

Supporting Information

First Example of an Enone-Alkene [2+2+2] Photocycloaddition: 1,3- Photocycloaddition of Tetramethylethylene Across 2,7- Cyclooctadienone

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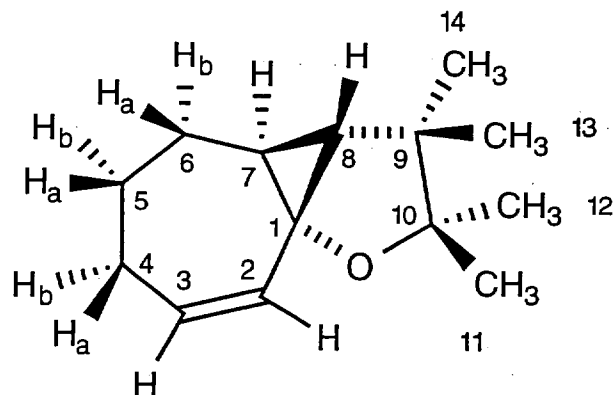
Experimental

9,9,10,10-Tetramethyl-11-oxatricyclo[6.3.0.0^{1,7}]undec-2-ene (7).

Cyclooctadienone¹ (817 mg, 6.7 mmol) and tetramethylethylene (20 mL) were dissolved in 50 mL of distilled hexane and irradiated ($\lambda > 340$ nm, uranium glass filter) for 14 h with 450 watt Hanovia lamp. The crude photolysis mixture was filtered through a short column of silica gel eluting with dichloromethane to give 450 mg of 7 as a clear oil (33% yield). An analytical sample was obtained by flash chromatography (10:1, hexanes/diethyl ether). Alternatively, analytical samples could be obtained by preparative GC (5% OV101, 5ft. x .25 in., 150 °C).

¹H NMR: (750 MHz) 5.90 (ddt J = 11.3, 2.2, 1.1; 1H), 5.43 (ddd J = 4.5, 6.0, 11.3; 1H), 2.25 (m, 1H), 2.06 (m, 1H), 1.99 (m, 1H), 1.63 (m, 1H), 1.57 (m, 1H), 1.39 (m, 1H), 1.19 (d J = 4.5, 1H), 1.03 (m, 1H), 1.22 (s, 3H), 1.05 (s, 3H), 0.96 (s, 3H), 0.90 (s, 3H); ¹³C NMR: 130.2 (d), 128.9 (d), 93.4 (s), 67.1 (s), 45.1 (d), 44.3 (s), 35.8 (d), 30.1 (t), 28.9 (t), 26.0 (q), 25.7 (q), 24.6 (t), 23.7 (q), 22.9 (q); MS m/e 206 (M+); Anal. Calcd for C₁₄H₂₂O: C, 81.50; H, 10.75. Found C, 81.36; H, 10.84.

(1) Garbisch, E. W. *J. Org. Chem.* **1965**, *30*, 2109-2120.

¹H and ¹³C NMR Chemical Shift Assignments and Proton-Proton Coupling Constants**Chemical Shift Assignments**

Positions	Protons (δ)	Carbons (δ)
1	----	93.4
2	5.88	130.2
3	5.43	128.9
4	4a: 2.25 4b: 2.06	30.1
5	5a: 1.63 5b: 1.39	24.6
6	6a: 1.99 6b: 1.03	28.9
7	1.57	35.8
8	1.19	45.1
9	----	44.3
10	----	67.1
11	1.22	26.0
12	1.05	25.7
13	0.96	22.9
14	0.90	23.7

Proton-Proton Coupling Constants (Hz)

$$J_{2,3} = 11$$

$$J_{2,4a} = 1; J_{2,4b} = 2$$

$$J_{2,7} = 1$$

$$J_{3,4a} = 4.5; J_{3,4b} = 6$$

$$J_{4a,4b} = 21$$

$$J_{4a,5a} = 5; J_{4a,5b} = 9$$

$$J_{4b,5a} = 9; J_{4b,5b} = 5$$

$$J_{5a,5b} = 14$$

$$J_{5a,6a} = 8; J_{5a,6b} = 3$$

$$J_{5b,6a} = 3; J_{5b,6b} = 8$$

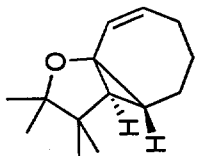
$$J_{6a,6b} = 14$$

$$J_{6a,7} = 5; J_{6b,7} = 9$$

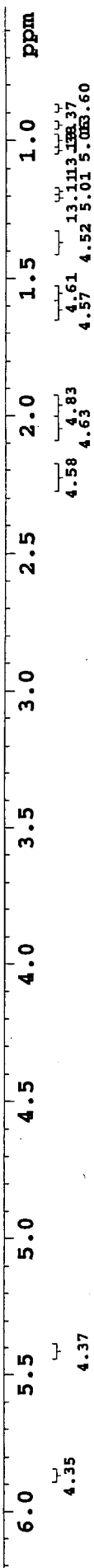
$$J_{7,8} = 4.5$$

8-S

750 MHz ¹H NMR

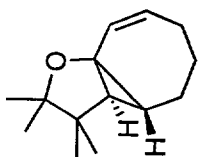


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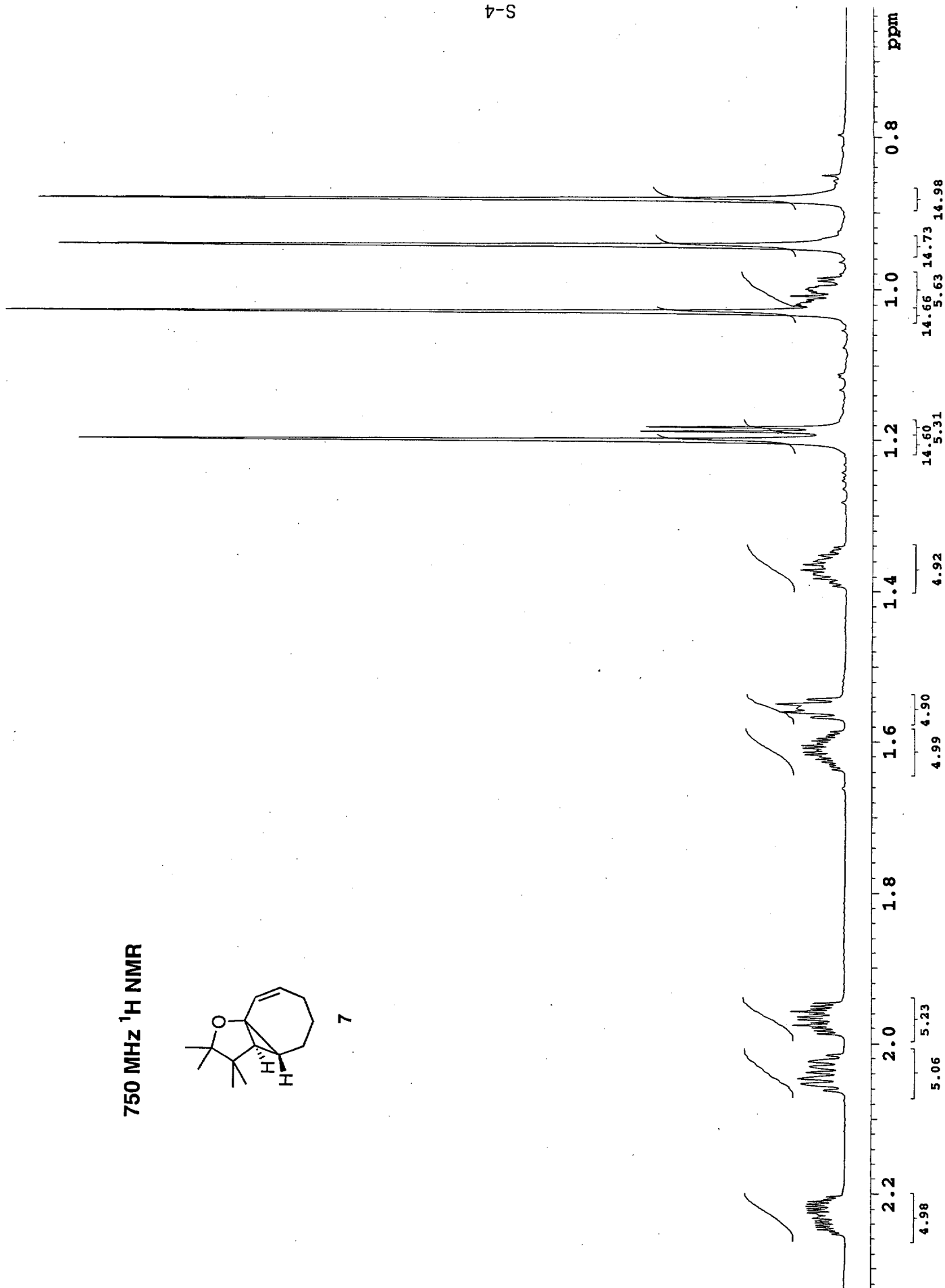


S-4

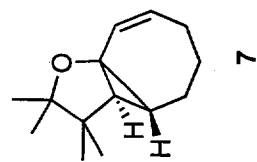
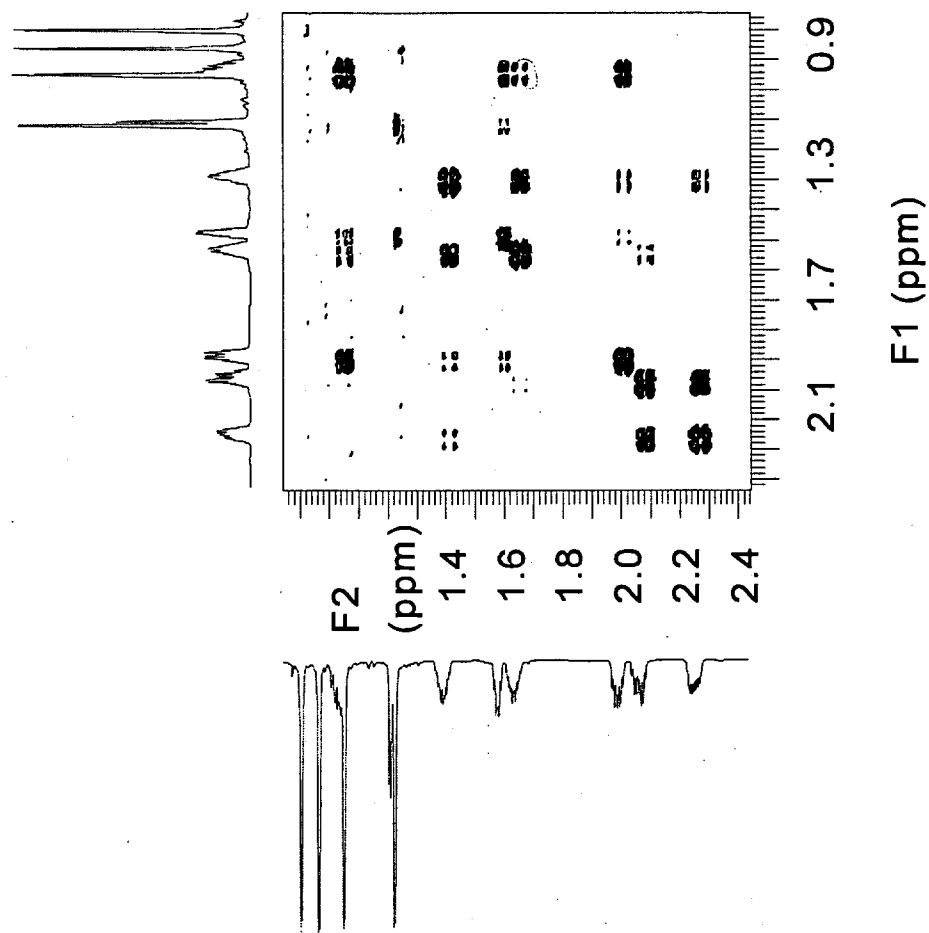
750 MHz ¹H NMR

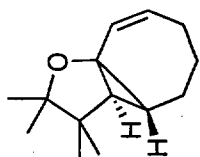


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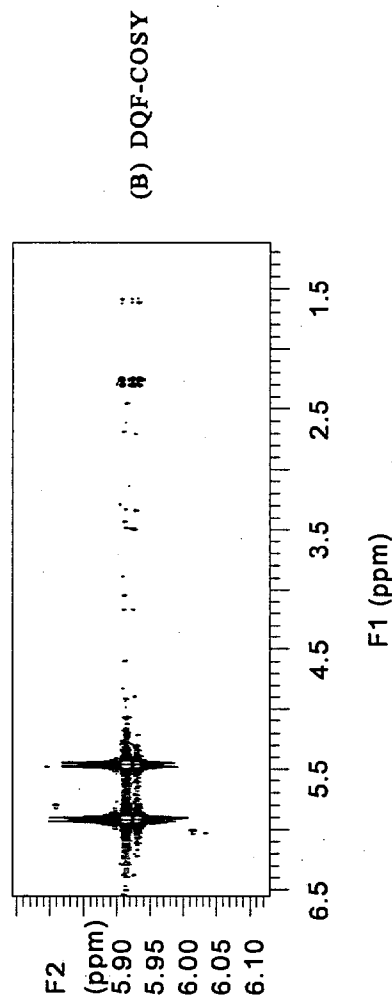
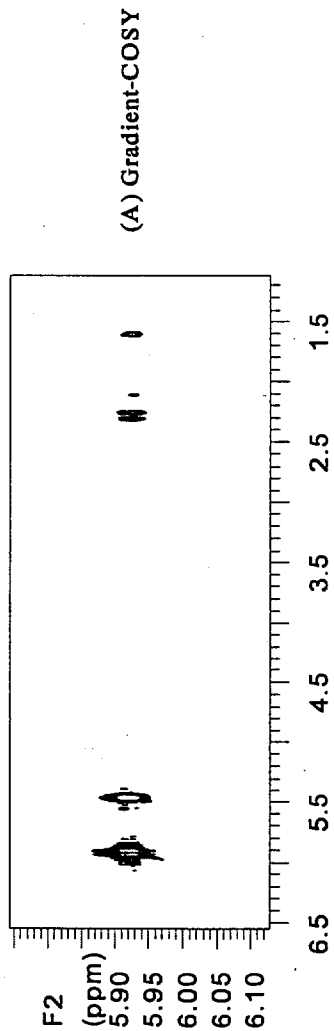
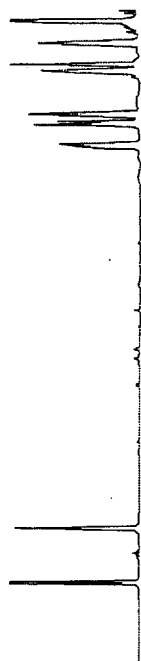
The Aliphatic Region Expansion of DQF-COSY 2D NMR Spectra





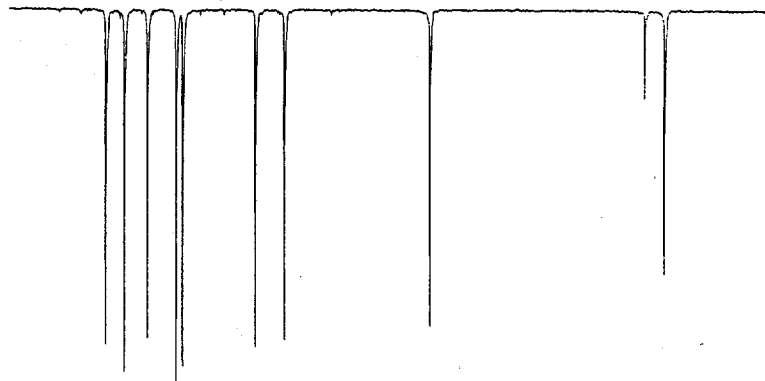
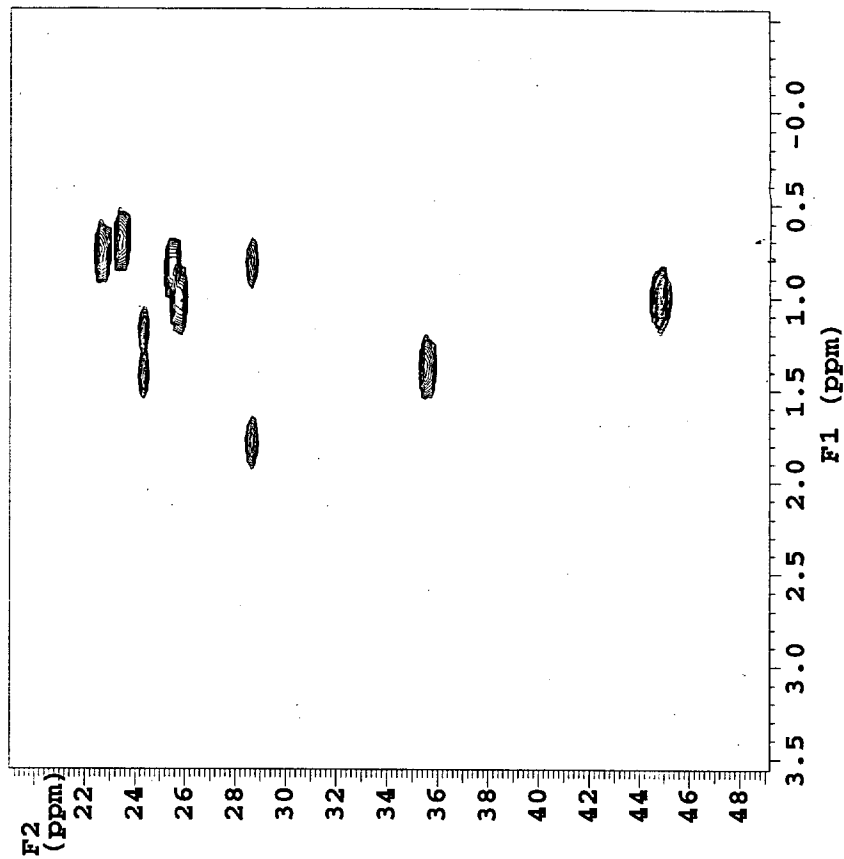
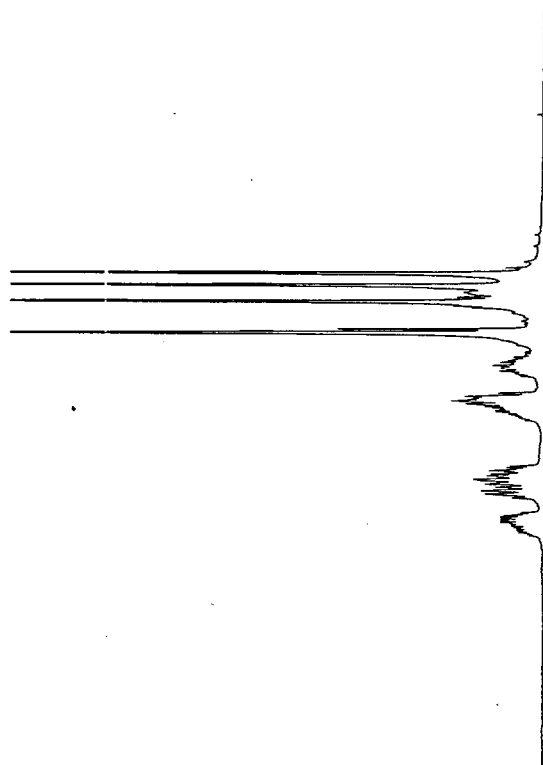
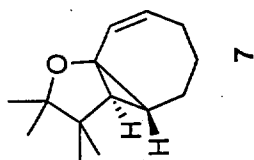
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The Expansions of COSY 2D NMR Spectra



Cl3-H1 Hetcor

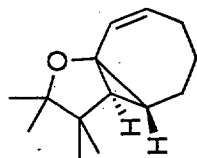
HETCOR



8-S

C13-H1 Hetcor

HETCOR



7

