

Enantioselective Epoxidation of Conjugated *cis*-Enynes by Chiral Dioxirane

Christopher P. Burke and Yian Shi*

*Department of Chemistry
Colorado State University
Fort Collins, CO 80523*

Phone: 970-491-7424
Fax: 970-491-1801
Email: yian@lamar.colostate.edu

Supporting Information

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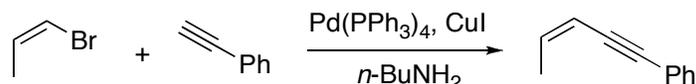
Synthesis and characterization of conjugated *cis*-enynes and epoxides.

General Methods. All commercially available reagents were used without further purification. All glassware used for the epoxidation was carefully washed with soap and water to be free of any trace metals which catalyze the decomposition of Oxone. Column chromatography was performed with silica gel (200-400 mesh). Solvents were evaporated under reduced pressure. Melting points are uncorrected.

Representative procedure for Sonogashira coupling: Pd(PPh₃)₄ (0.60 g, 0.50 mmol) was added at rt to a solution of vinyl halide (23.4 mmol) in benzene (25 mL) under Ar and was stirred for 45 min. A solution of alkyne (11.7 mmol) in *n*-BuNH₂ (12.0 mL, 120.0 mmol) was then added followed by CuI (0.35 g, 1.91 mmol) (the reaction is exothermic, so the flask was placed in a water bath before addition of CuI). After stirring at rt overnight, petroleum ether (or Et₂O) (50 mL) was added and the mixture was poured into sat. aq. NH₄Cl and extracted with more petroleum ether. The combined organic extracts were washed with sat. aq. NH₄Cl, H₂O, brine, dried (Na₂SO₄), and filtered. The residue was then concentrated and purified by column (pet. ether to 1:1 pet. ether-Et₂O).

Ratovelomana, V.; Linstumelle, G. *Synth. Commun.* **1981**, *11*, 917.

Table 1, entry 1



The enyne was prepared via Sonogashira coupling of *cis*-1-bromo-1-propene and phenylacetylene (87%): Colorless oil; IR (NaCl): 1490 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ

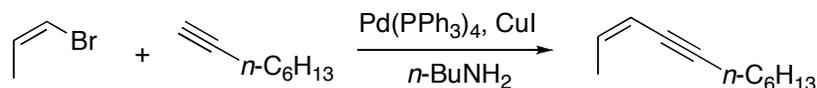
7.49-7.43 (m, 2H), 7.35-7.29 (m, 3H), 6.06 (dq, $J = 10.8, 6.9$ Hz, 1H), 5.71 (dq, $J = 10.8, 1.5$ Hz, 1H), 1.98 (dd, $J = 6.9, 1.5$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 138.9, 131.6, 128.5, 128.2, 123.9, 110.2, 94.1, 86.4, 16.3.



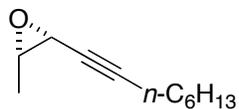
Colorless oil; $[\alpha]_{\text{D}}^{25} = -40.3$ (c 0.65, CHCl_3) (93% ee); IR (NaCl): 2227, 1490, 1349 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.49-7.45 (m, 2H), 7.35-7.30 (m, 3H), 3.65 (d, $J = 4.0$ Hz, 1H), 3.27 (qd, $J = 5.2, 4.0$ Hz, 1H), 1.51 (d, $J = 5.2$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 132.1, 128.9, 128.5, 122.3, 85.5, 84.3, 54.7, 46.1, 15.0.

(a) Lee, N.H.; Jacobsen, E.N. *Tetrahedron Lett.* **1991**, 32, 6533. (b) Sasaki, H.; Irie, R.; Hamada, T.; Suzuki, K.; Katsuki, T. *Tetrahedron* **1994**, 50, 11827. (c) Tian, H.; She, X.; Shu, L.; Yu, H.; Shi, Y. *J. Am. Chem. Soc.* **2000**, 122, 11551. (d) Tian, H.; She, X.; Yu, H.; Shu, L.; Shi, Y. *J. Org. Chem.* **2002**, 67, 2435.

Table 1, entry 2



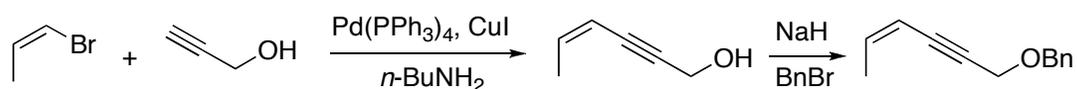
The enyne was prepared via Sonogashira coupling of *cis*-1-bromo-1-propene and 1-hexyne (82%): Colorless oil; IR (NaCl): 2931, cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.89 (dq, $J = 10.6, 6.8$ Hz, 1H), 5.50-5.45 (m, 1H), 2.35 (td, $J = 7.2, 2.0$ Hz, 2H), 1.86 (dd, $J = 6.8, 1.6$ Hz, 3H), 1.60-1.51 (m, 2H), 1.46-1.38 (m, 2H), 1.35-1.27 (m, 4H), 0.90 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 137.1, 110.6, 95.3, 77.3, 31.6, 29.1, 28.8, 22.8, 19.8, 15.9, 14.3.



Colorless oil; $[\alpha]_D^{25} = -34.2$ (c 0.37, CHCl_3) (90% ee); IR (NaCl): 2240, 1456, 1349 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 3.40 (dt, $J = 4.0, 1.6$ Hz, 1H), 3.11 (qd, $J = 5.2, 4.0$ Hz, 1H), 2.20 (td, $J = 7.2, 1.6$ Hz, 2H), 1.53-1.47 (m, 2H), 1.42-1.22 (m, 8H), 1.40 (d, $J = 5.2$ Hz, 3H), 0.88 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 86.8, 75.1, 54.1, 46.0, 31.5, 28.64, 28.60, 22.7, 19.0, 14.8, 14.2.

(a) Lee, N.H.; Jacobsen, E.N. *Tetrahedron Lett.* **1991**, 32, 6533. (b) Tian, H.; She, X.; Shu, L.; Yu, H.; Shi, Y. *J. Am. Chem. Soc.* **2000**, 122, 11551. (c) Tian, H.; She, X.; Yu, H.; Shu, L.; Shi, Y. *J. Org. Chem.* **2002**, 67, 2435.

Table 1, entry 3



The enyne alcohol was prepared via Sonogashira coupling of *cis*-1-bromo-1-propene and propargyl alcohol (56%): Yellow oil; IR (NaCl): 3334, 2199, 1363, 1011 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.01 (dq, $J = 10.8, 6.8$ Hz, 1H), 5.54-5.48 (m, 1H), 4.44 (d, $J = 2.4$ Hz, 2H), 1.88 (dd, $J = 6.8, 1.6$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 139.5, 109.5, 91.9, 82.6, 51.9, 16.2.

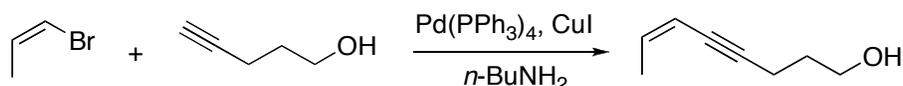
Sodium hydride (0.45 g of a 60% dispersion in mineral oil, 11.2 mmol) was placed in a flask and the mineral oil was removed by washing with pet. ether. THF (16 mL) was then added and the mixture was dropped to 0 °C. *cis*-4-Hexen-2-yn-1-ol (0.98 g, 10.2 mmol) was then added with stirring and the mixture was warmed to rt over about 0.5 h. Benzylbromide (1.75 g, 10.3 mmol) was added and the mixture was allowed to stir overnight. The reaction was then quenched by addition of water and the mixture was extracted with Et_2O . The combined organic phases were washed with brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by

column (pet. ether) to yield the benzyl ether as a colorless oil (1.10 g, 58%); IR (NaCl): 1355, 1088 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.41-7.28 (m, 5H), 6.03 (dq, $J = 10.8, 6.8$ Hz, 1H), 5.58-5.53 (m, 1H), 4.65 (s, 2H), 4.36 (d, $J = 2.0$ Hz, 2H), 1.91 (dd, $J = 6.8, 2.0$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 139.4, 137.8, 128.6, 128.3, 128.0, 109.7, 89.7, 83.4, 71.6, 58.1, 16.2.

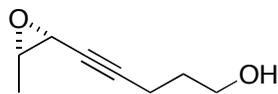


Colorless oil; $[\alpha]_{\text{D}}^{25} = -34.8$ (c 0.31, CHCl_3) (92% ee); IR (NaCl): 1348, 1074 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.28 (m, 5H), 4.61 (s, 2H), 4.24 (d, $J = 1.6$ Hz, 2H), 3.50 (dt, $J = 4.0, 1.6$ Hz, 1H), 3.20 (qd, $J = 5.6, 4.0$ Hz, 1H), 1.46 (d, $J = 5.6$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 137.4, 128.7, 128.3, 128.2, 81.7, 71.8, 57.5, 54.2, 45.6, 15.0. Anal. Calcd. for $\text{C}_{13}\text{H}_{14}\text{O}_2$: C, 77.20; H, 6.98. Found: C, 77.42; H, 6.70.

Table 1, entry 4

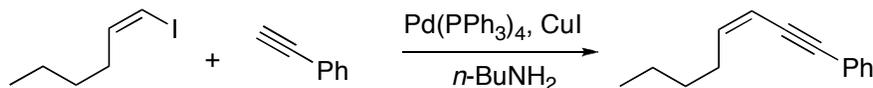


The enyne was prepared via Sonogashira coupling of *cis*-1-bromo-1-propene with 4-pentyn-1-ol (77%): Yellow oil; IR (NaCl): 3346, 1435, 1055 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.89 (dq, $J = 10.8, 6.8$ Hz, 1H), 5.48-5.42 (m, 1H), 3.77 (t, $J = 6.4$ Hz, 2H), 2.47 (td, $J = 6.8, 2.4$ Hz, 2H), 1.83 (dd, $J = 6.8, 1.6$ Hz, 3H), 1.81-1.78 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 137.4, 110.3, 94.0, 77.8, 61.8, 31.6, 16.2, 15.9.



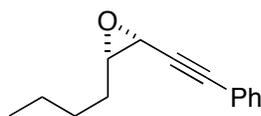
Colorless oil; $[\alpha]_D^{25} = -27.9$ (c 2.3, CHCl_3) (88% ee); IR (NaCl): 3384, 2241, 1350, 1055 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 3.76 (q, $J = 6.0$ Hz, 2H), 3.42 (dt, $J = 4.0, 2.0$ Hz, 1H), 3.14 (qd, $J = 5.6, 4.0$ Hz, 1H), 2.38 (td, $J = 7.2, 2.0$ Hz, 2H), 1.79 (quint., $J = 6.0$ Hz, 2H), 1.42 (d, $J = 5.6$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 85.9, 75.7, 61.7, 54.2, 46.0, 31.3, 15.5, 14.9. Anal. Calcd. for $\text{C}_8\text{H}_{12}\text{O}_2$: C, 68.54; H, 8.63. Found: C, 68.37; H, 8.68.

Table 1, entry 5



The enyne was prepared via Sonogashira coupling of *cis*-1-iodo-1-hexene* and phenylacetylene (76%): Colorless oil; IR (NaCl): 1466 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.32 (m, 2H), 7.25-7.19 (m, 3H), 5.89 (dt, $J = 10.8, 7.6$ Hz, 1H), 5.58 (dt, $J = 10.8, 1.2$ Hz, 1H), 2.32 (qd, $J = 7.6, 1.2$ Hz, 2H), 1.38-1.26 (m, 4H), 0.85 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 144.6, 131.6, 128.5, 128.2, 123.9, 109.2, 93.6, 86.7, 31.2, 30.3, 22.5, 14.1.

* Prepared according to the reported procedure: Dieck, H.A.; Heck, R.F. *J. Org. Chem.* **1975**, *40*, 1083.

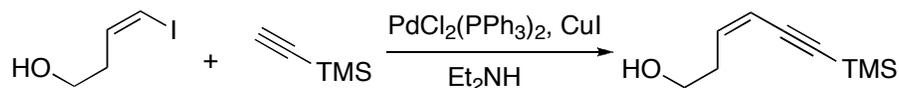


Colorless oil; $[\alpha]_D^{25} = -3.6$ (c 0.42, CHCl_3) (84% ee); IR (NaCl): 2227, 1491 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.48-7.44 (m, 2H), 7.36-7.29 (m, 3H), 3.66 (d, $J = 4.4$ Hz, 1H), 3.14 (td, $J = 6.0, 4.4$ Hz, 1H), 1.87-1.72 (m, 2H), 1.59-1.40 (m, 4H), 0.96 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR

(101 MHz, CDCl₃) δ 132.1, 128.9, 128.5, 122.4, 85.4, 84.5, 58.9, 45.9, 29.4, 28.3, 22.7, 14.3.

Anal. Calcd. for C₁₄H₁₆O: C, 83.96; H, 8.05. Found: C, 84.04; H, 7.78.

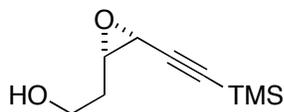
Table 1, entry 6



The enyne was prepared via Sonogashira coupling via a slightly different procedure than before:* to a solution of *cis*-4-iodo-3-buten-1-ol** (2.04 g, 10.3 mmol) in Et₂NH (10 mL) under Ar at rt was added PdCl₂(PPh₃)₂ (0.09 g, 0.13 mmol), CuI (0.49 g, 2.6 mmol), and trimethylsilylacetylene (1.01 g, 10.3 mmol) with stirring. After 2 h the mixture was diluted with Et₂O (50 mL), washed with H₂O, brine, dried (Na₂SO₄), filtered, and concentrated. The residue was then purified by column (9:1 to 3:2 pet. ether-EtOAc) to yield the enyne as a colorless oil (1.38 g, 80%): IR (NaCl): 3344, 2149, 1250 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.97 (dt, *J* = 10.8, 7.2 Hz, 1H), 5.59 (d, *J* = 10.8 Hz, 1H), 3.71 (t, *J* = 6.8 Hz, 2H), 2.58 (dt, *J* = 7.2, 6.8 Hz, 2H), 1.36 (s, 1H), 0.17 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 141.0, 111.9, 101.8, 99.7, 62.0, 34.0, 0.2.

*Marshall, J.A.; Bourbeau, M.P. *Org. Lett.* **2002**, *4*, 3931.

Prepared according to the reported procedure: Denmark, S.E.; Yang, S.M. *J. Am. Chem. Soc.* **2002, *124*, 2102.

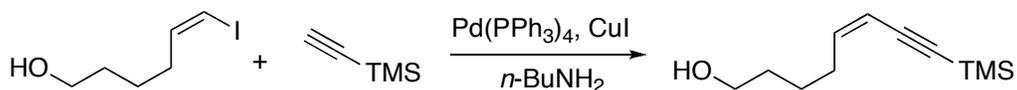


Colorless oil (note: epoxide should be purified by column without buffering with Et₃N); $[\alpha]_D^{25} = -42.6$ (*c* 0.31, CHCl₃) (94% ee); IR (NaCl): 3404, 2173, 1251 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.90 (td, *J* = 6.0, 1.6 Hz, 2H), 3.48 (d, *J* = 4.0, 1H), 3.26-3.22 (m, 1H), 2.08-1.92 (m,

2H), 0.19 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 100.3, 92.0, 60.2, 56.2, 45.2, 32.5, -0.1. Anal. Calcd. for $\text{C}_9\text{H}_{16}\text{O}_2\text{Si}$: C, 58.65; H, 8.75. Found: C, 58.90; H, 8.90.

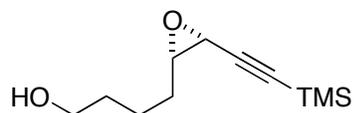
Mukai, C.; Sugimoto, Y-i.; Ikeda, Y.; Hanaoka, M. *Chem. Commun.* **1994**, 1161.

Table 1, entry 7

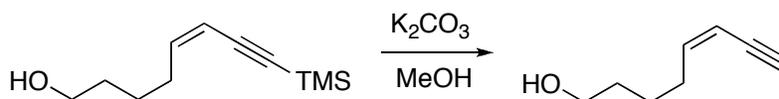


The enyne was prepared via Sonogashira coupling of *cis*-6-iodo-5-hexen-1-ol* and trimethylsilylacetylene (62%): Yellow oil; IR (NaCl): 3346, 2150, 1250 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.95 (dt, $J = 10.8, 7.6$ Hz, 1H), 5.51 (dt, $J = 10.8, 1.6$ Hz, 1H), 3.68 (t, $J = 6.4$ Hz, 2H), 2.37 (qd, $J = 7.6, 1.6$ Hz, 2H), 1.66-1.47 (m, 4H), 1.36 (s, 1H), 0.21 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 145.1, 109.8, 102.2, 99.0, 62.9, 32.3, 30.1, 25.0, 0.2.

* Prepared according to the reported procedure: Denmark, S.E.; Yang, S.M. *J. Am. Chem. Soc.* **2002**, *124*, 2102.

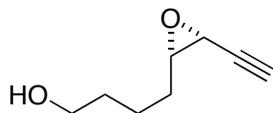


Colorless oil; $[\alpha]_{\text{D}}^{25} = -20.6$ (c 0.35, CHCl_3) (87% ee); IR (NaCl): 3383, 2176, 1251 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 3.69 (q, $J = 6.4$ Hz, 2H), 3.43 (d, $J = 4.0$ Hz, 1H), 3.04 (td, $J = 6.0, 4.0$ Hz, 1H), 1.83-1.56 (m, 6H), 0.19 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 100.5, 91.5, 62.9, 58.3, 45.5, 32.6, 29.2, 22.3, -0.1. Anal. Calcd. for $\text{C}_{11}\text{H}_{20}\text{O}_2\text{Si}$: C, 62.21; H, 9.49. Found: C, 62.20; H, 9.41.

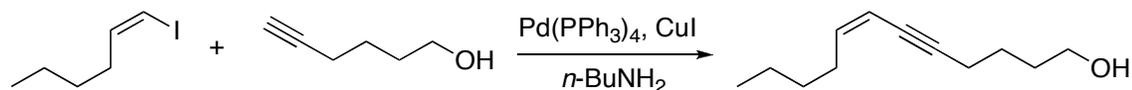
Table 1, entry 8

The desilylation was carried out according to the reported method:* *cis*-8-Trimethylsilyloct-5-en-7-yn-1-ol (0.71 g, 3.4 mmol) was treated with saturated methanolic K_2CO_3 solution (10.6 mL) and stirred at rt until the starting material disappeared as judged by TLC. The mixture was then extracted with Et_2O , and the combined organic layers were washed with brine, dried (Na_2SO_4), filtered and concentrated. The residue was purified by column (1:2 pet. ether- Et_2O) to yield the desilylated enyne as a colorless oil (0.42 g, 48%): IR (NaCl): 3289, 2096, 1066 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 6.01 (dt, $J = 10.8, 7.2$ Hz, 1H), 5.50-5.46 (m, 1H), 3.68 (t, $J = 6.0$ Hz, 2H), 3.09 (d, $J = 2.0$ Hz, 1H), 2.38 (qd, $J = 7.2, 1.2$ Hz, 2H), 1.66-1.58 (m, 2H), 1.56-1.47 (m, 2H), 1.40 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 108.7, 81.6, 80.7, 62.9, 32.3, 30.1, 25.1.

* Cai, C.; Vasella, A. *Helv. Chim. Acta* **1995**, 78, 732.

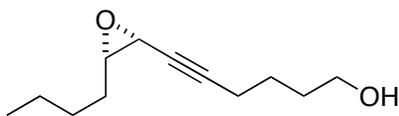


Colorless oil; $[\alpha]_D^{25} = -40.0$ (c 0.12, $CHCl_3$) (80% ee); IR (NaCl): 3382, 3291, 2120 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 3.69 (t, $J = 6.0$ Hz, 2H), 3.43 (dd, $J = 4.0, 1.8$ Hz, 1H), 3.05 (td, $J = 6.0, 4.0$ Hz, 1H), 2.36 (d, $J = 1.8$ Hz, 1H), 1.82-1.56 (m, 6H), 1.42 (brs, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 79.1, 73.9, 62.8, 57.9, 44.9, 32.5, 29.1, 22.4. Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.38; H, 8.39.

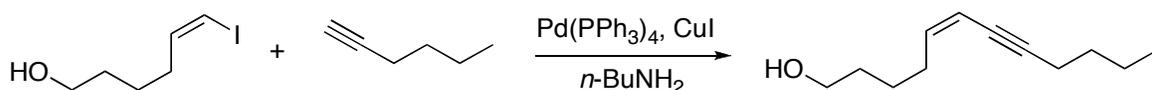
Table 1, entry 9

The enyne was prepared via Sonogashira coupling of *cis*-1-iodo-1-hexene* and 5-hexyn-1-ol (71%): Orange oil; IR (NaCl): 3344, 2213, 1721, 1061 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.83 (dt, *J* = 10.8, 7.2 Hz, 1H), 5.46-5.41 (m, 1H), 3.70 (t, *J* = 6.2 Hz, 2H), 2.40 (td, *J* = 6.8, 2.0 Hz, 2H), 2.30 (q, *J* = 7.2 Hz, 2H), 1.76-1.60 (m, 4H), 1.43-1.32 (m, 4H), 0.92 (t, *J* = 6.8, Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 143.1, 109.4, 94.0, 78.0, 62.7, 32.1, 31.2, 30.0, 25.3, 22.5, 19.5, 14.1.

* Dieck, H.A.; Heck, R.F. *J. Org. Chem.* **1975**, *40*, 1083.

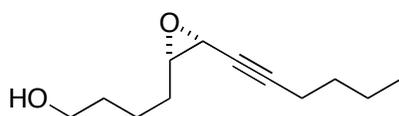


Colorless oil; [α]_D²⁵ = -14.1 (*c* 0.26, CHCl₃) (80% ee); IR (NaCl): 3385, 2240, 1457, 1061 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.68 (t, *J* = 6.4 Hz, 2H), 3.42 (dt, *J* = 4.4, 2.0 Hz, 1H), 3.00 (td, *J* = 6.0, 4.4 Hz, 1H), 2.29 (td, *J* = 6.8, 2.0 Hz, 2H), 1.77-1.36 (m, 10H), 1.26 (brs, 1H), 0.94 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 86.2, 75.7, 62.6, 58.3, 45.7, 32.0, 29.2, 28.3, 24.9, 22.7, 18.8, 14.2. Anal. Calcd. for C₁₂H₂₀O₂: C, 73.43; H, 10.27. Found: C, 73.19; H, 10.26.

Table 1, entry 10

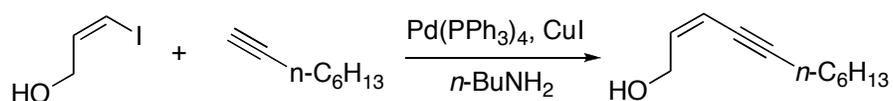
The enyne was prepared via Sonogashira coupling of *cis*-6-iodo-5-hexen-1-ol* and 1-hexyne (63%): Orange oil; IR (NaCl): 3333, 2210, 1458, 1061 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.81 (dt, $J = 10.8, 7.4$ Hz, 1H), 5.49-5.44 (m, 1H), 3.67 (t, $J = 6.6$ Hz, 2H), 2.37-2.30 (m, 4H), 1.66-1.28 (m, 8H), 0.93 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 142.1, 110.1, 94.9, 77.4, 63.0, 32.4, 31.2, 29.8, 25.2, 22.2, 19.4, 13.8.

* Prepared according to the reported procedure: Denmark, S.E.; Yang, S.M. *J. Am. Chem. Soc.* **2002**, *124*, 2102.



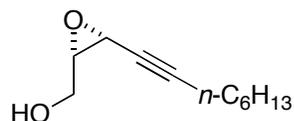
Colorless oil; $[\alpha]_{\text{D}}^{25} = -8.2$ (c 0.65, CHCl_3) (90% ee); IR (NaCl): 3358, 2239, 1458 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 3.69 (q, $J = 6.0$ Hz, 2H), 3.43 (dt, $J = 4.0, 1.6$ Hz, 2H), 3.01 (td, $J = 6.0, 4.0$ Hz, 1H), 2.23 (td, $J = 6.8, 1.6$ Hz, 2H), 1.81-1.28 (m, 10H), 0.91 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 86.9, 75.1, 62.9, 58.1, 45.8, 32.6, 30.7, 29.2, 22.4, 22.1, 18.7, 13.8. Anal. Calcd. for $\text{C}_{12}\text{H}_{20}\text{O}_2$: C, 73.43; H, 10.27. Found: C, 73.14; H, 10.15.

Table 1, entry 11



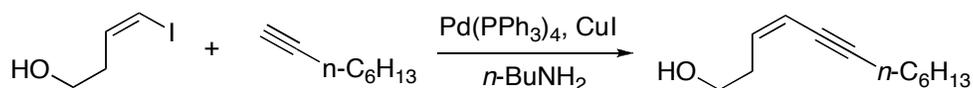
The enyne was prepared via Sonogashira coupling of *cis*-3-iodo-2-propen-1-ol* and 1-octyne (85%): Orange oil; IR (NaCl): 3326, 2216, 1020 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.01(dt, $J = 11.0, 6.4$ Hz, 1H), 5.61-5.56 (m, 1H), 4.40 (dd, $J = 6.4, 1.2$ Hz, 2H), 2.34 (td, $J = 6.8, 2.0$ Hz, 2H), 1.63 (s, 1H), 1.58-1.51 (m, 2H), 1.44-1.26 (m, 6H), 0.90 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 140.0, 111.5, 97.1, 76.4, 61.2, 31.5, 28.9, 28.8, 22.8, 19.7, 14.2.

*Prepared according to the reported procedure: Denmark, S.E.; Yang, S.M. *J. Am. Chem. Soc.* **2002**, *124*, 2102.



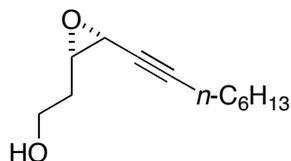
Colorless oil (note: epoxide should be purified by column without buffering with Et₃N); $[\alpha]_D^{25} = -41.4$ (*c* 0.22, CHCl₃) (97% ee); IR (NaCl): 3416, 2234, 1044 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.98-3.89 (m, 1H), 3.88-3.82 (m, 1H), 3.54 (dt, *J* = 4.4, 1.6 Hz, 1H), 3.26 (td, *J* = 6.0, 4.4 Hz, 1H), 2.22 (td, *J* = 7.2, 1.6 Hz, 2H), 1.70 (brs, 1H), 1.52 (quint., *J* = 7.2 Hz, 2H), 1.44-1.24 (m, 6H), 0.90 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 87.7, 74.3, 62.4, 57.4, 44.9, 31.5, 28.7, 28.5, 22.7, 19.0, 14.2. Anal. Calcd. for C₁₁H₁₈O₂: C, 72.49; H, 9.95. Found: C, 72.66; H, 9.71.

Table 1, entry 12



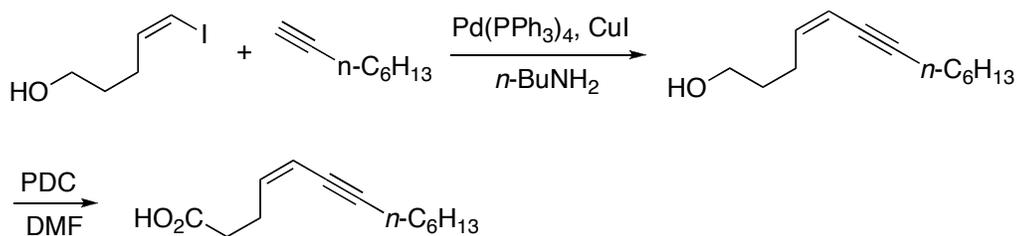
The enyne was prepared via Sonogashira coupling of *cis*-4-iodo-3-buten-1-ol* and 1-octyne (83%): Orange oil; IR (NaCl): 3330, 2217, 1048 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.87 (dt, *J* = 10.8, 7.2 Hz, 1H), 5.64-5.58 (m, 1H), 3.73 (q, *J* = 6.0 Hz, 2H), 2.58 (qd, *J* = 6.4, 1.2 Hz, 2H), 2.34 (td, *J* = 7.2, 2.0 Hz, 2H), 1.59-1.51 (m, 2H), 1.45-1.27 (m, 6H), 0.90 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 137.9, 112.5, 95.6, 62.2, 33.8, 31.5, 29.0, 28.8, 22.8, 19.7, 14.3.

*Prepared according to the reported procedure: Denmark, S.E.; Yang, S.M. *J. Am. Chem. Soc.* **2002**, *124*, 2102.



Colorless oil (note: epoxide should be purified by column without buffering with Et₃N); $[\alpha]_D^{25} = -36.8$ (*c* 0.37, CHCl₃) (97% ee); IR (NaCl): 3418, 2237, 1051 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.92-3.88 (m, 2H), 3.48 (dt, *J* = 6.0, 1.6 Hz, 1H), 3.23-3.19 (m, 1H), 2.23 (td, *J* = 7.2, 1.6 Hz, 2H), 2.06-1.91 (m, 2H), 1.62-1.24 (m, 8H), 0.90 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 87.5, 75.0, 60.4, 56.0, 45.4, 32.5, 31.5, 28.7, 28.6, 22.7, 19.0, 14.2. Anal. Calcd. for C₁₂H₂₀O₂: C, 73.43; H, 10.27. Found: C, 73.19; H, 10.07.

Table 1, entry 13

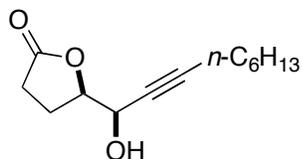


The enyne was prepared via Sonogashira coupling of 5-iodo-4-penten-1-ol* and 1-octyne. The crude alcohol was taken on to the next step without purification: Brown oil; IR (NaCl): 3340, 2211, 1456 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.83 (dt, *J* = 10.4, 7.2 Hz, 1H), 5.51 (m, 1H), 3.67 (t, *J* = 6.4 Hz, 2H), 2.40 (q, *J* = 7.2 Hz, 2H), 2.34 (td, *J* = 7.2 2.0 Hz, 2H), 1.69 (quint. *J* = 6.8 Hz, 2H), 1.55 (quint., *J* = 7.6 Hz, 2H), 1.45-1.37 (m, 2H), 1.37-1.24 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 141.4, 110.6, 95.4, 94.6, 62.3, 31.7, 31.6, 29.0, 28.8, 26.3, 22.8, 19.7, 14.3.

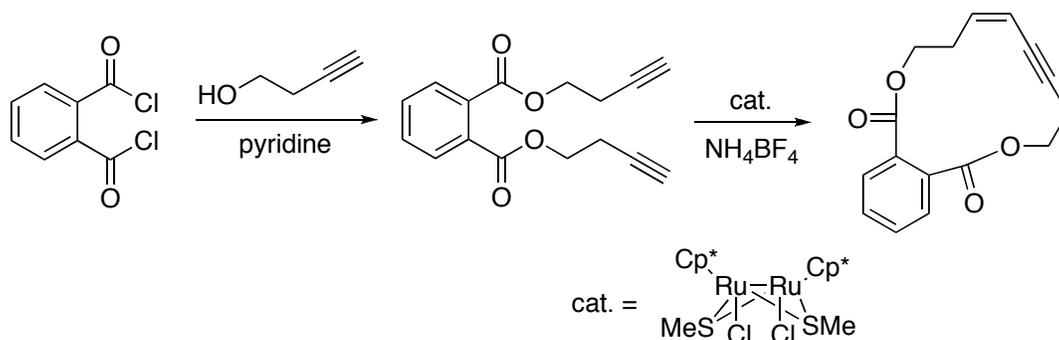
*Prepared according to the reported procedure: Denmark, S.E.; Yang, S.M. *J. Am. Chem. Soc.* **2002**, *124*, 2102.

The oxidation was carried out according to the reported method.* To a solution of *cis*-tridec-4-en-6-yn-1-ol (3.7 g, 21 mmol) in DMF (57 mL) was added PDC (26.5 g, 70.4 mmol) at rt with stirring under Ar. The mixture was stirred overnight and then filtered through a pad of silica gel while washing with Et₂O. The filtrate was concentrated and the residue was purified by column (7:1 hexanes-Et₂O to Et₂O) to yield the acid as a colorless oil (2.21 g, 50% over two steps): IR (NaCl): 2215, 1712 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 11.14 (brs, 1H), 5.84 (dt, *J* = 10.8, 7.2 Hz, 1H), 5.52 (m, 1H), 2.62 (q, *J* = 7.2 Hz, 2H), 2.49 (m, 2H), 2.35 (td, *J* = 6.8, 2.0 Hz, 2H), 1.55 (quint., *J* = 7.6 Hz, 2H), 1.46-1.36 (m, 2H), 1.36-1.24 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 178.9, 139.4, 111.5, 96.1, 33.3, 31.6, 29.0, 28.8, 25.3, 22.8, 19.8, 14.3.

* Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399.



Colorless oil; $[\alpha]_D^{25} = -19.3$ (*c* 0.29, CHCl₃) (96% ee); IR (NaCl): 3427, 2233, 1778 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.56 (ddd, *J* = 7.6, 6.0, 5.6 Hz, 1H), 4.46 (m, 1H), 2.70-2.50 (m, 2H), 2.40-2.30 (m, 1H), 2.26-2.14 (m, 4H), 1.56-1.47 (m, 2H), 1.42-1.23 (m, 6H), 0.90 (t, *J* = 7.2 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 177.0, 88.6, 81.9, 76.3, 65.2, 31.5, 28.7, 28.5, 28.4, 23.6, 22.7, 18.9, 14.3. Anal. Calcd for C₁₃H₂₀O₃: C, 69.61; H, 8.99. Found: C, 69.39; H, 9.16.

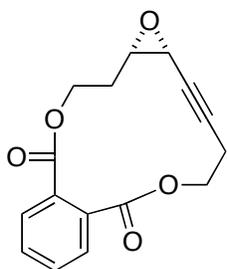
Table 1, entry 14

Phthaloyl dichloride (5.1 g, 25.0 mmol), 3-butyn-1-ol (3.4 g, 48 mmol), and pyridine (7.6 g, 96 mmol) were dissolved in CH_2Cl_2 (250 mL) at 0 °C with stirring. The mixture was allowed to gradually warm to rt and was stirred overnight. The mixture was then poured into sat. aq. NH_4Cl and the aq. phase was extracted with CH_2Cl_2 . The combined organic phases were then washed with H_2O , brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column (1:1 hexanes- Et_2O) to yield the diester as a colorless syrup (5.0 g, 74%): IR (NaCl): 3293, 2122, 1728 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.78-7.74 (m, 2H), 7.59-7.53 (m, 2H), 4.43 (t, J = 6.8 Hz, 4H), 2.66 (td, J = 6.8, 2.8 Hz, 4H), 2.04 (t, J = 2.8 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.4, 132.0, 131.5, 129.3, 80.1, 70.3, 63.4, 19.1.

The enyne was prepared according to the method of Nishibayashi et al.* NH_4BF_4 (0.036 g, 0.34 mmol) and phthalic acid dibut-3-ynyl ester (0.465 g, 1.72 mmol) were added to a solution of $[\text{Cp}^*\text{RuCl}(\mu_2\text{-SMe})_2\text{RuCp}^*\text{Cl}]$ (0.218 g, 0.342 mmol) in 850 mL dry MeOH. The reaction was followed by GC and was stirred at 60 °C for 24 h after which time an additional 0.12 g (0.19 mmol) of catalyst was added. After 48 h more, an additional 0.19 g (0.30 mmol) of catalyst was added. After stirring for 120 h total, the solvent was removed and the residue was purified by column (1:1 hexanes- Et_2O) to yield the enyne as white crystals (0.39 g, 84%): mp 108-109 °C; IR (NaCl): 2215, 1717, 1275, 1133 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.77-7.68 (m, 2H),

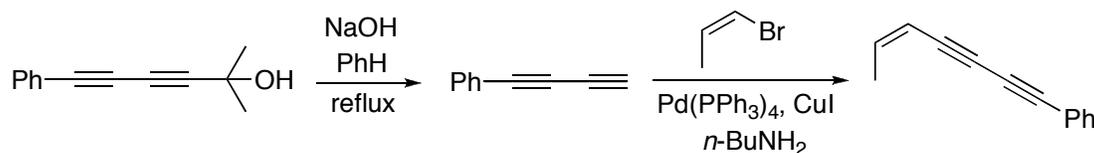
7.55-7.50 (m, 2H), 5.91 (dt, $J = 10.4, 8.0$ Hz, 1H), 5.54 (d, $J = 10.4$ Hz, 1H), 4.54 (t, $J = 5.2$ Hz, 2H), 4.41 (t, $J = 5.6$ Hz, 2H), 2.82-2.72 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.4, 167.2, 138.9, 133.0, 132.5, 131.3, 131.2, 129.5, 129.0, 112.6, 90.4, 79.2, 65.1, 62.9, 29.9, 20.6.

*Nishibayashi, Y.; Yamanashi, M.; Wakiji, I.; Hidai, M. *Angew. Chem. Int. Ed.* **2000**, *39*, 2909.



Colorless oil; $[\alpha]_{\text{D}}^{25} = -87.1$ (c 0.86, CHCl_3) (87% ee); IR (NaCl): 2245, 1728, 1293, 1129 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.79-7.71 (m, 2H), 7.60-7.53 (m, 2H), 4.84-4.76 (m, 1H), 4.73 (dt, $J = 11.2, 4.0$ Hz, 1H), 4.28 (td, $J = 11.2, 3.2$ Hz, 1H), 4.17 (ddd, $J = 10.4, 4.8, 3.2$ Hz, 1H), 3.44-3.42 (m, 1H), 3.11 (ddd, $J = 10.0, 4.0, 1.6$ Hz, 1H), 2.82-2.72 (m, 1H), 2.59 (dt, $J = 17.6, 2.8$ Hz, 1H), 2.34-2.26 (m, 1H), 2.23-2.11 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.5, 166.9, 132.9, 132.1, 131.5, 131.3, 129.6, 129.1, 82.9, 77.1, 63.3, 62.3, 56.9, 46.3, 28.3, 20.1. Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{O}_5$: C, 67.13; H, 4.93. Found: C, 67.36; H, 5.05.

Table 1, entry 15

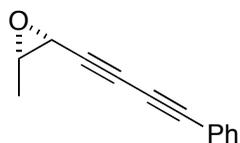


Powdered NaOH (0.66 g, 16.4 mmol) and 6-phenyl-3,5-hexadiyn-2-ol* (2.73 g, 14.8 mmol) were added to 29 mL of toluene and the mixture was refluxed under Ar until the starting material had disappeared by TLC (~1 h). The brown mixture was then cooled to rt, filtered through a pad

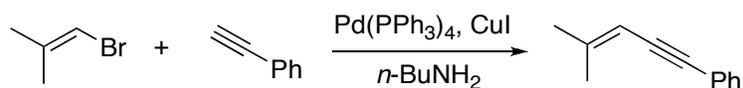
of SiO₂, and washed with 1:1 hexanes-Et₂O. The filtrate was concentrated to give a yellow oil which should be used immediately for the next step.

cis-1-Bromo-1-propene (3.6 g, 29.6 mmol) and Pd(PPh₃)₄ (0.76 g, 0.66 mmol) were then added to a flask with 33 mL of benzene. A solution of the above crude terminal diyne in 15 mL *n*-BuNH₂ (150 mmol) was then added to the benzene solution, followed by CuI (0.46 g, 2.4 mmol). The mixture was stirred at rt under Ar overnight and then hexane (50 mL) was added. The mixture was poured into sat. aq. NH₄Cl and washed with sat. aq. NH₄Cl, H₂O, brine, dried (Na₂SO₄), filtered, and concentrated. The residue was purified by column (hexanes) to give the endiynes as a colorless oil (0.88 g, 36%): IR (NaCl): 2214, 2149, 1490 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.54-7.46 (m, 2H), 7.41-7.30 (m, 3H), 6.20 (dq, *J* = 10.8, 6.8 Hz, 1H), 5.61 (dd, *J* = 10.8, 0.8 Hz, 1H), 1.97 (dd, *J* = 6.8, 0.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 143.3, 132.6, 129.3, 128.6, 122.2, 109.3, 81.9, 79.0, 78.2, 74.2, 16.8.

* (a) Dabdoub, M.J.; Baroni, A.C.M.; Lenardão, E.J.; Gianeti, T.R.; Hurtado, G. *Tetrahedron* **2001**, 57, 4271. (b) Jiang, M. X.-W.; Rawat, M.; Wulff, W.D. *J. Am. Chem. Soc.* **2004**, 126, 5970.



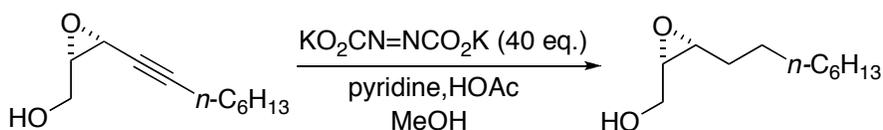
Colorless oil; [α]_D²⁵ = -48.4 (*c* 0.25, CHCl₃) (93% ee); IR (NaCl): 2232 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.53-7.48 (m, 2H), 7.42-7.31 (m, 3H), 3.57 (d, *J* = 4.0 Hz, 1H), 3.25 (qd, *J* = 5.2, 4.0 Hz, 1H), 1.49 (d, *J* = 5.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 132.9, 129.7, 128.7, 121.4, 78.01, 77.96, 73.5, 70.1, 55.1, 46.0, 15.2. Anal. Calcd for C₁₃H₁₀O: C, 85.69; H, 5.53. Found: C, 85.44; H, 5.45.

Table 1, entry 16

The enyne was prepared via Sonogashira coupling of 1-bromo-2-methylpropene and phenylacetylene (79%): Colorless oil; IR (NaCl): 2197, 1489 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.45-7.40 (m, 2H), 7.33-7.24 (m, 3H), 5.48 (s, 1H), 1.98 (s, 3H), 1.87 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 149.2, 131.5, 128.5, 127.9, 124.2, 105.4, 91.6, 87.9, 25.2, 21.4.



Colorless oil; $[\alpha]_D^{25} = +3.56$ (c 0.59, CHCl_3) (94% ee); IR (NaCl): 2221, 1490 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.47-7.43 (m, 2H), 7.36-7.28 (m, 3H), 3.44 (s, 1H), 1.52 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 132.1, 128.9, 128.5, 122.5, 85.5, 85.2, 61.2, 52.5, 23.7, 20.6. Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{O}$: C, 83.69; H, 7.02. Found: C, 83.80; H, 7.00.



(2S,3R)-2,3-epoxyundecan-1-ol: To a solution of the propargyl epoxide (0.096 g, 0.53 mmol) (96% ee) in MeOH (4 mL) and pyridine (0.86 mL) at rt was added potassium azodicarboxylate (1.03 g, 5.3 mmol) at the beginning. The same amount of potassium azodicarboxylate (1.03 g, 5.3 mmol) was subsequently added at the 12th, 24th, and 36th hour. Acetic acid (2.57 mL, 44.52 mmol, in 5 mL MeOH) was constantly added over 60 h via syringe pump. The reaction was then diluted with Et_2O and washed with water until no more gas bubbles evolved. The aqueous phase

was then extracted with Et₂O and the combined organic phases were washed with sat. aq. CuSO₄, H₂O, brine, dried (Na₂SO₄), filtered, and concentrated. The residue was purified by column (1:1 pet. ether-Et₂O) to yield the saturated epoxide as a white solid (0.05g, 53%): $[\alpha]_D^{25} = -2.7$ (*c* 0.37, CHCl₃); lit. $[\alpha]_D^{25} = -3.5$ (*c* 1.3, CHCl₃) (>80% ee)*; IR (NaCl): 3297, 1469 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.92-3.82 (m, 1H), 3.73-3.64 (m, 1H), 3.16 (dt, *J* = 7.2, 4.0 Hz, 1H), 3.08-3.02 (m, 1H), 1.66 (s, 1H), 1.62-1.22 (m, 14H), 0.89 (t, *J* = 6.8 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 61.2, 57.6, 57.0, 32.1, 29.7, 29.6, 29.4, 28.2, 26.9, 22.9, 14.3.

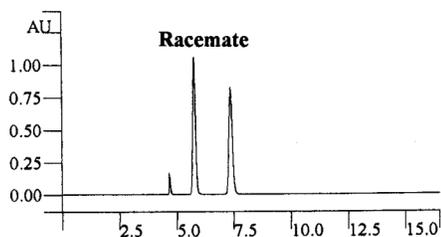
* Gao, Y.; Klunder, J.M.; Hanson, R.M.; Masamune, H.; Ko, S.Y.; Sharpless, K.B. *J. Am. Chem. Soc.* **1987**, *109*, 5765.

The chromatograms for the determination of enantiomeric excess of the epoxides from the asymmetric epoxidation of conjugated enynes catalyzed by ketone 2.

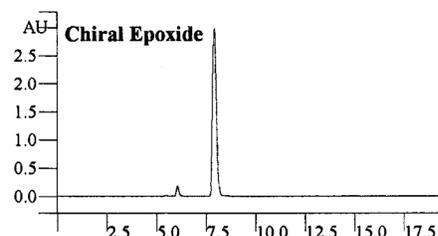
Table 1, Entry 1



HPLC Cond.: Column: Chiralcel OD (Column No. OD00CE-DL010), Chiral Technologies, Inc.
 Eluent: Hexanes/IPA (96/4); Flow Rate: 1.0mL/min; Detection: UV 254 nm

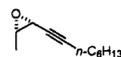


Peak No	Ret. Time (min)	Result ()	Minutes Area (counts)
1	5.754	49.7155	4514572
2	7.341	50.2845	4566234
Totals		100.0000	9080806

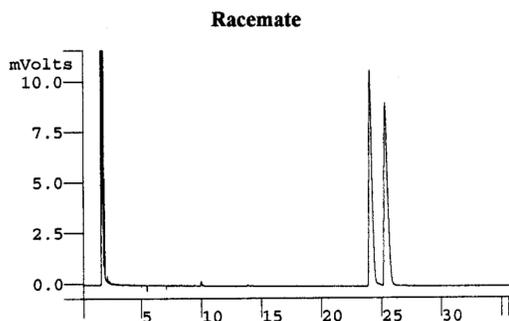


Peak No	Ret. Time (min)	Result ()	Minutes Area (counts)
1	6.029	3.6275	806710
2	7.887	96.3725	21431754
Totals		100.0000	22238464

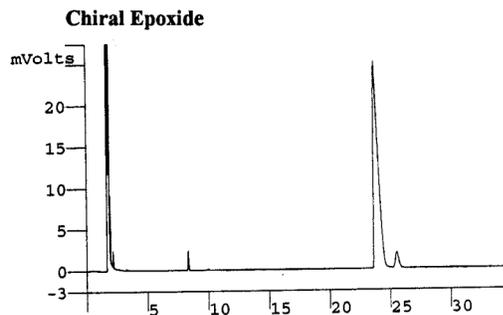
Table 1, Entry 2



GC Cond.: Column: Chiraldex B-DM (Cat. No. 77023), Adv. Separation Technologies, Inc.
 Oven: 100 °C; Carrier: Helium, head pressure 20 psi; Detection: FID 250 °C

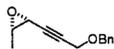


Peak No	Peak Name	Result ()	Ret. Time (min)	Minutes Area (counts)
1		49.9541	24.009	184553
2		50.0459	25.284	184892
Totals		100.0000		369445

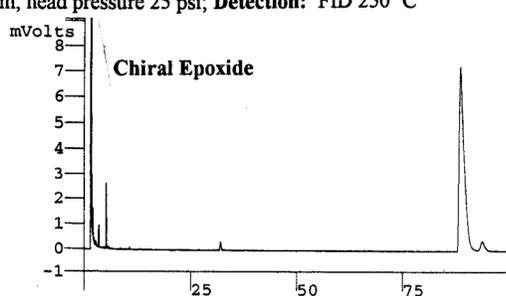
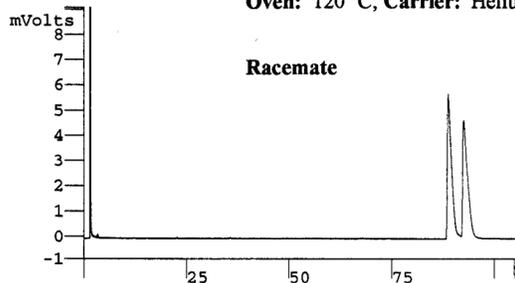


Peak No	Peak Name	Result ()	Ret. Time (min)	Minutes Area (counts)
1		95.0000	23.691	682403
2		5.0000	25.507	35916
Totals		100.0000		718319

Table 1, Entry 3



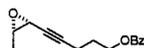
GC Cond.: Column: Chiraldex B-DM (Cat. No. 77023), Adv. Separation Technologies, Inc.
Oven: 120 °C; **Carrier:** Helium, head pressure 25 psi; **Detection:** FID 250 °C



Peak No	Peak Name	Result ()	Ret. Time (min)	Minutes Area (counts)
1		50.4584	88.622	386967
2		49.5416	92.418	379935
Totals		100.0000		766902

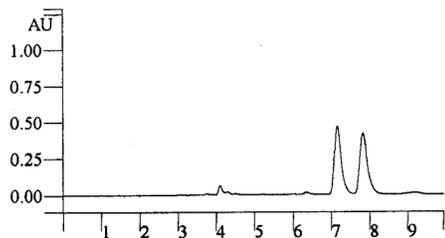
Peak No	Peak Name	Result ()	Ret. Time (min)	Minutes Area (counts)
1		96.0029	88.408	586139
2		3.9971	93.761	24404
Totals		100.0000		610543

Table 1, Entry 4

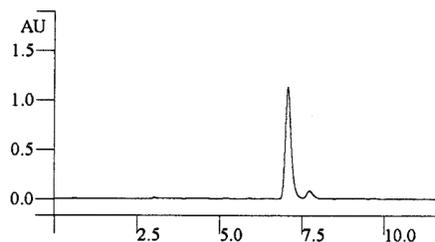


HPLC Cond.: Column: Chirapak AD (Column No. AD00CE-EA001), Chiral Technologies, Inc.
Eluent: Hexanes/IPA (92/8); **Flow Rate:** 1.0mL/min; **Detection:** UV 270 nm

Racemate



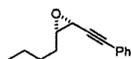
Chiral Epoxide



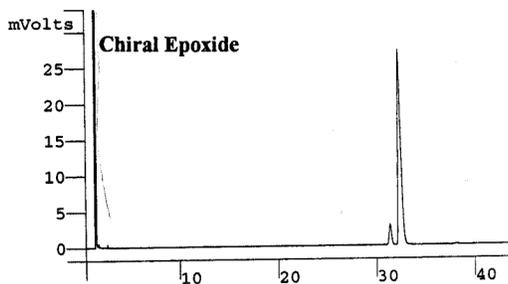
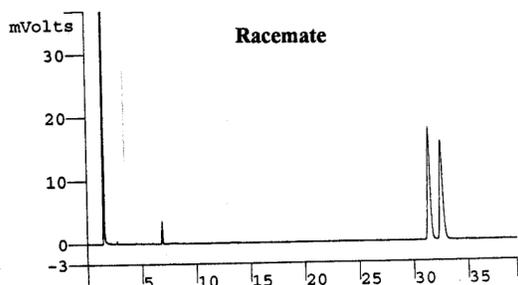
Peak No	Ret. Time (min)	Result ()	Minutes Area (counts)
1	7.146	50.0215	3027775
2	7.819	49.9785	3025178
		100.0000	6052953

Peak No	Ret. Time (min)	Result ()	Minutes Area (counts)
1	7.044	93.9168	7234500
2	7.714	6.0832	468598
		100.0000	7703098

Table 1, Entry 5



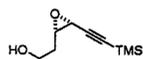
GC Cond.: Column: Chiraldex B-DM (Cat. No. 77023), Adv. Separation Technologies, Inc.
Oven: 135 °C; Carrier: Helium, head pressure 25 psi; Detection: FID 250 °C



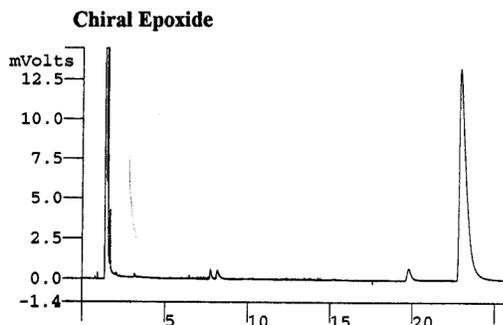
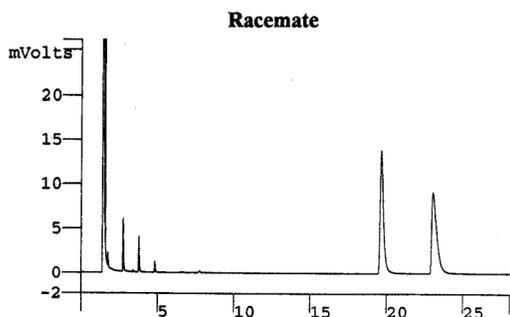
Peak No	Peak Name	Result ()	Ret. Time (min)	Minutes Area (counts)
1		49.8305	31.358	315240
2		50.1695	32.466	317384
Totals		100.0000		632624

Peak No	Peak Name	Result ()	Ret. Time (min)	Minutes Area (counts)
1		7.7968	31.361	48673
2		92.2031	32.263	575590
Totals		99.9999		624263

Table 1, Entry 6



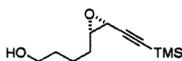
GC Cond.: Column: Chiraldex B-DM (Cat. No. 77023), Adv. Separation Technologies, Inc.
Oven: 110 °C; Carrier: Helium, head pressure 25 psi; Detection: FID 250 °C



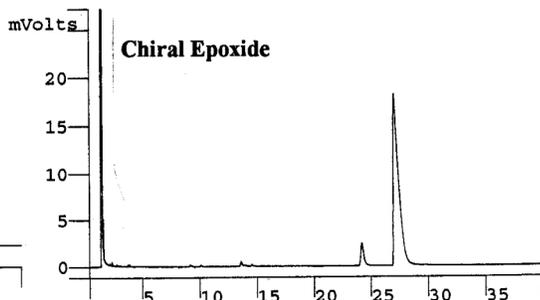
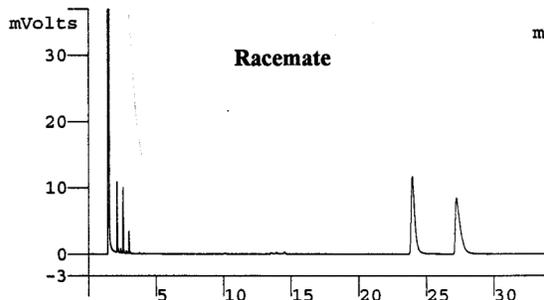
Peak No	Peak Name	Result ()	Ret. Time (min)	Minutes Area (counts)
1		50.0373	19.636	209856
2		49.9627	23.036	209543
Totals		100.0000		419399

Peak No	Peak Name	Result ()	Ret. Time (min)	Minutes Area (counts)
1		3.0681	19.759	11889
2		96.9319	22.864	375619
Totals		100.0000		387508

Table 1, Entry 7

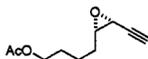


GC Cond.: Column: Chiraldex B-DM (Cat. No. 77023), Adv. Separation Technologies, Inc.
 Oven: 130 °C; Carrier: Helium, head pressure 25 psi; Detection: FID 250 °C

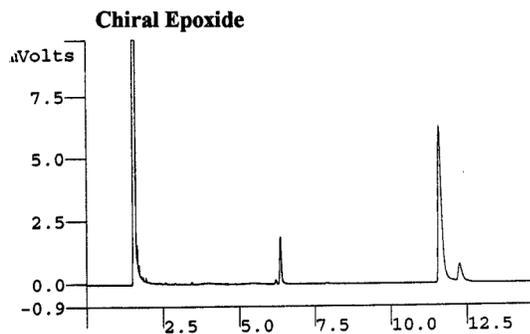
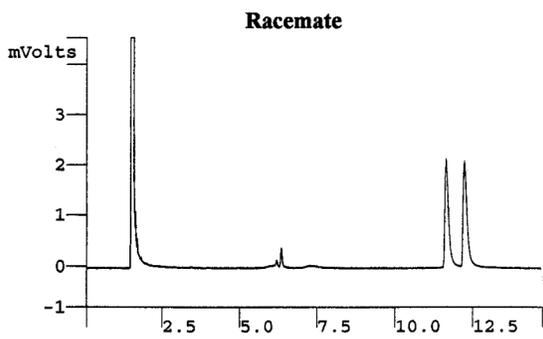


Peak No	Peak Name	Result ()	Ret. Time (min)	Area (counts)	Minutes	Peak No	Peak Name	Result ()	Ret. Time (min)	Area (counts)	Minutes
1		49.6323	23.931	213597		1		6.7327	24.167	42739	
2		50.3677	27.214	216762		2		93.2673	27.029	592055	
Totals		100.0000		430359		Totals		100.0000		634794	

Table 1, Entry 8

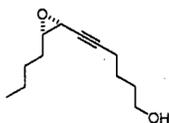


GC Cond.: Column: Chiraldex B-DM (Cat. No. 77023), Adv. Separation Technologies, Inc.
 Oven: 125 °C; Carrier: Helium, head pressure 25 psi; Detection: FID 250 °C



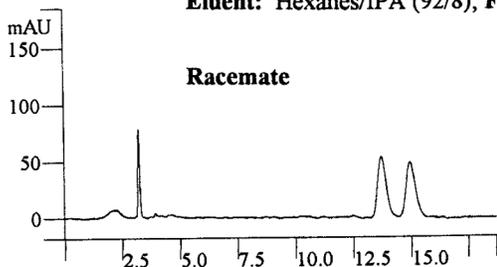
Peak No	Peak Name	Result ()	Ret. Time (min)	Area (counts)	Minutes	Peak No	Peak Name	Result ()	Ret. Time (min)	Area (counts)	Minutes
1		49.5730	11.626	17749		1		90.2378	11.579	51732	
2		50.4270	12.217	18055		2		9.7622	12.257	5597	
Totals		100.0000		35804		Totals		100.0000		57329	

Table 1, Entry 9

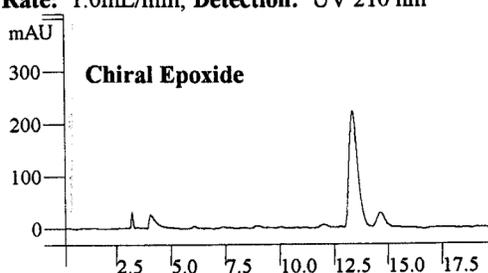


HPLC Cond.: Column: Chiralcel OD (Column No. OD00CE-DL010), Chiral Technologies, Inc.

Eluent: Hexanes/IPA (92/8); **Flow Rate:** 1.0mL/min; **Detection:** UV 210 nm

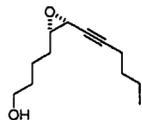


Peak No	Ret. Time (min)	Result ()	Minutes Area (counts)
1	13.686	50.2666	721994
2	14.934	49.7334	714334
		100.0000	1436328



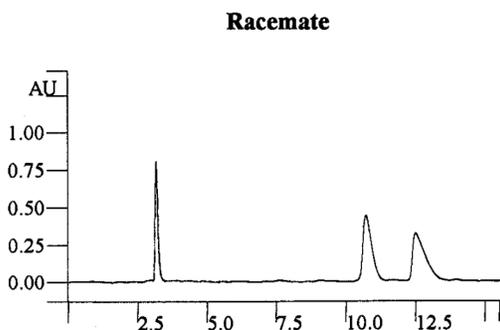
Peak No	Ret. Time (min)	Result ()	Minutes Area (counts)
1	13.339	90.0670	3212628
2	14.659	9.9330	354304
		100.0000	3566932

Table 1, Entry 10

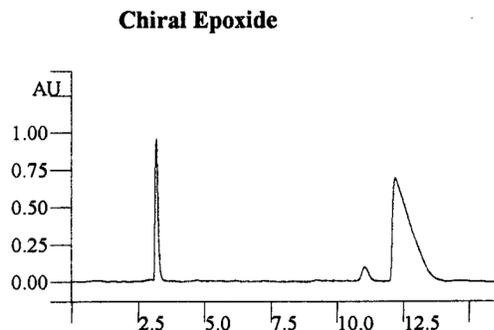


HPLC Cond.: Column: Chiralcel OJ (Column No. OJ00CE-DE008), Chiral Technologies, Inc.

Eluent: Hexanes/IPA (92/8); **Flow Rate:** 1.0mL/min; **Detection:** UV 210 nm

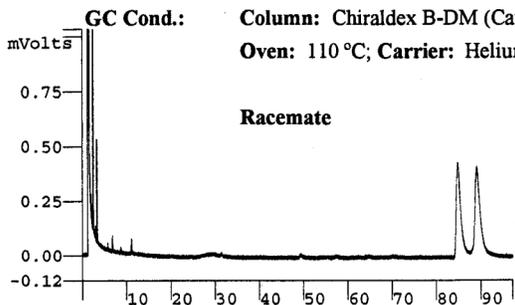


Peak No	Ret. Time (min)	Result ()	Minutes Area (counts)
1	10.704	49.5158	5191821
2	12.493	50.4842	5293368
		100.0000	10485189

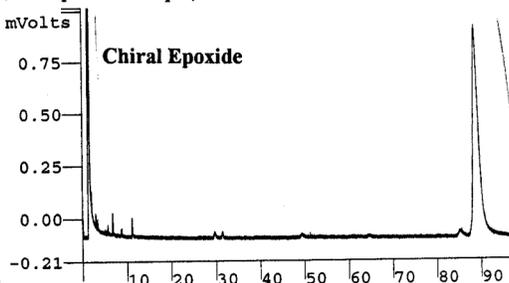


Peak No	Ret. Time (min)	Result ()	Minutes Area (counts)
1	11.014	4.8570	873081
2	12.161	95.1430	17102756
		100.0000	17975836

Table 1, Entry 11

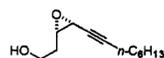


Peak No	Peak Name	Result ()	Ret. Time (min)	Area (counts)
1		49.6269	84.719	29469
2		50.3731	89.128	29912
Totals		100.0000		59381

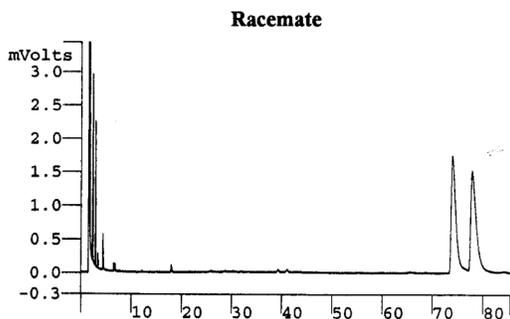


Peak No	Peak Name	Result ()	Ret. Time (min)	Area (counts)
1		1.7002	85.567	1540
2		98.2998	88.494	89032
Totals		100.0000		90572

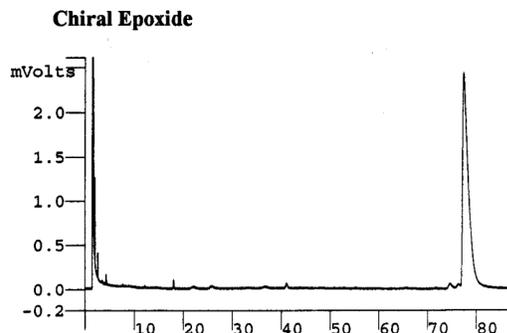
Table 1, Entry 12



GC Cond.: Column: Chiraldex B-DM (Cat. No. 77023), Adv. Separation Technologies, Inc.
Oven: 125 °C; Carrier: Helium, head pressure 25 psi; Detection: FID 250 °C

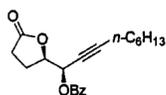


Peak No	Peak Name	Result ()	Ret. Time (min)	Area (counts)
1		50.1102	73.851	107289
2		49.8898	77.746	106817
Totals		100.0000		214106

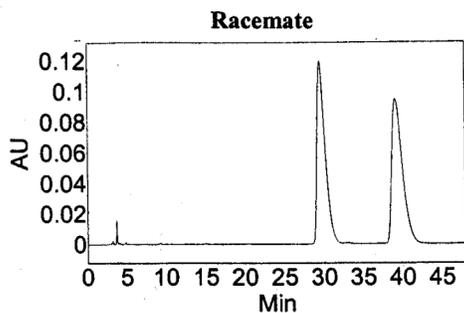


Peak No	Peak Name	Result ()	Ret. Time (min)	Area (counts)
1		1.4356	74.537	2848
2		98.5644	77.316	195542
Totals		100.0000		198390

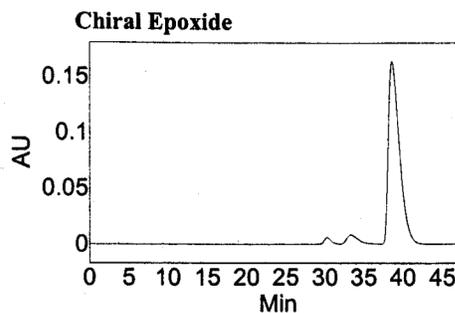
Table 1, Entry 13



HPLC Cond.: Column: Chiralcel OD (Column No. OD00CE-DL010), Chiral Technologies, Inc.
Eluent: Hexanes/IPA (85/15); **Flow Rate:** 1.0mL/min; **Detection:** UV 240 nm

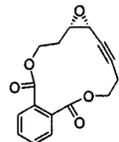


Index	Time [Min]	Area % [%]
1	29.525	49.716
2	39.108	50.284
Total		100.000

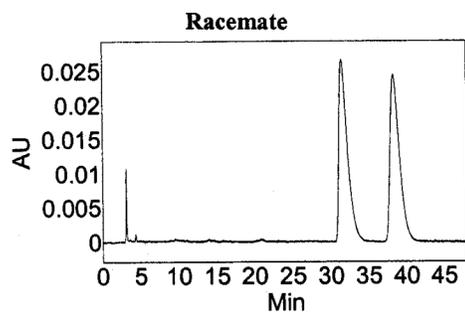


Index	Time [Min]	Area % [%]
2	30.248	2.121
1	38.553	97.879
Total		100.000

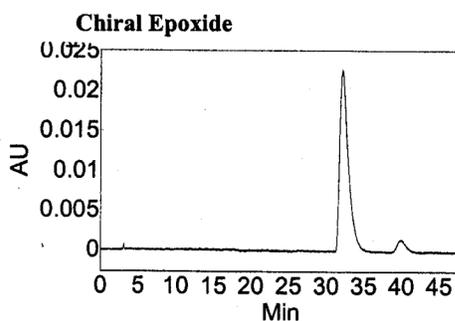
Table 1, Entry 14



HPLC Cond.: Column: Chiralcel OD (Column No. OD00CE-DL010), Chiral Technologies, Inc.
Eluent: Hexanes/IPA (90/10); **Flow Rate:** 1.0mL/min; **Detection:** UV 270 nm

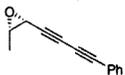


Index	Time [Min]	Area % [%]
1	31.460	50.165
2	38.278	49.835
Total		100.000

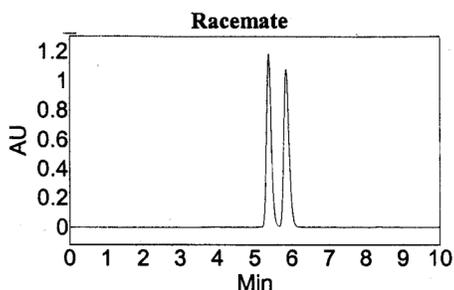


Index	Time [Min]	Area % [%]
1	32.080	93.378
2	39.902	6.622
Total		100.000

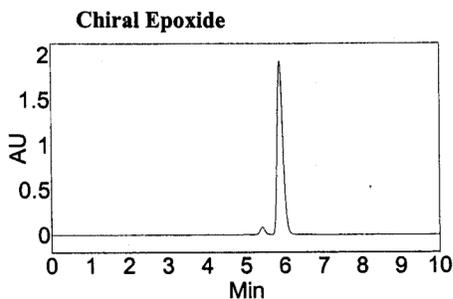
Table 1, Entry 15



HPLC Cond.: Column: Chiralcel OD (Column No. OD00CE-DL010), Chiral Technologies, Inc.
 Eluent: Hexanes/IPA (97/03); Flow Rate: 1.0mL/min; Detection: UV 254 nm

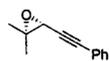


Index	Time (Min)	Area % [%]
1	5.383	50.001
2	5.847	49.999
Total		100.000

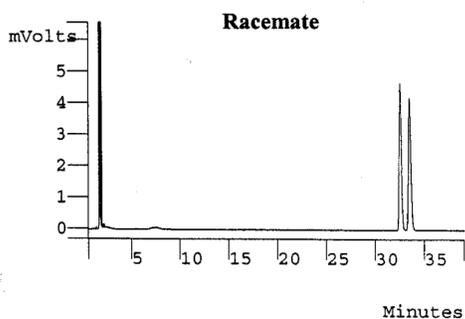


Index	Time (Min)	Area % [%]
1	5.408	3.575
2	5.870	96.425
Total		100.000

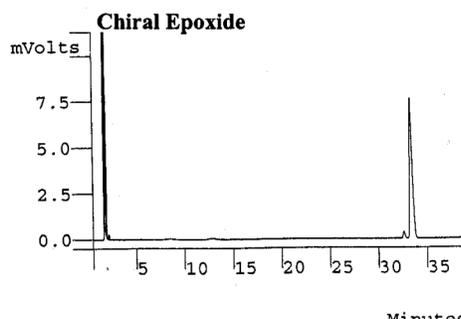
Table 1, Entry 16



GC Cond.: Column: Chiraldex B-DM (Cat. No. 77023), Adv. Separation Technologies, Inc.
 Oven: 110 °C; Carrier: Helium, head pressure 20 psi; Detection: FID 250 °C



Peak No	Peak Name	Result ()	Ret. Time (min)	Area (counts)
1		49.8989	32.466	71182
2		50.1011	33.426	71470
Totals		100.0000		142652



Peak No	Peak Name	Result ()	Ret. Time (min)	Area (counts)
1		3.0543	32.607	4579
2		96.9457	33.274	145330
Totals		100.0000		149909

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

INOVA-400 "narnia"

Pulse 30.8 degrees

Acq. time 2.291 sec

Width 6982.6 Hz

16 repetitions

OBSERVE H1, 400.1063121 MHz

DATA PROCESSING

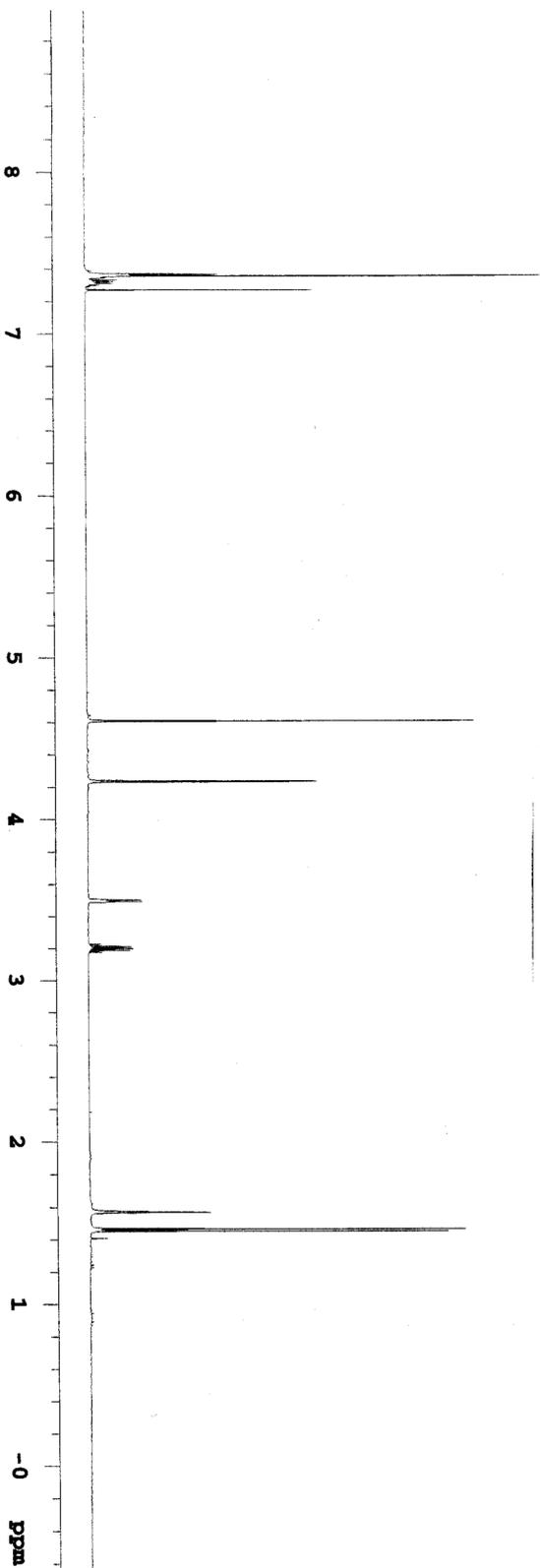
Gauss apodization 0.971 sec

FW size 65536

Total time 0 min, 41 sec



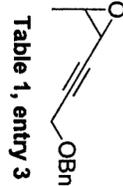
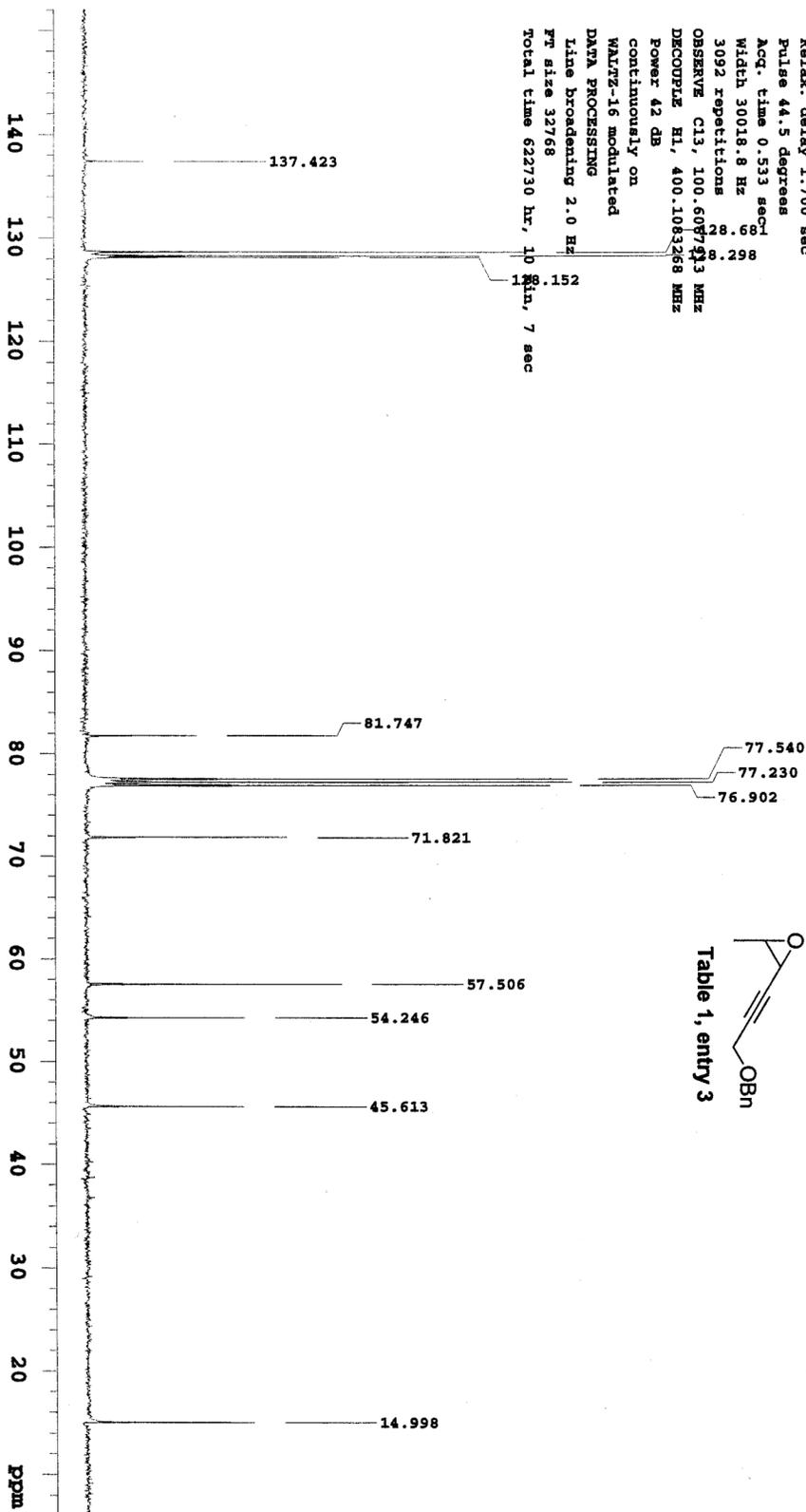
Table 1, entry 3



13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "harnia"

Relax. delay 1.700 sec
Pulse 44.5 degrees
Acq. time 0.533 sec
Width 30018.8 Hz
3092 repetitions
OBSERVE C13, 100.607513 MHz
DECODE H1, 400.1083268 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
line broadening 2.0 Hz
FT size 32768
Total time 622730 hr, 10 min, 7 sec



STANDARD 1H OBSERVE

Pulse Sequence: s2pu1
Solvent: CDCl3
Ambient temperature:
File: INOVA-500 "epoxide"
Relax. delay 0.000 sec
Pulse 28.7 degrees
Acq. time 2.667 sec
Width 6000.0 Hz
16 repetitions
OBSERVE H1, 300.1592196 MHz
DATA PROCESSING
Data acquisition 0.936 sec
F1 size 82768
Total time 0 min, 48 sec



13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature
INOVA-400 "narnia"

Relax. delay 1.700 sec

Pulse 44.5 degrees

Acq. time 0.533 sec

Width 30018.8 Hz

375 repetitions

OBSERVE C13, 100.6067894 MHz

DECOUPLE H1, 400.1083268 MHz

Power 42 dB

continuously on

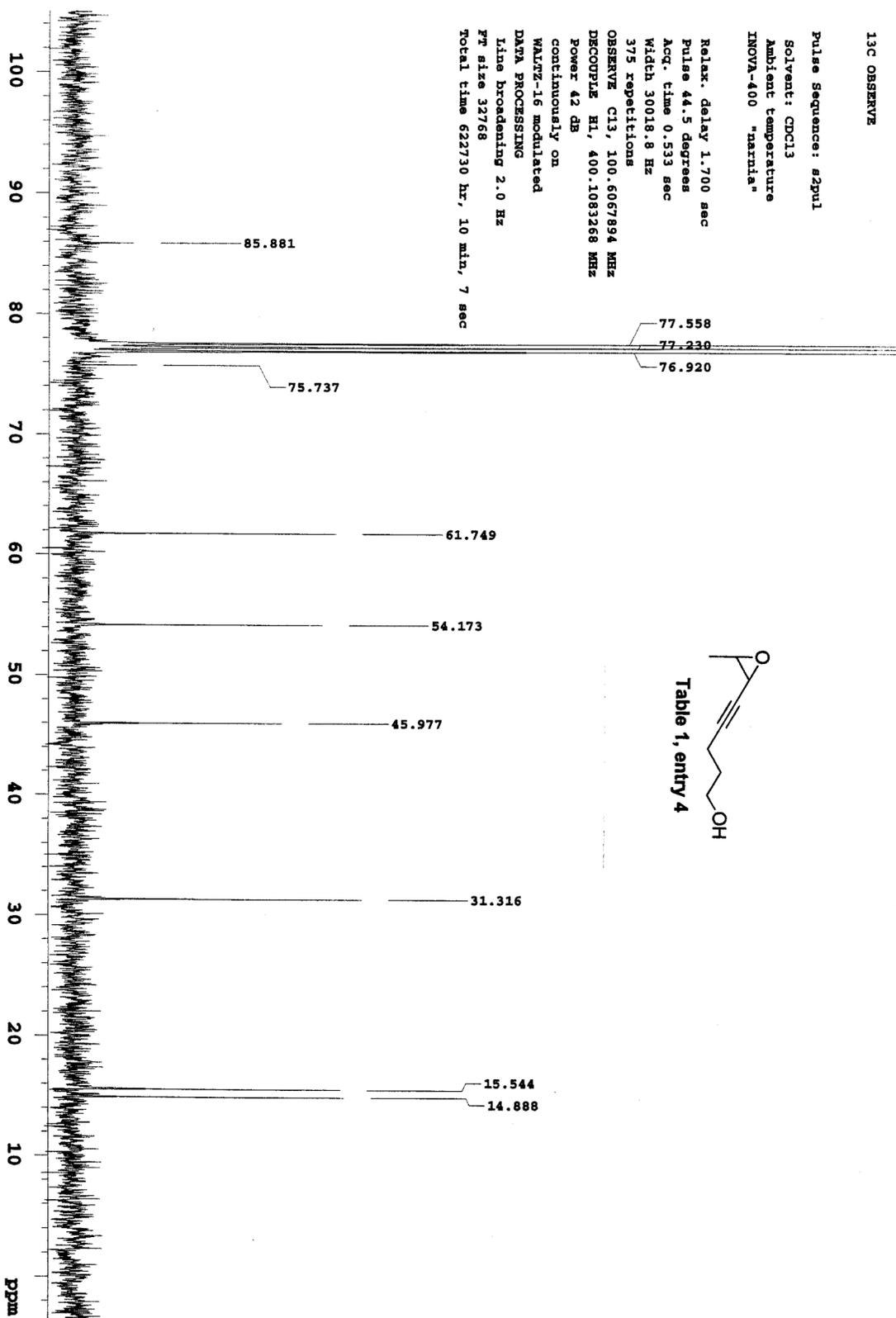
WALTZ-16 modulated

DATA PROCESSING

Line broadening 2.0 Hz

FT size 32768

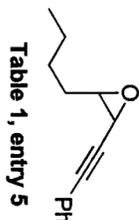
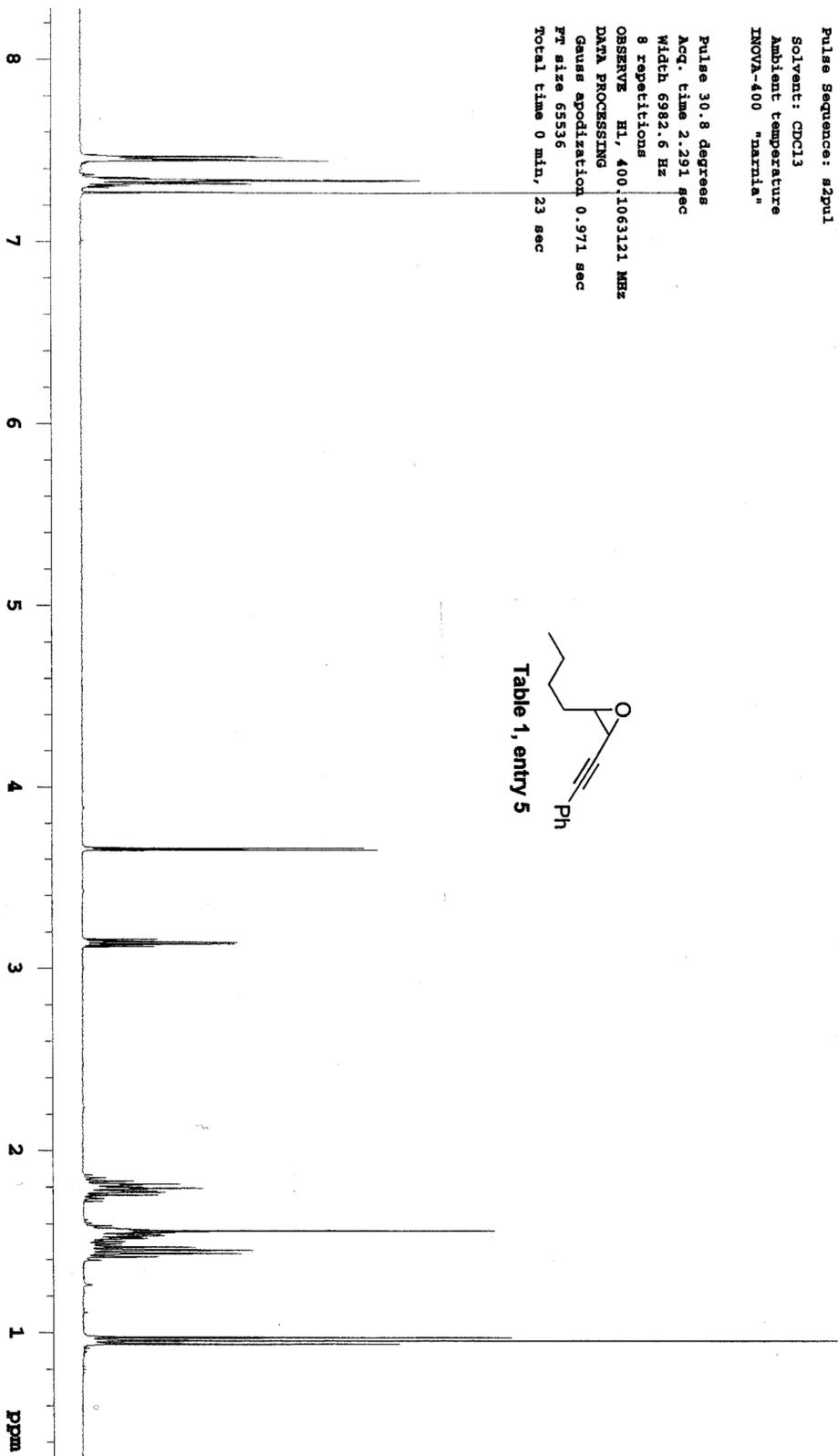
Total time 622730 hr, 10 min, 7 sec



STANDARD 1H OBSERVE

Pulse Sequence: szpul
Solvent: CDCl3
Ambient temperature
INOVA-400 "narnia"

Pulse 30.8 degrees
Acq. time 2.291 sec
Width 6982.6 Hz
8 repetitions
OBSERVE H1, 400.1063121 MHz
DATA PROCESSING
Gauss apodization 0.971 sec
PT size 65536
Total time 0 min, 23 sec



13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

INOVA-400 "narnia"

Relax. delay 1.700sec

Pulse 44.5 degrees

Acq. time 0.533 sec

Width 30018.8 Hz

1182 repetitions

OBSERVE C13, 100.6067894 MHz

DECOUPLE H1, 400.1083268 MHz

Power 42 dB

continuously on

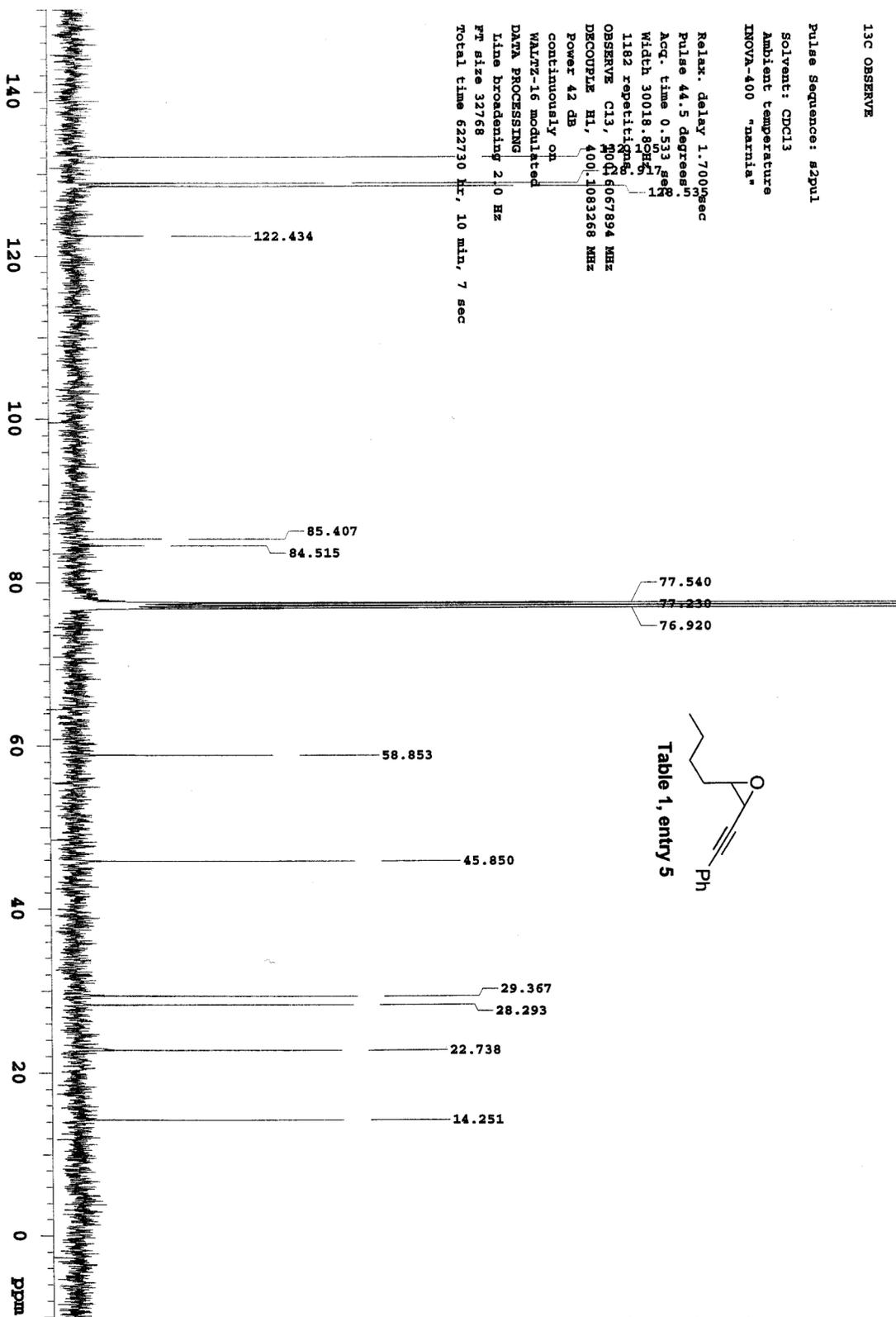
WALTZ-16 modulated

DATA PROCESSING

line broadening 2.0 Hz

FT size 32768

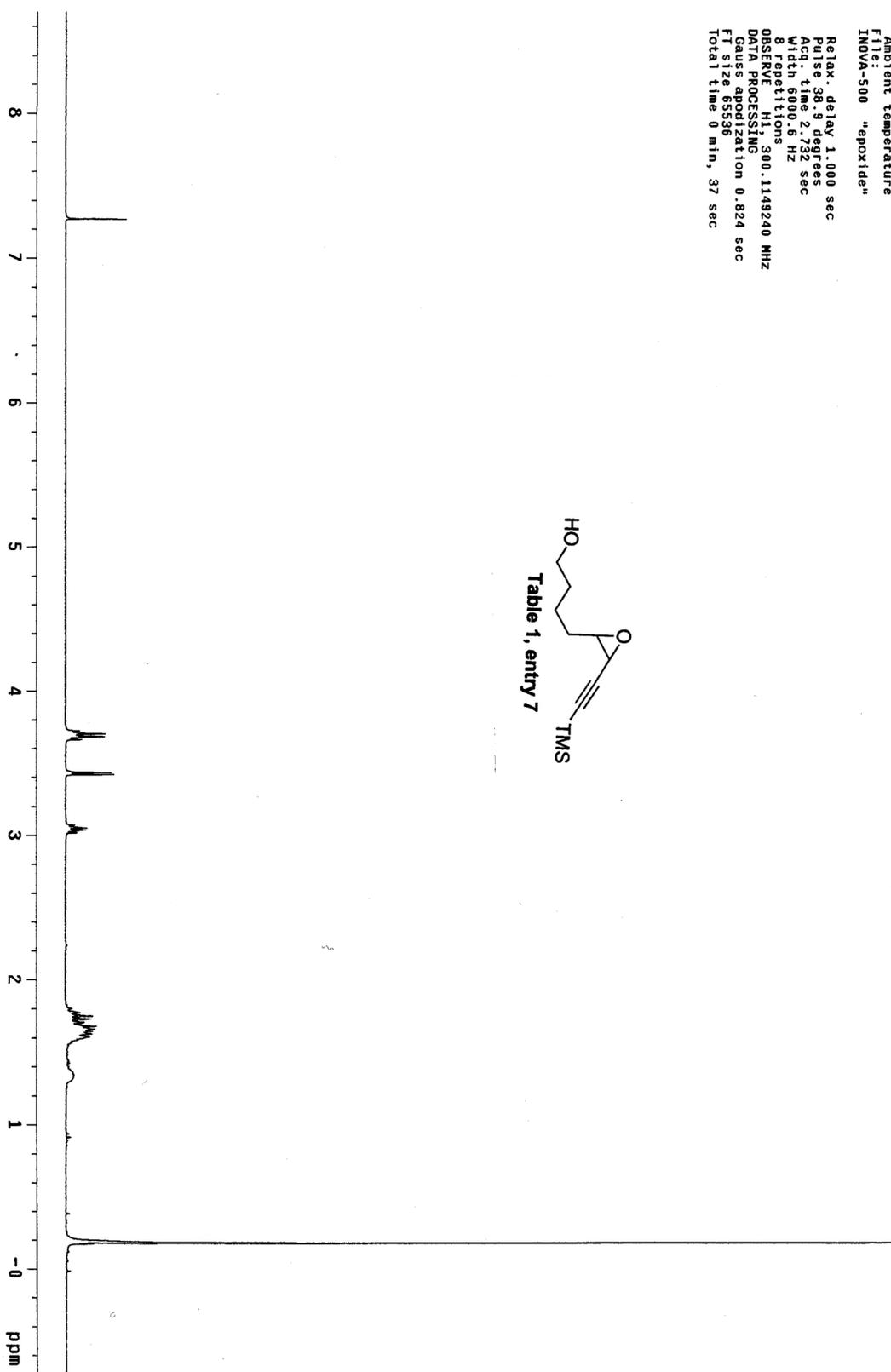
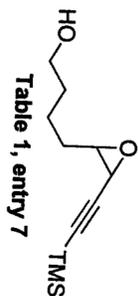
Total time 622730 hr, 10 min, 7 sec



STANDARD 1H OBSERVE

Pulse Sequence: szpul
Solvent: CDCl3
Ambient temperature
File: INOVA-500 "apoxide"

Relax. delay 1.000 sec
Pulse 38.3 degrees
Acq. time 2.732 sec
Width 4000.6 Hz
Observed 11 ions 300.1149240 MHz
DATA PROCESSING
Gauss apodization 0.824 sec
FT size 65536
Total time 0 min, 37 sec



¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

INNOVA-400 "narrina"

Relax. delay 1.700 sec

Pulse 44.5 degrees

Acq. time 0.533 sec

Width 30018.8 Hz

185 repetitions

OBSERVE C13, 100.6067894 MHz

DECOUPLE H1, 400.1083268 MHz

Power 42 dB

continuously on

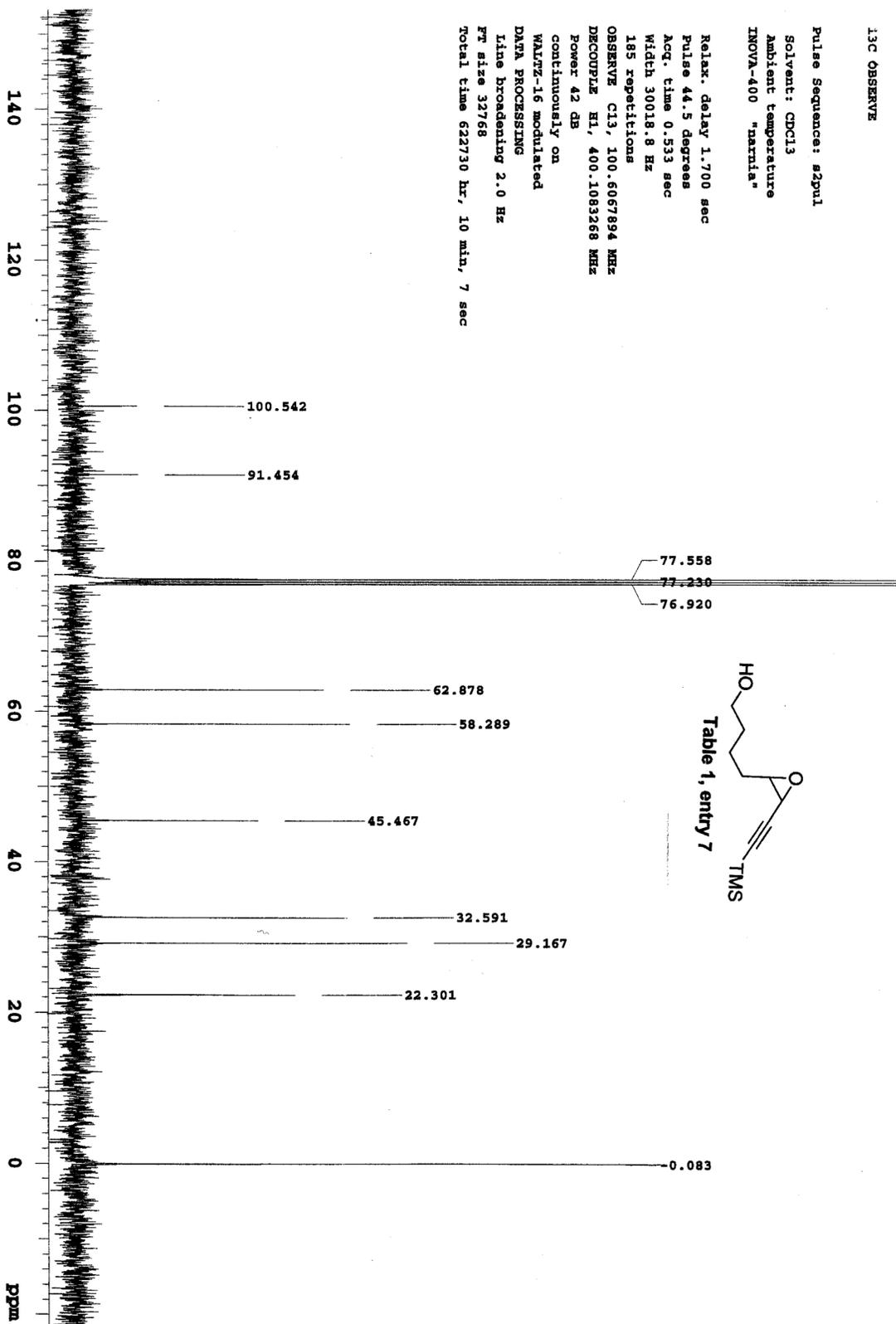
WALTZ-16 modulated

DATA PROCESSING

Line broadening 2.0 Hz

FT size 32768

Total time 622730 hr, 10 min, 7 sec



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

INOVA-400 "harnia"

Pulse 30.8 degrees

Acq. time 2.291 sec

Width 6982.6 Hz

8 repetitions

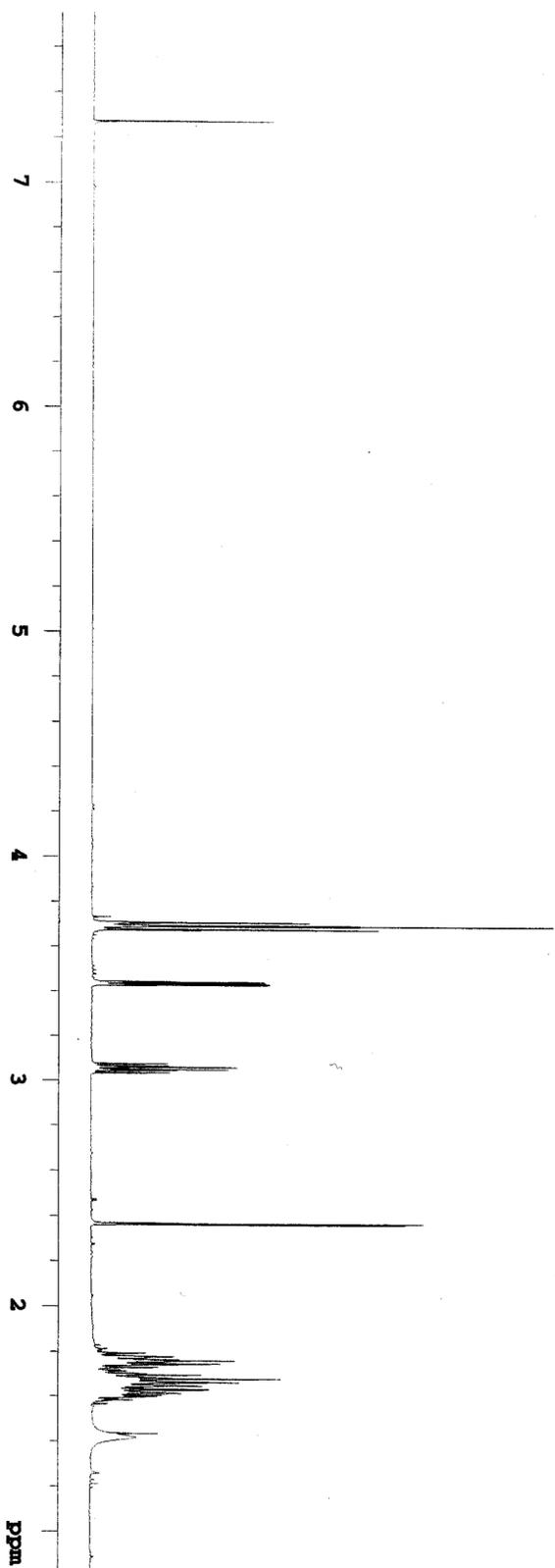
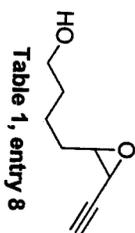
OBSERVE H1, 400.1063119 MHz

DATA PROCESSING

Gauss apodization 0.971 sec

Fr size 65536

Total time 0 min, 23 sec

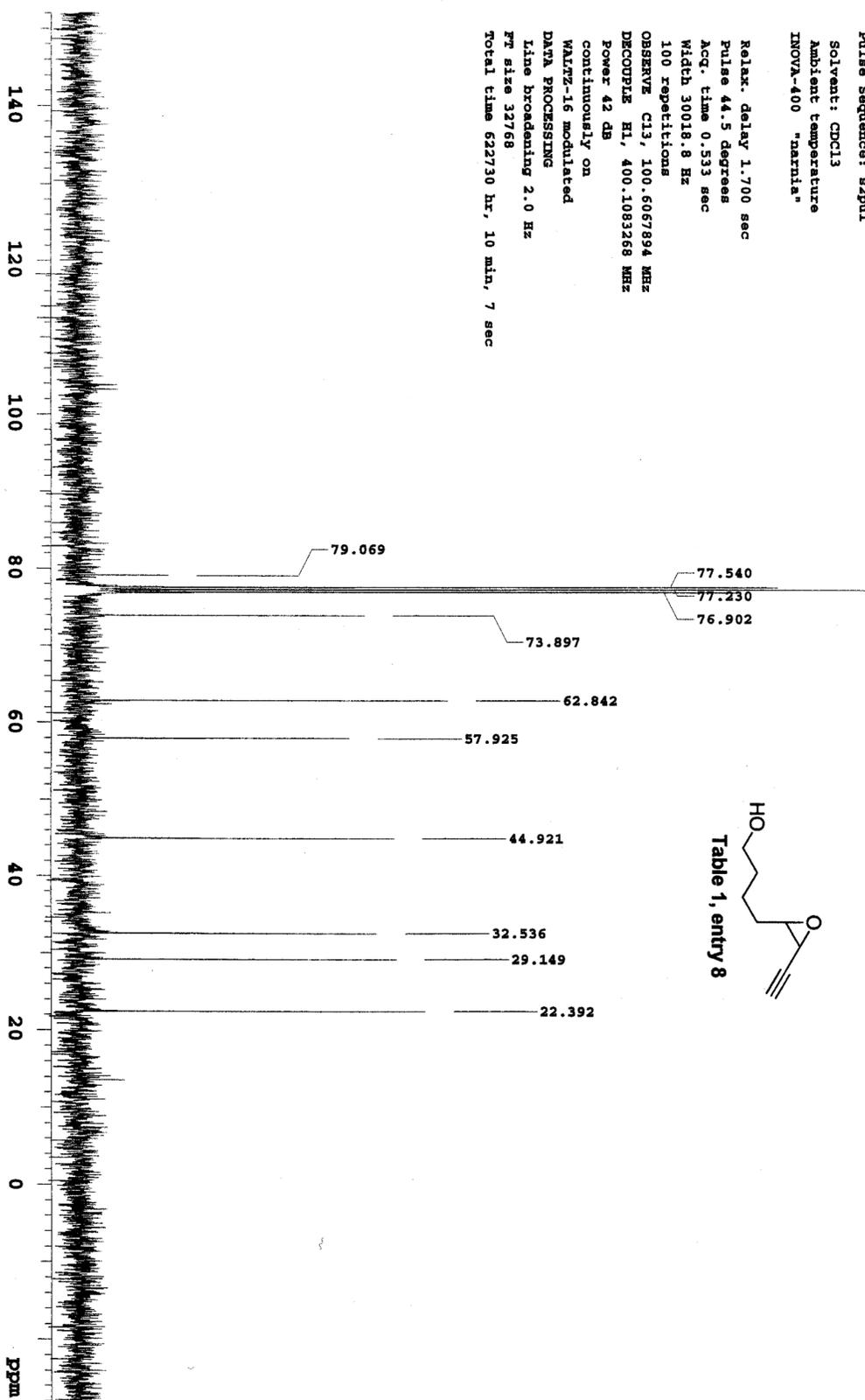


¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃
Ambient temperature
INOVA-400 "narnia"

Relax. delay 1.700 sec
Pulse 44.5 degrees
Acq. time 0.533 sec
Width 30018.8 Hz
100 repetitions
OBSERVE C13, 100.6067894 MHz
DECOUPLE H1, 400.1083268 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
RF size 32768
Total time 632730 hr, 10 min, 7 sec



STANDARD 1H OBSERVE

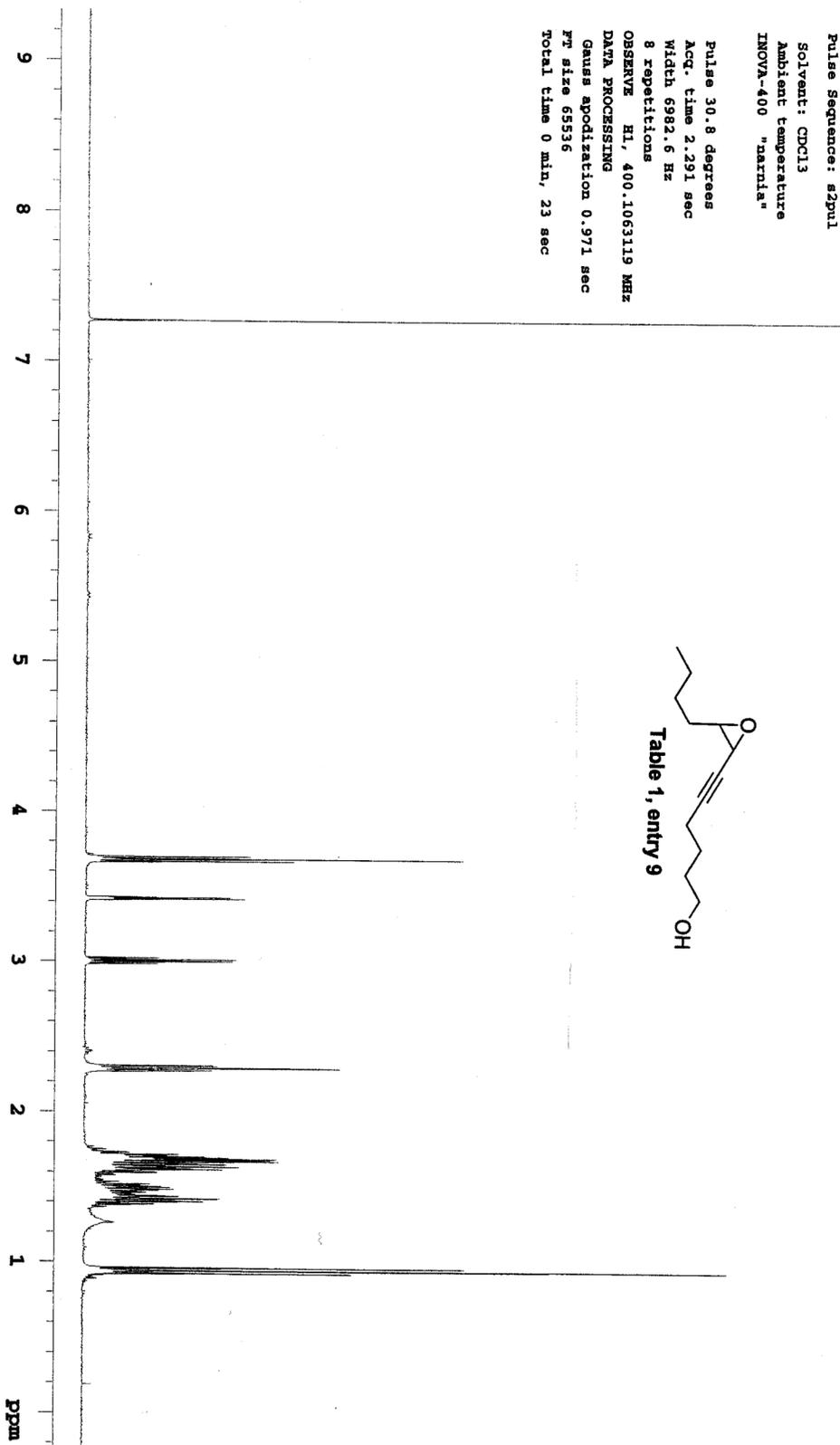
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "narda"

Pulse 30.8 degrees
Acq. time 2.291 sec
Width 6982.6 Hz
8 repetitions

OBSERVE H1, 400.1063119 MHz
DATA PROCESSING
Gauss apodization 0.971 sec
F2 size 65536
Total time 0 min, 23 sec



Table 1, entry 9



13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

INOVA-400 "narris"

Relax. delay 1.700 sec

Pulse 44.5 degrees

Acq. time 0.533 sec

Width 30018.8 Hz

1420 repetitions

OBSERVE C13, 100.6067894 MHz

DECOUPLE H1, 400.1083268 MHz

Power 42 dB

continuously on

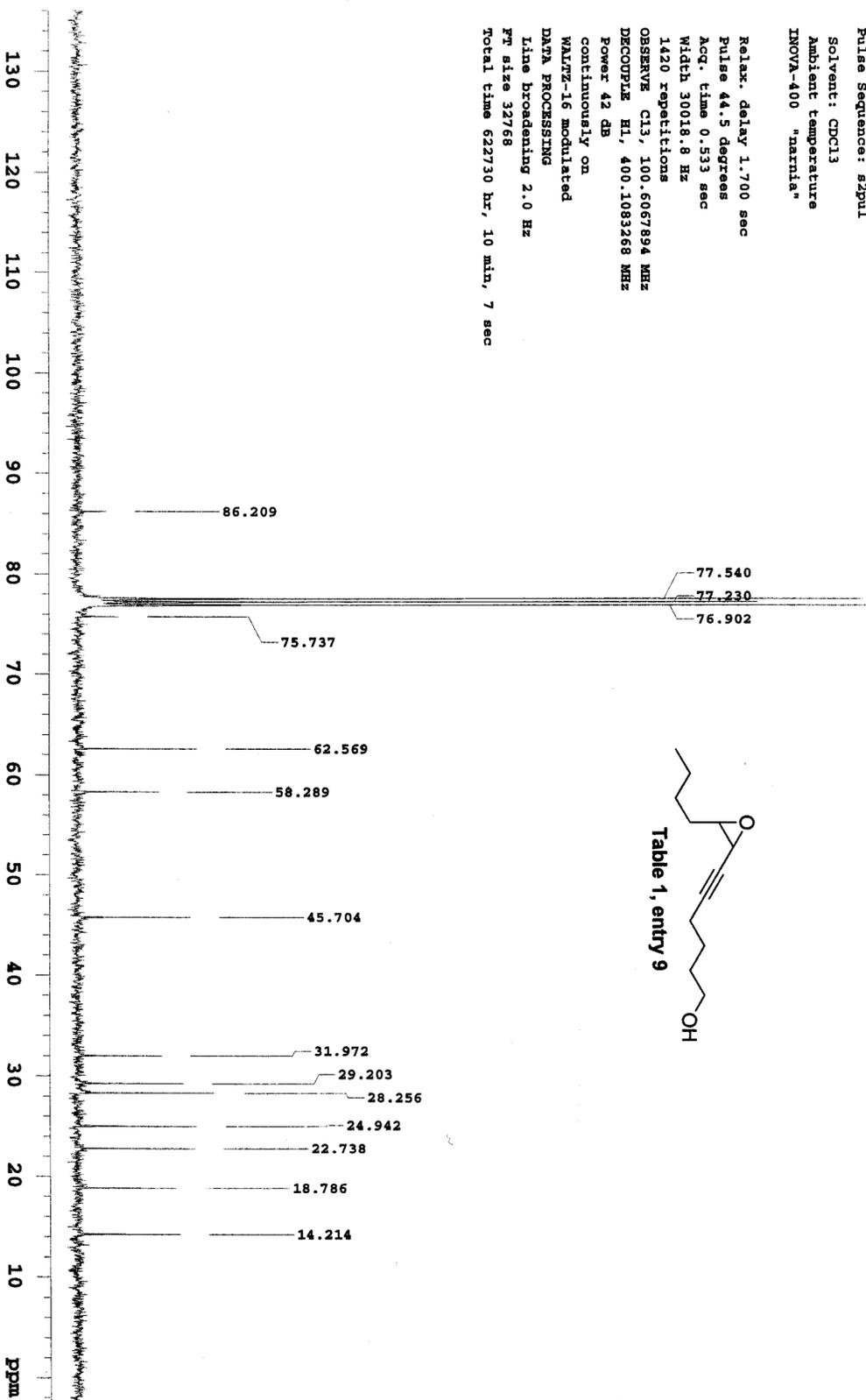
WALTZ-16 modulated

DATA PROCESSING

Line broadening 2.0 Hz

FT size 32768

Total time 622730 hr, 10 min, 7 sec



STANDARD 1H OBSERVE

Pulse Sequence: s2pui

Solvent: CDCl3

Ambient temperature

INOVA-400 "haria"

Pulse 30.8 degrees

Acq. time 2.291 sec

Width 6982.6 Hz

8 repetitions

OBSERVE H1, 400.1063121 MHz

DATA PROCESSING

Gauss apodization 0.971 sec

FF size 65536

Total time 0 min, 23 sec

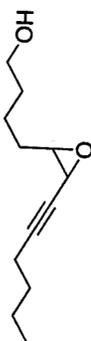
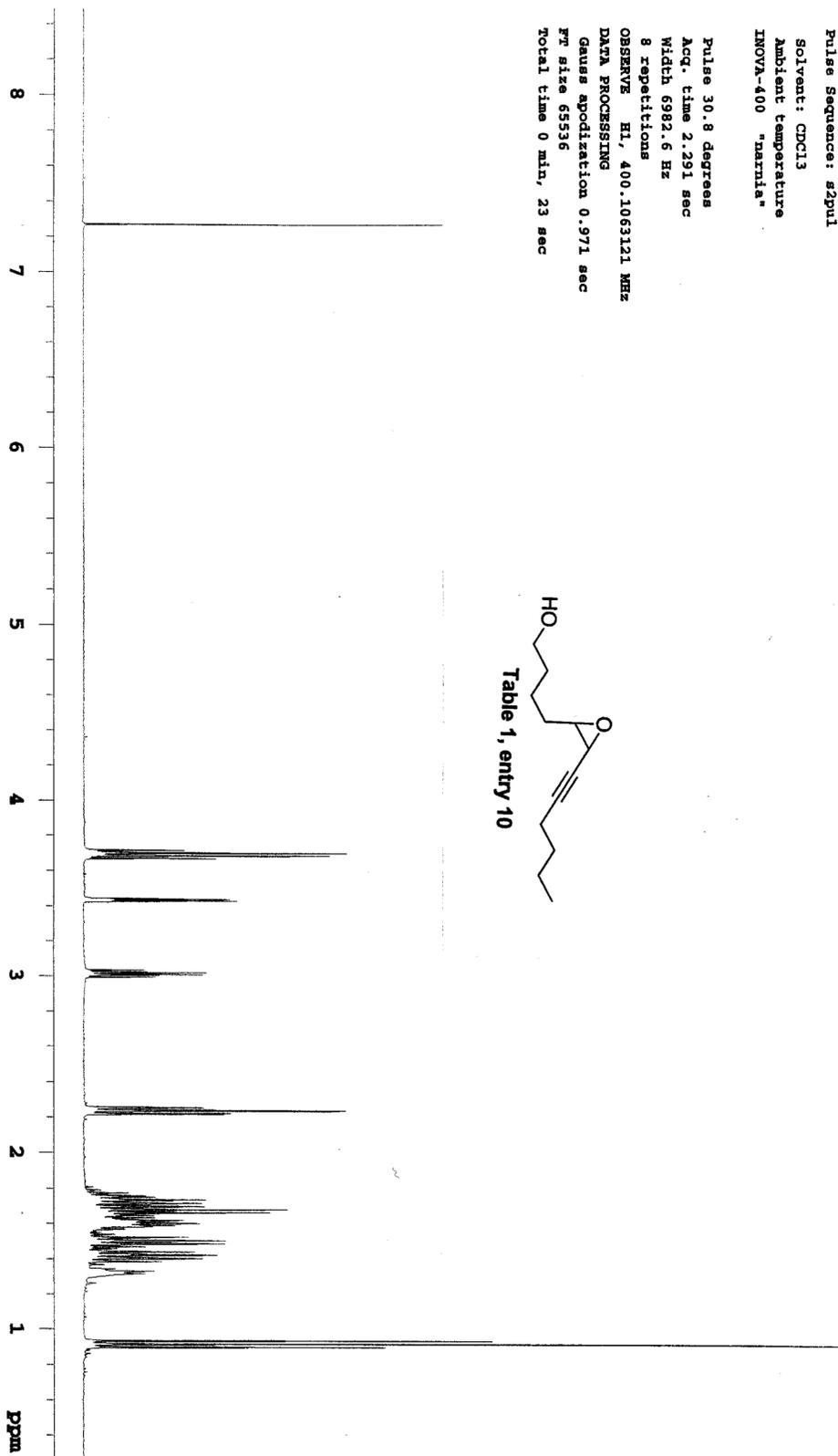


Table 1, entry 10



13C OBSERVE

Pulse Sequence: s2pml

Solvent: CDCl3
Ambient temperature
INOVA-400 "narnia"

Relax. delay 1.700 sec
Pulse 44.5 degrees
Acq. time 0.533 sec
Width 30018.8 Hz

307 repetitions
OBSERVE C13, 100.6067894 MHz
DECOUPLE H1, 400.1083268 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
line broadening 2.0 Hz
FT size 32768
Total time 622730 hr, 10 min, 7 sec

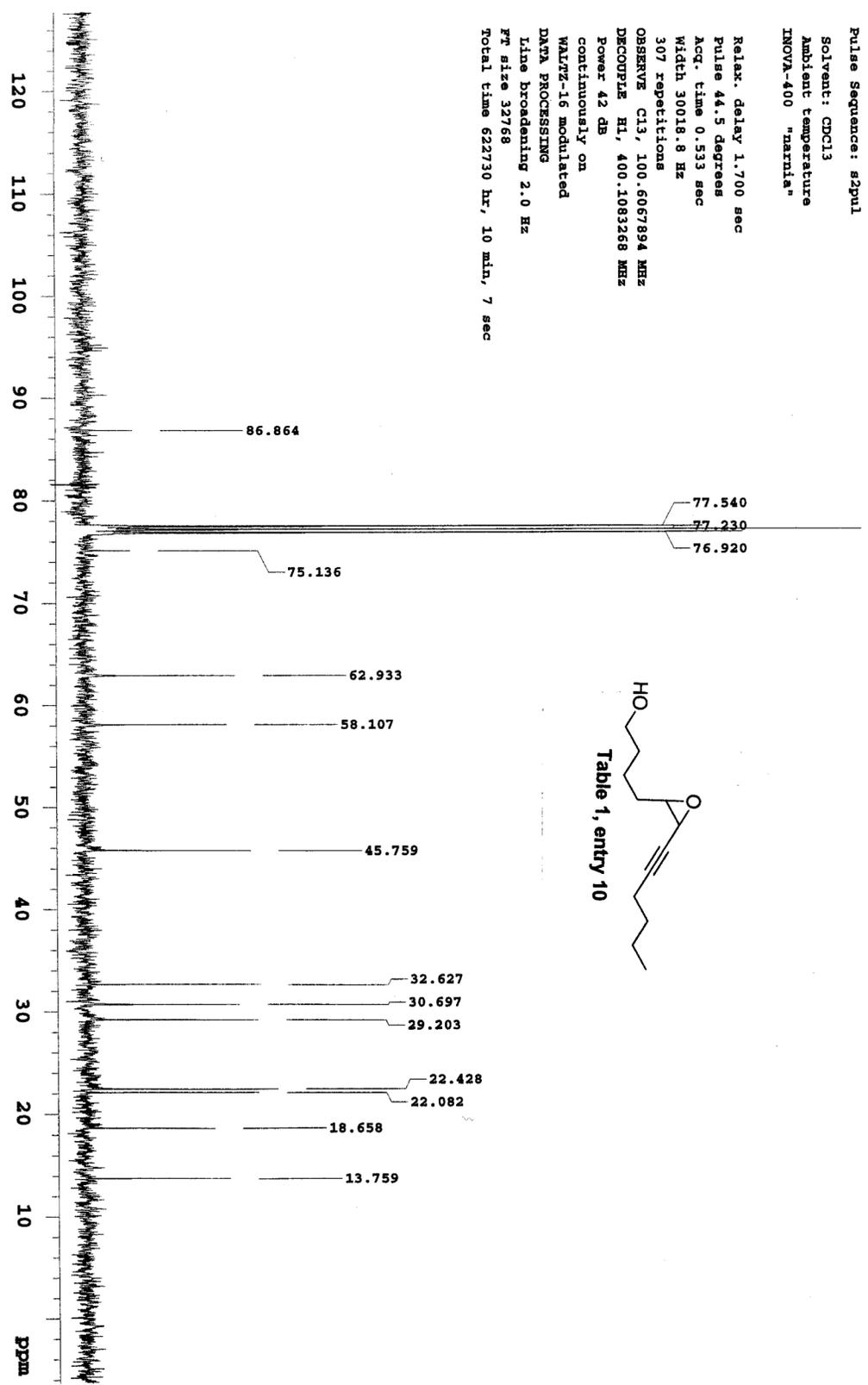
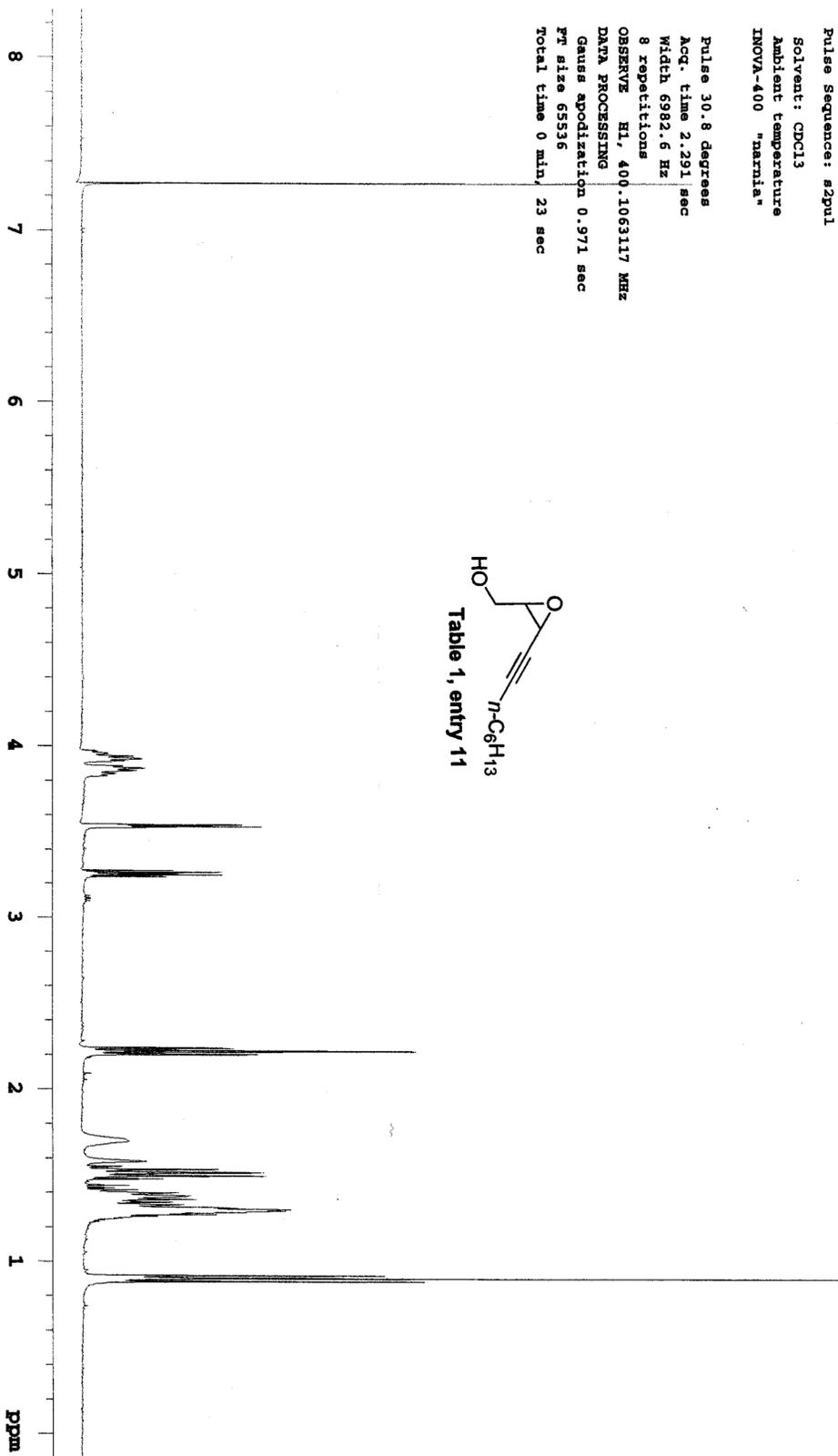


Table 1, entry 10

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "narnia"

Pulse 30.8 degrees
Acq. time 2.291 sec
Width 6982.6 Hz
8 repetitions
OBSERVE H1, 400.1063117 MHz
DATA PROCESSING
Gauss apodization 0.971 sec
FT size 65536
Total time 0 min, 23 sec



13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

INOVA-400 "maria"

Relax. delay 1.700 sec

Pulse 44.5 degrees

Acq. time 0.533 sec

Width 30018.8 Hz

570 repetitions

OBSERVE C13, 100.6067894 MHz

DECOUPLE H1, 400.1083268 MHz

Power 42 dB

continuously on

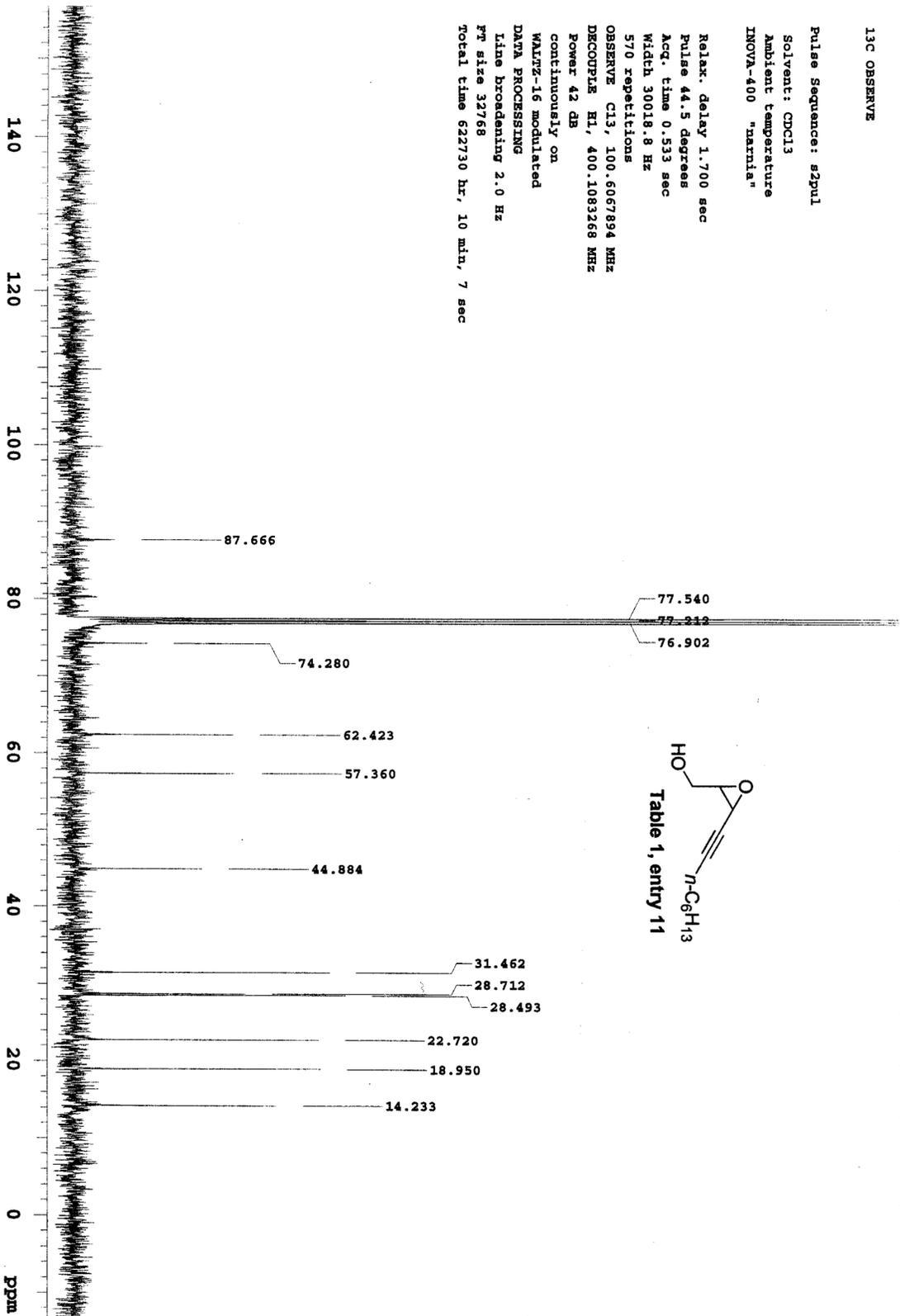
WALTZ-16 modulated

DATA PROCESSING

Line broadening 2.0 Hz

FT size 32768

Total time 622730 hr, 10 min, 7 sec



STANDARD 1H OBSERVE

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

INOVA-400 "narnia"

Pulse 30.8 degrees

Acq. time 2.291 sec

Width 6982.6 Hz

8 repetitions

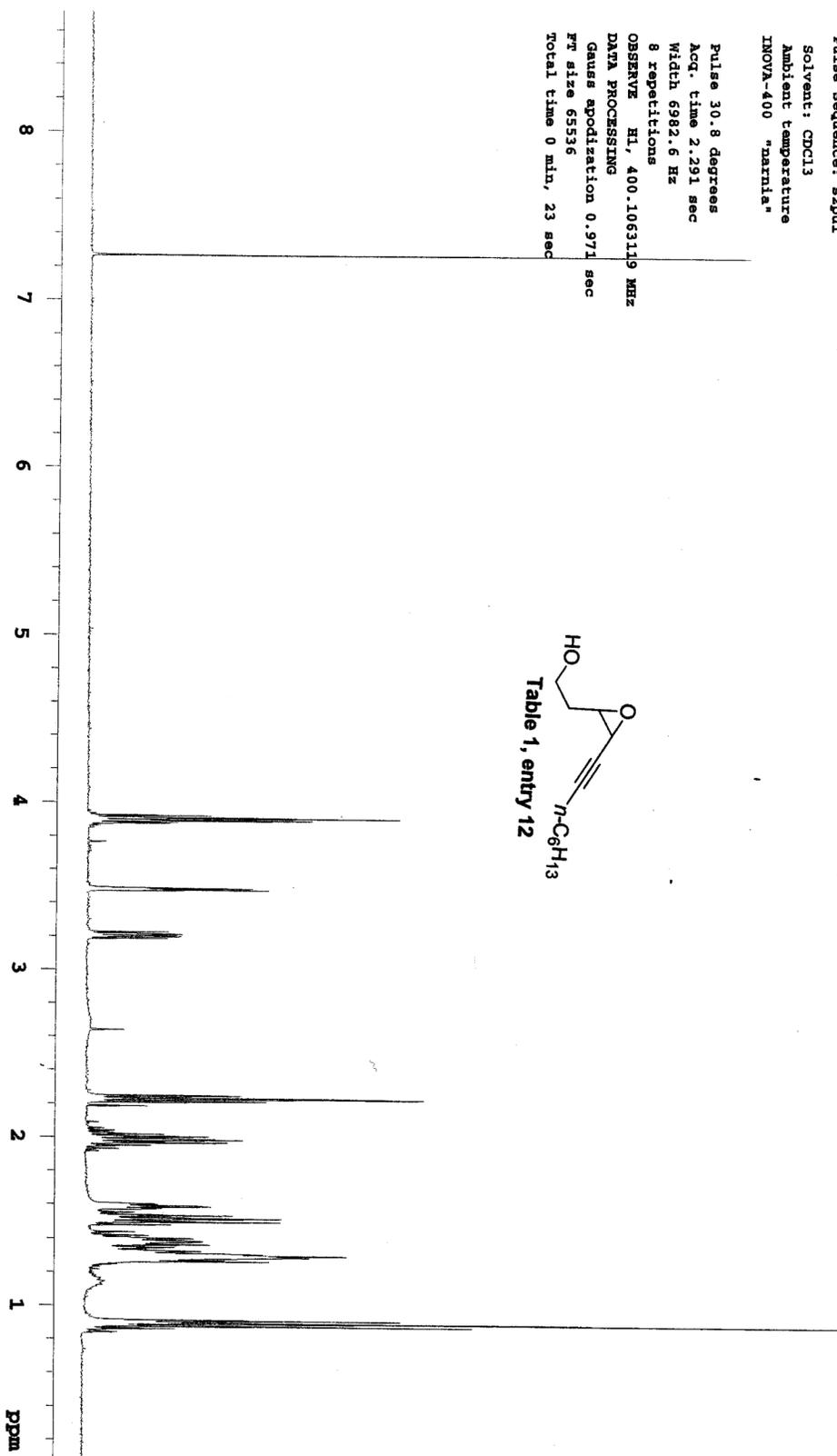
OBSERVE H1, 400.1063119 MHz

DATA PROCESSING

Gauss apodization 0.971 sec

FT size 65536

Total time 0 min, 23 sec



¹³C OBSERVE

Pulse Sequence: s2pul1

Solvent: CDCl₃

Ambient temperature

INNOVA-400 "narnia"

Relax. delay 1.700 sec

Pulse 44.5 degrees

Acq. time 0.533 sec

Width 30018.8 Hz

280 repetitions

OBSERVE C13, 100.6067894 MHz

DECOUPLE H1, 400.1083268 MHz

Power 42 dB

continuously on

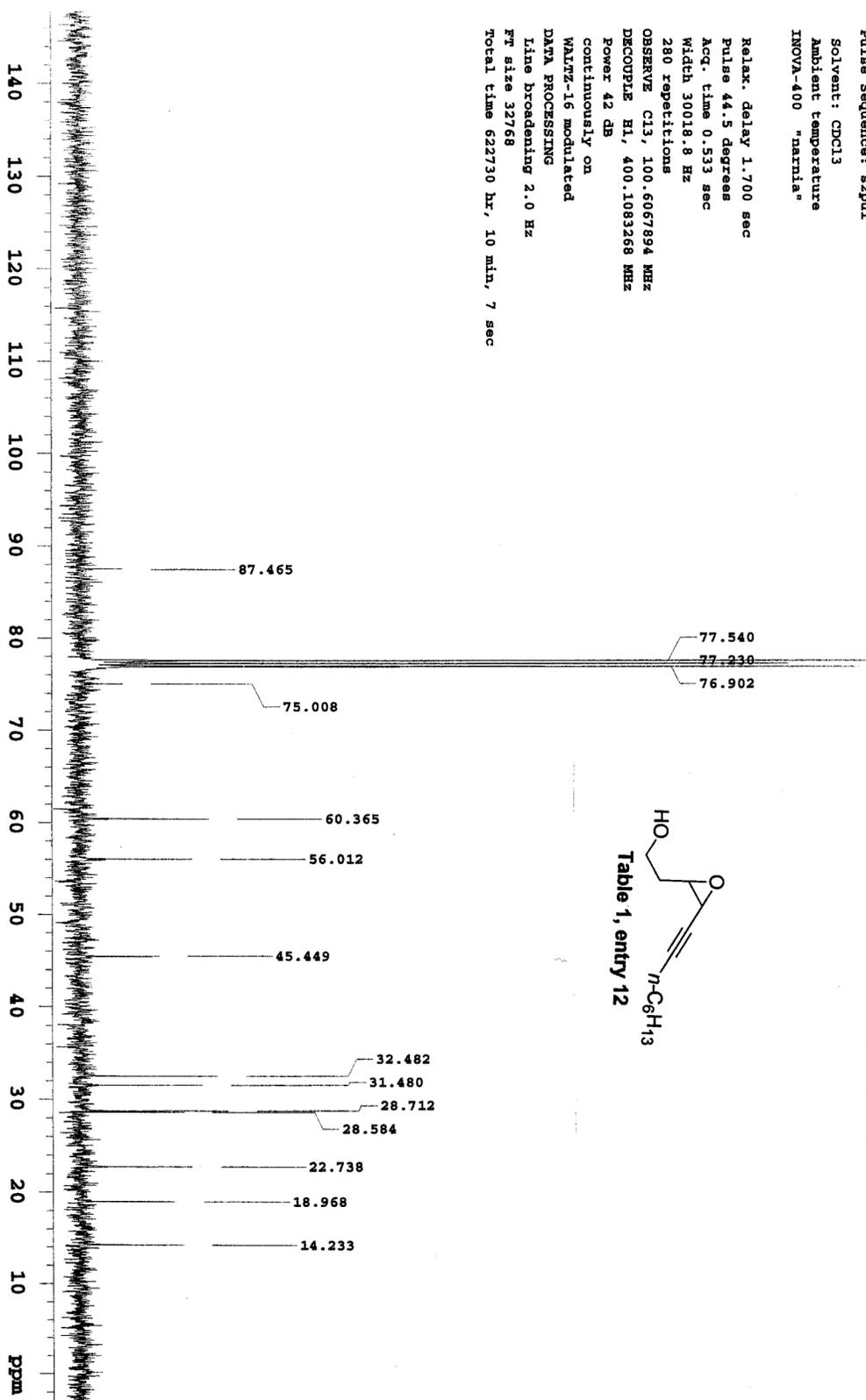
WALTZ-16 modulated

DATA PROCESSING

line broadening 2.0 Hz

FT size 32768

Total time 622730 hr, 10 min, 7 sec



STANDARD 1H OBSERVE

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

INOVA-400 "gamma"

Pulse 30.8 degrees

Acq. time 2.291 sec

Width 6982.6 Hz

8 repetitions

OBSERVE H1, 400.1063112 MHz

DATA PROCESSING

Gauss apodization 0.971 sec

FT size 65536

Total time 0 min, 23 sec

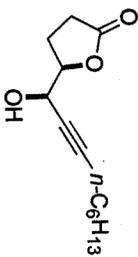
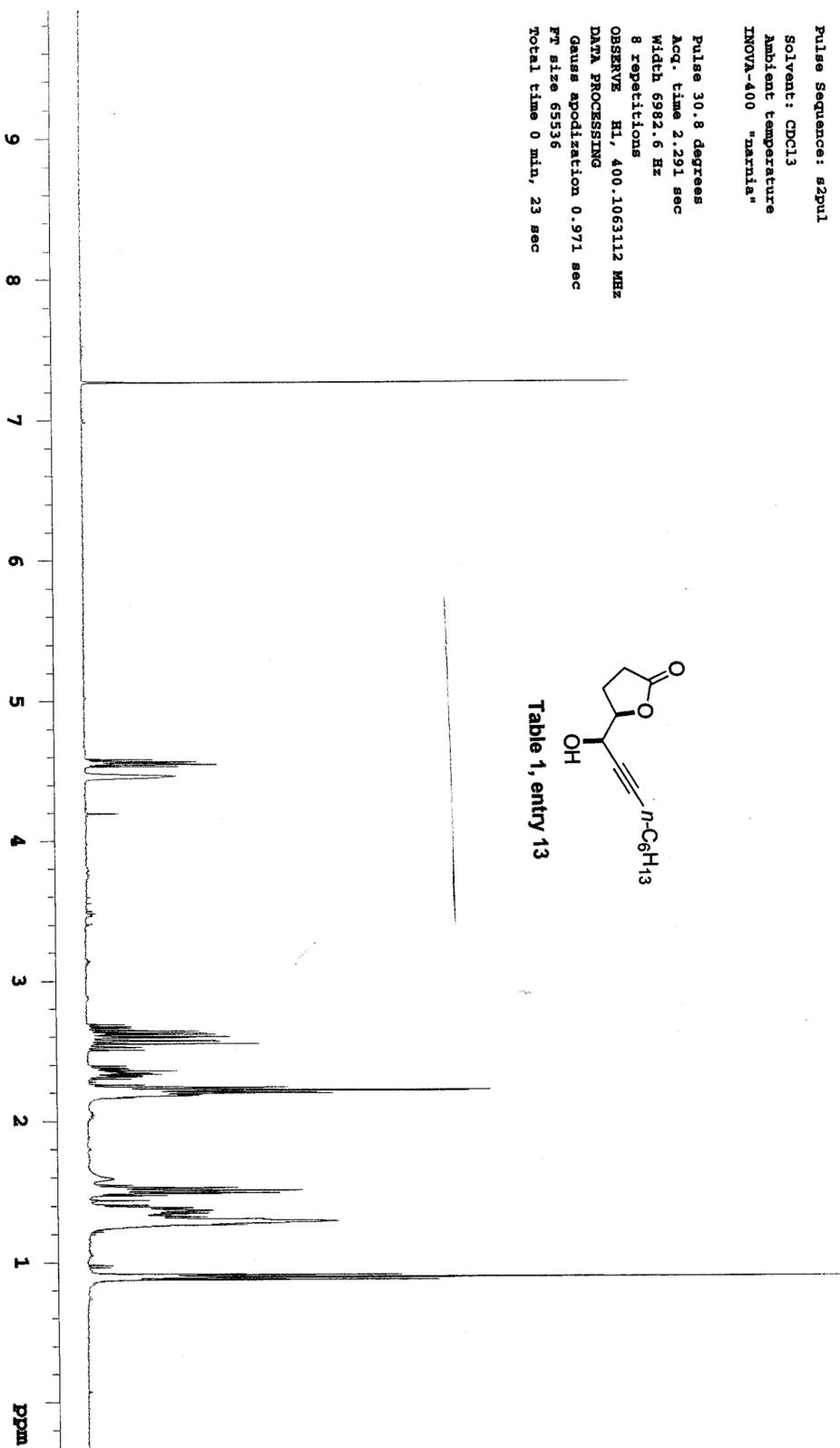


Table 1, entry 13



¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

INOVA-400 "narrisa"

Relax. delay 1.700 sec

Pulse 44.5 degrees

Acq. time 0.533 sec

Width 30018.8 Hz

510 repetitions

OBSERVE C13, 100.6067894 MHz

DECOUPLE H1, 400.1083268 MHz

Power 42 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 2.0 Hz

FM size 32768

Total time 622730 hr, 10 min, 7 sec

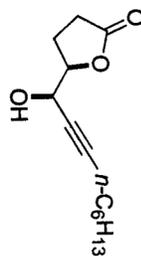
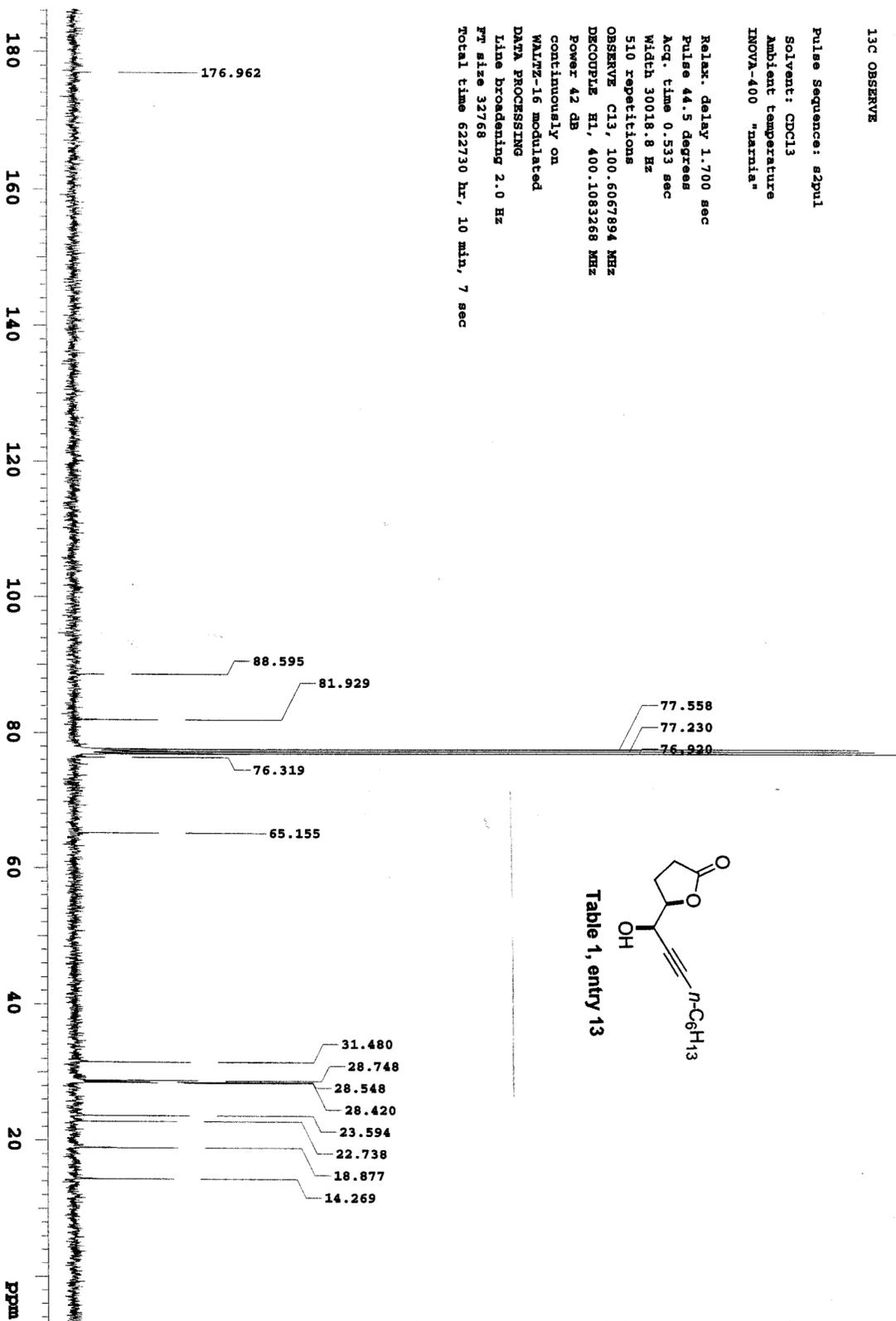


Table 1, entry 13

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

INOVA-400 "narnia"

Pulse 31.0 degrees

Acq. time 2.291 sec

Width 6982.6 Hz

4 repetitions

OBSERVE H1, 400.1063131 MHz

DATA PROCESSING

Gauss apodization 0.971 sec

FT size 65536

Total time 0 min, 13 sec

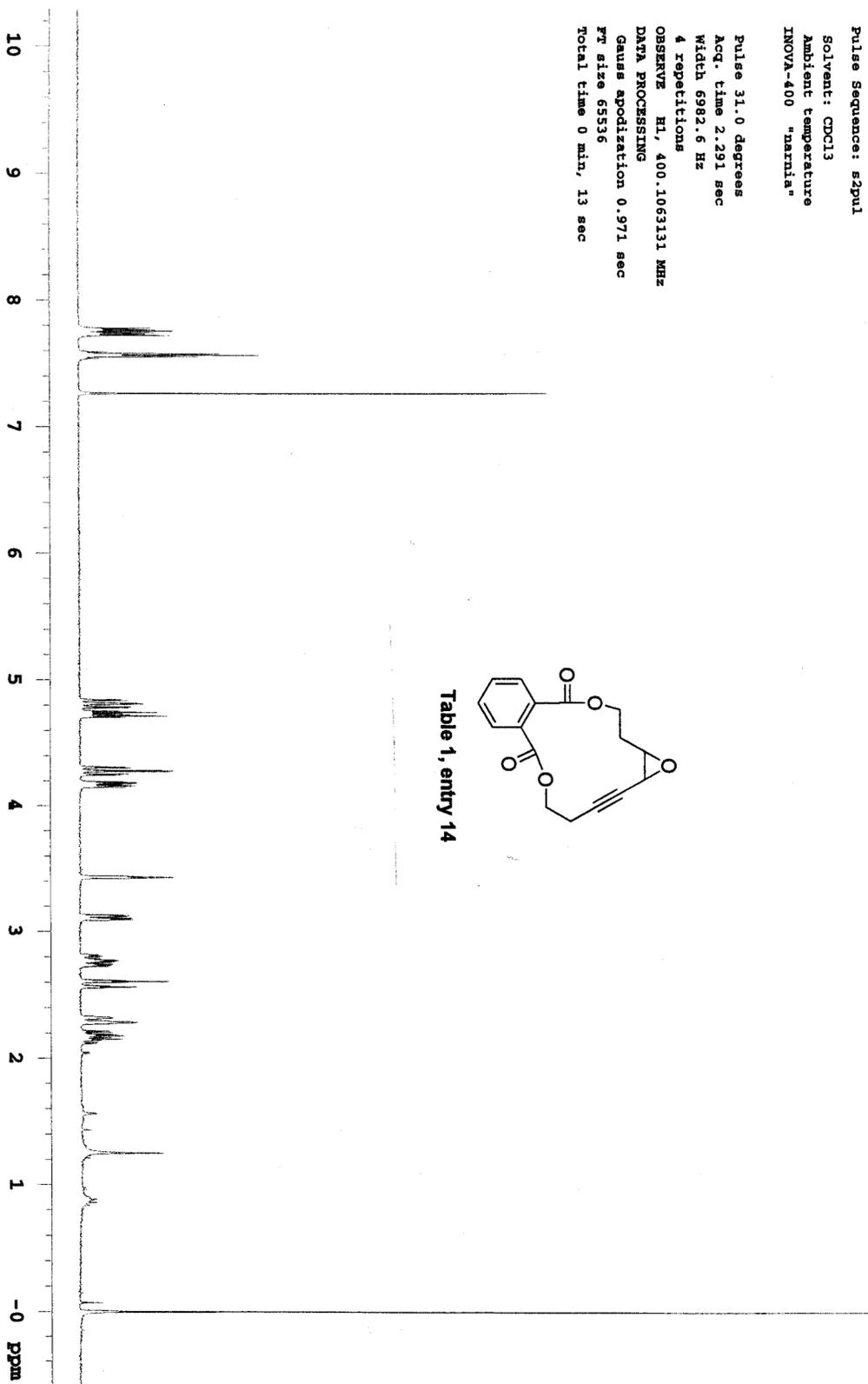
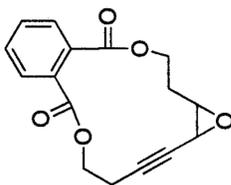


Table 1, entry 14



13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "gamma"

Relax. delay 1.700 sec
Pulse 44.5 degrees
Acq. time 0.533 sec
Width 30018.8 Hz
610 repetitions
OBSERVE C13, 100.6067913 MHz
DECUPLE H1, 400.1083268 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
F2 size 32768
Total time 622730 hr, 10 min, 7 sec

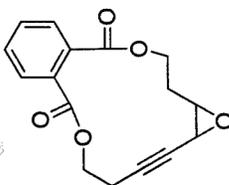
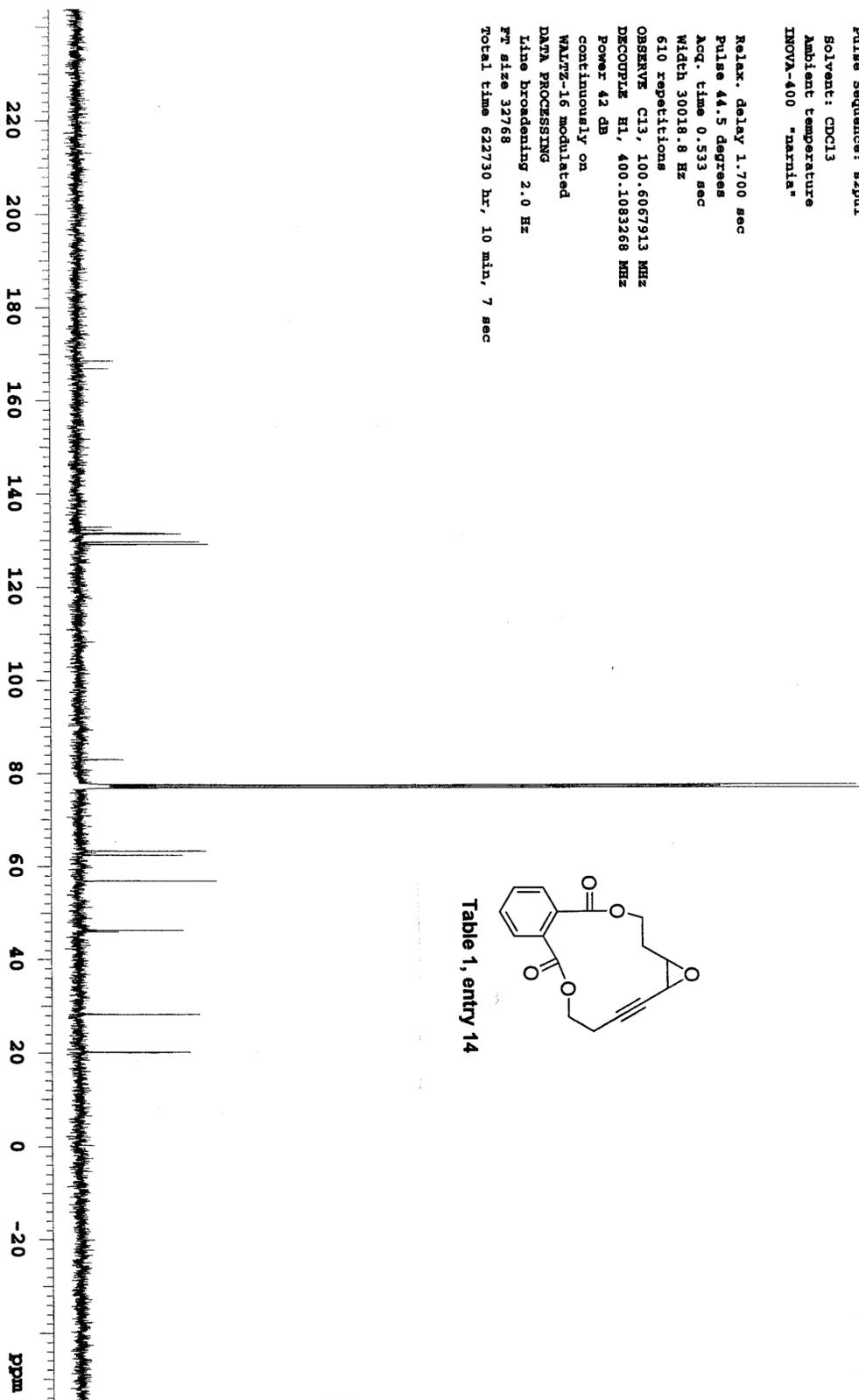


Table 1, entry 14

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

INOVA-400 "narrina"

Pulse 30.8 degrees

Acq. time 2.291 sec

Width 6982.6 Hz

8 repetitions

OBSERVE H1, 400.1063125 MHz

DATA PROCESSING

Gauss apodization 0.971 sec

FM size 65536

Total time 0 min, 23 sec

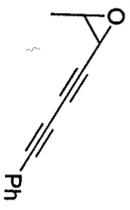
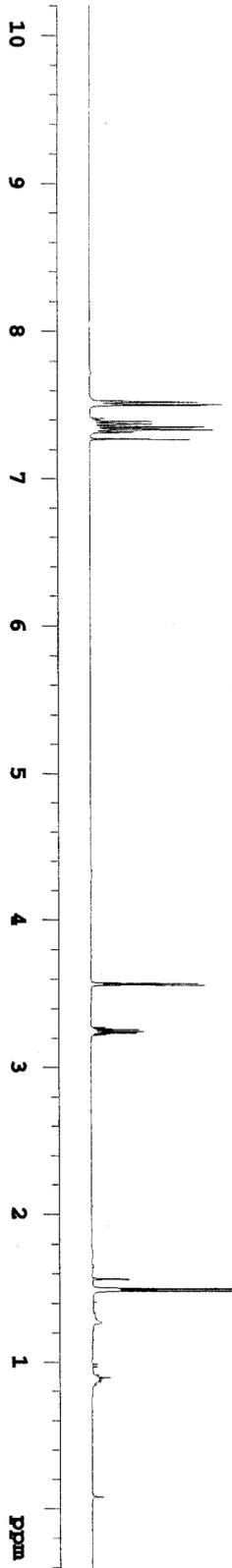


Table 1, entry 15



13C OBSERVE

Pulse Sequence: e2pul

Solvent: CDCl3
Ambient temperature
INOVA-400 "narrida"

Relax. delay 1.700 sec
Pulse 44.5 degrees
Acq. time 0.533 sec
Width 30018.8 Hz
366 repetitions
OBSERVE C13, 100.607894 MHz
DECOUPLE H1, 400.1083268 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
line broadening 2.0 Hz
FT size 32768
Total time 622730 hr, 10 min, 7 sec

