Supporting Information

Synthesis of benzofurans via acid catalysed transacetalistion/Fries-type O→C rearrangement/Michael addition/ring-opening aromatisation cascade of *β*-pyrones

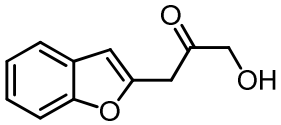
Siddheshwar K. Bankar, Jopaul Mathew, and S. S. V. Ramasastry*

Organic Synthesis and Catalysis Lab, Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Mohali, Sector 81, S A S Nagar, Manuali PO, Punjab 140 306, INDIA

E-mail: ramsastry@iisermohali.ac.in

General experimental methods: Starting compounds such as furan, furfural, (*S*)-1-(furan-2-yl)ethanol, phenols, and Lewis/Brønsted acids etc., were purchased from Sigma-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 visualised 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. 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 SMP30 and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker Biospin Avance III 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 utilised 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 in $(CD_3)_2SO$ (δ 2.50 ppm). Carbon chemical shifts are internally referenced to the deuterated solvent signals in $CDCl_3$ (δ 77.1 ppm) or in $(CD_3)_2SO$ (δ 39.5 ppm). Single crystal X-ray analysis was carried on an XtaLabmini diffractometer. High-resolution mass spectra were recorded on a Waters QTOF mass spectrometer. Optical rotations were recorded on Rudolph APIII/2W.

General procedure for the optimisation of reaction parameters. An oven-dried 5 mL glass vial was charged with acetoxy pyranone **2a** (0.2 mmol, 1 equiv), phenol **3a** (0.22 mmol, 1.1 equiv) and an appropriate solvent (1 mL). A catalyst (10 mol%, 0.1 equiv) was then introduced at 0-5 ^{o}C. The reaction mixture was stirred at the same temperature for 30 min, and continued stirring at room temperature until starting material disappeared as monitored by TLC. The reaction mixture was quenched with aqueous sodium bicarbonate solution, diluted with ethyl acetate (1-2 mL) and the layers were separated. The aqueous layer further extracted with ethyl acetate (1-2 mL) The organic layers were combined, dried over anhydrous Na_2SO_4, concentrated, and purified by silica gel column chromatography (hexanes/ethyl acetate) to afford the product **4a** as a pale yellow oil**.**

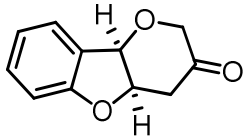


4a

1-(Benzofuran-2-yl)-3-hydroxypropan-2-one (4a).

This compound was isolated as pale yellow oil. R_f = 0.2 (Hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3454, 2923, 1738, 1454, 1365, 1228, 1216. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.30-7.35 (m, 2H), 6.67 (s, 1H), 4.42 (s, 2H), 3.94 (s, 2H), 3.01 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 204.6, 155.0, 149.2, 128.2, 124.3, 123.0, 120.8, 111.1, 105.9, 67.9, 38.9**. HRMS (ESI):** *m/z* calcd for $C_{11}H_{11}O_3$ $(M+H)^+$: 191.0708; Found: 191.0711.

An intermediate during the transformation of **2a** to **4a**, the pyran-fused benzofuran **4a'** is isolable. The spectral data is given below.



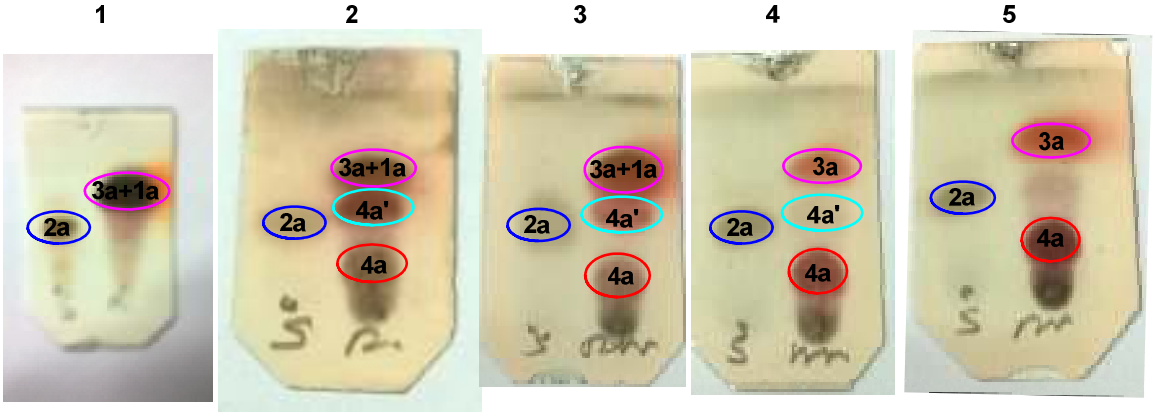
4a'

4,4a-Dihydro-2*H*-pyrano[2,3-*b*]benzofuran-3(9a*H*)-one (4a').

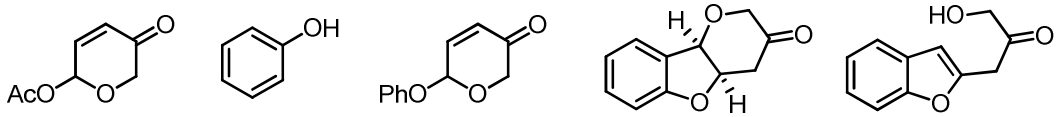
This compound was isolated as pale yellow oil. Following the general procedure, in a separate reaction, 30 mg of **2a** afforded 18 mg of **4a'** (50% yield). R_f = 0.4 (EtOAc/Hexane = 3/7). **IR (thin film, neat):** ν_{max}/cm^{-1} 2969, 1737, 1494, 1434, 1365, 1228, 1216, 995, 909. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 3.0 Hz, 1H), 7.35-7.31 (m, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 5.54 (d, *J* = 7.3 Hz, 1H), 5.19 (dt, *J* = 7.4 and 3.6 Hz, 1H), 3.94 (d, *J* = 18.1 Hz, 1H), 3.55 (d, *J* = 18.1 Hz, 1H), 3.10-3.05 (m, 2H). **^{13}C NMR** (100 MHz,

$CDCl_3$): δ 207, 160.6, 131.6, 126.9, 122.6, 121.8, 110.2, 79.2, 75.8, 68.7, 39.7. **HRMS (ESI):** *m/z* calcd for $C_{11}H_9O_3$ $(M–H)^+$: 189.0552; Found: 189.0547.

TLC monitoring of the reaction between 2a and 3a.



[eluent: 30% EtOAc/hexanes]

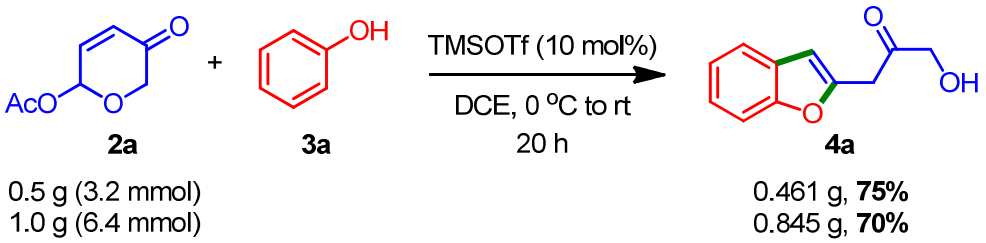


2a **3a** **1a** **4a'** **4a**

The reaction of **2a** and **3a** in the presence of 10 mol% TMSOTf was monitored by TLC. It can be observed from the above TLCs that **2a** transforms initially to the non-polar phenyl ether **1a** (TLC-1) [**Note**: R_f of **1a** and **3a** are same]. Phenyl ether **1a** then slowly transforms to the pyran-fused benzofuran **4a'** and **4a'** converts to the benzofuran derivative **4a** eventually (TLC-5), leaving behind little excess of the phenol **3a** employed in the reaction (TLCs-4&5).

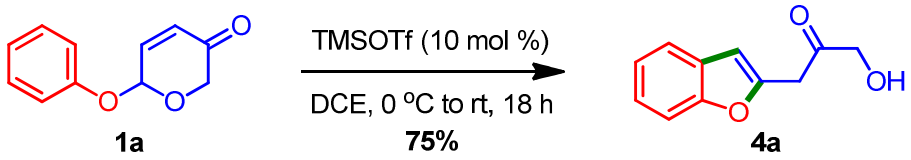
While **1a** is reasonably stable upon isolation; isolated samples of the pyran-fused benzofuran **4a'** were found to convert to benzofuran **4a** even at room temperature over a period of time.

Large scale reactions to verify the scalability of the present method. Two 'gram' scale reactions were carried out to demonstrate the scalability and practicality of the cascade process. Reactions performed on 0.5 g (3.2 mmol) and 1 g (6.4 mmol) scale of **2a** under the optimised conditions resulted in the formation of **4a** consistently in about 70% yield indicating the robustness of the present method.



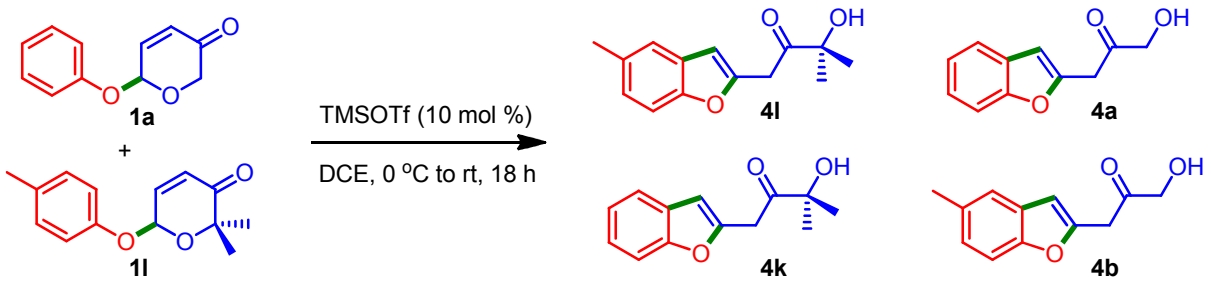
2a 0.5 g (3.2 mmol) 1.0 g (6.4 mmol) | **3a** | **4a** 0.461 g, **75%** 0.845 g, **70%**

Conversion of phenyl ether 1a to benzofuran 4a. The intermediate phenyl ether **1a** during the transformation of **2a** to **4a** was isolated and subjected to the optimised conditions. Benzofuran **4a** was obtained in 75%.

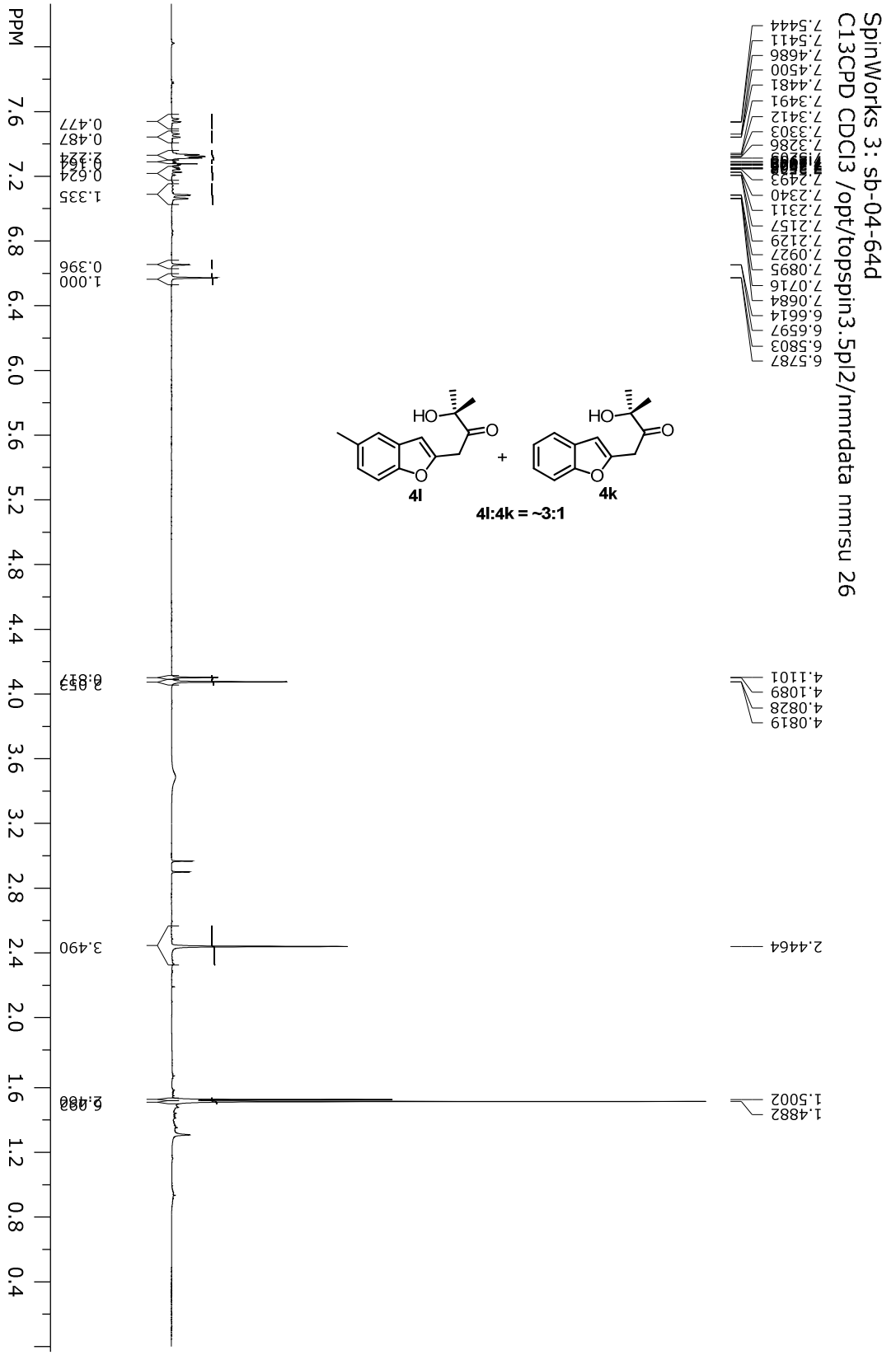


1a | **4a**

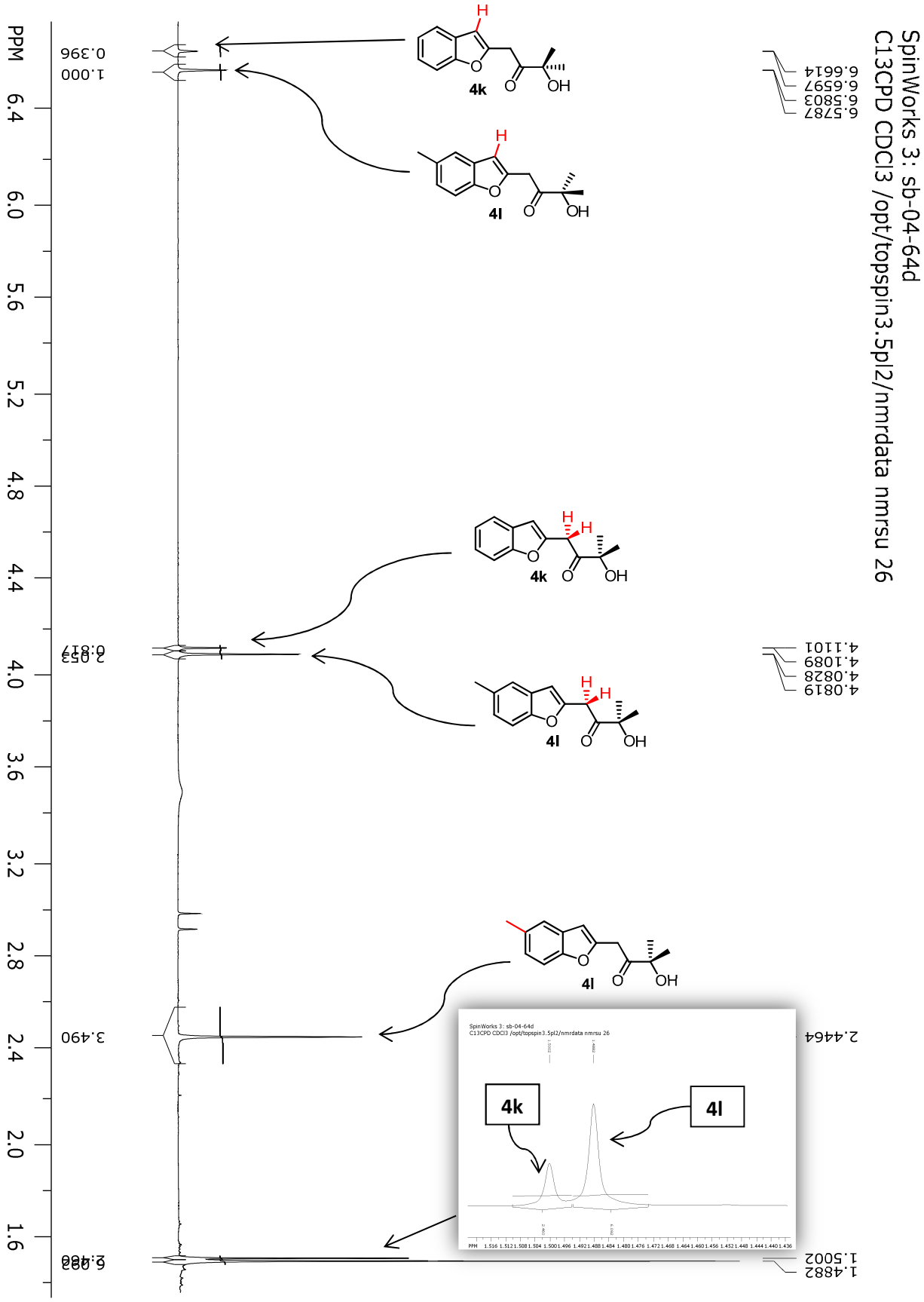
Cross-over experiment between 1a and 1l. In order to validate the intermolecular nature of the Fries-type O→C rearrangement step during the conversion of **2a** to **4a**, a cross-over experiment between the phenyl ethers **1a** and **1l** was planned. Accordingly, a 1:1 mixture of the phenyl ethers **1a** and **1l** was subjected to the optimised conditions. Crude reaction mixture and the fractions obtained after column chromatography purification were subjected to ^{1}H-NMR analysis, *which gave conclusive information regarding the intermolecular nature of the Fries-type O→C rearrangement step.*



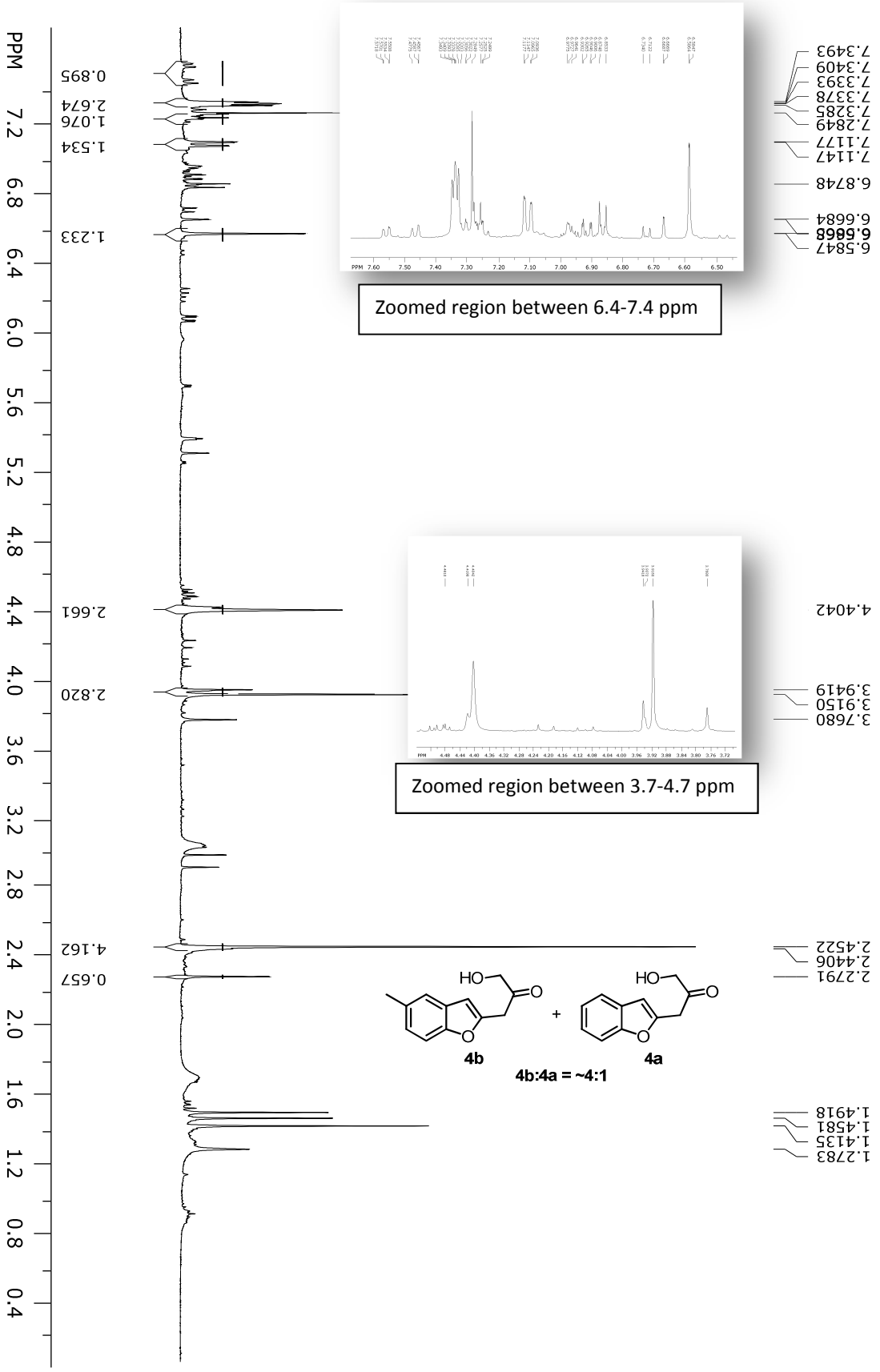
[1]H-NMR spectrum: Purified fraction-1



^{1}H-NMR spectra of the purified fraction-1
(Zoomed region between 6.70 to 1.40 ppm)



[1]H-NMR spectrum: Purified fraction-2



^{1}H-NMR spectrum of the purified fraction-2
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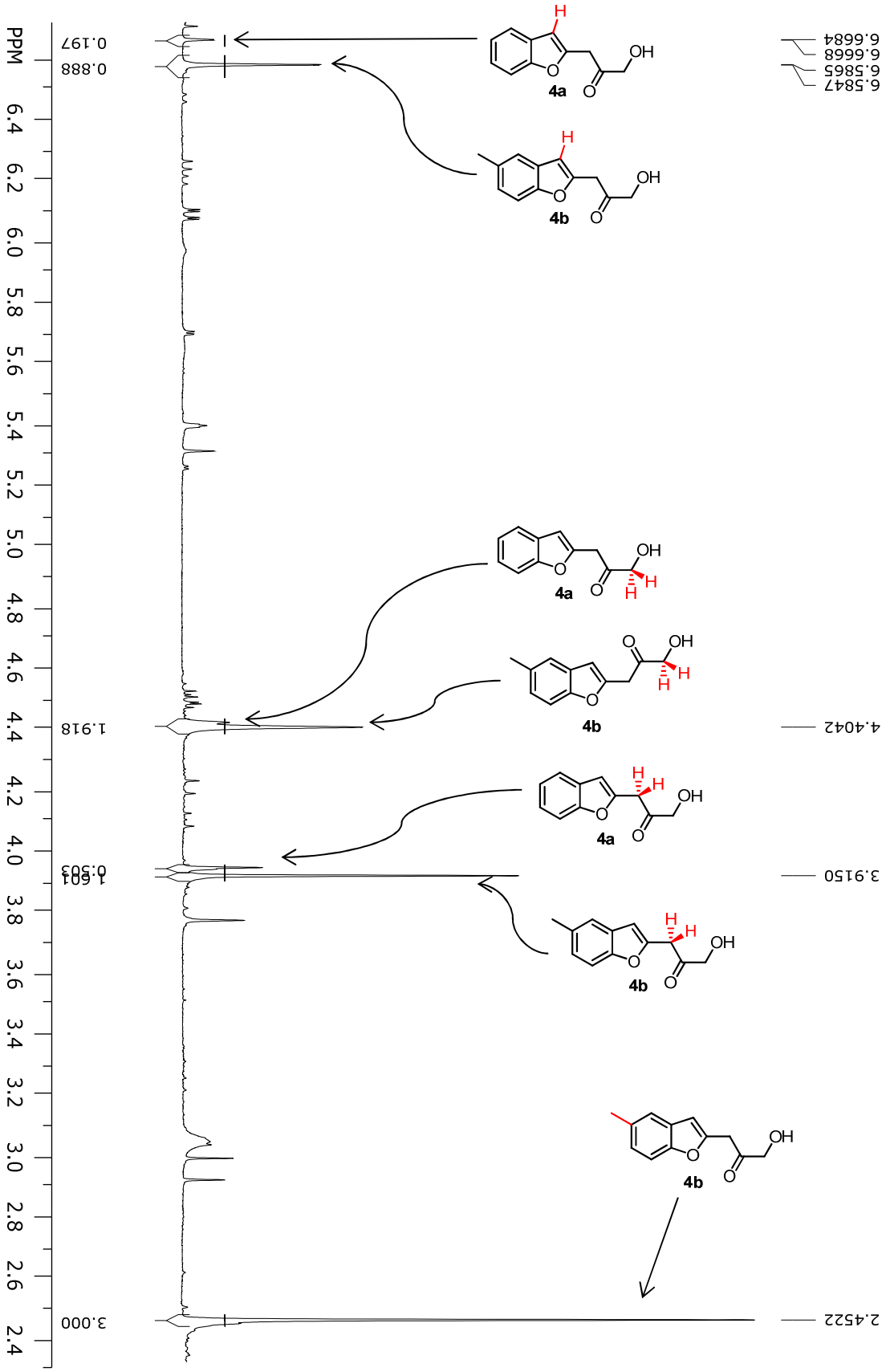
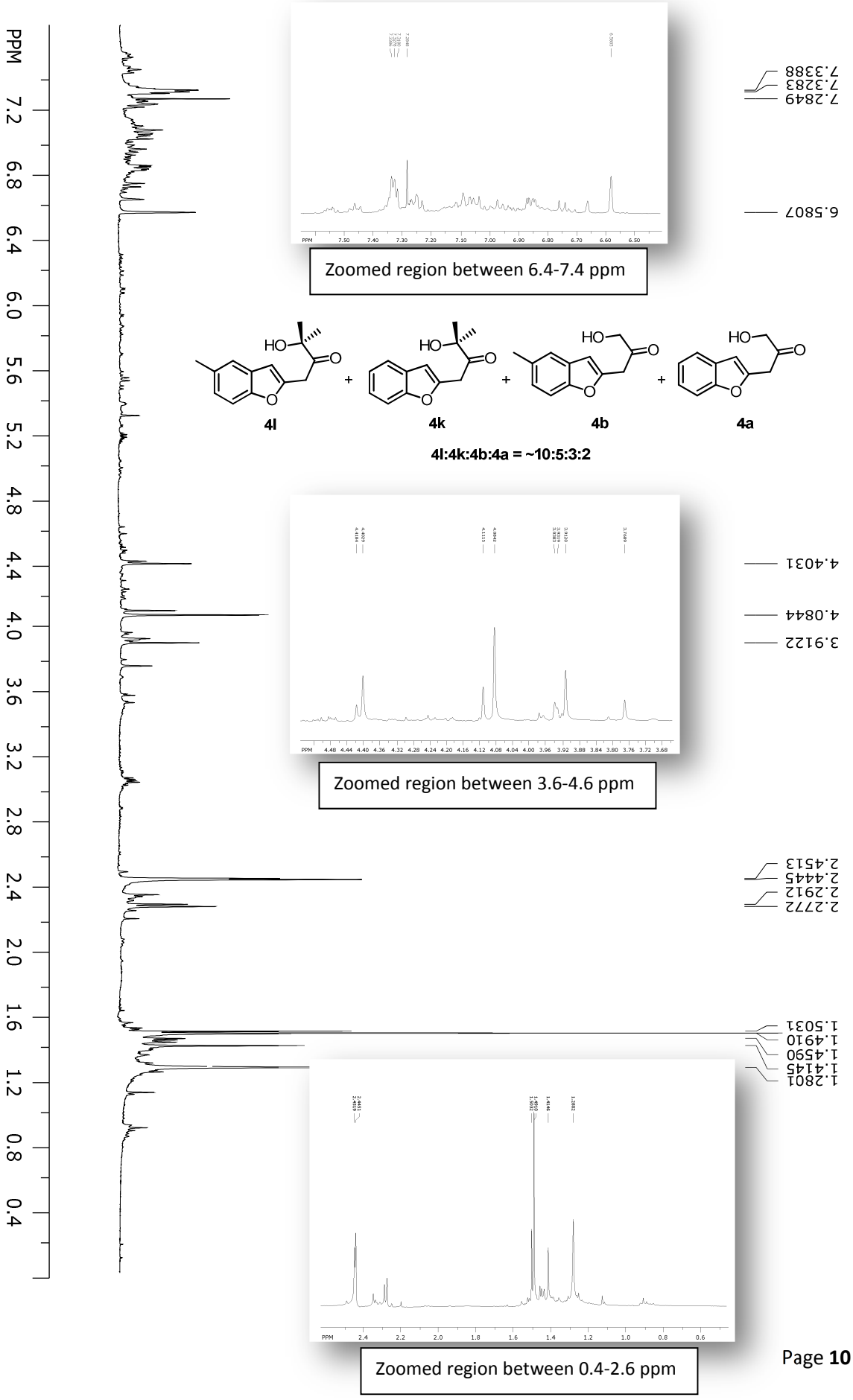
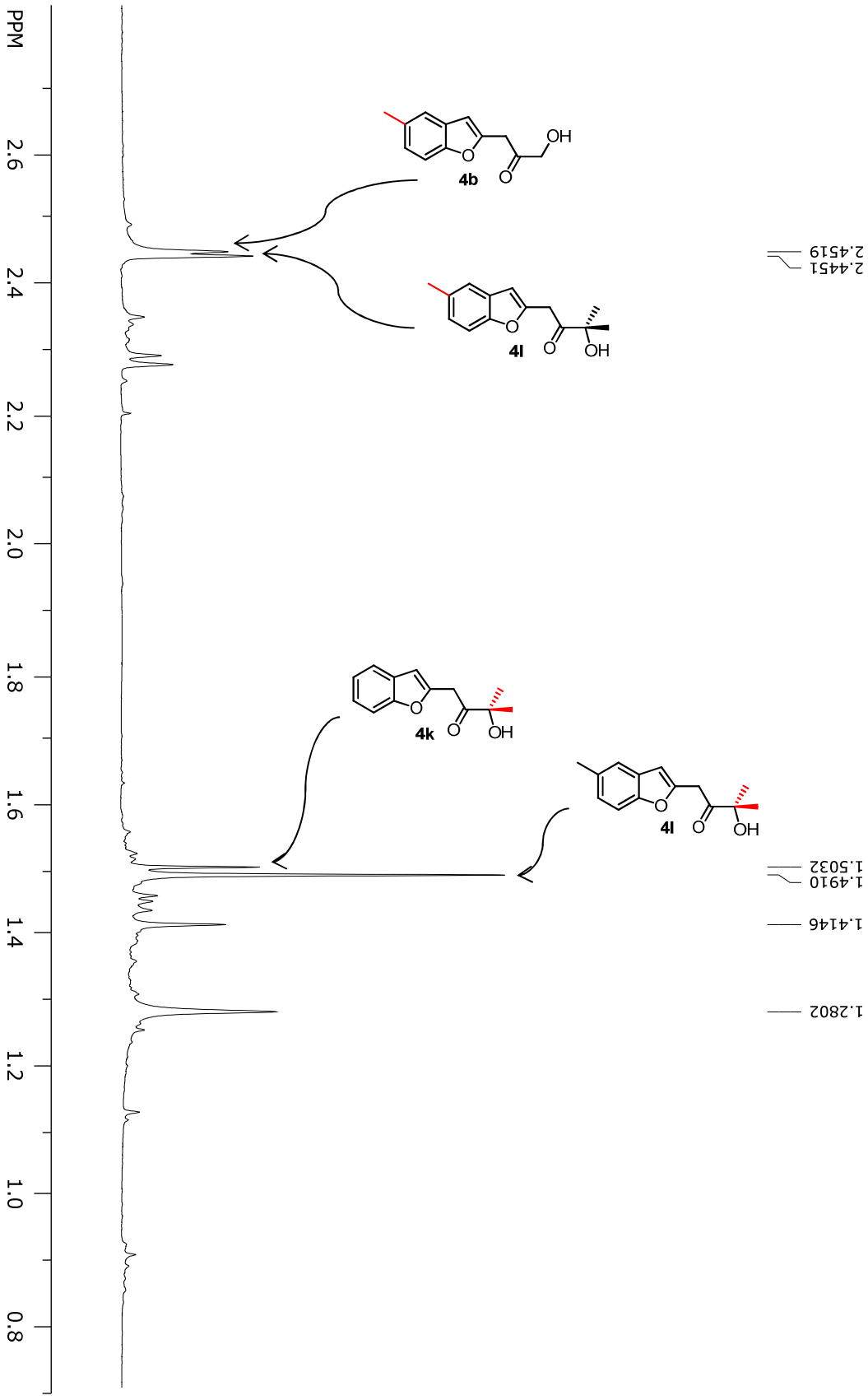


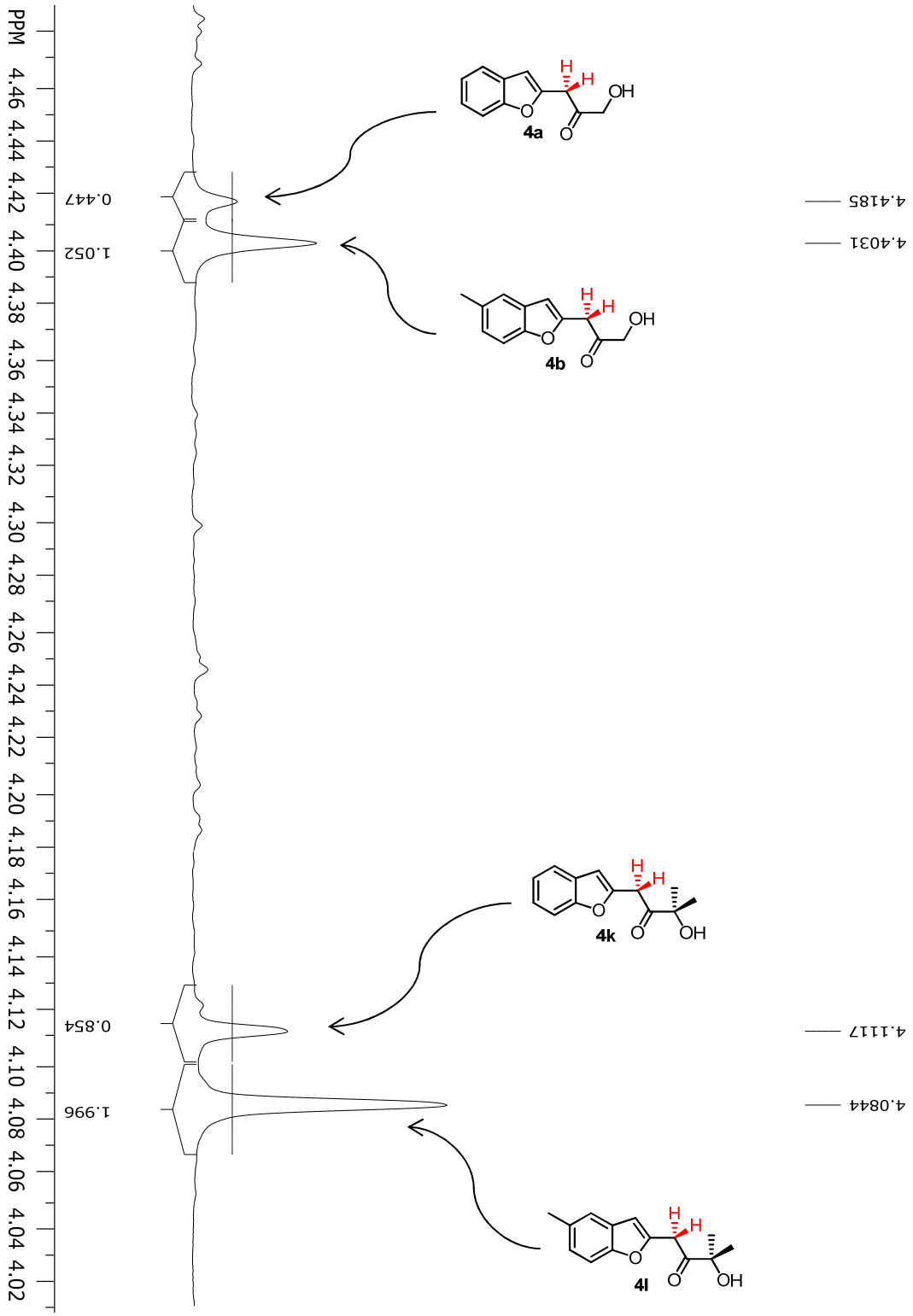
[1]H-NMR spectrum: Crude reaction mixture



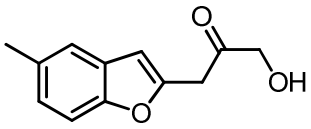
^{1}H-NMR spectrum of the crude reaction mixture
(Zoomed region from 2.70 to 0.70 ppm)



^{1}H-NMR spectra of the crude reaction mixture
(Zoomed region between 4.47 to 4.00 ppm)



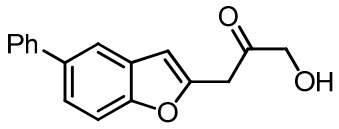
General procedure for the substrate screening. An oven-dried 5 mL glass vial was charged with the acetoxy pyranones **2** (0.2 mmol, 1 equiv), phenols **3** (0.22 mmol, 1.1 equiv), 1,2-dichloroethane (1 mL) and trimethylsilyl trifluoromethanesulfonate (TMSOTf, 10 mol%, 0.1 equiv) was added at 0-5 ^{o}C. Then the reaction mixture was stirred at same temperature for 30 min, and continued at room temperature until starting material disappeared as monitored by TLC. The reaction mixture was quenched with aqueous sodium bicarbonate solution, diluted with ethyl acetate (1-2 mL) and the layers were separated. The aqueous layer further extracted with ethyl acetate (1-2 mL) The organic layers were combined, dried over anhydrous Na_2SO_4, concentrated, and purified by silica gel column chromatography (hexanes/ethyl acetate) to afford the respective product (**4**).



4b

1-Hydroxy-3-(5-methylbenzofuran-2-yl)propan-2-one (4b).

This compound was isolated as colourless solid. Following the general procedure, 30 mg of **2a** afforded 33 mg of **4b** (85% yield). M.P = 103-104 ^{o}C. R_f = 0.2 (Hexane/EtOAc = 7/3). **IR** (thin film, neat): ν_{max} /cm^{-1} 3352, 2923, 2855, 1723, 1471, 1261, 1050, 800. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.35-7.34 (m, 2H), 7.11-7.09 (m, 1H), 6.59 (q, *J* = 1.0 Hz, 1H), 4.41 (s, 2H), 3.92 (s, 2H), 3.02 (s, 1H), 2.45 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ, 204.7, 153.4, 149.3, 132.5, 128.3, 125.5, 120.7, 110.5, 105.7, 67.9, 39.0, 21.5. **HRMS (ESI):** *m/z* calcd for $C_{12}H_{11}O_3$ $(M–H)^+$: 203.0708; Found: 203.0709.

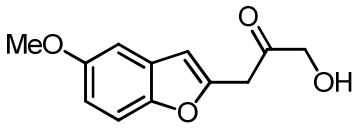


4c

1-Hydroxy-3-(5-phenylbenzofuran-2-yl)propan-2-one (4c).

This compound was isolated as colourless solid. Following the general procedure, 30 mg of **2a** afforded 41 mg of **4c** (80% yield). M.P = 97-99 ^{o}C. R_f = 0.2 (Hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3453, 2924, 2855, 1737, 1460, 1365, 1216, 764. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75-7.74 (m, 1H), 7.64-7.61 (m, 2H), 7.53-7.50 (m, 2H), 7.49-7.47 (m, 2H), 7.39-7.37 (m, 1H), 6.72 (d, *J* = 0.5 Hz, 1H), 4.44 (s, 2H), 3.96 (s, 2H), 3.10 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 204.5, 154.6, 150.0, 141.4, 136.8, 128.8, 128.7 (2C), 127.4 (2C), 126.9,

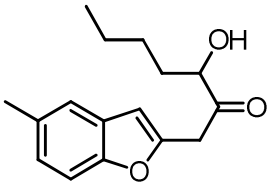
124.0, 119.4, 111.2, 106.2, 68.0, 38.9. HRMS (ESI): *m/z* calcd for $C_{17}H_{13}O_3$ $(M–H)^+$: 265.0865; Found: 265.0858.



4d

1-Hydroxy-3-(5-methoxybenzofuran-2-yl)propan-2-one (4d).

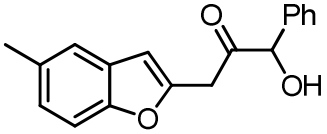
This compound was isolated as pale yellow liquid. Following the general procedure, 30 mg of **2a** afforded 32 mg of **4d** (75% yield).R_f = 0.2 (Hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3424, 2924, 1730, 1476, 1206, 1030. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.8 Hz, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 6.90 (dd, *J* = 8.8 and 2.4 Hz, 1H), 6.60 (d, *J* = 0.7 Hz, 1H), 4.41 (s, 2H), 3.91 (s, 2H), 3.86 (s, 3H), 3.01 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 204.6, 156.0, 150.05, 150.02, 128.8, 112.9, 112.5, 106.1, 103.3, 67.9, 55.9, 39.0 **HRMS (ESI):** *m/z* calcd for $C_{12}H_{13}O_4$ $(M+H)^+$: 221.0814; Found: 221.0818



4e

3-Hydroxy-1-(5-methylbenzofuran-2-yl)heptan-2-one (4e).

This compound was isolated as pale yellow oil. Following the general procedure, 30 mg of **2c** afforded 29 mg of **4e** (78%). R_f = 0.5 (EtOAc/Hexane = 1/4). IR (thin film, neat): ν_{max}/cm^{-1} 3429, 2925, 2856, 1721, 1515, 1472, 1267, 1082, 822. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34-7.32 (m, 2H), 7.09 (dd, *J* = 8.6 and 1.2 Hz, 1H), 6.58 (d, *J* = 0.7 Hz, 1H), 4.37-4.35 (m, 1H), 3.98 (s, 2H), 3.33 (d, *J* = 4.6 Hz, 1H), 2.45 (s, 3H), 1.94-1.90 (m, 1H), 1.68-1.63 (m, 2H) 1.47-1.40 (m, 3H) 0.95-0.91 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.2, 153.3, 149.8, 132.3, 128.4, 125.4, 120.6, 110.5, 105.5, 76.2, 38.2, 33.2, 26.8, 22.4, 21.3, 13.9. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{21}O_3$ $(M+H)^+$: 261.1491; Found: 261.1496.

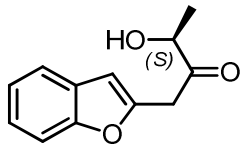


4f

1-Hydroxy-3-(5-methylbenzofuran-2-yl)-1-phenylpropan-2-one (4f).

This compound was isolated as Pale yellow oil. Following the general procedure, 30 mg of **2d** afforded 29 mg of **4f** (80% yield). R_f = 0.3 (Hexane/EtOAc = 7/3). IR (thin film, neat):

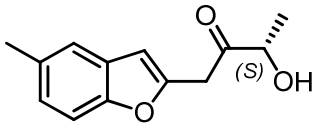
ν_{max}/cm^{-1} 3467, 2923, 2853, 1724, 1452, 1261, 1044, 800. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44-7.36 (m, 5H), 7.32-7.30 (m, 2H), 7.09 (dd, *J* = 8.4 and 1.6 Hz, 1H), 6.44 (d, *J* = 0.7 Hz, 1H) 5.31 (s, 1H), 4.26 (s, 1H), 3.92-3.75 (m, 2H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 204.3, 153.3, 149.5, 137.2, 132.3, 129.1, 129.0, 128.43, 128.41, 127.6, 125.3, 120.6, 110.5, 105.6, 79.4, 38.0, 21.3. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{15}O_3$ $(M–H)^+$: 279.1021; Found: 279.1025.



4g

(*S*)-1-(Benzofuran-2-yl)-3-hydroxybutan-2-one (4g).

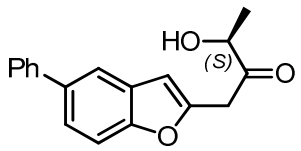
This compound was isolated as yellow oil. Following the general procedure, 30 mg of **2e** afforded 27 mg of **4g** (75% yield). R_f = 0.3 (Hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3435, 2925, 1723, 1455, 1614, 1252, 952, 795. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57-7.54 (m, 1H), 7.47-7.45 (m, 1H), 7.31-7.22 (m, 2H), 6.67-6.65 (m, 1H), 4.46 (q, *J* = 7.1 Hz, 1H), 4.02 (dd, *J* = 2.2 and 0.7 Hz, 2H), 3.43 (s, 1H), 1.49 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.3, 154.9, 149.7, 128.3, 124.2, 122.9, 120.8, 111.0, 105.8, 72.5, 37.9, 19.7. HRMS (ESI): *m/z* calcd for $C_{12}H_{11}O_3$ $(M–H)^+$: 203.0708; Found: 203.0702. **Optical rotation:** $[\alpha]_D^{23}$ +9.239 (*c* 0.02, $CHCl_3$).



4h

(*S*)-3-Hydroxy-1-(5-methylbenzofuran-2-yl)butan-2-one (**4h**).

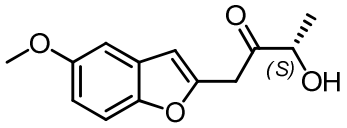
This compound was isolated as yellow oil. Following the general procedure, 30 mg of **2e** afforded 31 mg of **4h** (80% yield). R_f = 0.3 (Hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3445, 2925, 1723, 1474, 1264, 1053, 952. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34-7.32 (m, 2H),7.09 (dd, *J* = 8.3 and 1.2 Hz, 1H), 6.58 (d, *J* = 0.7 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 1H), 3.99 (s, 2H), 2.45 (s, 3H), 3.41 (s, 1H), 1.48 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.4, 153.3, 149.8, 132.3, 128.4, 125.4, 120.6, 110.5, 105.5, 72.5, 38.0, 21.3, 19.7. **HRMS (ESI)**: *m/z* calcd for $C_{13}H_{13}O_3$ $(M–H)^+$: 217.0865; Found: 217.0869. **Optical rotation:** $[\alpha]_D^{23}$ +7.048 (*c* 0.06, $CHCl_3$).



4i

(*S*)-3-Hydroxy-1-(5-phenylbenzofuran-2-yl)butan-2-one (4i).

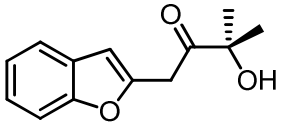
This compound was isolated as Pale brown oil. Following the general procedure, 30 mg of **2e** afforded 36 mg of **4i** (72% yield). R_f = 0.3 (Hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3441, 2935, 1724, 1602, 1464, 1233, 796, 763. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (t, *J* = 1.2 Hz, 1H), 7.64-7.61 (m, 2H), 7.52-7.45 (m, 5H), 6.72 (s, 1H), 4.47 (q, *J* = 7.1 Hz, 1H), 4.04 (d, *J* = 2.2 Hz, 2H), 3.39 (s, 1H), 1.51 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.2, 154.5, 150.5, 141.5, 136.7, 128.9, 128.7 (2C), 127.4 (2C), 126.9, 123.9, 119.3, 111.2, 106.0, 72.5, 37.9, 19.7. HRMS (ESI): *m/z* calcd for $C_{18}H_{15}O_3$ $(M–H)^+$: 279.1021; Found: 279.1014. **Optical rotation:** $[\alpha]_D^{23}$ –5.993 (*c* 0.03, $CHCl_3$).



4j

(*S*)-3-Hydroxy-1-(5-methoxybenzofuran-2-yl)butan-2-one (4j).

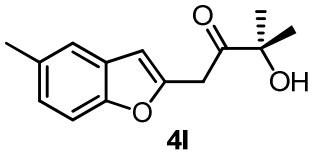
This compound was isolated as pale yellow oil. Following the general procedure, 30 mg of **2e** afforded 29 mg of **4j** (70% yield). R_f = 0.3 (Hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3456, 1724, 1477, 1029, 1206, 795. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 2.4 Hz, 1H), 7.01 (d, *J* = 2.4 Hz, 1H), 6.89 (dd, *J* = 8.9 and 2.6 Hz, 1H), 6.60 (d, *J* = 0.7 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 1H), 3.99 (d, *J* = 1.2 Hz, 2H), 3.85 (s, 3H), 3.41 (s, 1H), 1.48 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.3, 156.0, 150.5, 149.9, 128.9, 112.8, 111.5, 105.9, 103.3, 72.5, 55.9, 38.0, 19.7. HRMS (ESI): *m/z* calcd for $C_{13}H_{13}O_4$ $(M–H)^+$: 233.0814; Found: 233.0815. **Optical rotation:** $[\alpha]_D^{23}$ +5.992 (*c* 0.08, $CHCl_3$) for a sample with *ee* 98%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AS column (90:10 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 78.8 min, τ_{minor} = 36.1 min).



4k

1-(Benzofuran-2-yl)-3-hydroxy-3-methylbutan-2-one (4k).

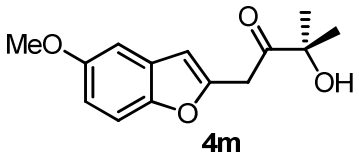
This compound was isolated as pale yellow oil. Following the general procedure, 30 mg of **2f** afforded 25 mg of **4k** (70% yield). R_f = 0.3 (Hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3446, 2926, 1719, 1454, 1366, 1194, 1051, 1252, 794. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56-7.54 (m, 1H), 7.47-7.45 (m, 1H), 7.28-7.25 (m, 2H), 6.66 (q, *J* = 1.0 Hz, 1H), 4.11 (d, *J* = 1.0 Hz, 2H), 3.48 (s, 1H), 1.51(s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 209.1, 154.8, 150.4, 128.4, 124.0, 122.8, 120.7, 111.0, 105.6, 76.9, 35.9, 26.5 ($2CH_3$). HRMS (ESI): *m/z* calcd for $C_{13}H_{13}O_3$ $(M–H)^+$: 217.0865; Found: 217.0860.



4l

3-Hydroxy-3-methyl-1-(5-methylbenzofuran-2-yl)butan-2-one (4l).

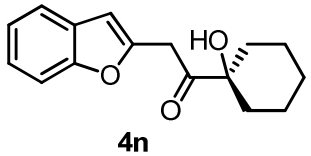
This compound was isolated as pale yellow solid. Following the general procedure, 30 mg of **2f** afforded 28 mg of **4l** (74% yield). M.P = 63-68 ^oC. R_f = 0.4 (Hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3440, 2925, 2855, 1719, 1474, 1377, 1265, 1204, 1051, 952, 798. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34-7.33 (m, 2H), 7.09 (d, *J* = 0.5 Hz, 1H), 6.58 (q, *J* = 0.8 Hz, 1H), 40.8 (d, *J* = 0.8 Hz, 2H), 3.47 (s, 1H), 2.45 (s, 3H), 1.49 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 209.1, 153.2, 150.5, 132.2, 128.5, 125.2, 120.6, 110.5, 105.3, 76.8, 36.0, 26.5, 21.3 (2C). HRMS (ESI): *m/z* calcd for $C_{14}H_{15}O_2$ $(M–OH)^+$: 215.1072; Found: 215.1064.



4m

3-Hydroxy-1-(5-methoxybenzofuran-2-yl)-3-methylbutan-2-one (4m).

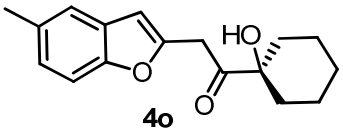
This compound was isolated as colourless oil. Following the general procedure, 30 mg of **2f** afforded 28 mg of **4m** (70% yield). R_f = 0.4 (Hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3451, 2927, 1719, 1612, 1476, 1206, 1168, 1031, 954,798, 842. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.8 Hz, 1H), 7.01 (d, *J* = 2.5 Hz, 1H), 6.68 (dd, *J* = 8.9 and 2.6 Hz, 1H), 6.60 (s, 1H), 4.08 (s, 2H), 3.86 (s, 3H), 3.45 (s, 1H), 1.49 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 209.1, 155.9, 151.2, 149.8, 129.0, 112.6, 111.4, 105.8, 103.3, 76.8, 55.9, 36.0, 26.5 (2C). HRMS (ESI): *m/z* calcd for $C_{14}H_{15}O_4$ $(M–H)^+$: 247.0971; Found: 247.0975.



4n

2-(Benzofuran-2-yl)-1-(1-hydroxycyclohexyl)ethanone (**4n**).

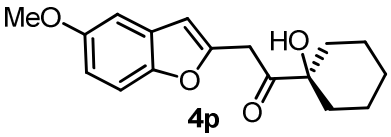
This compound was isolated as pale yellow oil. Following the general procedure, 30 mg of **2h** afforded 21 mg of **4n** (60% yield). R_f = 0.4 (Hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max} /cm^{-1} 3440, 2933, 2857, 1713, 1595, 1453, 1251, 986, 955. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55-7.53 (m, 1H), 7.46-7.44 (m, 1H), 725-7.24 (m, 2H), 6.64 (d, *J* = 0.8 Hz, 1H), 4.13 (d, *J* = 0.5 Hz, 2H), 3.15 (s, 1H), 1.86-1.69 (m, 10H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 209.3, 154.8, 150.8, 128.5, 123.9, 122.7, 120.7, 111.0, 105.5, 78.6, 36.1, 33.7 (2C), 25.1, 20.9 (2C). HRMS (ESI): *m/z* calcd for $C_{16}H_{17}O_3$ $(M–H)^+$: 257.1178; Found: 257.1170.



4o

1-(1-Hydroxycyclohexyl)-2-(5-methylbenzofuran-2-yl)ethanone (4o).

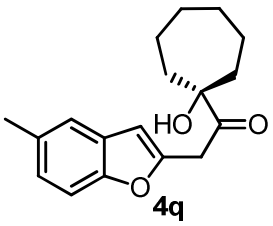
This compound was isolated as pale brown oil. Following the general procedure, 30 mg of **2h** afforded 27.6 mg of **4o** (70% yield). R_f = 0.3 (Hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 3451, 2924, 1704, 1204, 1174, 800. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.37-7.31 (m, 2H), 7.07 (d, *J* = 8.6 Hz, 1H), 6.56 (s, 1H), 4.10 (s, 2H), 3.20 (s, 1H), 2.45 (s, 3H), 1.84-1.59 (m, 10H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 209.4, 153.2, 150.8, 132.1, 128.6, 125.1, 120.5, 110.4, 105.2, 78.6, 36.2, 33.7 (2C), 25.1, 21.3, 20.9 (2C). **HRMS (ESI)**: *m/z* calcd for $C_{17}H_{19}O_3$ $(M–H)^+$: 271.1334; Found: 271.1322.



4p

1-(1-Hydroxycyclohexyl)-2-(5-methoxybenzofuran-2-yl)ethanone (4p).

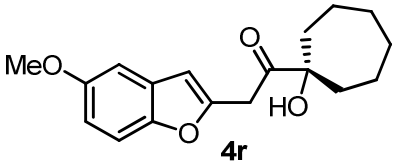
This compound was isolated as pale brown solid Following the general procedure, 30 mg of **2h** afforded 26 mg of **4p** (66% yield). M.P = 93-95 ^oC. R_f = 0.4 (Hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3409, 2927, 1714, 1510, 1206, 1034, 827. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33 (d, *J* = 8.8 Hz, 1H), 7.00 (d, *J* = 2.7 Hz, 1H), 6.86 (dd, *J* = 8.90 and 2.60 Hz, 1H), 6.57 (s, 1H), 4.09 (s, 2H), 3.85 (s, 3H), 3.17 (s, 1H), 1.79-1.59 (m, 10H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 209.4, 155.9, 151.6, 149.8, 129.1, 112.4, 111.4, 105.6, 103.3, 78.6, 55.9, 36.2, 33.6 (2C), 25.1, 20.9 (2C). HRMS (ESI): *m/z* calcd for $C_{17}H_{19}O_4$ $(M–H)^+$: 287.1284; Found: 287.1278.



4q

1-(1-Hydroxycycloheptyl)-2-(5-methylbenzofuran-2-yl)ethanone (4q).

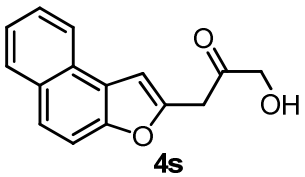
This compound was isolated as light yellow solid. Following the general procedure, 30 mg of **2i** afforded 27 mg of **4q** (75% yield). M.P = 92-94 ^{o}C. R_f = 0.5 (Hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max} /cm^{-1} 3430, 2927, 1713, 1511, 1476, 1205, 1034, 828. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34-7.32 (m, 2H), 7.09-7.06 (m, 1H), 6.56 (d, *J* = 0.7 Hz, 1H), 4.09 (d, *J* = 0.7 Hz, 2H), 3.26 (s, 1H), 2.45 (s, 3H), 2.03-1.97 (m, 2H), 1.85-1.68 (m, 10H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 209.5, 153.2, 150.9, 132.1, 125.1, 120.5, 150.0, 110.4, 105.2, 81.5, 37.6 (2C), 36.1, 29.2 (2C) 22.9 (2C), 21.3. HRMS (ESI): *m/z* calcd for $C_{18}H_{23}O_3$ $(M+H)^+$: 287.1647; Found: 287.1639.



4r

1-(1-Hydroxycycloheptyl)-2-(5-methoxybenzofuran-2-yl)ethanone (4r).

This compound was isolated as pale yellow solid. Following the general procedure, 30 mg of **2i** afforded 27.5 mg of **4r** (76% yield). M.P = 102-104 ^{o}C. R_f = 0.5 (Hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max}/cm^{-1} 3430, 2927, 1713, 1511, 1476, 1205, 1034, 828. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33 (d, *J* = 8.8 Hz, 1H), 7.00 (d, *J* = 2.7 Hz, 1H), 6.86 (dd, *J* = 8.9 and 2.6 Hz, 1H), 6.57 (s, 1H), 4.08 (s, 2H), 3.84 (s, 3H), 3.23 (s, 1H), 2.01-1.96 (m, 2H), 1.81-1.60 (m, 10H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ209.4, 155.9, 151.8, 149.8, 129.1, 112.4, 111.4, 105.6, 103.3, 81.5, 55.9, 37.6 (2C), 36.1, 29.2 (2C) 22.8 (2C). HRMS (ESI): *m/z* calcd for $C_{18}H_{21}O_4$ $(M-H)^+$: 301.1440; Found: 301.1447.

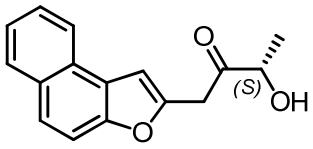


4s

1-Hydroxy-3-(naphtho[2,1-*b*]furan-2-yl)propan-2-one (4s).

This compound was isolated as light brown solid. Following the general procedure, 30 mg of **2a** afforded 42 mg of **4s** (90% yield). M.P = 97-99 ^{o}C. R_f = 0.2 (Hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3410, 2892, 1727, 1394, 1155, 1040, 944, 809. **^{1}H NMR** (400

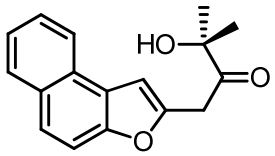
MHz, $(CD_3)_2SO$): δ 8.24 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.77 (q, *J* = 8.90 Hz, 2H), 7.61 (td, *J* = 7.60 Hz, 1H), 7.53-7.51 (m, 1H), 7.36 (s, 1H), 4.28 (s, 2H), 4.16 (s, 2H), 3.50 (s, 1H). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$): δ 206.6, 152.0, 151.8, 130.3, 129.0, 127.4, 126.8, 125.0, 124.9, 124.0, 123.9, 112.6, 105.0, 67.9, 38.5. HRMS (ESI): *m/z* calcd for $C_{15}H_{13}O_3$ $(M+H)^+$: 241.0865; Found: 241.0869.



4t

***(S)*-3-Hydroxy-1-(naphtho[2,1-*b*]furan-2-yl)butan-2-one (4t).**

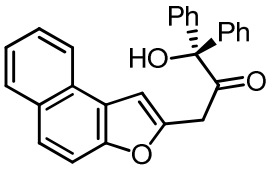
This compound was isolated as Pale yellow semisolid. Following the general procedure, 30 mg of **2e** afforded 41 mg of **4t** (90% yield). R_f = 0.2 (Hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3434, 1721, 1577, 1383, 951, 807. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.12-8.10 (m, 1H), 7.97-7.95 (m, 1H), 7.74-7.72 (m, 1H), 7.64-7.60 (m, 2H), 7.51 (ddd, *J* = 8.2, 6.9, and 1.3 Hz, 1H), 7.154-7.150 (m, 1H), 4.52-4.45 (m, 1H), 4.10 (dd, *J* = 2.8 and 0.8 Hz, 2H), 3.46 (s, 1H), 1.51-149 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.5, 152.4, 149.0, 130.3, 128.7, 127.4, 126.3, 125.1, 124.6, 123.6, 123.4, 112.1, 104.9, 72.5, 38.0, 19.7. HRMS (ESI): *m/z* calcd for $C_{16}H_{13}O_3$ $(M–H)^+$: 253.0865; Found: 253.0870. **Optical rotation:** $[\alpha]_D^{23}$ +6.327 (*c* 0.06, $CHCl_3$) for a sample with *ee* 93%. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralpak AS column (90:10 *n*-Hexane/2-Propanol, 1.0 mL/min, 254 nm, τ_{major} = 63.7 min, τ_{minor} = 21.8 min).



4u

3-Hydroxy-3-methyl-1-(naphtho[2,1-*b*]furan-2-yl)butan-2-one (4u).

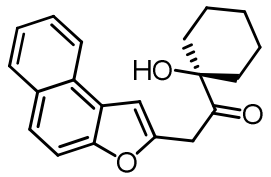
This compound was isolated as light yellow solid. Following the general procedure, 30 mg of **2f** afforded 40 mg of **4u** (92% yield). M.P = 89-91 ^oC. R_f = 0.3 (Hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3500, 2922, 1713, 1463, 1385, 1191, 952, 802. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.13-8.10 (m, 1H), 7.96 (d, *J* = 8 Hz, 1H), 7.73-7.64 (m, 1H), 7.62-7.59 (m, 2H), 7.58-7.50 (m, 1H), 7.16 (d, *J* = 0.8 Hz, 1H), 4.20 (s, 2H), 3.49 (s, 1H), 1.53 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 209.2, 152.3, 149.6, 130.3, 128.7, 127.4, 126.2, 124.9, 124.5, 123.6, 123.4, 112.1, 104.7, 76.9, 36.1, 26.5 (2C). HRMS (ESI): *m/z* calcd for $C_{17}H_{15}O_3$ $(M–H)^+$: 267.1021; Found: 267.1011.



4v

1-Hydroxy-3-(naphtho[2,1-*b*]furan-2-yl)-1,1-diphenylpropan-2-one (4v).

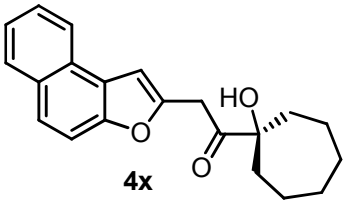
This compound was isolated as pale yellow oil. Following the general procedure, 30 mg of **2j** afforded 31 mg of **4v** (80% yield). R_f = 0.3 (Hexane/EtOAc = 7/3). IR (thin film, neat): ν_{max}/cm^{-1} 3500, 2922, 1713, 1463, 1385, 1191, 952, 802. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.74-7.70 (m, 1H), 7.63-7.57 (m, 2H), 7.51-7.44 (m, 11H), 6.99 (s, 1H), 4.56 (s, 1H), 4.21 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 206.1, 152.3, 149.6, 141.0, 130.2, 128.7, 128.5, 128.1, 127.5, 126.2, 124.8, 124.4, 123.6, 123.4, 112.2, 104.6, 86.0, 38.4. HRMS (ESI): *m/z* calcd for $C_{27}H_{20}NaO_3$ $(M+Na)^+$: 415.1310; Found: 415.1299.



4w

1-(1-Hydroxycyclohexyl)-2-(naphtho[2,1-*b*]furan-2-yl)ethanone (4w).

This compound was isolated as white solid. Following the general procedure, 30 mg of **2h** afforded 37 mg of **4w** (90% yield). M.P = 125-127 ^{o}C. R_f = 0.5 (Hexane/EtOAc = 1/4). IR (thin film, neat): ν_{max} /cm^{-1} 3489, 2941, 1696, 1379, 1150, 993, 799. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.73-7.70 (m, 1H), 7.64-7.57 (m, 2H), 7.52-7.48 (m, 1H), 7.15 (d, *J* = 0.5 Hz, 1H), 4.23 (d, *J* = 6.5 Hz, 2H) 3.17 (s, 1H) 1.89-1.70 (m, 10H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 209.5, 152.3, 150.0, 130.2, 128.7, 127.4, 126.2, 124.8, 124.4, 123.7, 123.4, 112.1, 104.6, 78.7, 36.3, 33.7 (2C), 25.1, 21.0 (2C). HRMS (ESI): *m/z* calcd for $C_{20}H_{19}O_3$ $(M–H)^+$: 307.1334; Found: 307.1342

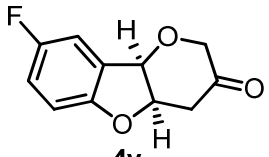


4x

1-(1-Hydroxycycloheptyl)-2-(naphtho[2,1-*b*]furan-2-yl)ethanone (4x).

This compound was isolated as light brown solid. Following the general procedure, 30 mg of **2i** afforded 40 mg of **4x** (92% yield). M.P = 110-112 ^{o}C. R_f = 0.5 (Hexane/EtOAc = 4/1). IR

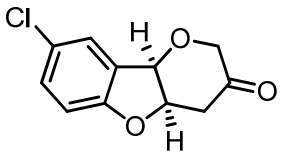
(thin film, neat): ν_{max}/cm^{-1} 3405, 2925, 1711, 1629, 1602, 1385, 1211, 1046, 846. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.13-8.10 (m, 1H), 7.97-7.94 (m, 1H), 7.73-7.71 (m, 1H), 7.64-7.57 (m, 2H), 7.52-7.48 (m, 1H), 7.15 (d, *J* = 0.8 Hz, 1H), 4.21 (d, *J* = 0.8 Hz, 2H), 3.23 (s, 1H), 2.07-2.01 (m, 2H) 1.88-1.68 (m, 10H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 209.5, 152.3, 150.1, 130.2, 128.7, 127.5, 126.2, 124.8, 124.4, 123.7, 123.4, 112.1, 104.6, 81.5, 37.7 (2C), 36.2, 29.2 (2C), 22.9 (2C). HRMS (ESI): *m/z* calcd for $C_{21}H_{21}O_3$ $(M-H)^+$: 321.1491; Found: 321.1501.



4y

8-Fluoro-4,4a-dihydro-2*H*-pyrano[3,2-*b*]benzofuran-3(9b*H*)-one (4y).

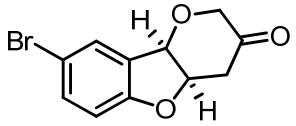
This compound was isolated as colorless oil. Following the general procedure, 30 mg of **2a** afforded 28 mg of **4y** (70% yield). R_f = 0.5 (EtOAc/Hexane = 3/7). **IR (thin film, neat):** ν_{max}/cm^{-1} 1738, 1510, 1484, 1221, 1194, 794, 835. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.16 (dd, *J* = 7.5 and 2.8 Hz, 1H), 7.04-7.03 (m, 1H), 6.80-6.77 (m, 1H), 5.52 (d, *J* = 7.3 Hz, 1H), 5.24-5.22 (m, 1H), 3.97 (d, *J* = 18.1 Hz, 1H), 3.56 (d, *J* = 18.1 Hz, 1H), 3.05 (dd, *J* = 6.0 and 3.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.3, 157.9 (d, *J* = 238.2 Hz, 1C), 156.6 (d, *J* = 1.2 Hz, 1C), 123.7 (d, *J* = 8.1 Hz, 1C), 118.5 (d, *J* = 24.4 Hz, 1C), 113.3 (d, *J* = 24.05 Hz, 1C), 110.8 (d, *J* = 8.2 Hz, 1C), 79.9, 75.8 (d, *J* = 1.5 Hz, 1C), 68.7, 39.6. **HRMS (ESI):** *m/z* calcd for $C_{11}H_{10}FO_3$ $(M+H)^+$: 209.0614; Found: 209.0608.



4z

8-Chloro-4,4a-dihydro-2*H*-pyrano[3,2-*b*]benzofuran-3(9b*H*)-one (4z).

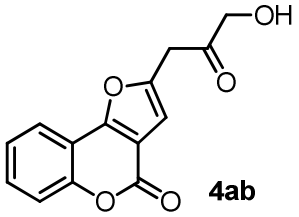
This compound was isolated as colourless oil. Following the general procedure, 30 mg of **2a** afforded 34 mg of **4z** (78 % yield. R_f = 0.5 (EtOAc/Hexane = 3/7). **IR (thin film, neat):** ν_{max}/cm^{-1} 1731, 1587, 1489, 1470, 1233, 1087, 823, 605. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 2.2 Hz, 1H), 7.31-7.27 (m, 1H), 6.80-6.76 (m, 1H), 5.23 (dt, *J* = 7.3 and 3.7 Hz, 1H), 3.99-3.64 (m, 1H), 3.58-3.54 (m, 1H), 3.10-2.99 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.4, 159.2, 131.6, 129.4, 126.9, 116.6, 111.4, 80.0, 75.5, 68.7, 39.5**.** HRMS (ESI): *m/z* calcd for $C_{11}H_8ClO_3$ $(M-H)^+$: 223.0162; Found: 223.0163.



4aa

8-Bromo-4,4a-dihydro-2*H*-pyrano[3,2-*b*]benzofuran-3(9*bH*)-one (4aa).

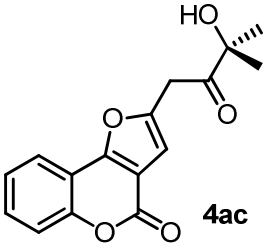
This compound was isolated as a pale brown oil. Following the general procedure, 30 mg of **2a** afforded 39 mg of **4aa** (75 % yield). R_f = 0.5 (EtOAc/Hexane = 3/7). **IR (thin film, neat):** ν_{max}/cm^{-1} 1731, 1587, 1489, 1470, 1233, 1087, 823, 605. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 2.2 Hz, 1H), 7.43 (dd, *J* = 8.6 and 2.2 Hz, 1H), 6.76-6.73 (m, 1H), 5.52 (d, *J* = 7.3 Hz, 1H), 5.23 (dt, *J* = 7.3 and 3.7 Hz, 1H), 3.98 (d, *J* = 18.1 Hz, 1H), 3.26 (d, *J* = 18.1 Hz, 1H), 3.10-2.99 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.1, 183.6, 134.5, 129.8, 113.5, 111.9, 109.7, 79.9, 75.4, 68.7, 39.5**.** HRMS (ESI): *m/z* calcd for $C_{11}H_8BrO_3$ $(M–H)^+$: 266.9657; Found: 266.9649.



4ab

2-(3-Hydroxy-2-oxopropyl)-4*H*-furo[3,2-*c*]chromen-4-one (4ab).

This compound was isolated as pale yellow liquid. Following the general procedure, 30 mg of **2a** afforded 35 mg of **4ab** (70% yield). R_f = 0.2 (Hexane/EtOAc = 7/3). **IR** (thin film, neat): ν_{max}/cm^{-1} 3427, 2929, 1733, 1632, 1059, 897. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.84 (dd, *J* = 7.8 and 1.5 Hz, 1H), 7.56-7.52 (m, 1H), 7.46-7.44 (m, 1H), 7.36 (td, *J* = 7.5 and 1.1 Hz, 1H), 6.89 (s, 1H), 4.45 (s, 2H), 4.01 (s, 2H) 3.01 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 203.6. 158.0, 157.7, 152.5, 149.8, 130.9, 124.6, 120.8, 117.4, 112.4, 111.5, 107.6, 68.1, 38.0. **HRMS (ESI):** *m/z* calcd for $C_{14}H_9O_5$ $(M–H)^+$: 257.0450; Found: 257.0451.

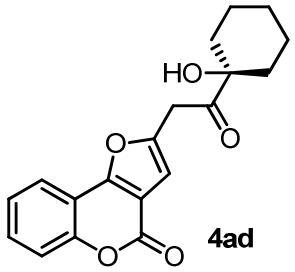


4ac

2-(3-Hydroxy-3-methyl-2-oxobutyl)-4*H*-furo[3,2-*c*]chromen-4-one (4ac).

This compound was isolated as pale yellow solid. Following the general procedure, 30 mg of **2f** afforded 37 mg of **4ac** (80% yield). M.P = 132-135 ^oC. R_f = 0.3 (Hexane/EtOAc = 7/3). IR

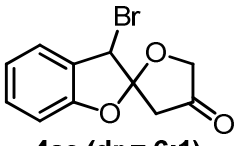
(thin film, neat): ν_{max}/cm^{-1} 3428, 2934, 2856, 1732, 1461, 1062, 974, 795. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.84 (dd, *J* = 7.8 and 1.5 Hz, 1H), 7.52-7.43 (m, 2H), 7.36-7.32 (m, 1H), 6.87 (s, 1H), 4.19 (d, *J* = 0.7 Hz, 2H), 3.26 (s, 1H), 1.52 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 208.3, 158.2, 157.4, 152.4, 151.2, 130.6, 124.5, 120.8, 117.3, 112.6, 112.5, 107.3, 76.9, 35.4, 26.6 (2C). HRMS (ESI): *m/z* calcd for $C_{16}H_{14}NaO_5$ $(M+Na)^+$: 309.0739; Found: 309.0729.



4ad

2-(2-(1-Hydroxycyclohexyl)-2-oxoethyl)-4H-furo[3,2-*c*]chromen-4-one (4ad).

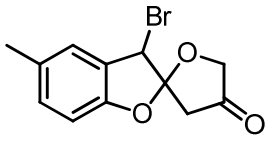
This compound was isolated as Pale yellow solid. Following the general procedure, 30 mg of **2h** afforded 28 mg of **4ad** (63% yield). M.P = 131-133 ^{o}C. R_f = 0.5 (Hexane/EtOAc = 4/1). IR (thin film, neat): ν_{max} /cm^{-} 3457, 2934, 1734, 1632, 1448, 1164, 1100, 947. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.83 (dd, *J* = 7.8 and 1.5Hz, 1H), 7.54-7.50 (m, 1H), 7.45-7.43 (m, 1H), 7.36-7.32 (m, 1H), 6.84 (s, 1H), 4.20 (s, 2H), 3.20 (s, 1H), 1.86-1.65 (m, 10H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 208.7, 158.2, 157.3, 152.4, 151.6, 130.6, 124.5, 120.8, 117.3, 112.6, 111.5, 107.1, 78.7, 35.7, 33.7 (2C), 25.1, 20.9 (2C). **HRMS (ESI):** *m/z* calcd for $C_{19}H_{19}O_5$ $(M+H)^+$: 327.1232; Found: 327.1222.



4ae (dr = 6:1)

3-Bromo-3*H*,3'*H*-spiro[benzofuran-2,2'-furan]-4'(5'*H*)-one (4ae).

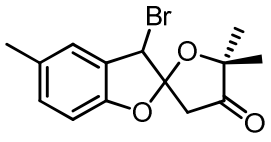
This compound was isolated as pale yellow oil. Following the general procedure, 30 mg of **4a** afforded 31 mg of **4ae** (73% yield. R_f = 0.6 (EtOAc/Hexane = 2/8). **IR (thin film, neat)**: ν_{max}/cm^{-1} 2918, 1770, 1594, 1467, 1322, 1284, 1166, 1034, 906, 880, 751, 672. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 8.9 Hz, 1H), 7.08-7.05 (m, 1H), 6.93-6.90 (m, 1H), 5.49 (s, 1H), 4.34-4.33 (m, 2H), 3.29-3.24 (m, 1H), 3.04 (d, *J* = 18.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 209.5, 157.3, 134.2, 131.2, 126.0, 122.7, 117.5, 111.1, 72.5, 50.6, 46.2. **HRMS (ESI)**: *m/z* calcd for $C_{11}H_{10}BrO_3$ $(M+H)^+$: 268.9813; Found: 268.9802.



4af (dr = 1:1)

3-Bromo-5-methyl-3*H*,3'*H*-spiro[benzofuran-2,2'-furan]-4'(5'*H*)-one (4af).

This compound was isolated as yellow oil. Following the general procedure, 30 mg of **4b** afforded 32 mg of **4af** (76% yield. R_f = 0.6 (EtOAc/Hexane = 2/8). **IR (thin film, neat):** ν_{max}/cm^{-1} 2918, 1771, 1491, 1307, 1277, 1036, 909, 795. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.28 7.26 (m, 1H), 7.13 (t, *J* = 8.9 Hz, 1H), 6.80 (dd, *J* = 8.2 and 4.3 Hz, 1H), 5.39 (m, 1H), 4.37-4.25 (m, 2H), 3.27-2.91 (m, 2H), 2.35 (d, *J* = 3.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 209.6, 155.5, 132.0, 126.2, 118.0, 110.7, 72.4, 61.8, 50.9, 46.2, 29.7, 20.8**. HRMS (ESI)**: *m/z* calcd for $C_{12}H_{10}BrO_3$ $(M–H)^+$: 280.9814; Found: 280.9802.



4ag (dr = 7:1)

3-Bromo-5,5',5'-trimethyl-3*H*,3'*H*-spiro[benzofuran-2,2'-furan]-4'(5'*H*)-one (4ag).

This compound was isolated as white solid. Following the general procedure, 30 mg of **4l** afforded 32 mg of **4ag** (80% yield.) M.P = 103-104 ^oC R_f = 0.6 (EtOAc/Hexane = 1/9). **IR (thin film, neat):** ν_{max}/cm^{-1} 2923, 1761, 1489, 1304, 1108, 839, 814. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.26-7.25 (m, 1H), 7.11-7.02 (m, 1H), 6.80-6.77 (m, 1H), 5.39 (s, 1H), 3.41-3.36 (m, 1H), 3.11-3.06 (m, 1H), 2.34 (s, 3H), 1.45 (s, 3H) 1.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 213.5, 155.3, 132.0, 131.8, 126.8, 126.1, 115.0, 110.6, 85.3, 52.3, 45.3, 25.1, 25.0, 20.8**.** HRMS (ESI): *m/z* calcd for $C_{14}H_{14}BrO_3$ $(M-H)^+$: 309.0127; Found: 309.0138.

Crystal structure of 4l (CCDC 1437901): Structure of the benzofuran derivative **4l** was confirmed by single crystal X-ray diffraction analysis.

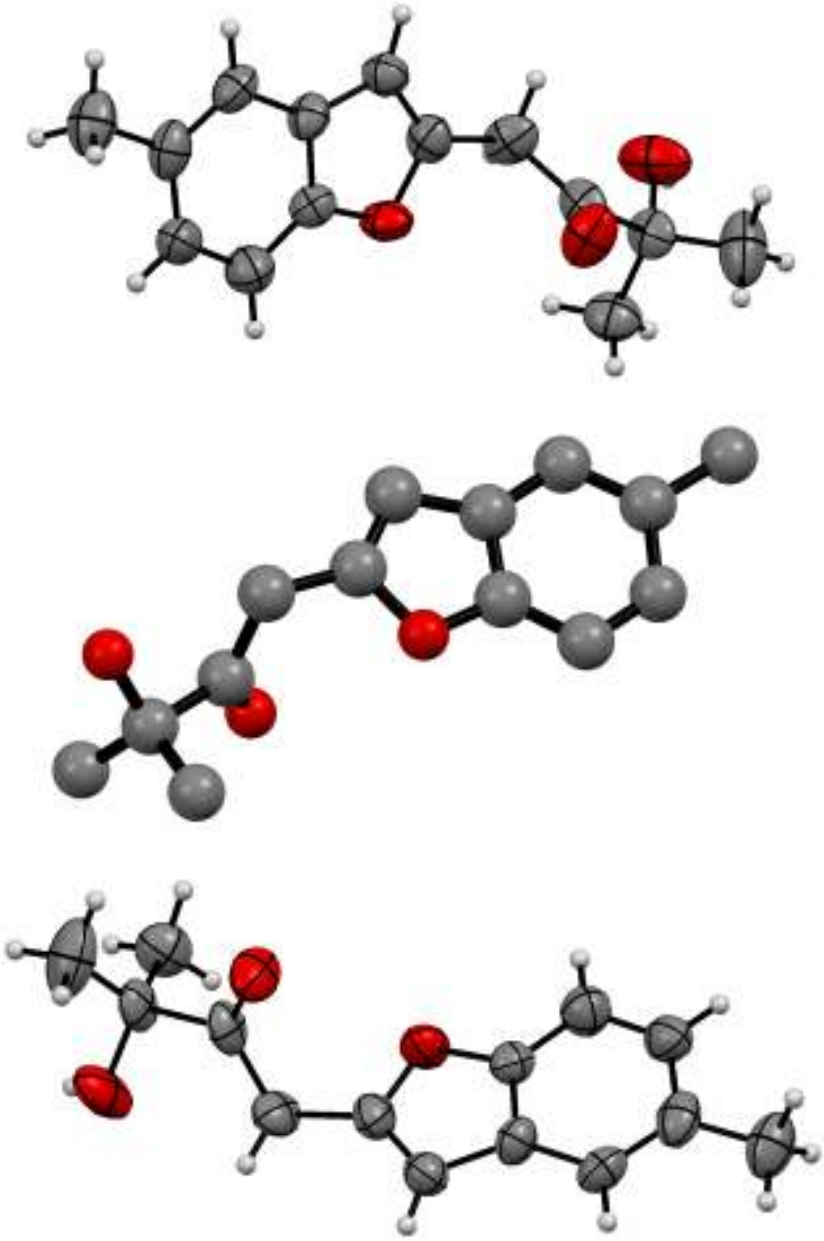


Fig. 1S ORTEP diagram of **4l** with 30% ellipsoidal probability.

Crystal Data for $C_{14}H_{16}O_3$ (M =232.28 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 14.498(2) Å, b = 5.9876(8) Å, c = 14.857(2) Å, β = 103.208(7)°, V = 1255.6(3) Å^3, Z = 4, T = 293 K, μ(Mo Kα) = 0.086 mm^{-1}, $Dcalc$ = 1.2287 g/cm^3, 12978 reflections measured (7.08° ≤ 2Θ ≤ 54.94°), 2864 unique (R_{int} = 0.0530, R_{sigma} = 0.0293) which were used in all calculations. The final R_1 was 0.0546 (I>=2u(I)) and wR_2 was 0.1671 (all data).

Table 1. Crystal data and structure refinement for JP-02-10.	
Identification code	JP-02-10
Empirical formula	$C_{14}H_{16}O_3$
Formula weight	232.28
Temperature/K	293
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.498(2)
b/Å	5.9876(8)
c/Å	14.857(2)
α/°	90
β/°	103.208(7)
γ/°	90
Volume/Å^3	1255.6(3)
Z	4
ρ_{calc}g/cm^3	1.2287
μ/mm^{-1}	0.086
F(000)	496.3
Crystal size/mm^3	0.3 × 0.22 × 0.16
Radiation	Mo Kα (λ = 0.71075)
2Θ range for data collection/°	7.08 to 54.94
Index ranges	$-18 \le h \le 18$, $-7 \le k \le 7$, $-19 \le l \le 19$
Reflections collected	12978
Independent reflections	2864 [R_{int} = 0.0530, R_{sigma} = 0.0293]
Data/restraints/parameters	2864/0/157
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0546, wR_2 = 0.1515
Final R indexes [all data]	R_1 = 0.0688, wR_2 = 0.1671
Largest diff. peak/hole / e Å^{-3}	0.22/-0.17

Table 2. **Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for JP-02-10.**

Atom	*x*	*y*	*z*	U(eq)
O1	1776.5(5)	4548.3(6)	3605.2(5)	52.7(3)
O2	-363.8(5)	3694.0(6)	3063.8(5)	70.4(4)
O3	-225.5(5)	-1828.9(6)	3735.3(5)	72.5(4)
C4	2341.1(5)	6873.3(6)	4809.8(5)	46.9(3)
C5	-437.1(5)	-270.7(6)	2995.2(5)	50.0(4)
C6	-21.1(5)	1955.1(6)	3399.4(5)	49.0(4)
C7	1727.0(6)	5241.0(6)	5081.6(5)	52.4(4)
C8	2884.6(5)	8678.2(6)	5227.0(5)	54.2(4)
C9	1415.0(5)	3906.6(6)	4346.5(5)	49.3(4)
C10	3399.7(5)	9914.3(6)	4726.9(6)	55.6(4)
C11	2339.7(5)	6369.5(6)	3903.1(5)	47.7(3)
C12	3984.2(6)	11874.8(6)	5163.0(6)	76.9(6)
C13	57.5(6)	-928.2(6)	2237.2(6)	64.8(5)
C14	3367.4(6)	9335.4(6)	3814.6(6)	61.3(4)
C15	2838.9(6)	7568.1(6)	3382.1(5)	59.0(4)
C16	827.1(6)	1862.9(6)	4195.7(6)	57.2(4)
C17	-1492.0(6)	-81.2(6)	2623.3(6)	81.4(6)

Table 3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for JP-02-10. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	63.6(7)	48.0(6)	46.6(6)	-6.3(5)	12.5(5)	-4.9(4)
O2	78.0(8)	33.6(5)	87.1(9)	3.0(5)	-7.0(7)	3.3(5)
O3	120.5(11)	34.6(6)	65.5(8)	-9.1(6)	27.6(7)	4.1(5)
C4	49.1(8)	44.5(7)	45.8(8)	4.3(6)	8.0(6)	-0.2(5)
C5	59.6(9)	33.2(7)	57.8(9)	-2.5(6)	15.0(7)	-0.8(6)
C6	58.5(9)	32.2(7)	56.7(9)	0.5(6)	14.0(7)	0.4(6)
C7	60.2(9)	52.5(8)	44.5(8)	-1.6(7)	11.8(6)	2.1(6)
C8	54.0(8)	53.5(8)	52.2(9)	0.9(7)	6.5(7)	-7.6(7)
C9	55.6(8)	41.9(7)	48.8(8)	1.2(6)	8.5(6)	4.4(6)
C10	43.1(8)	46.9(8)	71.8(11)	1.3(6)	2.5(7)	-0.8(7)
C11	49.4(8)	43.6(7)	48.4(8)	-0.6(6)	7.7(6)	-0.5(6)
C12	60.9(11)	58.5(10)	104.4(16)	-9.4(8)	4.5(10)	-12.3(10)
C13	76.6(12)	54.7(9)	65.4(10)	8.7(8)	21.5(9)	-3.8(8)
C14	53.2(9)	61.5(9)	68.8(11)	-6.8(7)	13.1(7)	8.2(8)
C15	62.9(9)	65.8(9)	49.5(9)	-6.3(8)	15.2(7)	2.4(7)
C16	68.3(10)	39.8(7)	59.6(9)	-2.7(7)	6.9(7)	6.0(6)
C17	59.0(11)	69.0(11)	117.1(18)	-10.4(9)	22.3(11)	-20.8(11)

Table 4. Bond Lengths for JP-02-10.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C9	1.3781(11)	C5	C17	1.5070(11)
O1	C11	1.3735(7)	C6	C16	1.5000(10)
O2	C6	1.2109(7)	C7	C9	1.3454(9)
O3	C5	1.4212(9)	C8	C10	1.3825(11)
C4	C7	1.4406(9)	C9	C16	1.4788(8)
C4	C8	1.3964(8)	C10	C12	1.5050(8)
C4	C11	1.3800(11)	C10	C14	1.3894(12)
C5	C6	1.5281(7)	C11	C15	1.3761(11)
C5	C13	1.5186(12)	C14	C15	1.3765(8)

Table 5. Bond Angles for JP-02-10.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	O1	C9	105.70(6)	C10	C8	C4	119.67(7)
C8	C4	C7	136.29(8)	C7	C9	O1	111.37(6)
C11	C4	C7	105.20(5)	C16	C9	O1	114.89(6)
C11	C4	C8	118.51(7)	C16	C9	C7	133.61(8)
C6	C5	O3	105.81(6)	C12	C10	C8	120.42(7)
C13	C5	O3	110.40(5)	C14	C10	C8	119.27(5)
C13	C5	C6	107.86(6)	C14	C10	C12	120.31(7)
C17	C5	O3	110.77(6)	C4	C11	O1	110.87(6)
C17	C5	C6	110.78(5)	C15	C11	O1	125.67(7)
C17	C5	C13	111.05(6)	C15	C11	C4	123.46(5)

C5	C6	O2	120.00(6)	C15	C14	C10	122.56(7)
C16	C6	O2	122.80(5)	C14	C15	C11	116.53(7)
C16	C6	C5	117.18(4)	C9	C16	C6	115.43(5)
C9	C7	C4	106.86(7)				

Table 6. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for JP-02-10.

Atom	*x*	*y*	*z*	U(eq)
H3	-164.3(5)	-3077.7(6)	3530.0(5)	108.8(6)
H7	1575.2(6)	5130.9(6)	5655.3(5)	62.9(5)
H8	2900.0(5)	9046.9(6)	5838.4(5)	65.0(5)
H12a	4172.6(6)	11657.6(6)	5819.7(6)	115.3(9)
H12b	4537.5(6)	12000.8(6)	4914.1(6)	115.3(9)
H12c	3615.3(6)	13216.7(6)	5033.4(6)	115.3(9)
H13a	726.1(6)	-1057.8(6)	2492.5(6)	97.1(7)
H13b	-186.0(6)	-2335.6(6)	1977.3(6)	97.1(7)
H13c	-55.0(6)	193.0(6)	1762.8(6)	97.1(7)
H14	3716.6(6)	10174.5(6)	3483.2(6)	73.6(5)
H15	2820.1(6)	7203.2(6)	2769.8(5)	70.9(5)
H16a	611.5(6)	1552.8(6)	4754.8(6)	68.6(5)
H16b	1223.0(6)	622.5(6)	4097.2(6)	68.6(5)
H17a	-1736.0(6)	-1480.5(6)	2354.9(6)	122.0(9)
H17b	-1790.0(6)	291.5(6)	3117.9(6)	122.0(9)
H17c	-1622.1(6)	1065.9(6)	2160.1(6)	122.0(9)

Crystal structure of 4ag (CCDC 1441109): Structure of the spiroketal **4ag** was confirmed by single crystal X-ray diffraction analysis.

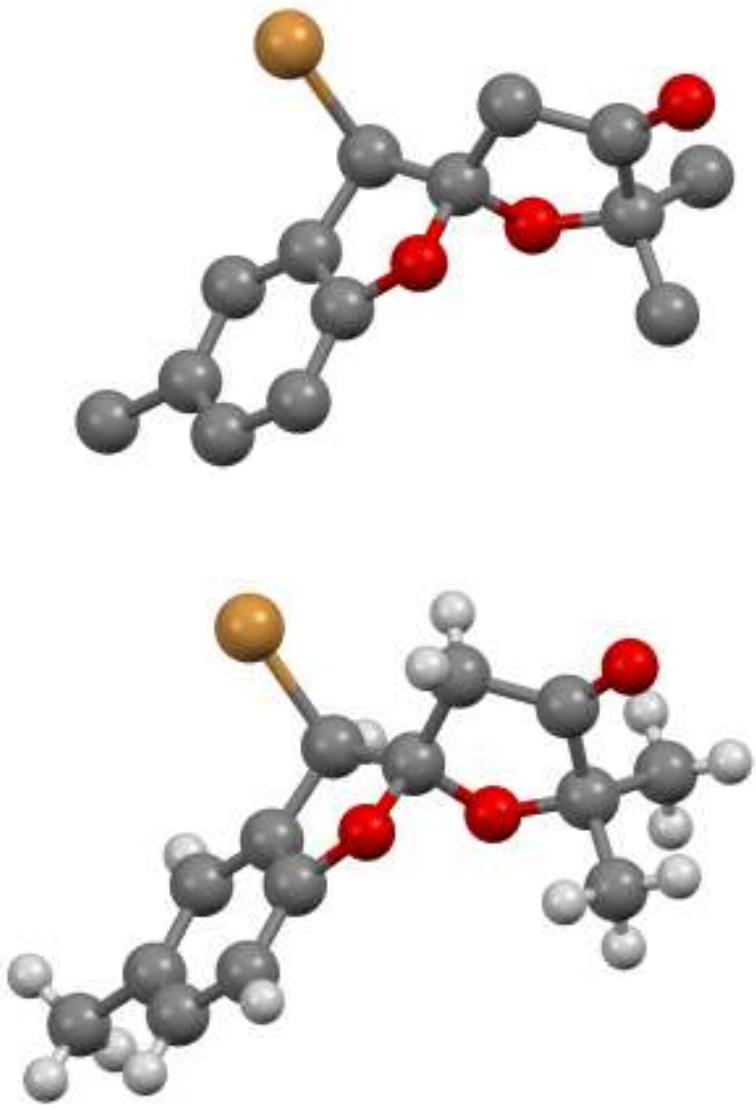


Fig. 2S ORTEP diagram of **4ag** with 30% ellipsoidal probability.

Crystal Data for $C_{14}H_{15}BrO_3$ (M =311.18 g/mol): triclinic, space group P-1 (no. 2), a = 7.839(2) Å, b = 11.990(3) Å, c = 15.335(2) Å, α = 102.87(3)°, β = 98.14(3)°, γ = 90.09(3)°, V = 1390.1(6) Å^3, Z = 4, T = 293 K, μ(Mo Kα) = 2.954 mm^{-1}, *Dcalc* = 1.4867 g/cm^3, 14261 reflections measured (6.2° ≤ 2Θ ≤ 55.32°), 6245 unique (R_{int} = 0.0658, R_{sigma} = 0.0900) which were used in all calculations. The final R_1 was 0.1126 (I>=2u(I)) and wR_2 was 0.3416 (all data).

Table 1. Crystal data and structure refinement for SB-04-132-2

Identification code	**SB-04-132-2**
Empirical formula	$C_{14}H_{15}BrO_3$
Formula weight	311.18
Temperature/K	293
Crystal system	Triclinic
Space group	P-1
a/Å	7.839(2)
b/Å	11.990(3)
c/Å	15.335(2)
α/°	102.87(3)
β/°	98.14(3)
γ/°	90.09(3)
Volume/Å^3	1390.1(6)
Z	4
ρ_{calc}g/cm^3	1.4867
μ/mm^{-1}	2.954
F(000)	631.2
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	Mo Kα (λ = 0.71075)
2Θ range for data collection/°	6.2 to 55.32
Index ranges	$-9 \le h \le 10$, $-15 \le k \le 15$, $-19 \le l \le 19$
Reflections collected	14261
Independent reflections	6245 [R_{int} = 0.0658, R_{sigma} = 0.0900]
Data/restraints/parameters	6245/0/330
Goodness-of-fit on F^2	1.548
Final R indexes [I>=2σ (I)]	R_1 = 0.1126, wR_2 = 0.2676
Final R indexes [all data]	R_1 = 0.1847, wR_2 = 0.3416
Largest diff. peak/hole / e Å^{-3}	2.25/-2.42

Table 2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for SB-04-132-2. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor

Atom	*X*	*y*	*z*	U(eq)
Br1	1804.4(16)	9578.8(10)	9134.9(7)	74.7(5)
Br2	6518.9(18)	7898.0(11)	9143.6(7)	86.9(5)
O1	5185(8)	5326(5)	7462(4)	49.7(15)
O2	282(8)	11084(5)	7475(4)	53.7(16)
O3	-2407(9)	10687(5)	7752(4)	60.0(17)
C4	380(11)	9142(7)	7275(5)	44.0(19)
O5	2479(8)	5912(5)	7746(4)	55.2(16)
C6	5427(10)	7173(7)	7259(5)	46(2)
C7	4208(12)	6008(7)	8123(6)	50(2)
C9	-126(12)	9571(7)	8185(6)	50(2)
C10	4778(12)	7259(7)	8134(6)	52(2)
C11	5654(13)	6016(8)	6925(6)	58(3)
C12	669(11)	10071(8)	6886(6)	52(2)

C14	5731(13)	7970(9)	6766(7)	65(3)
O15	2618(15)	3928(7)	9112(6)	112(3)
C16	754(11)	8074(7)	6793(6)	51(2)
C17	-713(14)	10786(7)	8111(6)	57(3)
C18	2883(13)	4689(8)	8766(7)	60(3)
C19	1250(14)	10004(10)	6082(6)	69(3)
C20	1317(14)	7952(10)	5976(7)	74(3)
C21	1665(13)	5015(9)	7966(7)	62(3)
C22	-2138(16)	12397(8)	8813(8)	72(3)
C23	4388(13)	5530(8)	8961(6)	59(3)
O24	-2371(11)	13353(6)	9232(6)	93(3)
C25	-461(11)	11770(7)	8968(6)	53(2)
C26	1554(13)	8890(11)	5641(6)	69(3)
C27	-3291(15)	11722(9)	8023(7)	72(3)
C28	1594(17)	6737(11)	5389(8)	98(4)
C29	6607(16)	6450(15)	5653(7)	94(4)
C31	6356(13)	7563(12)	5948(8)	73(3)
C32	6274(17)	5619(11)	6127(7)	86(4)
C33	-3622(16)	12320(10)	7254(9)	88(4)
C34	6640(20)	8441(14)	5373(8)	113(5)
C35	1252(17)	3965(10)	7212(8)	88(4)
C38	-5009(15)	11393(11)	8324(10)	101(5)
C42	-26(13)	5422(11)	8332(10)	93(4)

Table 3. Anisotropic Displacement Parameters ($Å^2×10^3$) for SB-04-132-2. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br1	86.5(9)	76.3(8)	61.7(7)	24.6(6)	12.8(6)	15.0(6)
Br2	112.0(11)	83.8(9)	57.5(7)	-26.7(7)	8.1(6)	3.3(6)
O1	69(4)	39(3)	47(3)	8(3)	24(3)	13(3)
O2	67(4)	37(3)	62(4)	8(3)	21(3)	14(3)
O3	69(4)	45(3)	63(4)	25(3)	8(3)	7(3)
C4	49(5)	50(5)	33(4)	7(4)	7(4)	6(4)
O5	54(4)	51(3)	63(4)	8(3)	-1(3)	24(3)
C6	39(4)	48(5)	45(4)	-9(4)	-7(4)	4(4)
C7	58(6)	41(4)	47(4)	15(4)	3(4)	2(4)
C9	60(6)	41(5)	54(5)	3(4)	13(4)	19(4)
C10	49(5)	39(4)	69(6)	1(4)	20(5)	7(4)
C11	64(6)	58(6)	50(5)	18(5)	22(5)	0(4)
C12	45(5)	67(6)	48(5)	3(4)	11(4)	17(4)
C14	64(6)	67(6)	58(6)	-2(5)	-12(5)	18(5)
O15	197(11)	66(5)	79(5)	15(6)	5(6)	43(5)
C16	52(5)	45(5)	49(5)	7(4)	-4(4)	-2(4)
C17	84(7)	45(5)	49(5)	32(5)	17(5)	20(4)
C18	52(6)	51(5)	89(7)	10(4)	33(5)	25(5)
C19	75(7)	88(8)	46(5)	13(6)	13(5)	16(5)
C20	60(6)	85(8)	65(6)	27(6)	-1(5)	-5(6)

C21	54(6)	62(6)	78(7)	3(5)	19(5)	31(5)
C22	98(8)	41(5)	81(7)	23(5)	33(7)	8(5)
C23	74(7)	54(5)	55(5)	10(5)	13(5)	21(5)
O24	110(7)	56(4)	108(6)	23(4)	39(5)	-3(4)
C25	47(5)	47(5)	65(6)	2(4)	13(4)	8(4)
C26	54(6)	117(10)	40(5)	-4(6)	20(4)	16(6)
C27	88(8)	65(6)	74(7)	36(6)	32(6)	25(6)
C28	100(9)	102(9)	65(7)	43(8)	6(7)	-30(7)
C29	77(8)	153(13)	46(6)	21(9)	16(6)	3(8)
C31	45(6)	112(10)	62(6)	-22(6)	-9(5)	30(7)
C32	121(10)	79(8)	58(6)	24(7)	33(7)	0(6)
C33	76(8)	80(8)	104(9)	7(6)	-13(7)	29(7)
C34	130(12)	162(14)	61(7)	-24(11)	15(7)	58(9)
C35	112(10)	66(7)	81(8)	-23(7)	-18(7)	22(6)
C38	71(8)	85(9)	153(13)	12(7)	61(9)	10(8)
C42	41(6)	99(9)	156(13)	-17(6)	18(7)	58(9)

Table 4. Bond Lengths for SB-04-132-2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C9	1.944(9)	C12	C19	1.359(13)
Br2	C10	1.928(10)	C14	C31	1.398(16)
O1	C7	1.461(9)	O15	C18	1.185(11)
O1	C11	1.374(11)	C16	C20	1.364(14)
O2	C12	1.405(10)	C17	C25	1.547(12)
O2	C17	1.435(11)	C18	C21	1.567(14)
O3	C17	1.358(12)	C18	C23	1.503(13)
O3	C27	1.431(11)	C19	C26	1.393(15)
C4	C9	1.486(11)	C20	C26	1.360(16)
C4	C12	1.409(12)	C20	C28	1.566(14)
C4	C16	1.383(11)	C21	C35	1.507(15)
O5	C7	1.390(10)	C21	C42	1.550(14)
O5	C21	1.377(11)	C22	O24	1.210(11)
C6	C10	1.483(12)	C22	C25	1.532(14)
C6	C11	1.389(12)	C22	C27	1.479(16)
C6	C14	1.383(13)	C27	C33	1.505(14)
C7	C10	1.561(12)	C27	C38	1.561(15)
C7	C23	1.509(12)	C29	C31	1.335(17)
C9	C17	1.551(11)	C29	C32	1.401(18)
C11	C32	1.367(13)	C31	C34	1.549(16)

Table 5. Bond Angles for SB-04-132-2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	O1	C7	108.0(6)	C25	C17	O2	107.7(8)
C17	O2	C12	108.4(6)	C25	C17	O3	108.9(7)
C27	O3	C17	112.1(8)	C25	C17	C9	119.2(7)
C12	C4	C9	109.7(7)	C21	C18	O15	125.2(10)
C16	C4	C9	133.9(8)	C23	C18	O15	129.9(11)

C16	C4	C12	116.1(7)	C23	C18	C21	104.8(8)
C21	O5	C7	110.6(7)	C26	C19	C12	113.6(10)
C11	C6	C10	106.0(8)	C26	C20	C16	119.8(10)
C14	C6	C10	133.2(8)	C28	C20	C16	120.9(12)
C14	C6	C11	120.8(9)	C28	C20	C26	119.1(11)
O5	C7	O1	107.8(6)	C18	C21	O5	106.6(8)
C10	C7	O1	102.6(7)	C35	C21	O5	115.6(9)
C10	C7	O5	104.7(7)	C35	C21	C18	109.2(8)
C23	C7	O1	109.6(7)	C42	C21	O5	109.7(8)
C23	C7	O5	108.2(8)	C42	C21	C18	106.7(8)
C23	C7	C10	123.1(7)	C42	C21	C35	108.6(10)
C4	C9	Br1	111.3(6)	C25	C22	O24	123.3(11)
C17	C9	Br1	113.5(6)	C27	C22	O24	126.4(11)
C17	C9	C4	100.5(7)	C27	C22	C25	109.9(8)
C6	C10	Br2	111.6(6)	C18	C23	C7	102.7(8)
C7	C10	Br2	112.7(6)	C22	C25	C17	100.0(8)
C7	C10	C6	104.6(7)	C20	C26	C19	124.0(9)
C6	C11	O1	113.8(7)	C22	C27	O3	104.7(8)
C32	C11	O1	124.0(9)	C33	C27	O3	110.1(9)
C32	C11	C6	122.1(10)	C33	C27	C22	113.0(10)
C4	C12	O2	108.5(7)	C38	C27	O3	107.5(9)
C19	C12	O2	125.7(9)	C38	C27	C22	109.7(9)
C19	C12	C4	125.8(9)	C38	C27	C33	111.5(11)
C31	C14	C6	117.0(10)	C32	C29	C31	123.4(10)
C20	C16	C4	120.6(9)	C29	C31	C14	121.0(11)
O3	C17	O2	109.3(7)	C34	C31	C14	117.4(12)
C9	C17	O2	104.2(7)	C34	C31	C29	121.5(12)
C9	C17	O3	107.2(8)	C29	C32	C11	115.7(11)

Table 6. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for SB-04-132-2.

Atom	*X*	*y*	*z*	U(eq)
H16	621(11)	7433(7)	7028(6)	62(3)
H26	1944(13)	8782(11)	5084(6)	83(4)
H19	1427(14)	10640(10)	5848(6)	82(3)
H14	5529(13)	8742(9)	6970(7)	78(3)
H29	7025(16)	6214(15)	5106(7)	113(5)
H32	6461(17)	4847(11)	5912(7)	104(4)
H9	-1097(12)	9108(7)	8266(6)	60(3)
H10	3771(12)	7742(7)	8154(6)	63(3)
H23a	5473(13)	5152(8)	9043(6)	71(3)
H23b	4312(13)	6127(8)	9496(6)	71(3)
H25a	-371(11)	11484(7)	9517(6)	64(3)
H25b	545(11)	12254(7)	8991(6)	64(3)
H28a	2530(80)	6380(40)	5690(30)	146(7)
H28b	560(50)	6270(30)	5300(60)	146(7)
H28c	1870(120)	6810(13)	4810(30)	146(7)
H33a	-2544(17)	12500(70)	7080(40)	132(6)
H33b	-4320(100)	11830(30)	6750(20)	132(6)

H33c	-4220(110)	13010(40)	7440(20)	132(6)
H34a	5700(80)	8370(70)	4890(50)	169(8)
H34b	6680(150)	9201(15)	5750(20)	169(8)
H34c	7700(70)	8300(60)	5130(60)	169(8)
H35a	390(80)	4140(20)	6750(30)	133(6)
H35b	2280(30)	3730(50)	6960(40)	133(6)
H35c	820(110)	3360(30)	7448(15)	133(6)
H38a	-5730(50)	10930(70)	7815(17)	152(7)
H38b	-4758(17)	10970(70)	8790(50)	152(7)
H38c	-5590(60)	12076(11)	8550(60)	152(7)
H42a	236(17)	6040(50)	8860(40)	140(6)
H42b	-780(50)	5680(70)	7870(20)	140(6)
H42c	-580(60)	4800(20)	8490(60)	140(6)

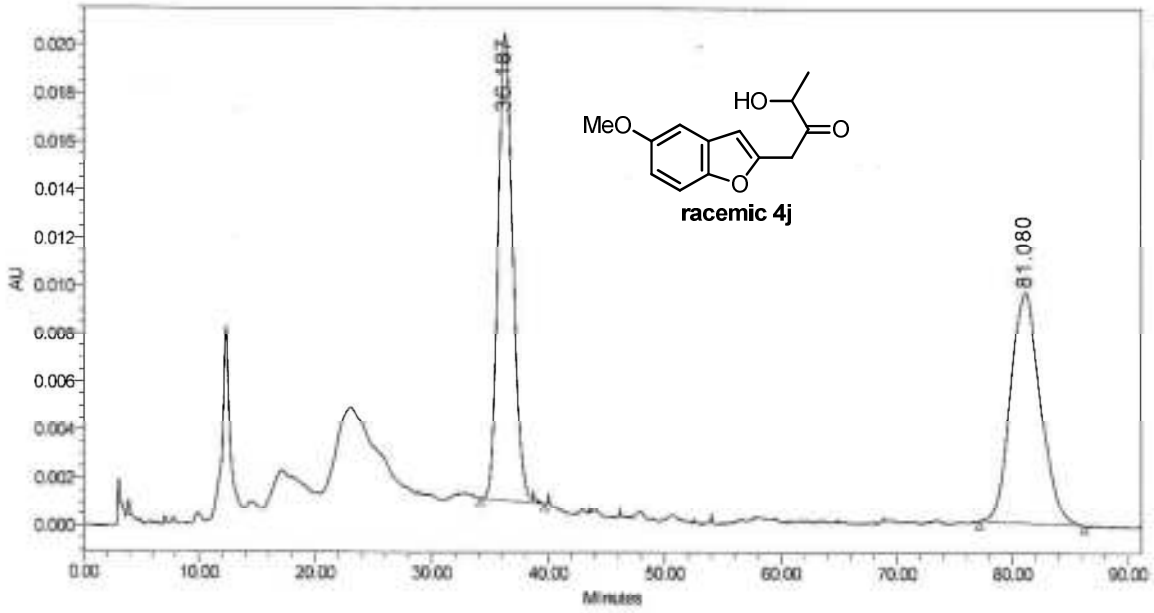
Determination of enantiomeric excess (ee) of 4j and 4t by chiral HPLC.

Empower 3

Vishnu

SAMPLE INFORMATION

Sample Name:	sb-04-48 chir-AS10%	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	1	Acq. Method Set:	Bishnu MBH
Injection #:	4	Processing Methoc	sb448
Injection Volume:	10.00 ul	Channel Name:	254.0nm
Run Time:	120.0 Minutes	Proc. Chnl. Descr.:	PDA 254.0 nm
Date Acquired:	04-11-2015 14:08:13 IST		
Date Processed:	04-11-2015 20:50:37 IST		



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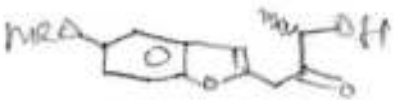
1	36.187	1705615	49.63	19361
2	81.080	1731281	50.37	9606



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Report Method: Vishnu
Report Method Id 4230
Page: 1 of 1

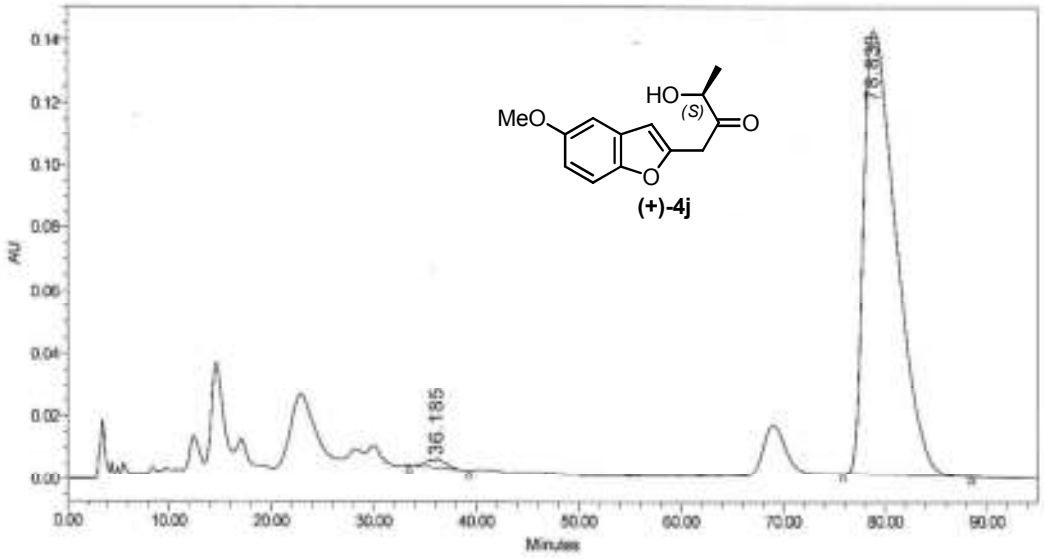
Project Name: YR_01
Date Printed:
04-11-2015
20:53:06 Asia/Calcutta

Empower 3

Vishnu

SAMPLE INFORMATION

Sample Name:	sb-04-48 chir-AS10%	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	1	Acq. Method Set:	Bishnu MBH
Injection #:	3	Processing Method:	sb448chiral
Injection Volume:	10.00 ul	Channel Name:	254.0nm
Run Time:	120.0 Minutes	Proc. Chnl. Descr.:	PDA 254.0 nm
Date Acquired:	04-11-2015 12:17:31 IST		
Date Processed:	04-11-2015 20:51:29 IST		



	RT	Area	% Area	Height
1	36.185	359271	1.14	2654
2	78.830	31277624	98.86	141411

Reported by User: System
Report Method: Vishnu
Report Method ID: 4230
Page: 1 of 1

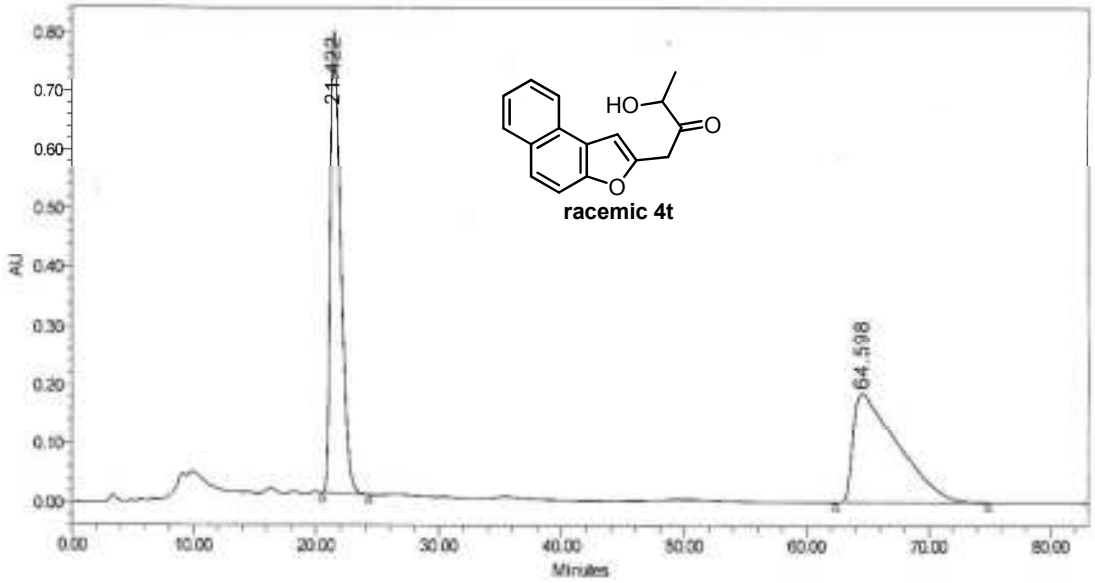
Project Name: YR_01
Date Printed:
04-11-2015
20:52:54 Asia/Calcutta

Empower 3

Vishnu

SAMPLE INFORMATION

Sample Name:	sb-04-45 np chir-AS10%	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	1	Acq. Method Set:	Bishnu MBH
Injection #:	5	Processing Methoc	sb448naprac
Injection Volume:	10.00 ul	Channel Name:	254.0nm
Run Time:	120.0 Minutes	Proc. Chnl. Descr.:	PDA 254.0 nm
Date Acquired:	04-11-2015 15:51:36 IST		
Date Processed:	04-11-2015 20:54:15 IST		



racemic 4t

	RT	Area	% Area	Height
1	21.422	46302803	49.54	785844
2	64.598	47160151	50.46	186658

Reported by User: System
Report Method: Vishnu
Report Method II 4230
Page: 1 of 1

Project Name: YR_01
Date Printed:
04-11-2015
20:56:31 Asia/Calcutta

Empower 3

Vishnu

SAMPLE INFORMATION

Sample Name:	sb-04-48 np chir-AS10%	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	1	Acq. Method Set:	Bishnu MBH
Injection #:	6	Processing Method:	sb448npchiral
Injection Volume:	10.00 ul	Channel Name:	254.0nm
Run Time:	120.0 Minutes	Proc. Chnl. Descr.:	PDA 254.0 nm
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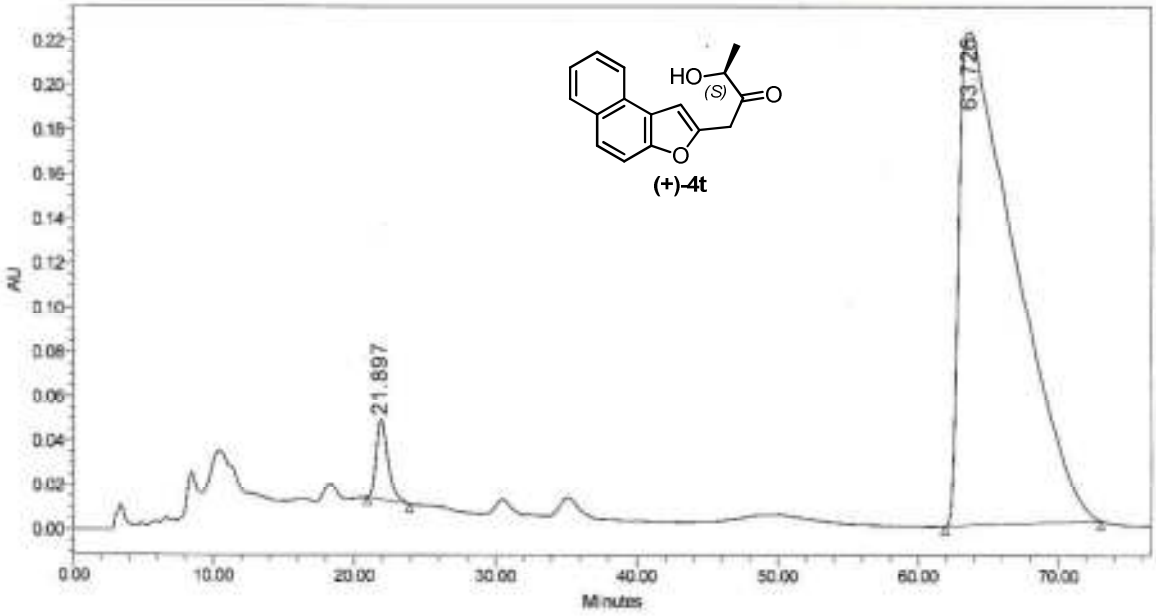
Date Processed:	04-11-2015 20:55:20 IST		



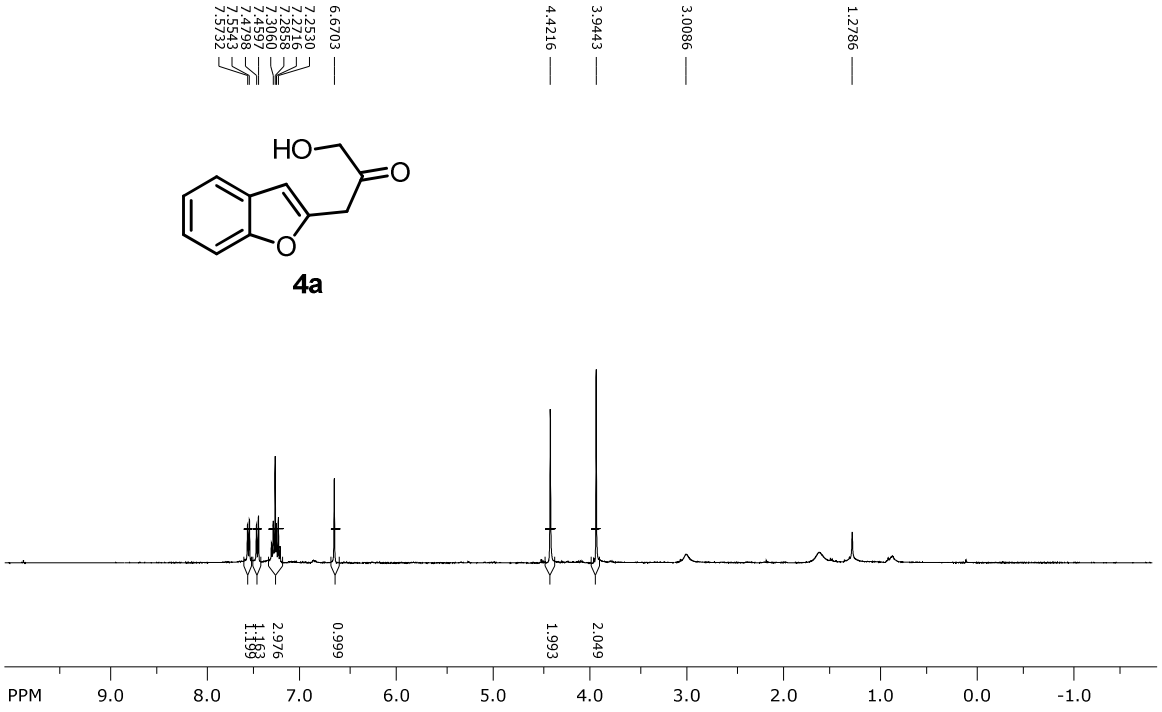
	RT	Area	% Area	Height
1	21.897	2097106	3.30	36077
2	63.726	61473269	96.70	222088

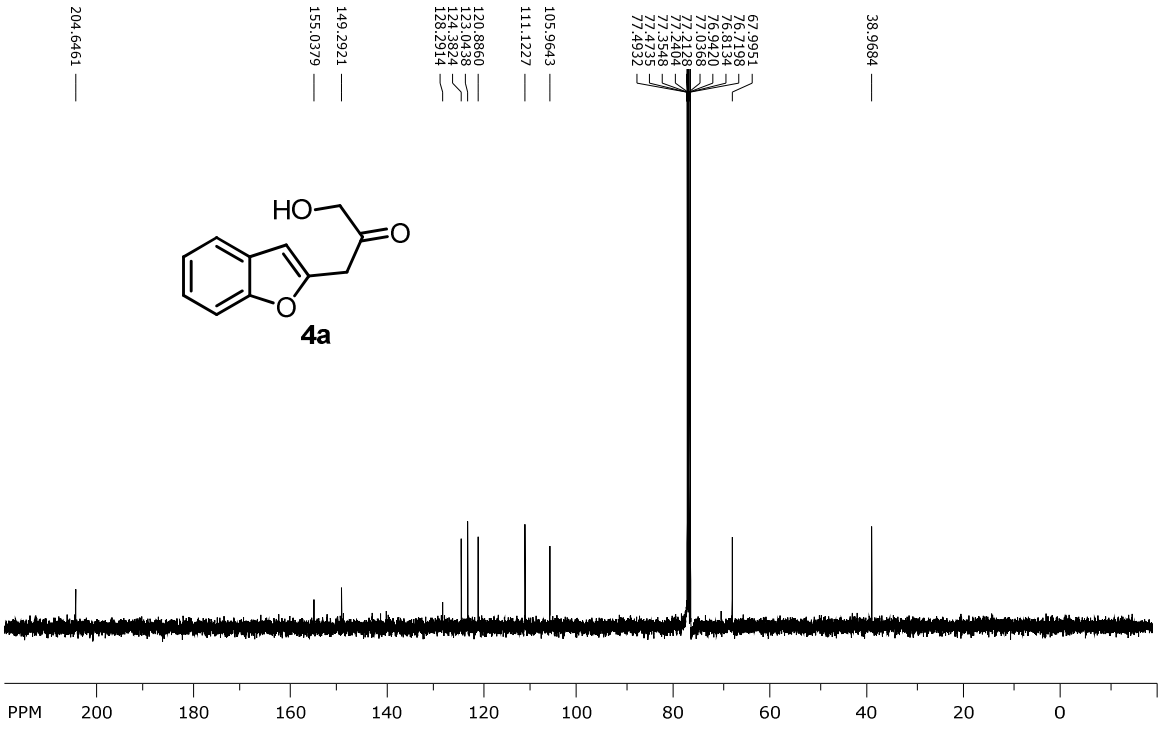
Reported by User: System
Report Method: Vishnu
Report Method ID: 4230
Page: 1 of 1

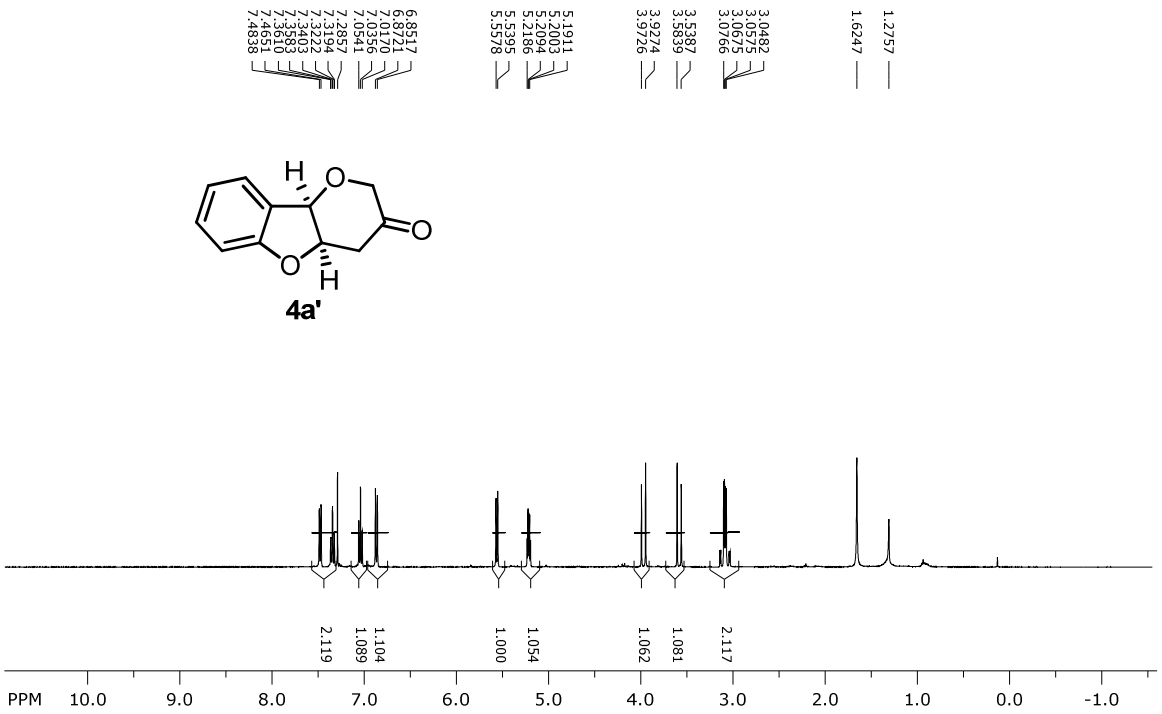
Project Name: YR_01
Date Printed:
04-11-2015
20:56:47 Asia/Calcutta

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

(**Note**: In general, in a ^{1}H NMR spectrum recorded in $CDCl_3$, a peak at around δ 1.6 refers to moisture in the solvent/sample and a peak at about δ 1.2 refers to oil/grease present in the sample. In a ^{13}C NMR spectrum recorded in $CDCl_3$, a peak at about δ 29.7 usually represents oil/grease)



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7.3610
7.3583
7.3403
7.3222
7.3194
7.2857
7.0541
7.0356
7.0170
6.8721
6.8517
5.5578
5.5395
5.2186
5.2094
5.2003
5.1911
3.9726
3.9274
3.5839
3.5587
3.0766
3.0675
3.0575
3.0482
1.6247
1.2757
4a'
2.119
1.089
1.104
1.000
1.054
1.062
1.081
2.117
PPM
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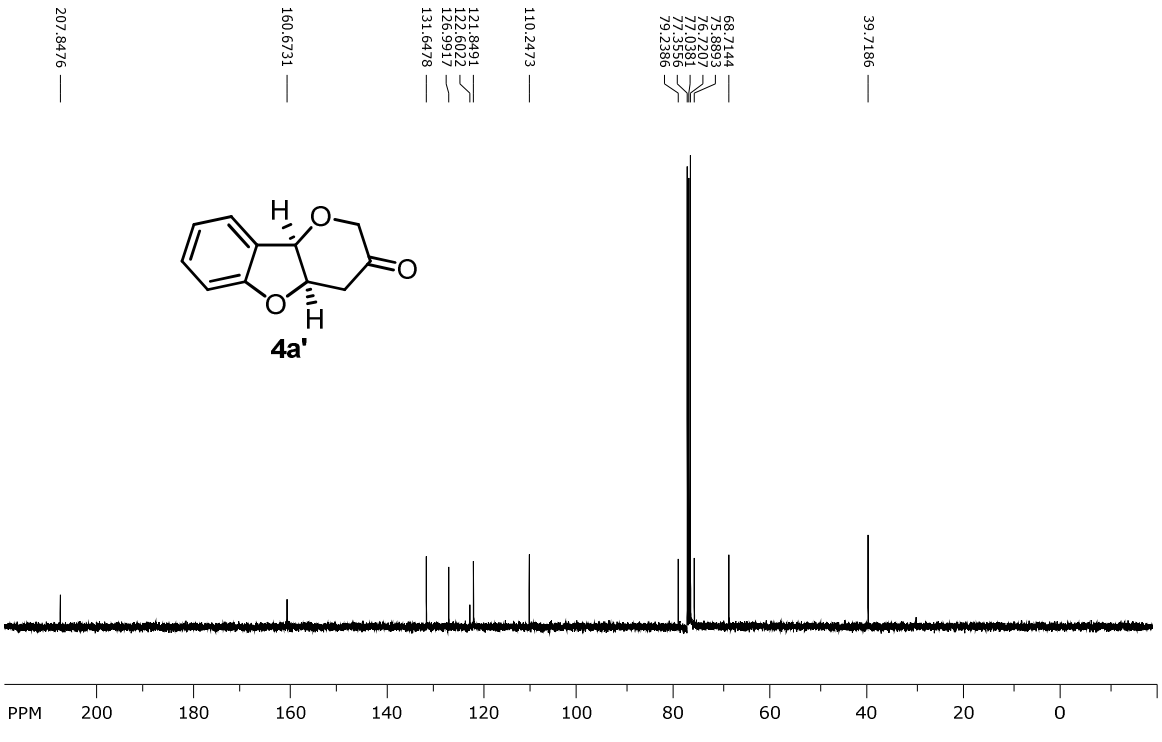
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0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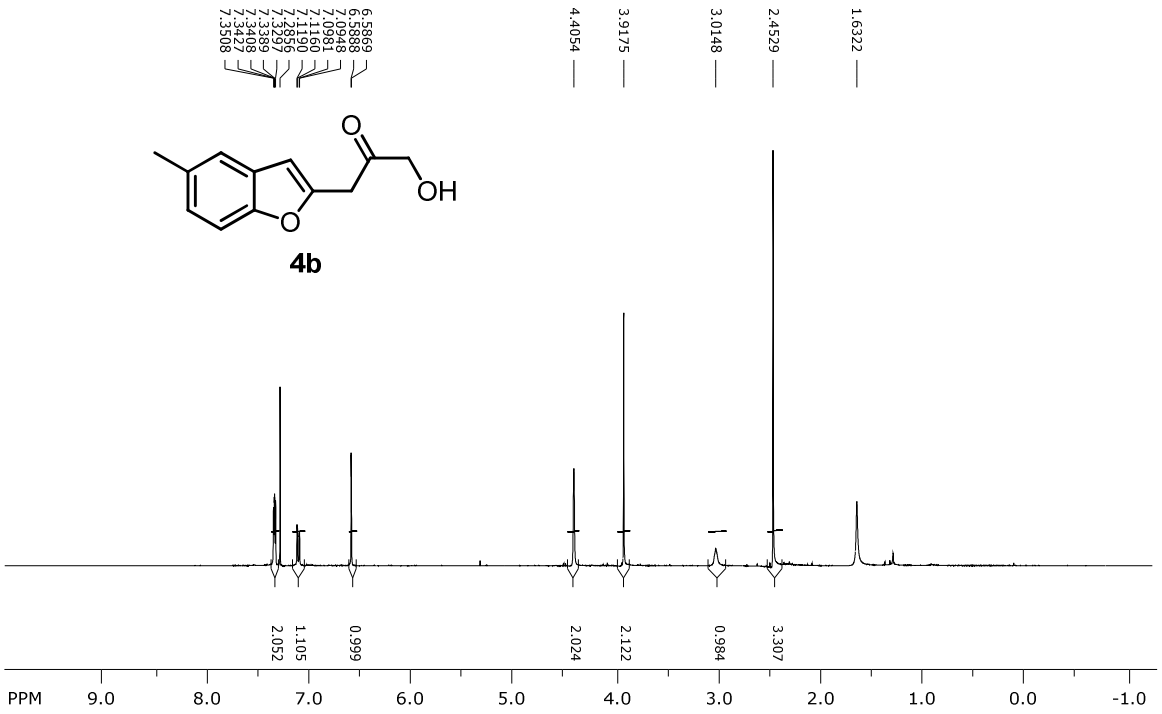
131.6478
126.9917
122.6022
121.8491
110.2473
79.2386
77.3556
77.0381
75.8893
68.7144
39.7186
4a'
PPM
200
180
160
140
120
100
80
60
40
20
0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7.3408
7.3389
7.3297
7.2856
7.1190
7.1160
7.0981
7.0948
6.5868
6.5868
4.4054
3.9175
3.0148
2.4529
1.6322
O
OH
O
4b
2.052
1.105
0.999
2.024
2.122
0.984
3.307
PPM
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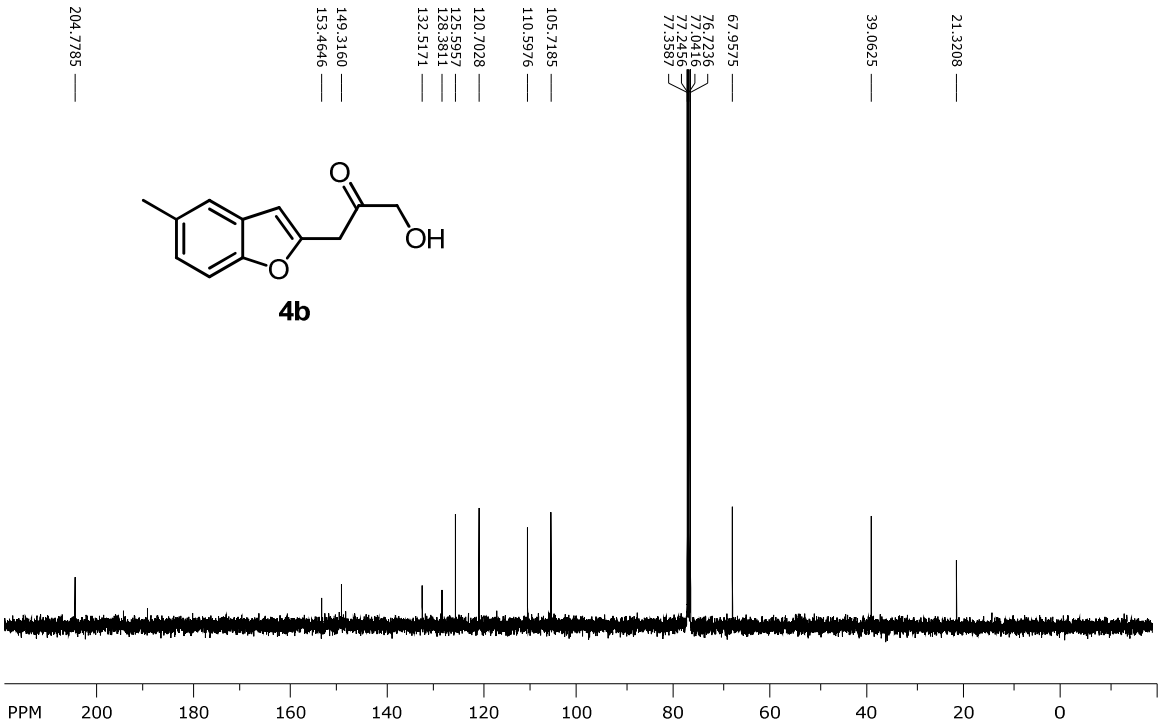
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0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128.3811
125.5957
120.7028
110.5976
105.7185
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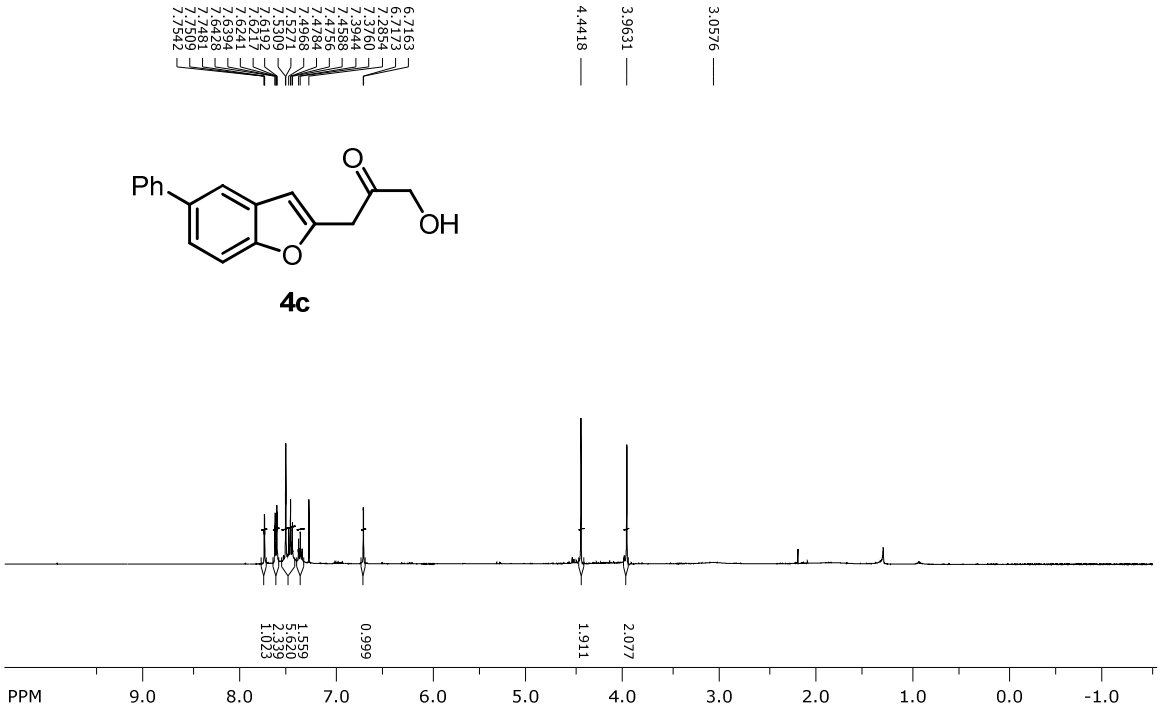
77.2456
77.0416
76.7236
67.9575
39.0625
21.3208
O
OH
O
4b
PPM
200
180
160
140
120
100
80
60
40
20
0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7.7481
7.6428
7.6241
7.6217
7.6192
7.5309
7.5271
7.4968
7.4784
7.4756
7.4588
7.3944
7.3760
7.2854
6.7173
6.7163
4.4418
3.9631
3.0576
Ph
O
OH
O
4c
1.023
2.339
5.620
1.559
0.999
1.911
2.077
PPM
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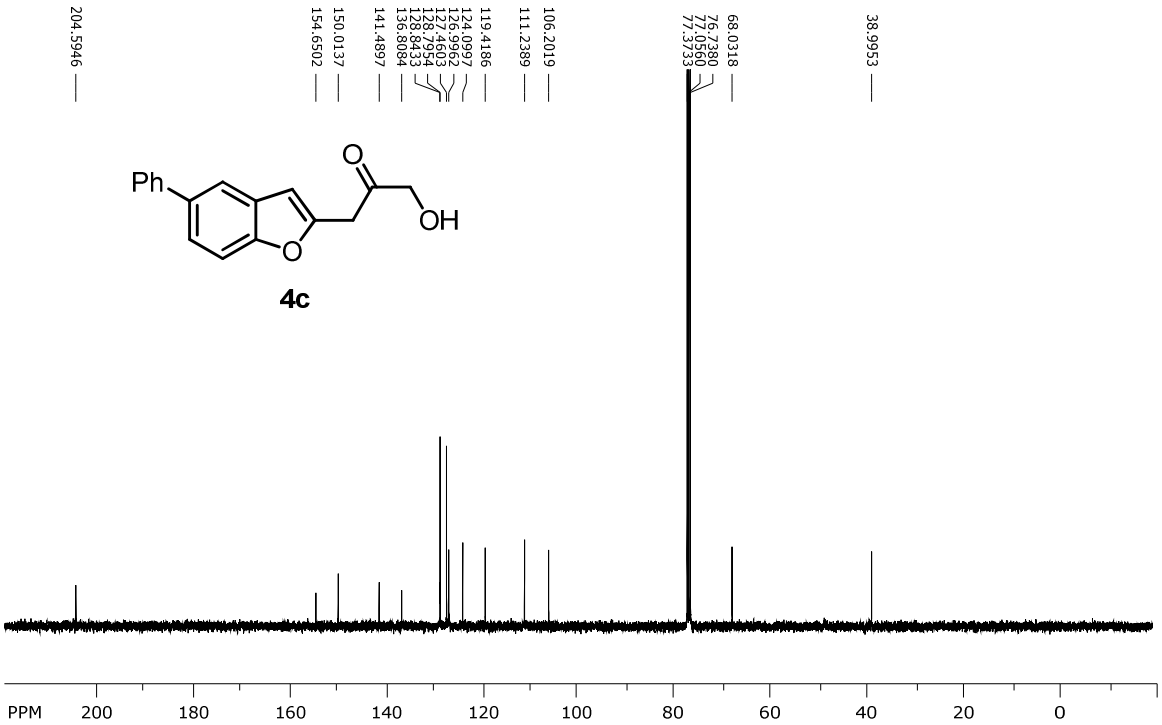
5.0
4.0
3.0
2.0
1.0
0.0
-1.0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128.7954
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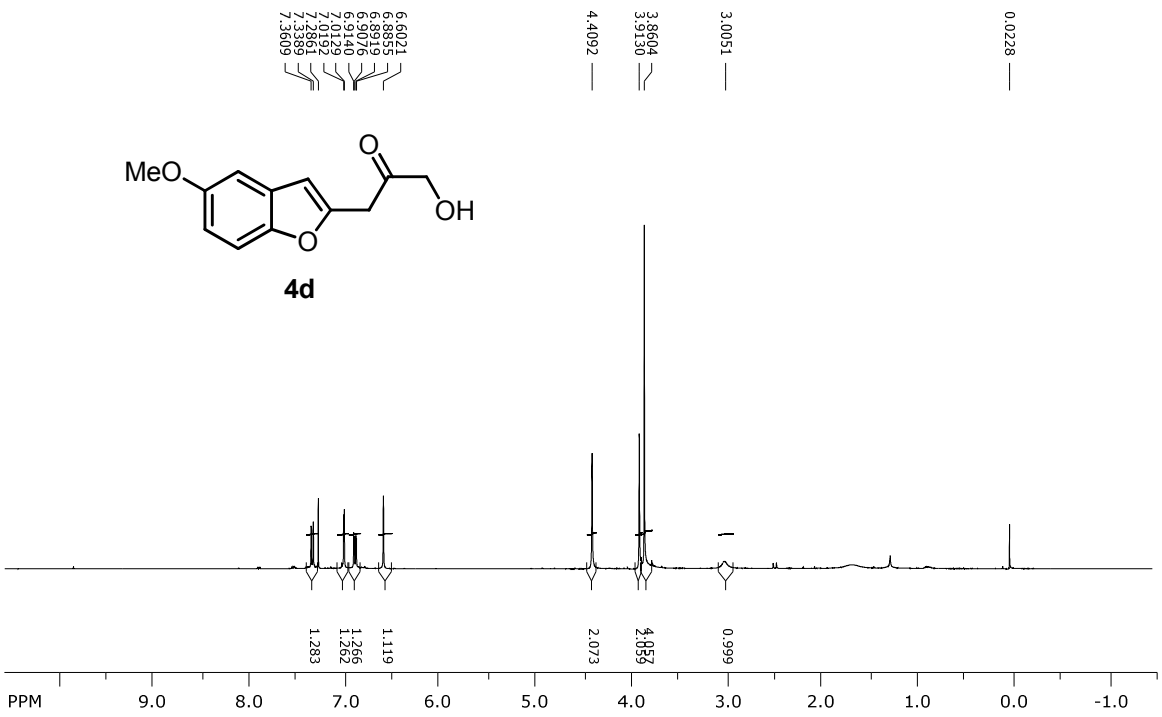
119.4186
111.2389
106.2019
77.3733
77.0560
76.7380
68.0318
38.9953
Ph
O
OH
O
4c
PPM
200
180
160
140
120
100
80
60
40
20
0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7.0267
7.0129
6.9140
6.9076
6.8919
6.8855
6.6021
4.4092
3.8604
3.9130
3.0051
0.0228
MeO
O
OH
O
4d
1.283
1.266
1.262
1.119
2.073
4.057
4.059
0.999
PPM
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7.0
6.0
5.0
4.0
3.0
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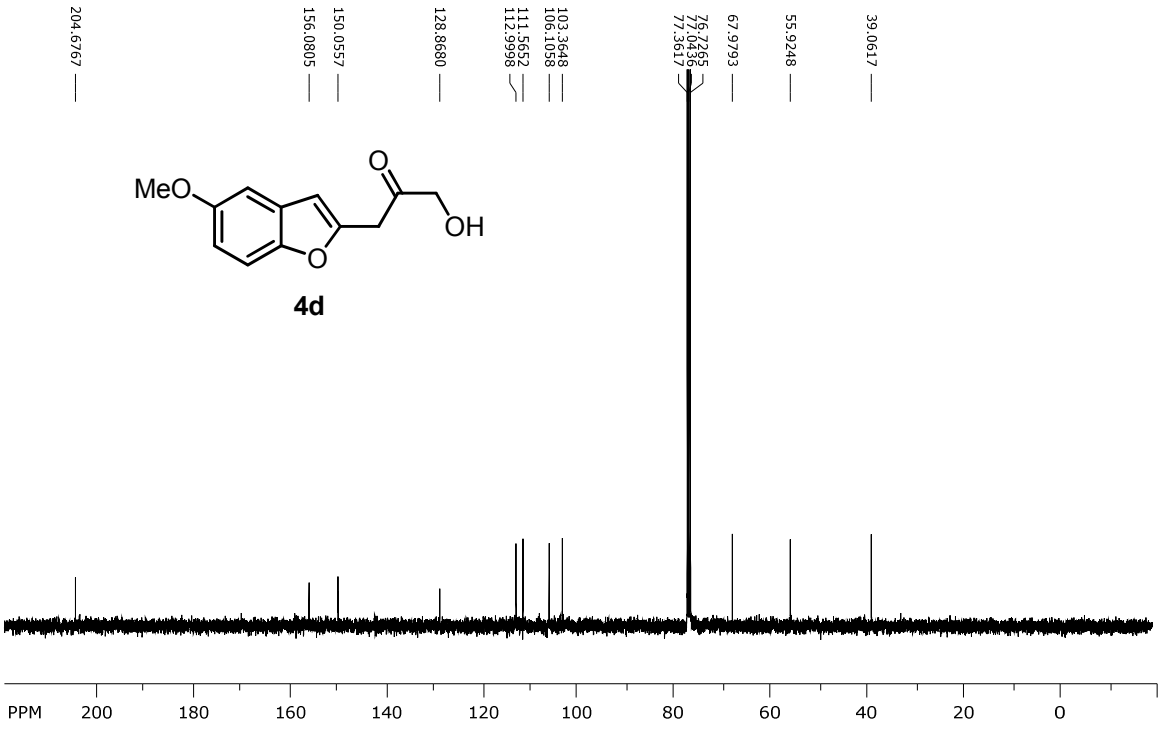
1.0
0.0
-1.0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128.8680
112.9998
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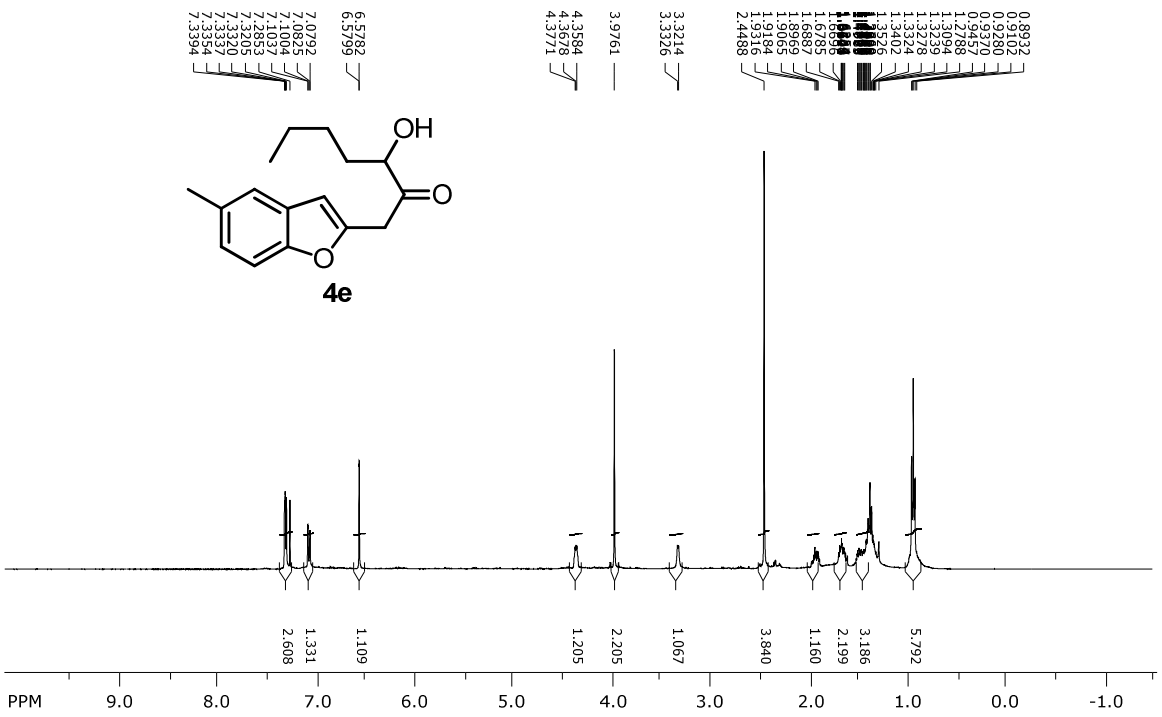
106.1058
103.3648
77.3617
67.9793
55.9248
39.0617
MeO
O
OH
O
4d
PPM
200
180
160
140
120
100
80
60
40
20
0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O
O
4e
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7.3354
7.3337
7.3320
7.3205
7.2853
7.1037
7.1004
7.0825
7.0792
6.5799
6.5782
4.3771
4.3578
4.3584
3.9761
3.3326
3.3214
2.4488
1.9316
1.9184
1.9065
1.8969
1.6887
1.6785
1.3326
1.3402
1.3324
1.3278
1.3239
1.3094
1.2788
0.9457
0.9270
0.9280
0.8932
2.608
1.331
1.109
1.205
2.205
1.067
3.840
1.160
2.199
3.186
5.792
PPM
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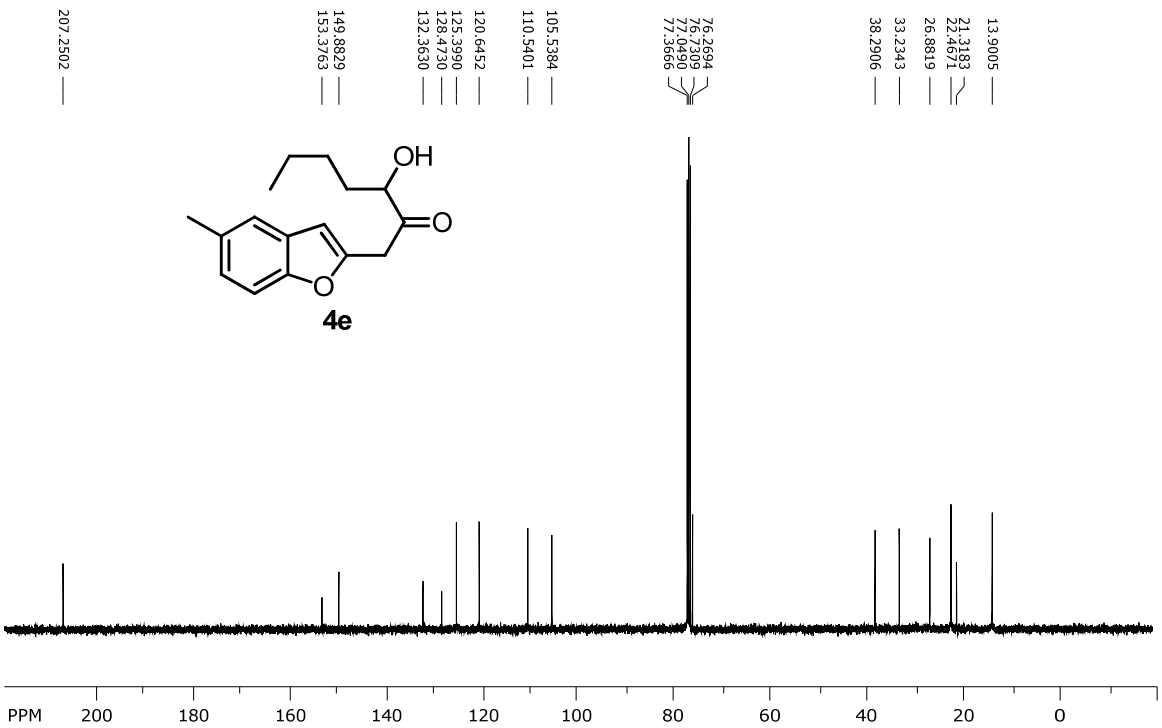
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0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O
O
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105.5384
77.3666
77.0490
76.7309
76.2694
38.2906
33.2343
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140
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100
80
60
40
20
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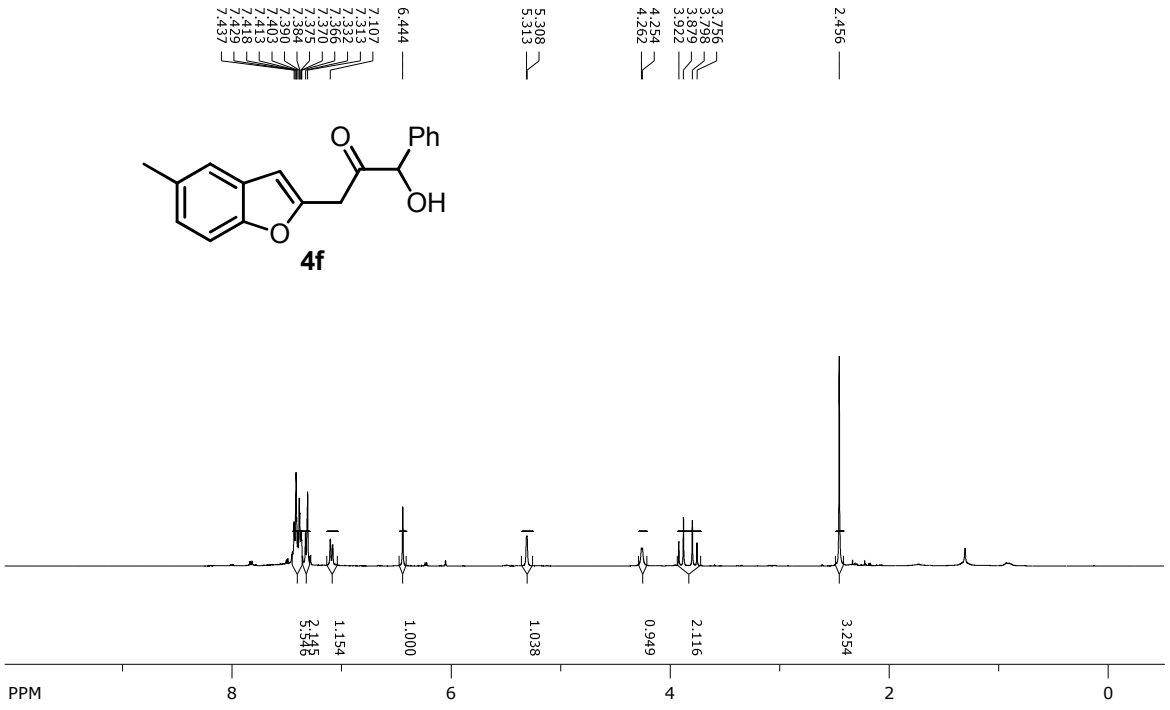
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7.370
7.366
7.332
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6.444
5.313
5.308
4.262
4.254
3.922
3.879
3.798
3.756
2.456
O
Ph
OH
O
4f
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1.038
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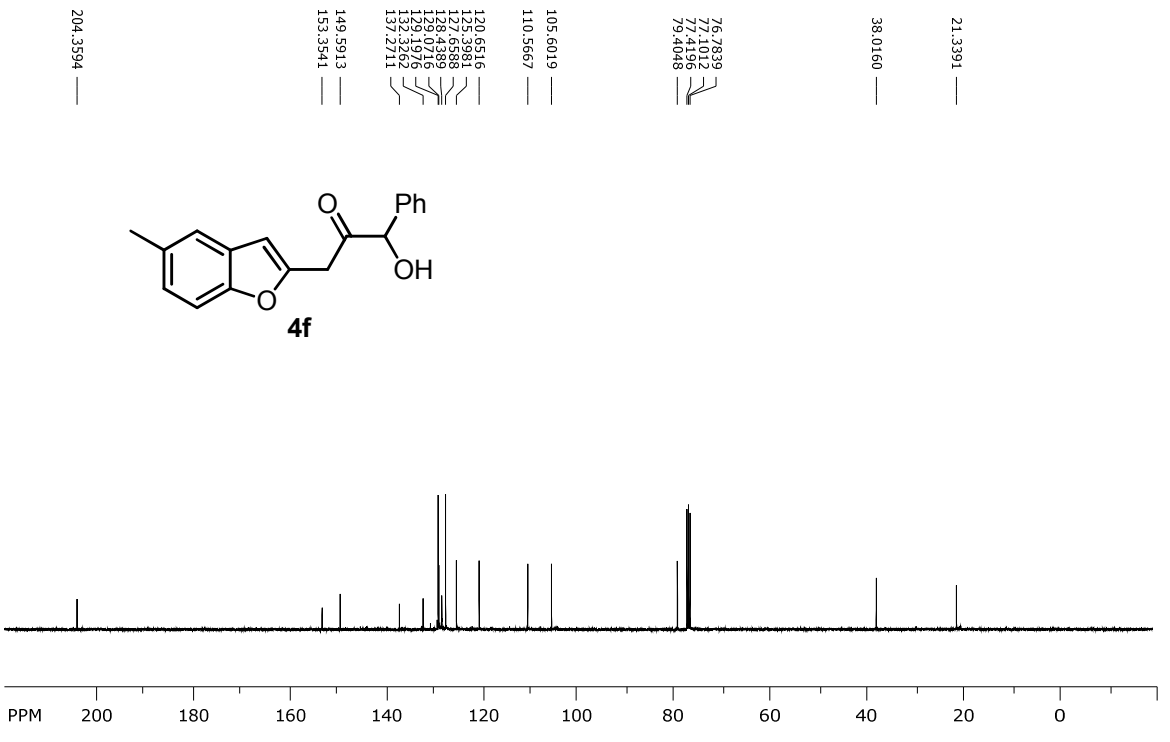
PPM
8
6
4
2
0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110.5667
105.6019
79.4048
77.4196
77.0322
76.7839
38.0160
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Ph
OH
O
4f
PPM
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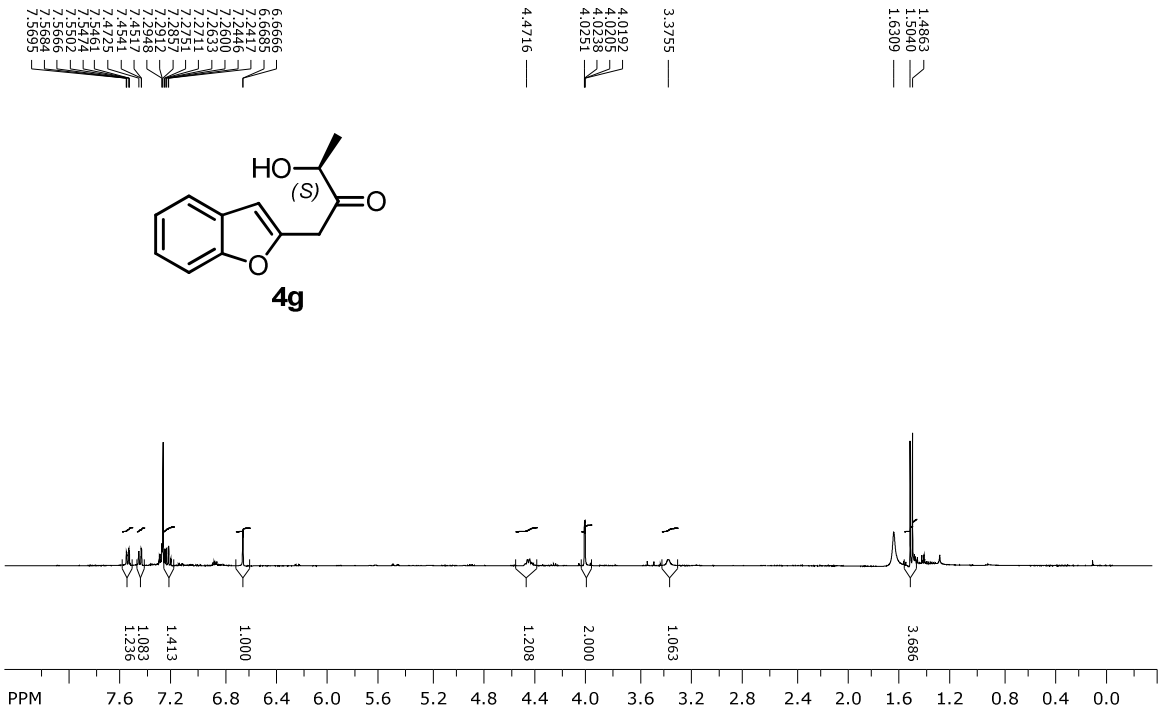
140
120
100
80
60
40
20
0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7.4517
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7.2912
7.2857
7.2751
7.2633
7.2600
7.2446
7.2417
6.6685
6.6666
4.4716
4.0251
4.0238
4.0205
4.0192
3.3755
1.6309
1.5040
1.4863
HO
(S)
O
O
4g
1.236
1.083
1.413
1.000
1.208
2.000
1.063
3.686
PPM
7.6
7.2
6.8
6.4
6.0
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5.2
4.8
4.4
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2.4
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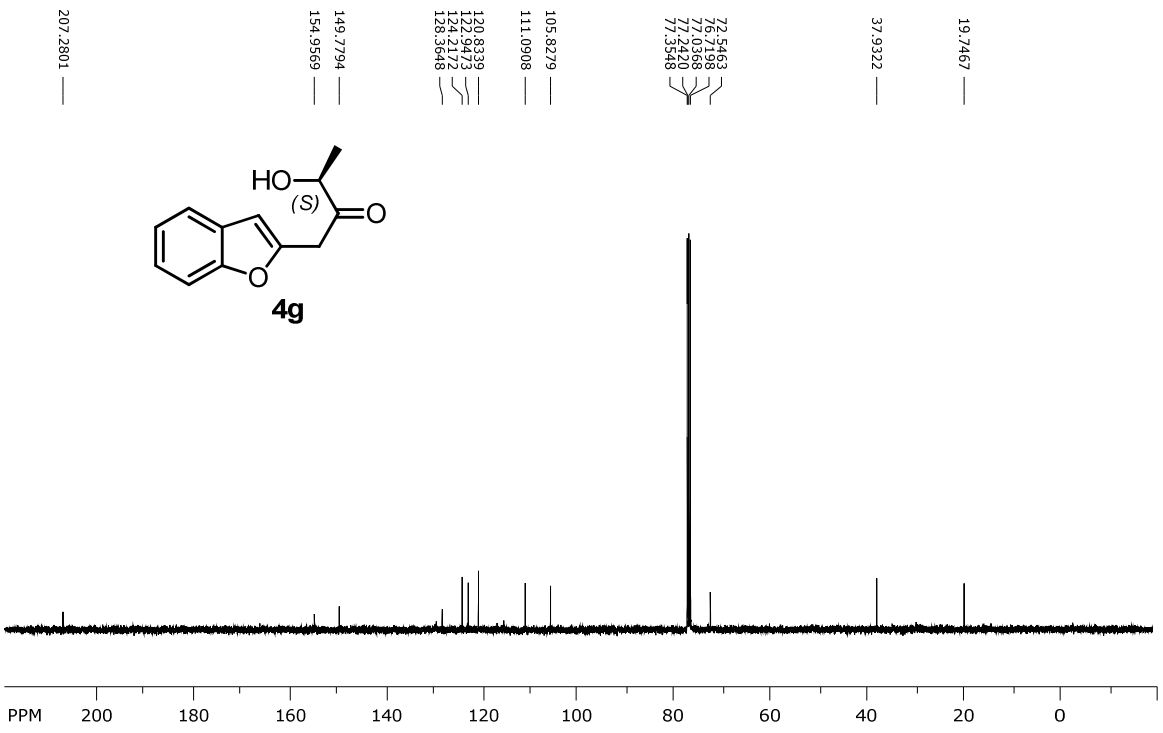
0.0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77.2420
77.0368
76.7198
72.5463
37.9322
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(S)
O
O
4g
PPM
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140
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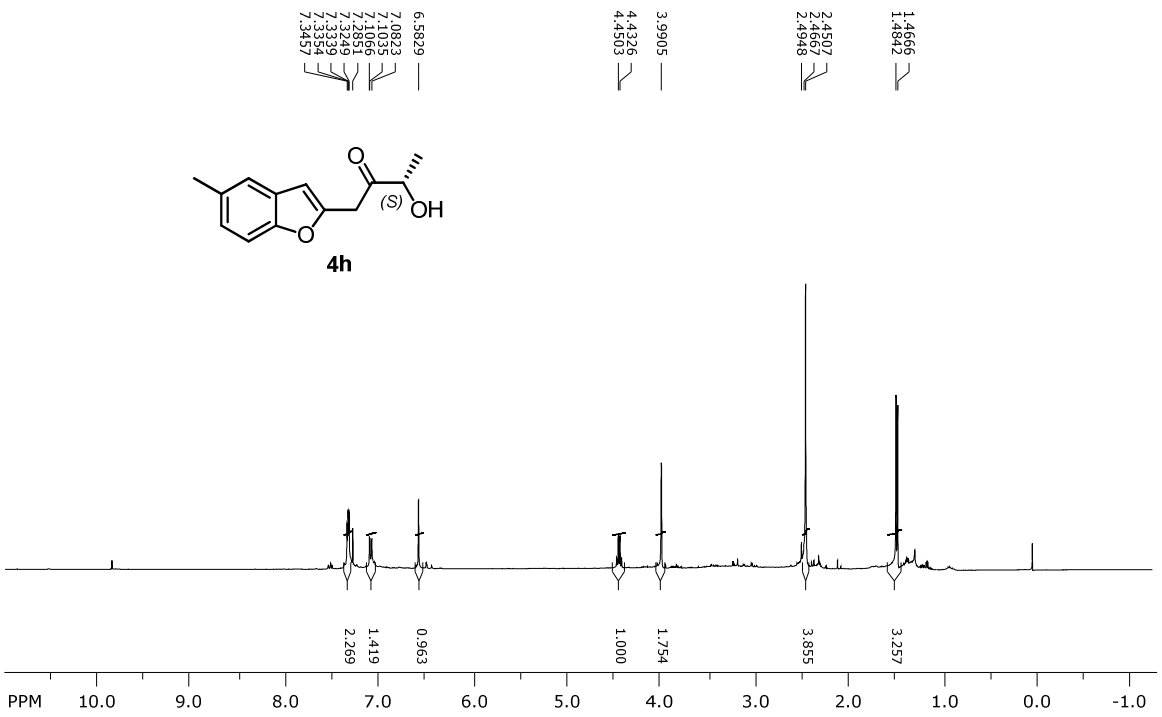
60
40
20
0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7.1035
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6.5829
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4.4326
3.9905
2.4948
2.4667
2.4507
1.4842
1.4666
(S)
OH
O
4h
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3.257
PPM
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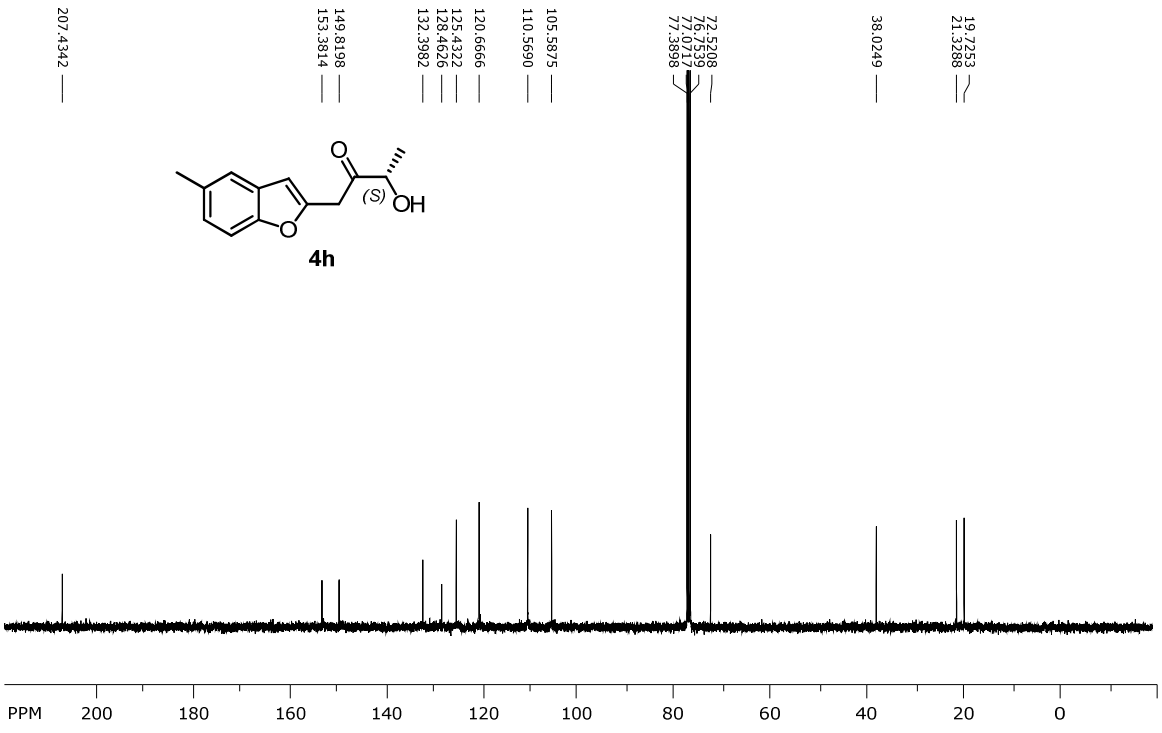
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76.7539
72.5208
38.0249
21.3288
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(S)
OH
O
4h
PPM
200
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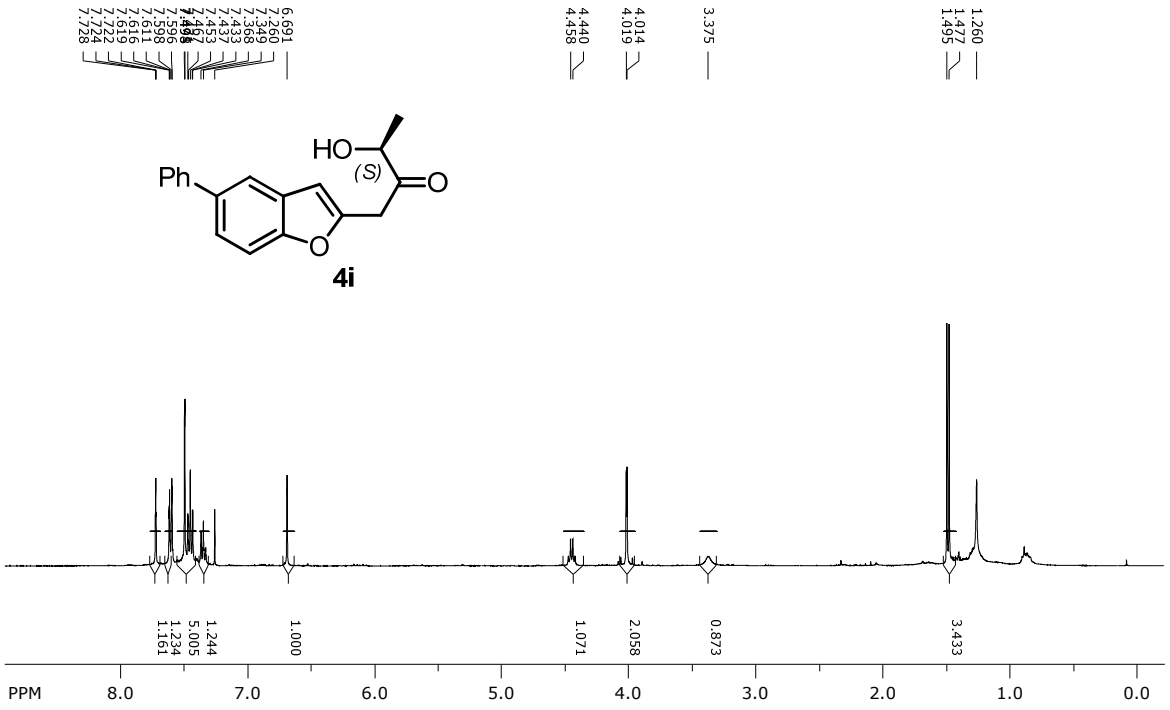
160
140
120
100
80
60
40
20
0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7.611
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7.453
7.437
7.433
7.368
7.349
7.260
6.691
4.458
4.440
4.019
4.014
3.375
1.495
1.477
1.260
HO
(S)
O
Ph
O
4i
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1.234
5.005
1.244
1.000
1.071
2.058
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PPM
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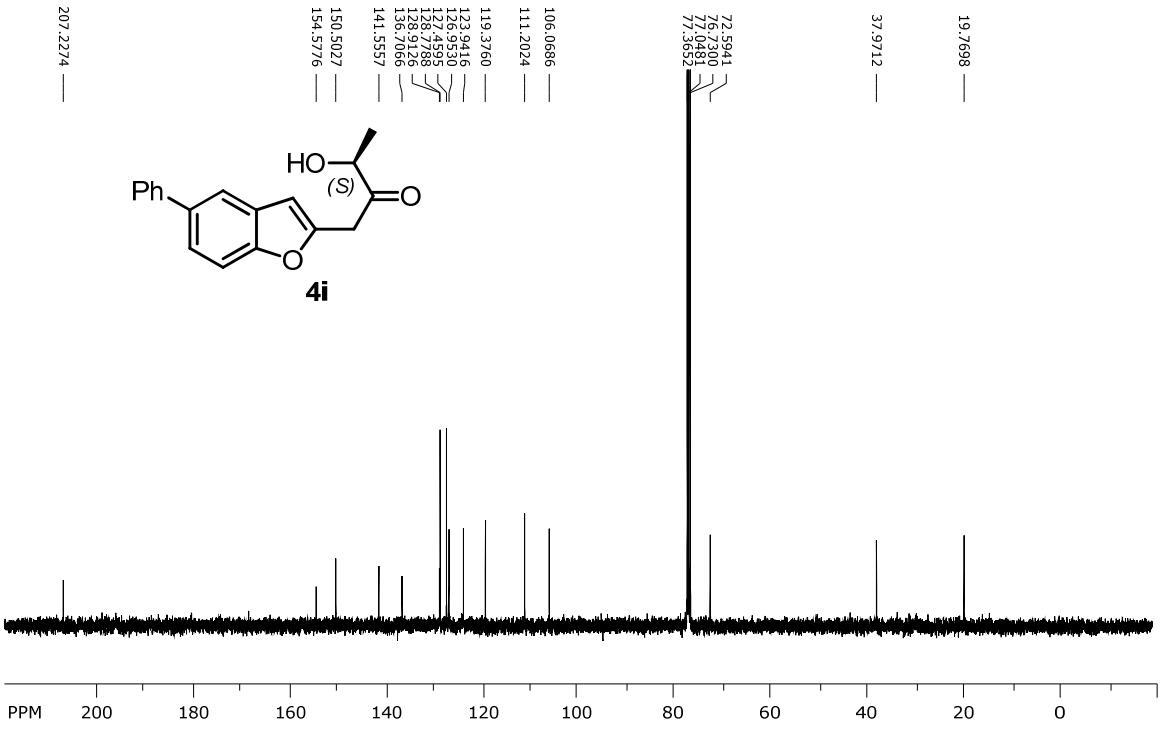
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128.7788
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127.5510
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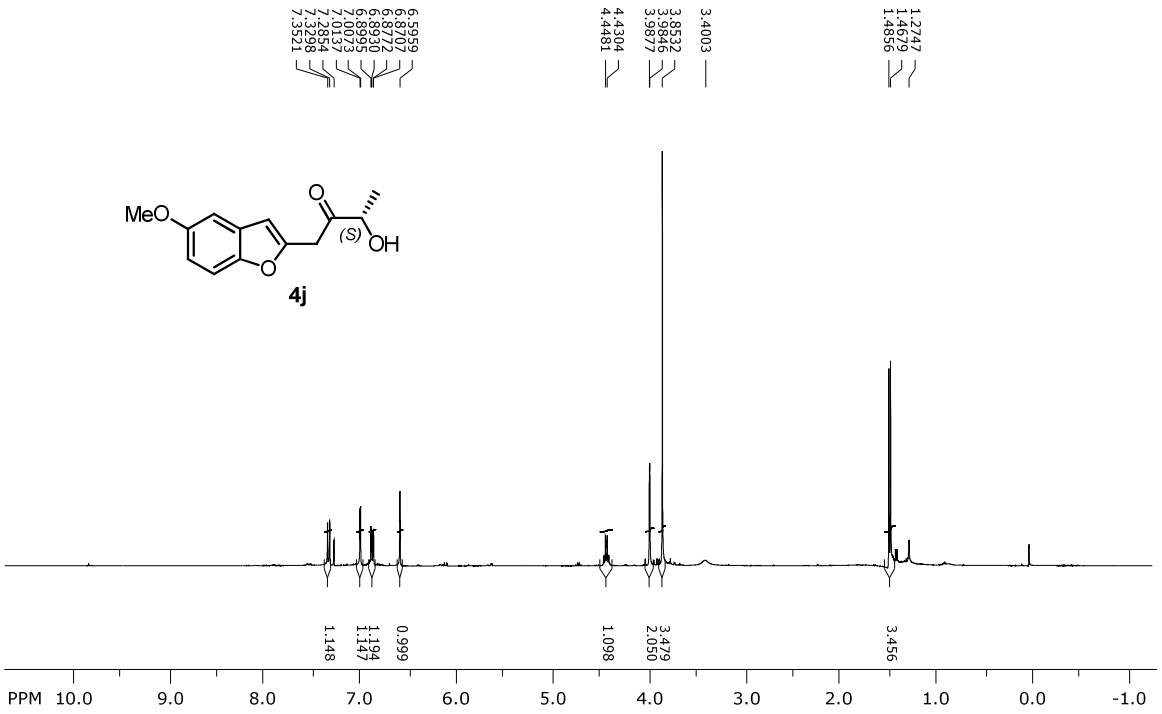
119.3760
111.2024
106.0686
77.3652
77.0481
76.7300
72.5941
37.9712
19.7698
HO
(S)
O
Ph
O
4i
PPM
200
180
160
140
120
100
80
60
40
20
0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1.4856
1.4679
1.2747
MeO
O
(S)
OH
4j
1.148
1.147
1.194
0.999
1.098
2.050
3.479
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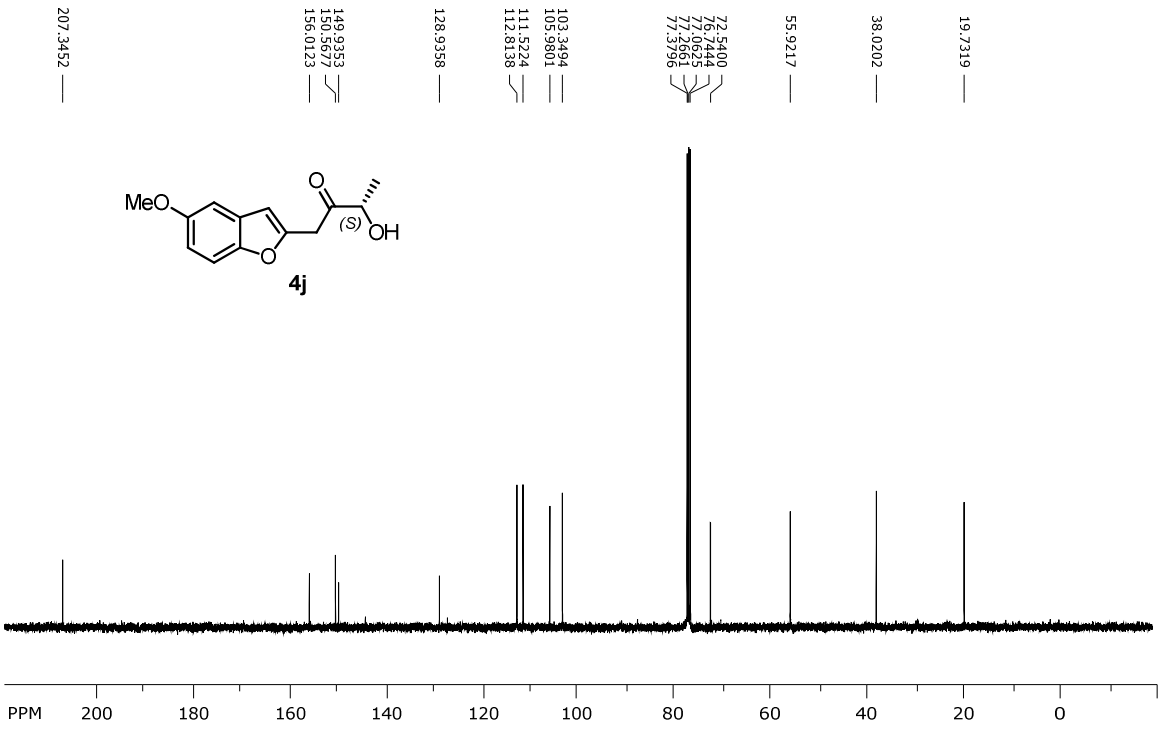
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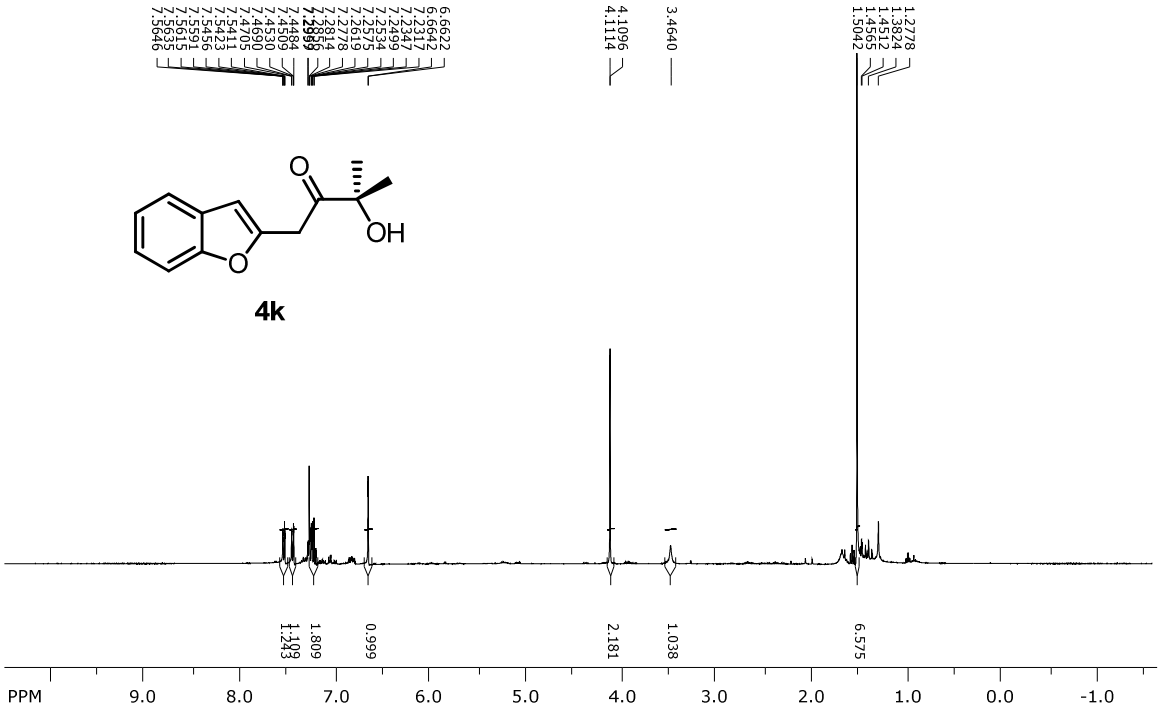
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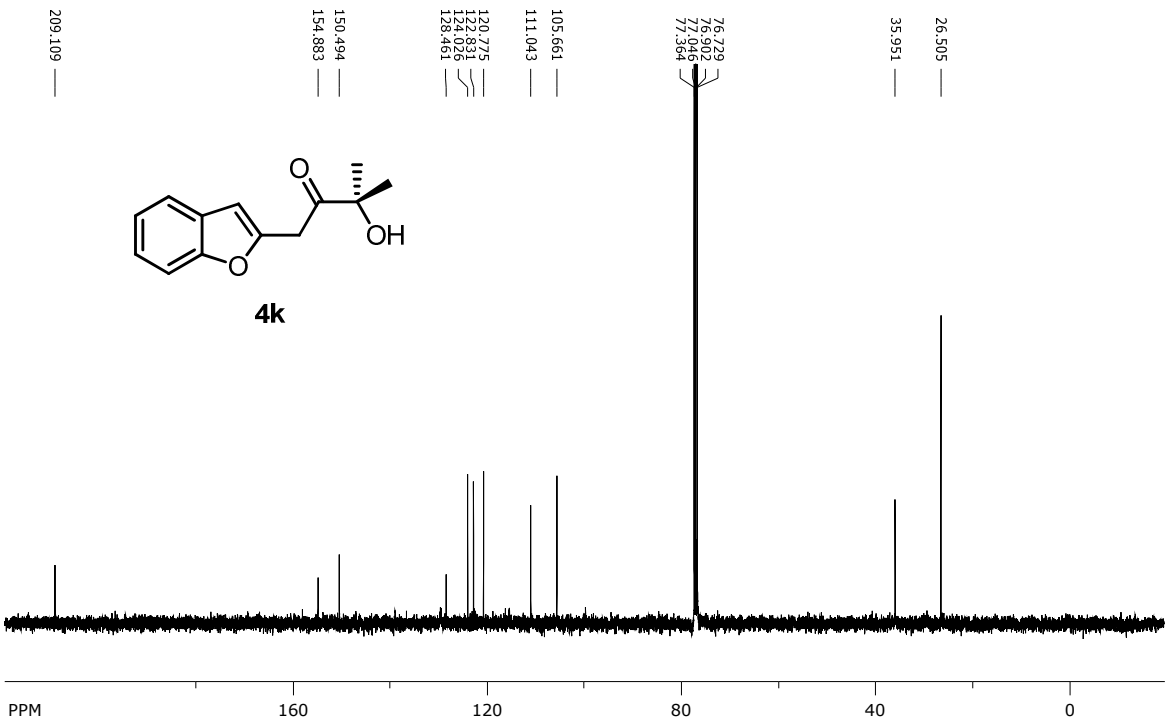
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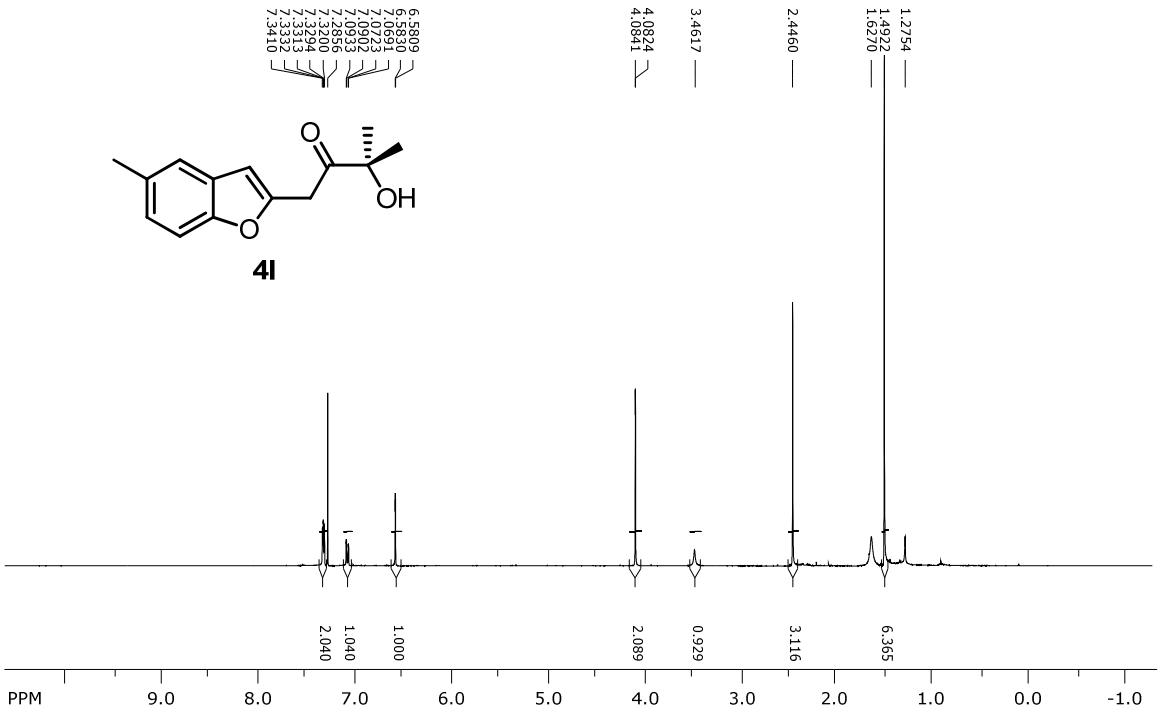
4k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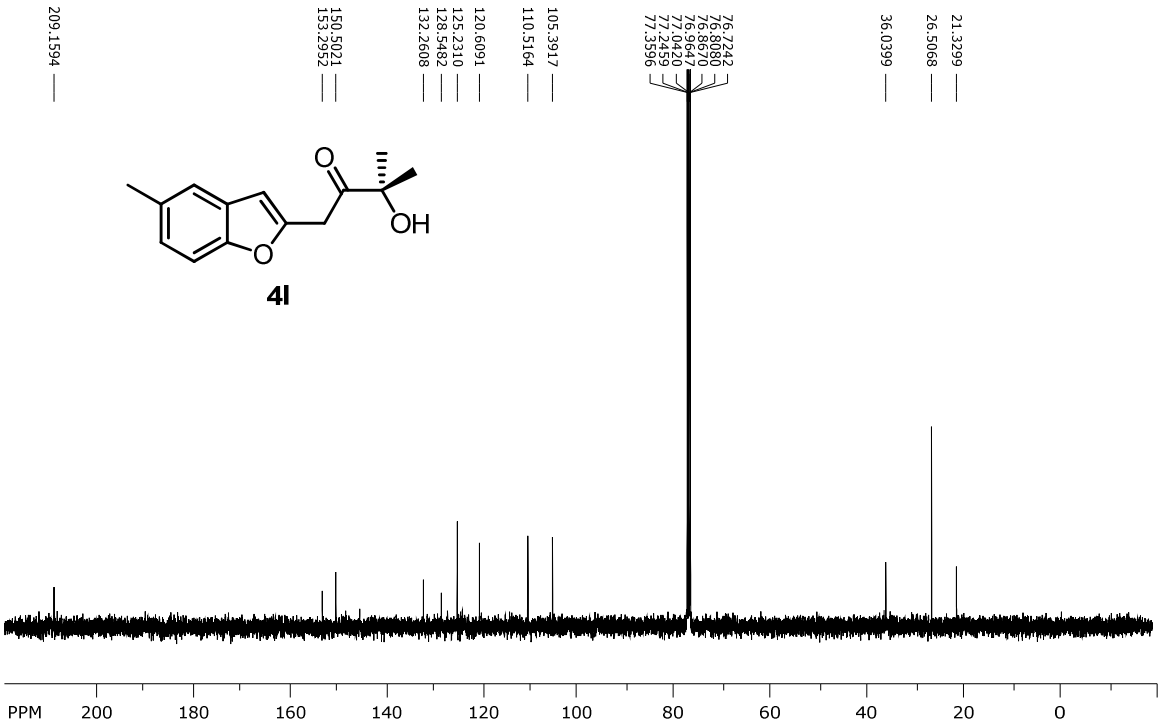
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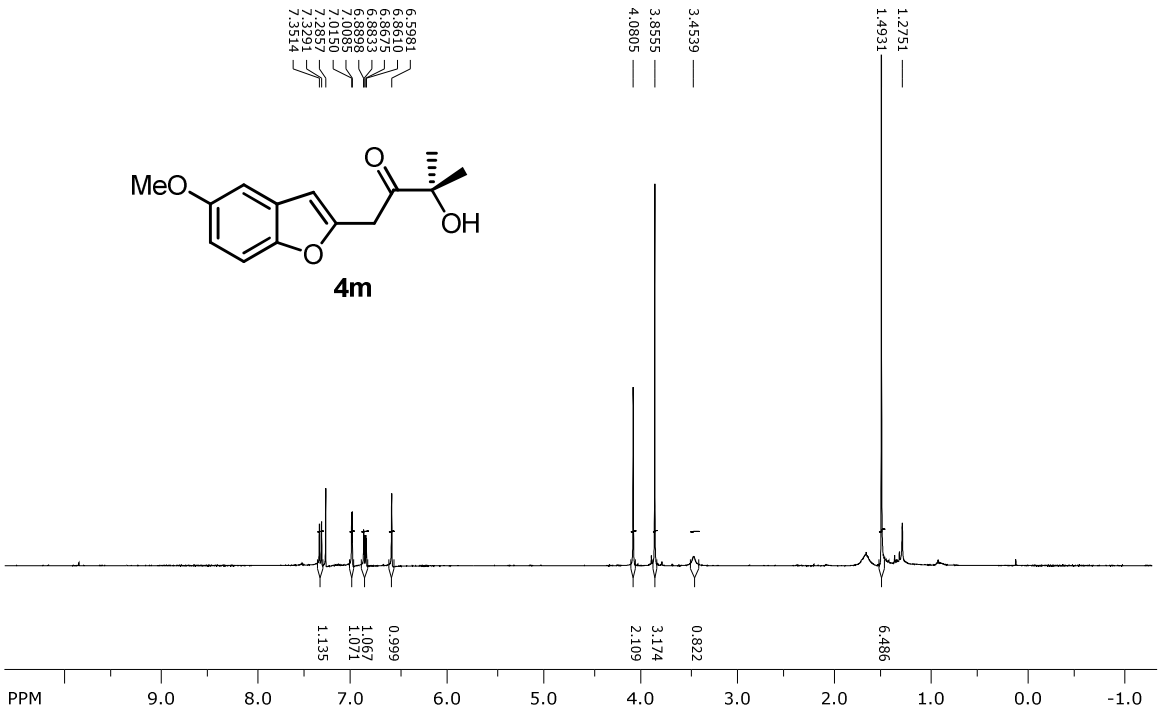
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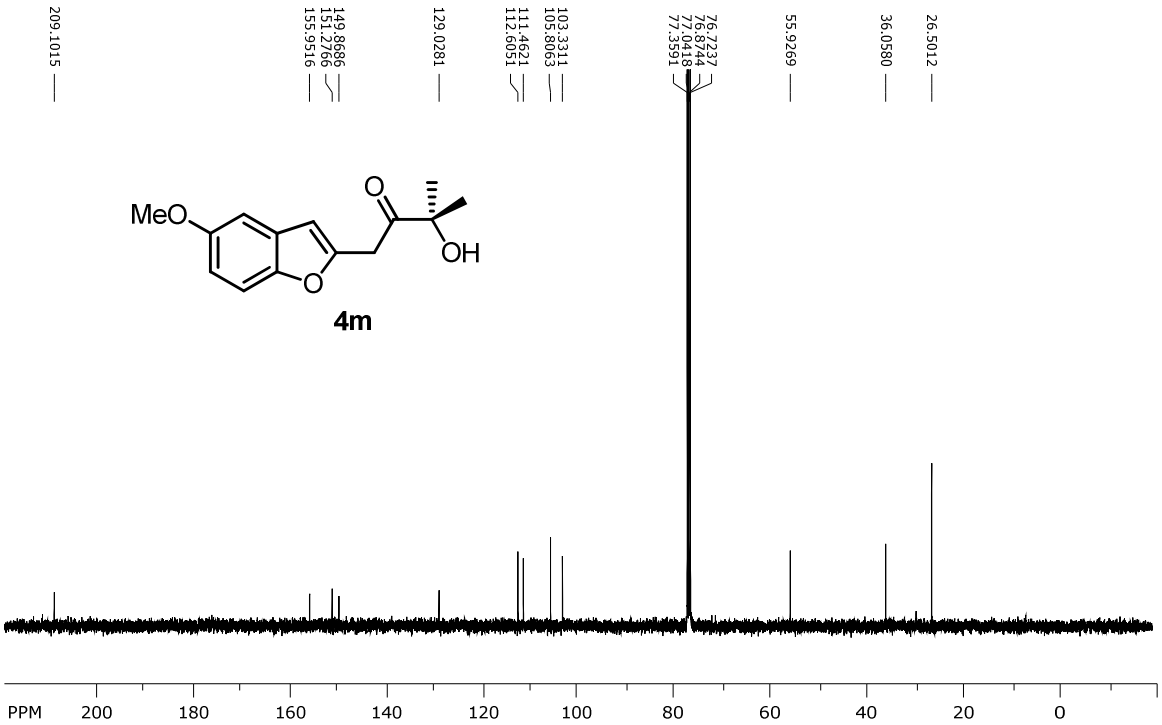
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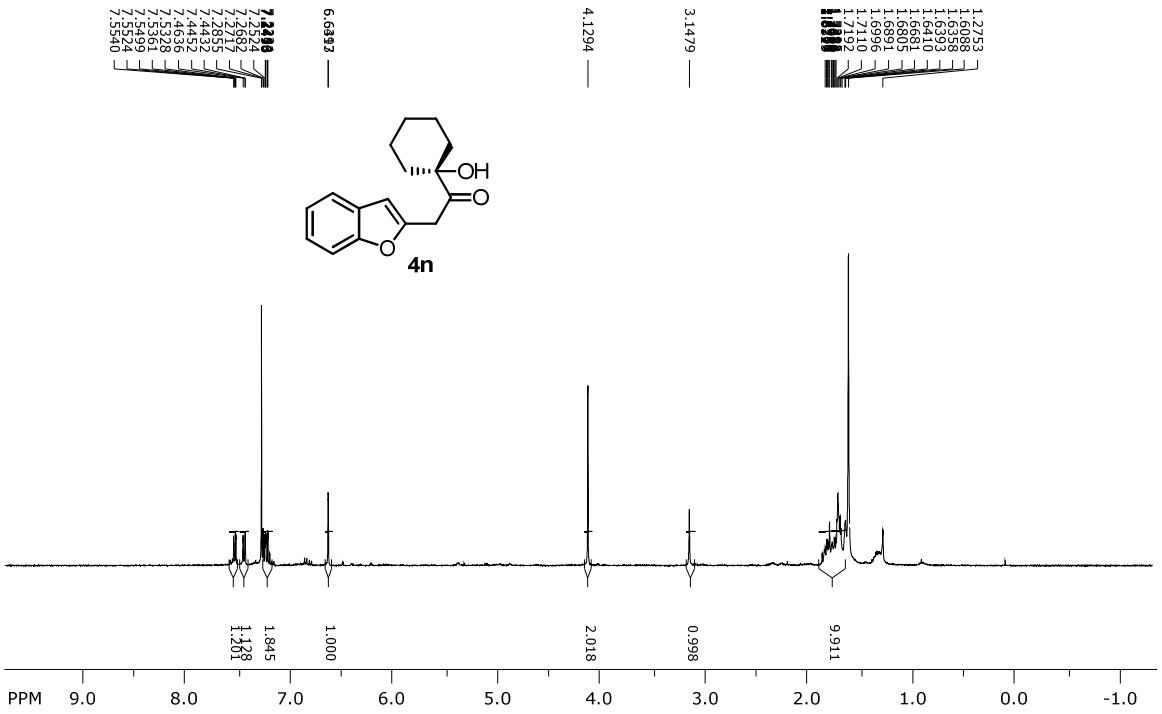
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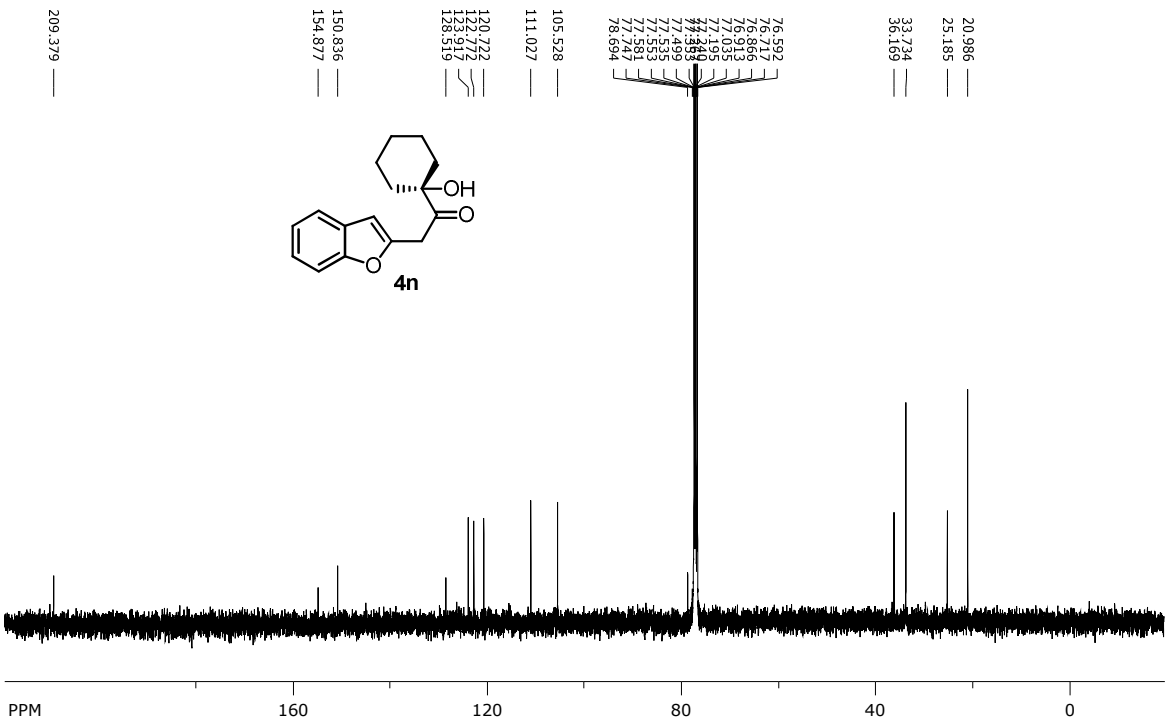
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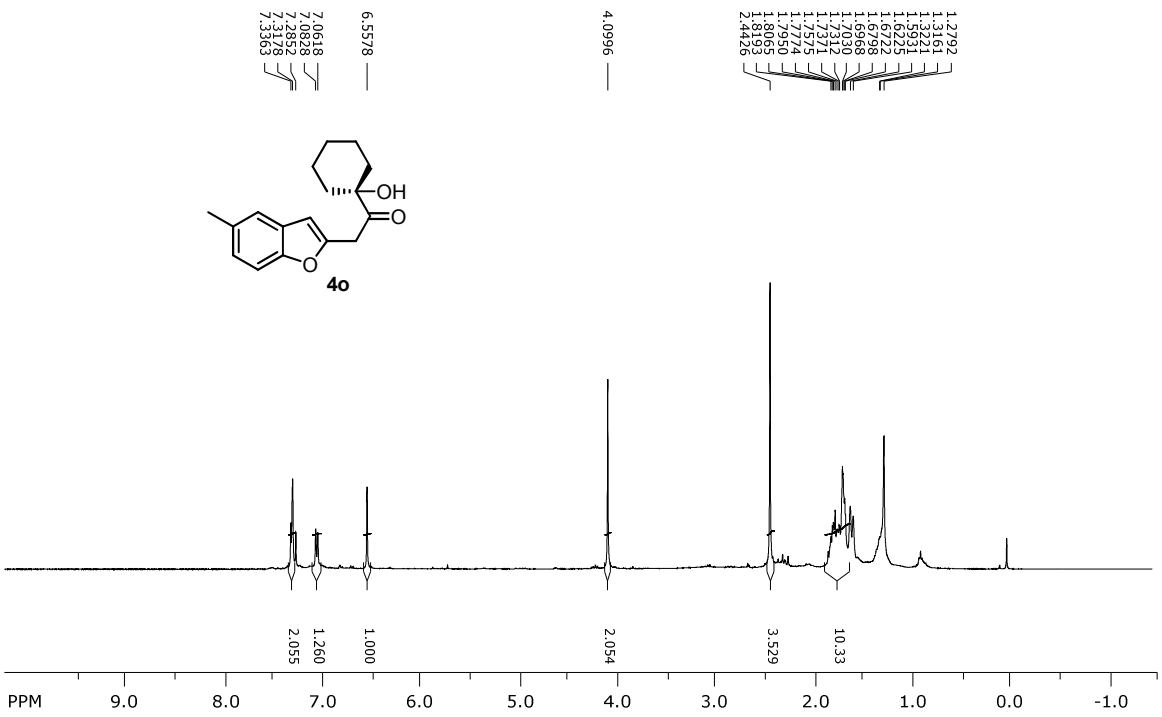
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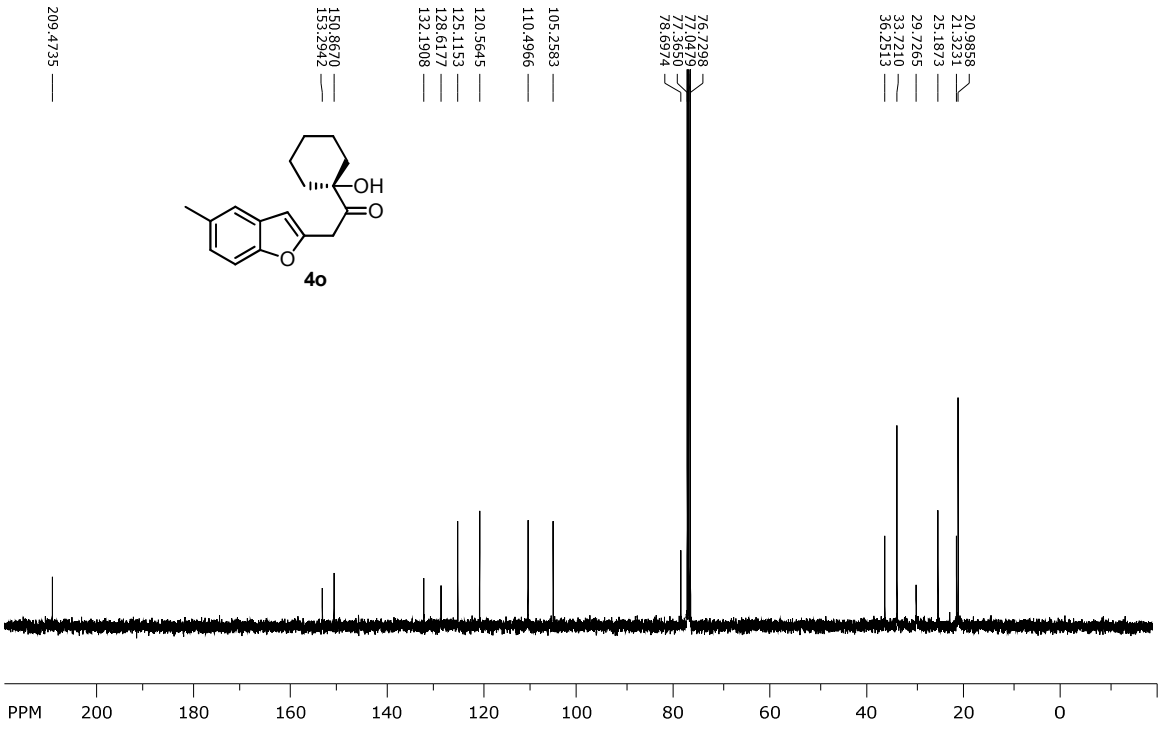
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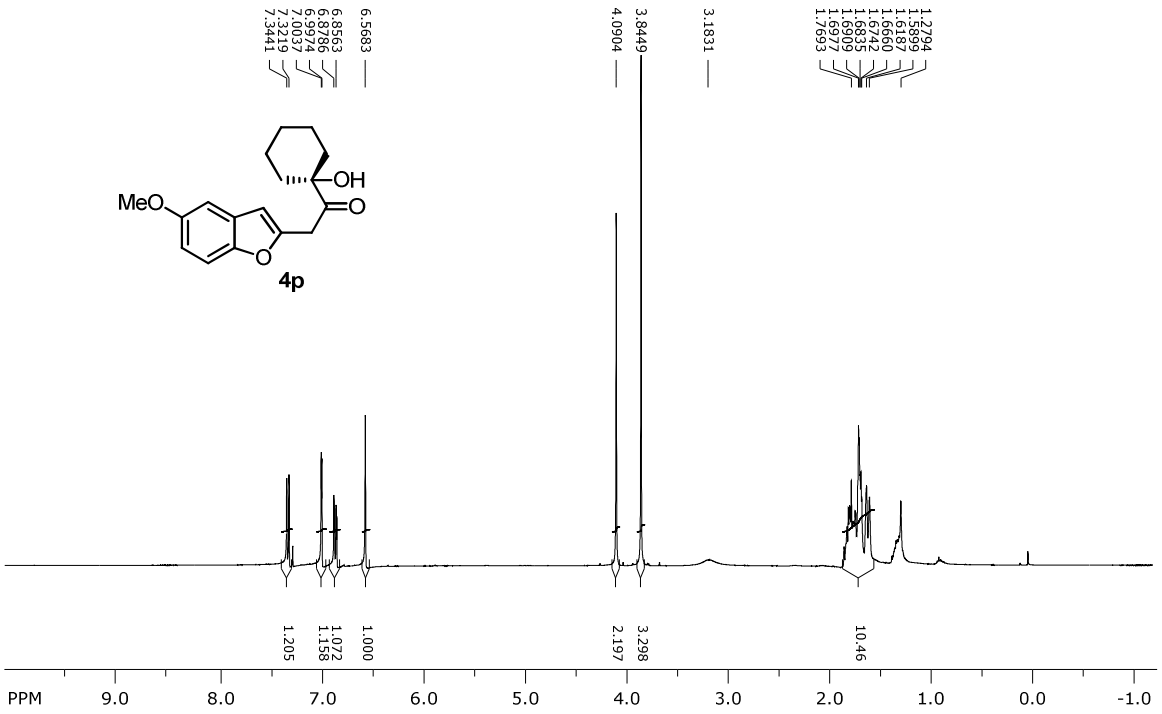
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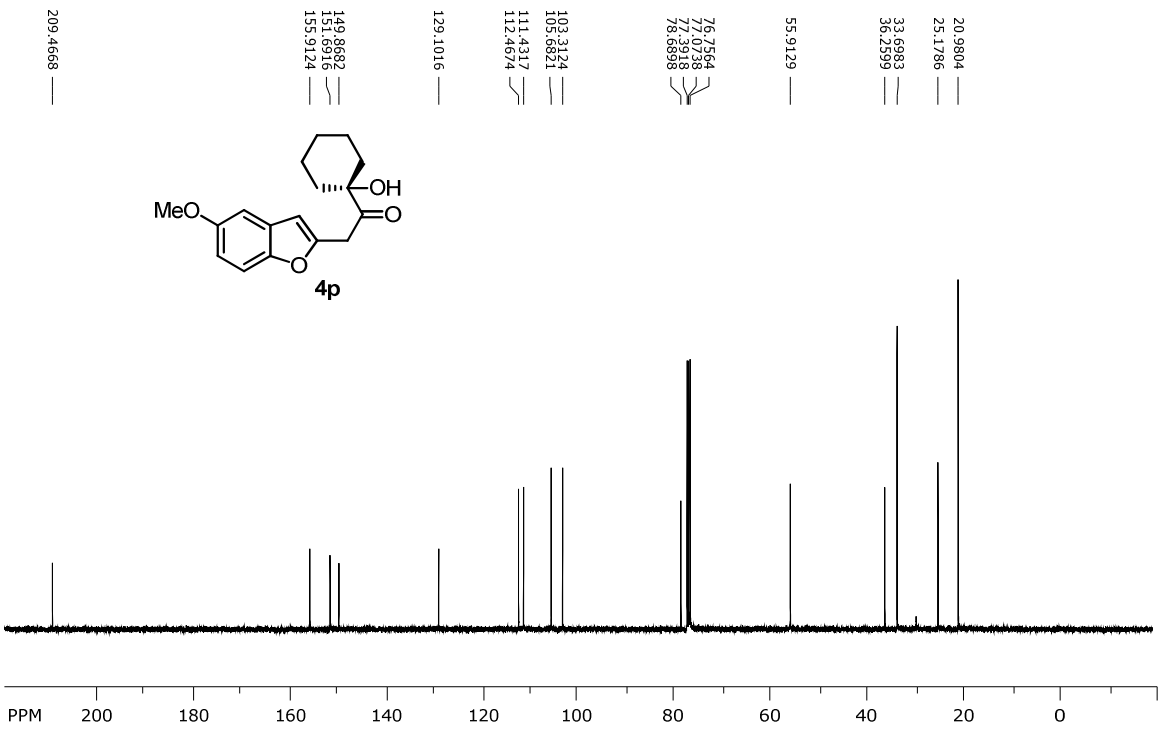
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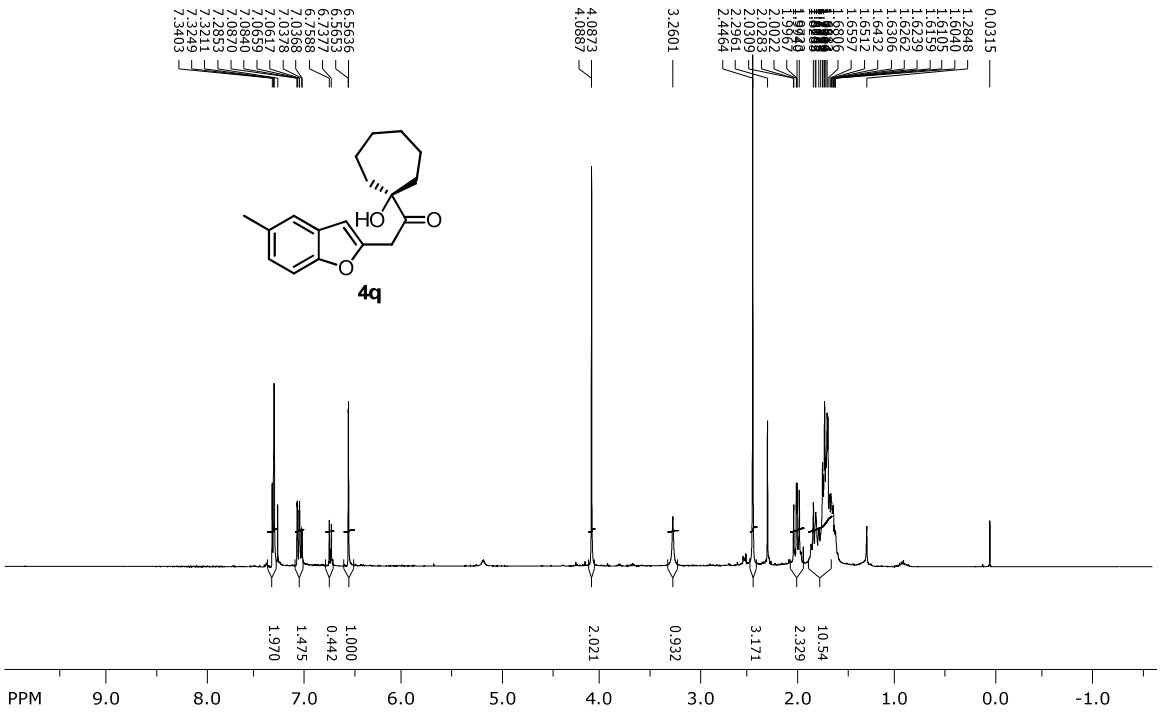
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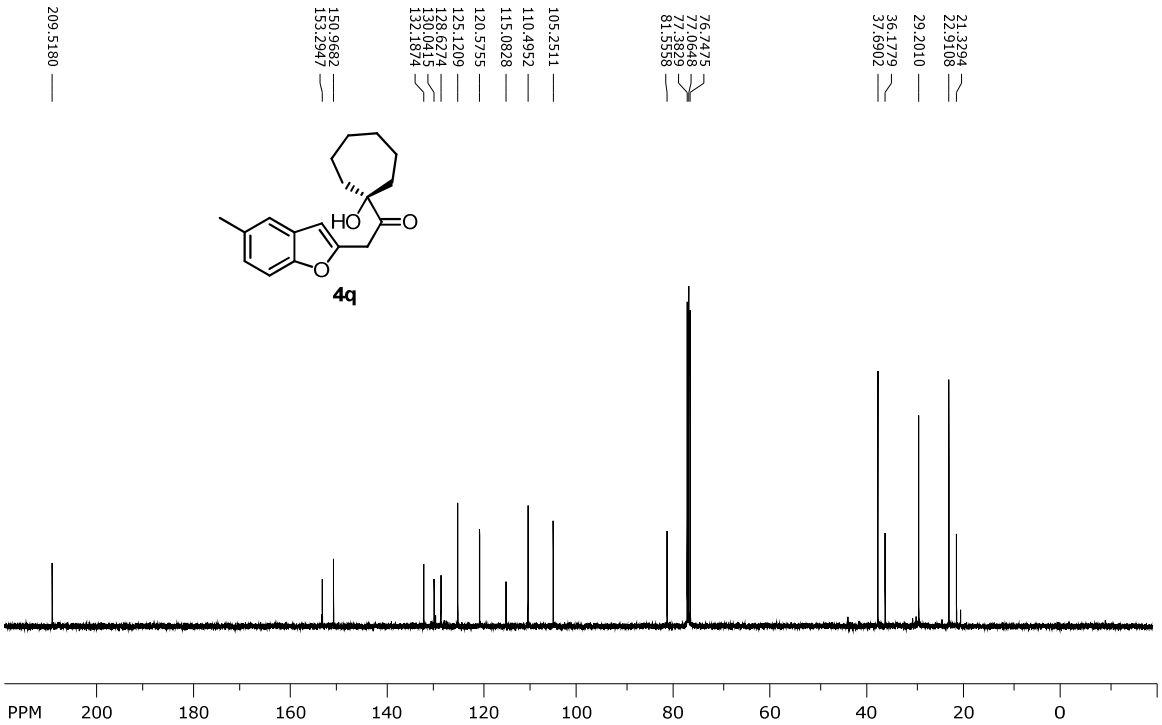
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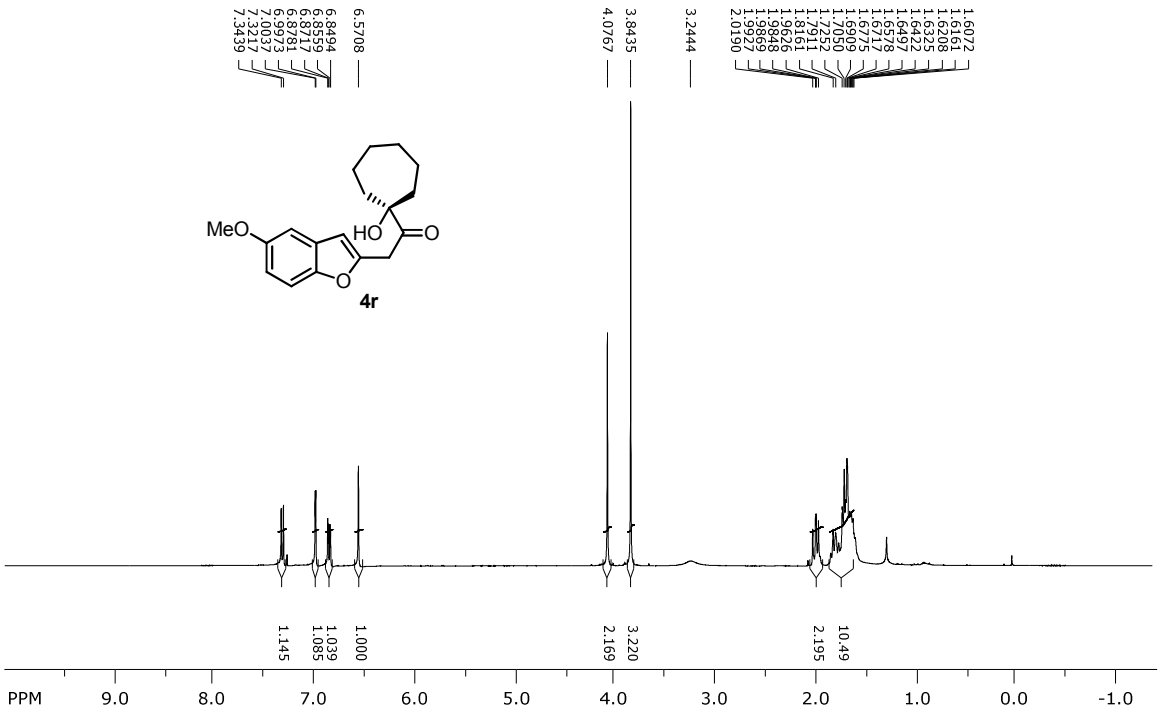
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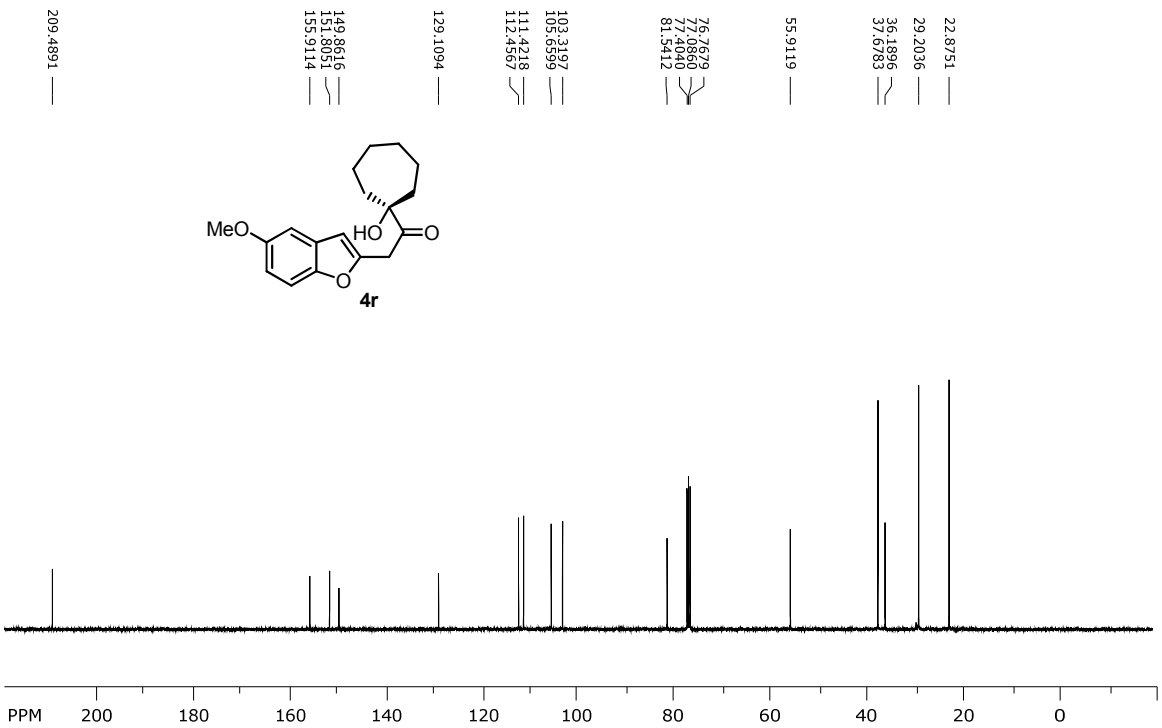
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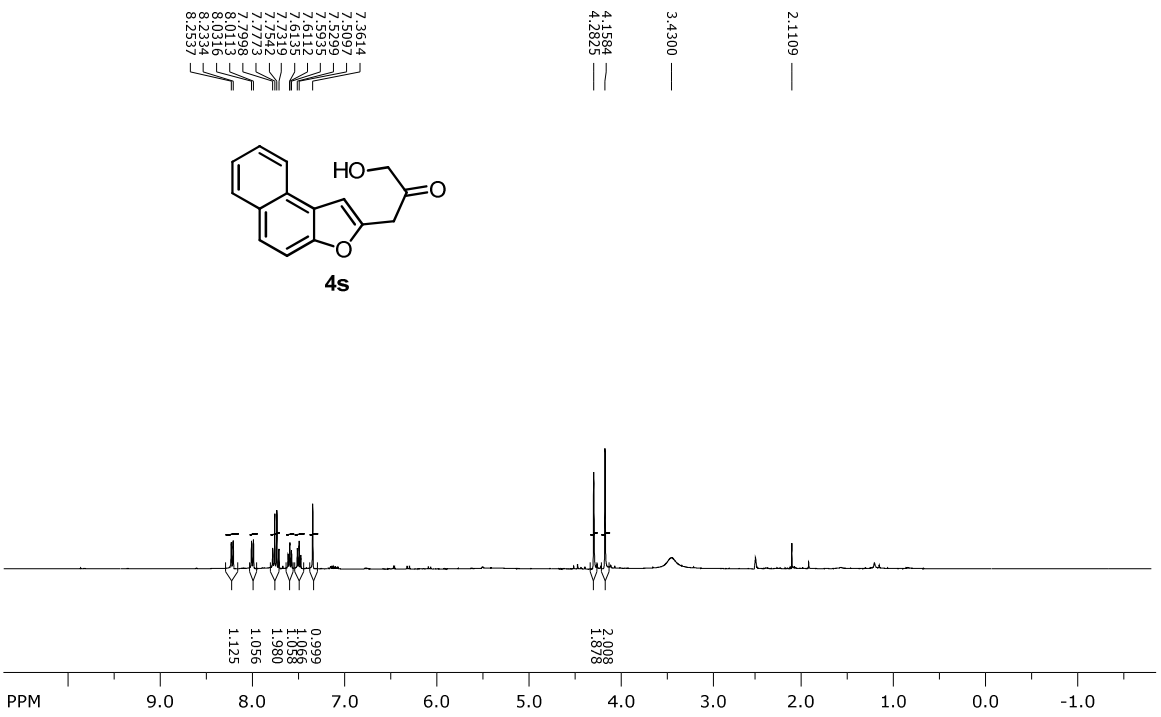
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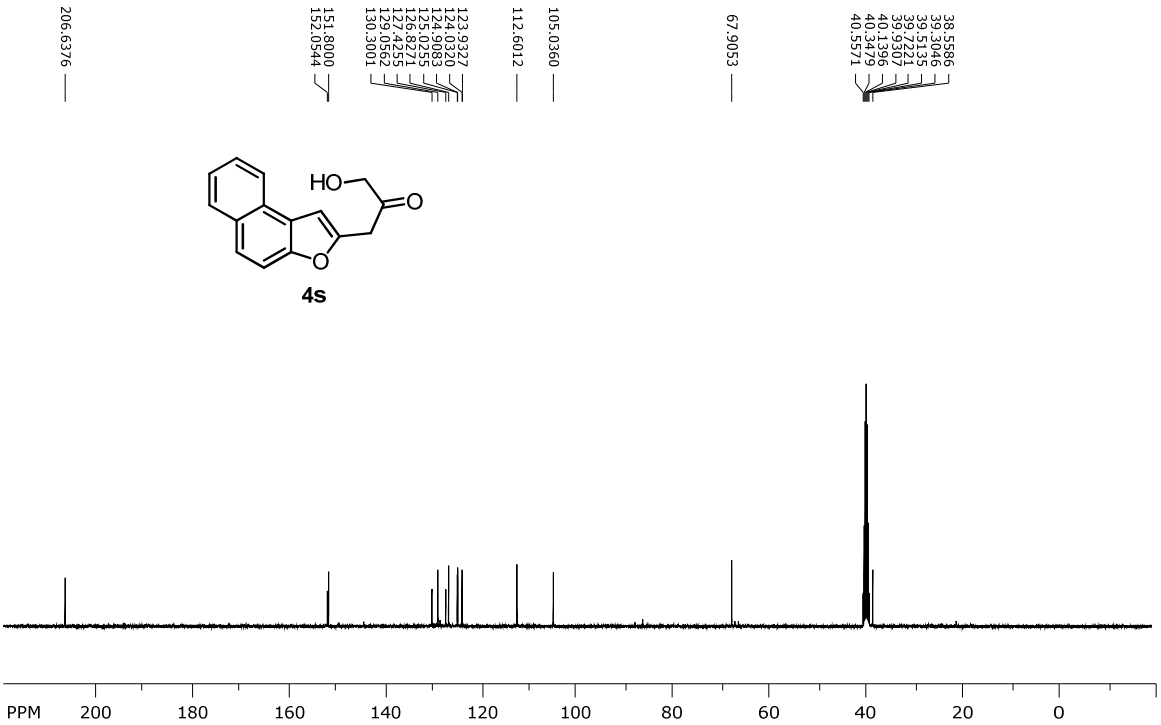
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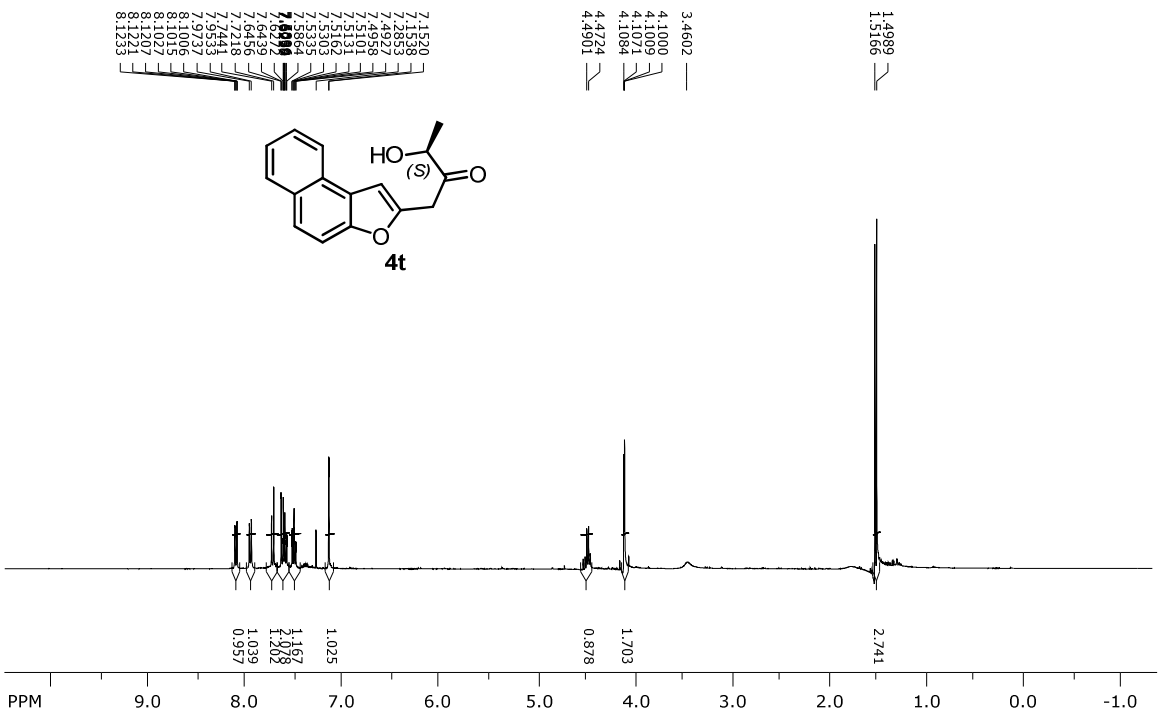
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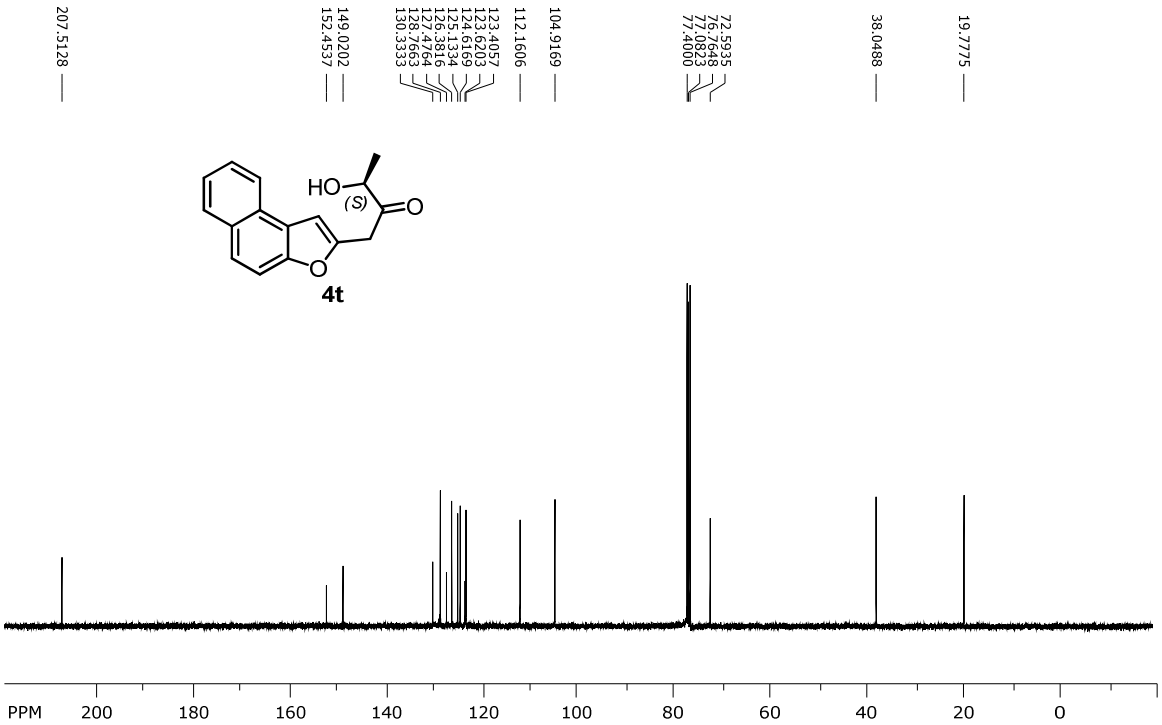
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PPM
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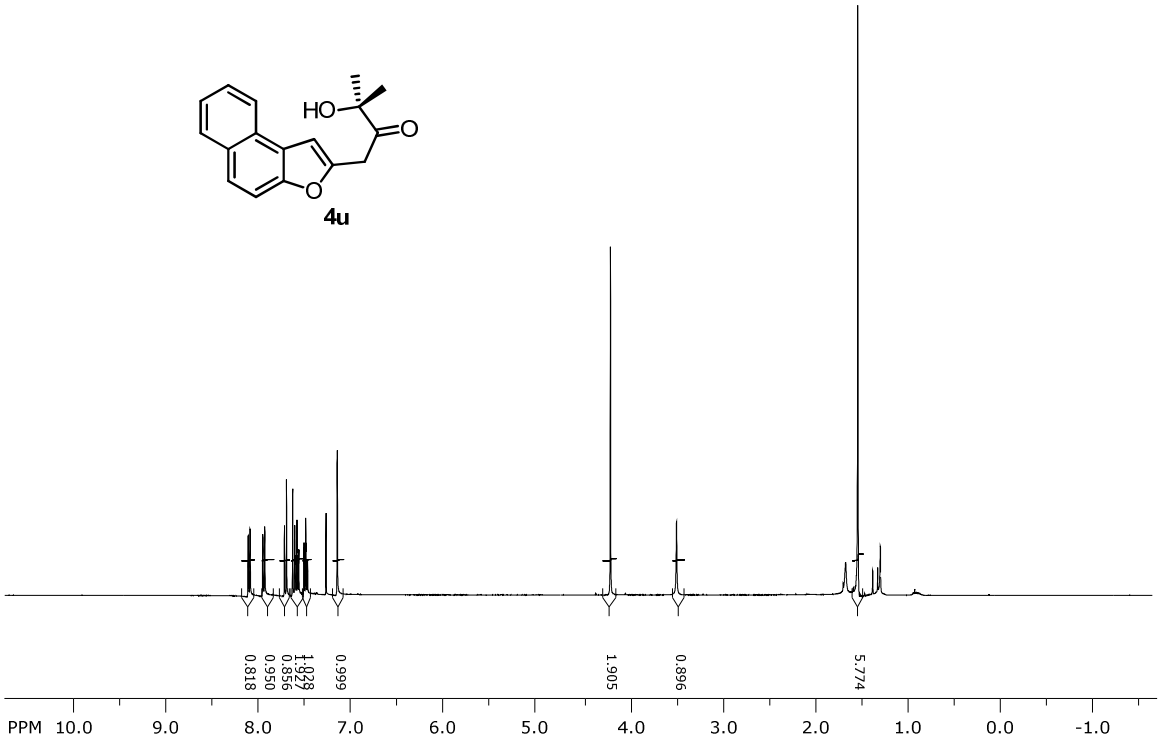
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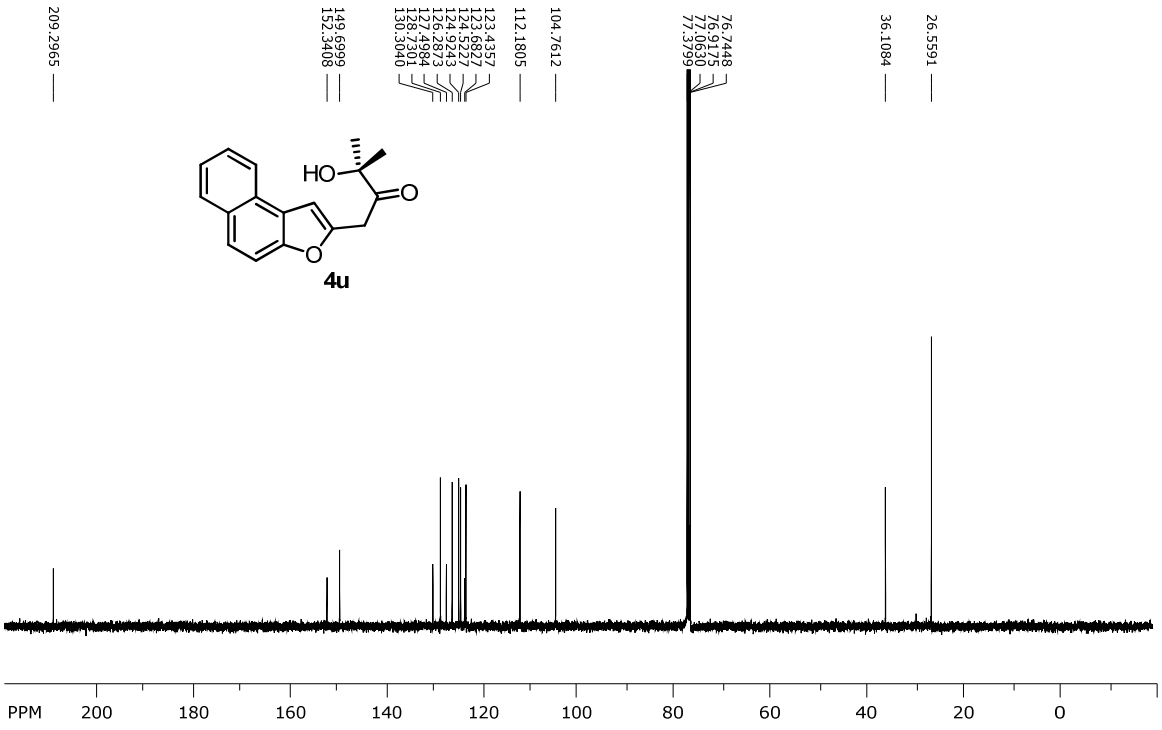
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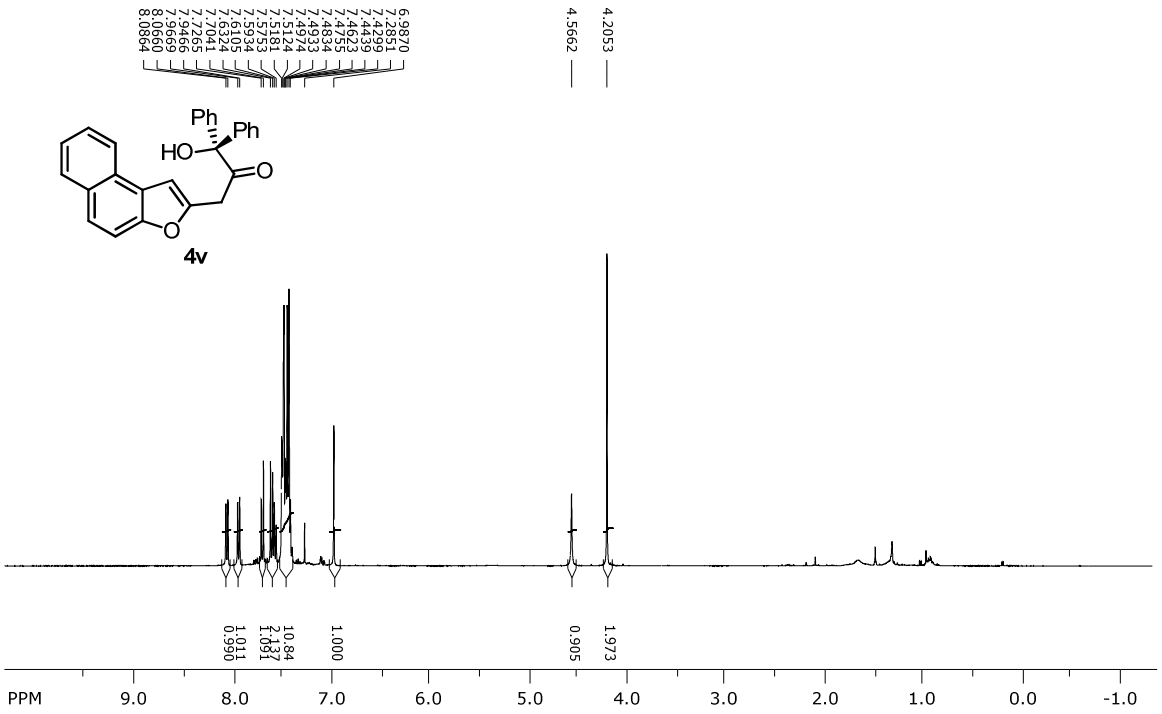
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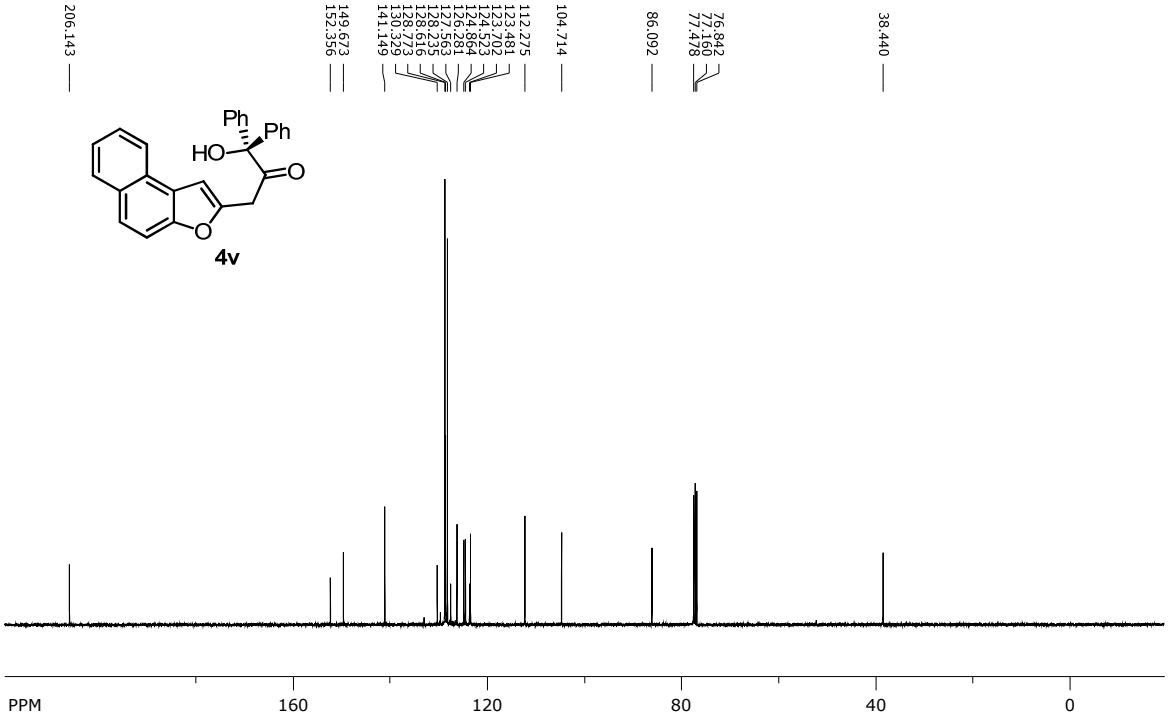
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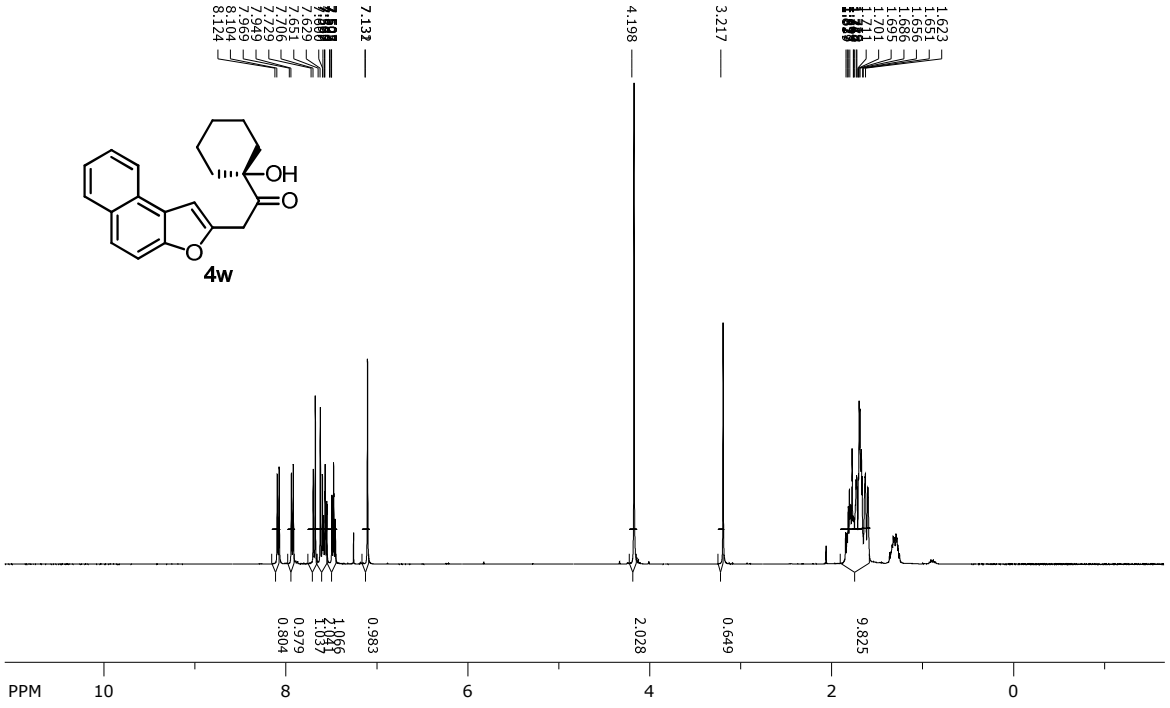
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4
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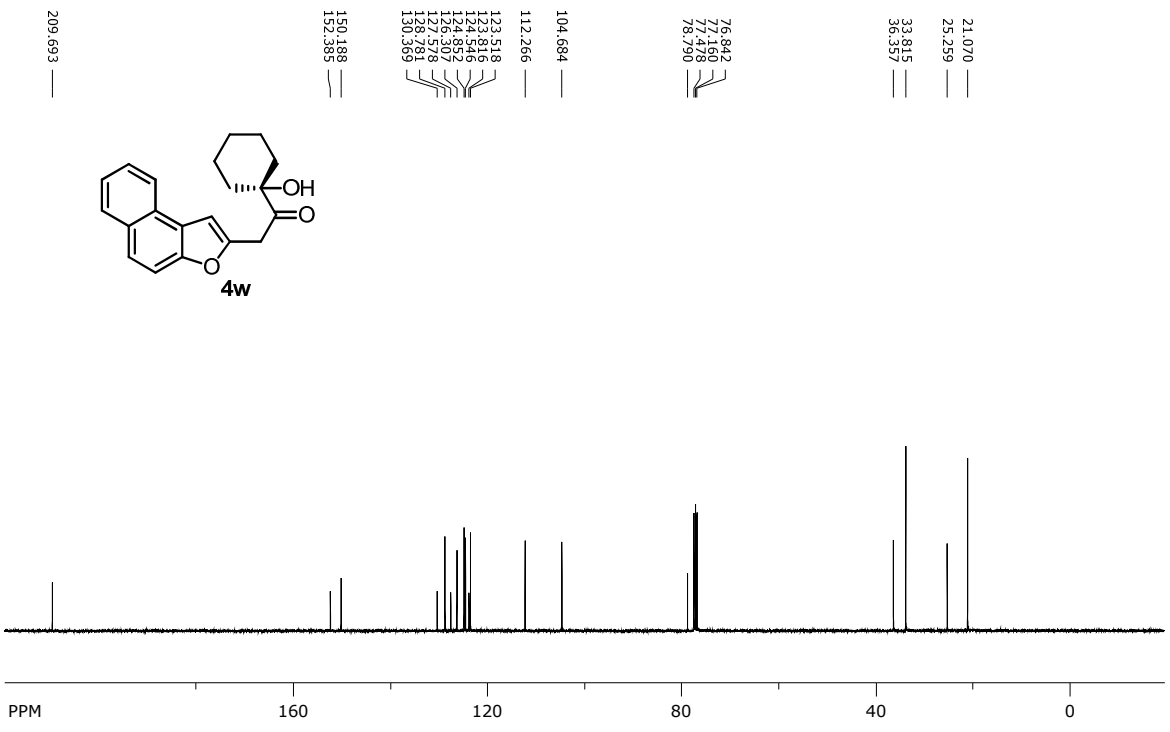
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150.188
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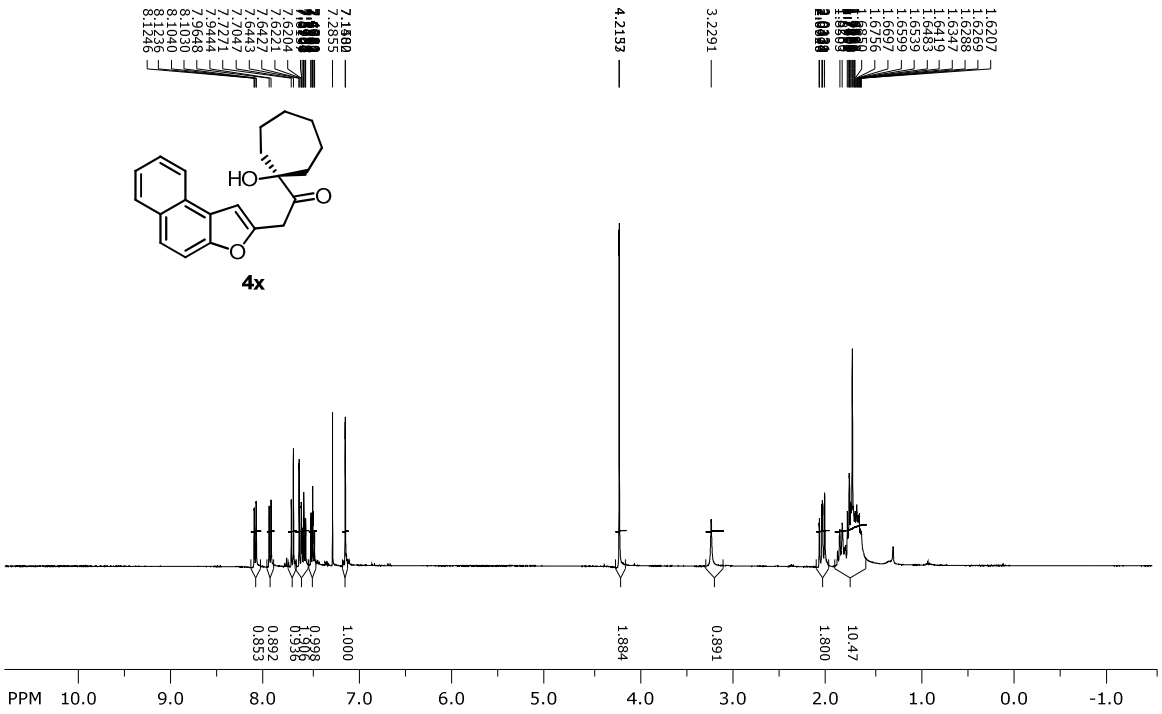
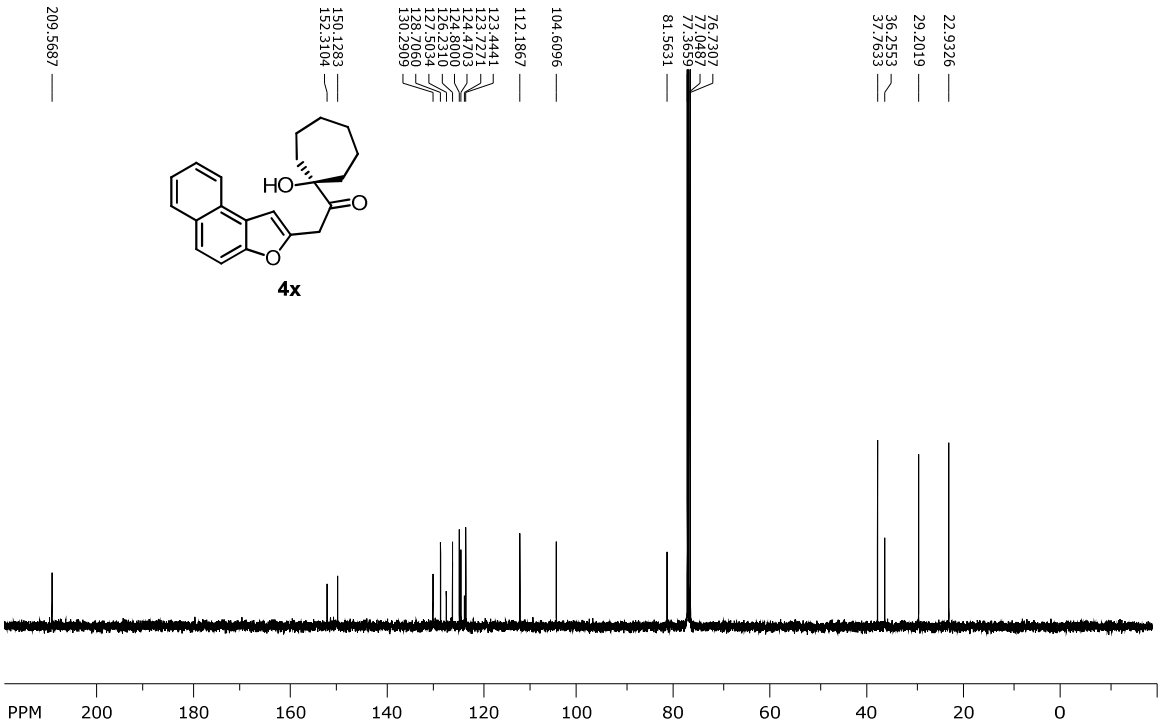
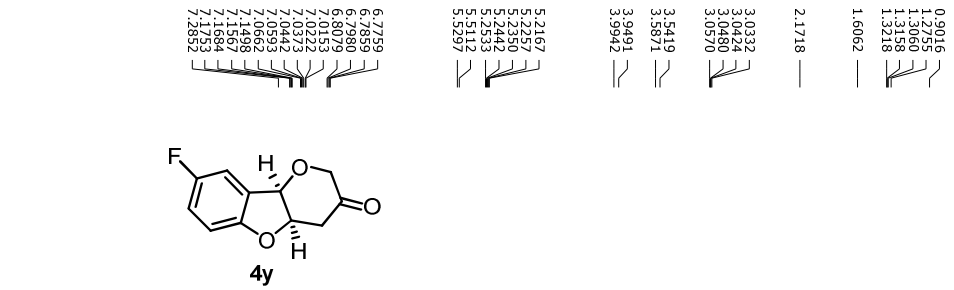
124.852
124.546
123.816
123.518
112.266
104.684
78.790
77.478
77.160
76.842
36.357
33.815
25.259
21.070
OH
O
O
4w
PPM
160
120
80
40
0


HO
O
O
4x
PPM 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0


HO
O
O
4x
PPM 200 180 160 140 120 100 80 60 40 20 0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7.1684
7.1567
7.1498
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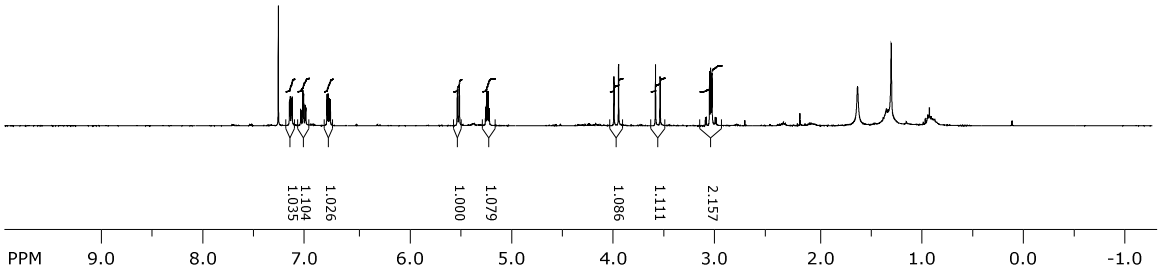
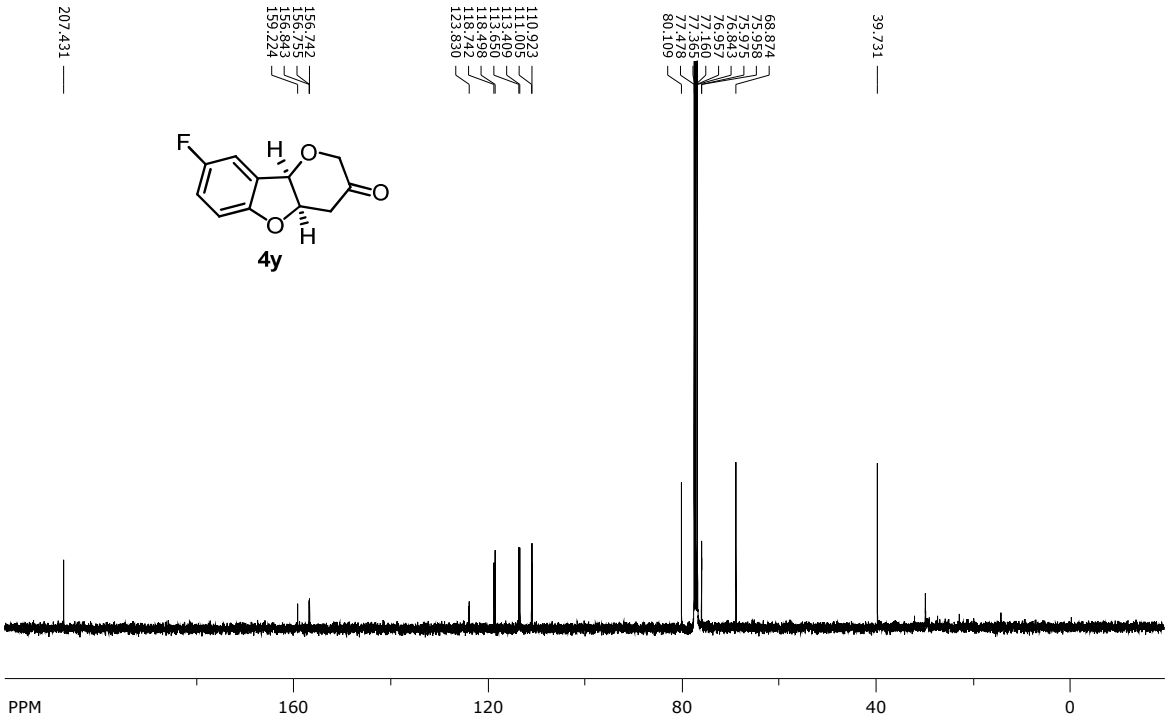
7.0593
7.0442
7.0322
7.0153
6.8079
6.7980
6.7859
6.7759
5.5297
5.5112
5.2533
5.2442
5.2350
5.2257
5.2167
3.9942
3.9491
3.5871
3.5419
3.0570
3.0480
3.0424
3.0332
2.1718
1.6062
1.3218
1.3098
1.2965
1.2755
0.9016
F
H
O
O
O
H
4y


1.035
1.104
1.026
1.000
1.079
1.086
1.111
2.157
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0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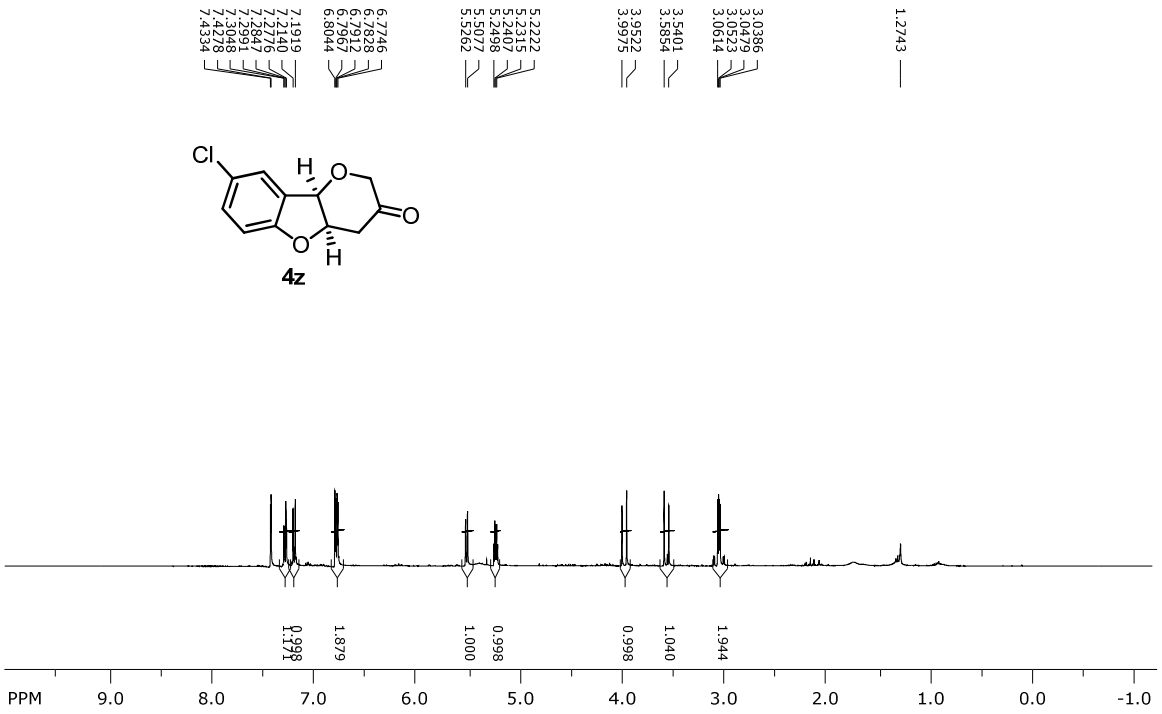
159.224
156.843
156.745
156.742
123.830
118.742
118.498
113.650
113.490
111.005
110.923
80.109
77.478
77.365
77.160
76.957
75.875
75.958
68.874
39.731
F
H
O
O
O
H
4y
PPM
160
120
80
40
0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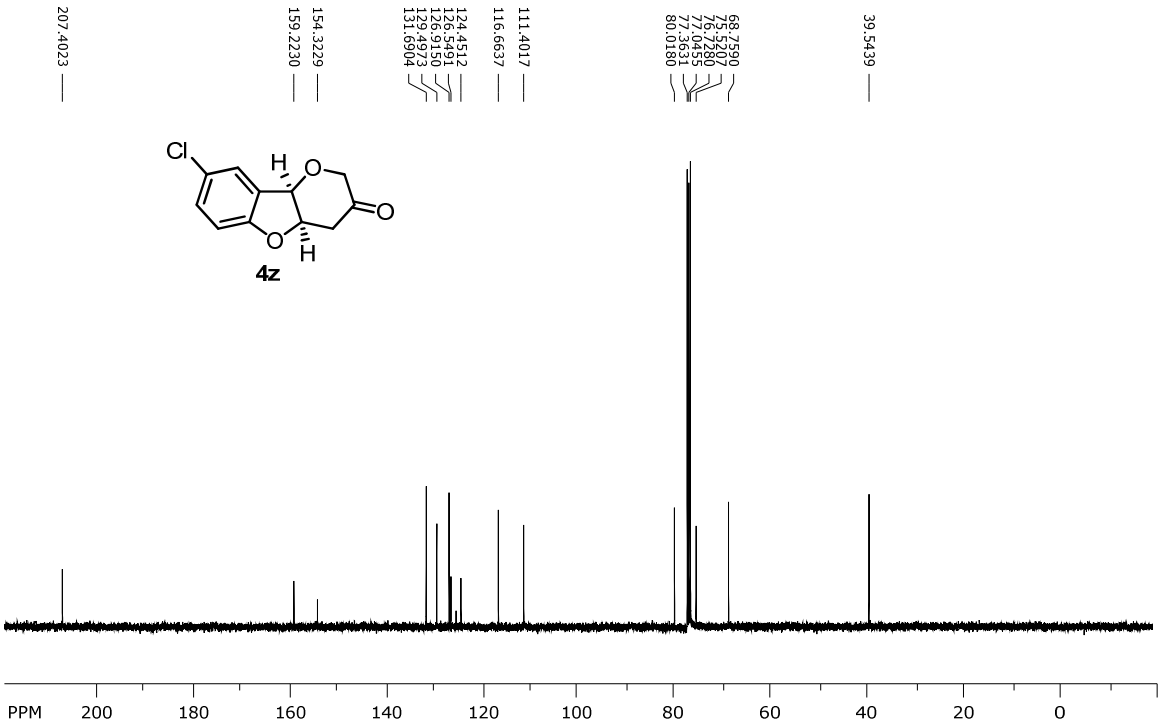
7.3048
7.2991
7.2649
7.2140
7.1919
6.8044
6.7967
6.7912
6.7828
6.7746
5.5262
5.5077
5.2498
5.2407
5.2317
5.2222
3.9975
3.9522
3.5854
3.5401
3.0614
3.0523
3.0433
3.0386
1.2743
Cl
H
O
O
O
H
4z
1.998
1.171
1.879
1.000
0.998
0.998
1.040
1.944
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0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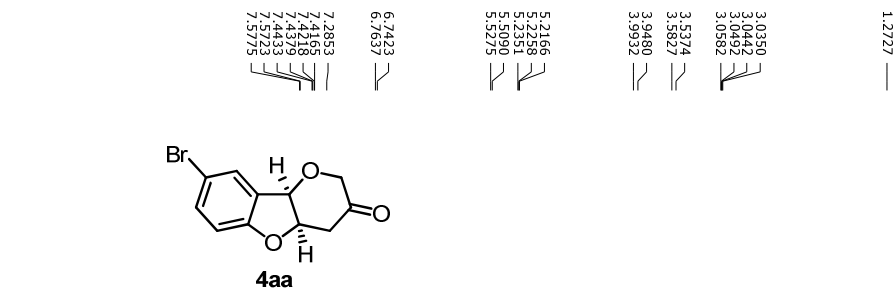
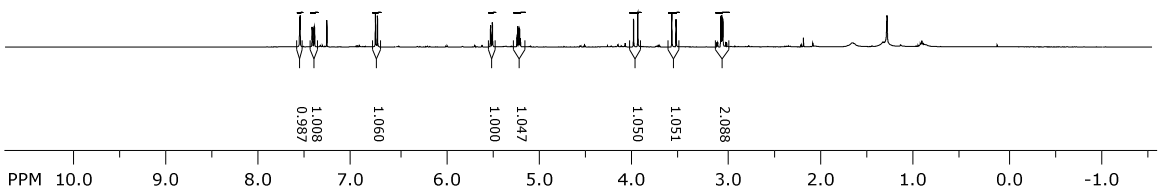
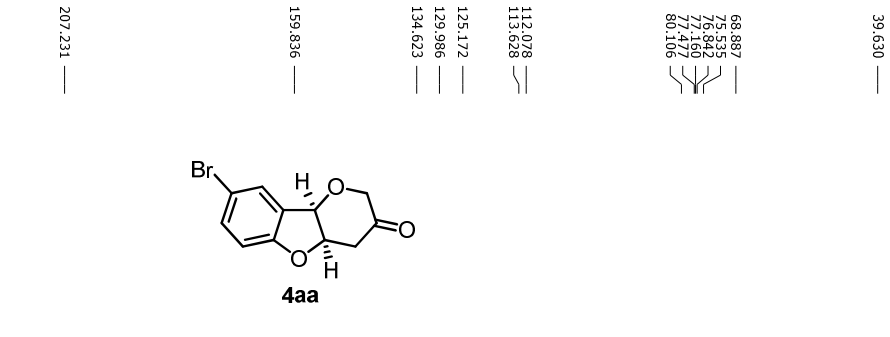
159.2230
154.3229
131.6904
129.4973
126.9150
126.5491
124.4512
116.6637
111.4017
80.0180
77.3631
77.0455
76.7280
75.5207
68.7590
39.5439
Cl
H
O
O
O
H
4z
PPM
200
180
160
140
120
100
80
60
40
20
0


7.5775
7.5723
7.4433
7.4379
7.4218
7.4165
7.2853
6.7637
6.7423
5.5275
5.5090
5.2351
5.2258
5.2166
3.9932
3.9480
3.5827
3.5374
3.0582
3.0492
3.0350
1.2727
Br
H
O
O
O
H

4aa


0.987
1.008
1.060
1.000
1.047
1.050
1.051
2.088
PPM 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0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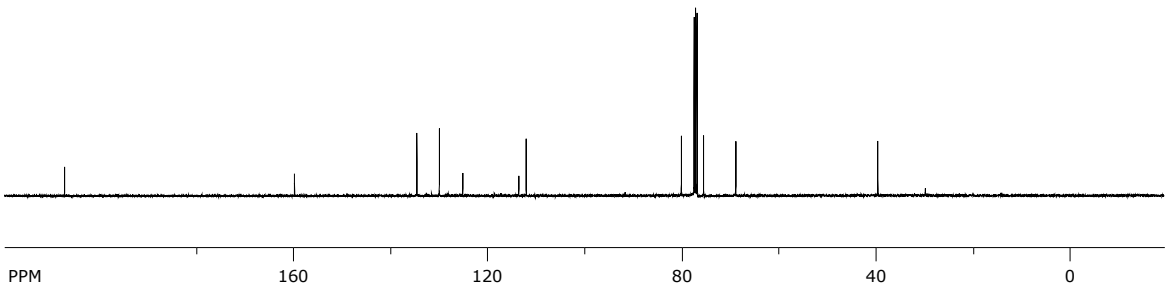
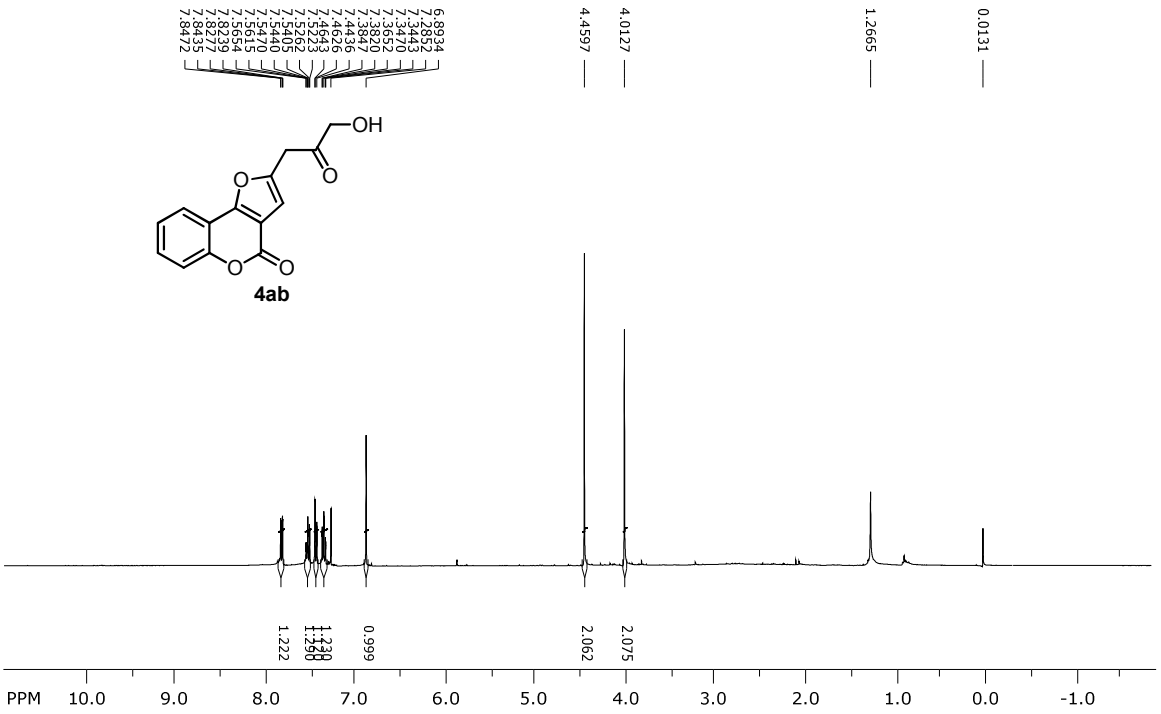
159.836
134.623
129.986
125.172
113.628
112.078
80.106
77.477
77.160
76.842
75.535
68.887
39.630
Br
H
O
O
O
H

4aa


PPM 160 120 80 40 0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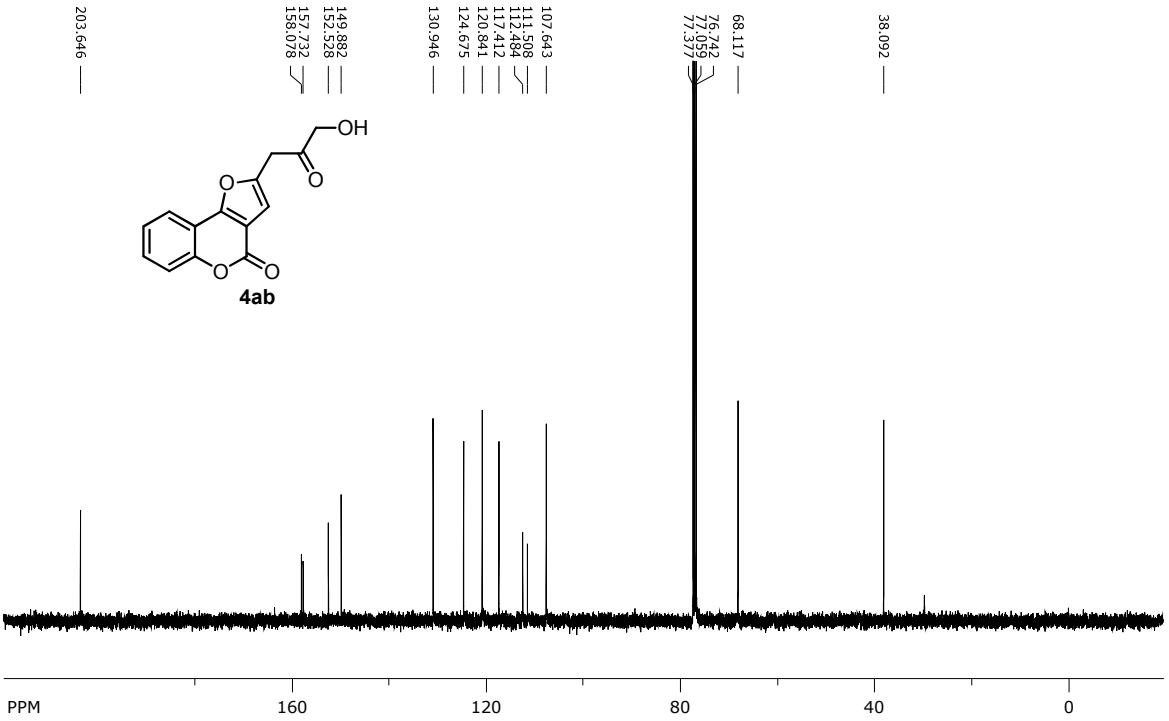
7.2852
7.3443
7.3470
7.3652
7.3820
7.3847
7.4436
7.4626
7.5223
7.5262
7.5405
7.5440
7.5470
7.5615
7.5654
7.8239
7.8277
7.8433
7.8472
4.4597
4.0127
1.2665
0.0131
OH
O
O
O
O
4ab
1.222
1.230
1.250
1.290
0.999
2.062
2.075
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0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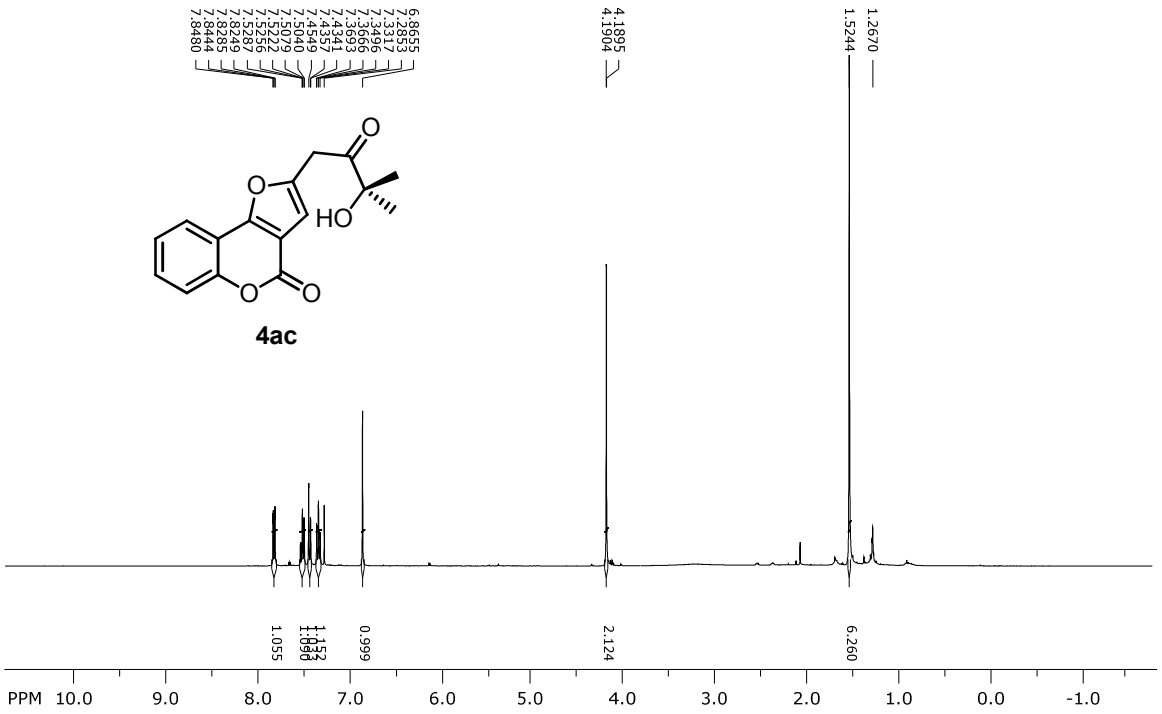
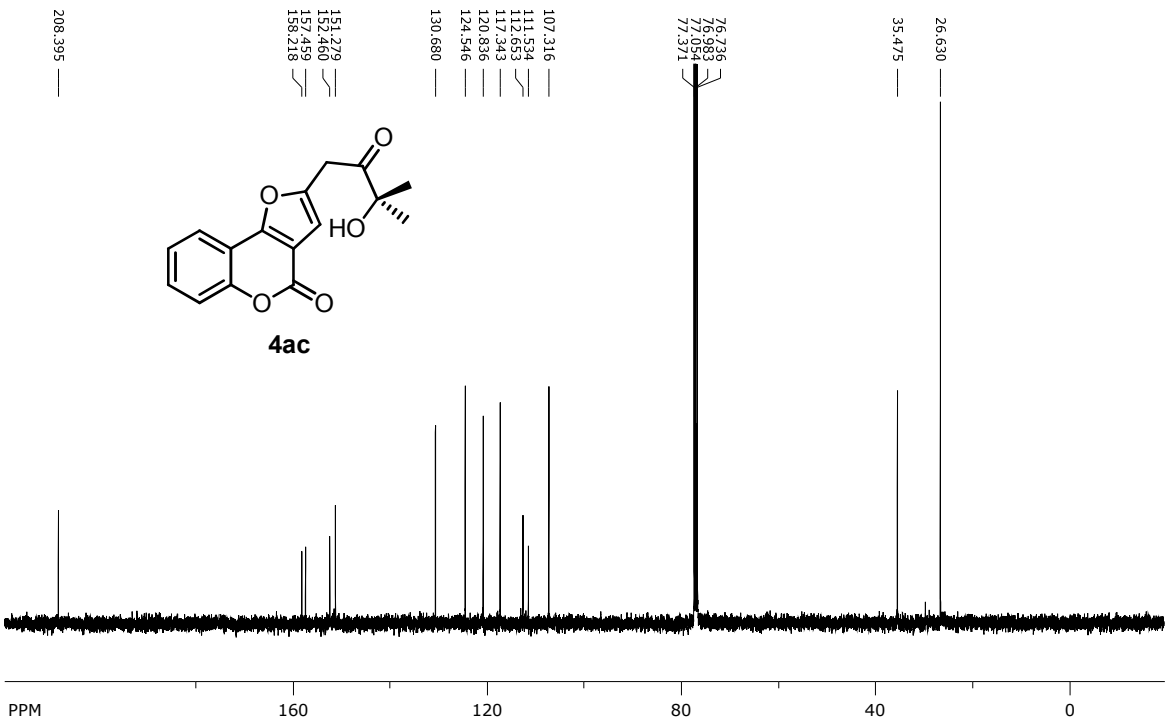
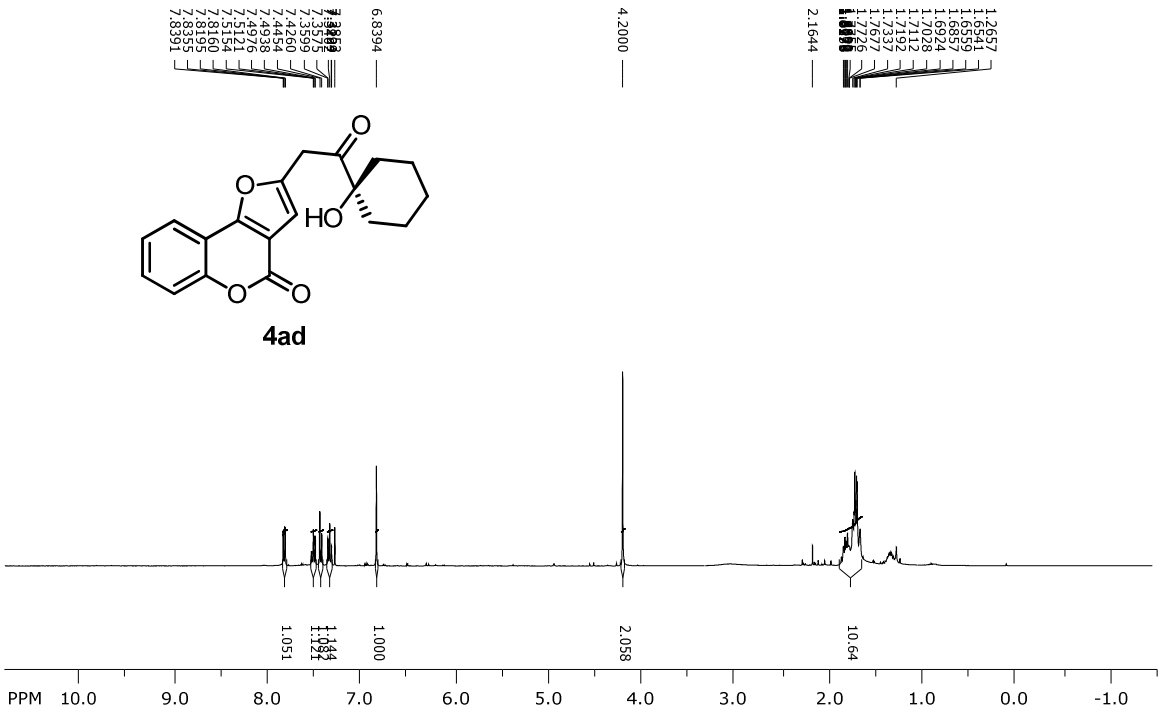
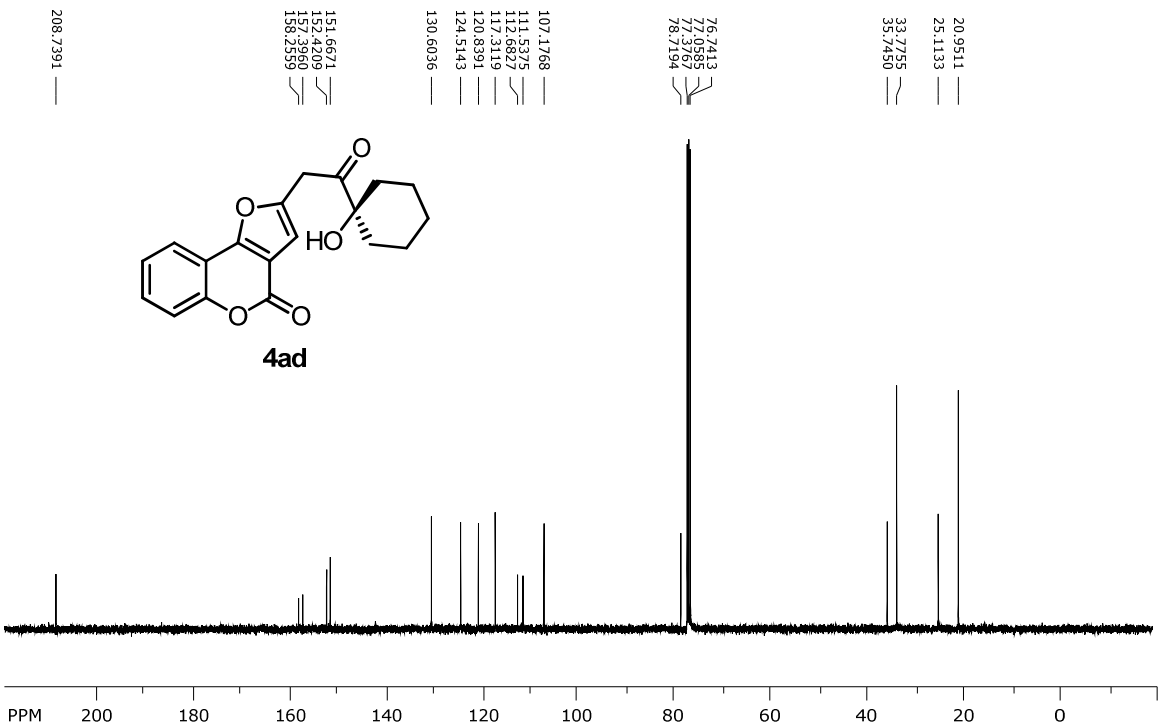
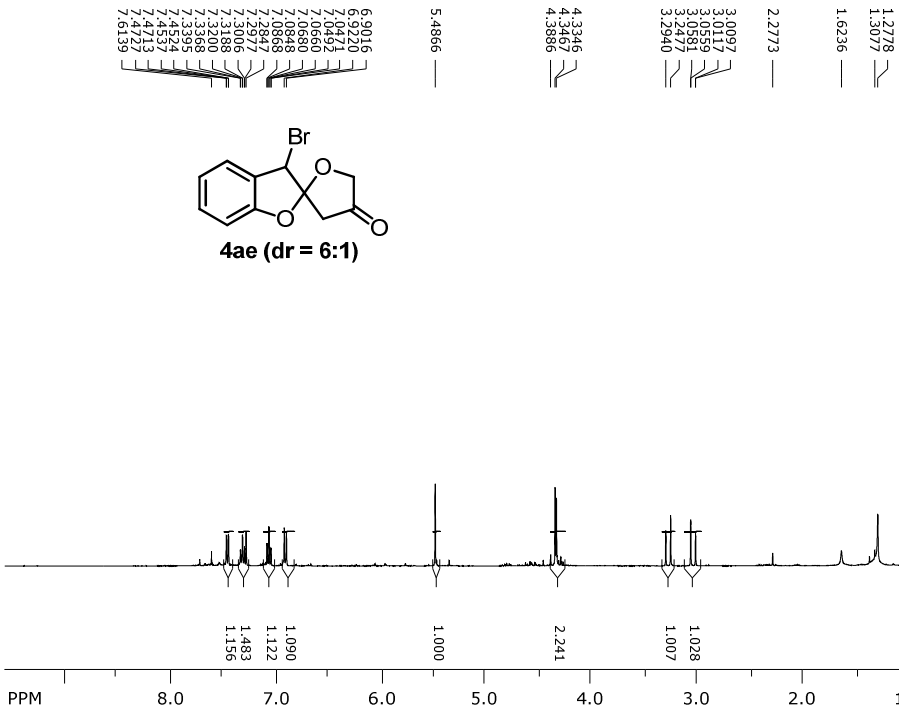
158.078
157.732
152.528
149.882
130.946
124.675
120.841
117.412
112.484
111.508
107.643
77.377
77.059
76.742
68.117
38.092
OH
O
O
O
O
4ab
PPM
160
120
80
40
0


4ac
PPM 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0


4ac
PPM 160 120 80 40 0


4ad
PPM 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0


4ad
PPM 200 180 160 140 120 100 80 60 40 20 0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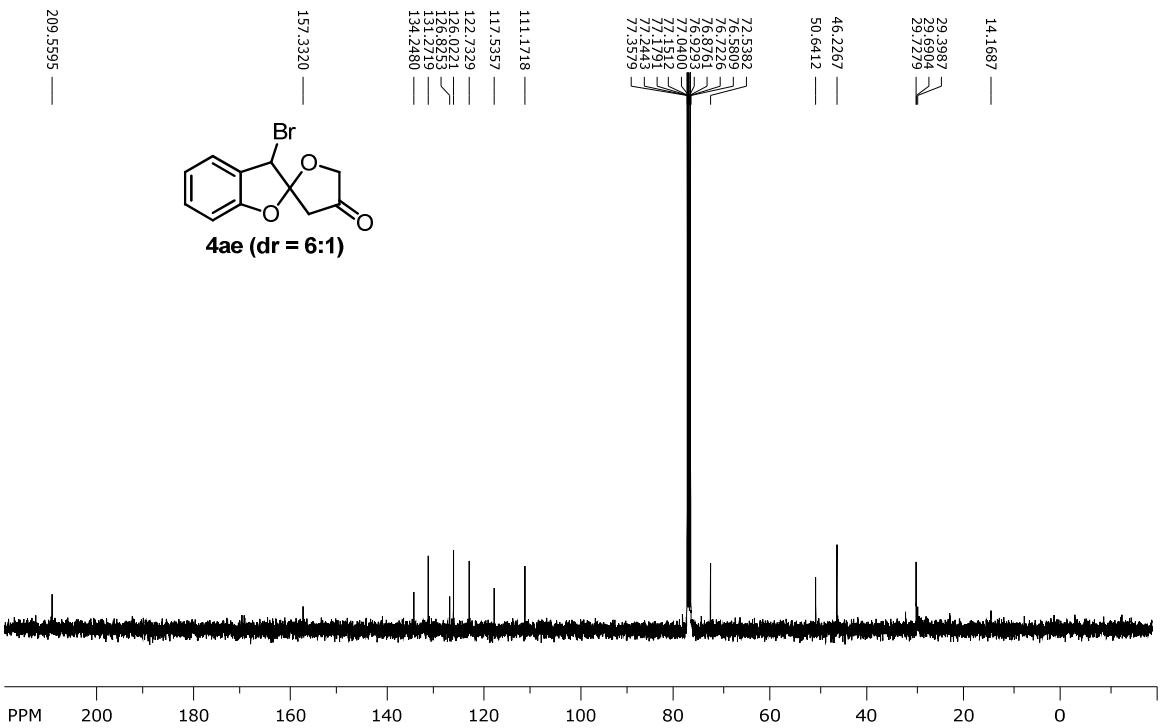
7.4727
7.4713
7.4537
7.4524
7.3395
7.3369
7.3188
7.3006
7.2977
7.2847
7.0868
7.0680
7.0660
7.0462
6.9220
6.9016
5.4866
4.3886
4.3869
4.3346
3.2940
3.2477
3.0581
3.0559
3.0117
3.0097
2.2773
1.6236
1.3077
1.2778
Br
O
O
O
4ae (dr = 6:1)
1.156
1.483
1.122
1.090
1.000
2.241
1.007
1.028
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0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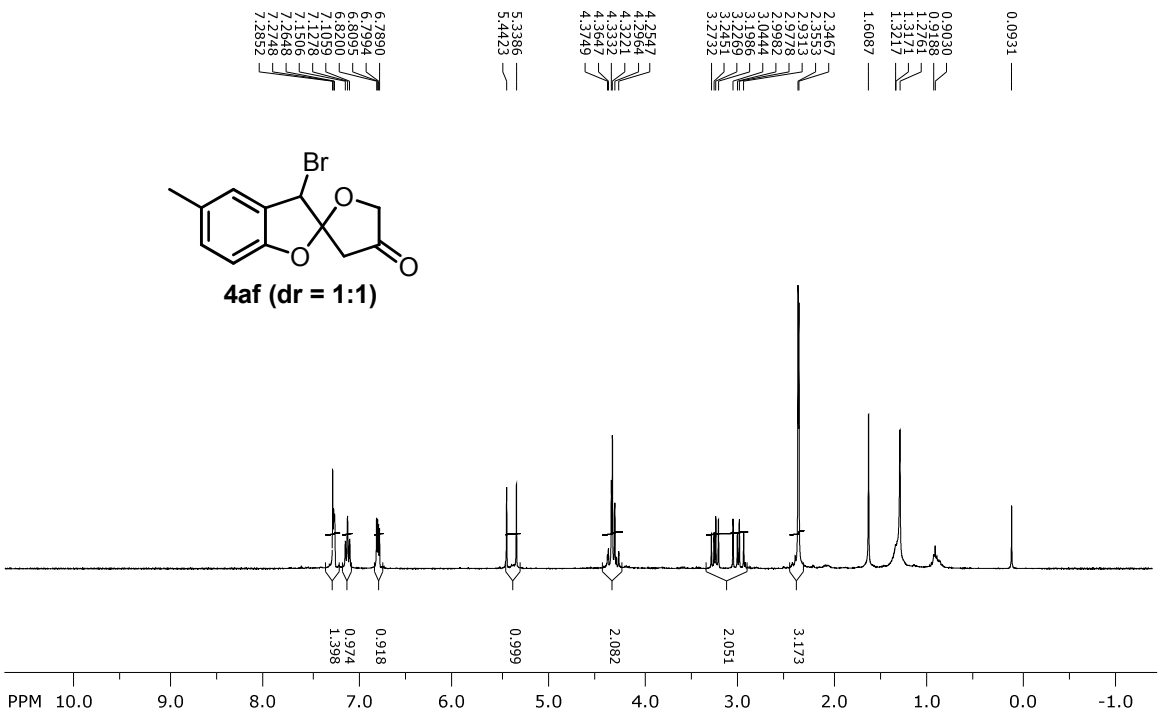
134.2480
131.2719
126.8253
126.0221
122.7329
117.5357
111.1718
77.3579
77.2443
77.1791
77.1512
77.0400
76.9293
76.8761
76.7226
76.5809
72.5382
50.6412
46.2267
29.7279
29.6904
29.3987
14.1687
Br
O
O
O
4ae (dr = 6:1)
PPM
200
180
160
140
120
100
80
60
40
20
0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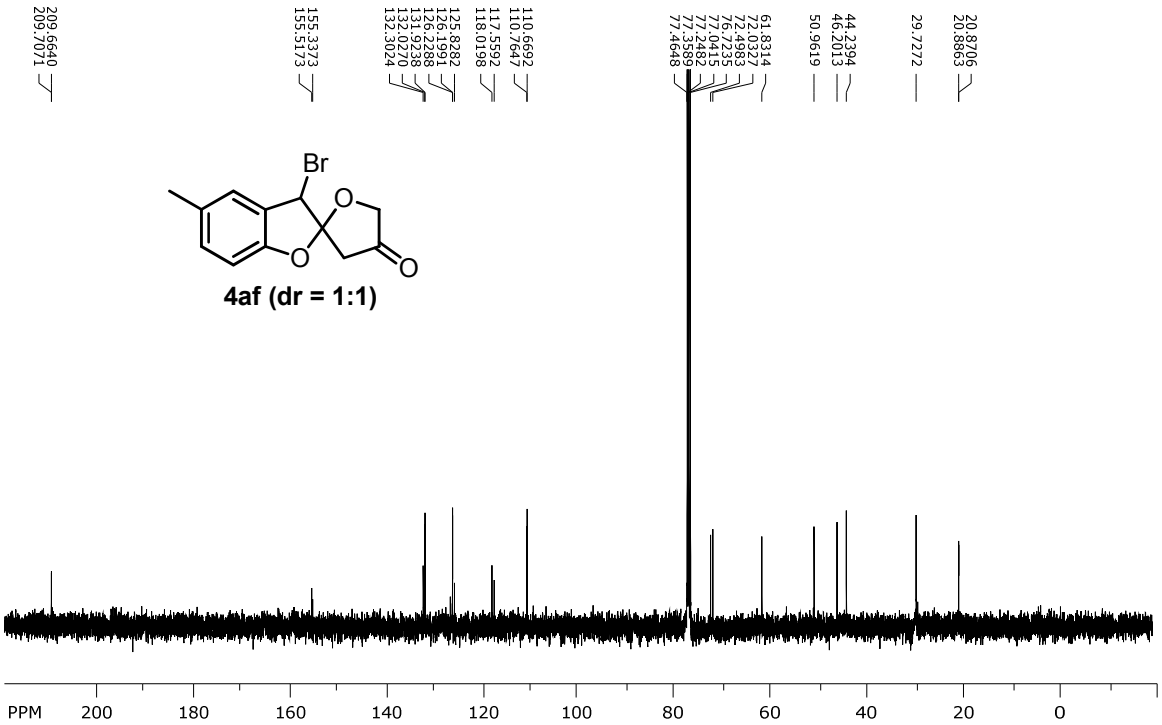
7.2748
7.2648
7.1506
7.1278
7.1059
6.8005
6.7994
6.7890
5.4423
5.3386
4.3749
4.3647
4.3332
4.3221
4.2964
4.2547
3.2732
3.2451
3.2269
3.1986
3.0444
2.9982
2.9778
2.9313
2.3563
2.3467
1.6087
1.3217
1.3171
1.2761
0.9188
0.9030
0.0931
Br
O
O
O
4af (dr = 1:1)
1.398
0.974
0.918
0.999
2.082
2.051
3.173
PPM 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0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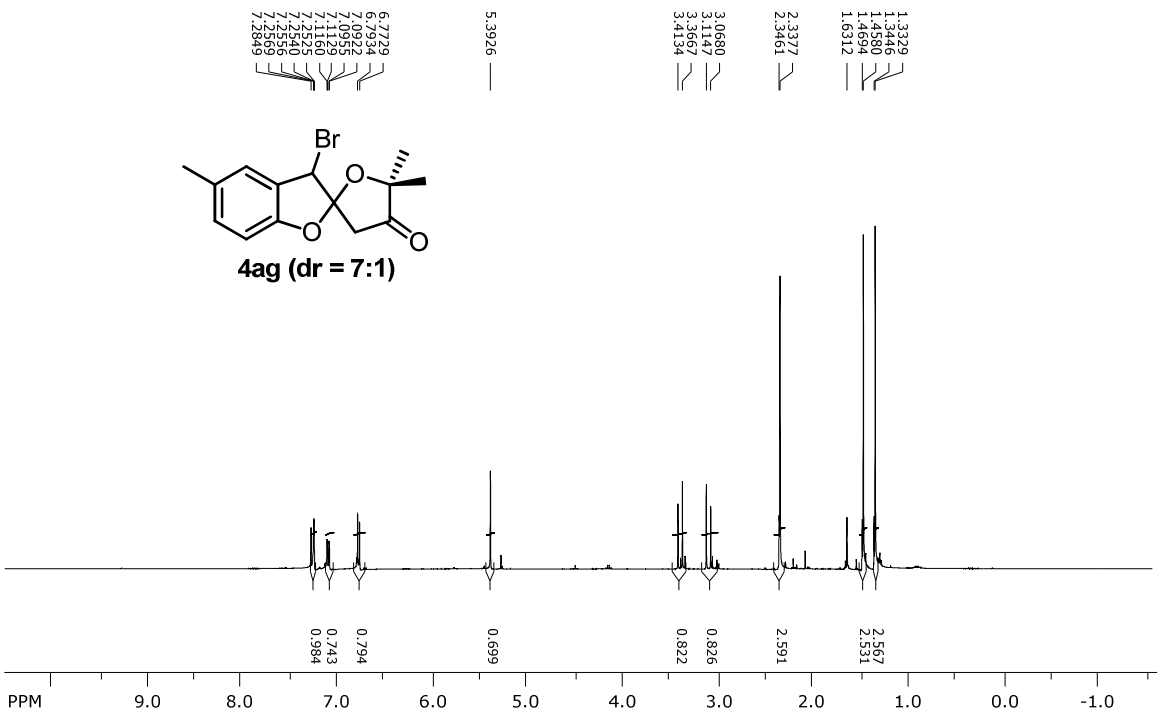
209.6640
155.5173
155.3373
132.3024
132.0270
131.9238
126.2288
126.1991
125.8282
118.0198
117.5592
110.7647
110.6692
77.4648
77.3589
77.2482
77.0415
76.7235
72.4983
72.0327
61.8314
50.9619
46.2013
44.2394
29.7272
20.8863
20.8706
Br
O
O
O
4af (dr = 1:1)
PPM 200 180 160 140 120 100 80 60 40 20 0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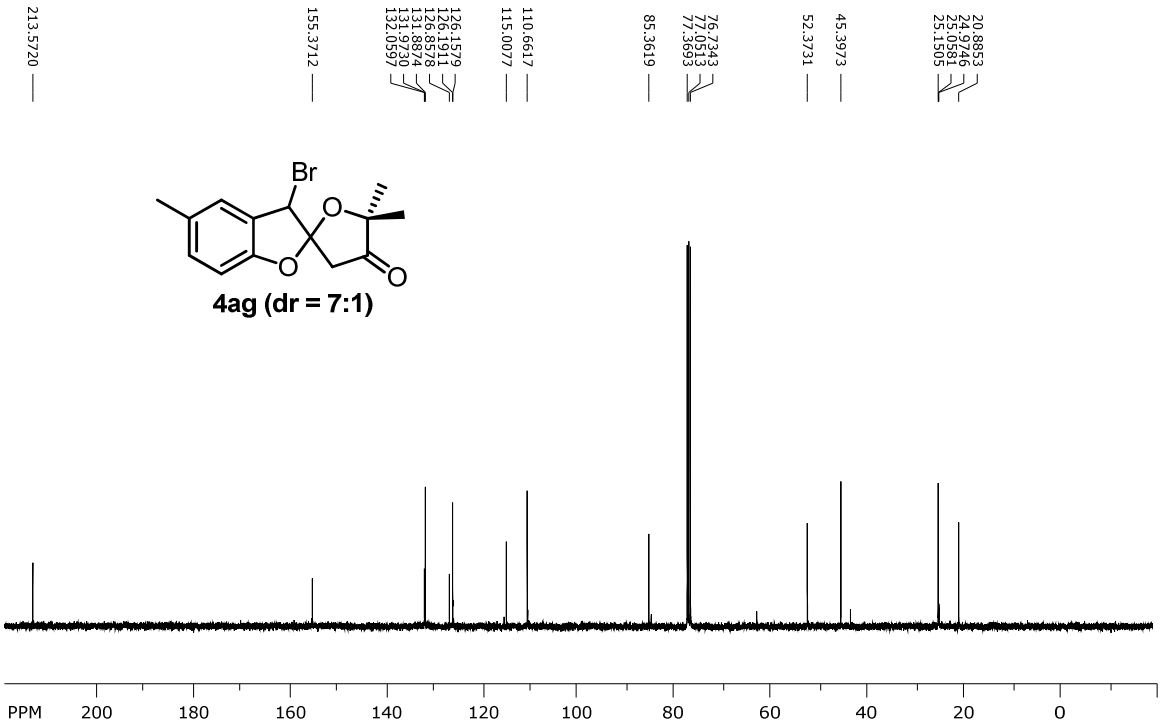
7.2856
7.2869
7.2540
7.2525
7.1160
7.1129
7.0955
7.0922
6.7934
6.7729
5.3926
3.4134
3.3667
3.1147
3.0680
2.3461
2.3377
1.6312
1.4694
1.4580
1.3446
1.3329
Br
O
O
O
4ag (dr = 7:1)
0.984
0.743
0.794
0.699
0.822
0.826
2.591
2.531
2.567
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0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155.3712
132.0597
131.9730
131.8874
126.8578
126.1911
126.1579
115.0077
110.6617
85.3619
77.3693
77.0513
76.7343
52.3731
45.3973
25.1505
25.0581
24.9746
20.8853
Br
O
O
O
4ag (dr = 7:1)
PPM
200
180
160
140
120
100
80
60
40
20
0