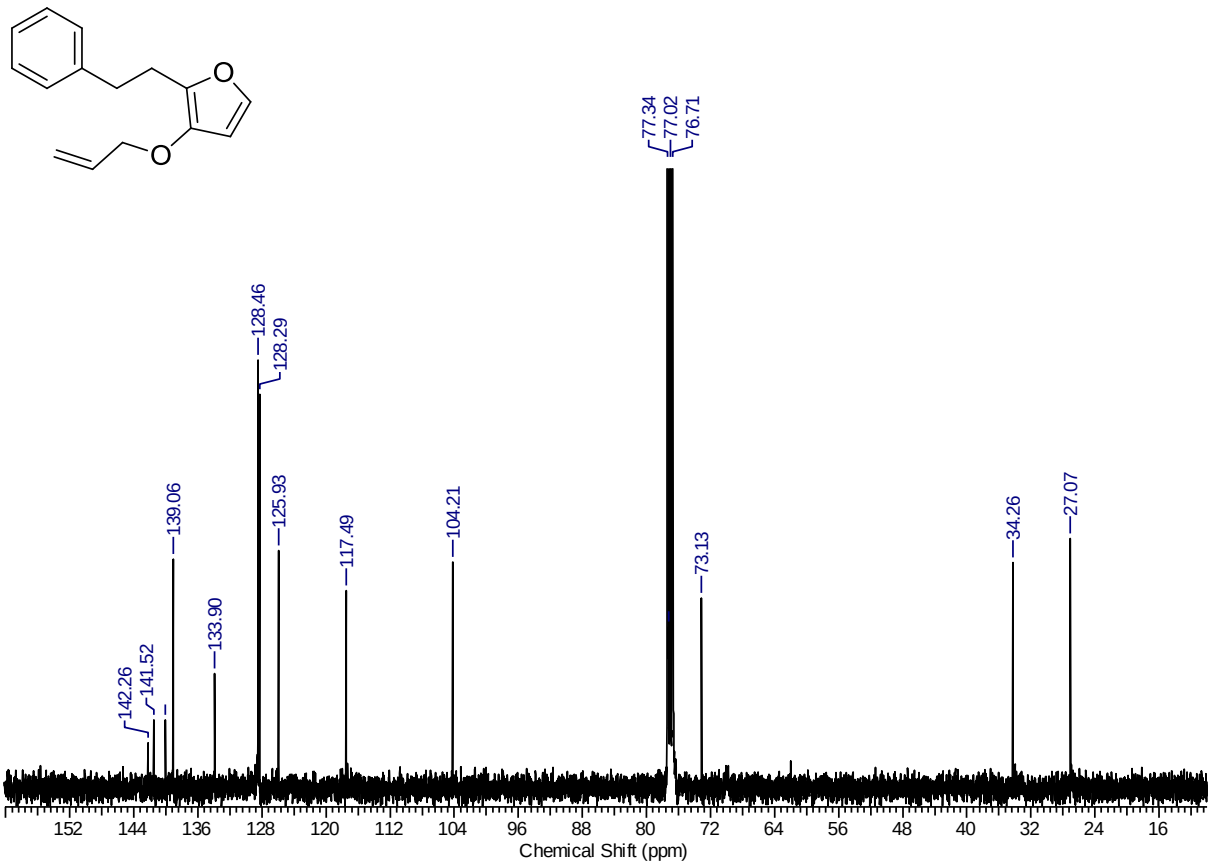
3-Phenethoxy-2-phenethylfuran 5b



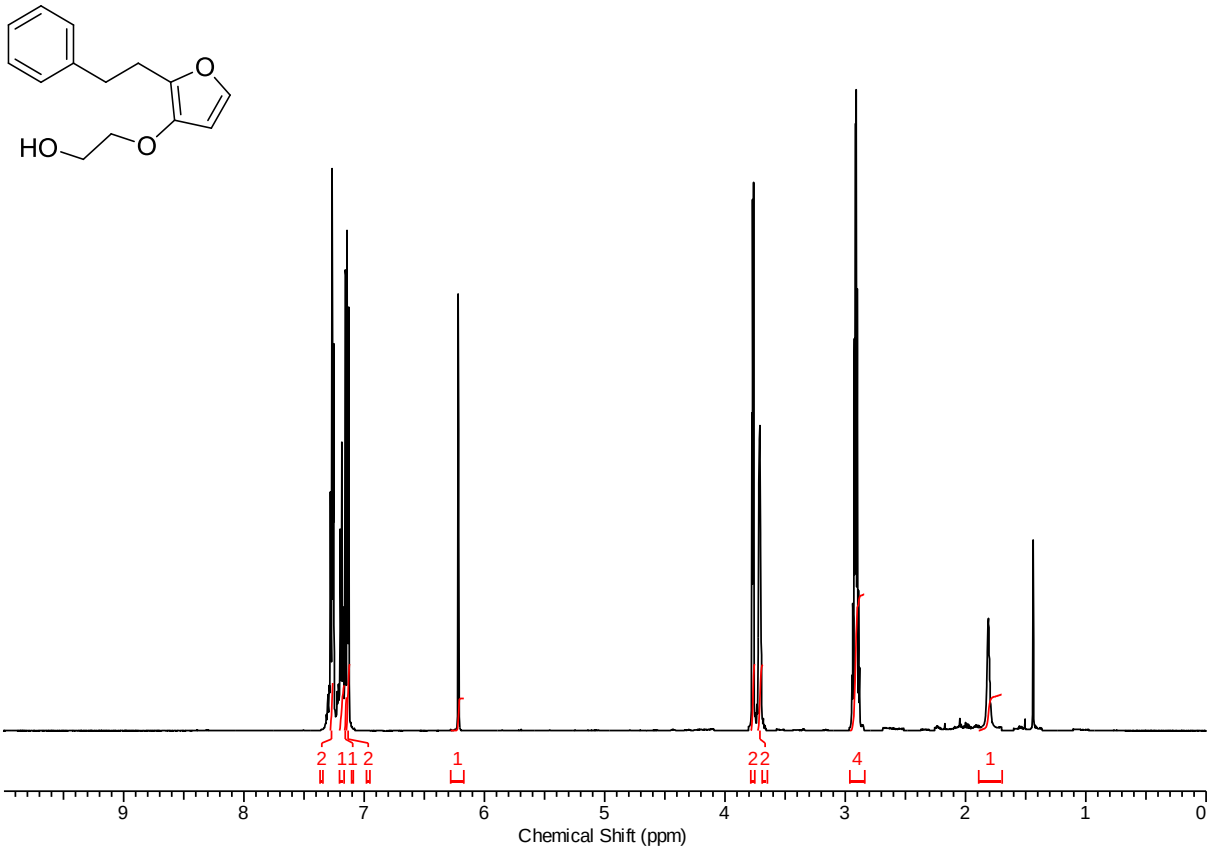


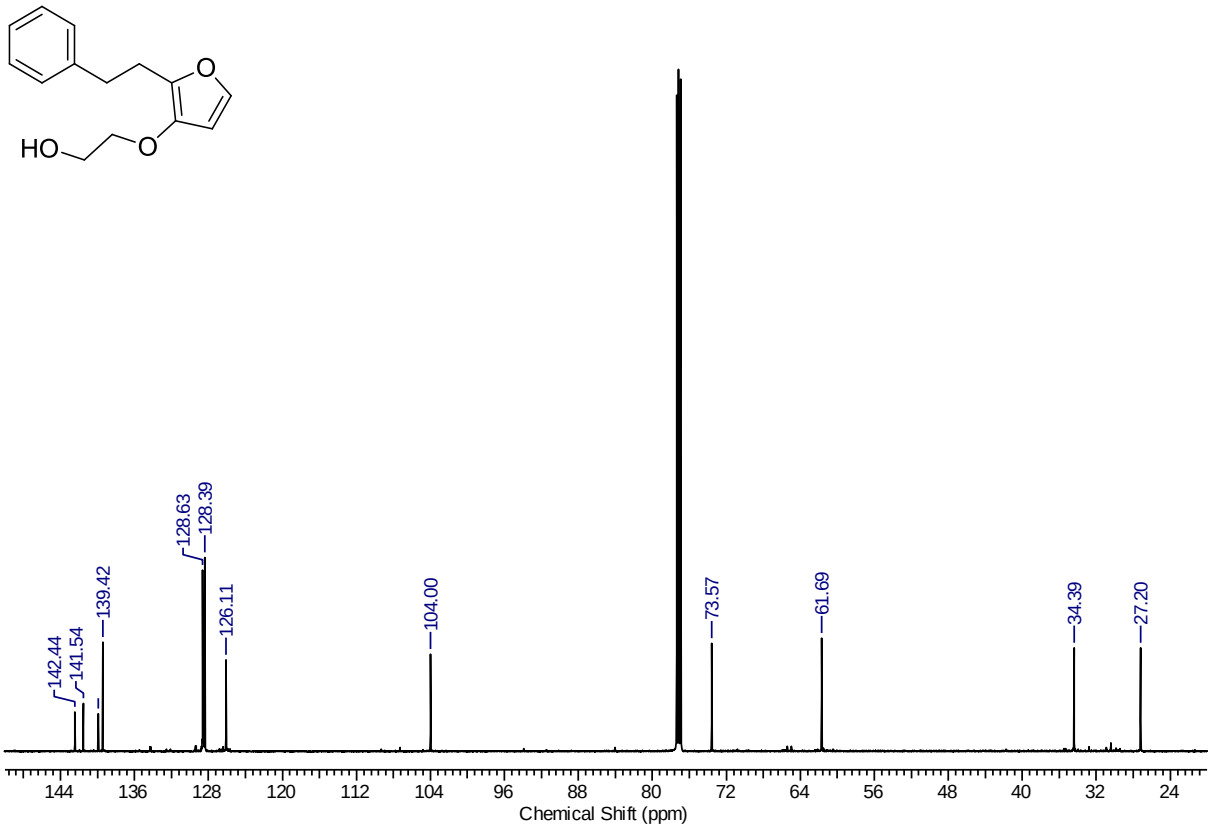
3-(Allyloxy)-2-phenethylfuran 6b



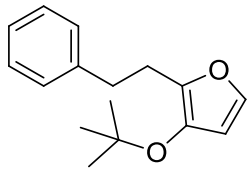


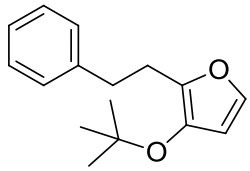
2-((2-Phenethylfuran-3-yl)oxy)ethanol 7b



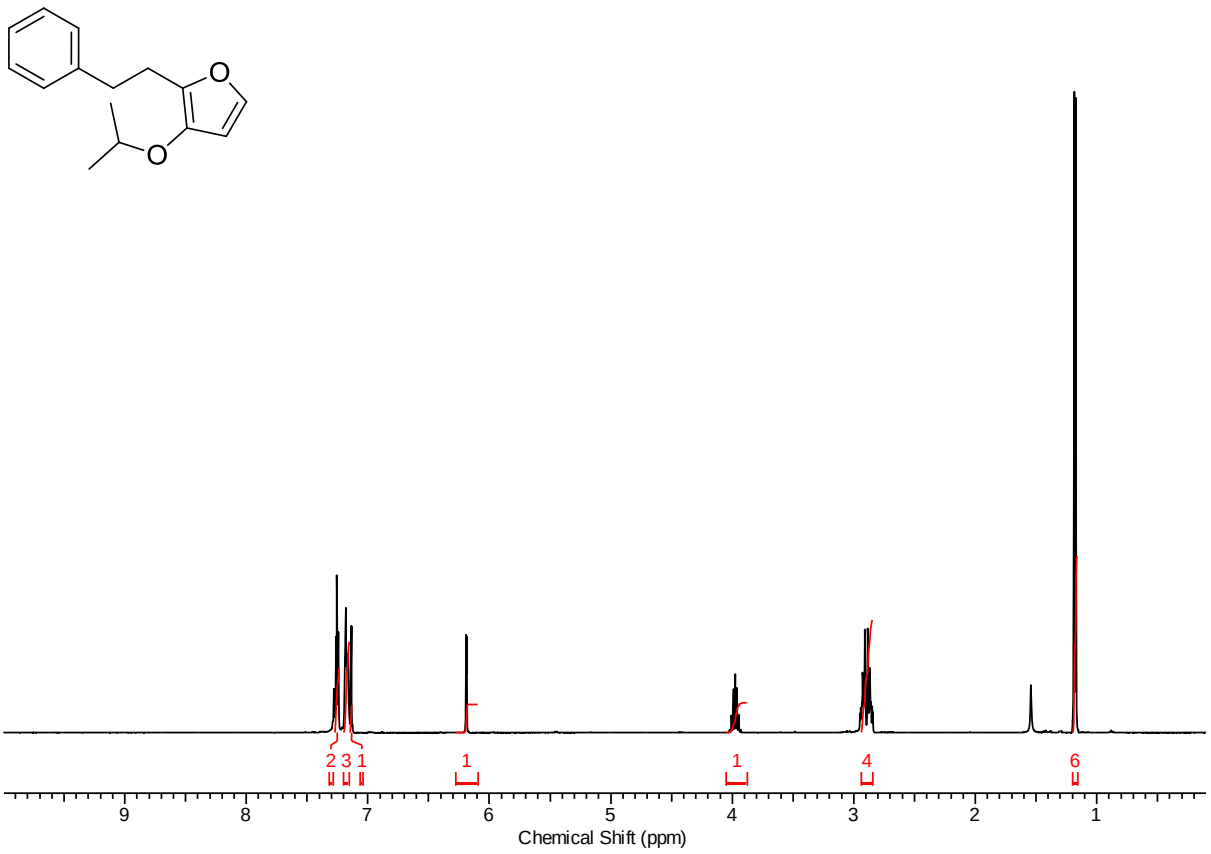


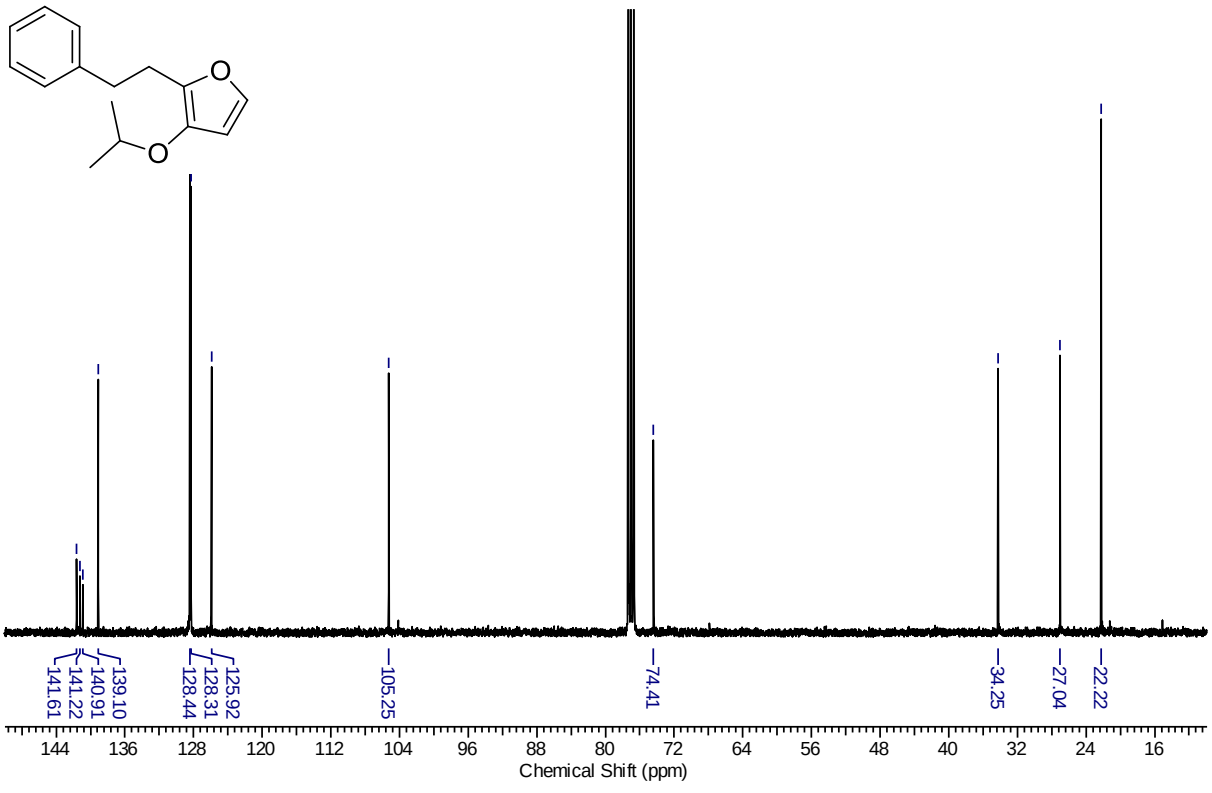
3-(*tert*-Butoxy)-2-phenethylfuran 8b



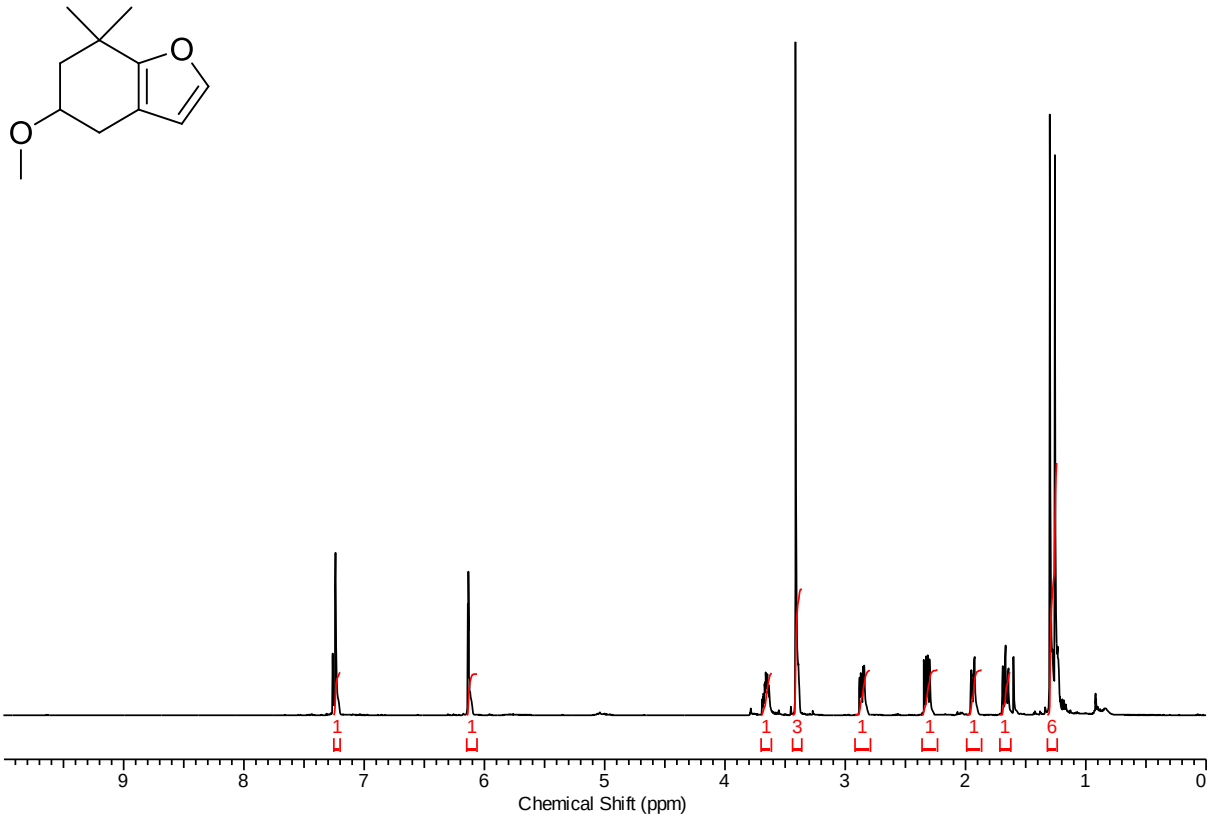


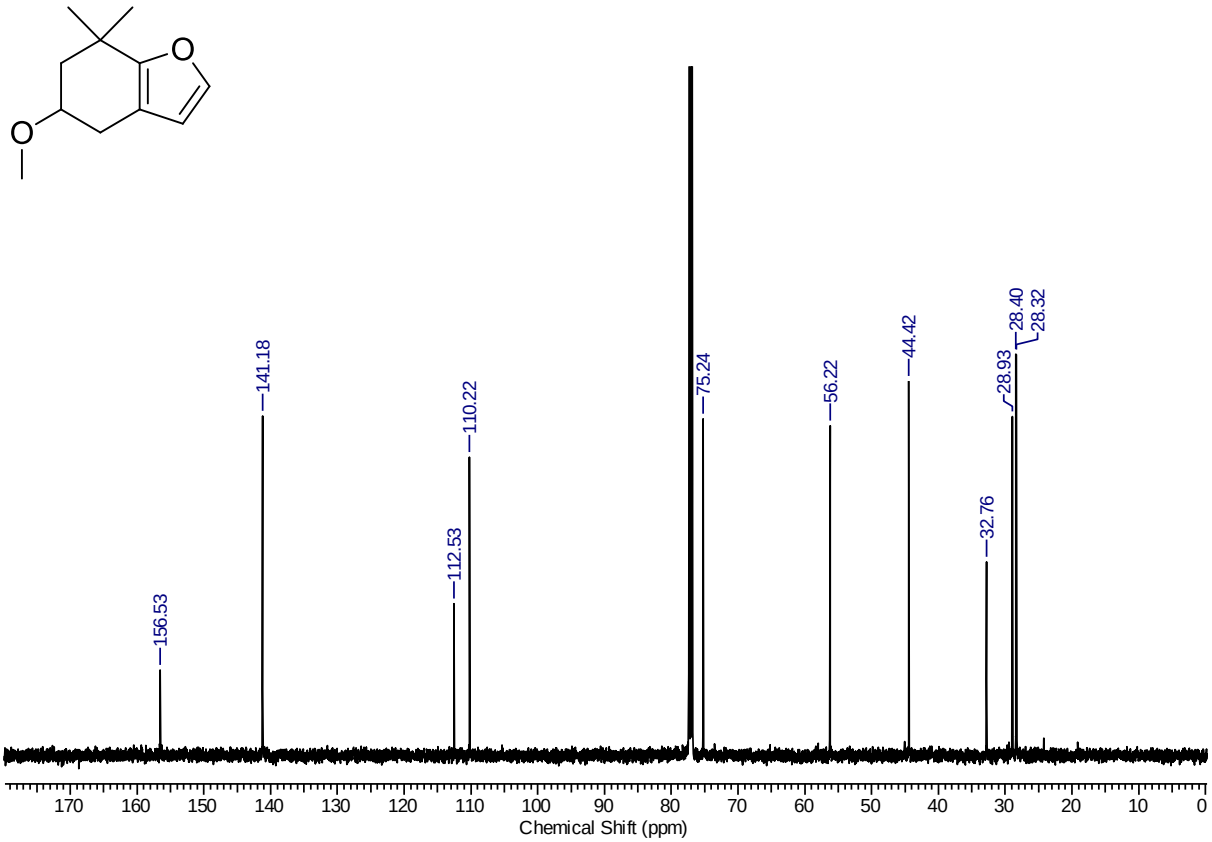
3-Isopropoxy-2-phenethylfuran 9b



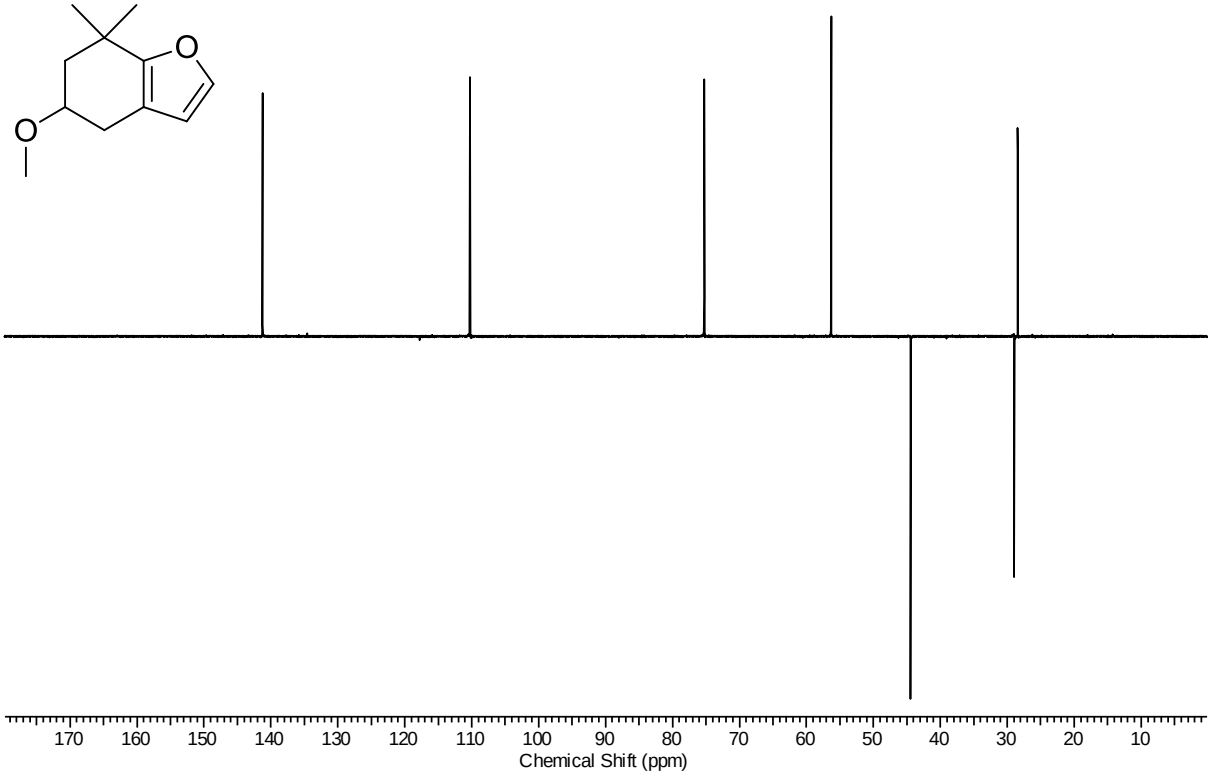


5-Methoxy-7,7-dimethyl-4,5,6,7-tetrahydrobenzofuran 10a

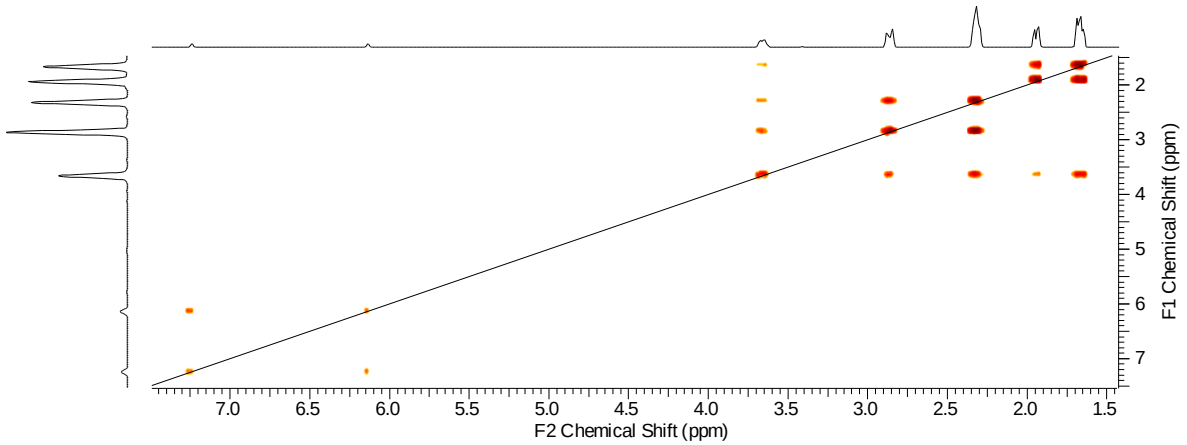




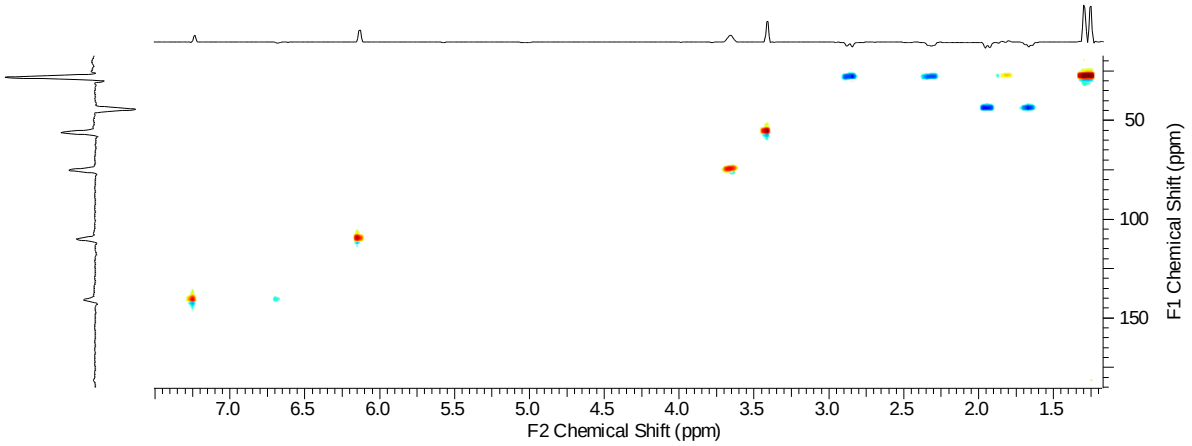
^{13}C DEPT



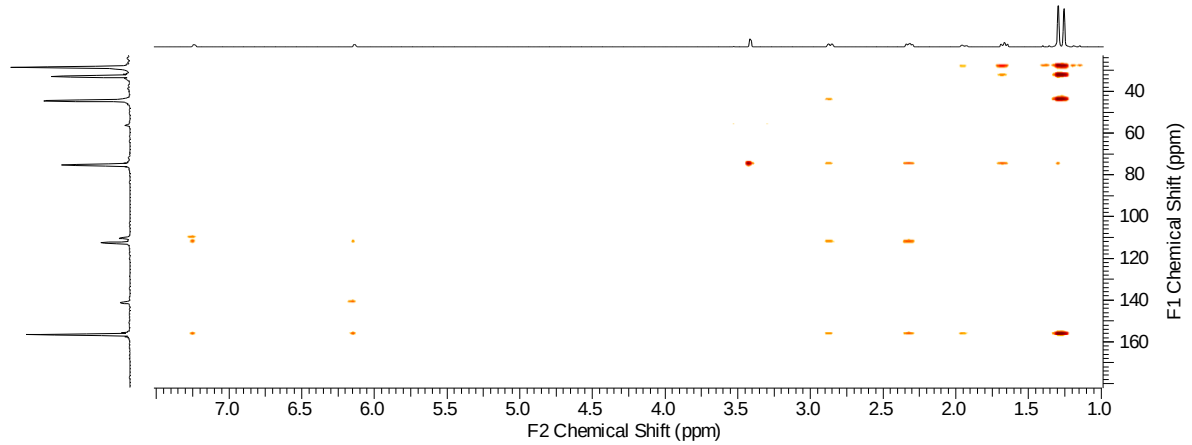
COSY



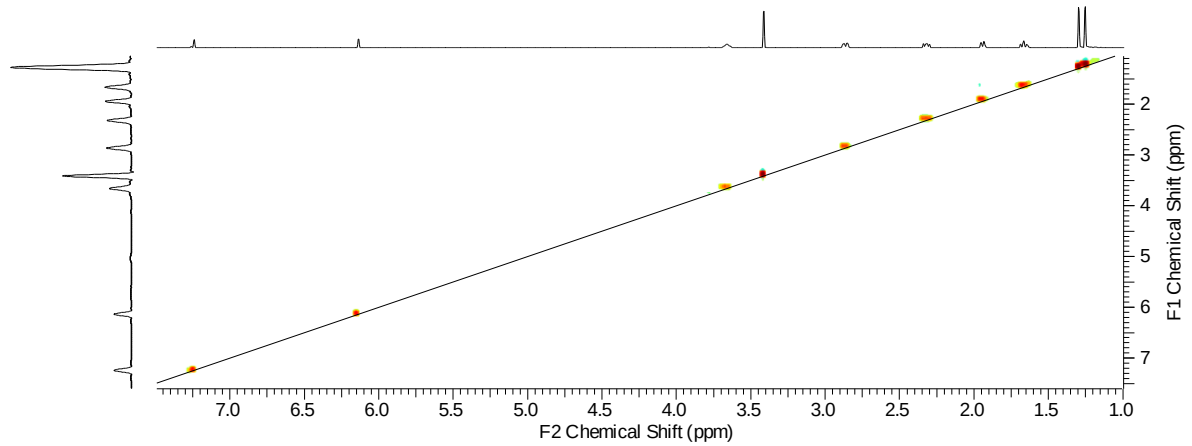
HSQC



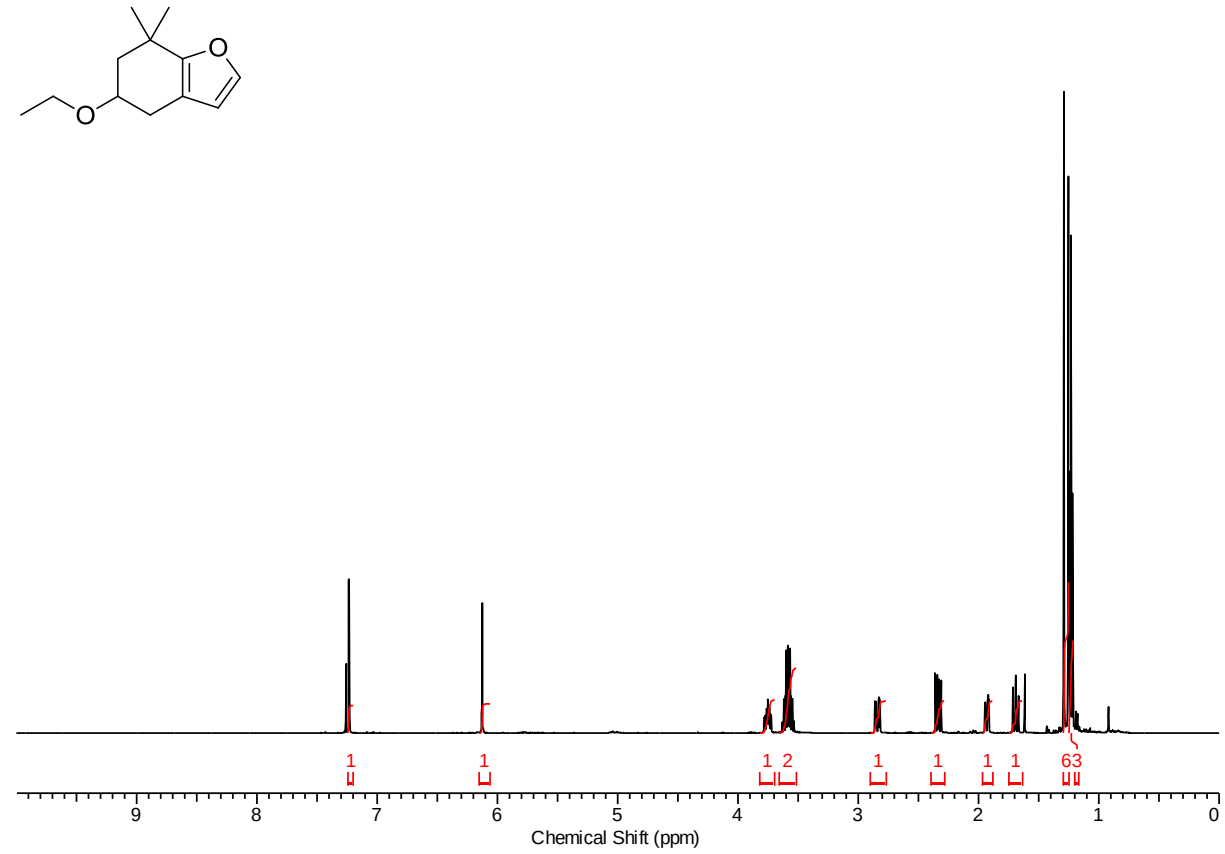
HMBC

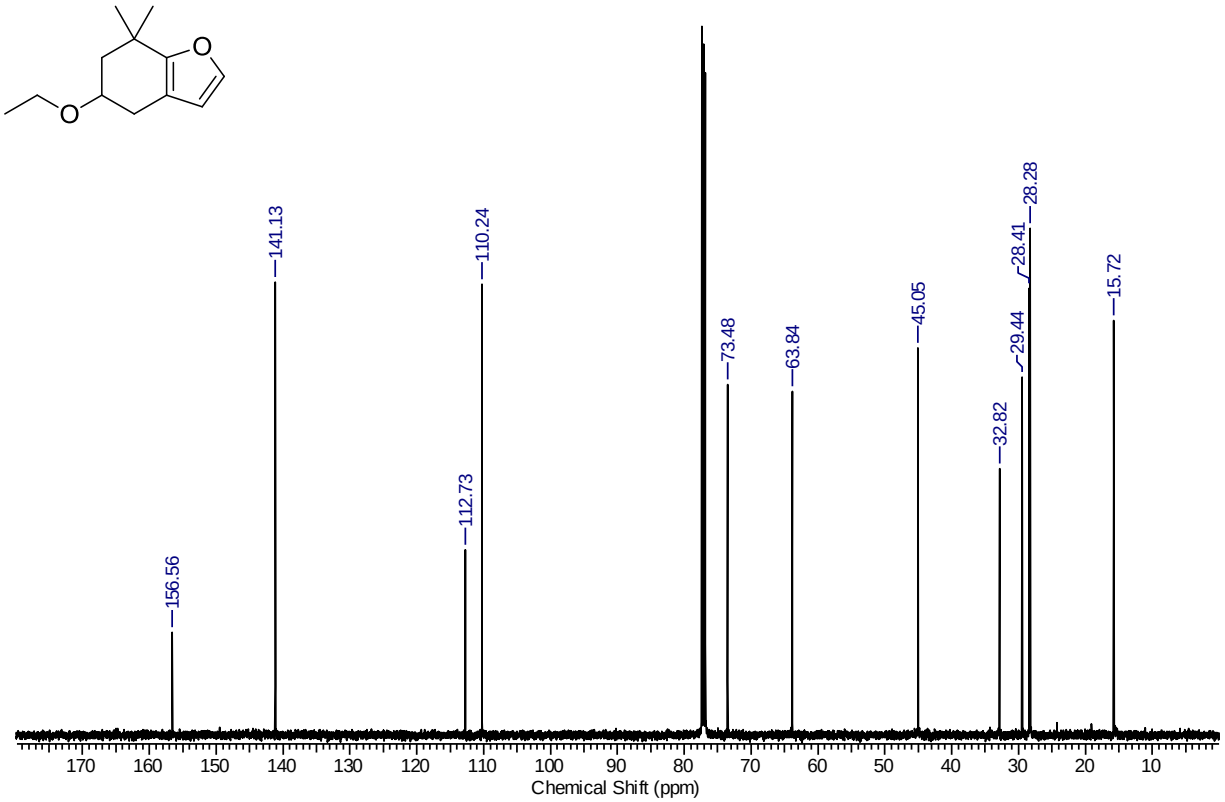


NOESY

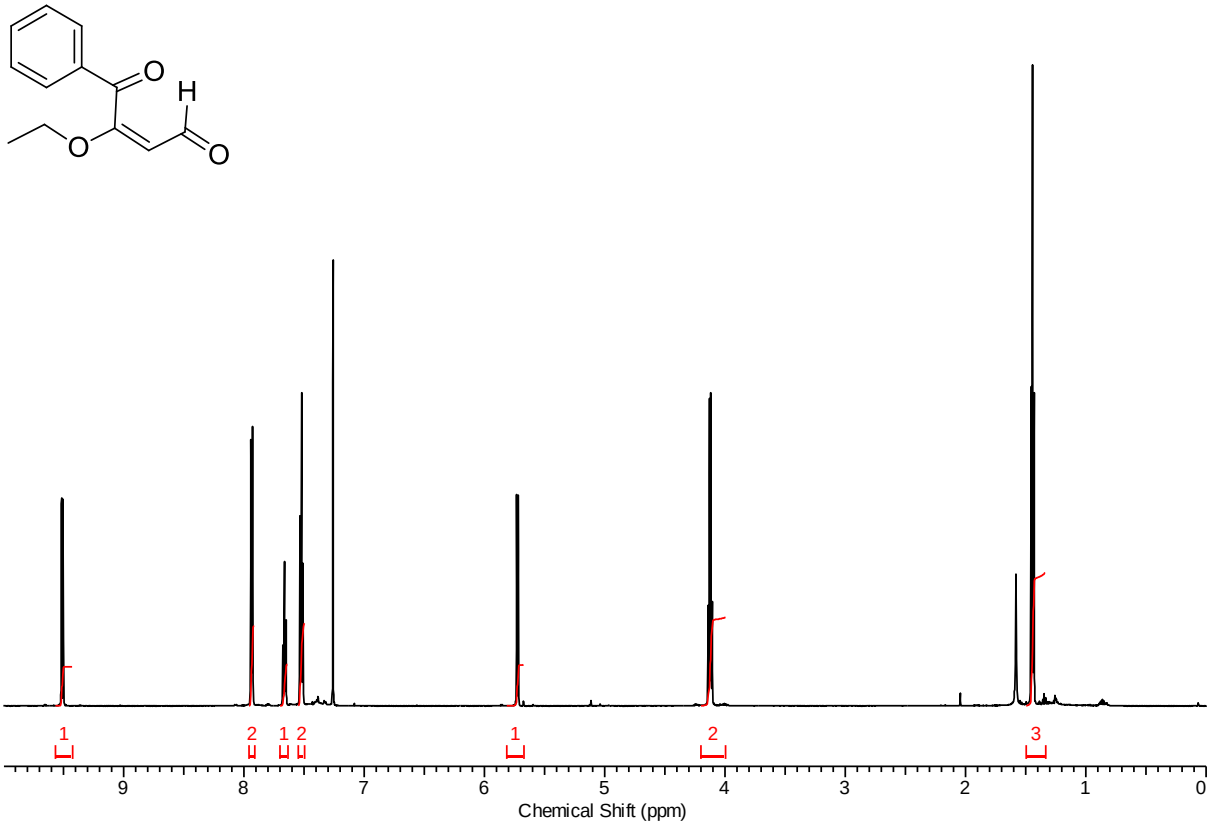


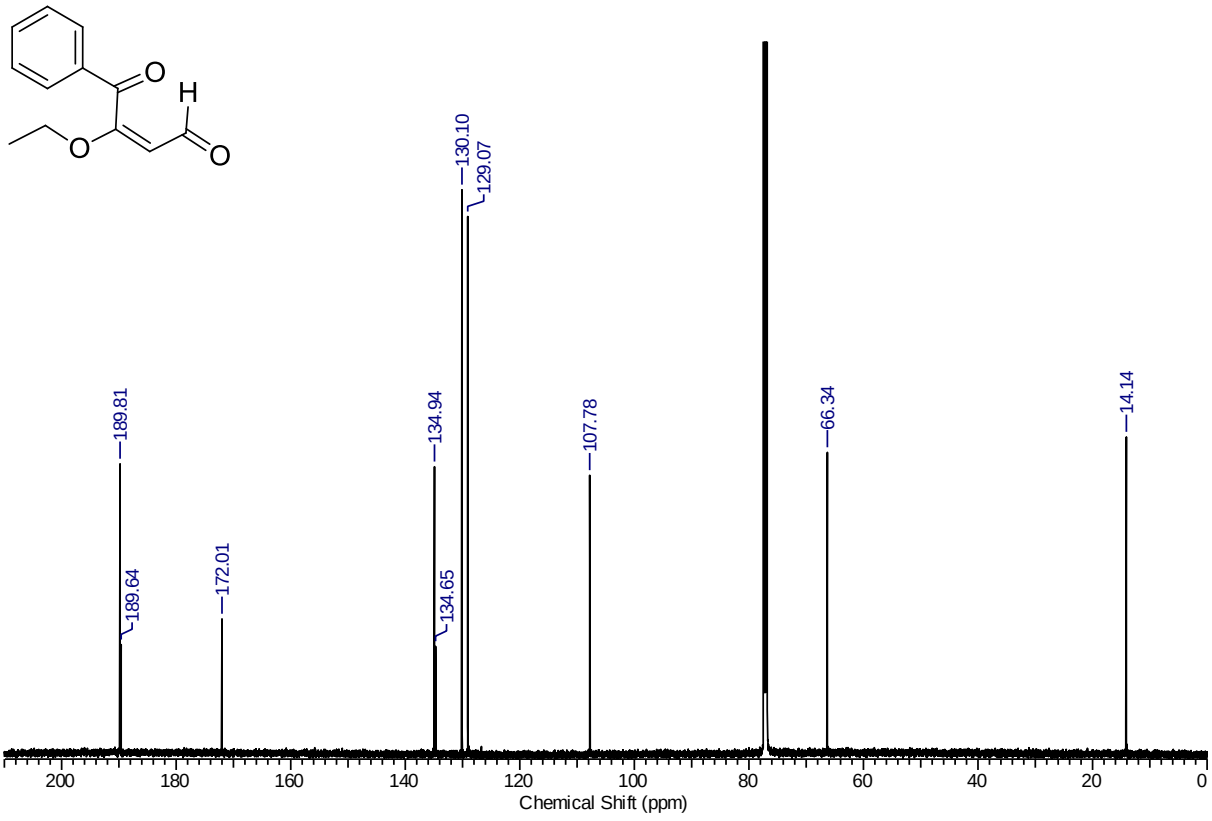
5-Ethoxy-7,7-dimethyl-4,5,6,7-tetrahydrobenzofuran 10b



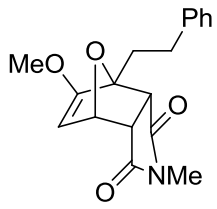


(*E*)-3-Ethoxy-4-oxo-4-phenylbut-2-enal A

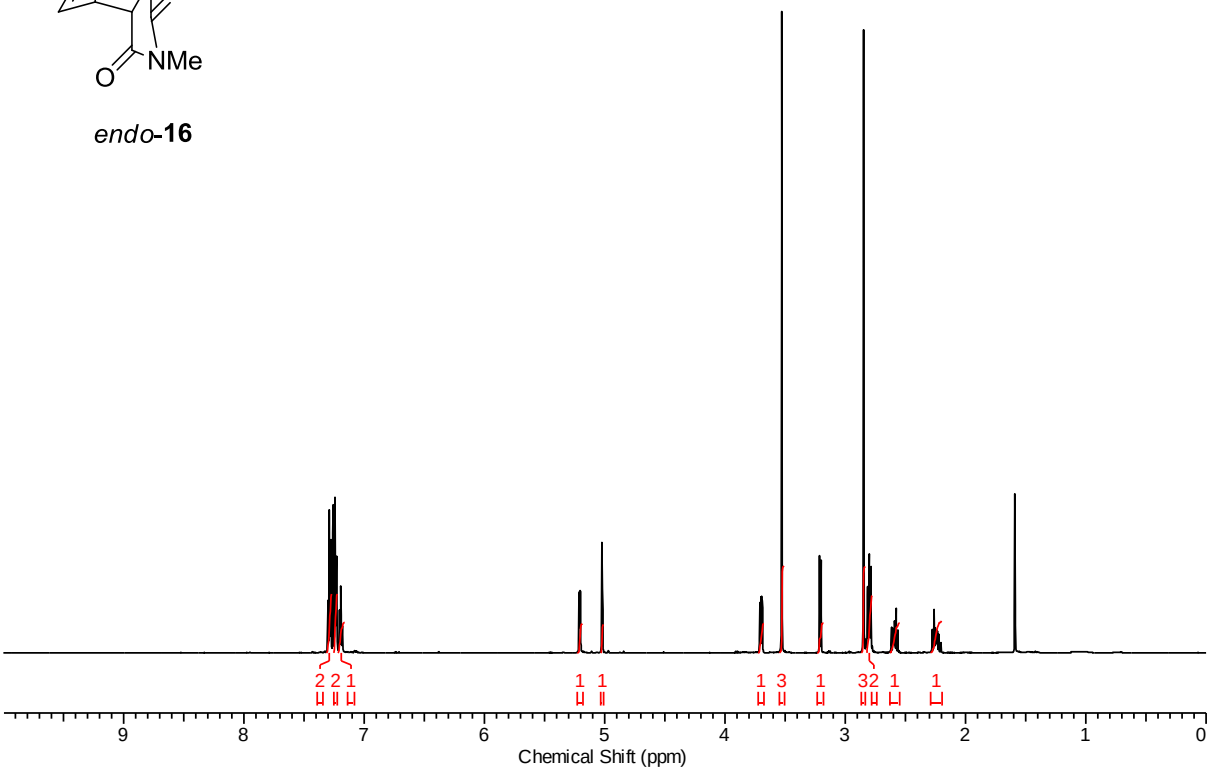


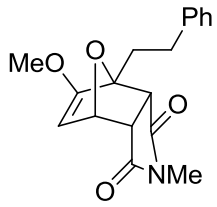


***endo*-16**



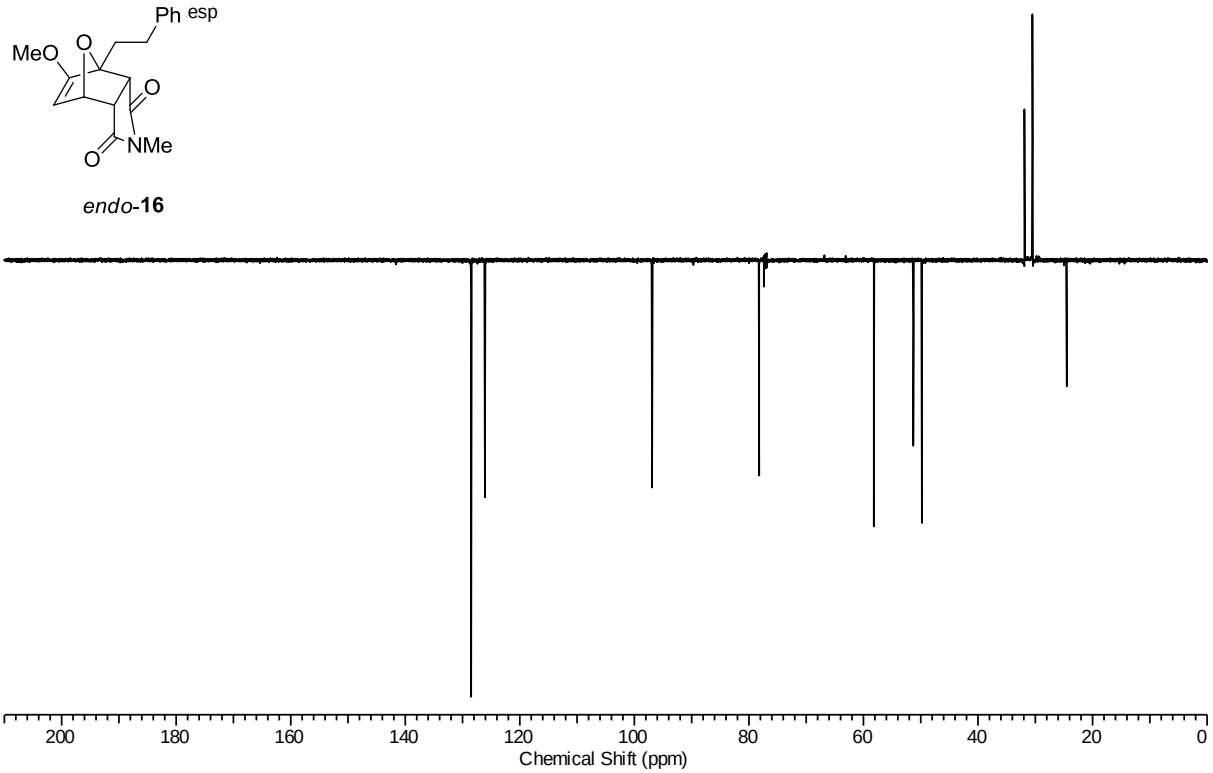
endo-**16**





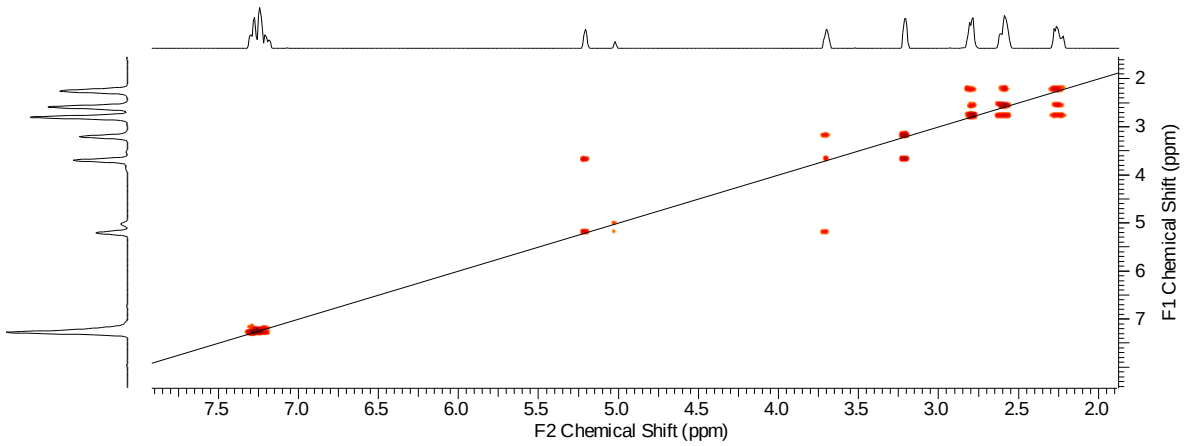
endo-**16**

^{13}C DEPT

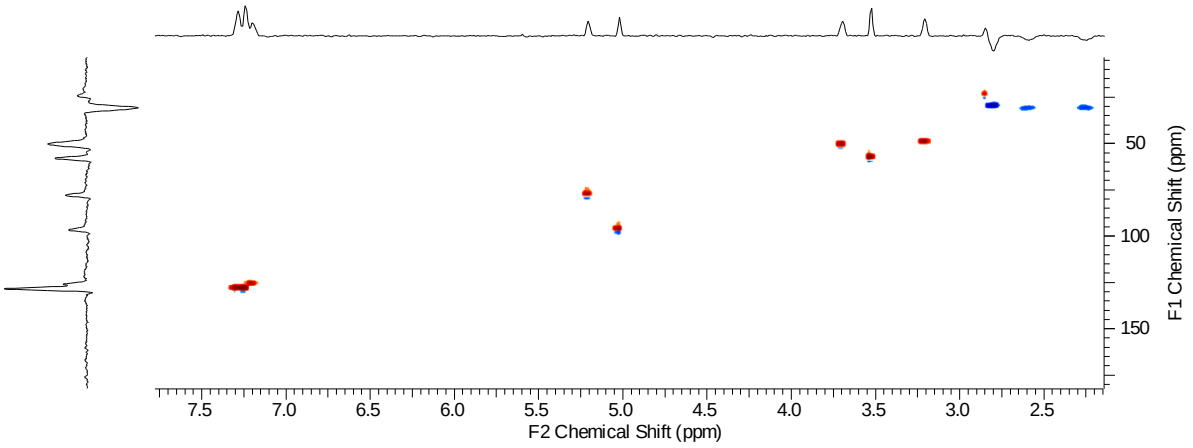


endo-**16**

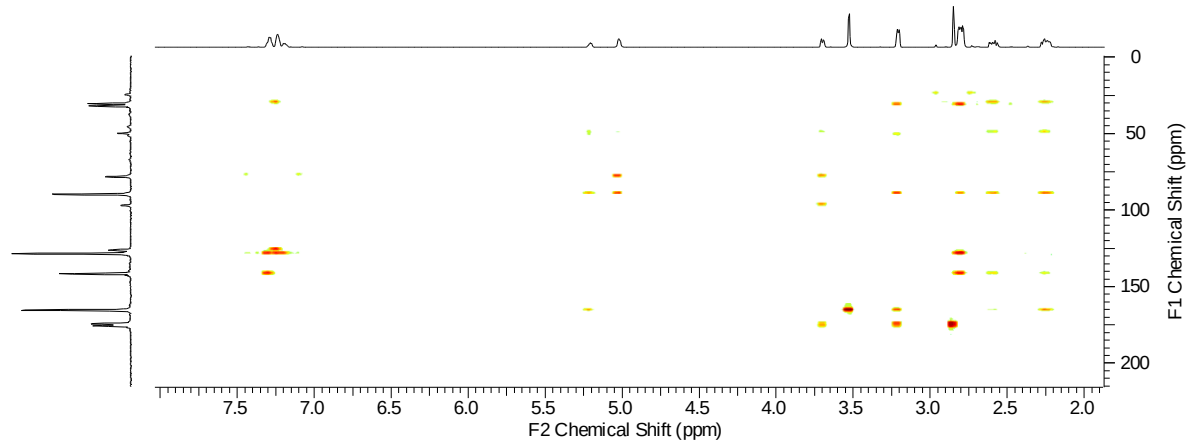
COSY



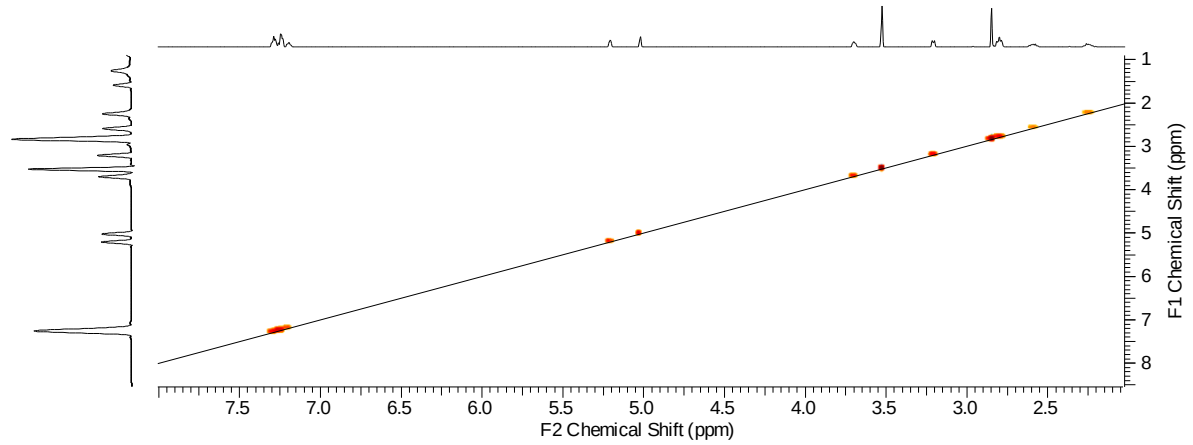
HSQC



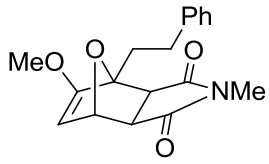
HMBC



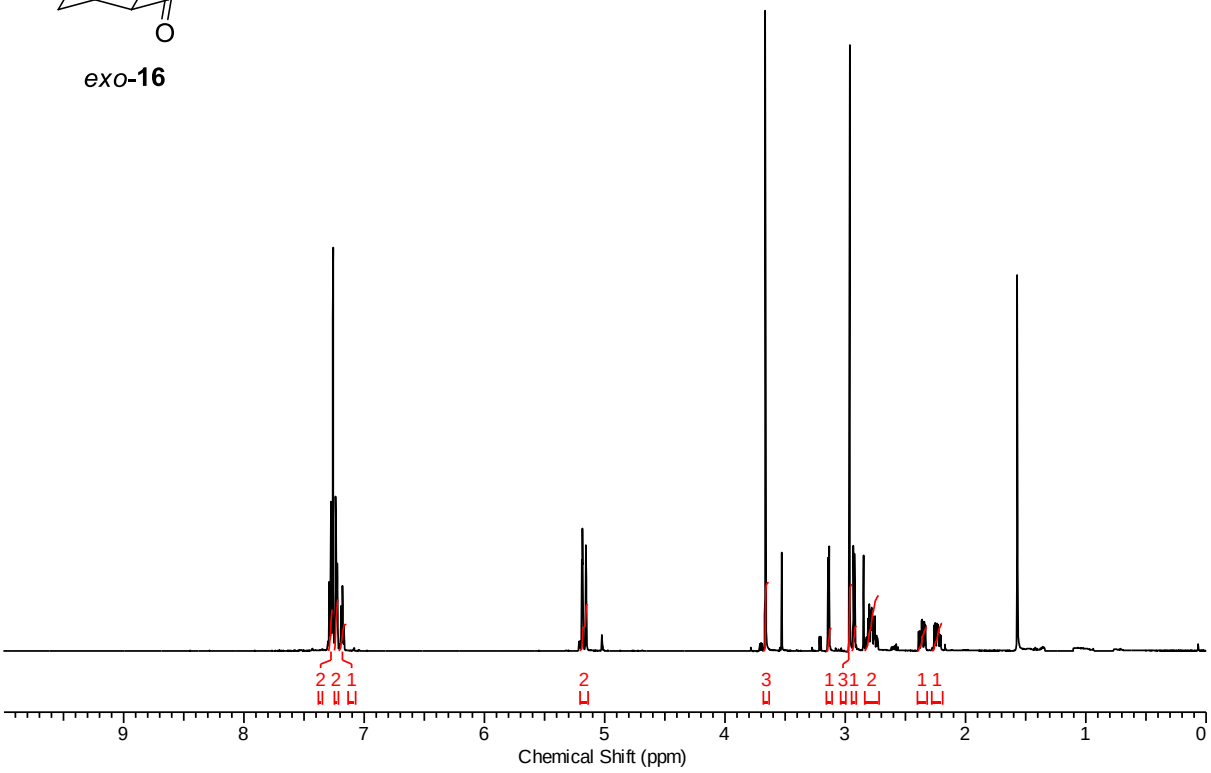
NOESY

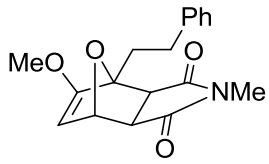


exo-16 (also contains *endo*-16)



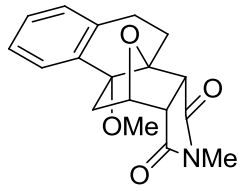
exo-**16**

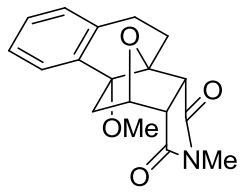




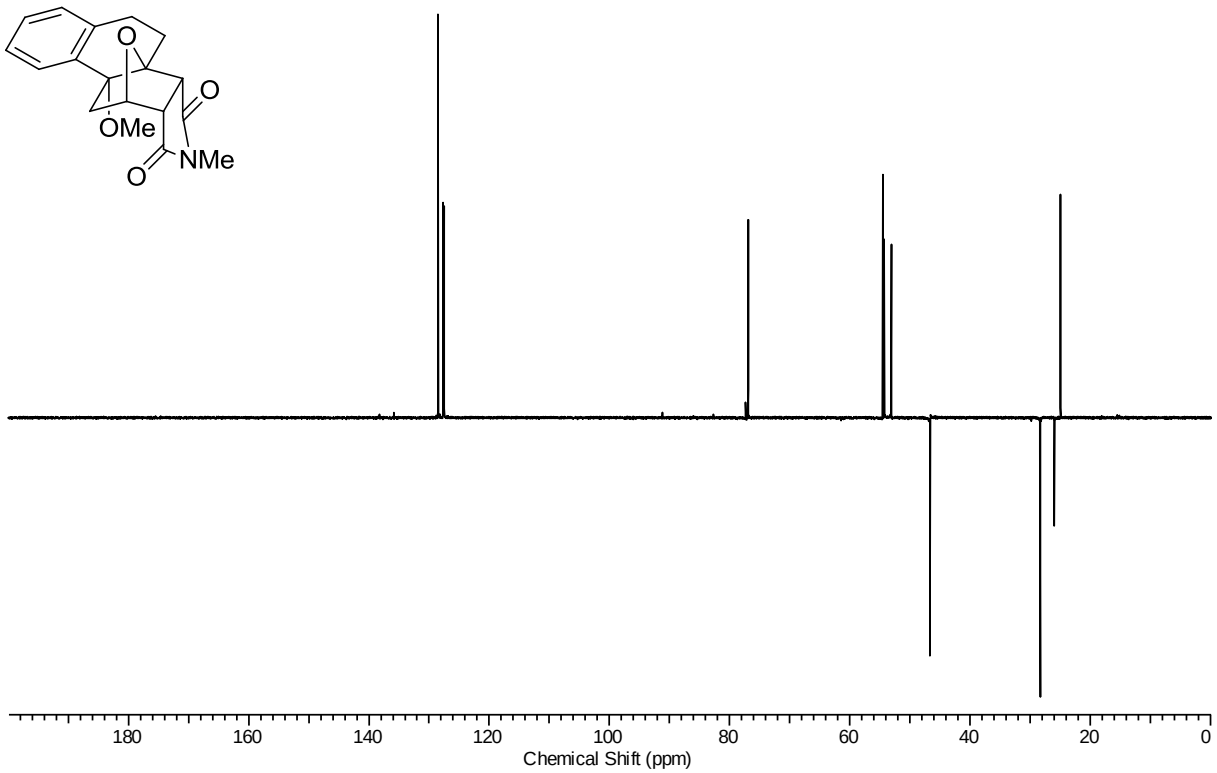
exo-**16**

(3aR,3bS,11S,11aS)-9b-methoxy-2-methyl-4,5,9b,10,11,11a-hexahydro-3b,11-epoxynaphtho[2,1-e]isoindole-1,3(2H,3aH)-dione 17

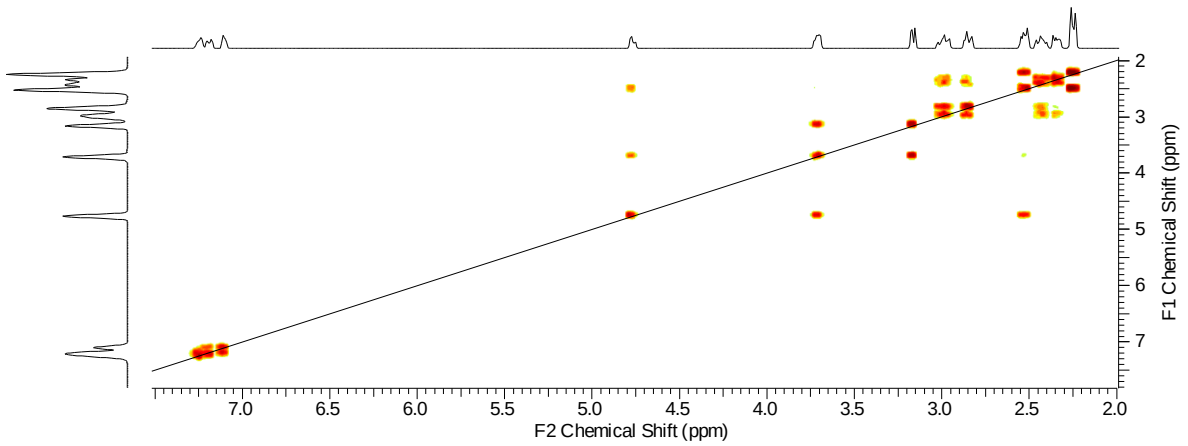




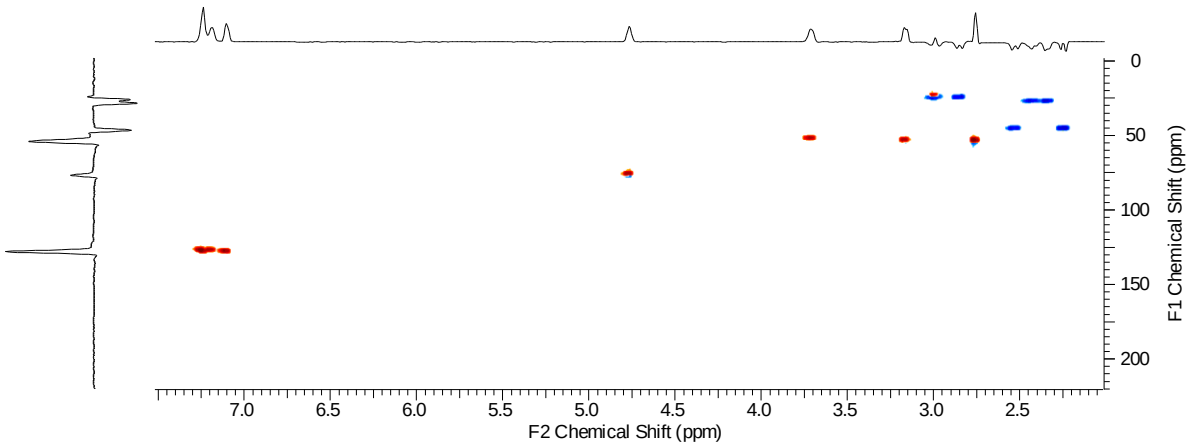
^{13}C DEPT



COSY



HSQC



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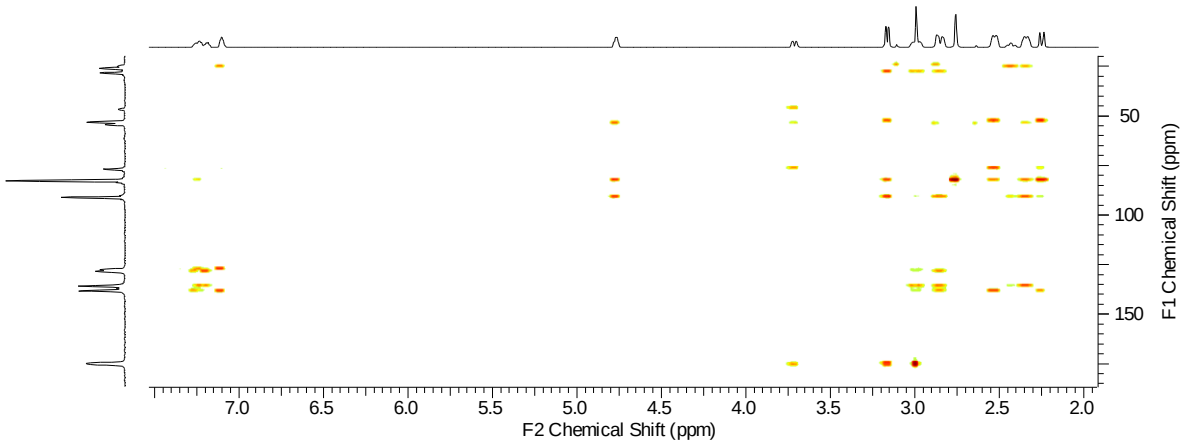

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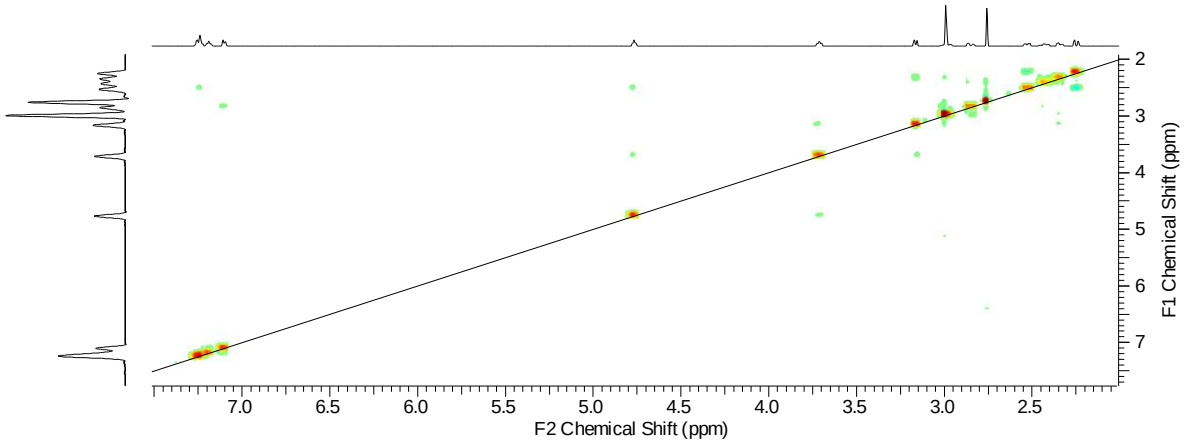
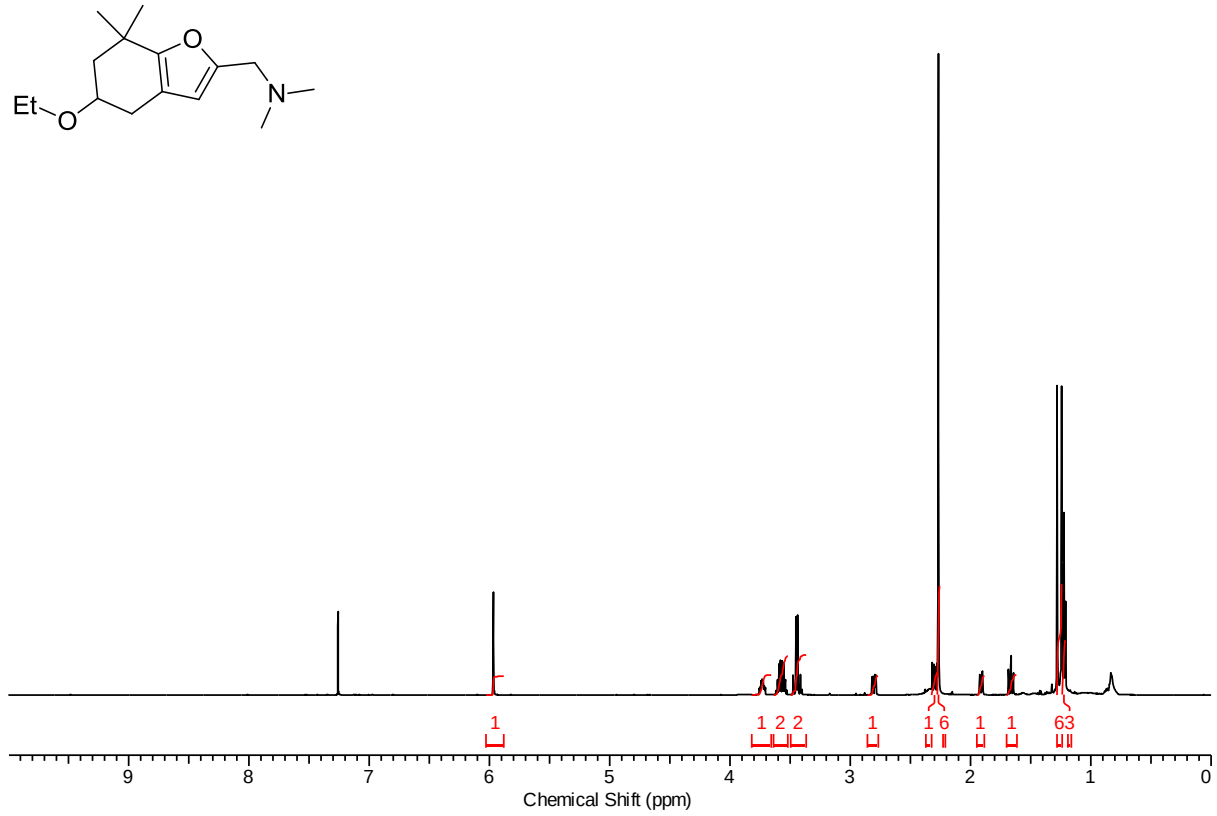
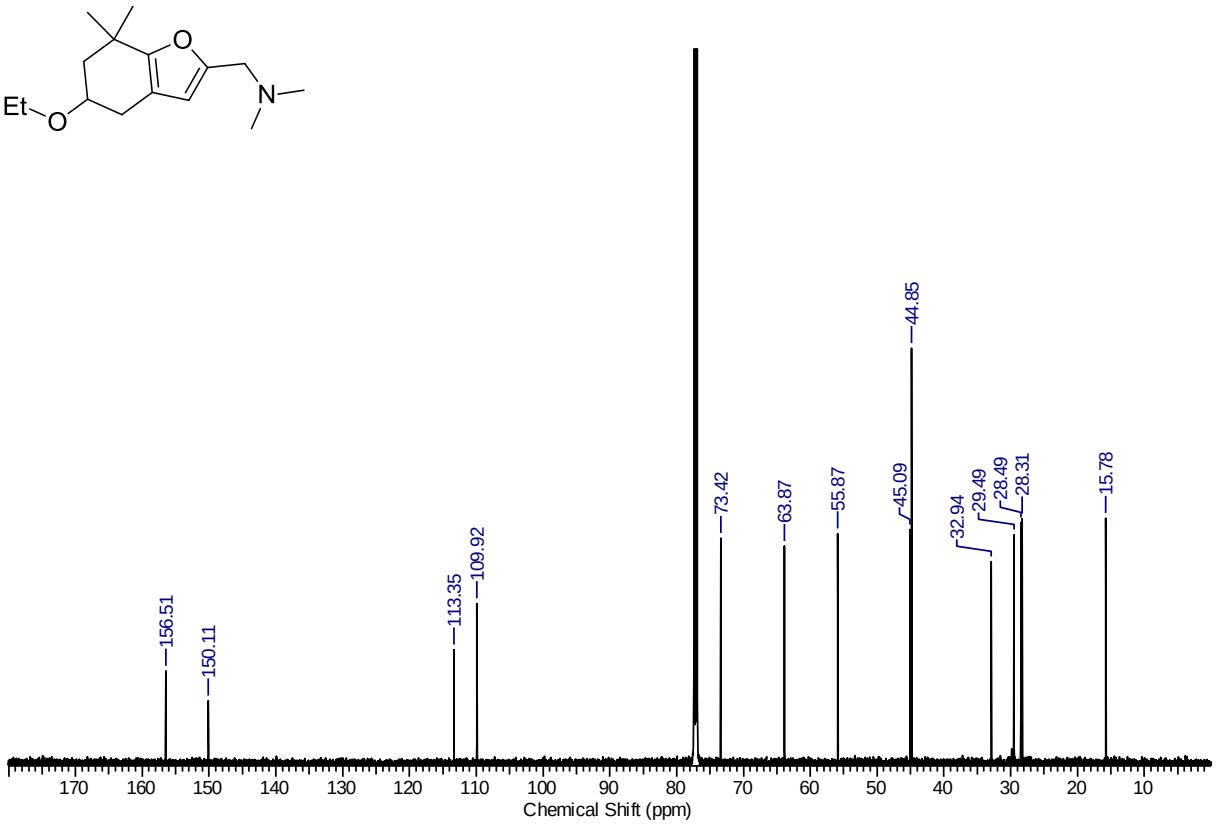
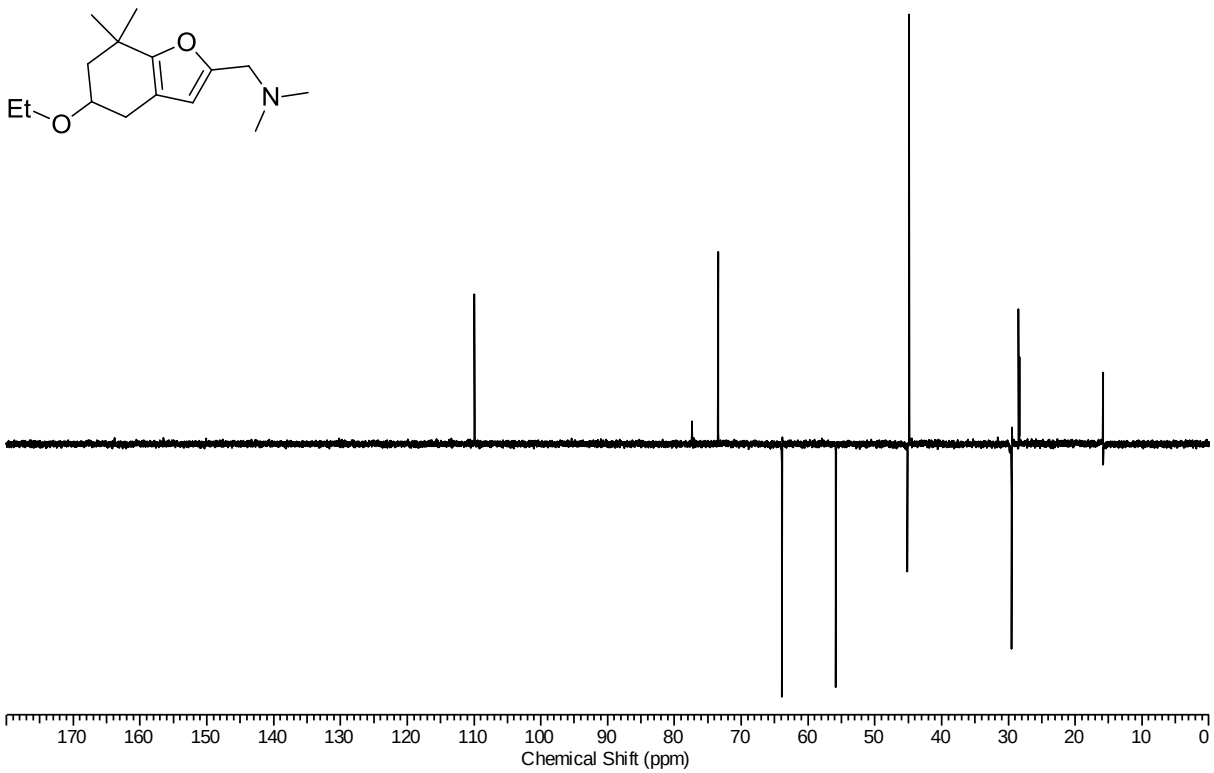


1-(5-Ethoxy-7,7-dimethyl-4,5,6,7-tetrahydrobenzofuran-2-yl)-N,N-dimethylmethanamine 18





^{13}C DEPT



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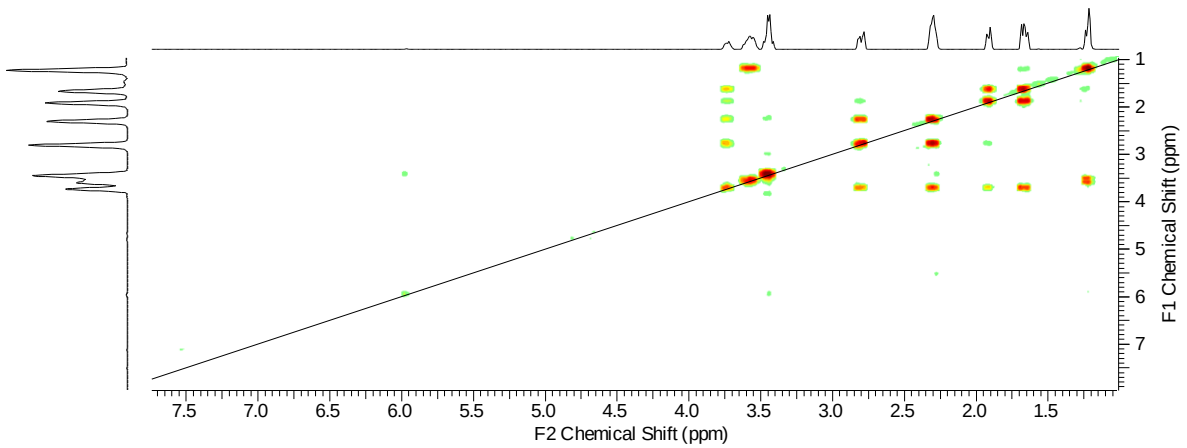

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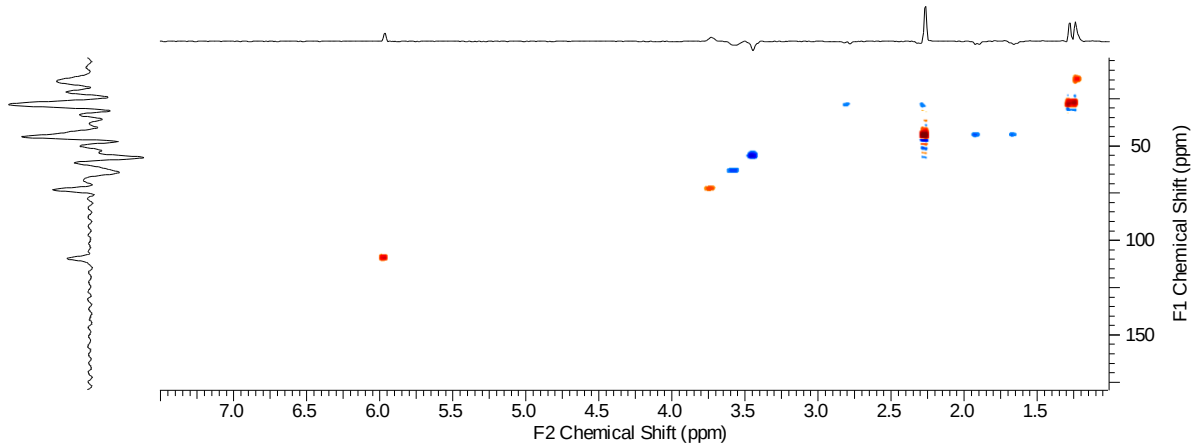

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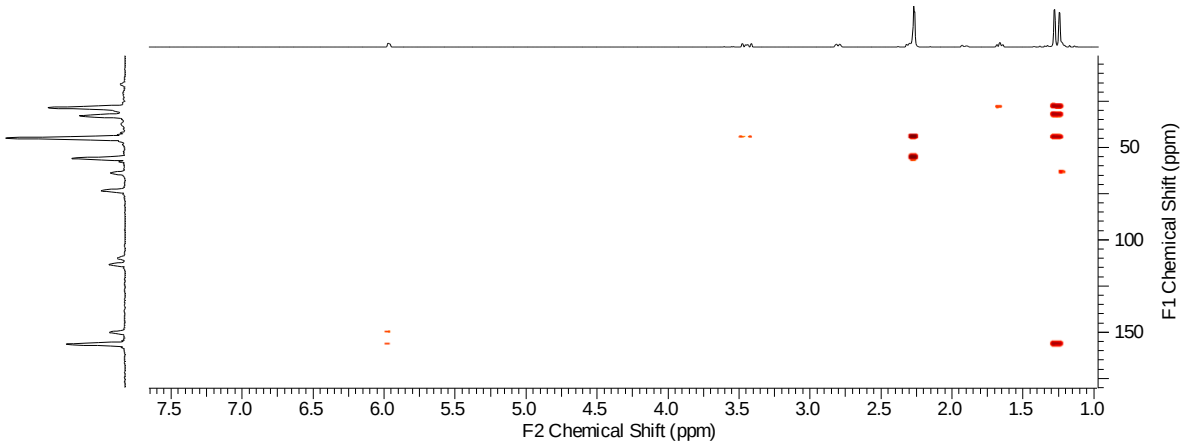

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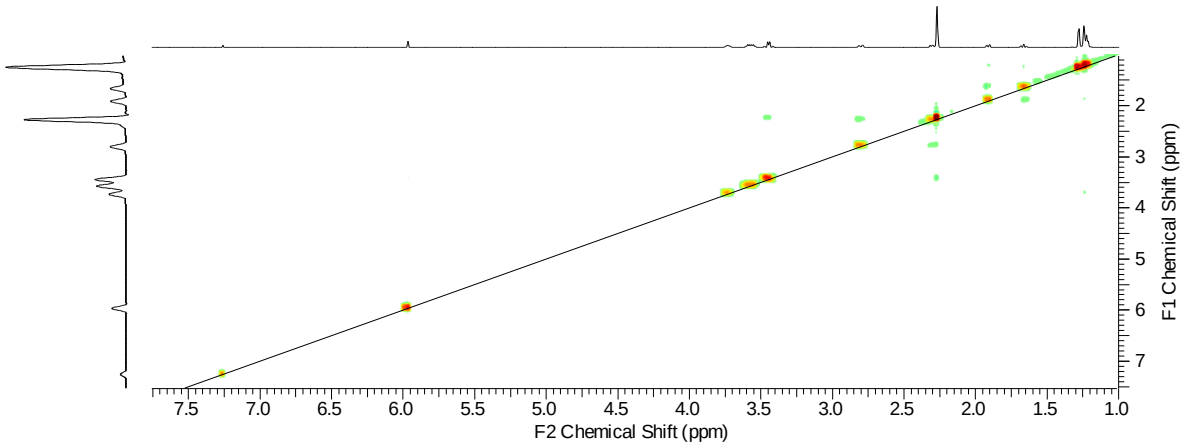
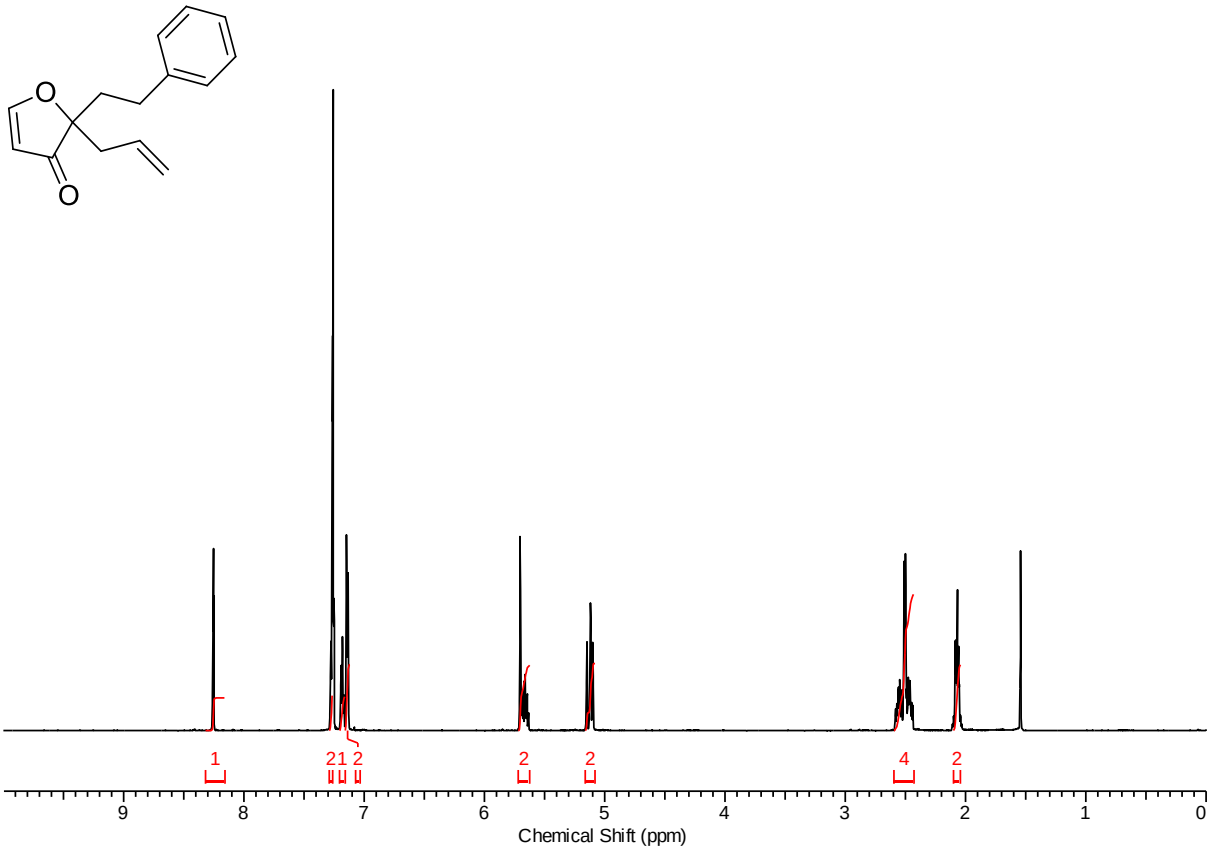
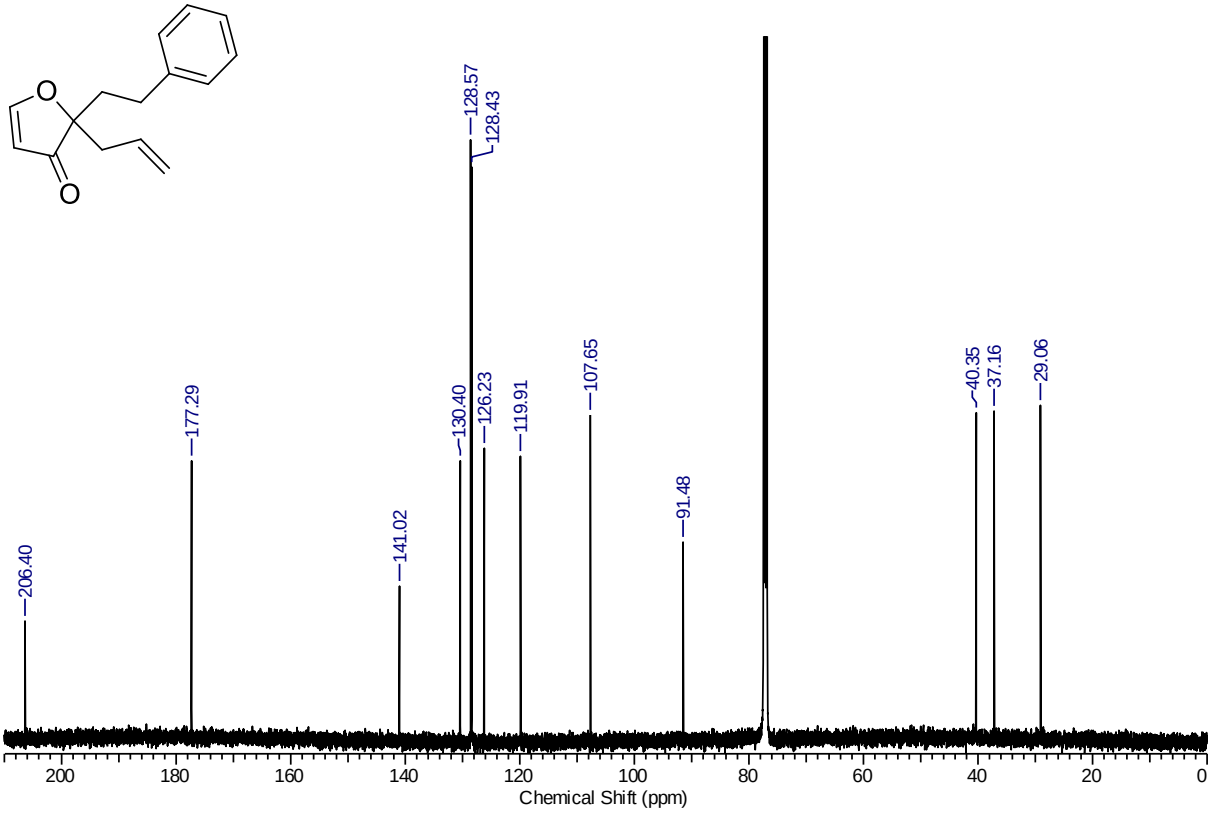


2-Allyl-2-phenethylfuran-3(2H)-one 19





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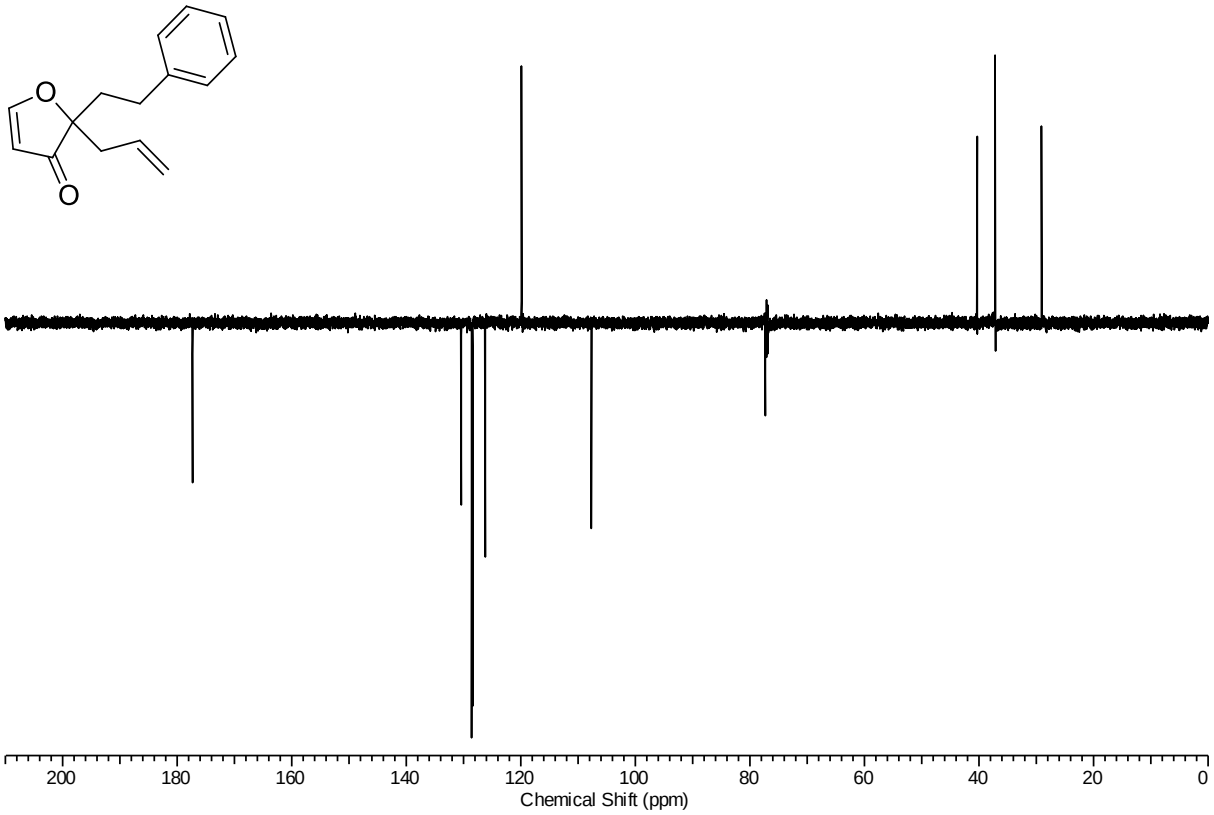

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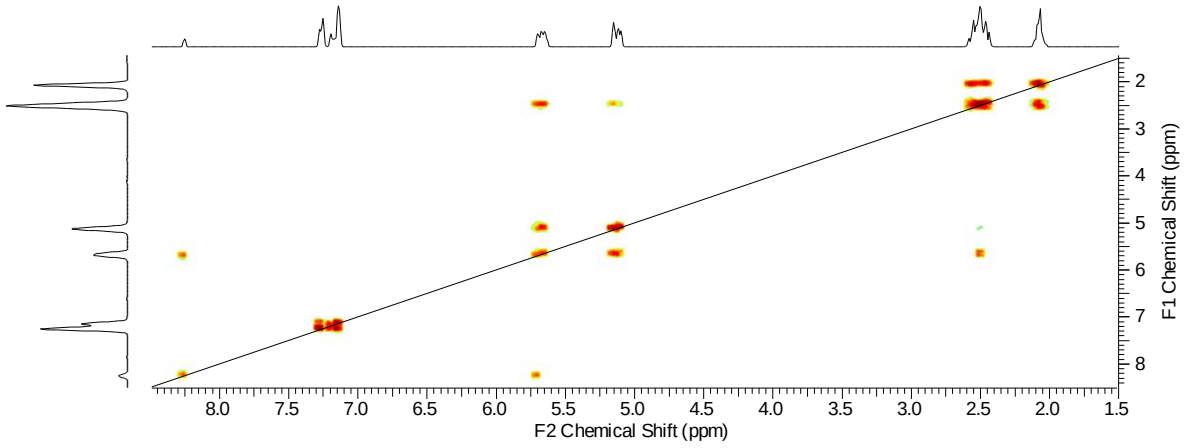

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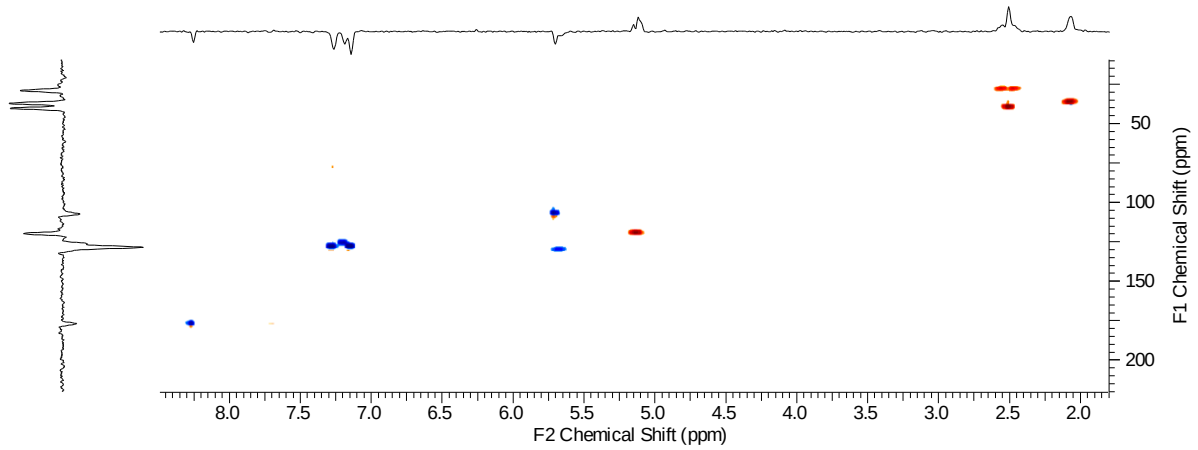

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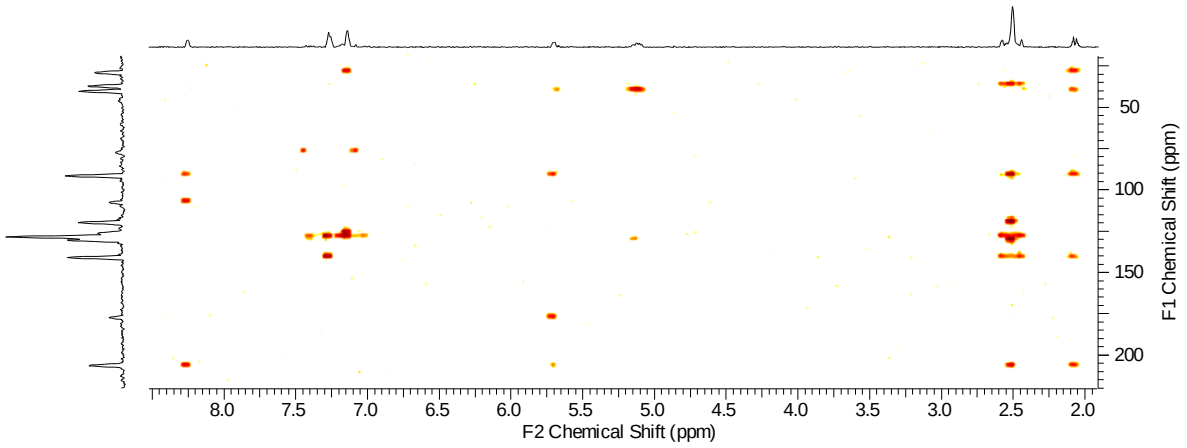

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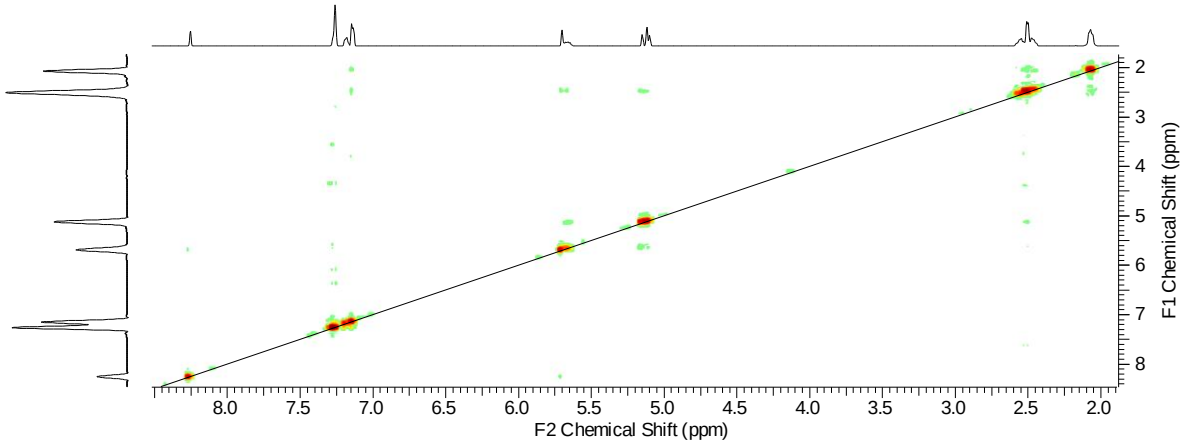
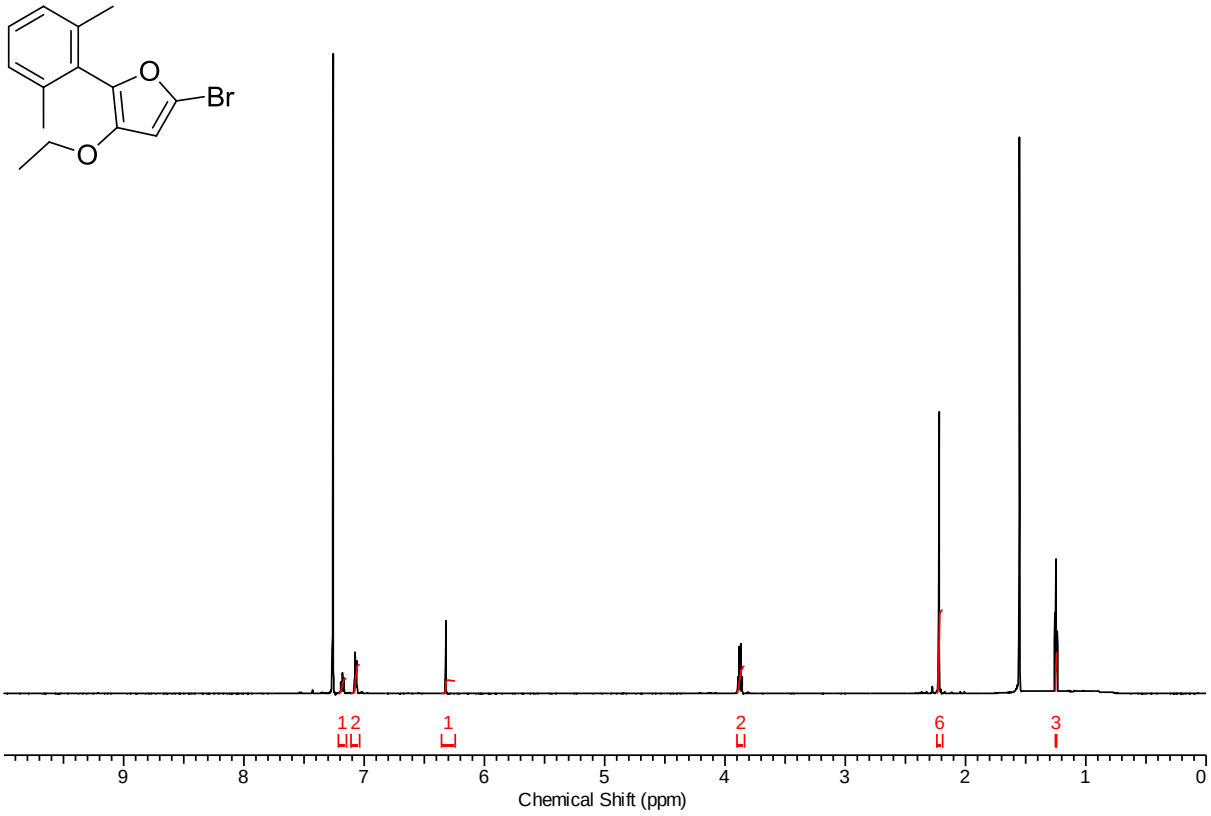
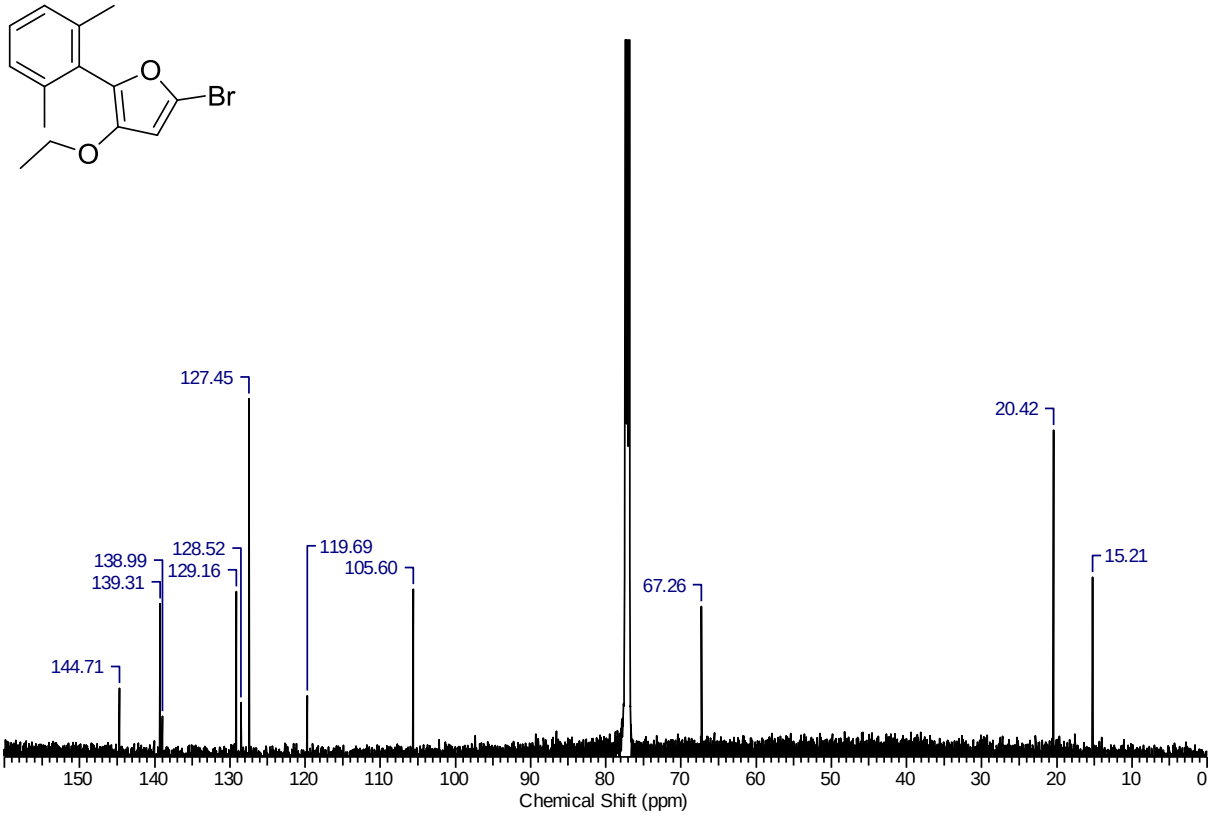


5-Bromo-2-(2,6-dimethylphenyl)-3-ethoxyfuran 20





5. References

1. I. Coric, S. Mueller, B. List, *J. Am. Chem. Soc.* **2010**, *132*, 17370–17373.

2. D. E. Frantz, R. Fässler, E. M. Carreira, *J. Am. Chem. Soc.* **2000**, *122*, 1806-1807.