Supporting Information

Taming Furfuryl Cations to the Synthesis of Privileged Structures and Novel Scaffolds

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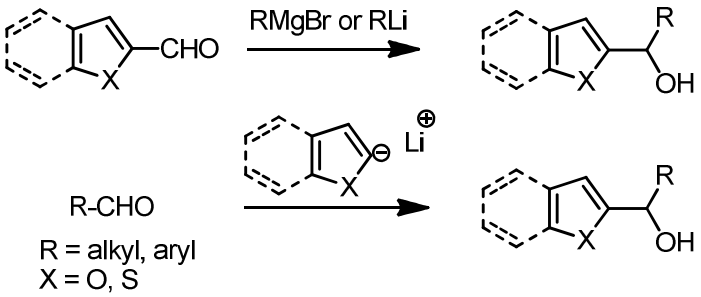
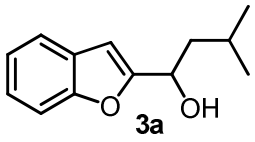
General Methods: Essential starting materials furan, 5-methyl furan, 5-methyl furfural, benzofuran, 3-methyl benzofuran, 5-methyl thiophene, 5-methyl 2-thiophenecarboxaldehyde, nitromethane were purchased from Aldrich and were used without further purification. For thin layer chromatography (TLC), silica aluminum foils with fluorescent indicator 254 nm (from Aldrich) were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), and acetic acid (10 mL) in ethanol (900 mL) followed by heating. Column chromatography was performed using SD Fine silica gel 100-200 mesh (approximately 15–20 g per 1 g of the crude product). Dry THF was obtained by distillation over sodium and stored over sodium wire. Dry methylene chloride was prepared by distilling over calcium hydride. All the commercial reagents were used as such without further purification. IR spectra were recorded on a Perkin – Elmer FT IR spectrometer as thin films or KBr pellet, as indicated, with ν_{max} in inverse centimetres. Melting points were recorded on a digital melting point apparatus Stuart SMP10 and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometer. NMR shifts are reported as delta (δ) units in parts per million (ppm) and coupling constants (*J*) are reported in Hertz (Hz). The following abbreviations are utilized to describe peak patterns when appropriate: br=broad, s=single, d=doublet, t=triplet, q=quartet and m=multiplet. Proton chemical shifts are given in δ relative to tetramethylsilane (δ 0.00 ppm) in $CDCl_3$ or to the residual proton signals of the deuterated solvent in CD_3OD (δ 3.31 ppm). Carbon chemical shifts are internally referenced to the deuterated solvent signals in $CDCl_3$ (δ 77.1 ppm) or CD_3OD (δ 49.00 ppm). High-resolution mass spectra were recorded on Bruker maXis mass spectrometer.

Synthesis of furfuryl and thiophenyl alcohols: Furfuryl and thiophenyl alcohols were prepared based on literature procedures,[1] either by the addition of organolithium reagents or organomagnesium reagents to aldehydes (for example: furfural, 5-methyl furan-2-carboxaldehyde, 5-methyl thiophene-2-carboxaldehyde, benzofuran-3-carboxaldehyde, etc) or by the generation of furyllithium/ thiophenyllithium/ benzofuranyllithium and addition to aldehydes (for example: isovaleraldehyde, 2-methyl pentanal, 2-octynal, benzaldehyde, acetaldehyde, propiophenone, etc) as in the following general scheme.



Some of the furfuryl and thiophenyl alcohols employed in this study are already known in the literature with complete characterization data.[2] Spectroscopic data of the newly synthesized alcohols is presented below. Most of the furfuryl alcohols employed in this study are found to be unstable and decompose upon storage even at 0-5 ^{o}C, they decompose even on silica gel and even in deuterated chloroform. But, benzofuranyl alcohols and thiophenyl alcohols are found to be reasonably stable upon cold storage.



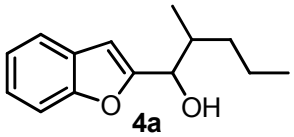
3a

1-(Benzofuran-2-yl)-3-methylbutan-1-ol (3a).

Pale yellow oil. R_f = 0.5 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 3367, 2956, 2871, 1457, 1253, 1172, 807, 745. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46 (d, *J* =7.2 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.20-7.11 (m, 2H), 6.53 (s, 1H), 4.87 (t, *J* = 7.7 Hz, 1H), 1.95 (d, *J*

[1] J. M. Winne, S. Catak, M. Waroquier and V. V. Speybroeck, *Angew. Chem., Int. Ed.,* 2011, **50**, 11990.
[2] For alcohol **1**: M. Kusakabe, Y. Kitano, Y. Kobayashi and F. Sato, *J. Org. Chem.*, 1989, **54**, 2085.
For alcohols **5a** and **28a**: M. I. Toşa, P. V. Podea, C. Paizs and F. D. Irimie, *Tetrahedron: Asymmetry,* 2008, **19**, 2068.
For alcohol **6a:** F. Schevenels and I. E. Marko, *Org. Lett.,* 2012, **14**, 1298.
For alcohol **9a**: M. S. Azevedo, G. B. C. Alves, J. N. Cardoso, R. S. C. Lopes and C. C. Lopes, *Synthesis,* 2004, 1262.
For alcohol **11a**: A. Massa, F. R. Siniscalchi, V. Bugatti, A. Lattanzi and A. Scettri, *Tetrahedron: Asymmetry,* 2002, **13**, 1277.
For alcohol **12a**: Reference-1
For alcohol **17a**: A. R. Kelly, M. H. Kerrigan and P. J. Walsh, *J. Am. Chem. Soc.,* 2008, **130**, 4097.
For alcohol **37**: A. S. K. Hashmi, T. Häffner, W. Yang, S. Pankajakshan, S. Schäfer, L. Schultes, F. Rominger and W. Frey, *Chem. Eur. J.,* 2012, **18**, 10480.

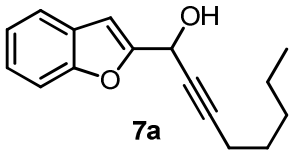
=5.9 Hz, 1H), 1.80-1.68 (m, 3H), 0.90 (d, *J* = 5.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): 159.7, 154.7, 128.1, 124.1, 122.7, 121.0, 111.1, 102.4, 66.0, 44.5, 24.6, 23.0, 22.1. HRMS (ESI): *m/z* calcd for $C_{13}H_{16}O_2Na$ (M+Na): 204.1150. Found: 204.1148.



4a
(2:1)

1-(Benzofuran-2-yl)-2-methylpentan-1-ol (4a, Major).

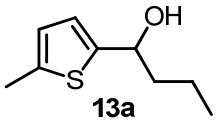
Pale yellow oil. R_f = 0.5 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 3408, 2960, 2872, 14543, 1380, 1253, 1171, 1151, 963, 803, 744. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.0 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.19-7.10 (m, 2H), 6.52 (s, 1H), 4.59 (d, *J* = 5.5 Hz, 1H), 2.08 (br s, 1H), 1.37- 1.05 (m, 5H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.86–0.78 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.2, 154.6, 128.2, 123.9, 122.7, 120.9, 111.2, 103.4, 73.0, 38.3, 35.2, 20.2, 15.5, 11.4. HRMS (ESI): *m/z* calcd for $C_{14}H_{18}O_2Na$ (M+Na): 241.1204. Found: 241.1206.



7a

1-(Benzofuran-2-yl)oct-2-yn-1-ol (7a).

Pale yellow oil. R_f = 0.6 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max} /cm^{-1} 3408, 2934, 2863, 1454, 1173, 1003, 746. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.17 (d, *J* = 8.1 Hz, 1H), 7.25 (d, *J* = 8.1, 1H), 7.27-7.10 (m, 2H), 6.71 (s, 1H), 5.49 (s, 1H), 2.34 (s, 1H), 2.19 (dt, *J* = 7.1 and 2.0 Hz, 2H), 1.51-1.44 (m, 2H), 1.32- 1.21 (m, 4H), 0.81 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.0, 155.2, 127.8, 124.6, 122.9, 121.3, 111.4, 104.0, 87.7, 76.4, 58.8, 31.0, 28.1, 22.2, 18.7, 13.9. HRMS (ESI): *m/z* calcd for $C_{16}H_{18}O_2Na$ (M+Na): 265.1204. Found: 265.1201.

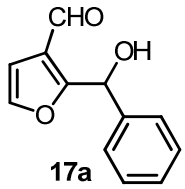


13a

1-(5-Methylthiophen-2-yl)butan-1-ol (13a).

Colorless oil. R_f = 0.6 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 3374, 2958, 2928, 2870, 1455, 1097, 1020, 800. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.73 (d, *J* = 3.3 Hz, 1H), 6.61 (d, *J* = 3.3 Hz, 1H), 4.48 (t, *J* = 6.9 Hz, 1H), 2.48 (s, 3H), 1.90-1.69 (m, 2H), 1.53-1.28 (m, 2H), 0.96 (t, *J* = 6.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): 146.5, 139.0, 124.5, 123.6, 70.1,

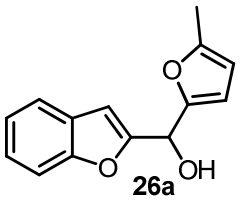
41.1, 19.2, 15.4, 13.8. HRMS (ESI): *m/z* calcd for $C_9H_{14}OSNa$ (M+Na): 193.0663. Found: 193.0662.



17a

2-(Hydroxy(phenyl)methyl)furan-3-carbaldehyde (17a).

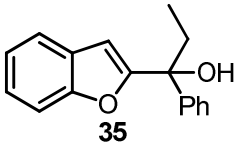
Pale yellow oil. R_f = 0.6 (hexane/EtOAc = 3/2). IR (thin film, neat): ν_{max}/cm^{-1} 3323, 2972, 2927, 2874, 1680, 1579, 1457, 1359, 1254, 1027, 755. **^{1}H NMR** (400 MHz, $CDCl_3$): 9.87 (s, 1H), 7.30-7.20 (m, 6H), 6.67 (s, 1H), 5.97 (s, 1H), 4.51 (br s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 187.3, 163.4, 141.6, 140.7, 129.5 (2CH), 128.4 (2CH), 125.7, 122.8, 108.6, 67.5. HRMS (ESI): *m/z* calcd for $C_{12}H_{10}O_3Na$ (M+Na): 225.0528. Found: 225.0528.



26a

Benzofuran-2-yl(5-methylfuran-2-yl)methanol (26a).

Pale yellow oil. R_f = 0.6 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 3390, 1614, 1557, 1451, 1220, 1020, 779, 674. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.2 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.20-7.12 (s, 2H), 7.14 (s, 1H), 6.17 (s, 1H), 5.88 (s, 1H), 5.87 (s, 1H), 2.53 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): 156.6, 154.9, 152.8, 150.8, 128.0, 124.4, 122.9, 111.2, 111.4, 109.2, 106.4, 104.1, 64.6, 13.6. HRMS (ESI): *m/z* calcd for $C_{14}H_{12}O_2Na$ (M+Na): 251.0684. Found: 251.0682.

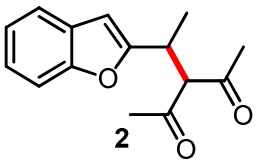


35

2-(Benzofuran-2-yl)-1-phenylpropan-2-ol (35).

Light yellow oil. R_f = 0.6 (hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max} /cm^{-1} 3154, 2936, 2974, 1452, 1354, 1252, 1170, 975, 750. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57-7.13 (m, 9H), 6.63 (s, 1H), 2.64 (s, 1H), 2.38 (q, *J* = 7.3 Hz, 1H), 2.23 (q, *J* = 7.3 Hz, 1H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.3, 154.8, 143.7, 128.2 (2C), 127.6, 127.4, 126.0 (2C), 124.2, 123.0, 121.1, 111.4, 103.2, 76.2, 29.8, 8.0. HRMS (ESI): *m/z* calcd for $C_{17}H_{16}O_2Na$ (M+Na): 275.1048. Found: 275.1048.

General procedure for catalyst screening (Table 1). To a solution of furfuryl alcohol **1** (0.1 mmol, 1 equiv) in anhydrous dichloromethane (1 mL) were added acetylacetone (0.11 mmol, 1.1 equiv) followed by a catalyst (0.02 mmol, 0.2 equiv) at room temperature. The reaction mixture was stirred at room temperature until the alcohol was consumed as monitored by TLC. Quenched the reaction mixture with aqueous saturated sodium bicarbonate solution (1-2 mL). Diluted with dichloromethane (1-2 mL) and the layers were separated. The aqueous layer was further extracted with dichloromethane (1-2 mL). The organic layers were combined, dried over Na_2SO_4, concentrated, and purified by silica gel column chromatography (20% hexanes/ethyl acetate) to afford product **2**.



2

3-(1-(Benzofuran-2-yl)ethyl)pentane-2,4-dione (2).

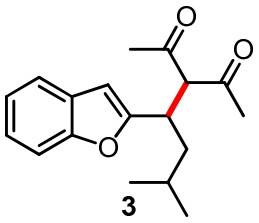
Pale yellow oil. R_f = 0.6 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max} /cm^{-1} 2936, 2880, 1724, 1700, 1598, 1455, 1422, 1358, 1253, 1167, 1011, 942. 809. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.19-7.10 (m, 2H), 6.34 (s, 1H), 4.10 (d, *J* = 10.2 Hz, 1H), 3.77 (dq, *J* = 10.2 and 6.7 Hz, 1H), 2.15 (s, 3H), 1.96 (s, 3H), 1.23 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.8, 202.6, 159.0, 154.5, 128.2, 123.8, 122.8, 120.7, 110.9, 102.7, 73.1, 33.7, 30.0, 29.3, 17.4. HRMS (ESI): *m/z* calcd for $C_{15}H_{16}O_3Na$ (M+Na): 267.0997. Found: 267.0994.

General procedure for solvent screening (Table-2). To a solution of furfuryl alcohol **1** (0.1 mmol, 1 equiv) in an appropriate solvent (1 mL) were added acetylacetone (0.11 mmol, 1.1 equiv) followed by $BiCl_3$ (0.02 mmol, 0.2 equiv) at room temperature. The reaction was stirred at room temperature until the alcohol was consumed as monitored by TLC and the reaction mixture was quenched with aqueous saturated sodium bicarbonate solution (1-2 mL). Diluted the reaction mixture with ethyl acetate (1-2 mL) and the layers were separated. The aqueous layer was further extracted with ethyl acetate (1-2 mL). The organic layers were combined, dried over Na_2SO_4, concentrated, and purified by silica gel column chromatography (20% hexanes/ethyl acetate) to afford product **2**.

General procedure for $BiCl_3$ catalyzed reactions of furfuryl alcohols with different nucleophiles (Scheme-1). To a solution of furfuryl alcohol (0.1 mmol, 1 equiv) in

nitromethane (1 mL) were added an appropriate nucleophile (0.11 mmol, 1.1 equiv) followed by $BiCl_3$ (0.02 mmol, 0.2 equiv) at room temperature. The reaction mixture was stirred at room temperature until the alcohol was consumed as monitored by TLC. Quenched the reaction mixture with aqueous saturated sodium bicarbonate solution (1-2 mL). Diluted the reaction mixture with ethyl acetate (1-2 mL) and the layers were separated. The aqueous layer was further extracted with ethyl acetate (1-2 mL). The organic layers were combined, dried over Na_2SO_4, concentrated, and purified by silica gel column chromatography (hexanes/ethyl acetate) to afford product.

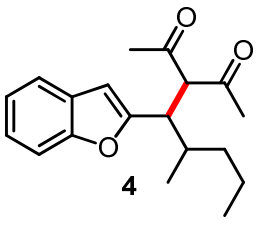
Note: The reaction is found to be air or moisture insensitive. This reaction can be carried out using Laboratory grade solvents. This reaction doesn't require any precautions such as working under nitrogen atmosphere.



3

3-(1-(Benzofuran-2-yl)-3-methylbutyl)pentane-2,4-dione (3).

Colorless oil. R_f = 0.6 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 2969, 2894, 1732, 1683, 1450, 1366, 1265, 1074, 745. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 7.1 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.18-7.07 (m, 2H), 6.40 (s, 1H), 4.16 (d, *J* = 10.0 Hz, 1H), 3.79 (dt, *J* = 11.5 and 3.3 Hz, 1H), 3.01 (s, 3H), 1.80 (s, 3H), 1.73-1.65 (m, 1H), 1.33-1.28 (m, 1H), 1.13-1.04 (m, 1H), 0.85 (d, *J* = 6.4 Hz, 3H), 0.72 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.7, 202.4, 156.9, 154.3, 128.2, 123.8, 122.8, 120.4, 111.0, 102.2, 73.2, 41.3, 37.9, 29.5, 25.4, 24.3, 23.7, 20.8. HRMS (ESI): *m/z* calcd for $C_{18}H_{22}O_3Na$ (M+Na): 309.1467. Found: 309.1463.

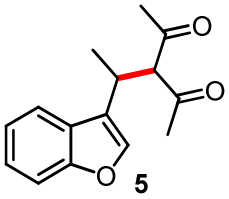


4

3-((-1-(Benzofuran-2-yl)-2-methylpentyl)pentane-2,4-dione (4).

Pale yellow oil. R_f = 0.7 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 2961, 2873, 1731, 1699, 1583, 1421, 1358, 1254, 1170, 748. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.18-7.09 (m, 2H), 6.36 (s, 1H), 4.46 (d, *J* = 11.8 Hz,

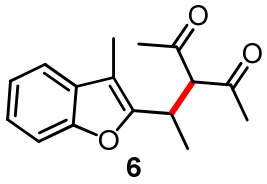
1H), 3.81(dd, *J* = 12.0 and 3.1 Hz , 1H), 2.21 (s, 3H), 1.90 (s, 3H), 1.60-1.54 (m, 1H), 1.40-1.00 (m, 4H), 0.89 (d, *J* = 4.1 Hz, 3H), 0.87-0.75 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.7, 202.5, 156.1, 154.4, 128.2, 127.6, 123.6, 120.6, 110.9, 105.4, 70.9, 45.0, 37.9, 33.8, 29.7, 28.8, 20.5, 18.6, 14.1. HRMS (ESI): *m/z* calcd for $C_{19}H_{24}O_3Na$ (M+Na): 323.1623. Found: 323.1622.



5

3-(-1-(Benzofuran-3-yl)ethyl)pentane-2,4-dione (5).

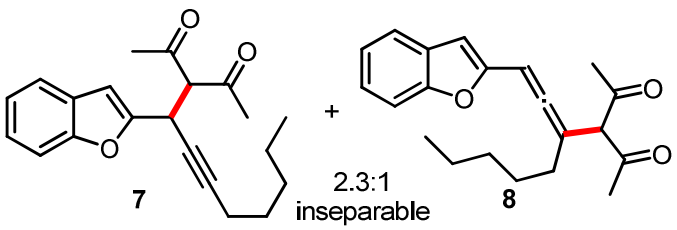
Pale yellow oil. R_f = 0.7 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 2936, 2880, 1724, 1700, 1598, 1455, 1422, 1358, 1253, 1167, 1011, 942, 809, 752. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61-7.06 (m, 5H), 4.12 (d, *J* = 11.2 Hz, 1H), 3.77 (m, 1H), 2.27 (s, 3H), 1.84 (s, 3H), 1.22 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 203.2, 203.2, 154.4, 142.2, 126.3, 124.6, 122.8, 122.0, 119.8, 111.0, 75.0, 30.4, 30.1, 29.0, 19.5. HRMS (ESI): *m/z* calcd for $C_{15}H_{16}O_3Na$ (M+Na): 267.0997. Found: 267.0994.



6

3-(1-(3-Methylbenzofuran-2-yl)ethyl)pentane-2,4-dione (6).

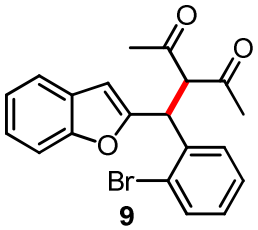
Pale yellow oil. R_f = 0.7 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 2969, 1736, 1732, 1561, 1377, 1248, 1099, 1045, 743. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43 (d, *J* =7.4 Hz, 1H), 7.43 (d, *J* =7.9 Hz, 1H), 7.17-7.09 (m, 2H), 4.30 (d, *J* = 12.7 Hz, 1H), 3.84, (dq, *J* = 12.7 and 7.0 Hz, 1H), 2.20 (s, 3H), 2.09 (s, 3H), 1.84 (s, 3H), 1.19 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.6, 202.4, 153.8, 153.2, 129.8, 123.7, 122.3, 119.2, 110.7, 110.5, 72.8, 31.8, 29.9, 29.7 17.8, 7.7. HRMS (ESI): *m/z* calcd for $C_{16}H_{19}O_3Na$ (M+Na+1): 259.1256. Found: 259.1253.



7 **8**

3-(1-(Benzofuran-2-yl)oct-2-ynyl)pentane-2,4-dione (7, Major).

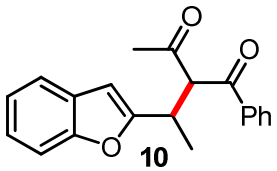
Pale yellow oil. R_f = 0.6 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 2956, 2932, 2860, 1720, 1705, 1599, 1454, 1357, 1254, 1172, 1149, 1009, 854. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 (m, 1H), 7.33 (m, 1H), 7.17- 7.08 (m, 2H), 6.35 (s, 1H), 4.65 (d, *J* = 10.2, 1H), 4.22 (d, *J* = 10.2 Hz, 1H), 2.30 (s, 3H), 2.16 (s, 3H), 2.10-1.06 (m, 2H), 1.51-1.16 (m, 6H), 0.86-0.78 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.2, 201.1, 154.4, 154.6, 128.0, 124.2, 122.9, 120.9, 111.1, 104.3, 85.7, 84.1, 71.9, 31.5, 30.9, 30.4, 29.3, 28.2, 22.1, 18.7, 13.9. HRMS (ESI): *m/z* calcd for $C_{21}H_{24}O_3Na$ (M+Na): 347.1618. Found: 347.1623.



9

3-((Benzofuran-2-yl)(2-bromophenyl)methyl)pentane-2,4-dione (9).

Yellow colored oil. R_f = 0.6 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 2932, 1723, 1703, 1471, 1358, 1252, 1172, 1022, 765. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51-7.56 (m, 8H), 5.59 (s, 1H), 5.57 (d, *J* = 10.1 Hz, 1H), 4.83 (d, *J* = 10.1 Hz, 1H), 2.14 (s, 3H), 1.98 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): 201.6, 201.4, 155.2, 154.7, 136.9, 133.6, 129.2, 129.1, 128.1, 128.0, 124.9, 124.0, 122.9, 120.9, 111.0, 104.4, 72.1, 43.2, 30.0, 28.4. HRMS (ESI): *m/z* calcd for $C_{20}H_{17}BrO_3Na$ (M+Na): 384.0361. Found: 384.0363.

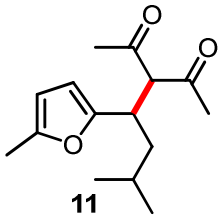


10

dr = 1:1

2-(1-(Benzofuran-2-yl)ethyl)-1-phenylbutane-1,3-dione (10).

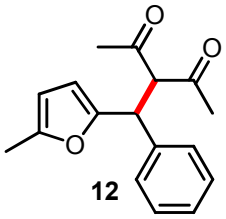
Pale yellow oil. R_f = 0.6 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 2956, 2869, 1722, 1675, 1454, 1255, 1180, 749. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.2 Hz, 2H), 7.43-7.27 (m, 4H), 7.20-7.00 (m, 3H), 6.30 (s, 1H), 4.93 (d, *J* = 10.1 Hz, 1H), 4.01 (m, 1H), 2.13 (s, 3H), 1.33 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): 202.5, 194.9, 159.2, 154.6, 136.8, 134.0, 128.9 (2CH), 128.5 (2H), 128.3, 123.8, 122.7, 120.7, 110.9, 102.9, 67.7, 34.4, 28.5, 17.9. HRMS (ESI): *m/z* calcd for $C_{20}H_{18}O_3Na$ (M+Na): 329.1154. Found: 329.1153.



11

3-(3-Methyl-1-(5-methylfuran-2-yl)butyl)pentane-2,4-dione (11).

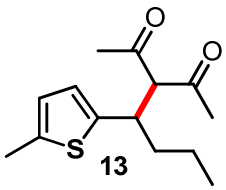
Pale yellow oil. R_f = 0.6 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 2954, 2871, 1726, 1701, 1374, 1226, 1073, 1018, 785. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.83 (d, *J* = 3.0 Hz, 1H), 5.75-5.73 (m, 1H), 3.97 (d, *J* = 10.8 Hz, 1H), 3.49 (dt, *J* = 11.4 and 3.3 Hz, 1H), 2.14 (s, 3H), 1.86 (s, 3H), 1.49 (s, 3H), 1.30-0.95 (m, 3H), 0.80 (d, *J* = 4.8 Hz, 3H), 0.72 (d, *J* = 4.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): 203.4, 203.1, 151.9, 151.8, 108.0, 105.9, 73.8, 41.2, 37.7, 29.9, 29.5, 25.4, 23.7, 20.9, 13.5. HRMS (ESI): *m/z* calcd for $C_{15}H_{22}O_3Na$ (M+Na): 273.1467. Found: 273.1461.



12

3-((5-Methylfuran-2-yl)(phenyl)methyl)pentane-2,4-dione (12)

Pale yellow oil. R_f = 0.6 (hexane/EtOAc = 9/1). IR (thin film, neat): ν_{max}/cm^{-1} 2926, 1727, 1724, 1450, 1371, 1243, 1035, 787, 701. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.22-7.15 (m, 6H), 5.80 (d, *J* = 3.0 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 2.17 (s, 3H), 2.08 (s, 3H), 1.83 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): 202.5, 202.4, 152.2, 151.6, 139.0, 128.8, 128.3, 128.2, 127.8, 127.3, 107.4, 106.2, 73.4, 45.1, 30.3, 28.8, 13.5. HRMS (ESI): *m/z* calcd for $C_{17}H_{18}O_3Na$ (M+Na): 293.1154. Found: 293.1153.

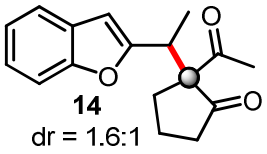


13

3-(1-(5-Methylthiophen-2-yl)butyl)pentane-2,4-dione (13).

Colorless oil. R_f = 0.4 (hexane/EtOAc = 9/1). IR (thin film, neat): ν_{max}/cm^{-1} 2979, 1724, 1723, 1455, 1362, 1254, 1178, 781. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.56 (d, *J* = 3.1 Hz, 1H), 6.50 (d, *J* = 3.1 Hz, 1H), 4.11 (d, *J* = 11.2 Hz, 1H), 3.70 (m, 1H), 2.41 (s, 3H), 2.23 (s, 3H), 1.94 (s, 3H), 1.47-1.36 (m, 2H), 1.27-1.17 (m, 2H), 0.83 (t, *J* = 11.2 Hz, 3H). **^{13}C NMR** (100

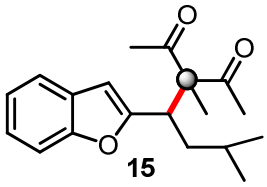
MHz, $CDCl_3$): 203.1, 203.1, 147.4, 141.9, 138.3, 125.6, 124.7, 41.4, 37.6, 29.7, 24.8, 20.0, 14.2, 13.6. HRMS (ESI): *m/z* calcd for $C_{14}H_{20}O_2NaS$ (M+Na): 275.1082. Found: 275.1078.



14
dr = 1.6:1

2-Acetyl-2-(1-(benzofuran-2-yl)ethyl)cyclopentanone (14, major).

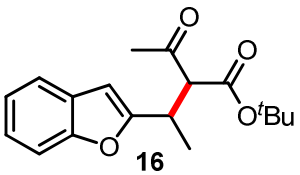
Light yellow oil. R_f = 0.70 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 3440, 2970, 1737, 1704, 1456, 1358, 1454, 1256, 1143, 1043, 815, 749, 582. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42-7.27 (m, 2H), 7.17-7.06 (m, 2H), 6.29 (s, 1H), 4.01 (q, *J* = 6.9 Hz, 1H), 2.53-2.54 (m, 1H), 2.2 (s, 3H), 2.19-2.06 (m, 1H), 1.96-1.71 (m, 4H), 1.62-1.41 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 214.8, 202.7, 158.7, 154.4, 128.0, 123.9, 122.8, 120.7, 111.0, 104.5, 73.4, 39.5, 37.6, 26.4, 25.5, 19.3, 15.0. HRMS (ESI): *m/z* calcd for $C_{17}H_{18}O_3Na$ (M+Na): 293.1154. Found: 293.1153.



15

3-(1-(Benzofuran-2-yl)-3-methylbutyl)-3-methylpentane-2,4-dione (15).

Pale yellow oil. R_f = 0.7 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 1732, 1698, 1454, 1373, 1094, 1046, 911, 736. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.3 Hz, 1H),7.32 (d, *J* = 7.5 Hz, 1H), 7.18-7.08 (m, 2H), 6.41 (s, 1H), 4.03 (dd, *J* = 1.2 and 2.3 Hz, 1H), 2.08 (s, 3H), 1.92 (s, 3H), 1.76 (m, 1H), 1.43 (s, 3H), 1.26 (m, 1H), 0.98 (m , 1H), 0.88 (d, *J* = 6.6 , 3H), 0.75 (d, *J* = 6.6, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 206.0, 206.1, 157.1, 154.5, 128.1, 123.7, 122.7, 120.6, 111.0, 105.6, 71.1, 40.8, 37.9, 27.1, 26.9, 26.0, 23.9, 21.0, 14.9. HRMS (ESI): *m/z* calcd for $C_{19}H_{24}O_3Na$ (M+Na): 323.1623. Found: 323.1623.

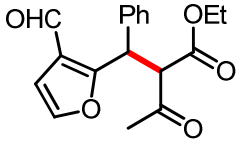


16
(dr = 1.3:1)

***tert*-Butyl 2-acetyl-3-(benzofuran-2-yl)butanoate (16, Major).**

Colorless oil. R_f = 0.7 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 2982, 1714, 1732, 1258, 1145, 745. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45-7.31 (m, 2H), 7.17-7.08 (m, 2H), 6.38 (s, 1H), 3.77 (d, *J* = 11.2 Hz, 1H), 3.72-3.66 (m, 1H), 2.20 (s, 3H), 1.38 (s, 9H),

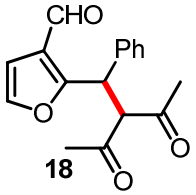
1.33 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.1, 201.9, 167.2, 159.5, 128.4, 123.6, 122.6, 120.6, 110.8, 102.6, 82.4, 65.2, 33.3, 29.9, 27.8, 17.4. HRMS (ESI): *m/z* calcd for $C_{18}H_{22}O_4Na$ (M+Na): 325.1416. Found: 325.1414.



17
(dr = 1:1)

Ethyl 2-((3-formylfuran-2-yl)(phenyl)methyl)-3-oxobutanoate (17).

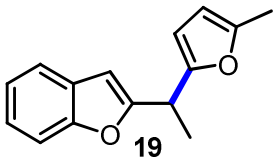
Pale yellow oil. R_f = 0.5 (hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max} /cm^{-1} 2936, 2880, 1735, 1700, 1598, 1455, 1422, 1358, 1253, 1167, 1011, 942. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 7.30-7.24 (m, 2H), 7.23-7.10 (m, 4H), 6.65 (s, 1H), 5.24 (d, *J* = 4.2 Hz, 1H), 4.61 (d, *J* = 4.2 Hz, 1H), 3.88 (q, *J* = 7.1 Hz, 2H), 2.16 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.4, 184.7, 166.7, 162.4, 142.6, 137.4, 129.1, 128.2 (2CH), 127.9 (2CH), 122.3, 108.9, 63.1, 61.9, 42.7, 31.0, 14.0. HRMS (ESI): *m/z* calcd for $C_{18}H_{18}O_5Na$ (M+Na): 337.1052. Found: 337.1050.



18

2-(2-Acetyl-3-oxo-1-phenylbutyl)furan-3-carbaldehyde (18).

Pale yellow oil. R_f = 0.3 (hexane/EtOAc = 9/1). IR (thin film, neat): ν_{max}/cm^{-1} 2961, 2927, 2874, 2743, 1731, 1702, 1680, 1458, 1457, 1381, 1359, 1254, 755. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.94 (s, 1H), 7.38-7.13 (m, 6H), 6.58 (s, 1H), 5.30 (d, *J* = 11.8 Hz, 1H), 4.84 (d, *J* = 11.8 Hz, 1H), 2.08 (s, 3H), 1.92 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.2, 200.8, 184.7, 161.6, 142.6, 137.1, 129.2, 128.2 (2C), 128.0 (2C), 122.1, 109.1, 71.6, 43.1, 30.3, 29.4. HRMS (ESI): *m/z* calcd for $C_{17}H_{16}O_4Na$ (M+Na): 307.0946. Found: 307.0947.

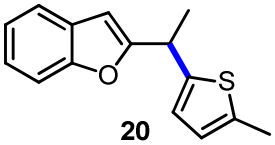


19

2-(1-(5-Methylfuran-2-yl)ethyl)benzofuran (19).

Pale yellow oil. R_f = 0.6 (hexane/EtOAc = 9/1). IR (thin film, neat): ν_{max}/cm^{-1} 2933, 1454, 1245, 1120, 1168, 1019, 787, 744. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53-7.45 (m, 2H), 7.28-7.19 (m, 2H), 6.46 (s, 1H), 6.05 (d, *J* = 2.9 Hz, 1H), 5.93 (d, *J* = 2.9 Hz, 1H), 4.33 (q, *J* = 7.2,

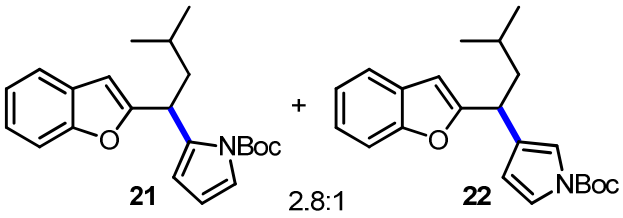
1H), 2.29 (s, 3H), 1.71 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.0, 154.7, 153.8, 151.1, 128.6, 123.4, 122.5, 120.5, 111.0, 106.0, 106.1, 101.9, 33.5, 17.9, 13.6. HRMS (ESI): *m/z* calcd for $C_{15}H_{14}O_2Na$ (M+Na): 249.0892. Found: 249.0891.



20

2-(1-(5-Methylthiophen-2-yl)ethyl)benzofuran (20).

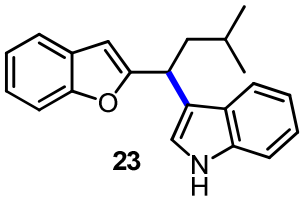
Colorless oil. R_f = 0.6 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max}/cm^{-1} 2974, 2925, 1585, 1453, 1374, 1253, 1166, 1046, 929, 881, 800, 744. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41-7.38 (m, 2H), 7.16-7.06 (m, 2H), 6.66 (s, 1H), 6.56 (s, 1H), 6.62 (d, *J* = 3.2 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 1H), 2.34 (s, 3H), 1.67 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.4, 154.7, 144.1, 138.3, 128.5, 124.6, 124.0, 123.5, 122.5, 120.6, 111.0, 101.7, 35.1, 21.0, 15.3. HRMS (ESI): *m/z* calcd for $C_{15}H_{14}OSNa$ (M+Na): 265.0663. Found: 265.0658.



21 2.8:1 **22**

***tert*-Butyl 3-(1-(benzofuran-2-yl)-3-methylbutyl)-1*H*-pyrrole-1-carboxylate (21, Major).**

Colorless oil. R_f = 0.6 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max}/cm^{-1} 2957, 1742, 1455, 1369, 1324, 1254, 1162, 1123, 738. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40 (m, 2H), 7.15 (m, 3H), 6.23 (s, 1H), 6.13 (s, 1H), 6.10 (t, *J* = 3.3 Hz, 1H), 5.08 (t, *J* = 7.6 Hz, 1H), 2.01-1.94 (m, 1H), 1.87- 1.80 (m, 1H), 1.68-1.61 (m, 1H), 1.47 (s, 9H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.2, 154.6, 149.3, 135.5, 128.8, 122.3, 120.3, 119.9, 111.8, 110.9, 109.9, 102.1, 83.6, 43.2, 35.7, 27.9, 27.4 ($3CH_3$), 25.8, 22.8, 22.4. HRMS (ESI): *m/z* calcd for $C_{22}H_{27}NO_3Na$ (M+Na): 376.1889. Found: 376.1884.

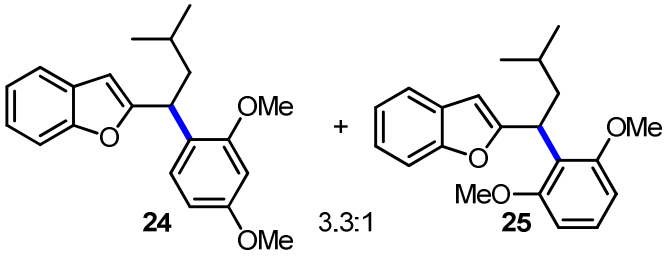


23

3-(1-(Benzofuran-2-yl)-3-methylbutyl)-1*H*-indole (23).

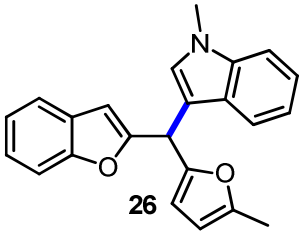
Pale yellow oil. R_f = 0.4 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max} /cm^{-1} 3376, 2963, 2927, 2852, 2874, 1597, 1455, 1254, 986. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92 (br s, 1H), 7.57 (d, *J* = 7.5, 1H), 7.40-7.21 (m, 3H), 7.14-6.91 (m, 5H), 6.30 (s, 1H), 4.42 (t, *J* = 7.8

Hz, 1H), 2.13-2.02 (m, 1H), 2.02-1.93 (m, 1H), 1.60-1.49 (m, 1H), 0.90 (d, J = 6.7 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.7, 154.7, 136.4, 128.8, 126.6, 123.0, 122.3, 122.0, 121.7, 120.3, 119.4, 119.3, 117.0, 111.1, 111.0, 102.0, 43.1, 34.8, 25.8, 22.6, 22.5. HRMS (ESI): *m/z* calcd for $C_{21}H_{21}NONa$ (M+Na): 326.1521. Found: 326.1520.



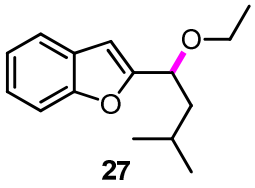
2-(1-(2,4-Dimethoxyphenyl)-3-methylbutyl)benzofuran (24, Major).

Pale yellow oil. R_f = 0.7 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max} /cm^{-1} 2955, 1505, 1456, 1294, 1257, 1207, 1040, 940, 748. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39-7.04 (m, 4H), 6.45-6.34 (m, 3H), 6.31 (s, 1H), 4.56 (t, J = 7.8 Hz, 1H), 3.74 (s, 3H), 3.70 (s, 3H), 1.95 (m, 1H), 1.78 (m, 1H),0.93 (m, 1H), 0.83 (d, J = 6.56 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.0, 159.3, 157.8, 154.6, 129.9, 128.8, 128.6, 123.1, 122.2, 120.2, 110.9, 104.3, 102.1, 96.5, 55.6, 55.2, 43.1, 34.8, 25.8, 22.5 (2C). HRMS (ESI): *m/z* calcd for $C_{21}H_{24}O_3Na$ (M+Na): 347.1623. Found: 347.1621.



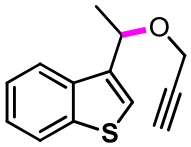
2-((Benzofuran-2-yl)(5-methylfuran-2-yl)methyl)-1-methyl-1*H*-indole (26).

Pale yellow oil. R_f = 0.6 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max} /cm^{-1} 2920, 1583, 1562, 1453, 1372, 1242, 1245, 1132, 1021, 784, 741. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45-7.37 (m, 3H), 7.24-6.97 (m, 5H), 6.99 (s, 1H), 6.38 (s, 1H), 5.94 (s, 1H), 5.84 (s, 1H), 5.72 (s, 1H), 3.71 (s, 3H), 2.20 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.2, 154.9, 152.0, 151.4, 137.1, 128.6, 127.7, 126.8, 123.5, 122.2, 121.7, 120.6, 119.5, 119.3, 112.5, 111.2, 109.3, 107.9, 106.2, 103.9, 37.0, 32.8, 13.2. HRMS (ESI): *m/z* calcd for $C_{23}H_{19}O_2NNa$ (M+Na): 364.1314. Found: 364.1318.



2-(1-Ethoxy-3-methylbutyl)benzofuran (27).

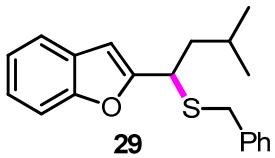
Colorless oil. R_f = 0.6 (hexane/EtOAc = 9/1). IR (thin film, neat): ν_{max} /cm^{-1} 2958, 2871, 1590, 1455, 1368, 1252, 1093, 746. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43-7.41 (m, 2H), 7.16-1.07 (m, 2H), 6.50 (s, 1H), 4.35 (q, *J* = 6.2, 1H), 3.45-3.40 (m, 1H), 3.33-3.29 (m, 1H), 1.81-1.77 (m, 1H), 1.64-1.57 (m, 2H), 1.02 (t, *J* = 6.2 Hz, 3H), 0.85-0.81 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.2, 154.9, 128.1, 123.9, 122.6, 120.8, 111.3, 103.8, 73.8, 64.5, 43.4, 24.6, 22.8, 22.3, 15.3. HRMS (ESI): *m/z* calcd for $C_{15}H_{20}O_2Na$ (M+Na): 255.1361. Found: 255.1364.



28

3-(1-(Prop-2-yn-1-yloxy)ethyl)benzo[*b*]thiophene (28).

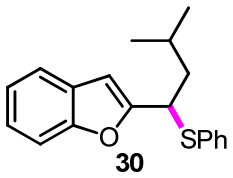
Colorless oil. R_f = 0.7 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max}/cm^{-1} 3292, 2979, 2932, 2855, 1457, 1427, 1442, 1372, 1354, 1254, 1007, 763. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03-8.00 (m,1H), 7.93-7.88 (m ,1H), 7.43-7.56 (m, 3H), 5.14 (q, *J* = 6.5 Hz, 1H), 4.22 (dd, *J* = 15.7 and 2.4 Hz, 1H), 4.03 (dd, *J* = 15.6 and 2.4 Hz, 1H), 2.46 (t, *J* = 2.4 Hz, 1H), 1.68 (d, *J* = 6.5 Hz ,3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 141.1, 37.4, 124.4, 124.1, 123.3, 122.9, 122.6, 80.0, 137.2, 74.2, 72.3, 55.6, 21.8. HRMS (ESI): *m/z* calcd for $C_{13}H_{12}OSNa$ (M+Na): 239.0507. Found: 239.0502.



29

2-(1-(Benzylthio)-3-methylbutyl)benzofuran (29).

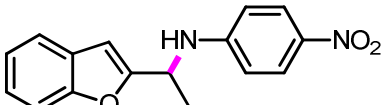
Colorless oil. R_f = 0.6 (hexane/EtOAc = 9/1). IR (thin film, neat): ν_{max}/cm^{-1} 3308, 2956, 2865, 1582, 1454, 1253, 786. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.50-7.43 (m, 2H), 7.28-7.16 (m, 7H), 6.49 (s, 1H), 3.83-3.38 (m, 1H), 3.60 (s, 2H), 1.91-1.84 (m, 1H), 1.74-1.58 (m, 2H), 0.82 (d, *J* = 7.4 Hz, 3H), 0.76 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.0, 138.0, 129.5, 129.0, 128.5, 128.4, 127.0, 123.9, 122.8, 120.7, 111.3, 103.0, 43.3, 42.3, 41.9, 35.6, 25.9, 22.2. HRMS (ESI): *m/z* calcd for $C_{20}H_{22}OSNa$ (M+Na): 333.1289. Found: 333.1288.



30

2-(3-Methyl-1-(phenylthio)butyl)benzofuran (30).

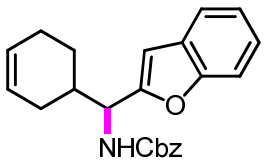
Colorless oil. R_f = 0.7 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 3015, 2958, 1583, 1454, 1253, 1216, 738. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45-7.40 (m, 2H), 7.29-7.13 (m, 7H), 6.28 (s, 1H), 4.30 (t, *J* = 7.1 Hz, 1H), 2.03-1.92 (m, 1H), 1.85 -1.70 (m, 2H), 0.90 (d, *J* = 6.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.5, 154.7, 133.7, 133.4, 129.1, 128.7 (2C), 128.2, 127.5, 123.8, 122.6, 120.6, 111.1, 103.9, 45.4, 42.2, 26.0, 22.5, 22.1. HRMS (ESI): *m/z* calcd for $C_{19}H_{20}OSNa$ (M+Na): 319.1133; Found; 319.1130.



31

N-(1-(Benzofuran-2-yl)ethyl)-4-nitrobenzenamine (31).

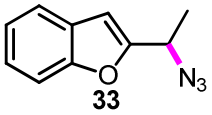
Pale yellow solid. M.P. = 137-139 ˚C. R_f = 0.6 (hexane/EtOAc = 4/1). IR (KBr): ν_{max}/cm^{-1} = 3372, 1599, 1473, 1311, 1110, 751. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.02-7.98 (m, 2H), 7.44-7.36 (m, 2H), 7.22-7.12 (m, 2H), 7.38-7.28 (m, 2H), 6.56-6.49 (m, 2H), 4.80-4.75 (m, 1H), 1.66 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.8, 154.8, 151.8, 138.6, 127.9, 126.3 (2C), 124.2, 122.9, 121.0, 111.8 (2C), 111.1, 102.7, 47.4, 20.7. HRMS (ESI): *m/z* calcd for $C_{16}H_{14}N_2O_3Na$ (M+Na): 305.0902. Found: 305.0901.



32

Benzyl (benzofuran-2-yl)(cyclohex-3-enyl)methylcarbamate (32).

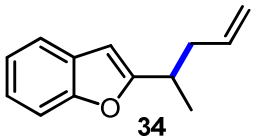
Colorless viscous oil. R_f = 0.6 (hexane/EtOAc = 1/4). IR (thin film): ν_{max}/cm^{-1} 3104, 2954, 2867, 1698, 1530, 1045, 745. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.4 Hz, 1H), 7.44 (d, *J* = 6.9 Hz, 1H), 7.20 (m, 7H), 6.62 (s, 1H), 5.73-5.64 (m, 2H), 5.21 (brs, 1H), 5.12 (ABq, *J* = 5.2 Hz, 2H), 4.85 (d, *J* = 6.6 Hz, 1H), 2.26 (m, 1H), 2.16-2.00 (m, 2H), 2.00-1.77 (m, 2H), 1.50-1.24 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.2, 156.1, 136.2, 128.5 (2CH), 128.2 (2C), 128.0, 128.3, 127.0, 126.9, 125.5, 124.0, 122.8, 120.9, 111.1, 103.9, 67.0, 54.3, 37.5, 28.5, 27.8, 24.9. HRMS (ESI): *m/z* calcd for $C_{23}H_{23}O_3NNa$ (M+Na): 384.1576. Found: 384.1572.



33

2-(1-Azidoethyl)benzofuran (33).

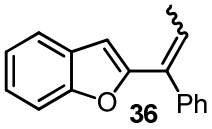
Colorless oil. R_f = 0.7 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max} /cm^{-1} 2929, 2106, 1454, 1153, 1043, 820, 746. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.49-7.39 (m, 2H), 7.24-7.13 (m, 2H), 6.59 (s, 1H), 4.6 (q, *J* = 6.8 Hz, 1H), 1.59 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.9, 154.9, 127.7, 124.6, 123.0, 121.2, 111.3, 103.6, 54.4, 18.0. HRMS (ESI): *m/z* calcd for $C_{10}H_9N_3ONa$ (M+Na): 210.0644. Found: 210.0644.



34

2-(Pent-4-en-2-yl)benzofuran (34).

Colorless oil. R_f = 0.80 (hexane/EtOAc = 9/1). IR (thin film, neat): ν_{max} /cm^{-1} 3072, 2928, 2977, 1587, 1454, 1253, 1170, 1123, 729. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46- 7.44 (m, 2H), 7.39-7.37 (m, 2H), 6.34 (s, 1H), 5.79-5.64(m, 1H), 5.06-4.97 (m, 2H), 3.02-2.97 (m, 1H), 2.58-2.34 (m, 2H), 1.29 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.1, 154.5, 136.0, 128.7, 123.1, 122.3, 120.3, 116.7, 110.8, 100.9, 39.5, 33.4, 18.2. HRMS (ESI): *m/z* calcd for $C_{13}H_{15}OK$ (M+K+1): 226.0760. Found: 226.0876.

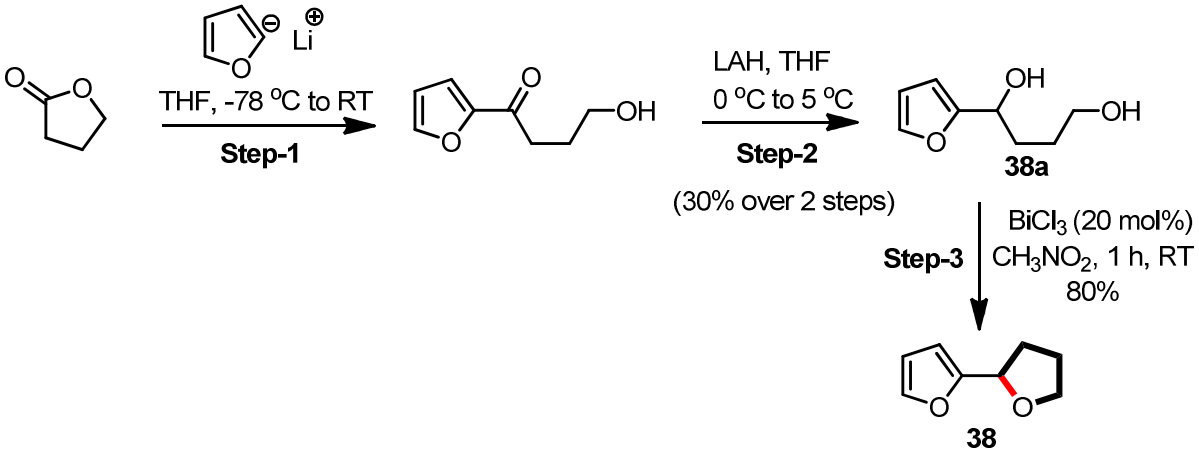


36

2-(1-Phenylprop-1-en-2-yl)benzofuran (36).

Light yellow oil. R_f = 0.7 (hexane/EtOAc = 9/1). IR (thin film, neat): ν_{max} /cm^{-1} 3057, 1556, 1494, 1471, 1452, 1303, 1279, 1256, 1007, 940, 801, 784, 762. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45-7.01 (m, 9H), 6.60 (q, *J* = 7.2 Hz, 1H), 5.99 (s, 1H), 2.06 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.5, 154.7, 132.7, 129.9, 128.2 (2C), 128.1 (2C), 127.6, 125.0, 124.2, 122.7, 120.8, 111.2, 107.3, 103.8, 15.0. HRMS (ESI): *m/z* calcd for $C_{17}H_{14}OK$ (M+K): 273.0682. Found: 273.0885.

Synthesis of the diol 38a and the cyclic ether 38 (Scheme-2). The cyclic ether **38** was synthesized from diol **38a** as shown in the following scheme.

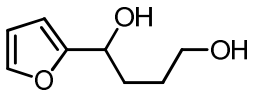


Step-1: The reaction was carried out by adding furyllithium to butyrolactone (500 mg, 5.8 mmol), obtained the keto-alcohol (1.08 g crude), following literature procedure.[3] Proceeded to next step without further purification.

Step-2: To a solution of crude keto-alcohol (1.08 g, 6.9 mmol) in anhydrous THF (10 mL) at 0-5 ^{o}C was added a weighed amount of LAH (697 mg, 8.39 mmol) in three portions under nitrogen atmosphere. The reaction mixture was stirred at the same temperature until the starting material was consumed as monitored by TLC and the reaction mixture was diluted carefully with ethyl acetate and subsequently quenched with saturated ammonium chloride solution (1 mL). Filtered the reaction mixture through short celite pad, concentrated and purified by silica gel column chromatography (50% hexanes/ethyl acetate) to afford an *unstable* diol **38a**[4] (335 mg, 30% over 2 steps).

Step-3: To a solution of the diol **38a** (0.1 mmol, 1 equiv) in nitromethane (1 mL) was added $BiCl_3$ (0.02 mmol, 0.2 equiv) at room temperature. The reaction was stirred at room temperature until the alcohol was consumed as monitored by TLC and the reaction mixture was quenched with aqueous saturated sodium bicarbonate solution (1-2 mL). Diluted the reaction mixture with ethyl acetate (1-2 mL) and the layers were separated. The aqueous layer was further extracted with ethyl acetate (1-2 mL). The organic layers were combined, dried over Na_2SO_4, concentrated, and purified by silica gel column chromatography (2-3% hexanes/ethyl acetate) to afford the cyclic ether **38** in 80% yield.

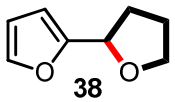
[3] H, Guo and G. A. O'Doherty, *Org. Lett.,* 2006, **8**, 1609.
[4] (*a*) D. Hongxun, Z. Weike and B. Junchai, *Tetrahedron Lett.,* 1987, **28**, 2599; (*b*) T. Irkinshaw, D. Cheshire and A. Mete, *PCT. Intl. Appl.,* (2001) WO20011062713.



38a

1-(Furan-2-yl)butane-1,4-diol (38a).

Pale yellow oil. R_f = 0.5 (hexane/EtOAc = 5/5). IR (thin film, neat): ν_{max}/cm^{-1} 3626, 2931, 1427, 1374, 1131, 849, 745. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.27 (s, 1H), 6.24 (s, 1H), 6.17 (s, 1H), 4.62 (t, *J* = 6.5 Hz, 1H), 3.56 (t, *J* = 6.9 Hz, 2H), 3.14 (br s, 2H), 1.80 (m, 2H), 1.58 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.7, 141.7, 110.1, 105.7, 67.5, 62.4, 32.6, 28.7. HRMS (ESI): *m/z* calcd for $C_8H_{12}O_3Na$ (M+Na): 179.0684. Found: 179.0682.

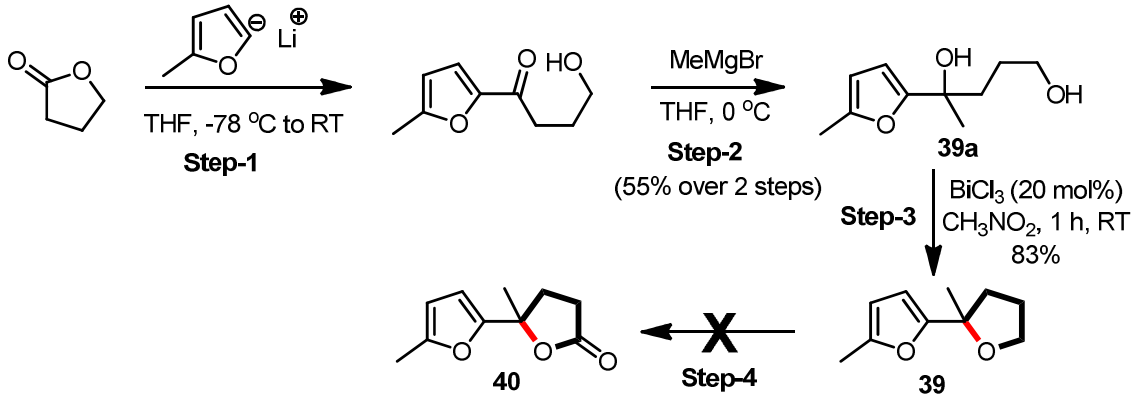


38

2-(Tetrahydrofuran-2-yl)furan (38).

Colorless oil. R_f = 0.4 (hexane/EtOAc = 9.5/0.5). IR (thin film, neat): ν_{max}/cm^{-1} 2970, 2932, 2876, 1454, 1381, 1254, 1219, 1078, 1020, 751. **^{1}H NMR** (400 MHz, $CDCl_3$+CCl_4): δ 7.30 (s, 1H), 6.25 (s, 1H), 6.18 (s, 1H), 4.84 (t, *J* = 6.5 Hz, 1H), 3.90 (q, *J* = 6.8 Hz, 1H), 3.83-3.81 (m, 1H), 2.17-1.85 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$+CCl_4): δ 155.1, 142.2, 110.0, 106.5, 73.8, 68.2, 30.3, 25.9. HRMS (ESI): *m/z* calcd for $C_8H_{10}O_2Na$ (M +Na): 161.0578. Found: 161.0577.

Synthesis of the diol 39a and the cyclic ether 39, and efforts towards the total synthesis of γ-lactone natural product 40 (Scheme-2). The cyclic ether **6** was synthesized from diol **1at** as shown in the following scheme.

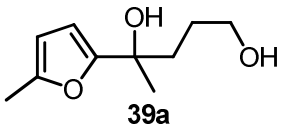


Step-1: The reaction was carried out by adding furyllithium to butyrolactone (500 mg, 5.8 mmol), obtained the keto-alcohol (660 mg crude), following literature procedure.[4] Proceeded to next step without further purification.

Step-2: To a solution of crude keto-alcohol (660 mg, 3.92 mmol) in anhydrous THF (7 mL) at 0 °C under nitrogen atmosphere was added slowly methylmagnesium bromide solution (1.4 M in THF:toluene (1:3), 9.3 mL, 13.1 mmol). The reaction mixture was stirred at the same temperature until the starting material was consumed as monitored by TLC and the reaction mixture was carefully quenched with saturated ammonium chloride solution (~10 mL) at 0-5 °C. Layers were separated and the aqueous layer was further extracted with ethyl acetate (2 x 5 mL). The combined organic phase was dried (Na_2SO_4) and concentrated under reduced pressure. Crude was purified by silica gel column chromatography (50% hexanes/ethyl acetate) to afford rather an *unstable* diol **39a** (265 mg, 55% over 2 steps).

Step-3: Following the procedure described for the synthesis of the cyclic ether **38**, the diol **39a** afforded the cyclic ether **39** in 83% yield.

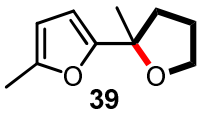
Step-4: All our efforts[5] to convert the cyclic ether **39** to butyrolactone natural product **40** were unsuccessful.



39a

4-(5-Methylfuran-2-yl)pentane-1,4-diol (39a).

Pale yellow oil. R_f = 0.60 (hexane/EtOAc = 1/1). IR (thin film, neat): ν_{max}/cm^{-1} 3351, 2929, 2919, 1454, 1254, 1171, 958, 754. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.07 (s, 1H), 5.90 (s, 1H), 3.94 (t, *J* = 6.12 Hz, 2H), 2.28 (s, 3H), 1.91 (m, 2H), 1.73 (m, 2H), 1.58 (m, 2H) 1.46 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): 157.9, 156.9, 119.4, 108.9, 79.8, 62.3, 29.7, 27.0, 20.0, 13.4. HRMS (ESI): *m/z* calcd for $C_{10}H_{16}O_3Na$ (M +Na): 193.0841. Found: 193.0839.



39

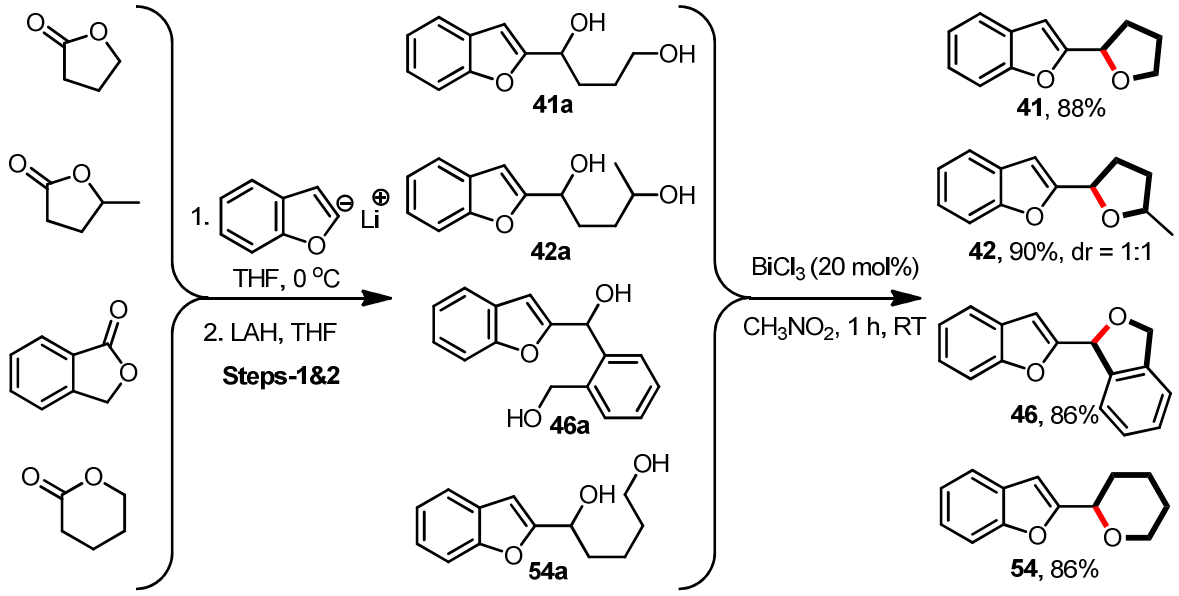
2-(Tetrahydro-2-methylfuran-2-yl)-5-methylfuran (39).

Colorless oil. R_f = 0.80 (hexane/EtOAc = 9.5/0.5); IR (thin film, neat): ν_{max}/cm^{-1} 2956, 2925, 2624, 1686, 1536, 1467, 1220, 969, 771, 750. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.97 (s, 1H), 5.78 (s, 1H), 3.91-3.72 (m, 1H), 2.29-2.20 (m, 1H), 2.18 (s, 6H), 1.97-1.86 (m, 2H), 1.79-1.71 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$ +CCl_4): δ 156.8, 151.3, 105.7, 105.3, 79.3, 67.8,

[5] **$Co(acac)_2$:** (a) E. Hata, T. Takai and T. Mukaiyama, *Chem. Lett.,* 1993, 1513; (b) M. T. Reetz and K. Ttillner, *Tetrahedron Lett.,* 1995, **36**, 9461.
$CoCl_2$: P. Li and H. Alper, *J. Mol. Catal.,*1992, **72**, 143.
$CrO_2(OAc)_2$: H. Frauenrath and T. Philipps, *Tetrahedron,* 1986, **42**, 1135.
$TMSONO_2$-CrO_3: S. P. Shahi, A. Gupta, S. V. Pitre, M. V. R. Reddy, R. Kumareswaran and Y. D. Vankar, *J. Org. Chem.,* 1999, **64**, 4509.
$ZnCr_2O_7$: H. Firouzabadi, A. R. Sardarian, H. Moosavipour and G. M. Afshari, *Synthesis,* 1985, 285.

37.0, 26.0 (2C), 13.6. HRMS (ESI): *m/z* calcd for $C_{10}H_{14}O_2Na$ (M +Na): 189.0891. Found: 189.0891.

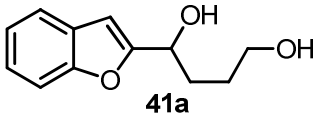
Synthesis of the diols 41a, 42a, 46a and 54a, and cyclic ethers 41, 42, 46 and 54 (Scheme-2). The cyclic ethers **41**, **42**, **46** and **54** were synthesized from the respective diols **41a**, **42a**, **46a** and **54a** as shown in the following scheme.



Step-1: Followed literature procedure[4] by adding benzofuranyllithium to the respective lactone at 0-5 °C to obtain keto-alcohols. Proceeded to next step without further purification.

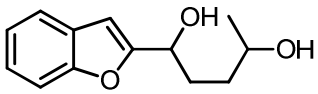
Step-2: The diols **41a**, **42a**, **46a** and **54a** were obtained by following the procedure as described for the synthesis of diol **38a** in 50-60% yield range over two steps. These diols are found to be *unstable* upon storage.

Step-3: Following the procedure described for the synthesis of the cyclic ether **38**, the diols **41a**, **42a**, **46a** and **54a** afforded the cyclic ethers **41**, **42**, **46** and **54**.



1-(Benzofuran-2-yl)butane-1,4-diol (41a).

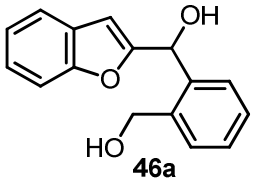
Pale yellow oil. R_f = 0.6 (hexane/EtOAc = 3/7). IR (thin film, neat): ν_{max}/cm^{-1} 3336, 2938, 1453, 1253, 1054, 745. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.21-7.11 (m, 2H), 6.55 (s, 1H), 4.30 (dd, *J* = 7.6 and 3.0 Hz, 1H), 3.65 (dt, *J* = 6.1 and 2.4 Hz, 2H), 2.07-1.09 (m, 2H), 1.71-1.63 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): 159.4, 154.7, 128.1, 124.0, 122.7, 121.0, 111.1, 102.5, 68.1, 62.6, 32.8, 28.6. HRMS (ESI): *m/z* calcd for $C_{12}H_{14}O_3Na$ (M+Na): 229.0841. Found: 229.0839.



42a

1-(Benzofuran-2-yl)pentane-1,4-diol (42a).

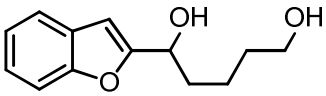
Pale yellow oil. R_f = 0.6 (hexane/EtOAc = 1/4). IR (thin film, neat): ν_{max}/cm^{-1} 3324, 2924, 1563, 1260, 1021, 765, 561. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 (d, *J* =7.4 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.29-7.18 (m, 2H), 6.61 (s, 1H), 4.86 (t, *J* = 5.9 Hz, 1H), 3.49 (m, 1H), 2.13-1.94 (m, 2H), 1.70-1.48 (m, 2H), 1.19 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): 159.6, 154.7, 128.2, 123.9, 122.7, 121.0, 111.1, 102.3, 68.3, 67.8, 35.3, 32.5, 23.5. HRMS (ESI): *m/z* calcd for $C_{13}H_{16}O_3Na$ (M+Na): 243.0997. Found: 243.0996.



46a

Benzofuran-2-yl(2-(hydroxymethyl)phenyl)methanol (46a).

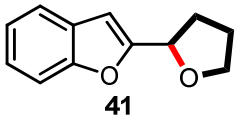
Pale yellow oil. R_f = 0.6 (hexane/EtOAc = 3/7). IR (thin film, neat): ν_{max}/cm^{-1} 3332, 2927, 1453, 1253 745. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 7.0 Hz, 1H), 7.37 (d, *J* = 7.3 Hz, 1H), 7.35-7.12 (m, 6H), 6.57 (s, 1H), 6.09 (s, 1H), 4.63 (AB q, *J* = 12.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): 157.9, 155.0, 139.1, 138.3, 130.1, 128.5 (2CH), 128.0, 124.2, 122.9 (2CH), 121.1, 111.3, 104.0, 69.3, 63.8. HRMS (ESI): *m/z* calcd for $C_{16}H_{14}O_3Na$ (M+Na): 277.0841. Found: 277.0836.



54a

1-(Benzofuran-2-yl)pentane-1,5-diol (54a).

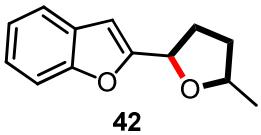
Pale yellow oil. R_f = 0.60 (hexane/EtOAc = 2/3). IR (thin film, neat): ν_{max}/cm^{-1} 3338, 2938, 1453, 1253, 1173, 1069. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.1 Hz, 1H), 7.29 (d, *J* = 7.4 Hz , 1H), 7.13-7.02 (m, 2H), 6.42 (s, 1H), 4.65 (t, *J* = 6.8 Hz, 1H), 3.43 (t, *J* = 5.8 Hz, 2H), 2.79 (br s, 2H), 1.77-1.72 (m, 2H), 1.48-1.20 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): 159.6, 154.7, 126.1, 124.0, 122.7, 121.0, 111.1, 102.3, 67.9, 62.2, 35.0, 31.9, 21.6. HRMS (ESI): *m/z* calcd for $C_{13}H_{16}O_3Na$ (M+Na): 243.0997. Found: 243.0993.



41

2-(Tetrahydrofuran-2-yl)benzofuran (41).

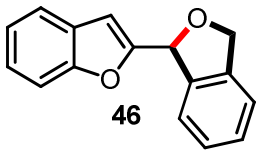
Pale yellow oil. R_f = 0.60 (hexane/EtOAc = 9/1). IR (thin film, neat): ν_{max} /cm^{-1} 2938, 1453, 1340, 1533, 1054, 1130, 745. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.19-7.08 (m, 2H), 6.53 (s, 1H), 4.93 (t, *J* = 6.6 Hz, 1H), 3.98 (q, *J* = 8.12 Hz, 1H), 3.88 (q, 8.12 Hz, 1H), 2.28-1.71 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.1, 155.0, 128.1, 124.0, 122.6, 120.9, 111.2, 103.0, 74.3, 68.7, 31.6, 25.9. HRMS (ESI): *m/z* calcd for $C_{12}H_{12}O_2Na$ (M +Na): 211.0735. Found: 211.0732.



42
dr = 1:1

2-(Tetrahydro-5-methylfuran-2-yl)benzofuran (42).

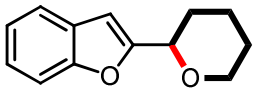
Light yellow Colored liquid. R_f = 0.6 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 2924, 2855, 1563, 1434, 1260, 1218, 1021, 959, 784, 765, 561. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.4 Hz, 1H), 7.40 (d, *J* = 8.1 Hz,1H), 7.20-7.10 (m, 2H), 6.57 (s, 1H), 5.13 (t, *J* = 6.6 Hz, 1H), 4.31-4.23 (m, 1H), 1.69-1.54 (m, 4H), 1.36 (d, *J* = 6.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.5, 155.0, 128.7, 123.9, 122.6, 120.9, 110.1, 103.0, 75.8, 74.5, 33.7, 31.0, 21.0. HRMS (ESI): *m/z* calcd for $C_{13}H_{14}O_2Na$ (M +Na): 225.0891; Found: 225.0891.



46

2,3-Dihydro-2,2'-bibenzofuran (46).

Pale yellow oil. R_f = 0.6 (hexane/EtOAc = 9/1). IR (thin film, neat): ν_{max}/cm^{-1} 3050, 2858, 1602, 1456, 1353, 1254, 1172, 1030, 854. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.31-7.11 (m, 5H), 6.85 (s, 1H), 6.30 (s, 1H), 5.28 (dd, *J* = 12.1 and 2.5 Hz, 1H), 5.16 (d, *J* = 12.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.8, 155.4, 139.5, 138.4, 128.3, 128.0, 127.6, 124.4, 122.8, 122.4, 121.2 (2CH), 111.5, 104.5, 79.5, 73.3. HRMS (ESI): *m/z* calcd for $C_{16}H_{12}O_2Na$ (M+Na): 259.0735. Found: 259.0732.



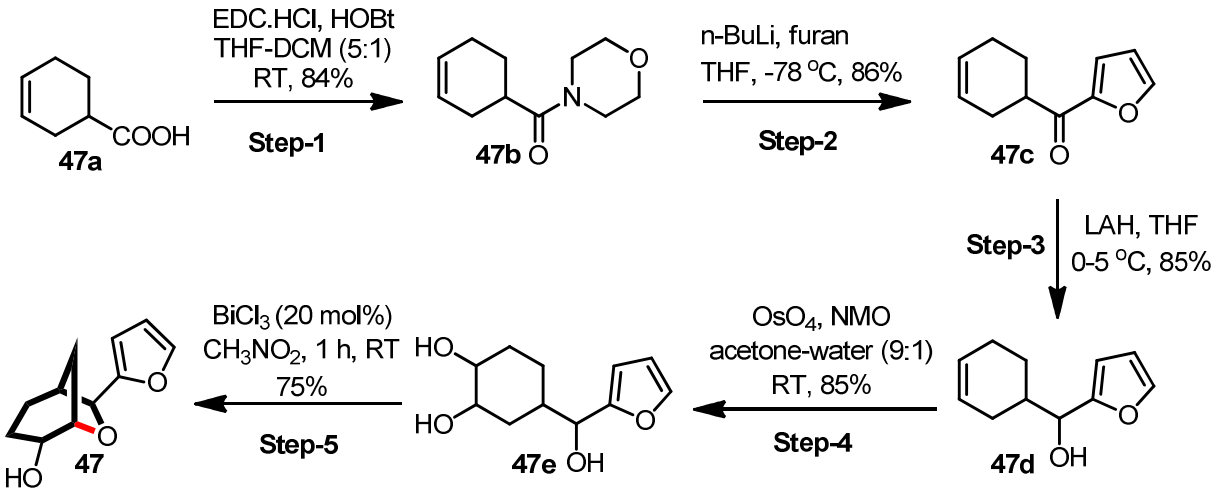
54

2-(Tetrahydro-2*H*-pyran-2-yl)benzofuran (54).

Pale yellow oil. R_f = 0.70 (hexane/EtOAc = 9/1). IR (thin film, neat): ν_{max}/cm^{-1} 2941, 2851, 1371, 1453, 1173, 1086, 1046, 1010, 784. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 7.04, Hz, 1H), 7.18-7.07 (m, 2H), 6.52 (s, 1H), 4.45 (dd, *J* = 10.6 and

2.0 Hz, 1H), 4.06-4.00 (m, 1H), 3.55 (dt, J = 11.3 and 1.36 Hz, 1H), 1.94-1.79 (m, 3H), 1.65-1.48 (m, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 157.8, 154.7, 128.1, 124.1, 122.6, 121.0, 111.3, 102.7, 73.4, 68.8, 29.8, 25.7, 23.1. HRMS (ESI): *m/z* calcd for $C_{13}H_{14}O_2Na$ (M +Na): 225.0891. Found: 225.0895.

Synthesis of the triol 47e and the bicyclic ether 47 (Scheme-2). The bicyclic ether **47** was synthesized from triol **47e** as shown in the following scheme.



Step-1: To a solution of the acid **47a** (500 mg, 4 mmol) in THF-DCM (5:1, 12 mL) at RT were added EDC.HCl (1.15 g, 6 mmol) and HOBt (811 mg, 6 mmol) under nitrogen atmosphere. The reaction mixture was stirred at the same temperature until the starting material was consumed as monitored by TLC (15 h). Decanted the reaction mixture from the solids. Washed the solids with ethyl acetate (2 x 5 mL). The combined organic phase was concentrated and purified by column chromatography (50% hexanes/ethyl acetate) to afford the amide **47b** as colorless viscous oil (650 mg, 84%).

Step-2: Addition of furyllithium to amide **47b** (208 mg, 2.4 mmol), obtained ketone **47c** (146 mg, 86% yield) following literature procedure.[6]

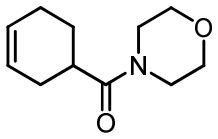
Step-3: The alcohol **47d** was obtained as described for the synthesis of diol **38a**. Ketone **47c** (310 mg, 1.9 mmol) was reduced using LAH to obtain alcohol **47d** (266 mg, 85% yield).

Step-4: To a solution of alcohol **47d** (30 mg, 018 mmol) in acetone-water (1 mL, 9:1) were added NMO (31.6 mg, 027 mmol) followed by OsO_4 (1 mg, 2 mol%) at RT and stirred the reaction mixture until the starting material was consumed as monitored by TLC (20 h). Slurry of sodium thiosulfate in 1 mL water was added to the reaction mixture. Stirred for 1 h at RT, filtered through celite and the residue was washed with ethyl acetate. The aqueous phase was

[6] M. O'Brien, A. Leach, R. J. Armstrong, K. Chonga and R. Sheridanb, *Org. Biomol. Chem.,* 2012, **10**, 2392.

separated and extracted with ethyl acetate (2 x 2 mL). The combined organic phase was dried (Na_2SO_4) and concentrated under reduced pressure. Crude product was purified by column chromatography (ethyl acetate) to afford the triol **47e** (30 mg, 85%).

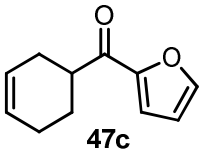
Step-5: Following the procedure described for the synthesis of the cyclic ether **38**, the triol **47e** afforded the bicyclic ether **47**.



47b

(Cyclohex-3-enyl)(morpholino)methanone (47b).

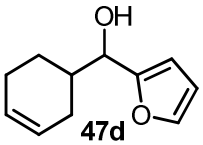
Colorless viscous oil. R_f = 0.6 (hexane/EtOAc = 2/3). IR (thin film): ν_{max}/cm^{-1} 3369, 2855, 1621, 1436, 1234, 1053, 994. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.62 (br s, 2H), 3.60 (t, *J* = 4.1 Hz, 4H), 3.50 (br s, 4H), 2.68-2.57 (tt, *J* = 10.9 and 4.1 Hz, 1H), 2.33 (m, 1H), 2.12-1.92 (m, 3H), 1.77-1.6 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 174.4, 126.5, 125.6, 66.9 ($4CH_2$), 36.2, 28.0, 25.5, 24.8. HRMS (ESI): *m/z* calcd for $C_{11}H_{17}O_2NNa$ (M+Na): 218.1157. Found: 218.1156.



47c

(Cyclohex-3-enyl)(furan-2-yl)methanone (47c).

Pale yellow oil. R_f = 0.6 (hexane/EtOAc = 9/1). IR (thin film, neat): ν_{max}/cm^{-1} 2938, 2878, 1667, 1453, 1373, 1051, 954, 754. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 3.9 Hz, 1H), 7.14 (d, *J* = 3.5 Hz, 1H), 6.46 (dd, *J* = 3.9 and 3.5 Hz, 1H), 5.67 (m, 2H), 3.21-3.19 (m, 1H), 2.34-2.23 (m, 1H), 2.17-2.06 (m, 2H), 1.94-1.87 (m, 1H), 1.71-1.60 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.5, 152.3, 146.3, 126.5, 125.5, 117.2, 112.1, 42.2, 27.3, 25.3, 24.8. HRMS (ESI): *m/z* calcd for $C_{11}H_{12}O_2Na$ (M+Na): 199.0735. Found: 199.0727.

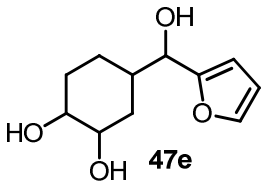


47d

(Cyclohex-3-enyl)(furan-2-yl)methanol (47d).

Pale yellow oil. R_f = 0.6 (hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3425, 2938, 288, 1453, 1373, 1254, 1109, 1051, 954, 867, 754. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.30 (s, 1H), 6.26 (s, 1H), 6.17 (s, 1H), 5.66-5.50 (m, 2H), 4.39 (d, *J* = 7.6 Hz, 1H), 2.09- 1.99 (m, 2H), 1.97-1.83 (m, 2H), 1.76-1.62 (m, 1H), 1.36-1.21 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$):

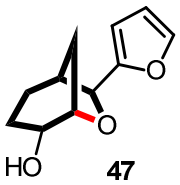
δ 155.0, 141.8, 127.1, 126.0, 110.7, 106.5, 77.3, 72.0, 38.4, 27.5, 24.9, 24.7, 24.5. HRMS (ESI): *m/z* calcd for $C_{11}H_{14}O_2Na$ (M+Na): 217.0631. Found: 217.0832.



47e

4-(Furan-2-yl(hydroxy)methyl)cyclohexane-1,2-diol (47e).

Pale yellow oil. R_f = 0.6 (EtOAc). IR (thin film, neat): ν_{max}/cm^{-1} 3324, 2924, 1563, 1260, 1021, 765, 561. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 (s, 1H), 6.31 (s, 1H), 6.2 (s, 1H), 4.34 (dt, J = 9.5 and 2.8 Hz, 1H), 3.98 (s, 1H), 3.63-3.47 (m, 2H), 1.96-1.81 (m, 2H), 1.51-1.32 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.3, 141.4, 109.5, 106.1, 71.5, 71.3, 68.6, 41.3, 29.3, 27.8, 21.3. HRMS (ESI): *m/z* calcd for $C_{11}H_{16}O_4K$ (M+K): 251.0686. Found: 251.0654.

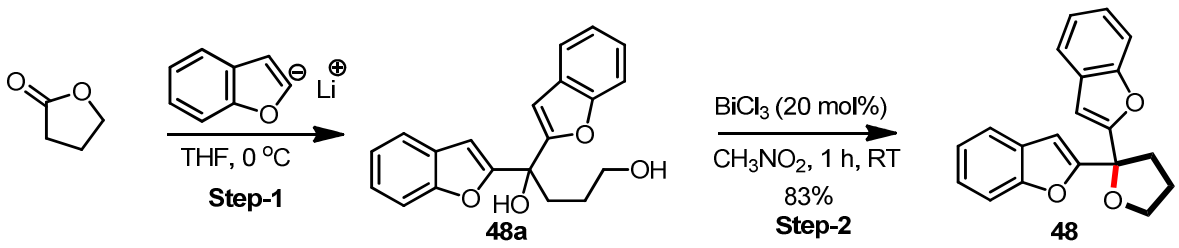


47

7-(Furan-2-yl)-6-oxabicyclo[3.2.1]octan-4-ol (47).

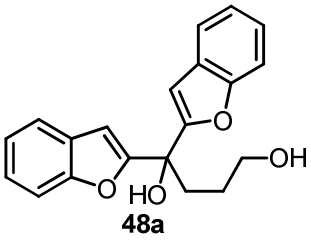
Colorless oil. R_f = 0.5 (hexane/EtOAc = 3/2). IR (thin film, neat): ν_{max}/cm^{-1} 2924, 2855, 1563, 1434, 1260, 1218, 1021, 959, 784, 765, 561. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30 (s, 1H), 6.39 (s, 1H), 6.20 (s, 1H), 4.88 (s, 1H), 4.40 (d, *J* = 6.7 Hz, 1H), 4.15 (q, *J* = 7.0 Hz, 2H), 3.54 (t, *J* = 7.8 Hz, 1H), 2.53 (s, 1H), 2.35-1.90 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.7, 141.9, 106.1 (2C), 81.5, 77.9, 71.9, 38.3, 34.2, 29.2, 28.1. HRMS (ESI): *m/z* calcd for $C_{11}H_{14}O_3Na$ (M +Na): 217.0841. Found: 217.0860.

Synthesis of the diol 48a and the bicyclic ether 48 (Scheme-2). The bicyclic ether **48** was synthesized from diol **48a** as shown in the following scheme.



Step-1: The diol **48a** was synthesized in a procedure described for the diols **41a**, **42a**, **46a** and **54a** using 2 equivalents of benzofuranyllithium.

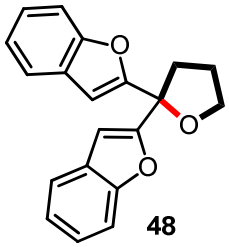
Step-2: Following the procedure described for the synthesis of the cyclic ether **38**, the diol **48a** afforded the bicyclic ether **48** in 83% yield.



48a

1,1-Di(benzofuran-2-yl)butane-1,4-diol (48a).

Pale yellow oil. R_f = 0.6 (hexane/EtOAc = 1/1). IR (thin film, neat): ν_{max}/cm^{-1} 3334, 2927, 1453, 1253 745, 542. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.31-7.20 (m, 4H), 6.79 (s, 2H), 3.74 (t, *J* = 5.8 Hz, 2H), 2.62 (t, *J* = 7.0 Hz, 2H), 1.77-1.68 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): 158.7 (2C), 154.8 (2C), 128.0 (2C), 124.2 (2CH), 122.9 (2CH), 121.2 (2CH), 111.3 (2CH), 103.8 (2CH), 72.7, 62.7, 36.0, 26.6. HRMS (ESI): *m/z* calcd for $C_{20}H_{18}O_4Na$ (M+Na): 345.1103. Found: 345.1102.

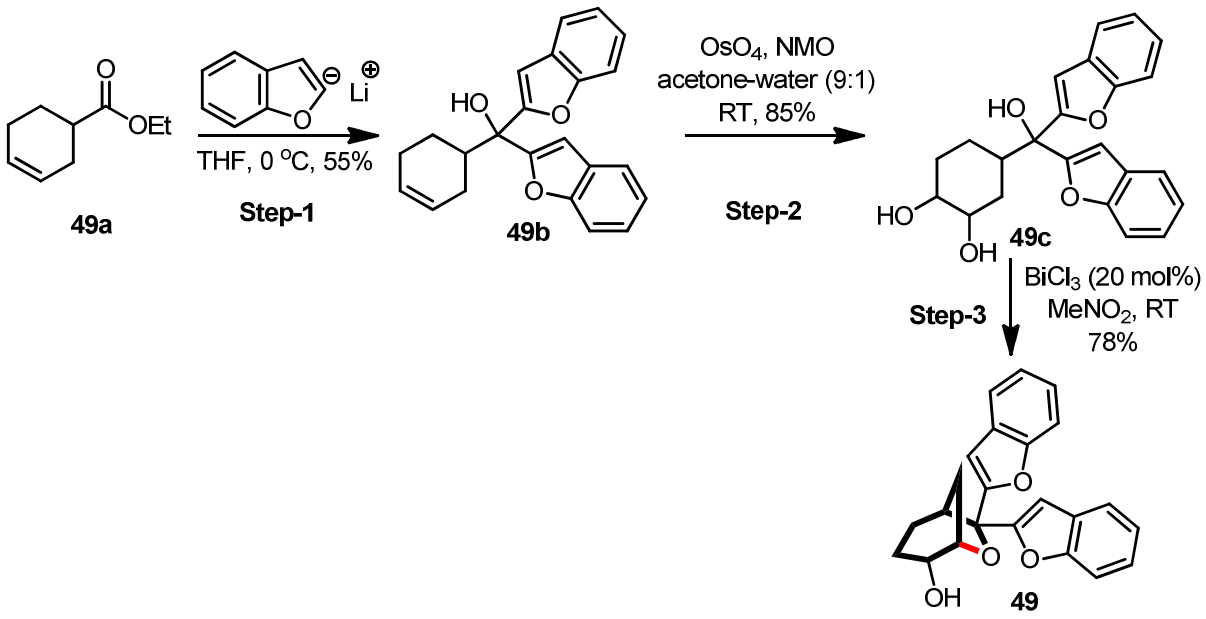


48

2,2'-(Tetrahydrofuran-2,2-diyl)bis(benzofuran) (48).

Pale yellow Colored oil; R_f = 0.60 (hexane/EtOAc = 9/1); IR (thin film, neat): νmax /cm^{-1} 3050, 2858, 1602, 1456, 1353, 1254, 1172, 1030, 854; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.3 Hz, 2H), 7.44 (d, *J* = 7.48 Hz, 2H), 7.16-7.17 (m, 4H), 6.70 (s, 2H), 4.17 (t, *J* = 6.84 Hz, 2H), 2.74 (t, *J* = 6.9 Hz, 2H), 2.17- 21.0 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.5 (2C), 155.16 (2C), 128.0 (2CH), 124.0 (2CH), 122.8 (2CH), 121.1 (2CH), 111.4 (2CH), 104.3 (2CH), 80,8 , 69.3, 35.6, 26.0. HRMS (ESI): *m/z* calcd for $C_{20}H_{16}O_3Na$ (M+Na): 327.0997. Found: 327.0996.

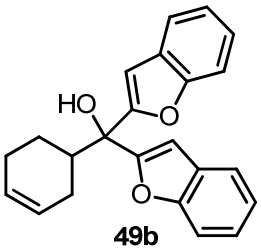
Synthesis of the triol 49a and the bicyclic ether 49 (Scheme-2). The bicyclic ether **49** was synthesized from the triol **49a** as shown in the following scheme.



Step-1: Addition of benzofuranyllithium to ester **49a** (500 mg, 3.2 mmol) by following the procedure as described for the diol **48a**, obtained the tertiary alcohol **49b** (312 mg, 55%).

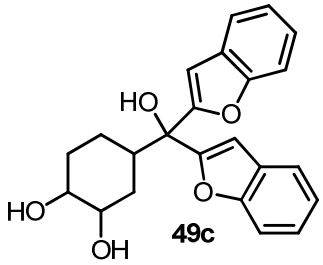
Step-2: Dihydroxylation of the tertiary alcohol **49b** (200 mg, 0.58 mmol) afforded the triol **49c** (209 mg, 85%) following the procedure as described for the triol **47e**.

Step-3: Following the procedure described for the synthesis of the cyclic ether **38**, the triol **49c** afforded the bicyclic ether **49**.



Di(benzofuran-2-yl)(cyclohex-3-enyl)methanol (49b).

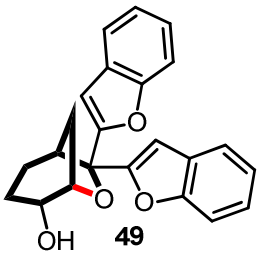
Pale yellow oil. R_f = 0.6 (hexane/EtOAc = 1/1). IR (thin film, neat): ν_{max}/cm^{-1} 3025, 2929, 2840, 1672, 1567, 1467, 1396, 1256, 1012, 883, 792. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.6 Hz, 2H), 7.42-7.37 (m, 2H), 7.22-7.11 (m, 4H), 6.73 (s, 1H), 6.72 (s, 1H), 5.57 (2dt, *J* = 4.2 and 1.4 Hz, 2H), 2.88 (s, 1H), 2.71 (tt, *J* = 11.1, 9.9 and 2.3 Hz, 1H), 2.15-1.99 (m, 2H), 1.83 (dt, *J* = 12.5 and 2.4 Hz, 1H), 1.78 (dt, *J* = 12.5 and 2.4 Hz, 1H), 1.45-1.32 (m, 1H), 1.29-1.13 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): 157.9 (2C), 154.7 (2C), 128.0 (2C), 126.8, 126.2, 124.2 (2CH), 122.9 (2CH), 121.1 (2CH), 111.1 (2CH), 103.9 (2CH), 76.1, 41.9, 25.9, 25.8, 23.3. HRMS (ESI): *m/z* calcd for $C_{23}H_{20}O_3Na$ (M+Na): 367.1310. Found: 367.1299.



49c

4-(Di(benzofuran-2-yl)(hydroxy)methyl)cyclohexane-1,2-diol (49c).

Pale yellow viscous oil. R_f = 0.6 (hexane/EtOAc = 1/4). IR (thin film, neat): ν_{max}/cm^{-1} 3385, 2926, 2853, 1454, 1252, 1158, 791. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.47-7.36 (m, 4H), 7.19-7.06 (m, 4H), 6.70 (s, 2H), 3.89 (s, 2H), 3.80 (s, 1H), 3.36 (s, 1H), 3.21 (s, 1H), 2.80 (tt, *J* = 12.4 and 3.8 Hz, 1H), 1.73-1.19 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): 158.0, 157.9, 154.7 (2C), 128.0 (2C), 124.2 (2CH), 122.9 (2CH), 121.7 (2CH), 111.4 (2CH), 103.8 (2CH), 76.0, 71.6, 69.4, 42.5, 31.5, 24.6, 19.7. HRMS (ESI): *m/z* calcd for $C_{23}H_{22}O_5Na$ (M+Na): 401.1362. Found: 401.1363.



49

7,7-Di(benzofuran-2-yl)-6-oxa-bicyclo[3.2.1]octan-4-ol (49).

Colorless solid. M. P. = 161-163 ^oC. R_f = 0.6 (hexane/EtOAc = 3/2). IR (KBr): ν_{max}/cm^{-1} 3386, 2929, 145, 1248, 1166, 1094, 1093, 1010, 750, 462. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59-7.46 (m, 4H), 7.32-7.16 (m, 4H), 6.90 (s, 1H), 6.74 (s, 1H), 4.67 (d, *J* = 7.8 Hz, 1H), 3.64 (t, *J* = 6.6 Hz, 1H), 3.27 (s, 1H), 2.55-2.45 (m, 1H), 1.94-1.81 (m, 3H), 1.70-1.60 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.8, 157.7, 154.9, 154.9, 128.0, 124.1, 124.0, 122.9, 122.8, 127.9, 121.1, 121.0, 111.5, 111.4, 103.9, 102.9, 84.1, 82.6, 72.1, 41.1, 35.3, 29.7, 25.8. HRMS (ESI): *m/z* calcd for $C_{23}H_{20}O_3Na$ (M +Na): 383.1259. Found: 383. 1269.

Crystal Structure Report of bicyclic ether 49 (CCDC 931682)

Structure of the bicyclic ether **49** was further confirmed by single crystal X-ray diffraction analysis. Following are the details.

A colorless rectangular-like specimen of $C_{23}H_{18}O_4$, approximate dimensions 0.25 mm x 0.25 mm x 0.30 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

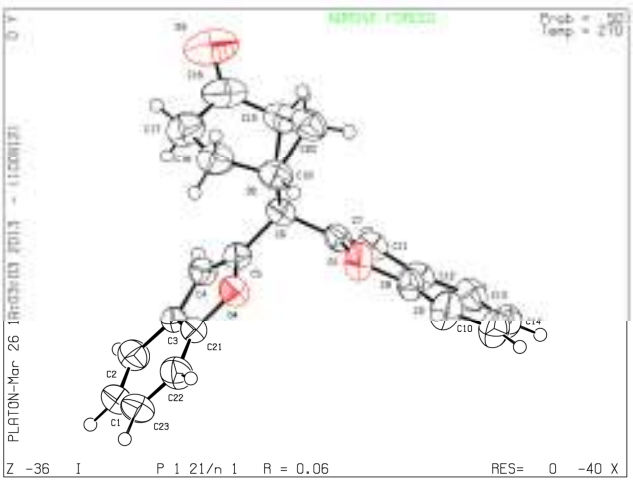


Table 1: Data collection details for SCI125_SE106.

Axis	dx/ mm	2θ/°	ω/°	φ/°	χ/°	Width /°	Frames	Time /s	Wavelength /Å	Voltage/ kV	Current/mA	Temperature /K
Phi	59.195	27.50	10.40	-13.87	-31.85	0.50	646	20.00	0.71073	50	30.0	n/a
Phi	59.195	-12.50	-23.38	-313.05	82.04	0.50	739	20.00	0.71073	50	30.0	n/a

A total of 1385 frames were collected. The total exposure time was 7.69 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 11037 reflections to a maximum θ angle of 25.35° (0.83 Å resolution), of which 3149 were independent (average redundancy 3.505, completeness = 99.1%, R_{int} = 5.12%, R_{sig} = 9.81%) and 1449 (46.01%) were greater than $2\sigma(F^2)$.The final cell constants of a = 10.594(7) Å, b = 12.392(8) Å, c = 13.698(9) Å, β = 105.41(2)°, volume = 1734.(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 1466 reflections above 20 σ(I) with 4.507° < 2θ < 40.20°.Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.914.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/n 1, with Z = 4 for the formula unit, $C_{23}H_{18}O_4$.The final anisotropic full-matrix least-squares refinement on F^2 with 244 variables converged at R1 = 5.69%, for the observed data and wR2 = 15.34% for all data. The goodness-of-fit was 0.933. The largest peak in the final difference electron density synthesis was 0.303 $e^-/Å^3$ and the

largest hole was -0.208 $e^-/Å^3$ with an RMS deviation of 0.048 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.373 g/cm^3 and F(000), 752 e^-.

Table 2. Sample and crystal data for SCI125_SE106.

Identification code	SCI125_SE106	
Chemical formula	$C_{23}H_{18}O_4$	
Formula weight	358.37	
Temperature	270(2) K	
Wavelength	0.71073 Å	
Crystal size	0.25 x 0.25 x 0.30 mm	
Crystal habit	colorless rectangular	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 10.594(7) Å	α = 90°
	b = 12.392(8) Å	β = 105.41(2)°
	c = 13.698(9) Å	γ = 90°
Volume	1734.(2) $Å^3$	
Z	4	
Density (calculated)	1.373 Mg/cm^3	
Absorption coefficient	0.094 mm^{-1}	
F(000)	752	

Table 3. Data collection and structure refinement for SCI125_SE106.

Theta range for data collection	2.17 to 25.35°
Index ranges	-10<=h<=12, -11<=k<=14, -14<=l<=16
Reflections collected	11037
Independent reflections	3149 [R(int) = 0.0512]
Coverage of independent reflections	99.1%
Absorption correction	multi-scan
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F^2

Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3149 / 0 / 244	
Goodness-of-fit on F^2	0.933	
Final R indices	1449 data; $I>2\sigma(I)$	R1 = 0.0569, wR2 = 0.1176
	all data	R1 = 0.1540, wR2 = 0.1534
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0708P)^2+0.0000P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.303 and -0.208 eÅ^{-3}	
R.M.S. deviation from mean	0.048 eÅ^{-3}	

Table 4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for SCI125_SE106.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
O1	0.4844(2)	0.97676(18)	0.85050(14)	0.0602(7)
O2	0.35822(19)	0.04261(16)	0.58827(14)	0.0510(6)
O3	0.3612(3)	0.2620(3)	0.4447(2)	0.1216(12)
O4	0.19821(19)	0.04400(16)	0.78775(14)	0.0501(6)
C1	0.8256(3)	0.9447(3)	0.7326(3)	0.0690(11)
C2	0.8894(3)	0.9431(3)	0.6592(3)	0.0611(10)
C3	0.0169(3)	0.9785(2)	0.6824(2)	0.0428(8)
C4	0.1146(3)	0.9871(2)	0.6299(2)	0.0453(8)
C5	0.2195(3)	0.0265(2)	0.6952(2)	0.0411(8)
C6	0.3553(3)	0.0483(2)	0.6919(2)	0.0435(8)
C7	0.4430(3)	0.9618(3)	0.7478(2)	0.0434(8)
C8	0.5603(3)	0.8888(3)	0.8873(2)	0.0501(9)
C9	0.6241(3)	0.8716(3)	0.9861(2)	0.0704(11)
C10	0.6956(3)	0.7800(3)	0.0069(3)	0.0709(11)
C11	0.4876(3)	0.8709(3)	0.7207(2)	0.0457(8)
C12	0.5648(3)	0.8211(3)	0.8101(2)	0.0446(8)
C13	0.6389(3)	0.7285(3)	0.8331(2)	0.0576(9)

	x/a	y/b	z/c	U(eq)
C14	0.7026(3)	0.7094(3)	0.9321(3)	0.0635(10)
C15	0.4390(4)	0.1288(3)	0.5686(3)	0.0684(10)
C16	0.3509(4)	0.2178(3)	0.5191(3)	0.0841(13)
C17	0.2516(4)	0.2515(3)	0.5731(3)	0.0752(11)
C18	0.3040(3)	0.2471(3)	0.6856(3)	0.0656(10)
C19	0.4047(3)	0.1611(2)	0.7252(2)	0.0558(9)
C20	0.5146(3)	0.1695(3)	0.6723(3)	0.0685(10)
C21	0.0716(3)	0.0140(2)	0.7783(2)	0.0452(8)
C22	0.0087(4)	0.0184(3)	0.8525(2)	0.0634(10)
C23	0.8835(4)	0.9820(3)	0.8275(3)	0.0705(10)

Table 5. Bond lengths (Å) for SCI125_SE106.

O1-C8	1.369(3)	O1-C7	1.370(3)
O2-C6	1.430(3)	O2-C15	1.438(4)
O3-C16	1.188(4)	O4-C5	1.363(3)
O4-C21	1.364(3)	C1-C2	1.352(4)
C1-C23	1.363(5)	C1-H1	0.93
C2-C3	1.375(4)	C2-H2	0.93
C3-C21	1.361(4)	C3-C4	1.412(4)
C4-C5	1.321(4)	C4-H4	0.93
C5-C6	1.476(4)	C6-C7	1.490(4)
C6-C19	1.520(4)	C7-C11	1.313(4)
C8-C9	1.359(4)	C8-C12	1.360(4)
C9-C10	1.352(4)	C9-H9	0.93
C10-C14	1.364(4)	C10-H10	0.93
C11-C12	1.421(4)	C11-H11	0.93
C12-C13	1.379(4)	C13-C14	1.366(4)
C13-H13	0.93	C14-H14	0.93
C15-C16	1.487(5)	C15-C20	1.519(4)
C15-H15	0.98	C16-C17	1.496(5)
C17-C18	1.494(4)	C17-H17A	0.97
C17-H17B	0.97	C18-C19	1.503(4)
C18-H18A	0.97	C18-H18B	0.97
C19-C20	1.530(4)	C19-H19	0.98
C20-H20A	0.97	C20-H20B	0.97

C21-C22	1.357(4)	C22-C23	1.356(5)
C22-H22	0.93	C23-H23	0.93

Table 6. Bond angles (°) for SCI125_SE106.

C8-O1-C7	105.5(2)	C6-O2-C15	108.7(2)
C5-O4-C21	105.7(2)	C2-C1-C23	121.8(3)
C2-C1-H1	119.1	C23-C1-H1	119.1
C1-C2-C3	118.6(3)	C1-C2-H2	120.7
C3-C2-H2	120.7	C21-C3-C2	117.8(3)
C21-C3-C4	106.6(3)	C2-C3-C4	135.6(3)
C5-C4-C3	106.4(3)	C5-C4-H4	126.8
C3-C4-H4	126.8	C4-C5-O4	111.8(3)
C4-C5-C6	134.3(3)	O4-C5-C6	113.8(2)
O2-C6-C5	107.4(2)	O2-C6-C7	107.4(2)
C5-C6-C7	109.5(2)	O2-C6-C19	104.2(2)
C5-C6-C19	114.8(3)	C7-C6-C19	112.9(2)
C11-C7-O1	111.5(3)	C11-C7-C6	133.9(3)
O1-C7-C6	114.6(3)	C9-C8-C12	124.5(3)
C9-C8-O1	125.4(3)	C12-C8-O1	110.1(3)
C10-C9-C8	116.4(3)	C10-C9-H9	121.8
C8-C9-H9	121.8	C9-C10-C14	121.3(3)
C9-C10-H10	119.4	C14-C10-H10	119.4
C7-C11-C12	107.2(3)	C7-C11-H11	126.4
C12-C11-H11	126.4	C8-C12-C13	118.1(3)
C8-C12-C11	105.8(3)	C13-C12-C11	136.1(3)
C14-C13-C12	118.2(3)	C14-C13-H13	120.9
C12-C13-H13	120.9	C10-C14-C13	121.6(3)
C10-C14-H14	119.2	C13-C14-H14	119.2
O2-C15-C16	107.6(3)	O2-C15-C20	105.3(3)
C16-C15-C20	106.9(3)	O2-C15-H15	112.2
C16-C15-H15	112.2	C20-C15-H15	112.2
O3-C16-C15	122.9(5)	O3-C16-C17	122.2(5)
C15-C16-C17	114.9(4)	C18-C17-C16	112.5(3)
C18-C17-H17A	109.1	C16-C17-H17A	109.1
C18-C17-H17B	109.1	C16-C17-H17B	109.1
H17A-C17-H17B	107.8	C17-C18-C19	115.6(3)

C17-C18-H18A	108.4	C19-C18-H18A	108.4
C17-C18-H18B	108.4	C19-C18-H18B	108.4
H18A-C18-H18B	107.5	C18-C19-C6	112.9(3)
C18-C19-C20	109.7(3)	C6-C19-C20	99.5(3)
C18-C19-H19	111.4	C6-C19-H19	111.4
C20-C19-H19	111.4	C15-C20-C19	98.2(3)
C15-C20-H20A	112.1	C19-C20-H20A	112.1
C15-C20-H20B	112.1	C19-C20-H20B	112.1
H20A-C20-H20B	109.8	C22-C21-C3	124.7(3)
C22-C21-O4	125.7(3)	C3-C21-O4	109.6(3)
C23-C22-C21	116.1(3)	C23-C22-H22	122.0
C21-C22-H22	122.0	C22-C23-C1	121.1(3)
C22-C23-H23	119.5	C1-C23-H23	119.5

Table 7. Anisotropic atomic displacement parameters (Å^2) for SCI125_SE106.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.0603(14)	0.0724(17)	0.0439(14)	-0.0087(12)	0.0069(11)	0.0184(13)
O2	0.0546(14)	0.0564(15)	0.0446(13)	-0.0021(11)	0.0179(10)	-0.0129(11)
O3	0.169(3)	0.109(3)	0.098(2)	0.016(2)	0.056(2)	-0.024(2)
O4	0.0440(14)	0.0633(15)	0.0423(13)	-0.0066(11)	0.0104(10)	-0.0034(11)
C1	0.047(2)	0.075(3)	0.087(3)	0.016(2)	0.022(2)	-0.0056(19)
C2	0.051(2)	0.065(2)	0.065(2)	0.0033(19)	0.0105(19)	-0.0095(18)
C3	0.0375(19)	0.0430(19)	0.046(2)	0.0044(15)	0.0079(15)	0.0003(16)
C4	0.0433(19)	0.051(2)	0.0408(18)	-0.0015(15)	0.0092(16)	-0.0045(16)
C5	0.0447(19)	0.0412(19)	0.0384(18)	-0.0020(15)	0.0126(15)	-0.0008(15)
C6	0.0424(19)	0.052(2)	0.0367(18)	-0.0067(16)	0.0118(14)	-0.0068(16)
C7	0.0359(18)	0.057(2)	0.0369(19)	-0.0067(16)	0.0092(14)	-0.0053(16)

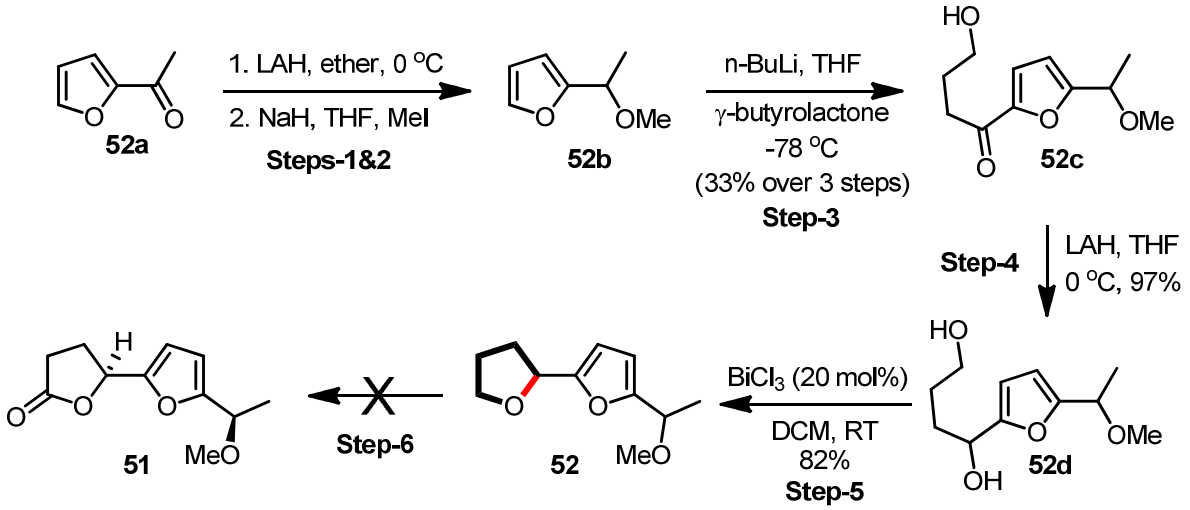
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C8	0.045(2)	0.058(2)	0.047(2)	-0.0044(18)	0.0127(16)	0.0101(18)
C9	0.079(3)	0.084(3)	0.046(2)	-0.006(2)	0.0119(19)	0.025(2)
C10	0.070(3)	0.083(3)	0.056(2)	0.002(2)	0.0101(19)	0.018(2)
C11	0.0438(19)	0.052(2)	0.0430(19)	-0.0118(16)	0.0148(16)	-0.0079(16)
C12	0.0370(18)	0.052(2)	0.047(2)	-0.0057(18)	0.0157(15)	-0.0076(16)
C13	0.052(2)	0.056(2)	0.064(3)	-0.0101(18)	0.0153(18)	-0.0048(18)
C14	0.058(2)	0.060(2)	0.071(3)	0.002(2)	0.015(2)	0.0085(18)
C15	0.067(2)	0.071(3)	0.076(3)	0.001(2)	0.035(2)	-0.011(2)
C16	0.104(3)	0.083(3)	0.069(3)	0.006(3)	0.030(3)	-0.032(3)
C17	0.089(3)	0.062(3)	0.077(3)	0.005(2)	0.026(2)	0.000(2)
C18	0.077(3)	0.048(2)	0.076(3)	-0.0103(19)	0.028(2)	-0.008(2)
C19	0.056(2)	0.051(2)	0.061(2)	-0.0084(18)	0.0159(17)	-0.0135(18)
C20	0.057(2)	0.065(2)	0.085(3)	-0.007(2)	0.021(2)	-0.0202(19)
C21	0.040(2)	0.047(2)	0.051(2)	0.0054(16)	0.0159(16)	0.0018(16)
C22	0.062(3)	0.080(3)	0.053(2)	0.0007(19)	0.0240(18)	0.005(2)
C23	0.064(3)	0.083(3)	0.077(3)	0.017(2)	0.041(2)	0.006(2)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for SCI125_SE106.

	x/a	y/b	z/c	U(eq)
H1	-0.2602	-0.0803	0.7178	0.083
H2	-0.1520	-0.0815	0.5945	0.073
H4	0.1067	-0.0314	0.5628	0.054
H9	0.6190	-0.0798	1.0366	0.085
H10	0.7407	-0.2352	1.0735	0.085
H11	0.4716	-0.1559	0.6551	0.055
H13	0.6453	-0.3196	0.7825	0.069
H14	0.7520	-0.3532	0.9490	0.076
H15	0.4971	0.1049	0.5279	0.082

	x/a	y/b	z/c	U(eq)
H17A	0.2232	0.3245	0.5531	0.09
H17B	0.1758	0.2046	0.5527	0.09
H18A	0.2312	0.2359	0.7150	0.079
H18B	0.3423	0.3166	0.7089	0.079
H19	0.4390	0.1656	0.7989	0.067
H20A	0.5445	0.2432	0.6699	0.082
H20B	0.5883	0.1233	0.7033	0.082
H22	0.0491	0.0447	0.9168	0.076
H23	-0.1636	-0.0175	0.8760	0.085

Synthesis of the diol 52d and efforts towards the first total synthesis of furanopolyketide 51 (Scheme-2). The diol **52d** required for the $BiCl_3$ catalyzed cyclization is prepared as shown in the following scheme starting from acetylfuran **52a**.



Steps-1, 2&3: To a solution of acetylfuran **52a** (1 g, 9.1 mmol) in dry diethyl ether at 0-5 °C was added LAH (1.13 g, 13.6 mmol) in portions under nitrogen atmosphere. After 30 min, diluted the reaction mixture with diethyl ether and subsequently quenched with saturated ammonium chloride solution (1-2 mL). Filtered the reaction mixture through short celite pad,

washed the contents with diethyl ether. Concentrated the ether layer on a rotary evaporator at 35-40 ^{o}C (without applying vacuum) and proceeded to next step without further purification.

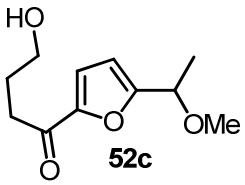
The crude alcohol obtained above was converted to methoxy ether **52b** in a procedure that was reported earlier,[7] obtained after distillation 500 mg of methoxy ether **52b**.

Following the procedure reported for the synthesis of diol **38a**, the methoxy ether **52b** (500 mg, 3.96 mmol) was converted to the keto-alcohol **52c** (631 mg, 33% over three steps).

Step-4: The keto-alcohol **52c** (200 mg, 0.94 mmol) was converted to the diol **52d** (193 mg, 97%) following the procedure described for the diol **38a**.

Step-5: General procedure (described for the synthesis of the cyclic ether **38)** was followed for the conversion of **52d** to **52**, but surprisingly the yield was poor (16%). When the reaction was performed in dichloromethane as solvent, the cyclic ether **52** was obtained in 82% yield.

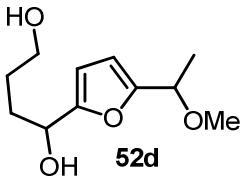
Step-6: At this stage, our task is reduced to converting the tetrahydrofuran moiety in **52** to butyrolactone as in the natural product **51**. The bisether **52** is found to be very sensitive to oxidative conditions. All our efforts[6] to convert the tetrahydrofuran **52** to the lactone **51** were unsuccessful, most likely because of the presence of competing methoxy ether functionality and a sensitive furan moiety. IR of the crude reaction mixture shows carbonyl stretch at 1770 cm^{-1}, but ^{1}H NMR of shows the absence of OMe group and furan moiety.



52c

4-Hydroxy-1-(5-(1-methoxyethyl)furan-2-yl)butan-1-one (52c).

Pale yellow oil. R_f = 0.6 (hexane/EtOAc = 3/7). IR (thin film, neat): ν_{max}/cm^{-1} 3325, 2954, 2874, 1674, 1458, 1256, 1109, 754, 567. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.17 (d, *J* = 3.5 Hz, 1H), 6.41 (d, *J* = 3.5 Hz, 1H), 4.42 (q, *J* = 6.6 Hz, 1H), 3.70 (dt, *J* = 6.0 and 0.88 Hz, 2H), 3.32 (s, 3H), 2.96 (t, *J* = 7.0 Hz, 2H), 1.97 (m, 2H), 1.51 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 189.5, 160.6, 151.8, 118.1, 108.9, 72.4, 62.0, 56.8, 35.0, 26.8, 19.7. HRMS (ESI): *m/z* calcd for $C_{11}H_{16}O_4Na$ (M+Na): 235.0947. Found: 235.0950.

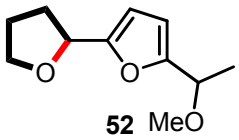


52d

1-(5-(1-Methoxyethyl)furan-2-yl)butane-1,4-diol (52d).

[7] L. Wang, S. K. Meegalla, C. –L. Fang, N. Taylor and R. Rodrigo, *Can. J. Chem.,* 2002, **80**, 728.

Pale yellow oil. R_f = 0.6 (EtOAc/MeOH = 9/1). IR (thin film, neat): ν_{max}/cm^{-1} 3354, 2954, 2874, 1253, 1108, 1098, 854, 763. **^{1}H NMR** (400 MHz, CD_3OD): δ 6.28 (d, *J* = 2.7 Hz, 1H), 6.23 (d, *J* = 2.7 Hz, 1H), 4.62 (t, *J* = 6.5 Hz, 1H), 4.38 (q, *J* = 6.5 Hz, 1H), 3.57 (t, *J* = 6.5 Hz, 2H), 3.26 (s, 3H), 1.92-1.79 (m, 2H), 1.72-1.51 (m, 2H), 1.47 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, CD_3OD): δ 156.0, 153.0, 107.0, 105.8, 71.0, 66.8, 61.3, 54.8, 31.7, 28.3, 18.0. HRMS (ESI): *m/z* calcd for $C_{11}H_{18}O_4Na$ (M+Na): 237.1103. Found: 237.1117.

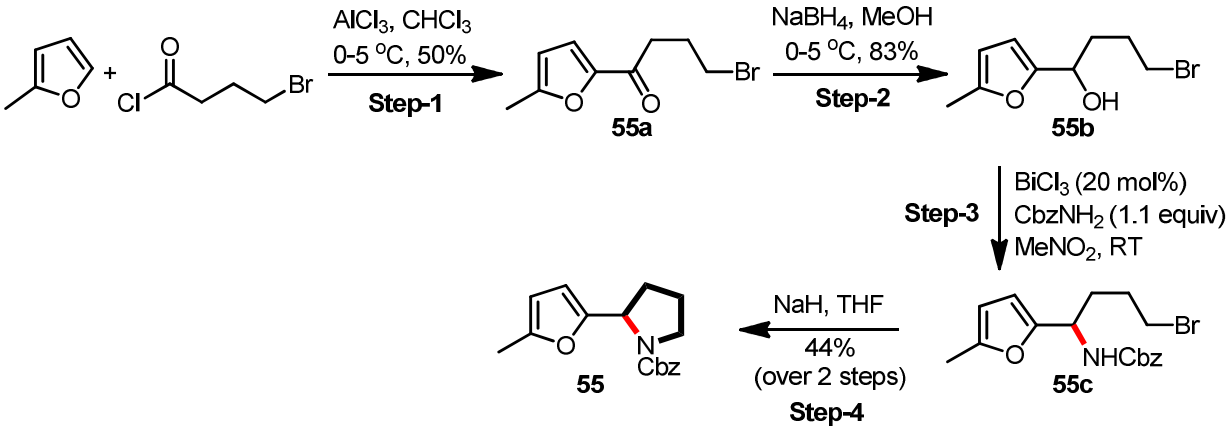


52

2-(Tetrahydrofuran-2-yl)-5-(1-methoxyethyl)furan (52).

Colorless oil. R_f = 0.5 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 2924, 2855, 1564, 1340, 240, 1174, 1110, 784, 543. **^{1}H NMR** (400 MHz, C_3D_6O): δ 6.25 (s, 2H), 4.83 (t, *J* = 6.4 Hz, 1H), 4.32 (q, *J* = 6.6 Hz, 1H), 3.87 (t, *J* = 6.8 Hz, 1H), 3.78 (t, *J* = 6.8 Hz, 1H), 3.20 (s, 3H), 2.23 (m, 1H), 2.08 (m, 3H), 1.42 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (100 MHz, C_3D_6O): δ 155.2, 155.0, 107.4, 106.6, 73.5, 71.6, 67.5, 55.1, 30.1, 25.6, 18.8. HRMS (ESI): *m/z* calcd for $C_{11}H_{16}O_3Na$ (M+Na): 219.0997. Found: 219.0995.

Synthesis of the alcohol 55b, amine 55c and pyrrolidine 55 (Scheme-2). Pyrrolidine **55** was synthesized as shown in the following scheme.



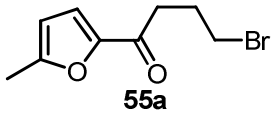
Step-1: 4-Bromobutanoyl chloride (400 mg, 2.1 mmol) was dissolved in dry chloroform (3 mL) under an atmosphere of nitrogen and $AlCl_3$ (1.4 g, 10.7 mmol) was added at 0-5 °C. The reaction mixture was stirred for 2 h when a solution of 2-methylfuran (236 mg, 3.4 mmol) in chloroform (2 mL) was added drop wise over 15 minutes. The reaction mixture was stirred for a further 1 h when it was poured carefully onto ice. The organic layer was separated, washed sequentially with water and saturated sodium bicarbonate solution, dried (Na_2SO_4)

and evaporated to dryness. Purification by column chromatography (hexanes/ethyl acetate: 15/1) afforded pale brown viscous oil **55a** (440 mg, 50%).

Step-2: To a solution of crude bromoketone **55a** (150 g, 0.65 mmol) in methanol (2 mL) at 0-5 ^{o}C was added a weighed amount of sodium borohydride (28 mg, 0.78 mmol) under nitrogen atmosphere. The reaction mixture was stirred at the same temperature until the starting material was consumed as monitored by TLC (20 min) and the reaction mixture was diluted carefully with saturated ammonium chloride solution (1 mL). Solvent (methanol) was removed under reduced pressure. Diluted with water (2 mL) and extracted with ethyl acetate (2 x 5 mL). Combined the organic layers, concentrated and purified by alumina column chromatography (20% hexanes/ethyl acetate) to afford an *unstable* bromoalcohol **55b** (125 mg, 83%).

Step-3: Following the procedure described for the synthesis of the cyclic ether **38**, the bromoalcohol **55b** afforded the amine **55c**.

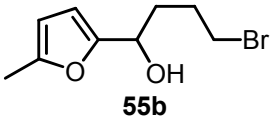
Step-4: The amine **55c** was converted to cyclic amine **55** following sodium hydride mediated cyclization procedure described in literature.[8]



55a

4-Bromo-1-(5-methylfuran-2-yl)butan-1-one (55a).

Brown viscous oil. M.P. = 54-56 ^{o}C. R_f = 0.6 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 2945, 2854, 1687, 1545, 1098, 754. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.05 (s, 1H), 6.07 (s, 1H), 3.41 (t, *J* = 6.3 Hz, 2H), 2.86 (t, *J* = 7.0 Hz, 2H), 2.29 (s, 3H), 2.16 (q, *J* = 6.7 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 187.2, 157.9, 151.2, 119.4, 109.0, 36.6, 32.3, 27.3, 14.1. HRMS (ESI): *m/z* calcd for $C_9H_{11}BrO_2K$ (M+K): 268.9579. Found: 268.9573.



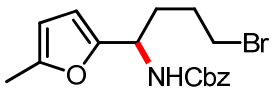
55b

4-Bromo-1-(5-methylfuran-2-yl)butan-1-ol (55b).

Pale yellow oil, rapidly decomposes at room temperature. R_f = 0.6 (hexanes/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 3439, 2923, 2977, 2871, 1449, 1384, 1052, 1019, 793. **^{1}H NMR** (400 MHz, CD_3OD): δ 6.22 (s, 1H), 5.93 (s, 1H), 4.17 (t, *J* = 5.9 Hz, 1H), 3.29 (t, *J* = 1.6 Hz,

[8] J. –I. Yamaguchi and M. Ueki, *Chem Lett.,* **1996**, 621.

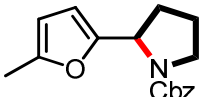
2H), 2.28 (s, 3H), 2.05-1.79 (m, 4H). **^{13}C NMR** (100 MHz, CD_3OD): δ 152.9, 152.2, 109.1, 105.5, 75.5, 32.7, 32.1, 28.9, 12.0.



55c

Benzyl 4-bromo-1-(5-methylfuran-2-yl)butylcarbamate (55c).

Pale yellow oil. R_f = 0.5 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max} /cm^{-1} 3320, 1698, 1567, 1434, 1301, 1246, 1038, 746, 698. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.44-7.31 (m, 5H), 6.08 (s, 1H), 5.89 (s, 1H), 5.19 (s, 2H), 4.79 (dd, *J* = 6.4 and 1.3 Hz, 1H), 3.42 (t, *J* = 6.0 Hz, 2H), 2.27 (s, 3H), 2.06-1.84 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.6, 151.7, 136.3, 128.5 (4CH), 128.2, 128.1, 107.0, 106.0, 66.9, 48.6, 32.2, 32.9, 29.15, 13.6. HRMS (ESI): *m/z* calcd for $C_{17}H_{19}BrNNaO_3$ (M+Na-1): 387.0446. Found: 387.0525.

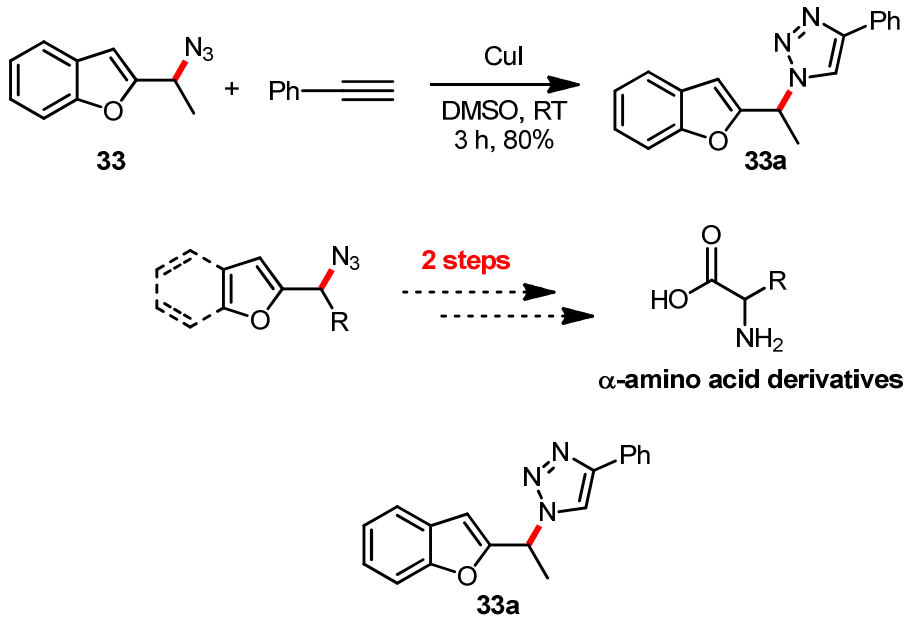


55

Benzyl 2-(5-methylfuran-2-yl)pyrrolidine-1-carboxylate (55).

Pale yellow oil. R_f = 0.5 (hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max} /cm^{-1} 2984 1698, 1567, 1434, 1301, 1246, 1038, 746. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.41-7.17 (m, 5H), 5.85 (s, 1H), 5.86 (s, 1H), 5.10 (m, 2H), 4.94 (t, *J* = 6.3 Hz, 1H), 3.54-3.42 (m, 2H), 2.63 (s, 3H), 2.13-2.03 (m, 2H), 1.96-1.88 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.8, 154.4, 153.5, 145.3, 122.5 (2CH), 122.3, 122.2 (2CH), 106.3, 103.6, 66.9, 54.9, 46.6, 32.0, 22.9, 13.6. HRMS (ESI): *m/z* calcd for $C_{17}H_{19}NO_3K$ (M+K): 324.1002. Found: 324.1889.

Elaboration of azide 33 to the triazole 33a. Azide **33** was elaborated to the triazole **33a** *via* Cu-catalyzed click reaction.[9] This class of products could be medicinally significant and amenable to further synthetic elaborations.[10] Furanyl azides can also be converted to α-amino acid derivatives[11] as in the following scheme.

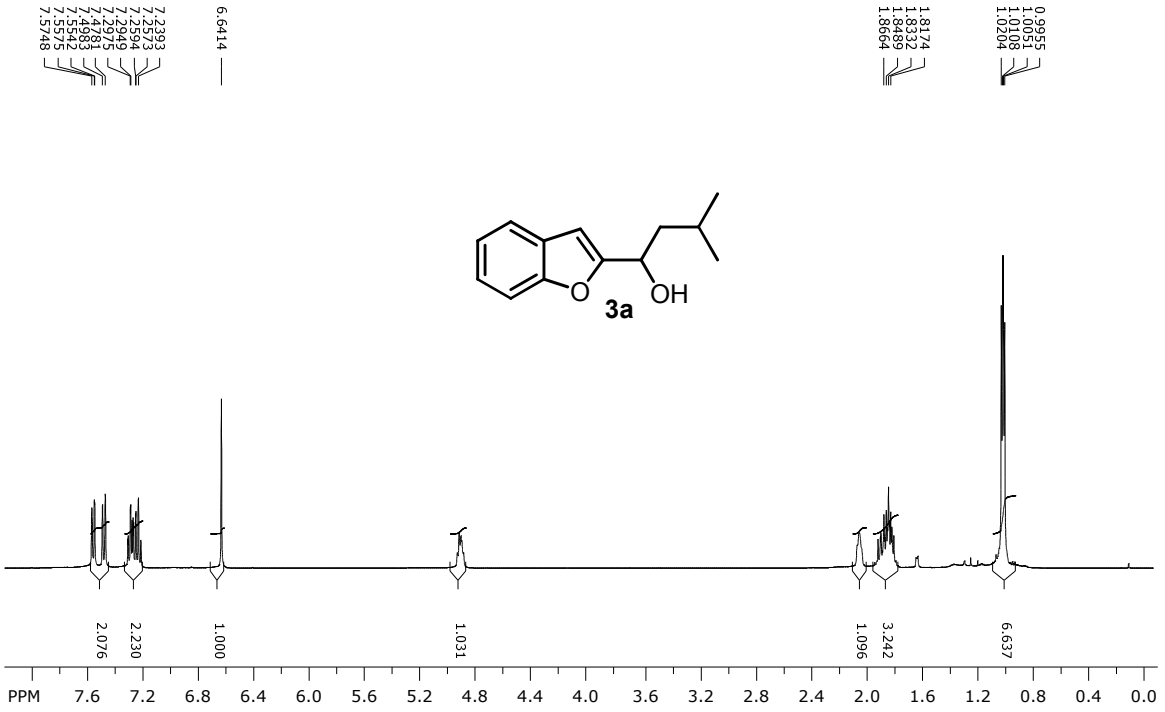


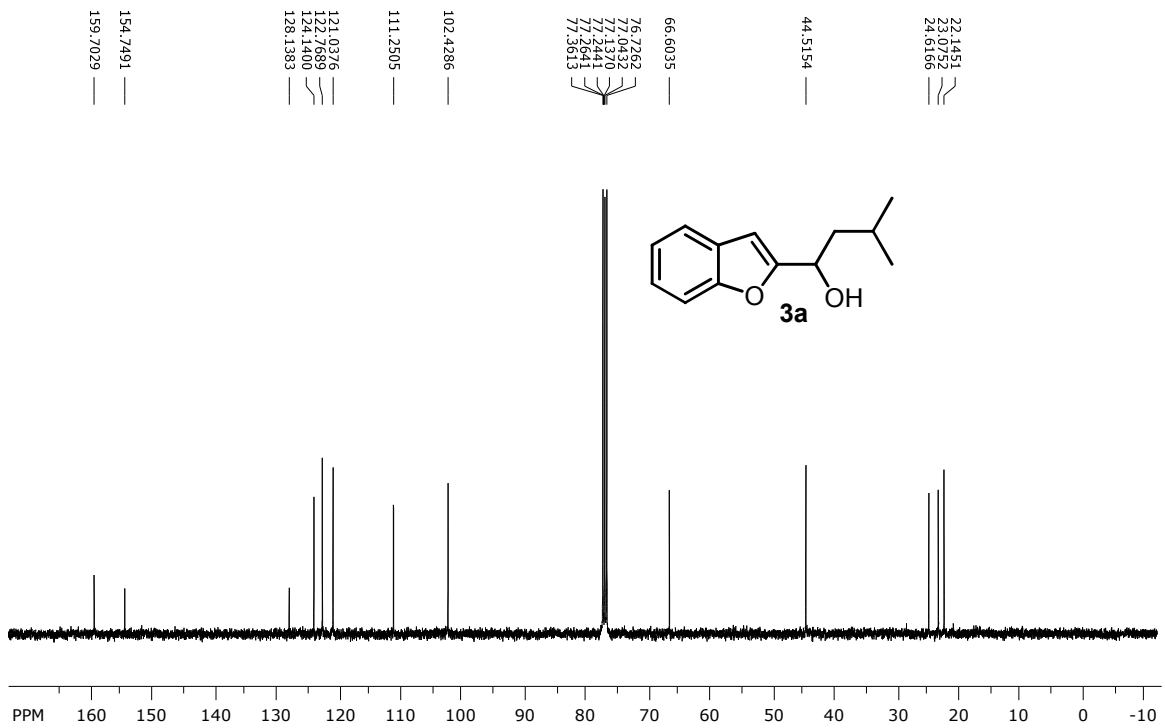
1-(1-(Benzofuran-2-yl)ethyl)-4-phenyl-1H-1,2,3-triazole (33a).

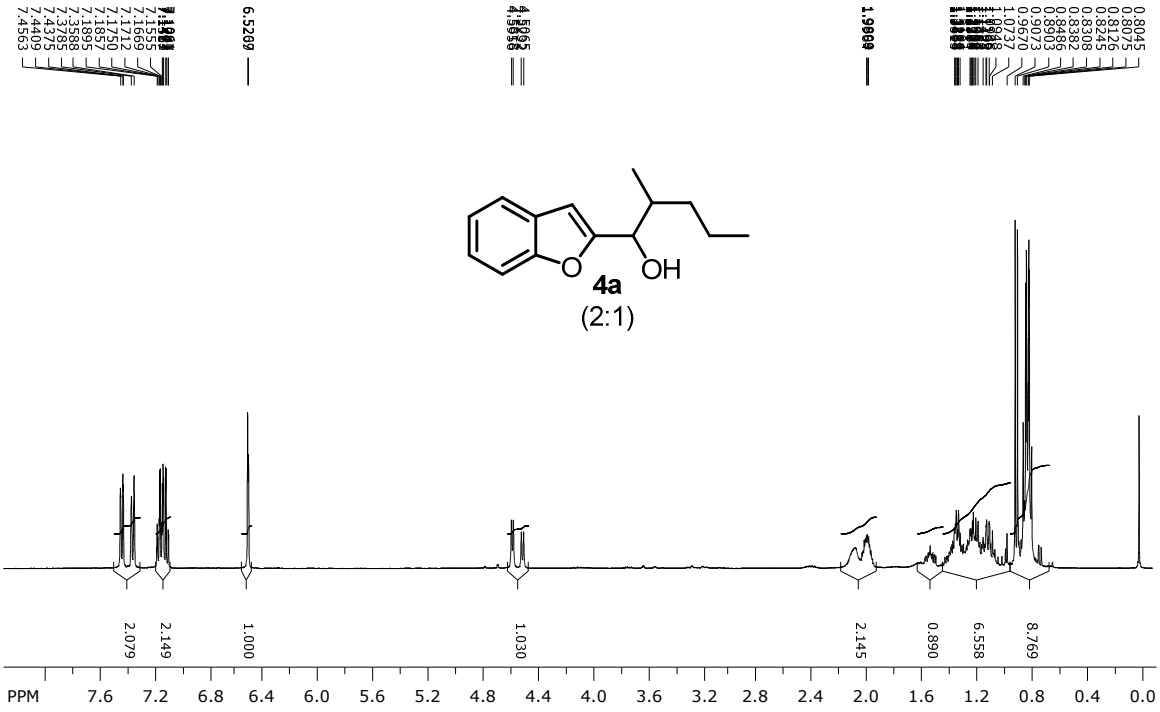
Colorless solid. M. P. = 130-132°C. R_f = 0.6 (hexane/EtOAc = 4/1). IR (KBr): ν_{max}/cm^{-1} 3010, 1608, 1454, 1357, 1218, 1177, 1078, 754. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.71-7.70 (m, 3H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.33 (tt, *J* = 7.5 and 1.6 Hz, 2H), 7.24 (tt, *J* = 8.6 and 2.1 Hz, 2H), 7.18 (dt, *J* = 7.56 and 1.04 Hz, 1H), 6.71 (s, 1H), 6.04 (q, *J* = 7.0 Hz, 1H), 2.07 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.0, 154.0, 147.9, 130.5, 128.8 (2C), 128.2, 127.5 (2C), 125.7, 125.1, 123.3, 121.4, 118.0, 111.5, 105.0, 54.4, 19.6. HRMS (ESI): *m/z* calcd for $C_{18}H_{15}ON_3Na$ (M+Na): 312.1113. Found: 312.1113.

[9] J. E. Moses and A. D. Moorhouse, *Chem. Soc. Rev.,* 2007, **36**, 1249.
[10] S. Chuprakov, S. W. Kwok and V. V. Fokin, *J. Am. Chem. Soc.,* 2013, **135**, 4652 and references cited therein.
[11] J. –N. Desrosiers, A. Côté and A. B. Charette, *Tetrahedron,* 2005, **61**, 6186.

^{1}H and ^{13}C-NMR data of all new compounds reported in this study



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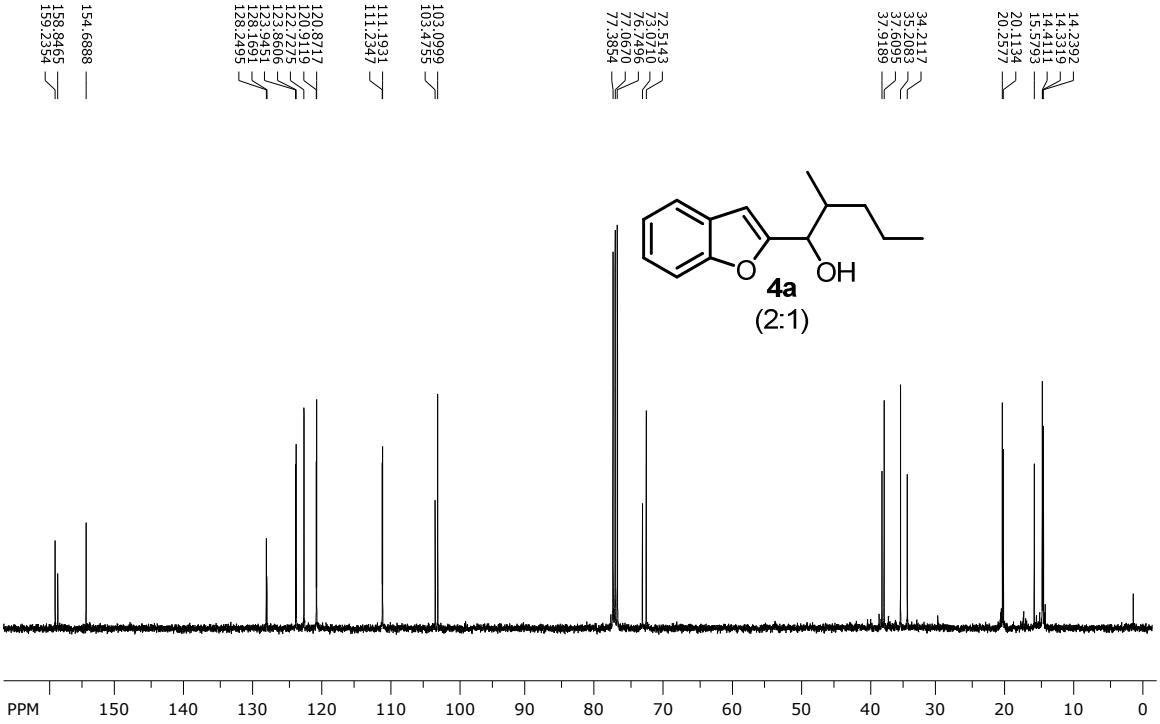
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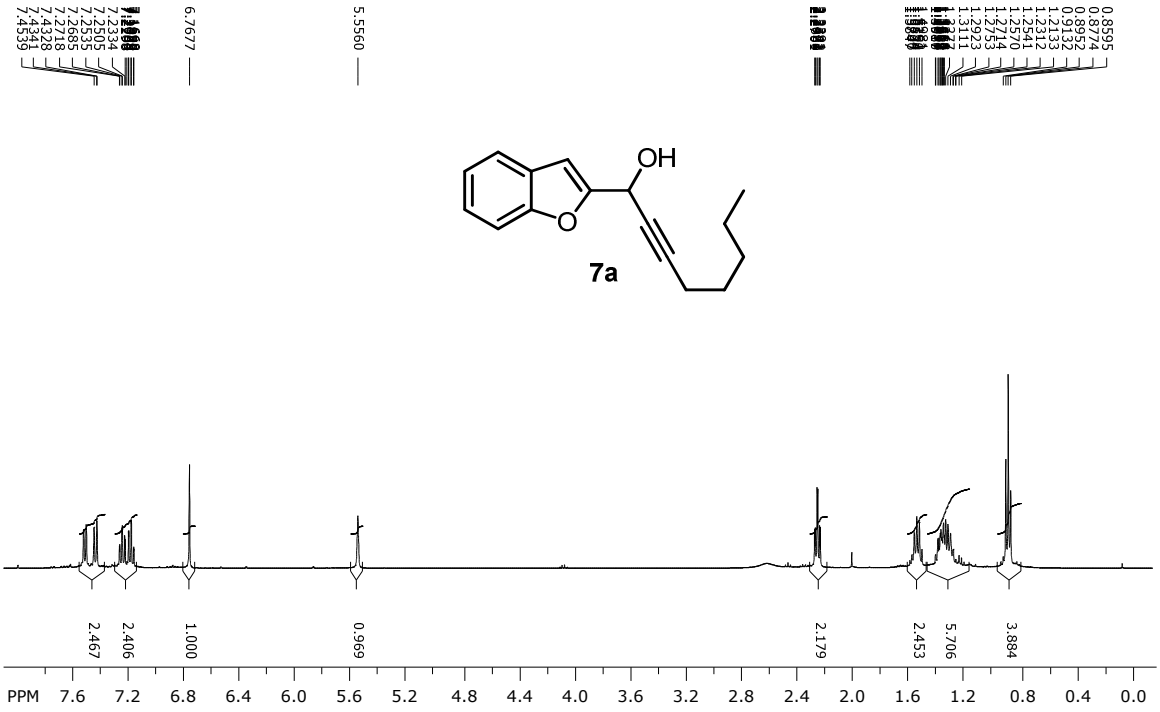

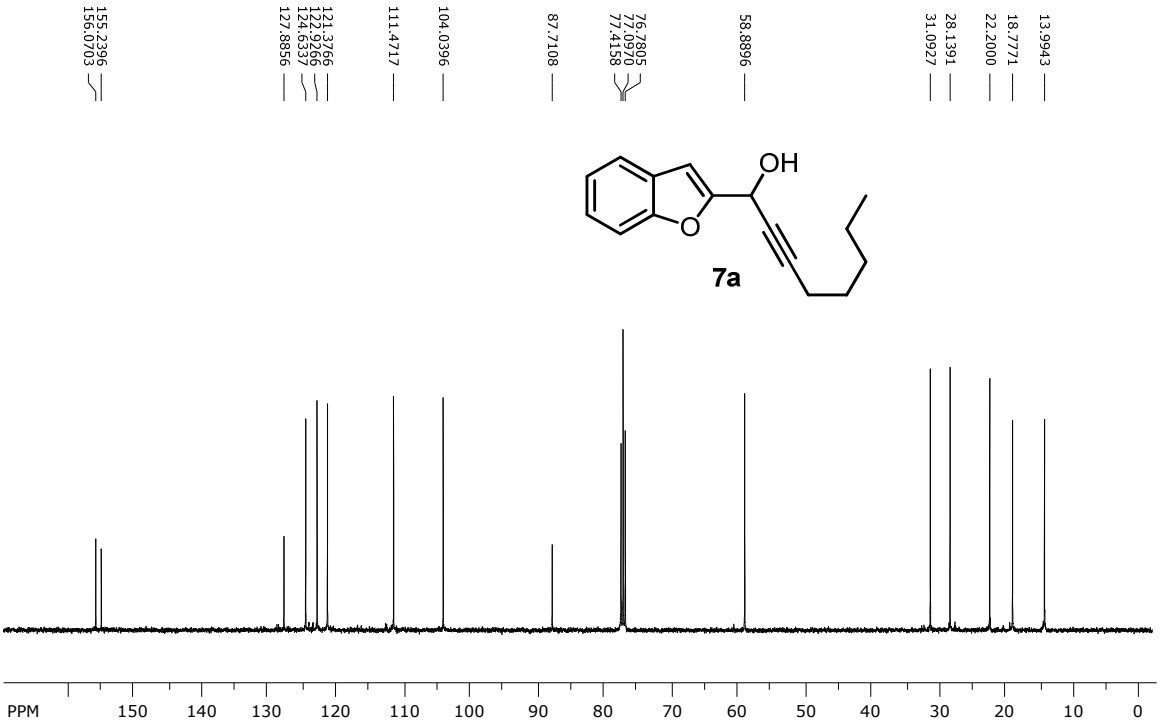

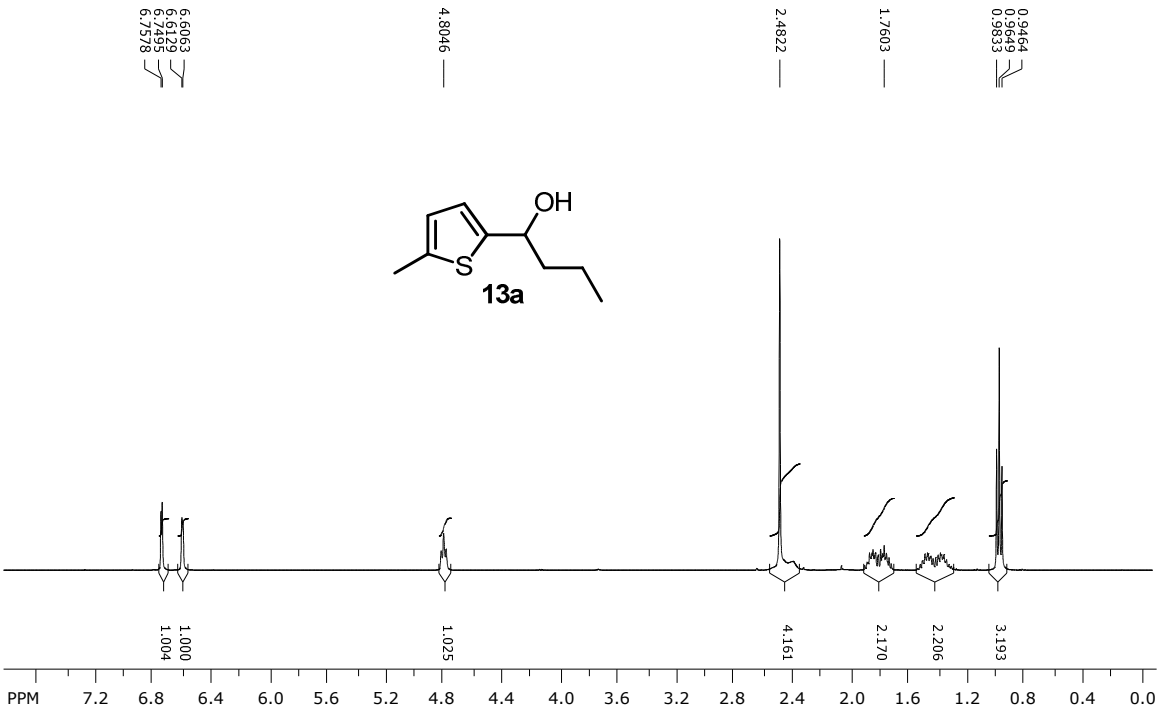

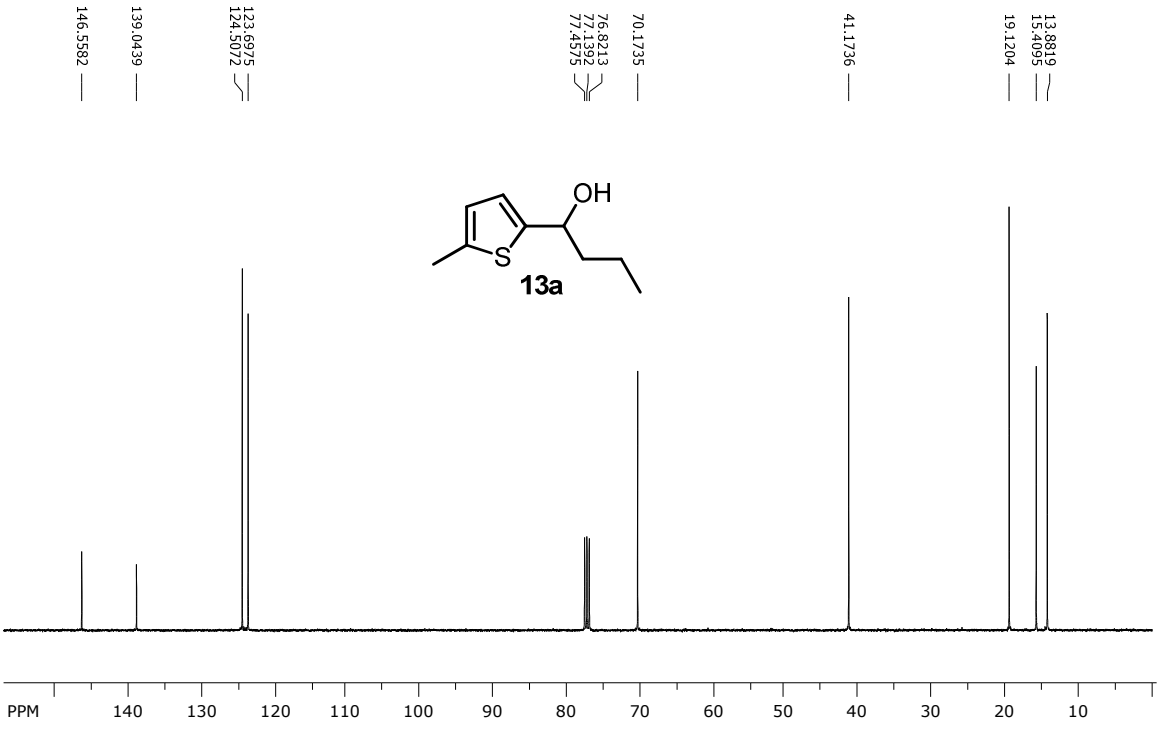

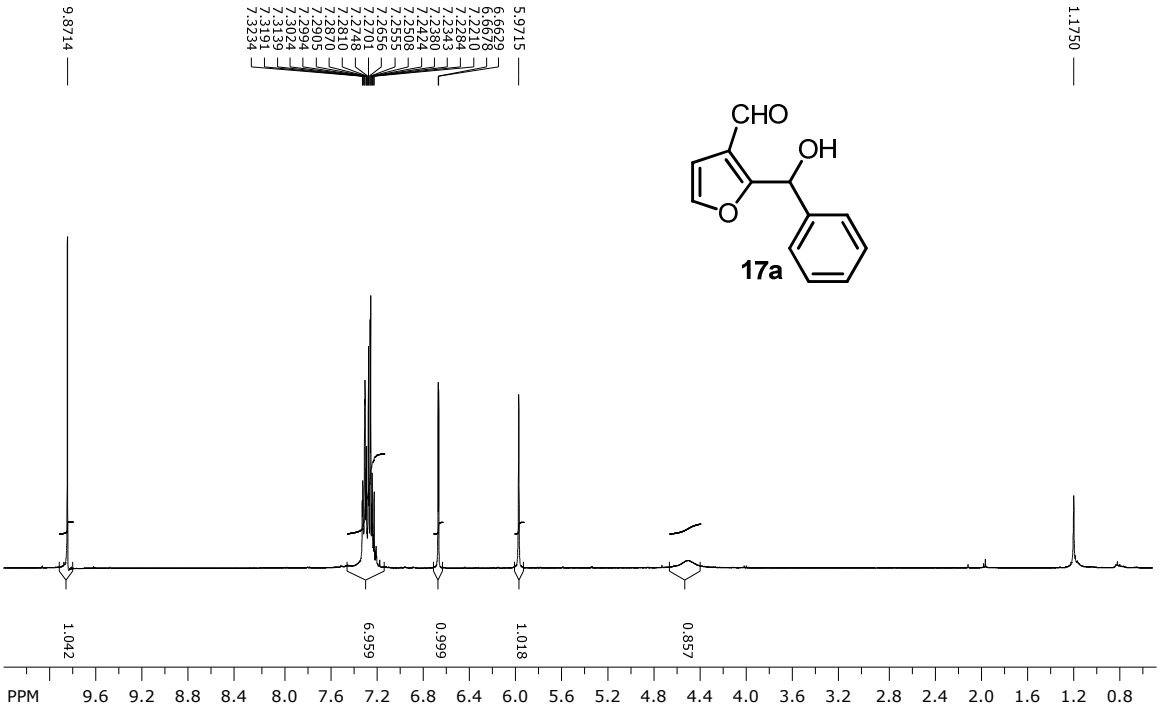

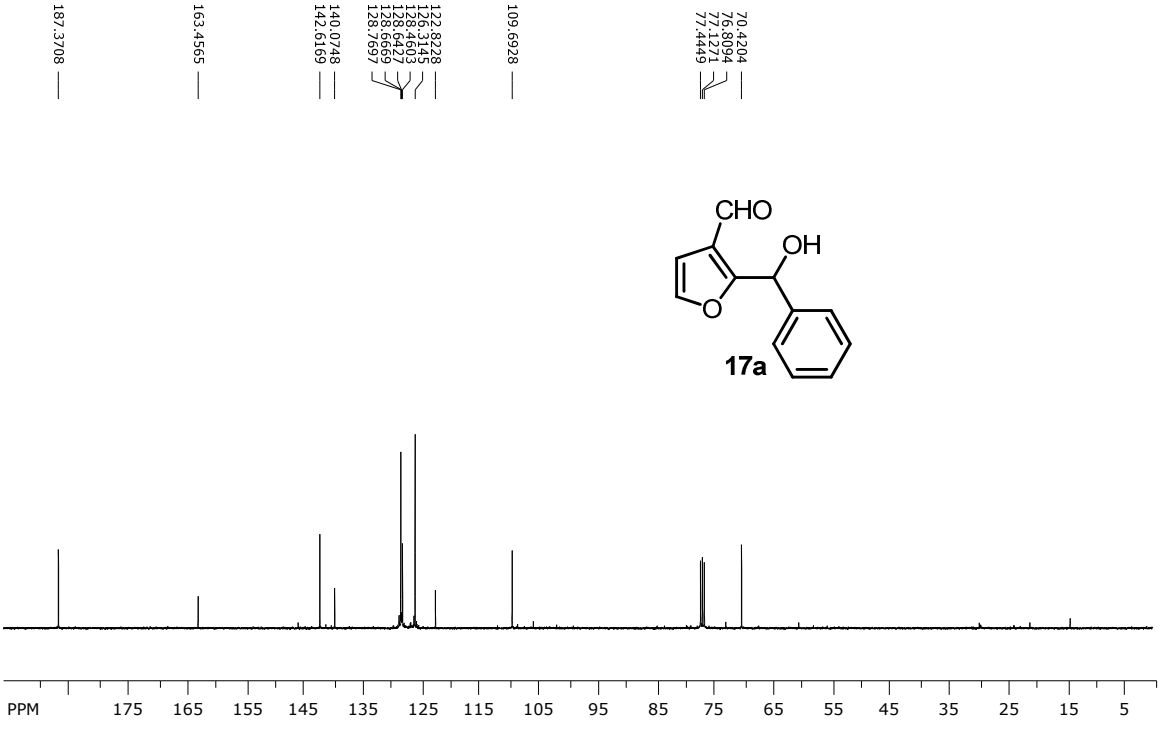

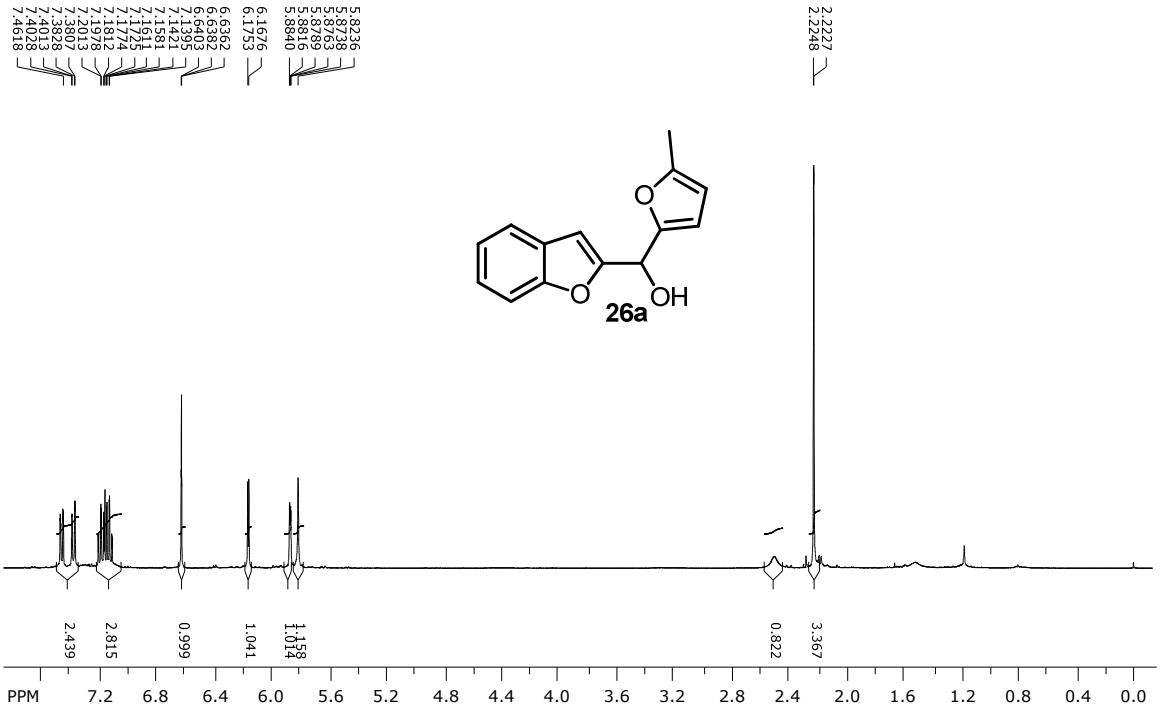

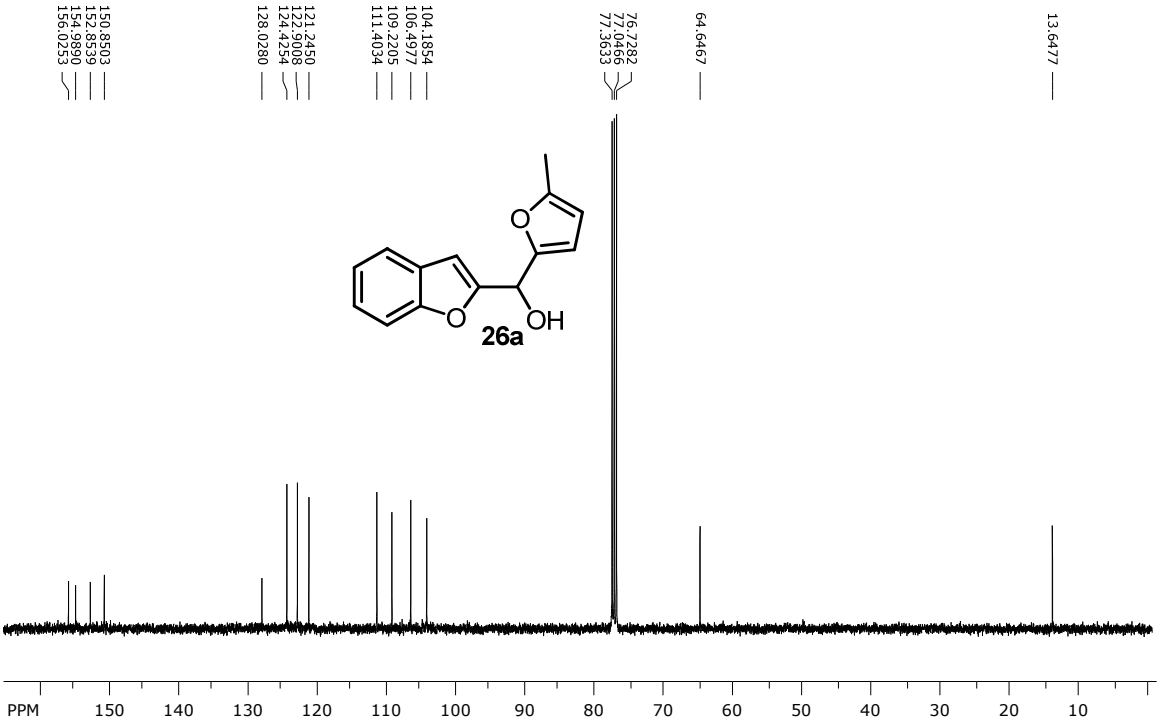

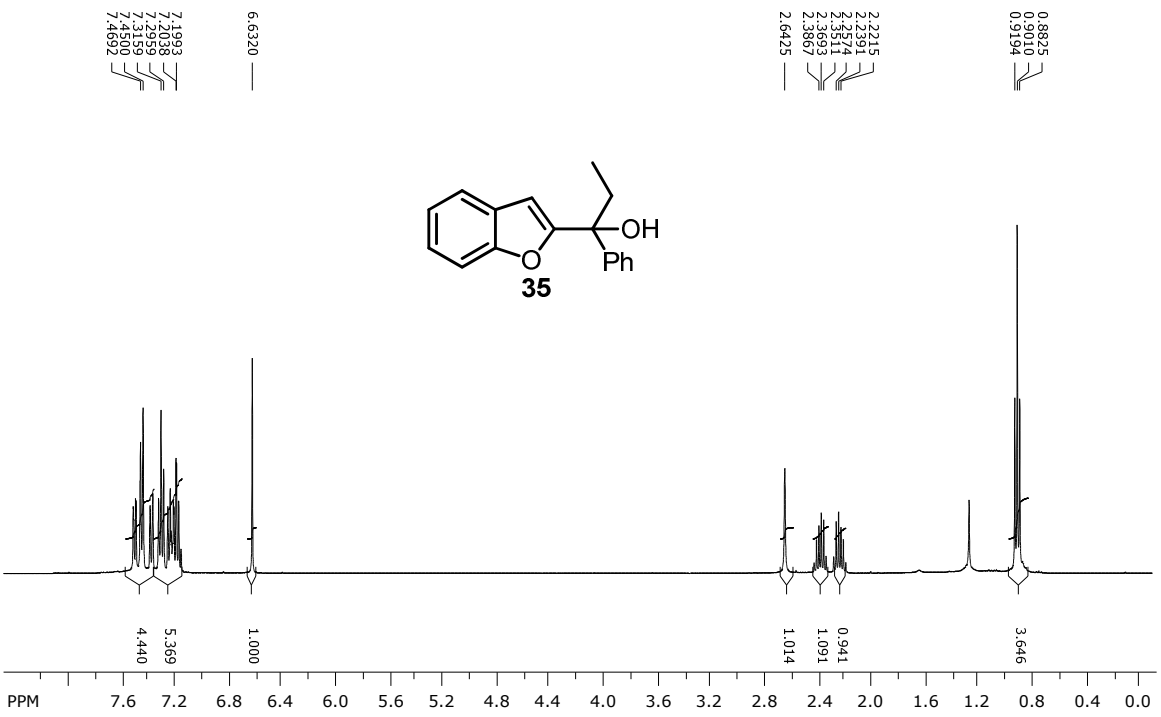

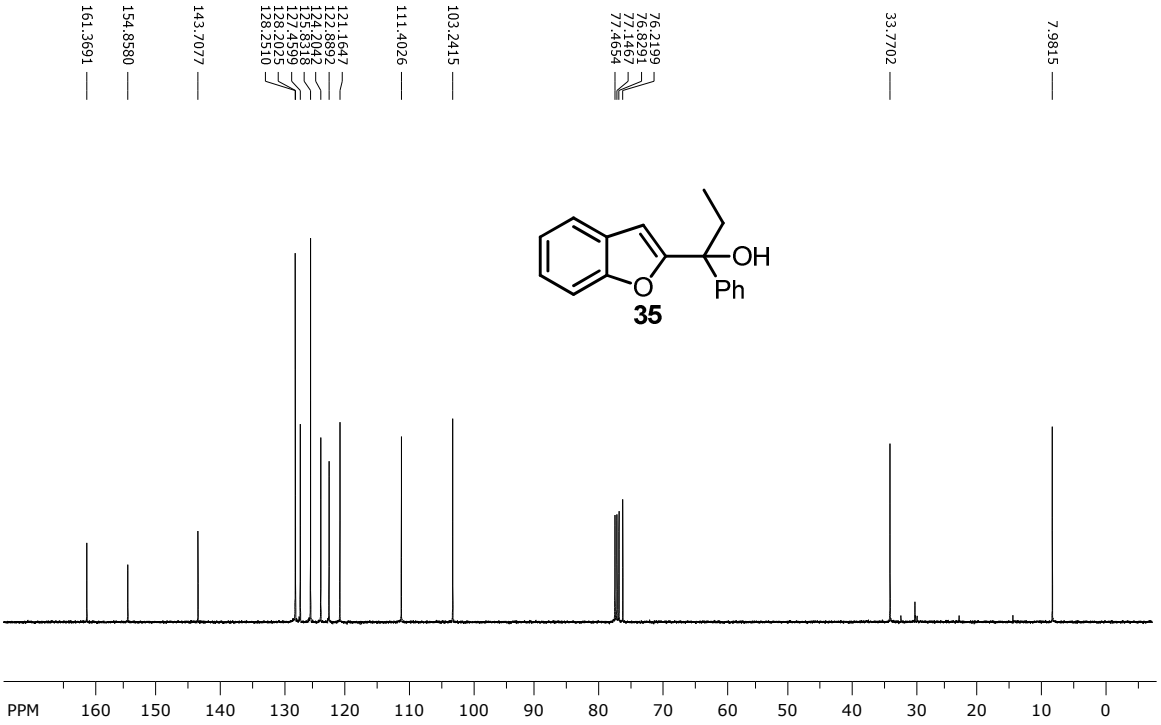

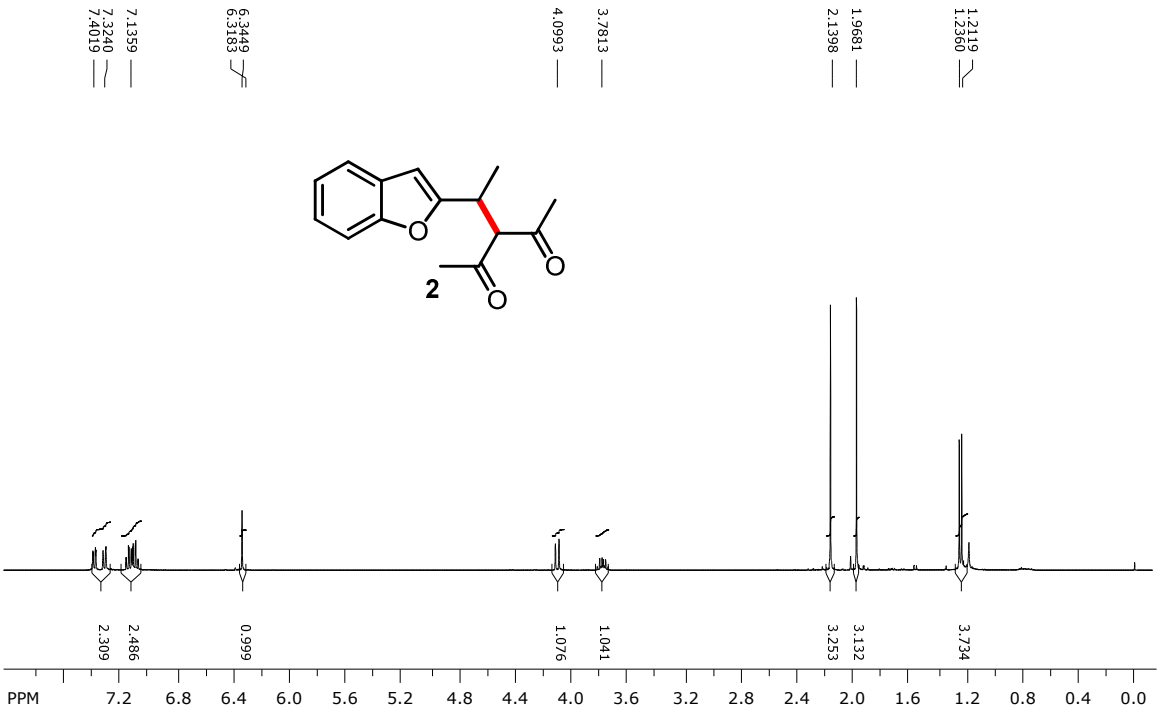
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3.734
PPM
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6.4
6.0
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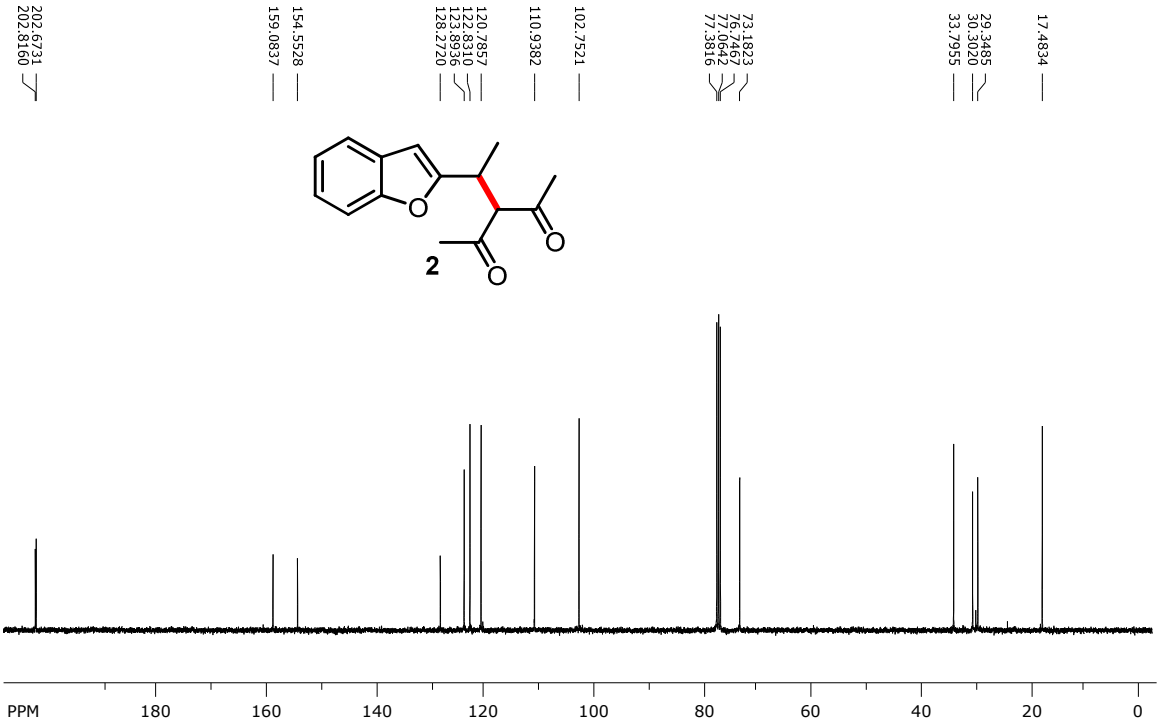
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20
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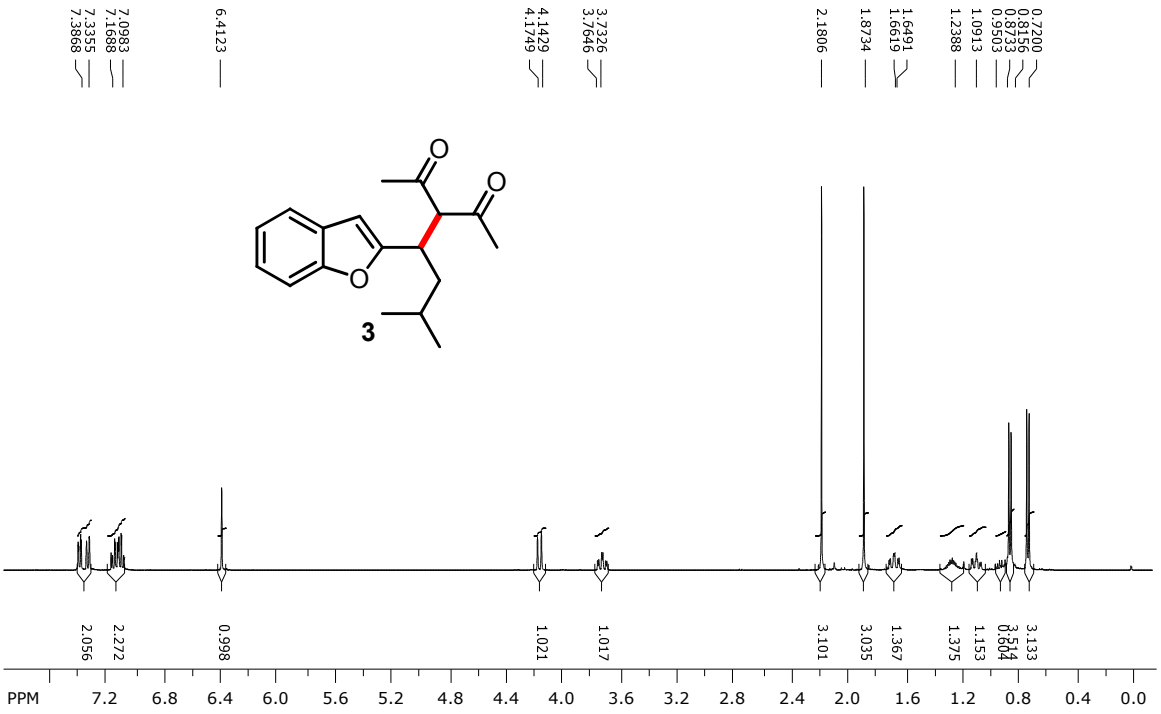
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1.2388
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2.272
0.998
1.021
1.017
3.101
3.035
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1.375
1.153
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PPM
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6.0
5.6
5.2
4.8
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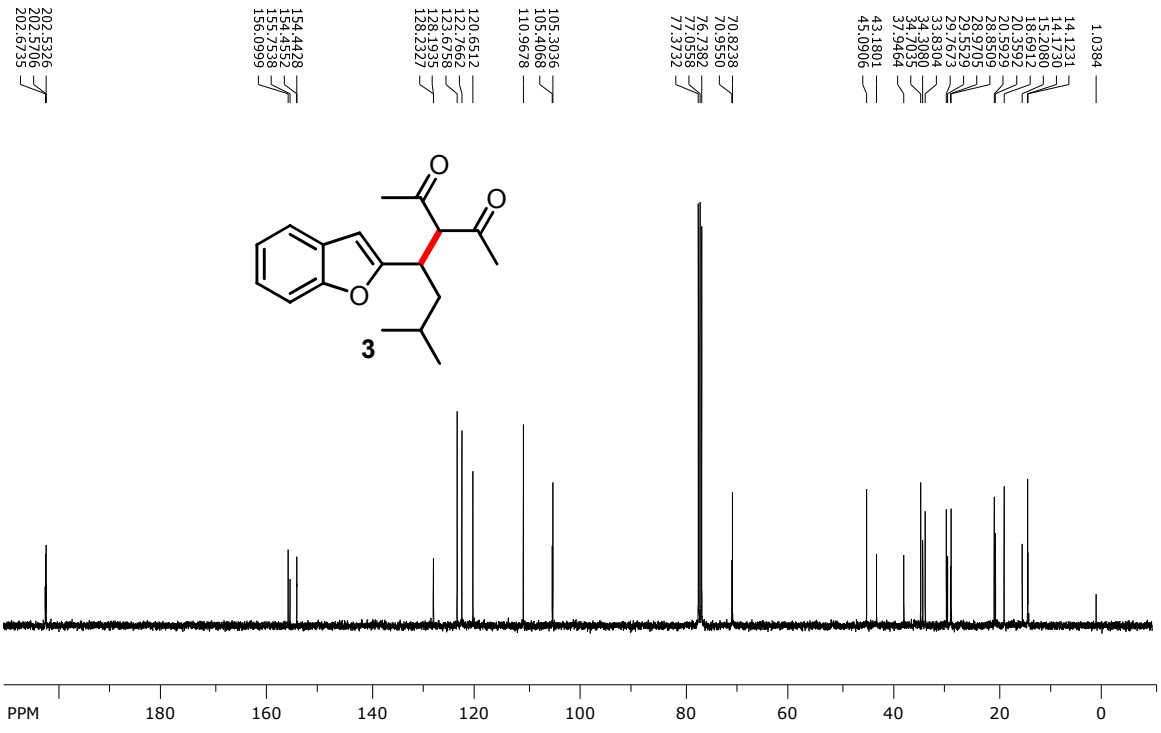
0.0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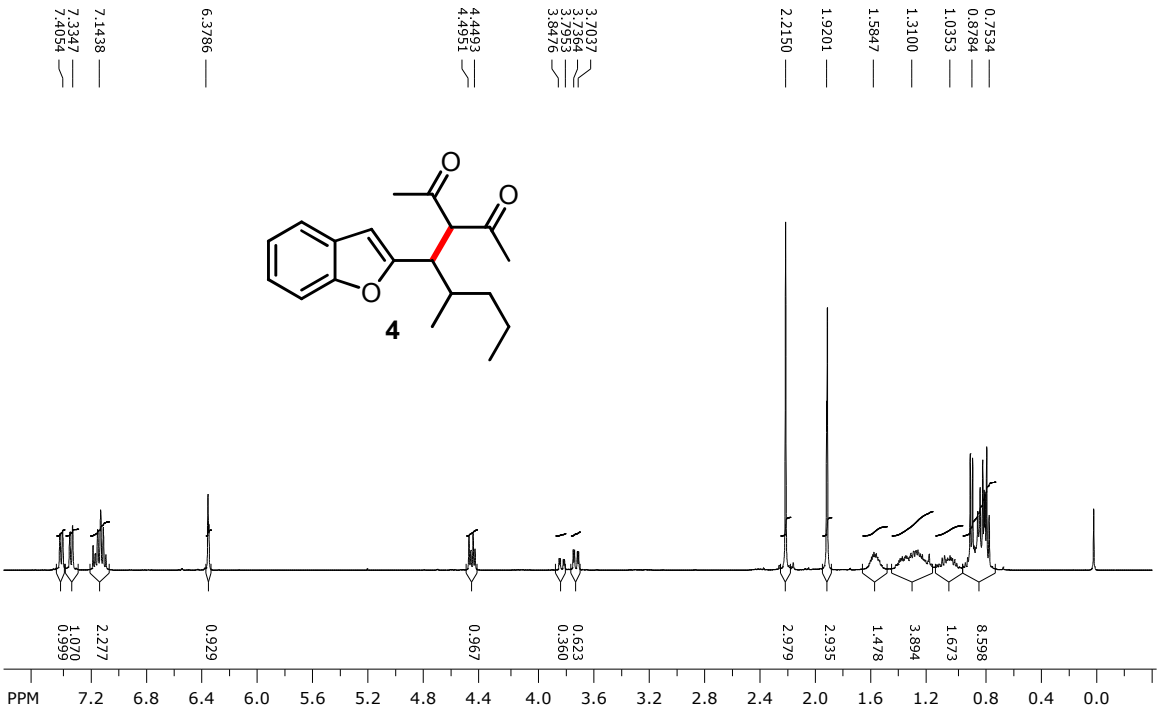

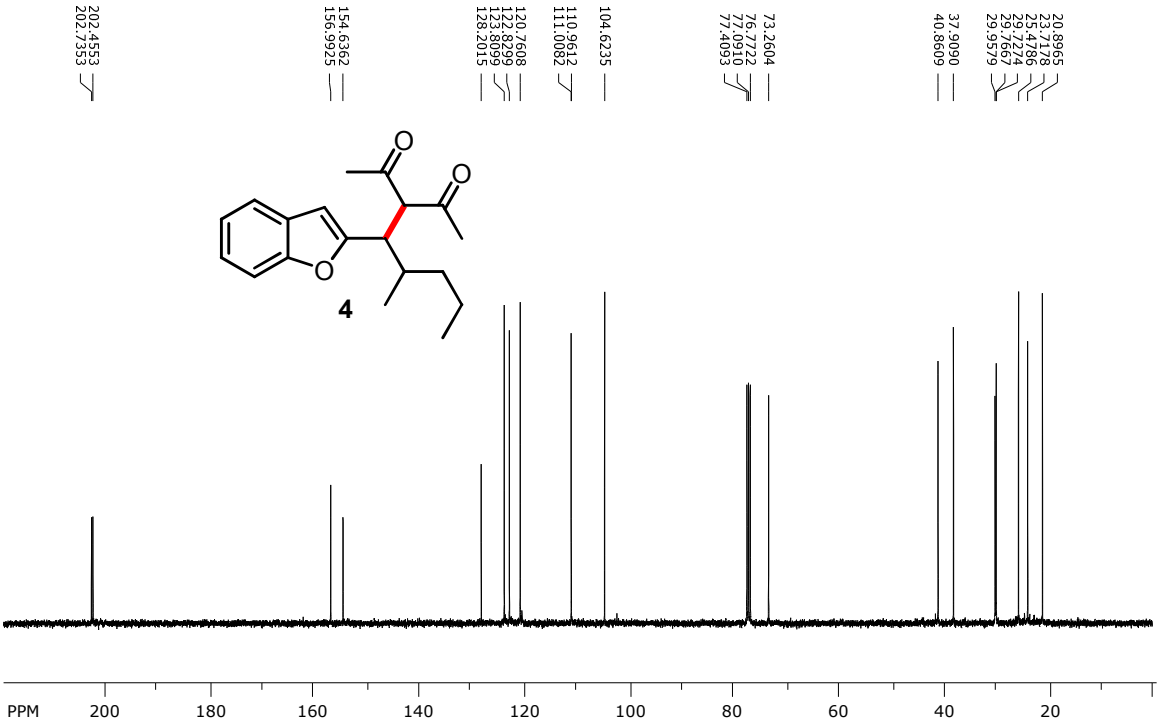

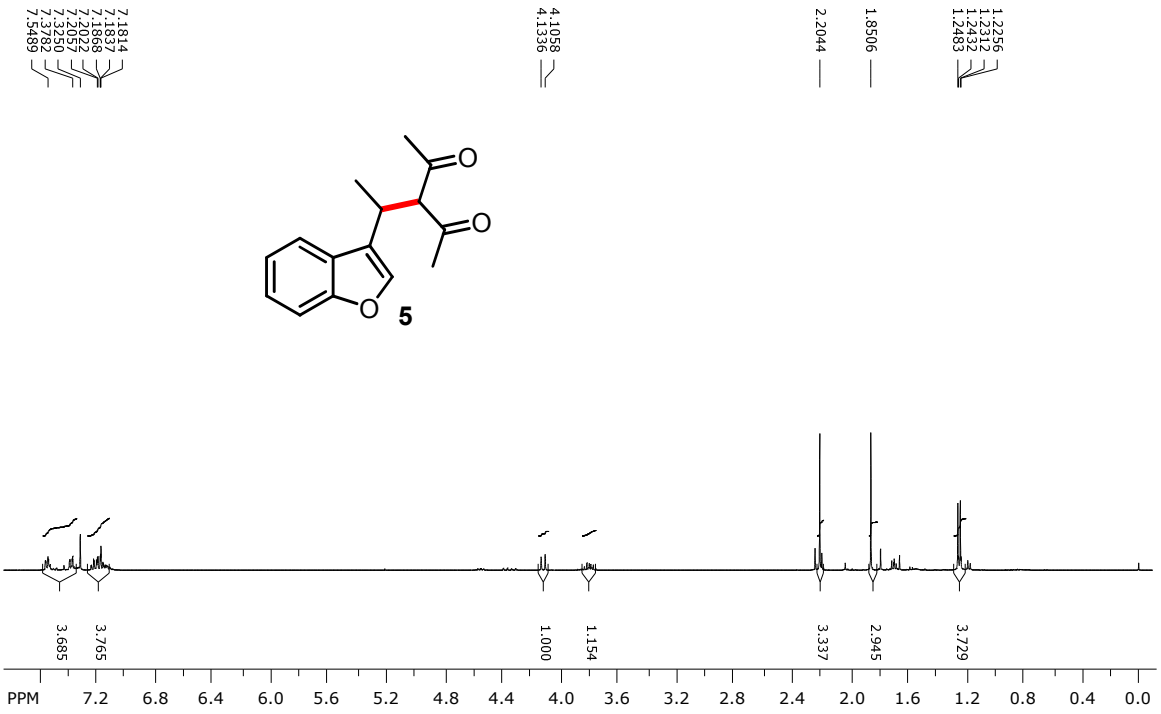
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4.1058
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1.2483
1.2432
1.2312
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O
O
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3.765
1.000
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3.729
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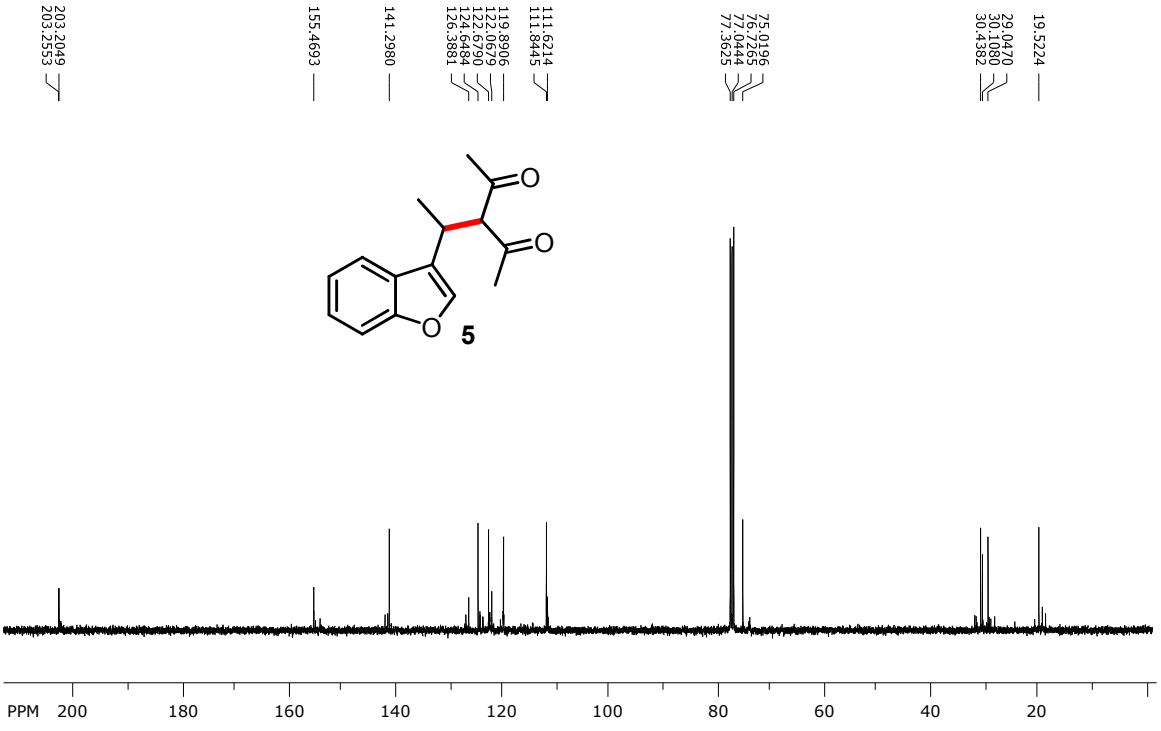
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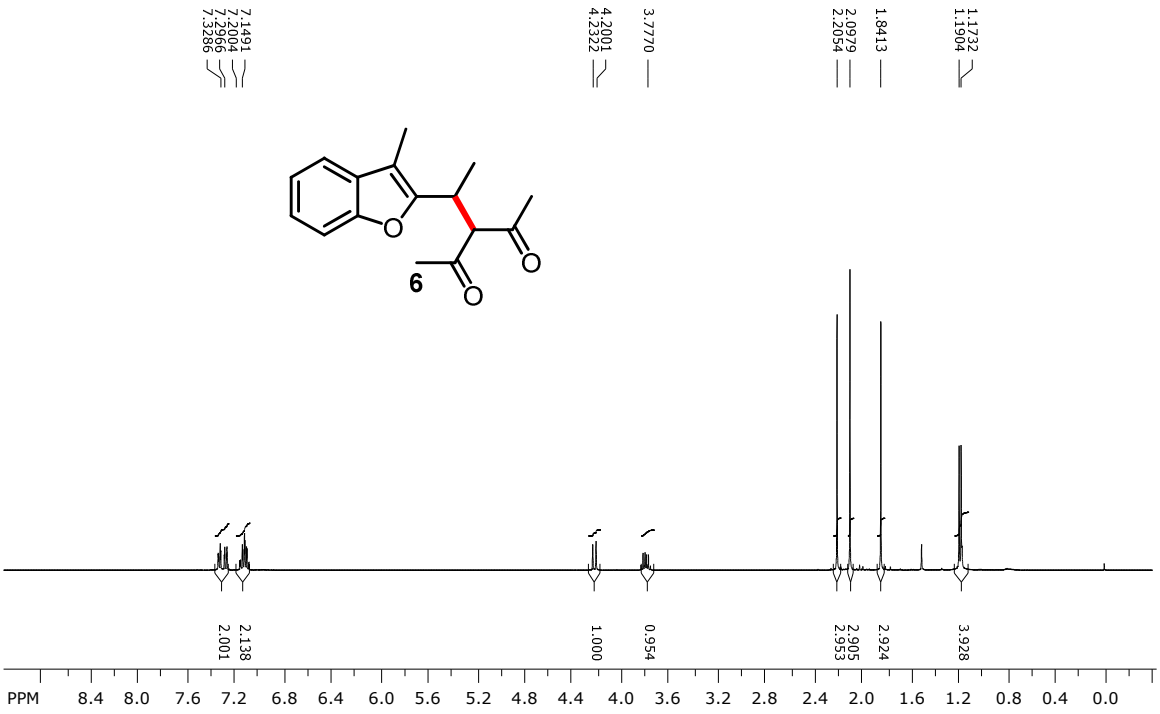

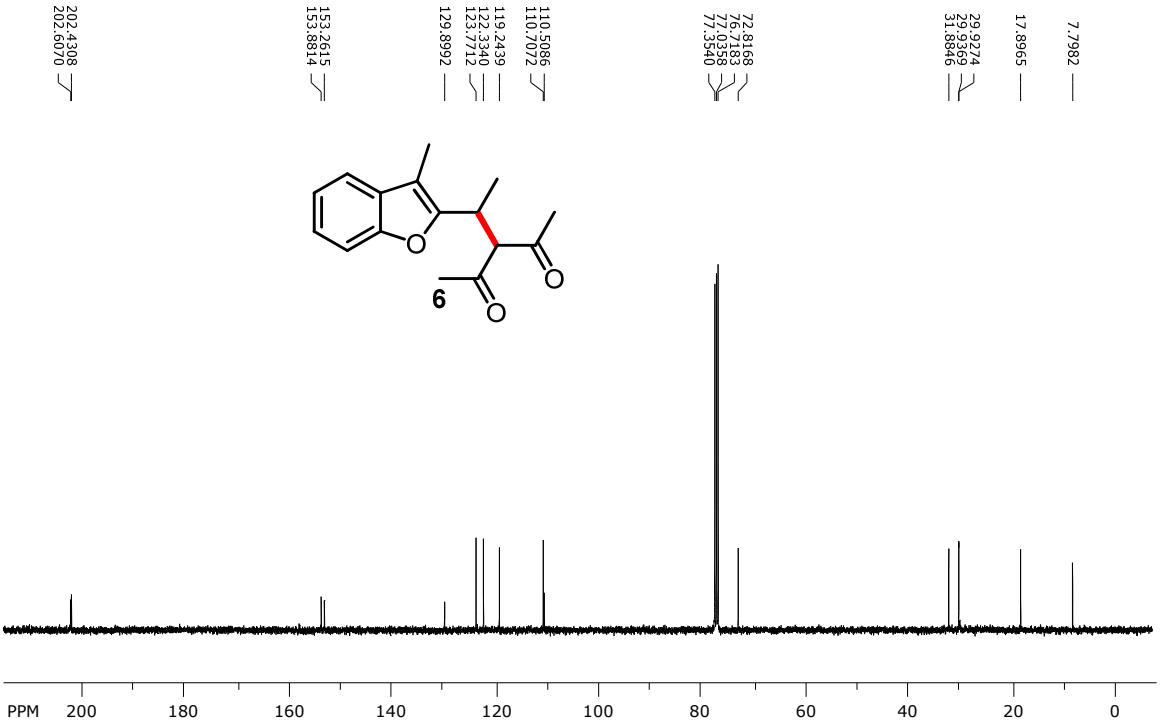

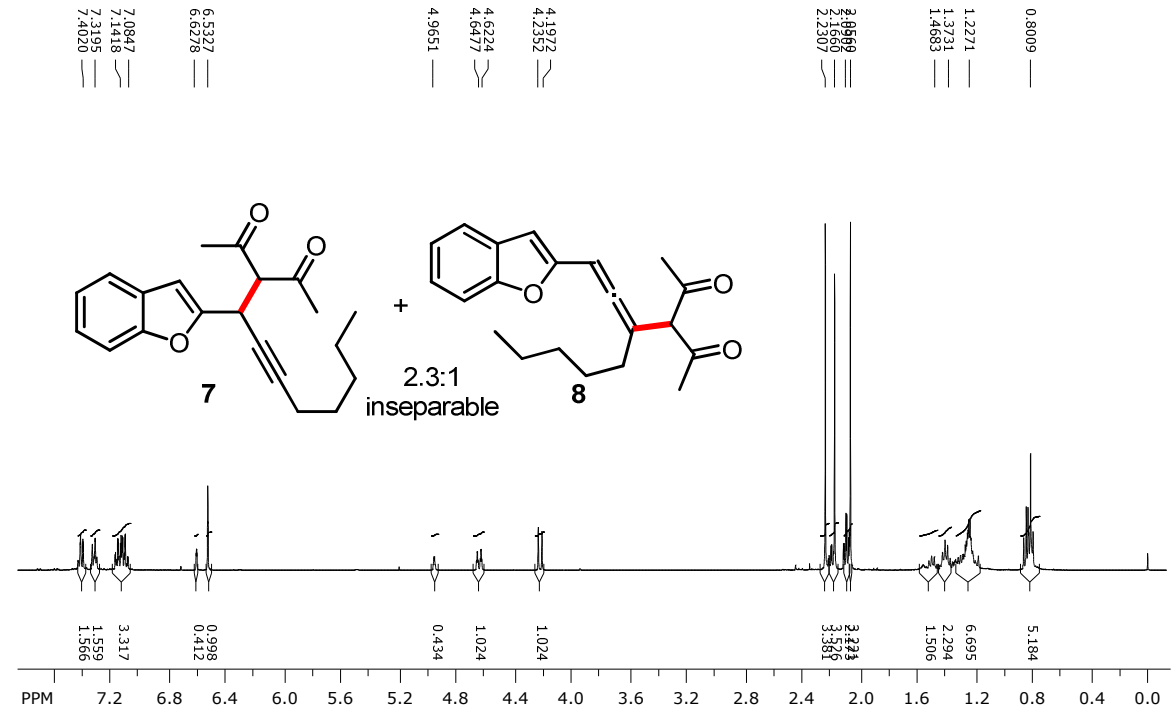
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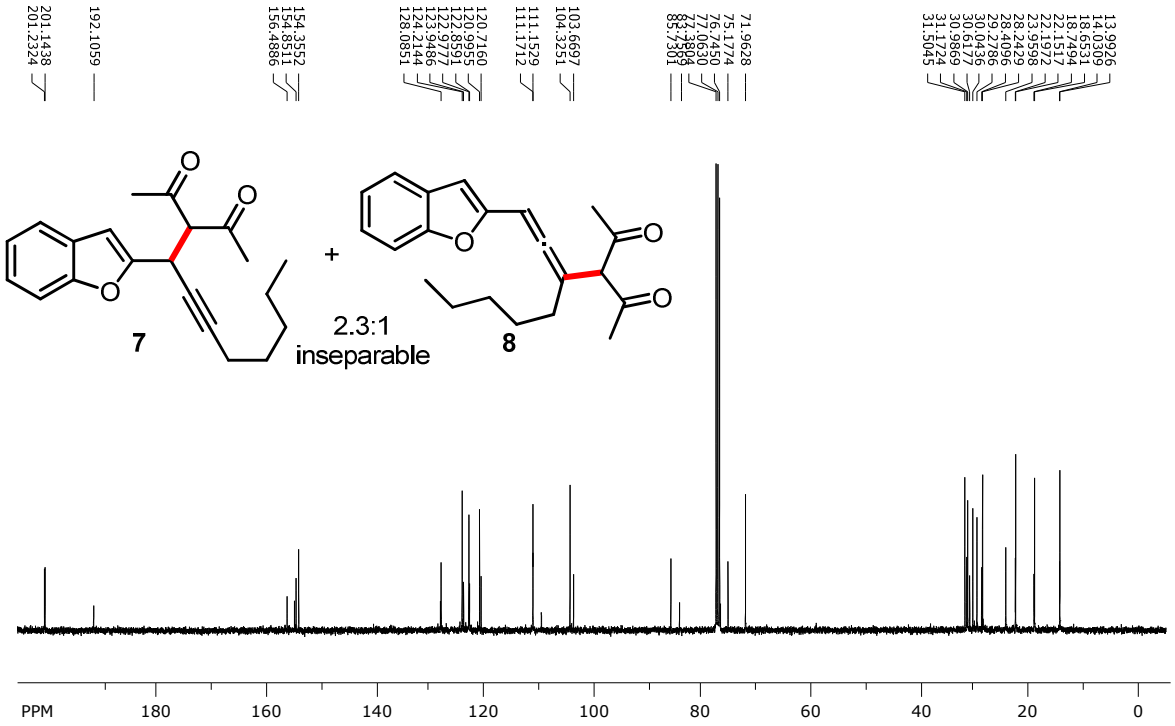
PPM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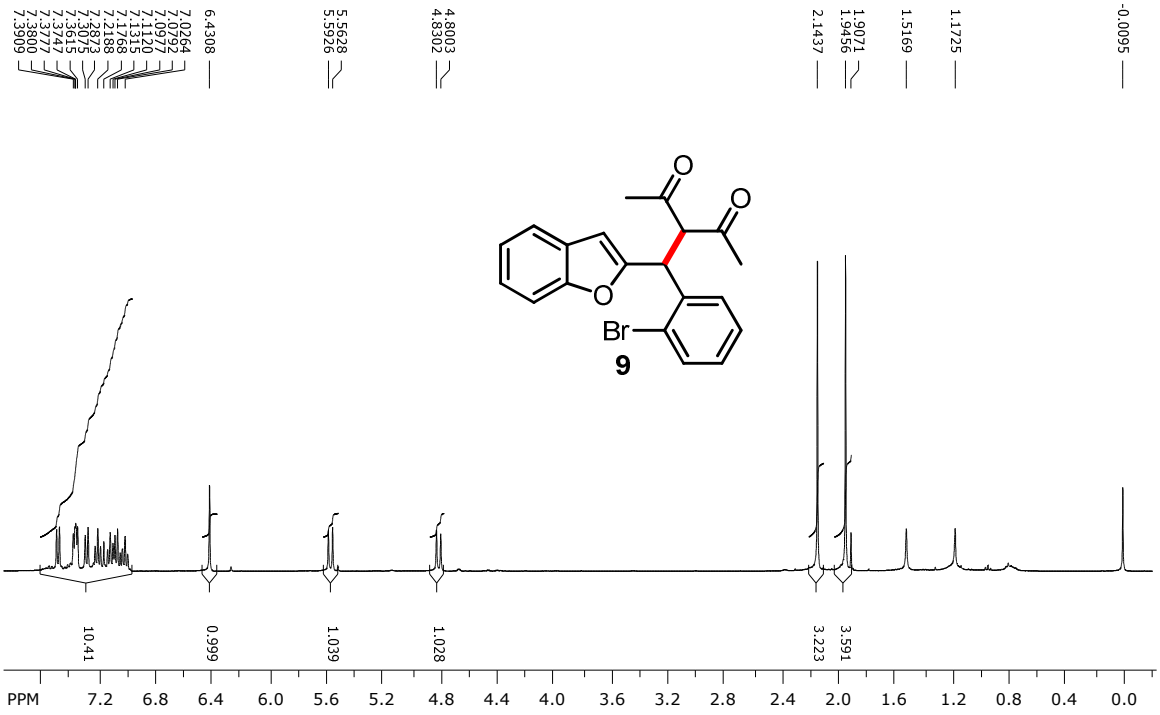

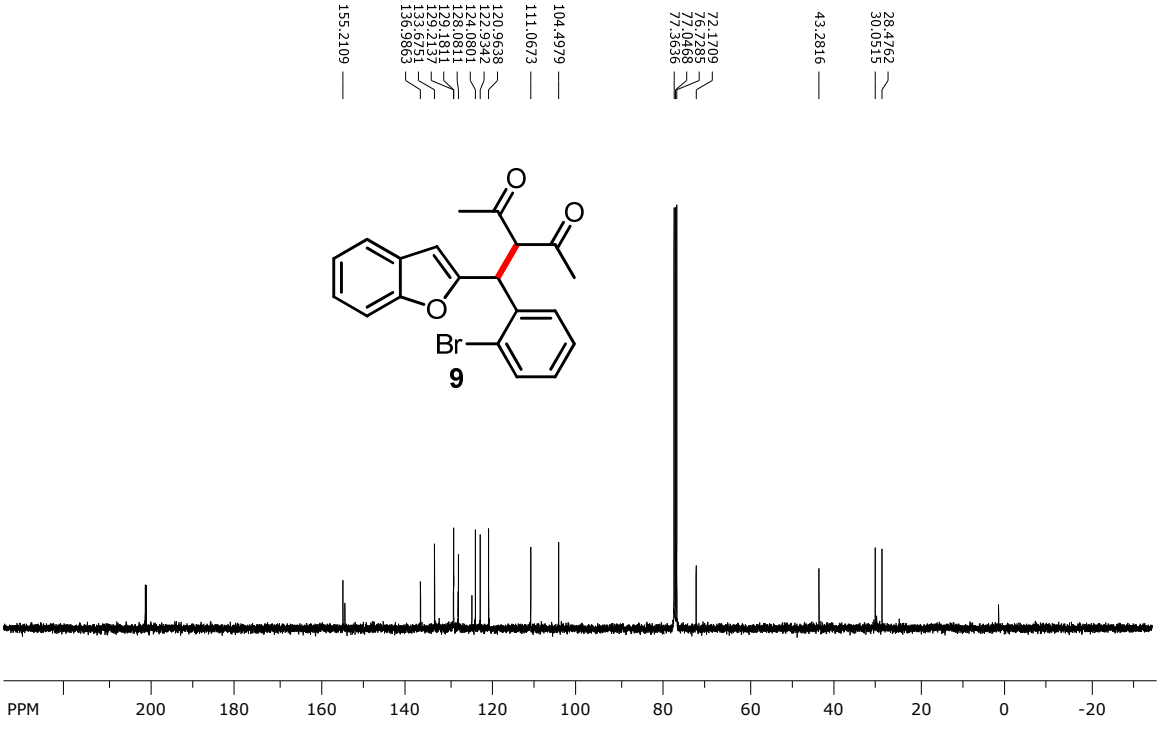

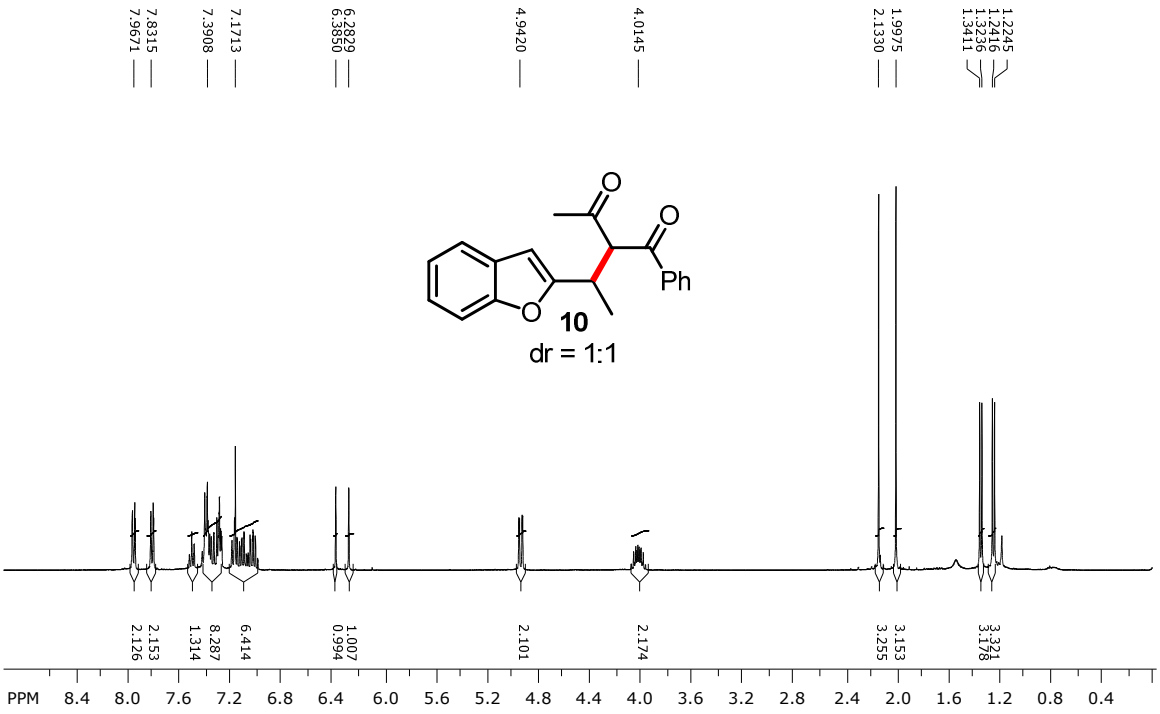

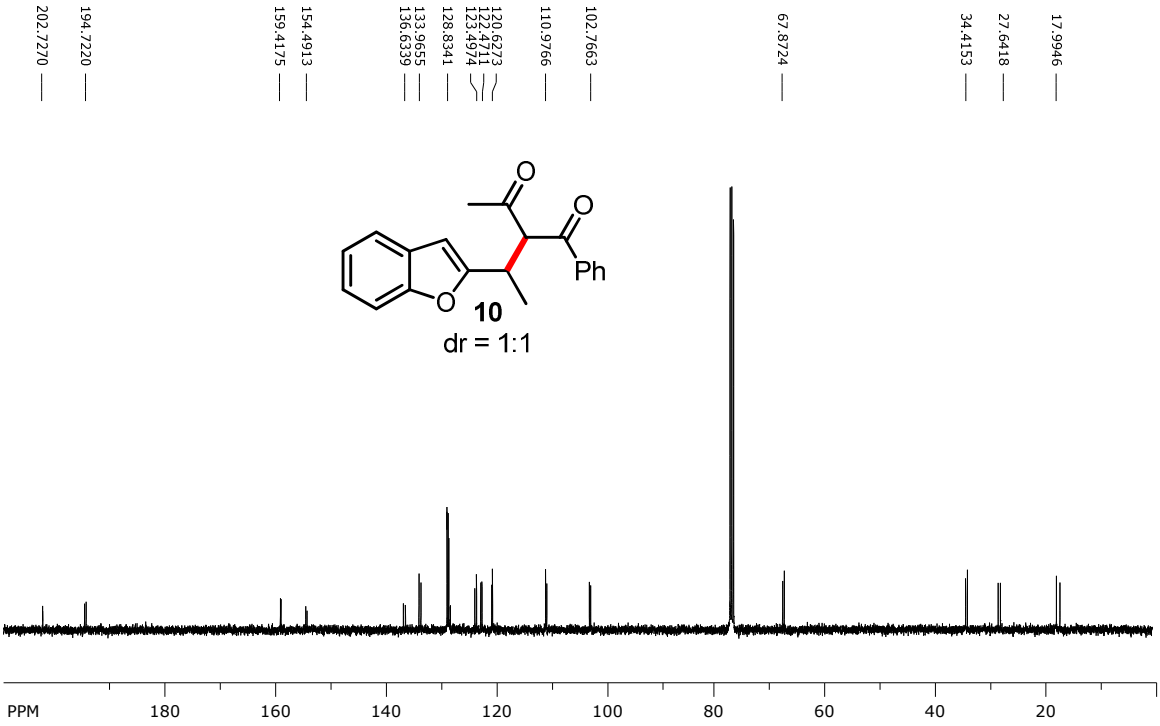

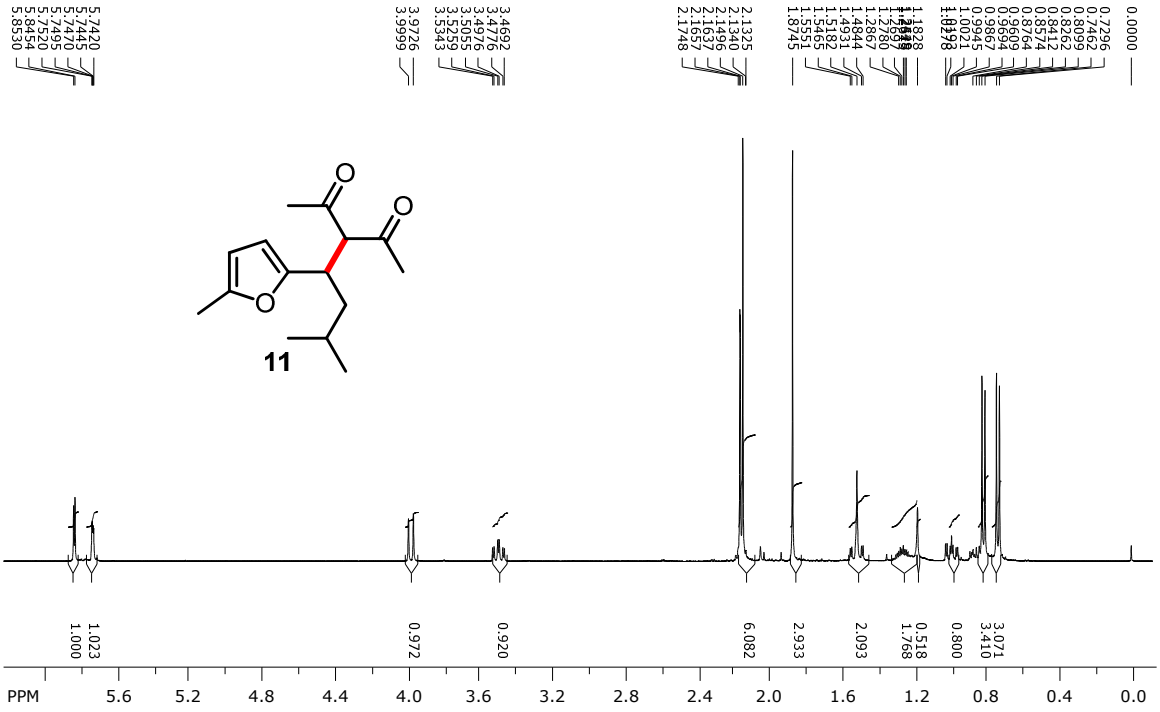
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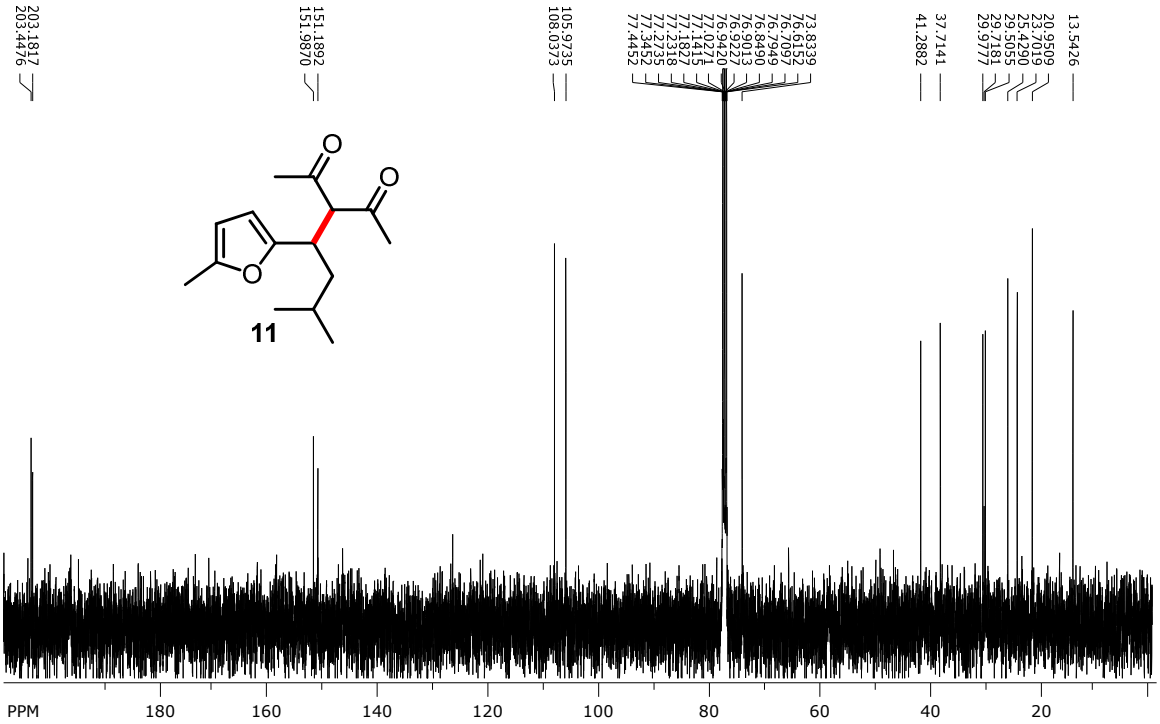
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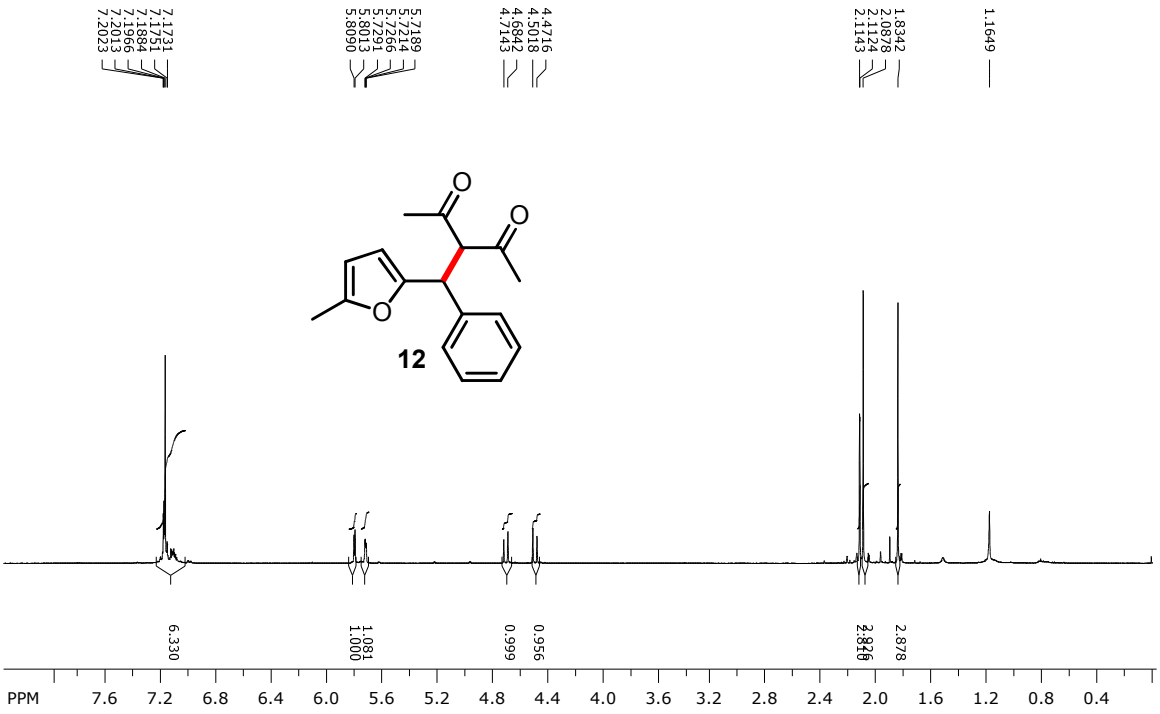
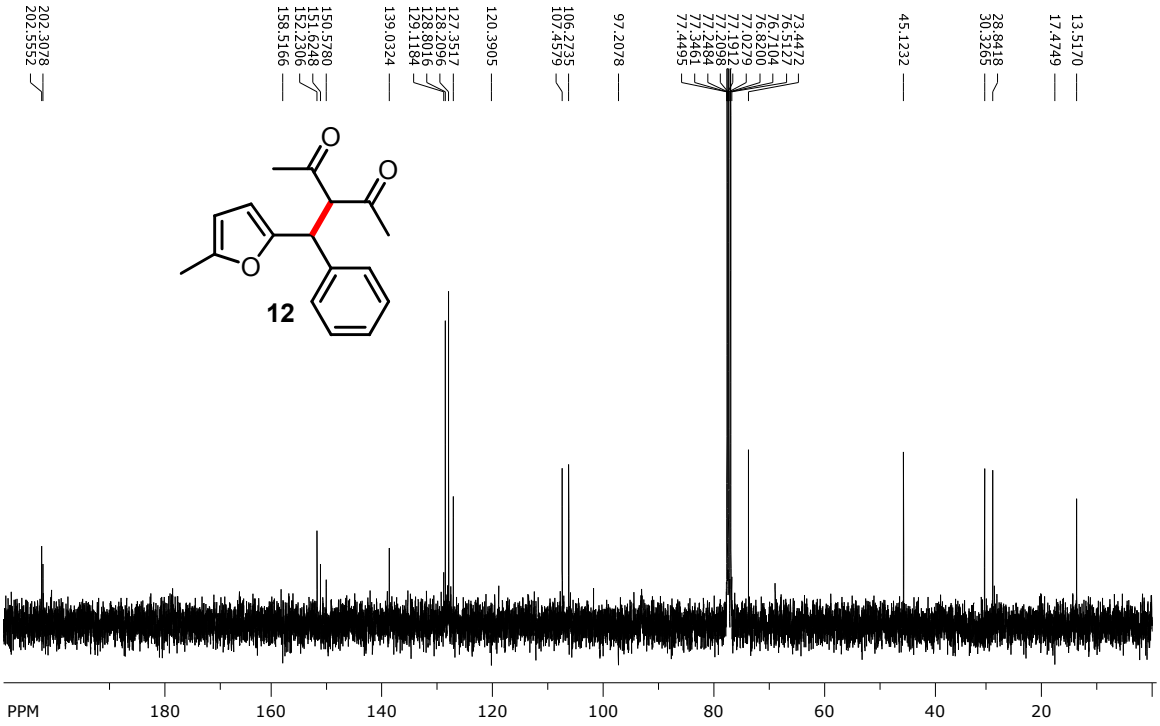
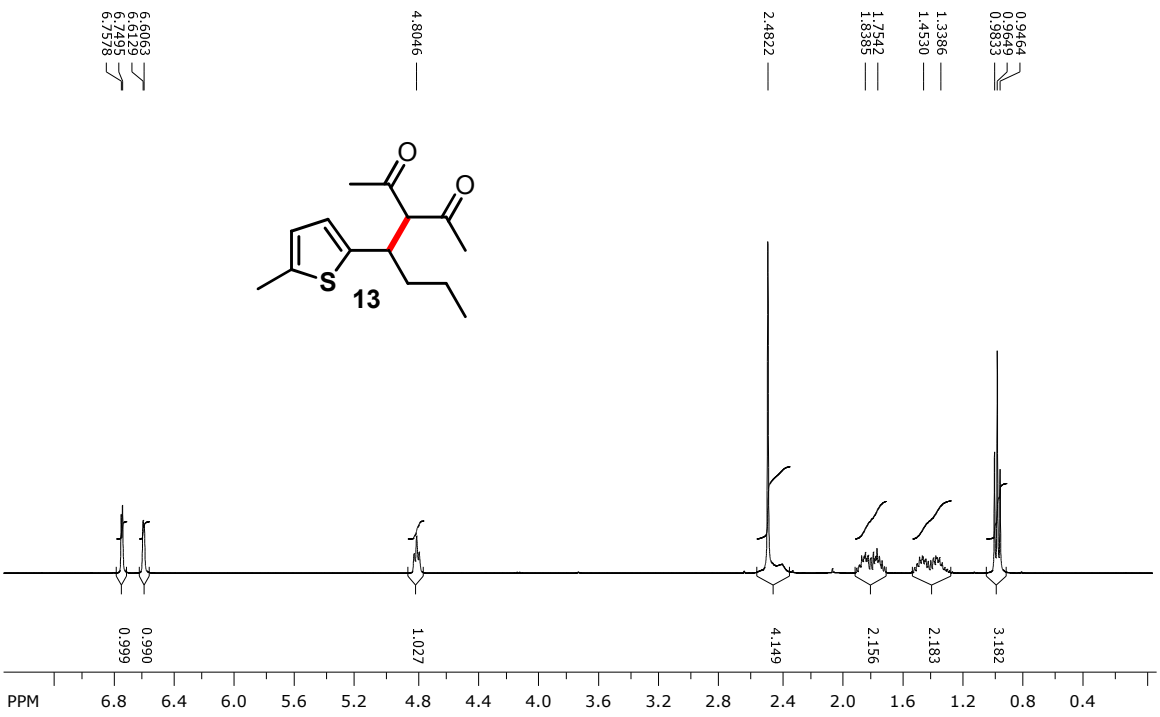
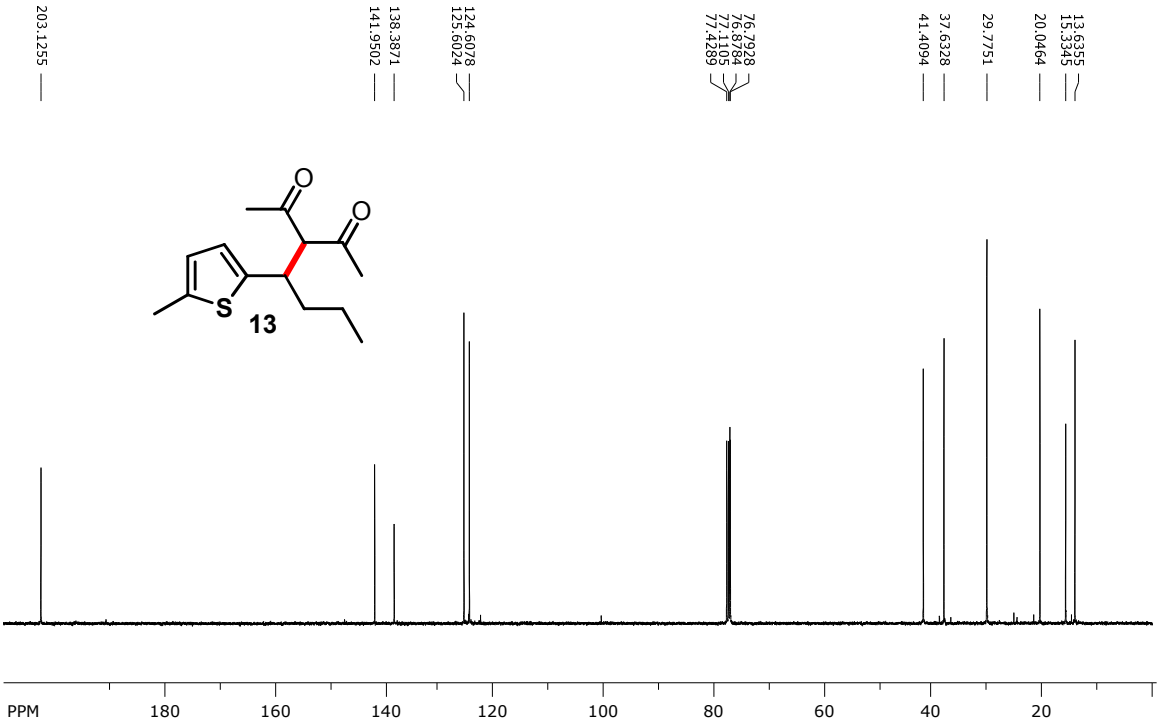
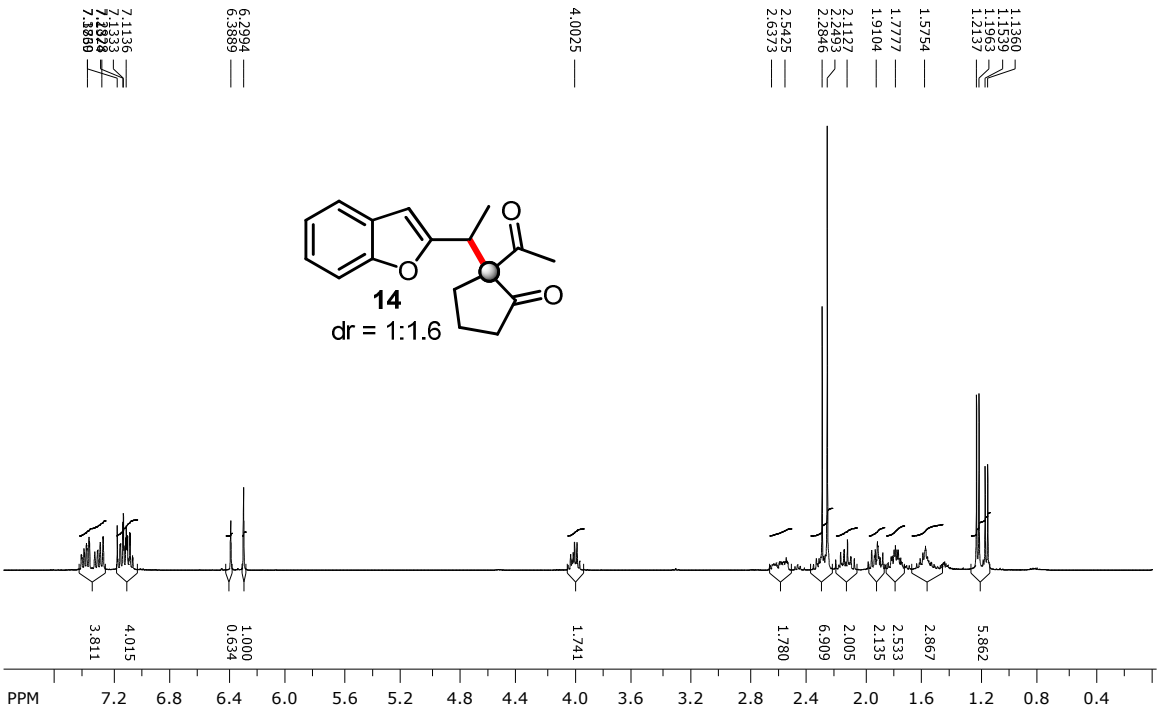
PPM







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5.2
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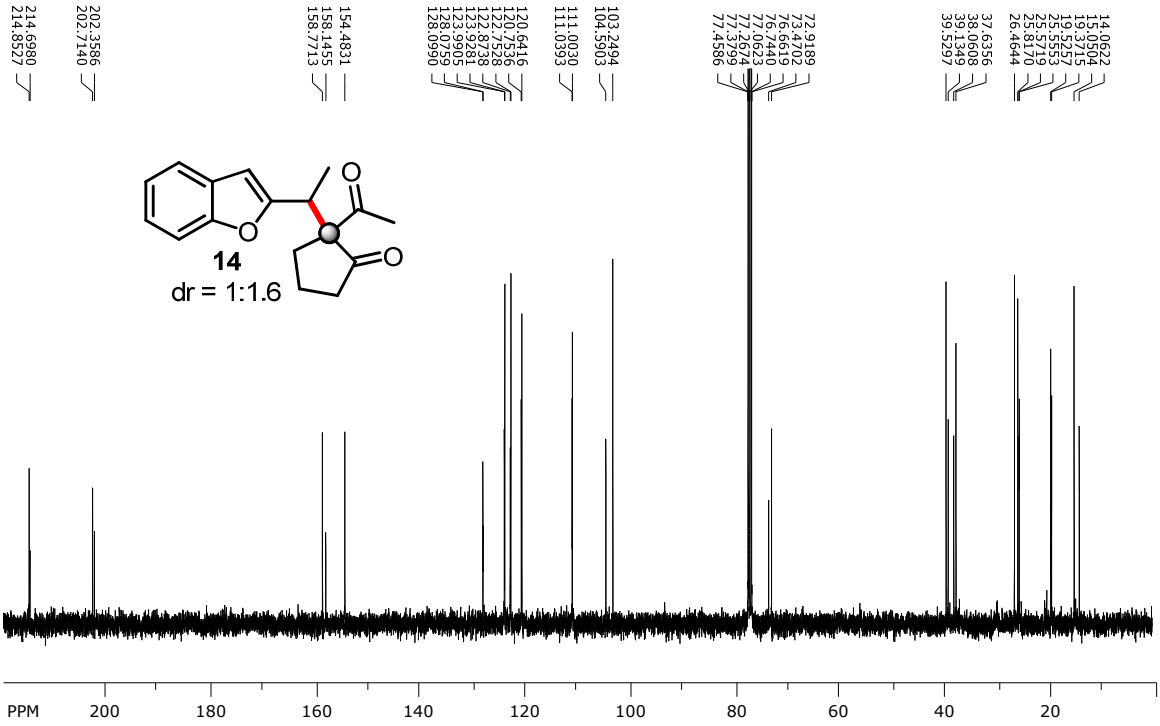
0.4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120.7536
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PPM
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40
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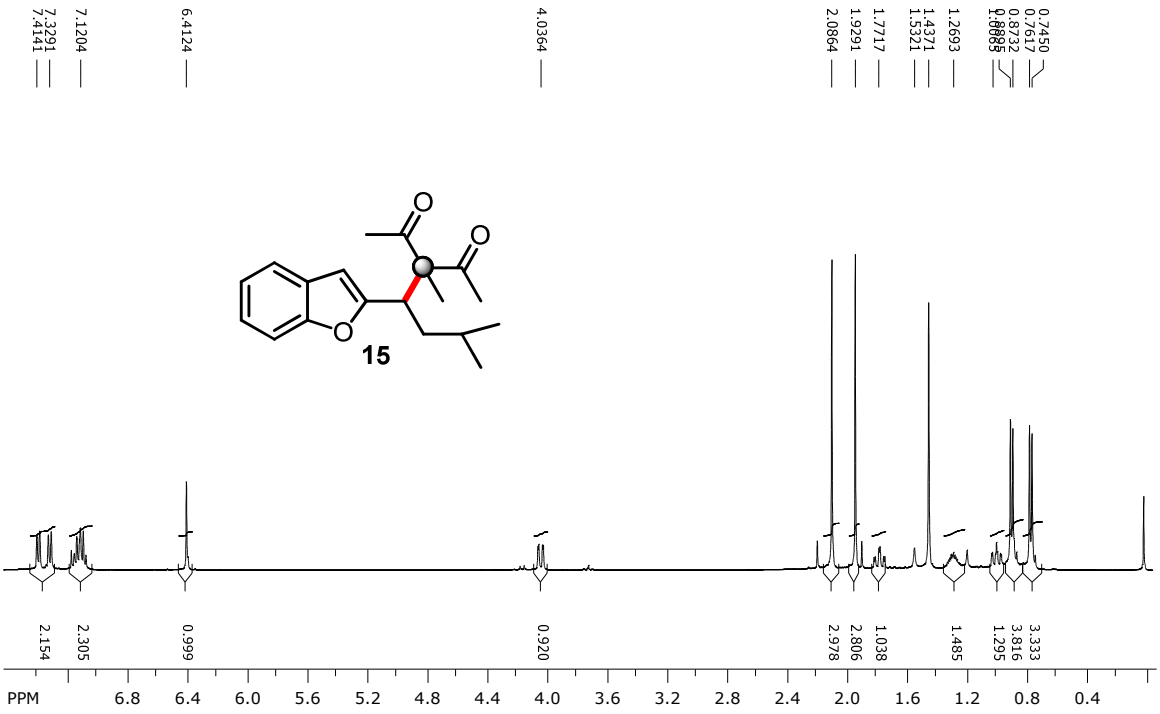
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0.7617
0.7450
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1.038
1.485
1.295
3.816
3.333
PPM
6.8
6.4
6.0
5.6
5.2
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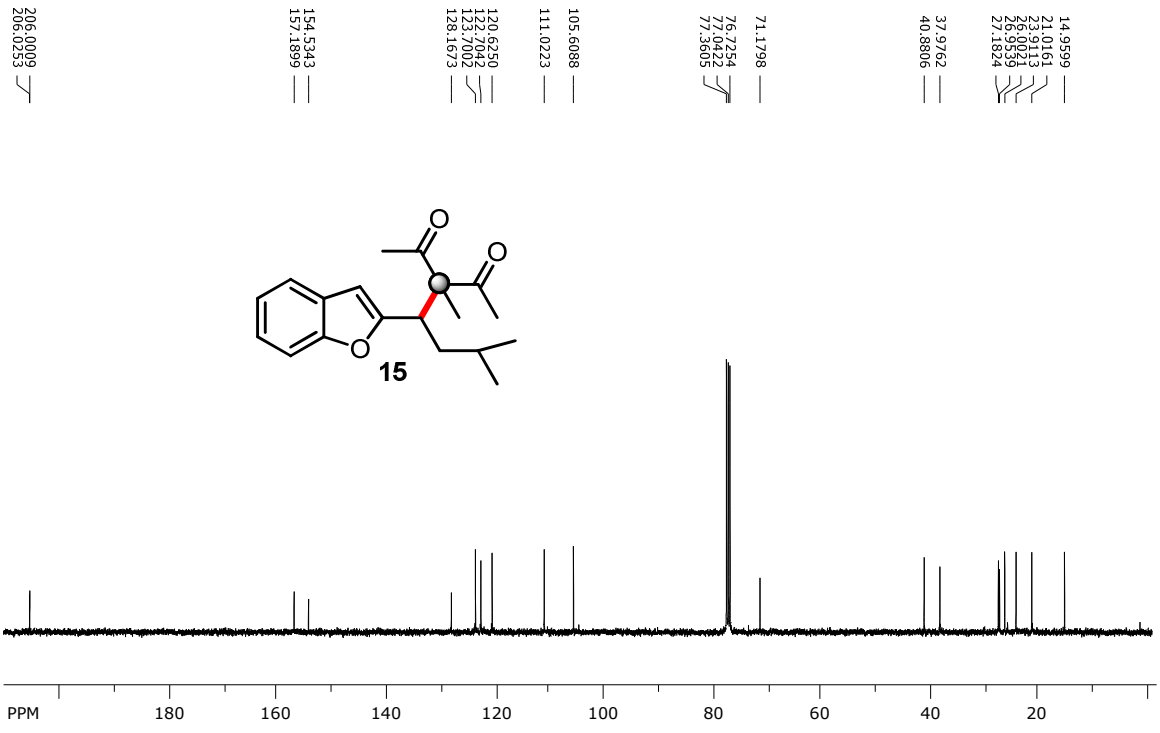
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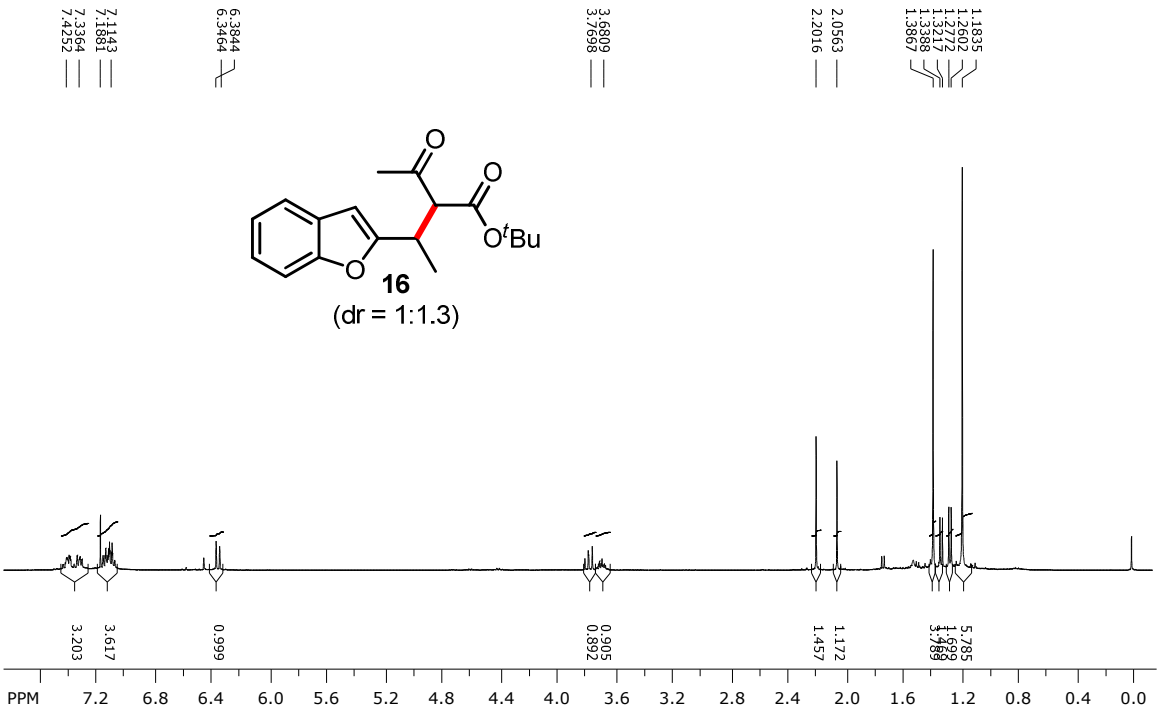
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1.3217
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1.1835
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O
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O
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PPM
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6.0
5.6
5.2
4.8
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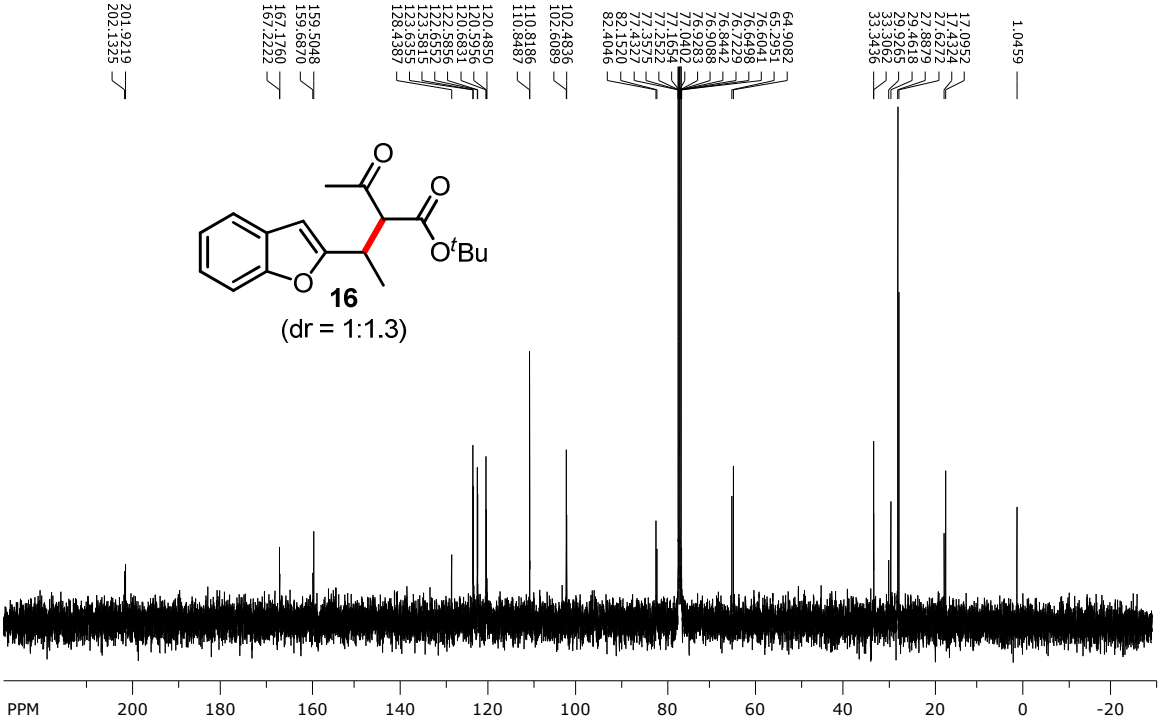
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O
O
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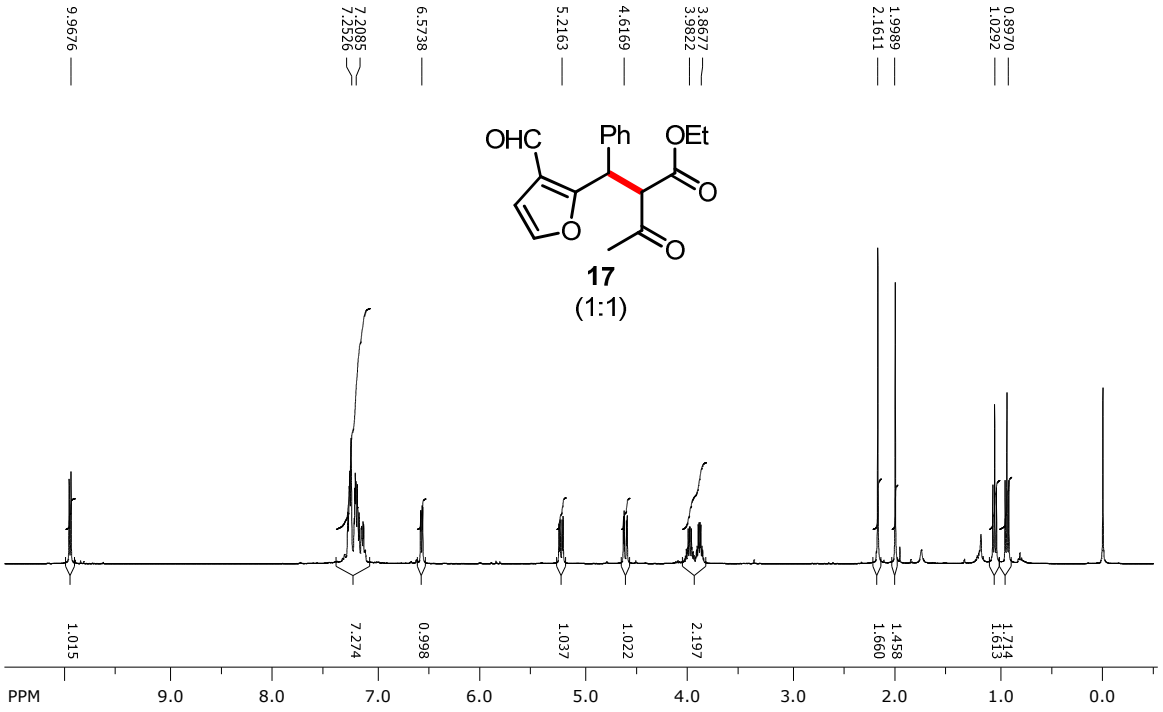

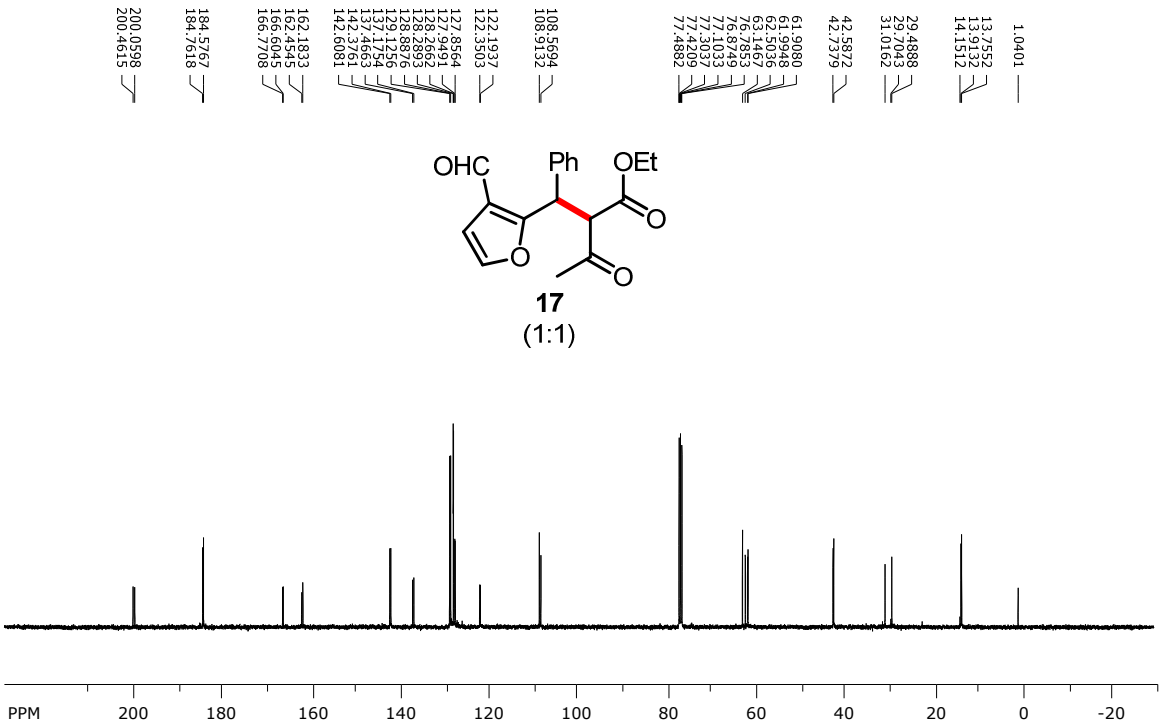

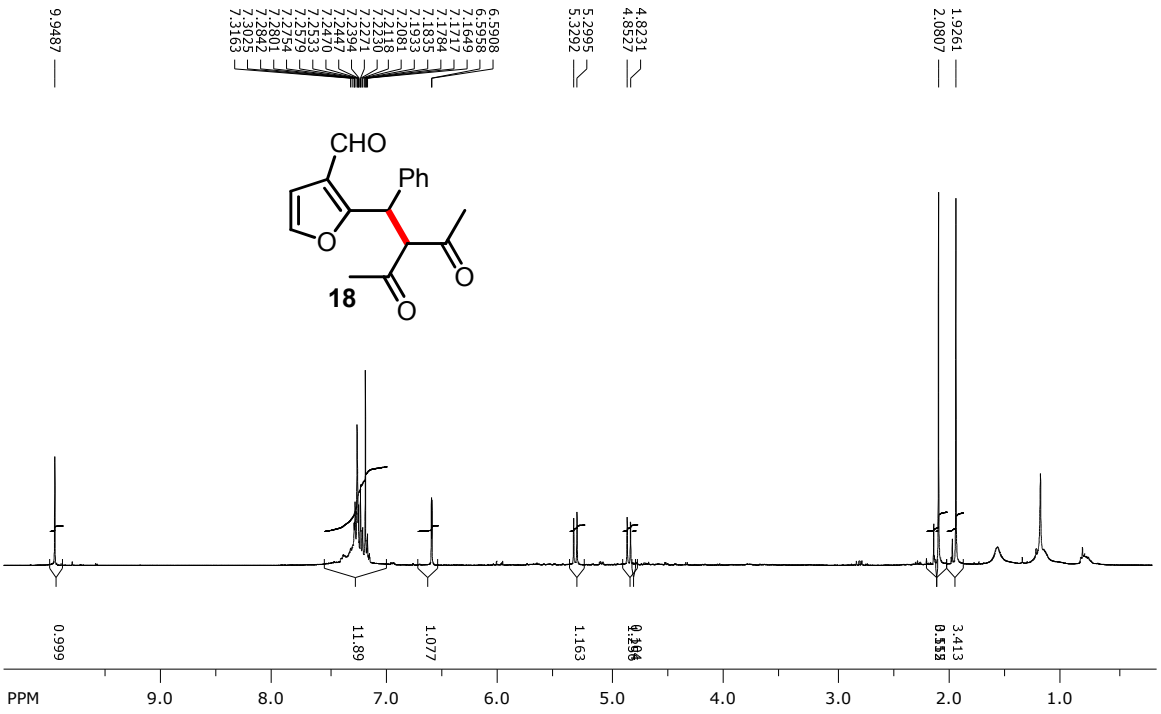
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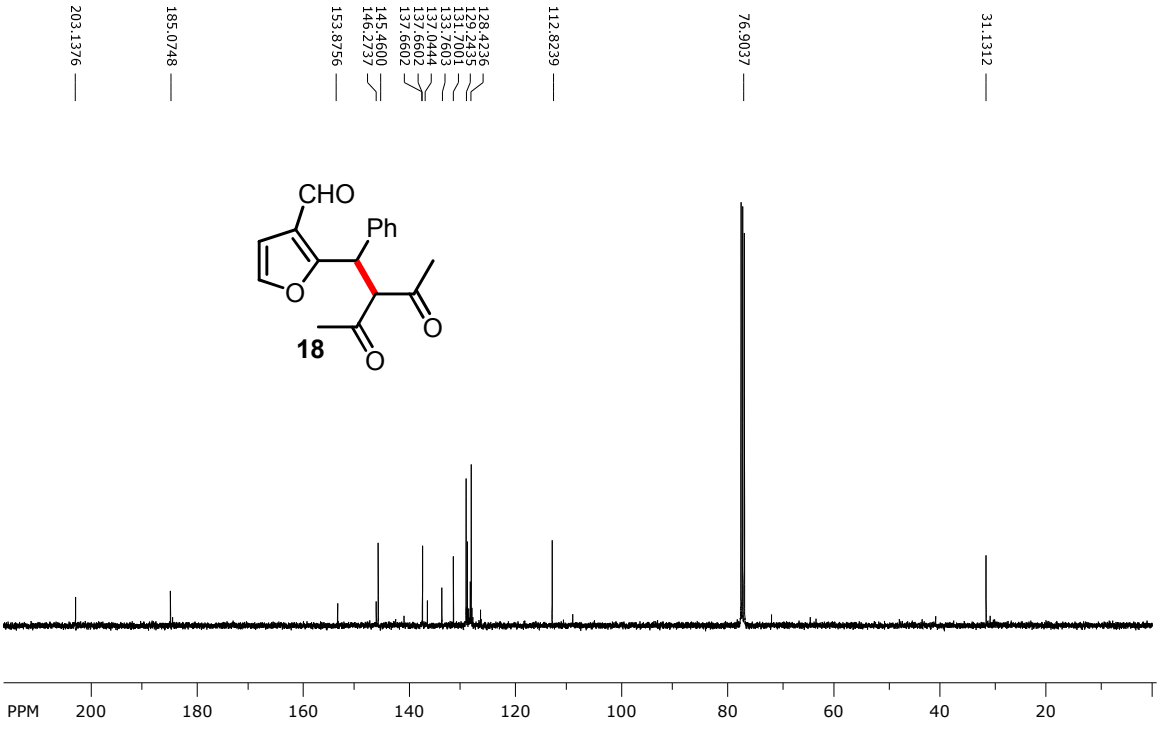
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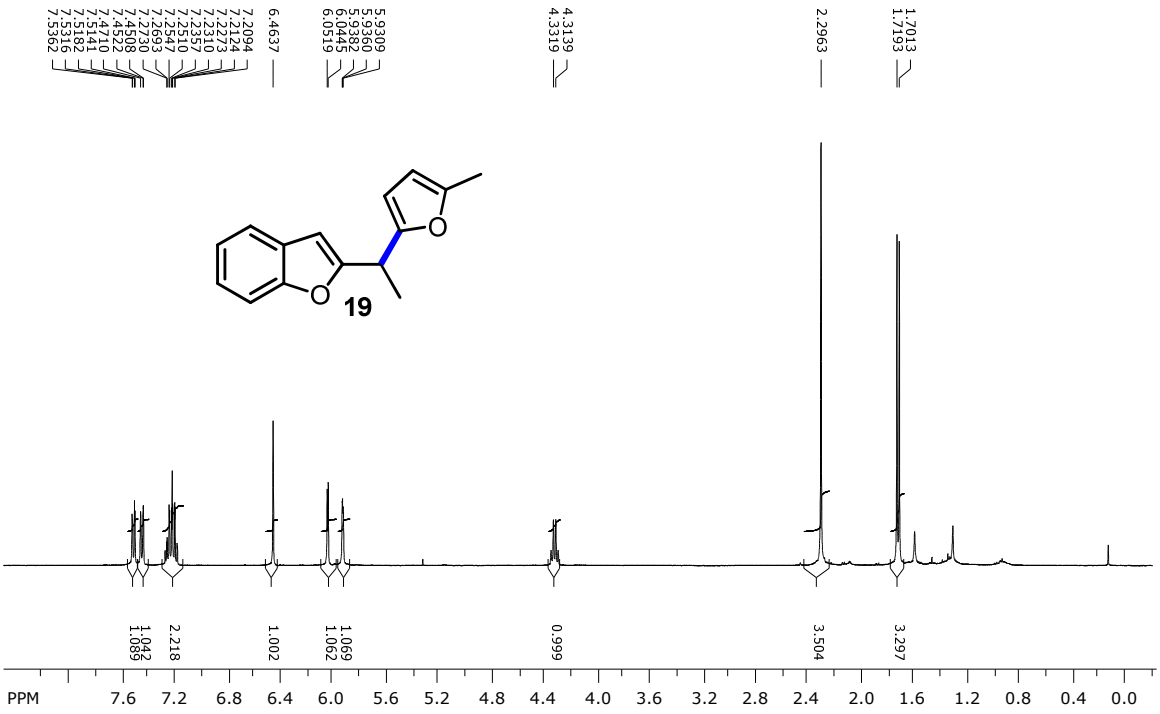

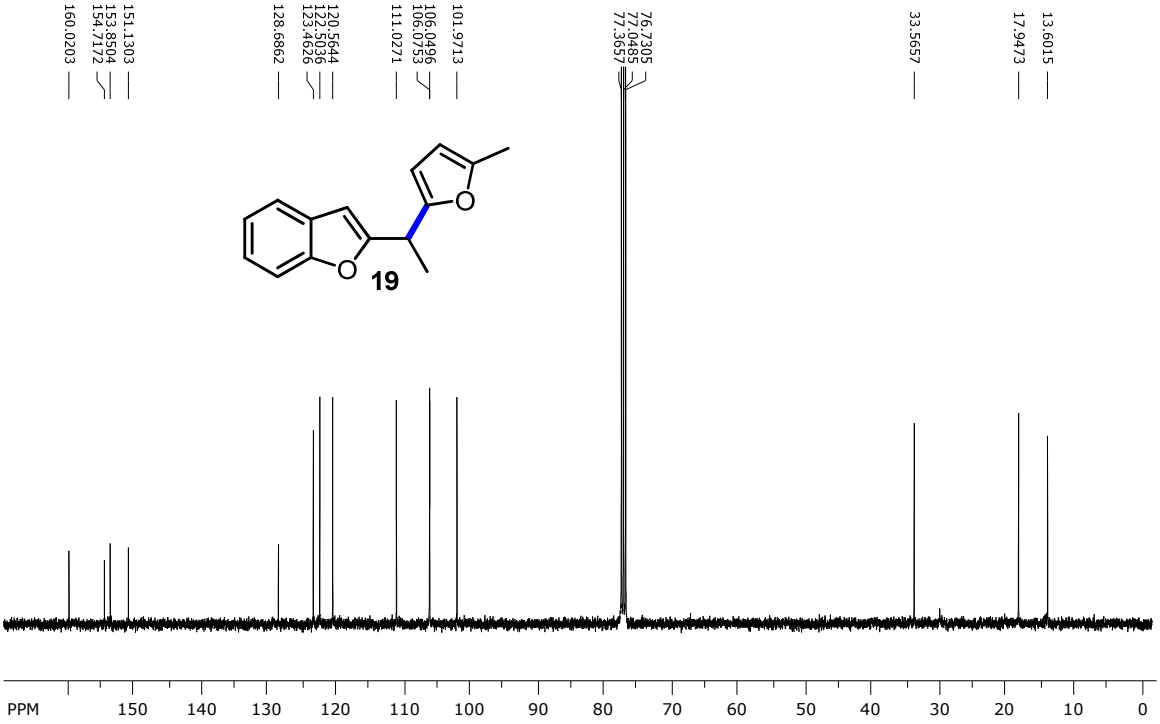

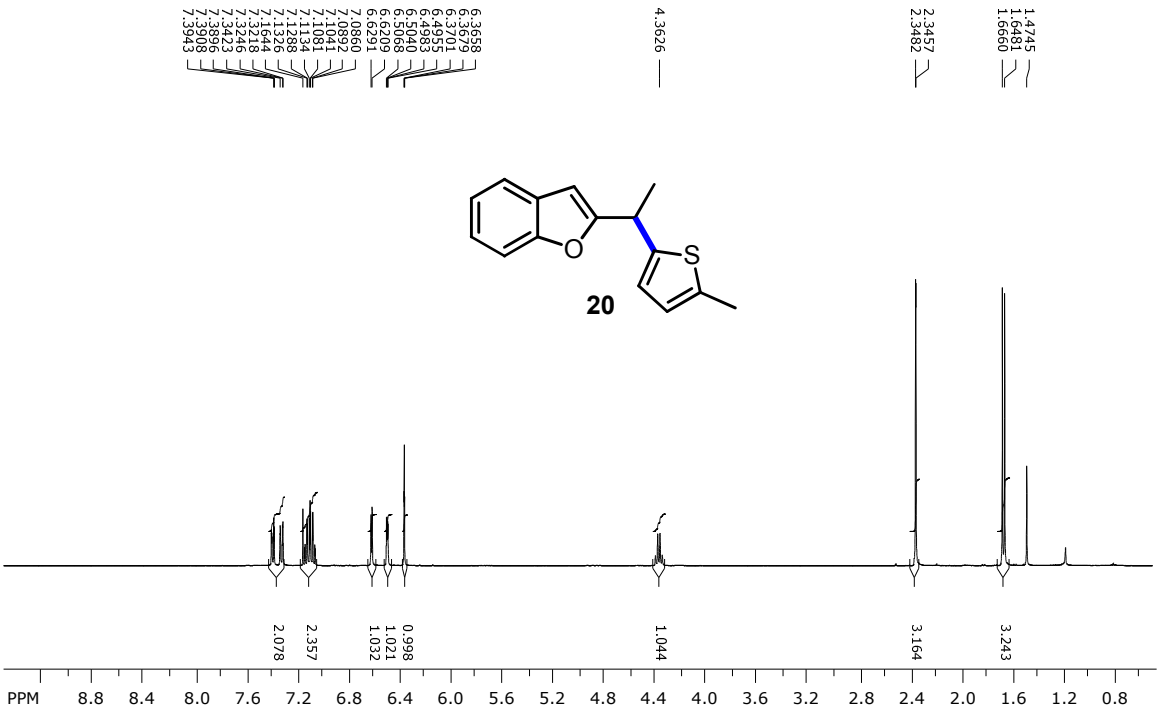

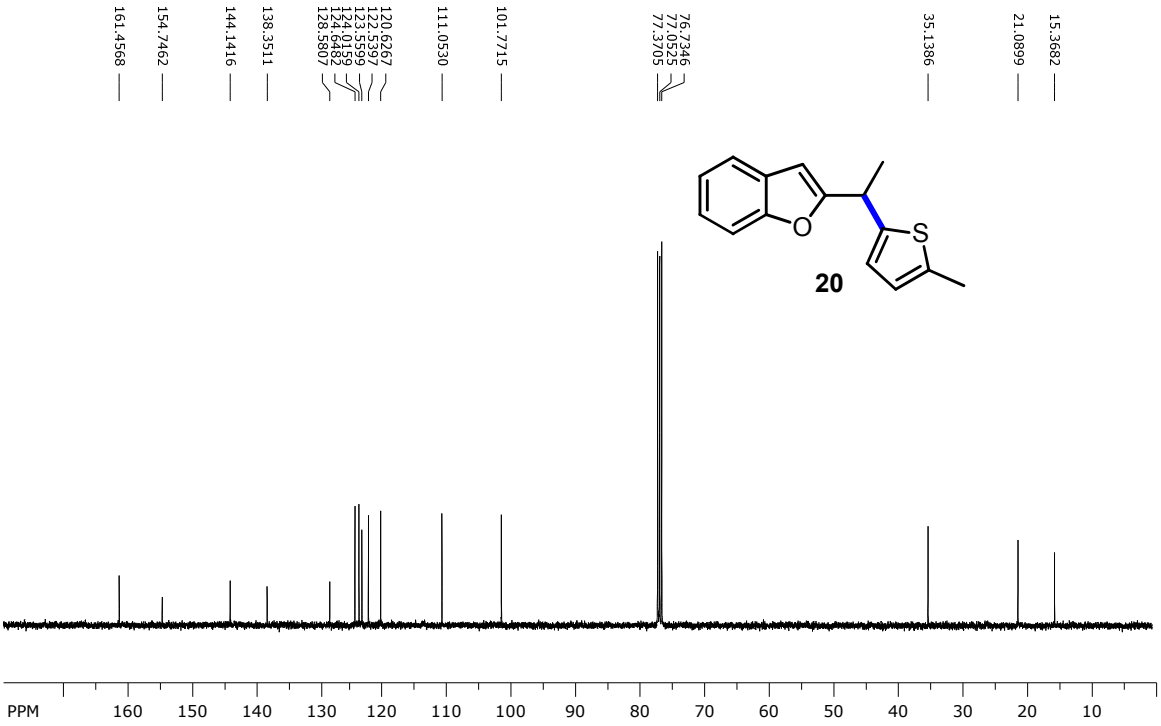

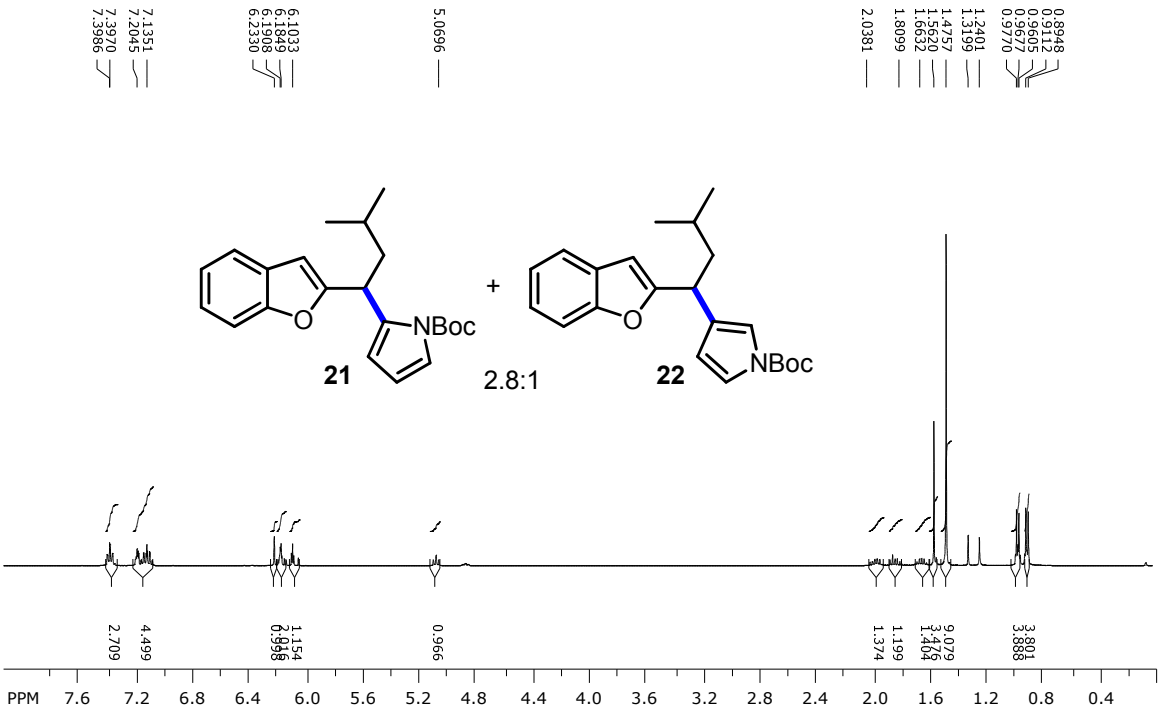
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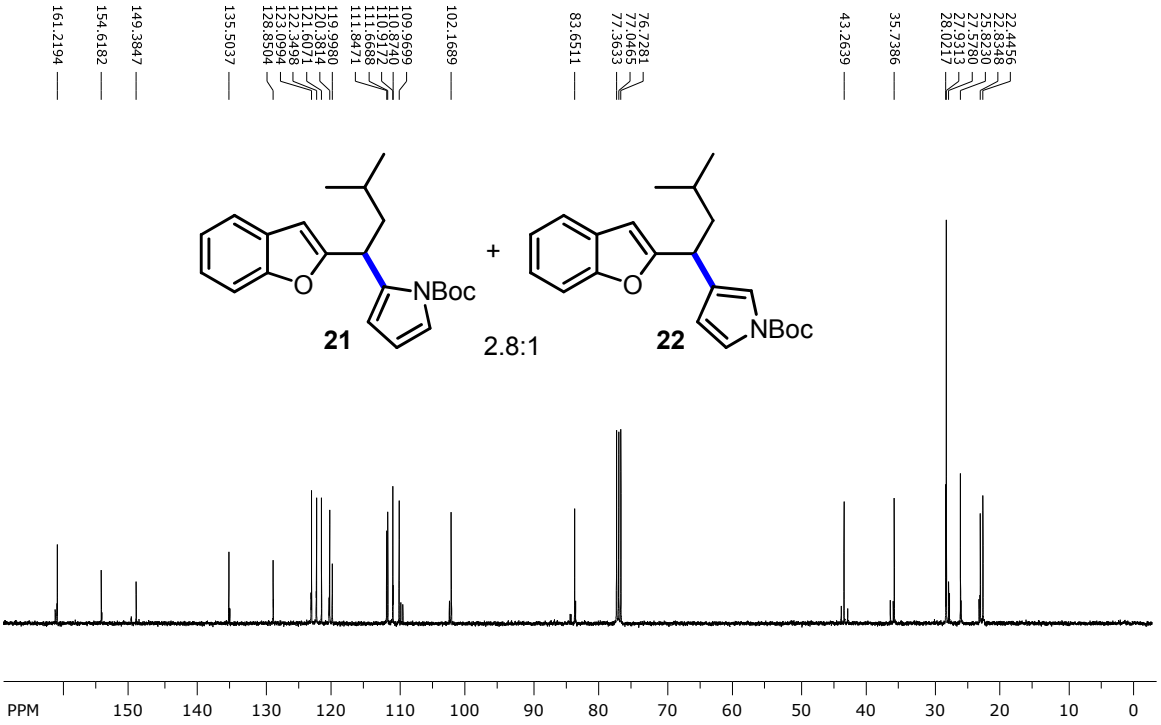
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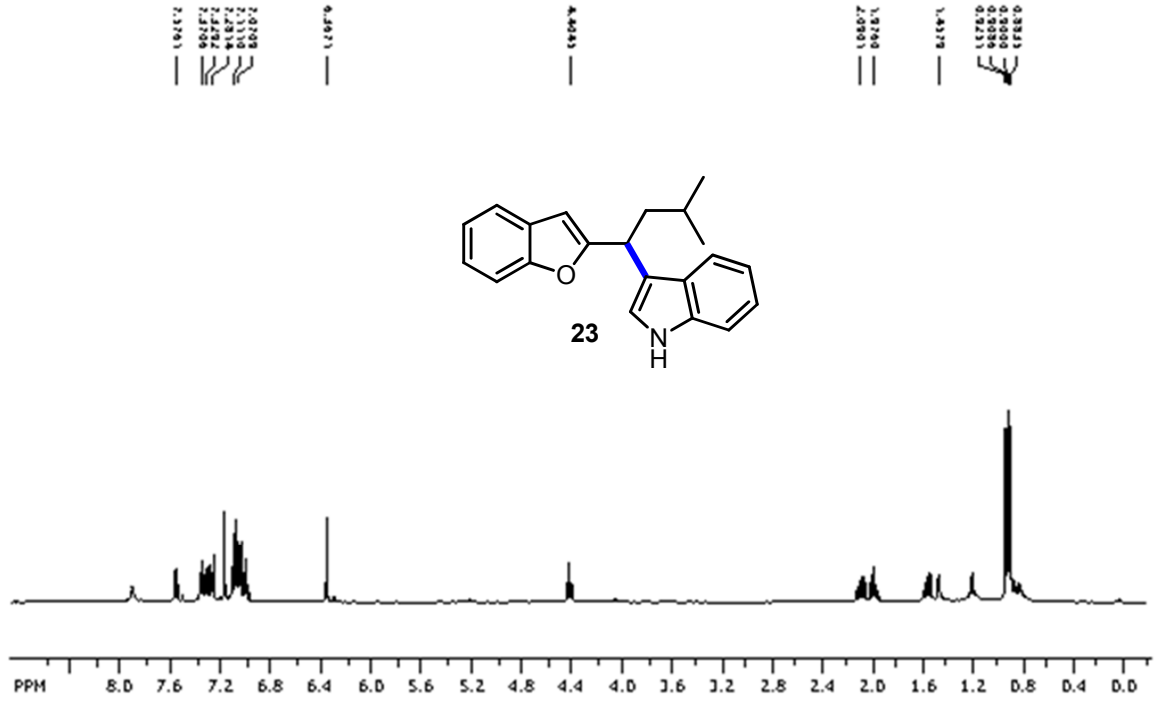
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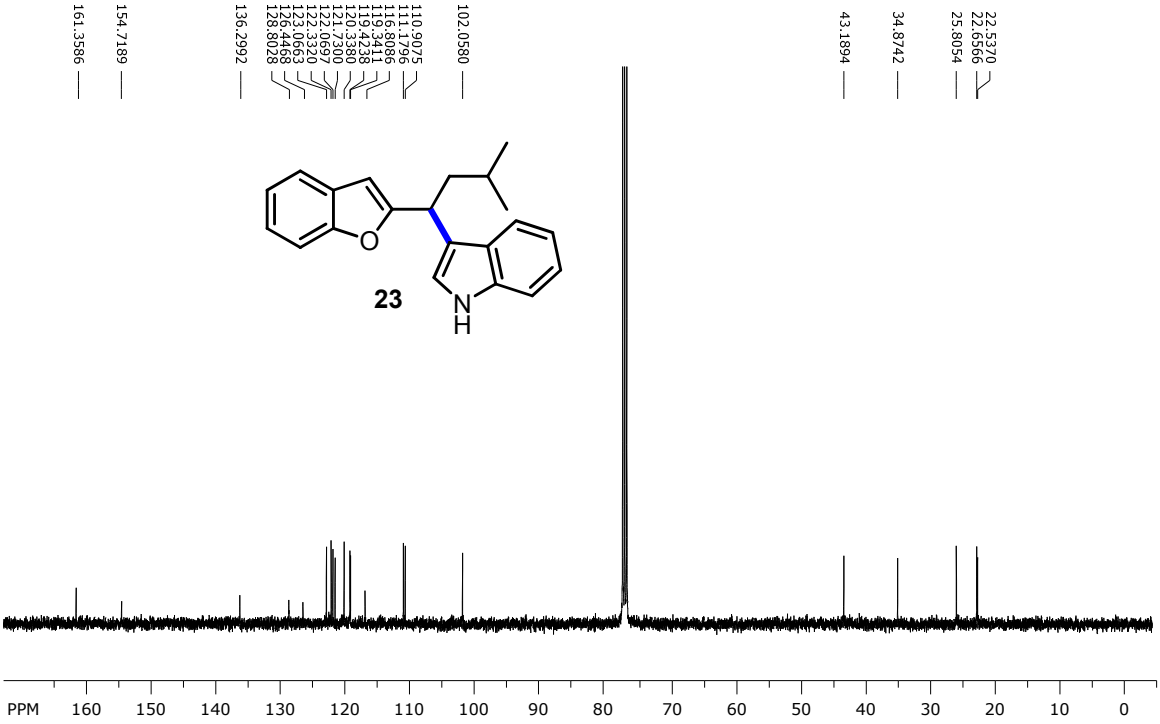
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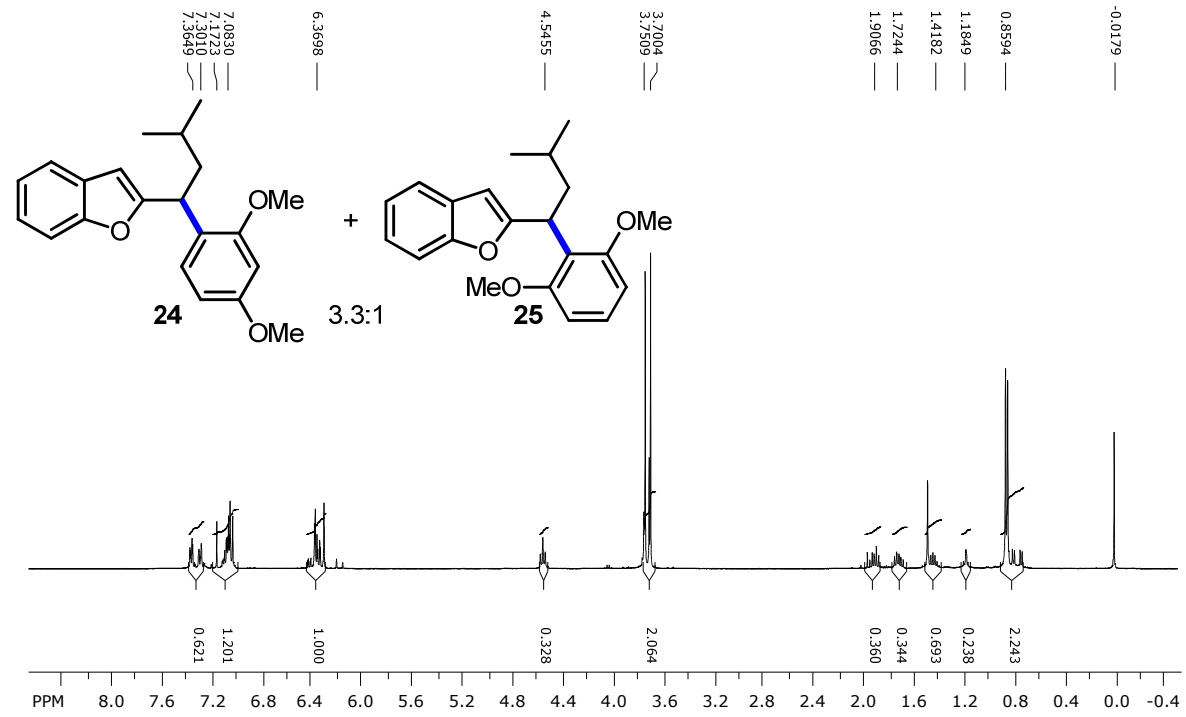

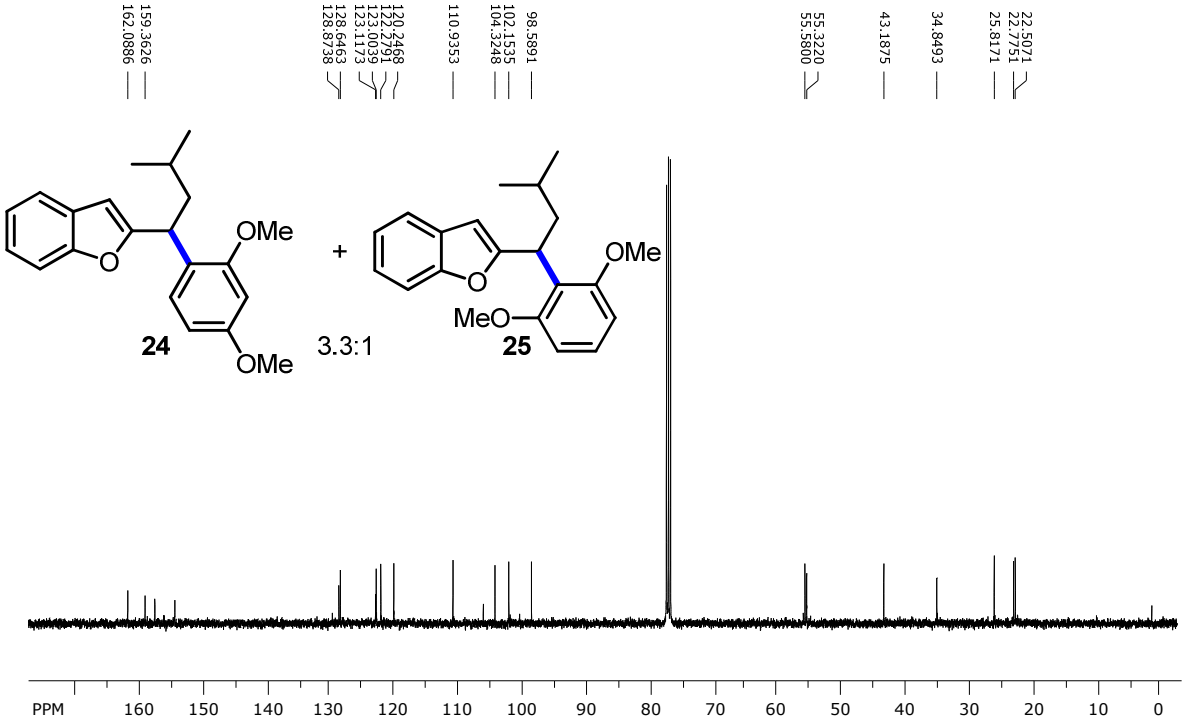

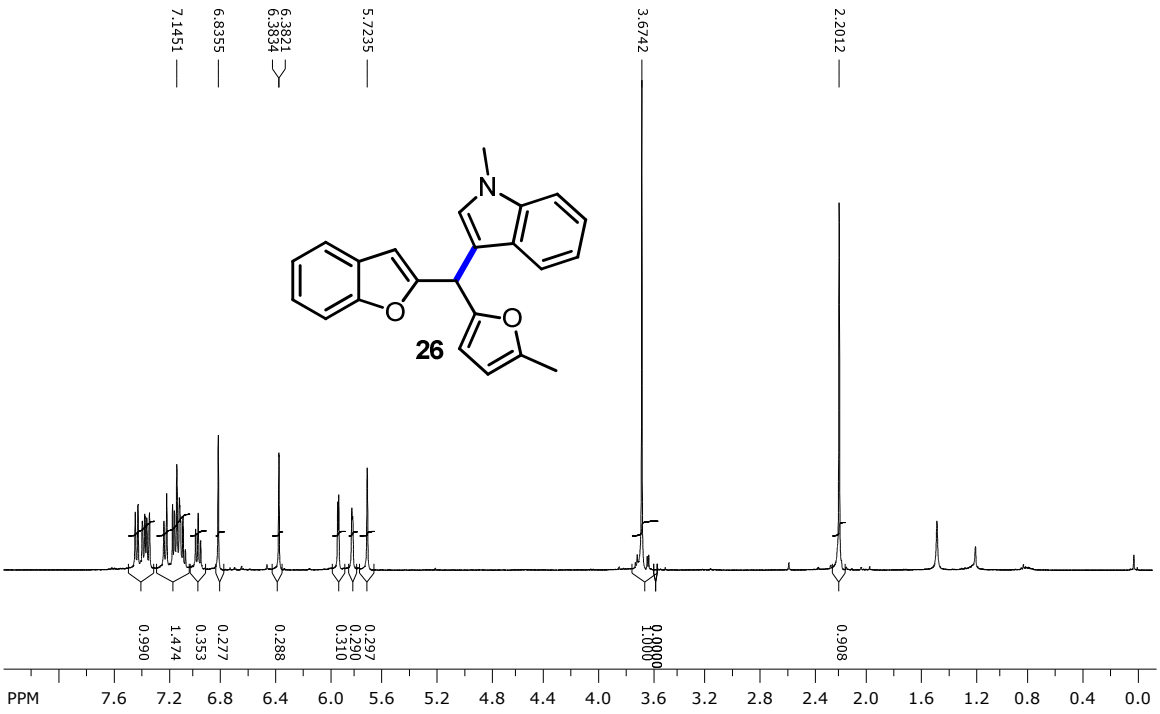

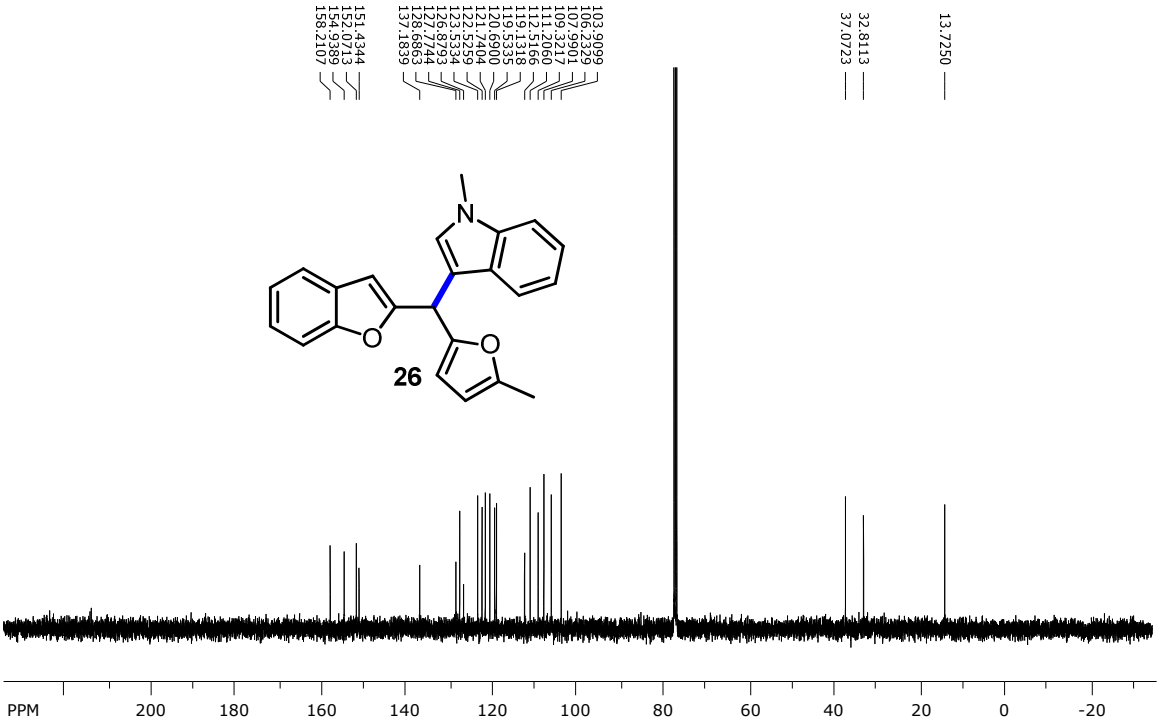

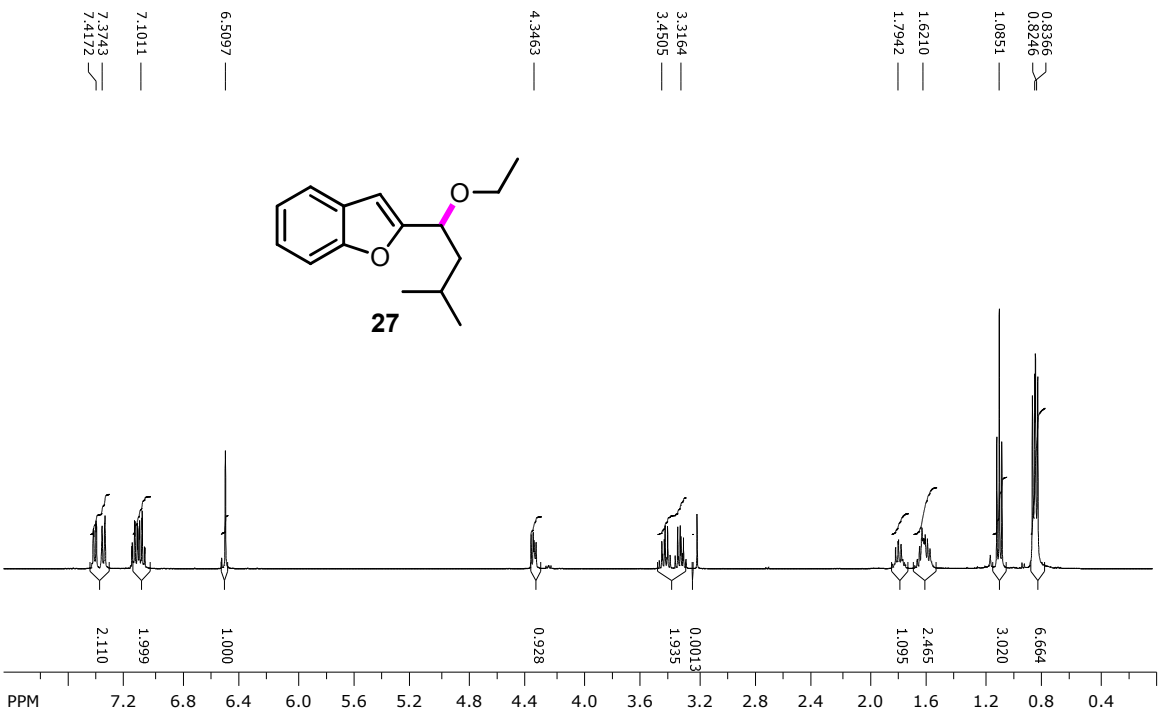

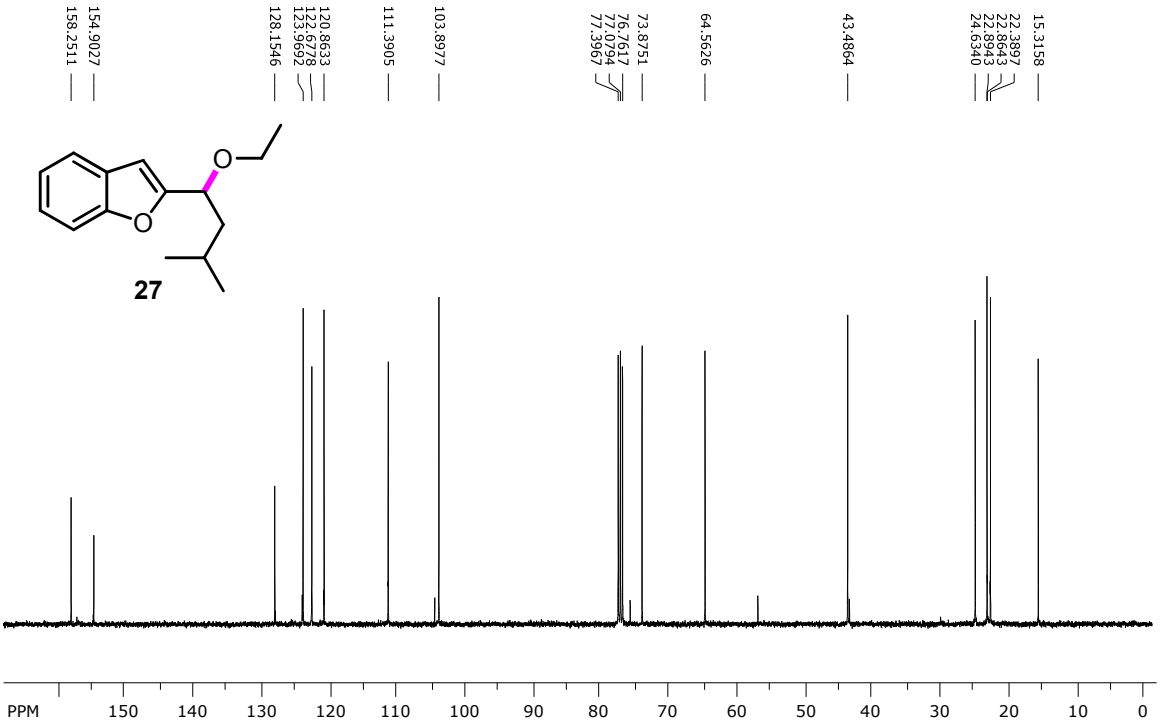

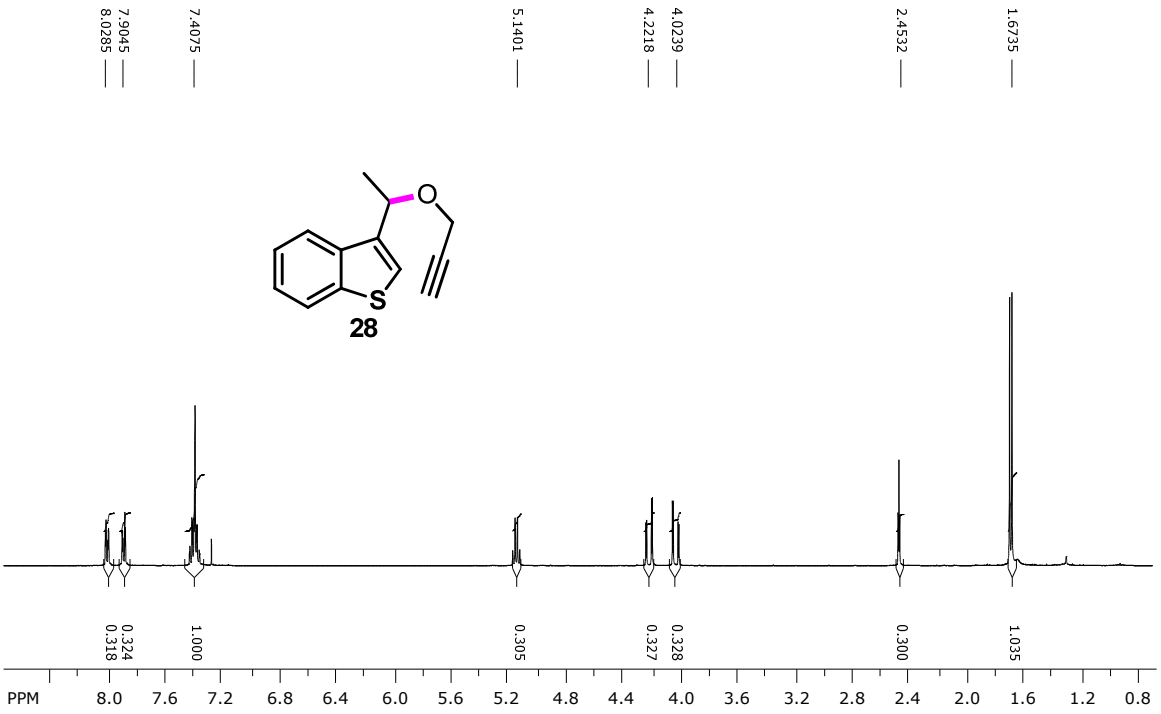

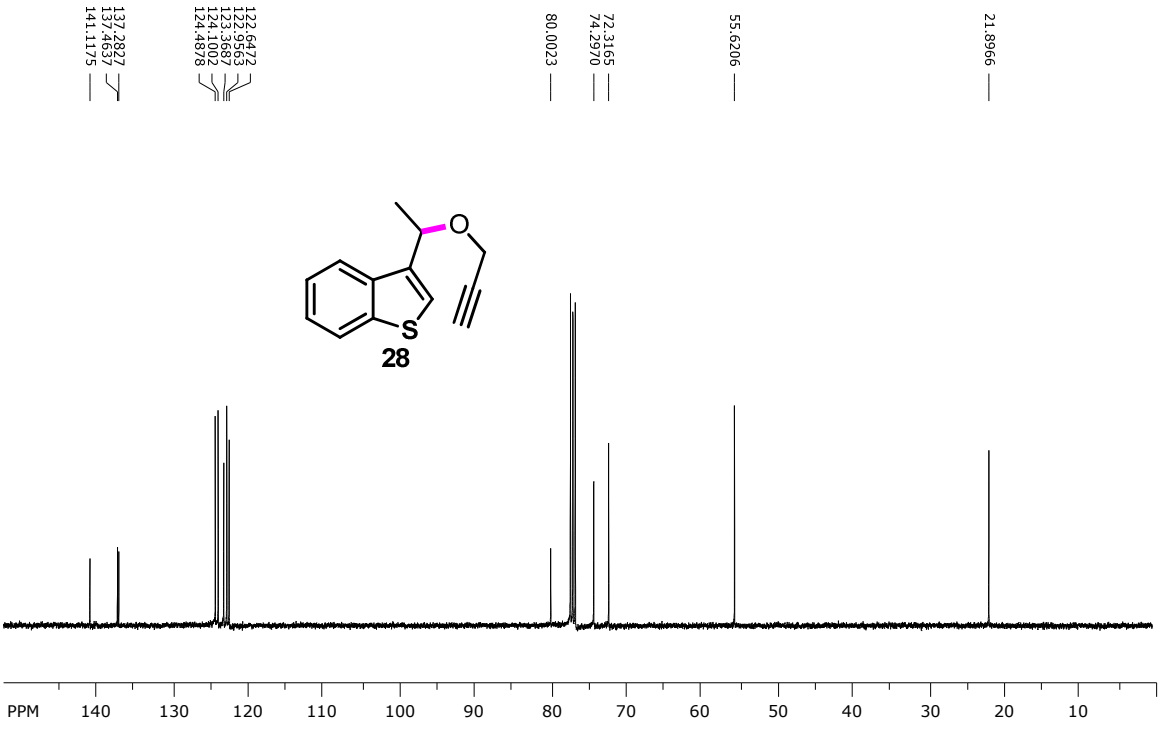

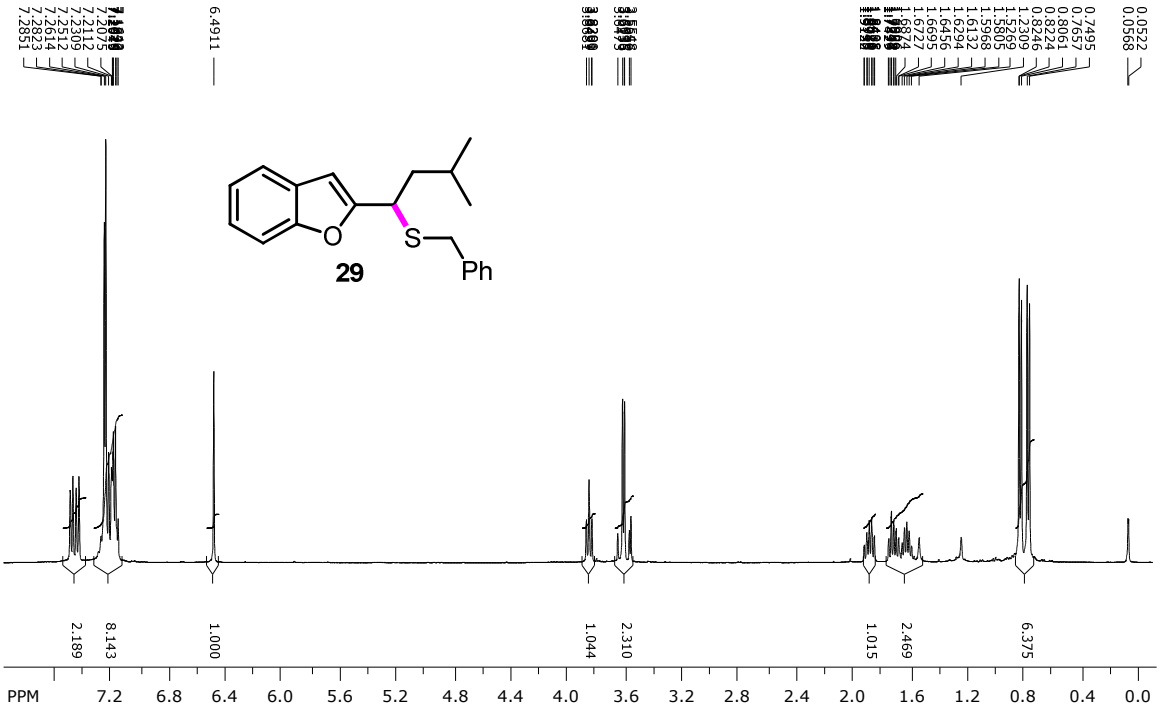

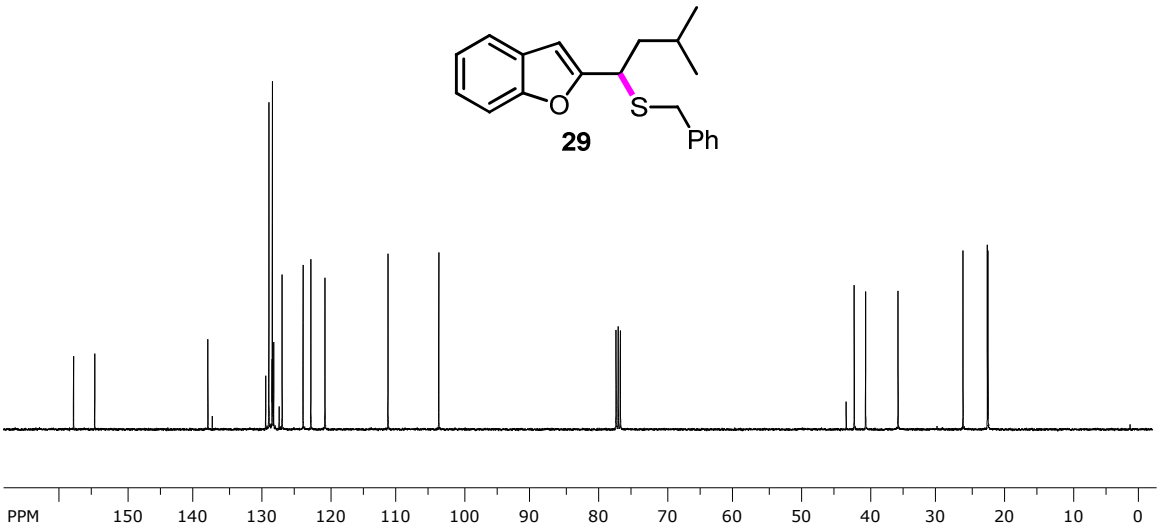

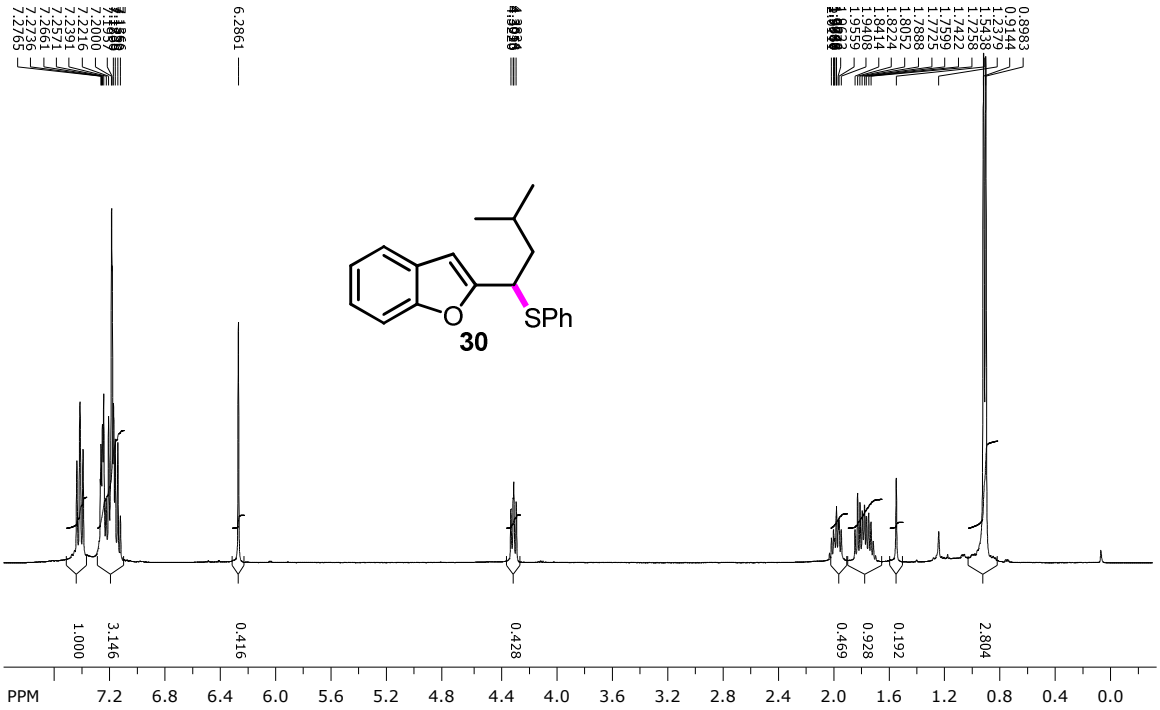

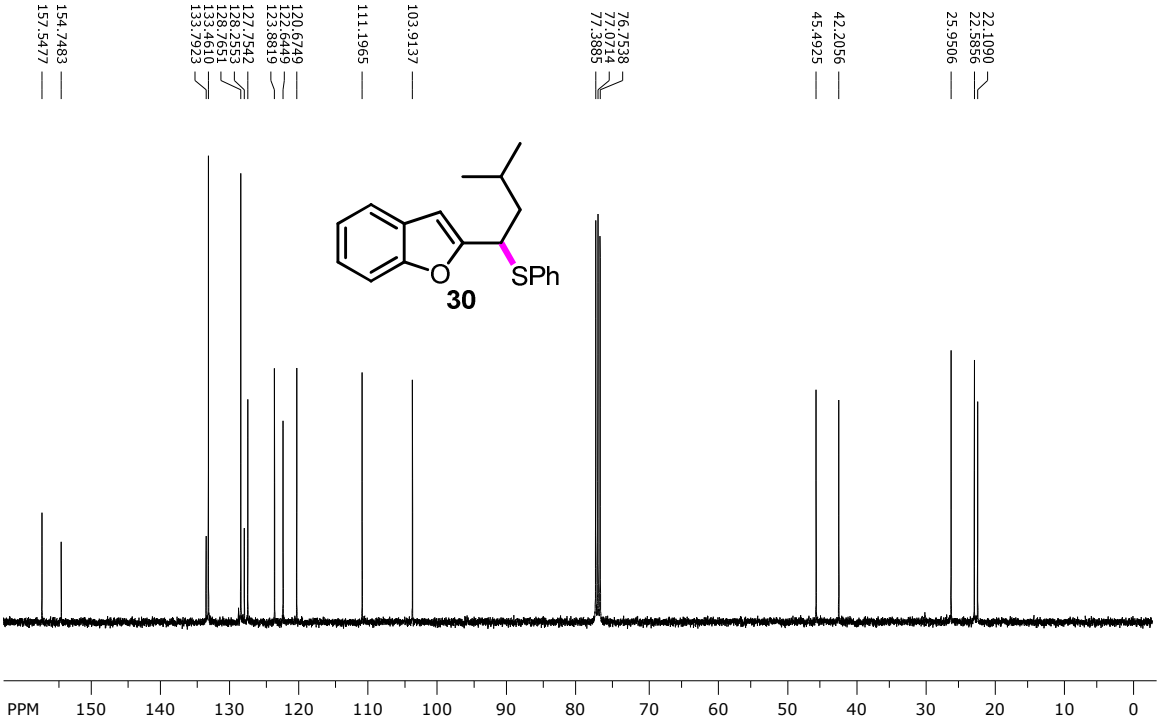

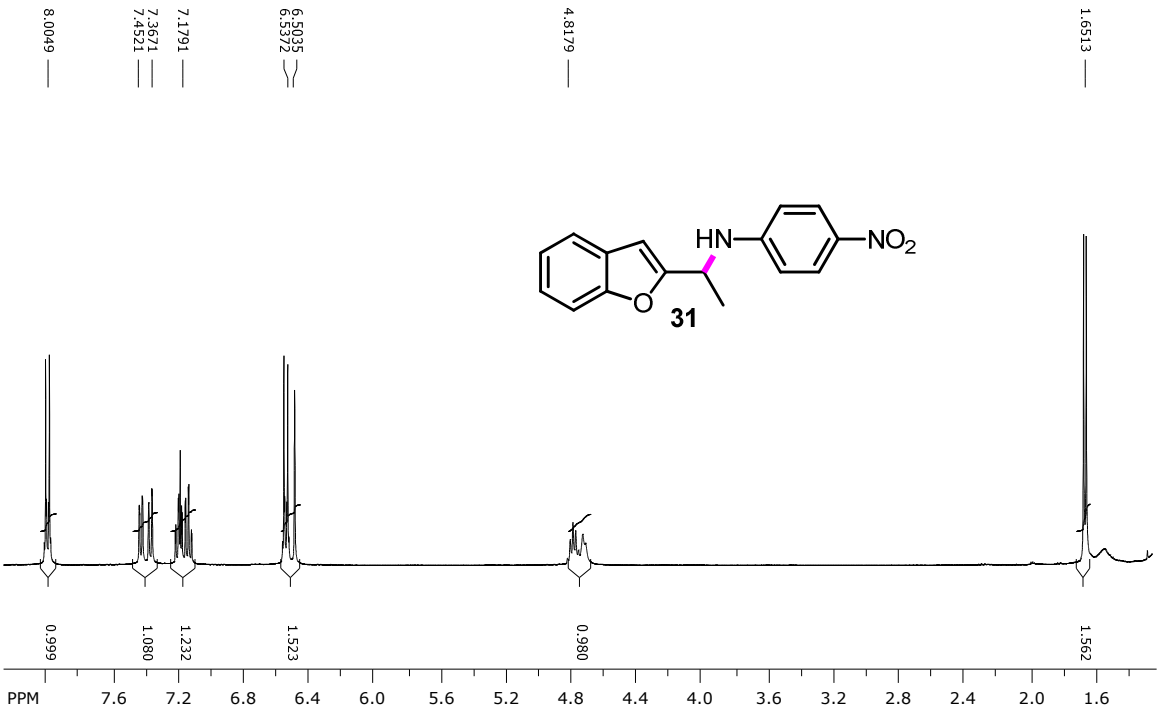

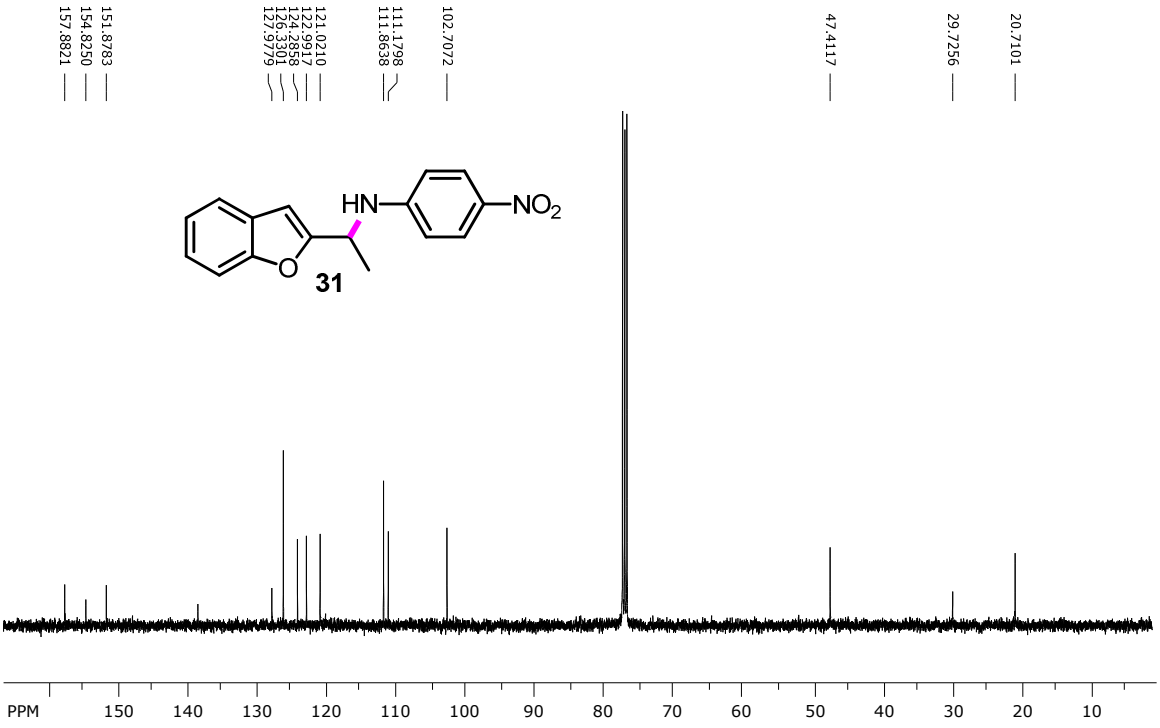

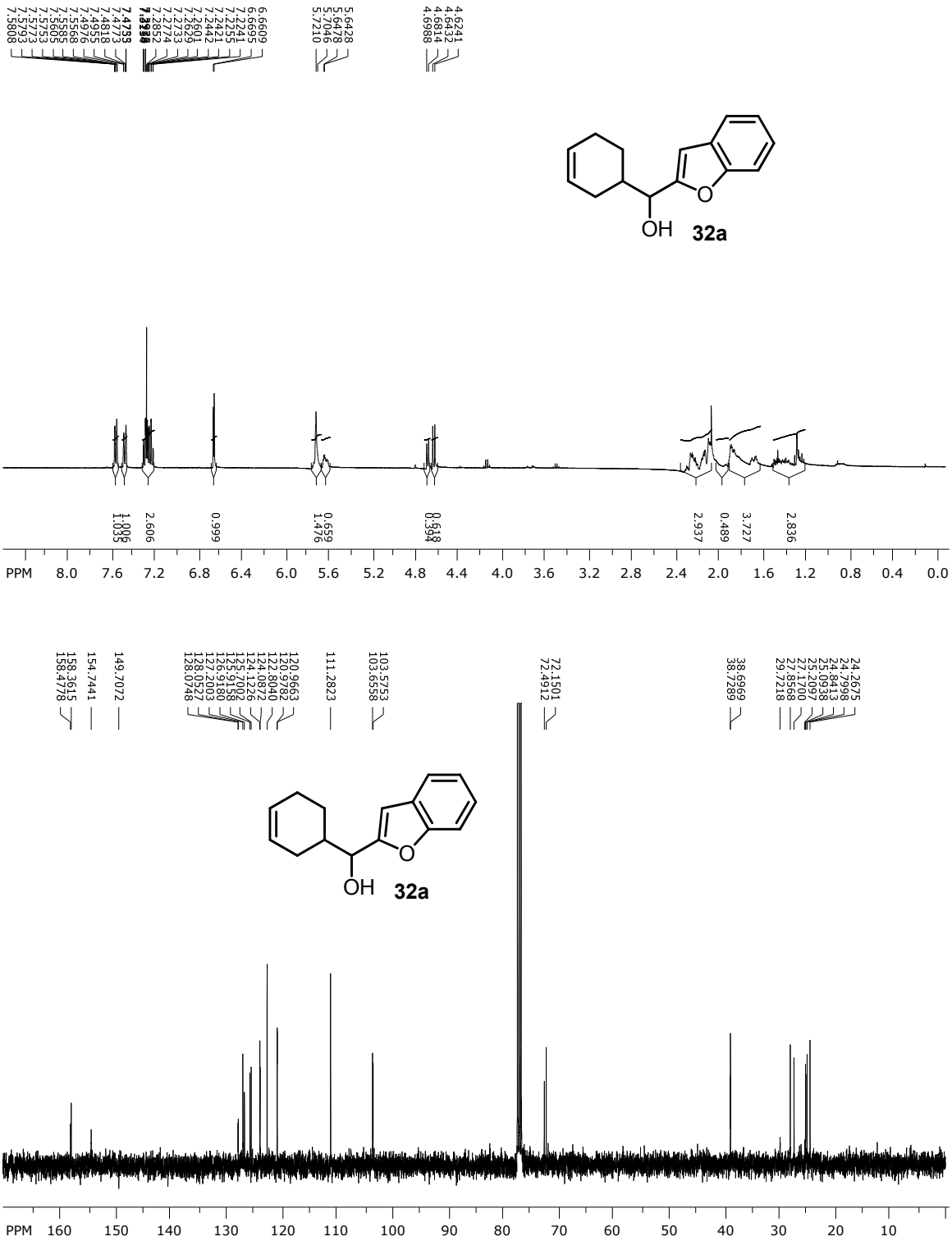
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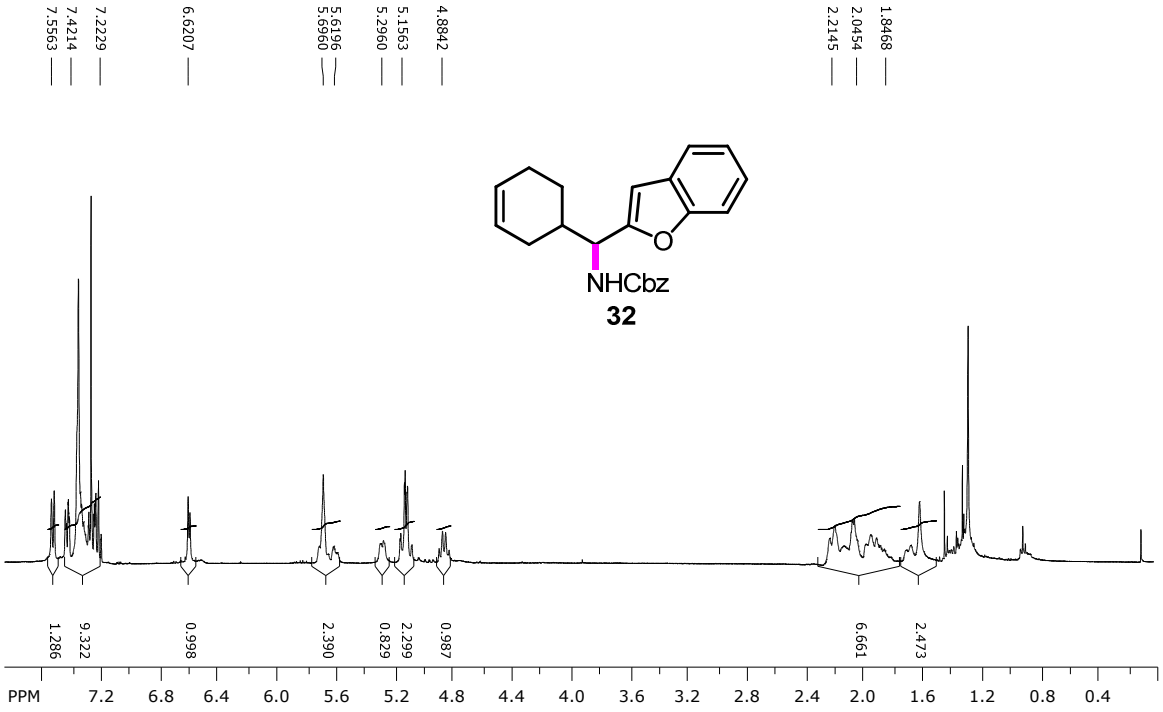

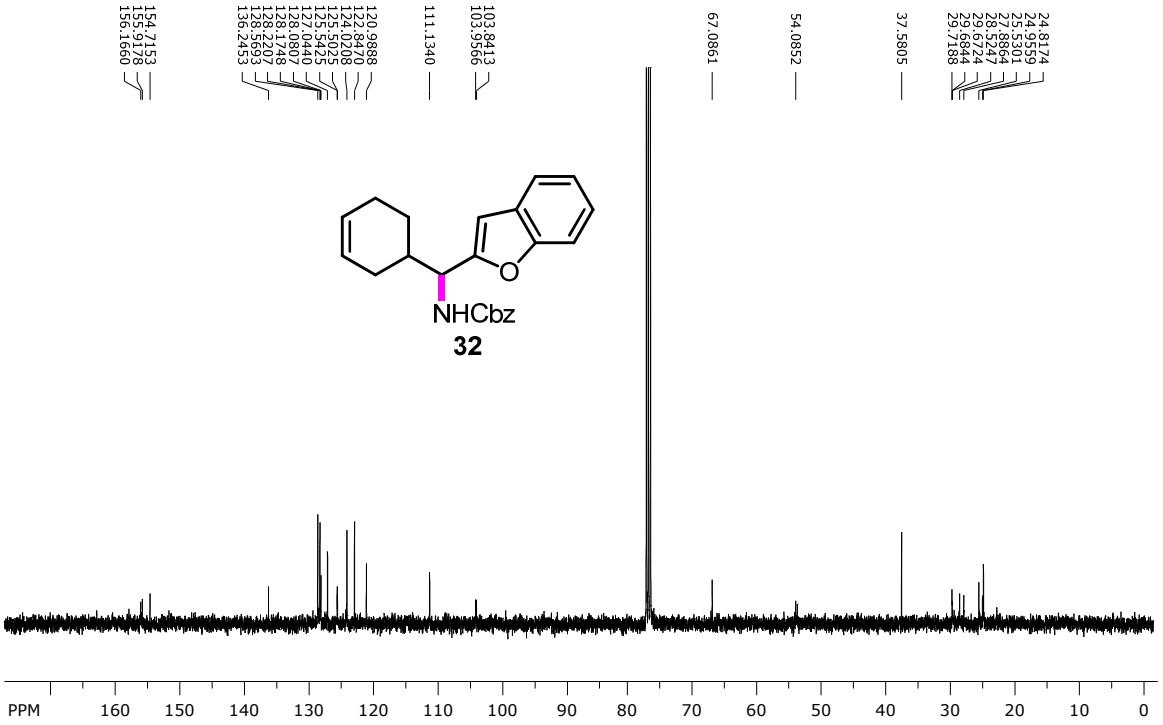

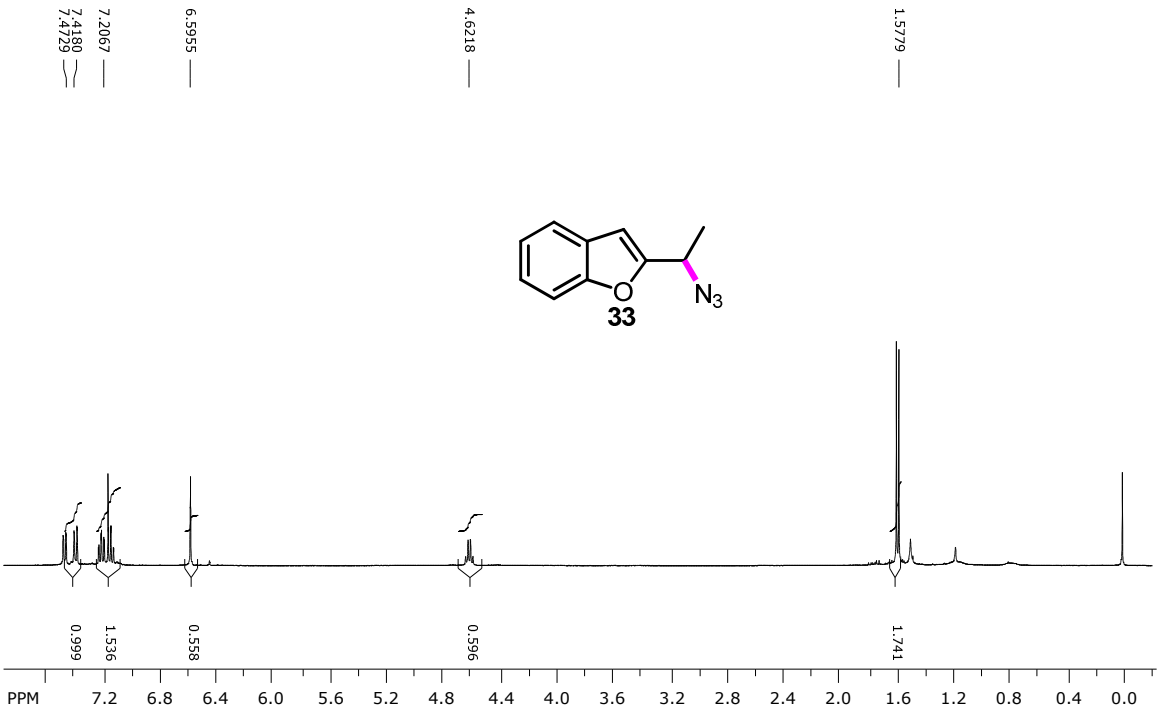

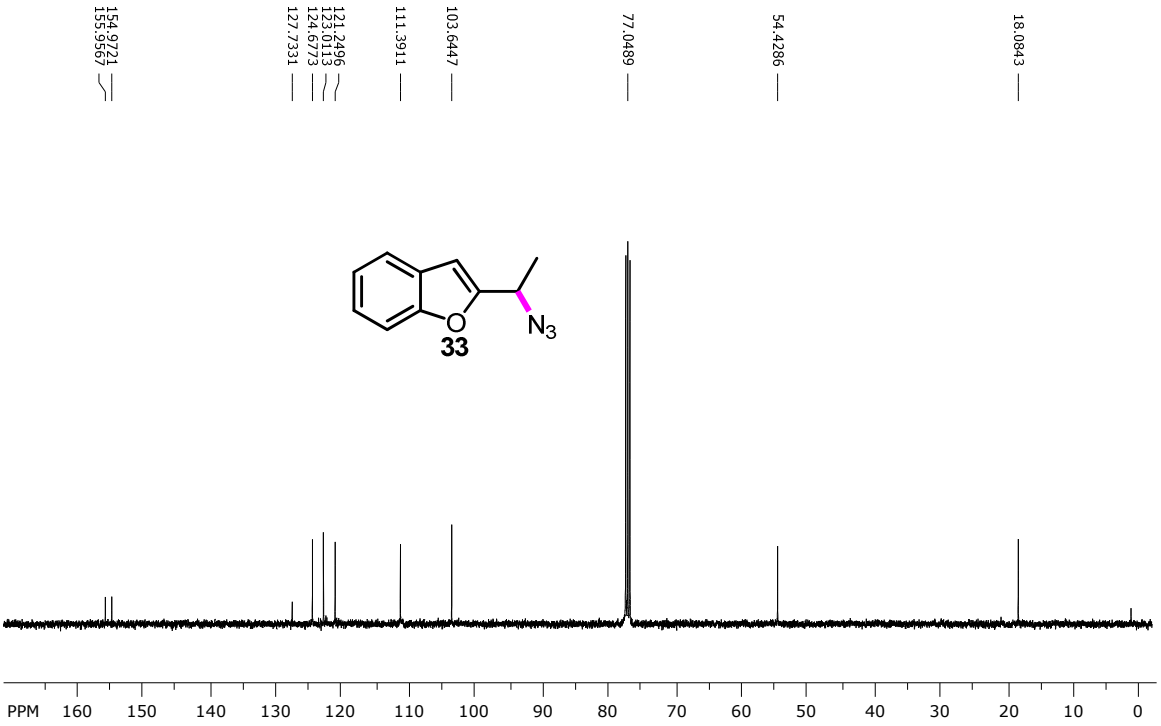

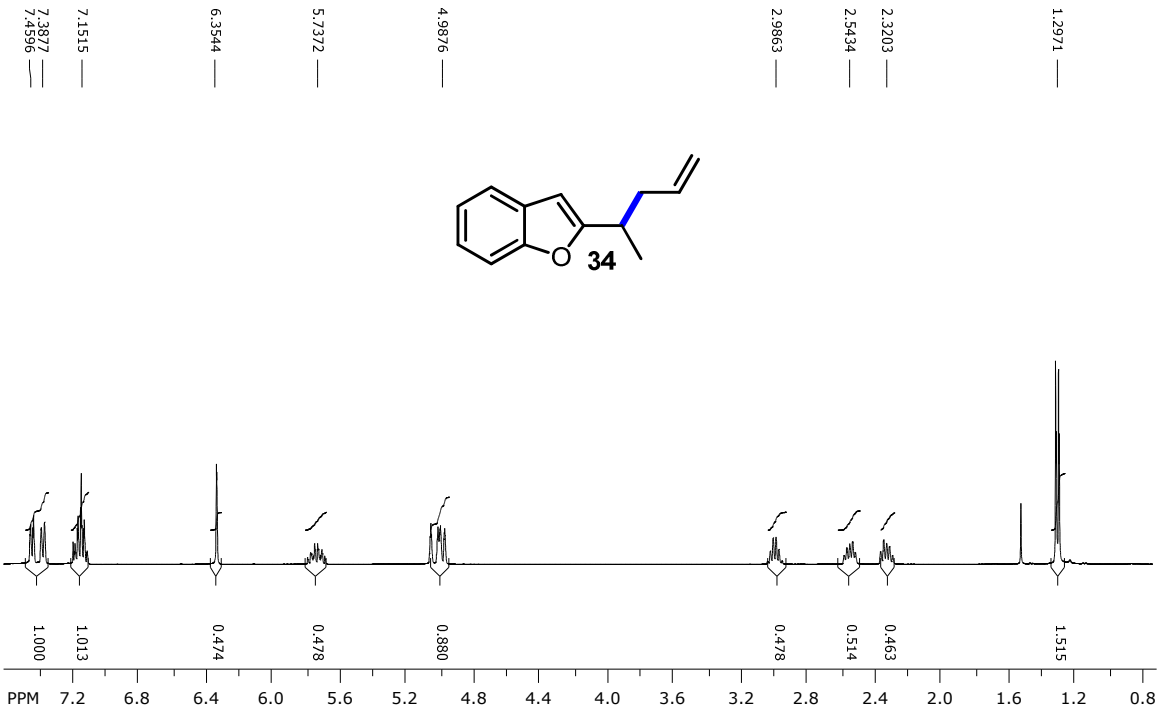

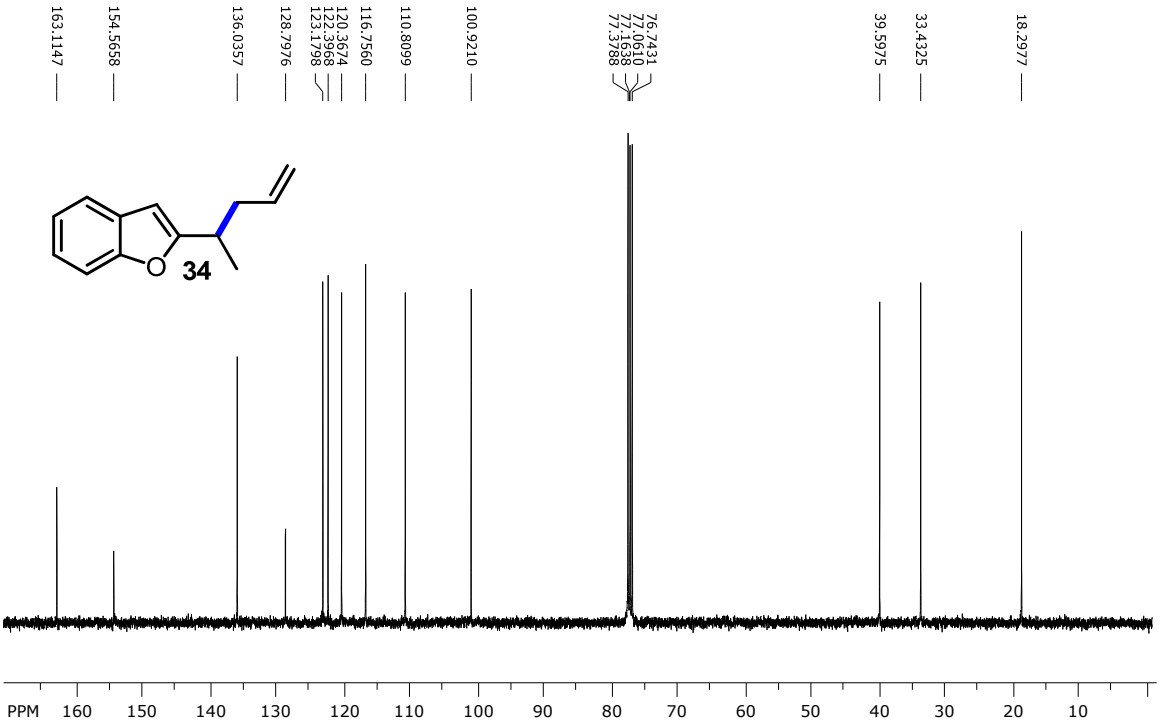

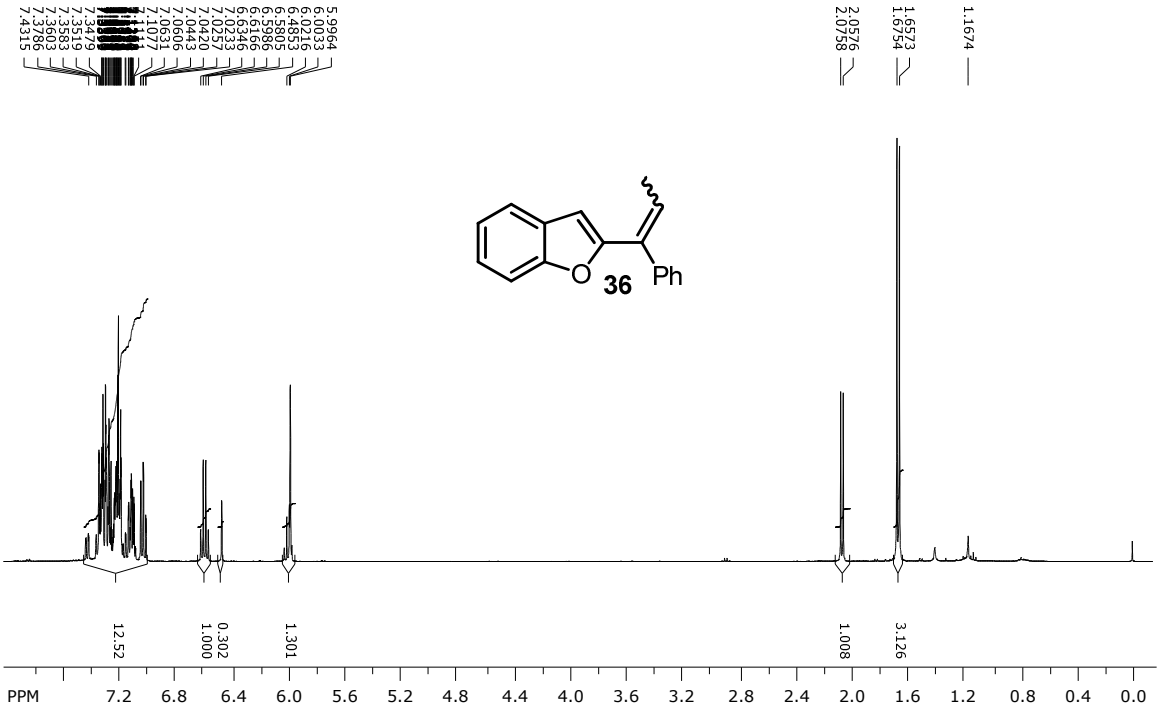

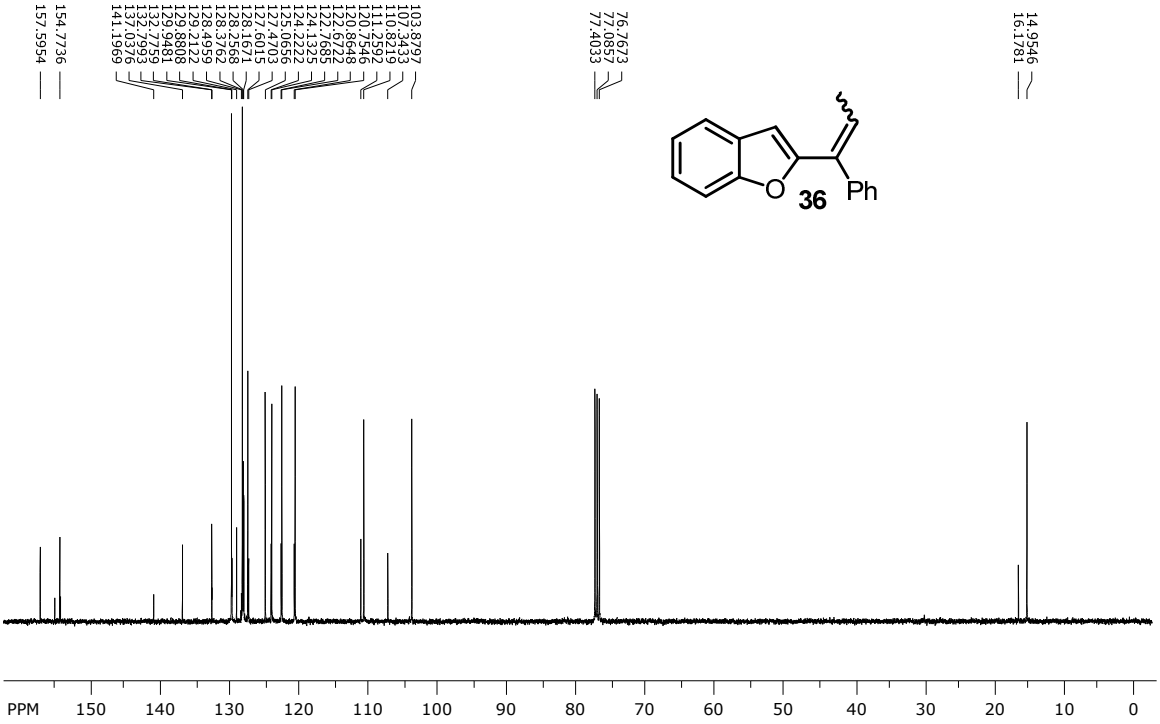

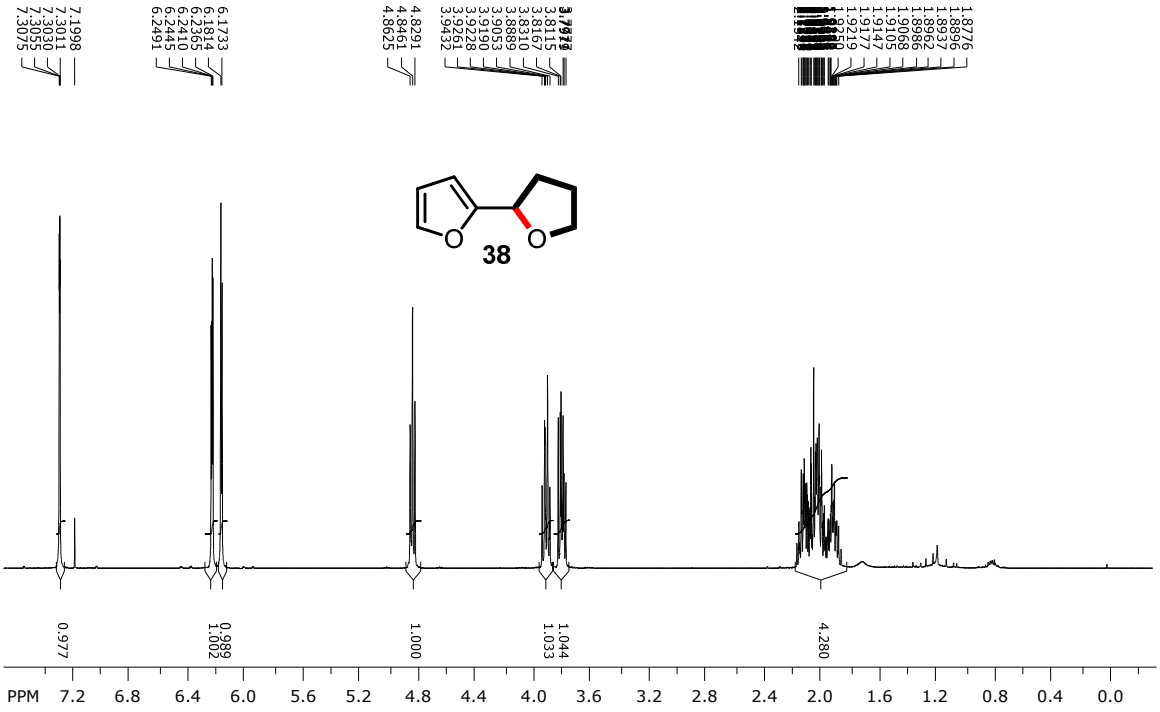

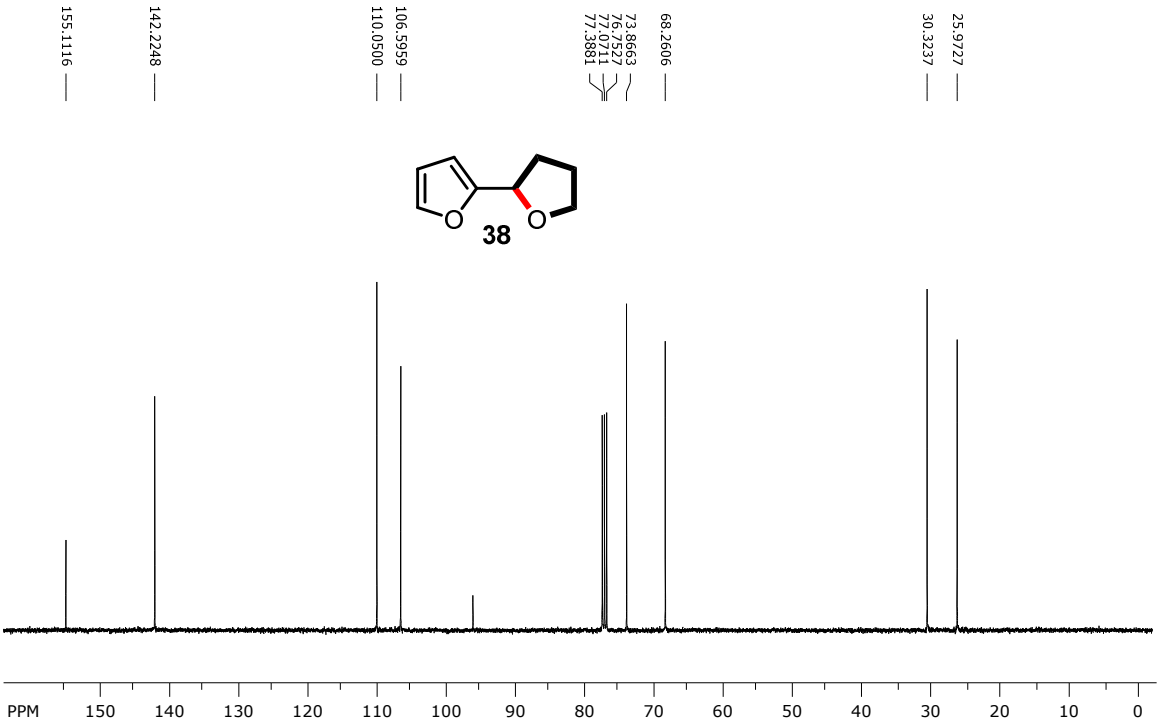

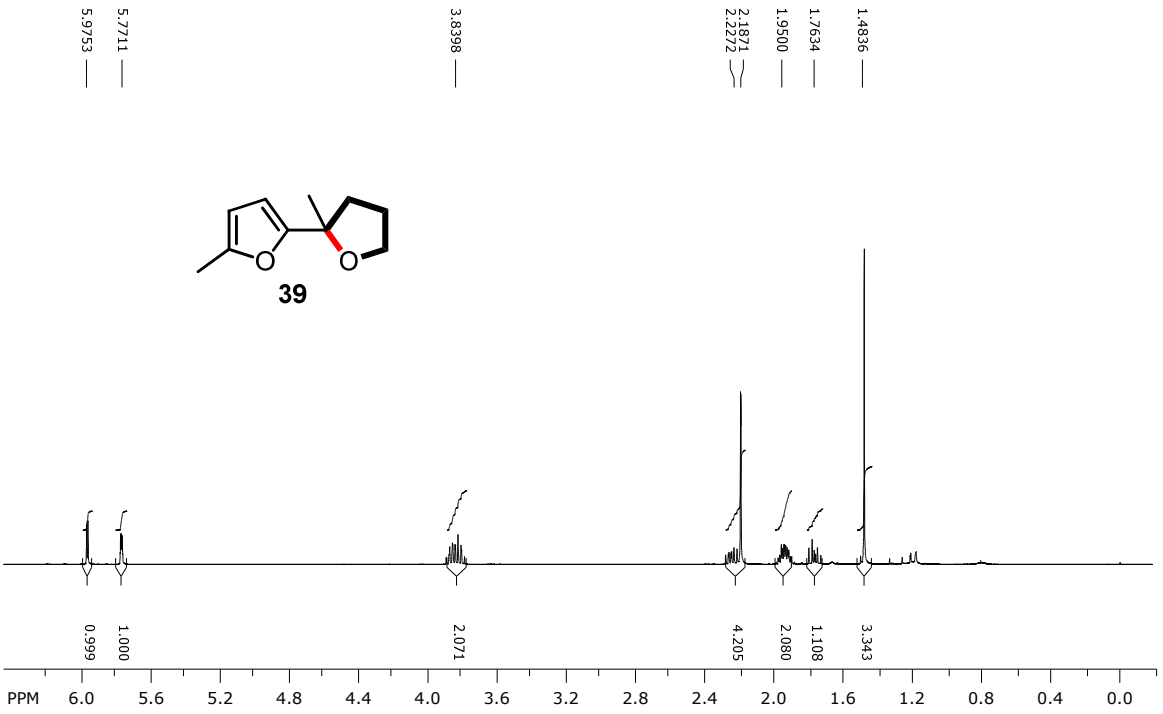

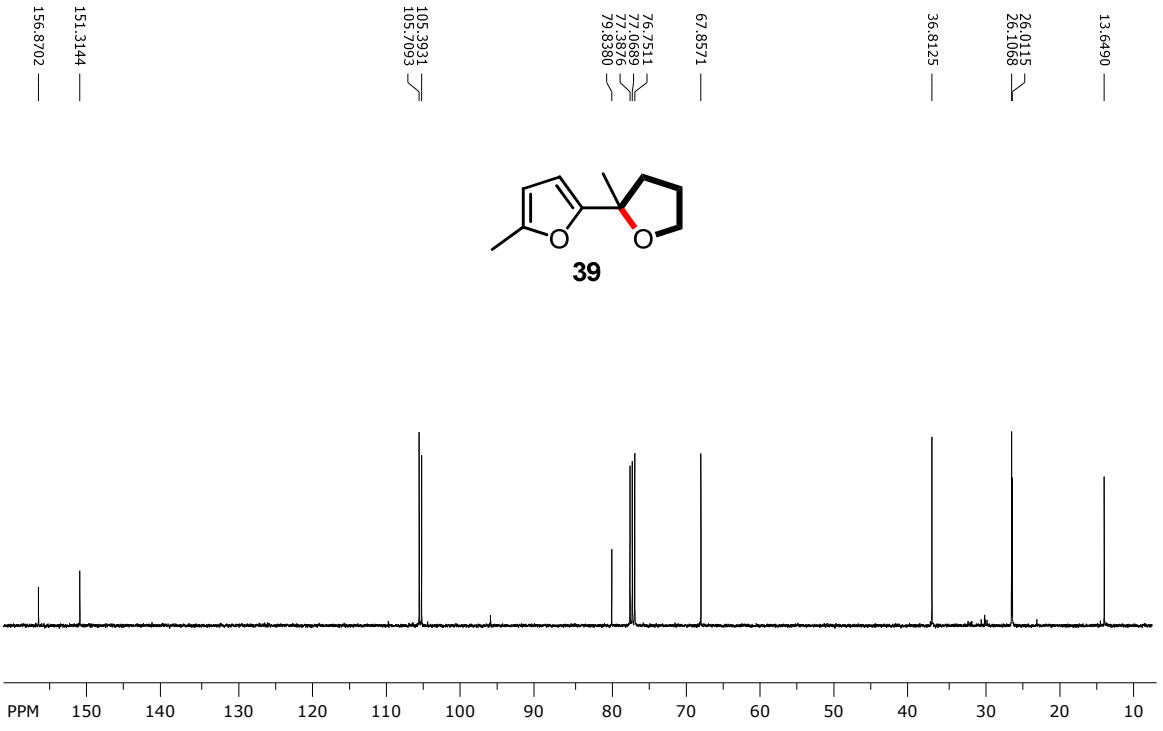

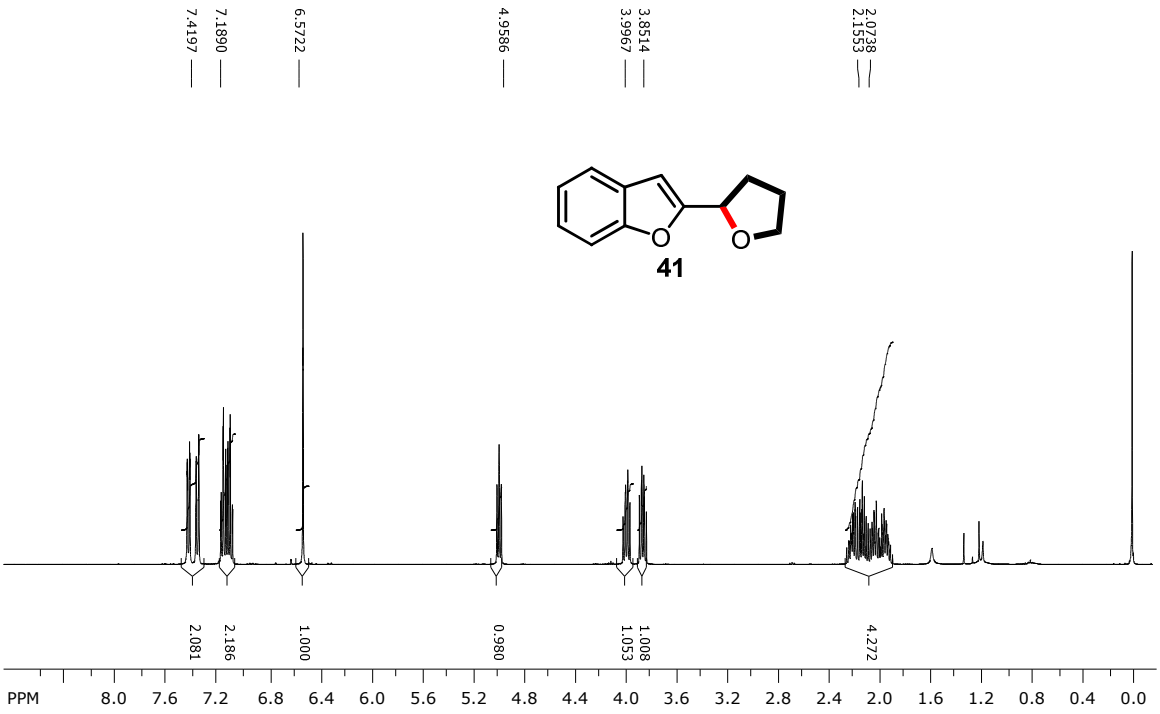

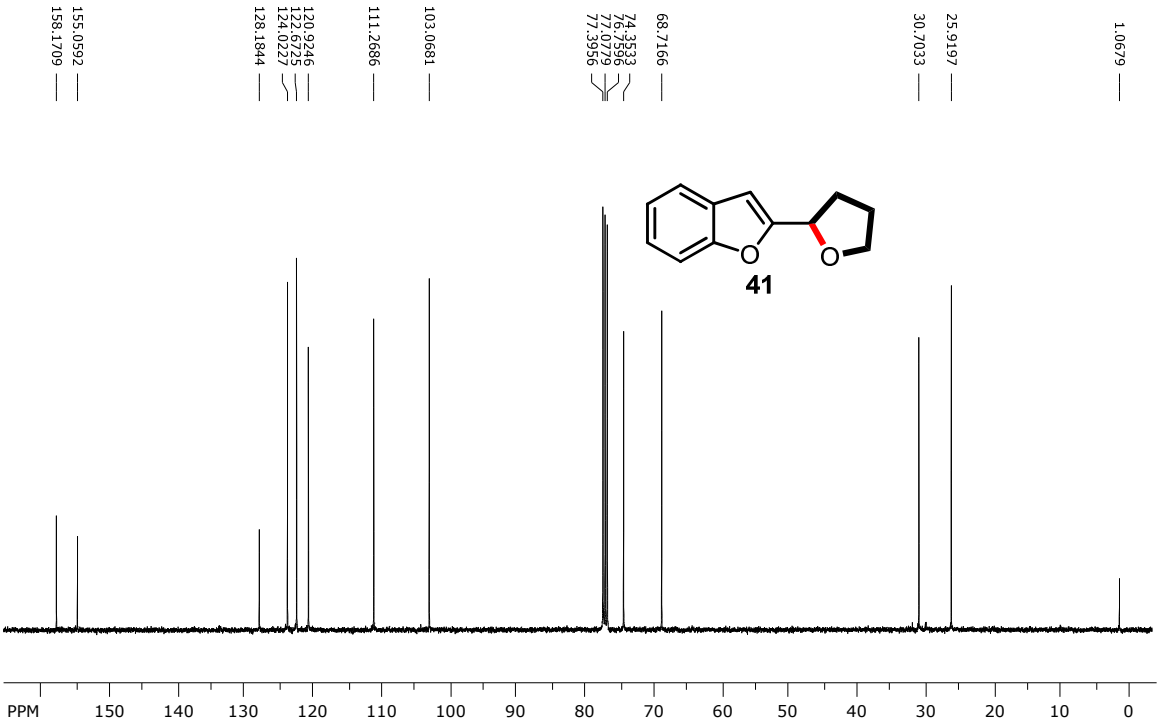

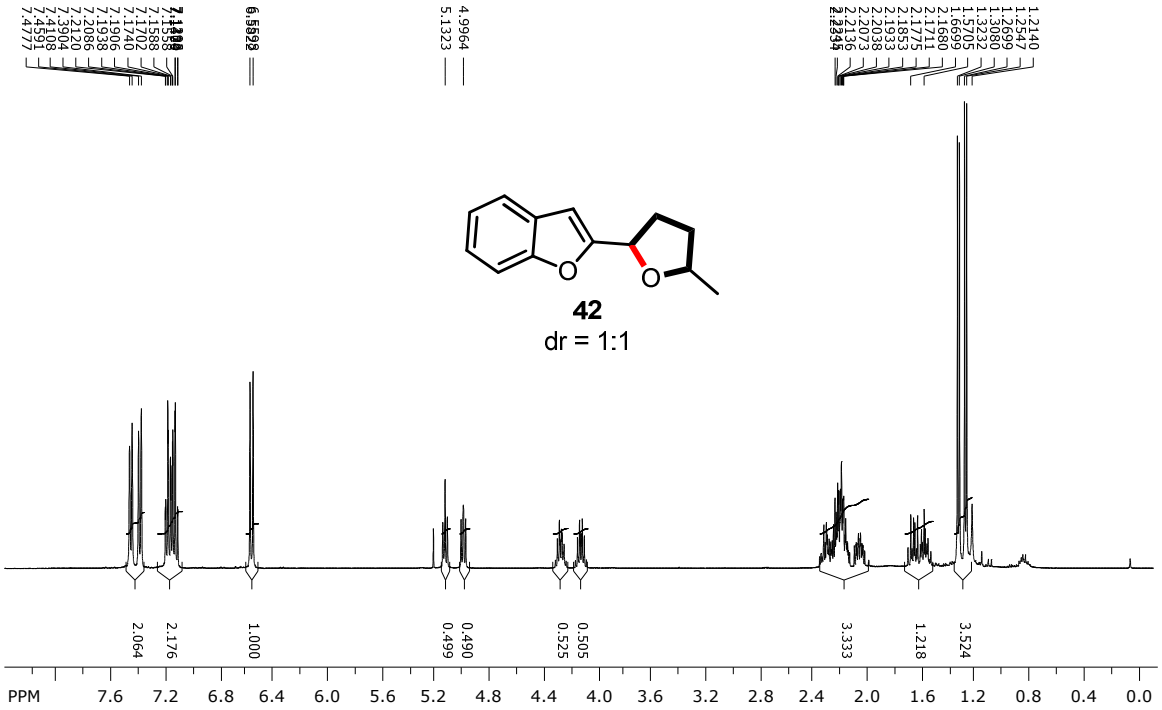

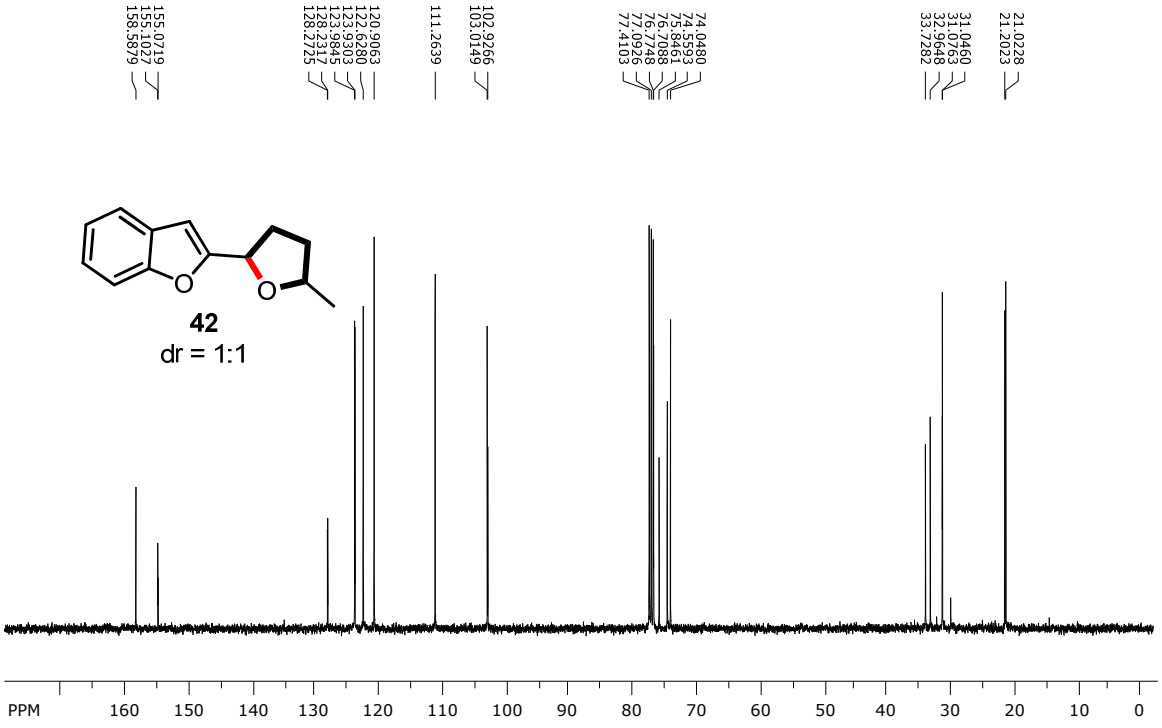

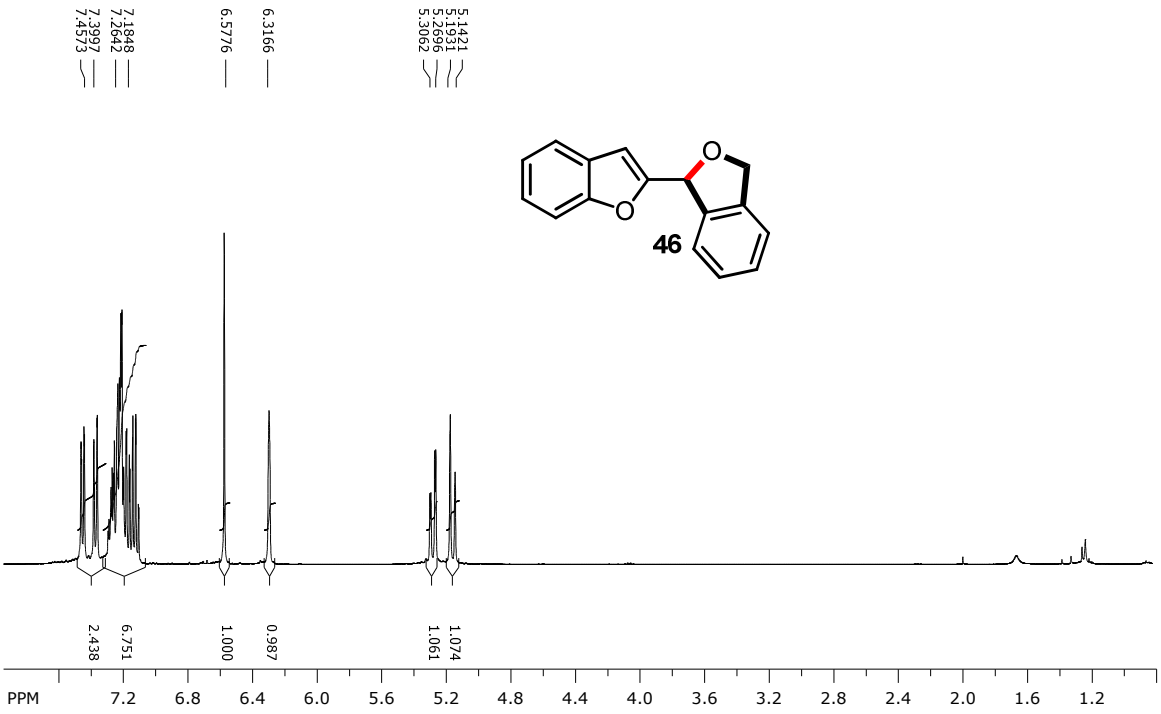

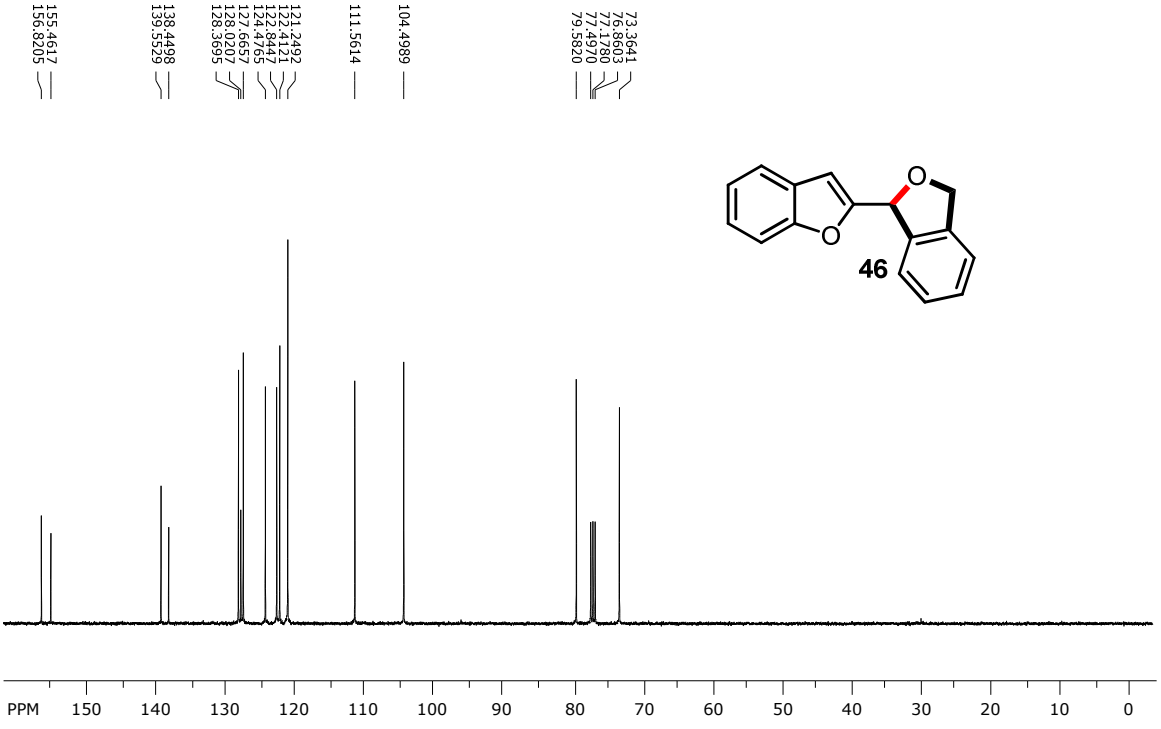

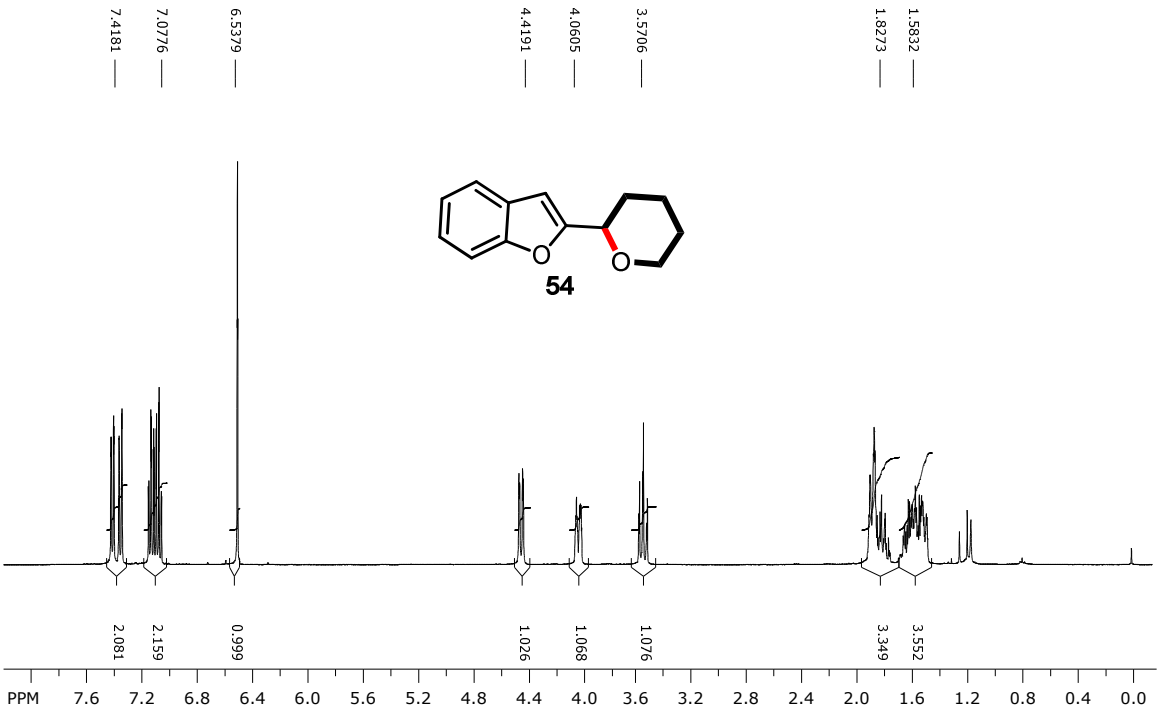

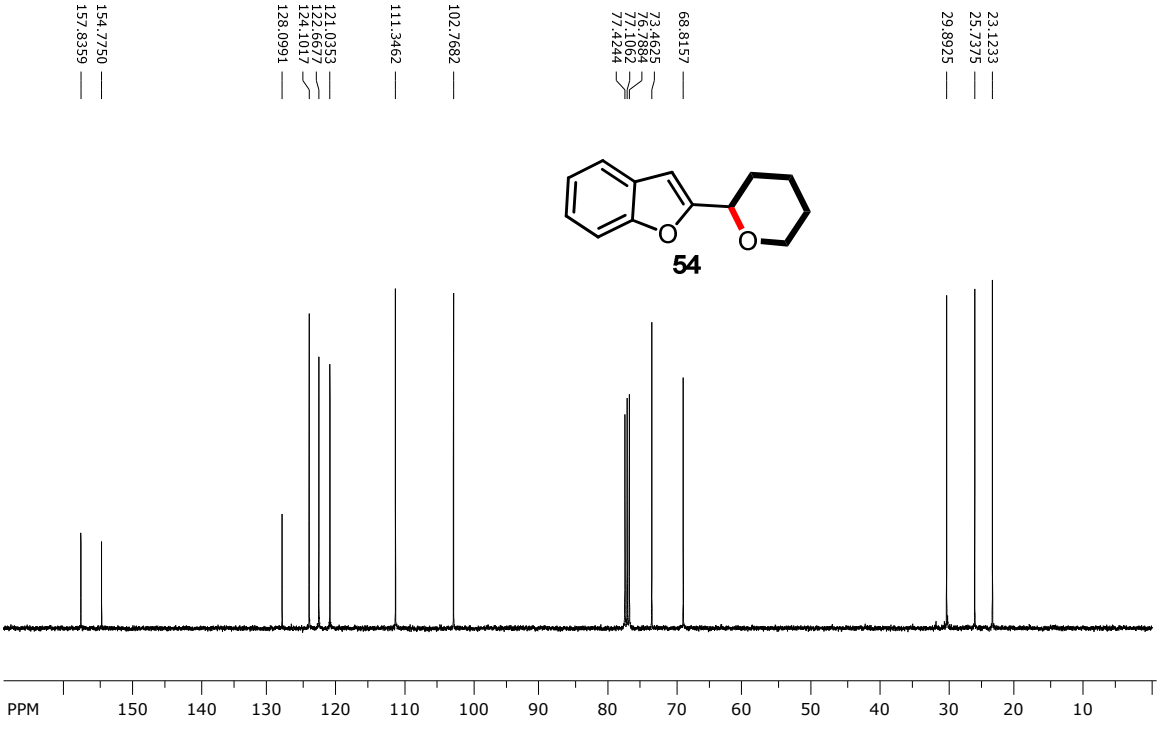

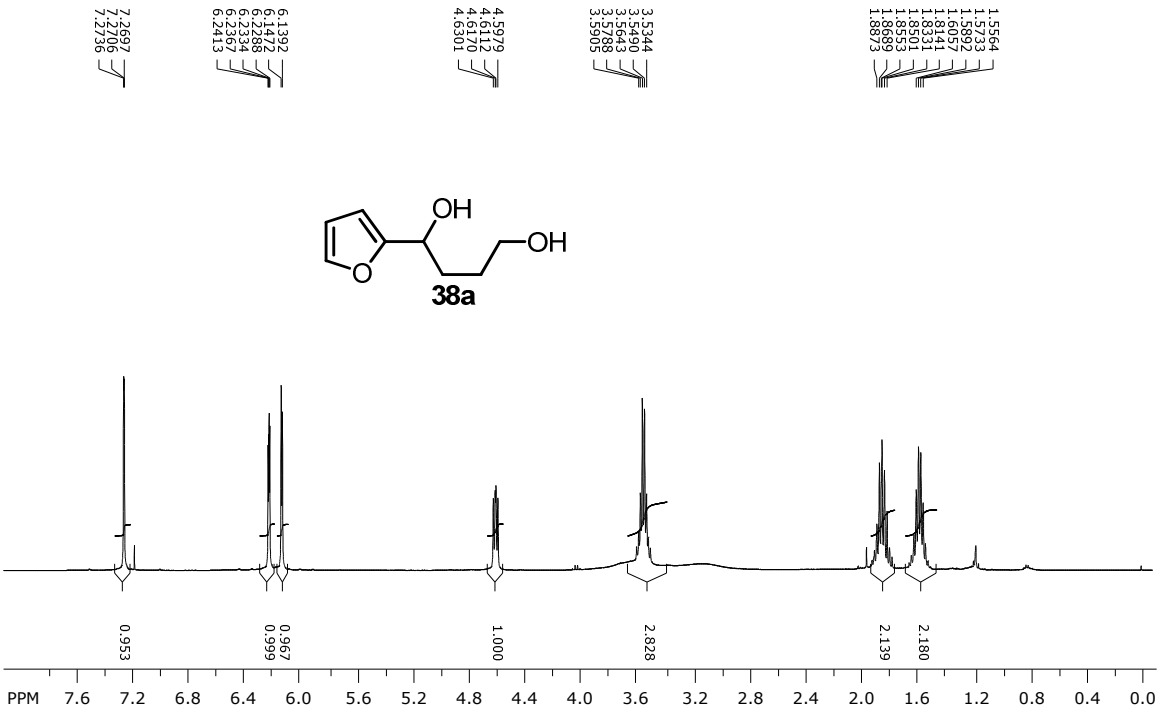

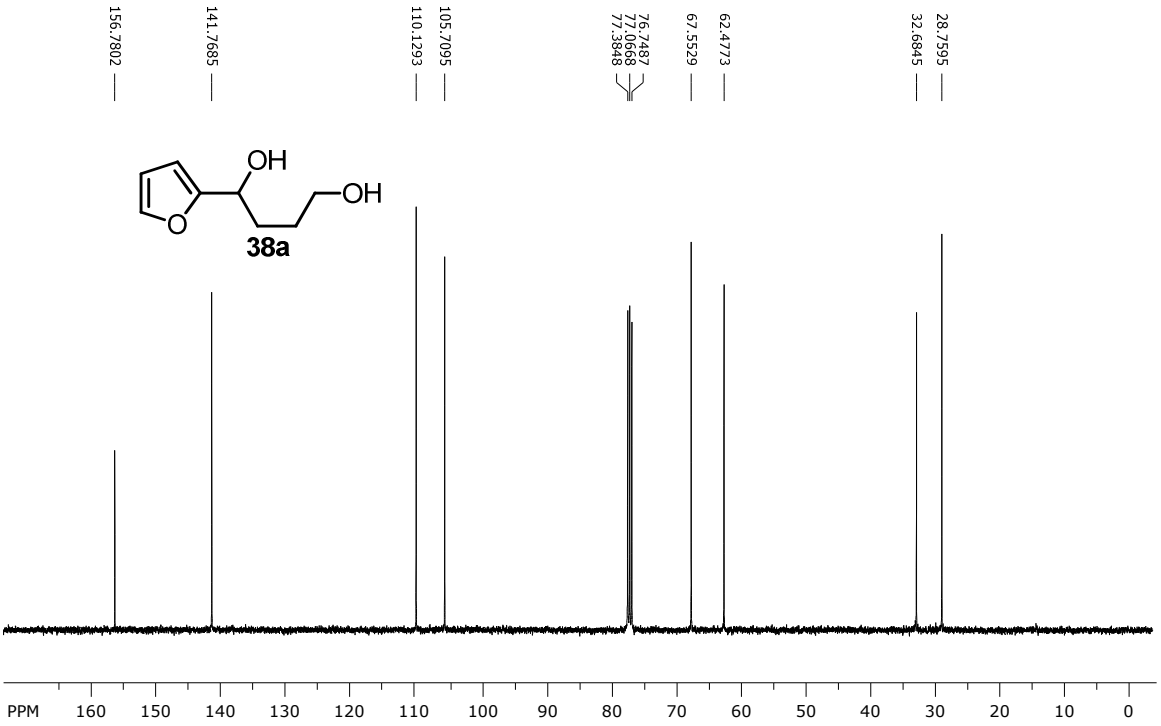

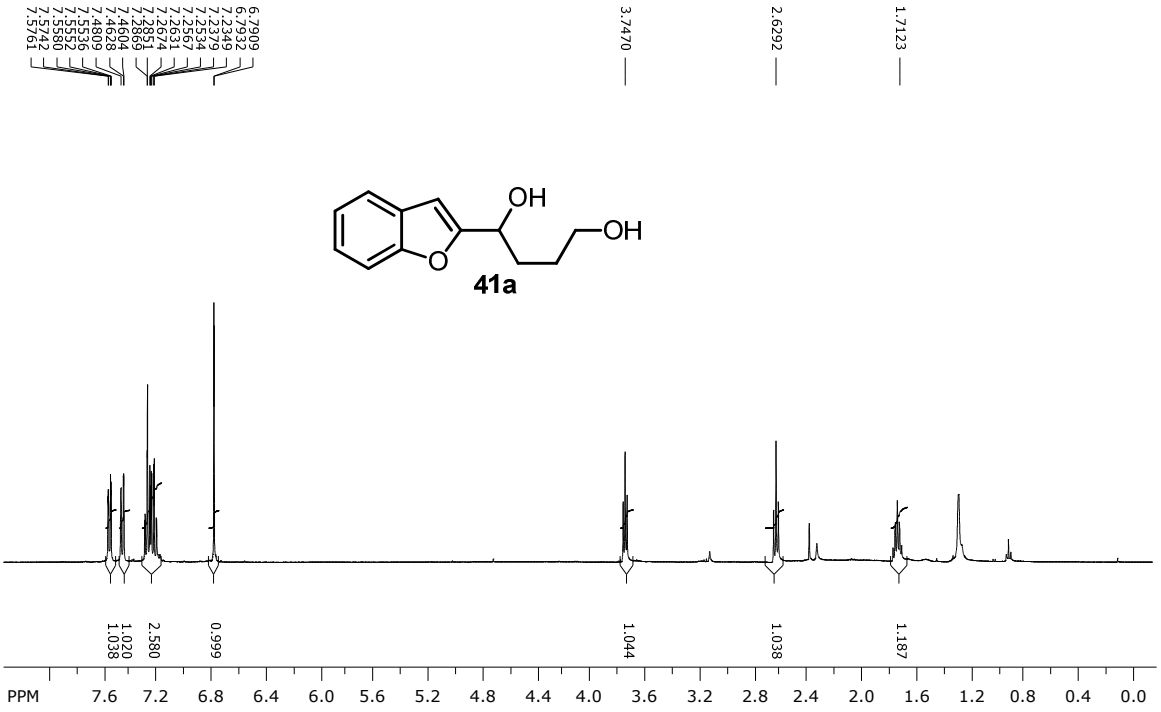
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OH
O
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1.020
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1.044
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PPM
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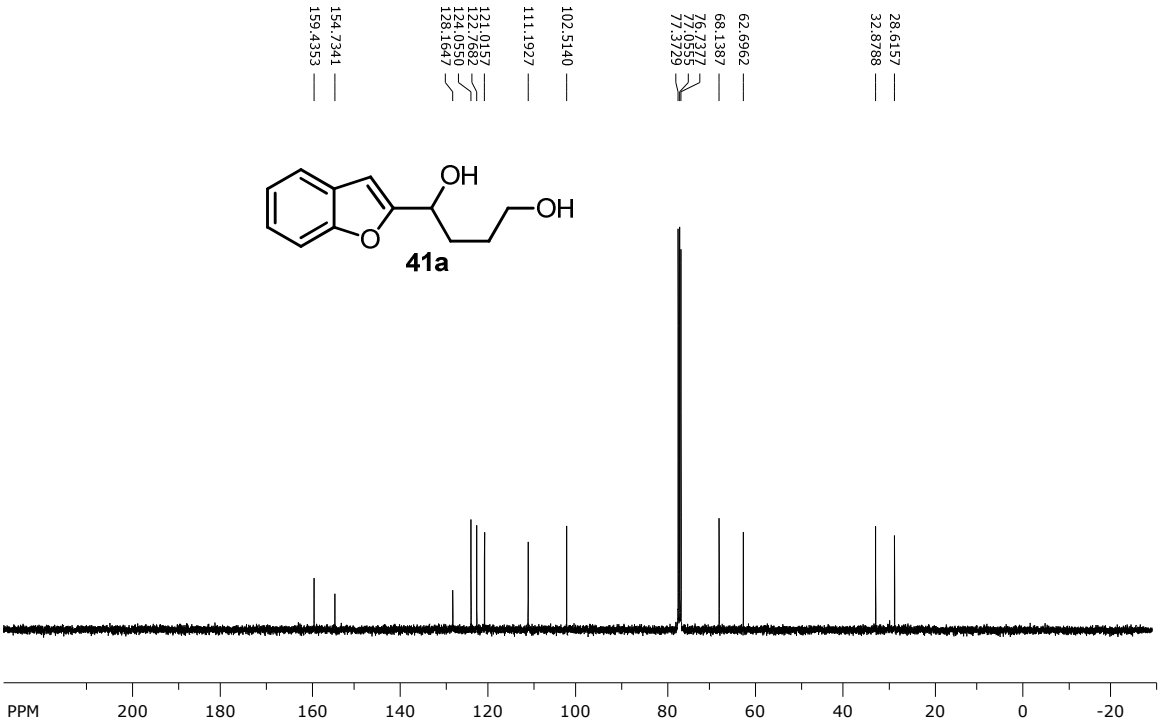
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32.8788
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O
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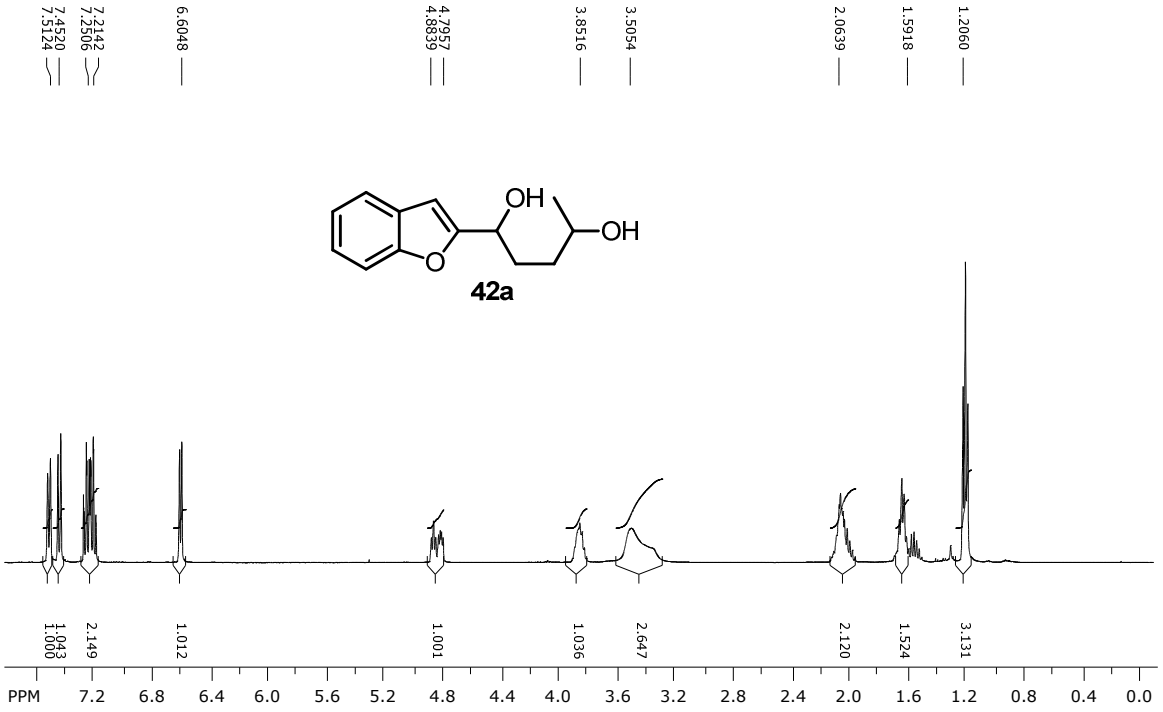

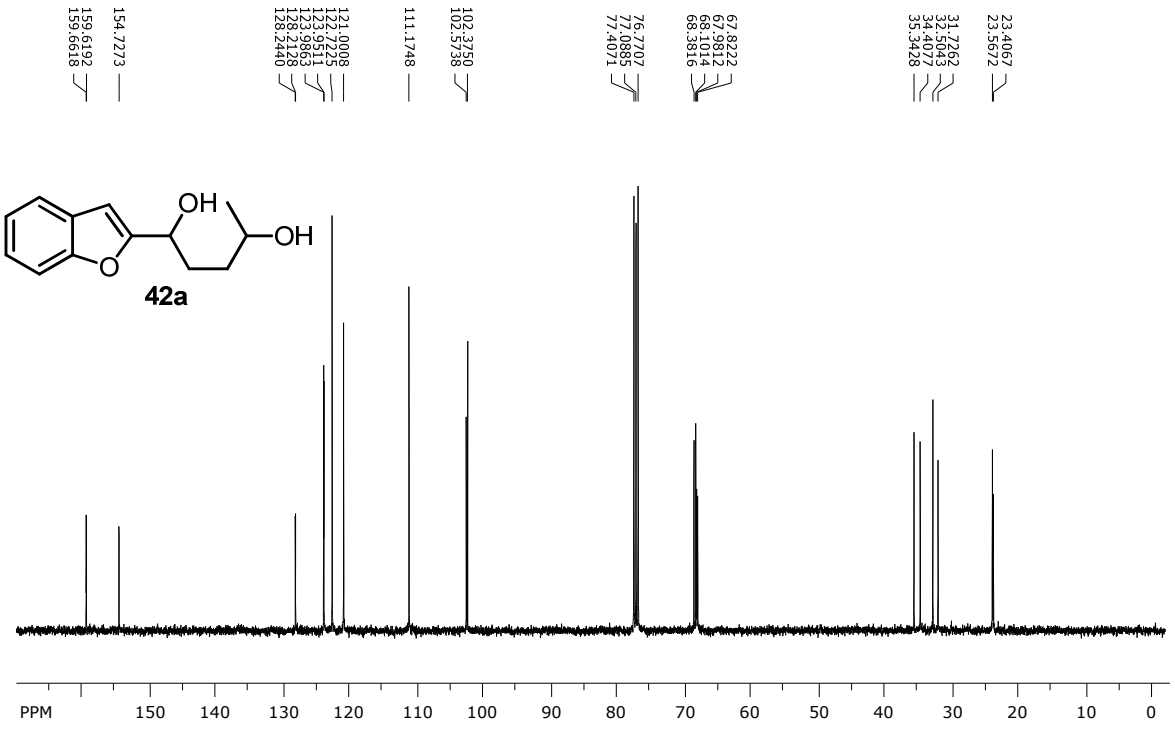

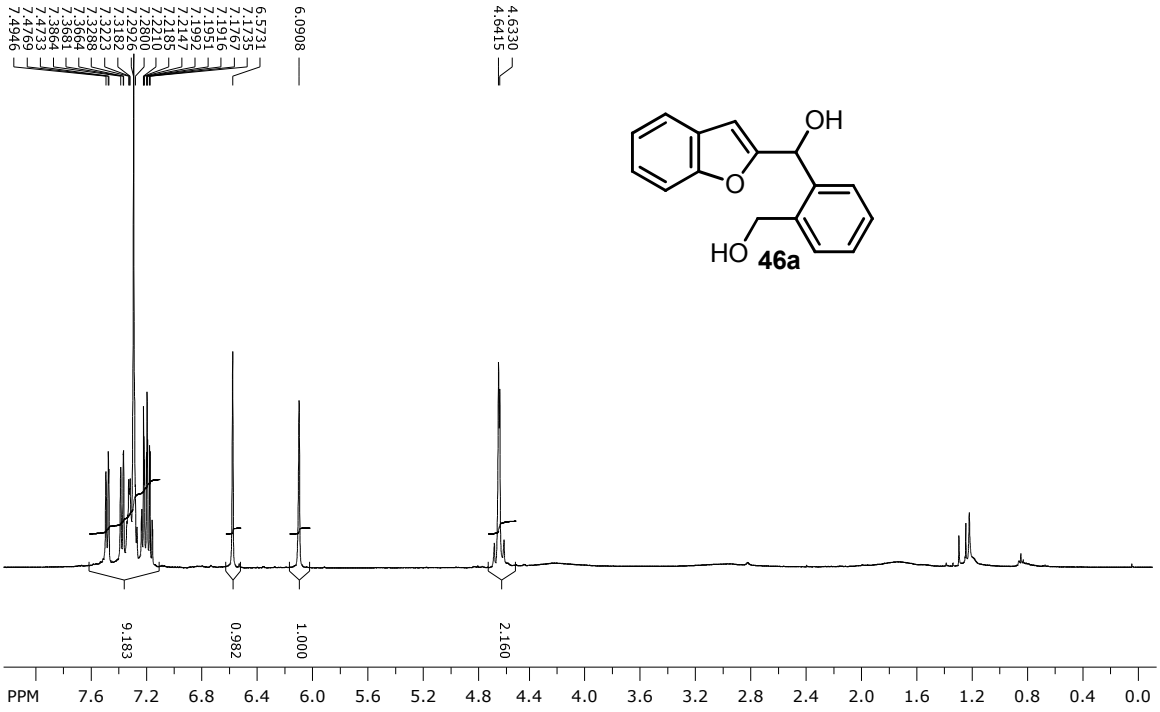

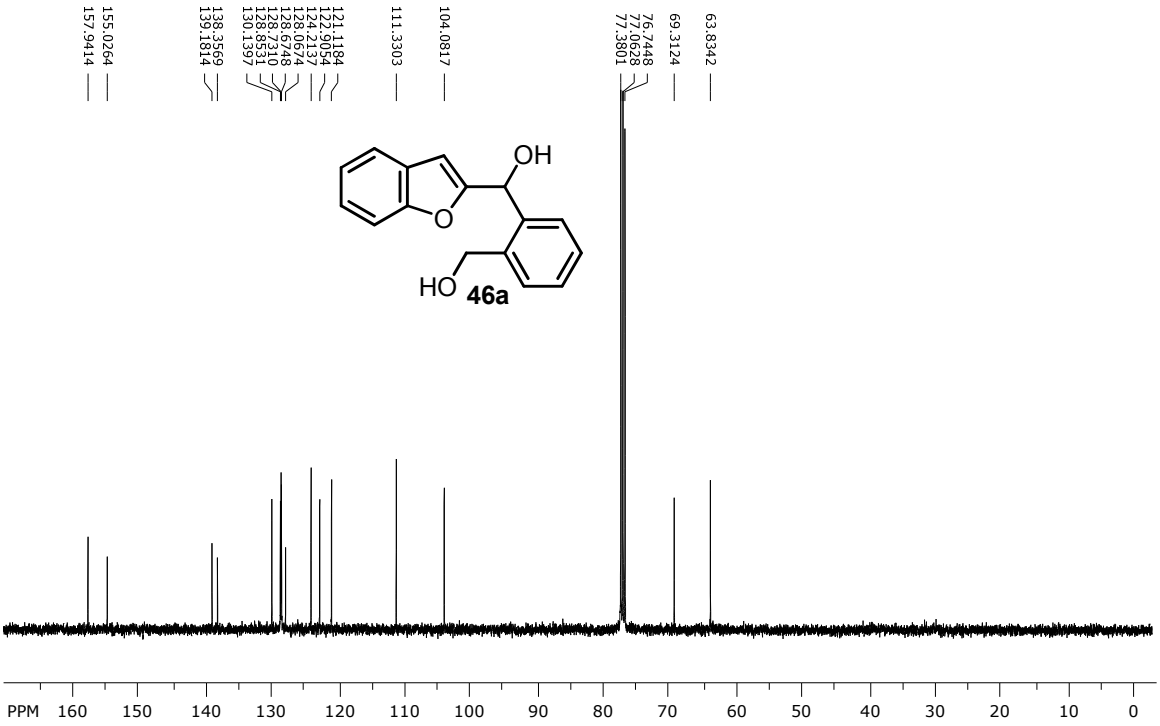

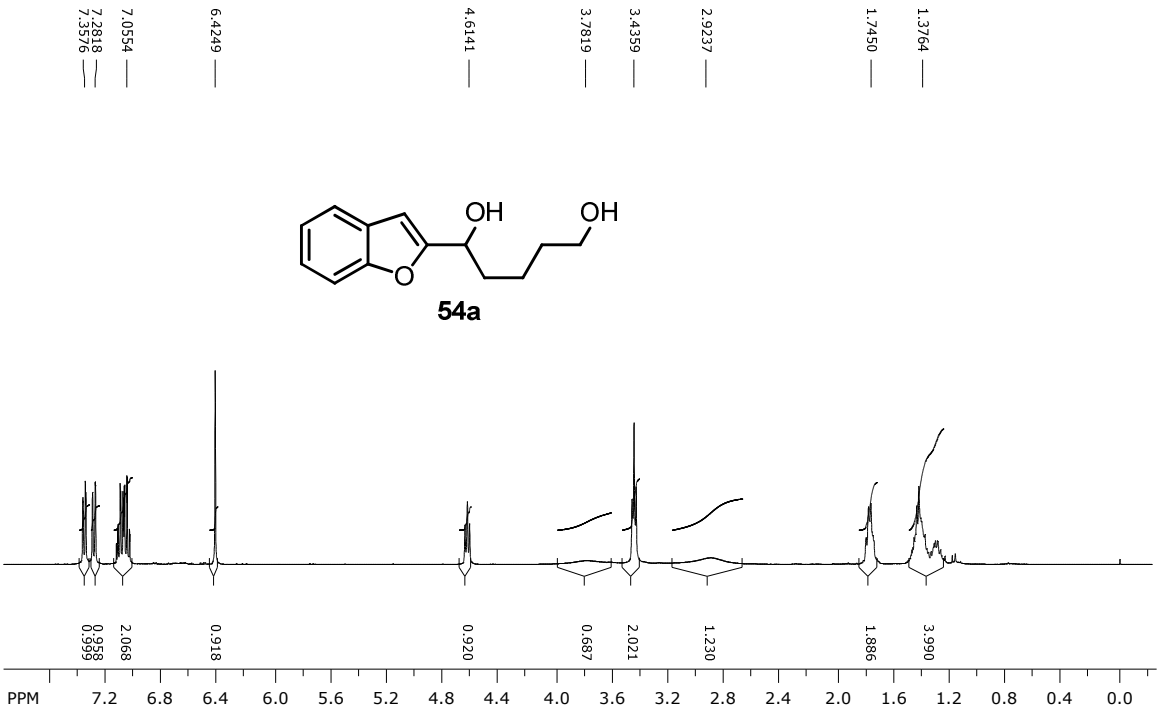

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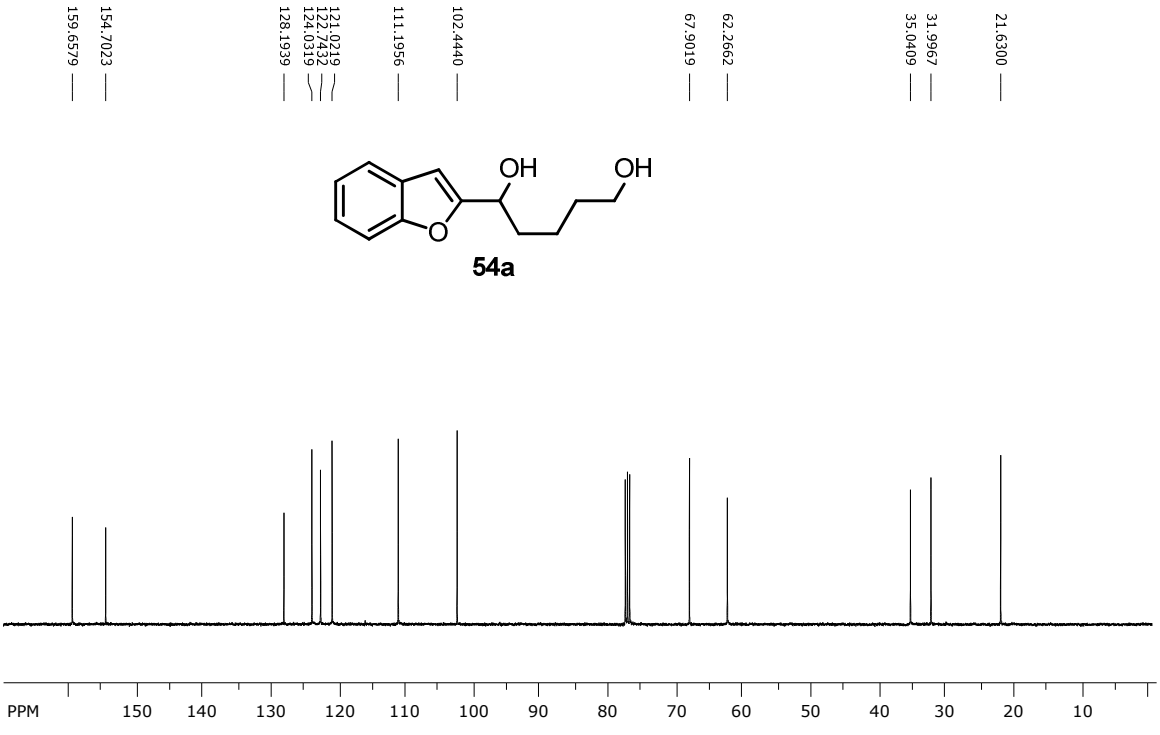

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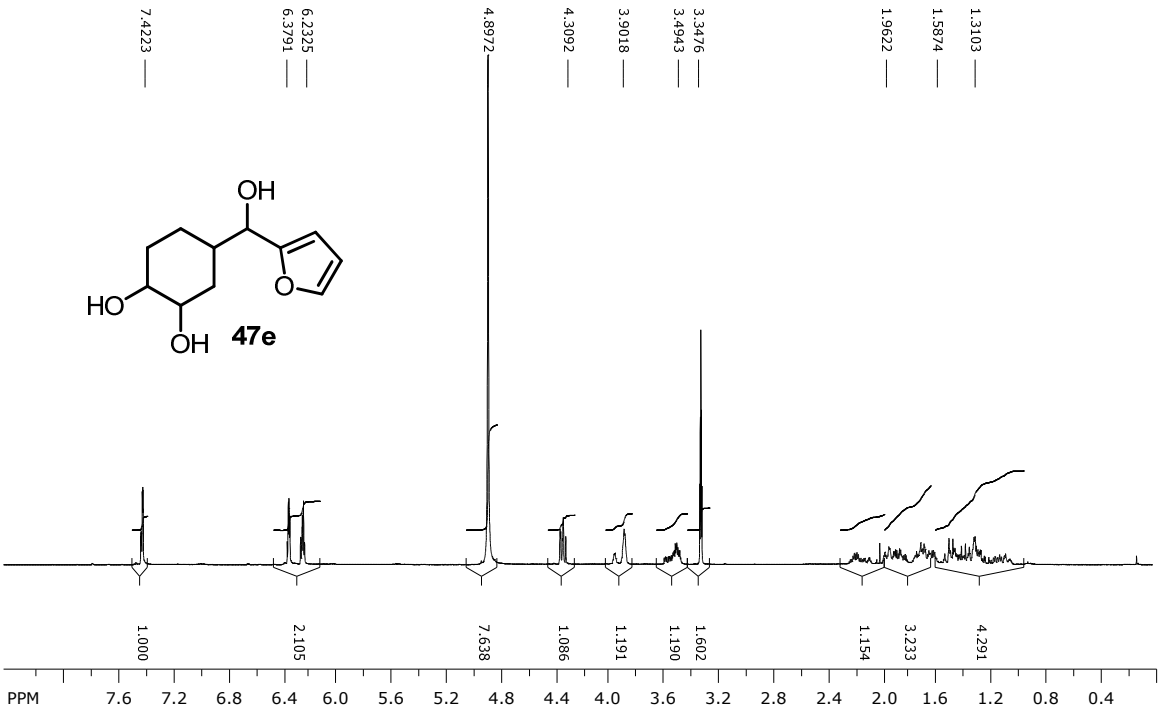
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1.191
1.190
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3.233
4.291
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7.2
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6.4
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5.2
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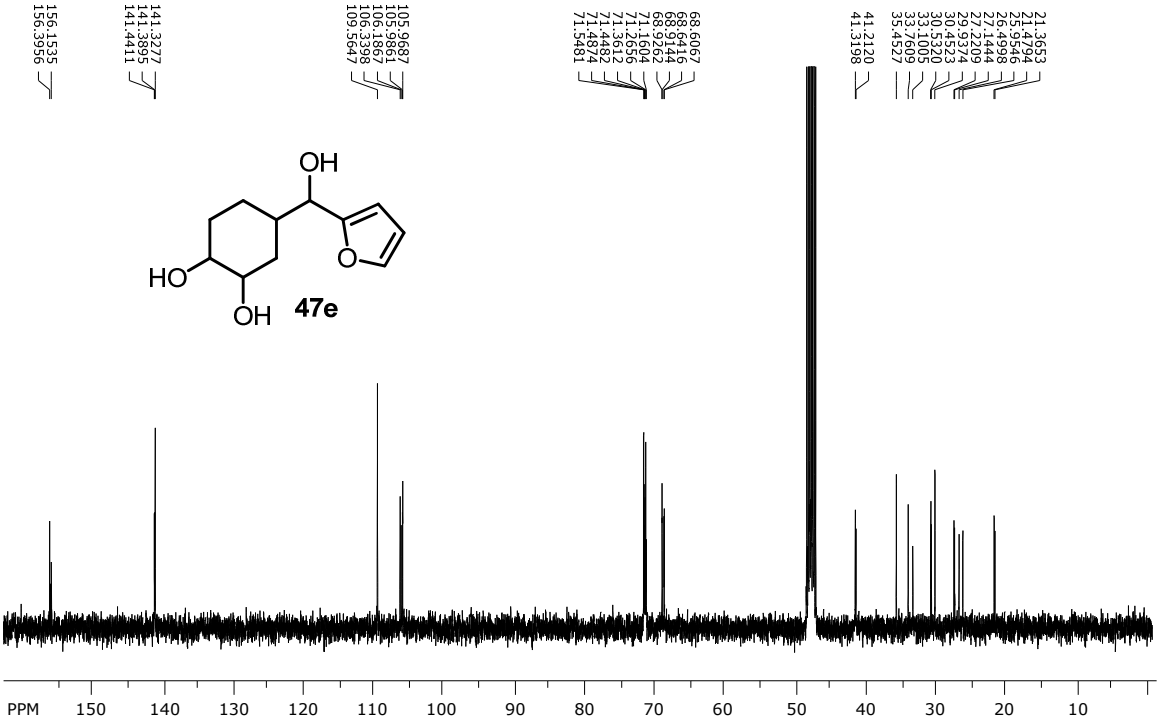
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71.2656
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30.4523
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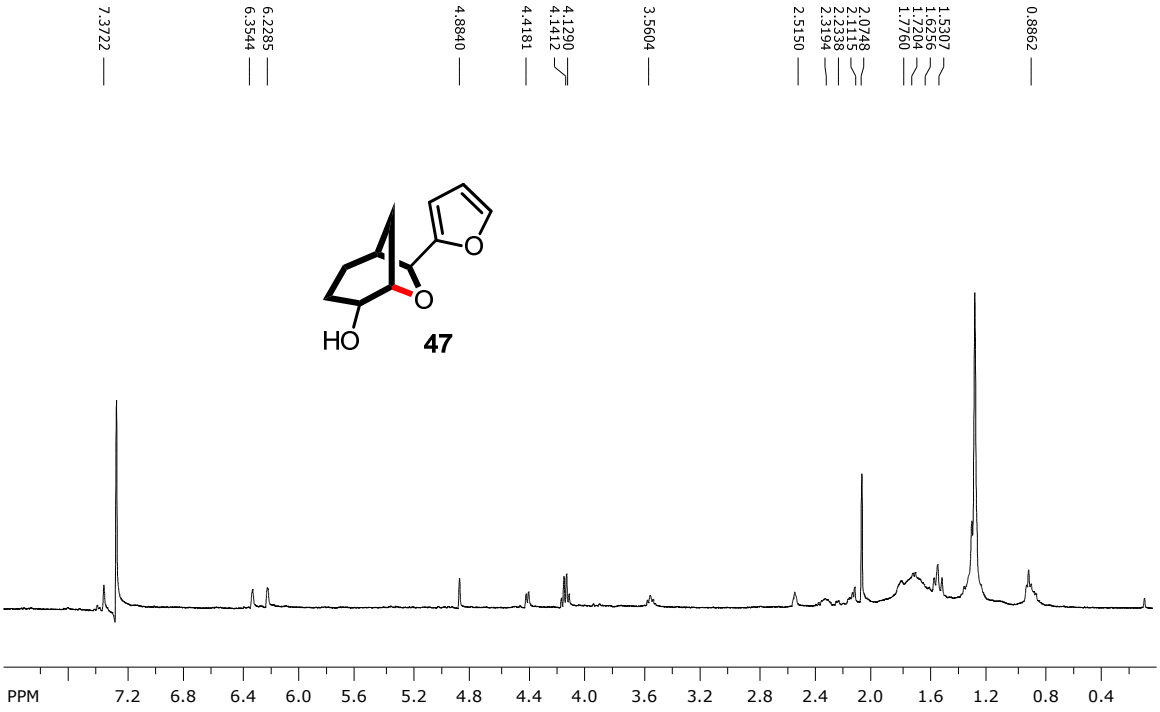

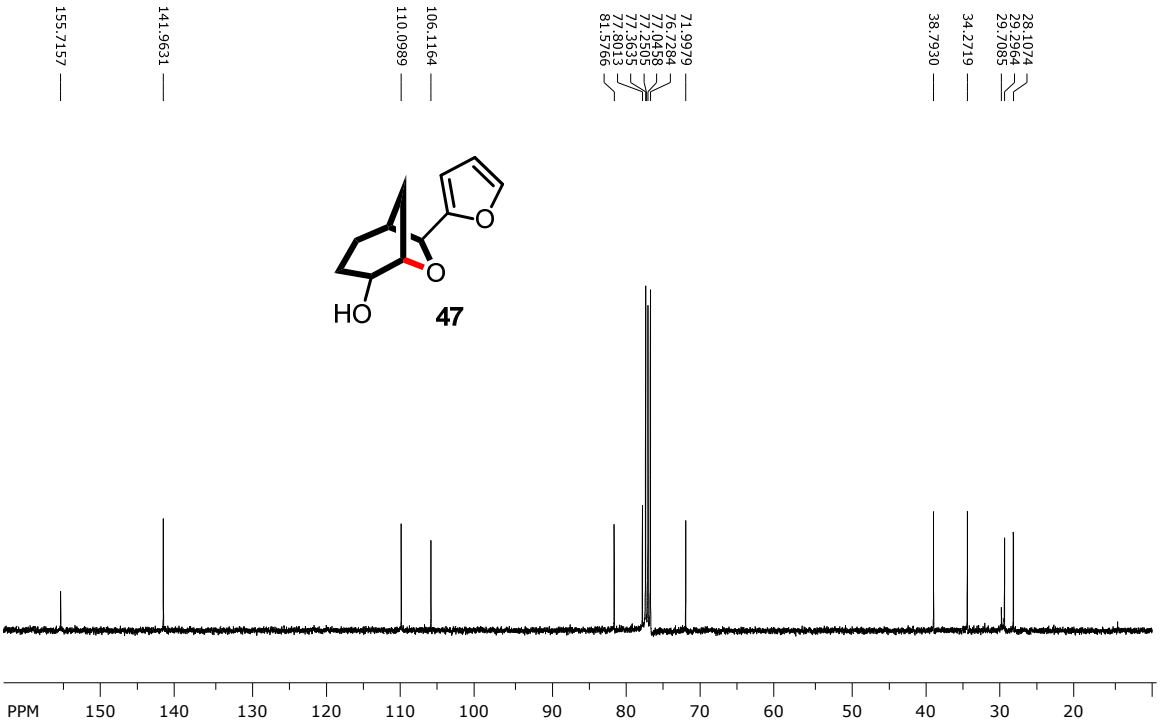

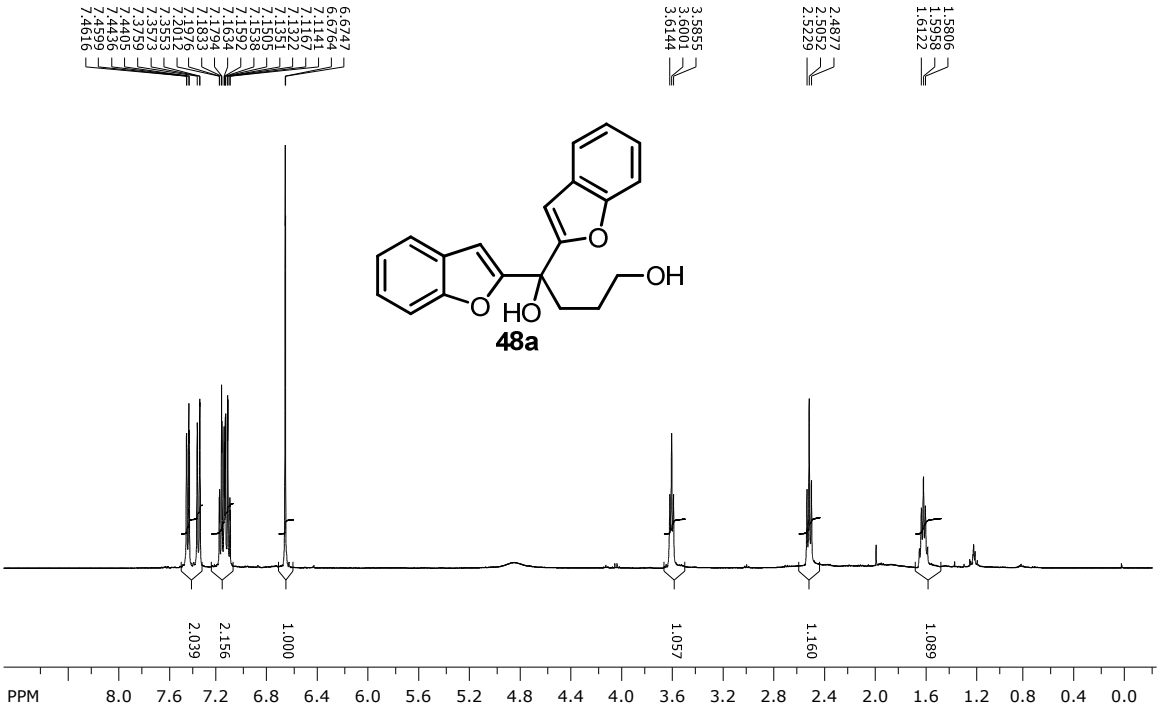
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O
O
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6.4
6.0
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5.2
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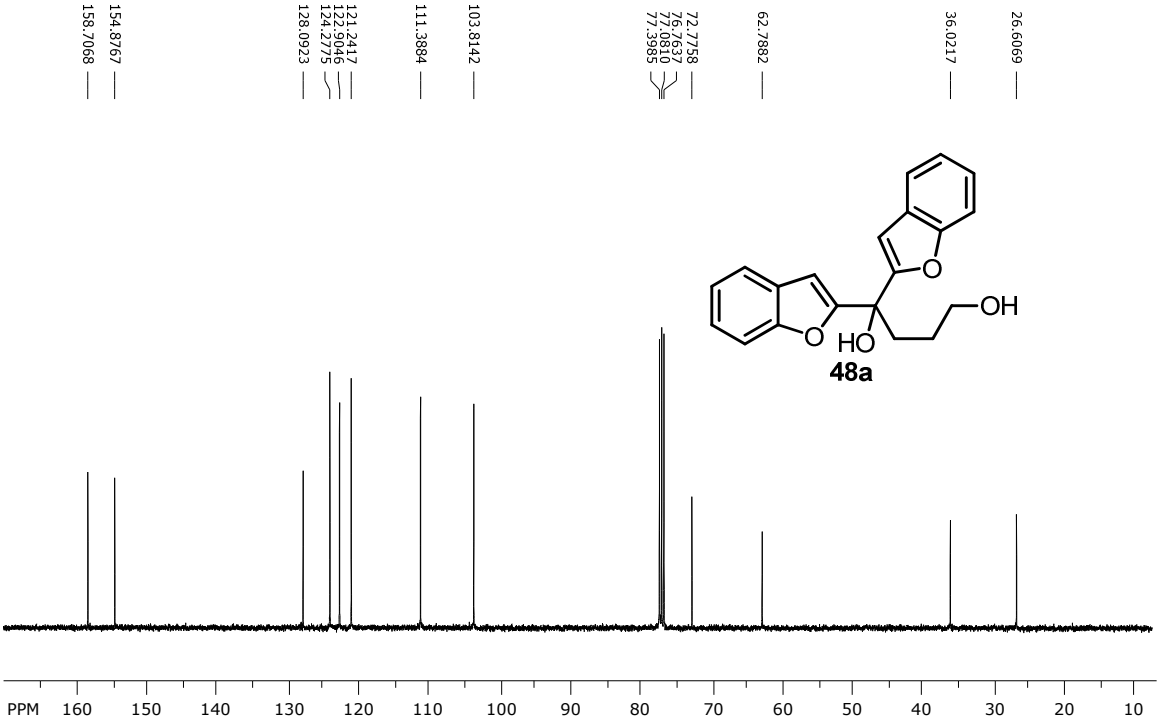
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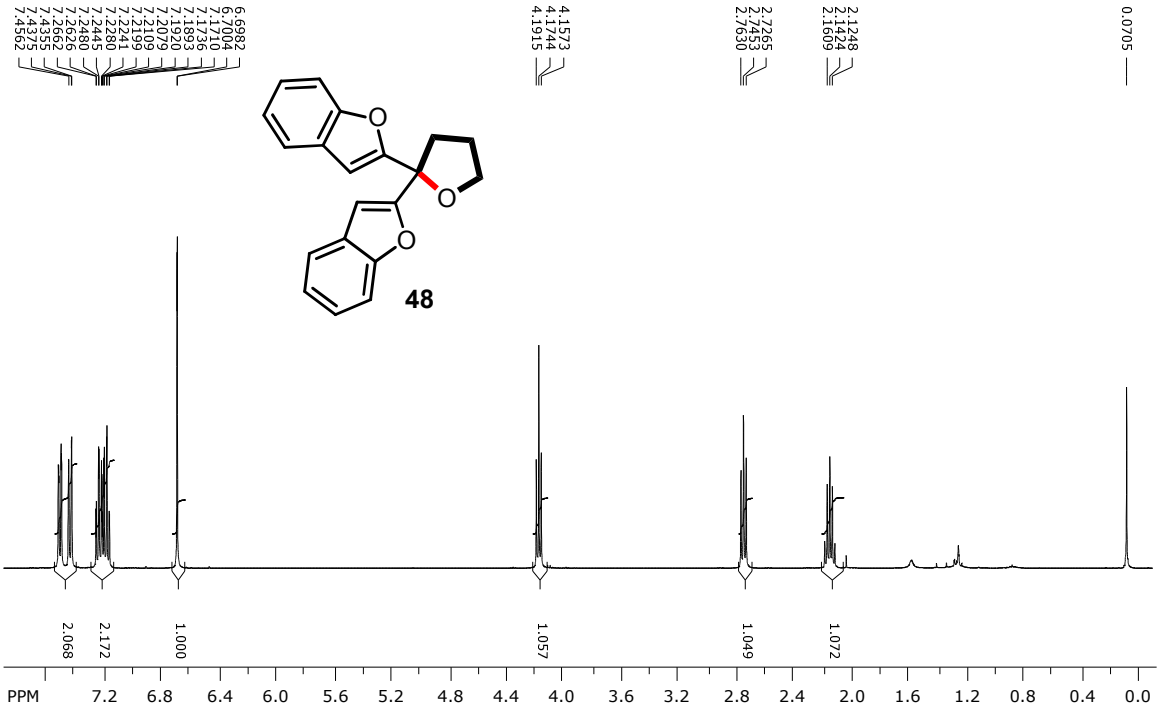
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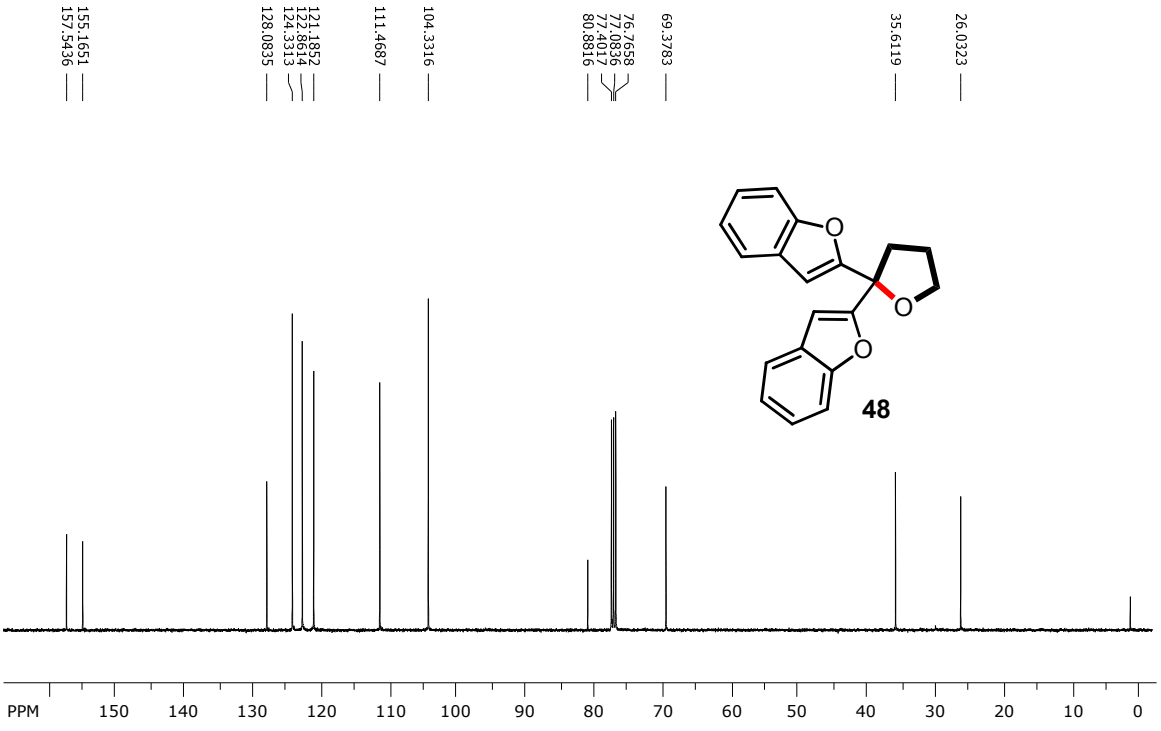
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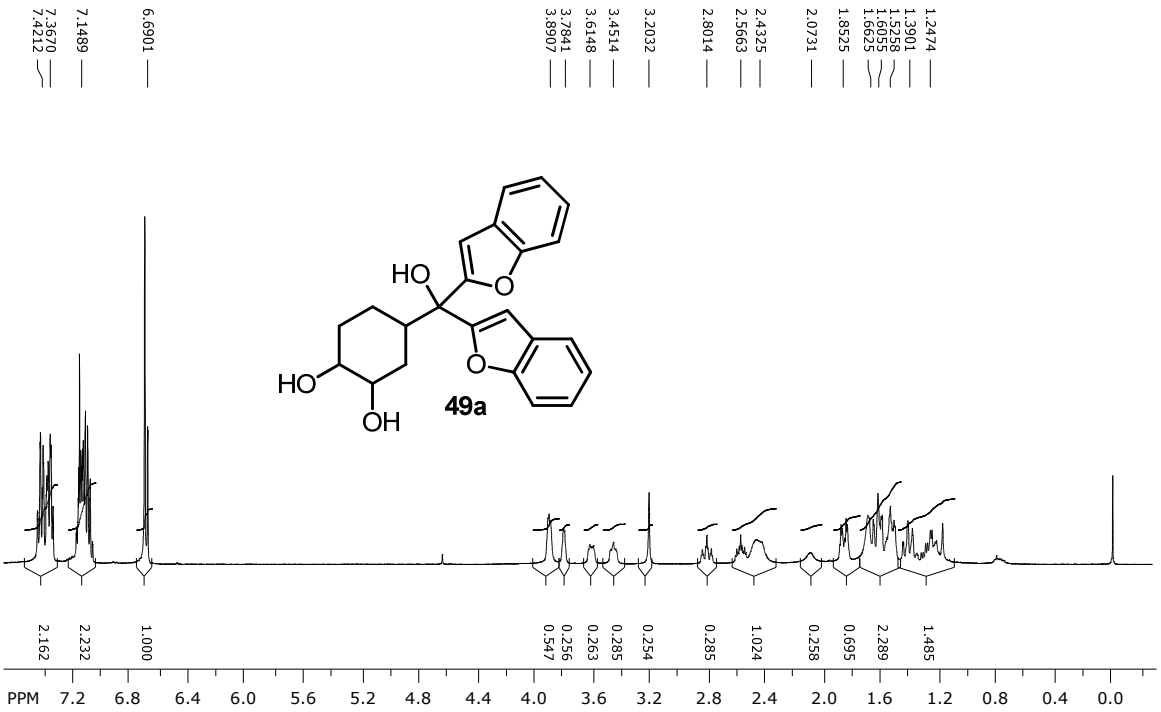
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O
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0.263
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0.254
0.285
1.024
0.258
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2.289
1.485
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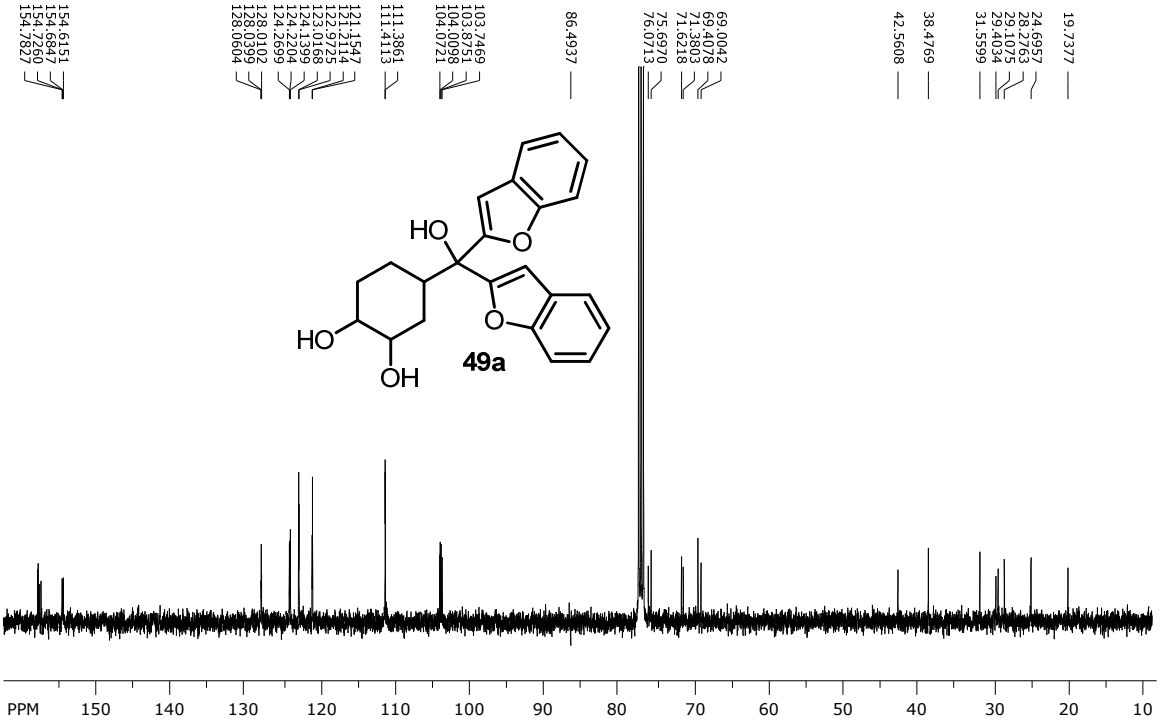
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OH
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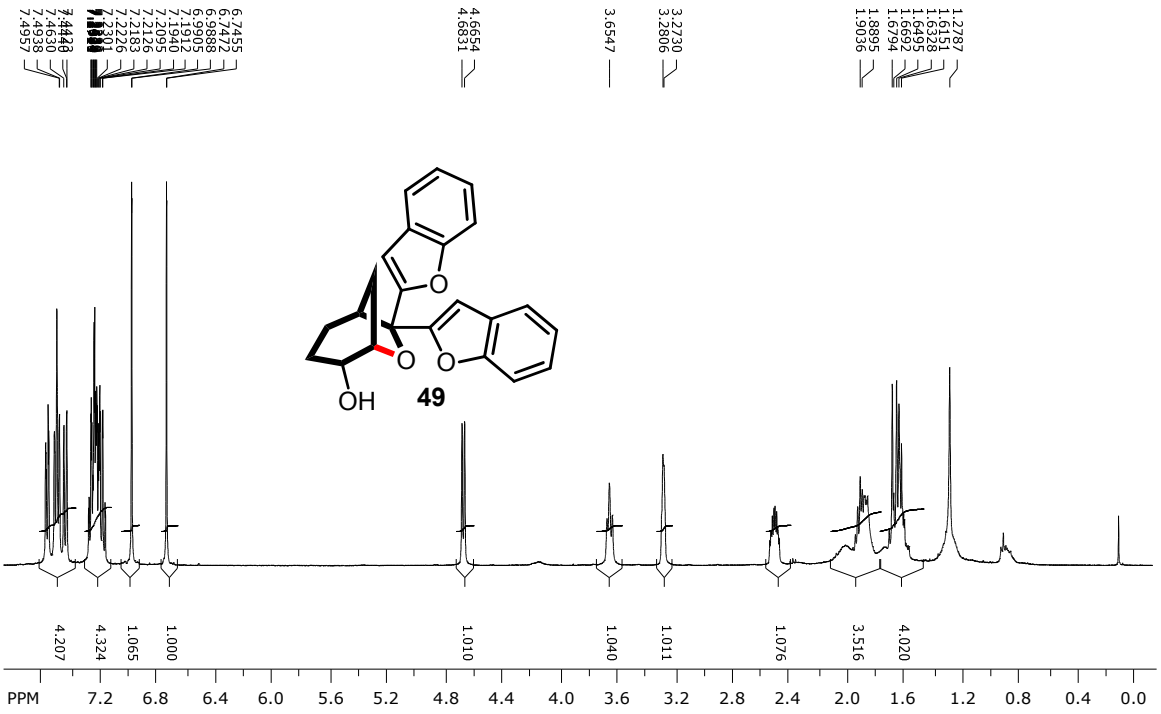
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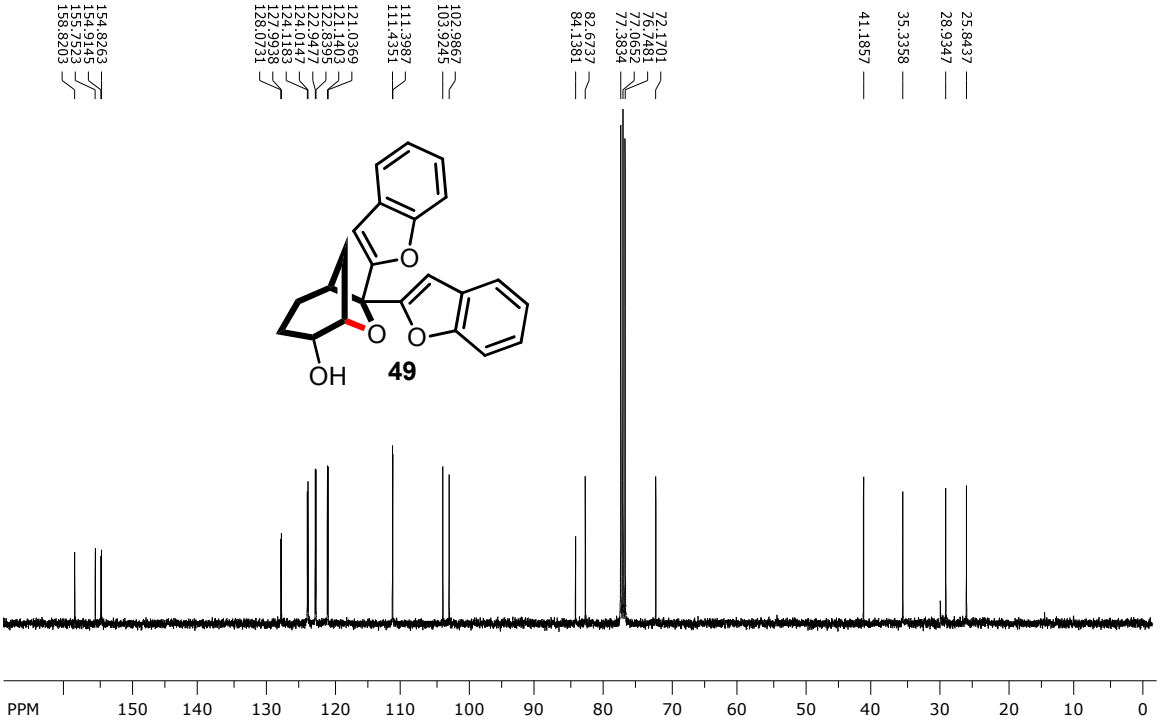
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PPM
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10
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