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Supporting Information

Silver-Catalyzed Asymmetric Synthesis of 2,3-Dihydrobenzofurans: A New Chiral Synthesis of Pterocarpans

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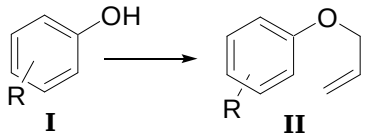
Synthetic Procedures

General procedure for the allylation of phenols Ia-d: Preparation of allylphenyl ethers IIa-c: To a stirred solution of the corresponding phenol **Ia-c** in acetone, K_2CO_3 and allyl bromide were added. The resulting solution was heated to reflux for 4-6 hours. The mixture was then diluted with CH_2Cl_2 and washed with NaOH 2M. The organic layer was dried over anhyd. Na_2SO_4, and the solvent was removed. The residue was purified by silica gel column chromatography.



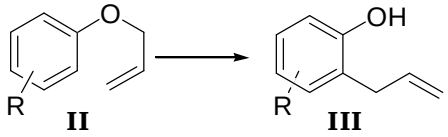
Allyl *p*-methoxyphenyl ether (IIa): Reaction of *p*-methoxyphenol (5 g, 40.27 mmol) with K_2CO_3 (5.56 g, 40.27 mmol) and allyl bromide (5.45 mL, 48.32 mmol) in acetone (30 mL) followed by workup as described above yielded **IIa** (6.31g, 38.47 mmol, 95%), as colourless oil: R_f=0.30 (hexane/Et_2O, 85:15); IR (film) ν_{max} 3074, 2999, 2942, 2839,1593, 1509, 1457, 1227, 1034, 827 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ= 6.87 (4H, m, H-2, 3, 5, 6), 6.09 (1H, ddt, *J*= 17.3, *J*= 10.4, *J*= 5.2 Hz, H-2'), 5.43 (1H, dq, *J*= 17.3, *J*= 1.6 Hz, H-3'*trans*), 5.30 (1H, dq, *J*= 10.4, *J*= 1.6 Hz, H-3'*cis*), 4.51 (2H, dt, *J*= 5.2, *J*= 1.6 Hz, H- 1'), 3.79 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.88 (C, C-4*), 152.72 (C, C-1*), 133.60 (CH, C-2'), 117.37 (CH_2, C-3'), 115.69 (CH, C-3, C-5), 114.56 (CH, C-2, C-6), 69.46 (CH_2, C-1'), 55.63 (OCH_3). * may be interchanged; HREIMS (*m/z*) calcd. for $C_{10}H_{12}O_2$ 164.0837 $[M]^+$, found 164.0836.

Allyl *m*-methoxyphenyl ether (IIb): Reaction of *m*-methoxyphenol (6 g, 48.3 mmol) with K_2CO_3 (6.67 g, 48.3 mmol) and allyl bromide (7.5 mL, 66.38 mmol) in acetone (40 mL) followed by workup as described above yielded **IIb** (7.69g, 46.93 mmol, 97%), as colourless oil: R_f=0.27 (hexane/Et_2O, 9:1); IR (film) ν_{max} 3082, 2939, 2836, 1600, 1492, 1453, 1287, 1152 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ= 7.20 (1H, dt, *J*= 7.9, *J*= 0.9 Hz, H-5), 6.50 (3H, m, H-2, 4, 6), 6.08 (1H, ddt, *J*= 17.2, *J*= 10.5, *J*= 5.4 Hz, H-2'), 5.44 (1H, dq, *J*= 17.2, *J*= 1.6 Hz, H-3'*trans*), 5.32 (1H, dq, *J*= 10.5, *J*= 1.6 Hz, H-3'*cis*), 4.55 (2H, dt, *J*= 5.4, *J*= 1.6 Hz, H- 1'), 3.81 (3H, s, OCH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.78* (C, C-3), 159.81* (C, C-1), 133.22 (CH, C-2'), 129.79 (CH, C-5), 117. 59 (CH_2, C-3'), 106.83# (CH, C-4), 106.39# (CH,

C-6), 101.20 (CH, C-2), 68.77, (CH_2, C-1'), 55.19 (OCH_3). *, # may be interchanged; HREIMS (*m/z*) calcd. for $C_{10}H_{12}O_2$ 164.0837 $[M]^+$, found 164.0838.

Allyl 3,4-methylenedioxyphenyl ether (IIc): Reaction of sesamol (4 g, 28.96 mmol) with K_2CO_3 (4 g, 28.96 mmol) and allyl bromide (2.75 mL, 31.8 mmol) in acetone (30 mL) followed by workup as described above yielded **IIc** (4.72 g, 38.47 mmol, 92%), as colourless oil: R_f=0.32 (hexane/Et_2O, 9:1); IR (film) ν_{max} 3081, 2987, 2888, 2777,1628, 1490, 1245, 1187, 1134, 1034, 930, 819, 615 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ= 6.72 (1H, d, *J*= 8.5 Hz, H-5), 6.54 (1H, d, *J*= 2.4 Hz, H-2), 6.36 (1H, dd, *J*= 8.5, *J*= 2.4 Hz, H-6), 6.05 (1H, ddt, *J*= 17.5, *J*= 10.6, *J*= 5.3 Hz, H-2'), 5.93 (2H, s, OCH_2O), 5.42 (1H, dq, *J*= 17.5, *J*= 1.3 Hz, H-3'*trans*), 5.30 (1H, dq, *J*= 10.6, *J*= 1.3 Hz, H-3'*cis*), 4.48 (2H, dt, *J*= 5.3, *J*= 1.3 Hz, H-1'). ^{13}C RMN ($CDCl_3$, 75 MHz) δ 154.02? (C, C-1), 148.15 (C, C-3), 141.64 (C, C-4), 133.31 (CH, C-2'), 117.61 (CH_2, C-3'), 107.86* (CH, C-5), 105.86* (CH, C-6), 101.08 (OCH_2O), 98.23 (CH, C-2), 69.69 (CH_2, C-1'). * may be interchanged; HREIMS (*m/z*) calcd. for $C_{10}H_{10}O_3$ 178.0629 $[M]^+$, found 178.0627.

General procedure for the Claisen rearrangement of allylphenyl ethers IIa-c: Preparation of 2-allylphenols IIIa-d: Compounds **IIa-c** were dissolved under N_2 atmosphere in *N*,*N*-dimethylaniline. The solution was heated to reflux for 10-12h. The reaction mixture was diluted with CH_2Cl_2, and washed with HCl 5%. The dried (Na_2SO_4) extract was concentrated *in vacuo* and purified by chromatography over silica gel.



II **III**

2-Allyl-4-methoxy-phenol (IIIa): Reaction of allyl *p*-methoxyphenyl ether (6.31 g, 38.47 mmol) with *N*,*N*-dimethylaniline (10 mL, 79.38 mmol) followed by workup as described above yielded **IIIa** (5.86 g, 35.78 mmol, 93%) as colourless oil: R_f=0.30 (hexane/Et_2O, 9:1); IR (film) ν_{max}, 3414, 3074, 2944, 2836, 1615, 1504, 1437, 1207, 808 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.68-6.79 (3H, m, H-3, 5, 6), 6.03 (1H, ddt, *J*= 17.8, *J*= 9.8, *J*= 6.3 Hz, H-2'), 5.17 (2H, m, H-3'), 5.01 (1H, bs, OH), 3.79 (3H, s, OCH_3) 3.41 (2H, dt, *J*= 6.3, *J*= 1.6 Hz, H-1'); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.66 (C, C-4), 147.92 (C, C-1), 136.16 (CH, C-2'), 126.62 (C, C-2), 116.41 (CH_2, C-3'), 116.41 (CH, C-6*), 115.92 (CH, C-3*), , 112.57 (CH,

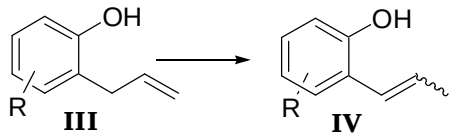
C-5), 55.71 (OCH_3), 35.11 (CH_2, C-1'). * may be interchanged; HREIMS (*m/z*) calcd. for $C_{10}H_{12}O_2$ 164.0837 $[M]^+$, found 164.0835.

2-Allyl-5-methoxyphenol (IIIb) and 2-Allyl-3-methoxyphenol (IIId): Reaction of allyl-*m*-methoxyphenyl ether (7.6 g, 46.34 mmol) with *N*,*N*-dimethylaniline (15 mL, 119 mmol) followed by workup as described above yielded **IIIb** and **IIId.** Compound **IIIb** (2.84 g, 17.2 mmol, 37%) as colourless oil: R_f=0.34 (hexane/Et_2O, 9:1); IR (film) ν_{max} 3432, 3077, 2938, 2837, 1619, 1595, 1518, 1434, 1285, 1202, 1161, 1113, 1036, 959, 915, 834, 632 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ= 7.03 (1H, d, *J*= 8.2 Hz, H-3), 6.49 (1H, dd, *J*= 8.2, *J*= 2.7 Hz, H-4), 6.45 (1H, d, *J*= 2.7 Hz, H-6), 6.03 (1H, ddt, *J*= 17.7, *J*= 9.5, *J*= 6.5 Hz, H-2'), 5.39 (1H, bs, OH), 5.14-5.22 (2H, m, H-3'), 3.79 (3H, s, OCH_3) 3.38 (2H, d, *J*= 6.5 Hz, H-1'). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.46* (C, C-5), 154.95* (C, C-1), 136.80 (CH, C-2'), 130.81 (CH, C-3), 117.54 (C, C-2), 116.11 (CH_2, C-3'), 106.24 (CH, C-4), 102.01 (CH, C-6), 55.28 (OCH_3), 34.38 (CH_2, C-1'). * may be interchanged; HREIMS (*m/z*) calcd. for $C_{10}H_{12}O_2$ 164.0837 $[M]^+$, found 164.0836.Compound **IIId** (4 g, 24.4 mmol, 53%) as colourless oil: R_f=0.30 (hexane/Et_2O, 9:1); IR (film) ν_{max}, 3446, 3075, 2947, 2838, 1598, 1468, 1329, 1282, 1210, 1075, 997, 777, 735 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.12 (1H, t, *J*= 8.3 Hz, H-5), 6.54* (1H, bd, *J*= 8.3 Hz, H-4), 6.53* (1H, bd, *J*= 8.3 Hz, H-6), 6.03 (1H, ddt, *J*= 17.2, *J*= 10.0, *J*= 6.0 Hz, H-2'), 5.23 (1H, bs, OH), 5.15 (1H, ddt, *J*= 17.2, *J*= 1.7, *J*= 1.7 Hz, H-3'*trans*), 5.12 (1H, ddt, *J*= 10.0, *J*= 1.7, *J*= 1.7 Hz, H-3'*cis*), 3.84 (3H, s, OCH_3) 3.51 (2H, dt, *J*= 6.0, *J*= 1.7 Hz, H-1'). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 155.70 (C, C-3), 152.50 (C, C-1), 133.81 (CH, C-2'), 124.98 (CH, C-5), 112.75 (CH_2, C-3'), 111.19 (C, C-2), 106.25* (C, C-4), 100.82* (CH, C-6), 53.28 (OCH_3), 24.78 (CH_2, C-1') * may be interchanged; HREIMS (*m/z*) calcd. for $C_{10}H_{12}O_2$ 164.0837 $[M]^+$, found 164.0838.

2-Allyl-4,5-methylenedioxyphenol (IIIc): Reaction of allyl- 3,4-methylenedioxyphenyl ether **(IIc)** (4.72 g, 26.38 mmol) with *N*,*N*-dimethylaniline (10 mL, 79.38 mmol) followed by workup as described above yielded **IIIc** (4.30 g, 24.0 mmol, 91%) as white solid. m.p 74-76 ºC: R_f=0.29 (hexane/Et_2O, 85:15); IR (film) ν_{max}, 3256, 2905, 1637, 1505, 1458, 1212, 1166, 1035, 918 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 6.60 (1H, s, H-3), 6.45 (1H, s, H-6), 5.97 (1H, ddt, *J*= 17.5, *J*= 9.5, *J*= 6.3 Hz, H-2'), 5.90 (2H, s, OCH_2O), 5.12-5.20 (2H, m, H-3'), 4.83 (1H, bs, OH), 3.33 (2H, dt, *J*= 6.3, *J*= 1.5 Hz, H-1'). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.56 (C, C-1), 146.68 (C, C-5), 141.42 (C, C-4), 136.34 (CH, C-2'), 116.60 (C, C-2),

116.41 (CH_2, C-3'), 109.47 (CH, C-3), 100.95 (OCH_2O), 98.62 (CH, C-6), 35.03 (CH_2, C-1'). HREIMS (*m/z*) calcd. for $C_{10}H_{10}O_3$ 178.0629 $[M]^+$, found 178.0626.

General procedure for the isomerization of 2-allylphenols (IIIa-c): Preparation of 2-(1-propenyl)phenols (IVa-c): Allylphenols were dissolved in DMSO, under N_2 atmosphere, and sodium *tert*-butoxide was added. The mixture was stirred at 60ºC for 12 h, then was cooled to 0ºC and quenched by addition of HCl 5%. The aqueous layer was extracted with CH_2Cl_2. After washing with brine, the dried (Na_2SO_4) extract was concentrated *in vacuo* and purified by chromatography over silica gel.



4-Methoxy-2-(1-propenyl)phenol (IVa): Reaction of 2-allyl-4-methoxy-phenol (5.86 g, 35.78 mmol) with sodium *tert*-butoxide (13.7 g, 143 mmol) in DMSO (125 mL) followed by workup as described above yielded **IVa** (4.86 g, 29.6 mmol, 83%) as colourless oil and a mixture of *cis* /*trans* isomers (1:12): R_f=0.29 (hexane/Et_2O, 9:1); IR (film) ν_{max}, 3472, 2947, 2838, 1605, 1499, 1435, 1354, 1276, 1204, 810 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz), *(signals of trans isomer)* δ 6.62 (1H, dq, *J*= 15.8 Hz, *J*= 1.8 Hz, H-1'), 6.22 (1H, dq, *J*= 15.8, *J*= 6.7 Hz, H-2'), 1.92 (3H, dd, *J*= 6.7, *J*= 1.8 Hz, H-3'), *(signals of cis isomer)* δ 6.41 (1H, dq, *J*= 11.5, *J*=1.9 Hz, H-1'), 6.00 (1H, dq, *J*= 11.5, *J*= 6.4 Hz, H-2'), 1.77 (3H, dd, *J*= 6.4, *J*=1.9 Hz, H-3'), *(signals of both)* δ 6.91 (1H, d, *J*= 2.9 Hz, H-3), 6.74 (1H, d, *J*= 8.8 Hz, H-6), 6.68 (1H, dd, *J*= 8.8, *J*= 2.9 Hz, H-5), 5.38 (1H, bs, OH), 3.79 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) *(signals of trans isomer)*, δ 128.03 (CH, C-1'), 125.31 (CH, C-2'), 18.77 (CH_3, C-3'). *(signals of cis isomer)* δ 130.80 (CH, C-1'), 124.15 (CH, C-2'), 14.54 (CH_3, C-3'). *(signals of both)* δ 153.54 (C, C-4), 146.60 (C, C-1), 125.88 (C, C-2), 116.50 (CH, C-6), 113.49 (CH, C-5), 111.98 (CH, C-3), 55.77 (OCH_3); HREIMS (*m/z*) calcd. for $C_{10}H_{12}O_2$ 164.0837 $[M]^+$, found 164.0834.

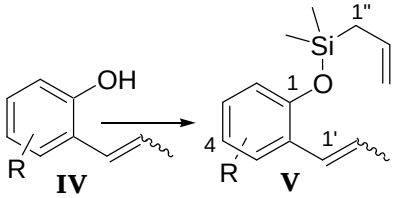
5-Methoxy-2-(1-propenyl)phenol (IVb): Reaction of 2-allyl-5-methoxy-phenol (2.68 g, 16.3 mmol) with sodium *tert*-butoxide (6.2 g, 65.3 mmol) in DMSO (80 mL) followed by workup

as described above yielded **IVb** (2.2 g, 13.5 mmol, 83%) as colourless oil and a mixture of *cis* /*trans* isomers (1:4): R_f=0.31 (hexane/Et_2O, 85:15); IR (film) ν_{max}, 3512, 2957, 2839, 2248, 1613, 1509, 1443, 1291, 1158, 1109, 959, 834 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz), (*signals of trans isomer*) δ= 7.21 (1H, d, *J*= 8.9, Hz, H-3), 6.09 (1H, dq, *J*= 15.7, *J*= 6.5 Hz, H-2'), 3.78 (3H, s, OCH_3), 1.91 (3H, dd, *J*= 6.5, *J*= 1.7 Hz, H-3'). (*signals of cis isomer*) δ= 7.04 (1H, d, *J*= 9.2, Hz, H-3), 5.99 (1H, dq, *J*= 10.9, *J*= 6.5 Hz, H-2'), 3.81 (3H, s, OCH_3), 1.73 (3H, dd, *J*= 6.5, *J*= 1.7 Hz, H-3'). (*signals of both*) δ 6.50 (3H, m, H-1', H-4, OH), 6.40 (1H, d, *J*= 2.4 Hz, H-6).^{13}C NMR ($CDCl_3$, 75 MHz) (*signals of trans isomer*), δ= 128.07* (CH, C-1'), 126.37* (CH, C-3), 124.98 (CH, C-2'), 106.59 (CH, C-4), 101.45 (CH, C-6), 18.77 (CH_3, C-3'). (*signals of cis isomer*) δ=130.39* (CH, C-1'), 130.15* (CH, C-3), 123.70 (CH, C-2'), 106.29 (CH, C-4), 100.67 (CH, C-6), 14.48 (CH_3, C-3'). (*signals of both*) δ 159.57 (C, C-5), 153.36 (C, C-1), 117.95 (C, C-2), 55.26 (OCH_3) * may be interchanged; HREIMS (*m/z*) calcd. for $C_{10}H_{12}O_2$ 164.0837 $[M]^+$, found 164.0838.

4,5-Methylenedioxy-2-(1-propenyl)phenol (IVc): Reaction of 2-allyl-4,5-methylenedioxy phenol (5 g, 27.93 mmol) with sodium *tert*-butoxide (8 g, 143 mmol) in DMSO (140 mL) followed by workup as described above yielded **IVc** (2.2 g, 13.5 mmol, 83%) as white solid. m.p 68-70 ºC; and a mixture of *cis* /*trans* isomers (1:8): R_f=0.30 (hexane/Et_2O, 85:15); IR (film) ν_{max}, 3476, 2899, 1627, 1489, 1442, 1287, 1239, 1170,1038, 933, 863, 753 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz), (*signals of trans isomer*) δ= 6.79 (1H, s, H-3), 6.53 (1H, dd, *J*= 15.7, *J*= 1.7 Hz, H-1'), 6.40 (1H, s, H-6), 6.04 (1H, dq, *J*= 15.7, *J*= 6.6 Hz, H-2'), 5.90 (2H, s, OCH_2O), 1.90 (3H, dd, *J*= 6.6, *J*= 1.7 Hz, H-3'). (*signals of cis isomer*) δ= 6.59 (1H, s, H-3), 6.48 (1H, s, H-6), 5.92 (2H, s, OCH_2O), 1.73 (3H, dd, *J*= 7.1, *J*=1.9 Hz, H-3'). (*signals of both*) δ= 4.93 (1H, bs, OH). ^{13}C NMR ($CDCl_3$, 75 MHz) (*signals of trans isomer*) δ= 124.78 (CH, C-2'), 105.82 (CH, C-3), 98.12 (CH, C-6), 18.70 (CH_3, C-3'). (*signals of cis isomer*) δ 123.89 (CH, C-2'), 108.31 (CH, C-3), 97.48 (CH, C-6), 14.48 (CH_3, C-3'). (*signals of both*) δ= 147.12* (C, C-1), 146.93* (C, C-5), 141.76 (C, C-4), 126.41 (CH, C-1'), 117.32 (C, C-2), 100.97 (OCH_2O). * may be interchanged; HREIMS (*m/z*) calcd. for $C_{10}H_{10}O_3$ 178.0629 $[M]^+$, found 178.0629.

General procedure for the sililation of 2-(1-propenyl)phenols (IVa-c and IVe): Preparation of allyl(2-(1-propenyl)phenoxy)dimethylsilanes (Va-c and Ve): 2-(1-

Propenyl)phenols were dissolved in anhydrous CH_2Cl_2 at 0ºC under N_2 atmosphere. NEt_3 anhydrous and allylchlorodimethylsilane were added. The reaction mixture was stirred at 0ºC for 4h, and then, a saturated solution of $NaHCO_3/H_2O$ was added The reaction mixture was extracted with CH_2Cl_2. The organic layer was dried over anhyd. Na_2SO_4, and concentrated *in vacuo*. The residue was purified by flash chromatography.



Allyl(4-methoxy-2-(1-propenyl)phenoxy)dimethylsilane (Va): Reaction of 4-methoxy-2-(1-propenyl)phenol (**IVa**) (4.86 g, 29.6 mmol) with NEt_3 anhydrous (4.9 mL, 35.52 mmol) and allylchlorodimethylsilane (4.75 mL, 32.56 mmol) in anhydrous CH_2Cl_2 (200 mL) followed by workup as described above yielded **Va** (10.7 g, 41 mmol, 87%) (*cis*:*trans* 1:12); R_f=0.35 (hexane/Et_2O, 98:2); as a colourless oil: IR (film) ν_{max}, 2956, 1626, 1489, 1429, 1262, 1215, 904, 827 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz), (*signals of the mayor isomer)* δ=?6.96 (1H, d, *J*= 2.9 Hz, H-3), 6.74 (1H, d, *J*= 8.7 Hz, H-6), 6.67 (1H, dd, *J*= 8.7, *J*=2.9 Hz, H-5), 6.64 (1H, dq, *J*= 15.8, *J*= 1.9 Hz, H-1'), 6.20 (1H, dq, *J*= 15.8, *J*= 6.5 Hz, H-2'), 5.84 (1H, ddt, *J*= 16.8, *J*= 10.0, *J*=8.1 Hz, H-2''), 4.97 (2H, m, H-3''), 3.79 (3H, s, OCH_3), 1.91 (3H, dd, *J*=6.5, *J*=1.9 Hz, H-3'), 1.79 (2H, d, *J*= 8.1 Hz, H-1''), 0.26 (6H, s, $SiMe_2$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ= 154.23 (C, C-4), 145.80 (C, C-1), 133.34 (CH, C-2''), 129,81 (C, C-2), 126.15* (CH, C-1'), 126.13* (CH, C-2'), 120.37 (CH, C-6), 114.24 (CH_2, C-3''), 113.02 (CH, C-5), 110.89 (CH, C-3), 55.49 (OCH_3), 24.63 (CH_2, C-1''), 18.74 (CH_3, C-3'), -1.75 ($SiMe_2$). * may be interchanged. HREIMS (*m/z*) calcd. for $C_{15}H_{22}O_2Si$ 262.1389 $[M]^+$, found 262. 1385.

Allyl(5-methoxy-2-(1-propenyl)phenoxy)dimethylsilane (Vb): Reaction of 5-methoxy-2-(1-propenyl)phenol (**IVb**) (2.15 g, 13.16 mmol) with NEt_3 anhydrous (2.2 mL, 15.8 mmol) and allylchlorodimethylsilane (2.3 mL, 15.8 mmol) in anhydrous CH_2Cl_2 (60 mL) followed by workup as described above yielded **Vb** (3 g, 11.47 mmol, 87%) (*cis*:*trans* 1:4); R_f=0.37 (hexane/Et_2O, 98:2); as a colourless oil: IR (film) ν_{max}, 2957, 1608, 1497, 1434, 1264, 1164, 1038, 997 cm^{-1}.^1H NMR ($CDCl_3$, 300 MHz), (*signals of trans isomer*) δ 7.35 (1H, d, *J*= 8.8 Hz, H-3), 5.86 (1H, ddt, *J*= 17.0, *J*= 9.7, *J*=8.1 Hz, H-2''), 3.79 (3H, s, OCH_3), 1.91 (3H, dd, *J*= 6.4, *J*= 1.6 Hz, H-3'), 1.82 (2H, bd, *J*= 8.1 Hz, H-1''), 0.31 (6H, s, Me_2Si). (*signals of cis*

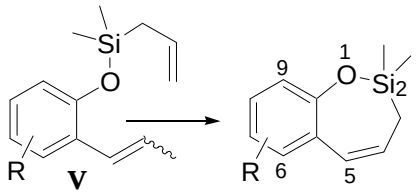
isomer) δ= 7.23 (1H, d, *J*= 8.1 Hz, H-3), 5.76 (1H, ddt, *J*= 11.3, *J*= 7.3, *J*=6.5 Hz, H-2''), 3.81 (3H, s, OCH_3), 1.85 (3H, dd, *J*= 6.4, *J*= 1.6 Hz, H-3'), 1.79 (2H, bd, *J*= 8.1 Hz, H-1''), 0.31 (6H, s, Me_2Si). (signals of both) δ 6.59 (1H, m, H-1'), 6.54 (1H, dd, *J*= 8.8, *J*= 2.4 Hz, H-4), 6.39 (1H, d, *J*= 2.4 Hz, H-6), 6.09 (1H, m, H-2'), 4.91-5.03 (2H, m, H-3''). ^{13}C NMR ($CDCl_3$, 75 MHz) (*signals of trans isomer*) δ= 133.22 (CH, C-2''), 126.78 (CH, C-3), 125.62 (CH, C-1'), 123.70 (CH, C-2'), 114.38 (CH_2, C-3''), 107.20 (CH, C-4), 105.90 (CH; C-6), 18.73 (CH_3, C-3'). (*signals of cis isomer*) δ= 133.30 (CH, C-2''), 130.57 (CH, C-3), 125.46 (CH, C-1'), 125.30 (CH, C-2'), 114.27 (CH_2, C-3''), 106.26* (CH, C-4), 106.11* (CH, C-6), 14.58 (CH_3, C-3'). (*signals of both*) δ= 159.21 (C, C-5), 152.67 (C, C-1), 122.40 (C, C-2), 55.18 (OCH_3), 24.63 (CH_2, C-1''), -1.77 (Me_2Si). * may be interchanged; HRFABMS (*m/z*) calcd. for $C_{15}H_{22}O_2Si$ 285.1287 $[M+Na]^+$, found 285.1288.

Allyl(4,5-methylenedioxy-2-(1-propenyl)phenoxy)dimethylsilane (Vc): Reaction of 4,5-methylenedioxy-2-(1-propenyl)phenol (**IVc**) (2.40 g, 13.4 mmol) with NEt_3 anhydrous (2.24 mL, 16.11 mmol) and allylchlorodimethylsilane (2.35 mL, 16.11 mmol) in anhydrous CH_2Cl_2 (60 mL) followed by workup as described above yielded **Vc** (3 g, 12.1 mmol, 90%) (*cis*:*trans* 1:8); R_f=0.35 (hexane/Et_2O, 98:2); as a colourless oil: IR (film) ν_{max}, 2962, 2891, 1626, 1481, 1431, 1249, 1177, 1039, 897, 844 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz), (*signals of trans isomer*) δ=6.90 (1H, s, H-3), 6.58 (1H, dd, *J*= 15.8, *J*= 1.8 Hz, H-1'), 6.36 (1H, s, H-6), 6.01 (1H, dq, *J*= 15.8, *J*= 6.7 Hz, H-2'), 5.91 (2H, s, OCH_2O), 1.88 (3H, dd, *J*= 6.7, *J*= 1.8 Hz, H-3'), 0.27 (6H, s, Me_2Si). (*signals of cis isomer*)?δ=6.78 (1H, s, H-3), 6.43 (1H,s, H-6), 5.94 (2H, s, OCH_2O), 1.84 (3H, dd, *J*=7.1, *J*= 2.0 Hz, H-3'), 0.24 (6H, s, Me_2Si). (*signals of both*) δ= 5.78 (1H, m, H-2''), 4.96 (2H, m, H-3''), 1.79 (2H, d, *J*= 8.0 Hz, H-1''). ^{13}C NMR ($CDCl_3$, 75 MHz) (*signals of trans isomer*) δ=?104.67 (CH, C-3), 101.73 (CH, C-6), 18.67 (CH_3, C-3'). (*signals of cis isomer*) 109.03 (CH, C-3), 101.91 (CH, C-6), 14.59 (CH_3, C-3'). (*signals of both*) 146.60* (C, C-1), 146.30* (C, C-5), 142.40 (C, C-4), 133.14 (CH, C-2''), 125.67 (CH, C-1'), 123.62 (CH, C-2'), 121.90 (C, C-2), 114.30 (CH_2, C-3''), 100.99 (CH_2, OCH_2O), 24.55 (CH_2, C-1''), -1.80 ($SiMe_2$). HREIMS (*m/z*) calcd. for $C_{15}H_{20}O_3Si$ 276.1182 $[M]^+$, found 276. 1180.

Allyl(2-(1-propenyl)phenoxy)dimethylsilane (Ve): Reaction of commercially available 2-propenylphenol (3 g, 22.4 mmol) with NEt_3 anhydrous (3.7 mL, 26.8 mmol) and allylchlorodimethylsilane (3.6 mL, 24.6 mmol) in anhydrous CH_2Cl_2 (110 mL) followed by

workup as described above yielded **Ve**. Compound **Ve** ***trans*** (mayor isomer) (4.55 g, 20 mmol, 90%) was purified by chromatography over silica gel (hexane/ Et_2O 98:2) as a colourless oil; IR (film) ν_{max}, 2961, 2912, 2881, 2854, 1630, 1596, 1483, 1449, 1253, 1159, 1039, 968, 915, 835 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz), δ= 7.46 (1H, dd, *J*= 7.7, *J*= 1.5 Hz, H-3), 7.13 (1H, td, *J*= 7.7, *J*= 1.5 Hz, H-5), 6.97 (1H, bt, *J*= 7.5 Hz, H-4), 6.84 (1H, dd, *J*= 8.0, *J*= 1.0 Hz, H-6), 6.71 (1H, bd, *J*= 15.9 Hz, H-1'), 6.22 (1H, dq, *J*= 15.9, *J*= 6.6 Hz, H-2'), 5.85 (1H, ddt, *J*= 16.7, *J*= 10.2, *J*= 8.2 Hz, H-2''), 5.02-4.93 (2H, m, H-3''), 1.93 (3H, dd, *J*= 6.6, *J*=1.7 Hz, H-3'), 1.82 (2H, d, *J*= 8.1 Hz, H-1''), 0.30 (6H, s, $SiMe_2$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ= 151.83 (C, C-1), 133.28 (CH, C-2''), 129,38 (C, C-2), 127.49 (CH) , 126.29 (CH), 126.10 (CH), 125.90 (CH), 121.70 (CH), 119.75 (CH), 114.34 (CH_2, C-3''), 24.69 (CH_2, C-1''), 18.83 (CH_3, C-3'), -1.67 (CH_3, $SiMe_2$). HREIMS (*m/z*) calcd. for $C_{14}H_{20}OSi$ 232.1283 $[M]^+$ found, 232.1279.

General procedure for the metathesis of allyl(2-(1-propenyl)phenoxy)dimethylsilanes (Va-c and Ve): Preparation of 2,2-dimethyl-2,3-dihydrobenzo[*f*][1,2]oxasilepins: Grubbs catalyst 2nd generation [1,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene) dichloro(phenylmethylene)-(tricyclohexylphosphine)ruthenium] was added to a stirred solution 0.02 M of allyl-(2-propenyl-phenoxy)-dimethylsilanes in anhyd. CH_2Cl_2, under N_2 atmosphere. The mixture was stirred under reflux for 30 min, and then, the solvent was removed *in vacuo*. The residue was purified by flash chromatography.



2,2-Dimethyl-7-methoxy-2,3-dihydrobenzo[*f*][1,2]oxasilepin (2): Reaction of allyl(4-methoxy-2-(1-propenyl)phenoxy)dimethylsilane (**Va**) (1.5 g, 5.7 mmol) with Grubbs catalyst 2nd generation (24 mg, 0.028 mmol) in anhyd. CH_2Cl_2 (285 mL) followed by workup as described above yielded **2** (1.13 g, 5.15 mmol, 90%) as a colourless oil: R_f=0.35 (hexane/Et_2O, 98:2); IR (film) ν_{max} 3013, 2950, 2839, 1609, 1490, 1418, 1259, 1220, 1144, 1042, 935, 890, 842, 811 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.87 (1H, d, *J*= 8.9 Hz, H-9), 6.73 (1H, dd, *J*= 8.9, *J*= 3.1 Hz, H-8), 6.63 (1H, d, *J*= 3.1 Hz, H-6), 6.33 (1H, d, *J*= 10.8 Hz, H-5), 6.09 (1H, dt, *J*= 10.8, *J*= 7.4 Hz, H-4), 3.78 (3H, s, OCH_3), 1.57 (2H, d, *J*= 7.4 Hz, H-

3), 0.31 (6H, $SiMe_2$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.81 (C, C-7), 147.10 (C, C-9a), 129.01 (C, C-5a), 128.62 (CH, C-4), 126.36 (CH, C-5), 121.83 (CH, C-9), 114.64 (CH, C-6), 113.87 (CH, C-8), 55.55 (OCH_3), 18.18 (CH_2, C-3), -0.73 ($SiMe_2$). HREIMS (m/z) calcd. for $C_{12}H_{16}O_2Si$ 220.0920 $[M]^+$, found 220.0919.

2,2-Dimethyl-2,3-dihydrobenzo[*f*][1,2]oxasilepin (5a): Reaction of allyl(2-(1-propenyl)phenoxy)dimethylsilane (**Ve**) (1.4 g, 6.2 mmol) with Grubbs catalyst 2nd generation (26 mg, 0.03 mmol) in anhyd. CH_2Cl_2 (310 mL) followed by workup as described above yielded **5a** (1.07 g, 5.6 mmol, 91%) as a colourless oil: R_f=0.34 (hexane/Et_2O, 98:2); IR (film) ν_{max} 3064, 3018, 2958, 2875, 1598, 1565, 1484, 1443 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ= 7.18 (1H, td, *J*= 7.6, *J*= 1.3 Hz, H-7)*, 7.13 (1H, dd, *J*= 7.7, *J*= 1.3 Hz, H-6), 6.99 (1H, td, *J*= 7.6, *J*= 1.3 Hz, H-8)*, 6.97 (1H, dd, *J*= 7.6, *J*= 1.3 Hz, H-9), 6.39 (1H, d, *J*=10.8 Hz, H-5), 6.10 (1H, dt, *J*= 10.8, *J*= 7.5 Hz, H-4), 1.61 (2H, d, *J*= 7.5 Hz, H-3), 0.37 (6H, $SiMe_2$).^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.18 (C, C-9a), 130.86 (CH, C-6), 128.50 (C, C-5a), 128.11 (CH, C-4), 127.86 (CH, C-7)*, 126.63 (CH, C-5), 121.39 (CH, C-8)*, 121.24 (CH, C-9), 18.24 (CH_2, C-3), -0.52 (CH_3, $SiMe_2$). HREIMS (*m*/*z*) calcd. for $C_{11}H_{15}OSi$ 191.0892 $[M+H]^+$, found 191.0885.

2,2-Dimethyl-7,8-methylenedioxy-2,3-dihydrobenzo[*f*][1,2]oxasilepin (5b): Reaction of allyl(4,5-methylenedioxy-2-(1-propenyl)phenoxy)dimethylsilane (**Vc**) (950 mg, 3.44 mmol) with Grubbs catalyst 2nd generation (15 mg, 0.017 mmol) in anhyd. CH_2Cl_2 (170 mL) followed by workup as described above yielded **5b** (725 mg, 3.1 mmol, 90%) as a colourless oil: R_f=0.35 (hexane/Et_2O, 98:2); IR (film) ν_{max} 3016, 2960, 2887, 1618, 1484, 1429, 1254, 1153, 1038, 905, 744 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ= 6.54 (1H, s, H-6), 6.49 (1H, s, H-9), 6.24 (1H, d, *J*= 10.9 Hz, H-5), 6.01 (1H, dt, *J*= 10.9, *J*= 7.7 Hz, H-4), 5.93 (2H, s, OCH_2O), 1.50 (2H, d, *J*= 7.7 Hz, H-3), 0.31 (6H, $SiMe_2$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ= 147.98* (C, C-8), 146.98* (C, C9a), 142.02 (C, C-7), 127.25 (CH, C-4), 126.20 (CH, C-5), 120.75 (C, C-5a), 108.70 (CH, C-6), 102.69 (CH, C-9), 101.13 (OCH_2O), 18.11 (CH_2, C-3), -0.71 ($SiMe_2$). *may be interchanged;. HREIMS (m/z) calcd. for $C_{12}H_{14}O_3Si$ 234.0712 $[M+H]^+$, found 234.0714.

2,2-Dimethyl-8-methoxy-2,3-dihydrobenzo[*f*][1,2]oxasilepin (5c): Reaction of allyl(5-methoxy-2-(1-propenyl)phenoxy)dimethylsilane (**Vb**) (814 mg, 3.12 mmol) with Grubbs

catalyst 2nd generation (13 mg, 0.015 mmol) in anhyd. CH_2Cl_2 (155 mL) followed by workup as described above yielded **5c** (635 mg, 2.89 mmol, 93%) as a colourless oil: R_f=0.35 (hexane/Et_2O, 98:2); IR (film) ν_{max} 3018, 2959, 2836, 1609, 1568, 1501, 1154, cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ= 7.01 (1H, d, *J*= 8.9 Hz, H-6), 6.57 (1H, dd, *J*= 8.9, *J*= 2.4 Hz, H-7), 6.51 (1H, d, *J*= 2.4 Hz, H-9), 6.31 (1H, d, *J*= 10.5 Hz, H-5), 5.97 (1H, dt, *J*= 10.5, *J*= 7.3 Hz, H-4), 3.81 (3H, s, OCH_3), 1.59 (2H, d, *J*= 7.3 Hz, H-3), 0.33 (6H, $SiMe_2$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ= 159.44 (C, C-8), 154.09 (C, C-9a), 131.51 (CH, C-6), 126.36* (CH, C-5), 126.28* (CH, C-4), 121.03 (C, C-5a), 107.85# (CH, C-9), 106.19# (CH, C-7), 55.23 (OCH_3), 18.10 (CH_2, C-3), -0.50 ($SiMe_2$). * and # may be interchanged;. HREIMS (m/z) calcd. for $C_{12}H_{16}O_2Si$ 220.0920 $[M]^+$, found 220.0922.

General procedure for the phenol protection in aromatic aldehydes: To a solution of the corresponding starting benzaldehyde in anhydrous CH_2Cl_2 under N_2 atmosphere, DMAP, anhyd. pyridine and pivaloyl chloride (or acetic anhydride) were added. The mixture was heated to reflux for 6 h, then quenched with HCl 5%, and extracted with CH_2Cl_2. The organic layer was dried over anhyd. Na_2SO_4, and the solvent was removed. The residue was purified by flash chromatography.

5-Methoxy-2-pivaloyloxybenzaldehyde (1): Reaction of 2-hydroxy-5-methoxybenzaldehyde (1 g, 6.57 mmnol) with DMAP (80 mg, 0.66 mmol), anhyd. pyridine (1.6 mL, 19.71 mmol) and pivaloyl chloride (2.3 mL, 18.4 mmol) in anhydrous CH_2Cl_2 (75 mL) followed by workup as described above yielded **1** (1.32 g, 5.6 mmol, 85%); R_f=0.28 (hexane/Et_2O, 9:1); as a colourless oil: ^1H NMR ($CDCl_3$, 300 MHz): δ(ppm) 10.10 (1H, s, CHO), 7.37 (1H, d, *J*=3.0 Hz, H-6), 7.17 (1H, dd, *J*=8.9, *J*=3.0 Hz, H-4), 7.05 (1H, d, *J*=8.9 Hz, H-3), 3.85 (3H, s, OCH_3), 1.41 (9H, s, $OCOC(CH_3)_3$; ^{13}C RMN: δ(ppm) 185.68 (CH), 175.25 (C), 157.21 (C), 140.66 (C), 130.53 (C), 123.64 (CH), 115.71 (CH), 111.97 (CH), 55.57 (CH_3), 38.52 (C), 27.06 (C).

2-Pivaloyloxybenzaldehyde (4a): Reaction of 2-hydroxybenzaldehyde (1 g, 8.18 mmnol) with DMAP (100 mg, 0.8 mmol), anhyd. pyridine (1 mL, 12.27 mmol) and pivaloyl chloride (2 mL, 16.37 mmol) in anhydrous CH_2Cl_2 (40 mL) followed by workup as described above yielded **4a** (1.55 g, 7.5 mmol, 92%); R_f=0.28 (hexane/Et_2O, 8:2) as a colourless oil; ^1H NMR

($CDCl_3$, 300 MHz) δ= 10.13 (1H, s, CHO), 7.89 (1H, dd, *J*= 7.7, *J*= 1.6 Hz, H-6), 7.61 (1H, dt, *J*= 8.1, *J*= 1.6 Hz, H-4), 7.36 (1H, t, *J*= 7.7 Hz, H-5), 7.13 (1H, d, *J*= 8.1 Hz, H-3), 1.41 (9H, s, $OCOC(CH_3)_3$). ^{13}C RMN ($CDCl_3$, 75 MHz) δ= 188.30 (CH, CHO), 176.62 (C, $OCOC(CH_3)_3$), 152.45 (C, C-2), 135.23 (CH), 130.04 (CH), 128.26 (C, C-1), 126.18 (CH), 123.28 (CH), 39.31 (C, $C(CH_3)_3$), 27.06 (CH_3, $C(CH_3)_3$). HREIMS (*m*/*z*) calcd. for $C_{12}H_{14}O_3$ 206.0943 $[M]^+$, found 206.0946.

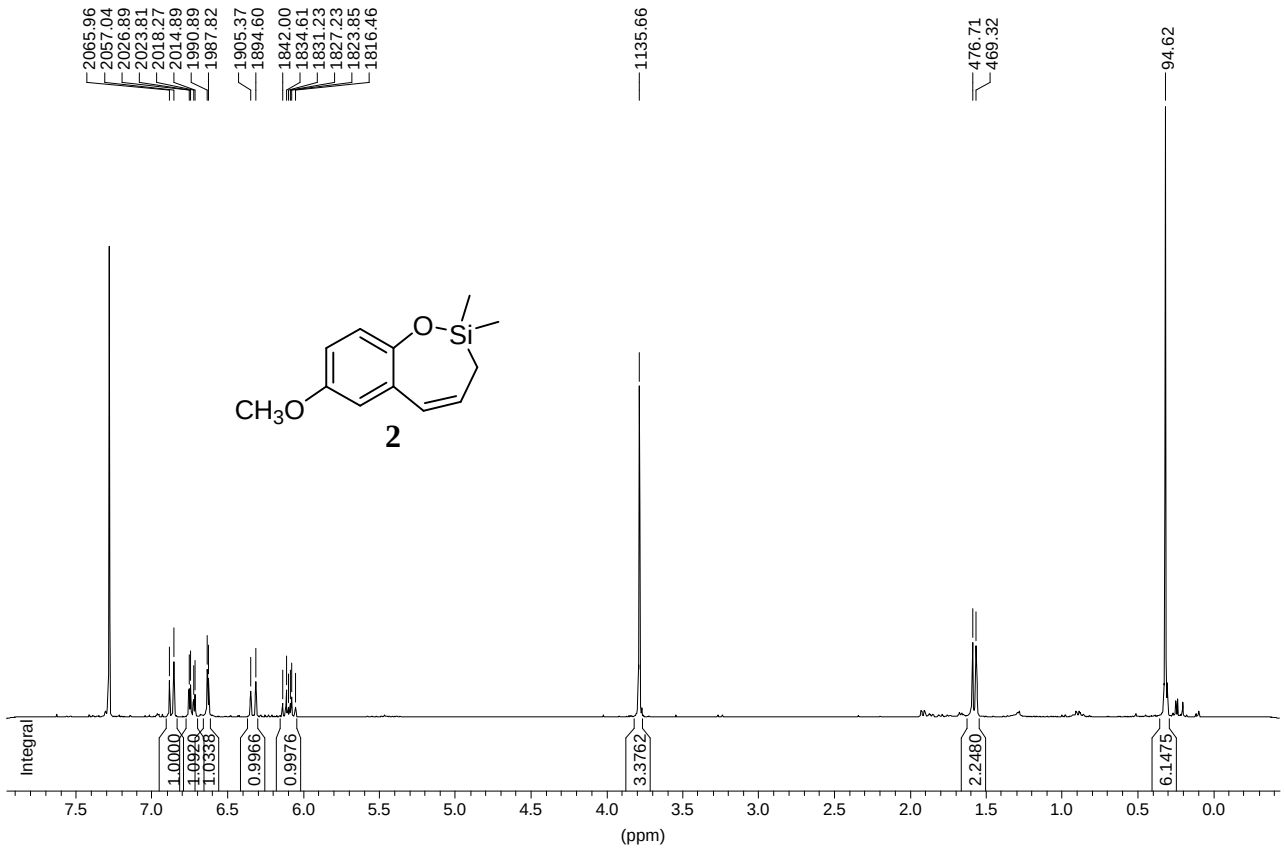
2-Acetylbenzaldehyde (4b): Reaction of 2-hydroxybenzaldehyde (1 g, 8.18 mmol) with DMAP (100 mg, 0.8 mmol), anhyd. pyridine (1 mL, 12.27 mmol) and acetic anhydride (1.2 mL, 12.27 mmol) in anhydrous CH_2Cl_2 (40 mL) followed by workup as described above yielded **4b** (1.2 g, 7.3 mmol, 92%); R_f=0.28 (hexane/Et_2O, 8:2) as a colourless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 10.11 (1H, d, *J*= 1.2 Hz, CHO), 7.88 (1H, dt, *J*= 7.8, *J*= 1.2 Hz, H-6), 7.63 (1H, ddd, *J*= 8.4, *J*= 7.4, *J*= 1.3 Hz, H-4), 7.40 (1H, dd, *J*= 7.8, *J*= 7.4 Hz, H-5), 7.18 (1H, bd, *J*= 8.4, H-3), 2.38 (3H, s, CH_3). ^{13}C RMN ($CDCl_3$, 75 MHz) δ= 188.74 (CH, CHO), 169.20 (C, $OCOCH_3$), 151.42 (C, C-2), 135.26 (CH, C-4), 131.24 (CH, C-6), 127.98 (C, C-1), 126.38 (CH, C-5), 123.44 (CH, C-3), 20.77 (CH3, $OCOCH_3$).

2,4-Dipivaloyloxybenzaldehyde (4c): Reaction of 2,4-dihydroxybenzaldehyde (3 g, 21.72 mmol) with DMAP (265 mg, 2.2 mmol), anhyd. pyridine (5.3 mL, 65.16 mmol) and pivaloyl chloride (10.7 mL, 86.9 mmol) in anhydrous CH_2Cl_2 (150 mL) followed by workup as described above yielded **4c** (4.2 g, 19.1 mmol, 87%); R_f=0.28 (hexane/Et_2O, 9:1); as a white solid foam: IR (film) ν_{max} 2975, 2936, 2873, 1759, 1695, 1605, 1479, 1395, 1272, 1239, 1097, 1028 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ= 10.07 (1H, s, CHO), 7.89 (1H ,d, *J*= 8.5 Hz, H-6), 7.10 (1H, dd, *J*= 8.5, *J*= 2.1 Hz, H-5), 6.97 (1H, d, *J*= 2.1 Hz, H-3), 1.39 (9H, s, $C(CH_3)_3$), 1.34 (9H, s, $C(CH_3)_3$). ^{13}C RMN ($CDCl_3$, 75 MHz) δ= 187.13 (CH, CHO), 176.17 (C, COO), 175.84 (C, COO), 156.05* (C, C-2), 153.21* (C, C-4), 130.94 (CH, C-6), 125.74 (C, C-1), 119.49 (CH, C-5), 116.75 (CH, C-3), 39.24 (C, $C(CH_3)_3$), 27.03 (CH_3, $C(CH_3)_3$). * may be interchanged.

4-Methoxy-2-pivaloyloxybenzaldehyde (4d): Reaction of 2-hydroxy-4-methoxybenzaldehyde (1 g, 6.57 mmnol) with DMAP (80 mg, 0.66 mmol), anhyd. pyridine (1.6 mL, 19.71 mmol) and pivaloyl chloride (2.3 mL, 18.4 mmol) in anhydrous CH_2Cl_2 (75 mL) followed by workup as described above yielded **4d** (1.42 g, 6.1 mmol, 92%); R_f=0.28

(hexane/Et_2O, 9:1); as a colourless oil: IR (film) ν_{max} 2974, 2860, 1756, 1692, 1609, 1463, 1256, 1106, 1028, 894, 816 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ= 9.95 (1H, s, CHO) 7.80 (1H, d, *J*= 8.8 Hz, H-6), 6.84 (1H, dd, *J* = 8.8, *J* = 2.5 Hz, H-5), 6.59 (1H, d, *J*= 2.5 Hz, H-3), 3.83 (3H, s, OCH_3), 1.38 (9H, s, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ= 186.92 (CH, <u>C</u>HO), 176.40 (C, <u>C</u>OO), 165.12 (C, C-2), 154.23 (C, C-4), 131.82 (CH, C-6), 121.85 (C, C-1), 112.23 (CH, C-5), 108.34 (CH, C-3), 55.73 ($O\underline{C}H_3$), 39.28 (C, $\underline{C}(CH_3)_3$), 27.03 (CH_3, $C(\underline{C}H_3)_3$).

4-Pivaloyloxybenzaldehyde (4e): Reaction of 4-hydroxybenzaldehyde (1 g, 8.18 mmnol) with DMAP (100 mg, 0.8 mmol), anhyd. pyridine (1 mL, 12.27 mmol) and pivaloyl chloride (2 mL, 16.37 mmol) in anhydrous CH_2Cl_2 (40 mL) followed by workup as described above yielded **4e** (1.57 g, 7.6 mmol, 93%); R_f=0.28 (hexane/Et_2O, 8:2); as a white solid: m.p. 96-98ºC; ^1H NMR ($CDCl_3$, 300 MHz) δ= 9.97 (1H, s, CHO), 7.91 (2H,d, *J*= 8.8 Hz, H-2, 6), 7.24 (2H, d, *J*= 8.8 Hz, H-3, 5), 1.36 (9H, s, $OCOC(CH_3)_3$). ^{13}C RMN ($CDCl_3$, 75 MHz) δ= 191.00 (CH, <u>C</u>HO), 176.35 (C, <u>C</u>OO), 155.86 (C, C-4), 133.77 (C, C-1), 131.12 (CH, C-3, 5), 122.28 (CH, C-2, 6), 39.16 (C, $\underline{C}(CH_3)_3$), 26.95 (CH_3, $C(\underline{C}H_3)_3$). HREIMS (*m*/*z*) calcd. for $C_{12}H_{14}O_3$ 206.0943 $[M]^+$, found 206.0941.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2014.89
1990.89
1987.82
1905.37
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1842.00
1834.61
1831.23
1827.23
1823.85
1816.46
1135.66
476.71
469.32
94.62
O
Si
CH3O
2
Integral
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1.0920
1.0338
0.9966
0.9976
3.3762
2.2480
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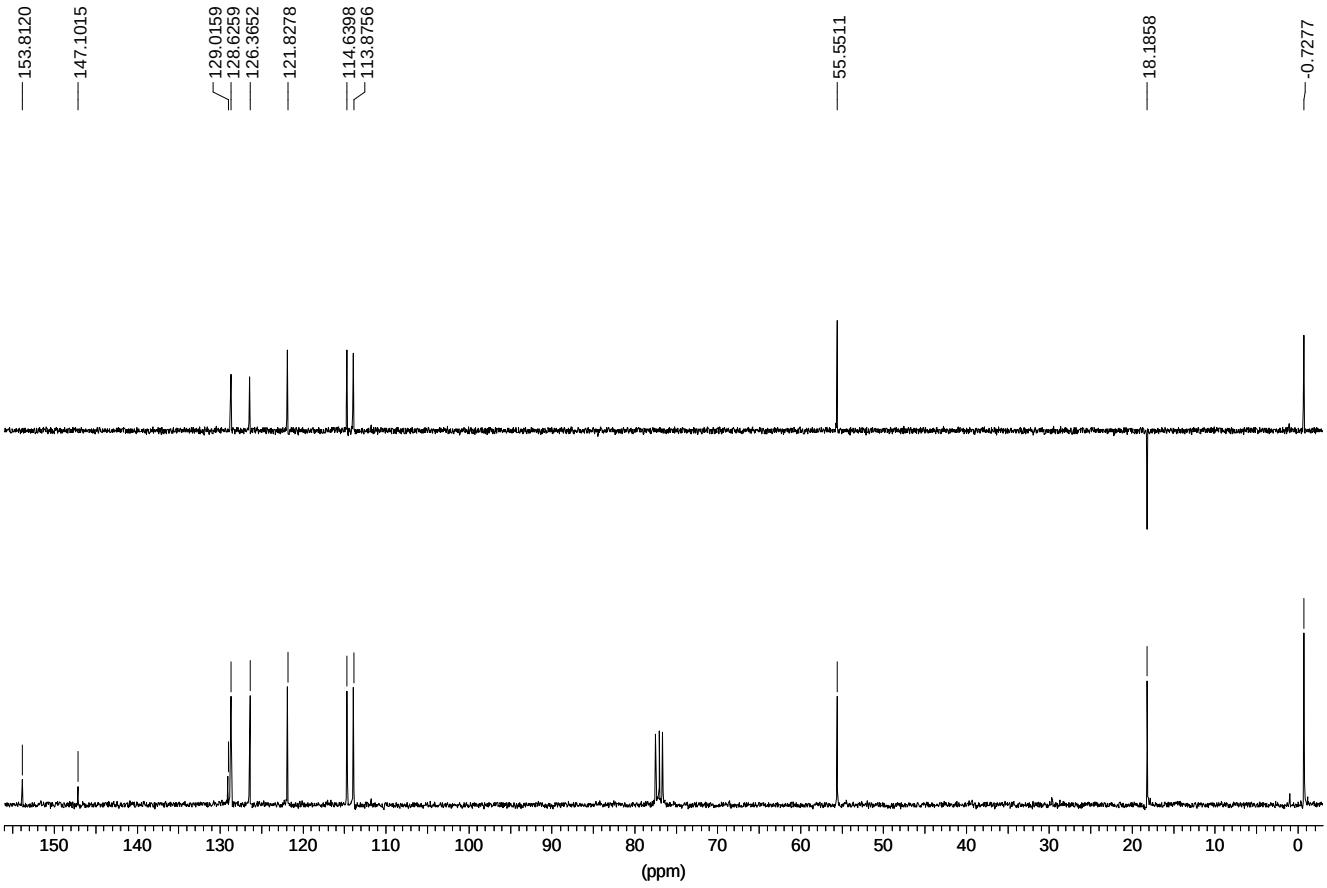
(ppm)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18.1858
-0.7277
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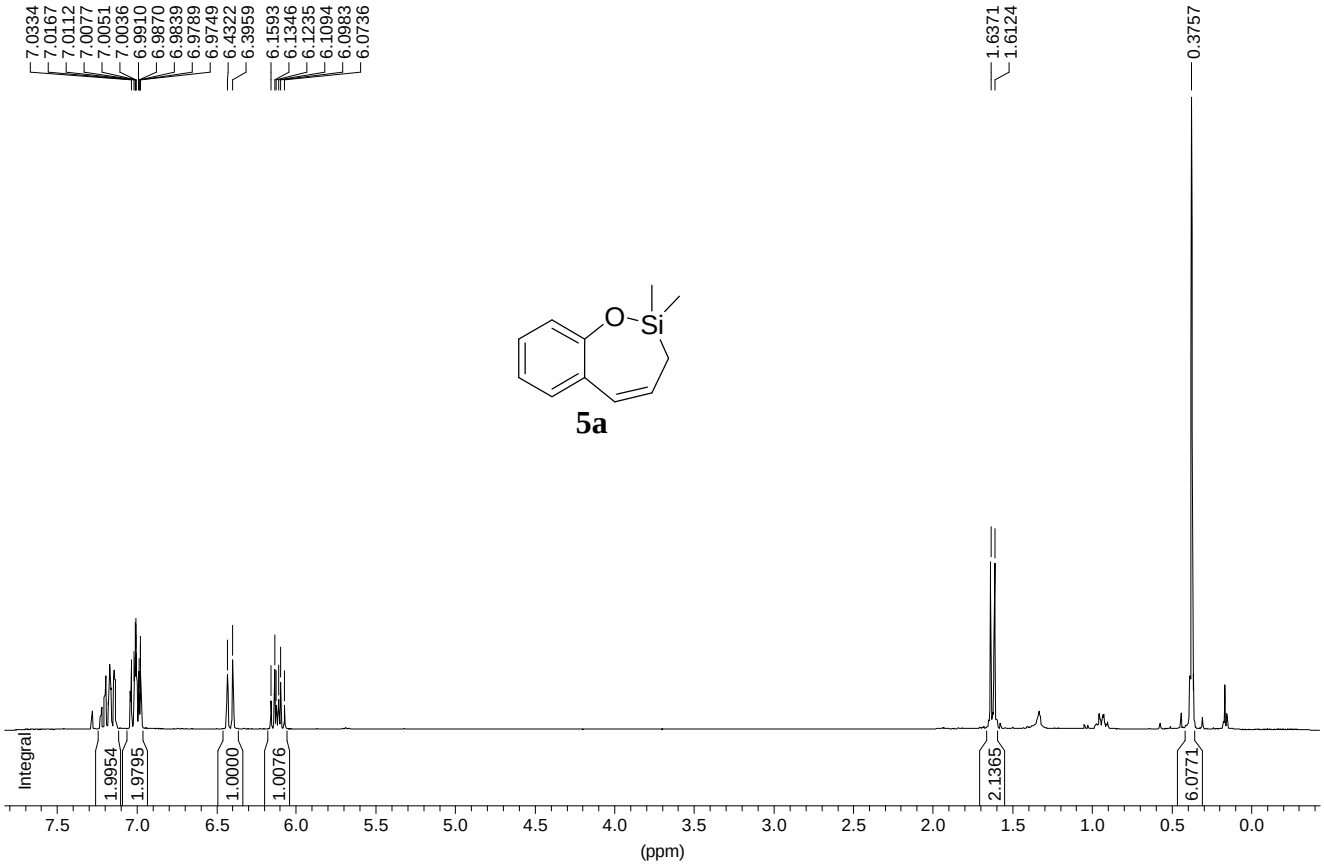
(ppm)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7.0112
7.0077
7.0051
7.0036
6.9910
6.9870
6.9839
6.9789
6.9749
6.4322
6.3959
6.1593
6.1346
6.1235
6.1094
6.0983
6.0736
1.6371
1.6124
0.3757
O
Si
Integral
1.9954
1.9795
1.0000
1.0076
2.1365
6.0771
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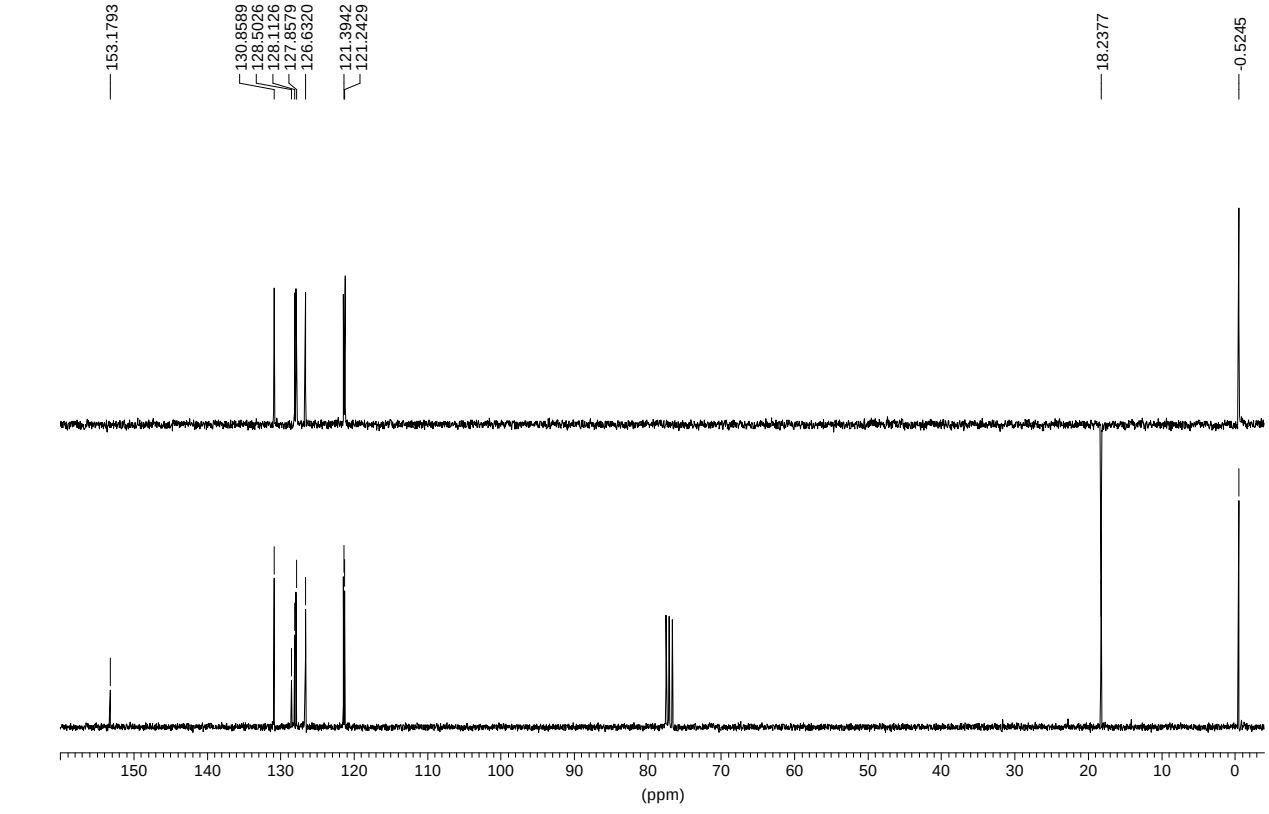
(ppm)

5a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130.8589
128.5026
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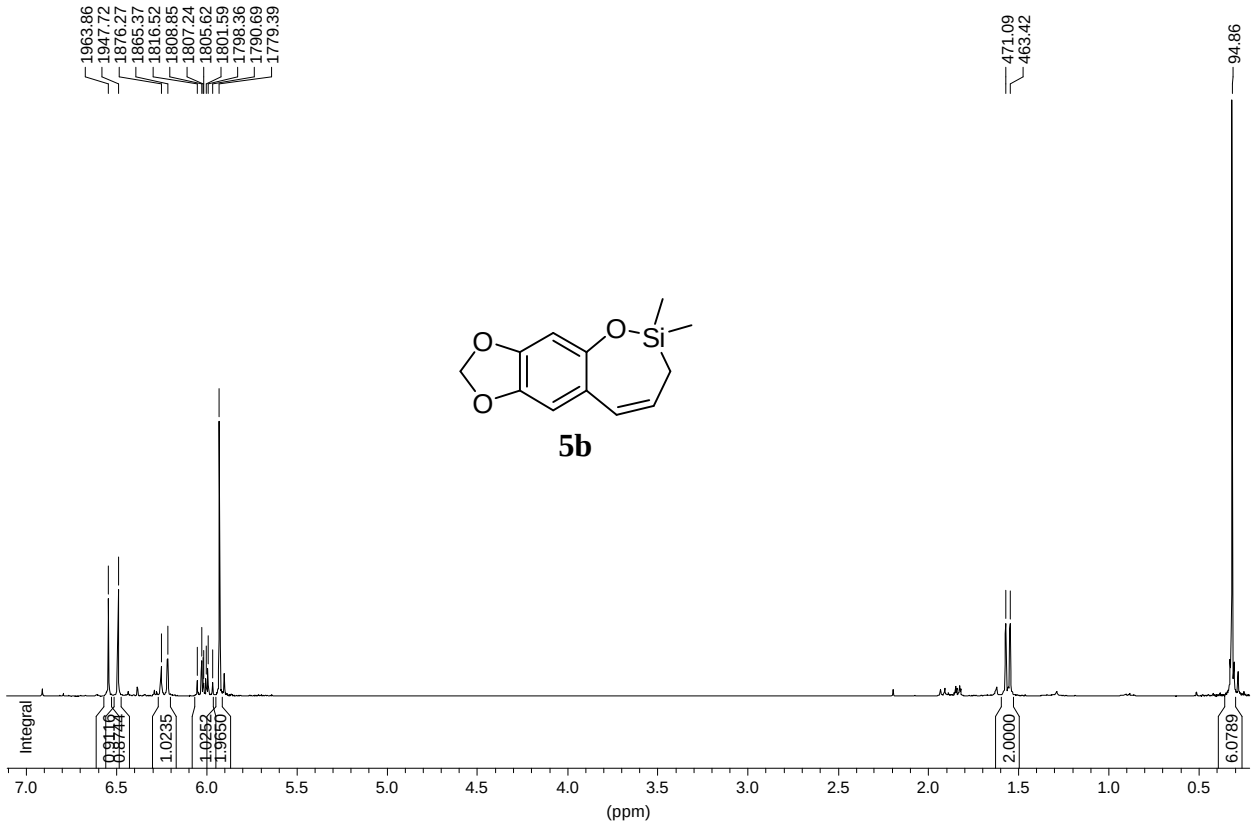
(ppm)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1807.24
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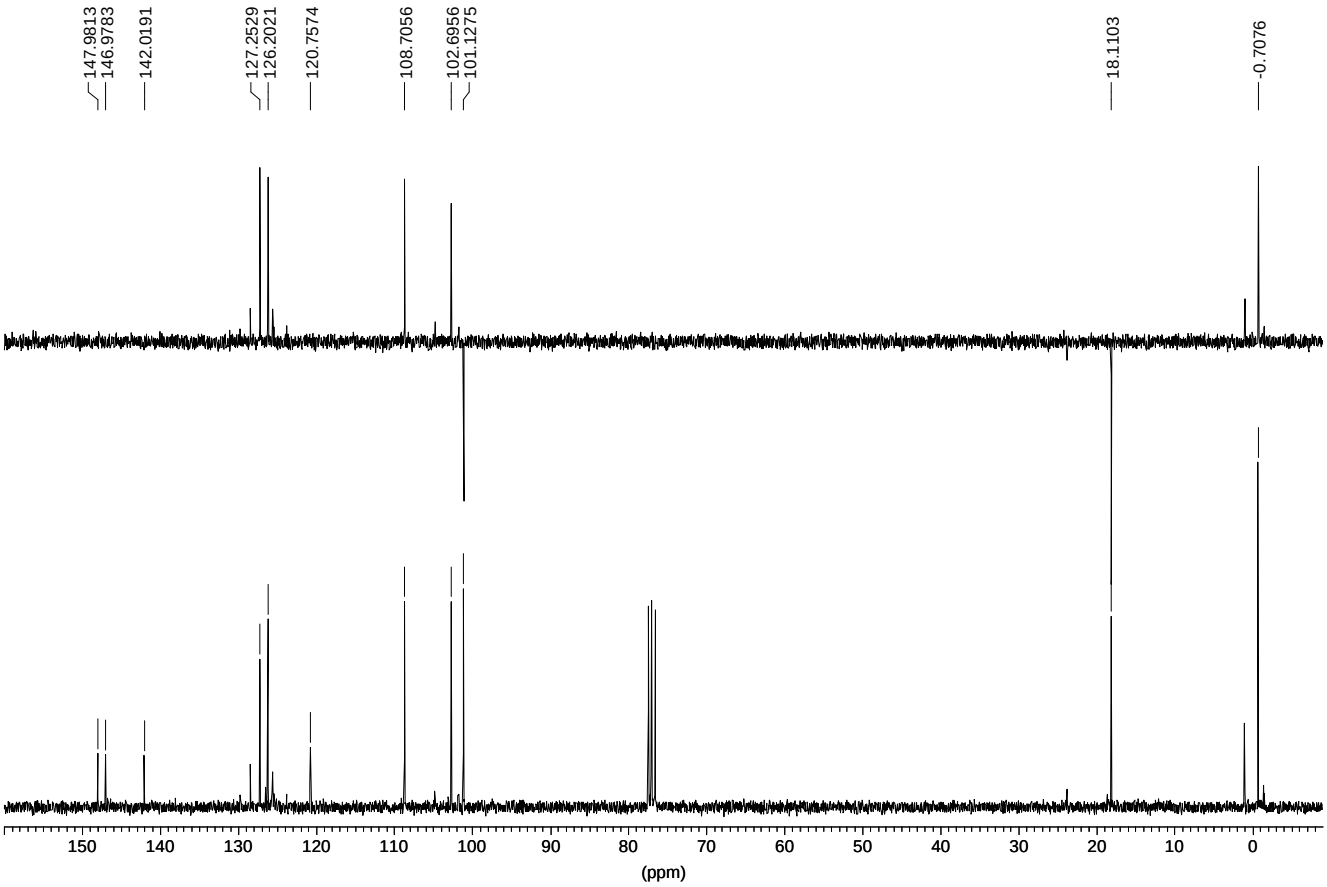
1790.69
1779.39
471.09
463.42
94.86
O
O
O
Si
Integral
0.9110
0.8744
1.0235
1.0252
1.9650
2.0000
6.0789
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

5b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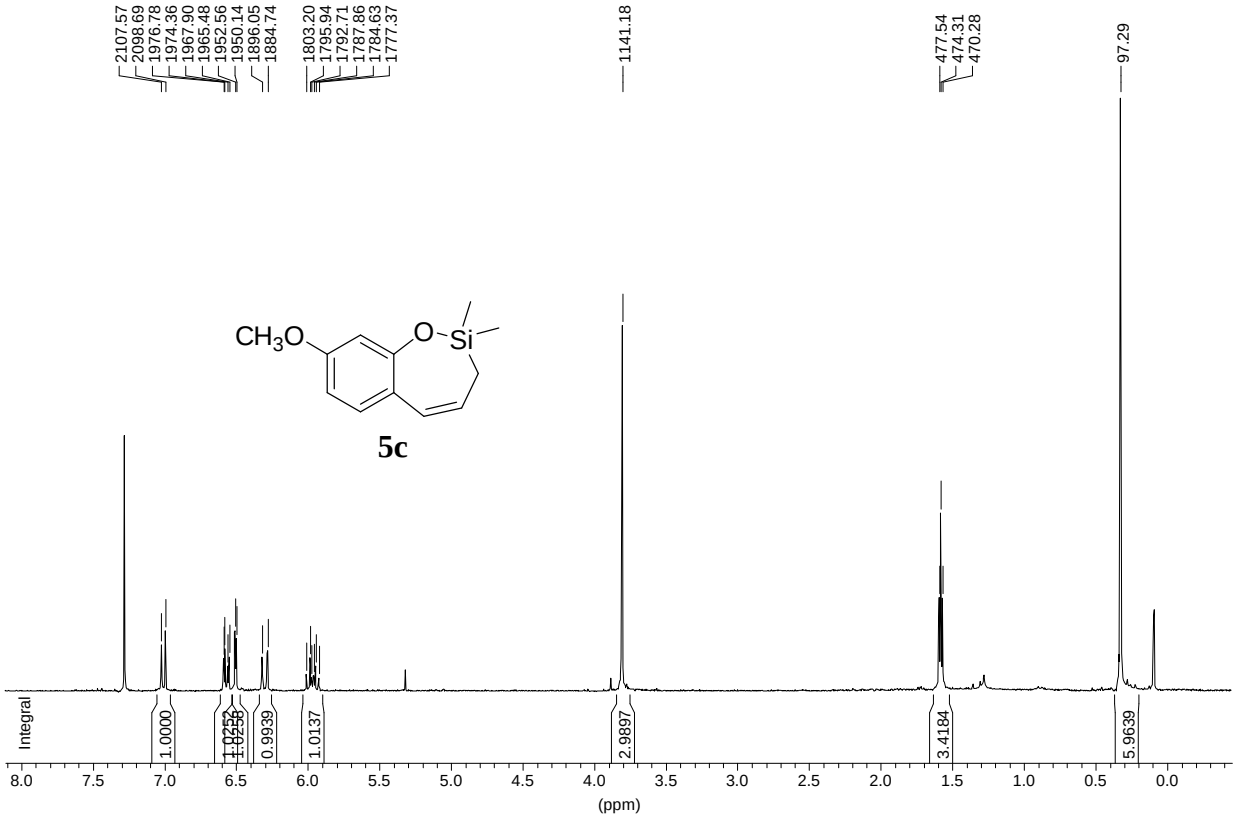
(ppm)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1967.90
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1952.56
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1792.71
1787.86
1784.63
1777.37
1141.18
477.54
474.31
470.28
97.29
CH3O
O
Si
Integral
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3.4184
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7.5
7.0
6.5
6.0
5.5
5.0
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1.0
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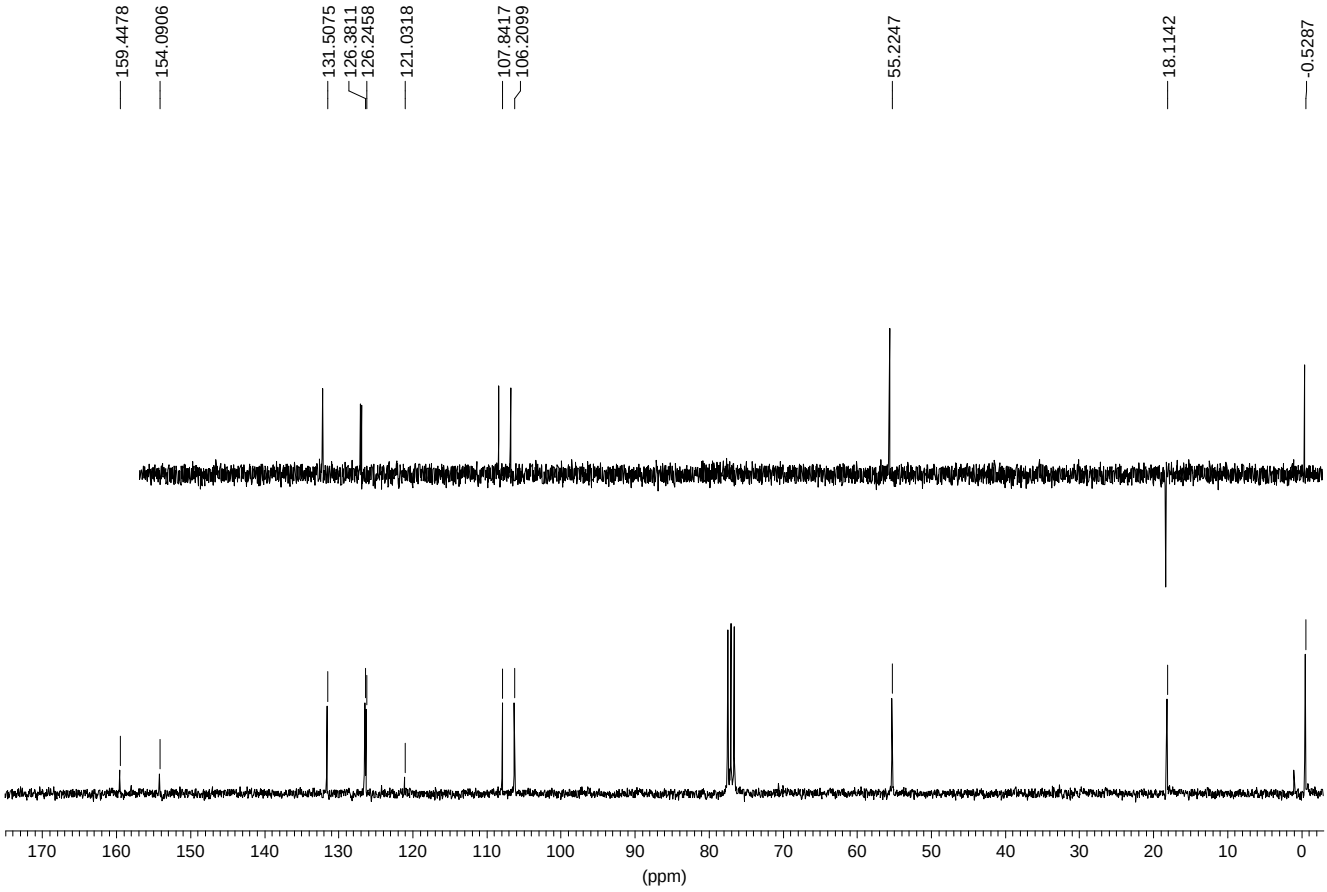
0.0
(ppm)

5c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126.2458
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55.2247
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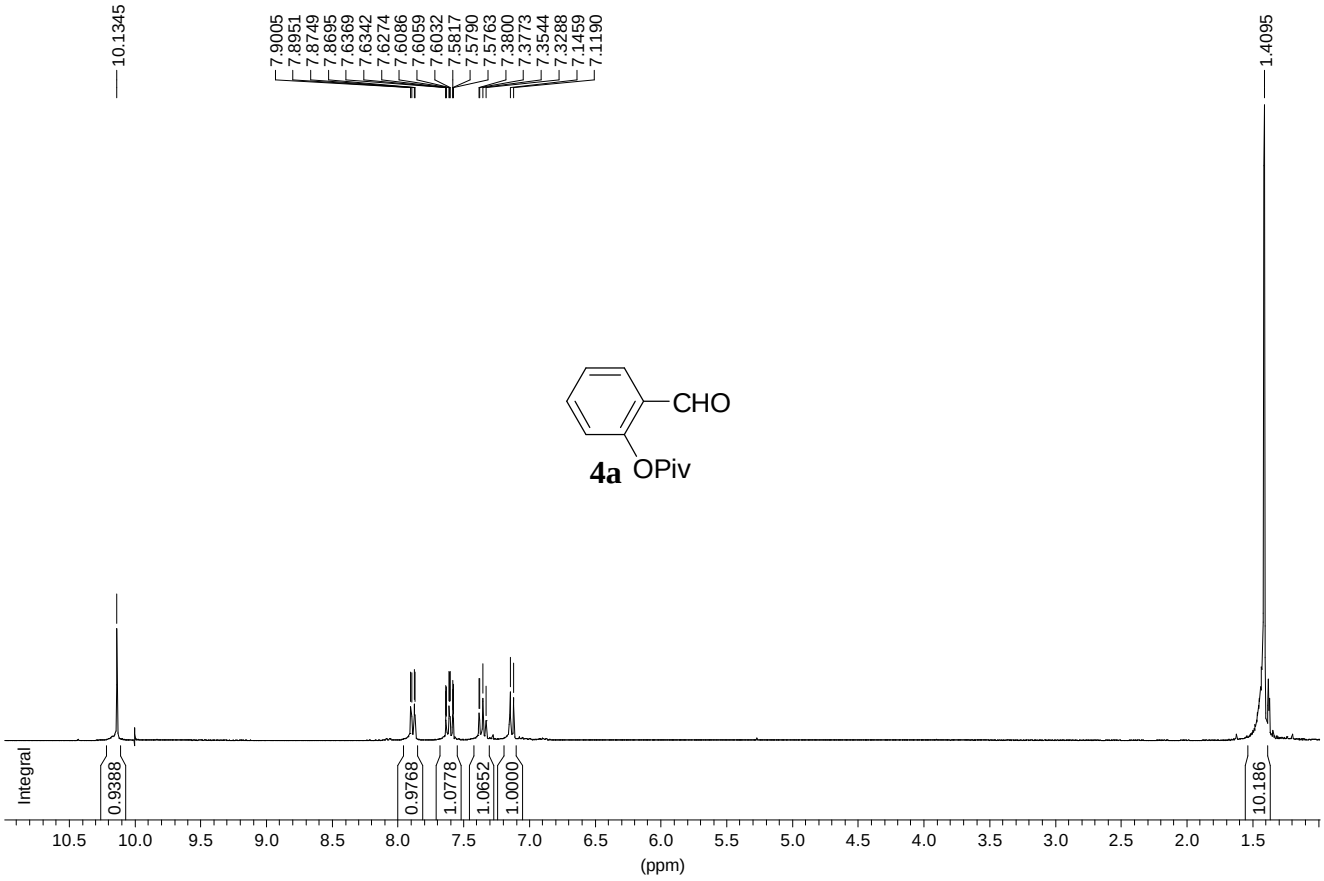
(ppm)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7.6032
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7.5790
7.5763
7.3800
7.3773
7.3544
7.3288
7.1459
7.1190
1.4095
CHO
OPiv
4a
Integral
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1.0000
10.186
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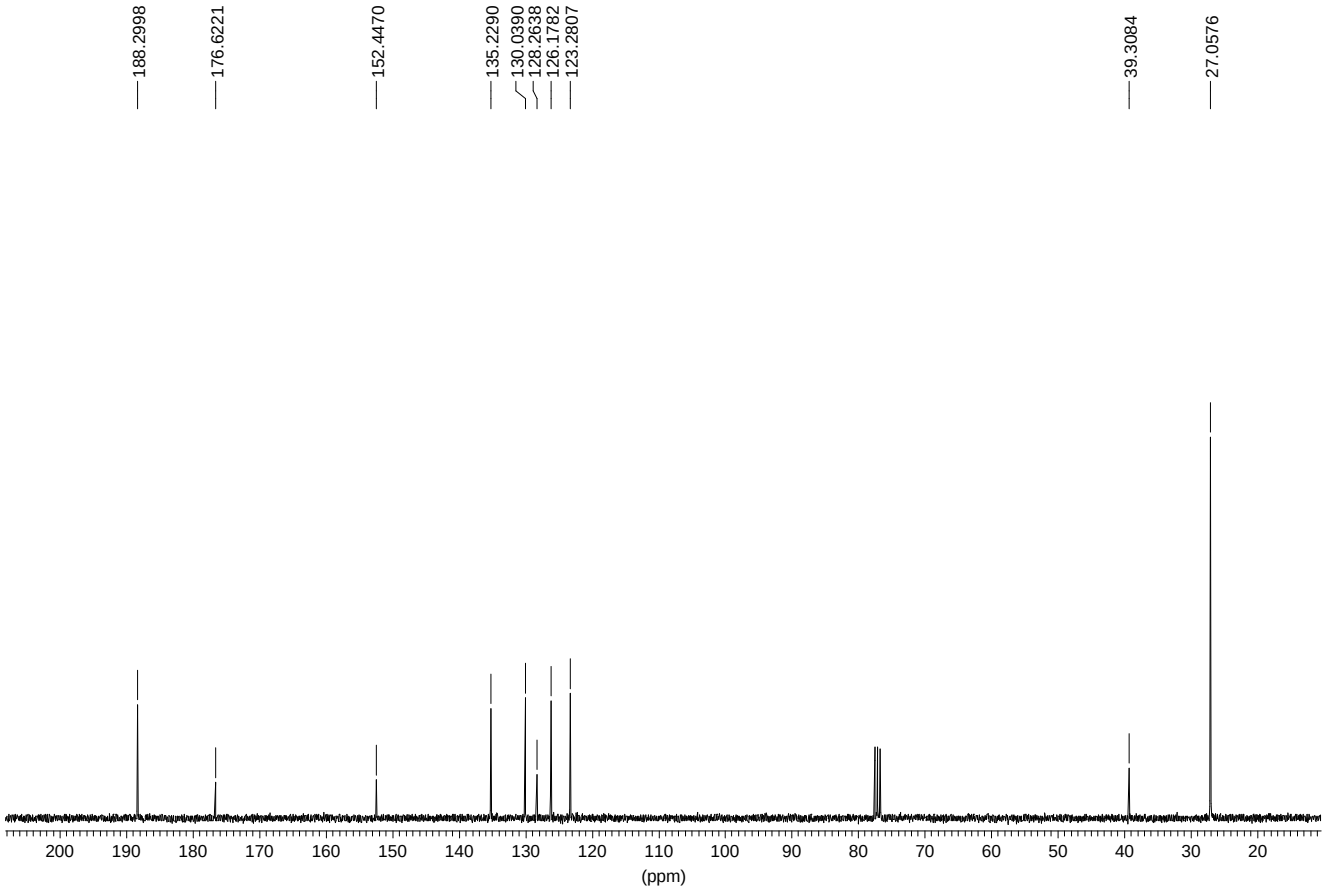
(ppm)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39.3084
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150
140
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120
110
100
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80
70
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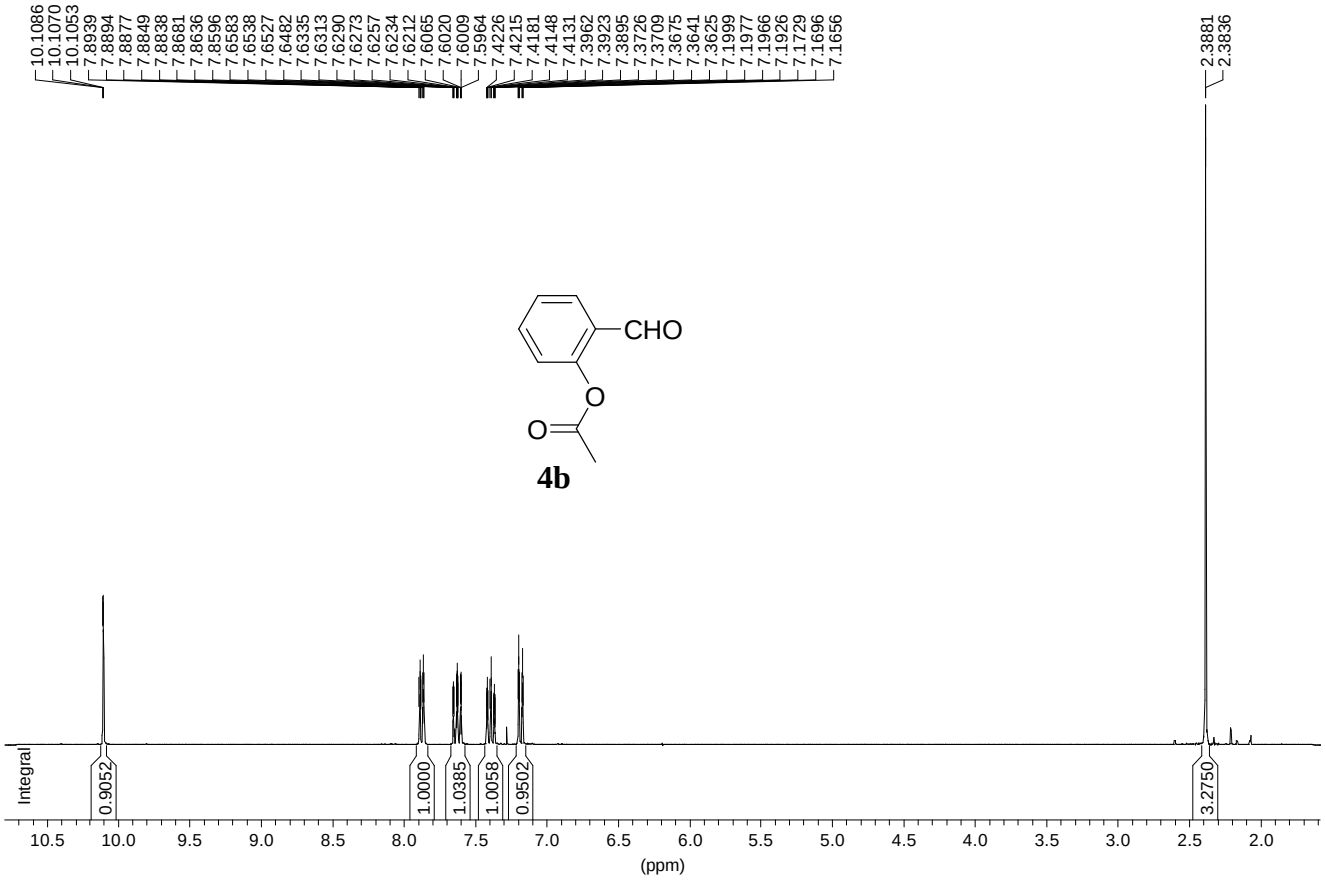
30
20
(ppm)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7.8596
7.6583
7.6538
7.6527
7.6482
7.6335
7.6313
7.6290
7.6273
7.6257
7.6234
7.6212
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7.6020
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7.4181
7.4148
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7.3923
7.3895
7.3726
7.3709
7.3675
7.3641
7.3625
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7.1977
7.1966
7.1926
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7.1656
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2.3836
CHO
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O
4b
Integral
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0.9502
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10.0
9.5
9.0
8.5
8.0
7.5
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6.0
5.5
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4.0
3.5
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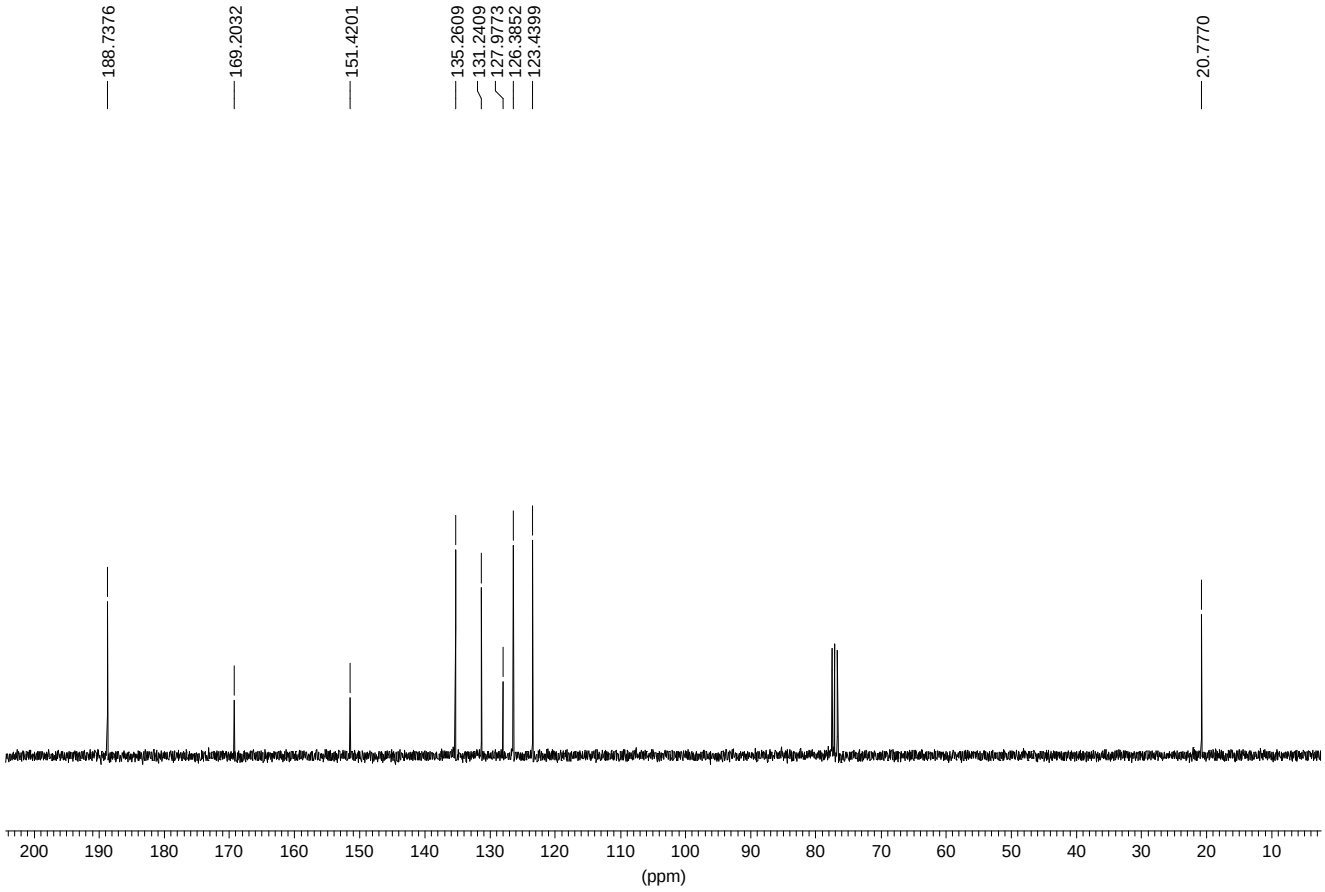
2.0
(ppm)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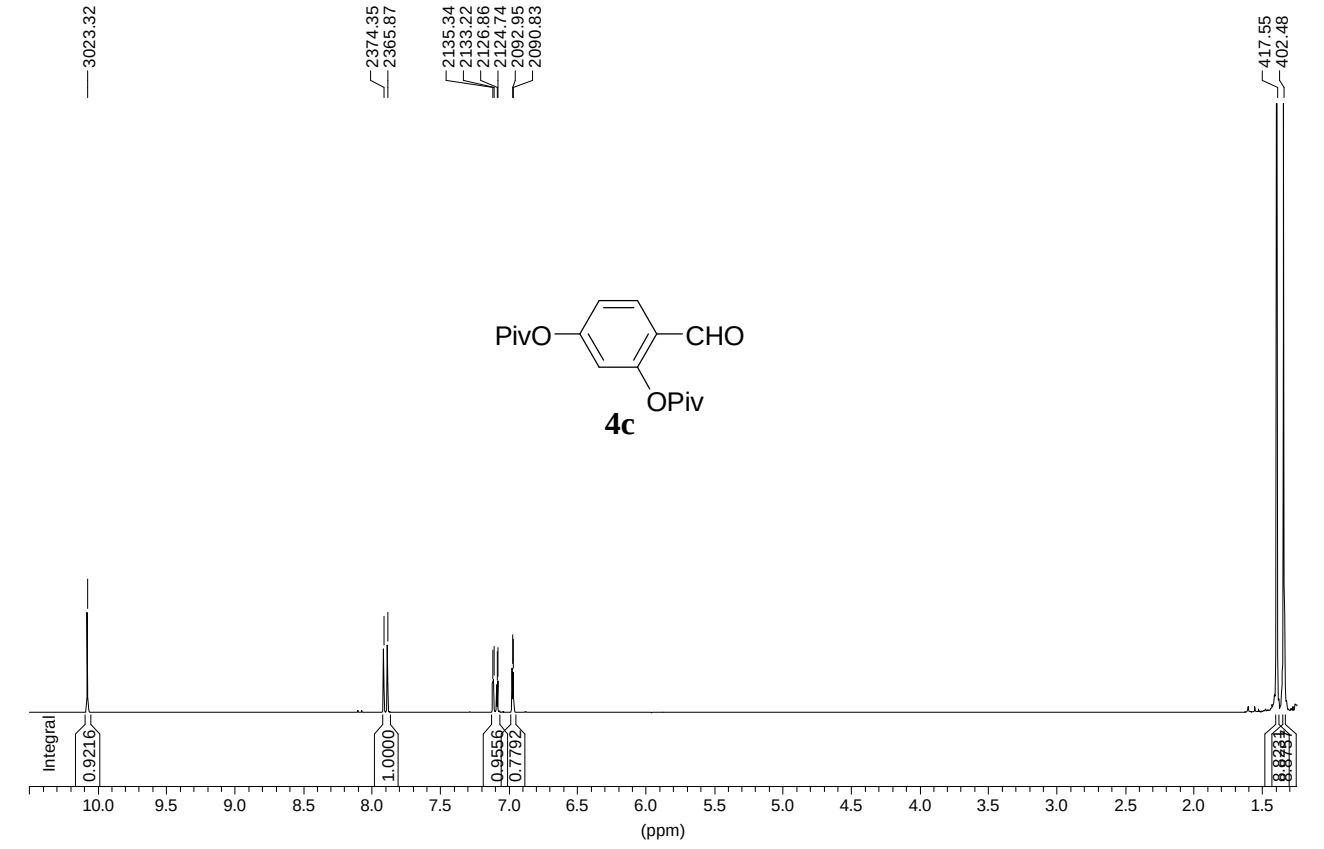
(ppm)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PivO
CHO
OPiv
4c
Integral
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0.9556
0.7792
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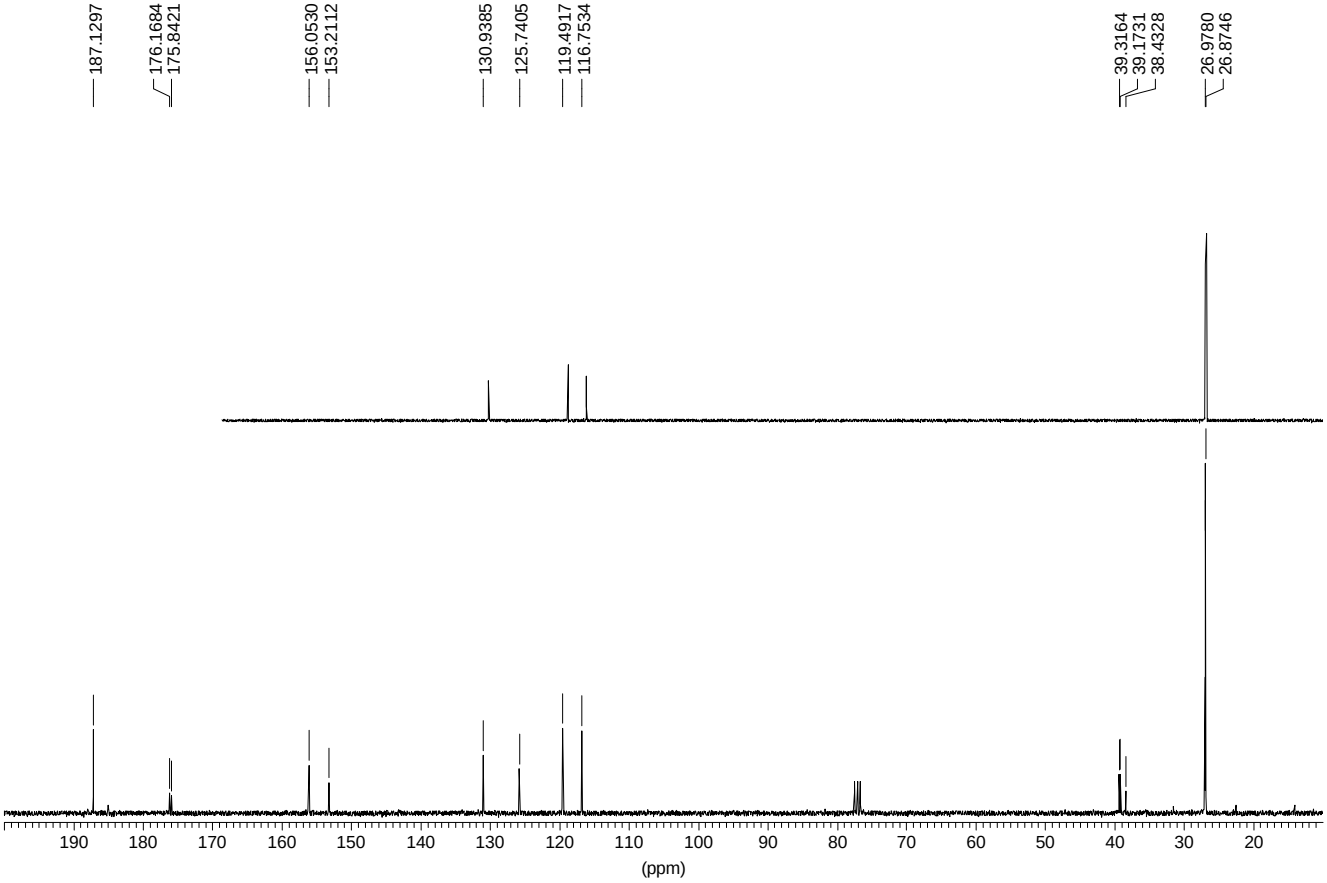
(ppm)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39.1731
38.4328
26.9780
26.8746
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150
140
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120
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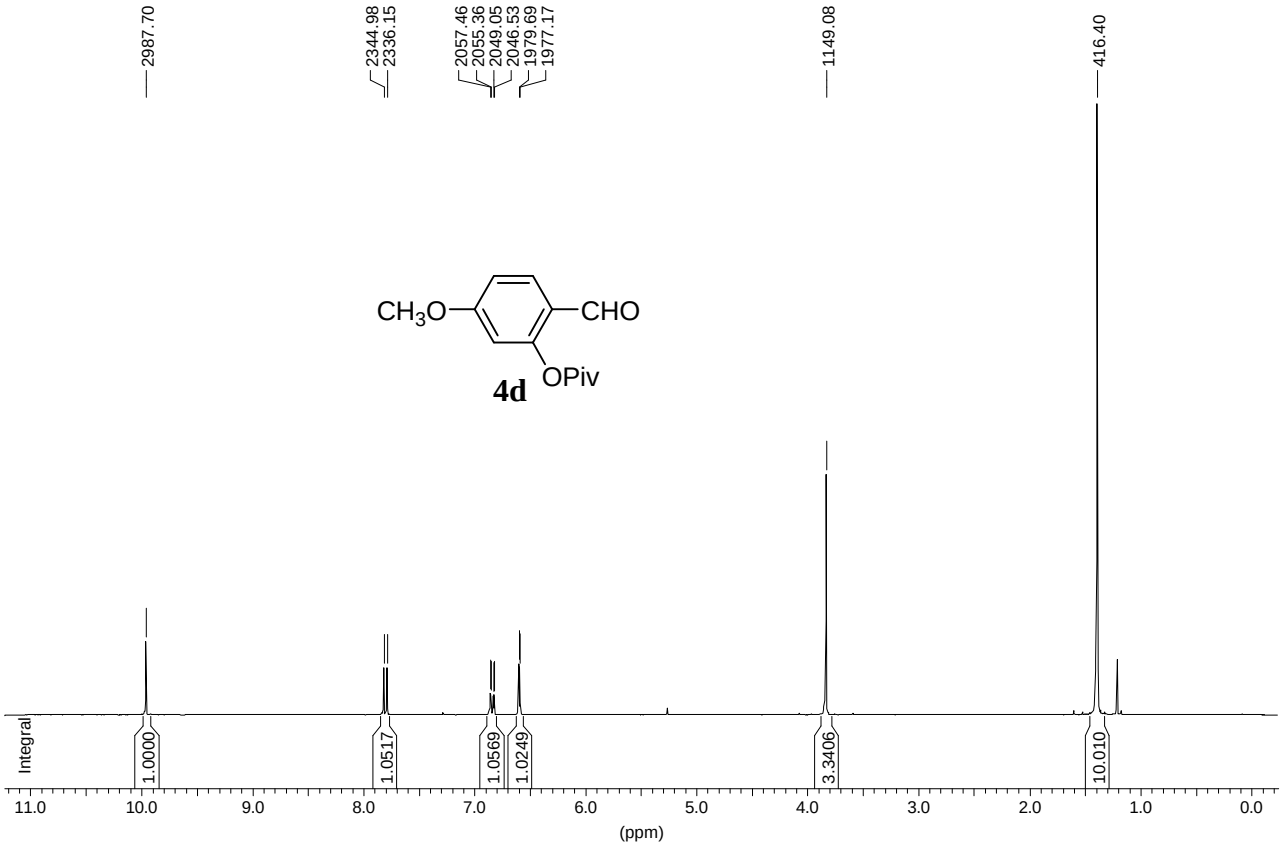
30
20
(ppm)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2055.36
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2046.53
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416.40
CH3O
CHO
OPiv
Integral
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11.0
10.0
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7.0
6.0
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2.0
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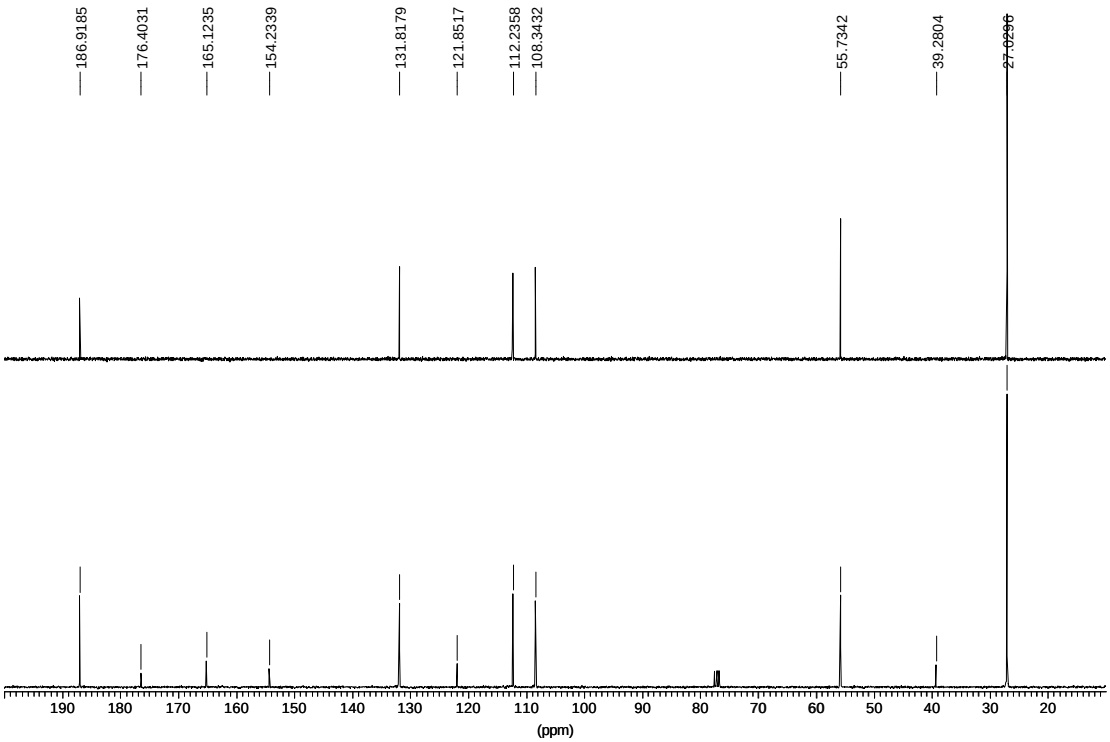
(ppm)

4d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120
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80
70
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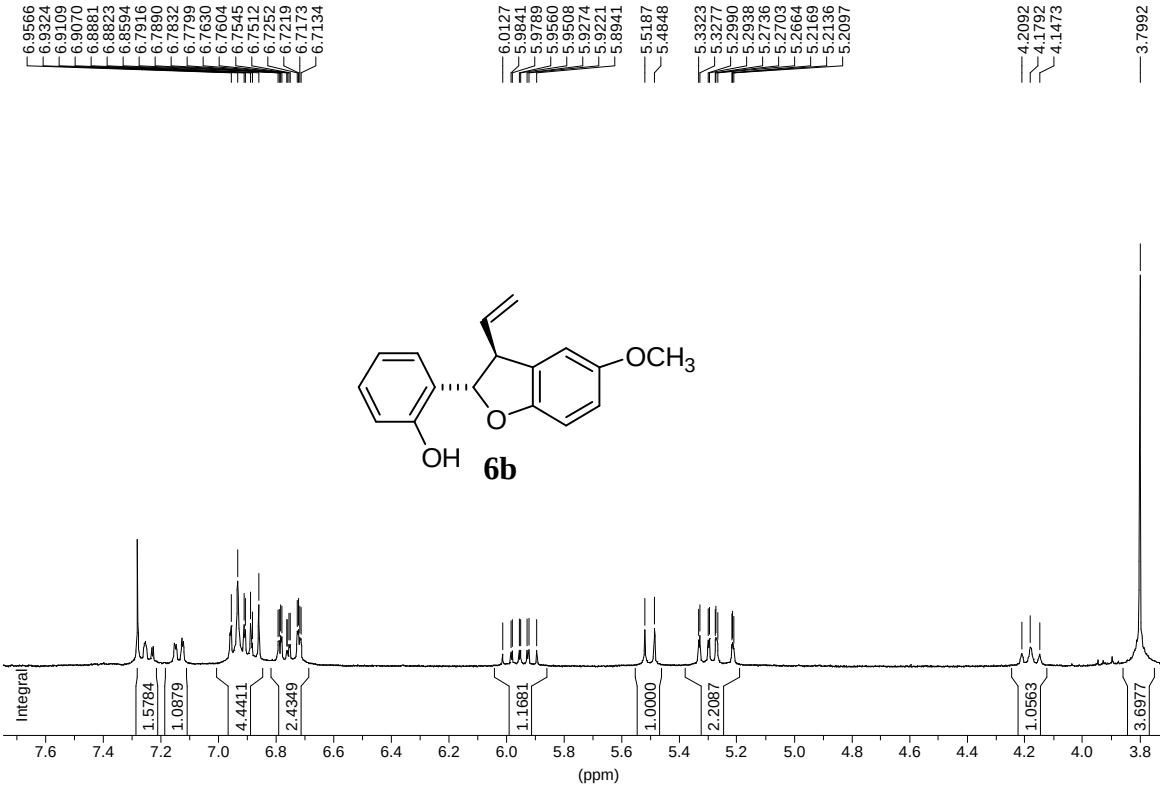
30
20
(ppm)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6.7630
6.7604
6.7545
6.7512
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5.2169
5.2136
5.2097
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4.1792
4.1473
3.7992
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O
OH
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Integral
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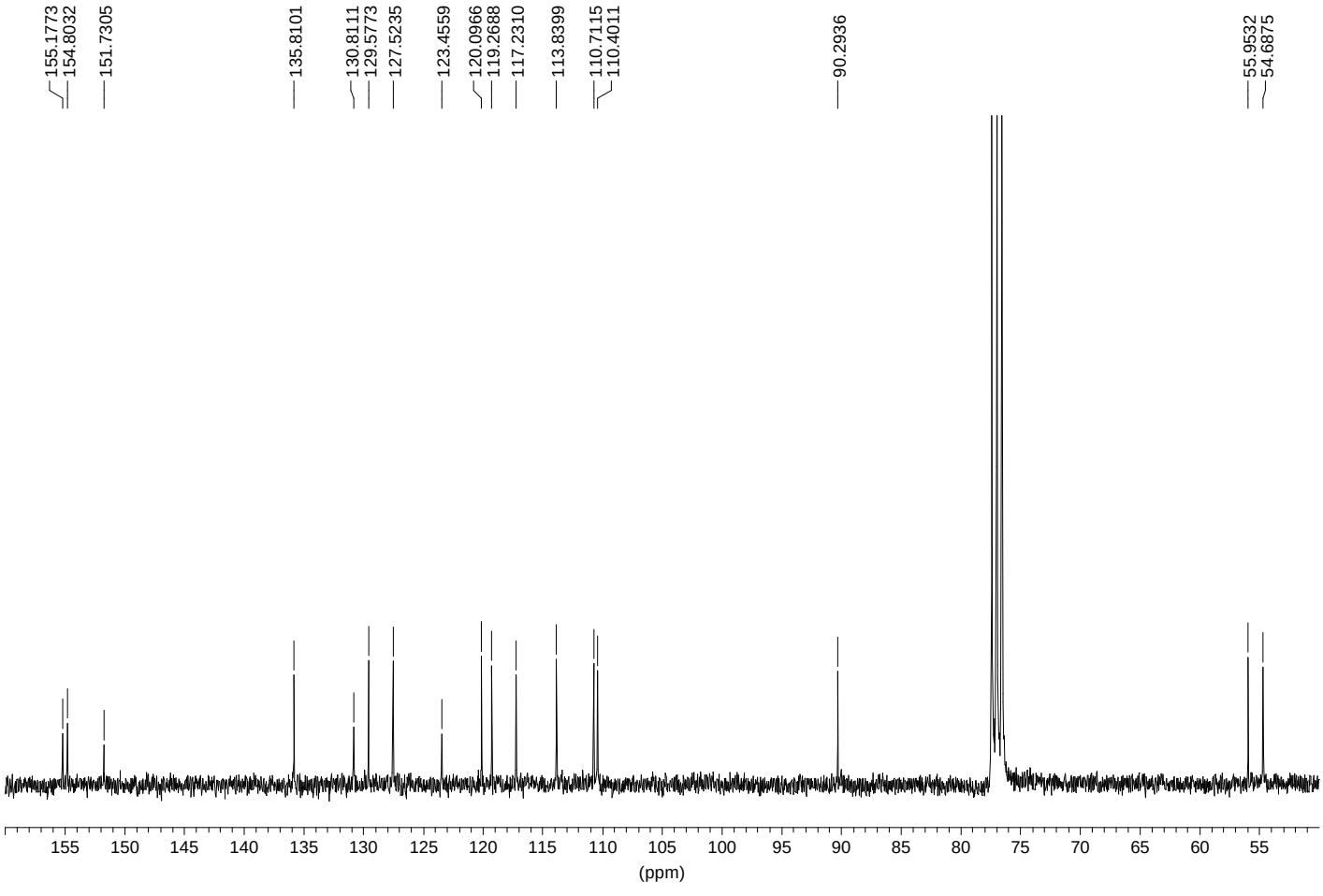
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113.8399
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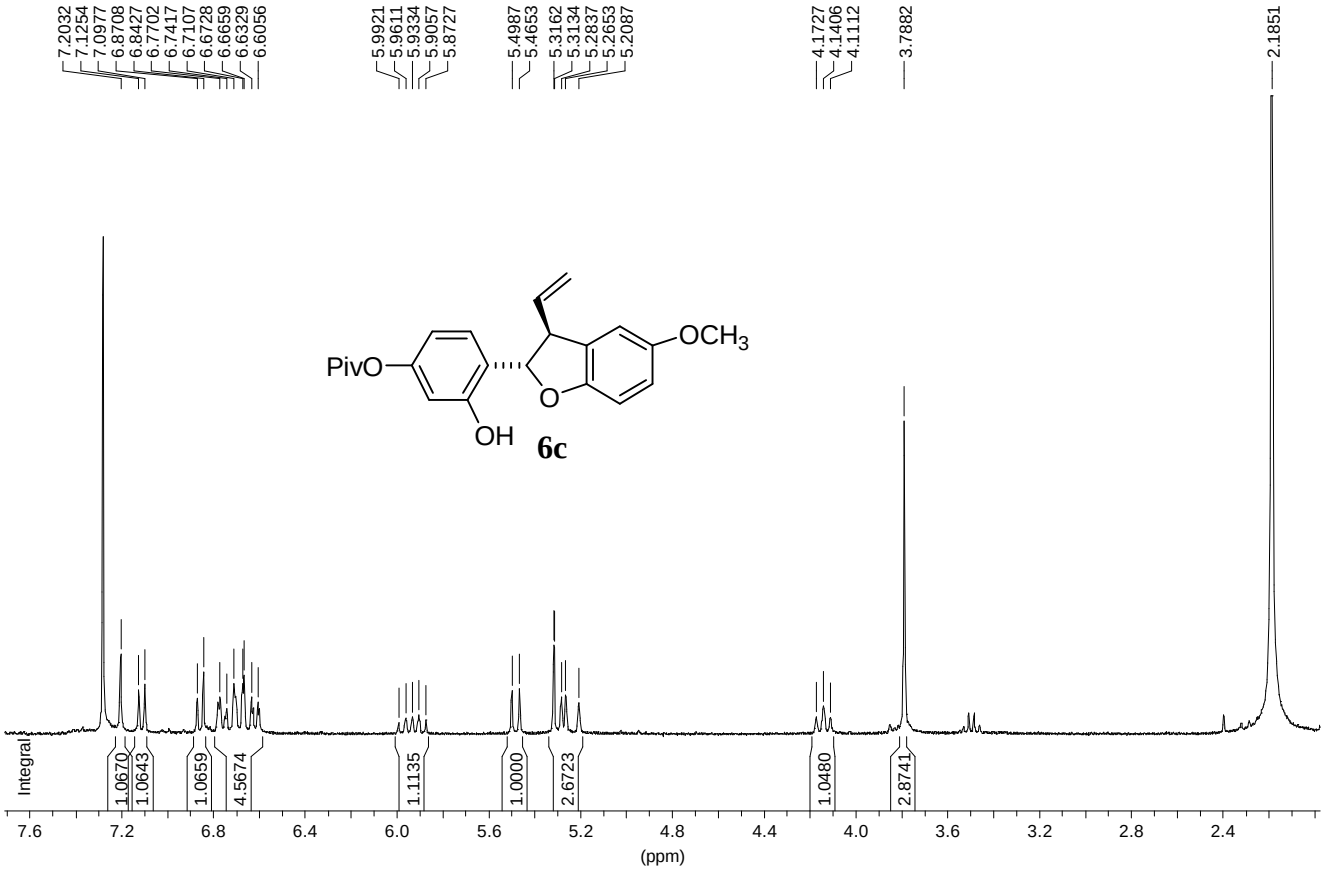
(ppm)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5.4653
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3.7882
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PivO
OCH3
O
OH
6c
Integral
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7.6
7.2
6.8
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3.6
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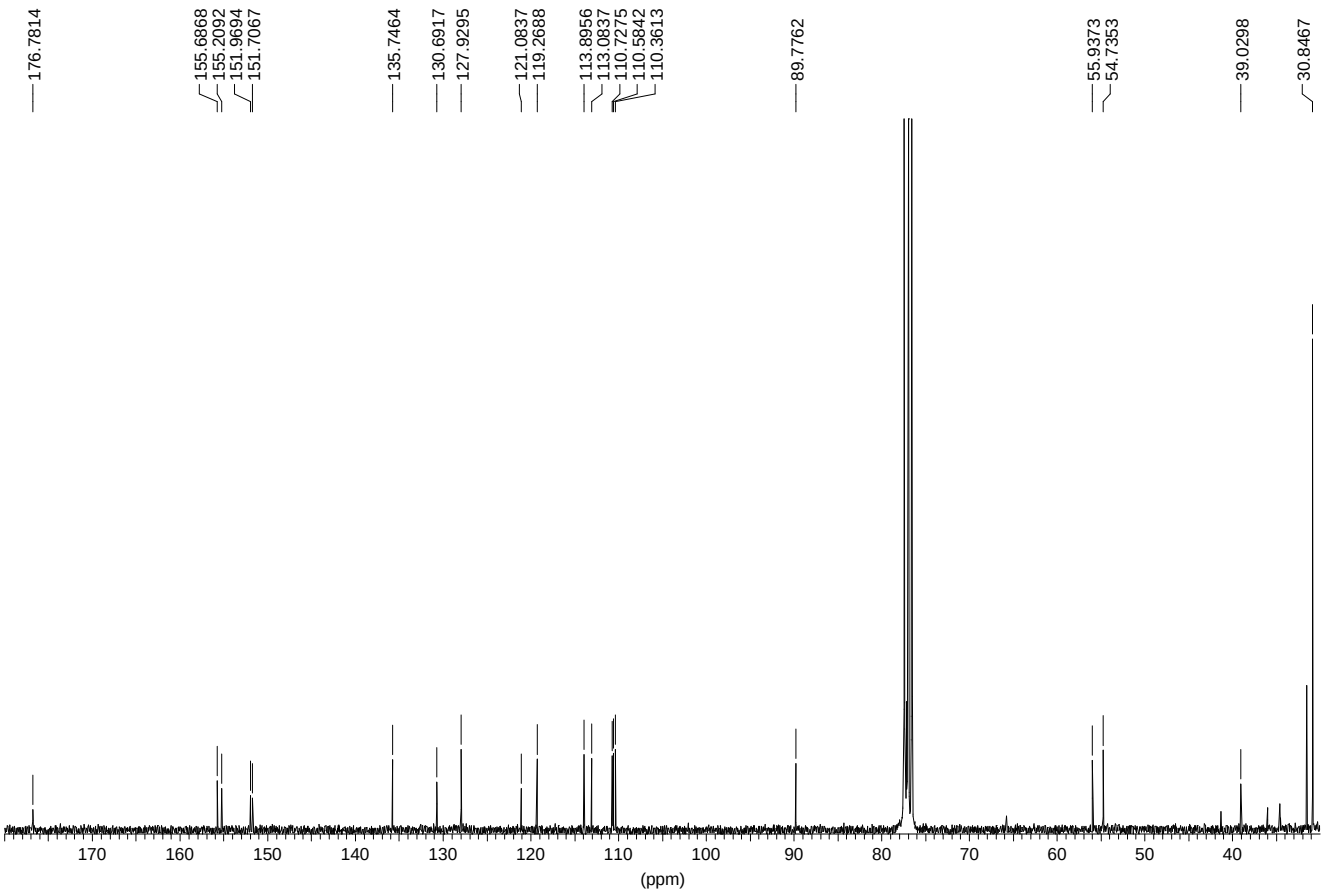
2.4
(ppm)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113.0837
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110.5842
110.3613
89.7762
55.9373
54.7353
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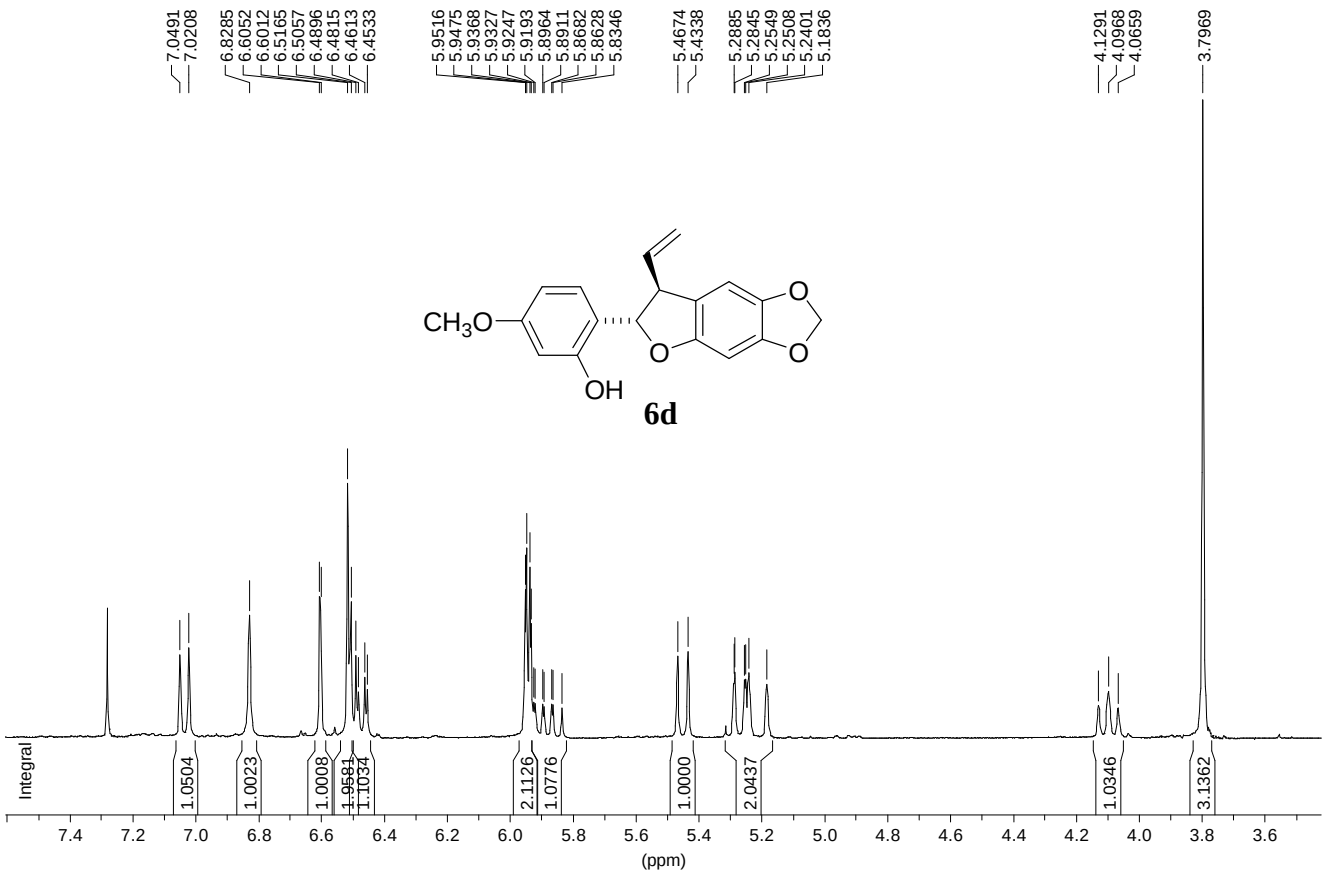
(ppm)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5.9193
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O
OH
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7.0
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6.6
6.4
6.2
6.0
5.8
5.6
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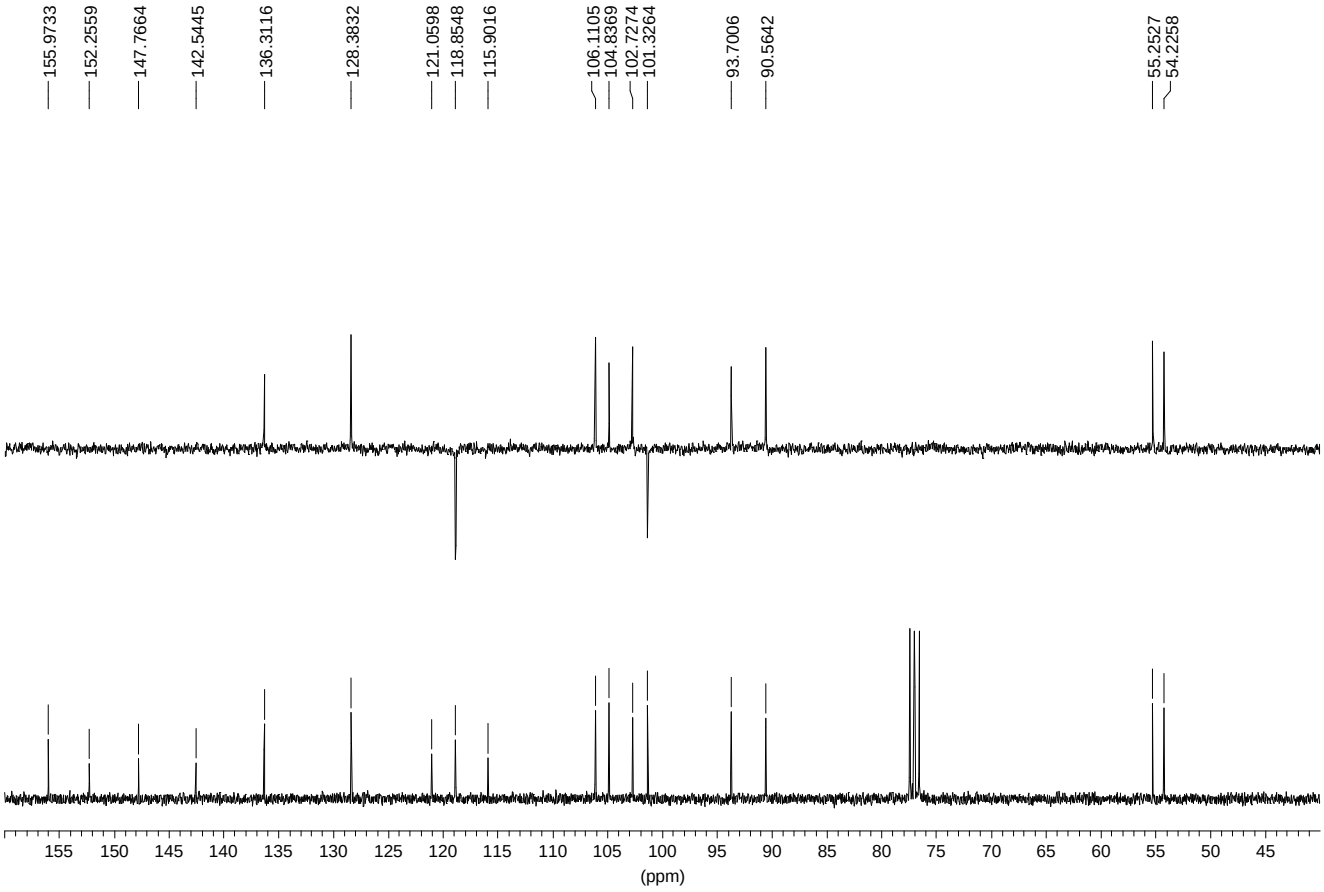
4.4
4.2
4.0
3.8
3.6
(ppm)

6d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102.7274
101.3264
93.7006
90.5642
55.2527
54.2258
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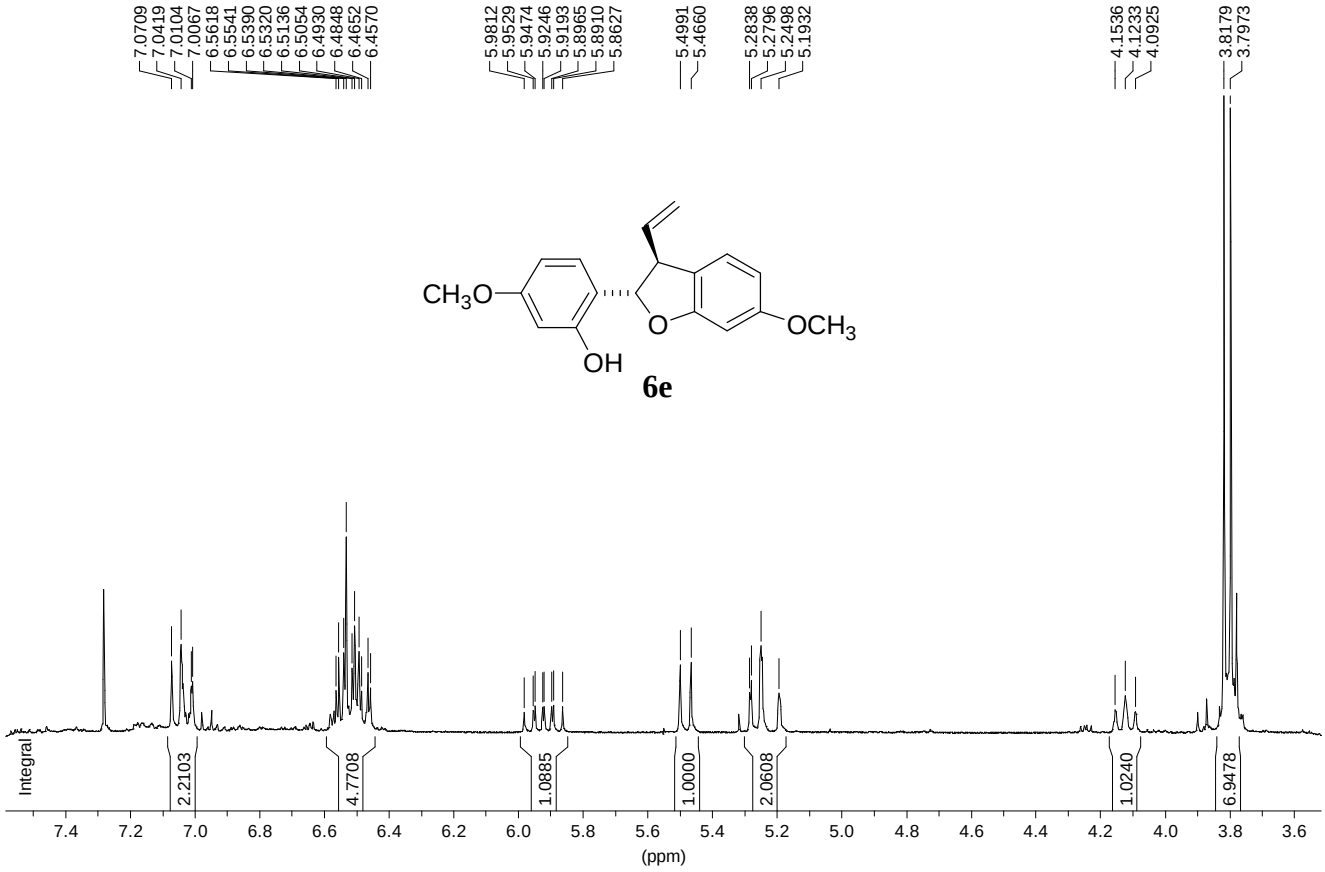
(ppm)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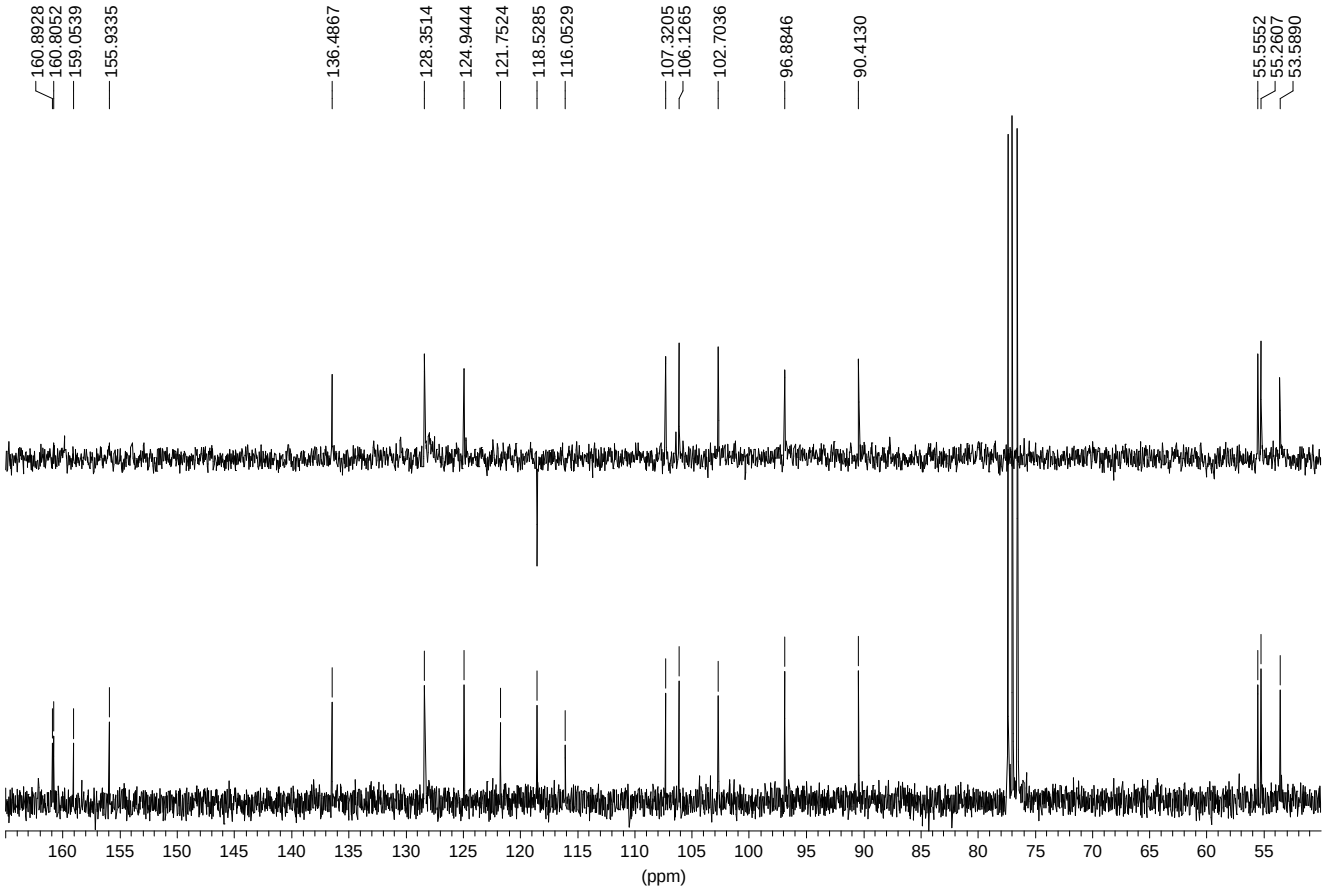
6.4930
6.4848
6.4652
6.4570
5.9812
5.9529
5.9474
5.9246
5.9193
5.8965
5.8910
5.8627
5.4991
5.4660
5.2838
5.2796
5.2498
5.1932
4.1536
4.1233
4.0925
3.8179
3.7973
CH3O
OH
O
OCH3
6e
Integral
2.2103
4.7708
1.0885
1.0000
2.0608
1.0240
6.9478
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6
(ppm)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118.5285
116.0529
107.3205
106.1265
102.7036
96.8846
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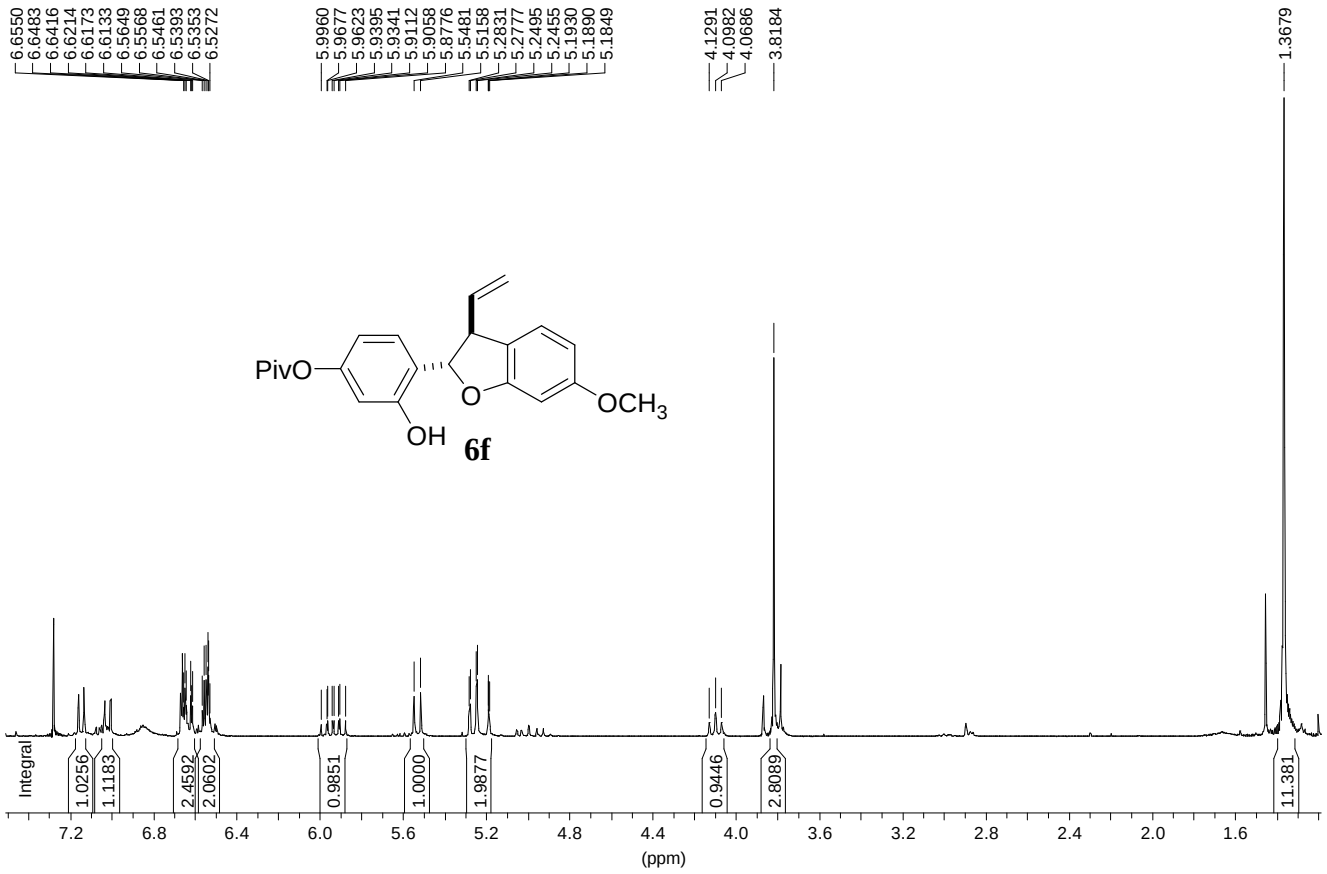
55.5552
55.2607
53.5890
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55
(ppm)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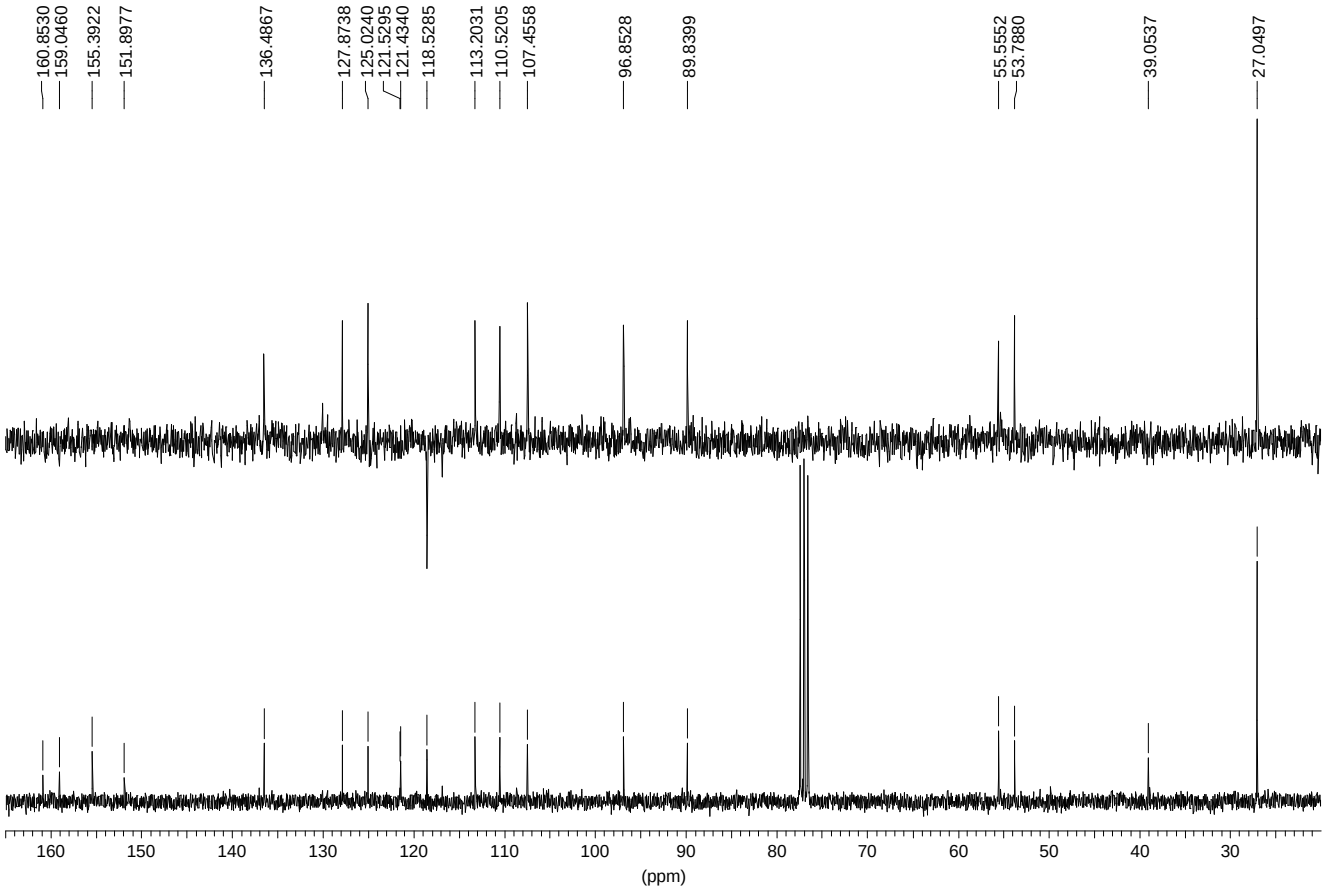
6.5353
6.5272
5.9960
5.9677
5.9623
5.9395
5.9341
5.9112
5.9058
5.8776
5.5481
5.5158
5.2831
5.2777
5.2495
5.2455
5.1930
5.1890
5.1849
4.1291
4.0982
4.0686
3.8184
1.3679
PivO
O
OCH3
OH
6f
Integral
1.0256
1.1183
2.4592
2.0602
0.9851
1.0000
1.9877
0.9446
2.8089
11.381
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
(ppm)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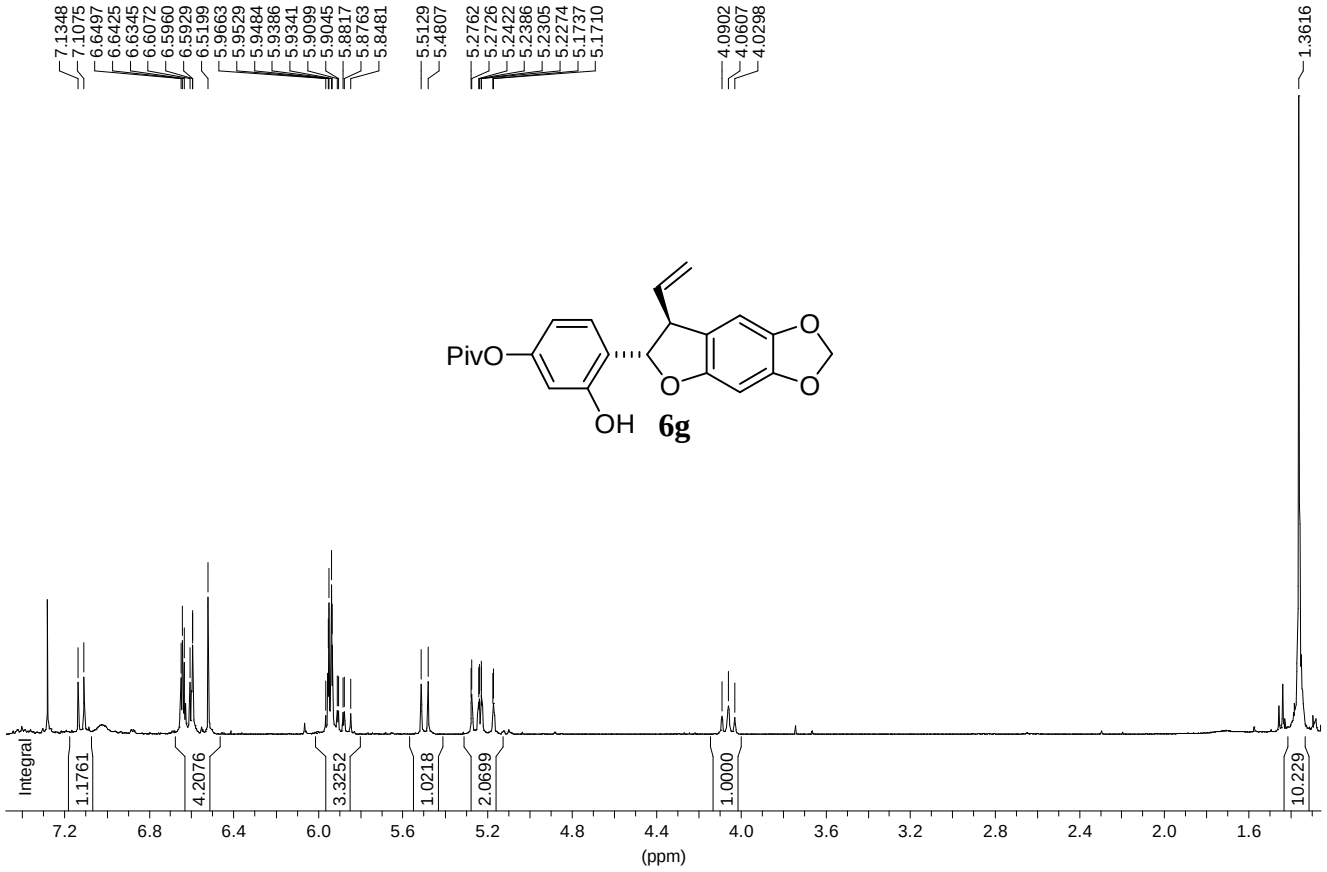
113.2031
110.5205
107.4558
96.8528
89.8399
55.5552
53.7880
39.0537
27.0497
160
150
140
130
120
110
100
90
80
70
60
50
40
30
(ppm)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6.5199
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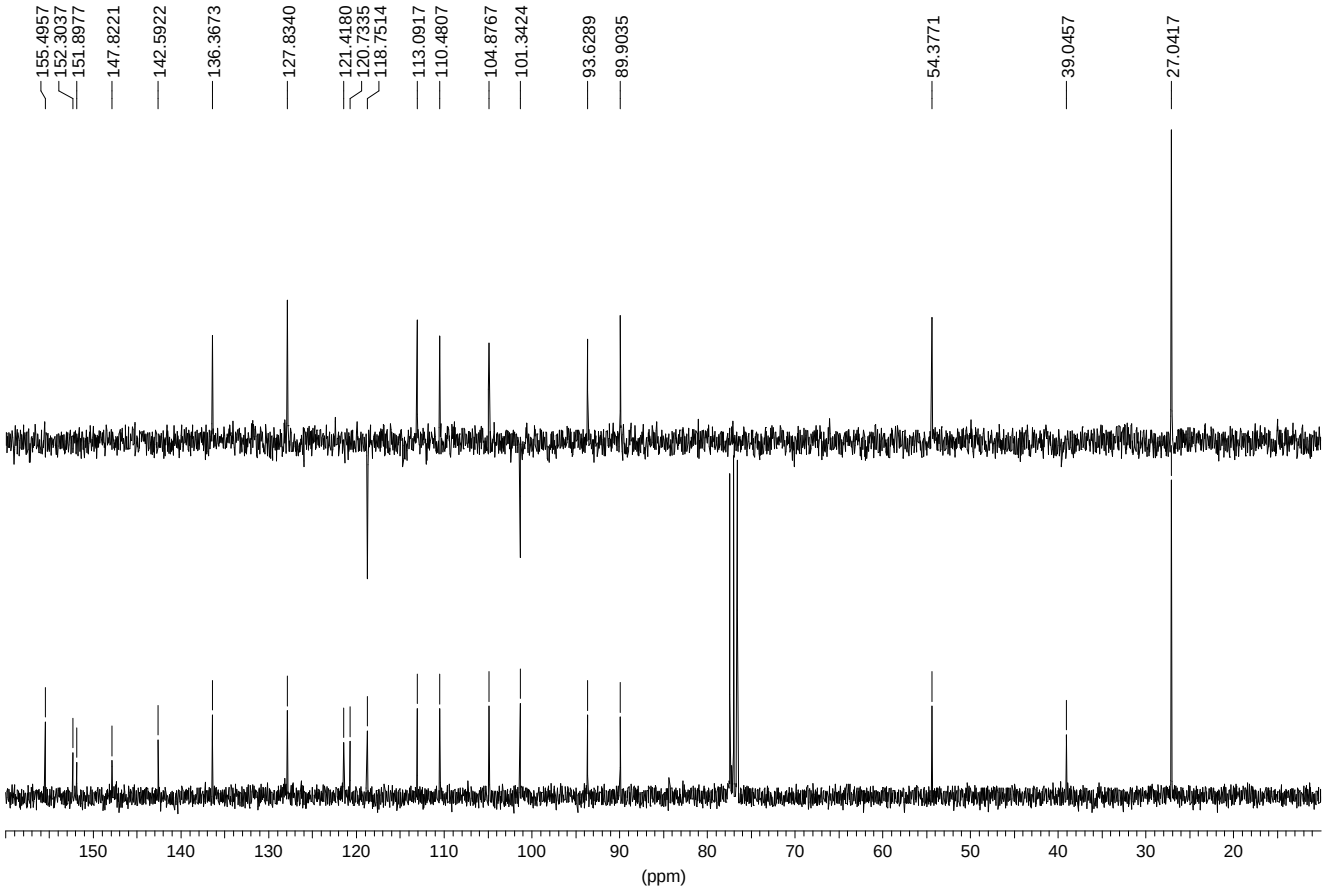
5.9529
5.9484
5.9386
5.9341
5.9099
5.9045
5.8817
5.8763
5.8481
5.5129
5.4807
5.2762
5.2726
5.2422
5.2386
5.2305
5.2274
5.1737
5.1710
4.0902
4.0607
4.0298
1.3616
PivO
OH
6g
Integral
1.1761
4.2076
3.3252
1.0218
2.0699
1.0000
10.229
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
(ppm)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113.0917
110.4807
104.8767
101.3424
93.6289
89.9035
54.3771
39.0457
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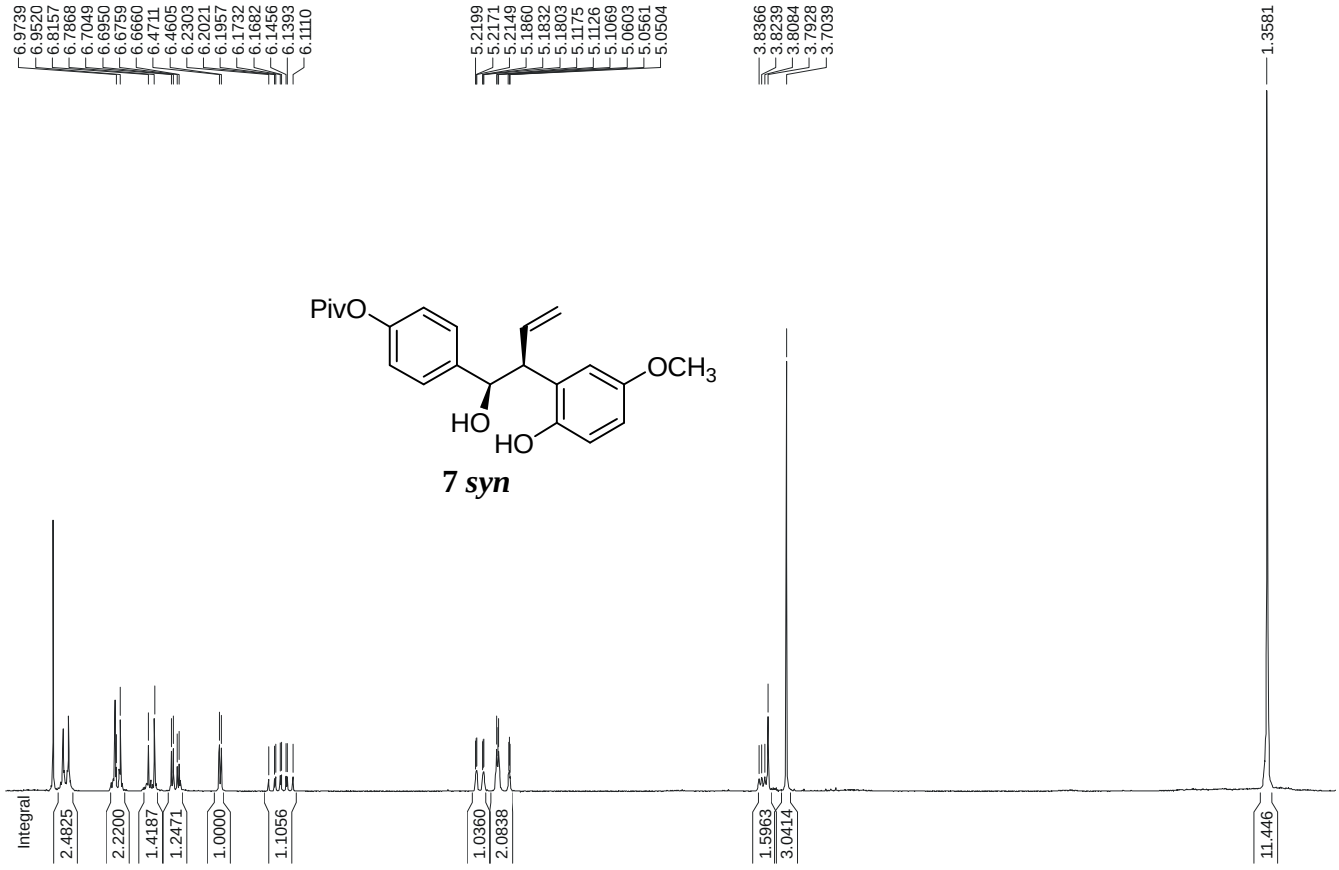
150
140
130
120
110
100
90
80
70
60
50
40
30
20
(ppm)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6.8157
6.7868
6.7049
6.6950
6.6759
6.6660
6.4711
6.4605
6.2303
6.2021
6.1957
6.1732
6.1682
6.1456
6.1393
6.1110
5.2199
5.2171
5.2149
5.1860
5.1832
5.1803
5.1175
5.1126
5.1069
5.0603
5.0561
5.0504
3.8366
3.8239
3.8084
3.7928
3.7039
1.3581
PivO
OCH3
HO
HO
Integral
2.4825
2.2200
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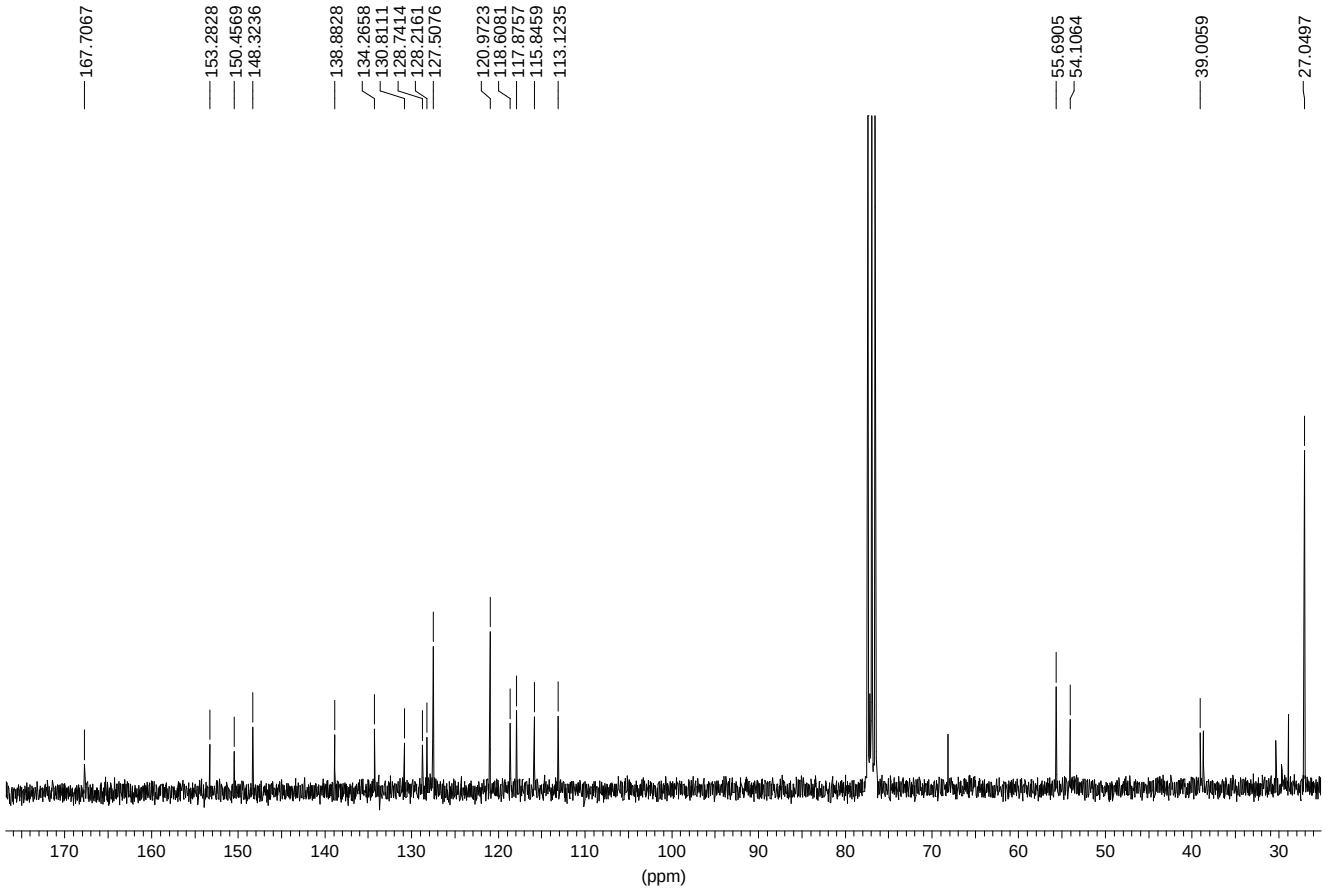
1.0000
1.1056
1.0360
2.0838
1.5963
3.0414
11.446

7 *syn*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150.4569
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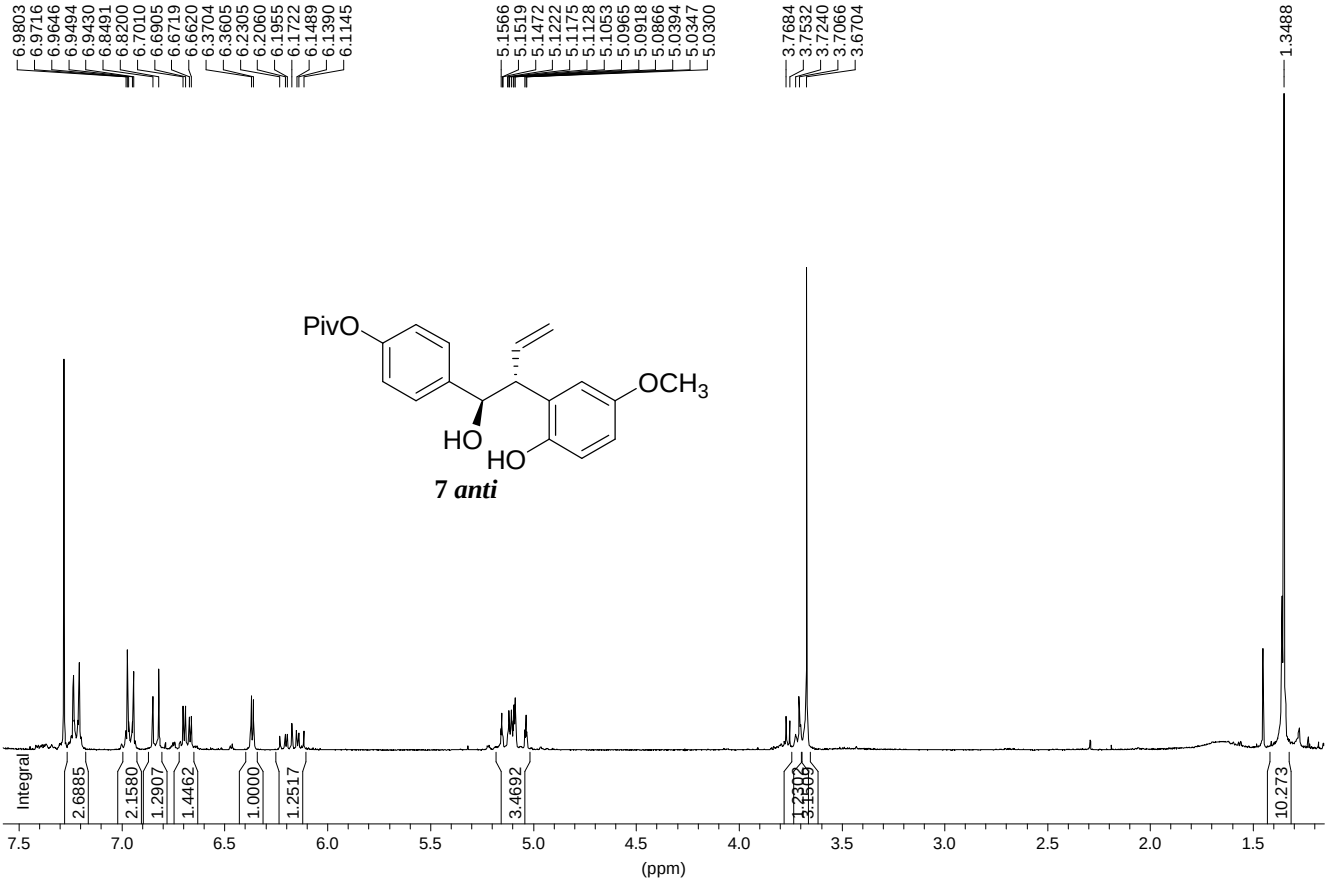
128.2161
127.5076
120.9723
118.6081
117.8757
115.8459
113.1235
55.6905
54.1064
39.0059
27.0497
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
(ppm)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6.9430
6.8491
6.8200
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6.6905
6.6719
6.6620
6.3704
6.3605
6.2305
6.2060
6.1955
6.1722
6.1489
6.1390
6.1145
5.1566
5.1519
5.1472
5.1222
5.1175
5.1128
5.1053
5.0965
5.0918
5.0866
5.0394
5.0347
5.0300
3.7684
3.7532
3.7240
3.7066
3.6704
1.3488
PivO
OCH3
HO
HO
7 anti
Integral
2.6885
2.1580
1.2907
1.4462
1.0000
1.2517
3.4692
1.2306
3.1506
10.273
7.5
7.0
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5.0
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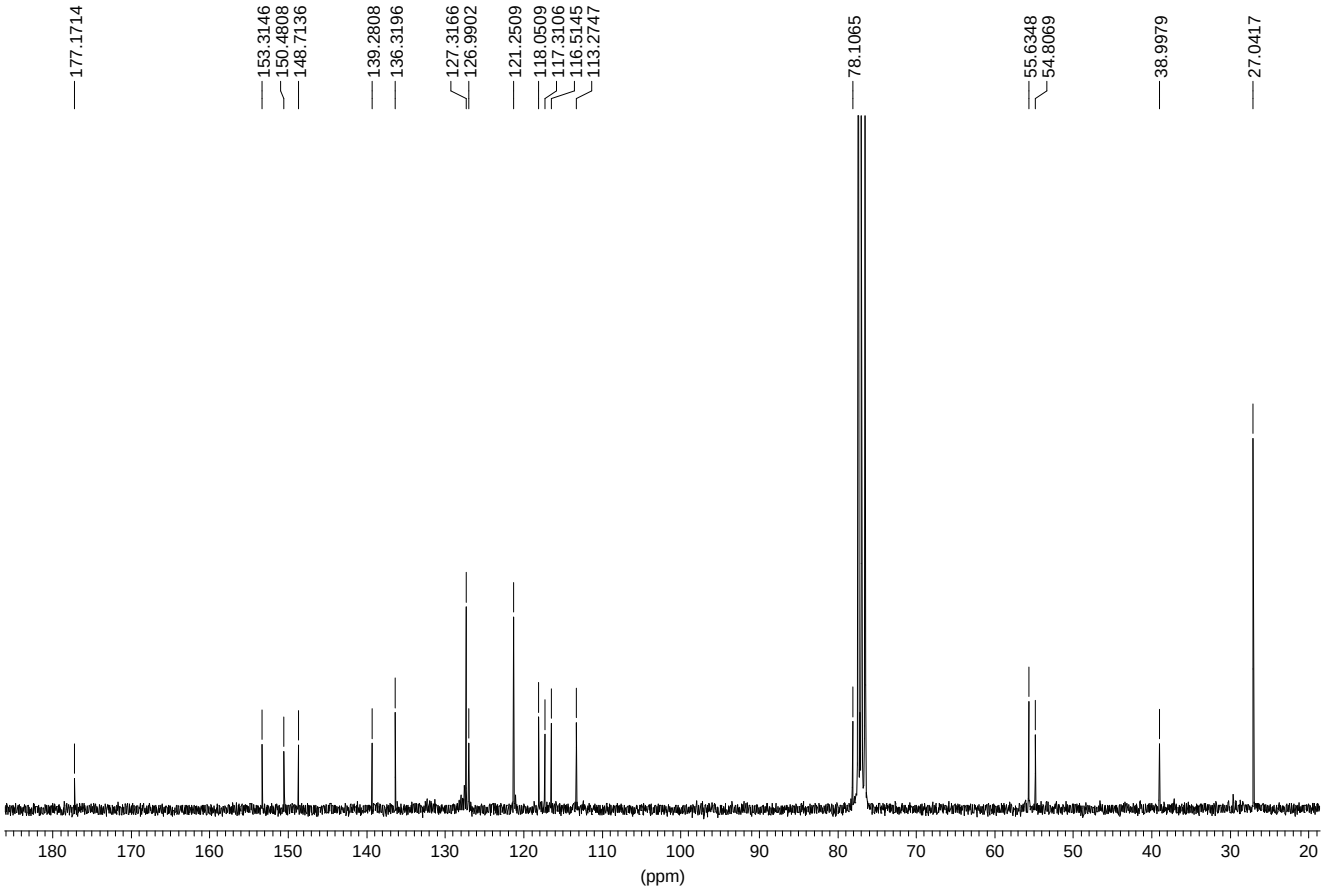
4.0
3.5
3.0
2.5
2.0
1.5
(ppm)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116.5145
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78.1065
55.6348
54.8069
38.9979
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180
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150
140
130
120
110
100
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80
70
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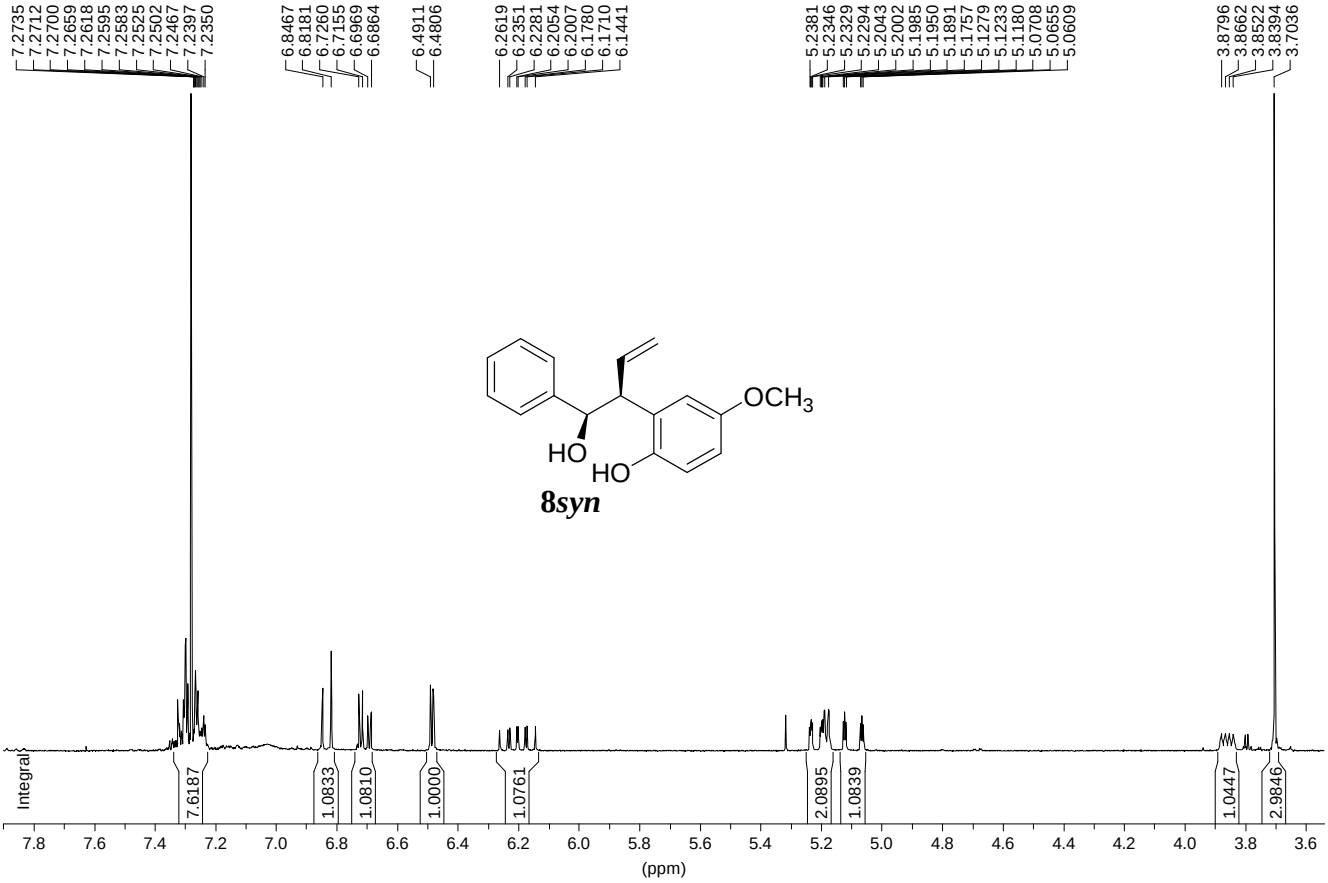
40
30
20
(ppm)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7.2350
6.8467
6.8181
6.7260
6.7155
6.6969
6.6864
6.4911
6.4806
6.2619
6.2351
6.2281
6.2054
6.2007
6.1780
6.1710
6.1441
5.2381
5.2346
5.2329
5.2294
5.2043
5.2002
5.1985
5.1950
5.1891
5.1757
5.1279
5.1233
5.1180
5.0708
5.0655
5.0609
3.8796
3.8662
3.8522
3.8394
3.7036
OCH3
HO
HO
Integral
7.6187
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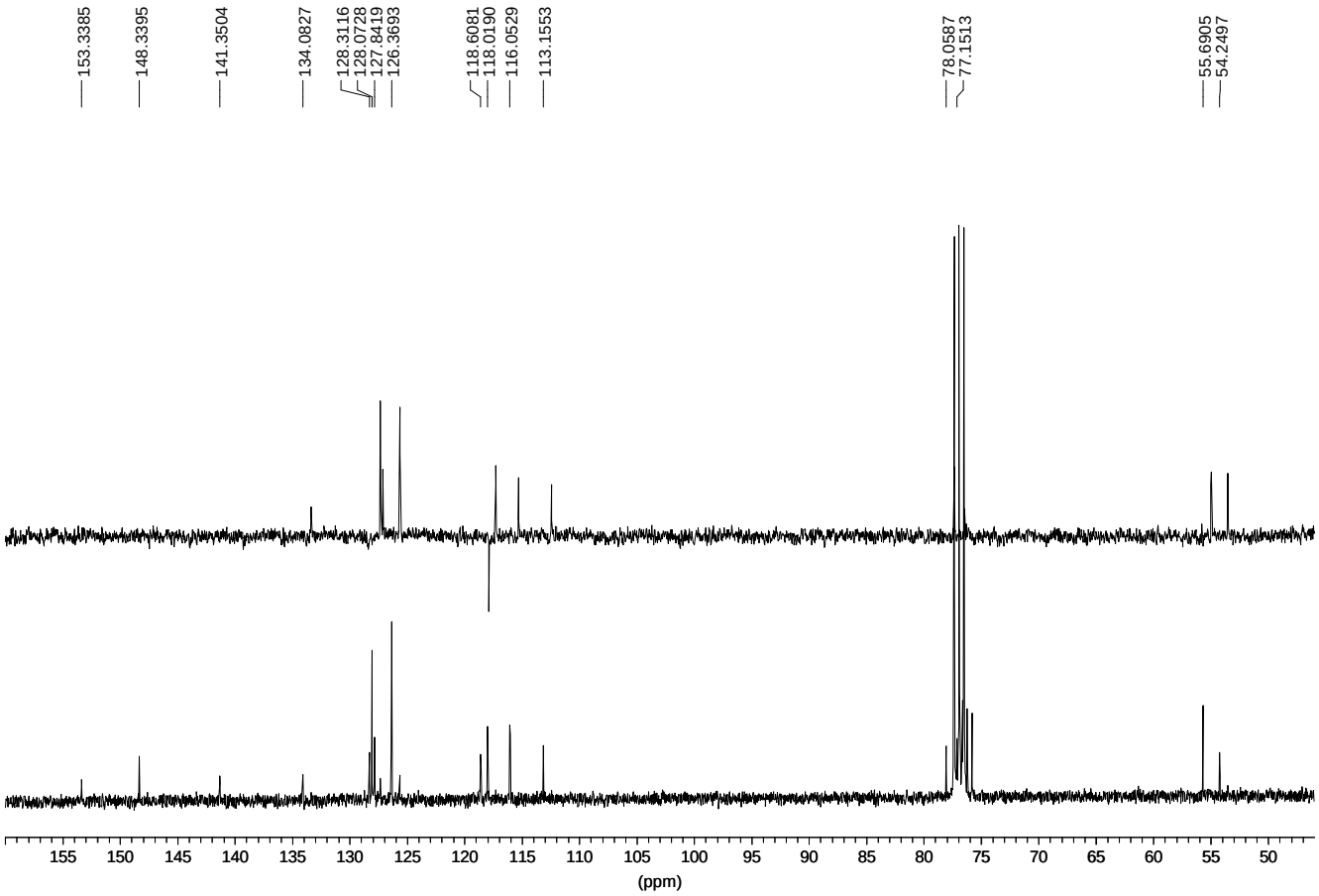
1.0810
1.0000
1.0761
2.0895
1.0839
1.0447
2.9846
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6
(ppm)

8*syn*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127.8419
126.3693
118.6081
118.0190
116.0529
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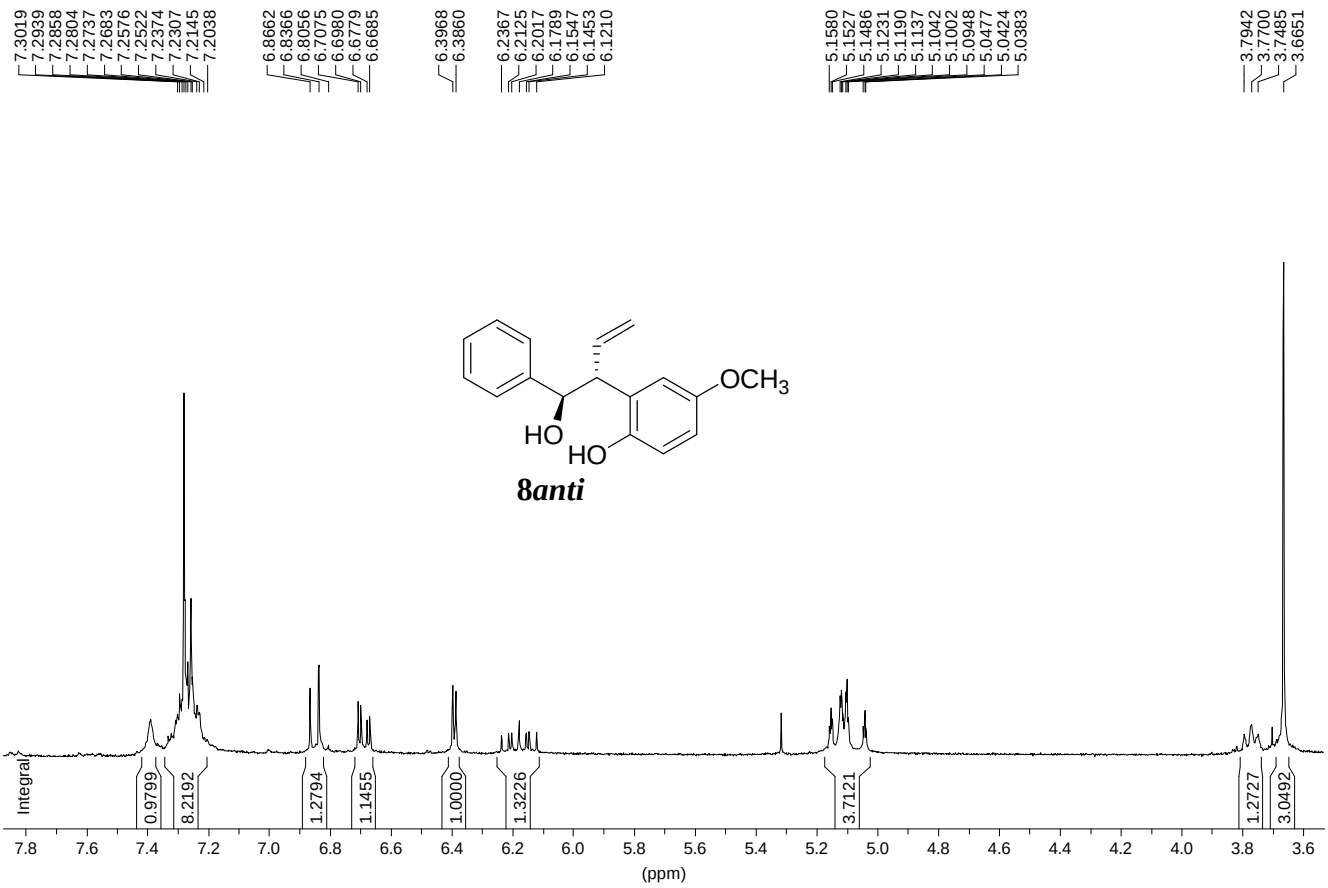
77.1513
55.6905
54.2497
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50
(ppm)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7.2038
6.8662
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6.8056
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6.6980
6.6779
6.6685
6.3968
6.3860
6.2367
6.2125
6.2017
6.1789
6.1547
6.1453
6.1210
5.1580
5.1527
5.1486
5.1231
5.1190
5.1137
5.1042
5.1002
5.0948
5.0477
5.0424
5.0383
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3.7700
3.7485
3.6651
OCH3
HO
HO
8anti
Integral
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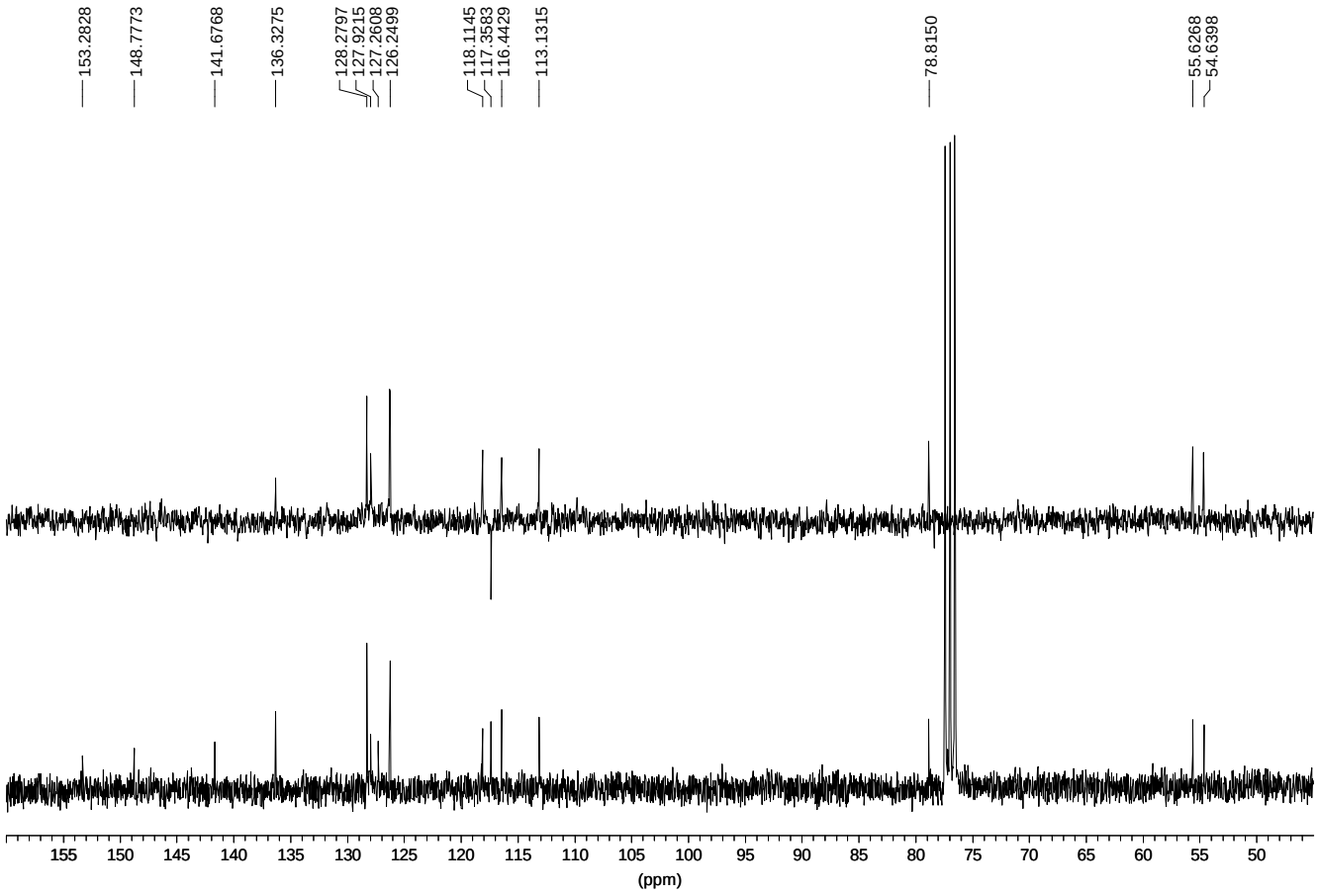
1.0000
1.3226
3.7121
1.2727
3.0492
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6
(ppm)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54.6398
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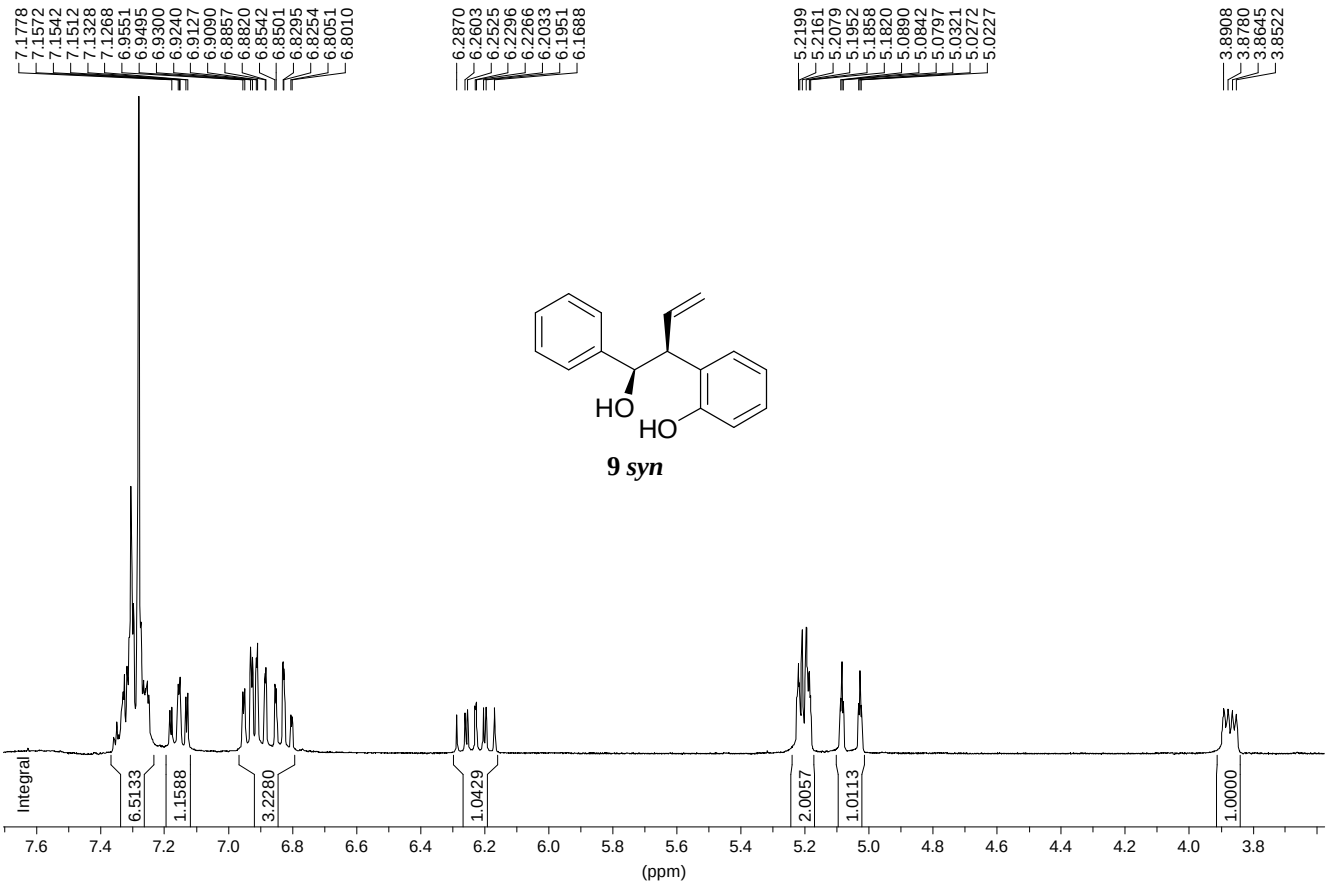
(ppm)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6.9090
6.8857
6.8820
6.8542
6.8501
6.8295
6.8254
6.8051
6.8010
6.2870
6.2603
6.2525
6.2296
6.2266
6.2033
6.1951
6.1688
5.2199
5.2161
5.2079
5.1952
5.1858
5.1820
5.0890
5.0842
5.0797
5.0321
5.0272
5.0227
3.8908
3.8780
3.8645
3.8522
HO
HO
Integral
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1.1588
3.2280
1.0429
2.0057
1.0113
1.0000
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
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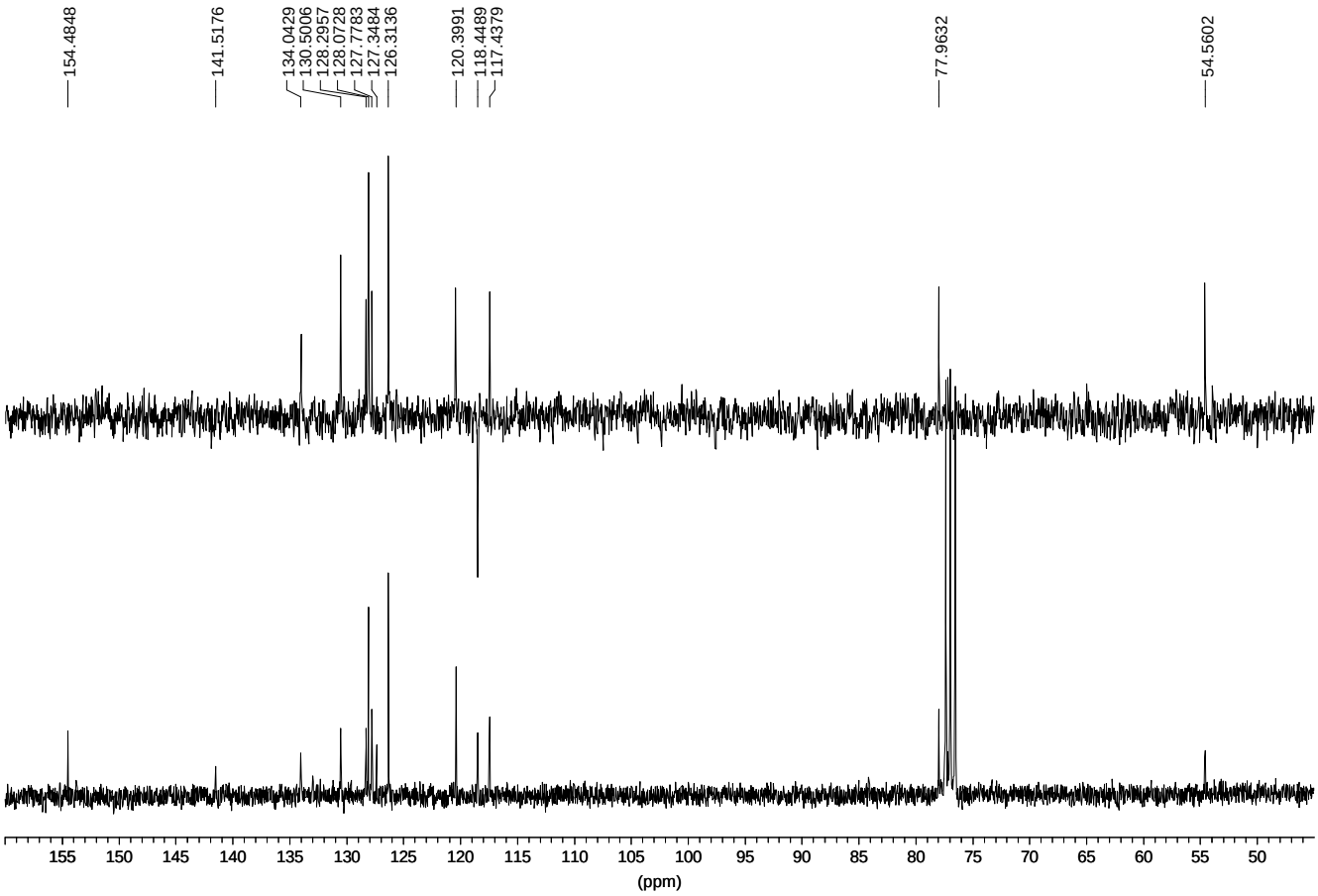
5.0
4.8
4.6
4.4
4.2
4.0
3.8
(ppm)

9 ***syn***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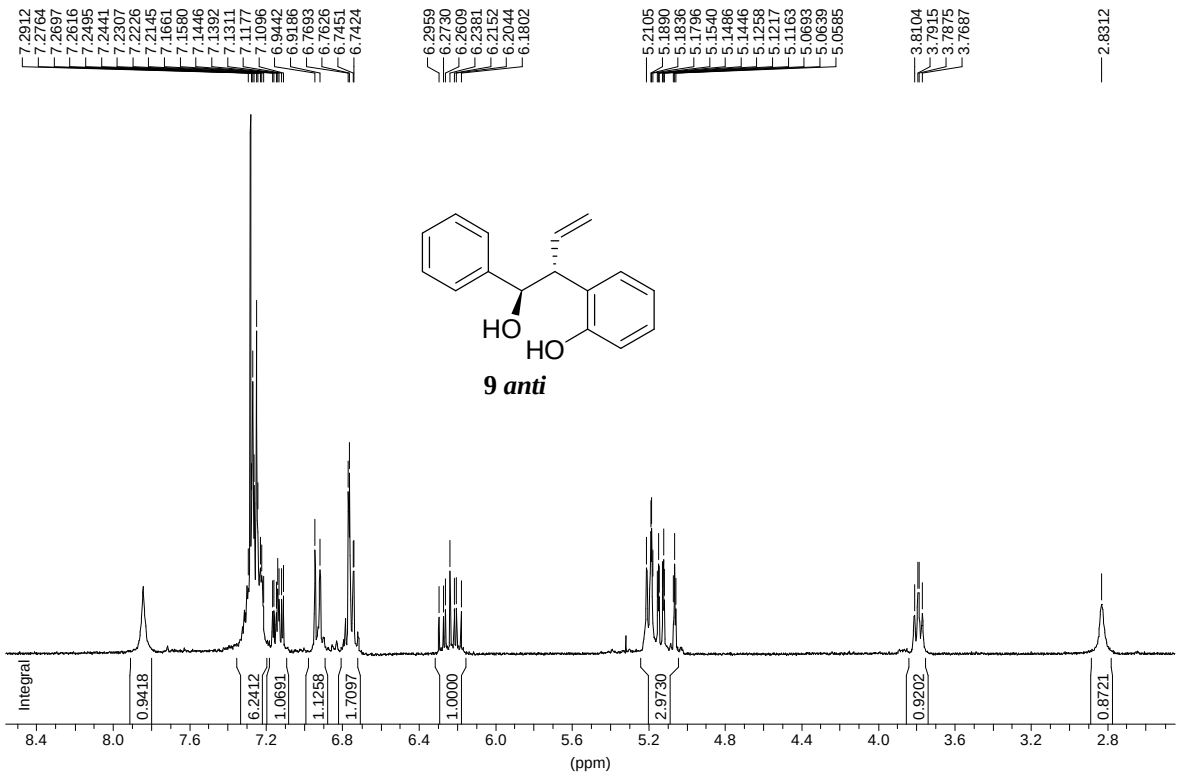
54.5602
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50
(ppm)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7.1580
7.1446
7.1392
7.1311
7.1177
7.1096
6.9442
6.9186
6.7693
6.7626
6.7451
6.7424
6.2959
6.2730
6.2609
6.2381
6.2152
6.2044
6.1802
5.2105
5.1890
5.1836
5.1796
5.1540
5.1486
5.1446
5.1258
5.1217
5.1163
5.0693
5.0639
5.0585
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3.7915
3.7875
3.7687
2.8312
HO
HO
Integral
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6.2412
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1.1258
1.7097
1.0000
2.9730
0.9202
0.8721
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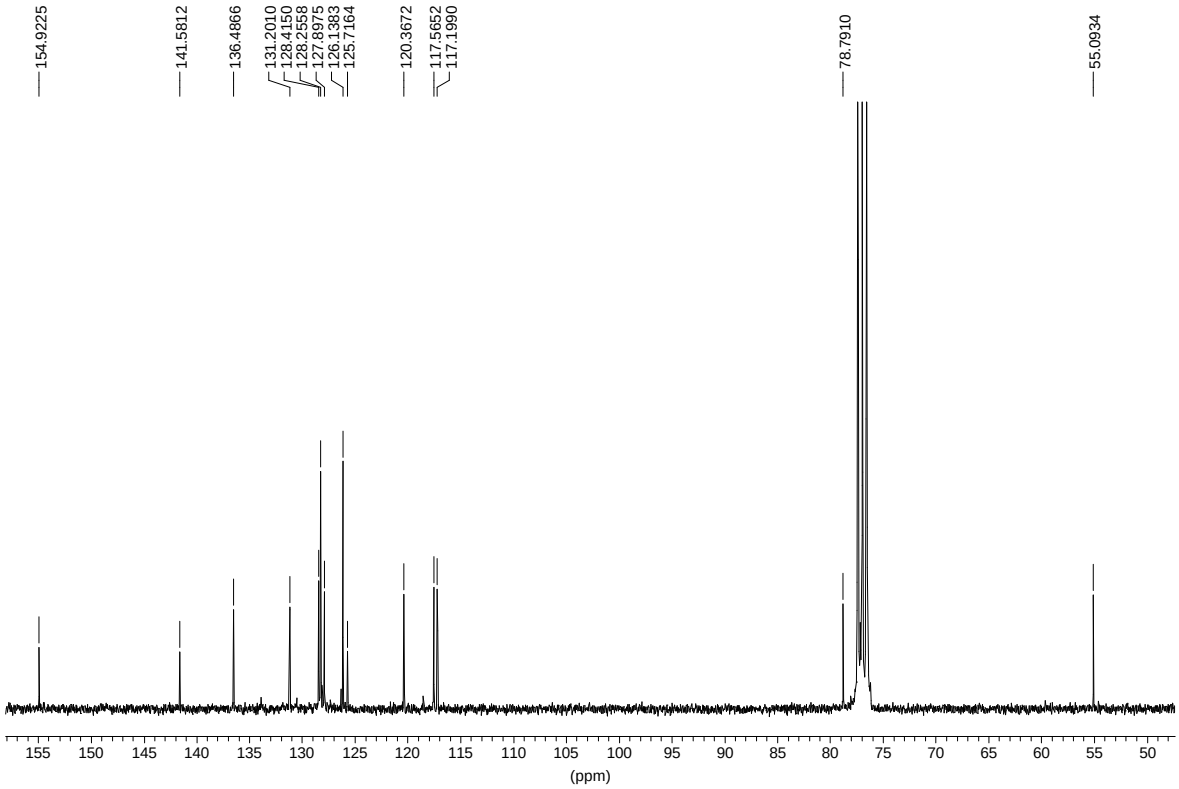
(ppm)

9 ***anti***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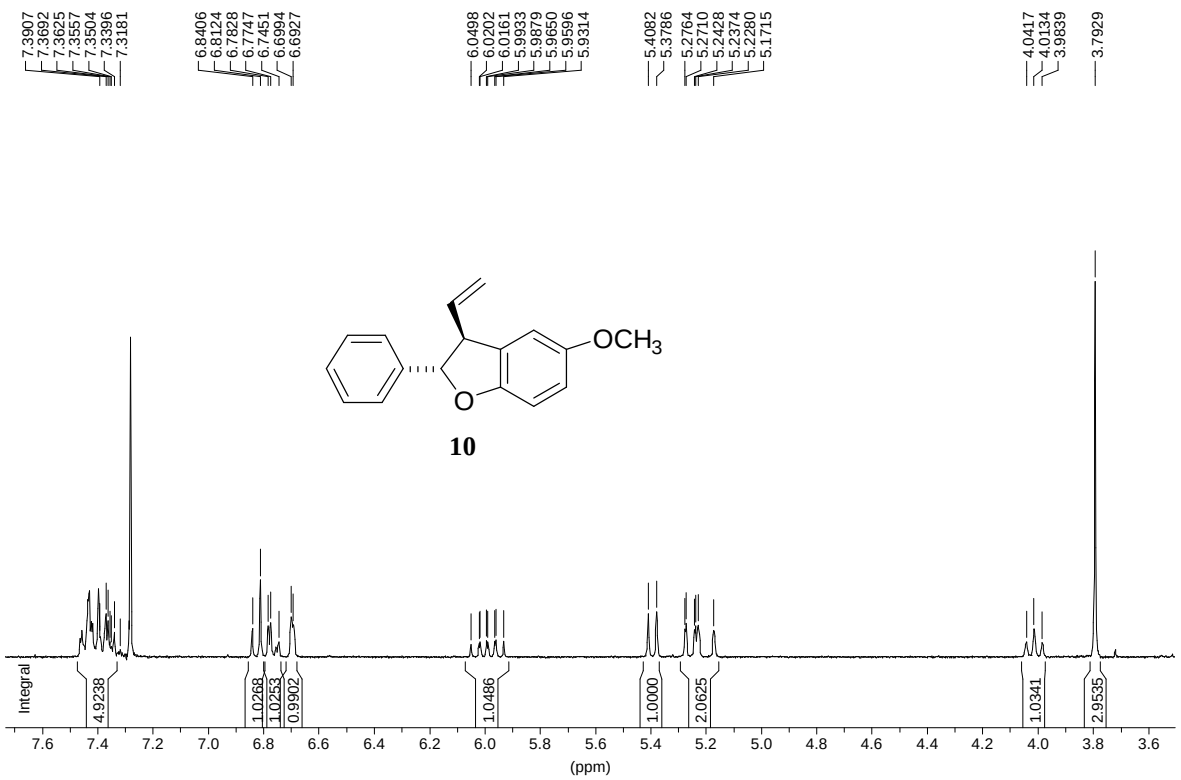
(ppm)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6.7828
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6.7451
6.6994
6.6927
6.0498
6.0202
6.0161
5.9933
5.9879
5.9650
5.9596
5.9314
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5.2710
5.2428
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4.0417
4.0134
3.9839
3.7929
OCH3
O
10
Integral
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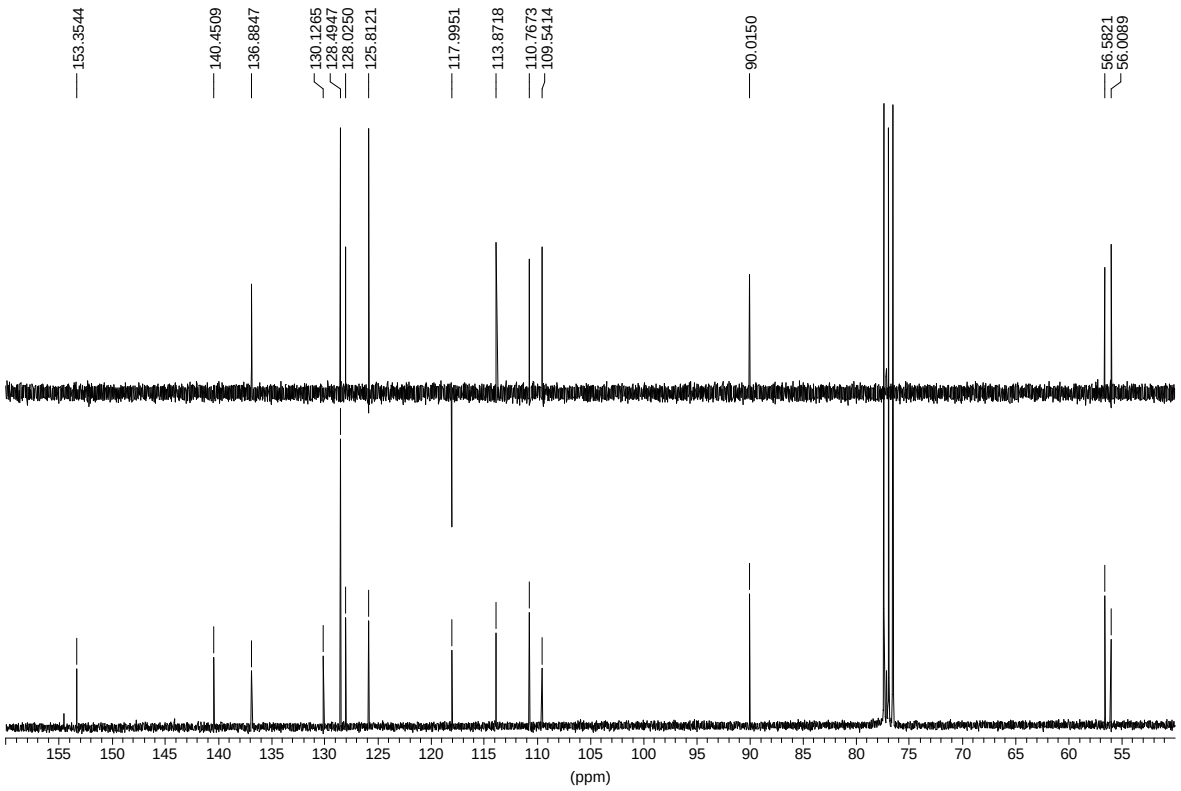
1.0268
1.0253
0.9902
1.0486
1.0000
2.0625
1.0341
2.9535
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6
(ppm)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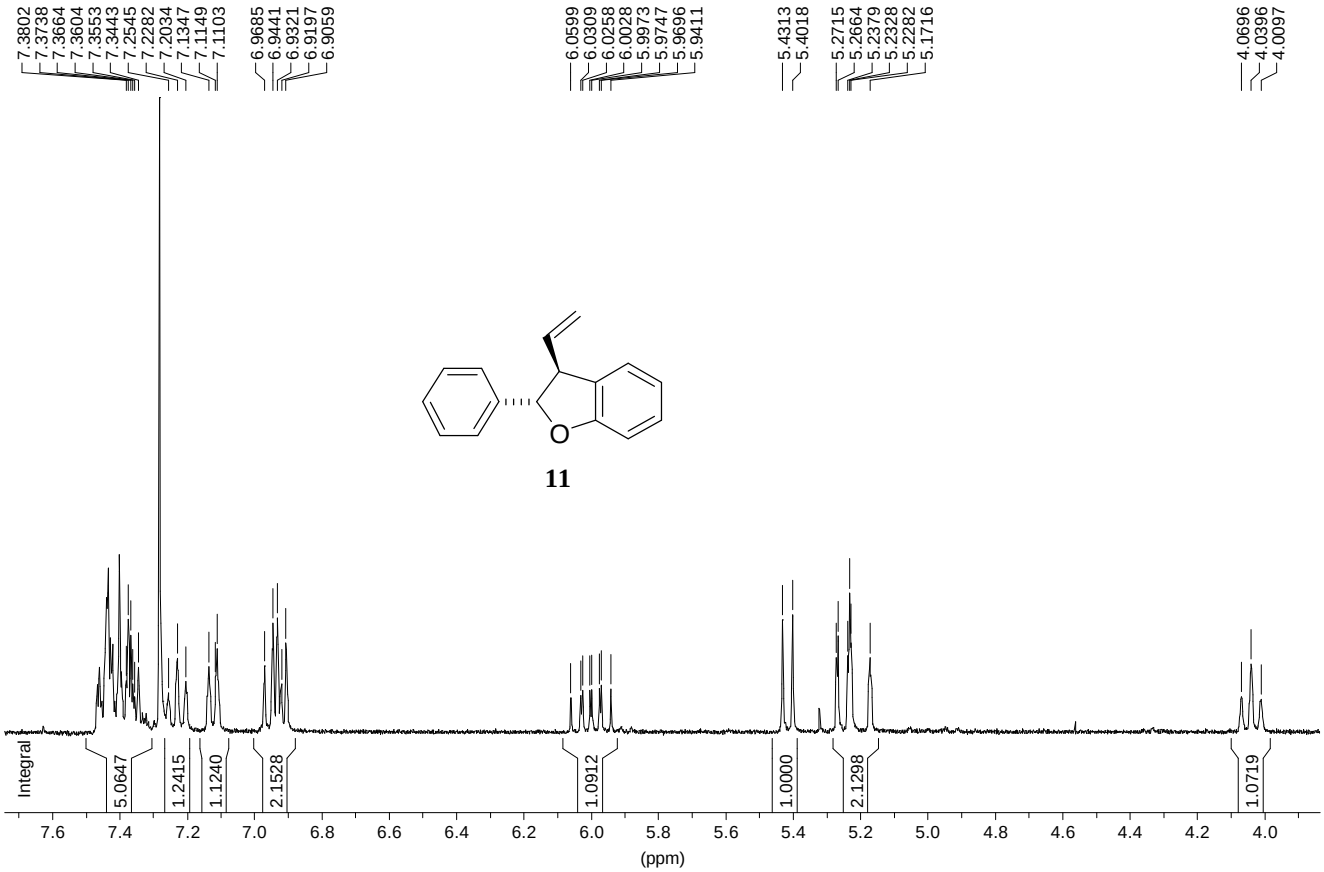
90.0150
56.5821
56.0089
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55
(ppm)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7.1149
7.1103
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6.9197
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6.0258
6.0028
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5.9696
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5.2282
5.1716
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4.0097
O
Integral
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2.1528
1.0912
1.0000
2.1298
1.0719
7.6
7.4
7.2
7.0
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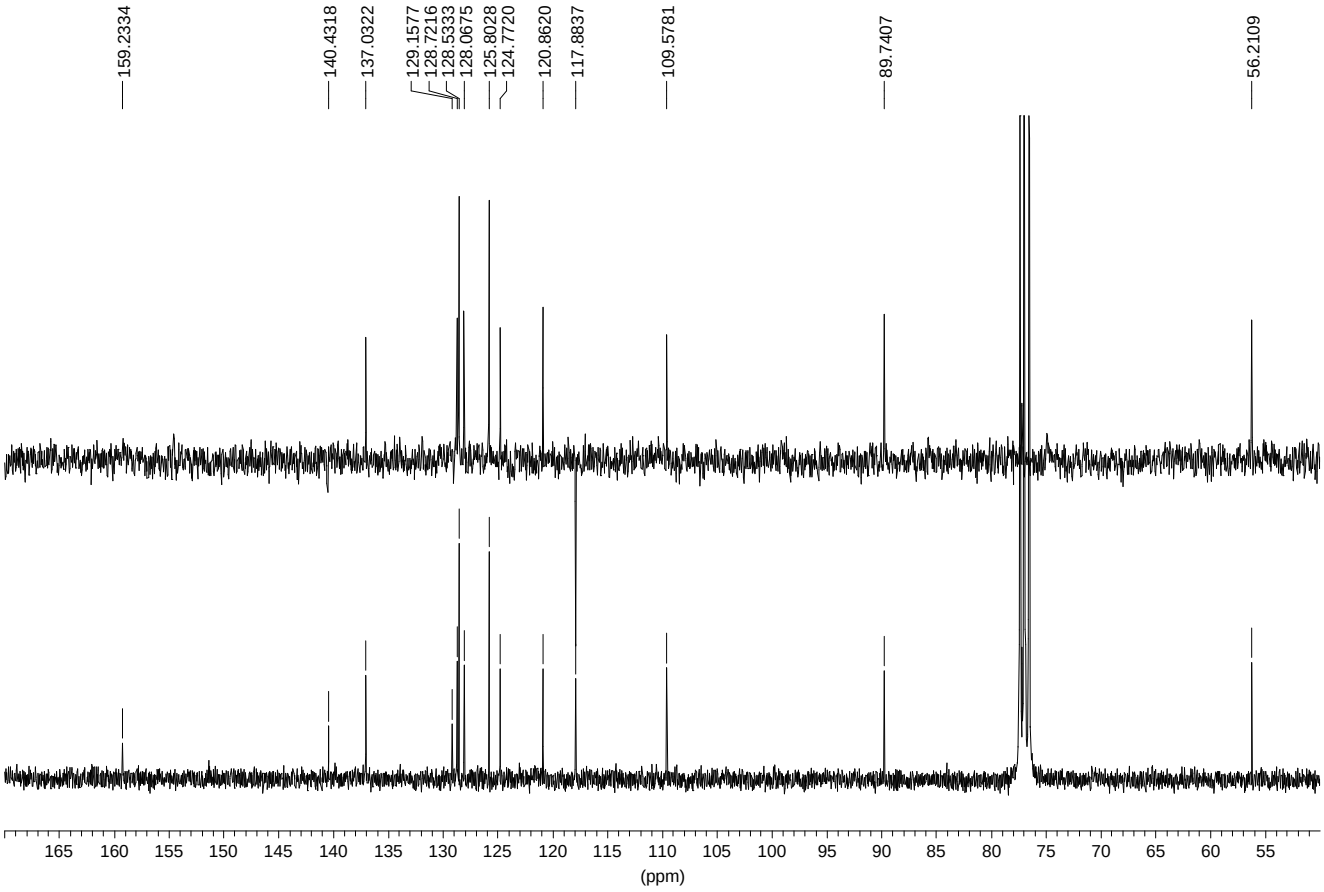
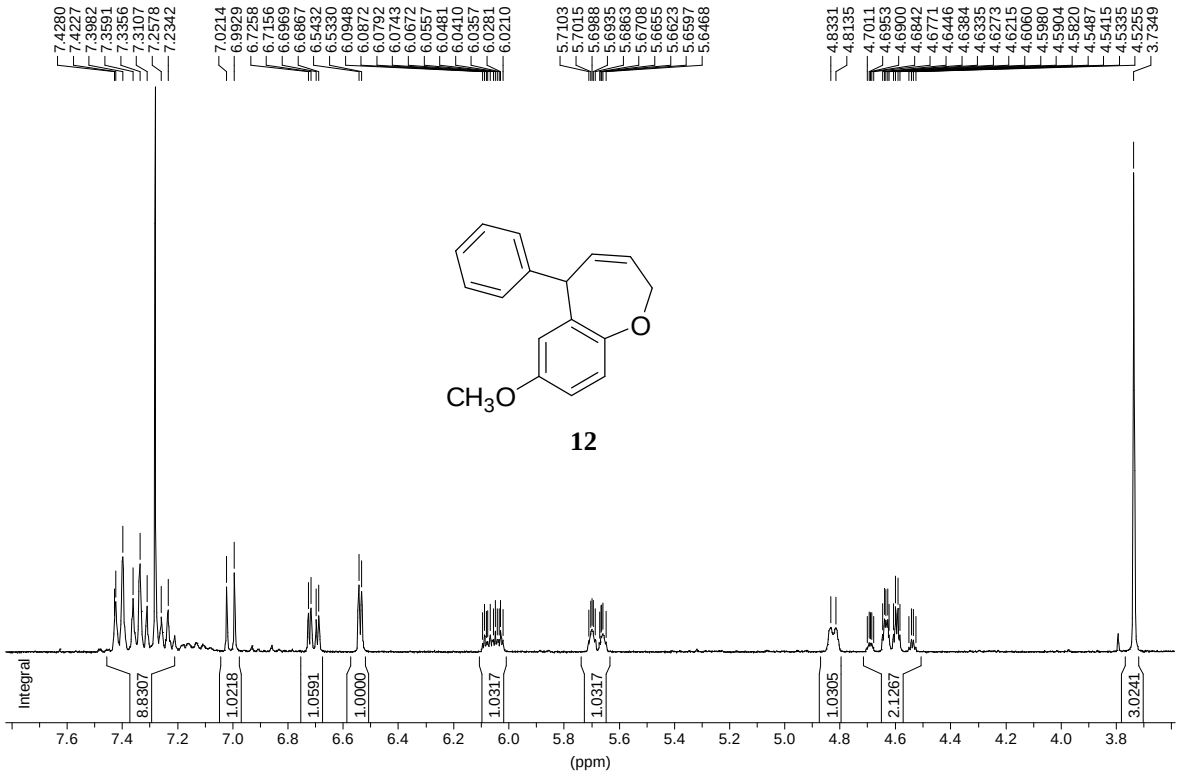
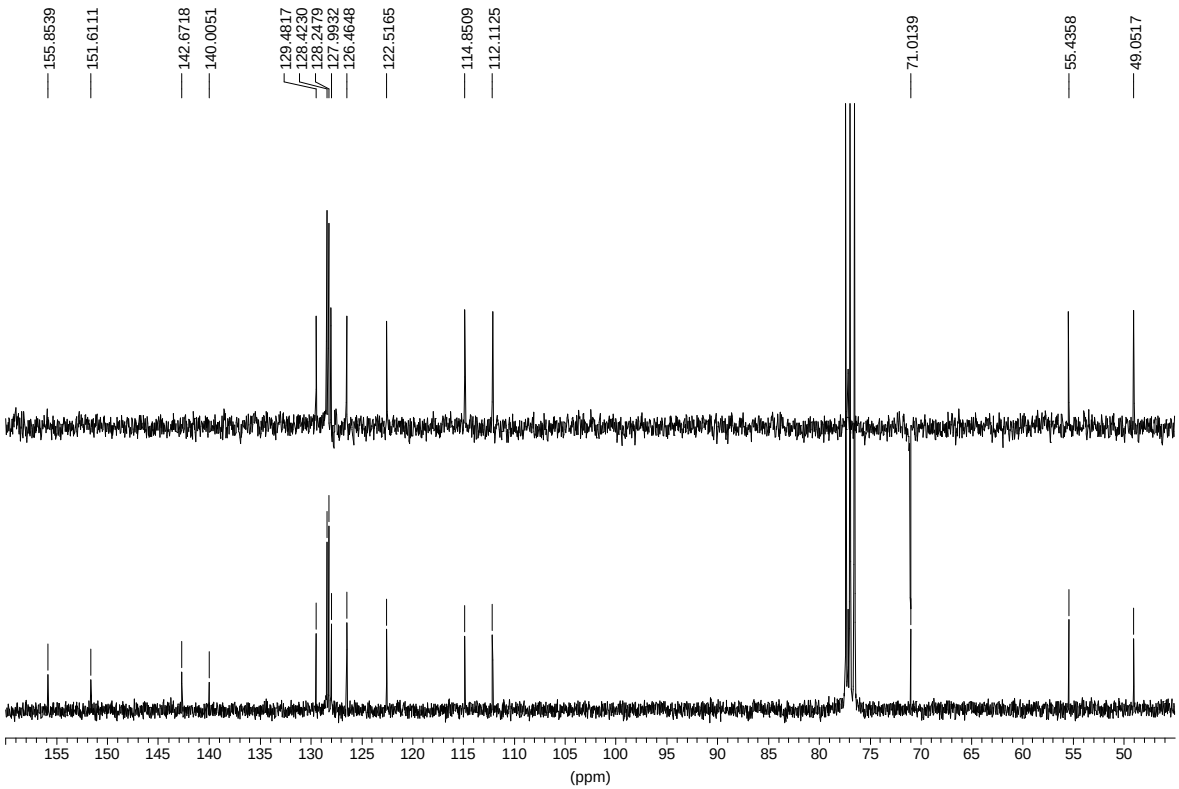
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
(ppm)

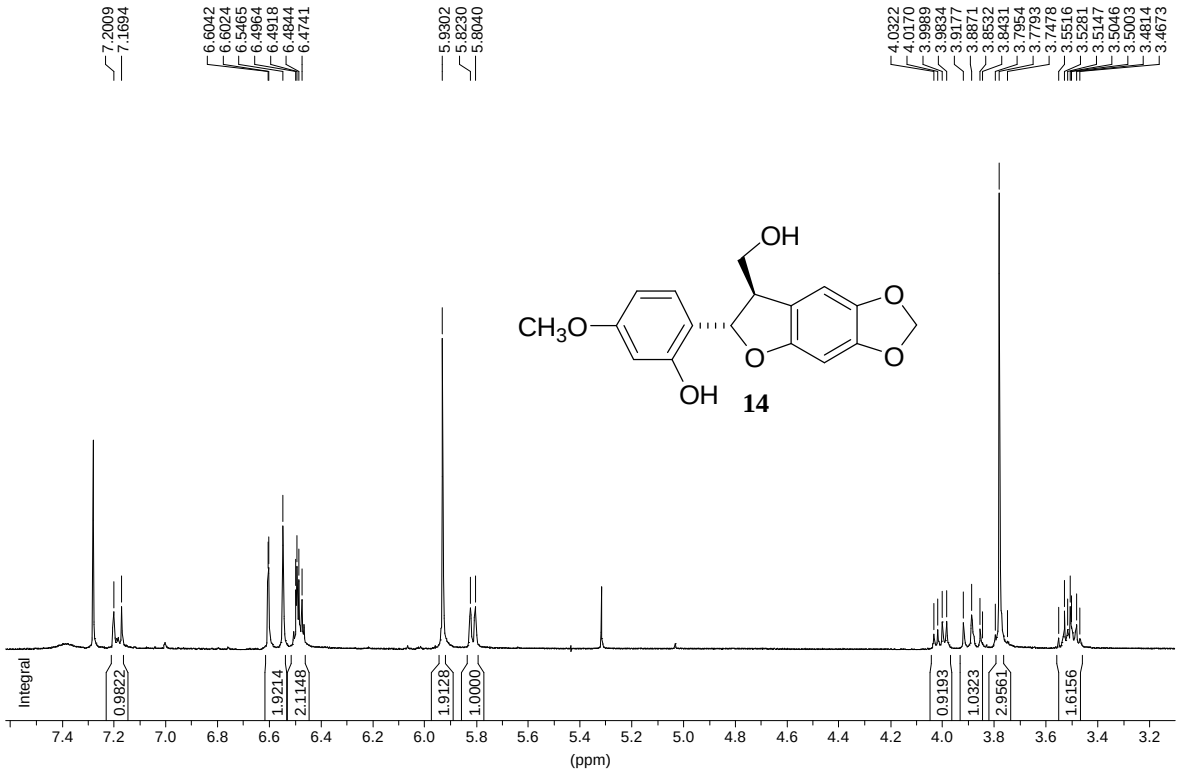
11

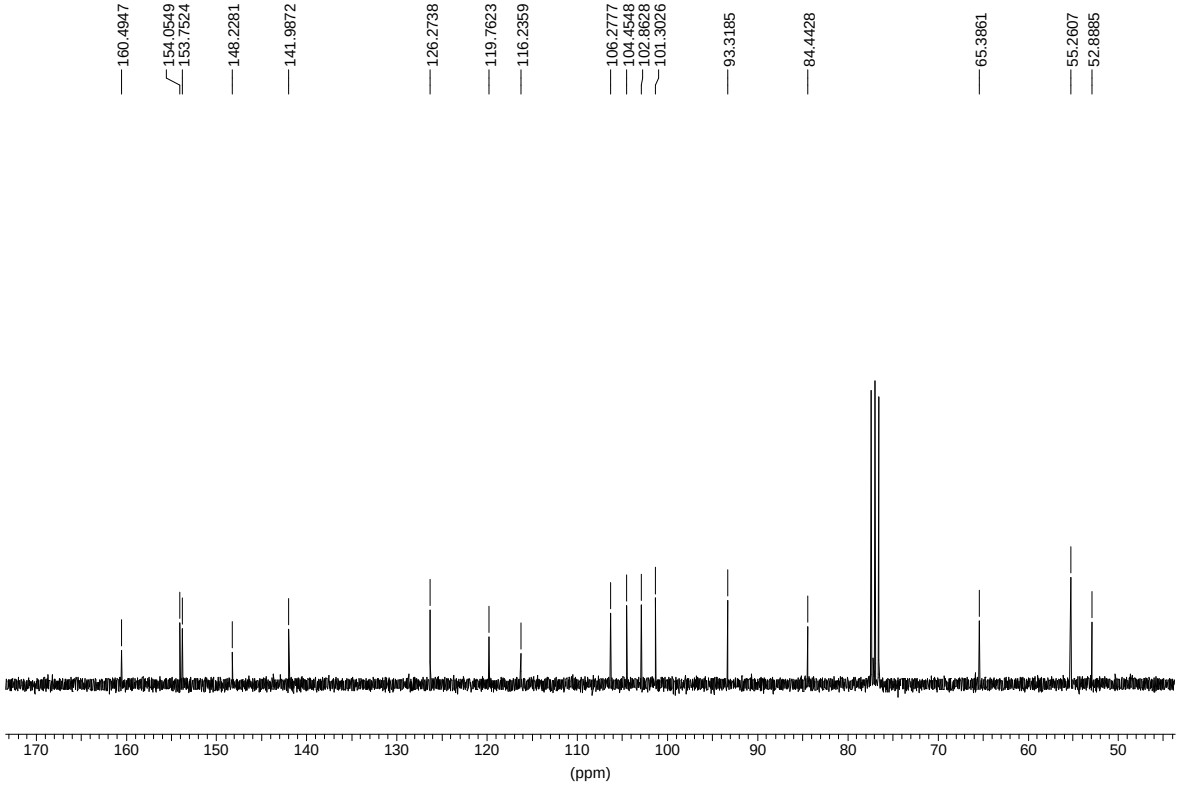

159.2334
140.4318
137.0322
129.1577
128.7216
128.5333
128.0675
125.8028
124.7720
120.8620
117.8837
109.5781
89.7407
56.2109
165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55
(ppm)

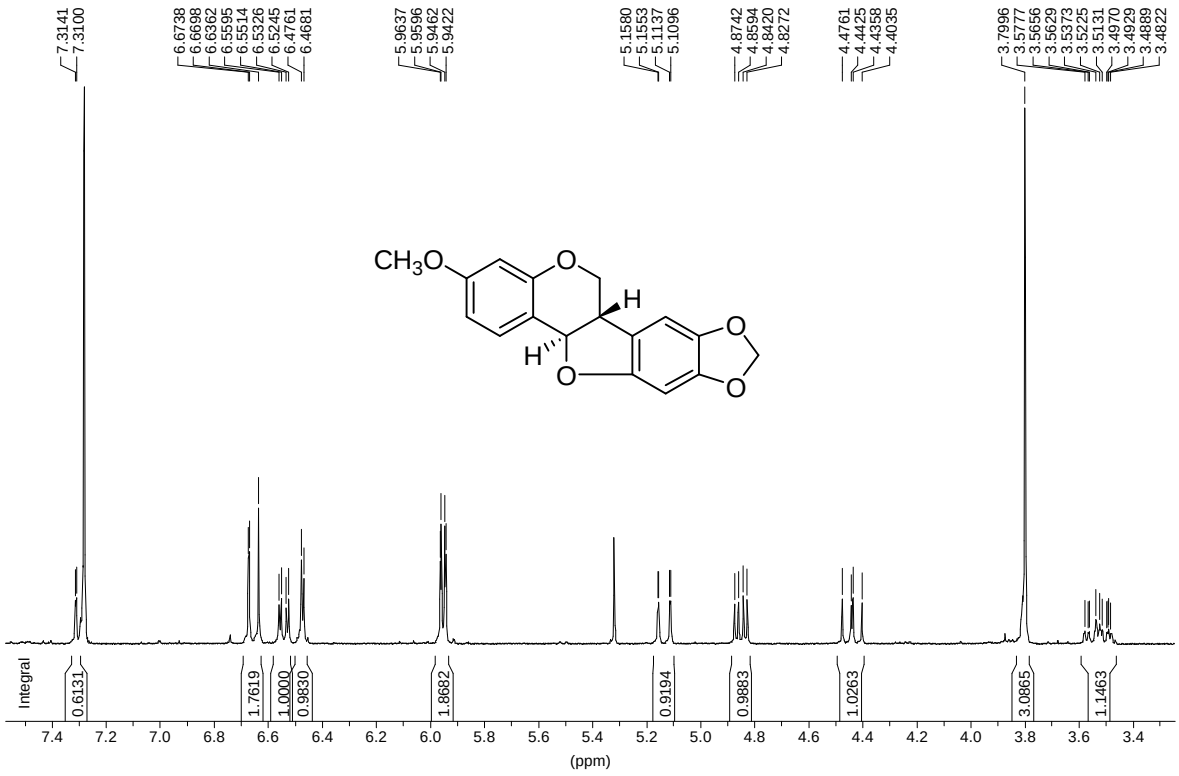

7.4280
7.4227
7.3982
7.3591
7.3356
7.3107
7.2578
7.2342
7.0214
6.9929
6.7258
6.7156
6.6969
6.6867
6.5432
6.5330
6.0948
6.0872
6.0792
6.0743
6.0672
6.0557
6.0481
6.0410
6.0357
6.0281
6.0210
5.7103
5.7015
5.6988
5.6935
5.6863
5.6708
5.6655
5.6623
5.6597
5.6468
4.8331
4.8135
4.7011
4.6953
4.6900
4.6842
4.6771
4.6446
4.6384
4.6335
4.6273
4.6215
4.6060
4.5980
4.5904
4.5820
4.5487
4.5415
4.5335
4.5255
3.7349
O
CH3O
Integral
8.8307
1.0218
1.0591
1.0000
1.0317
1.0317
1.0305
2.1267
3.0241
(ppm)

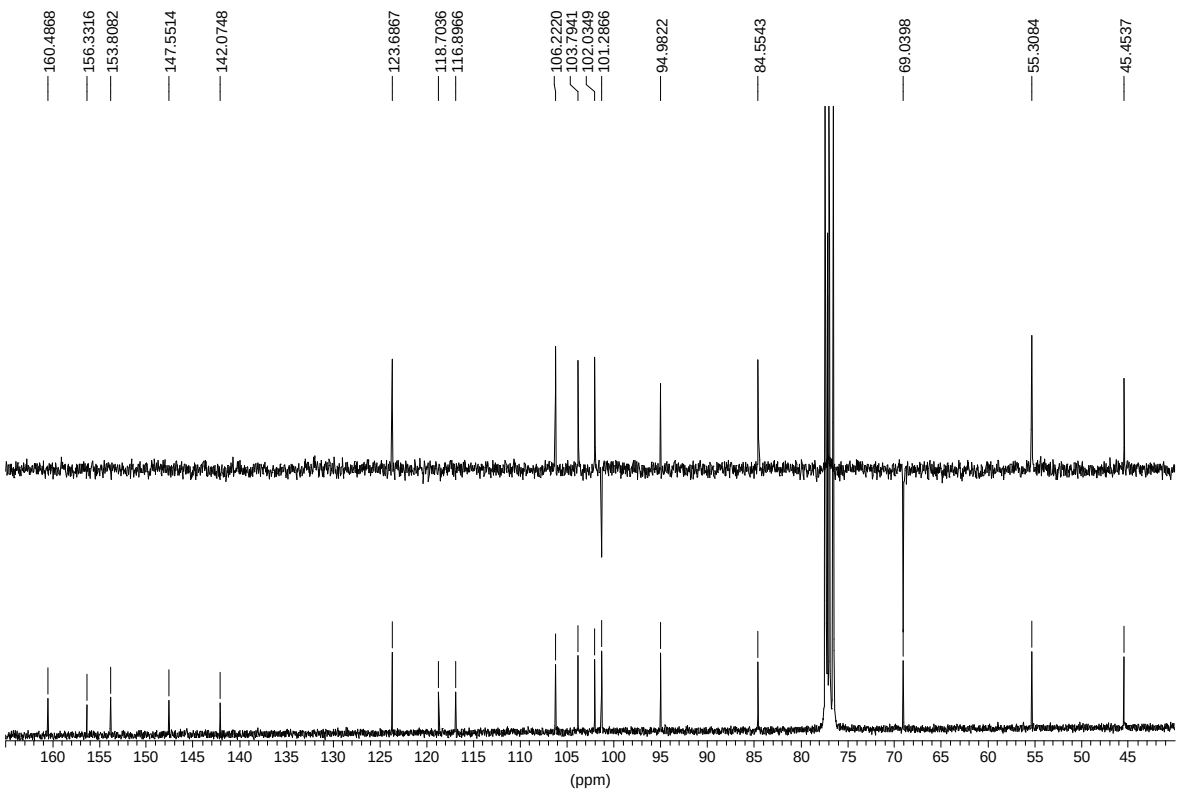
12


155.8539
151.6111
142.6718
140.0051
129.4817
128.4230
128.2479
127.9932
126.4648
122.5165
114.8509
112.1125
71.0139
55.4358
49.0517
(ppm)

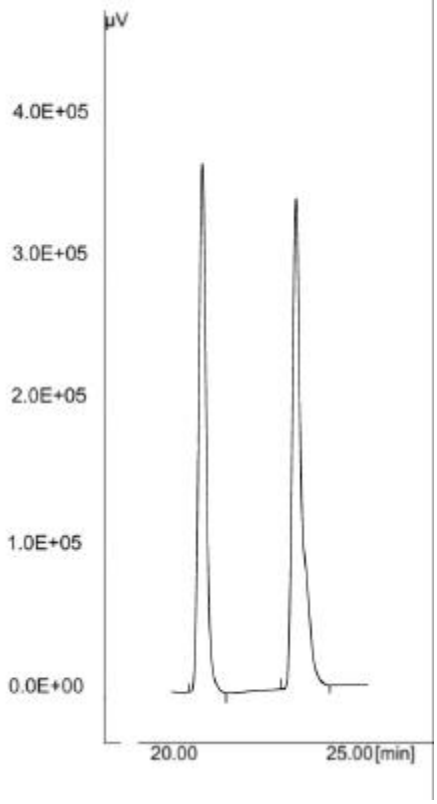

7.2009
7.1694
6.6042
6.6024
6.5465
6.4964
6.4918
6.4844
6.4741
5.9302
5.8230
5.8040
4.0322
4.0170
3.9989
3.9834
3.9177
3.8871
3.8532
3.8431
3.7954
3.7793
3.7478
3.5516
3.5281
3.5147
3.5046
3.5003
3.4814
3.4673
OH
CH3O
O
O
O
OH
14
Integral
0.9822
1.9214
2.1148
1.9128
1.0000
0.9193
1.0323
2.9561
1.6156
(ppm)


160.4947
154.0549
153.7524
148.2281
141.9872
126.2738
119.7623
116.2359
106.2777
104.4548
102.8628
101.3026
93.3185
84.4428
65.3861
55.2607
52.8885
(ppm)


7.3141
7.3100
6.6738
6.6698
6.6362
6.5595
6.5514
6.5326
6.5245
6.4761
6.4681
5.9637
5.9596
5.9462
5.9422
5.1580
5.1553
5.1137
5.1096
4.8742
4.8594
4.8420
4.8272
4.4761
4.4425
4.4358
4.4035
3.7996
3.5777
3.5656
3.5629
3.5373
3.5225
3.5131
3.4970
3.4929
3.4889
3.4822
CH3O
O
H
H
O
O
O
Integral
0.6131
1.7619
1.0000
0.9830
1.8682
0.9194
0.9883
1.0263
3.0865
1.1463
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
(ppm)

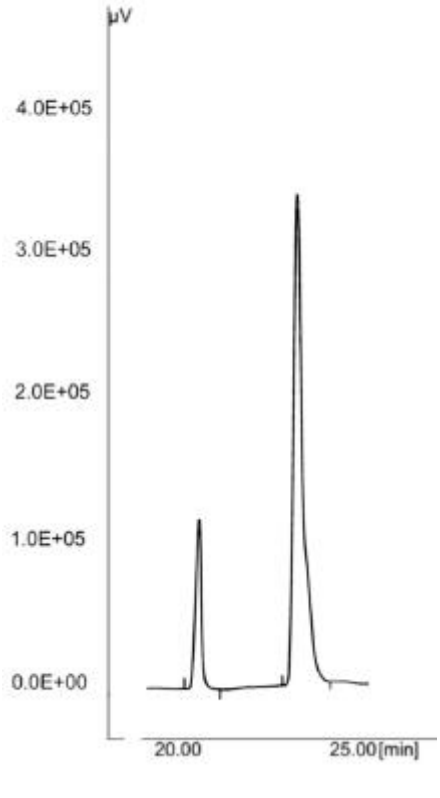


Chiral HPLC cromatogram of **6d:**



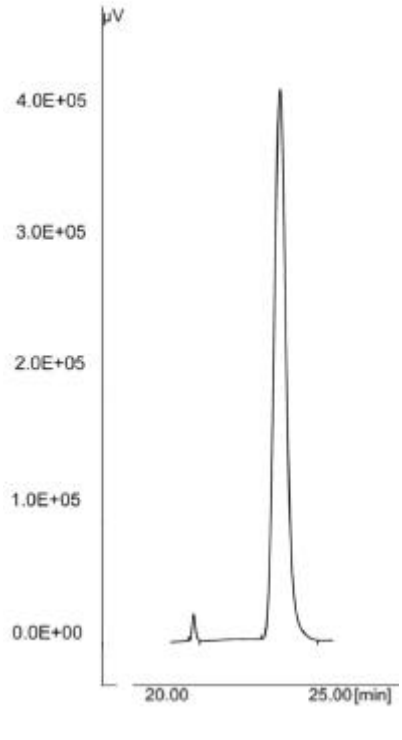
racemic

(entry 5, table 2)



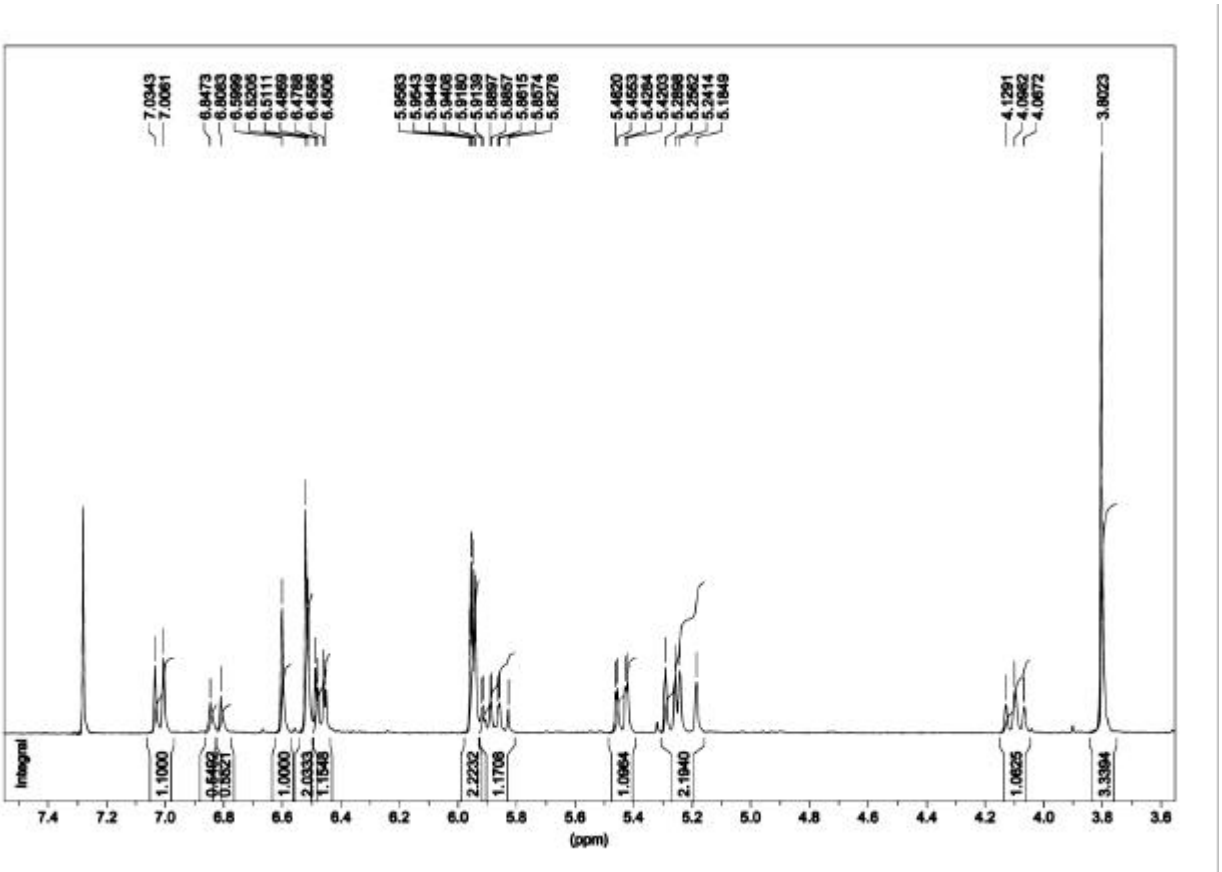
57% e.e.

(entry 6, table 3)

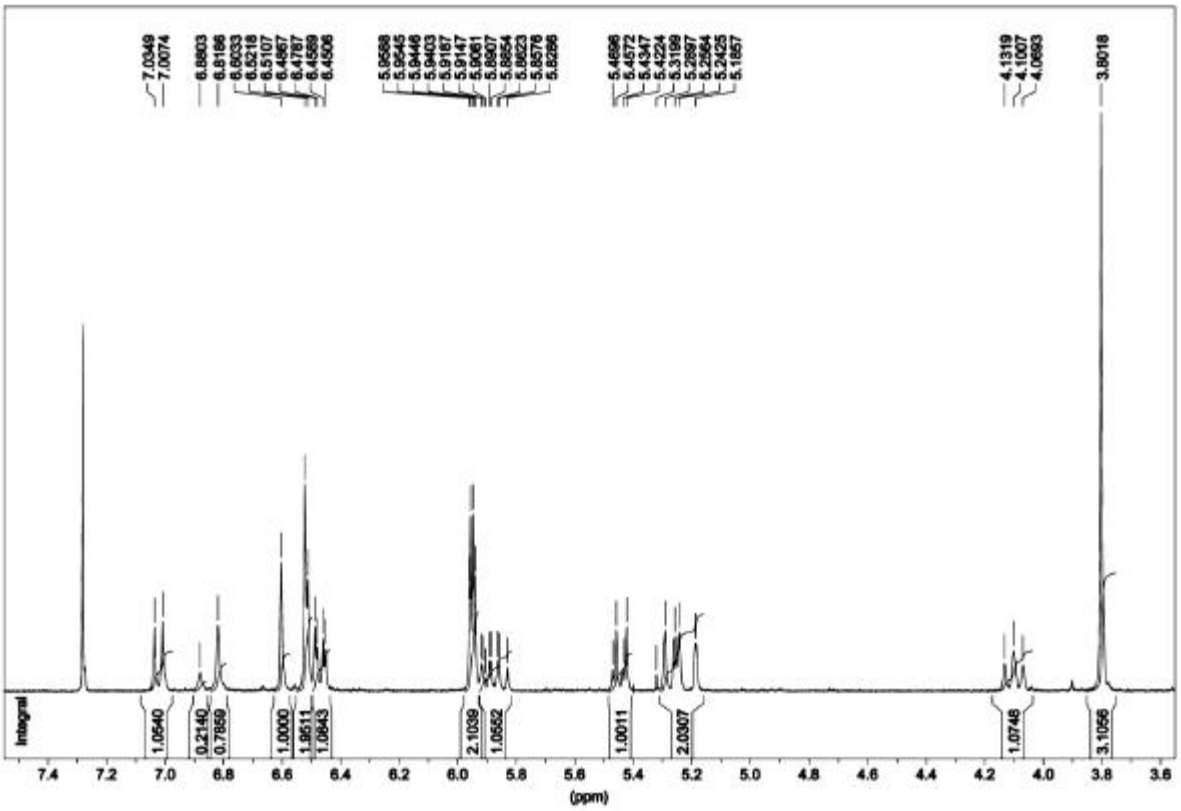


84% e.e.

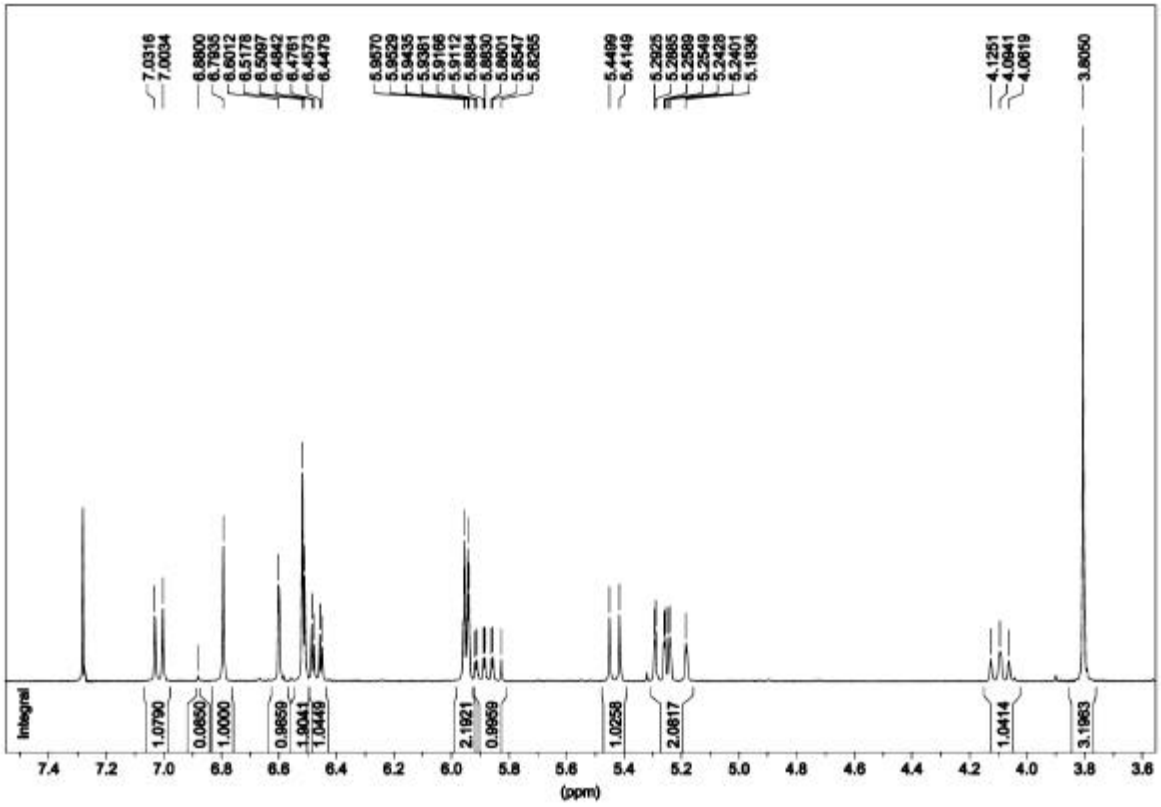
(entry 8, table 3)



^{1}H NMR of **(±)-6d** with added Eu(hfc)$_3$ (entry 5, table 2)



^{1}H NMR of **(+)-6d** with added Eu(hfc)$_3$ (entry 6, table 3)



^{1}H NMR of **(+)-6d** with added Eu(hfc)$_3$ (entry 8, table 3)

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Supporting Information