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Supporting Information

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Supporting Information

Ortho-TMS Benzaldehyde, An Effective Linchpin for Type II Anion Relay Chemistry (ARC): Application in Diversity-Oriented Synthesis.

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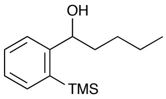
Experimental

I. Materials and Methods

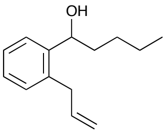
Except as otherwise indicated, reactions were carried out under an argon atmosphere in flame- or oven-dried glassware. In aqueous work-up, all organic solutions were dried over sodium sulfate or magnesium sulfate, and filtered prior to rotary evaporation at water aspirator pressure. All solvents were freshly distilled and dried by standard techniques just before use. Diethyl ether and THF were distilled from sodium/benzophenone. After storing over 4A molecular sieves for several days, HPLC grade dichloromethane was used without further purification. Hexamethylphosphoramide (HMPA) was freshly distilled from calcium hydride under vacuum. TMSCl was distilled and stored over 4A molecular sieves activated with microwave. 2-Methyl-1,3-dithiane, KO-*t*-Bu (1.0 M in THF), *t*-BuLi (1.7M in THF), *n*-BuLi (2.5M in THF) and Copper (I) iodide (99.999% metals basis) were purchased from Aldrich. Reactions were monitored by thin layer chromatography (TLC) with 0.25-mm E. Merck pre-coated silica gel plates (Kieselgel $60F_{254}$, Merck). Spots were detected by viewing under a UV light, colorizing with charring after dipping in anisaldehyde solution composed of acetic acid, sulfuric acid, and MeOH or in $KMnO_4$ solution composed of potassium carbonate, sodium hydroxide, and water. Silica gel for flash chromatography (particle size 0.040-0.063 mm) was supplied by Silicycle and Sorvent technologies. Yields refer to chromatographically and spectroscopically pure compounds unless otherwise noted. ^1H and ^{13}C spectra were recorded on a Bruker AM-500 spectrometer. Chemical shifts are reported as δ values relative to internal chloroform (δ 7.26 for ^1H and δ 77.0 for ^{13}C). IR spectra were measured as neat oils on a Perkin-Elmer Model 1600 FTIR. Optical rotations were measured on a Jasco polarimeter. High resolution mass spectra were obtained at the University of Pennsylvania Mass Spectrometry Service Center.

II. Procedure



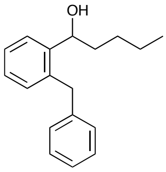
4

Compound 4. To a solution of *o*-TMS benzaldehyde **3** (108.6 mg, 0.60 mmol, 1.0 equiv.) in Et_2O (1 mL) at –78 °C was added *n*-BuLi (2.5M in hexane, 0.29 mL, 0.72 mmol, 1.2 equiv.) dropwise. After being stirred for 30 min, the reaction mixture was quenched with a saturated aqueous NH_4Cl (3 mL) and extracted with Et_2O (10 mL x 3). The combined layers were separated, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was dissolved in THF (2 mL) and treated with TBAF (1.0M in THF, 0.72 mL, 0.72 mmol, 1.2 equiv.) at ambient temperature. After being stirred for 30 min, the mixture was then extracted with Et_2O (10 mL x 3). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash chromatography on silica gel, using diethyl ether/hexane (1/10), provided **4** (126.3 mg, 0.53 mmol, 88% yield) as pale yellow oil. R_f 0.4 (hexane/diethyl ether = 10/1); IR (film) 3389 (s), 3056 (m), 2956 (s), 2859 (s), 1466 (m), 1433 (m), 1250 (s), 1047 (s), 764 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 7.8 Hz, 1H), 7.52 (dd, J = 7.5 and 1.2 Hz, 1H), 7.45-7.41 (m, 1H), 7.30-7.27 (m, 1H), 4.92 (dd, J = 8.8 and 4.1 Hz, 1H), 1.88-1.80 (m, 2H), 1.75-1.68 (m, 1H), 1.64-1.58 (m, 1H), 1.43-1.30 (m, 3H), 0.95 (t, J = 7.1 Hz, 3H), 0.38 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.8, 137.2, 134.3, 129.7, 126.9, 125.4, 73.7, 38.8, 28.7, 22.8, 14.0, 0.74; high resolution mass spectrum (CI) m/z 219.1563 [$(M-OH)^+$; calcd for $C_{14}H_{23}Si$: 219.1568].



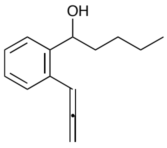
6a

Compound 6a. To a solution of *o*-TMS benzaldehyde **3** (111.3 mg, 0.62 mmol, 1.0 equiv.) in Et_2O (1 mL) at –78 °C was added *n*-BuLi (2.5M in hexane, 0.3 mL, 0.75 mmol, 1.2 equiv.) dropwise. After stirring for 30 min, the resulting solution was added into a mixture of CuI (142.6 mg, 0.75 mmol, 1.2 equiv.) and HMPA/THF (1 mL/1 mL) via cannula at 0 °C. The resulting solution was warmed to ambient temperature. After stirring for 30 min, allyl bromide (0.11 mL, 1.24 mmol, 2.0 equiv.) was added at ambient temperature and the reaction stirred for additional 2 h, before a saturated aqueous NH_4Cl (3 mL) solution was added. The resulting mixture was then extracted with Et_2O (10 mL x 3), and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was dissolved in THF (2 mL) and treated with TBAF (1.0M in THF, 0.75 mL, 0.75 mmol, 1.2 equiv.) at ambient temperature. After being stirred for 30 min, the mixture was extracted with Et_2O (10 mL x 2) and CH_2Cl_2 (10 mL x2). The combined organic layers dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash chromatography on silica gel, using ethyl acetate/hexane (1/15), provided **6a** (87.7 mg, 0.43 mmol, 69% yield) as pale yellow oil. R_f 0.42 (hexane/diethyl ether = 5/1); IR (film) 3365 (s), 3075 (w), 2956 (s), 2859 (s), 1451 (m), 1277 (w), 1046 (m), 757 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 7.6 Hz, 1H), 7.28-7.21 (m, 2H), 7.16 (d, J = 7.2 Hz, 1H), 6.04-5.96 (m, 1H), 5.09-5.07 (m, 1H), 5.02-4.98 (m, 1H), 4.94 (dd, J = 8.1 and 4.9 Hz, 1H), 3.46 (ddd, J = 30.9, 15.9 and 6.2 Hz, 2H), 1.82-1.67 (m, 3H), 1.52-1.45 (m, 1H), 1.39-1.29 (m, 3H), 0.91 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 137.6, 136.3, 129.9, 127.4, 126.8, 125.7, 115.8, 70.3, 38.1, 36.7, 28.4, 22.6, 14.0; high resolution mass spectrum (CI) m/z 186.1405 [$(M-H_2O)^+$; calcd for $C_{14}H_{18}$: 186.1408].



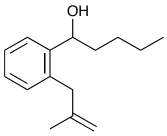
6b

Compound 6b. Under the conditions similar to those used for **6a**, *o*-TMS benzaldehyde **3** (112 mg, 0.63 mmol, 1.0 equiv.) gave **6b** (88.4 mg, 0.35 mmol, 55% yield) as colorless oil upon flash chromatography (ethyl acetate/hexane = 1/10), and preparative thin layer chromatography (ethyl acetate/benzene = 1/20). R_f 0.45 (hexane/diethyl ether = 5/1); IR (film) 3376 (s), 3062 (m), 2955 (s), 2858 (s), 1493 (s), 1453 (s), 1045 (m), 758 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.5 Hz, 1H), 7.39-7.12 (m, 8H), 4.92 (dd, *J* = 8.0 and 5.0 Hz, 1H), 4.08 (dd, *J* = 26.5 and 16.0 Hz, 2H), 1.73-1.66 (m, 2H), 1.57-1.50 (m, 1H), 1.42-1.35 (m, 1H), 1.31-1.18 (m, 3H), 0.85 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.3, 140.9, 137.0, 130.7, 128.6, 128.5, 127.3, 127.0, 126.1, 126.0, 70.3, 38.7, 38.1, 28.3, 22.5, 14.0; high resolution mass spectrum (CI) *m/z* 237.1638 [(M-OH)$^+$; calcd for $C_{18}H_{21}$: 237.1643].



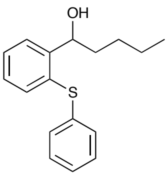
6c

Compound 6c. Under the conditions similar to those used for **6a**, *o*-TMS benzaldehyde **3** (112.7 mg, 0.63 mmol, 1.0 equiv.) gave **6c** (74.7 mg, 0.37 mmol, 58% yield) as pale yellow oil upon flash chromatography (diethyl ether/hexane = 1/10). R_f 0.42 (hexane/diethyl ether = 5/1); IR (film) 3362 (s), 3061 (w), 2956 (s), 2860 (s), 1941 (s), 1453 (s), 1047 (m), 760 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.46 (m, 1H), 7.44-7.42 (m, 1H), 7.26-7.21 (m, 2H), 6.49 (t, *J* = 7.0 Hz, 1H), 5.13 (d, *J* = 1.0 Hz, 1H), 5.11 (d, *J* = 1.0 Hz, 1H), 5.02-4.99 (m, 1H), 1.89 (s, 1H), 1.79-1.74 (m, 2H), 1.50-1.45 (m, 1H), 1.40-1.30 (m, 3H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.4, 141.4, 130.6, 127.8, 127.4, 127.2, 125.9, 90.4, 78.0, 71.1, 38.0, 28.2, 22.6, 14.0; high resolution mass spectrum (CI) m/z 202.1350 [(M)$^+$; calcd for $C_{14}H_{18}O$: 202.1358].



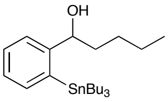
6d

Compound 6d. Under the conditions similar to those used for **6a**, *o*-TMS benzaldehyde **3** (106.1 mg, 0.59 mmol, 1.0 equiv.) gave **6d** (83.6 mg, 0.38 mmol, 64% yield) as colorless oil upon flash chromatography (ethyl acetate/hexane = 1/15). R_f 0.41 (hexane/diethyl ether = 5/1); IR (film) 3388 (s), 3072 (m), 2957 (s), 2859 (s), 1450 (s), 1433 (m), 1047 (m), 757 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.6 Hz, 1H), 7.29-7.26 (m, 1H), 7.23-7.14 (m, 1H), 7.13 (d, *J* = 1.0 Hz, 1H), 4.90 (dd, *J* = 8.0 and 5.0 Hz, 1H), 4.84 (s, 1H), 4.51 (s, 1H), 3.38 (dd, *J* = 27.5 and 16.0 Hz, 2H), 1.86 (br, 1H), 1.82-1.79 (m, 1H), 1.76 (s, 3H), 1.72-1.66 (m, 1H), 1.54-1.45 (m, 1H), 1.40-1.25 (m, 3H), 0.91 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5, 143.4, 136.0, 130.4, 127.1, 126.9, 125.7, 111.9, 70.2, 40.9, 37.9, 28.4, 22.8, 22.6, 14.0; high resolution mass spectrum (CI) *m/z* 200.1557 [$(M-H_2O)^+$; calcd for $C_{15}H_{20}$: 200.1565].



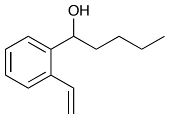
6e

Compound 6e. Under the conditions similar to those used for **6a**, *o*-TMS benzaldehyde **3** (117.5 mg, 0.66 mmol, 1.0 equiv.) gave **6e** (128.0 mg, 0.47 mmol, 71% yield) as colorless oil upon flash chromatography (diethyl ether/hexane = 1/10). R_f 0.43 (hexane/diethyl ether = 5/1); IR (film) 3058 (s), 3029 (m), 1582 (s), 1476 (s), 1439 (s), 1021 (s), 746 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.5 and 1.0 Hz, 1H), 7.37-7.32 (m, 2H), 7.29-7.26 (m, 2H), 7.23-7.20 (m, 4H), 5.24 (dd, *J* = 8.0 and 5.0 Hz, 1H), 2.04 (br, 1H), 1.76-1.65 (m, 2H), 1.49-1.35 (m, 1H), 1.34-1.27 (m, 3H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 136.7, 133.9, 131.8, 129.6, 129.2, 128.4, 128.0, 126.6, 126.5, 71.4, 38.0, 28.1, 22.5, 14.0; high resolution mass spectrum (CI) *m/z* 272.1229 [$(M)^+$; calcd for $C_{17}H_{20}OS$: 272.1235].



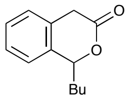
6f

Compound 6f. Under the conditions similar to those used for **6a**, *o*-TMS benzaldehyde **3** (122.1 mg, 0.68 mmol, 1.0 equiv.) gave **6f** (201.1 mg, 0.44 mmol, 65% yield) as colorless oil upon flash chromatography (diethyl ether/hexane = 1/15). R_f 0.61 (hexane/diethyl ether = 5/1); IR (film) 3436 (s), 3051 (m), 2956 (s), 2855 (s), 1463 (s), 1433 (m), 1253 (m), 1044 (s), 762 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2H), 7.37-7.33 (m, 1H), 7.26-7.23 (m, 1H), 4.58-4.54 (m, 1H), 1.82-1.77 (m, 2H), 1.71-1.66 (m, 1H), 1.57-1.51 (m, 7H), 1.40-1.33 (m, 9H), 1.11-1.16 (m, 7H), 0.94-0.90 (m, 11H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.5, 140.3, 136.7, 128.5, 127.0, 125.4, 77.3, 39.1, 29.2, 28.7, 27.4, 22.8, 14.0, 13.6, 10.9; high resolution mass spectrum (ES^+) *m/z* 477.2144 [$(M+Na)^+$; calcd for $C_{23}H_{42}OSnNa$: 477.2156].



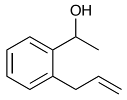
6g

Compound 6g. To a solution of *o*-TMS benzaldehyde **3** (106.1 mg, 0.59 mmol, 1.0 equiv.) in Et_2O (1 mL) at –78 °C was added *n*-BuLi (2.5M in hexane, 0.28 mL, 0.71 mmol, 1.2 equiv.) dropwise. After stirring for 30 min, the resulting solution was added into a mixture of CuI (135.2 mg, 0.71 mmol, 1.2 equiv.) and HMPA/THF (1 mL/1 mL) via cannula at 0 °C. The resulting solution was warmed to ambient temperature. After stirring for 30 min, vinyl bromide (1.18 mL, 1.18 mmol, 2.0 equiv.) and $Pd(PPh_3)_4$ (20.8 mg, 0.018 mmol, 0.03 equiv.) in THF (1 mL) were added at ambient temperature. After being stirred for 2 h, a saturated aqueous NH_4Cl (3 mL) solution was added, and the resulting mixture extracted with Et_2O (10 mL x 3). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was dissolved in THF (2 mL) and treated with TBAF (1.0M in THF, 0.71 mL, 0.71 mmol, 1.2 equiv.) at ambient temperature. After being stirred for 30 min, the mixture was then extracted with Et_2O (10 mL x 2) and CH_2Cl_2 (10 mL x2). The combined organic layers dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash chromatography on silica gel, using ethyl acetate/hexane (1/15), provided **6g** (63.5 mg, 0.33 mmol, 56% yield) as pale yellow oil. R_f 0.4 (hexane/diethyl ether = 5/1); IR (film) 3365 (s), 3063 (w), 2956 (s), 2860 (s), 1452 (m), 1043 (m), 760 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.49-7.46 (m, 2H), 7.32-7.29 (m, 1H), 7.27-7.24 (m, 1H), 7.06 (dd, *J* = 17.0 and 11.0 Hz, 1H), 5.62 (dd, *J* = 17.0 and 1.0 Hz, 1H), 5.32 (dd, *J* = 11.0 and 1.5 Hz, 1H), 5.02-4.99 (m, 1H), 1.88 (br, 1H), 1.79-1.70 (m, 2H), 1.48-1.23 (m, 4H), 0.91 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 135.6, 134.2, 128.0, 127.3, 126.1, 125.4, 116.4, 70.8, 38.1, 28.1, 22.6, 14.0; high resolution mass spectrum (CI) *m/z* 190.1354 [$(M)^+$; calcd for $C_{13}H_{18}O$: 190.1358].



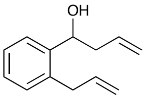
7

Compound 7. To a solution of *o*-TMS benzaldehyde **3** (110.9 mg, 0.62 mmol, 1.0 equiv.) in Et_2O (1 mL) at –78 °C was added *n*-BuLi (2.5M in hexane, 0.29 mL, 0.74 mmol, 1.2 equiv.) dropwise. After stirring for 30 min, the resulting solution was added into a mixture of CuI (140.9 mg, 0.74 mmol, 1.2 equiv.) and HMPA/THF (1 mL/1 mL) via cannula at 0 °C. The resulting solution was warmed to ambient temperature and stirred for 30 min, before the addition of ethyl bromoacetate (0.14 mL, 1.24 mmol, 2.0 equiv.) at ambient temperature. After being stirred for 2 h, 2% HCl in EtOH (2 mL) was added. After 30 min, the mixture was extracted with Et_2O (10 mL x 2) and CH_2Cl_2 (10 mL x2). The combined organic layers dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash chromatography on silica gel, using ethyl acetate/hexane (1/10), provided **7** (63.4 mg, 0.31 mmol, 50% yield) as pale yellow oil. R_f 0.3 (hexane/ethyl acetate = 3/1); IR (film) 3061 (w), 2954 (m), 2852 (w), 1752 (s), 1253 (s), 1171 (s), 843 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33-7.30 (m, 2H), 7.23-7.19 (m, 2H), 5.33 (t, *J* = 6.5 Hz, 1H), 3.73 (dd, *J* = 31.5 and 18.5 Hz, 2H), 2.01-1.96 (m, 2H), 1.64-1.55 (m, 1H), 1.50-1.38 (m, 3H), 0.94 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 134.8, 130.4, 128.4, 127.4, 127.2, 124.3, 80.9, 35.7, 34.1, 27.3, 22.4, 13.9; high resolution mass spectrum (ES^+) *m/z* 205.1232 [$(M+H)^+$; calcd for $C_{13}H_{17}O_2$: 205.1229].



8a

Compound 8a.[1] To a solution of *o*-TMS benzaldehyde **3** (126.4 mg, 0.71 mmol, 1.0 equiv.) in Et_2O (1 mL) at –78 °C was added MeLi (1.6M in diethyl ether, 0.53 mL, 0.85 mmol, 1.2 equiv.) dropwise. After stirring for 30 min, the resulting solution was added into a mixture of CuI (142.6 mg, 0.75 mmol, 1.2 equiv.) and HMPA/THF (1 mL/1 mL) via cannula at 0 °C. The resulting solution was warmed to ambient temperature. After stirring for 30 min, allyl bromide (0.12 mL, 1.42 mmol, 2.0 equiv.) was added at ambient temperature and the reaction stirred for additional 2 h, before a saturated aqueous NH_4Cl (3 mL) solution was added. The resulting mixture was then extracted with Et_2O (10 mL x 3), and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was dissolved in THF (2 mL) and treated with TBAF (1.0M in THF, 0.75 mL, 0.85 mmol, 1.2 equiv.) at ambient temperature. After being stirred for 30 min, the mixture was extracted with Et_2O (10 mL x 2) and CH_2Cl_2 (10 mL x2). The combined organic layers dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash chromatography on silica gel, using ethyl acetate/hexane (1/15), provided **8a** (77.7 mg, 0.48 mmol, 68% yield) as pale yellow oil upon flash chromatography (diethyl ether/hexane = 1/10). R_f 0.4 (hexane/diethyl ether = 5/1).



8b

Compound 8b. Under the conditions similar to those used for **8a**, *o*-TMS benzaldehyde **3** (119.4 mg, 0.67 mmol, 1.0 equiv.) gave **8b** (83.5 mg, 0.44 mmol, 66% yield) as pale yellow oil upon flash chromatography (ethyl acetate/hexane = 1/15). R_f 0.42 (hexane/diethyl ether = 5/1); IR (film) 3393 (s), 3075 (m), 2978 (m), 1639 (m), 1447 (m), 1045 (s), 758 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.5 and 1.5 Hz, 1H), 7.29-7.22 (m, 2H), 7.17

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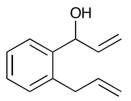
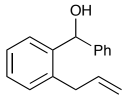
[1] Padwa, A.; Zhang, J. Z.; Zhi, L. *J. Org. Chem.* **2000**, *65*, 5223.

(dd, J = 7.5 and 1.5 Hz, 1H), 6.03-5.95 (m, 1H), 5.90-5.82 (m, 1H), 5.21-5.14 (m, 2H), 5.09 (ddd, J = 10.0, 3.0 and 1.5 Hz, 1H), 5.02-4.98 (m, 2H), 3.51-3.41 (m, 2H), 2.54-2.44 (m, 2H), 2.01 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 137.4, 136.2, 134.8, 129.9, 127.5, 126.8, 125.8, 118.1, 115.9, 69.3, 43.0, 36.7; high resolution mass spectrum (CI) *m/z* 171.1166 [$(M-OH)^+$; calcd for $C_{13}H_{15}$: 171.1174].



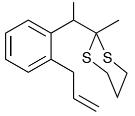
8c

Compound 8c.[2] Under the conditions similar to those used for **8a**, *o*-TMS benzaldehyde **3** (111.6 mg, 0.63 mmol, 1.0 equiv.) gave **8c** (74.6 mg, 0.43 mmol, 68% yield) as pale yellow oil upon flash chromatography (ethyl acetate/hexane = 1/15). R_f 0.4 (hexane/diethyl ether = 5/1).



8d

Compound 8d. Under the conditions similar to those used for **8a**, *o*-TMS benzaldehyde **3** (104.7 mg, 0.59 mmol, 1.0 equiv.) gave **8d** (79.4 mg, 0.354 mmol, 60% yield) as pale yellow oil upon flash chromatography (ethyl acetate/hexane = 1/15). R_f 0.4 (hexane/diethyl ether = 5/1); IR (film) 3361 (s), 3062 (s), 3028 (s), 2916 (w), 1451 (s), 1015 (s), 760 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.45 (m, 1H), 7.35-7.33 (m, 4H), 7.30-7.26 (m, 3H), 7.21-7.19 (m, 1H), 6.09 (s, 1H), 5.96-5.90 (m, 1H), 5.07 (dd, J = 10.0 and 1.5 Hz, 1H), 4.99 (dd, J = 17.0 and 1.5 Hz, 1H), 3.41 (ddd, J = 29.5, 15.5 and 6.0 Hz, 2H), 2.22 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.1, 141.4, 137.3, 137.2, 130.0, 128.4, 127.8, 127.5, 127.2, 126.9, 126.7, 116.0, 72.7, 36.8; high resolution mass spectrum (CI) m/z 206.1088 [$(M-H_2O)^+$; calcd for $C_{16}H_{14}$: 206.1096].



8e

Compound 8e. To a solution of 2-methyl-1,3-dithiane (96.7 mg, 0.72 mmol, 1.2 equiv.) in THF (1.0 mL) at -78 °C was added KO-*t*-Bu (1.0 M in THF, 0.79 mL, 0.79 mmol, 1.32 equiv.) and then *t*-BuLi (1.7 M in pentane, 0.47 mL, 0.79 mmol, 1.32 equiv.). The resulting solution was stirred for 30 min at -78 °C, and a solution of *o*-TMS benzaldehyde **3** (107.3 mg, 0.60 mmol, 1.0 equiv.) in THF (1 mL) was added. After stirring for 30 min, the resulting solution was added into a mixture of CuI (137.1 mg, 0.72 mmol, 1.2 equiv.) and HMPA/THF (1 mL/1 mL) via cannula at 0 °C. The resulting solution was warmed to ambient temperature. After stirring for 30 min, allyl bromide

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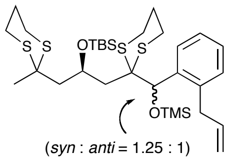
[2] Uozumi, Y.; Tsuji, H.; Hayashi, T. *J. Org. Chem.* **1998**, *63*, 6137.

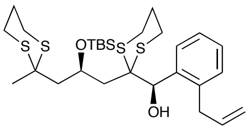
(0.104 mL, 1.20 mmol, 2.0 equiv.) was added at ambient temperature. After being stirred for 2 h, a saturated aqueous NH_4Cl (3 mL) solution was added. The resulting mixture was then extracted with Et_2O (10 mL x 3). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was dissolved in 2% HCl in EtOH (2 mL) at ambient temperature. After being stirred for 30 min, the mixture was then extracted with Et_2O (10 mL x 2) and CH_2Cl_2 (10 mL x2). The combined organic layers dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash chromatography on silica gel, using diethyl ether/hexane (1/9), provided **8e** (131.9 mg, 0.47 mmol, 78% yield) as pale yellow oil. R_f 0.38 (hexane/diethyl ether = 5/1); IR (film) 3446 (s), 3070 (w), 2973 (s), 2912 (s), 1448 (s), 1278 (m), 1026 (s), 760 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.68-7.65 (m, 1H), 7.27-7.22 (m, 2H), 7.20-7.17 (m, 1H), 6.04-5.96 (m, 1H), 5.27 (s, 1H), 5.11 (ddd, J = 10.5, 3.5 and 1.5 Hz, 1H), 5.04 (ddd, J = 17.5, 3.5 and 1.5 Hz, 1H), 3.78 (dd, J = 16.0 and 6.0 Hz, 1H), 3.50 (dd, J = 16.0 and 6.0 Hz, 1H), 3.09 (s, 1H), 3.04-2.99 (m, 1H), 2.92-2.87 (m, 1H), 2.81 (ddd, J = 14.0, 6.5 and 3.5 Hz, 1H), 2.72 (ddd, J = 14.5, 6.5 and 3.0 Hz, 1H), 2.11-2.02 (m, 1H), 1.98-1.90 (m, 1H), 1.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 137.2, 136.7, 129.6, 128.7, 128.1, 125.7, 116.1, 72.6, 54.9, 37.6, 27.7, 26.1, 24.5, 24.3; high resolution mass spectrum (CI) *m/z* 279.0879 $[(M-H)^+$; calcd for $C_{15}H_{19}OS_2$: 279.0877].



(*syn* : *anti* = 1.25 : 1)

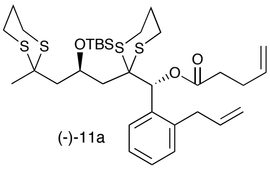
9

Compound 9. To a solution of 2-methyl-1,3-dithiane (1.24 g, 9.2 mmol, 1.2 equiv.) in THF (15 mL) at -78 °C was added KO-*t*-Bu (1.0 M in THF, 9.7 mL, 9.7 mmol, 1.26 equiv.) and then *t*-BuLi (1.7 M in pentane, 5.7 mL, 9.7 mmol, 1.26 equiv.). The resulting solution was stirred for 30 min at -78 °C, and a solution of epoxide (-)-**2** (2.24 g, 7.7 mmol, 1.0 equiv.) in THF (15 mL) was added. The resulting solution was stirred for 20 min at -78 °C and then a solution of aldehyde **3** (1.64 g, 9.2 mmol, 1.2 equiv.) in THF (15 mL) was added via cannula. After 30 min at -78 °C, the resulting solution was added into a mixture of CuI (142.6 mg, 0.75 mmol, 1.2 equiv.) and HMPA/THF (10 mL/10 mL) via cannula at 0 °C. The resulting solution was warmed to ambient temperature. After stirring for 30 min, allyl bromide (2.0 mL, 23.1 mmol, 3.0 equiv.) was added at ambient temperature, stirred for 1 h, and the reaction quenched with a saturated aqueous NH_4Cl solution (100 mL). The resulting mixture was then extracted with Et_2O (100 mL X 3) and the combined organic layers washed with brine (100 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash chromatography on silica gel, using diethyl ether/hexane (1/50) as eluant, provided a 1.25:1 diastereomeric mixture of **9** (3.13 g, 4.87 mmol, 63%) as pale yellow oil. R_f 0.8 (hexane/diethyl ether = 10/1); For **major diastereomer (*Syn*) of 9:** $[\alpha]^{20}_D$ +1.10 (c 1.0 $CDCl_3$); IR (film) 3072 (w), 2953 (s), 2855 (m), 1471 (m), 1252 (s), 1089 (s), 1045 (s), 774 (s) cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.95-7.94 (m, 1H), 7.26-7.16 (m, 2H), 7.15-7.13 (m, 1H), 5.96-5.88 (m, 1H), 5.22 (s, 1H), 5.17-5.11 (m, 2H), 4.65 (t, *J* = 8.5 Hz, 1H), 3.74 (dd, *J* = 16.0 and 7.5 Hz, 1H), 3.49 (dd, *J* = 16.0 and 6.5 Hz, 1H), 3.24-3.18 (m, 1H), 3.16-3.11 (m, 1H), 2.30-2.94 (m, 1H), 2.84-2.77 (m, 2H), 2.72-2.61 (m, 3H), 2.46-2.42 (m, 1H), 2.00-1.90 (m, 3H), 1.87-1.80 (m, 2H), 1.75-1.70 (m, 2H), 1.64 (s, 3H), 0.87 (s, 9H), 0.19 (s, 3H), 0.17 (s, 3H), -0.05 (s, 9H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 138.9, 137.6, 137.1, 130.6, 128.7, 127.7, 125.3, 116.5, 80.5, 68.8, 56.3, 51.1, 49.1, 47.2, 37.4, 29.4, 28.2, 27.2, 27.0, 26.7, 26.3, 25.2, 23.7, 18.0, 0.23, -2.73, -3.44; high resolution mass spectrum (ES$^+$) *m/z* 665.2469 [(M+Na)$^+$; calcd for $C_{31}H_{54}O_2S_4Si_2Na$: 665.2443].; For **minor diastereomer (*Anti*) of 9:** $[\alpha]^{20}_D$ +1.59 (*c* 0.75 CDCl$_3$); IR (film) 3072 (w), 2953 (s), 2855 (m), 1472 (m), 1252 (s), 1091 (s), 1021 (m), 775 (m) cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.86-7.85 (m, 1H), 7.23-7.17 (m, 2H), 7.15-7.13 (m, 1H), 5.97-5.89 (m, 1H), 5.32 (s, 1H), 5.17-5.12 (m, 2H), 4.57 (t, *J* = 9.0 Hz, 1H), 3.67 (dd, *J* = 15.5 and 7.0 Hz, 1H), 3.43 (dd, *J* = 15.5 and 6.5 Hz, 1H), 3.38-3.32 (m, 2H), 3.20-3.11 (m, 2H), 3.09-3.03 (m, 1H), 2.71-2.61 (m, 4H), 2.06-2.02 (m, 2H), 1.88-1.76 (m, 4H), 1.74 (d, *J* = 16.0 Hz, 1H), 1.63 (s, 3H), 0.78 (s, 9H), 0.06 (s, 3H), -0.04 (s, 9H), -0.21 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 138.8, 137.7, 137.0, 130.4, 128.7, 127.7, 125.4, 116.6, 81.1, 68.8, 56.3, 50.6, 49.3, 46.0, 37.4, 29.4, 28.8, 27.2, 27.1, 26.7, 26.1, 25.3, 23.9, 17.9, 0.20, -3.49, -3.71; high resolution mass spectrum (ES$^+$) m/z 643.2623 [(M+H)$^+$; calcd for $C_{31}H_{55}O_2S_4Si_2$: 643.2612].



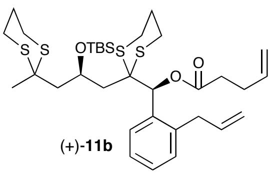
(-)-**10a**

Compounds (-)-**10a and** (+)-**10b**. To a solution of **9** (1.94 g, 3.02 mmol, 1.0 equiv.) in MeOH (40 mL) was added K_2CO_3 (4.17, 30.2 mmol, 10.0 equiv.) at ambient temperature. After stirring overnight at ambient temperature, H_2O (100 mL) was added. The resulting mixture was then extracted with Et_2O (50 mL X 3). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash chromatography on silica gel, using diethyl ether/hexane (1/10), provided two separable diastereomers (-)-**10a** as solid and (+)-**10b** as pale yellow oil (1.62 g, 2.84 mmol, 94%). **Compound** (-)-**10a:** $[\alpha]^{20}_D$ -0.90 (*c* 1.0 CDCl$_3$); R$_f$ 0.2 (hexane/diethyl ether = 10/1). IR (film) 3434 (m), 2927 (s), 2855 (s), 1471 (m), 1254 (s), 1090 (s), 1028 (s), 775 (s) cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.78-7.76 (m, 1H), 7.25-7.22 (m, 2H), 7.17-7.16 (m, 1H), 6.04-5.96 (m, 1H), 5.29 (s, 1H), 5.09 (dd, *J* = 10.0 and 1.5 Hz, 1H), 5.03 (dd, *J* = 17.0 and 2.0 Hz, 1H), 4.59-4.55 (m, 1H), 3.81 (dd, *J* = 16.0 and 6.5 Hz, 1H), 3.63 (br, 1H), 3.55 (dd, *J* = 16.0 and 6.0 Hz, 1H), 3.12-3.06 (m, 1H), 3.03-2.94 (m, 2H), 2.85-2.62 (m, 6H), 2.44 (dd, *J* = 15.5 and 6.5 Hz, 1H), 2.05-1.81 (m, 6H), 1.73 (s, 3H), 0.83 (s, 9H), 0.12 (s, 3H), -0.04 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 138.9, 137.5, 137.0, 129.6, 129.5, 128.0, 125.6, 115.9, 73.3, 68.4, 58.3, 50.7, 48.5, 46.3, 37.9, 29.5, 27.6, 27.1, 26.7, 26.2, 26.1, 25.2, 24.0, 18.1, -3.35, -3.4; high resolution mass spectrum (ES$^+$) *m/z* 593.2061 [(M+Na)$^+$; calcd for $C_{28}H_{46}O_2S_4SiNa$: 593.2048]. **Compound** (+)-**10b:** $[\alpha]^{20}_D$ +18.6 (*c* 0.5 $CDCl_3$); IR (film) 3440 (m), 2952 (s), 2856 (s), 1468 (m), 1254 (s), 1092 (s), 1026 (s), 775 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75-7.74 (m, 1H), 7.26-7.20 (m, 2H), 7.18-7.17 (m, 1H), 6.04-5.96 (m, 1H), 5.26 (s, 1H), 5.09 (dd, *J* = 10.5 and 1.5 Hz, 1H), 5.04 (dd, *J* = 17.0 and 1.5 Hz, 1H), 4.60-4.56 (m, 1H), 3.92 (d, *J* = 3.5 Hz, 1H), 3.79 (dd, *J* = 16.0 and 6.5 Hz, 1H), 3.58 (dd, *J* = 16.0 and 6.5 Hz, 1H), 3.06-3.01 (m, 1H), 2.97-2.92 (m, 1H), 2.91-2.67 (m, 7H), 2.44 (dd, *J* = 15.5 and 5.0 Hz, 1H), 2.32 (dd, *J* = 15.5 and 6.0 Hz, 1H), 1.96 (dd, *J* = 8.0 and 3.5 Hz, 1H), 1.94-1.80 (m, 4H), 1.72 (s, 3H), 0.91 (s, 9H), 0.22 (s, 3H), 0.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 137.5, 137.1, 129.6, 129.3, 127.8, 125.4, 116.0, 73.0, 68.9, 58.3, 49.9, 48.0, 45.0, 37.7, 29.3, 27.6, 27.0, 26.6, 26.2, 26.1, 25.1, 24.2, 18.1, -3.4; high resolution mass spectrum (ES$^+$) *m/z* 593.2049 [(M+Na)$^+$; calcd for $C_{28}H_{46}O_2S_4SiNa$: 593.2048].



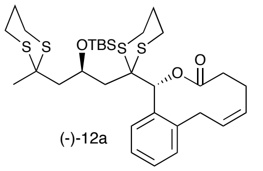
(-)-11a

Compounds (-)-**11a**. To a solution of (-)-**10a** (247.0 mg, 0.43 mmol, 1.0 equiv) in CH_2Cl_2 (12 mL) were added DCC (1.0 M in CH_2Cl_2, 4.3 mL, 4.3 mmol, 10.0 equiv.), DMAP (26.8 mg, 0.22 mmol, 0.5 equiv.) and 4-pentenoic acid (0.44 mL, 4.3 mmol, 10.0 equiv.) dropwise at ambient temperature. After stirring for 10 h, CH_2Cl_2 was evaporated, and then filtered through celite with diethyl ether. The filtrates were concentrated *in vacuo* and flash chromatography on silica gel, using diethyl ether/hexane (1/20), provided (-)-**11a** (267.8 mg, 0.41 mmol, 95%) as pale yellow oil. R_f 0.46 (hexane/diethyl ether = 5/1); $[\alpha]^{20}_D$ -7.40 (*c* 1.0 $CDCl_3$); IR (film) 3075 (w), 2952 (s), 2855 (s), 1739 (s), 1471 (m), 1253 (s), 1092 (s), 1022 (s), 775 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.25-7.23 (m, 1H), 7.20-7.16 (m, 2H), 6.48 (s, 1H), 6.08-6.00 (m, 1H), 5.84-5.76 (m, 1H), 5.14 (d, *J* = 6.5 Hz, 1H), 5.12 (s, 1H), 5.02 (dd, *J* = 16.0 and 1.5 Hz, 1H), 4.97 (dd, *J* = 10.5 and 1.5 Hz, 1H), 4.61-4.57 (m, 1H), 3.85 (dd, *J* = 15.5 and 6.5 Hz, 1H), 3.64 (dd, *J* = 15.5 and 7.5 Hz, 1H), 3.21-3.15 (m, 1H), 3.05-2.96 (m, 2H), 2.85-2.67 (m, 5H), 2.56-2.35 (m, 5H), 2.17 (dd, *J* = 15.5 and 7.5 Hz, 1H), 2.00-1.80 (m, 6H), 1.68 (s, 3H), 0.83 (s, 9H), 0.11 (s, 3H), -0.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5, 139.8, 136.9, 136.6, 134.5, 129.8, 129.2, 128.3, 125.4, 116.5, 115.5, 75.2, 68.3, 55.1, 50.9, 48.8, 46.0, 37.5, 33.8, 29.4, 28.6, 28.1, 27.0, 26.9, 26.7, 26.2, 25.2, 23.6, 18.0, -3.3, -3.5; high resolution mass spectrum (ES$^+$) *m/z* 675.2495 [(M+Na)$^+$; calcd for $C_{33}H_{52}O_3S_4SiNa$: 675.2467].



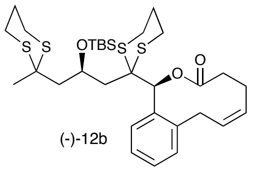
(+)-**11b**

Compounds (+)-11b. Under the conditions similar to those used for (-)-**11a**, (+)-**10b** (646.2 mg, 1.13 mmol, 1.0 equiv.) gave (+)-**11b** (711.9 mg, 1.09 mmol, 96% yield) as pale yellow oil upon flash chromatography (diethyl ether/hexane = 1/20). R_f 0.46 (hexane/diethyl ether = 5/1); $[\alpha]^{20}_{D}$ +33.1 (*c* 1.0 $CDCl_3$); IR (film) 3075 (w), 2927 (s), 2855 (s), 1740 (s), 1471 (m), 1255 (s), 1092 (s), 1022 (m), 775 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 1H), 7.30-7.24 (m, 1H), 7.21-7.16 (m, 2H), 6.54 (s, 1H), 6.07-5.99 (m, 1H), 5.83-5.76 (m, 1H), 5.17-5.13 (m, 2H), 5.02 (ddd, *J* = 17.0, 3.0 and 1.5 Hz, 1H), 4.96 (ddd, *J* = 10.0, 2.5 and 1.0 Hz, 1H), 4.64-4.59 (m, 1H), 3.83 (dd, *J* = 15.5 and 6.0 Hz, 1H), 3.59 (dd, *J* = 16.0 and 7.5 Hz, 1H), 3.29-3.23 (m, 1H), 3.16-3.10 (m, 1H), 3.03-2.97 (m, 3H), 2.73-2.62 (m, 4H), 2.53-2.44 (m, 2H), 2.43-2.35 (m, 2H), 2.16 (dd, *J* = 15.0 and 2.5 Hz, 1H), 2.10-1.99 (m, 2H), 1.94-1.75 (m, 4H), 1.64 (s, 3H), 0.90 (s, 9H), 0.16 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5, 139.9, 136.8, 136.5, 134.4, 129.5, 129.1, 128.3, 125.4, 116.7, 115.5, 74.7, 68.9, 54.8, 50.0, 49.0, 45.2, 37.4, 33.8, 29.3, 28.7, 28.6, 27.1, 26.8, 26.7, 26.2, 25.2, 23.8, 18.0, -3.32, -3.34; high resolution mass spectrum (ES^+) *m/z* 675.2479 [$(M+Na)^+$; calcd for $C_{33}H_{52}O_3S_4SiNa$: 675.2467].



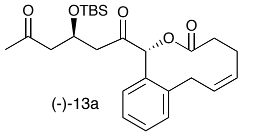
(-)-12a

Compounds (-)-**12a**. To a solution of (-)-**11a** (60.5 mg, 0.093 mmol, 1.0 equiv.) in CH_2Cl_2 (0.003M, 31 mL) at was added 2nd generation Grubbs catalyst (7.89 mg, 0.0093 mmol, 0.1 equiv.) at ambient temperature. After stirring for 2 h at 55 °C, CH_2Cl_2 was evaporated, and then the crude product was purified by flash chromatography on silica gel, using diethyl ether/hexane (1/10) to provide (-)-**12a** (45.1 mg, 0.072 mmol, 77%) as pale yellow oil. R_f 0.3 (hexane/diethyl ether = 5/1); $[\alpha]^{20}_{D}$ -27.9 (*c* 1.0 $CDCl_3$); IR (film) 2927 (s), 2855 (s), 1739 (s), 1459 (m), 1240 (s), 1092 (s), 1020 (m), 776 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.39 (d, *J* = 7.5 Hz, 1H), 7.26-7.13 (m, 3H), 6.39 (s, 1H), 5.44 (td, *J* = 11.0 and 4.0 Hz, 1H), 5.35-5.31 (m, 1H), 4.55-4.52 (m, 1H), 4.43 (t, *J* = 12.0 Hz, 1H), 3.33-3.28 (m, 1H), 3.22-3.16 (m, 1H), 3.12-2.96 (m, 5H), 2.81-2.66 (m, 4H), 2.59 (d, *J* = 14.5 Hz, 1H), 2.33-2.28 (m, 2H), 2.10-2.02 (m, 3H), 1.96-1.80 (m, 4H), 1.66 (s, 3H), 0.78 (s, 9H), 0.05 (s, 3H), -0.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 140.4, 133.0, 132.8, 132.2, 132.17, 128.5, 125.3, 124.7, 77.3, 68.3, 56.0, 50.4, 48.9, 44.1, 35.1, 34.5, 29.3, 27.2, 27.1, 26.7, 26.6, 26.1, 25.2, 24.2, 23.3, 17.8, -3.5, -4.0; high resolution mass spectrum (ES^+) *m/z* 625.2346 [$(M+H)^+$; calcd for $C_{31}H_{49}O_3S_4Si$: 625.2334].



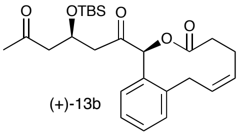
(-)-12b

Compounds (-)-**12b**. Under the conditions similar to those used for (-)-**12a**, (-)-**11b** (86.2 mg, 0.13 mmol, 1.0 equiv.) gave (-)-**12b** (66.9 mg, 0.107 mmol, 82% yield) as pale yellow oil upon flash chromatography (diethyl ether/hexane = 1/10). R_f 0.3 (hexane/diethyl ether = 5/1); $[\alpha]^{20}_{D}$ -4.53 (*c* 0.64 $CDCl_3$); IR (film) 2927 (s), 2855 (s), 1739 (s), 1421 (m), 1240 (s), 1090 (s), 1018 (s), 774 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.7 Hz, 1H), 7.27-7.13 (m, 3H), 6.43 (s, 1H), 5.43 (td, *J* = 11.0 and 4.0 Hz, 1H), 5.32 (td, *J* = 10.5 and 6.0 Hz, 1H), 4.62 (t, *J* = 8.0 Hz, 1H), 4.44 (t, *J* = 12.0 Hz, 1H), 3.23-3.14 (m, 2H), 3.10-2.92 (m, 4H), 2.77-2.72 (m, 3H), 2.68-2.61 (m, 3H), 2.31-2.23 (m, 2H), 2.08-1.94 (m, 4H), 1.85-1.80 (m, 3H), 1.62 (s, 3H), 0.90 (s, 9H), 0.28 (s, 3H), 0.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 140.2, 133.2, 132.9, 132.3, 132.1, 128.5, 125.1, 124.7, 77.8, 68.6, 55.9, 50.6, 48.8, 44.3, 34.9, 34.4, 29.4, 27.5, 27.0, 26.8, 26.6, 26.3, 25.1, 24.1, 22.3, 18.0, -2.9, -3.3; high resolution mass spectrum (ES^+) *m/z* 675.2364 [$(M+H)^+$; calcd for $C_{31}H_{49}O_3S_4Si$: 675.2334].



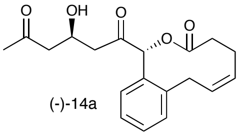
(-)-13a

Compounds (-)-**13a**. To a solution of dithiane (-)-**12a** (39.5 mg, 0.063 mmol, 1.0 equiv.) in aqueous CH_3CN (80%, 7.5 mL) at 0 °C was added NCS (50.5 mg, 0.378 mmol, 6.0 equiv.) and $AgNO_3$ (107.0 mg, 0.63 mmol, 10.0 equiv.). After being stirred for 5 min at 0 °C, a saturated aqueous $NaHSO_3$ (3 mL), and $NaHCO_3$ (3 mL) were added. The resulting mixture was then extracted with Et_2O (10 mL X 3). The combined organic layers were washed with brine (3 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash chromatography on silica gel, using ethyl acetate/hexane (1/4), provided (-)-**13a** (18.2 mg, 0.041 mmol, 65%) as pale yellow oil. R_f 0.3 (hexane/ethyl acetate = 3/1); $[\alpha]^{20}_{D}$ -140.4 (*c* 1.0 $CDCl_3$); IR (film) 2929 (s), 2856 (s), 1749 (s), 1726 (s), 1460 (w), 1250 (s), 1069 (s), 1007 (m), 778 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.0 Hz, 1H), 7.28-7.21 (m, 3H), 6.04 (s, 1H), 5.47 (td, *J* = 11.0 and 4.5 Hz, 1H), 5.39-5.35 (m, 1H), 4.61-4.56 (m, 1H), 4.11 (t, *J* = 12.0 Hz, 1H), 3.13 (ddd, *J* = 24.0, 13.5 and 3.0 Hz, 1H), 2.89 (dd, *J* = 12.5 and 4.0 Hz, 1H), 2.79 (dd, *J* = 16.5 and 6.5 Hz, 1H), 2.72-2.68 (m, 1H), 2.64 (dd, *J* = 16.5 and 6.0 Hz, 1H), 2.51 (d, *J* = 6.0 Hz, 2H), 2.29-2.22 (m, 1H), 2.12-2.09 (m, 1H), 2.09 (s, 3H), 0.81 (s, 9H), 0.04 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.5, 201.5, 170.2, 139.9, 132.7, 132.3, 131.0, 130.6, 129.2, 126.4, 125.6, 82.3, 65.1, 50.6, 46.2, 34.0, 32.5, 31.2, 25.7, 22.9, 17.8, -4.90, -4.97; high resolution mass spectrum (ES^+) *m/z* 445.2420 [$(M+H)^+$; calcd for $C_{25}H_{37}O_5Si$: 445.2410].



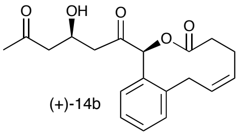
(+)-13b

Compounds (+)-**13b**. Under the conditions similar to those used for (-)-**13a**, (-)-**12b** (34.2 mg, 0.055 mmol, 1.0 equiv.) gave (+)-**13b** (16.5 mg, 0.037 mmol, 67% yield) as pale yellow oil upon flash chromatography (ethyl acetate/hexane = 1/4). R_f 0.3 (hexane/ethyl acetate = 4/1); $[\alpha]^{20}_D$ +82.3 (*c* 1.0 $CDCl_3$); IR (film) 2930 (s), 2857 (s), 1749 (s), 1726 (s), 1462 (w), 1250 (s), 1070 (s), 1011 (m), 778 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.0 Hz, 1H), 7.29-7.20 (m, 3H), 6.08 (s, 1H), 5.48 (td, *J* = 11.0 and 5.0 Hz, 1H), 5.40-5.34 (m, 1H), 4.54-4.50 (m, 1H), 4.12 (t, *J* = 12.0 Hz, 1H), 3.12 (ddd, *J* = 23.5, 13.0 and 2.5 Hz, 1H), 2.88 (dd, *J* = 12.5 and 4.5 Hz, 1H), 2.82 (dd, *J* = 16.5 and 6.0 Hz, 1H), 2.72-2.62 (m, 4H), 2.29-2.23 (m, 1H), 2.14 (s, 3H), 2.12-2.08 (m, 1H), 0.78 (s, 9H), 0.01 (s, 3H), -0.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.9, 201.5, 170.4, 140.1, 132.8, 132.4, 131.0, 130.5, 129.2, 126.4, 125.7, 82.2, 64.9, 50.3, 45.8, 34.0, 32.6, 31.4, 25.7, 23.0, 17.8, -4.9; high resolution mass spectrum (ES^+) *m/z* 445.2425 [$(M+H)^+$; calcd for $C_{25}H_{37}O_5Si$: 445.2410].



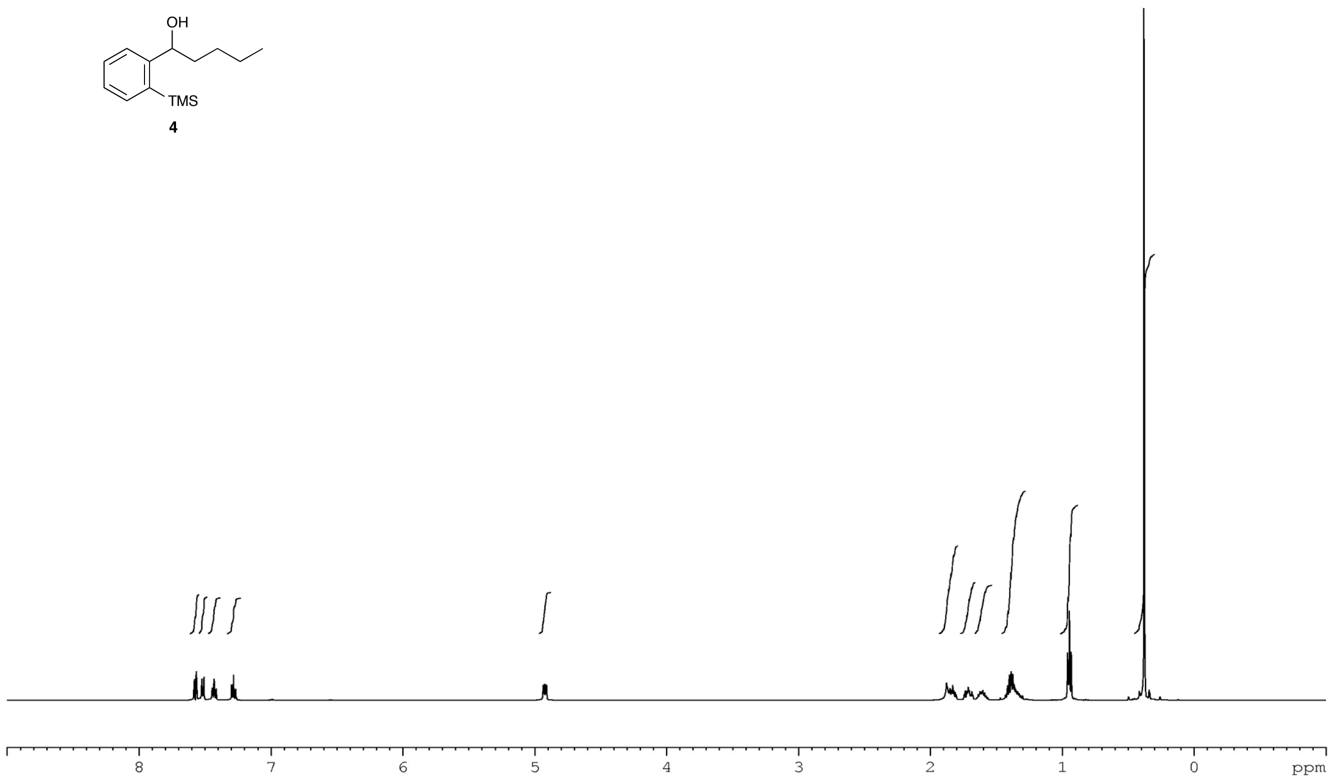
(-)-14a

Compounds (-)-**14a**. Silyl ether (-)-**13a** (16.1 mg, 0.036 mmol, 1.0 equiv.) was treated with 2% HCl in EtOH (3 mL). After stirring for 4 h at ambient temperature, a saturated aqueous NH_4Cl solution (5 mL) was added. The resulting mixture was then extracted with CH_2Cl_2 (10 mL X 3). The combined organic layers were washed with brine (5 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash chromatography on silica gel, using ethyl acetate/hexane (1/2), provided (-)-**14a** (9.9 mg, 0.03 mmol, 83%) as pale yellow oil. R_f 0.1 (hexane/ethyl acetate = 3/1); $[\alpha]^{20}_D$ -133.9 (*c* 0.18 $CDCl_3$); IR (film) 3462 (m), 3010 (m), 2920 (m), 2858 (m), 1721 (s), 1359 (m), 1241 (s), 1065 (s), 745 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36-7.22 (m, 4H), 6.10 (s, 1H), 5.49 (td, *J* = 10.5 and 4.5 Hz, 1H), 5.41-5.35 (m, 1H), 4.47-4.41 (m, 1H), 4.10 (t, *J* = 11.5 Hz, 1H), 3.30 (br, 1H), 3.14-3.06 (m, 1H), 2.91 (dd, *J* = 12.5 and 4.5 Hz, 1H), 2.84 (dd, *J* = 17.0 and 7.5 Hz, 1H), 2.72-2.53 (m, 4H), 2.31-2.25 (m, 1H), 2.13 (s, 3H), 2.12-2.07 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.3, 203.1, 170.5, 140.0, 132.7, 132.4, 130.9, 130.5, 129.3, 126.5, 125.8, 82.1, 64.2, 48.9, 44.8, 34.0, 32.6, 30.7, 22.9; high resolution mass spectrum (ES^+) *m/z* 353.1380 [$(M+Na)^+$; calcd for $C_{19}H_{22}O_5Na$: 353.1365].



(+)-14b

Compounds (+)-**14b**. Under the conditions similar to those used for (-)-**14a**, (+)-**13b** (15.8 mg, 0.036 mmol, 1.0 equiv.) gave (+)-**14b** (9.85 mg, 0.03 mmol, 83% yield) as pale yellow oil upon flash chromatography (ethyl acetate/hexane = 1/2). R_f 0.1 (hexane/ethyl acetate = 3/1); $[\alpha]^{20}_D$ +75.2 (*c* 0.25 $CDCl_3$); IR (film) 3485 (m), 3011 (m), 2922 (m), 2858 (m), 1720 (s), 1359 (m), 1242 (s), 1066 (s), 745 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.35-7.21 (m, 4H), 6.10 (s, 1H), 5.49 (td, *J* = 11.0 and 4.5 Hz, 1H), 5.41-5.35 (m, 1H), 4.47-4.42 (m, 1H), 4.10 (t, *J* = 11.8 Hz, 1H), 3.27 (br, 1H), 3.13-3.05 (m, 1H), 2.91 (dd, *J* = 13.0 and 4.5 Hz, 1H), 2.82 (dd, *J* = 17.0 and 5.5 Hz, 1H), 2.72-2.58 (m, 4H), 2.32-2.26 (m, 1H), 2.14 (s, 3H), 2.13-2.10 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.4, 203.2, 170.6, 140.0, 132.8, 132.4, 130.9, 130.4, 129.4, 126.6, 125.8, 82.0, 63.9, 48.8, 44.7, 33.9, 32.7, 30.7, 22.9; high resolution mass spectrum (ES^+) *m/z* 331.1557 [$(M+H)^+$; calcd for $C_{19}H_{23}O_5$: 331.1557].



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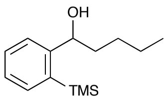

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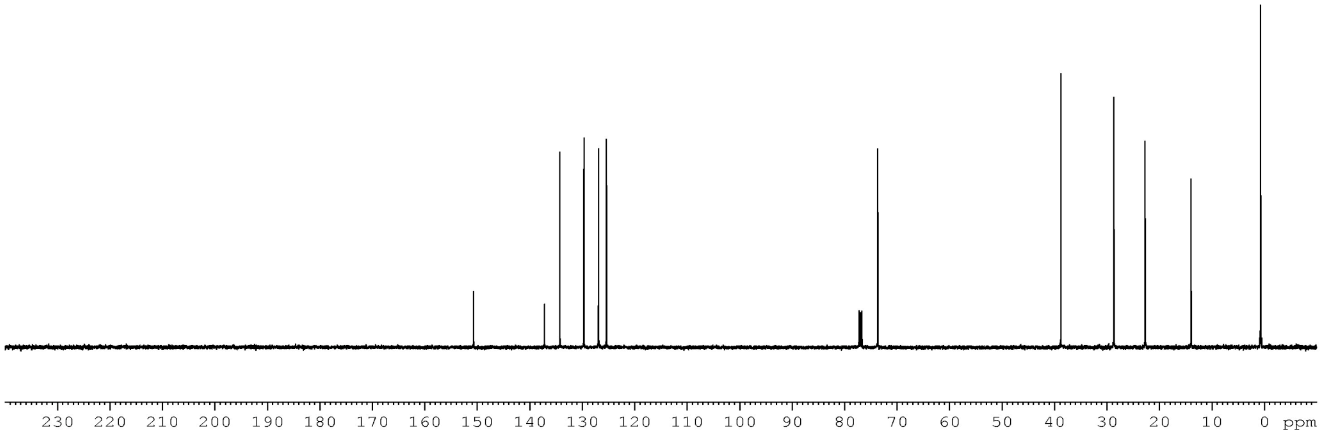
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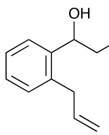

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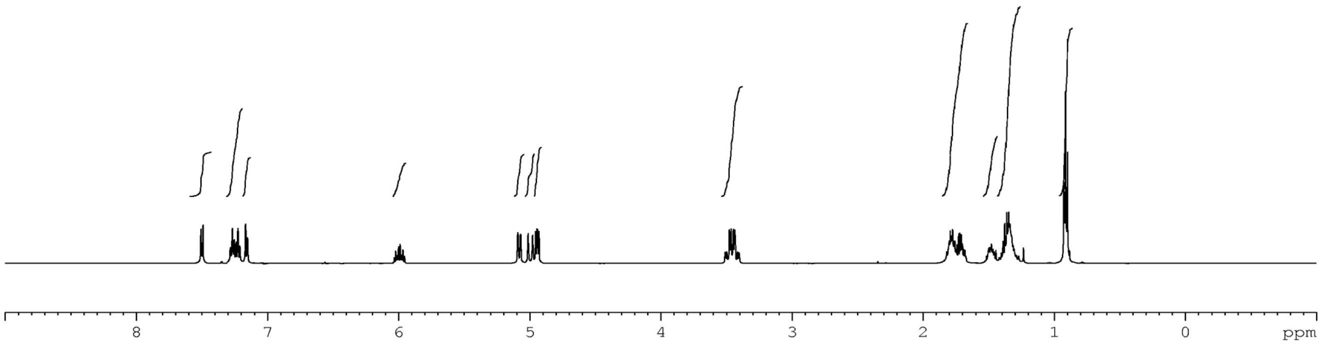

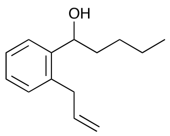

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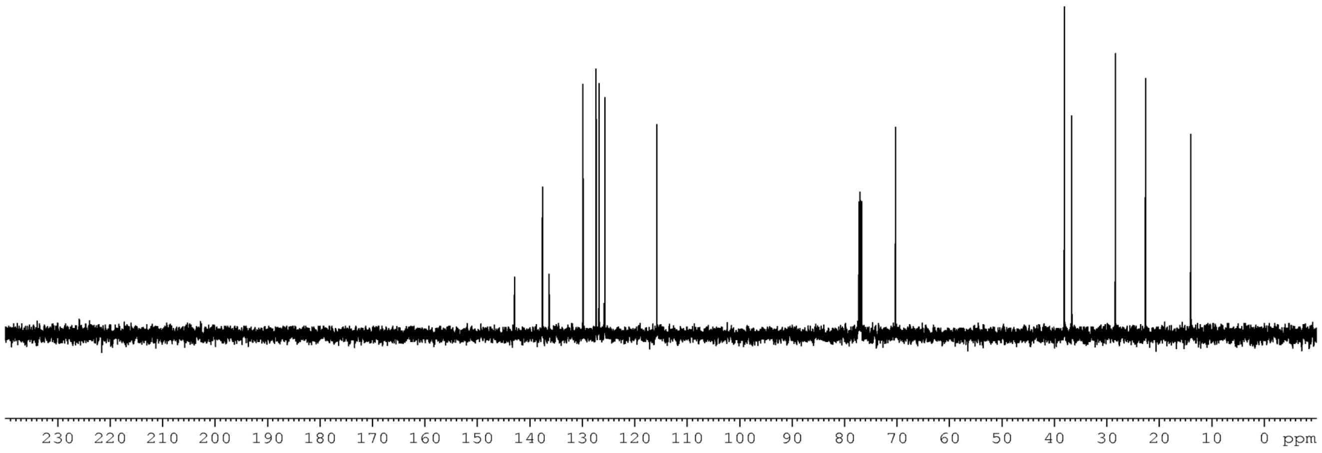

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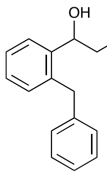

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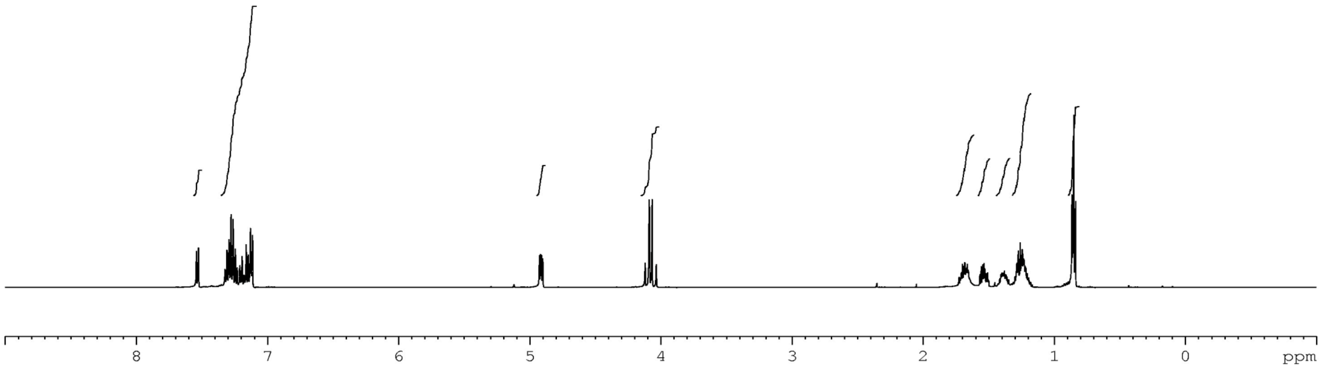

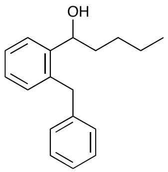

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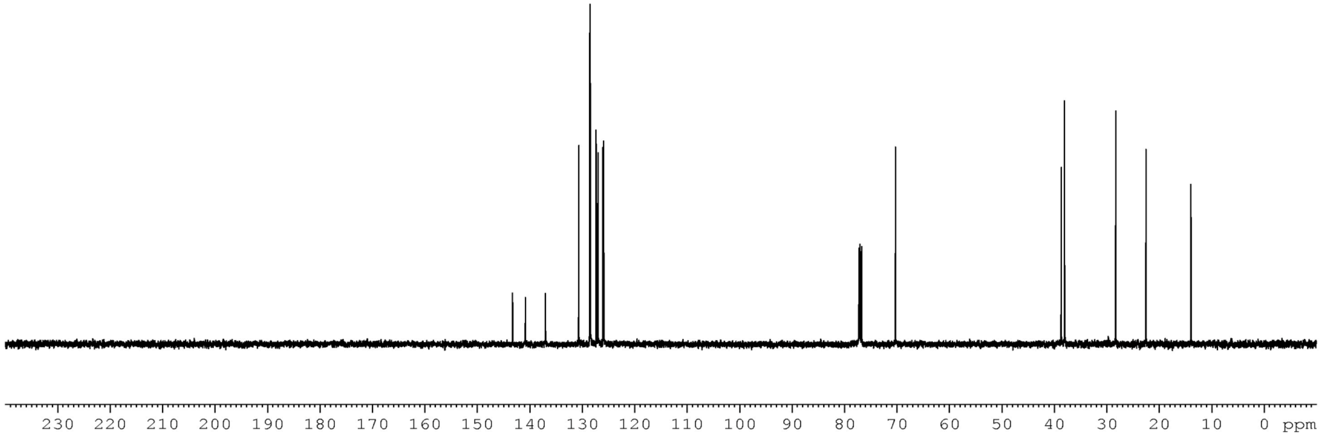

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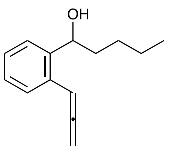

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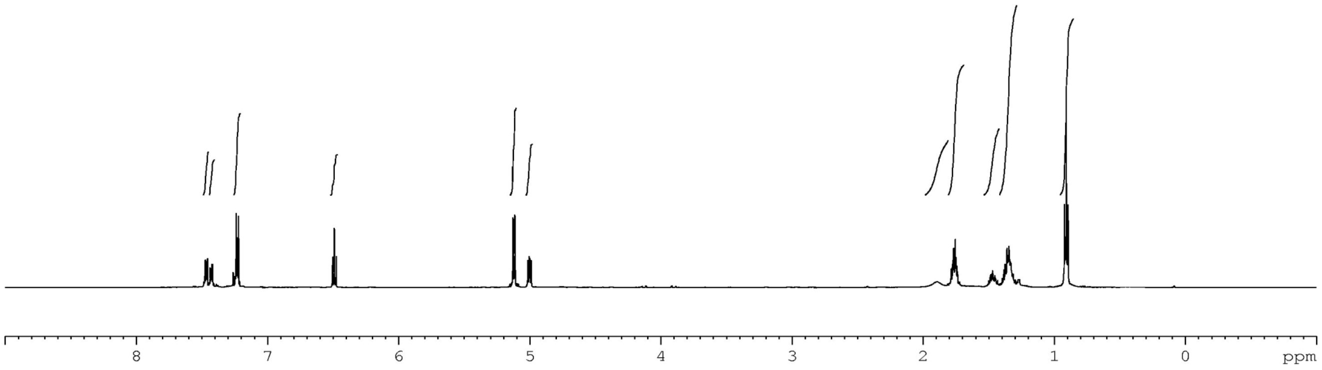

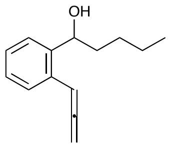
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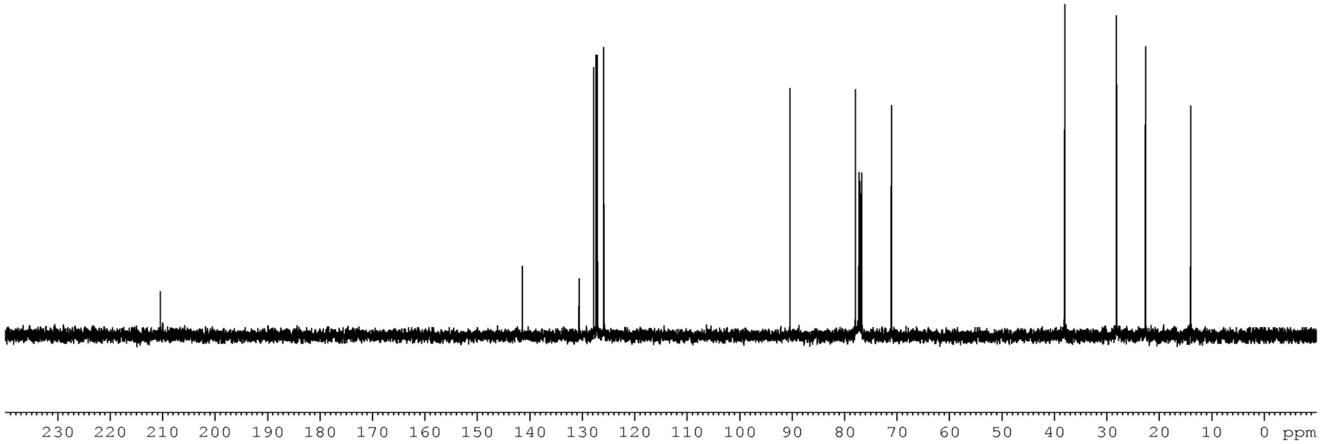
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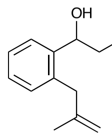

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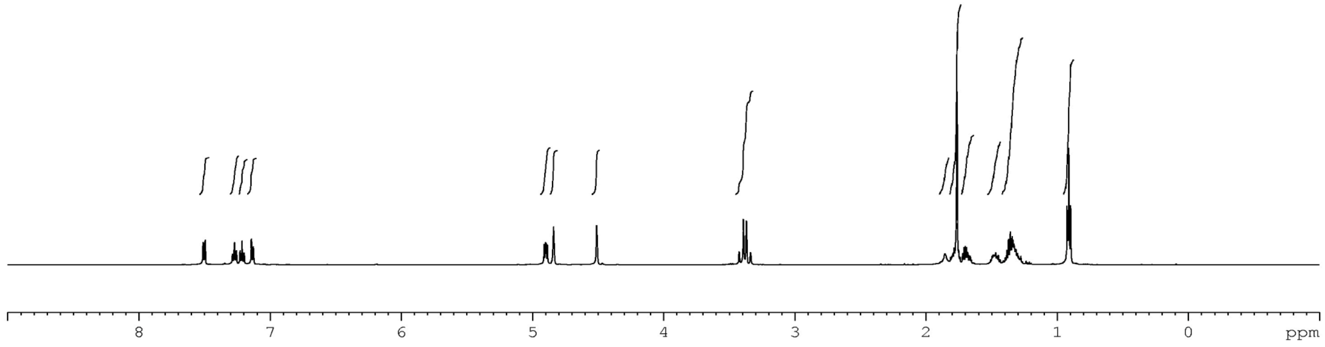

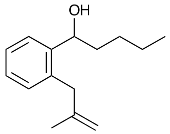
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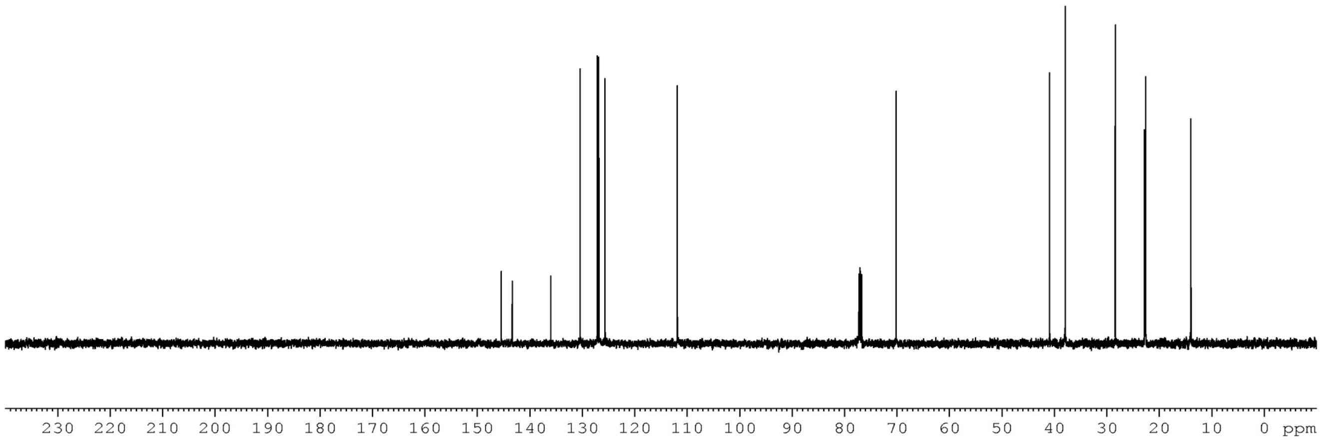
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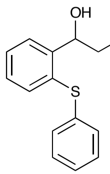

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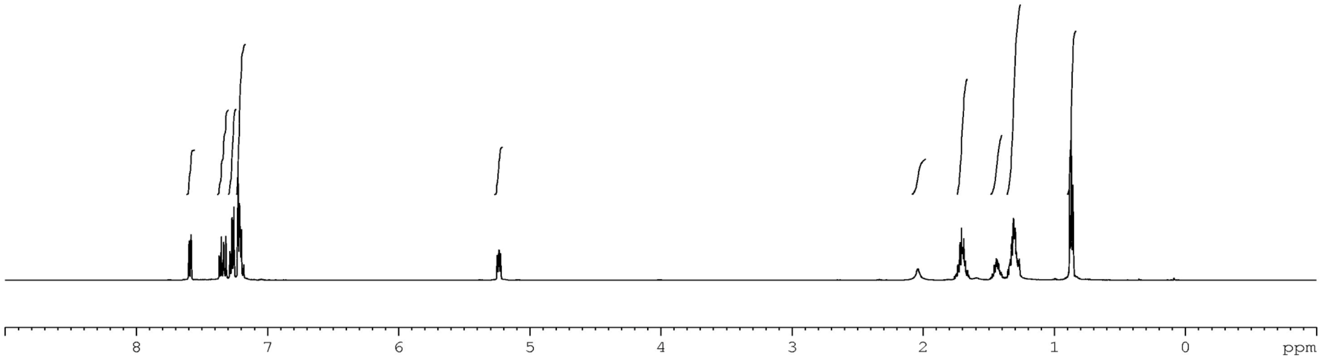

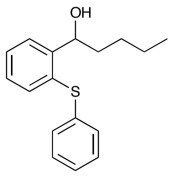
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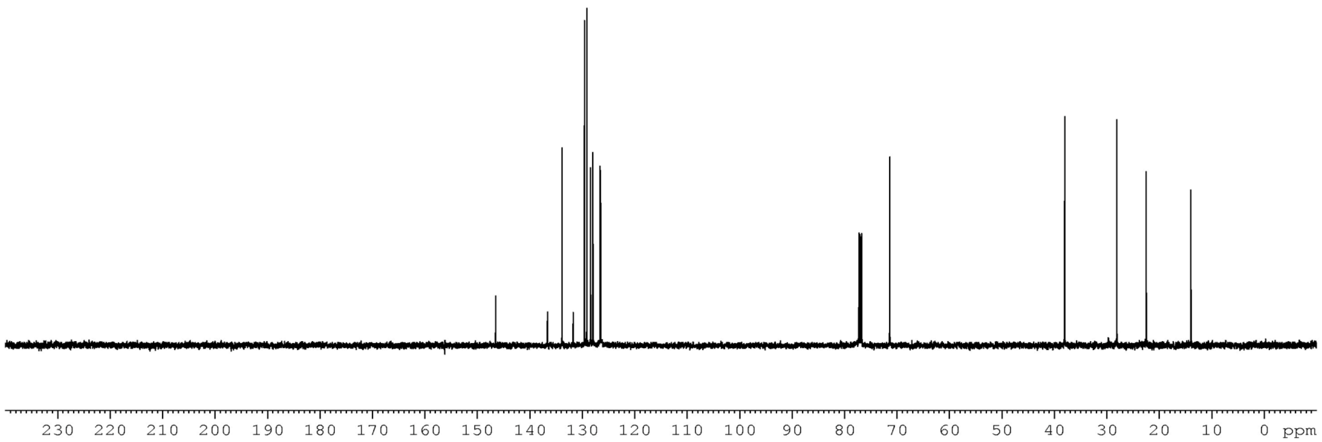
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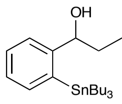

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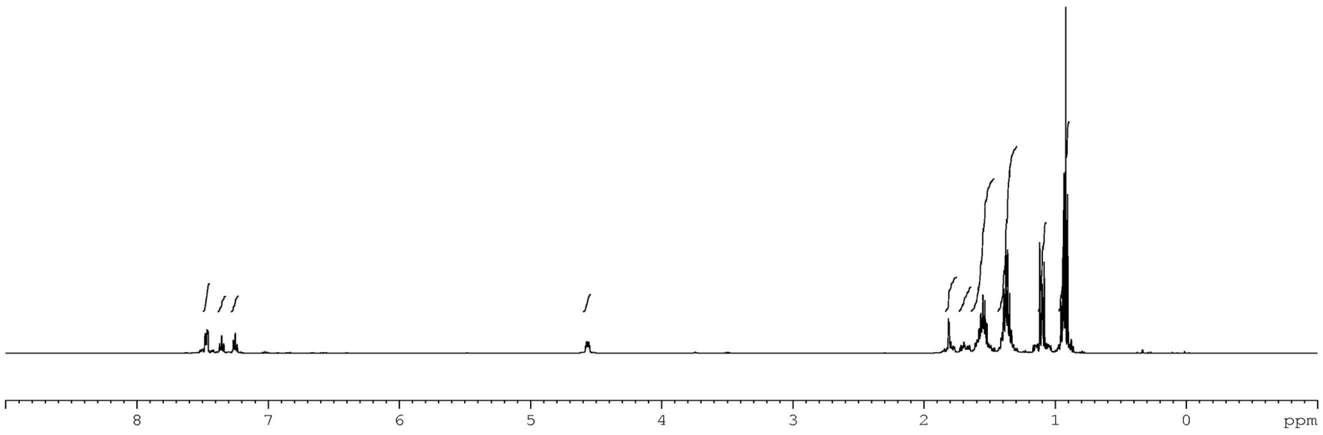

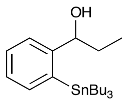
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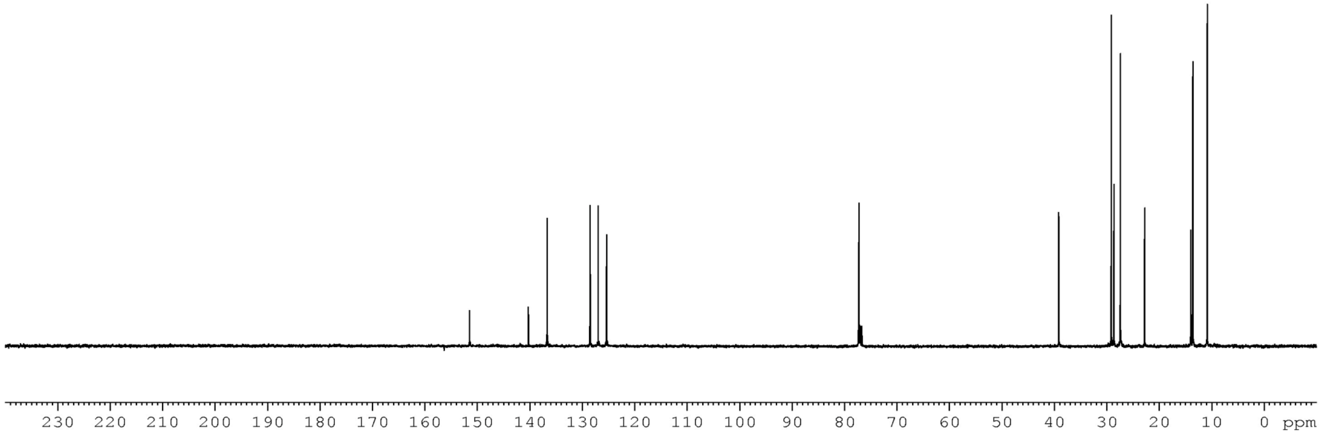
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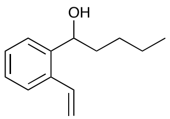

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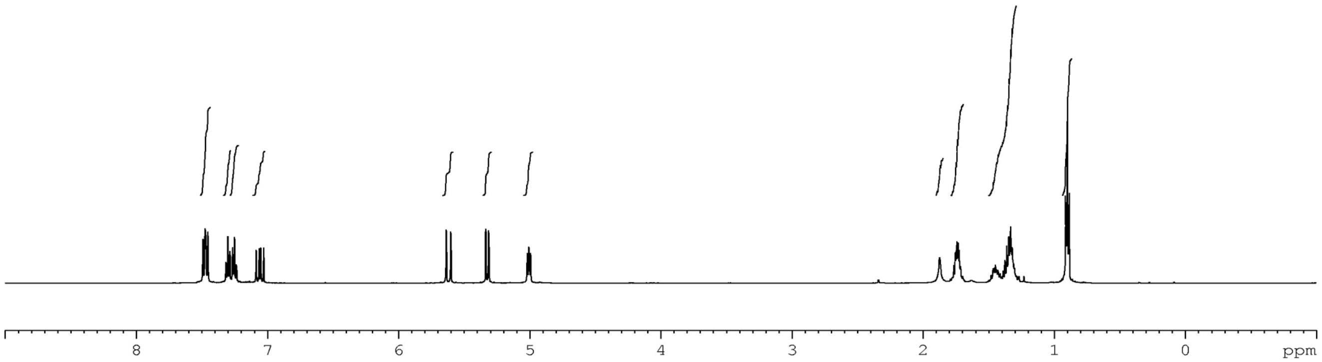

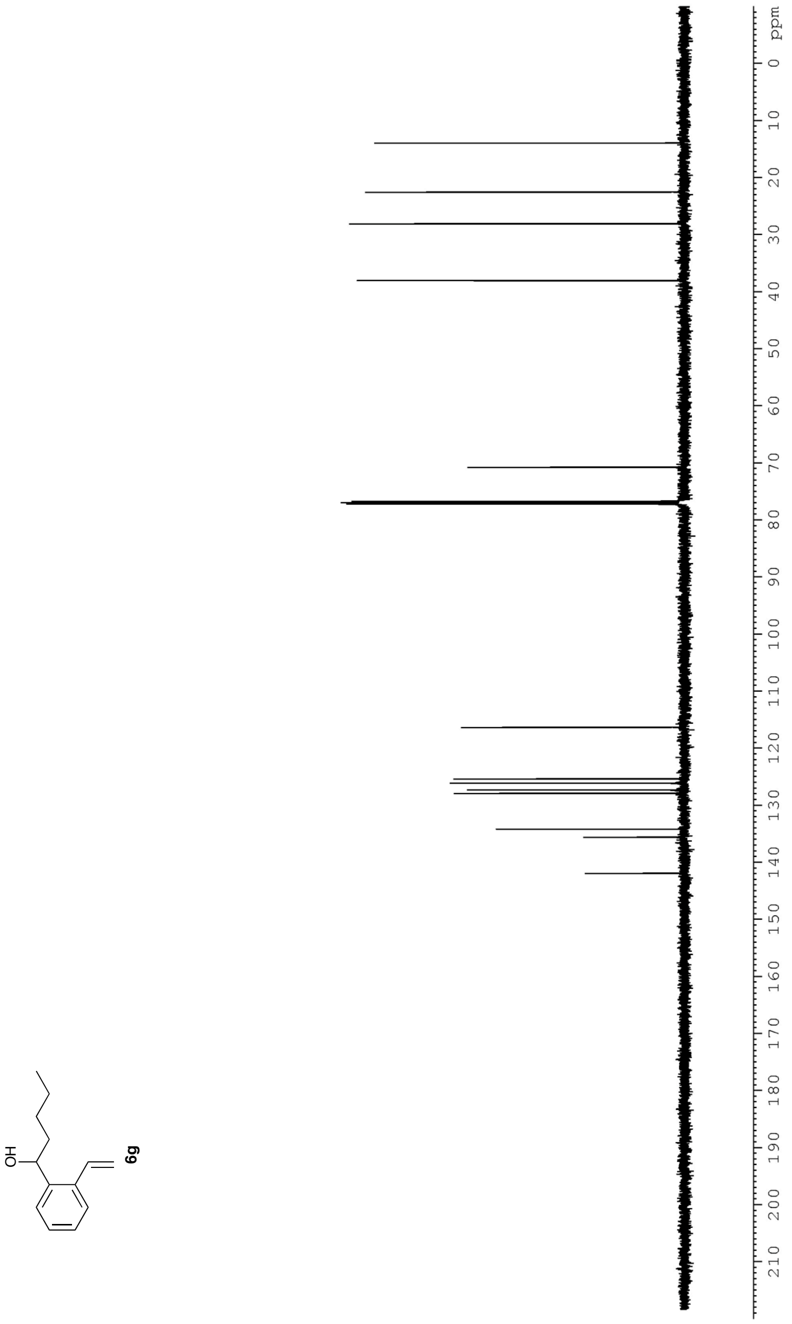

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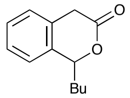

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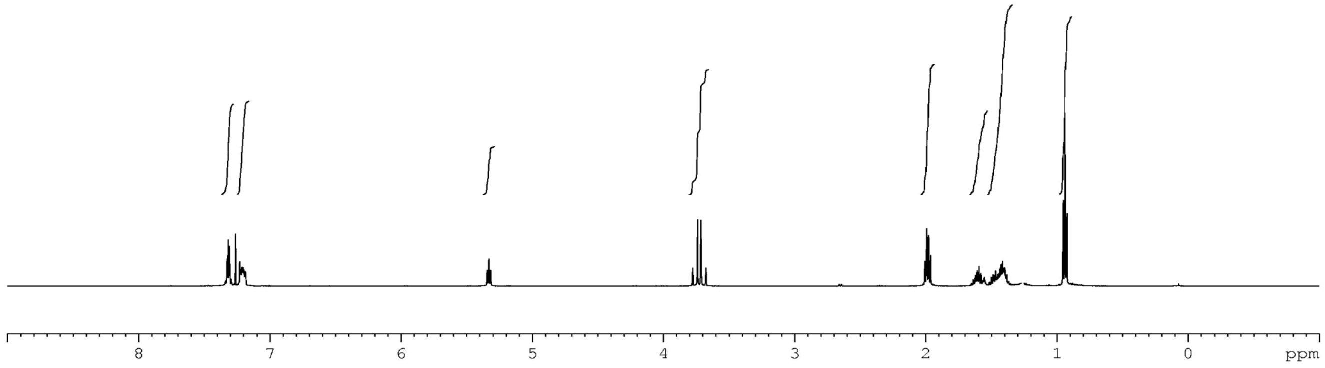

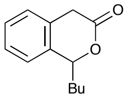
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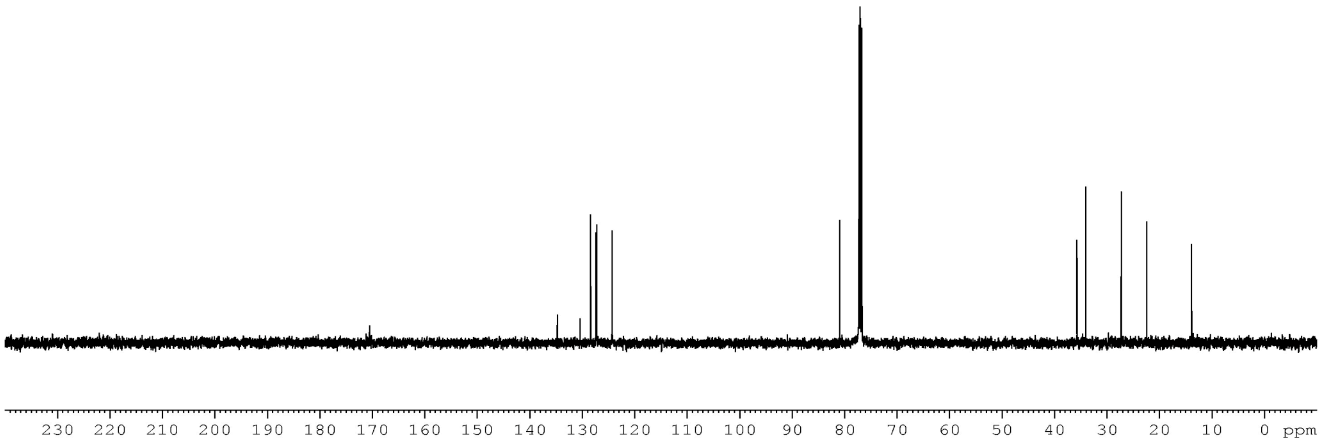
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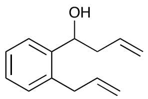

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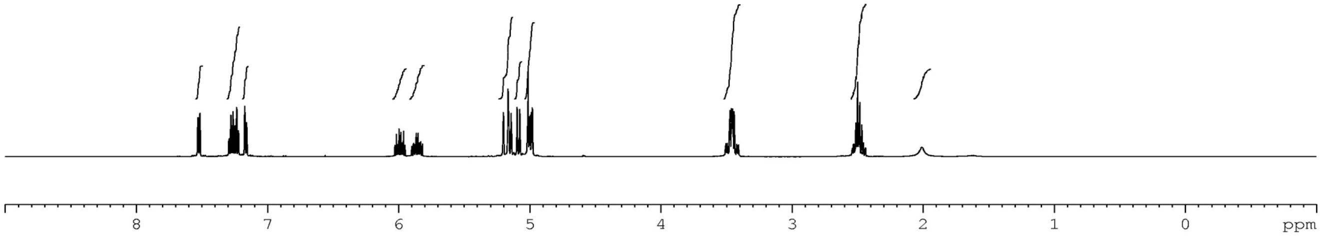

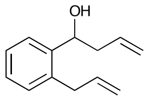

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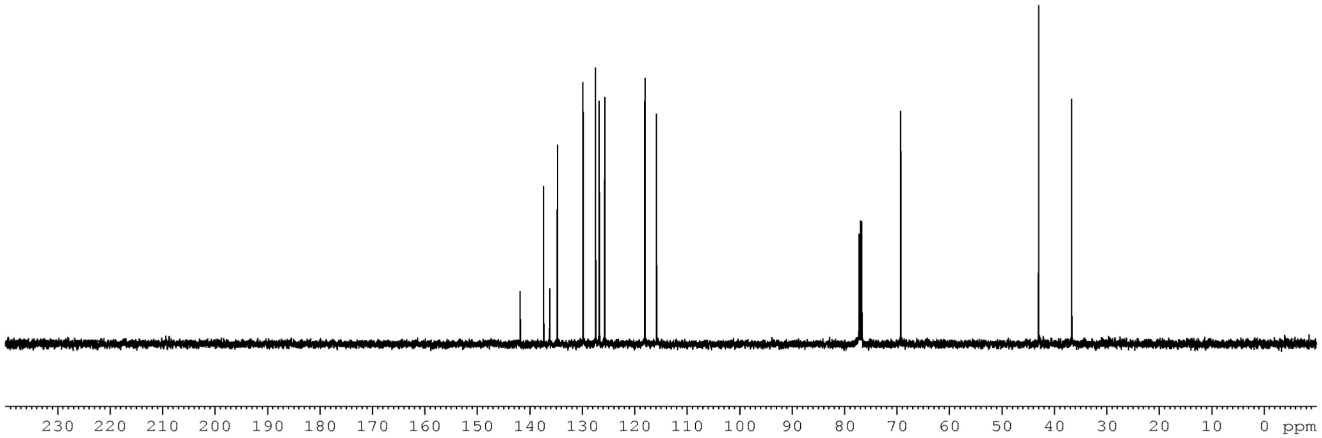
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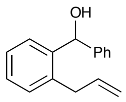

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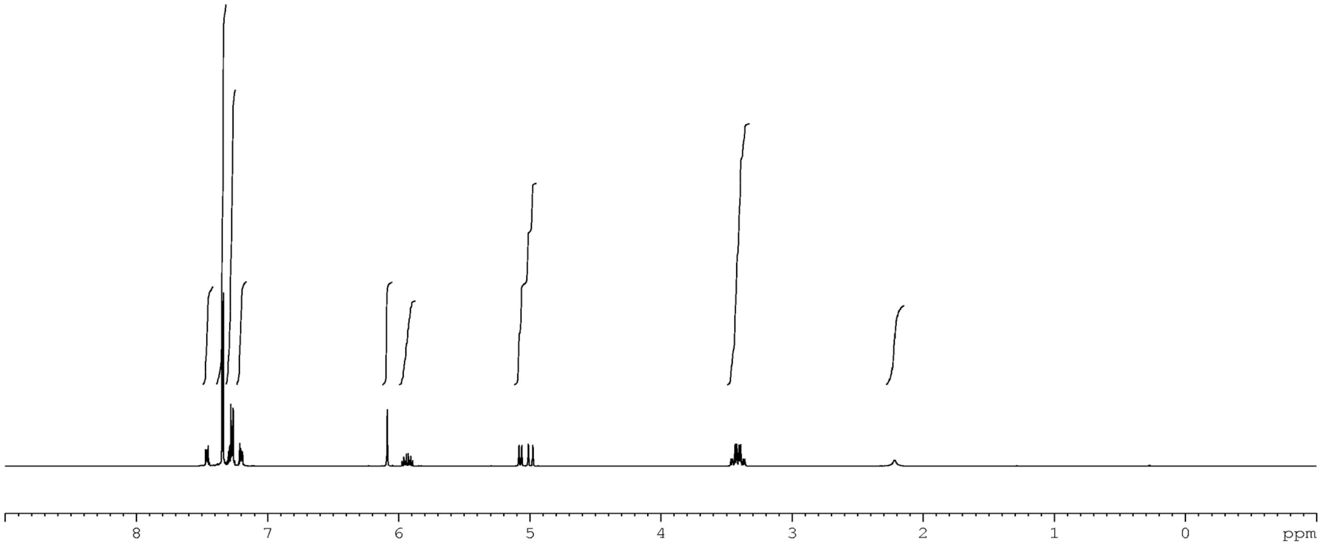

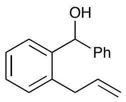
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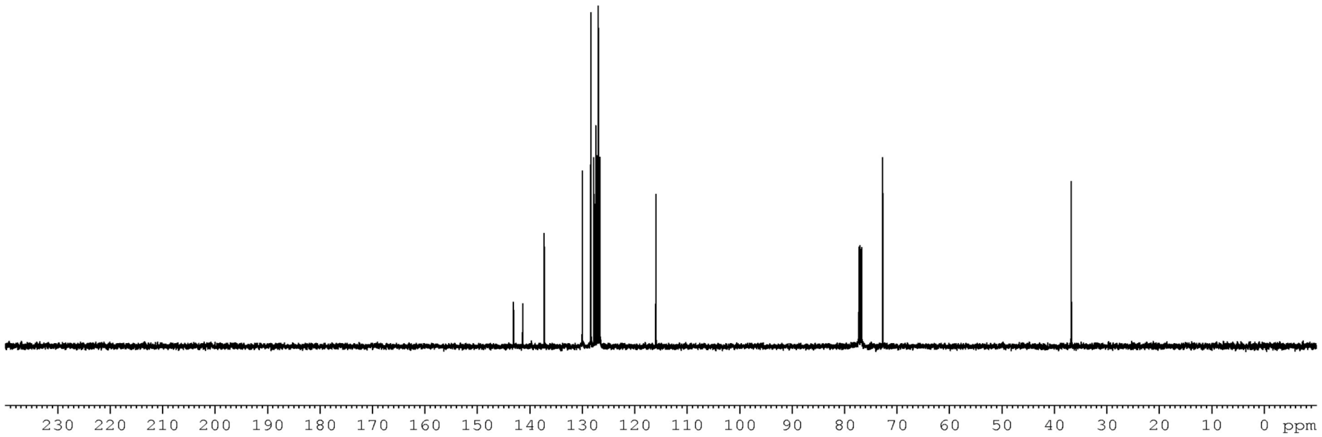
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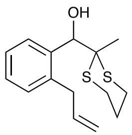

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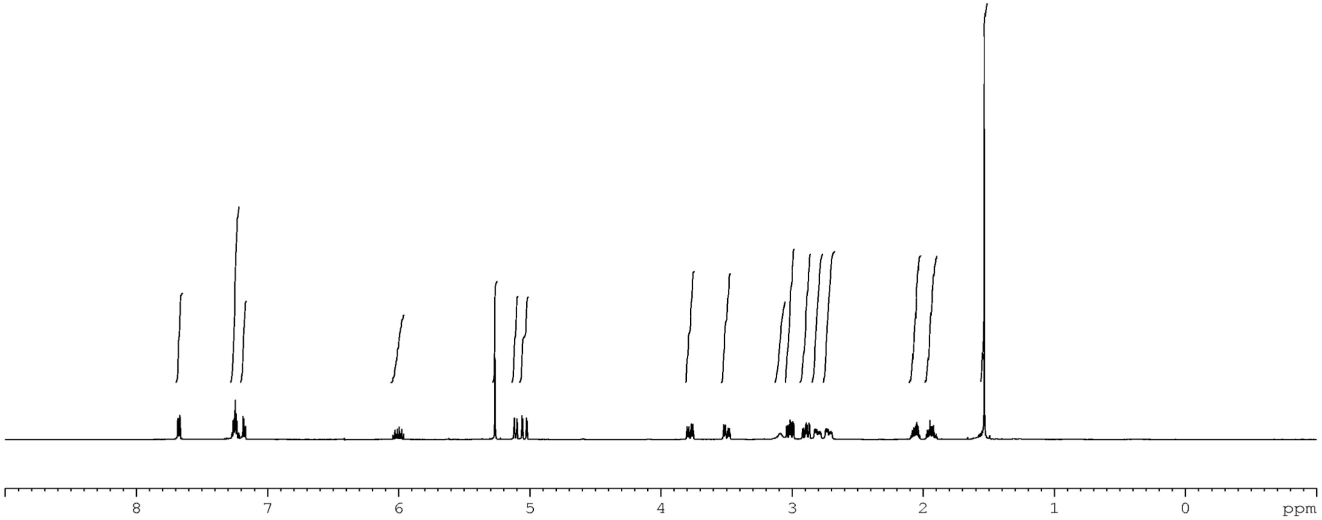

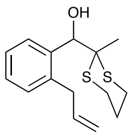
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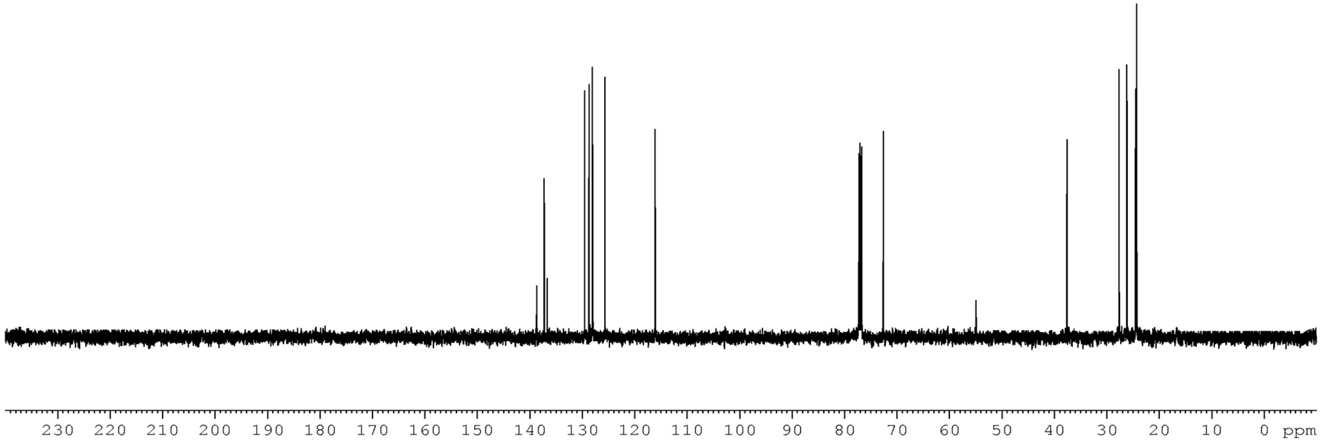
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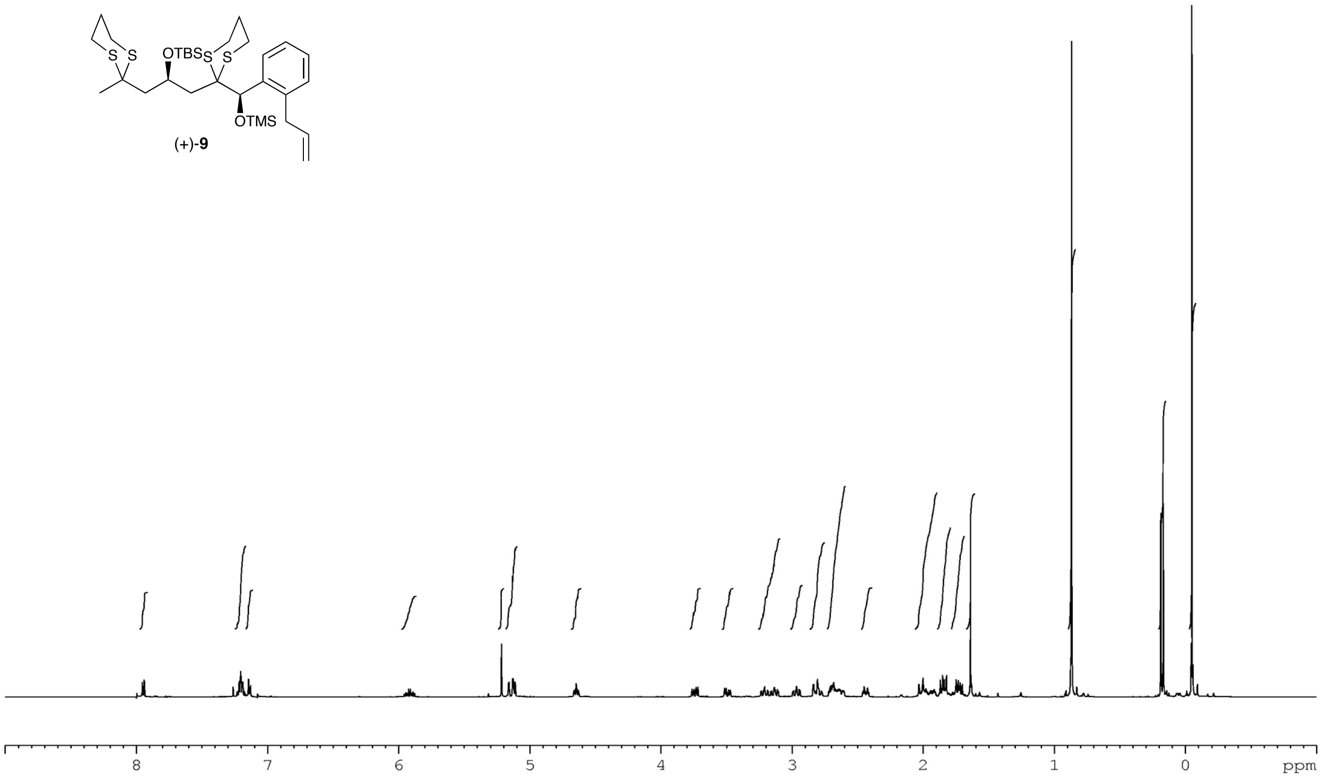

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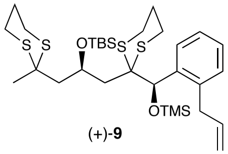

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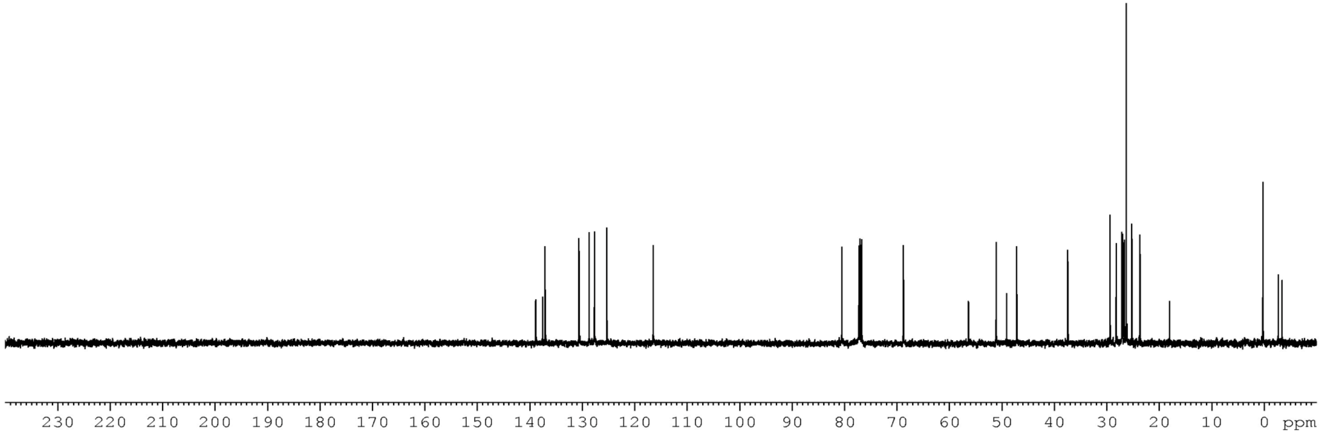

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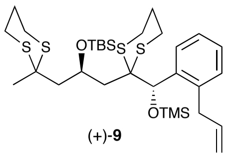

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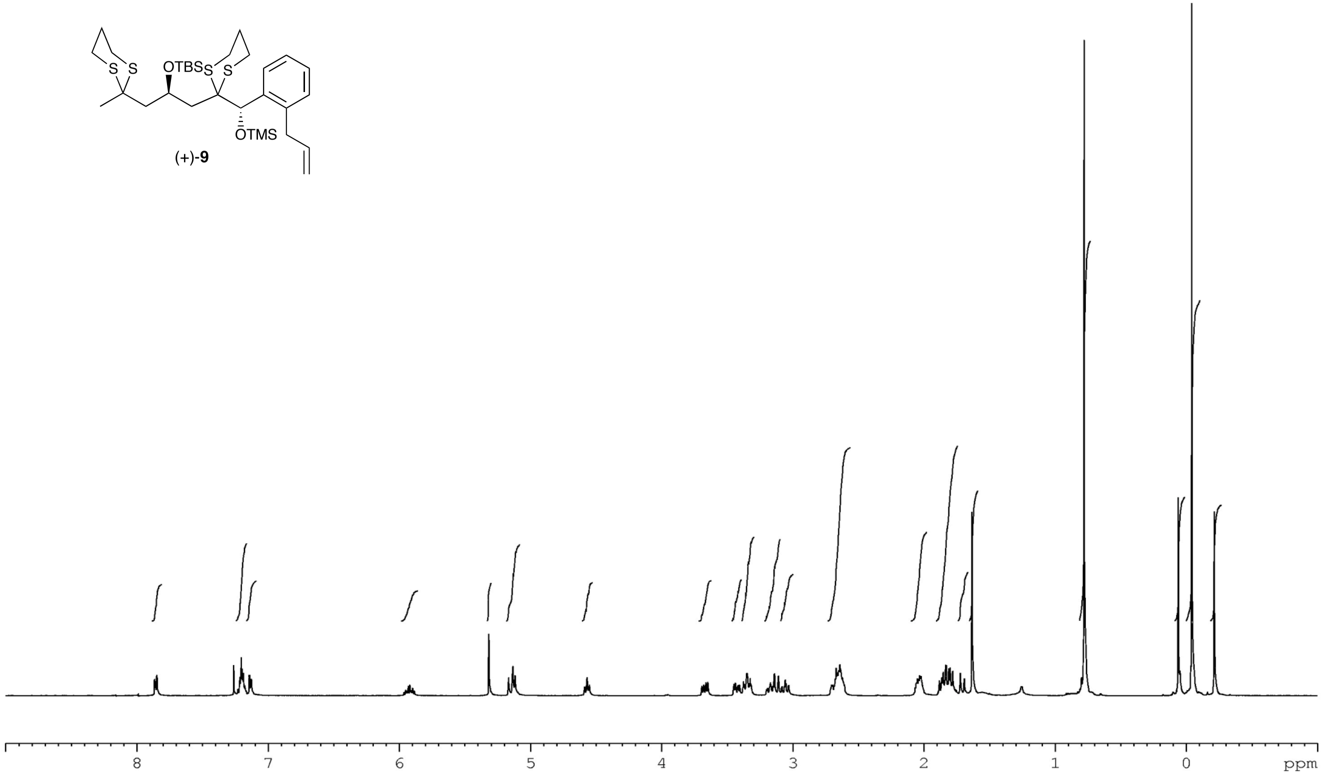

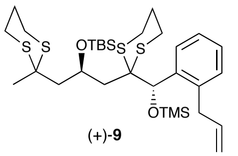
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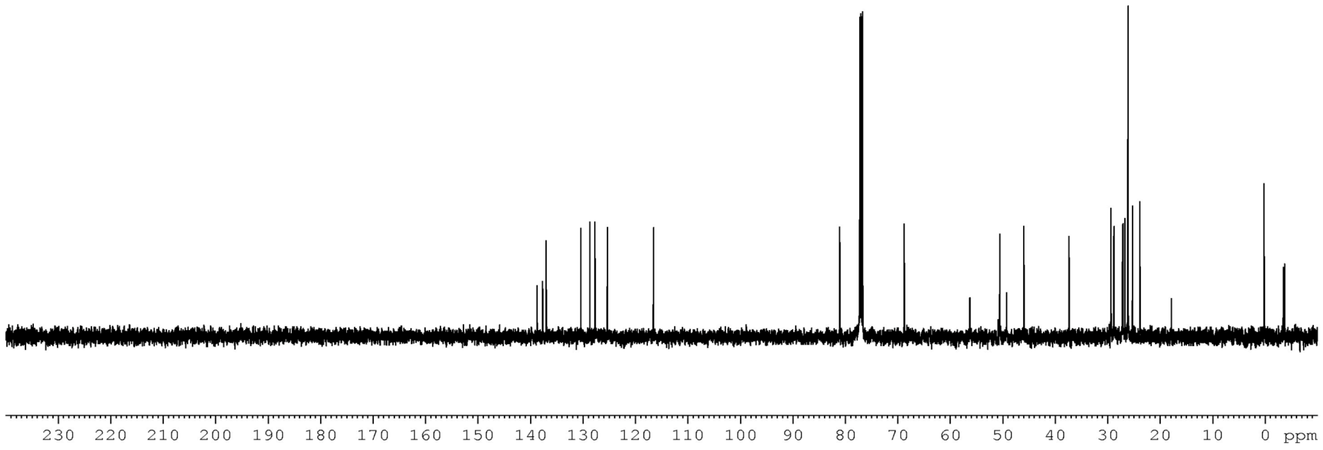
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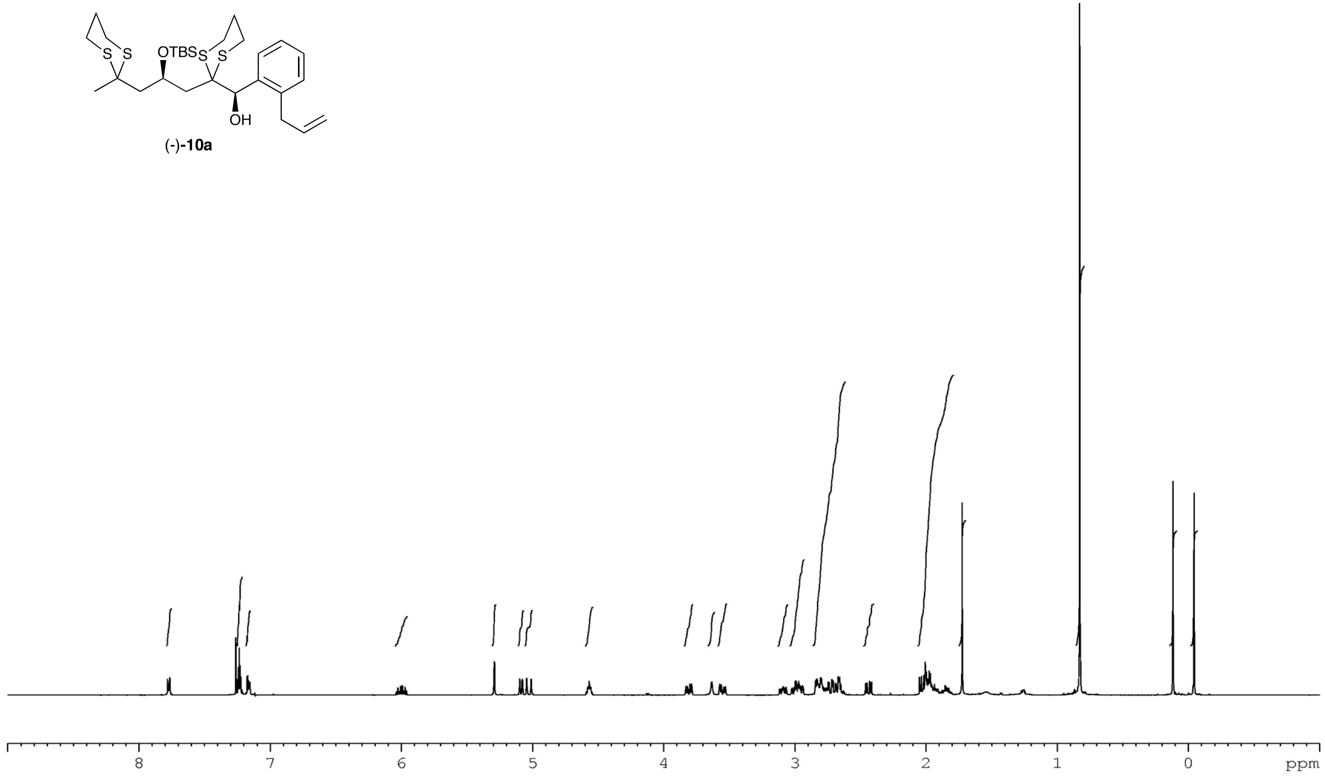

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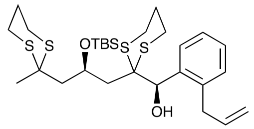

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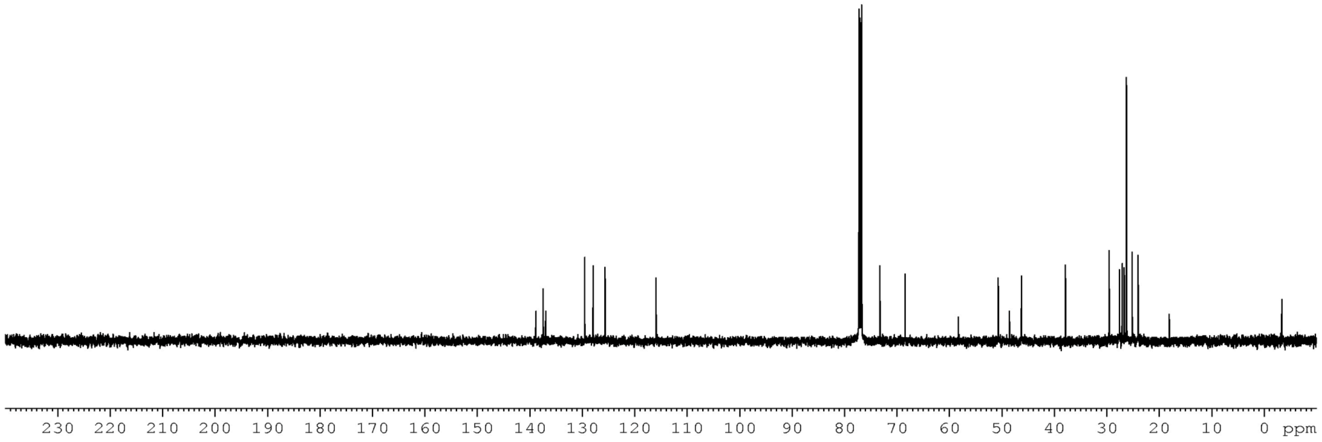
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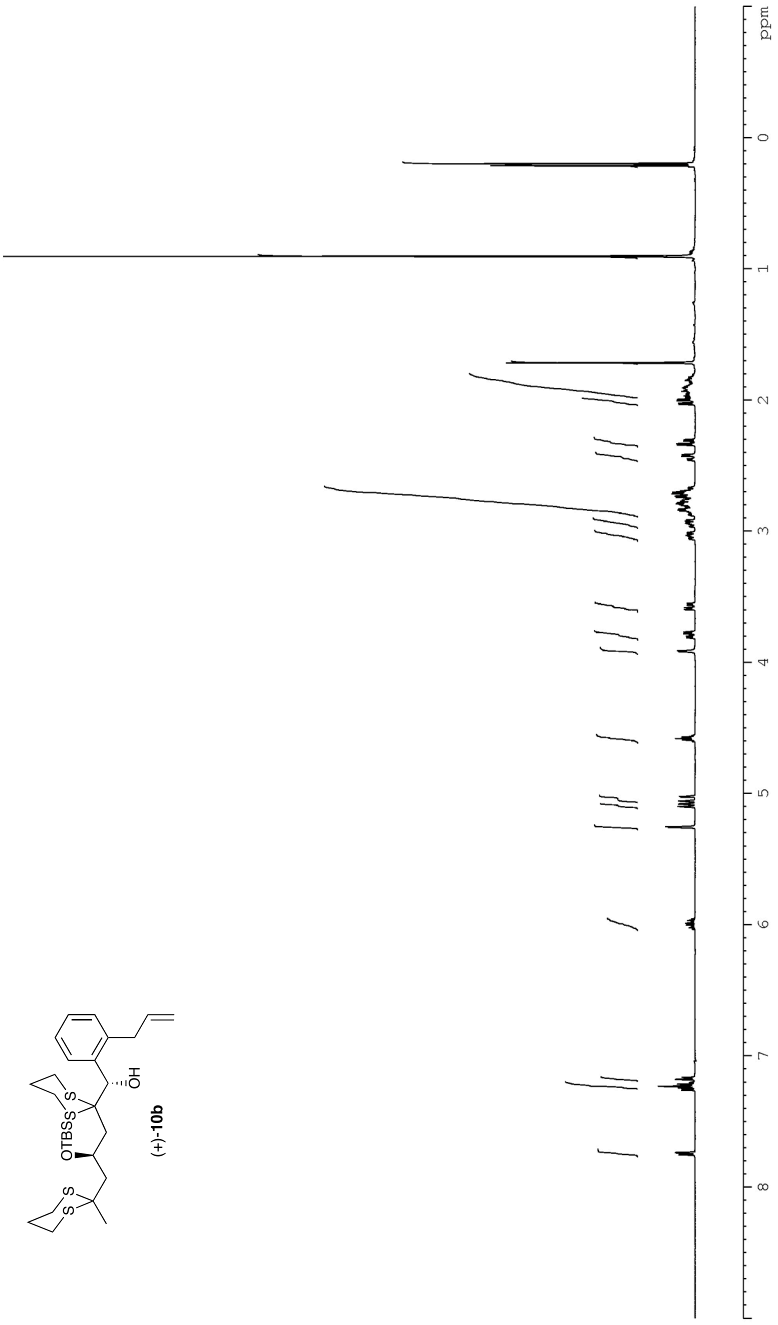
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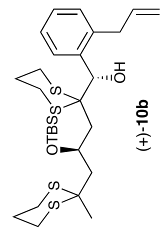

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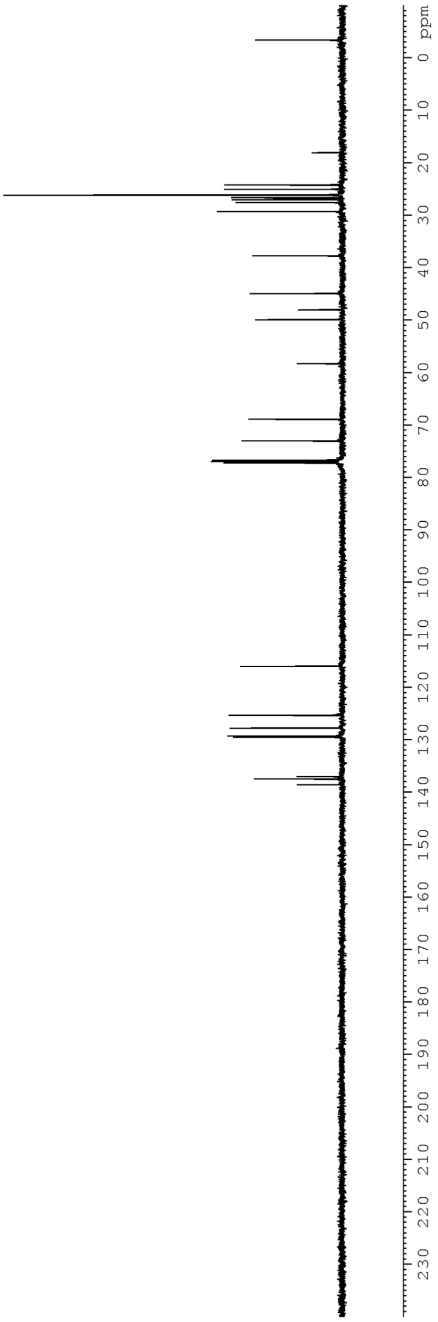

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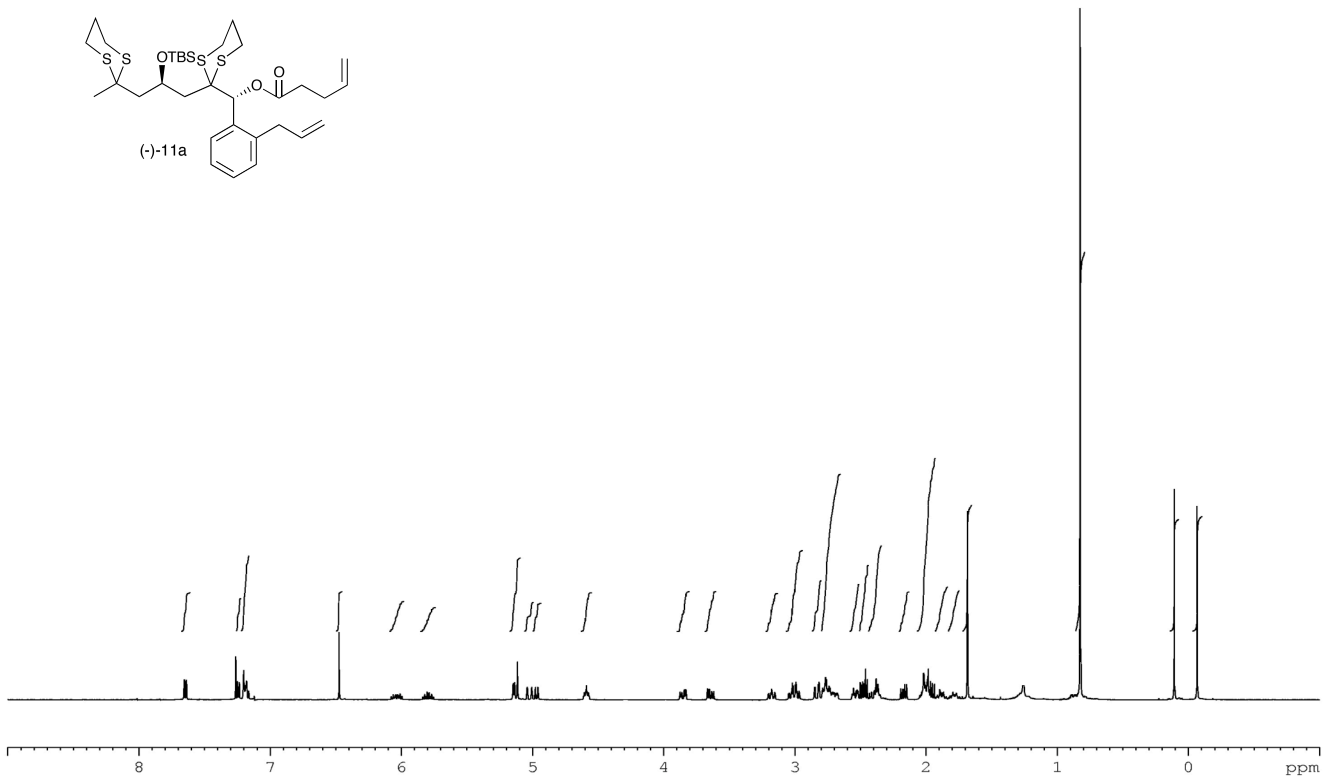
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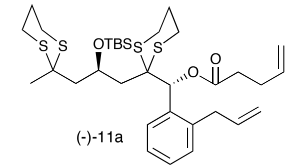

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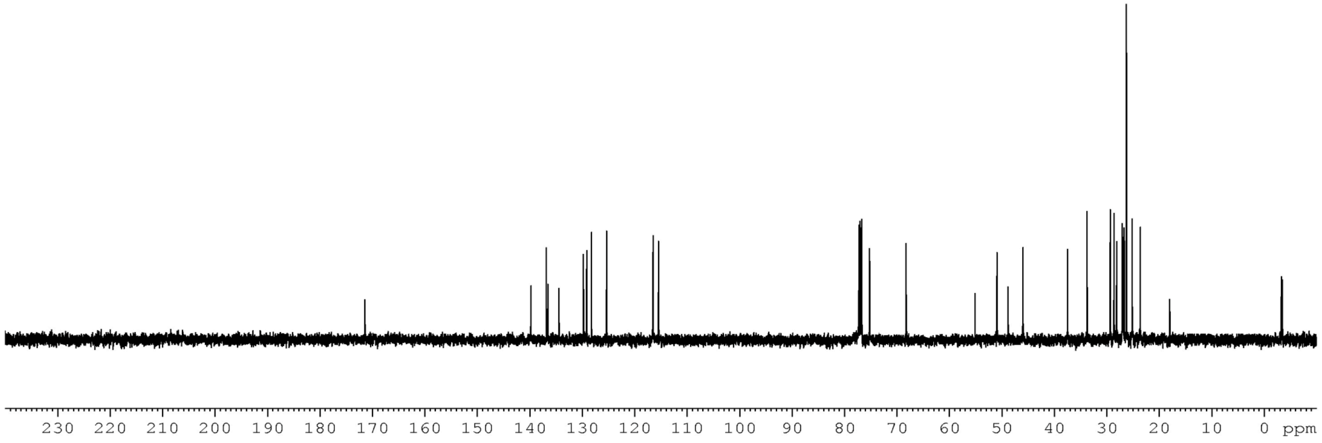
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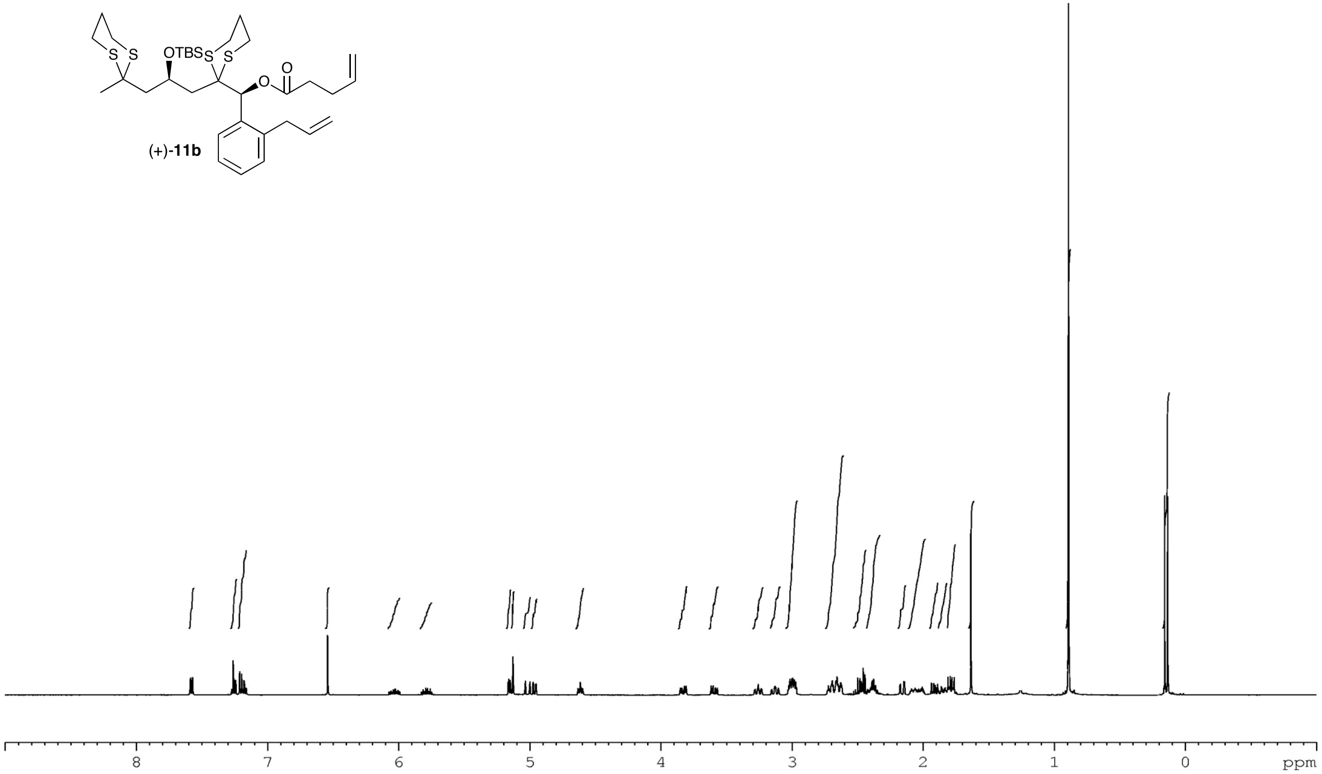

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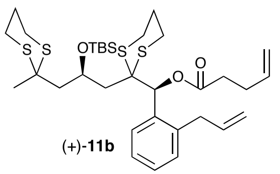
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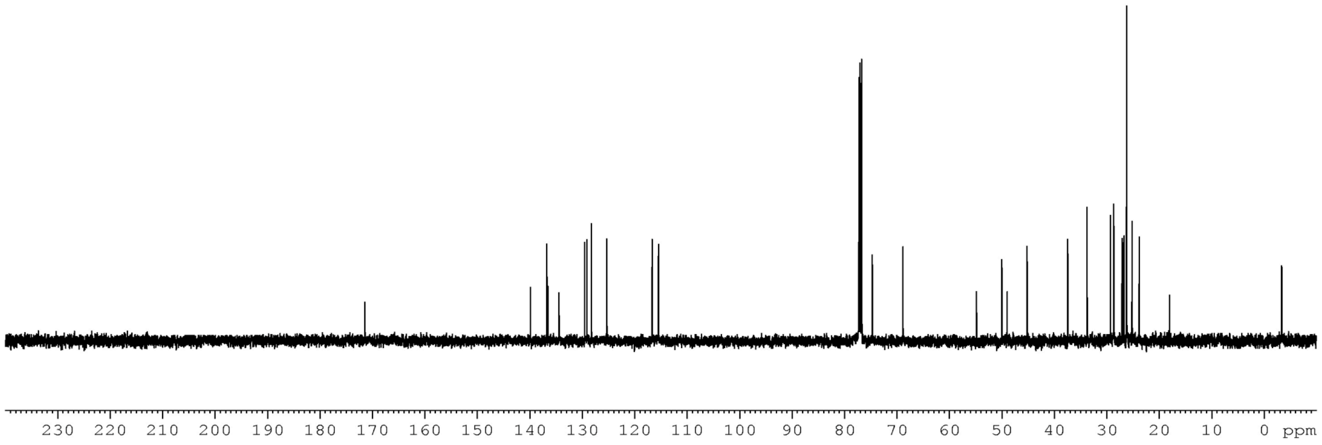
(+)-**11b**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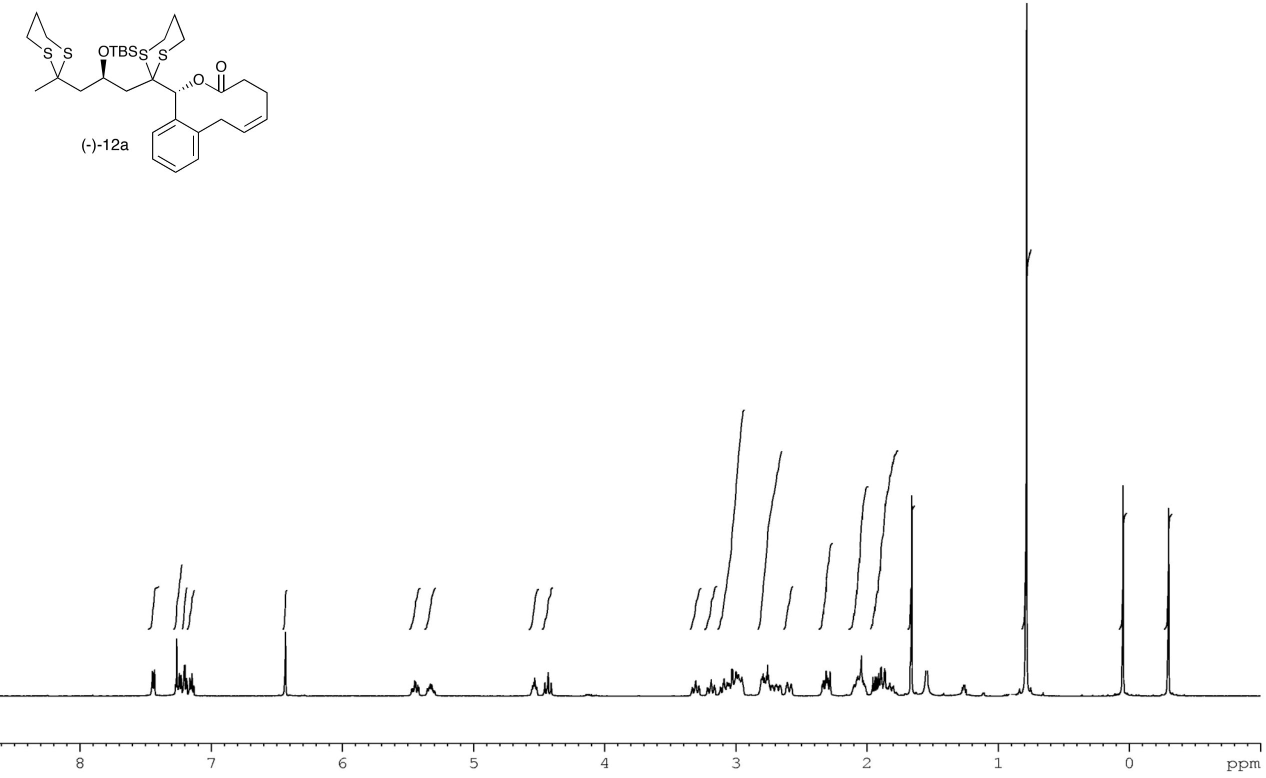
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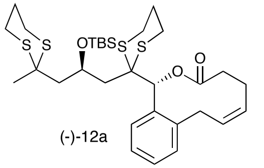
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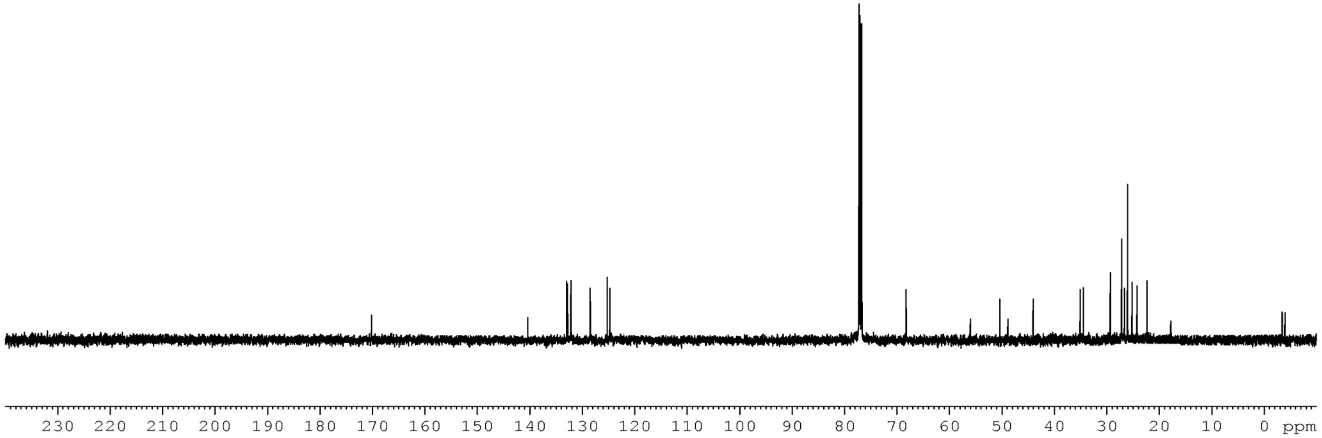
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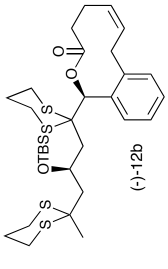

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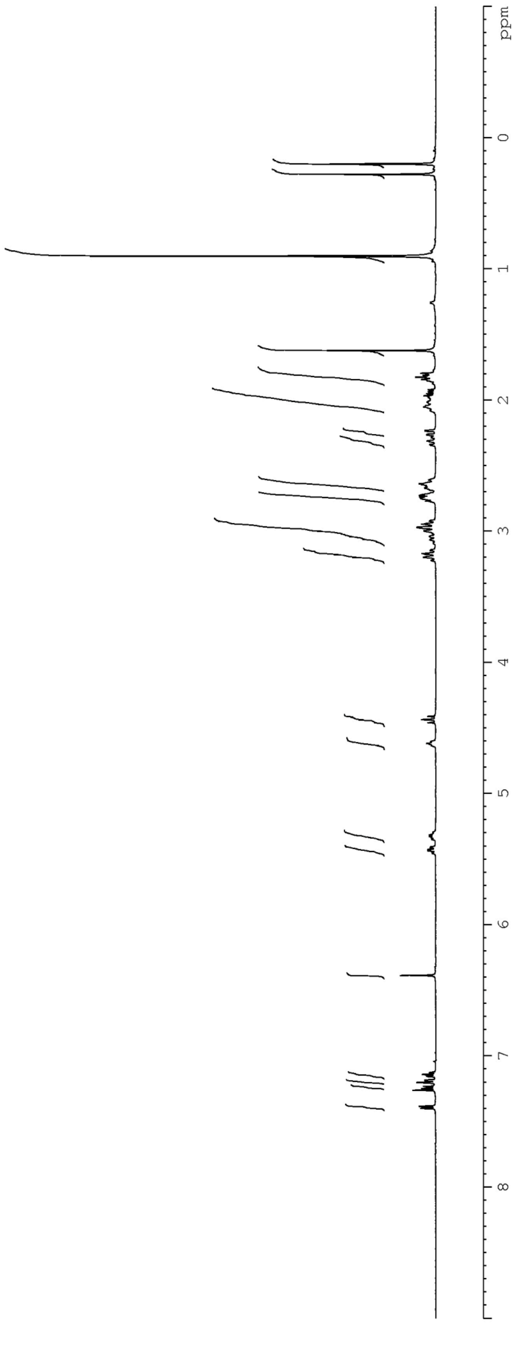

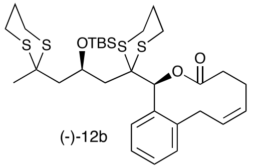

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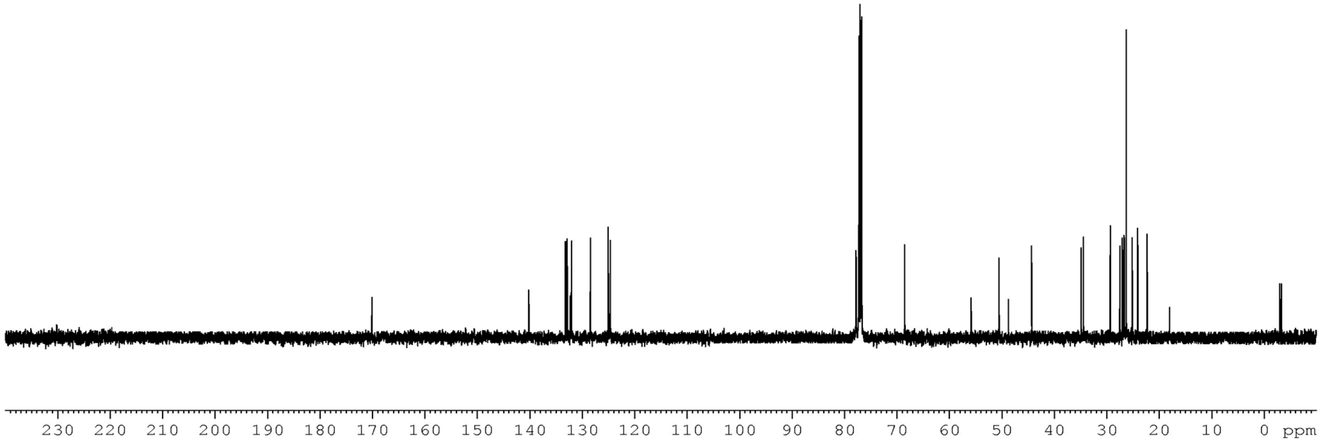
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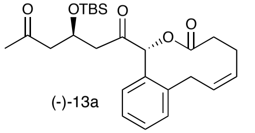

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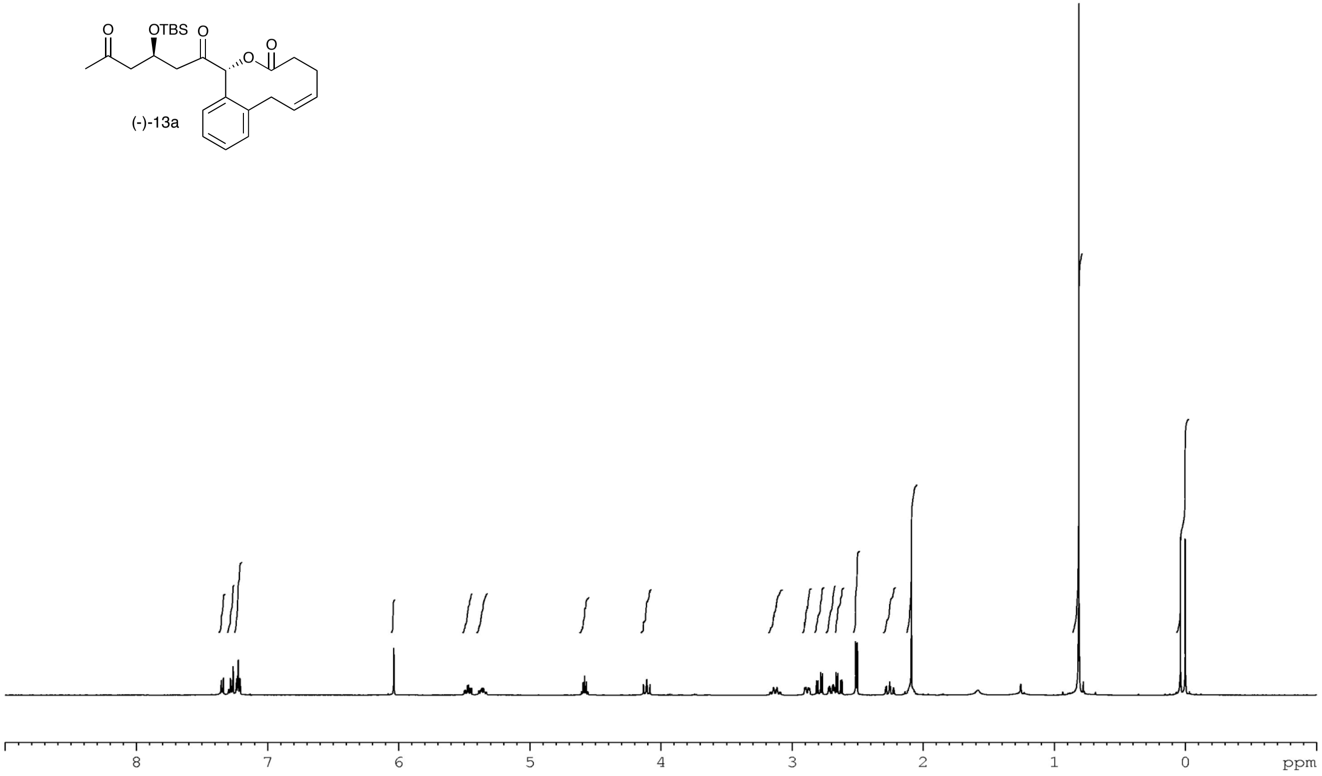

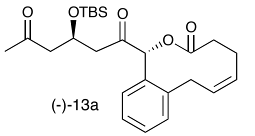

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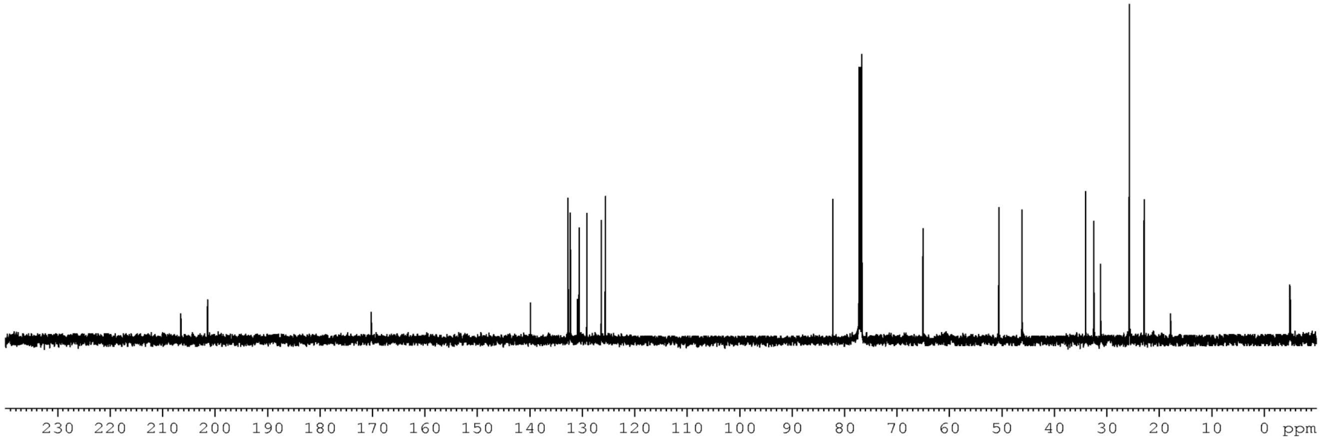

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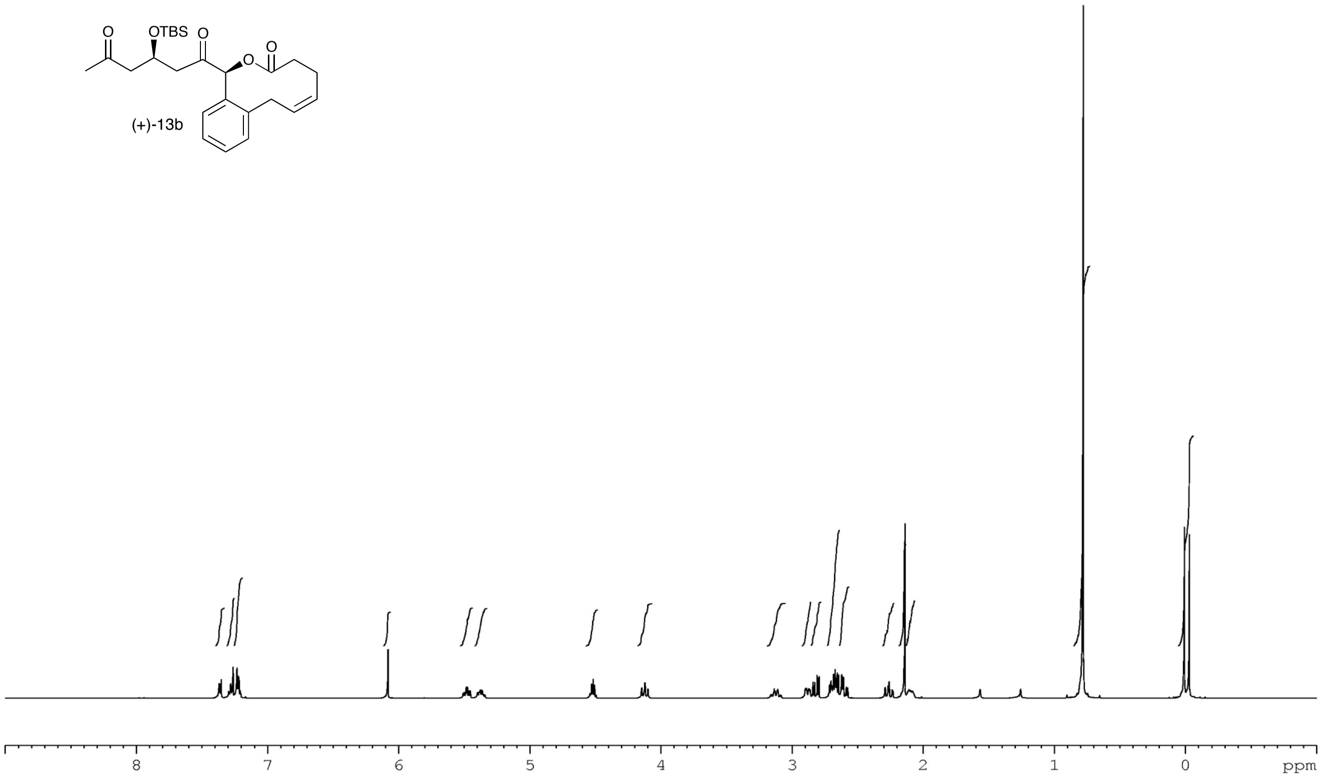

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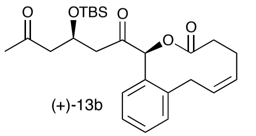

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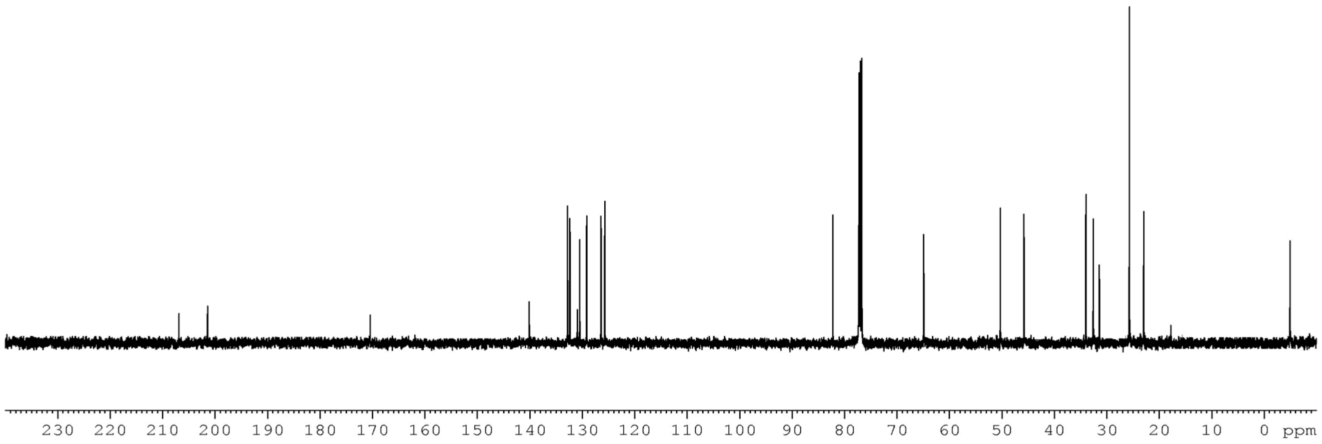
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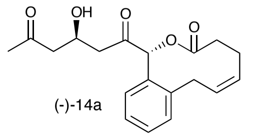

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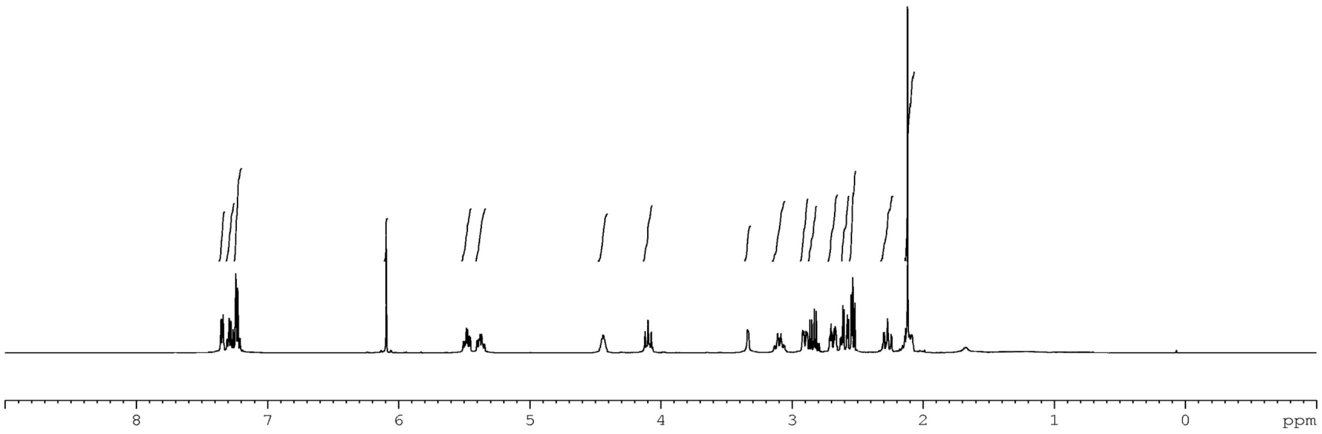

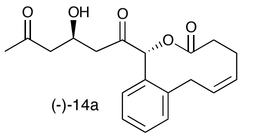

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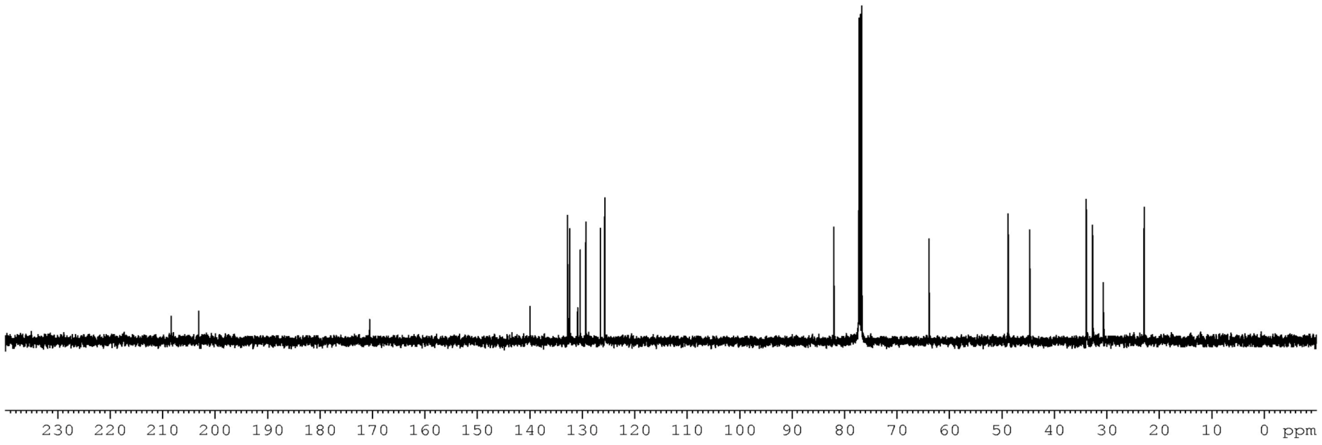
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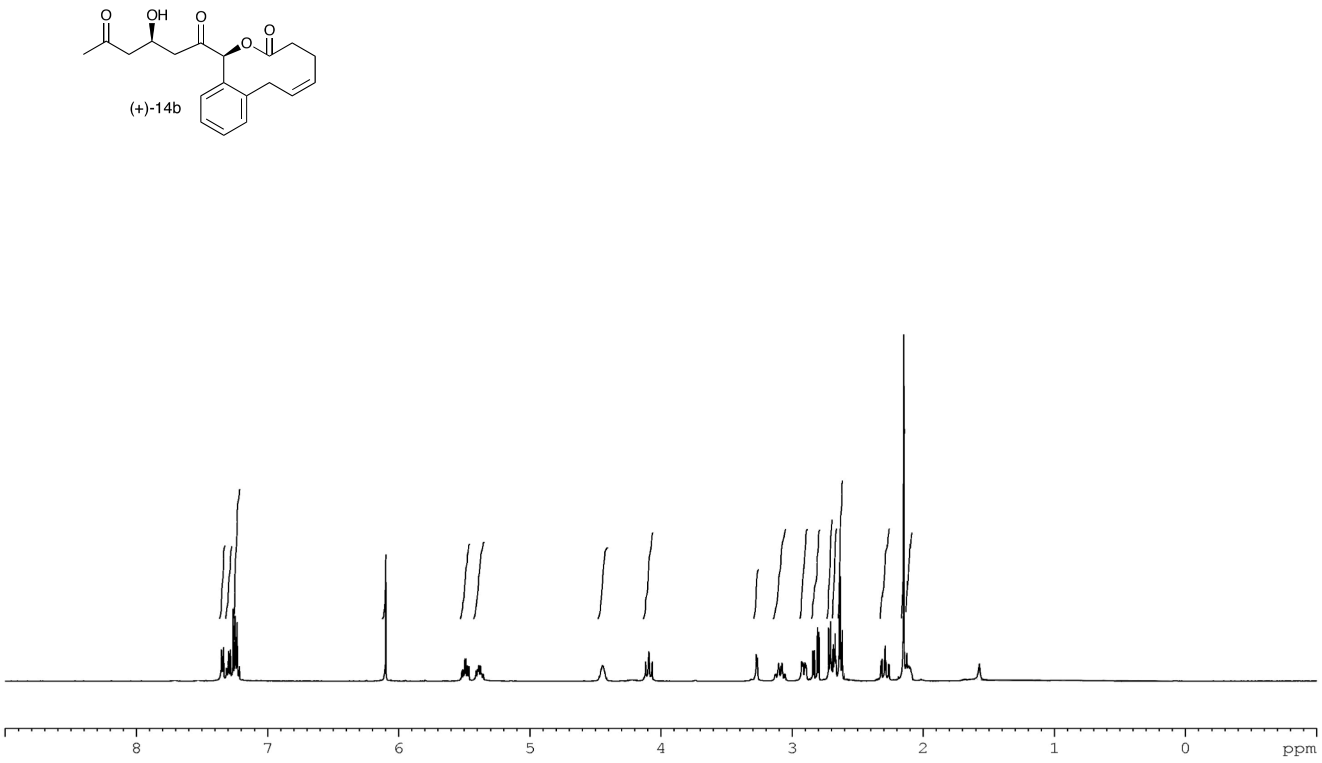

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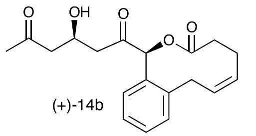
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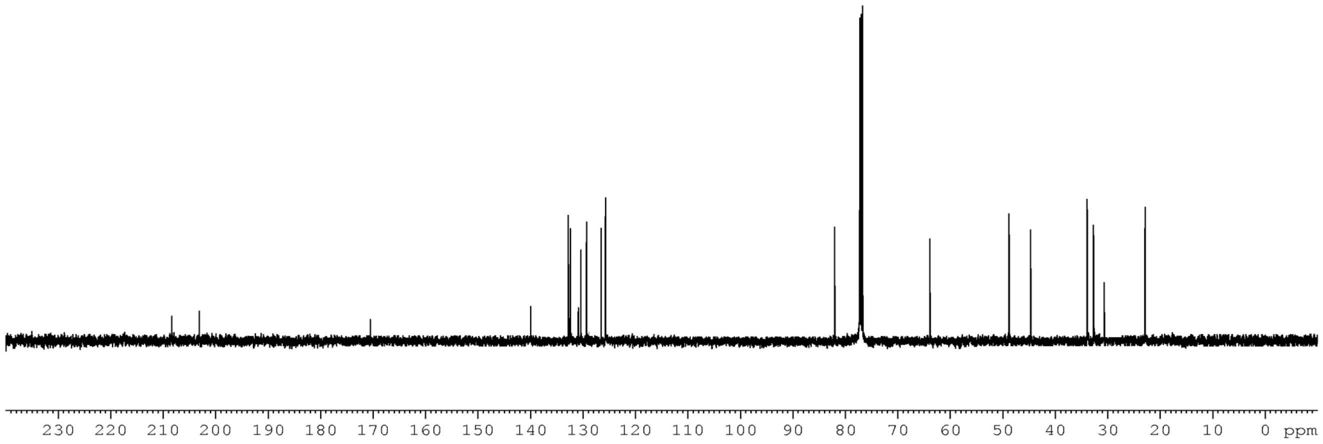
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