

**Supporting information**

**Triphenylphosphine Induced Ring-Contraction of 1,2-Dioxines**

Ben W. Greatrex and Dennis K. Taylor

*Department of Chemistry, University of Adelaide, Australia, 5005*

Page S2, General Experimental

Pages S2-S3 Characterization data for **1b**, **1c**, **8c-e**, **10**

Pages S5-S11  $^1\text{H}$  or  $^{13}\text{C}$  NMR spectra for **1c**, **8c,e**, **9a-c,f**, **10**, **11**, **12a-c**

**General Experimental**

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were recorded in  $\text{CDCl}_3$  solution using a 200 MHz, 300 MHz or 600 MHz instrument, with TMS (0 ppm,  $^1\text{H}$ ) and  $\text{CDCl}_3$  (77.0 ppm,  $^{13}\text{C}$ ) as internal standard. Thin-layer chromatography was performed using aluminium sheets silica gel 60 F<sub>254</sub>. THF was distilled from benzophenone ketyl and  $\text{CH}_2\text{Cl}_2$  distilled from  $\text{P}_2\text{O}_5$  immediately before use.

**General procedure for the synthesis of 1,2-dioxines;**

**4-Hexyl-3,6-dihydro-1,2-dioxine.** A solution of 2-hexyl-1,3-butadiene<sup>1,2</sup> (2.01 g, 14.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (90 ml) was irradiated for 6 hours with 3 x 500 W tungsten lamps. The solution was concentrated *in vacuo* and the product purified by flash chromatography (90:10 hexane/ethyl acetate) to give a colorless oil (1.54 g, 62%);  $R_f$  0.47 (5:95 ether/hexane); IR (neat) 1679, 1466, 1378, 1348, 1055, 1038, 774  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz)  $\delta$  0.89 (t,  $J = 7.2$  Hz, 3H), 1.26-1.48 (m, 8H), 2.02, (t,  $J = 8.1$  Hz, 2H), 4.45-4.47 (m, 2H), 4.55-4.58 (m, 2H), 5.62-5.65 (m, 1H);  $^{13}\text{C}$  NMR (50 MHz)  $\delta$  14.0, 22.5, 27.2, 28.9, 31.6, 32.4, 70.0, 72.5, 117.0, 135.8; EIMS  $m/z$  (%): 170 ( $\text{M}^+$ , 2), 152 (5), 95 (24), 82 (46), 68 (95), 43 (72), 41 (100).

**1a-Hexyl-tetrahydrooxireno[1,2-*c*]dioxine 8c.** To a stirred solution of 4-hexyl-3,6-dihydro-1,2-dioxine (1.15 g, 6.7 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 ml) at ambient temperature was added *m*-CPBA (3.05 g, 12.4 mmol). The solution was allowed to stir for 16 hours and then diluted with  $\text{CH}_2\text{Cl}_2$  (20 ml). The solution was washed with 10%  $\text{Na}_2\text{S}_2\text{O}_3$  (2 x 10 ml) then  $\text{NaHCO}_3$  (10 ml) and then brine (10 ml). The organic phase was dried and concentrated *in vacuo*, the residue was purified by squat chromatography to give a colorless oil (1.17 g, 93 %);  $R_f$  0.17 (7.5:82.5 ether/hexane); IR (neat) 1467, 1422, 1378, 1217, 1042, 731  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz)  $\delta$  0.92 (t,  $J = 7.2$  Hz, 3H), 1.26-1.50 (m, 8H), 1.63-1.82 (m, 2H), 3.31 (d,  $J = 3.3$  Hz, 1H), 4.27-4.49 (m, 4H);  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  14.0, 22.5, 24.1, 29.2, 31.6, 32.9, 54.7, 57.4, 70.2, 72.5; EIMS  $m/z$  (%): 186 ( $\text{M}^+$ , 1), 155 (14), 81 (32), 69 (85), 55 (77), 43 (100).

**4-(1-Adamantyl)-3,6-dihydro-1,2-dioxine 1b.** The reaction of 2-adamantyl-1,3-butadiene (2.70 g, 14.3 mmol) as per the general procedure afforded **1b** as a colorless solid (91%, 2.86 g); mp 65-66°C (sub);  $R_f$  0.46 (1:19 ether/hexane); IR (nujol): 1664,

1345, 1103, 1070, 1042, 945, 786, 722  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz):  $\delta$  1.57-1.72 (m, 12H), 2.01 (br s, 3H), 4.58-4.63 (m, 4H), 5.79-5.61 (m, 1H);  $^{13}\text{C}$  NMR (50 MHz):  $\delta$  144.1, 114.6, 70.4, 69.5, 40.9, 36.8, 35.7, 28.4. EIMS  $m/z$  (%): 220 ( $\text{M}^+$ , 12), 188 (40), 145 (15), 135 (100); Anal. Calcd for  $\text{C}_{14}\text{H}_{20}\text{O}_2$ : C, 76.33; H, 9.15. Found: C, 76.60; H, 9.20.

**1a-(1-Adamanty)perhydrooxireno[2,3-*d*][1,2]dioxine 8d.** The reaction of **1b** (500 mg, 2.27 mmol) with *m*-CPBA (1.0g, 4.05 mmol) according to the general procedure gave a colorless solid (95%, 510 mg); mp 57-59°C (sub);  $R_f$  0.20 (1:9 ether/hexane);  $^1\text{H}$  NMR (200 MHz):  $\delta$  1.61-1.76 (m, 12H), 2.02 (br s, 3H), 3.39 (ddd,  $J = 2.7, 0.9, 0.9$  Hz, 1H), 4.25 (br d,  $J = 13.5$  Hz, 1H), 4.30 (ddd,  $J = 13.5, 2.7, 0.8$  Hz, 1H), 4.42 (ddd,  $J = 13.5, 0.6, 0.6$  Hz, 1H), 4.52 (dd,  $J = 13.5, 0.9$  Hz, 1H);  $^{13}\text{C}$  NMR (50 MHz):  $\delta$  144.1, 114.6, 70.4, 69.5, 40.9, 36.8, 35.7, 28.4; IR (nujol): 1343, 1271, 1044, 1032, 988, 908, 809, 740  $\text{cm}^{-1}$ ; MS  $m/z$  (+EI): 236 ( $\text{M}^+$ , 49), 218 (13), 178 (6), 135 (100), 107 (9), 93 (22), 79 (23), 41 (14); Anal. Calcd for  $\text{C}_{14}\text{H}_{20}\text{O}_3$ : C, 71.16; H, 8.53. Found: C, 71.38; H, 8.49.

**4-Cyclohexyl-3,6-dihydro-1,2-dioxine 1c.** A solution of 2-cyclohexyl-1,3-butadiene<sup>3</sup> (1.16 g, 8.40 mmol) in  $\text{CH}_2\text{Cl}_2$  (90 ml) was irradiated for 6 hours with 3 x 500 W tungsten lamps. The solution was concentrated *in vacuo* and the product purified by flash chromatography (90:10 hexane/ethyl acetate) to give a colorless oil (0.88 g, 77 %);  $R_f$  0.45 (5:95 ether/hexane); IR (neat) 1673, 1449, 1347, 1037, 971, 943  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz)  $\delta$  1.10-1.36 (m, 5H), 1.66-1.93 (m, 6H), 4.51-4.59 (m, 4H), 5.59-5.62 (m, 1H);  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  26.1, 26.4, 31.6, 41.1, 70.1, 71.6, 115.4, 140.7; EIMS  $m/z$  (%): 168 (11), 121 (32), 95 (40), 67 (79), 58 (83), 41 (100).

**1a-Cyclohexyl-tetrahydrooxireno[1,2-*c*]dioxine 8e.** The reaction of **1c** (500 mg, 2.97 mmol) with *m*-CPBA (1.47 g, 5.96 mmol) as per the general procedure afforded **8e** as a colorless oil (0.53 g, 98 %); IR (neat) 1450, 1421, 1261, 1044, 875, 827, 737  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz)  $\delta$  1.00-1.32 (m, 5H), 1.41-1.51 (m, 1H), 1.67-1.84 (m, 5H), 3.29 (d,  $J = 2.1$  Hz, 1H), 4.26-4.44 (m, 4H);  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  25.8, 25.9, 26.0, 27.5, 28.1, 41.3, 53.6, 60.5, 70.2, 71.4; EIMS  $m/z$  (%): 184 ( $\text{M}^+$ , 10), 167 (25), 83

(74), 67 (52), 55 (100); HRMS calcd for (MH<sup>+</sup>) C<sub>10</sub>H<sub>17</sub>O<sub>3</sub>: 185.1177; found: 185.1171.

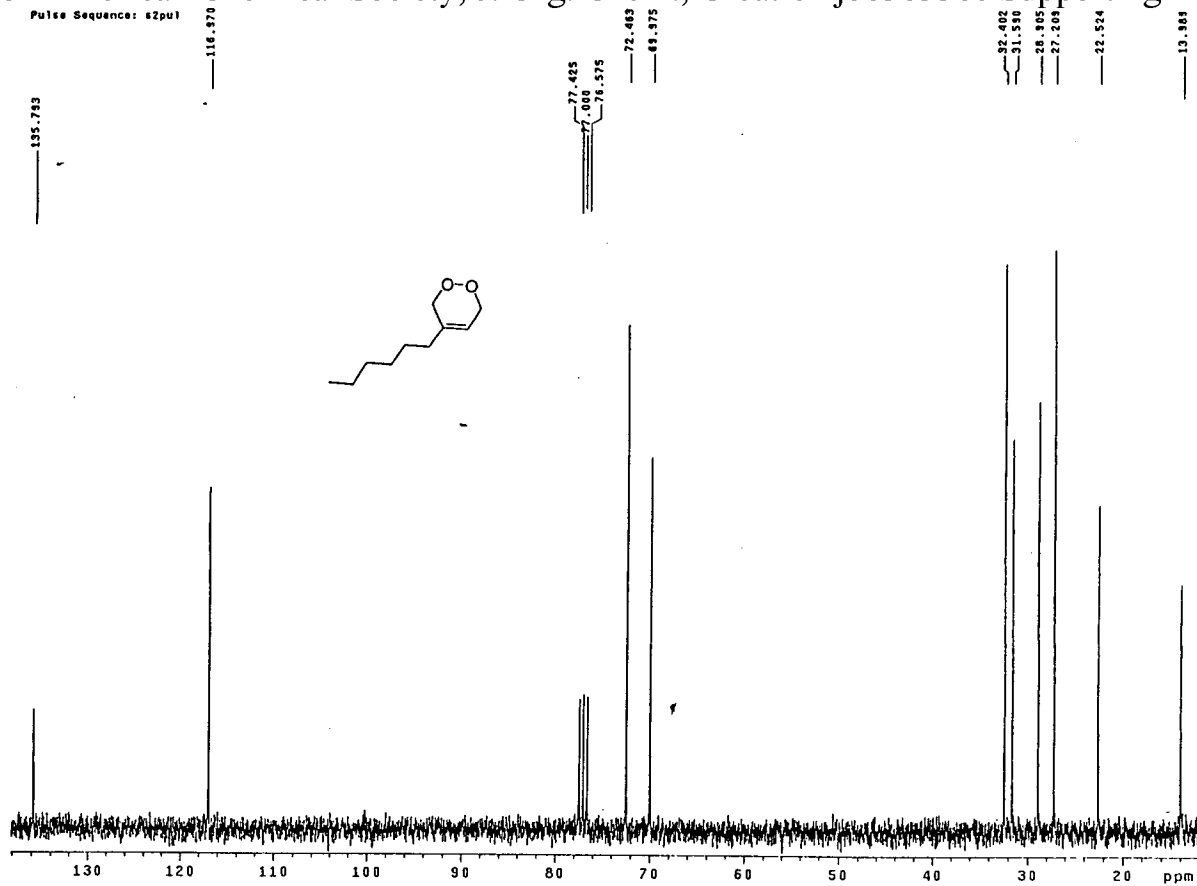
**4-Methyl-3-phenyl-3,6-dihydro-1,2-dioxine.** A solution of (*E*)-2-methyl-1-phenyl-1,3-butadiene (5.0 g, 28 mmol) and Rose Bengal (100 mg) in a water-jacketed flask cooled to 0° was irradiated with 3x500W-tungsten lamps for a period of 6 hours. The solution was then concentrated under reduced pressure and the product oil subjected to flash chromatography to yield the starting diene (1.04 g, 21%) and 1,2-dioxine **1b** (1.08, 18%); R<sub>f</sub> 0.45 (9:1 hexane/ethyl acetate); IR (neat) 3031, 2883, 1679, 1492, 1454 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz) δ 1.58 (d, *J* = 0.6 Hz, 3H), 4.55-4.74 (m, 2H), 5.32 (s, 1H), 5.87 (br s, 1H), 7.30-7.60 (m, 5H); <sup>13</sup>C NMR (50 MHz) δ 136.4, 133.4, 129.2, 128.8, 128.4, 119.8, 84.4, 70.0, 18.7; EIMS *m/z* (%): 176 (M<sup>+</sup>) (5), 158 (15), 144 (100), 129 (50); HRMS calcd for C<sub>11</sub>H<sub>12</sub>O<sub>2</sub>: 176.0837, found: 176.0831.

**(±) (1*aS*,2*R*,5*aS*)-1*a*-Methyl-2-phenylperhydrooxireno[2,3-*d*][1,2]dioxine 8g.** Epoxidation of 4-methyl-3-phenyl-3,6-dihydro-1,2-dioxine (700 mg, 3.97 mmol) as per the general procedure gave a colorless oil (370 mg, 48%); R<sub>f</sub> 0.20 (1:1 hexane/CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.46-7.42 (m, 5H), 5.25 (s, 1H), 4.61 (ddd, *J* = 13.2, 2.1, 0.6 Hz, 1H), 4.53 (dd, *J* = 13.2, 0.6 Hz, 1H), 3.41 (br s, 1H), 1.19 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 135.8, 129.0, 128.8, 128.5, 84.9, 69.6, 57.7, 56.1, 20.4; IR (neat): 3063, 3032, 2989, 2910, 1494, 1455, 1051, 701 cm<sup>-1</sup>; 192 (M<sup>+</sup>, 10), 105 (100); HRMS calcd for C<sub>11</sub>H<sub>12</sub>O<sub>3</sub>: 192.0786; found: 192.0780.

**(*S*)-{(2*S*,3*R*)-3-[(*R*)-1-hydroxy-1-phenylmethyl]oxiran-2-yl}(phenyl)methanol 10.** R<sub>f</sub> 0.15 (70:30 hexane/ethyl acetate); IR (nujol) 3392, 3189, 1040, 1025, 739, 700 cm<sup>-1</sup>; <sup>1</sup>H NMR (300) δ 3.05 (s, 2H), 3.23-3.27 (m, 2H), 4.80-4.83 (m, 2H), 7.33-7.53 (m, 10H); <sup>13</sup>C NMR (75) δ 59.9, 72.7, 125.8, 128.3, 128.8, 140.9; EIMS *m/z* (%) 256 (5), 238 (10), 220 (15); 149 (100).

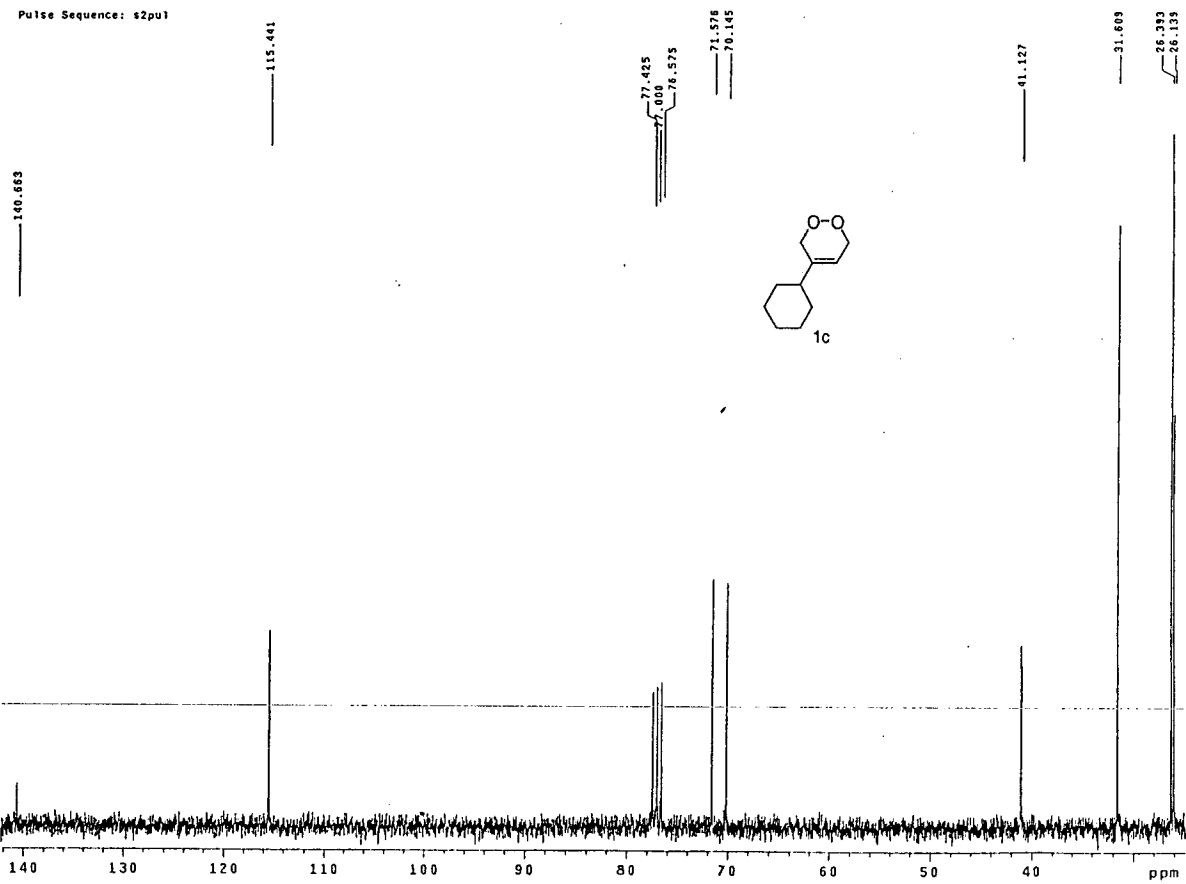
- (1) Greenand, M.; Hickinbothom, W. *J. Chem. Soc.* **1957**, 3262.
- (2) Fearnley, S.; Funk, R.; Gregg, R. *Tetrahedron* **2000**, *56*, 10275.
- (3) Hoshi, M.; Arase, A. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2693.

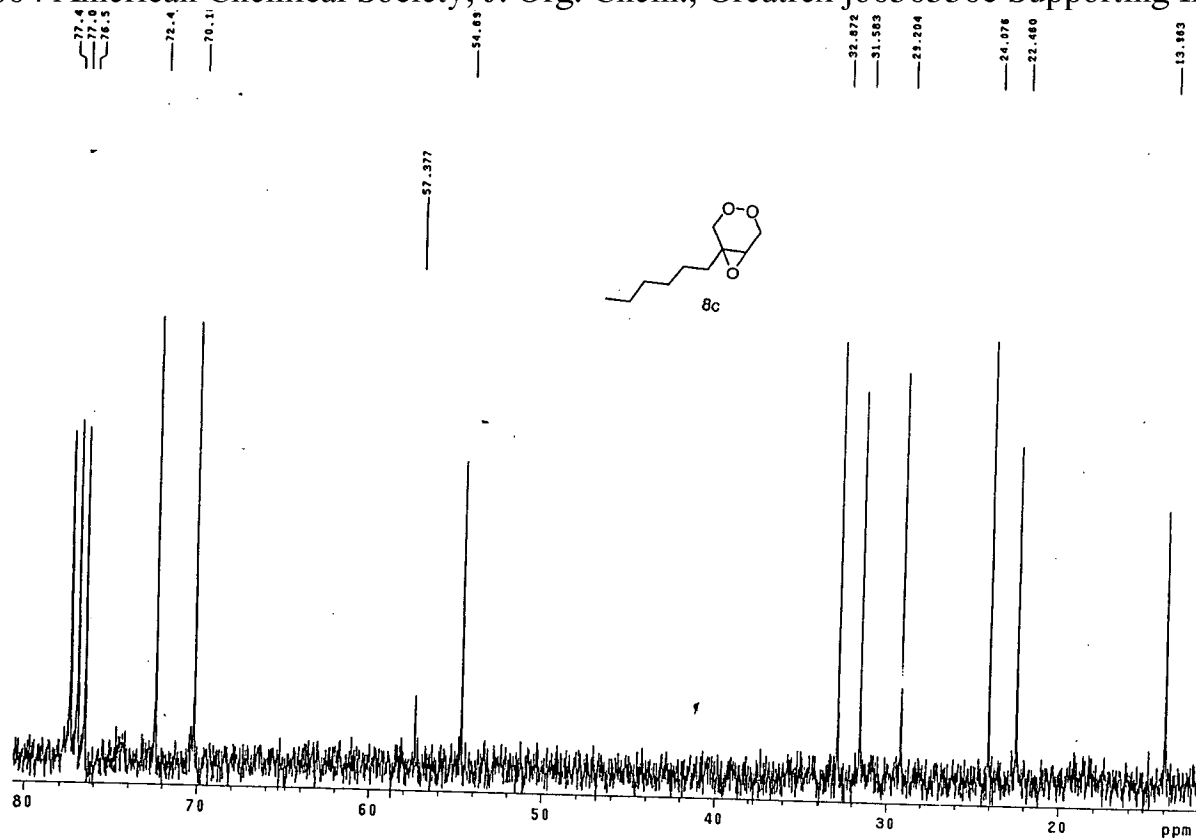
Pulse Sequence: s2pu1



13C OBSERVE

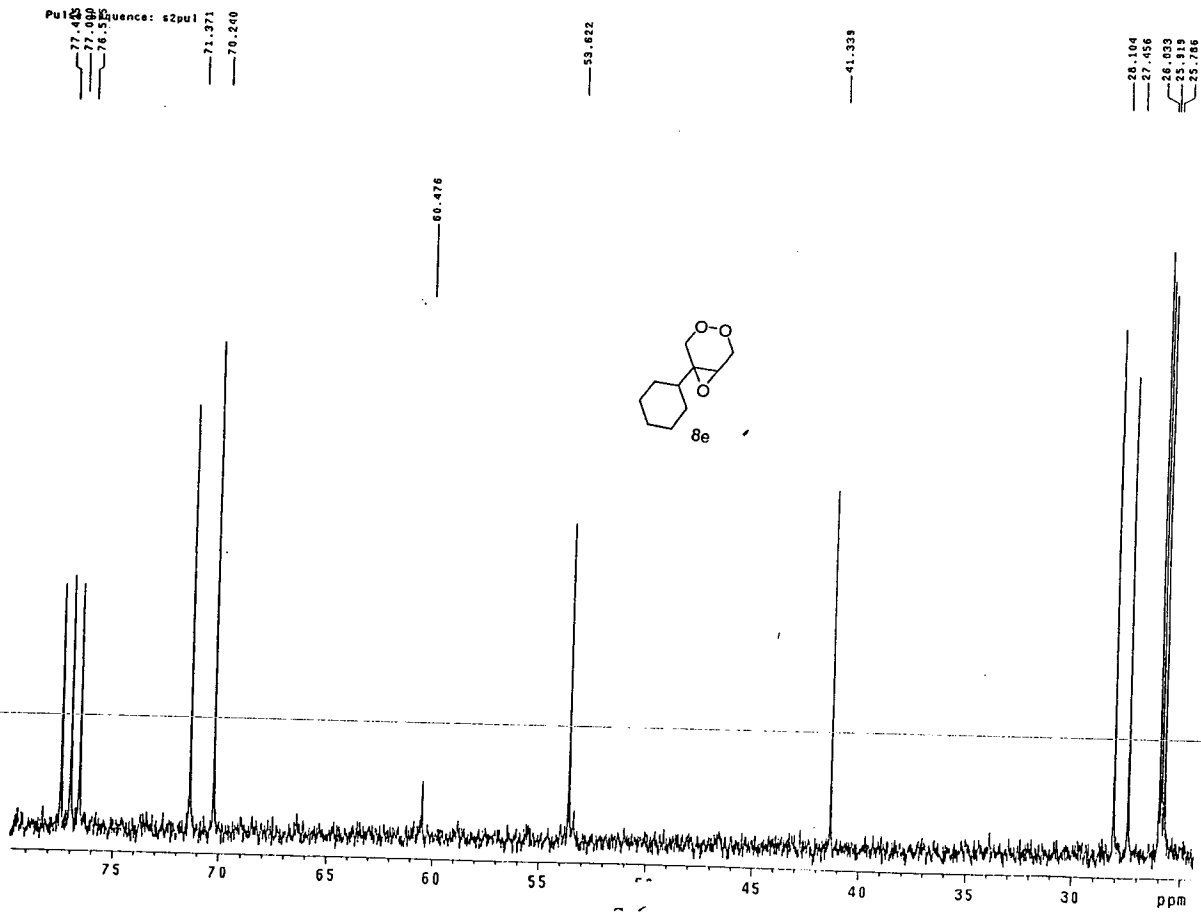
Pulse Sequence: s2pu1





13C OBSERVE

Pu124 Sequence: s2pu1

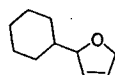




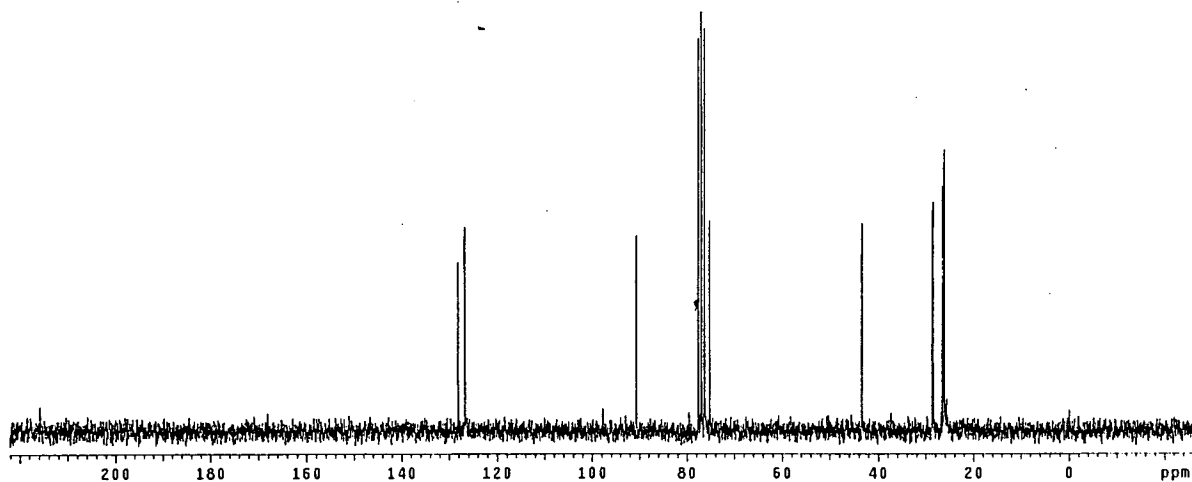




Pulse Sequence: scpul

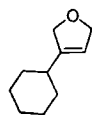


12a

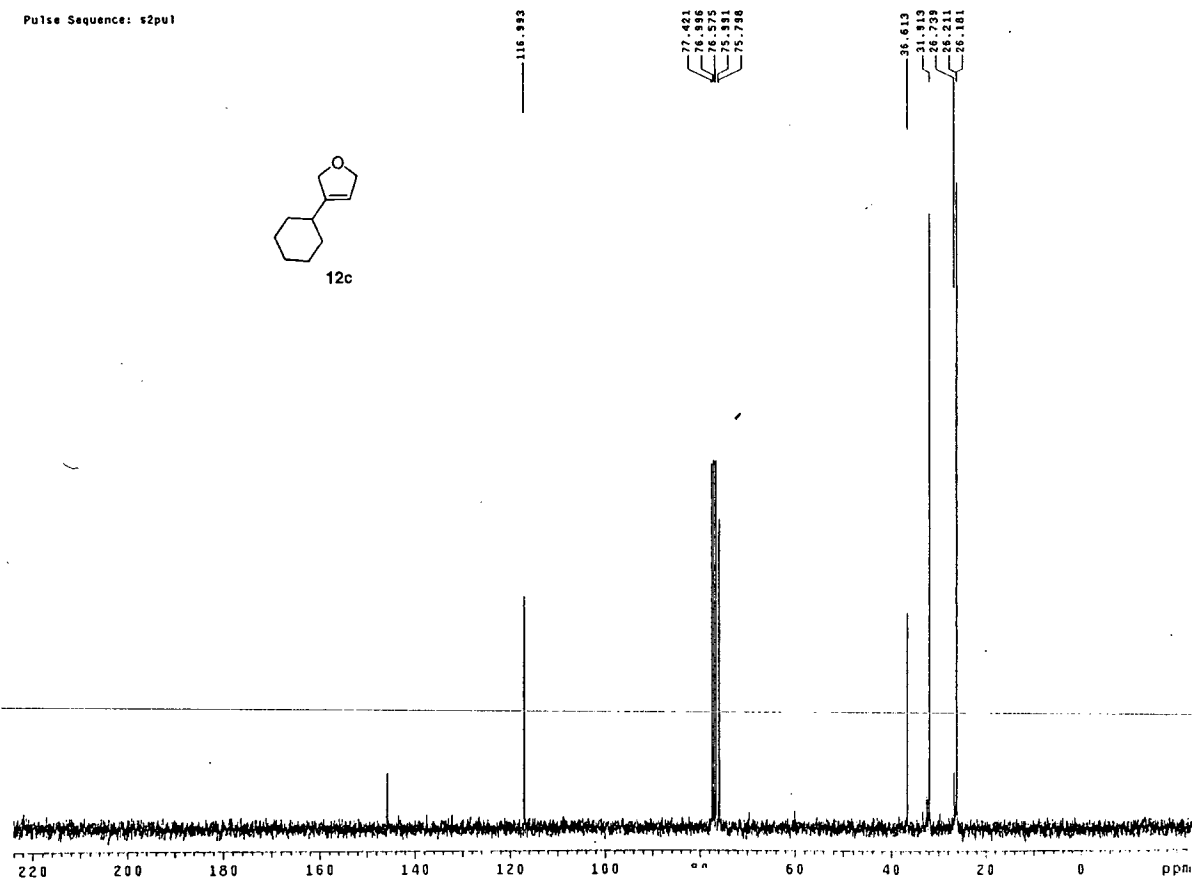


13C OBSERVE

Pulse Sequence: s2pul



12c



Pulse Sequence: s2pu1

