Direct, Enantioselective Generation of (*Z*)-Disubstituted Allylic Alcohols

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Supporting Information

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General Methods. All reactions were performed under a nitrogen atmosphere with oven-dried glassware using standard Schlenk or vacuum line techniques. The progress of reactions was monitored by thin-layer chromatography performed on Whatman precoated silica gel 60 Å K6F plates and visualized by ultra-violet light or by staining with phosphomolybdic acid. *t*BuOMe was distilled from Na/benzophenone and hexanes was dried through alumina columns. TEEDA was distilled and stored under nitrogen. The ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra were obtained on a Brüker AM-500 Fourier transform NMR spectrometer at 500 and 125 MHz, respectively. ^{1}H NMR spectra were referenced to tetramethylsilane in $CDCl_3$ or residual protonated solvent; $^{13}C\{^{1}H\}$ NMR spectra were referenced to residual solvent. Analysis of enantiomeric excess was performed using a Hewlett-Packard 1100 Series HPLC and a chiral column. The optical rotations were recorded using a JASCO DIP-370. Infrared spectra were obtained using a Perkin-Elmer Spectrum 100 Series spectrometer. All reagents were purchased from Aldrich or Acros unless otherwise described. 1-Bromo- and 1-chloroalkynes were made according to known procedures.[1,2] Characterization of 1-bromoalkynes was previously reported by us.[3] All commercially available aldehyde substrates were distilled prior to use. Silica gel (Silicaflash P60 40-63 μm, Silicycle) was used for air-flashed chromatography.

Caution. Dialkylzinc reagents and *t*-BuLi are pyrophoric. Care must be used when handling these reagents.

Characterization of 1-chloroalkyne

***tert*-Butyl-(4-chloro-but-3-ynyloxy)-diphenyl-silane (1a).** Compound **1a** was prepared from the corresponding alkyne[4] using the literature method.[2] It was purified by column chromatography on silica gel; (hexanes / EtOAc 95 / 5) to afford **1a** (3.19 g, 48.6% yield) as a liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.14 (s, 9H), 2.49 (t, J = 6.7 Hz, 2H), 3.82 (t, J = 6.9 Hz, 2H), 7.46 (m, 5H), 7.75 (m, 5H) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 19.4, 22.8, 27.0, 58.6, 62.4, 67.1, 128.0, 130.0, 133.8, 135.8 ppm; HRMS calcd for $C_{20}H_{24}O_1SiCl$ $(MH)^+$: 343.1285, found 343.1296.

1-Chloro-oct-1-yne (1b). Compound **1b** was prepared using the literature method.[2] The crude product was purified by column chromatography on silica gel (pentane) to give **1b** (1.80 g, 62% yield) as a liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.85 (m, 3H), 1.26 (m, 6H), 1.81 (m, 2H), 2.12 (t, J = 7.0 Hz, 2H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 14.2, 19.0, 22.7, 28.6, 28.7, 31.5, 57.1, 70.0 ppm.

1,6-Dichloro-hex-1-yne (1c). Compound **1c** was prepared using the literature method.[2] The crude product was purified by column chromatography on silica gel (pentane) to give **1c** (2.02 g, 67.4% yield) as a liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.65 (qui, J = 7.3 Hz, 2H), 1.85 (qui, J = 7.0 Hz, 2H), 2.23 (t, J = 6.9 Hz, 2H), 3.56 (t, J = 6.9 Hz, 2H), ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 18.3, 25.7, 31.7, 44.6, 58.0, 69.0 ppm.

Chloroethynyl-benzene (1d). Compound **1d** was prepared using the literature method.[2] The crude product was purified by column chromatography on silica gel (pentane) to give **1d** (1.62 g, 59% yield) as an oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.33 (m, 3H), 7.46 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 68.2, 69.6, 122.4, 128.6, 128.9, 132.2 ppm.

Characterization of 4-phenylethynyl-benzaldehyde (2d). Compound **2d** was prepared using the literature method.[5] The product was purified by chromatography in silica gel (hexanes / EtOAc 95 / 5) to give the product **2d** (555.7 mg, 98.6% yield) as yellowish solid.[5] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.39 (m, 3H), 7.57 (m, 2H), 7.68 (d, J = 8.3 Hz, 2H), 7.87 (d, J = 8.2 Hz, 2H), 10.03 (s, 1H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 89.0, 93.9, 122.9, 128.9, 129.4, 130.0, 132.2, 132.6, 135.8, 191.9 ppm; IR (neat): 3387, 3068, 3050, 2846, 2744, 2409, 1948, 1876, 1814, 1698, 1602, 1563, 1508, 1487, 1441, 1384, 1303, 1287, 1206, 1176, 1160 cm^{-1}; HRMS calcd for $C_{15}H_{10}O_1$ $(M)^+$: 206.0732 found 206.0721.

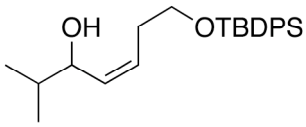
Catalytic Asymmetric Synthesis of (*Z*)-Disubstituted Allylic Alcohols

General Procedure A. Dicyclohexylborane (88 mg, 0.5 mmol) was weighed into a Schlenk flask under nitrogen and dry *t*-BuOMe (1 mL) was added. The 1-chloro-1-alkyne (0.5 mmol) was then added slowly to the reaction mixture at 0 °C. After 15 min, the reaction was warmed to room

temperature and stirred for 45 min during which time the dicyclohexylborane dissolved leaving a clear solution. *t*-BuLi (0.365 mL, 0.55 mmol, 1.5 M pentane solution) was added dropwise at -78 °C and stirred for 60 min, warmed to room temperature and stirred for an additional 60 min. A precipitate formed during this time. Diethylzinc (0.275 mL, 0.55 mmol, 2 M hexanes solution) was slowly added to the reaction mixture at -78 °C and stirred for 20 min. Addition of TEEDA (14 μL, 0.066 mmol) and hexanes (4 mL) was next performed at -78 °C, followed by warming to 0 °C and addition of (–)-MIB (166 μL, 0.017 mmol) and neat aldehyde (0.333 mmol). The reaction was then slowly warmed to room temperature and stirred 12-16 h. After the reaction was complete by TLC analysis, it was diluted with 3 mL hexanes and quenched with water. The organic layer was next separated and the aqueous solution extracted with EtOAc (2 × 10 mL). The combined organic layer was dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel.

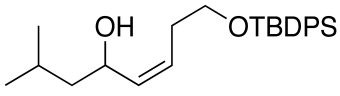
General Procedure B. This procedure is exactly the same as Procedure A except that the amount of TEEDA was adjusted to 30 mol %. Thus 21 μL (0.099 mmol) was used.

Preparation of (*Z*)-7-(*tert*-butyl-diphenyl-silanyloxy)-2-methyl-hept-4-en-3-ol (3aa). General



Procedure A was applied to isobutyraldehyde (15 μL, 0.166 mmol) and *tert*-butyl-(4-chloro-but-3-ynyloxy)-diphenyl-silane (80 μL, 0.25 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 95 / 5) to give **3aa** (38.0 mg, 61% yield) as an oil. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexanes : 2-propanol = 99 : 1, flow rate = 0.5 mL/min), t_r (1) = 15.0 min, t_r (2) = 16.7 min $[\alpha]_D^{20}$ = + 2.79 (*c* = 0.045, $CHCl_3$, 90% ee).[1]H NMR and ^{13}C NMR spectra for this compound compare with previously reported literature data.[3]

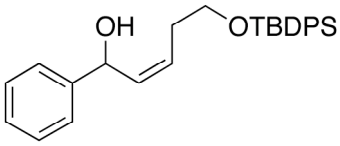
Preparation of (*Z*)-8-(*tert*-butyl-diphenyl-silanyloxy)-2-methyl-oct-5-en-4-ol (3ab). General



Procedure A was applied to isovaleraldehyde (35 μL, 0.332 mmol) and *tert*-butyl-(4-chloro-but-3-ynyloxy)-diphenyl-silane (160 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 95 / 5) to give **3ab** (97.9 mg, 74% yield) as an oil. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexanes : 2-propanol = 99 : 1, flow rate = 0.5 mL/min), t_r (1) = 14.9

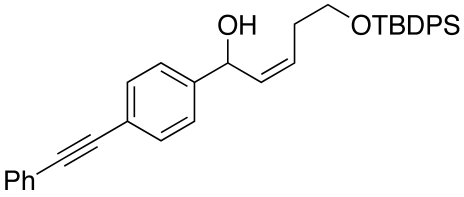
min, t_r (2) = 16.9 min $[\alpha]_D^{20}$ = + 10.20 (*c* = 0.039, $CHCl_3$, 76% ee). ^1H NMR and ^{13}C NMR spectra for this compound compare with previously reported literature data.[3]

Preparation of (*Z*)-5-(*tert*-butyl-diphenyl-silanyloxy)-1-phenyl-pent-2-en-1-ol (3ac). General



Procedure A was applied to benzaldehyde (34 µL, 0.332 mmol) and *tert*-butyl-(4-chloro-but-3-ynyloxy)-diphenyl-silane (160 µL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 95 / 5) to give **3ac** (83.8 mg, 61% yield) as an oil. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (hexanes : 2-propanol = 99 : 1, flow rate = 0.5 mL/min), t_r (1) = 38.2 min, t_r (2) = 44.6 min $[\alpha]_D^{20}$ = + 131.11 (*c* = 0.001, $CHCl_3$, 95% ee); ^1H NMR ($CDCl_3$, 500 MHz): δ 1.12 (s, 9H), 2,20 (br, 1H), 2.45-2.51 (m, 1H), 2.58-2.65 (m, 1H), 3.73-3.80 (m, 2H), 5.50-5.51 (dd, *J* = 1.9, 8.0 Hz, 1H), 5.60-5.67 (dt, *J* = 7.8, 11.2 Hz, 1H), 5.77-5.81 (dd, *J* = 8.5, 10.9 Hz, 1H), 7.40 (m 10H), 7.71 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 19.4, 27.1, 31.4, 63.5, 69.9, 126.1, 127.6, 127.9, 128.7, 128.8, 129.9, 133.8, 134.5, 135.8, 143.7 ppm; IR (neat): 3369, 3069, 2931, 1958, 1890, 1824, 1656, 1589, 1472, 1427, 1389 cm^{-1}; HRMS calcd for $C_{27}H_{32}NaO_2Si$ $(M+Na)^+$: 439.2069, found 439.2054.

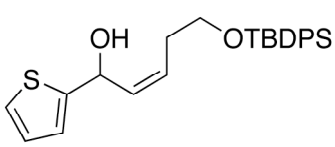
Preparation of (*Z*)-5-(*tert*-Butyl-diphenyl-silanyloxy)-1-(4-phenylethynyl-phenyl)-pent-2-en-1-



ol (3ad). General Procedure A was applied to 4-phenylethynyl-benzaldehyde (68.5 mg, 0.332 mmol, dissolved in 0.5 mL toluene) and *tert*-butyl-(4-chloro-but-3-ynyloxy)-diphenyl-silane (160 µL, 0.5 mmol). Upon addition of TEEDA, 3.5 mL of toluene were added instead of the 4 mL of hexanes to serve the same purpose. The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 95 / 5) to give **3ad** (145.0 mg, 84% yield) as an oil. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (hexanes : 2-propanol = 99 : 1, flow rate = 0.5 mL/min), t_r (1) = 52.2 min, t_r (2) = 64.3 min $[\alpha]_D^{20}$ = + 1.65 (*c* = 0.025, $CHCl_3$, 98% ee); ^1H NMR ($CDCl_3$, 500 MHz): δ 1.07 (s, 9H), 2,20 (br, 1H), 2.44-2.46 (m, 1H), 2.56-2.58 (m, 1H), 3.70-3.75 (m, 2H), 5.46-5.48 (d, *J* = 7.9 Hz, 1H), 5.63-5.67 (dt, *J* = 7.4, 11.2 Hz, 1H), 5.71-5.75 (dd, *J* = 9.0, 11.0 Hz, 1H), 7.35-7.57 (m, 15H), 7.70-7.73 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 19.4, 27.1, 31.4, 63.4, 69.5, 89.5, 89.6, 122.4, 123.5, 126.1, 127.9, 128.4, 128.6, 129.3, 130.0, 131.8, 132.0, 133.8, 134.2, 135.8,

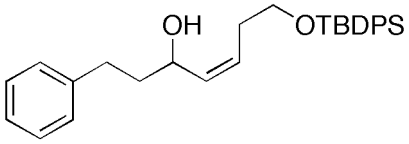
143.9 ppm; IR (neat): 3393, 3070, 3050, 2957, 2930, 2857, 1597, 1486, 1427, 1361, 1111 cm^{-1}; HRMS calcd for $C_{35}H_{36}NaO_2Si$ $(M+Na)^+$: 539.2382, found 539.2394.

Preparation of (*Z*)-5-(*tert*-butyl-diphenyl-silanyloxy)-1-phenyl-pent-2-en-1-ol (3ae). General



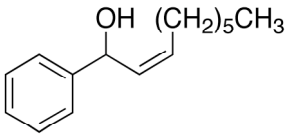
Procedure A was applied to thiophenecarboxaldehyde (31 μL, 0.332 mmol) and *tert*-butyl-(4-chloro-but-3-ynyloxy)-diphenyl-silane (160 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 95 / 5) to give **3ae** (98.8 mg, 69% yield) as an oil. Enantiomeric excess was determined by HPLC with a Chiralcel AS-H column (hexanes : 2-propanol = 99 : 1, flow rate = 0.5 mL/min), t_r (1) = 20.0 min, t_r (2) = 28.4 min $[\alpha]_D^{20}$ = + 55.97 (*c* = 0.093, $CHCl_3$, 93% ee); ^1H NMR ($CDCl_3$, 500 MHz): δ 1.08 (s, 9H), 2.27 (d, *J* = 4.0 Hz 1H), 2.39-2.46 (m, 1H), 2.49-2.56 (m, 1H), 3.69-3.78 (m, 2H), 5.65-5.70 (m, 2H), 5.82-5.86 (m, 1H), 6.93-6.97 (m, 2H), 7.24-7.27 (m, 1H), 7.39-7.46 (m, 5H), 7.68-7.71 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 19.4, 27.0, 31.3, 63.4, 66.3, 124.0, 125.0, 126.9, 127.9, 129.4, 129.9, 133.6, 133.8, 135.8, 147.7 ppm; IR (neat): 3390, 3070, 2930, 1960, 1891, 1826, 1656, 1589, 1471, 1427, 1389 cm^{-1}; HRMS calcd for $C_{25}H_{30}NaO_2SSi$ $(M+Na)^+$: 445.1633, found 445.1612.

Preparation of (*Z*)-7-(*tert*-butyl-diphenyl-silanyloxy)-1-phenyl-heptt-4-en-13-ol (3af). General



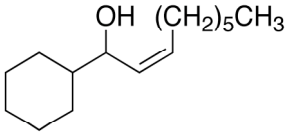
Procedure A was applied to hydrocinnamaldehyde (45 μL, 0.332 mmol) and *tert*-butyl-(4-chloro-but-3-ynyloxy)-diphenyl-silane (160 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 95 / 5) to give **3af** (104.8 mg, 72% yield) as an oil. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (hexanes : 2-propanol = 99.5 : 0.5, flow rate = 0.5 mL/min), t_r (1) = 30.0 min, t_r (2) = 36.6 min $[\alpha]_D^{20}$ = + 17.736 (*c* = 0.013, $CHCl_3$, 75% ee); ^1H NMR ($CDCl_3$, 500 MHz): δ 1.07 (s, 9H), 1.60 (br, 1H), 1.73-1.81 (m, 1H), 1.88-1.97 (m, 1H), 2.27-2.34 (m, 1H), 2.39-2.46 (m, 1H), 2.62-2.74 (m, 2H), 3.66-3.75 (m, 2H), 4.37-4.42 (m, 1H), 5.53-5.61 (m, 2H), 7.17-7.22 (m 3H), 7.26-7.31 (m, 2H), 7.36-7.47 (m, 6H), 7.66-7.71 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 19.4, 27.0, 31.3, 31.9, 39.0, 63.6, 67.2, 126.0, 127.9, 128.5, 129.0, 129.8, 133.8, 134.7, 135.8, 143.2 ppm; IR (neat): 3390, 3070, 3025, 2930, 2858, 1959, 1889, 1824, 1775, 1659, 1603, 1589, 1495, 1471, 1456, 1427, 1389 1361 cm^{-1}; HRMS calcd for $C_{29}H_{36}NaO_2Si$ $(M+Na)^+$: 467.2382, found 467.2397.

Preparation of (*Z*)- 1-phenyl-non-2-en-1-ol (3bc). General Procedure A was applied to



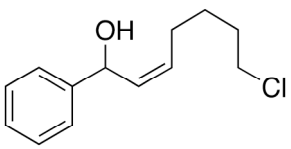
benzaldehyde (34 μL, 0.332 mmol) and 1-chloro-oct-1-yne (94 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 95 / 5) to give **3bc** (45.5 mg, 63% yield) as an oil. Enantiomeric excess was determined by HPLC with a Chiralcel AS-H column (hexanes : 2-propanol = 99.5 : 0.5, flow rate = 0.5 mL/min), t_r (1) = 26.0 min, t_r (2) = 29.0 min $[\alpha]_D^{20}$ = + 143.56 (*c* = 0.060, $CHCl_3$, 93% ee); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.90 (t, 3H), 1.31 (br, 8H), 1.84 (d, *J* = 8.0 Hz, 1H), 2.22 (m, 2H), 5.59 (m, 3H), 7.26-7.30 (m, 1H) 7.34-7.42 (m, 4H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 14.3, 22.8, 28.0, 29.2, 29.8, 31.9, 70.0, 126.1, 127.6, 128.7, 132.1, 132.7, 144.0 ppm; IR (neat): 3340, 3085, 3063, 3028, 3012, 2956, 2926, 2855, 1655, 1603, 1492, 1452, 1378, 1282, 1192, 1079, 1023 cm^{-1}; HRMS calcd for $C_{15}H_{22}O$ $(M)^+$: 218.1671, found 218.1665.

Preparation of (*Z*)- 1-cyclohexyl-non-2-en-1-ol (3bg). General Procedure A was applied to



cyclohexanecarboxaldehyde (40 μL, 0.332 mmol) and 1-chloro-oct-1-yne (94 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 95 / 5) to give **3bg** (60.2 mg, 81% yield) as an oil. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexanes : 2-propanol = 99.5 : 0.5, flow rate = 0.5 mL/min), t_r (1) = 17.0 min, t_r (2) = 19.0 min $[\alpha]_D^{20}$ = + 8.74 (*c* = 0.057, $CHCl_3$, 84% ee); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.88 (m, 6H), 1.48 (br, 12H), 1.68 (br, 4H), 1.93 (m, 1H), 2.05 (m, 3H), 4.14 (t, *J* = 7.9 Hz, 1H), 5.37 (dd, *J* = 9.0, 11.1 Hz, 1H), 5.52 (dt, *J* = 7.6, 13.2 Hz, 1H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 14.3, 22.8, 26.2, 26.4, 26.8, 28.0, 28.8, 29.0, 29.2, 29.9, 31.9, 44.2, 72.1, 131.2, 133.3 ppm; IR (neat): 3411, 3008, 2924, 2853, 2668, 1733, 1658, 1449, 1394, 1361, 1316, 1256, 1217, 1192, 1148, 1112, 1081, 1047, 1007 cm^{-1}; HRMS calcd for $C_{15}H_{27}O$ $(M-H)^+$: 223.2062, found 223.2056.

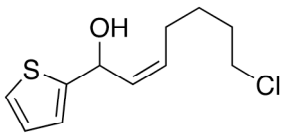
Preparation of (*Z*)-7-chloro-1-phenyl-hept-2-en-1-ol (3cc). General Procedure B was applied to



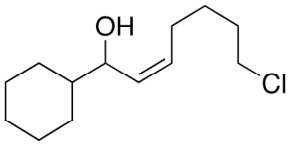
benzaldehyde (34 μL, 0.332 mmol) and 1,6-dichloro-hex-1-yne (66 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 95 / 5) to give **3cc** (62.4 mg, 84% yield) as an oil. Enantiomeric excess was determined by HPLC with a Chiralcel AS-H column (hexanes : 2-propanol = 99 : 1, flow rate = 0.5 mL/min), t_r (1) = 52.0 min, t_r (2) = 59.5 min $[\alpha]_D^{20}$ = + 101.3 (*c* = 0.203, $CHCl_3$, 88% ee); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.56 (m, 2H), 1.81 (m, 2H), 1.87 (d, *J* = 3.5

Hz, 1H), 2.26 (m, 2H), 3.54 (t, J = 6.60 Hz, 2H), 5.51-5.54 (dd, J = 3.6, 8.0 Hz, 1H), 5.55-5.59 (dt, J = 7.6, 10.7 Hz, 1H), 5.67 (dd, J = 8.9, 10.7 Hz, 1H), 7.27-7.31 (m, 1H), 7.34-7.42 (m, 4H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 26.9, 27.2, 32.3, 45.0, 70.0, 126.1, 127.8, 128.8, 131.6, 132.8, 143.8 ppm; IR (neat): 3352, 3062, 3012, 2937, 2864, 1951, 1881, 1810, 1654, 1602, 1492, 1451, 1384, 1300, 1276, 1191, 1076, 1036, 1009 cm^{-1}; HRMS calcd for $C_{13}H_{15}Cl$ $(M\text{-}H_2O)^+$: 206.0862, found 206.0851.

Preparation of (*Z*)-7-chloro-1-thiophen-2-yl-hept-2-en-1-ol (3ce). General Procedure B was applied to thiophenecarboxaldehyde (31 μL, 0.332 mmol) and 1,6-dichloro-hex-1-yne (66 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc: 95 / 5) to give **3ce** (56.0 mg, 73% yield) as an oil. Enantiomeric excess was determined by HPLC with a Chiralcel AS-H column (hexanes : 2-propanol = 99 : 1, flow rate = 0.5 mL/min), t_r (1) = 84.0 min, t_r (2) = 93.0 min $[\alpha]_D^{20}$ = + 167.9 (c = 0.031, $CHCl_3$, 94% ee); ^1H NMR ($CDCl_3$, 500 MHz): δ 1.57 (m, 2H), 1.79 (m, 2H), 1.99 (d, J = 3.3 Hz, 1H), 2.23 (m, 2H), 3.54 (t, J = 6.6 Hz, 2H), 5.61 (m, 1H), 5.75 (m, 2H), 6.98 (m, 2H), 7.27 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 26.9, 27.1, 32.2, 45.0, 66.3, 124.1, 125.3, 127.0, 132.0, 132.3 ppm; IR (neat): 3376, 3106, 3013, 2932, 2857, 2664, 1793, 1646, 1532, 1450, 1364, 1296, 1228, 1164, 1140, 1059, 1034 cm^{-1}; HRMS calcd for $C_{11}H_{14}ClS$ $(M\text{-}OH)^+$: 213.0505, found 213.0491.

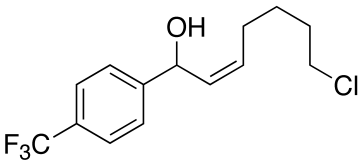


Preparation of (*Z*)-7-chloro-1-cyclohexyl-hept-2-en-1-ol (3cg). General Procedure B was applied to cyclohexanecarboxaldehyde (40 μL, 0.332 mmol) and 1,6-dichloro-hex-1-yne (66 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc: 95 / 5) to give **3cg** (57.1 mg, 74% yield) as an oil. Enantiomeric excess was determined by HPLC with a Chiralcel AS-H column (hexanes : 2-propanol = 99.5 : 0.5, flow rate = 0.5 mL/min), t_r (1) = 35.8 min, t_r (2) = 39.3 min $[\alpha]_D^{20}$ = + 21.4 (c = 0.040, $CHCl_3$, 88% ee); ^1H NMR ($CDCl_3$, 500 MHz): δ 0.98 (m, 2H), 1.24 (m, 2H), 1.39 (m, 2H), 1.55 (m, 2H), 1.69 (m, 2H), 1.79 (m, 4H), 1.94 (d, J = 3.3 Hz, 1H), 2.12 (m, 2H), 3.55 (t, J = 6.6 Hz, 2H), 4.13 (t, J = 7.9 Hz, 1H), 5.41 (dd, J = 9.4, 11.1 Hz, 1H), 5.55 (dt, J = 7.5, 11.3 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 26.2, 26.3, 26.7, 27.1, 27.2, 28.8, 29.0, 32.3, 44.2, 45.0, 72.1, 131.9, 132.2 ppm; IR (neat): 3370, 3005, 2926, 2853, 2667, 1707, 1655,

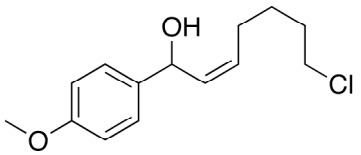


1450, 1307, 1273, 1140, 1080, 1050 cm^{-1}; HRMS calcd for $C_{13}H_{21}Cl$ $(M-H_2O)^+$: 212.1332, found 212.1321.

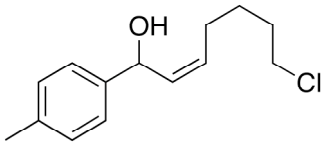
Preparation of (*Z*)-7-chloro-1-(4-trifluoromethyl-phenyl)-hept-2-en-1-ol (3ch). General Procedure A was applied to *p*-trifluoromethyl-benzaldehyde (45 μL, 0.332 mmol) and 1,6-dichloro-hex-1-yne (66 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 95 / 5) to give **3ch** (70.4 mg, 72% yield) as an oil. Enantiomeric excess was determined by HPLC with a Chiralcel AS-H column (hexanes : 2-propanol = 99 : 1, flow rate = 0.5 mL/min), t_r (1) = 48.0 min, t_r (2) = 55.8 min $[\alpha]_D^{20}$ = + 119.9 (*c* = 0.01, $CHCl_3$, 86% ee); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.58 (m, 3H), 1.83 (m, 2H), 2.28 (m, 2H), 3.56 (t, *J* = 6.5 Hz, 2H), 5.62 (m, 3H), 7.51 (d, *J* = 8.2 Hz, 2H) 7.62 (d, *J* = 8.2 Hz, 2H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 26.9, 27.3, 32.3, 44.5, 69.4, 125.7 (q), 126.4, 130.0, 132.1, 132.7, 147.5 ppm; $^{19}F\{^1H\}$ NMR ($CDCl_3$, 282 MHz): δ -62.64 (s) ppm; IR (neat): 3350, 3014, 2939, 2866, 2360, 2097, 1924, 1807, 1654, 1619, 1588, 1446, 1417, 1266, 1164, 1125, 1067, 1046, 1016 cm^{-1}; HRMS calcd for $C_{14}H_{14}ClF_3$ $(M-H_2O)^+$: 274.0736, found 274.0724.



Preparation of (*Z*)-7-chloro-1-(4-methoxy-phenyl)-hept-2-en-1-ol (3ci). General Procedure A was applied to *p*-methoxybenzaldehyde (40 μL, 0.332 mmol) and 1,6-dichloro-hex-1-yne (66 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 90 / 10) to give **3ci** (71.1 mg, 84% yield) as an oil. Enantiomeric excess was determined by HPLC with a Chiralcel AS-H column (hexanes : 2-propanol = 95 : 5, flow rate = 0.5 mL/min), t_r (1) = 32.0 min, t_r (2) = 42.0 min $[\alpha]_D^{20}$ = + 120.0 (*c* = 0.047, $CHCl_3$, 93% ee); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.58 (m, 3H), 1.81 (m, 2H), 2.25 (m, 2H), 3.56 (t, *J* = 6.6 Hz, 2H), 3.84 (s, 3H), 5.49-5.52 (dd, *J* = 3.6, 8.3 Hz, 1H), 5.53-5.59 (dd, *J* = 8.0, 10.9 Hz, 1H), 5.71 (dd, *J* = 9.1, 11.0 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 2H) 7.34 (d, *J* = 8.7 Hz, 2H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 26.9, 27.1, 32.3, 45.0, 55.5, 69.7, 114.2, 127.4, 131.2, 133.0, 136.1, 159.3 ppm; IR (neat): 3394, 2935, 1610, 1585, 1511, 1459, 1302, 1247, 1173, 1110, 1035 cm^{-1}; HRMS calcd for $C_{14}H_{17}ClO$ $(M-H_2O)^+$: 236.0968, found 236.0969.

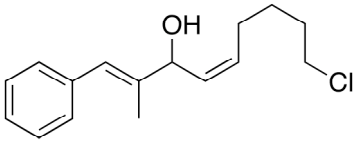


Preparation of (*Z*)-7-chloro-1-p-tolyl-hept-2-en-1-ol (3cj). General Procedure A was applied to *p*-



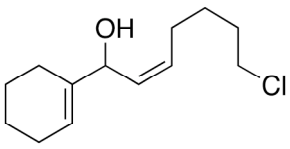
methylbenzaldehyde (39 μL, 0.332 mmol) and 1,6-dichloro-hex-1-yne (66 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc : 95 / 5) to give **3cj** (73.0 mg, 93% yield) as an oil. Enantiomeric excess was determined by HPLC with a Chiralcel AS-H column (hexanes : 2-propanol = 99 : 1, flow rate = 0.5 mL/min), t_r (1) = 74.0 min, t_r (2) = 90.0 min $[\alpha]_D^{20}$ = + 141.6 (*c* = 0.044, $CHCl_3$, 97% ee); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.57 (m, 2H), 1.80 (m, 3H), 2.23 (m, 2H), 2.27 (s, 3H), 3.54 (t, *J* = 6.6 Hz, 2H), 5.48-5.52 (dd, *J* = 3.6, 8.7 Hz, 1H), 5.53 (dt, *J* = 7.8, 10.5 Hz, 1H), 5.67 (dd, *J* = 8.4, 10.7 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.28 (m, 2H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 21.3, 26.9, 27.1, 32.3, 45.0, 69.9, 126.1, 129.5, 131.4, 132.9, 137.5, 140.1 ppm; IR (neat): 3368, 3012, 2932, 2861, 2361, 1903, 1654, 1512, 1452, 1230, 1193, 1177, 1111, 1039 cm^{-1}; HRMS calcd for $C_{14}H_{17}Cl$ $(M-H_2O)^+$: 220.1019, found 220.1027.

Preparation of (*Z*)-9-chloro-2-methyl-1-phenyl-nona-1,4-dien-3-ol (3ck). General Procedure B



was applied to α-methyl *trans* cinnamaldehyde (46 μL, 0.332 mmol) and 1,6-dichloro-hex-1-yne (66 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc: 95 / 5) to give **3ck** (64.6 mg, 73% yield) as an oil. Enantiomeric excess was determined by HPLC with a Chiralcel AS-H column (hexanes : 2-propanol = 99 : 1, flow rate = 0.5 mL/min), t_r (1) = 67.0 min, t_r (2) = 73.5 min $[\alpha]_D^{20}$ = + 167.9 (*c* = 0.03, $CHCl_3$, 88% ee); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.58 (qui, *J* = 7.4 Hz, 2H), 1.64 (d, *J* = 3.3 Hz, 1H), 1.82 (m, 2H), 1.88 (d, *J* = 1.3 Hz, 3H), 2.24 (m, 2H), 3.55 (t, *J* = 6.8 Hz, 2H), 4.99 (dd, *J* = 3.0, 7.5 Hz, 1H), 5.58 (m, 2H), 6.61 (s, 1H), 7.28 (m, 5H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 14.3, 26.9, 27.3, 32.3, 45.0, 73.5, 125.4, 126.7, 128.3, 129.2, 131.2, 132.5, 137.8, 139.8 ppm; IR (neat): 3370, 3020, 2937, 2861, 1949, 1886, 1654, 1599, 1575, 1491, 1444, 1413, 1383, 1360, 1300, 1180, 1010 cm^{-1}; HRMS calcd for $C_{16}H_{21}OCl$ $(M)^+$: 264.1281, found 264.1278.

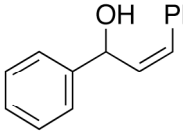
Preparation of (*Z*)-7-chloro-1-cyclohex-1-enyl-hept-2-en-1-ol (3cl). General Procedure A was



applied to cyclohexenecarboxaldehyde (38 μL, 0.332 mmol) and 1,6-dichloro-hex-1-yne (66 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc: 95 / 5) to give **3cl** (61.1 mg, 80% yield) as an oil. Enantiomeric excess was determined by HPLC with a Chiralcel AD-

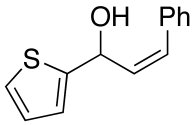
H column (hexanes : 2-propanol = 97.5 : 2.5, flow rate = 0.5 mL/min), t_r (1) = 28.2 min, t_r (2) = 32.9 min $[\alpha]_D^{20}$ = + 88.55 (*c* = 0.078, $CHCl_3$, 94% ee); ^1H NMR ($CDCl_3$, 500 MHz): δ 1.45 (d, *J* = 3.2 Hz, 1H), 1.52-1.67 (m, 6H), 1.80 (m, 2H), 2.04 (m, 4H), 2.16 (m, 2H), 3.54 (t, *J* = 6.6 Hz, 2H), 4.78 (d, *J* = 6.8 Hz, 1H), 5.48 (m, 2H), 5.75 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 22.7, 22.8, 24.4, 25.2, 26.9, 27.1, 32.3, 45.1, 72.2, 122.7, 131.6, 131.7, 139.7 ppm; IR (neat): 3350, 2929, 2858, 1655, 1437, 1268, 1137, 1006 cm^{-1}; HRMS calcd for $C_{13}H_{19}Cl$ $(M-H_2O)^+$: 210.1175, found 210.1176.

Preparation of (*Z*)-1,3-diphenyl-prop-2-en-1-ol (3dc). General Procedure A was applied to



benzaldehyde (34 μL, 0.332 mmol) and chloroethynyl-benzene (60 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc: 95 / 5) to give **3dc** (69.8 mg, 82% yield) as an oil. Enantiomeric excess was determined by HPLC with a Chiralcel AD column (hexanes : 2-propanol = 97.5 : 2.5, flow rate = 0.5 mL/min), t_r (1) = 38.4 min, t_r (2) = 52.3 min $[\alpha]_D^{20}$ = + 461.6 (*c* = 0.168, $CHCl_3$, 97% ee); ^1H NMR ($CDCl_3$, 500 MHz): δ 1.94 (d, *J* = 3.6 Hz, 1H), 5.58 (dd, *J* = 3.7, 9.4 Hz, 1H), 5.87 (dd, *J* = 9.4, 11.7 Hz, 1H), 6.63 (d, *J* = 11.0 Hz, 1H), 7.20-7.35 (m, 8H), 7.36-7.41 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 70.2, 126.5, 127.7, 128.0, 128.6, 128.9, 129.0, 131.6, 133.4, 136.6, 143.4 ppm; IR (neat): 3543, 3346, 3081, 3059, 3026, 2923, 1952, 1888, 1810, 1761, 1639, 1600, 1575, 1493, 1447, 1403, 1336, 1261, 1220, 1193, 1157, 1079, 1043, 1028, 1005 cm^{-1}; HRMS calcd for $C_{15}H_{14}O$ $(M)^+$: 210.1045, found 210.1053.

Preparation of (*Z*)-3-phenyl-1-thiophen-2-yl-prop-2-en-1-ol (3de). General Procedure A was



applied to thiophenecarboxaldehyde (31 μL, 0.332 mmol) and chloroethynyl-benzene (60 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc: 95 / 5) to give **3de** (45.0 mg, 63% yield) as an oil. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (hexanes : 2-propanol = 97.5 : 2.5, flow rate = 0.5 mL/min), t_r (1) = 49.2 min, t_r (2) = 60.1 min $[\alpha]_D^{20}$ = + 367.2 (*c* = 0.012, $CHCl_3$, 92% ee); ^1H NMR ($CDCl_3$, 500 MHz): δ 2.1 (d, *J* = 4.5 Hz, 1H), 5.79 (dd, *J* = 4.5, 9.4 Hz, 1H), 5.93 (dd, *J* = 9.7, 11.0 Hz, 1H), 6.66 (d, *J* = 11.0 Hz, 1H), 6.93 (m, 1H), 6.98 (m, 1H) 7.24 (m, 6H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 66.7, 124.6, 125.6, 127.1, 127.8, 128.6, 129.0, 131.8, 132.7 136.5, 147.8 ppm; IR (neat): 3554, 3443, 3103, 3060, 3025,

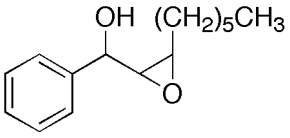
2923, 2853, 2626, 1952, 1886, 1800, 1725, 1644, 1599, 1576, 1493, 1447, 1413, 1352, 1286, 1265, 1229, 1204, 1178, 1036 cm^{-1}; HRMS calcd for $C_{13}H_{12}OS$ $(M)^+$: 216.0609, found 216.0611.

Diastereoselective Epoxidation of (*Z*)-Vinylzinc Reagents

General procedure C. Dicyclohexylborane (88 mg, 0.5 mmol) was weighed into a Schlenk flask under nitrogen and dry *t*-BuOMe (1 mL) was added. The 1-chloroalkyne (0.5 mmol) was then added slowly to the reaction mixture at 0 °C. After 15 min the reaction mixture was warmed to room temperature and stirred for 45 min resulting in a clear solution. *t*-BuLi (0.365 mL, 0.55 mmol, 1.5 M pentane solution) was added dropwise at -78 °C and stirred for 60 min. The solution was warmed to room temperature and stirred for an additional 60 min during which time a precipitate formed. Diethylzinc (0.275 mL, 0.55 mmol, 2 M hexanes solution) was slowly added to the reaction mixture at -78 °C and stirred for 20 min. Addition of TEEDA (14 μL, 0.066 mmol) and hexanes (4 mL) was performed while at -78 °C. The solution was warmed to 0 °C. (–)-MIB (166 μL, 0.017 mmol) and neat aldehyde (0.333 mmol) were then added. The reaction mixture was then slowly warmed to room temperature and stirred 12-16 h. After the reaction was complete by TLC analysis, the temperature was lowered to -20 °C and $ZnEt_2$ (0.275 mL, 0.55 mmol, 2 M solution in hexanes) was added. The solution was stirred for 30 min and TBHP (0.300 mL, 1.68 mmol, 5.5 M solution in decanes) was added. After 30 min the Ti(O*i*-Pr)$_4$ (48 μL, 0.067 mmol, 1.4 M solution in hexanes) was added and the reaction stirred until completion (about 16 h). The reaction was quenched with 2 mL saturated aq. NH_4Cl, allowed to stir for 30 minutes at room temperature, and poured into a separtory funnel with a solution of aq. $Na_2S_2O_3$. The organic and aqueous layers were separated, and the aqueous layer was extracted with diethyl ether (3 × 5 mL). The combined organic layers were then washed with 5 mL brine, 5 mL H_2O and dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the crude product was purified by column chromatography on deactivated silica gel. Analysis of diastereomeric excess was performed *via* NMR before purification. The relative stereochemistry was determined by comparison of NMR data for known epoxidation methods (vide **4cc**) and by derivatization and single crystal X-ray analysis.

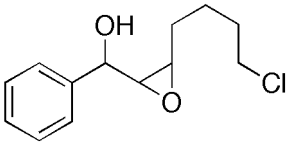
General Procedure D. This procedure is exactly the same as procedure A except that the amount of TEEDA necessary to obtain optimum results was adjusted to 30 mol %. Thus, 21 μL (0.099 mmol) were used.

Preparation of (3-Hexyl-oxiranyl)-phenyl-methanol (4bc). General Procedure C was applied to



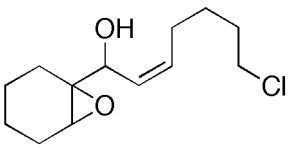
benzaldehyde (34 µL, 0.332 mmol) and 1-chloro-oct-1-yne (94 µL, 0.5 mmol). The crude product was purified by column chromatography on deactivated silica gel (hexanes / EtOAc: 90 / 10) to give **4bc** (40.1 mg, 52% yield) as an oil. $[\alpha]_D^{20}$ = + 35.9 (*c* = 0.026, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 0.92 (t, *J* = 7.1 Hz 3H), 1,37 (m, 8H), 1,71 (m, 2H), 2.53 (br, 1H), 3.09 (dt, *J* = 4.7, 7.7 Hz, 1H), 3.21 (dd, *J* = 4.3, 8.2 Hz, 1H), 4.60 (d, *J* = 8.0 Hz, 1H), 7.43 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 14.2, 22.7, 27.0, 28.8, 29.3, 31.9, 58.7, 61.5, 72.4, 126.4, 128.4, 128.9, 140.3 ppm; IR (neat): 3415, 3087, 3063, 3031, 2955, 2857, 1604, 1494, 1454, 1378, 1267, 1234, 1194, 1145, 1080, 1042 cm^{-1}; HRMS calcd for $C_{15}H_{21}O$ $(M\text{-}OH)^+$: 217.1592, found 217.1586.

Preparation of [3-(4-Chloro-butyl)-oxiranyl]-phenyl-methanol (4cc). General Procedure D was



applied to benzaldehyde (34 µL, 0.332 mmol) and 1,6-dichloro-hex-1-yne (66 µL, 0.5 mmol). The crude product was purified by column chromatography on deactivated silica gel (hexanes / EtOAc: 90 / 10) to give **4cc** (53.6 mg, 67% yield) as an oil. $[\alpha]_D^{20}$ = + 56.0 (*c* = 0.041, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 1.64 (m, 6H), 2.46 (d, *J* = 2.9 Hz, 1H), 3.1 (m, 1H), 3.20 (dd, *J* = 4.4, 8.4 Hz, 1H), 3.56 (t, *J* = 6.8 Hz, 2H), 4.58 (dd, *J* = 2.8, 8.0 Hz, 1H), 7.31 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 24.5, 28.0, 32.3, 44.9, 58.3, 61.4, 72.5, 126.4, 128.6, 129.0, 140.1 ppm; IR (neat): 3419, 3062, 3031, 2955, 2866, 1807, 1604, 1492, 1454, 1278, 1195, 1040 cm^{-1}; HRMS calcd for $C_{13}H_{16}OCl$ $(M\text{-}OH)^+$: 223.0889, found 223.0888.

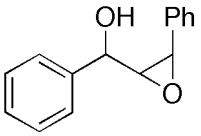
Preparation of (*Z*)-7-Chloro-1-(7-oxa-bicyclo[4.1.0]hept-1-yl)-hept-2-en-1-ol (4cl). General



Procedure C was applied to cyclohexenecarboxaldehyde (76 µL, 0.667 mmol) and 1,6-dichloro-hex-1-yne (132 µL, 1.0 mmol). The crude product was purified by column chromatography on deactivated silica gel (hexanes / EtOAc: 90 / 10) to give **4cl** (85.7 mg, 52% yield) as an oil. $[\alpha]_D^{20}$ = + 43.8 (*c* = 0.016, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 1.27 (m, 2H), 1.58 (m, 4H), 1.81 (m, 5H), 1.99 (m, 1H), 2.20 (m, 3H), 3.30 (d, *J* = 2.8 Hz, 1H), 3.56 (d, *J* = 7.0 Hz, 2H), 4.40 (d, *J* = 9.2 Hz, 1H), 5.33 (dd, *J* = 9.3, 10.9 Hz, 1H), 5.68 (dt, *J* = 7.3, 10.9 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 19.7, 20.2, 24.5, 25.0, 26.7, 27.2, 32.1, 44.8, 54.9, 62.1, 67.5, 128.1, 135.0 ppm; IR (neat): 3438, 2936, 2861, 2673,

1715, 1659, 1446, 1434, 1359, 1344, 1298, 1275, 1192, 1177, 1164, 1108, 1078, 1047 cm^{-1}; HRMS calcd for $C_{13}H_{21}O_2NaCl$ $(M+Na)^+$: 267.1128, found 267.1136.

Preparation of (*Z*)-phenyl-(3-phenyl-oxiranyl)-methanol (4dc). General Procedure C was applied to benzaldehyde (33 µL, 0.327 mmol) and chloroethynyl-benzene (60 µL, 0.5 mmol). The crude product was purified by column chromatography on deactivated silica gel (hexanes / EtOAc: 90 / 10) to give **4dc** (43.5 mg, 59% yield) as an oil. $[\alpha]_D^{20}$ = + 60.5 (*c* = 0.026, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 2.42 (d, *J* = 2.3 Hz, 1H), 3.44 (dd, *J* = 4.5, 8.5 Hz, 1H), 4.26 (d, *J* = 4.4 Hz, 1H), 4.30 (dd, *J* = 1.9, 8.5 Hz, 1H), 6,97 (m, 2H), 7.28 (m, 3H), 7.40 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 58.3, 63.4, 71.9, 126.1, 126.6, 128.3, 128.4, 128.6, 128.7, 135.0, 139.4 ppm; IR (neat): 3412, 3031, 2980, 2923, 1956, 1888, 1815, 1604, 1495, 1453, 1254, 1199 cm^{-1}; HRMS calcd for $C_{15}H_{18}NO_2$ $(M+NH_4)^+$: 244.1338, found 244.1326.



Determination of Absolute Configuration of Secondary Alcohols

The configuration of the secondary alcohols from addition reactions was determined by X-ray diffraction analysis. In the case of the epoxy alcohol epoxidation reagents with known diastereoselectivity were employed and the products compared by ^1H NMR spectrometry.

Epoxidation with *m*CPBA. To a solution of **3cc** (168 mg, 0.748 mmol) dissolved in CH_2Cl_2 (2 mL) *m*CPBA (142 mg, 0.823 mmol) was added. The solution was stirred magnetically at room temperature and the reaction progress was monitored by TLC. Upon completion, the reaction mixture was quenched by addition of 0.50 g of K_2CO_3 generating a suspension that was stirred another 30 min. The suspension was removed by filtration, the filtrate washed with saturated aq. $NaHCO_3$ (3 × 5 mL) and water (2 × 5 mL), the organic phase dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the crude product was purified by column chromatography on deactivated silica gel. Analysis of diastereomeric excess was performed by ^1H NMR spectroscopy. The epoxy alcohol **4cc** was obtained as a mixture of diastereomers (10 : 1).

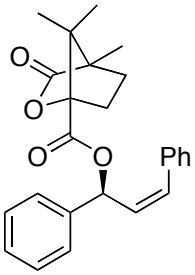
Epoxidation with $VO(acac)_2$/*t*-BuOOH. To a solution of **3cc** (180 mg, 0.8 mmol) in CH_2Cl_2 (2 mL) was added $VO(acac)_2$ (21 mg, 0.08 mmol). After stirring for 5 min at room temperature, *t*-

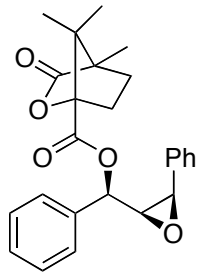
BuOOH was added (0.73 mL, 4 mmol, 5.5 M in decane) and the mixture changed from blue to red. The reaction progress was monitored by TLC until completion. The reaction was then quenched with 1M $Na_2S_2O_3$, diluted with EtOAc (3 mL) and the layers were separated. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to give a crude product that was purified by chromatography on deactivated silica gel. Analysis of diastereomeric excess was performed by ^1H NMR spectroscopy before purification. The epoxy alcohol **4cc** was obtained as a mixture of diastereomers (2.5 : 1).

Derivatization of alcohol for X-ray Diffraction Analysis.

General procedure E A solution of the desired alcohol (0.42 mmol) and (dimethylamino)pyridine (DMAP) (103 mg, 0.84 mmol) in 2 mL dichloromethane was treated with (–)-camphanic acid chloride (136 mg, 0.63 mmol), and the mixture was allowed to stand at room temperature for 2 h. The crude product was purified by column chromatography on silica gel to give the title compound. Clear crystals suitable for an X-ray diffraction study were formed by a slow vapor diffusion of dry hexanes into a THF solution of the compound.

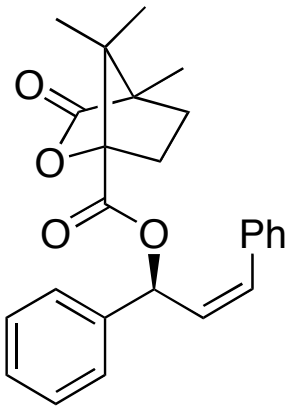
Preparation of (*Z*)-4,7,7-Trimethyl-3-oxo-2-oxa-bicyclo[2.2.1]heptane-1-carboxylic acid 1,3-diphenyl-allyl ester (derivative of 3dc). General procedure E was applied to **3dc** (90 mg, 0.42 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc: 95 / 5) to give the derivate of **3dc** (125 mg, 74% yield) as an oil. $[\alpha]_D^{20}$ = + 42.5 (*c* = 0.016, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 0.91 (s, 3H), 1.01 (s, 3H), 1.10 (s, 3H), 1.67 (m, 1H), 1.90 (m, 1H), 2.01 (m, 1H), 2.40 (m, 1H), 5.99 (dd, *J* = 9.7, 11.3 Hz, 1H), 6.74 (d, *J* = 11.2 Hz, 1H), 6.84 (d, *J* = 9.8 Hz, 1H), 7.37 (m, 10H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 9.9, 16.9, 17.0, 29.2, 30.7, 54.5, 55.0, 74.0, 91.2, 127.3, 128.0, 128.6, 128.7, 128.8, 128.9, 129.0, 133.1, 136.1, 139.2, 166.7, 178.4 ppm; IR (neat): 3060, 3028, 2969, 2876, 1955, 1888, 1790, 1751, 1664, 1601, 1576, 1494, 1448, 1397, 1378, 1356, 1318, 1264, 1228, 1168, 1125, 1102, 1061, 1017 cm^{-1}; HRMS calcd for $C_{25}H_{26}O_4$ $(M)^+$: 390.1831, found 390.1827.

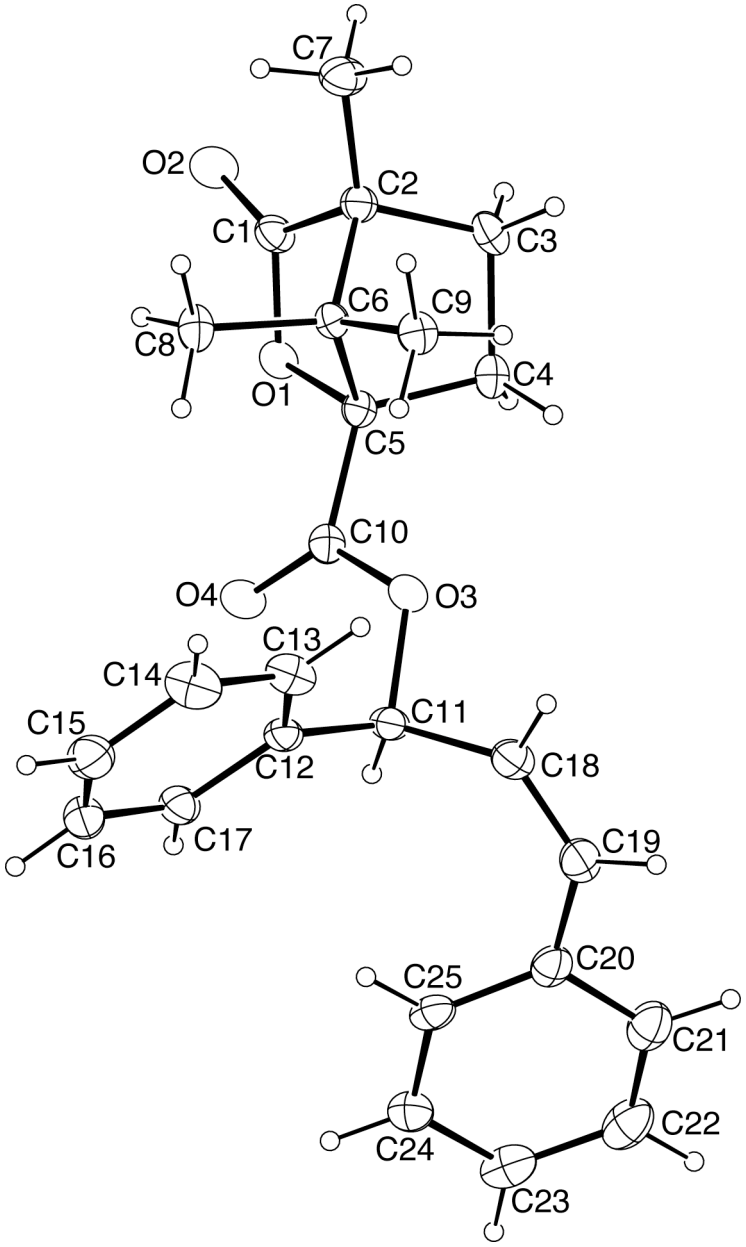


Preparation of 4,7,7-Trimethyl-3-oxo-2-oxa-bicyclo[2.2.1]heptane-1-carboxylic acid phenyl-(3-phenyl-oxiranyl)-methyl ester (derivative of 4dc). 

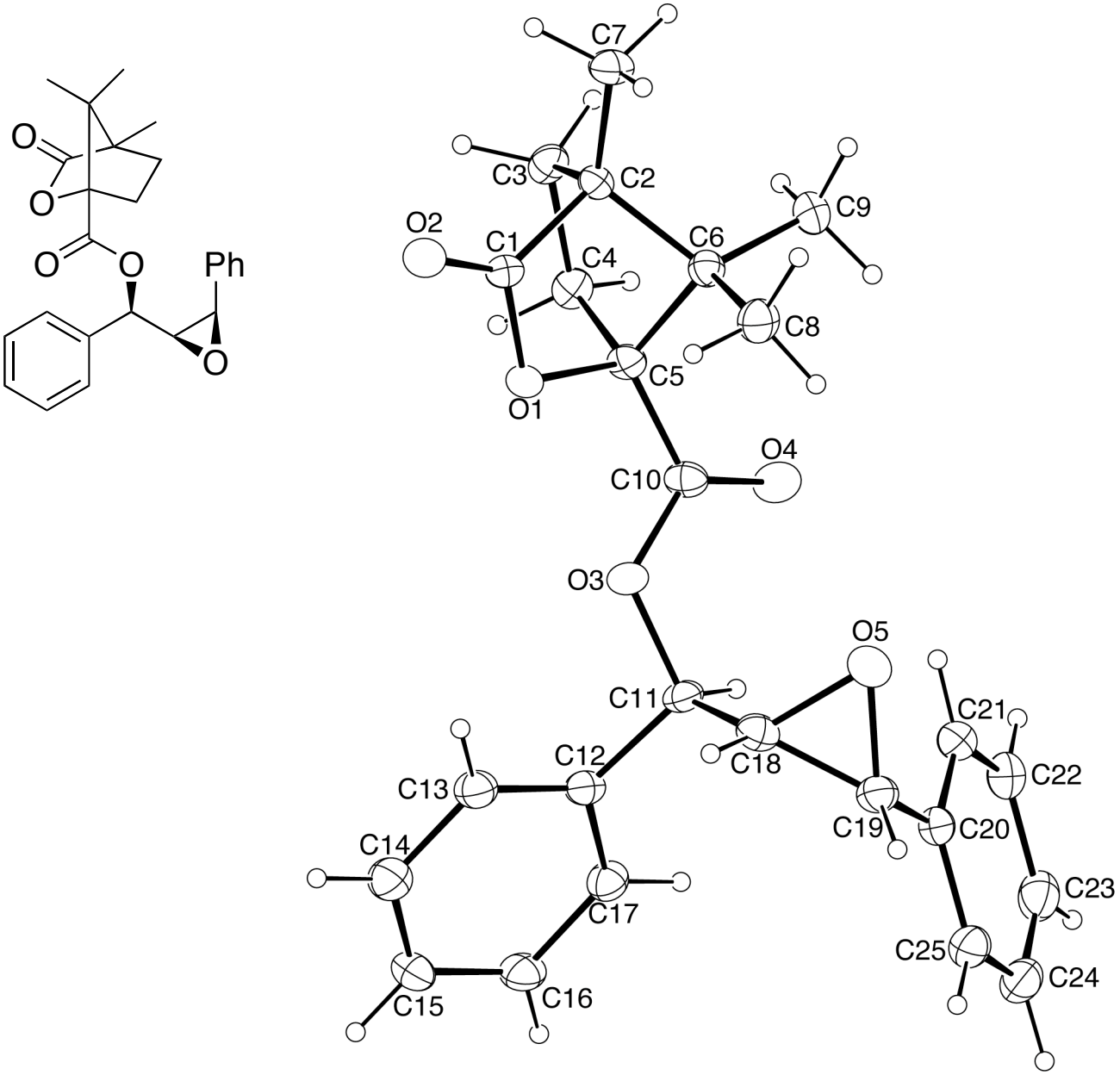
General Procedure E was applied to **4dc** (95 mg, 0.42 mmol). The crude product was purified by column chromatography on silica gel (hexanes / EtOAc: 95 / 5) to give the derivate of **4dc** (120 mg, 70% yield) as an oil. $[\alpha]_D^{20}$ = - 5.78 (*c* = 0.038, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 1.08 (s, 3H), 1.11 (s, 3H), 1.15 (s, 3H), 1.70 (m, 1H), 1.94 (m, 1H), 2.05 (m, 1H), 2.48 (m, 1H), 3.57 (dd, *J* = 4.3, 8.7 Hz, 1H), 4.20 (d, *J* = 4.3 Hz, 1H), 5.62 (d, *J* = 8.7 Hz, 1H), 6.89 (m, 2H), 7.25 (m, 3H), 7.40 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 10.1, 17.0, 17.1, 29.3, 30.9, 54.8, 55.2, 57.7, 60.9, 75.7, 91.6, 126.7, 126.8, 128.7, 128.8, 128.9, 129.1, 134.2, 135.7, 166.9, 178.8 ppm; IR (neat): 3110, 3063, 3034, 2974, 2935, 2874, 2337, 1959, 1901, 1789, 1732, 1606, 1587, 1497, 1454, 1396, 1379, 1360, 1343, 1322, 1269, 1223, 1165, 1125, 1099, 1064, 1022 cm^{-1}; HRMS calcd for $C_{25}H_{26}O_5Na$ $(M + Na)^+$: 429.1678, found 429.1698.

(1) Leroy, J. *Org. Synth.* **1997**, *74*, 212-216.
(2) Murray, R. E. *Synth. Commun.* **1980**, *10*, 345-349.
(3) Jeon, S.-J.; Fisher, E. L.; Carroll, P. J.; Walsh, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 9618-9619.
(4) Maleczka, R. E., Jr.; Gallagher, W. P. *Org. Lett.* **2001**, *3*, 4173-4176.
(5) Dyker, G.; Stirner, W.; Henkel, G. *Eur. J. Org. Chem.* **2000**, 1433-1441.

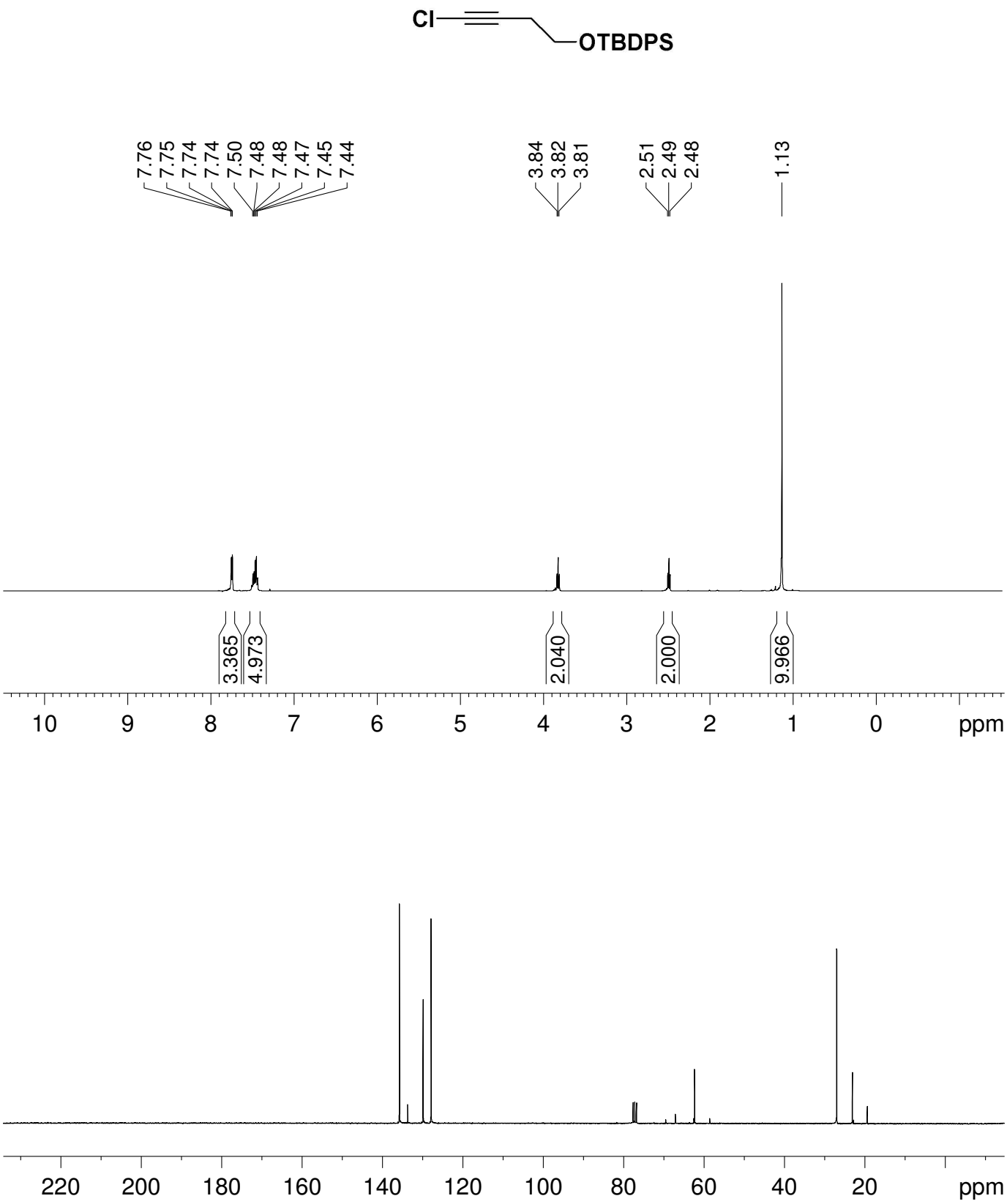




X-ray structure of **3dc** derivative



X-ray structure of **4dc** derivative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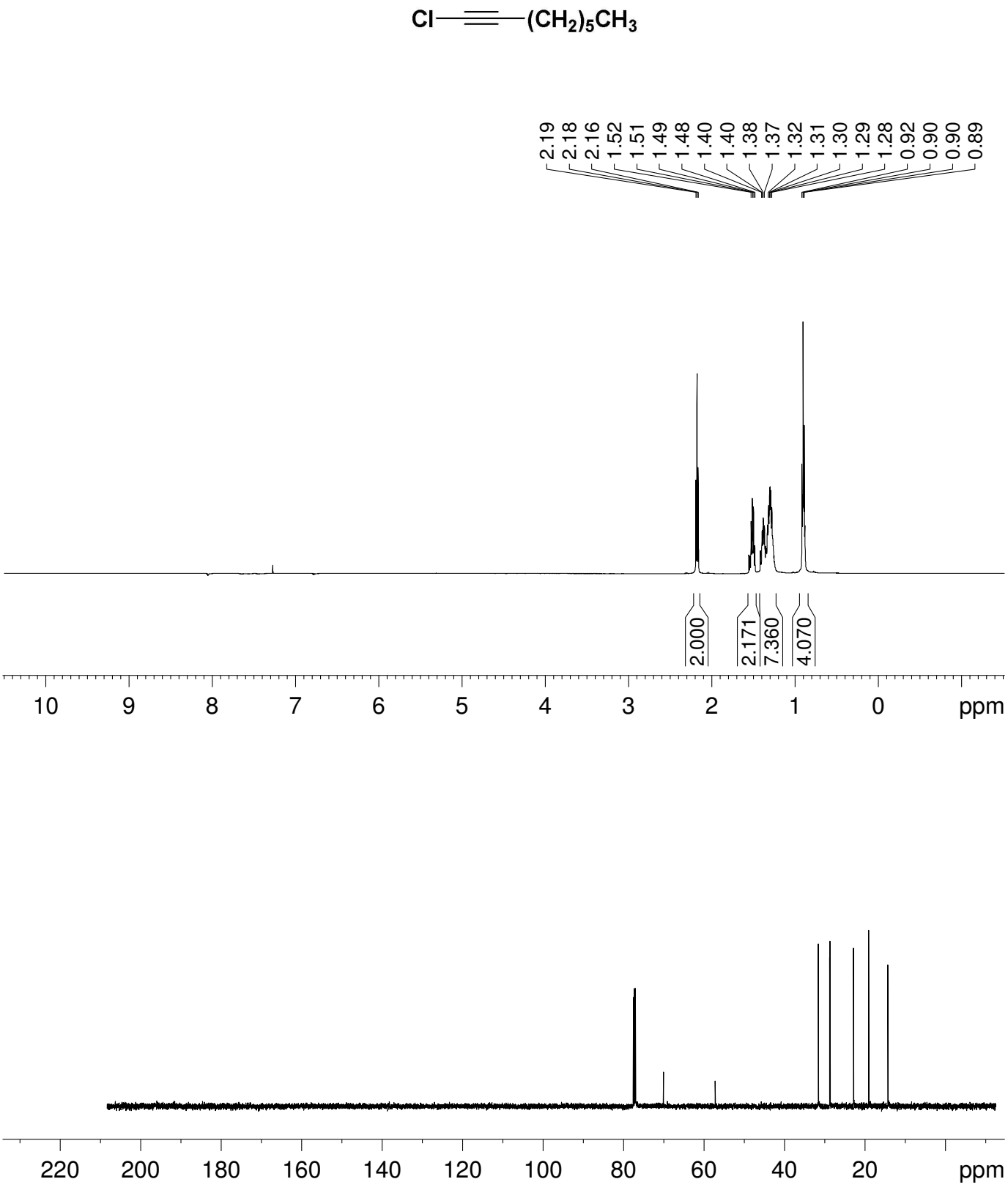
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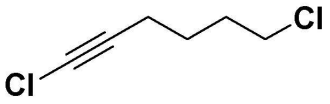
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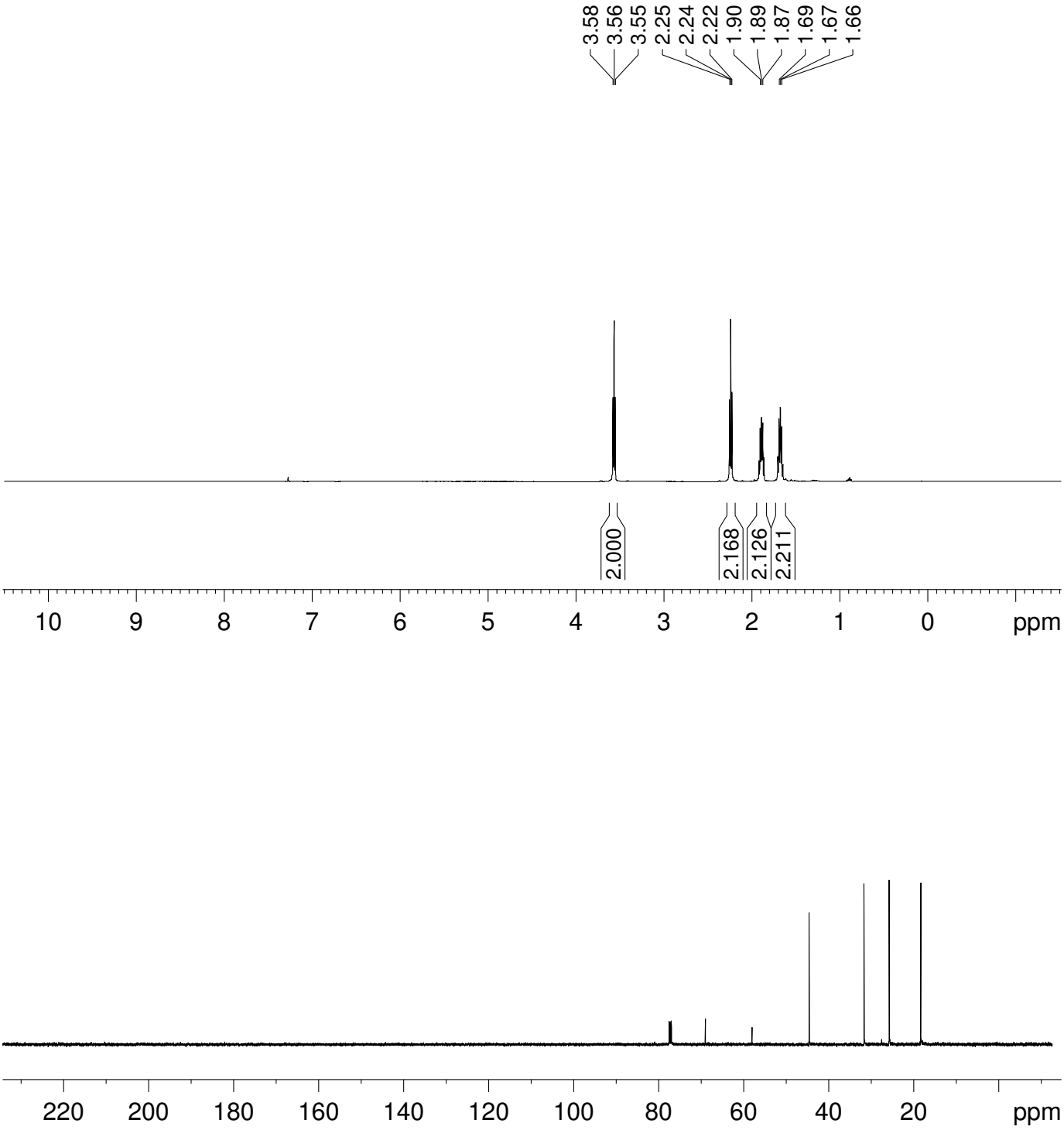
Cl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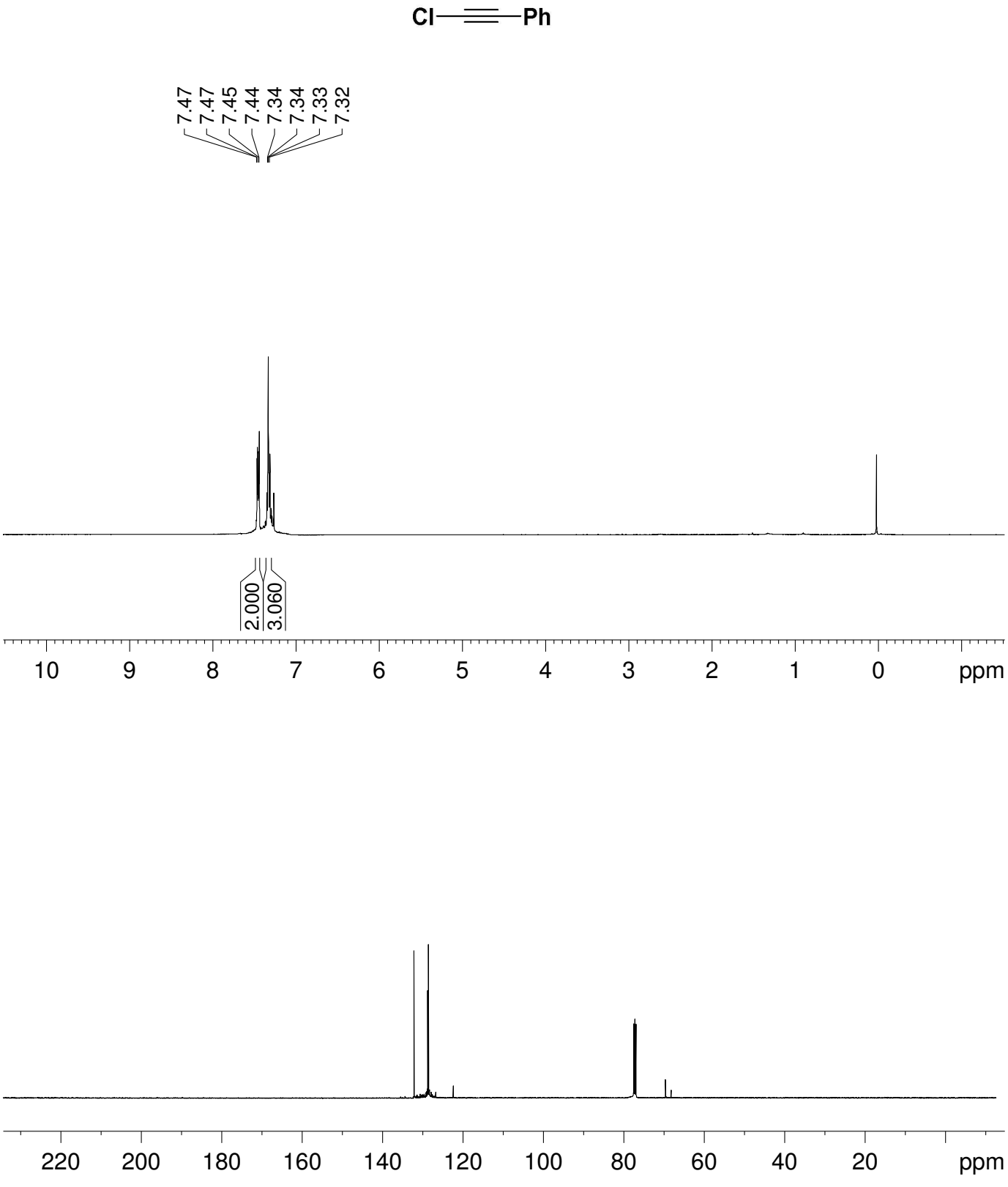
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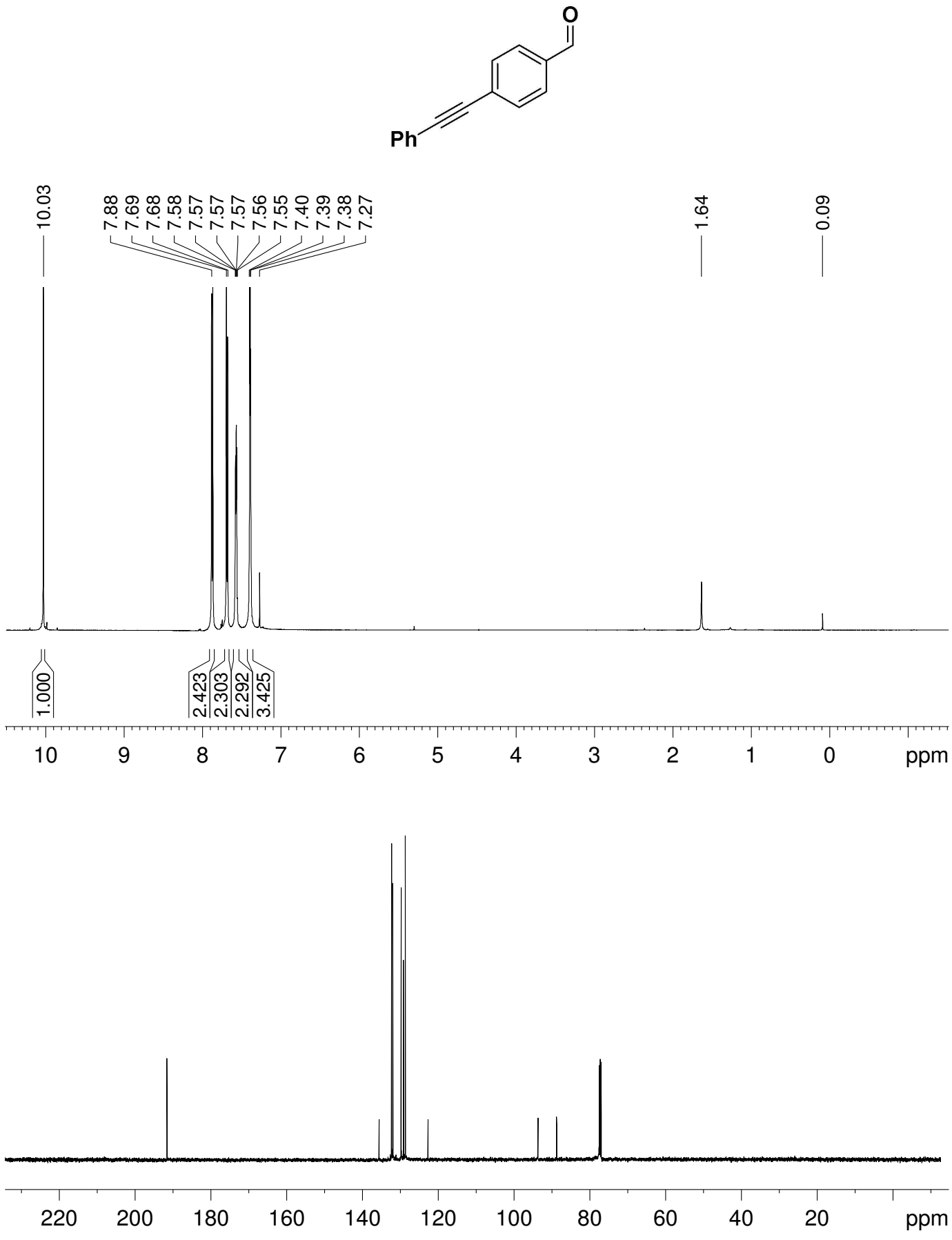
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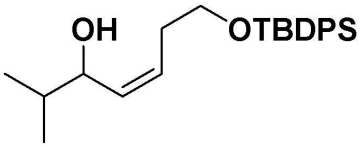
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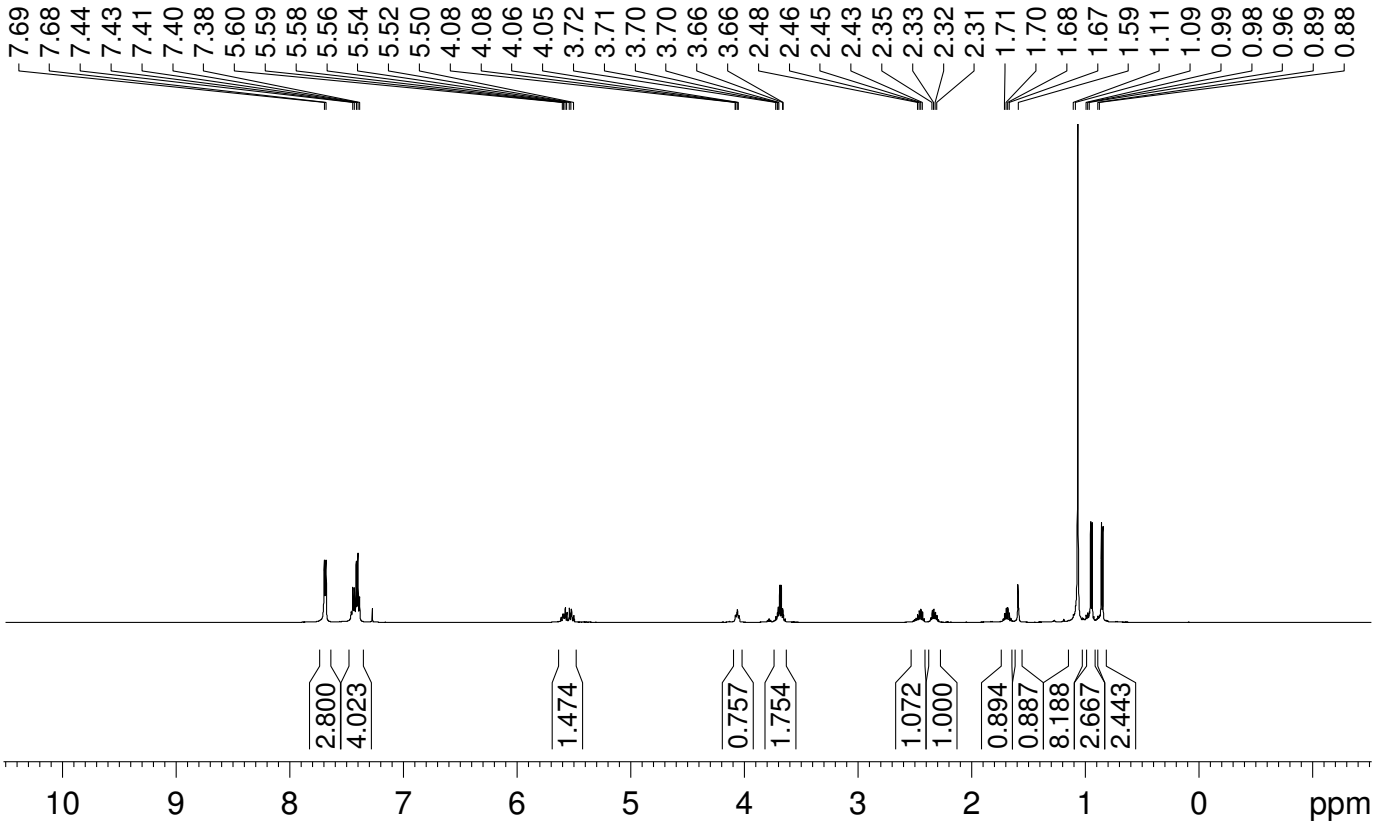
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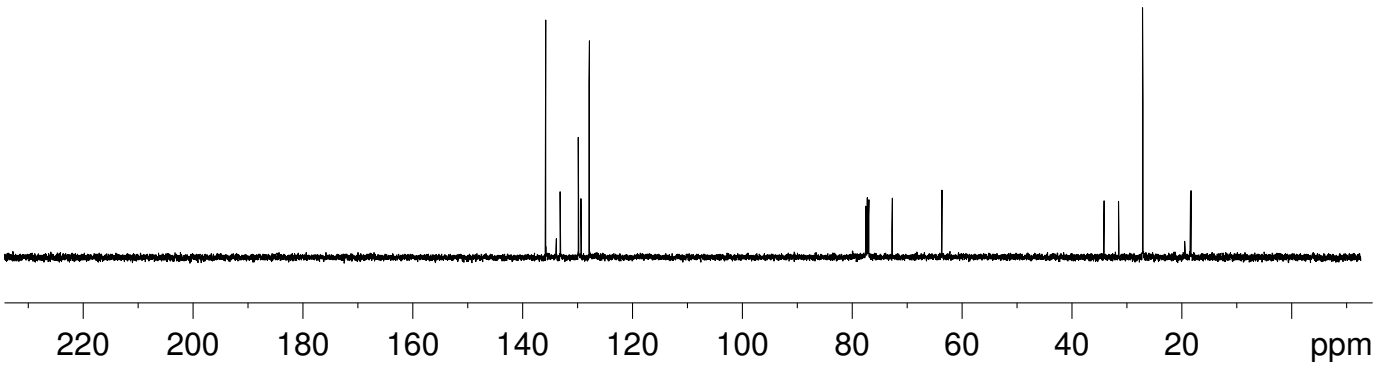
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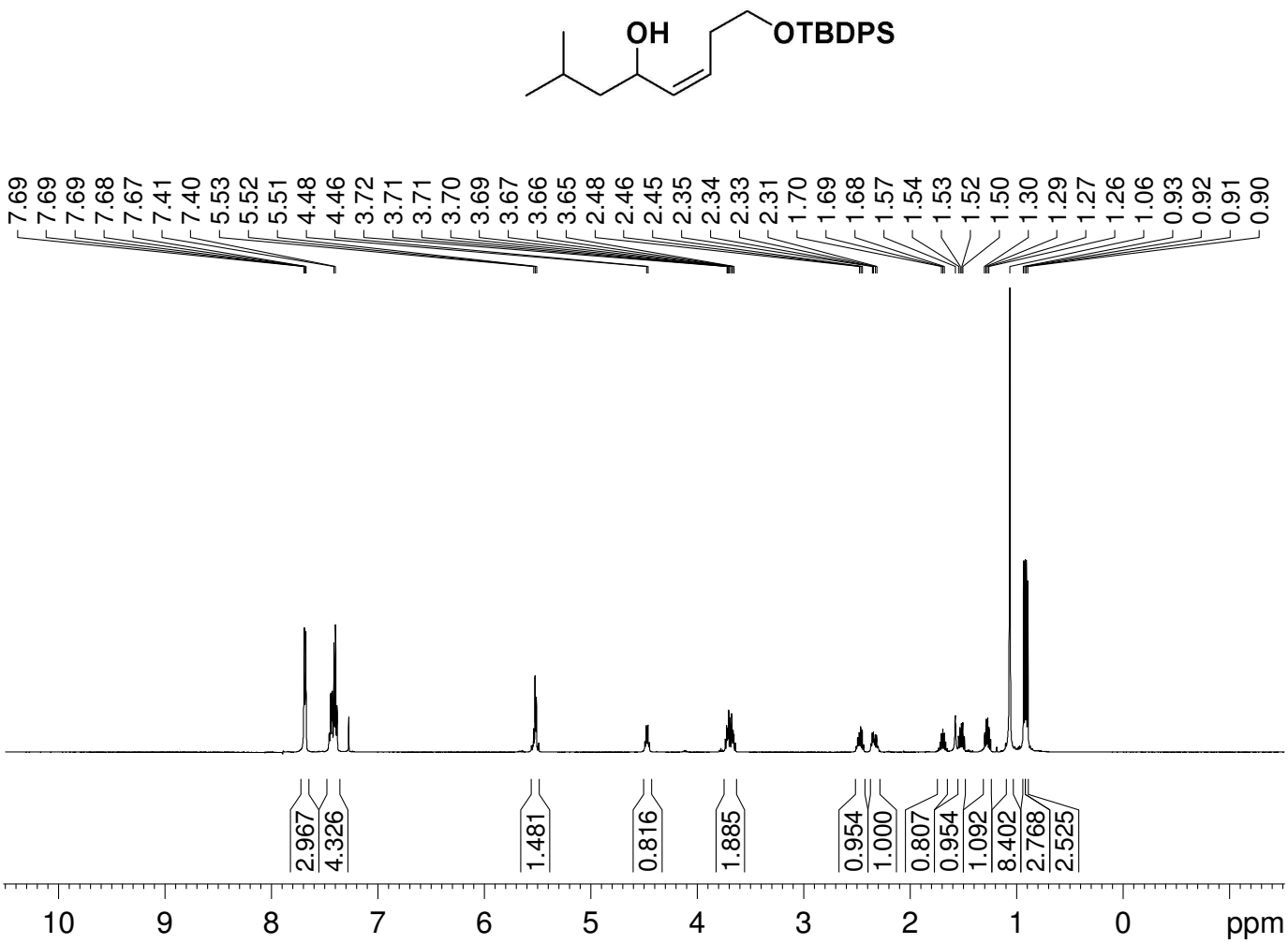
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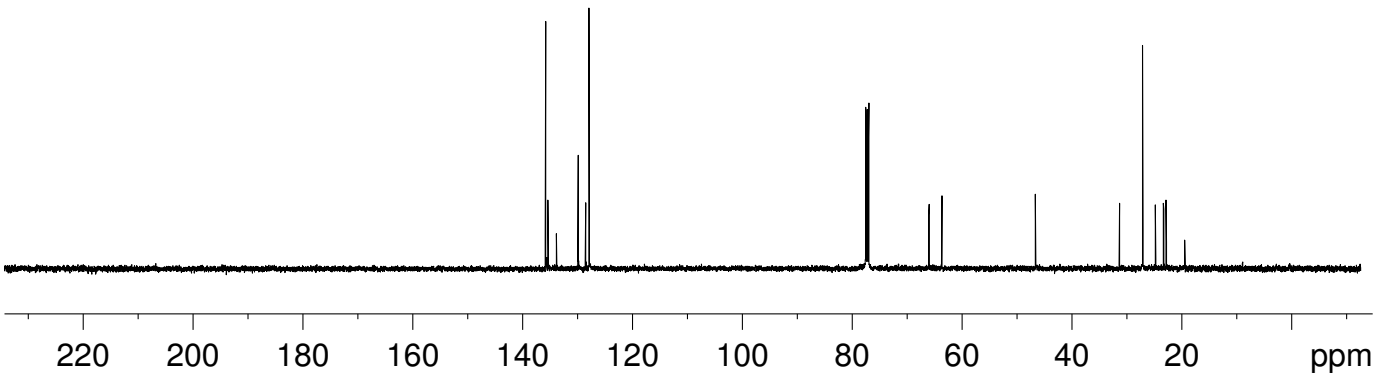
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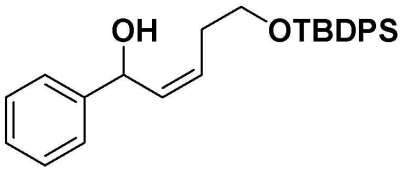
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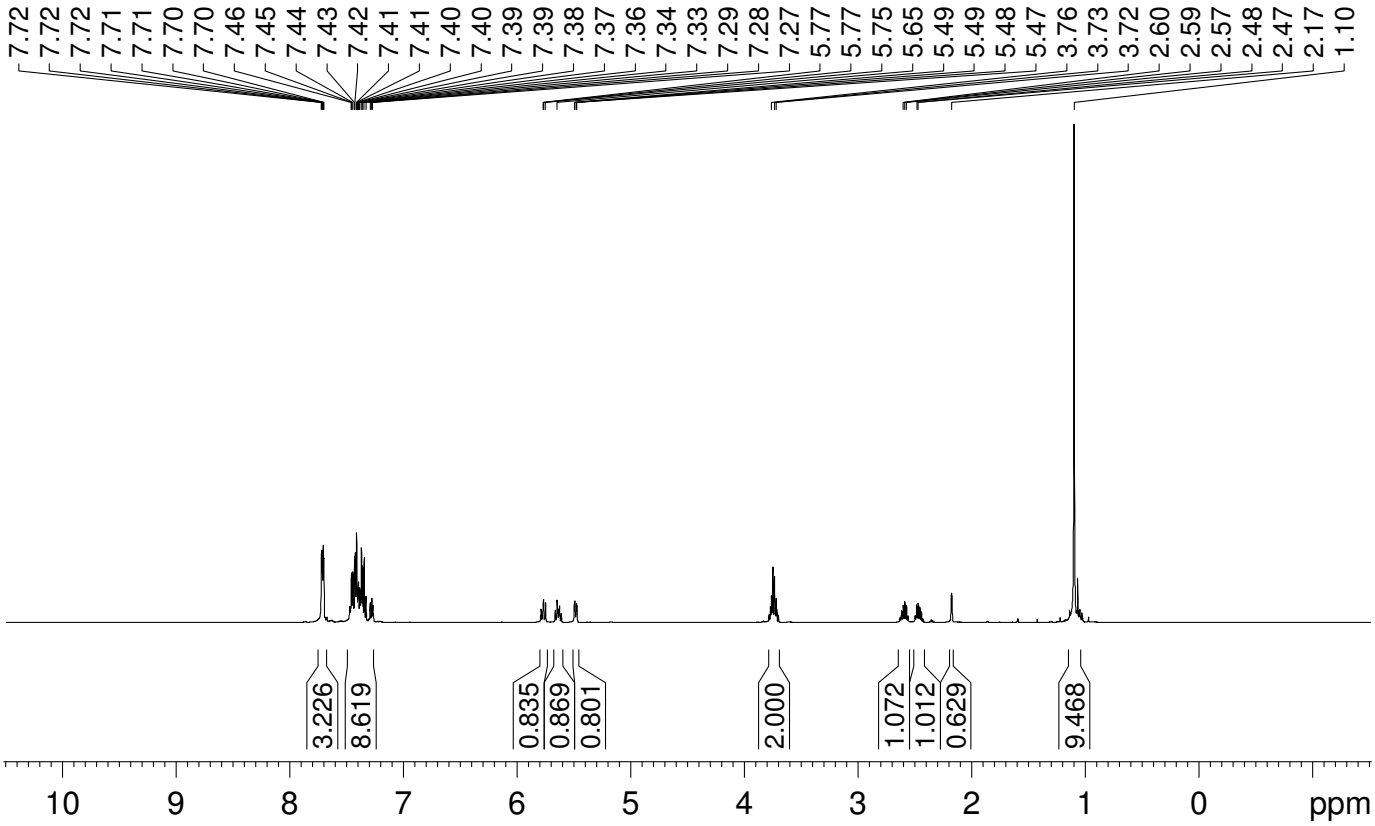
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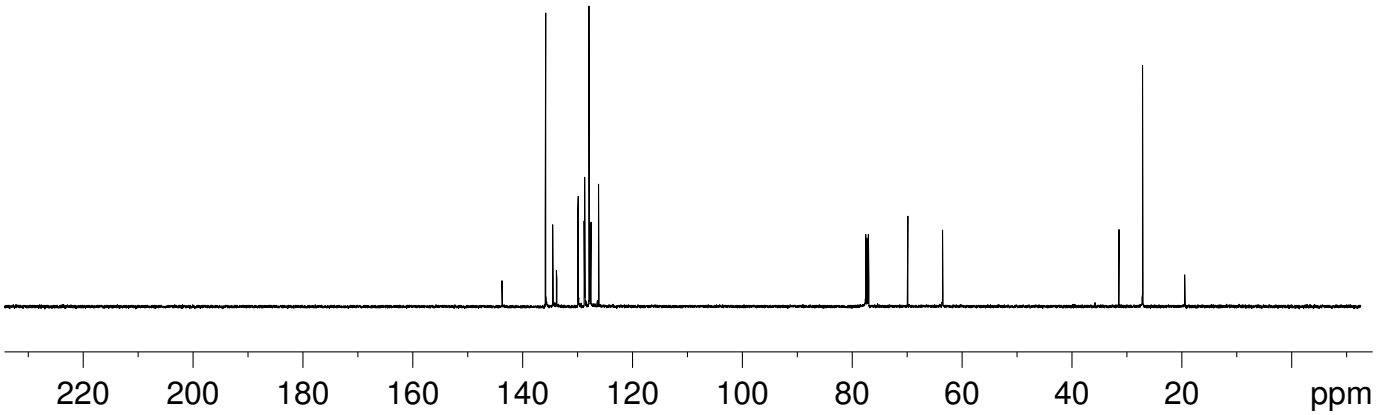
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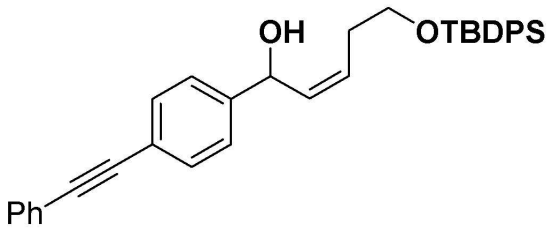
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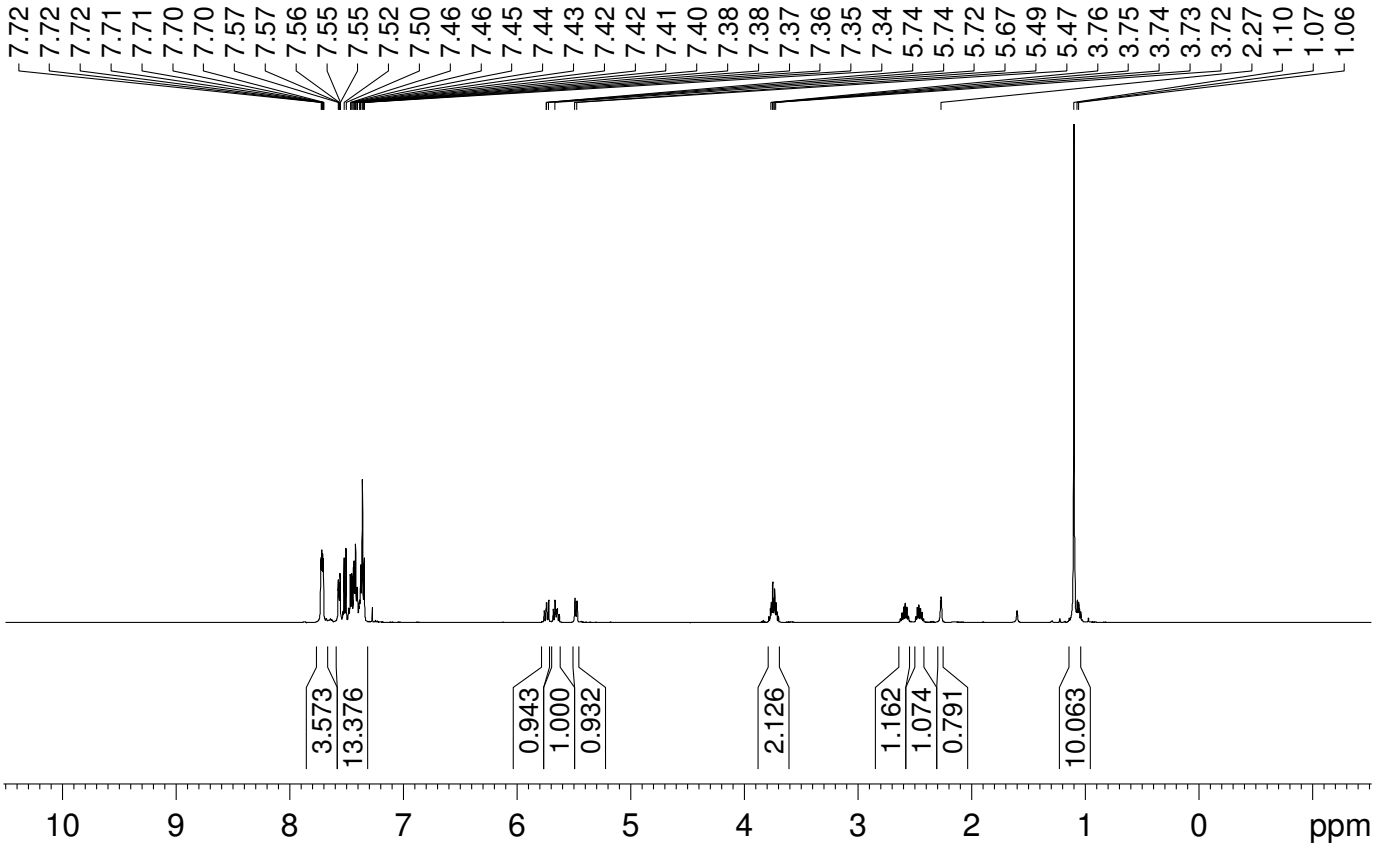
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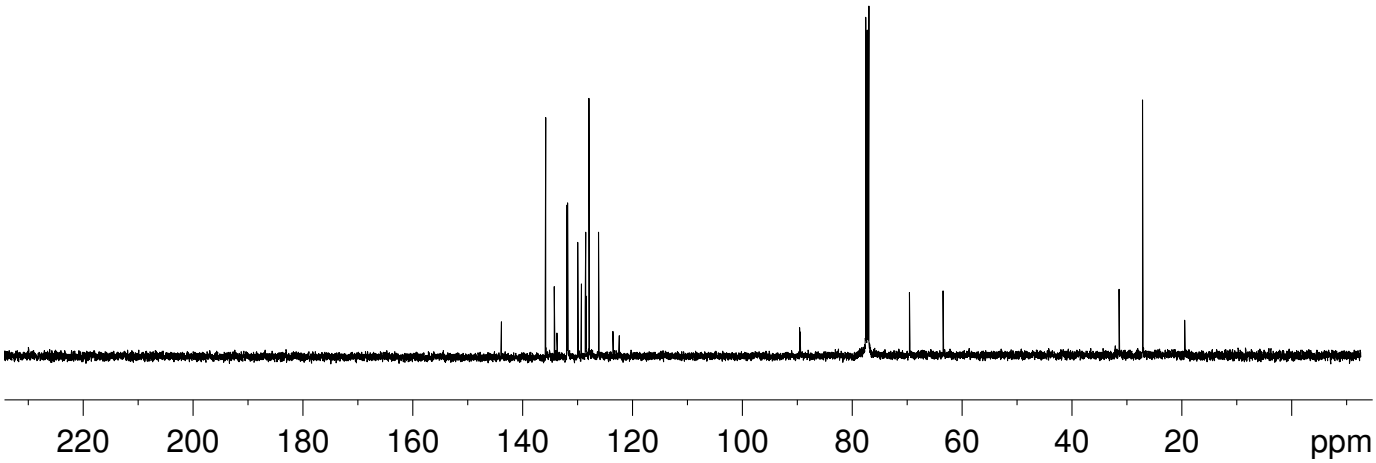
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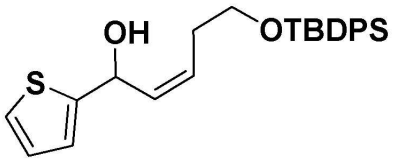
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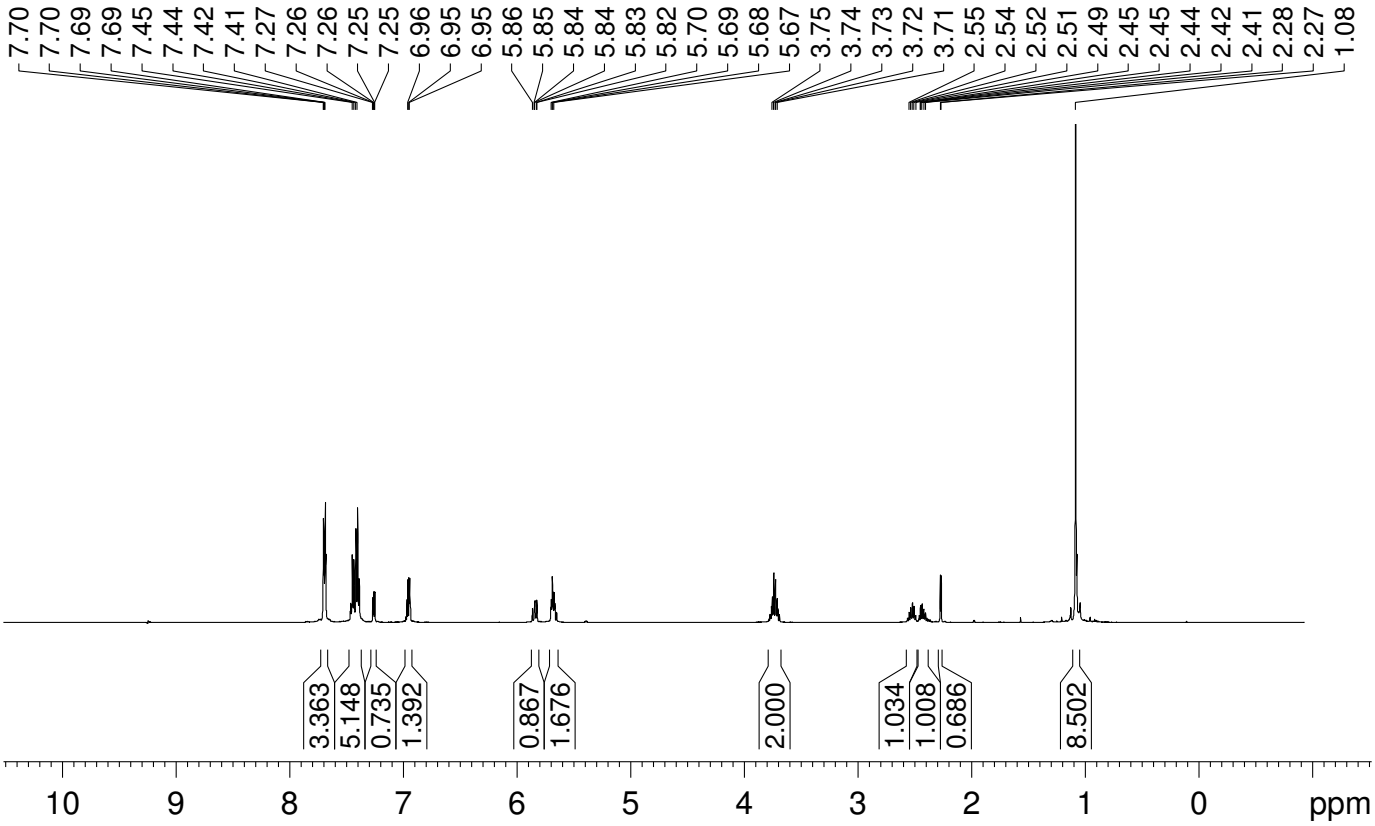
OTBDPS
S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7.26
7.26
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6.96
6.95
6.95
5.86
5.85
5.84
5.84
5.83
5.82
5.70
5.69
5.68
5.67
3.75
3.74
3.73
3.72
3.71
2.55
2.54
2.52
2.51
2.49
2.45
2.45
2.44
2.42
2.41
2.28
2.27
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3.363
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1.392
0.867
1.676
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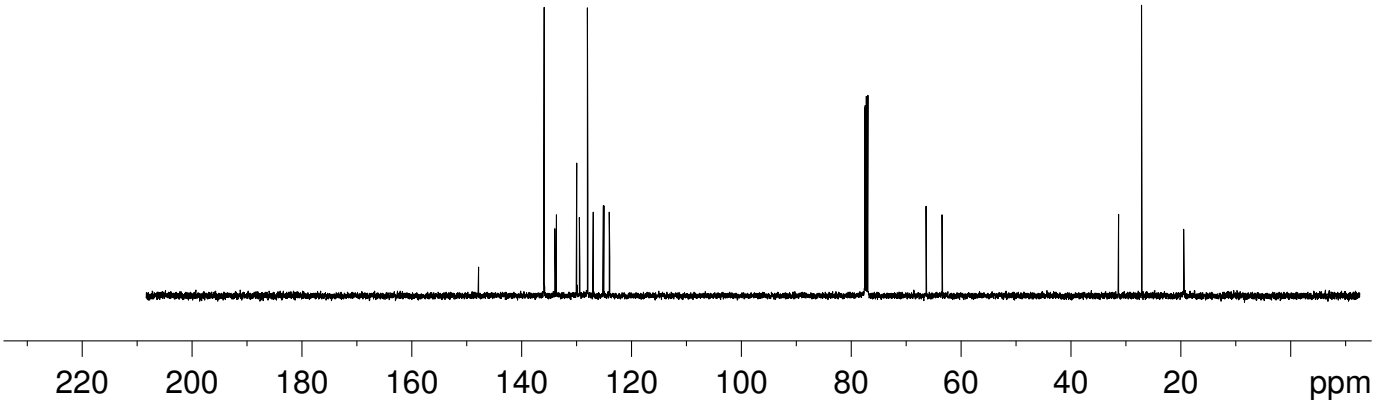
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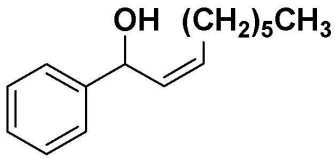
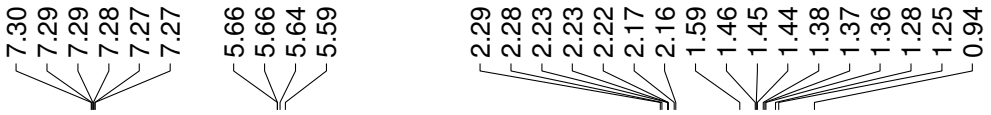

OH
(CH2)5CH3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5.66
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2.28
2.23
2.23
2.22
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1.46
1.45
1.44
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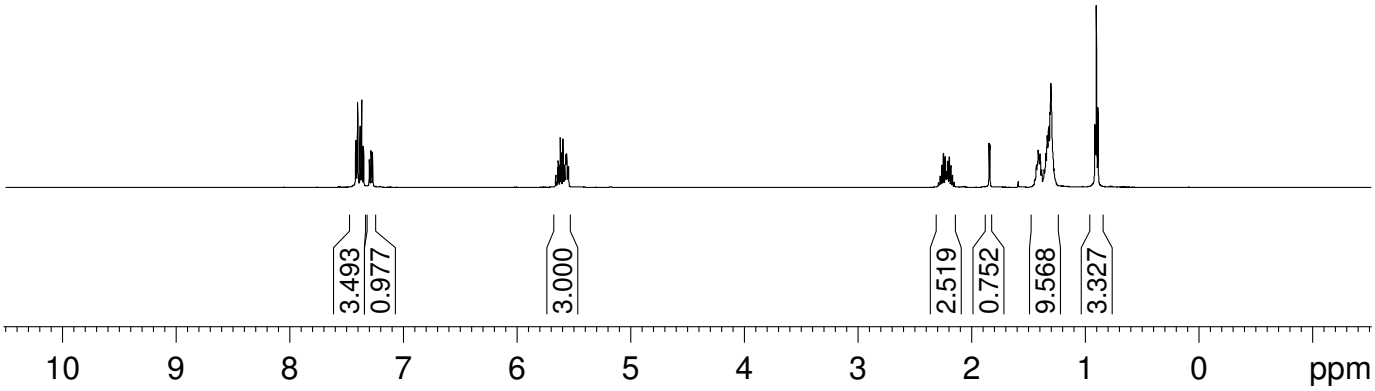
1.28
1.25
0.94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10
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6
5
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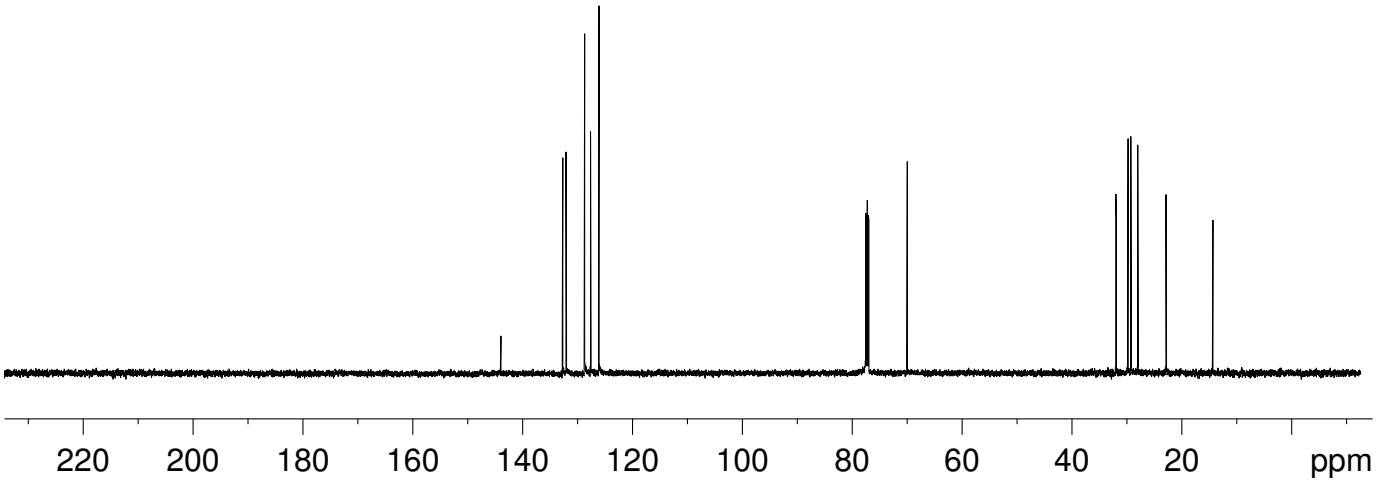
0
ppm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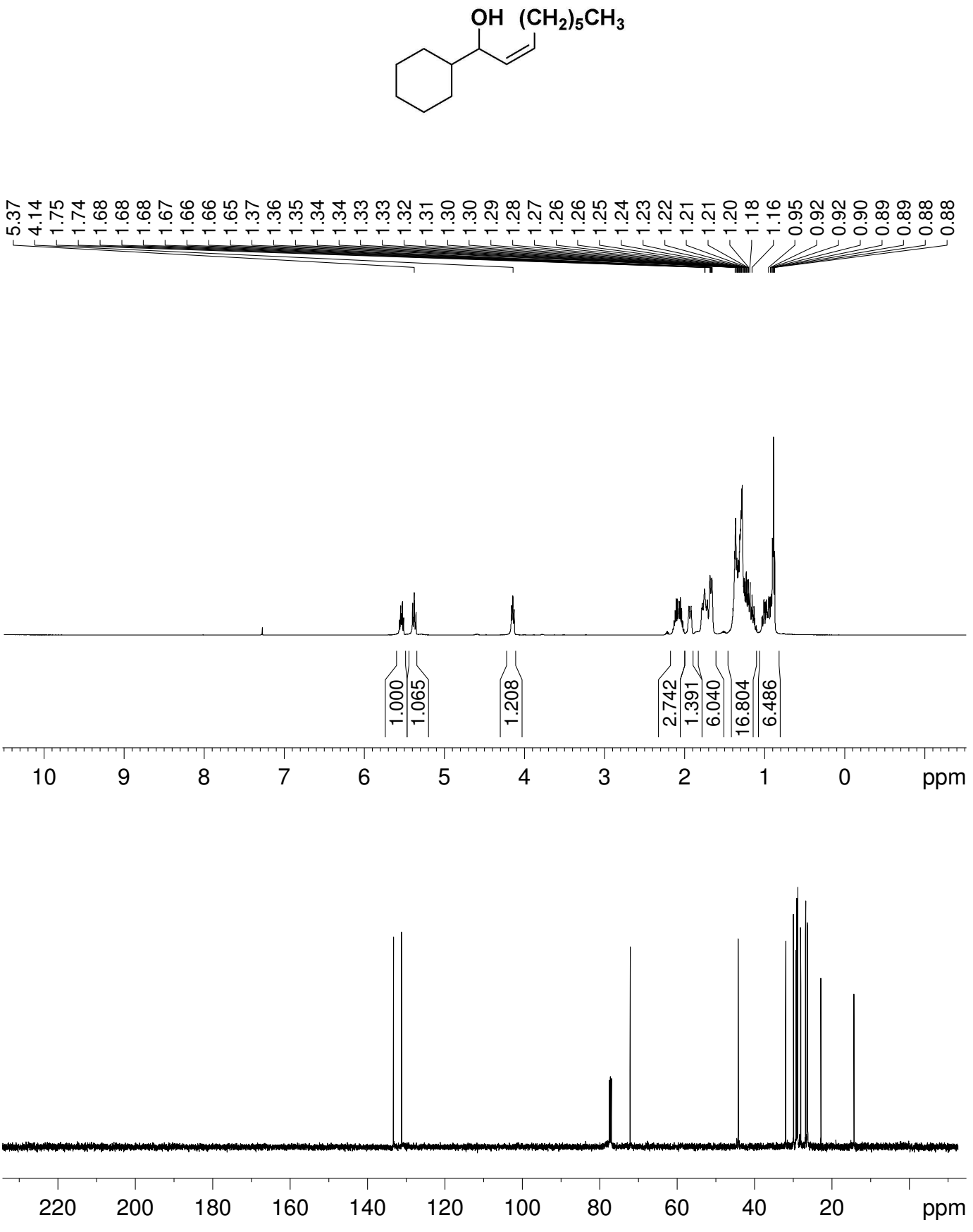
OH (CH2)5CH3
5.37 4.14 1.75 1.74 1.68 1.68 1.68 1.67 1.66 1.66 1.65 1.37 1.36 1.35 1.34 1.34 1.33 1.33 1.32 1.31 1.30 1.30 1.29 1.28 1.27 1.26 1.26 1.25 1.24 1.23 1.22 1.21 1.21 1.20 1.18 1.16 0.95 0.92 0.92 0.90 0.89 0.89 0.88 0.88
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10 9 8 7 6 5 4 3 2 1 0 ppm
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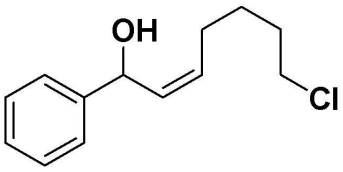
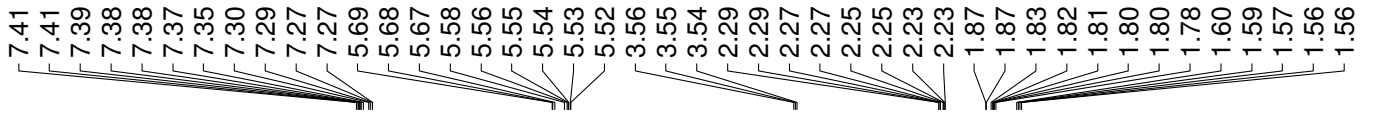

OH
Cl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5.68
5.67
5.58
5.56
5.55
5.54
5.53
5.52
3.56
3.55
3.54
2.29
2.29
2.27
2.27
2.25
2.25
2.23
2.23
1.87
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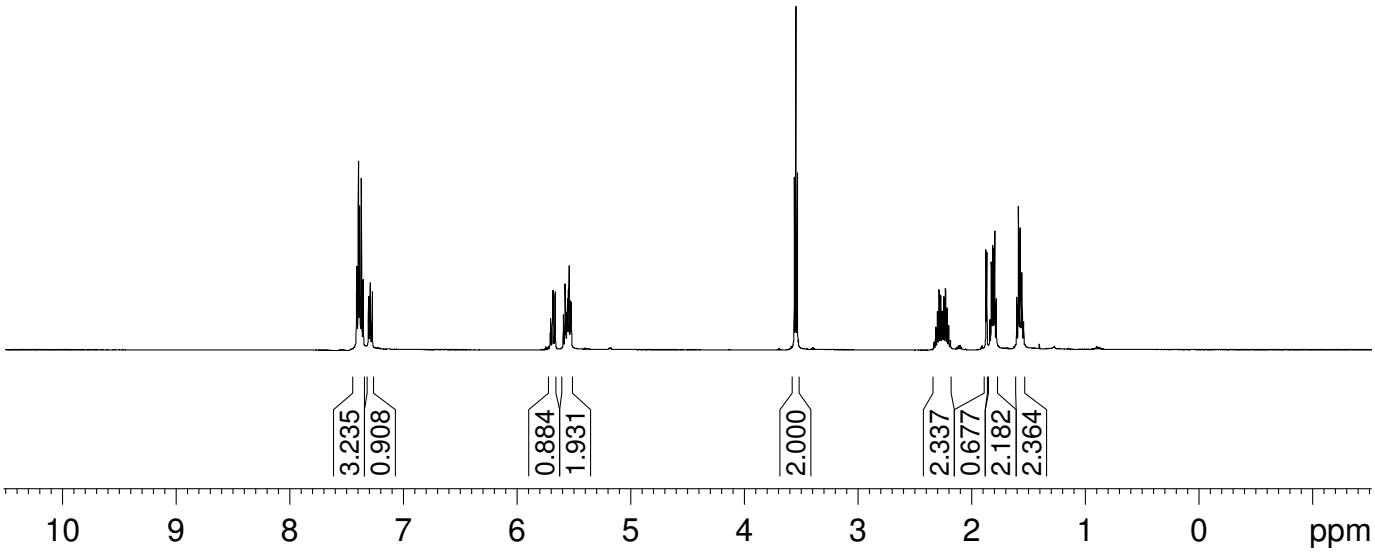
1.56
1.56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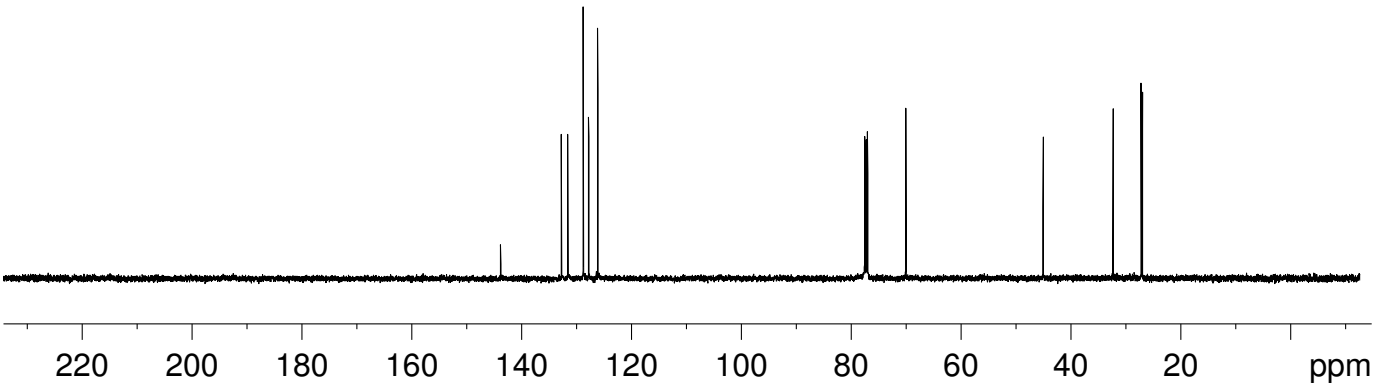
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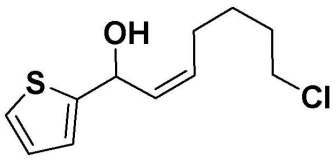
ppm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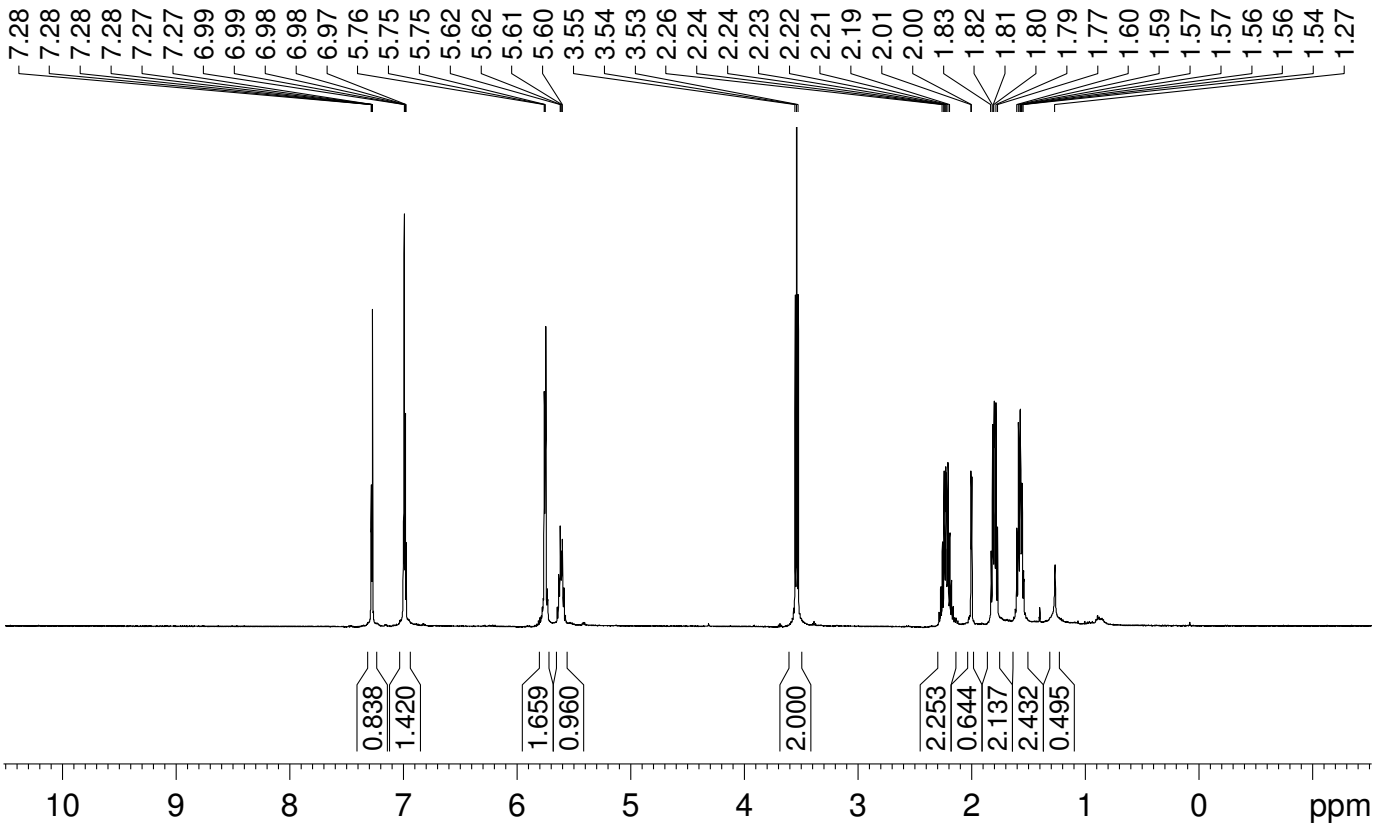
S
Cl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5.75
5.75
5.62
5.62
5.61
5.60
3.55
3.54
3.53
2.26
2.24
2.24
2.23
2.22
2.21
2.19
2.01
2.00
1.83
1.82
1.81
1.80
1.79
1.77
1.60
1.59
1.57
1.57
1.56
1.56
1.54
1.27
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0.960
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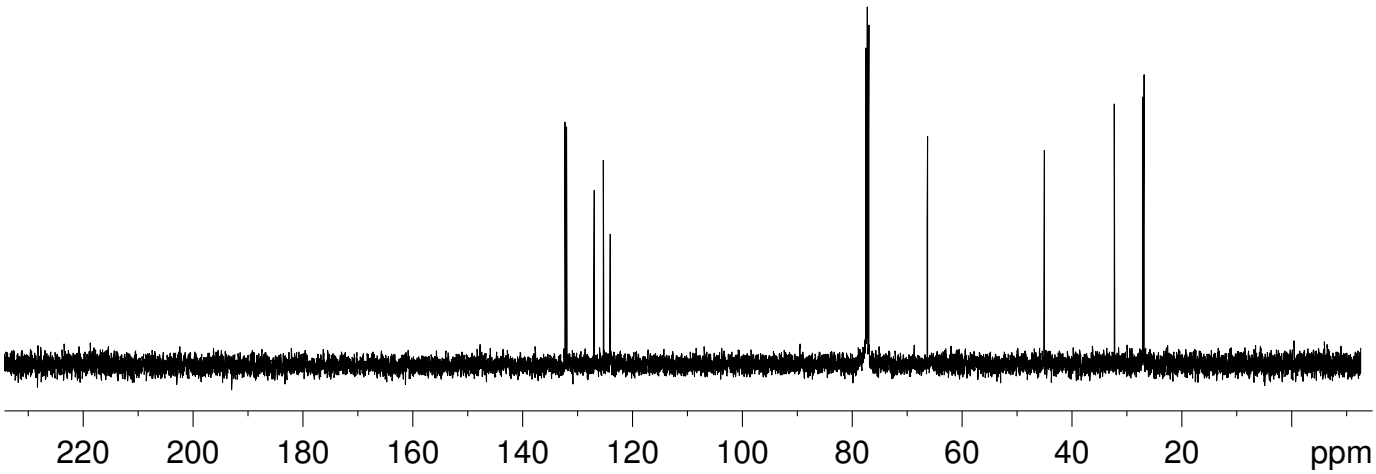
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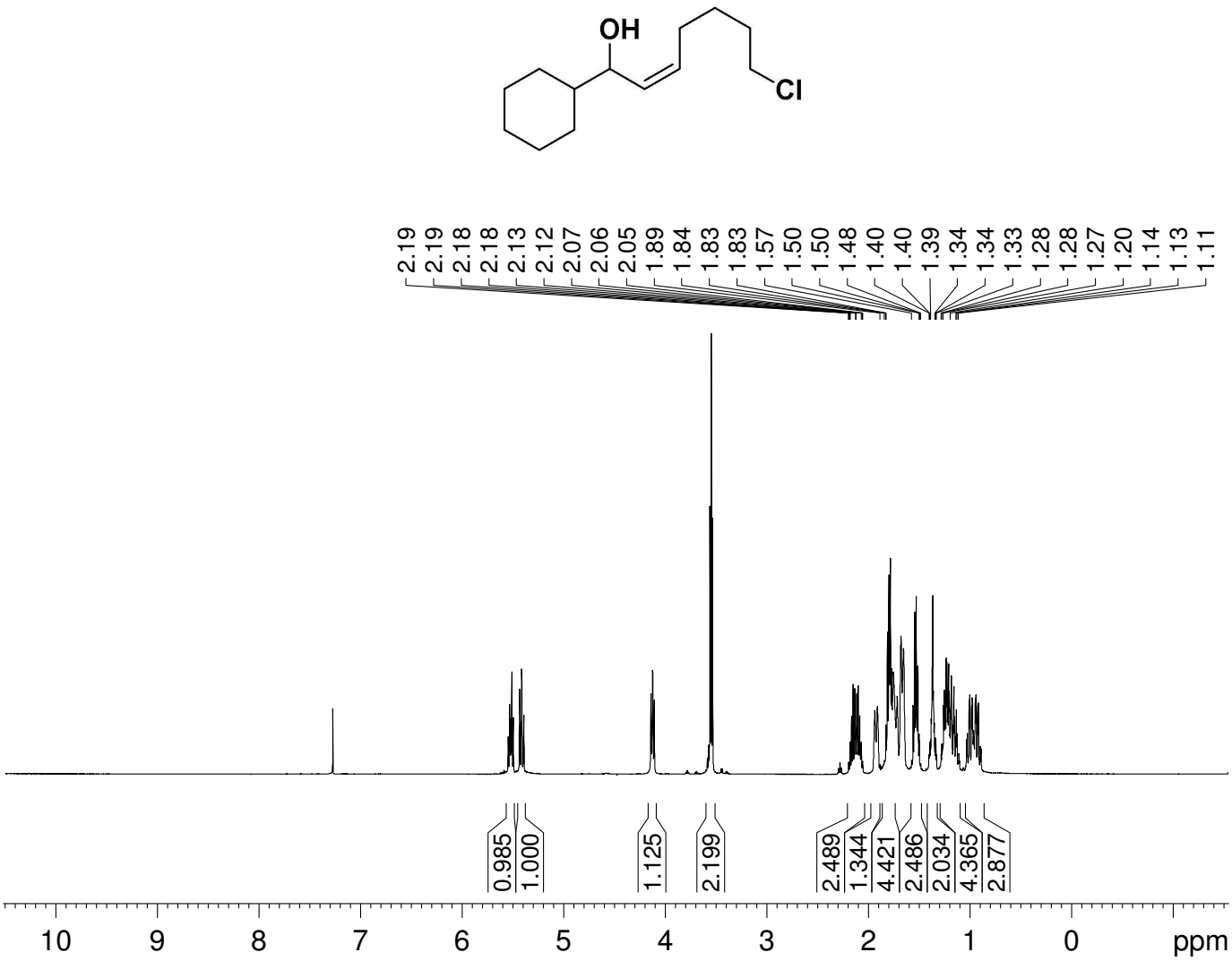
OH
Cl
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2.05
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1.50
1.50
1.48
1.40
1.40
1.39
1.34
1.34
1.33
1.28
1.28
1.27
1.20
1.14
1.13
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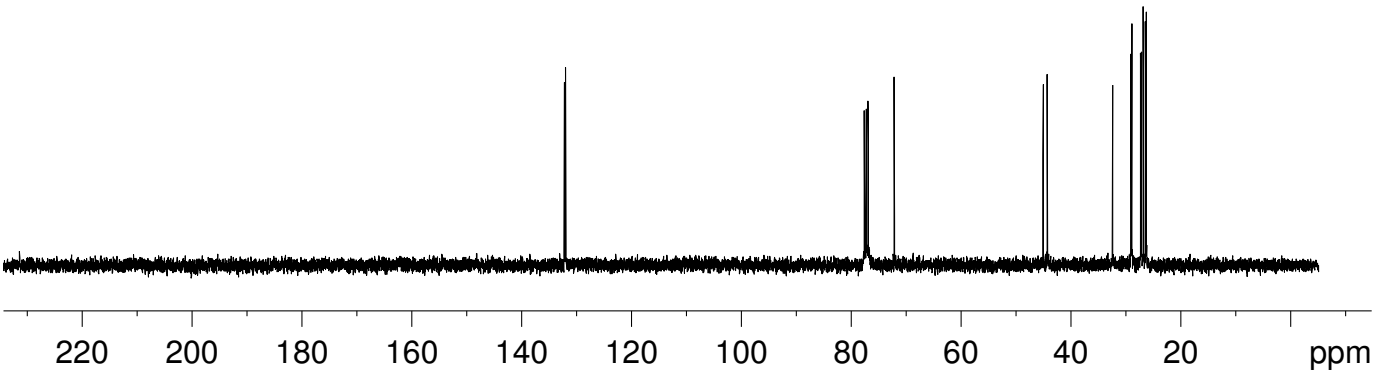
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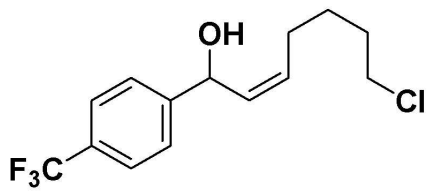
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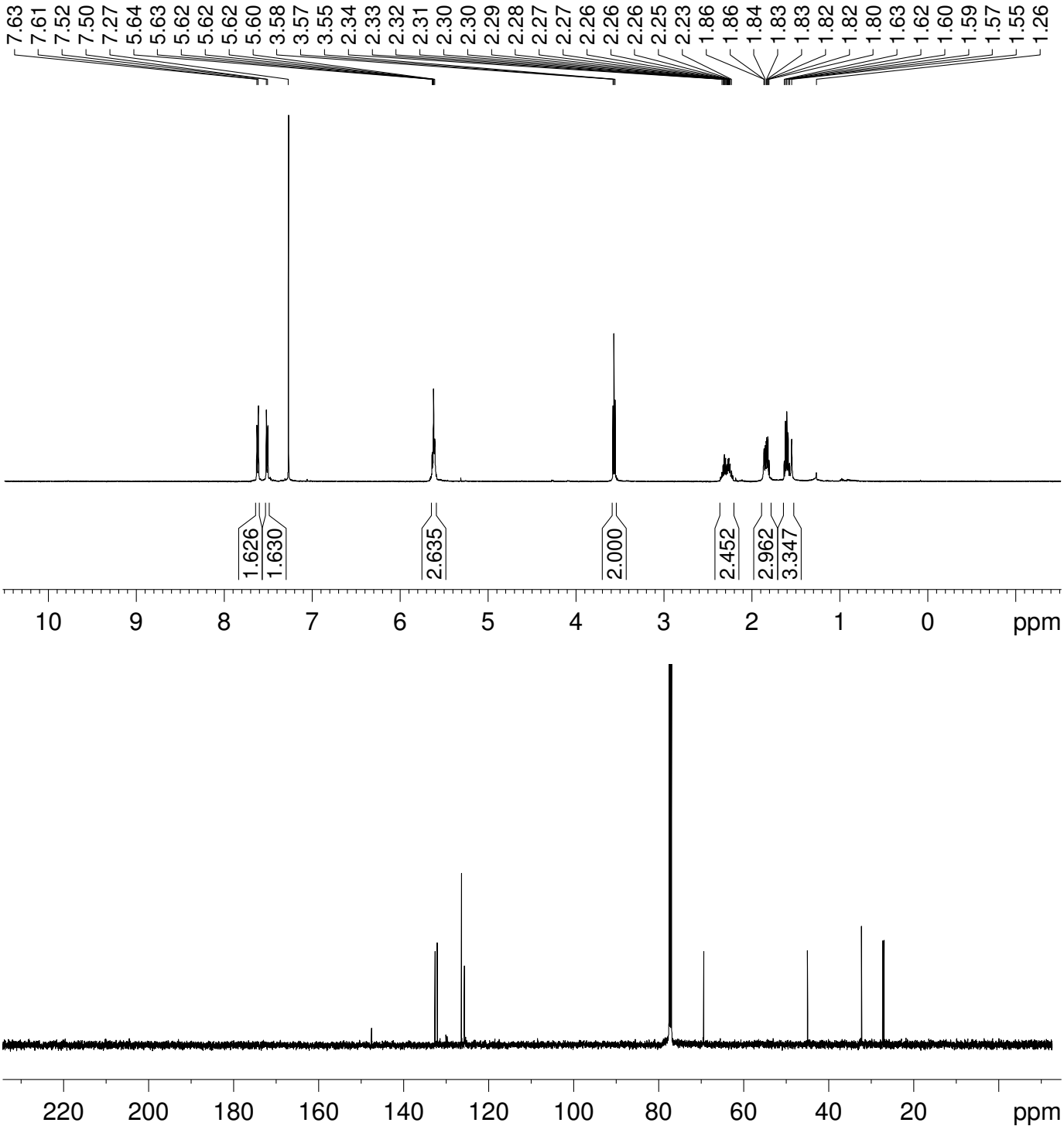
Cl
F3C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3.57
3.55
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2.32
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2.23
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1.83
1.82
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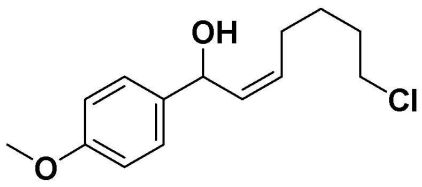
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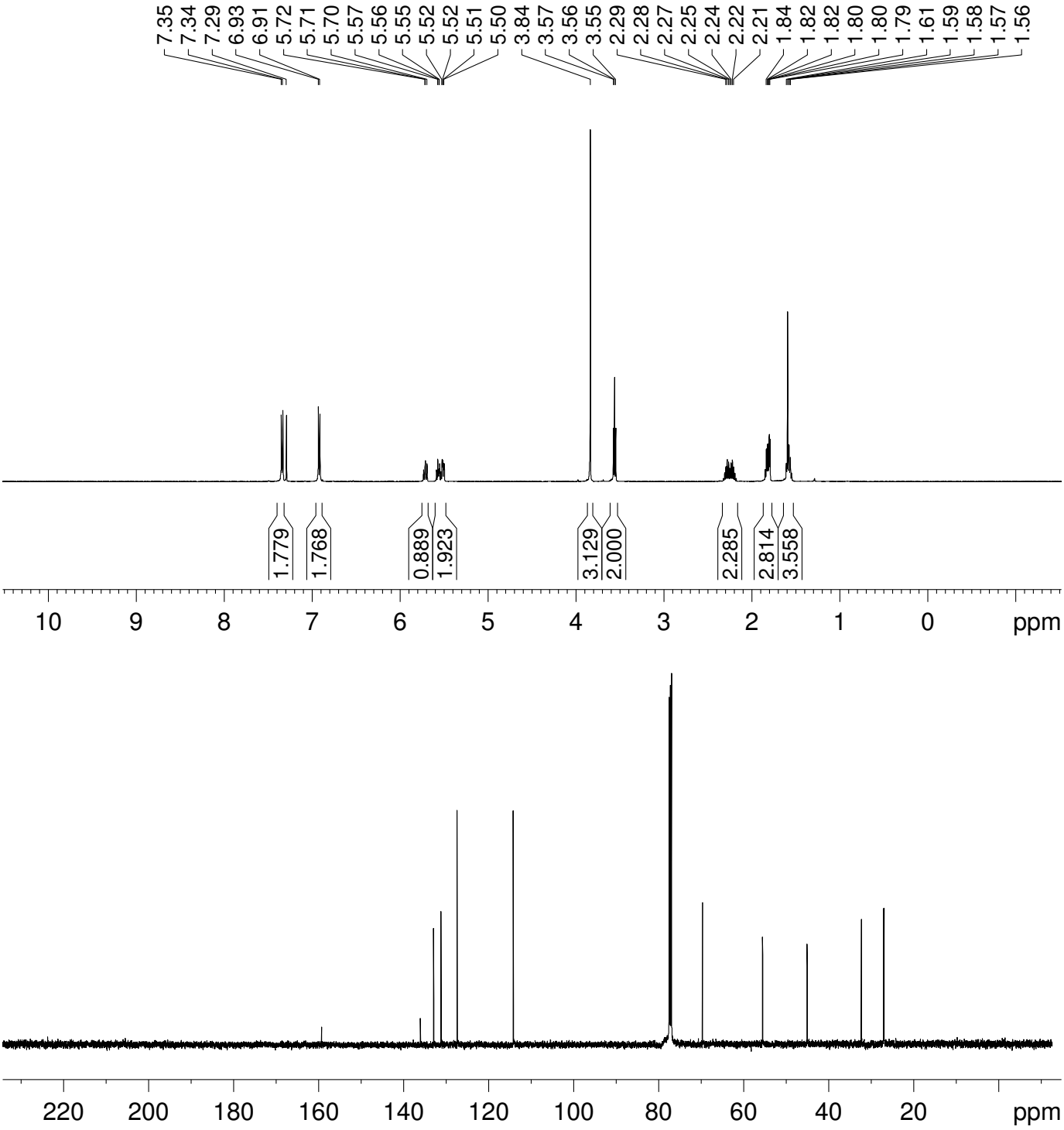
Cl
O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1.82
1.82
1.80
1.80
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1.61
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1.56
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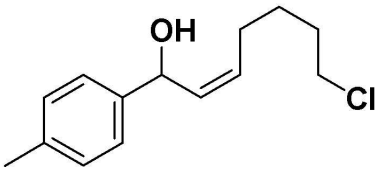
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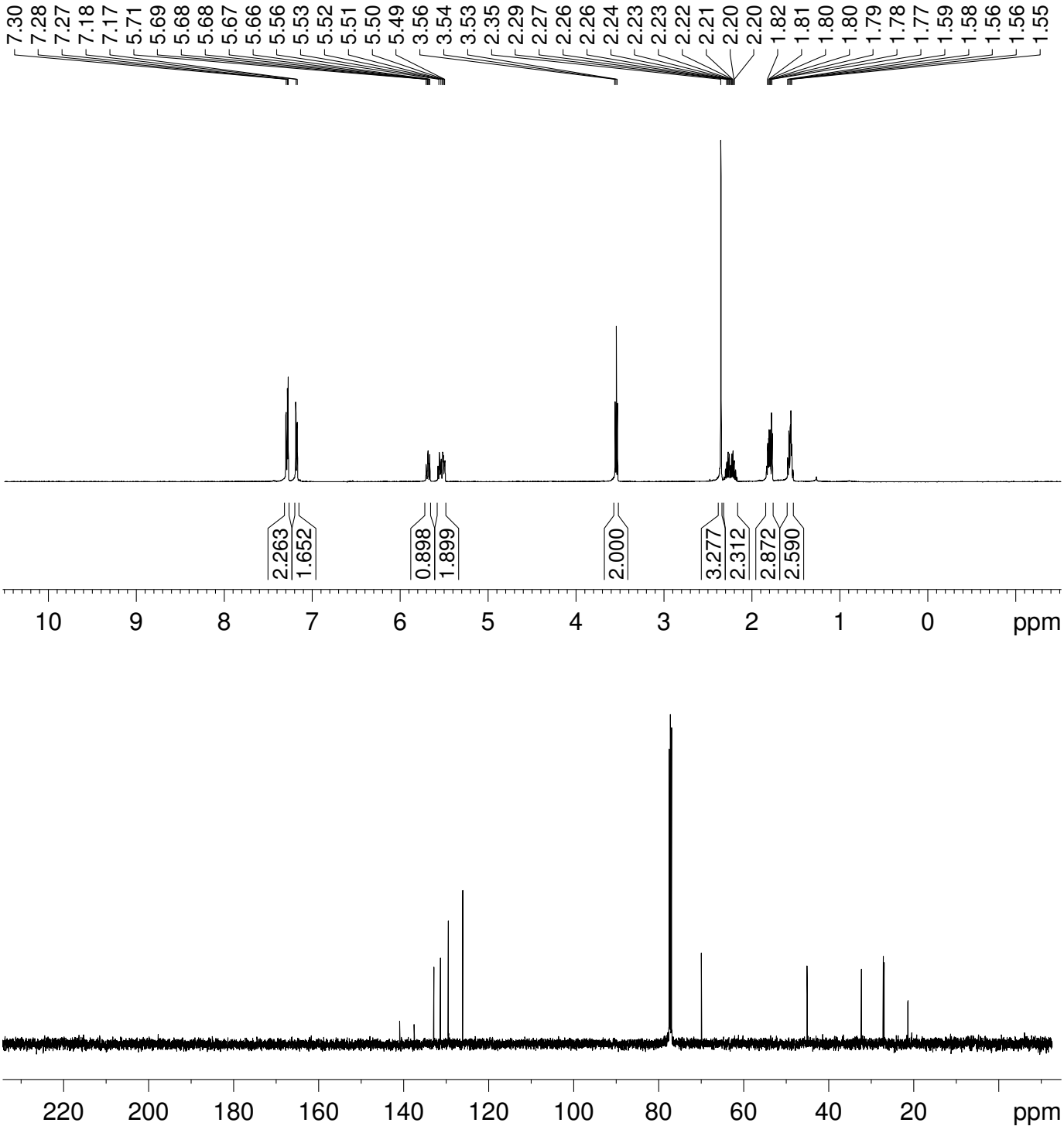
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2.24
2.23
2.23
2.22
2.21
2.20
2.20
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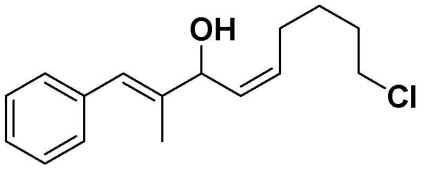
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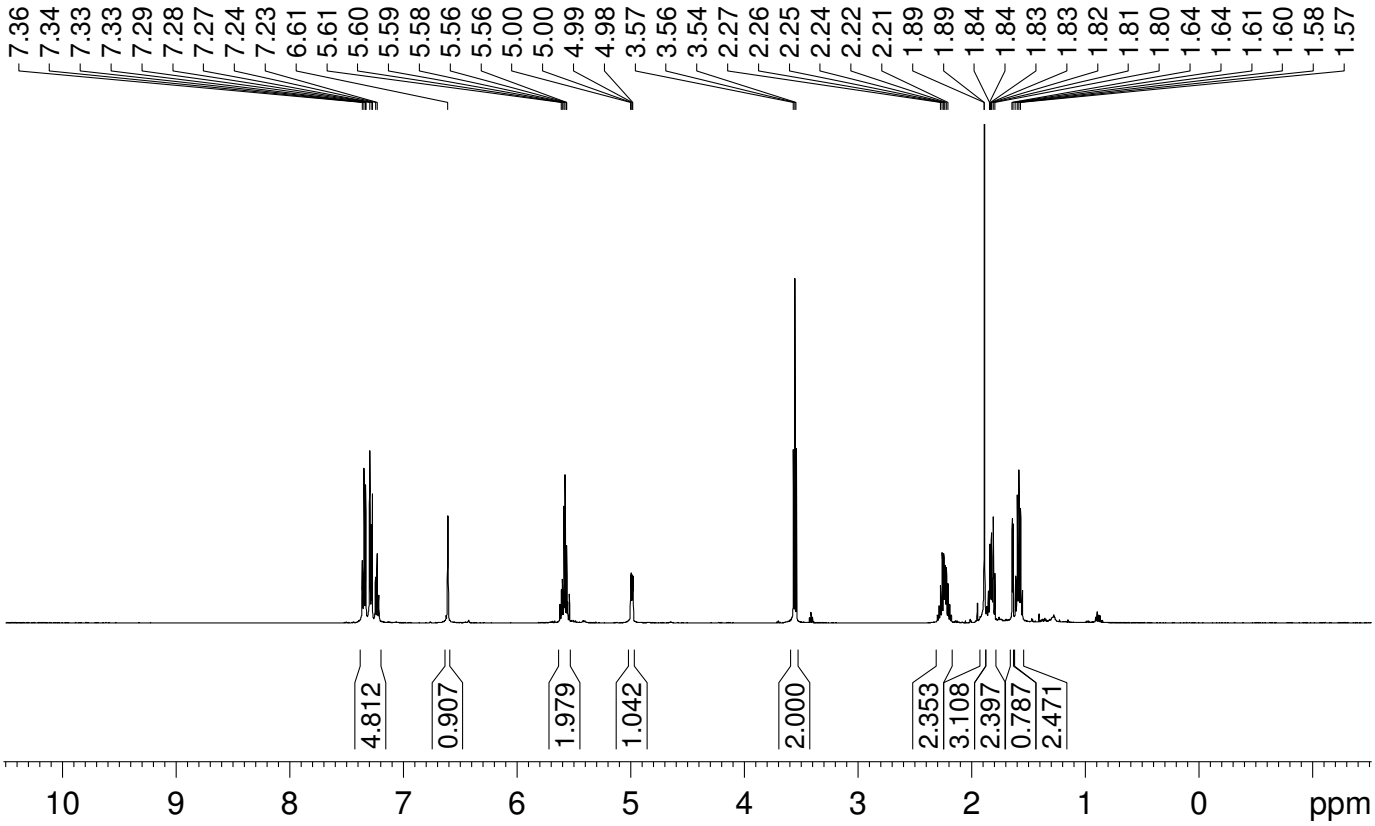
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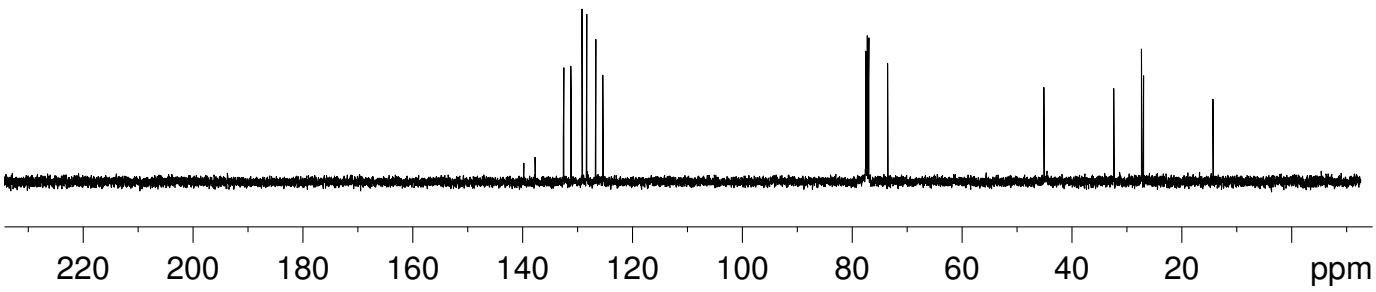
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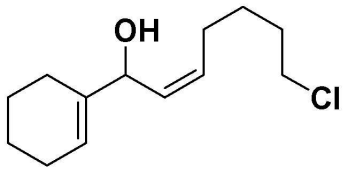
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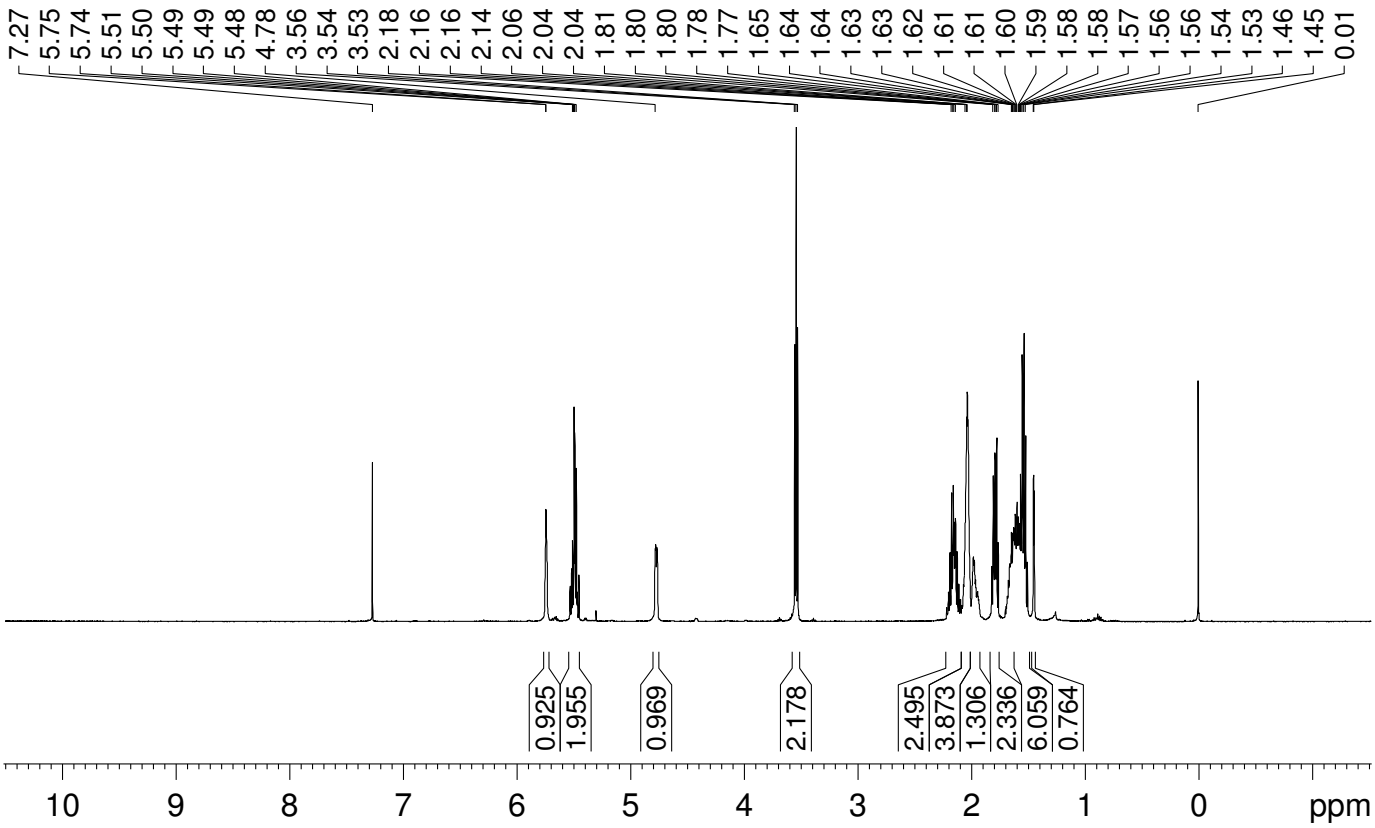
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1.77
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1.64
1.63
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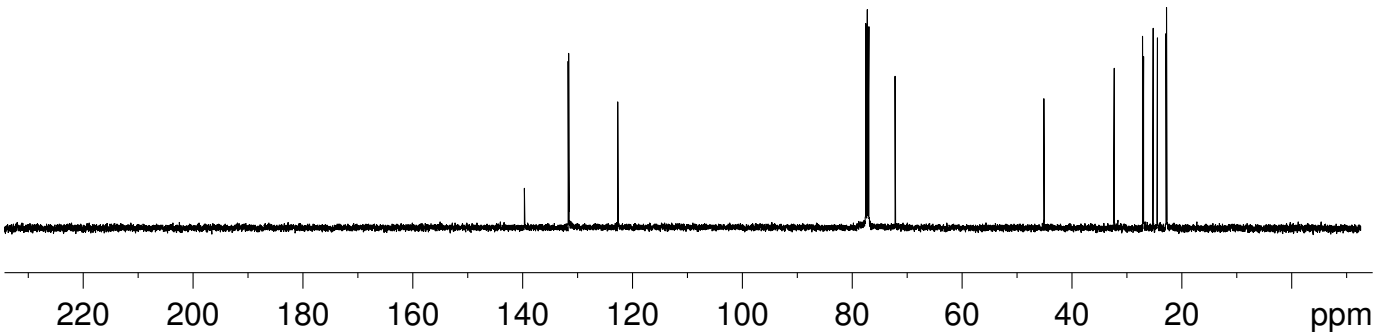
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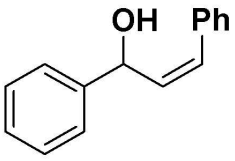
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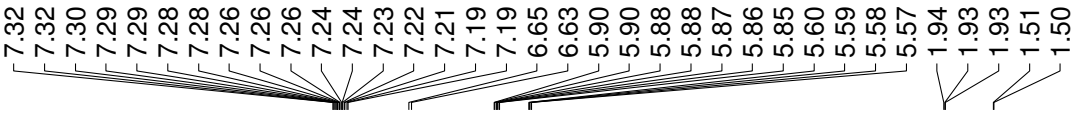
Ph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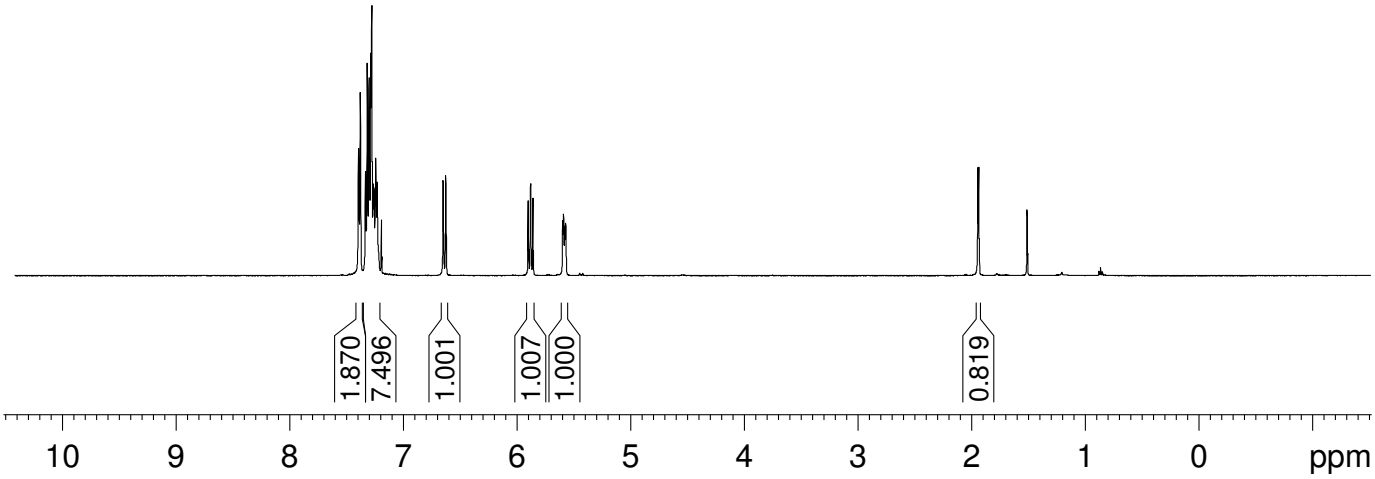
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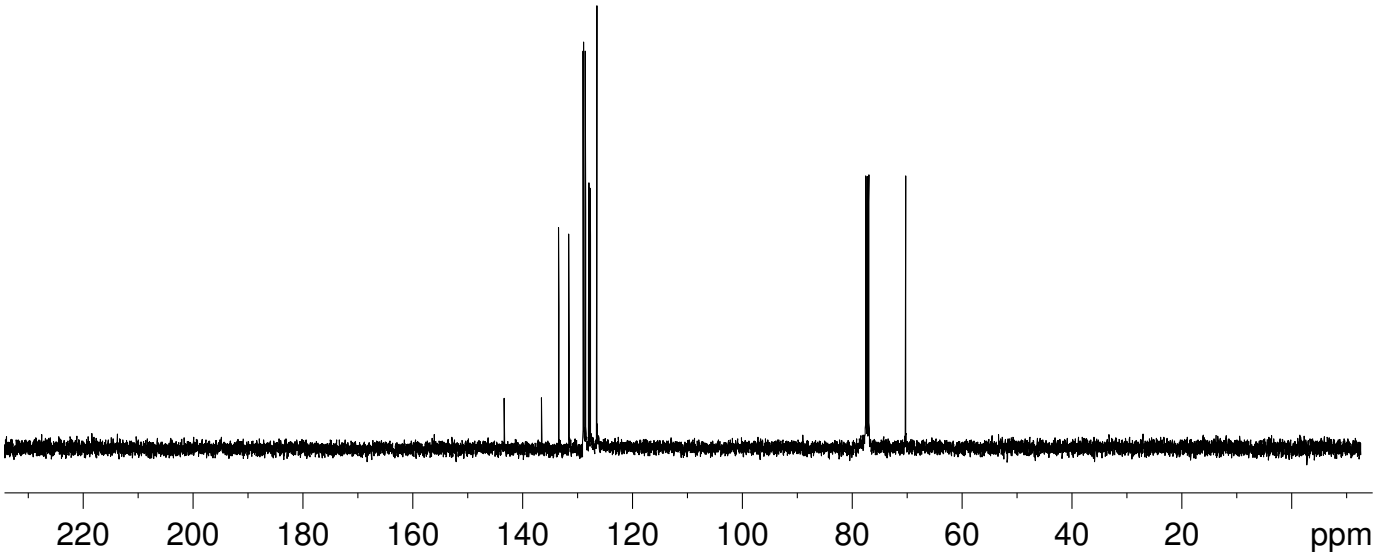
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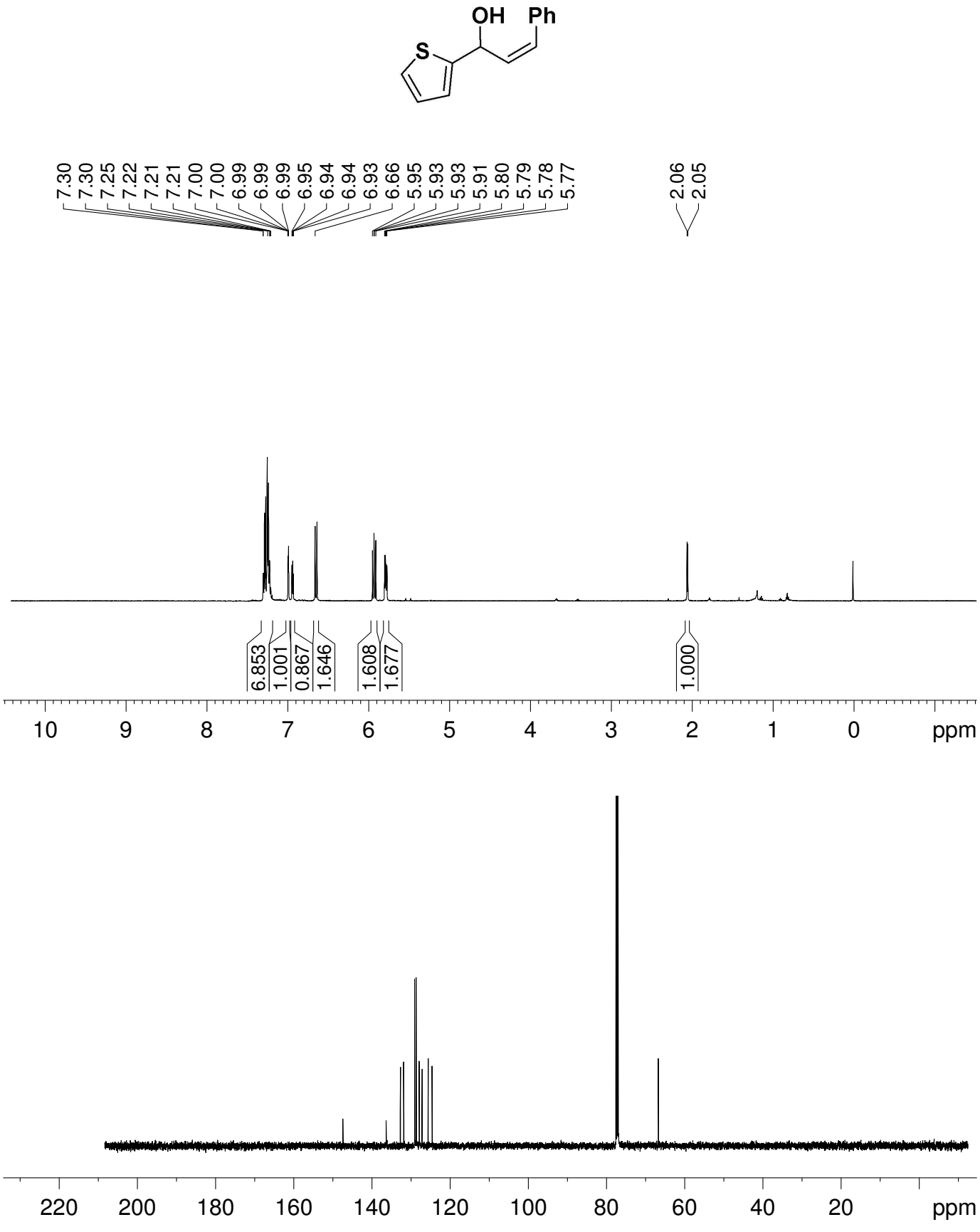
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Ph
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6.99
6.95
6.94
6.94
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2.05
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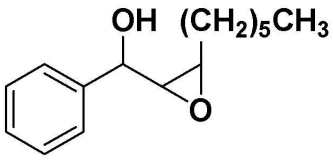
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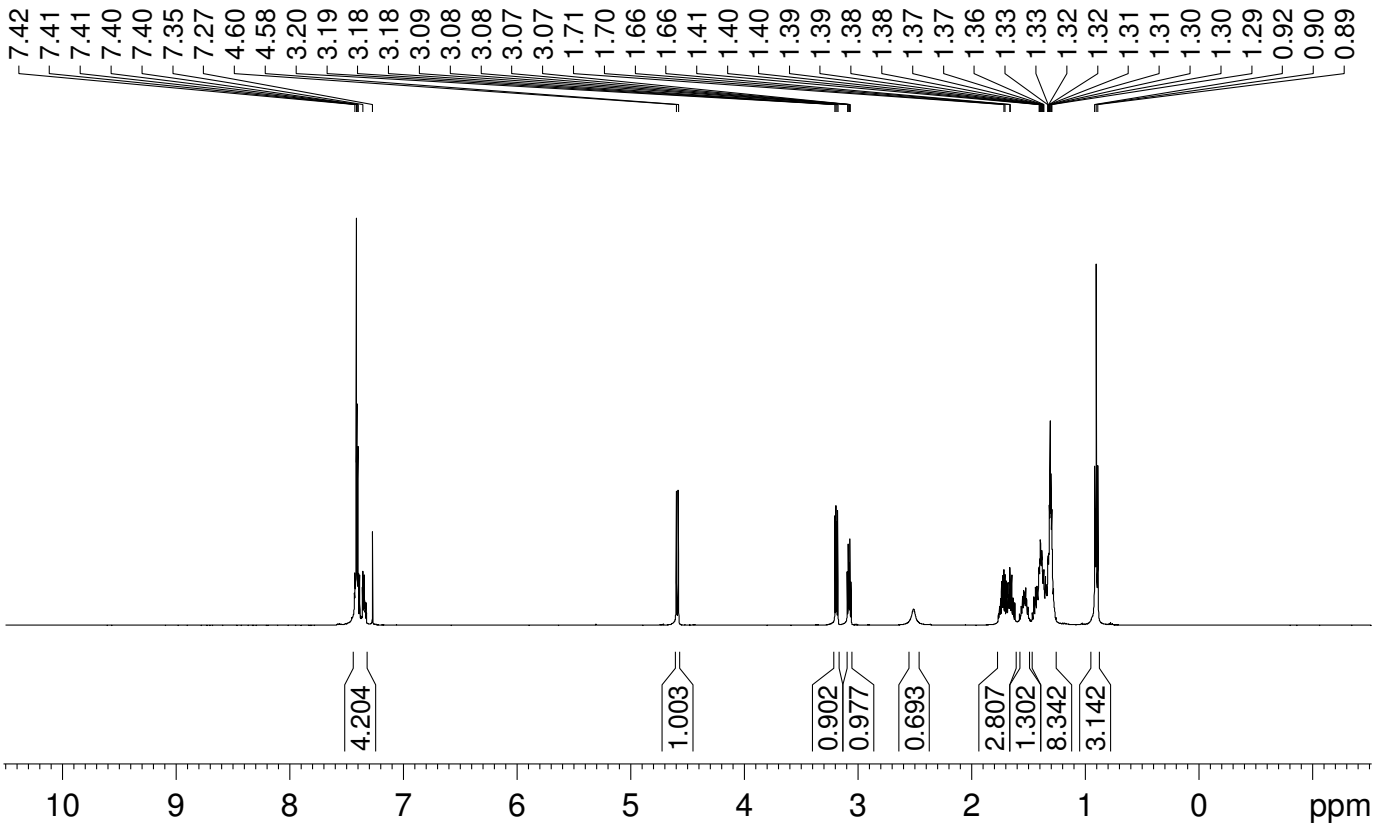
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3.08
3.08
3.07
3.07
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1.70
1.66
1.66
1.41
1.40
1.40
1.39
1.39
1.38
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1.37
1.36
1.33
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1.32
1.32
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1.31
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1.30
1.29
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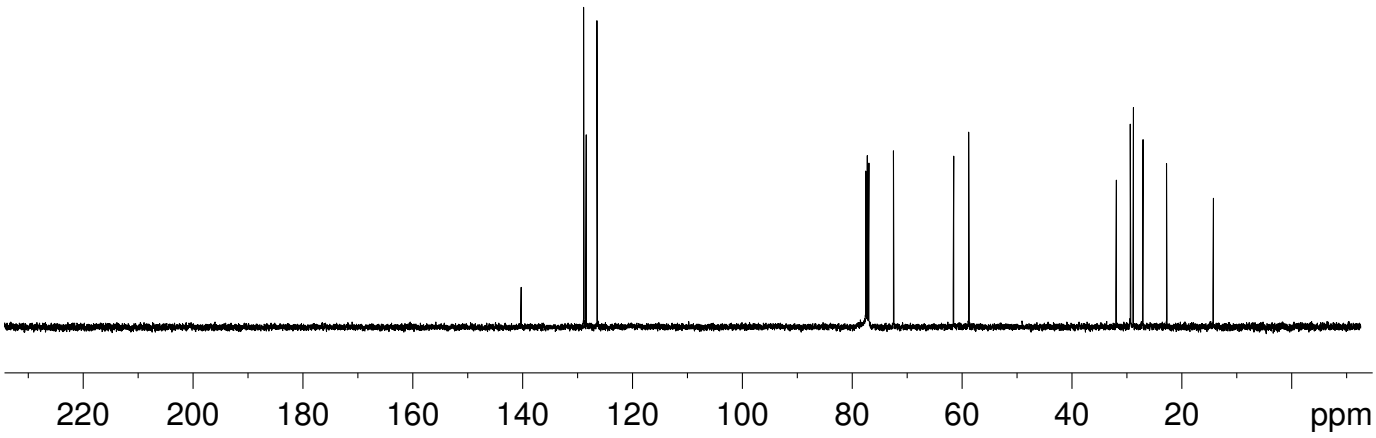
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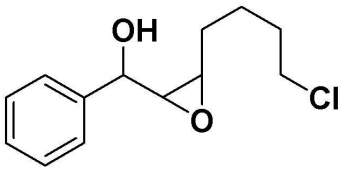
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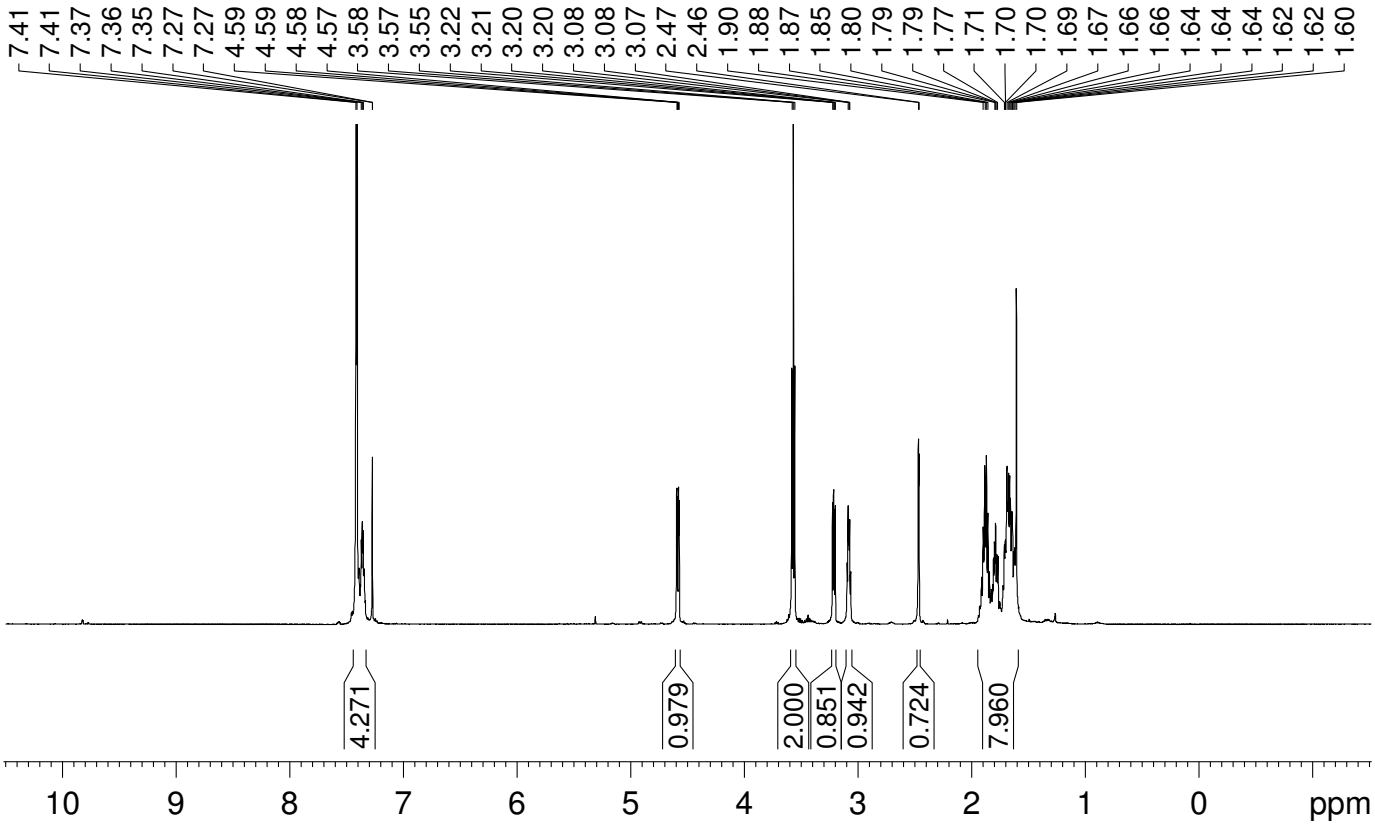
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4.58
4.57
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3.57
3.55
3.22
3.21
3.20
3.20
3.08
3.08
3.07
2.47
2.46
1.90
1.88
1.87
1.85
1.80
1.79
1.79
1.77
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1.70
1.69
1.67
1.66
1.66
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1.64
1.64
1.62
1.62
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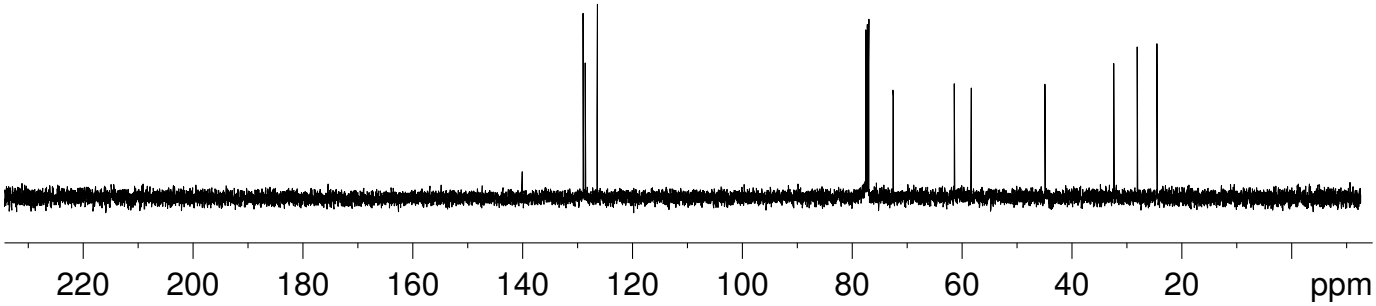
ppm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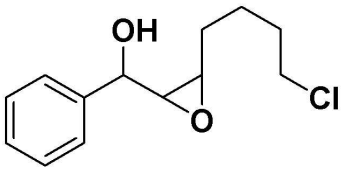
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O
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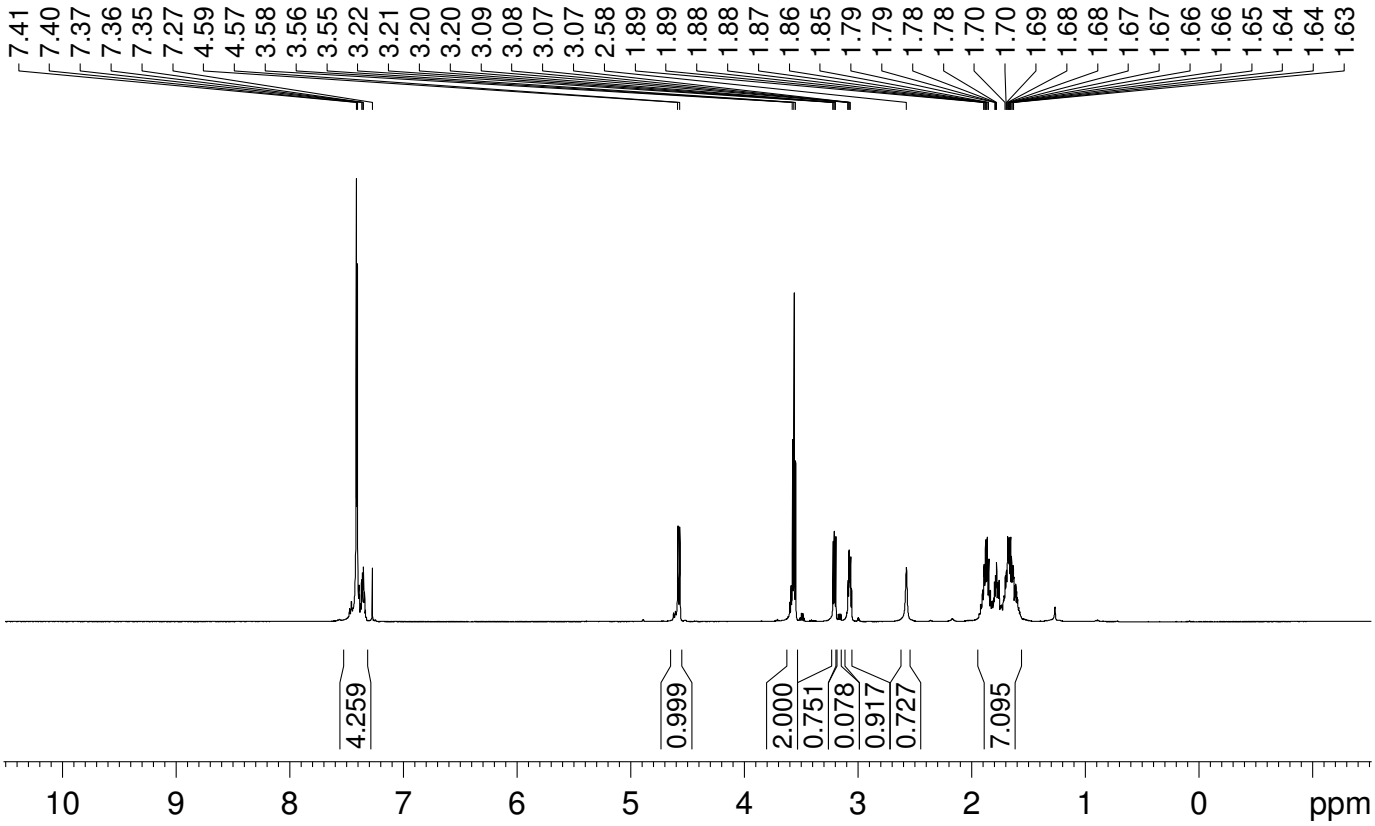
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7.27
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4.57
3.58
3.56
3.55
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3.21
3.20
3.20
3.09
3.08
3.07
3.07
2.58
1.89
1.89
1.88
1.88
1.87
1.86
1.85
1.79
1.79
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1.69
1.68
1.68
1.67
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1.66
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1.65
1.64
1.64
1.63
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0.999
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10
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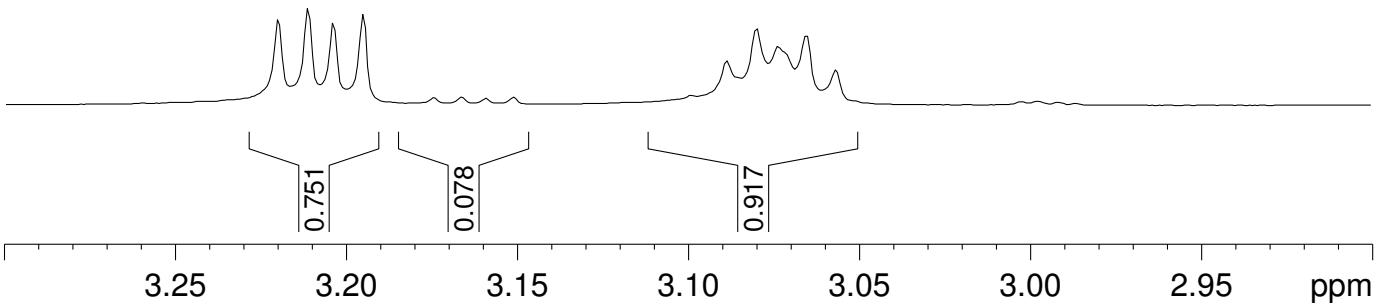
ppm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3.05
3.00
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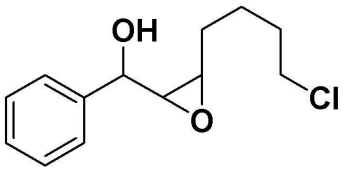
ppm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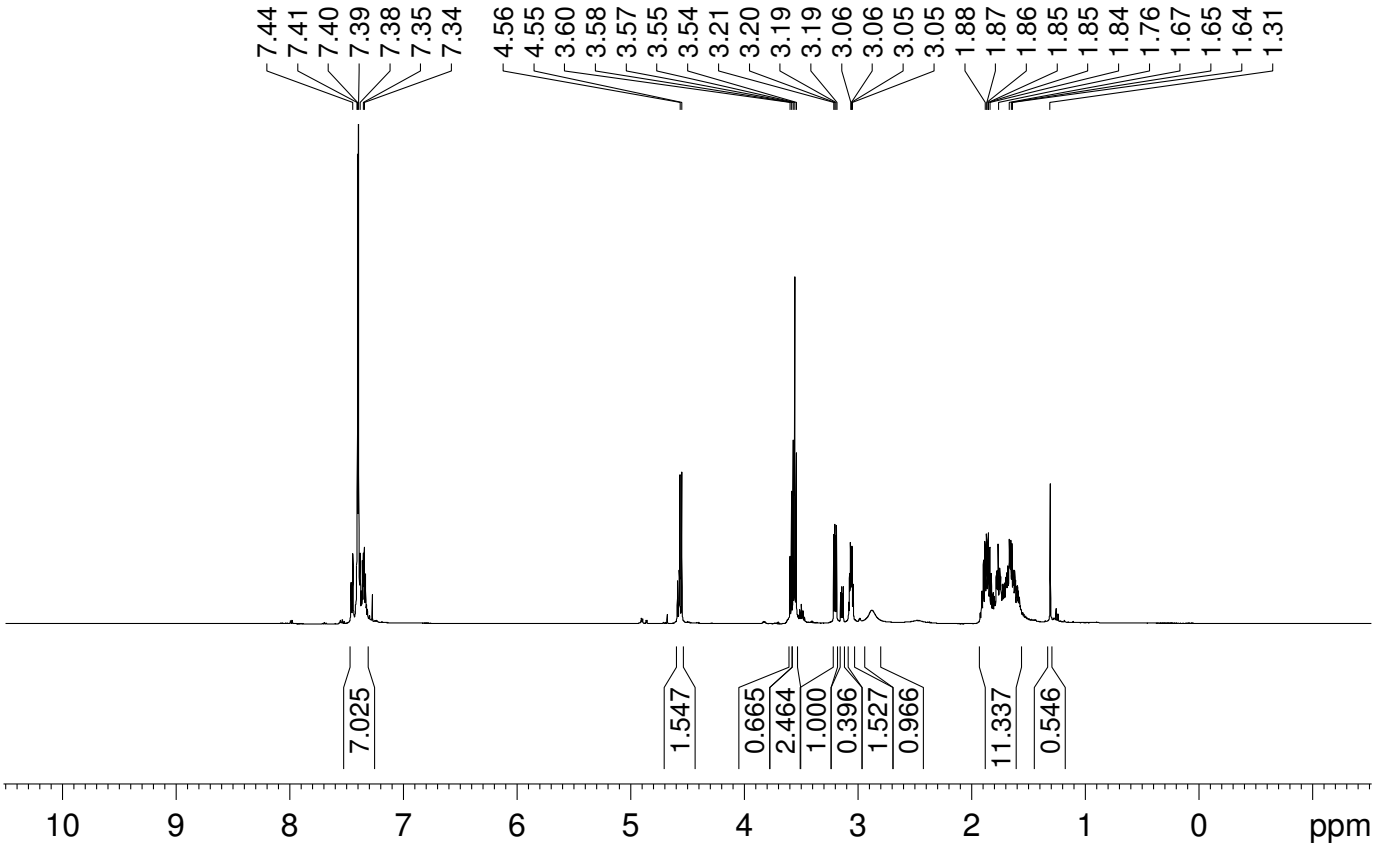
O
Cl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3.60
3.58
3.57
3.55
3.54
3.21
3.20
3.19
3.19
3.06
3.06
3.05
3.05
1.88
1.87
1.86
1.85
1.85
1.84
1.76
1.67
1.65
1.64
1.31
7.025
1.547
0.665
2.464
1.000
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1.527
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6
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3
2
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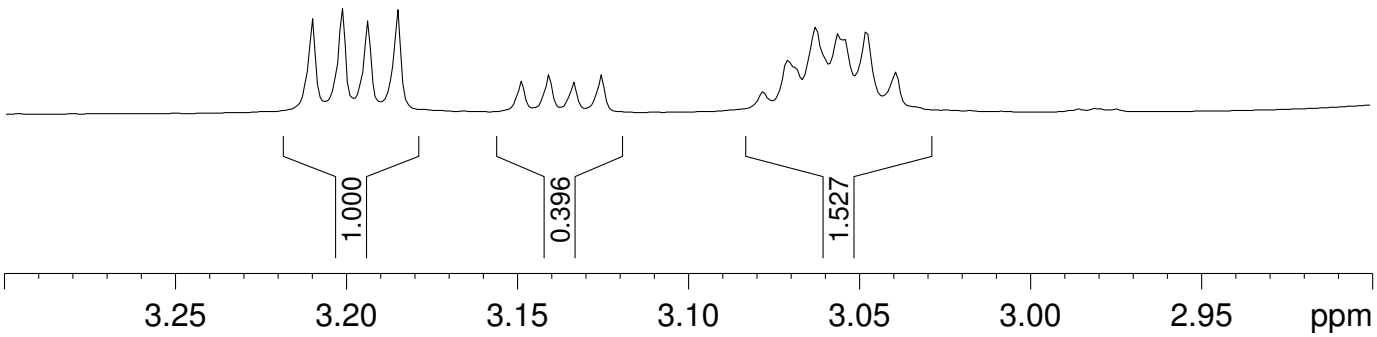
0
ppm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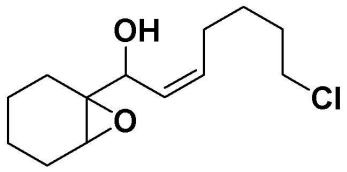
3.10
3.05
3.00
2.95
ppm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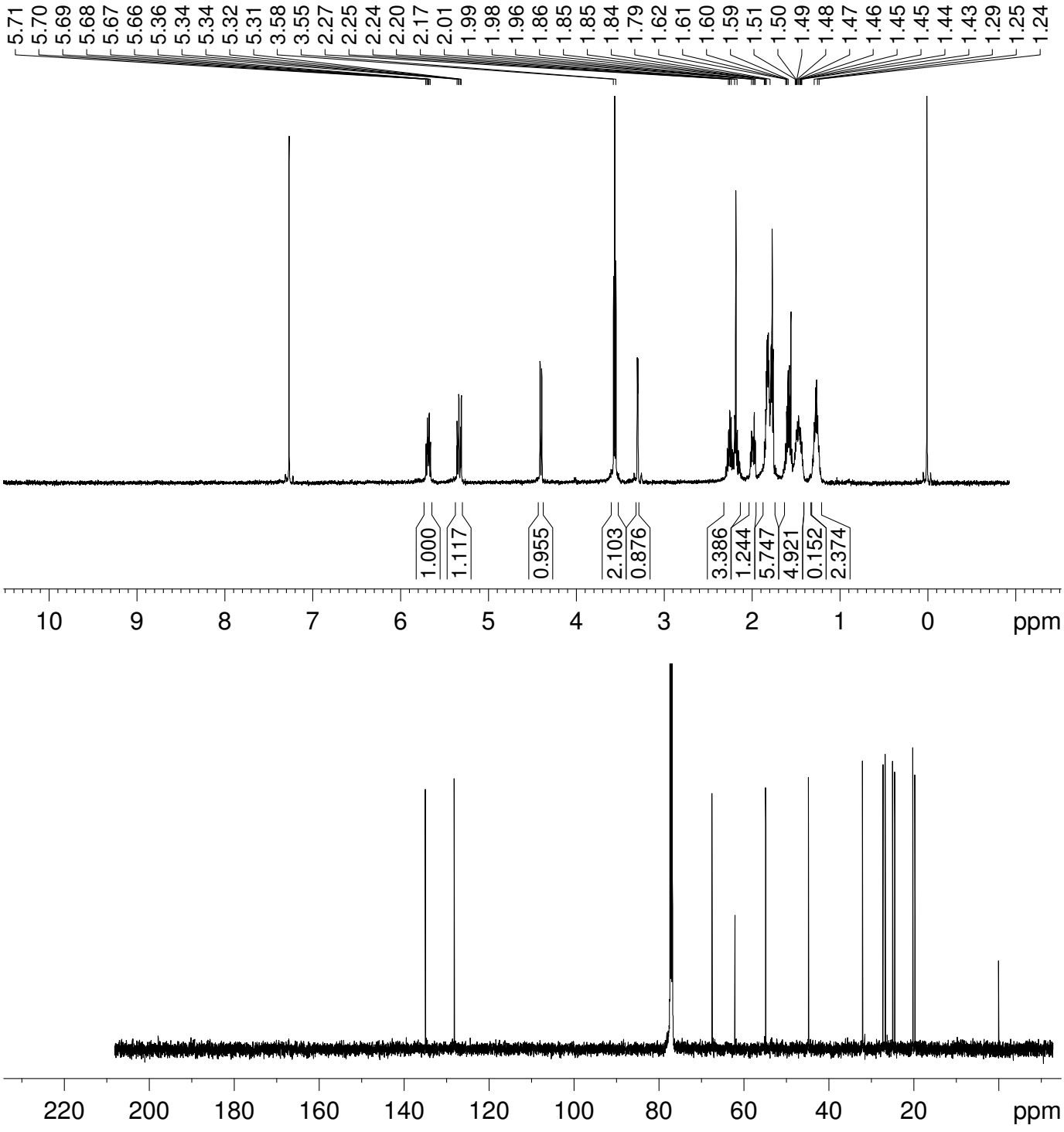
Cl
O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5.34
5.32
5.31
3.58
3.55
2.27
2.25
2.24
2.20
2.17
2.01
1.99
1.98
1.96
1.86
1.85
1.85
1.84
1.79
1.62
1.61
1.60
1.59
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1.48
1.47
1.46
1.45
1.45
1.44
1.43
1.29
1.25
1.24
1.000
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0.876
3.386
1.244
5.747
4.921
0.152
2.374
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9
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20
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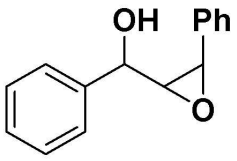
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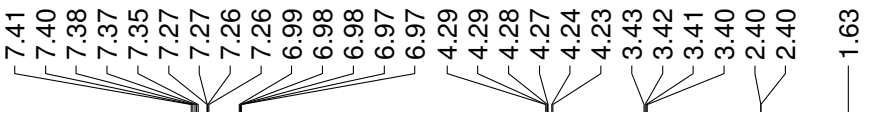
Ph
O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6.98
6.97
6.97
4.29
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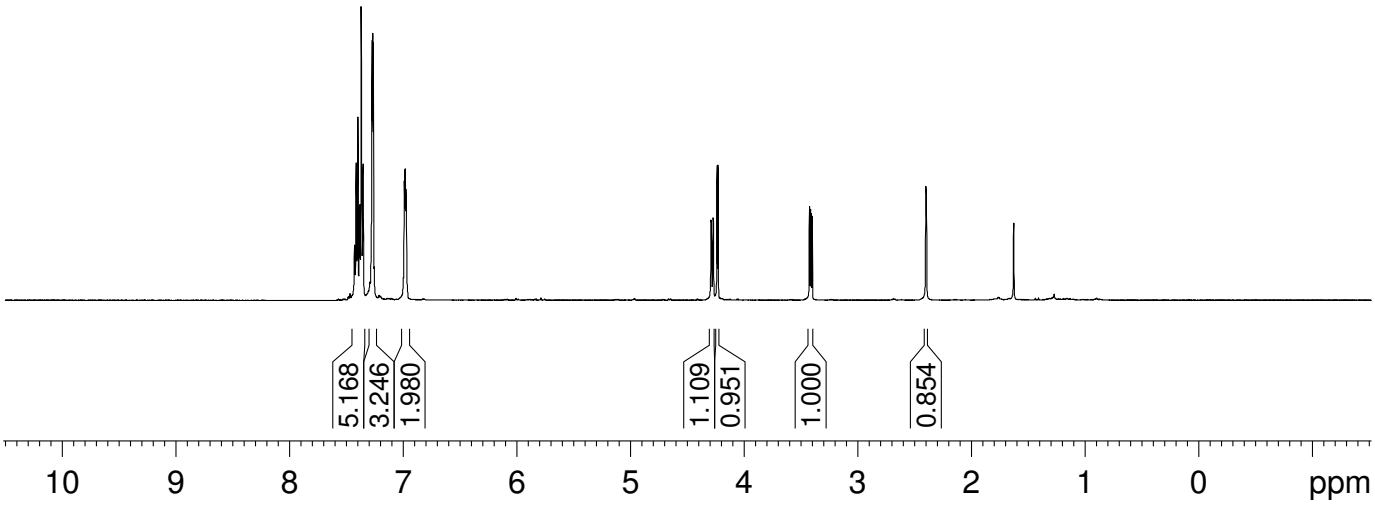
2.40
1.63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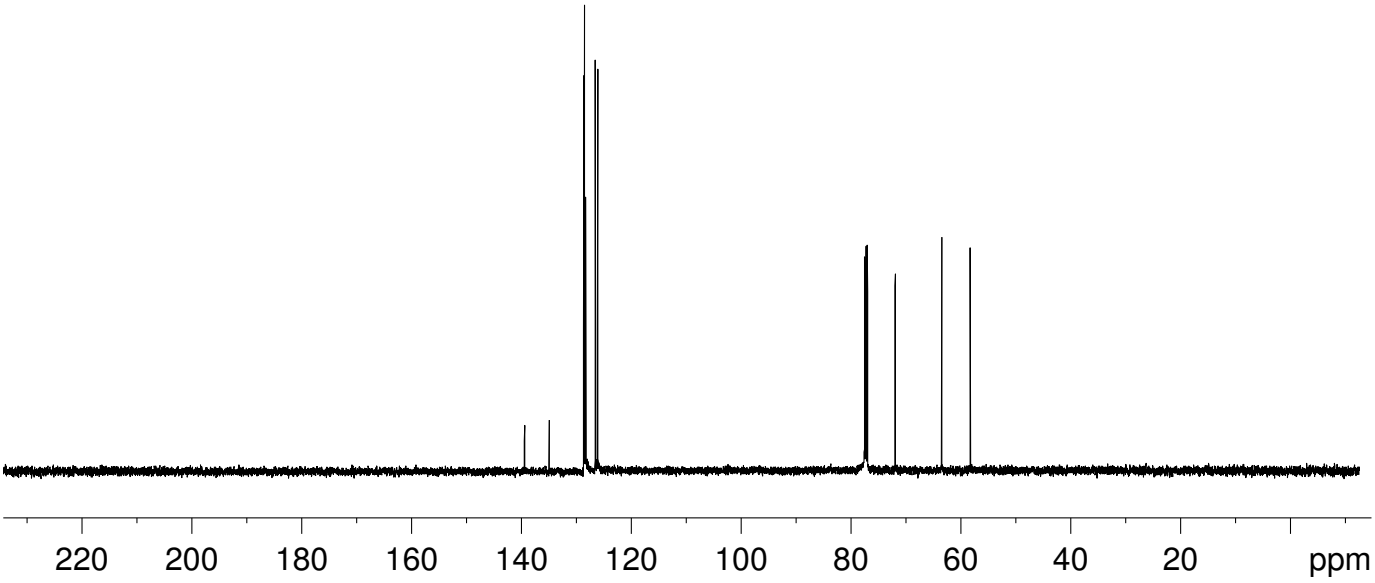
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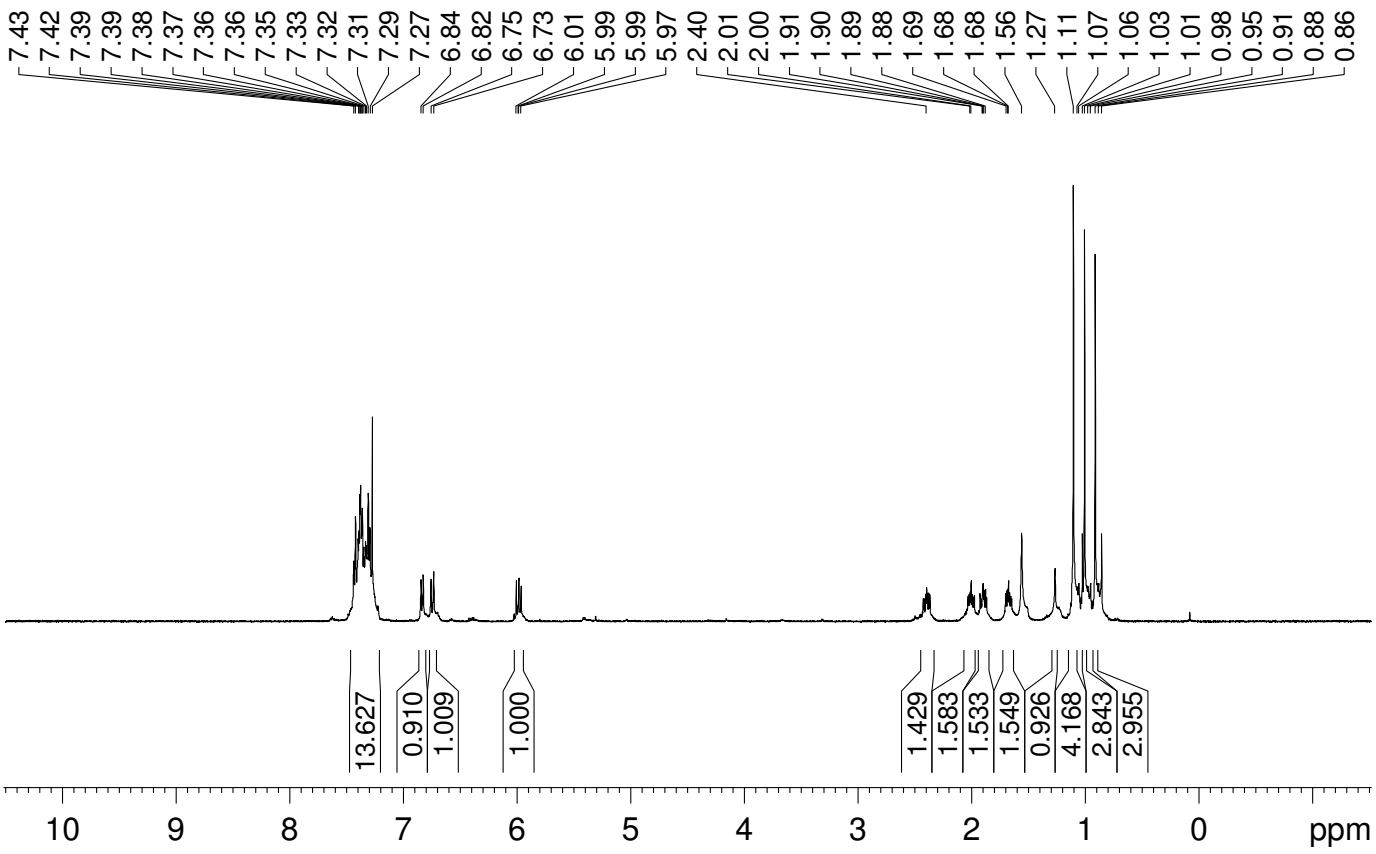
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7.32
7.31
7.29
7.27
6.84
6.82
6.75
6.73
6.01
5.99
5.99
5.97
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2.01
2.00
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1.88
1.69
1.68
1.68
1.56
1.27
1.11
1.07
1.06
1.03
1.01
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0.95
0.91
0.88
0.86
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1.533
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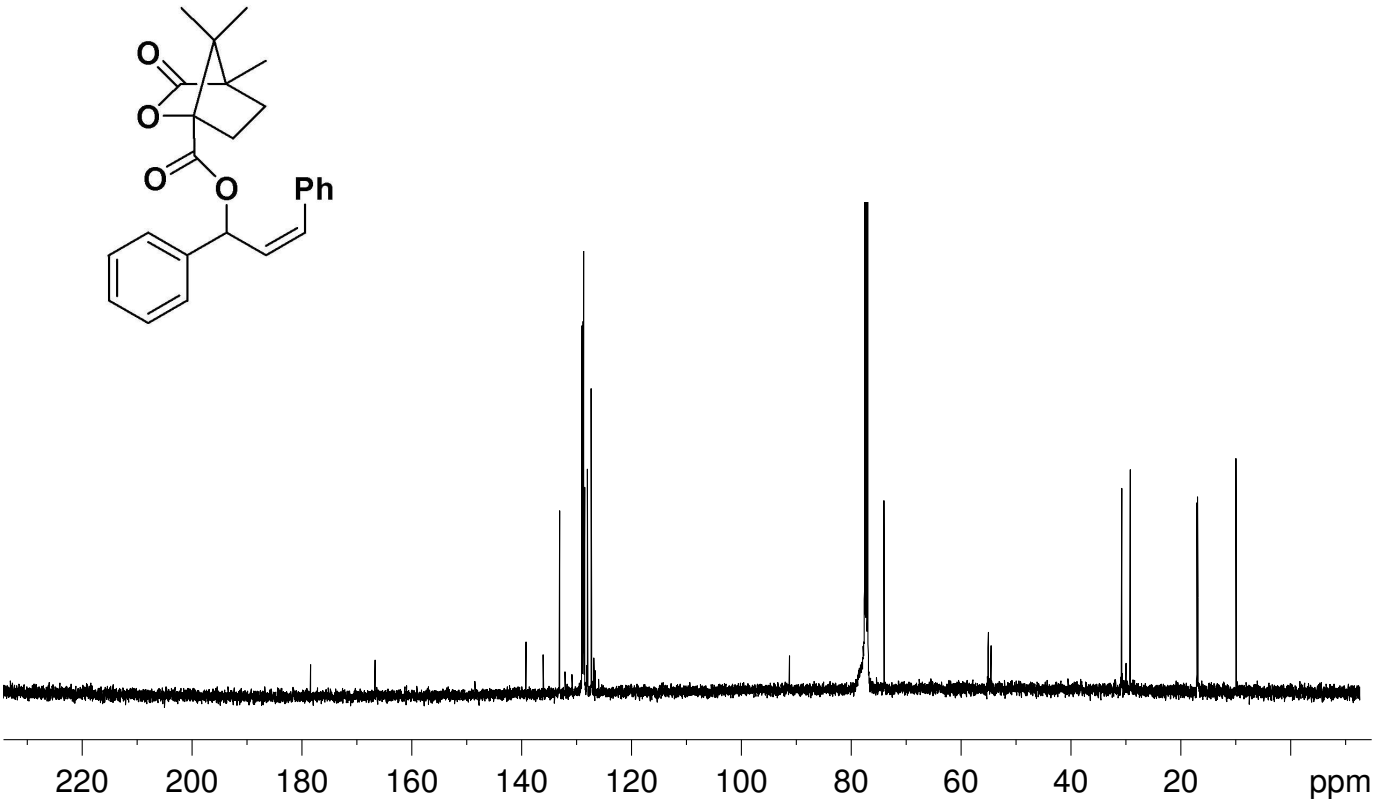
O
O
O
O
Ph
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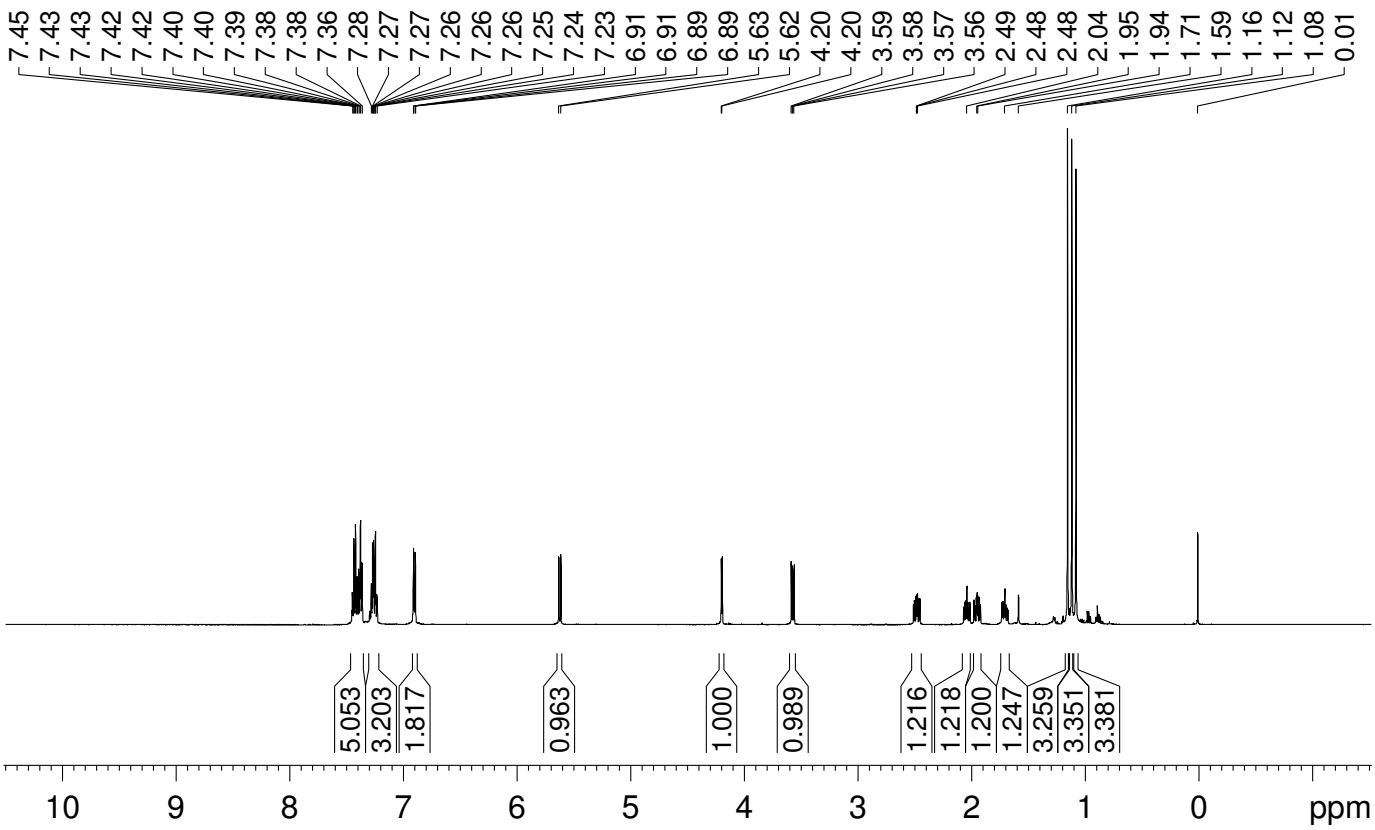
20
ppm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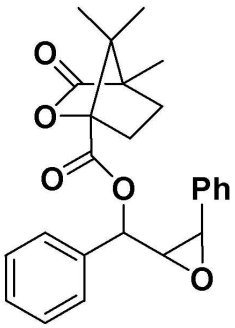
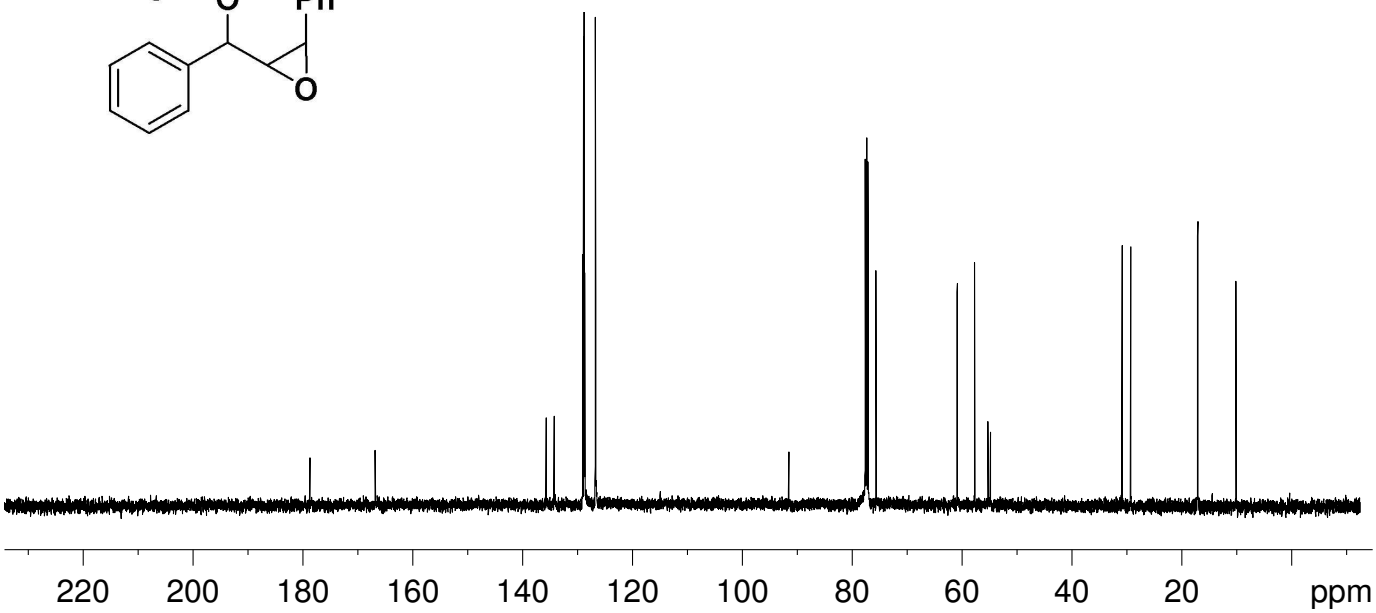
10 9 8 7 6 5 4 3 2 1 0 ppm


O
O
O
O
Ph
O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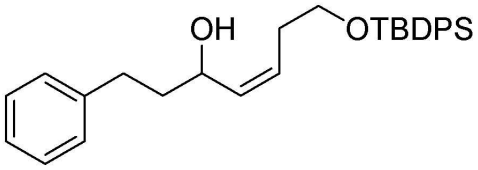
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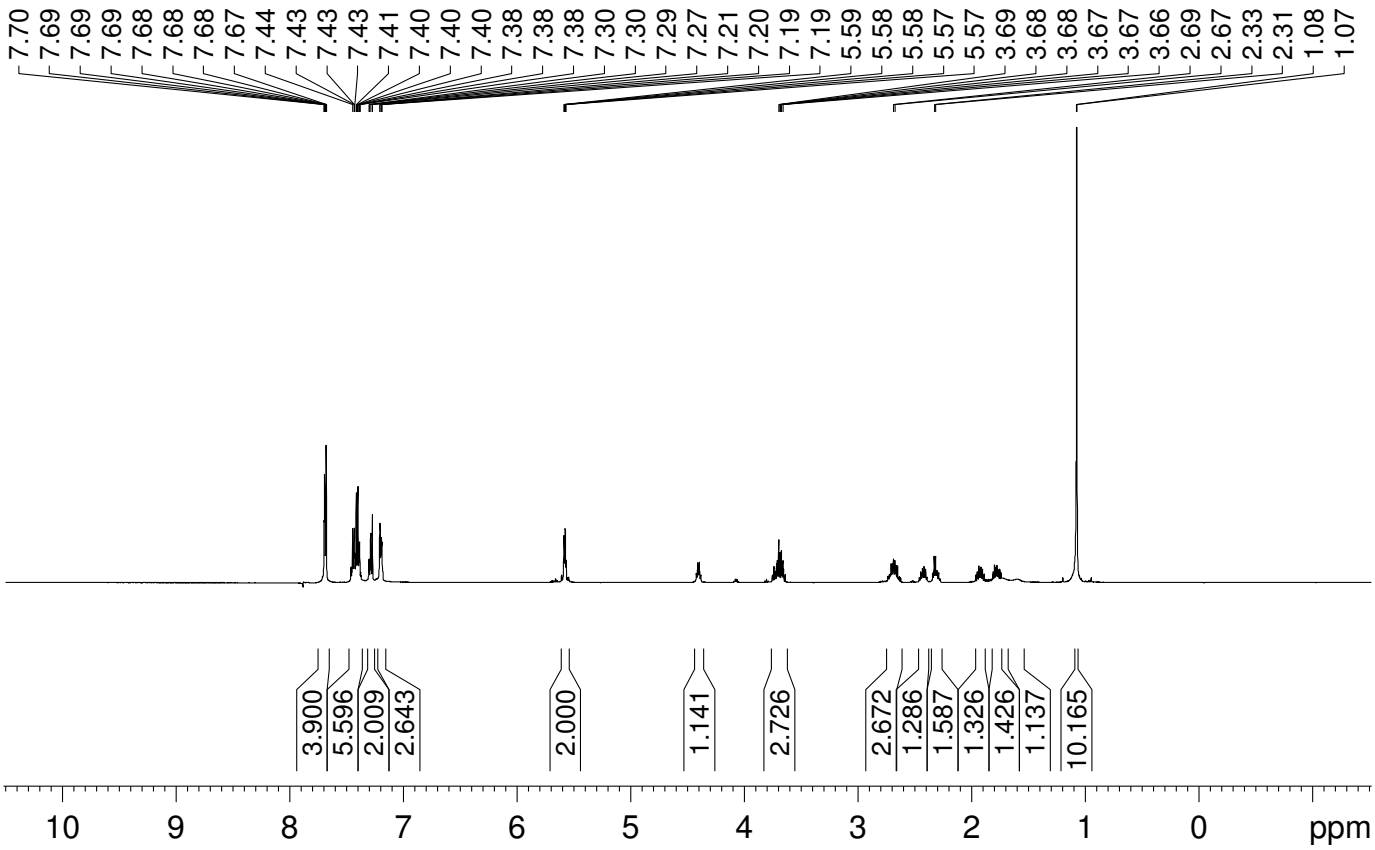
OTBDPS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7.40
7.40
7.40
7.38
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7.38
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7.30
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7.27
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7.19
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5.58
5.58
5.57
5.57
3.69
3.68
3.68
3.67
3.67
3.66
2.69
2.67
2.33
2.31
1.08
1.07
3.900
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2.009
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2.672
1.286
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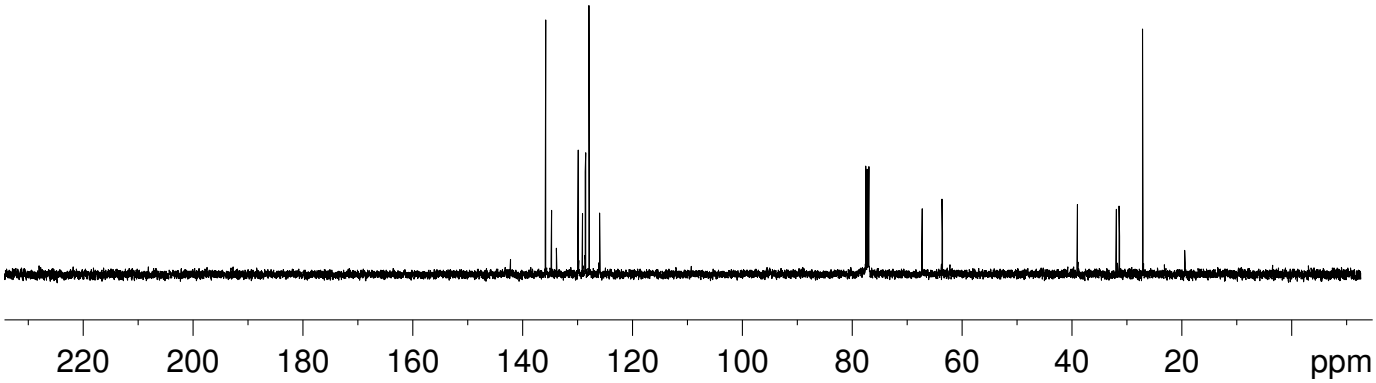
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ppm