

**Supporting Information for**  
**Et<sub>2</sub>AlCl-Promoted Asymmetric Phenylseleno Group Transfer Radical**  
**Cyclization Reactions of Unsaturated  $\beta$ -Hydroxy Esters**

Dan Yang,\* Qiang Gao, Bao-Fu Zheng, and Nian-Yong Zhu

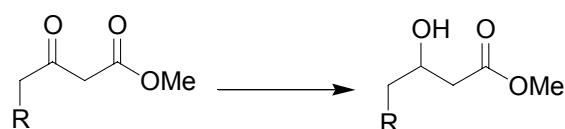
*Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong*

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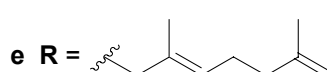
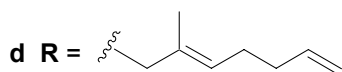
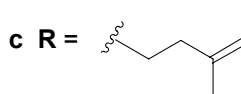
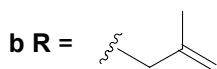
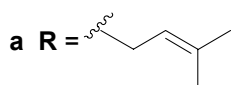
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### General procedure:

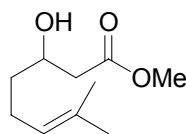
All reactions were performed in oven-dried flasks. Air and moisture-sensitive compounds were introduced *via* syringes through a rubber septum. THF and Benzene were distilled from sodium metal-benzophenone ketyl before use. Dichloromethane and toluene were distilled over calcium hydride. Flash column chromatography was performed on E. Merck silica gel 60 (230–400 mesh ASTM) using ethyl acetate/*n*-hexane as eluting solvents. A 125W high pressure mercury lamp was used as UV source. A 300W sunlamp was used as the photolysis source.



**6a-e**

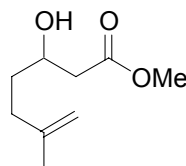


**Typical procedure for the preparation of unsaturated  $\beta$ -hydroxy esters** To a solution of 7-methyl-3-oxo-oct-6-enoic acid methyl ester<sup>1</sup> (2.5 g, 13.59 mmol) in MeOH (50 mL), was added NaBH<sub>4</sub> (516 mg, 13.59 mmol) in four portions at 0 °C. The mixture was stirred for further 5 min before the adding of acetone (20 mL). After the removal of all solvents, aqueous NH<sub>4</sub>Cl was added, and the mixture was extracted with Et<sub>2</sub>O. The combined organic extracts were washed with water, dried over Na<sub>2</sub>SO<sub>4</sub> and then concentrated. The crude residue was purified by flash column chromatography to give **6a** (2.1 g, 85%).



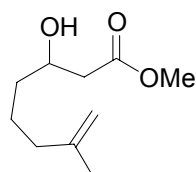
**6a**

**6a**:<sup>5</sup> A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1,  $R_f$  = 0.35;  $^1\text{H}$  NMR (400 MHz)  $\delta$  5.14–5.09 (m, 1H), 4.07–3.99 (m, 1H), 3.71 (s, 3H), 2.86 (d,  $J$  = 4.1 Hz, 1H), 2.51 (dd,  $J$  = 3.5, 16.4 Hz, 1H), 2.42 (dd,  $J$  = 8.7, 16.4 Hz, 1H), 2.10 (q,  $J$  = 7.5 Hz, 2H), 1.69 (s, 3H), 1.62 (s, 3H), 1.60–1.44 (m, 2H).



**6b**

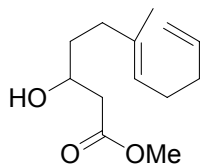
**6b**: A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1,  $R_f$  = 0.4;  $^1\text{H}$  NMR (300 MHz)  $\delta$  4.73 (t,  $J$  = 0.6 Hz, 1H), 4.67 (d,  $J$  = 0.8 Hz, 1H), 4.06–3.98 (m, 1H), 3.71 (s, 3H), 2.97 (br. s, 1H), 2.53 (dd,  $J$  = 3.6, 16.3 Hz, 1H), 2.44 (dd,  $J$  = 8.6, 16.3 Hz, 1H), 2.28–2.04 (m, 2H), 1.73 (s, 3H), 1.71–1.52 (m, 2H);  $^{13}\text{C}$  NMR (75.5 MHz)  $\delta$  173.3, 145.2, 110.3, 67.7, 51.7, 41.1, 34.4, 33.7, 22.4; IR ( $\text{CH}_2\text{Cl}_2$ ) 3688, 1729  $\text{cm}^{-1}$ ; LRMS (EI, 20 eV)  $m/z$  154 ( $\text{M}^+ - \text{H}_2\text{O}$ , 16), 149 (100); HRMS (EI) for  $\text{C}_9\text{H}_{14}\text{O}_2$  ( $\text{M}^+ - \text{H}_2\text{O}$ ): calcd 154.0994, found 154.0988.



**6c**

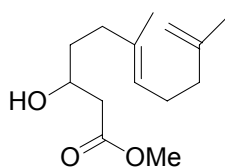
**6c**: A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1,  $R_f$  = 0.4;  $^1\text{H}$  NMR (300 MHz)  $\delta$  4.70 (apparent s, 1H), 4.67 (apparent s, 1H), 4.05–3.99 (m, 1H), 3.71 (s, 3H), 2.88 (br. s, 1H), 2.51 (dd,  $J$  = 3.6, 16.3 Hz, 1H), 2.41 (dd,  $J$  = 8.6, 16.3 Hz, 1H), 2.03 (apparent t,  $J$  = 6.6 Hz,

2H), 1.75 (s, 3H), 1.64–1.39 (m, 4H);  $^{13}\text{C}$  NMR (75.5 MHz)  $\delta$  173.4, 145.5, 110.1, 67.8, 51.7, 41.2, 37.5, 36.0, 23.4, 22.2; IR ( $\text{CH}_2\text{Cl}_2$ ) 3649, 1732  $\text{cm}^{-1}$ ; LRMS (EI, 20 eV)  $m/z$  168 ( $\text{M}^+ - \text{H}_2\text{O}$ , 100), 153 (52); HRMS (EI) for  $\text{C}_{10}\text{H}_{16}\text{O}_2$  ( $\text{M}^+ - \text{H}_2\text{O}$ ): calcd 168.1150, found 168.1133.



**6d**

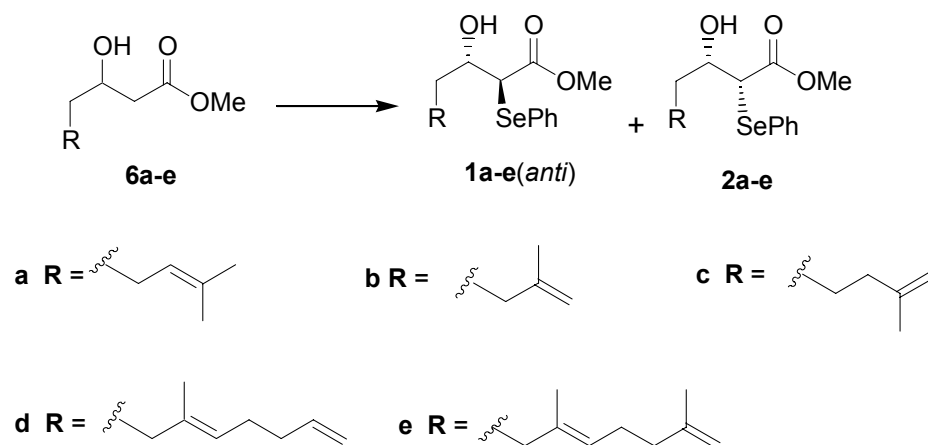
**6d**: A colorless oil; analytical TLC (silica gel 60),  $n$ -Hexane:EtOAc = 3:1,  $R_f$  = 0.3;  $^1\text{H}$  NMR (400 MHz)  $\delta$  5.84–5.77 (m, 1H), 5.18 (td,  $J$  = 1.1, 7.1 Hz, 1H), 5.17–4.92 (m, 2H), 4.01–3.96 (m, 1H), 3.71 (s, 3H), 2.83 (d,  $J$  = 4.0 Hz, 1H), 2.52 (dd,  $J$  = 3.4, 16.4 Hz, 1H) 2.42 (dd,  $J$  = 8.8, 16.4 Hz, 1H), 2.13–2.05 (m, 6H), 1.64–1.54 (m, 2H), 1.60 (s, 3H);  $^{13}\text{C}$  NMR (75.5 MHz)  $\delta$  173.4, 138.6, 134.8, 124.5, 114.5, 67.8, 51.7, 41.2, 35.6, 34.7, 33.9, 27.4, 16.0; IR ( $\text{CH}_2\text{Cl}_2$ ) 3527, 1730  $\text{cm}^{-1}$ ; LRMS (EI, 20 eV)  $m/z$  226 ( $\text{M}^+$ , 1), 208 (5), 93 (100); HRMS (EI) for  $\text{C}_{13}\text{H}_{20}\text{O}_2$  ( $\text{M}^+ - \text{H}_2\text{O}$ ): calcd 208.1463, found 208.1459.



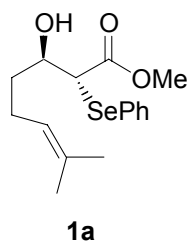
**6e**

**6e**: A colorless oil; analytical TLC (silica gel 60),  $n$ -Hexane:EtOAc = 3:1,  $R_f$  = 0.30;  $^1\text{H}$  NMR (300 MHz)  $\delta$  5.16 (td,  $J$  = 7.9, 1.2 Hz, 1H), 4.70 (s, 1H), 4.67 (s, 1H), 4.03–3.94 (m, 1H), 3.71 (s, 3H), 2.91 (br. s, 1H), 2.52 (dd,  $J$  = 3.6, 16.2 Hz, 1H), 2.42 (dd,  $J$  = 8.6, 16.3 Hz, 1H), 2.19–2.00 (m, 6H), 1.71 (s, 3H), 1.68–1.47 (m, 2H), 1.61 (s, 3H);  $^{13}\text{C}$  NMR (75.5 MHz)  $\delta$  173.3, 145.7, 134.5, 124.7, 109.9, 67.8, 51.6, 41.1, 37.7, 35.6, 34.6, 26.1, 22.4, 15.9; IR ( $\text{CH}_2\text{Cl}_2$ ) 3673, 1730  $\text{cm}^{-1}$ ; LRMS

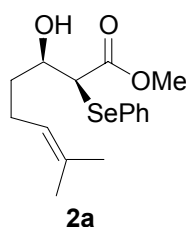
(EI, 20 eV)  $m/z$  240 ( $M^+$ , 5), 222 (100); HRMS (EI) for  $C_{14}H_{24}O_3$  ( $M^+$ ): calcd 240.1725, found 240.1716.



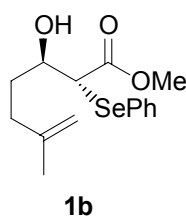
**Typical procedure for the preparation of unsaturated  $\alpha$ -phenylseleno  $\beta$ -hydroxy esters.** To a solution of (*i*-Pr)<sub>2</sub>NH (1.5 mL, 10.7 mmol) in THF (40 mL) under argon was added *n*-BuLi (2.5 M in hexane, 4 mL, 10 mmol) slowly at 0 °C. After 0.5 h, the solution was cooled to –35 °C, and the pre-cooled solution of **6a** (786 mg, 4.1 mmol) in THF (10 mL) was added. After 20 min, the solution was cooled to –78 °C, and the pre-cooled solution of PhSeBr (1.06 g, 4.51 mmol) in THF 15 mL was added slowly. The reaction was then stirred at –78 °C for 3 h before quenched with H<sub>2</sub>O. The mixture was extracted with ether. The combined extracts were washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and then concentrated. The crude product was purified by flash column chromatography to give **1a** (991 mg, 71%) and **2a** (95 mg, 7%).<sup>2</sup>



**1a**: A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1,  $R_f$  = 0.38;  $^1\text{H}$  NMR (400 MHz)  $\delta$  7.60–7.58 (m, 2H), 7.32–7.29 (m, 3H), 5.08 (tt,  $J$  = 1.3, 5.8 Hz, 1H), 3.95–3.88 (m, 1H), 3.66 (s, 3H), 3.62 (d,  $J$  = 7.0 Hz, 1H), 2.83 (d,  $J$  = 7.2 Hz, 1H), 2.18–2.08 (m, 2H), 1.88–1.80 (m, 1H), 1.63 (s, 3H), 1.61–1.52 (m, 1H), 1.59 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  173.2, 135.6, 132.7, 129.3, 129.2, 127.0, 123.6, 71.7, 52.2, 49.1, 34.8, 25.8, 24.3, 17.8; IR ( $\text{CH}_2\text{Cl}_2$ ) 3544, 1718  $\text{cm}^{-1}$ ; LRMS (EI, 20 eV)  $m/z$  342 ( $\text{M}^+$ , 11), 230 (33), 167 (100); HRMS (EI) for  $\text{C}_{16}\text{H}_{22}\text{O}_3\text{Se}$  ( $\text{M}^+$ ): calcd 342.0734, found 342.0737.

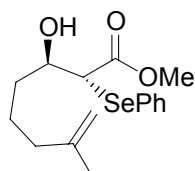


**2a**: A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1,  $R_f$  = 0.42;  $^1\text{H}$  NMR (400 MHz)  $\delta$  7.64–7.61 (m, 2H), 7.31–7.28 (m, 3H), 5.09 (tt,  $J$  = 1.4, 5.8 Hz, 1H), 3.95–3.89 (m, 1H), 3.65 (s, 3H), 3.62 (d,  $J$  = 5.2 Hz, 1H), 3.21 (d,  $J$  = 1.7 Hz, 1H), 2.13–2.05 (m, 2H), 1.83–1.71 (m, 1H), 1.67 (s, 3H), 1.64–1.52 (m, 1H), 1.59 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  173.7, 135.5, 135.4, 129.3, 129.2, 128.6, 123.7, 70.0, 52.3, 52.0, 34.5, 25.8, 24.3, 17.9; IR ( $\text{CH}_2\text{Cl}_2$ ) 3574, 1724  $\text{cm}^{-1}$ ; LRMS (EI, 20 eV)  $m/z$  342 ( $\text{M}^+$ , 9), 230 (48), 167 (100); HRMS (EI) for  $\text{C}_{16}\text{H}_{22}\text{O}_3\text{Se}$  ( $\text{M}^+$ ): calcd 342.0734, found 342.0730.



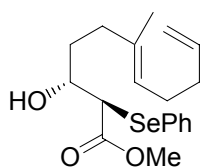
**1b**: A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1,  $R_f$  = 0.42;  $^1\text{H}$  NMR (300 MHz)  $\delta$  7.61–7.60 (m, 2H), 7.58–7.29 (m, 3H), 4.72 (s, 1H), 4.69 (s, 1H), 3.96–3.90 (m, 1H),

3.66 (s, 3H), 3.65 (d,  $J = 6.5$  Hz, 1H), 2.88 (d,  $J = 7.0$  Hz, 1H), 2.35–1.95 (m, 3H), 1.72 (s, 3H), 1.69–1.59 (m, 1H);  $^{13}\text{C}$  NMR (75.5 MHz)  $\delta$  173.0, 145.0, 135.4, 129.2, 128.7, 127.8, 110.5, 71.7, 52.1, 49.2, 33.8, 32.6, 22.4; IR ( $\text{CH}_2\text{Cl}_2$ ) 3500, 1730  $\text{cm}^{-1}$ ; LRMS (EI, 20 eV)  $m/z$  328 ( $\text{M}^+$ , 25), 230 (62), 149 (100); HRMS (EI) for  $\text{C}_{15}\text{H}_{20}\text{O}_3\text{Se}$  ( $\text{M}^+$ ): calcd 328.0578, found 328.0575.



**1c**

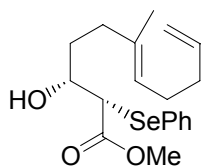
**1c:** A colorless oil; analytical TLC (silica gel 60),  $n$ -Hexane:EtOAc = 3:1,  $R_f$  = 0.45;  $^1\text{H}$  NMR (300 MHz)  $\delta$  7.61–7.58 (m, 2H), 7.32–7.20 (m, 3H), 4.70 (s, 1H), 4.66 (s, 1H), 3.98–3.89 (m, 1H), 3.65 (s, 3H), 3.63 (d,  $J = 7.1$  Hz, 1H), 2.88 (d,  $J = 7.1$  Hz, 1H), 2.01 (t,  $J = 7.5$  Hz, 2H), 1.82–1.76 (m, 1H), 1.69 (s, 3H), 1.67–1.48 (m, 3H);  $^{13}\text{C}$  NMR (75.5 MHz)  $\delta$  173.1, 145.4, 135.5, 129.1, 128.7, 127.7, 110.1, 71.9, 52.1, 49.1, 37.4, 34.2, 23.6, 22.3; IR ( $\text{CH}_2\text{Cl}_2$ ) 3611, 1717  $\text{cm}^{-1}$ ; LRMS (EI, 20 eV)  $m/z$  342 ( $\text{M}^+$ , 16), 230 (84), 149 (100); HRMS (EI) for  $\text{C}_{16}\text{H}_{22}\text{O}_3\text{Se}$  ( $\text{M}^+$ ): calcd 342.0735, found 342.0732.



**1d**

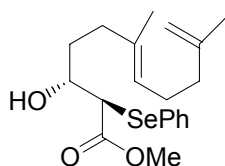
**1d:** A colorless oil; analytical TLC (silica gel 60),  $n$ -Hexane:EtOAc = 3:1,  $R_f$  = 0.35;  $^1\text{H}$  NMR (300 MHz)  $\delta$  7.61–7.58 (m, 2H), 7.34–7.29 (m, 3H), 5.92–5.72 (m, 1H), 5.15 (br. s 1H), 5.03–4.92 (m, 2H), 3.95–3.87 (m, 1H), 3.67 (s, 3H), 3.64 (d,  $J = 7.0$  Hz, 1H), 2.80 (d,  $J = 7.0$  Hz, 1H), 2.22–1.87 (m, 7H), 1.68–1.54 (m, 1H), 1.60 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  173.1, 138.6, 135.4, 134.6, 129.2, 128.7, 127.9, 124.7, 114.6, 71.7, 52.2, 49.2, 35.7, 33.9, 32.9, 27.4, 16.0; IR ( $\text{CH}_2\text{Cl}_2$ )

3520, 1723  $\text{cm}^{-1}$ ; LRMS (EI, 20 eV)  $m/z$  382 ( $\text{M}^+$ , 19), 230 (94), 147 (100); HRMS (EI) for  $\text{C}_{19}\text{H}_{26}\text{O}_3\text{Se}(\text{M}^+)$ : calcd 382.1048, found 382.1046.



**2d**

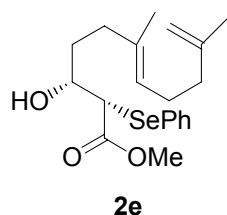
**2d**: A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1,  $R_f$  = 0.40;  $^1\text{H}$  NMR (300 MHz)  $\delta$  7.64–7.61 (m, 2H), 7.31–7.25 (m, 3H), 5.85–5.75 (m, 1H), 5.15 (br. s 1H), 5.02–4.75 (m, 2H), 3.95–3.90 (m, 1H), 3.66 (s, 3H), 3.65 (d,  $J$  = 5.2 Hz, 1H), 3.15 (dd,  $J$  = 0.9, 2.7 Hz, 1H), 2.18–1.00 (m, 6H), 1.81–1.62 (m, 2H), 1.58 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  173.6, 138.8, 135.5, 134.8, 129.3, 128.7, 128.4, 124.6, 114.6, 70.0, 52.3, 52.0, 35.8, 34.0, 32.7, 27.5, 16.0; IR ( $\text{CH}_2\text{Cl}_2$ ) 3522, 1721  $\text{cm}^{-1}$ ; LRMS (EI, 20 eV)  $m/z$  382 ( $\text{M}^+$ , 15), 230 (81), 147 (100); HRMS (EI) for  $\text{C}_{19}\text{H}_{26}\text{O}_3\text{Se}(\text{M}^+)$ : calcd 382.1048, found 382.1049.



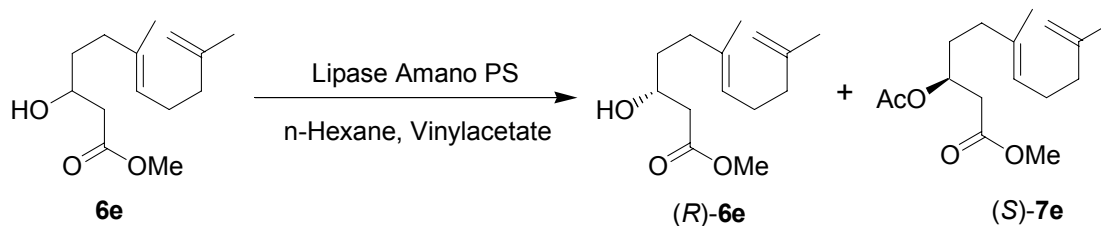
**1e**

**1e**: A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1,  $R_f$  = 0.35;  $^1\text{H}$  NMR (400 MHz)  $\delta$  7.61–7.58 (m, 2H), 7.36–7.29 (m, 3H), 5.16–5.13 (m, 1H), 4.70 (s, 1H), 4.67 (s, 1H), 3.94–3.88 (m, 1H), 3.66 (s, 3H), 3.64 (d,  $J$  = 7.0 Hz, 1H), 2.77 (d,  $J$  = 7.0 Hz, 1H), 2.16–2.00 (m, 6H), 1.97–1.89 (m, 1H), 1.72 (s, 3H), 1.60 (s, 3H), 1.64–1.56 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  173.2, 145.9, 135.6, 134.5, 129.4, 129.3, 128.8, 125.1, 110.0, 71.8, 52.3, 49.3, 37.8, 35.8, 33.0, 26.3, 22.6, 16.0; IR ( $\text{CH}_2\text{Cl}_2$ ) 3756, 1718  $\text{cm}^{-1}$ ; LRMS (EI, 20 eV)  $m/z$  396 ( $\text{M}^+$ , 4), 230 (79), 167 (100); HRMS (EI) for  $\text{C}_{20}\text{H}_{28}\text{O}_3\text{Se}(\text{M}^+)$ : calcd 396.1205, found 396.1202.





**2e:** A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1,  $R_f$  = 0.40;  $^1\text{H}$  NMR (400 MHz)  $\delta$  7.64–7.61 (m, 2H), 7.35–7.25 (m, 3H), 5.13 (td,  $J$  = 7.5, 1.0 Hz, 1H), 4.69 (s, 1H), 4.66 (s, 1H), 3.94–3.89 (m, 1H), 3.65 (s, 3H), 3.64 (d,  $J$  = 4.9 Hz, 1H), 3.19 (d,  $J$  = 2.1 Hz, 1H), 2.18–1.99 (m, 6H), 1.82–1.64 (m, 2H), 1.71 (s, 3H), 1.59 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  173.6, 145.8, 135.5, 134.4, 129.4, 129.3, 128.6, 124.9, 109.9, 69.9, 52.3, 51.9, 37.8, 35.7, 32.6, 26.3, 22.5, 15.9; IR ( $\text{CH}_2\text{Cl}_2$ ) 3756, 1718  $\text{cm}^{-1}$ ; LRMS (EI, 20 eV)  $m/z$  396 ( $\text{M}^+$ , 7), 230 (34), 157 (100); HRMS (EI) for  $\text{C}_{20}\text{H}_{28}\text{O}_3\text{Se}$  ( $\text{M}^+$ ): calcd 396.1205, found 396.1203.



**Typical procedure of Lipase-mediated transesterification.** To a solution of **6e** (1.66 g, 6.86 mmol) and vinyl acetate (5.81 mL, 54.8 mmol) in *n*-Hexane (50 mL) was added Lipase Amano PS (2.37 g) in one portion. The mixture was stirred at 40 °C for 60 h, and filtered through a celite pad. After the removal of the solvent, the residue was purified by flash column chromatography to give **(R)-6e** (726 mg, 45%, 94.8% *ee*) and the diester **(S)-7e** (1.05 g, 55%).

**(R)-6d** was prepared from **6d** in 45% yield and 94 *ee*%;  $[\alpha]_{\text{D}} -13.2^\circ$  ( $c$  1.87,  $\text{CH}_2\text{Cl}_2$ ). For characterization data, see those of **6d**.

**(R)-6e:**  $[\alpha]_{\text{D}} -12.4^\circ$  ( $c$  1.62,  $\text{CH}_2\text{Cl}_2$ ). For characterization data, see those of **6e**.

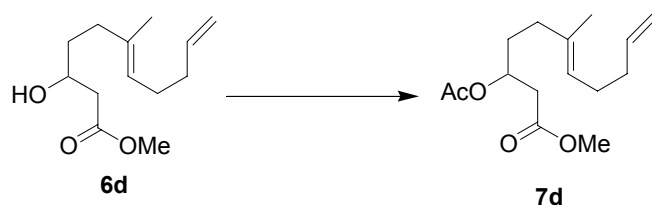
(*R*)-**6a**: Prepared according to Genet's procedure<sup>5</sup>: 99% yield, 96% *ee*; [ $\alpha$ ]<sub>D</sub> -16.7 ° (*c* 1.39, CH<sub>2</sub>Cl<sub>2</sub>). For characterization data, see those of **6a**.

(+)-**1a**, (+)-**1d** and (+)-**1e**: Prepared following the procedure for synthesis of **1a**.

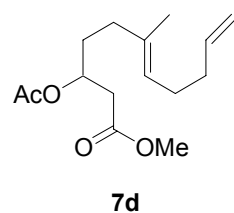
(+)-**1a**: [ $\alpha$ ]<sub>D</sub> +123.2 ° (*c* 1.19, CH<sub>2</sub>Cl<sub>2</sub>).

(+)-**1d**: [ $\alpha$ ]<sub>D</sub> +97.4 ° (*c* 1.08, CH<sub>2</sub>Cl<sub>2</sub>).

(+)-**1e**: [ $\alpha$ ]<sub>D</sub> +100.9 ° (*c* 1.06, CH<sub>2</sub>Cl<sub>2</sub>);

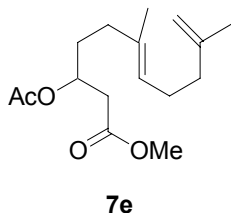


To a solution of **6d** (100 mg, 0.44 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added acetic anhydride (0.135 mL, 1.32 mmol) and pyridine (0.177 mL, 2.2 mmol) at room temperature and stirred overnight. The mixture was diluted with Et<sub>2</sub>O, and washed with 6 N HCl. The organic extracts were washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and then concentrated. The crude product was purified by flash column chromatography to give **7d** (117 mg, 99%).



**7d**: A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1, *R<sub>f</sub>* = 0.35; <sup>1</sup>H NMR (300 MHz)  $\delta$  5.87–5.74 (m, 1H), 5.20–5.14 (m, 2H), 5.03–4.93 (m, 2H), 3.67 (s, 3H), 2.59–2.56 (m, 2H), 2.08–2.06 (m, 4H), 2.03 (s, 3H), 2.05–1.99 (m, 2H), 1.78–1.65 (m, 2H), 1.59 (m, 2H); <sup>13</sup>C NMR (75.5 MHz)  $\delta$  170.8, 170.4, 138.6, 134.0, 124.6, 114.5, 70.3, 51.8, 38.9, 35.2, 33.8, 32.2,

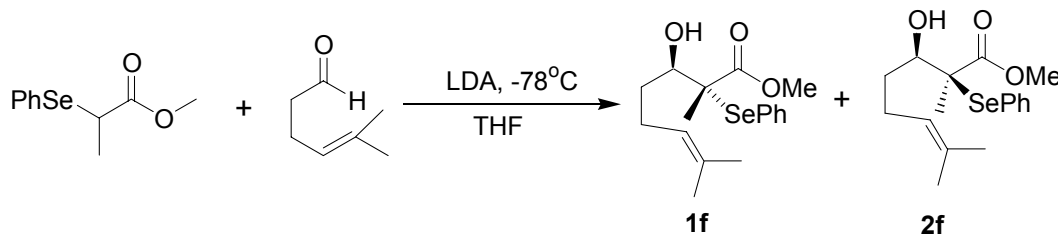
27.4, 21.1, 15.9; IR (CH<sub>2</sub>Cl<sub>2</sub>) 3077, 2965, 1739, 1241 cm<sup>-1</sup>; LRMS (EI, 20 eV) *m/z* 268 (M<sup>+</sup>, 1), 208 (42, M<sup>+</sup>-AcOH), 167 (61), 107 (100); HRMS (EI) for C<sub>13</sub>H<sub>20</sub>O<sub>2</sub> (M<sup>+</sup>-AcOH): calcd 208.1463, found 208.1467.



**7e:** A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1, *R<sub>f</sub>* = 0.35; <sup>1</sup>H NMR (400 MHz) δ 5.19–5.10 (m, 1H), 4.70 (s, 1H), 4.67 (s, 1H), 3.67 (s, 3H), 2.59–2.54 (m, 2H), 2.14–2.06 (m, 2H), 2.04–1.99 (m, 4H), 2.03 (s, 3H), 1.77–1.66 (m, 2H), 1.71 (s, 3H), 1.60 (s, 3H); <sup>13</sup>C NMR (100 MHz) δ 170.9, 170.5, 145.8, 133.9, 124.9, 110.0, 70.6, 51.8, 39.0, 37.8, 35.3, 32.3, 26.3, 22.6, 21.2, 15.9; IR (CH<sub>2</sub>Cl<sub>2</sub>) 3074, 2935, 1739, 1241 cm<sup>-1</sup>; LRMS (EI, 20 eV) *m/z* 222 (44, M<sup>+</sup>-AcOH), 135 (59), 107 (100); HRMS (EI) for C<sub>14</sub>H<sub>22</sub>O<sub>2</sub> (M<sup>+</sup>, M<sup>+</sup>-AcOH): calcd 222.1620, found 222.1610.

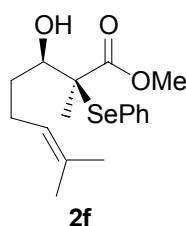
**(S)-7d:** [α]<sub>D</sub> -1.4 ° (*c* 0.6, CH<sub>2</sub>Cl<sub>2</sub>). For characterization data, see those of **7d**.

**(S)-7e:** [α]<sub>D</sub> -1.2 ° (*c* 0.7, CH<sub>2</sub>Cl<sub>2</sub>). For characterization data, see those of **7e**.

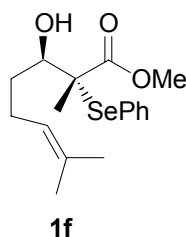


**Preparation of 1f and 2f:** To a solution of (*i*-Pr)<sub>2</sub>NH (0.47 mL, 3.36 mmol) in THF (30 mL) under argon was added *n*-BuLi (1.5 M in hexane, 2.0 mL, 3.0 mmol) slowly at 0 °C. After 0.5 h, the solution was cooled to -78 °C, and the pre-cooled solution of methyl-α-(phenylseleno)propionate<sup>3</sup>

(700 mg, 2.87 mmol) in THF (10 mL) was added and the mixture was stirred at this temperature for 1 h. 5-Methyl-hex-4-enal (439 mg, 4.2 mmol) was added dropwisely. The reaction was stirred at  $-78^{\circ}\text{C}$  overnight, and quenched with aqueous  $\text{NH}_4\text{Cl}$ . The mixture was extracted with ether. The organic extracts were washed with water and brine, and dried over  $\text{Na}_2\text{SO}_4$ . After removal of the solvent, the crude product was purified by flash column chromatography to give **1f** (553 mg, 56%) and **2f** (340 mg, 34%), respectively.<sup>4</sup>

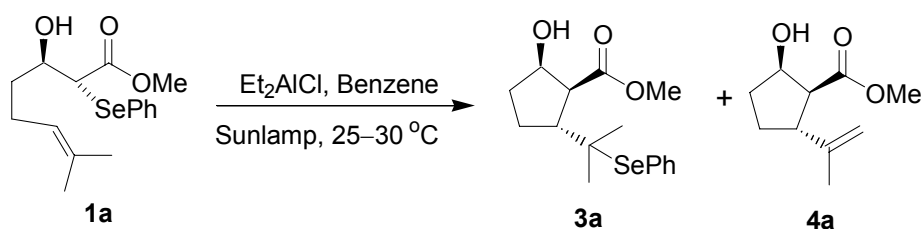


**2f**: A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1,  $R_f$  = 0.40;  $^1\text{H}$  NMR (400 MHz)  $\delta$  7.59–7.57 (m, 2H), 7.42–7.38 (m, 1H), 7.37–7.30 (m, 2H), 5.09–5.05 (m, 1H), 3.89 (ddd,  $J$  = 10.0, 2.7, 2.0 Hz, 1H), 3.57 (s, 3H), 2.90 (dd,  $J$  = 1.7, 2.9 Hz, 1H), 2.27–2.18 (m, 1H), 2.12–2.03 (m, 1H), 1.66 (s, 3H), 1.59 (s, 3H), 1.61–1.33 (m, 1H), 1.41 (s, 3H), 1.36–1.29 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  173.65, 138.1, 132.5, 129.6, 128.9, 126.6, 123.8, 72.67, 57.7, 52.0, 32.1, 25.8, 25.4, 17.8, 17.21; IR ( $\text{CH}_2\text{Cl}_2$ ) 3513, 1730  $\text{cm}^{-1}$ ; LRMS (EI, 20 eV)  $m/z$  356 ( $\text{M}^+$ , 20), 244 (82), 181 (100); HRMS (EI) for  $\text{C}_{17}\text{H}_{24}\text{O}_3\text{Se}$  ( $\text{M}^+$ ): calcd 356.0891, found 356.0891.

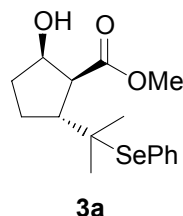


**1f**: A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1,  $R_f$  = 0.35;  $^1\text{H}$  NMR (400 MHz)  $\delta$  7.56–7.54 (m, 2H), 7.41–7.37 (m, 1H), 7.32–7.29 (m, 2H), 5.16–5.12 (m, 1H), 3.89 (dd,  $J$  = 10.4, 5.3 Hz, 1H), 3.64 (s, 3H), 2.73 (d,  $J$  = 6.4 Hz, 1H), 2.29–2.21 (m, 1H), 2.15–2.05 (m, 1H),

1.95–1.87 (ddt,  $J = 16.4, 1.4, 8.9$  Hz, 1H), 1.73 (s, 3H), 1.63 (s, 3H), 1.43 (s, 3H), 1.48–1.39 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  174.54, 138.1, 132.6, 129.6, 128.9, 126.7, 123.9, 74.68, 55.0, 52.3, 31.6, 25.9, 25.2, 18.1, 17.87; IR ( $\text{CH}_2\text{Cl}_2$ ) 3520, 1723  $\text{cm}^{-1}$ ; LRMS (EI, 20 eV)  $m/z$  356 ( $\text{M}^+$ , 12), 244 (55), 181 (100); HRMS (EI) for  $\text{C}_{17}\text{H}_{24}\text{O}_3\text{Se}$  ( $\text{M}^+$ ): calcd 356.0891, found 356.0889.

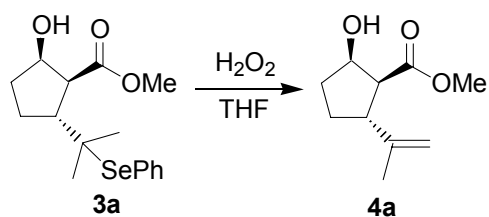


**Typical procedure for phenylseleno group transfer radical cyclization reactions.** Compound **1a** (200 mg, 0.58 mmol) was dissolved in dry benzene (20 mL) and the solution was degassed with argon for 15 min.  $\text{Et}_2\text{AlCl}$  (1 M in *n*-Hexane, 1.2 mL, 1.2 mmol) was added at room temperature. Ten min later, the mixture was irradiated with a 300 W sunlamp at 25–30  $^\circ\text{C}$  for 7.5 h. The reaction was monitored by TLC. To the reaction mixture was added saturated aqueous  $\text{Na}_2\text{CO}_3$  (10 mL), and the mixture was stirred for 0.5 h, then extracted with  $\text{Et}_2\text{O}$ . The aqueous solution was acidified to pH = 2 with 6 N HCl, and extracted with  $\text{Et}_2\text{O}$  again. The combined  $\text{Et}_2\text{O}$  layers were washed with water and brine, then dried over  $\text{Na}_2\text{SO}_4$ . After removal of the solvent, the crude product was purified by flash column chromatography to give **3a** (140 mg, 70%) and **4a** (14 mg, 7%).



**3a:** A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1,  $R_f$  = 0.25;  $^1\text{H}$  NMR (400 MHz)  $\delta$  7.63–7.61 (m, 2H), 7.38–7.33 (m, 1H), 7.32–7.30 (m, 2H), 4.42–4.39 (m, 1H), 3.72 (s, 3H), 2.98 (dd,  $J$  = 6.0, 8.6 Hz, 1H), 2.80 (dd,  $J$  = 8.9, 13.3 Hz, 1H), 2.62 (br. s, 1H), 2.09–2.00 (m, 1H), 1.94–1.78 (m, 2H), 1.74–1.64 (m, 1H), 1.33 (s, 3H), 1.25 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  175.3, 138.5, 128.78, 128.72, 127.3, 75.4, 52.3, 52.1, 51.9, 50.8, 34.7, 28.7, 28.5, 26.0; IR ( $\text{CH}_2\text{Cl}_2$ ) 3488, 1738  $\text{cm}^{-1}$ ; LRMS (EI, 20 eV)  $m/z$  342 ( $\text{M}^+$ , 7), 186 (12), 185 (100); HRMS (EI) for  $\text{C}_{16}\text{H}_{22}\text{O}_3\text{Se}$  ( $\text{M}^+$ ): calcd 342.0734, found 342.0734.

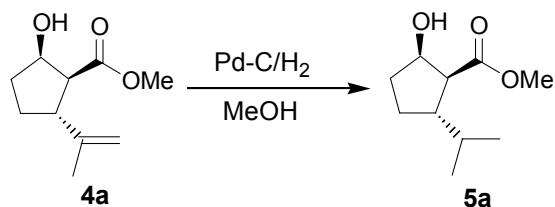
(–)-**3a:** Prepared from (+)-**1a**; 98.2% *ee*;  $[\alpha]_{\text{D}} -9.0^\circ$  ( $c$  0.55,  $\text{CH}_2\text{Cl}_2$ ).



**Oxidative elimination of 3a.** Compound **3a** (50 mg, 0.146 mmol) was dissolved in THF (3 mL).  $\text{H}_2\text{O}_2$  (0.05 mL, 6.1 M in  $\text{H}_2\text{O}$ ) was added at  $0^\circ\text{C}$ , and the solution was stirred overnight. The mixture was diluted with  $\text{Et}_2\text{O}$ , washed with water and brine, and dried over  $\text{Na}_2\text{SO}_4$ . After removal of the solvent, the crude product was purified by flash column chromatography to provide **4a** (22 mg, 80%) as a colorless oil.

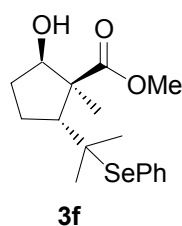
**4a:** A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1,  $R_f$  = 0.27;  $^1\text{H}$  NMR (400 MHz)  $\delta$  4.77 (t,  $J$  = 0.8 Hz, 1H), 4.74 (t,  $J$  = 1.4 Hz, 1H), 4.49–4.45 (m, 1H), 3.71 (s, 3H), 3.13 (apparent q,  $J$  = 9.2 Hz, 1H), 2.99 (d,  $J$  = 3.1 Hz, 1H), 2.70 (dd,  $J$  = 4.8, 11.0 Hz, 1H), 2.16–2.06 (m, 1H), 1.92 (tt,  $J$  = 14.9, 10.0 Hz, 1H), 1.82 (ddt,  $J$  = 14.1, 5.8, 2.5 Hz, 1H), 1.73 (s, 3H), 1.57–1.47 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  174.9, 154.9, 110.7, 74.5, 53.2, 51.9, 48.1, 34.1, 28.6,

19.9; LRMS (EI, 20 eV)  $m/z$  166 ( $M^+ - H_2O$ , 20), 149 (95), 107 (100); HRMS (EI) for  $C_{10}H_{14}O_2$  ( $M^+ - H_2O$ ): calcd 166.0994, found 166.0984.



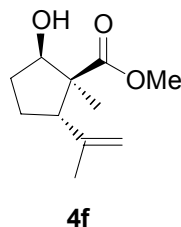
**Conversion of 4a to 5a:** To a solution of **4a** (20 mg, 0.11 mmol) in MeOH (3 mL) was added palladium on active carbon (10%, 4 mg). The mixture was stirred under 1 atm  $H_2$  at rt overnight. The mixture was filtered through celite, and the solvent was removed to give **5a** (20 mg, 100%).

**5a:** A colorless oil; analytical TLC (silica gel 60),  $n$ -Hexane:EtOAc = 3:1,  $R_f$  = 0.27;  $^1H$  NMR (400 MHz)  $\delta$  4.39–4.35 (m, 1H), 3.73 (s, 3H), 2.79 (d,  $J$  = 6.2 Hz, 1H), 2.55 (dd,  $J$  = 5.4, 9.7 Hz, 1H), 2.34 (tt,  $J$  = 16.6, 9.2 Hz, 1H), 1.99–1.91 (m, 1H), 1.87–1.75 (m, 2H), 1.68–1.60 (m, 1H), 1.40–1.31 (m, 1H), 0.89 (d,  $J$  = 6.8 Hz, 3H), 0.87 (d,  $J$  = 6.8 Hz, 3H).  $^{13}C$  NMR (100 MHz)  $\delta$  175.7, 74.9, 52.7, 51.7, 47.6, 34.3, 31.4, 25.6, 20.9, 19.1; LRMS (EI, 20 eV)  $m/z$  168 ( $M^+ - H_2O$ , 1), 153 (35), 149 (100); HRMS (EI) for  $C_{10}H_{16}O_2$  ( $M^+ - H_2O$ ): calcd 168.1150, found 168.1133.

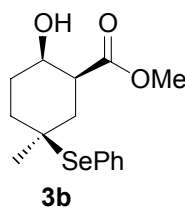


**3f:** A colorless oil; analytical TLC (silica gel 60),  $n$ -Hexane:EtOAc = 3:1,  $R_f$  = 0.28;  $^1H$  NMR (300 MHz)  $\delta$  7.63–7.60 (m, 2H), 7.37–7.30 (m, 3H), 3.85 (dd,  $J$  = 2.8, 5.1 Hz, 1H), 3.69 (s, 3H), 3.17 (br. s, 1H), 3.02 (dd,  $J$  = 8.2, 10.7 Hz, 1H), 2.23–2.16 (m, 1H), 2.13–2.02 (m, 1H), 1.94–1.84 (m, 1H), 1.75–1.64 (m, 1H), 1.39 (s, 3H), 1.33 (s, 3H), 1.26 (s, 3H);  $^{13}C$  NMR (100 MHz)  $\delta$  177.4,

138.5, 128.64, 128.63, 127.9, 82.8, 55.8, 54.7, 52.3, 49.6, 32.2, 30.3, 28.7, 24.7, 18.4; IR (CH<sub>2</sub>Cl<sub>2</sub>) 3497, 1715 cm<sup>-1</sup>; LRMS (EI, 20 eV) *m/z* 356 (M<sup>+</sup>, 4), 199 (90), 121 (100); HRMS (EI) for C<sub>17</sub>H<sub>24</sub>O<sub>3</sub>Se (M<sup>+</sup>): calcd 356.0891, found 356.0887.

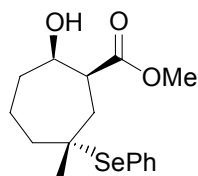


**4f**: A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1, *R<sub>f</sub>* = 0.28; <sup>1</sup>H NMR (400 MHz) δ 4.88 (s, 1H), 4.75 (s, 1H), 3.94 (apparent q, *J* = 5.9 Hz, 1H), 3.74 (s, 3H), 3.22 (dd, *J* = 7.3, 10.4 Hz, 1H), 2.86 (d, *J* = 6.2 Hz, 1H), 2.20–2.12 (m, 1H), 1.91–1.86 (m, 1H), 1.73–1.60 (m, 2H), 1.66 (s, 3H), 1.02 (s, 3H); <sup>13</sup>C NMR (75.5 MHz) δ 177.2, 144.0, 112.3, 82.2, 55.0, 52.1, 51.0, 33.2, 25.8, 23.5, 17.3; IR (CH<sub>2</sub>Cl<sub>2</sub>) 3505, 1715 cm<sup>-1</sup>; LRMS (EI, 20 eV) *m/z* 198 (M<sup>+</sup>, 4), 180 (28), 121 (100); HRMS (EI) for C<sub>11</sub>H<sub>16</sub>O<sub>2</sub> (M<sup>+</sup>–H<sub>2</sub>O): calcd 180.1150, found 180.1148.



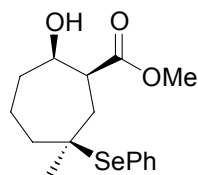
**3b**: A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1, *R<sub>f</sub>* = 0.30; <sup>1</sup>H NMR (300 MHz) δ 7.65–7.62 (m, 2H), 7.37–7.26 (m, 3H), 4.14 (br. s, 1H), 3.70 (s, 3H), 3.01 (br. s, 1H), 2.57 (ddd, *J* = 12.6, 3.62, 2.3 Hz, 1H), 2.40 (t, *J* = 12.7 Hz, 1H), 2.21 (td, *J* = 13.8, 5.6 Hz, 1H), 1.87 (td, *J* = 2.8, 12.7 Hz, 1H), 1.81–1.73 (m, 1H), 1.64–1.52 (m, 2H), 1.42 (s, 3H); <sup>13</sup>C NMR (75.5 MHz) δ 175.6, 138.3, 128.8, 128.7, 126.9, 64.9, 51.9, 45.3, 43.7, 35.9, 32.2, 28.5, 24.6; IR (CH<sub>2</sub>Cl<sub>2</sub>) 3528, 1716 cm<sup>-1</sup>; LRMS (EI, 20 eV) *m/z* 328 (M<sup>+</sup>, 27), 171 (100), 153 (54); HRMS (EI) for C<sub>15</sub>H<sub>20</sub>O<sub>3</sub>Se (M<sup>+</sup>): calcd 328.0578, found 328.0576.





**$\alpha$ -3c**

**$\alpha$ -3c:** A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1,  $R_f$  = 0.32;  $^1\text{H}$  NMR (300 MHz)  $\delta$  7.65–7.63 (m, 2H), 7.37–7.35 (m, 1H), 7.31–7.27 (m, 2H), 4.33 (br. s, 1H), 3.76 (s, 3H), 3.06 (d,  $J$  = 9.8 Hz, 1H), 2.97 (br. s, 1H), 2.27 (dd,  $J$  = 15.2, 9.7 Hz, 1H), 1.98–1.86 (m, 2H), 1.70–1.58 (m, 4H), 1.52–1.42 (m, 1H), 1.42 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  177.3, 138.6, 128.8, 128.7, 127.8, 68.3, 52.0, 50.9, 45.7, 42.4, 37.3, 34.4, 32.2, 18.0; IR ( $\text{CH}_2\text{Cl}_2$ ) 3528, 1723  $\text{cm}^{-1}$ ; LRMS (EI, 20 eV)  $m/z$  342 ( $\text{M}^+$ , 72), 185 (100), 153 (99); HRMS (EI) for  $\text{C}_{16}\text{H}_{22}\text{O}_3\text{Se}(\text{M}^+)$ : calcd 342.0735, found 342.0733.

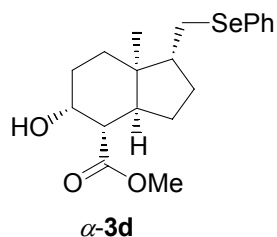


**$\beta$ -3c**

**$\beta$ -3c:** A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1,  $R_f$  = 0.30;  $^1\text{H}$  NMR (400 MHz)  $\delta$  7.64–7.62 (m, 2H), 7.37–7.35 (m, 1H), 7.32–7.28 (m, 2H), 4.26 (d,  $J$  = 1.4 Hz, 1H), 3.68 (s, 3H), 2.95 (t,  $J$  = 2.0 Hz, 1H), 2.82 (dd,  $J$  = 9.9, 14.4 Hz, 1H), 2.47 (d,  $J$  = 9.9 Hz, 1H), 2.06 (dd,  $J$  = 9.5, 15.7 Hz, 1H), 2.00–1.92 (m, 1H), 1.87–1.82 (m, 1H), 1.67 (dd,  $J$  = 0.8, 14.3 Hz, 1H), 1.52–1.48 (m, 1H), 1.46–1.39 (m, 1H), 1.43 (s, 3H), 1.33 (ddd,  $J$  = 0.8, 7.6, 11.8 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  176.7, 138.5, 128.8, 128.0, 68.3, 52.2, 49.4, 44.3, 41.9, 37.0, 35.4, 30.5, 18.5;

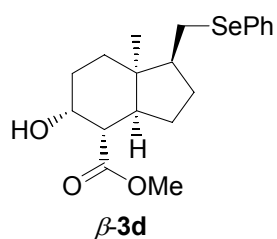
IR (CH<sub>2</sub>Cl<sub>2</sub>) 3559, 1717 cm<sup>-1</sup>; LRMS (EI, 20 eV) *m/z* 342 (M<sup>+</sup>, 16), 185 (90), 167 (79), 107 (100);

HRMS (EI) for C<sub>16</sub>H<sub>22</sub>O<sub>3</sub>Se (M<sup>+</sup>): calcd 342.0735, found 342.0739.



**α-3d**: A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1, *R<sub>f</sub>* = 0.28; <sup>1</sup>H NMR (300 MHz) δ 7.48–7.45 (m, 2H), 7.29–7.19 (m, 3H), 4.02 (br. s, 1H), 3.71 (s, 3H), 3.03 (dd, *J* = 2.8, 11.3 Hz, 1H), 2.88 (br. s, 1H), 2.62 (t, *J* = 10.8 Hz, 1H), 2.24–2.06 (m, 4H), 1.92 (tt, *J* = 5.9, 12.0 Hz, 1H), 1.79–1.62 (m, 2H), 1.48–1.25 (m, 4H), 0.87 (s, 3H); <sup>13</sup>C NMR (75.5 MHz) δ 176.6, 132.4, 130.7, 129.1, 126.8, 66.7, 54.8, 49.0, 44.3, 43.5, 40.9, 29.7, 28.7, 26.8, 26.1, 26.0, 23.3; IR (CH<sub>2</sub>Cl<sub>2</sub>) 3522, 1721 cm<sup>-1</sup>; LRMS (EI, 20 eV) *m/z* 382 (M<sup>+</sup>, 40), 207 (40), 147 (100); HRMS (EI) for C<sub>19</sub>H<sub>26</sub>O<sub>3</sub>Se (M<sup>+</sup>): calcd 382.1048, found 382.1048.

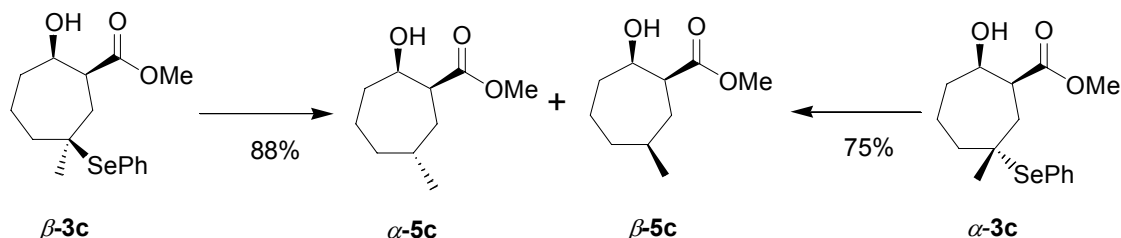
**(-)-α-3d**: Prepared from **(+)-1d**; [α]<sub>D</sub> -101.6 ° (*c* 0.74, CH<sub>2</sub>Cl<sub>2</sub>).



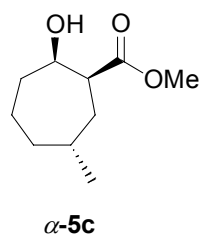
**β-3d**: A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1, *R<sub>f</sub>* = 0.30; <sup>1</sup>H NMR (300 MHz) δ 7.47–7.45 (m, 2H), 7.26–7.22 (m, 3H), 3.87–3.80 (m, 1H), 3.69 (s, 3H), 3.53 (d, *J* = 11.4 Hz, 1H), 3.06 (dd, *J* = 3.3, 11.3 Hz, 1H), 2.81 (d, *J* = 4.9 Hz, 1H), 2.58 (t, *J* = 11.4 Hz, 1H), 2.37 (t, *J* = 10.9 Hz, 1H), 2.04–1.97 (m, 1H), 1.92 (dd, *J* = 4.0, 12.0 Hz, 1H), 1.88–1.75 (m, 3H),

1.61–1.54 (m, 1H), 1.42–1.30 (m, 2H), 1.26–1.22 (m, 1H), 0.89 (s, 3H);  $^{13}\text{C}$  NMR (75.5 MHz)  $\delta$  175.9, 132.5, 130.9, 129.2, 126.8, 67.5, 51.6, 51.5, 49.4, 46.0, 42.1, 28.9, 28.2, 27.9, 26.8, 26.7, 22.9; IR ( $\text{CH}_2\text{Cl}_2$ ) 3501, 1724  $\text{cm}^{-1}$ ; LRMS (EI, 20 eV)  $m/z$  382 ( $\text{M}^+$ , 29), 207 (24), 147 (100); HRMS (EI) for  $\text{C}_{19}\text{H}_{26}\text{O}_3\text{Se}$  ( $\text{M}^+$ ): calcd 382.1048, found 382.1049.

(-)- **$\beta$ -3d**: Prepared from (+)-**1d**;  $[\alpha]_{\text{D}} -85.9^\circ$  ( $c$  1.90,  $\text{CH}_2\text{Cl}_2$ ).

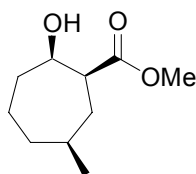


**Conversion of  $\alpha$ - or  $\beta$ -3c to 5c**: To a solution of  **$\alpha$ -3c** (32 mg, 0.09 mmol) in benzene (5 mL), were added  $n\text{-Bu}_3\text{SnH}$  (0.05 mL, 0.18 mmol) and  $\text{Et}_3\text{B}$  (0.2 mL, 1M in  $n$ -hexane) at rt.  $\text{O}_2$  (10 mL) was bubbled through the solution slowly. After 5 h, the solvent was removed and the residue was purified by flash column chromatography to provide  **$\alpha$ -5c** (7 mg, 44%) and  **$\beta$ -5c** (5 mg, 31%) as colorless oils.  **$\beta$ -3c** gave  **$\alpha$ -5c** and  **$\beta$ -5c** (total yield 88%) with same ratio under the same reaction condition.



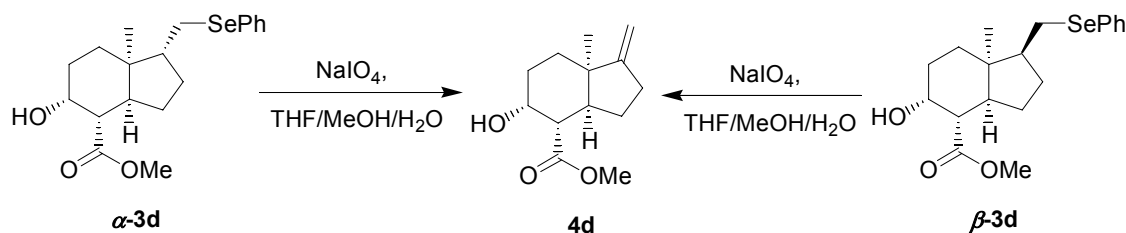
**$\alpha$ -5c**: A colorless oil; analytical TLC (silica gel 60),  $n\text{-Hexane}:\text{EtOAc} = 3:1$ ,  $R_f = 0.32$ ;  $^1\text{H}$  NMR (300 MHz)  $\delta$  4.14–4.08 (m, 1H), 3.71 (s, 3H), 2.97 (d,  $J = 4.7$  Hz, 1H), 2.72 (td,  $J = 2.4, 9.1$  Hz,

1H), 2.32 (ddd,  $J = 5.7, 9.1, 14.6$  Hz, 1H), 1.95–1.90 (m, 2H), 1.80–1.71 (m, 1H), 1.61–1.51 (m, 3H), 1.31 (ddd,  $J = 2.6, 5.8, 14.5$  Hz, 1H), 1.13–1.00 (m, 1H), 0.93 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (75.5 MHz)  $\delta$  177.2, 70.4, 51.8, 45.4, 36.3, 35.4, 31.3, 30.4, 23.0, 20.9; IR ( $\text{CH}_2\text{Cl}_2$ ) 3627, 1734  $\text{cm}^{-1}$ ; LRMS (EI, 20 eV)  $m/z$  168 ( $\text{M}^+ - \text{H}_2\text{O}$ , 11), 153 (100), 136 (72); HRMS (EI) for  $\text{C}_{10}\text{H}_{16}\text{O}_2$  ( $\text{M}^+ - \text{H}_2\text{O}$ ): calcd 168.1150, found 168.1148.



**$\beta$ -5c**

**$\beta$ -5c:** A colorless oil; analytical TLC (silica gel 60),  $n$ -Hexane:EtOAc = 3:1,  $R_f$  = 0.30;  $^1\text{H}$  NMR (300 MHz)  $\delta$  4.30–4.24 (m, 1H), 3.71 (s, 3H), 2.87 (d,  $J = 3.2$  Hz, 1H), 2.61 (td,  $J = 2.2, 9.7$  Hz, 1H), 1.89–1.65 (m, 7H), 1.35–1.20 (m, 2H), 0.93 (d,  $J = 6.3$  Hz, 3H);  $^{13}\text{C}$  NMR (75.5 MHz)  $\delta$  177.0, 69.6, 51.9, 49.0, 37.6, 35.1, 34.2, 31.9, 23.9, 20.6; IR ( $\text{CH}_2\text{Cl}_2$ ) 3629, 1734  $\text{cm}^{-1}$ ; LRMS (EI, 20 eV)  $m/z$  168 ( $\text{M}^+ - \text{H}_2\text{O}$ , 6), 153 (100); HRMS (EI) for  $\text{C}_{10}\text{H}_{16}\text{O}_2$  ( $\text{M}^+ - \text{H}_2\text{O}$ ): calcd 168.1150, found 168.1147.

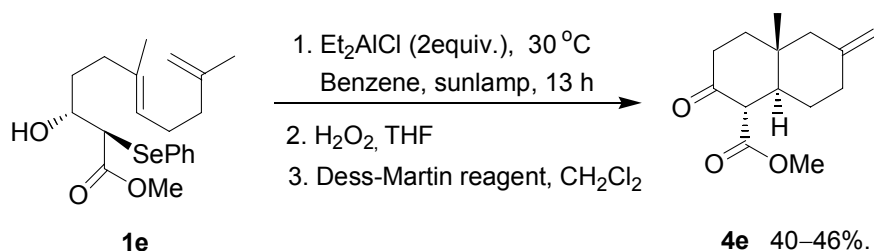


**Oxidative elimination of 3d:** Compound  $\alpha$ -3d (69 mg, 0.18 mmol) was dissolved in mixed solvent of THF (2 mL), MeOH (0.7 mL) and  $\text{H}_2\text{O}$  (0.3 mL).  $\text{NaIO}_4$  (39 mg, 0.18 mmol) was added at 0  $^\circ\text{C}$ . The reaction was warmed to rt slowly, and stirred overnight. The mixture was diluted with

Et<sub>2</sub>O, washed with water and brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the crude residue was purified by flash column chromatography to provided **4d** (33 mg, 80%). Oxidative elimination of **β-3d** gave **4d** in a similar yield.

**4d**: A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1, *R<sub>f</sub>* = 0.3; <sup>1</sup>H NMR (300 MHz) δ 4.87 (t, *J* = 2.1 H, 1H), 4.77 (t, *J* = 2.4 H, 1H), 4.06–4.04 (m, 1H), 3.72 (s, 3H), 2.94 (dd, *J* = 1.6, 2.4 Hz, 1H), 2.56–2.48 (m, 1H), 2.46–2.37 (m, 1H), 2.32–2.20 (m, 1H), 2.13 (dd, *J* = 2.2, 11.4 Hz, 1H), 2.00–1.89 (m, 1H), 1.83 (dd, *J* = 3.9, 9.9 Hz, 1H), 1.68 (dq, *J* = 13.7, 4.1 Hz, 1H), 1.63 (td, *J* = 3.8, 14.0 Hz, 1H), 1.53–1.45 (m, 1H), 1.42–1.37 (m, 1H), 1.02 (s, 3H); <sup>13</sup>C NMR (75.5 MHz) δ 176.6, 155.8, 104.2, 67.1, 51.9, 48.5, 45.3, 43.8, 29.5, 28.6, 27.7, 26.8, 25.0; IR (CH<sub>2</sub>Cl<sub>2</sub>) 3680, 1746 cm<sup>-1</sup>; LRMS (EI, 20 eV) *m/z* 224 (M<sup>+</sup>, 21), 206 (58), 147 (100); HRMS (EI) for C<sub>13</sub>H<sub>20</sub>O<sub>3</sub> (M<sup>+</sup>): calcd 224.1412, found 224.1413.

(–)-**4d**: Prepared from (–)-**α-3d** and (–)-**β-3d**; 97.1% *ee*; [α]<sub>D</sub> –50.0 ° (*c* 0.23, CH<sub>2</sub>Cl<sub>2</sub>).



The first two steps (started from **1e**, 184 mg, 0.46 mmol) were carried out according to procedure for the preparation of **3a** and **4a**. The crude mixture (90 mg) was diluted with CH<sub>2</sub>Cl<sub>2</sub>. Dess-Martin reagent (1.08 g, 15% solution in CH<sub>2</sub>Cl<sub>2</sub>) was added at rt in one portion. The mixture was stirred for 4.5 h and quenched with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aqueous solution. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the organic layers were washed with water and brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. After

removal of the solvent, the crude residue was purified by flash column chromatography to provided **4e** (52 mg, 46% for three steps).

**4e**: A colorless oil; analytical TLC (silica gel 60), *n*-Hexane:EtOAc = 3:1,  $R_f$  = 0.6;  $^1\text{H}$  NMR (300 MHz)  $\delta$  4.77 (d,  $J$  = 1.7 Hz, 1H), 4.66 (d,  $J$  = 1.9 Hz, 1H), 3.76 (s, 3H), 3.17 (d,  $J$  = 12.9 Hz, 1H), 2.51–2.40 (m, 2H), 2.35–2.28 (m, 1H), 2.12–1.92 (m, 4H), 1.73–1.66 (m, 2H), 1.52–1.45 (m, 1H), 1.30 (dq,  $J$  = 4.4, 12.2 Hz, 1H), 0.99 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  205.6, 170.3, 144.9, 110.4, 60.1, 52.0, 49.2, 46.3, 39.9, 37.8, 34.5, 33.8, 28.0, 16.3; IR ( $\text{CH}_2\text{Cl}_2$ ) 1744, 1720  $\text{cm}^{-1}$ ; LRMS (EI, 20 eV)  $m/z$  236 ( $\text{M}^+$ , 31), 203 (26), 130 (100); HRMS (EI) for  $\text{C}_{14}\text{H}_{20}\text{O}_3$  ( $\text{M}^+$ ): calcd 236.1414, found 236.1410.

(–)-**4e**: Prepared from (+)-**1e**; 96.8% *ee*;  $[\alpha]_{\text{D}} -24.0^\circ$  ( $c$  0.15,  $\text{CH}_2\text{Cl}_2$ ).<sup>6</sup>

## References:

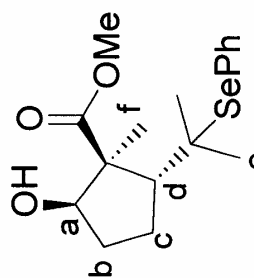
1. Huckin, S. N.; Weiler, L. *J. Am. Chem. Soc.* **1974**, *96*, 1082-1087. (b) Sum, P.-E.; Weiler, L. *Can. J. Chem.* **1979**, *57*, 1475–1480.
2. The relative stereochemistry of *trans* and *cis* products were determined according to the literature report: Nakamura, S.; Hayakawa, T.; Nishi, T.; Watanabe, Y.; Toru, T. *Tetrahedron* **2001**, *57*, 6703–6711.
3. Yamashita, T.; Yasuda, M.; Watanabe, M.; Kojima, R.; Tanabe, K.; Shima, K. *J. Org. Chem.* **1996**, *61*, 6438 – 6441
4. The relative stereochemistry of **4a** and **3a** was determined by comparing the  $^{13}\text{C}$ -NMR chemical shifts of C=O, CH-OH and  $\alpha$ -methyl. For **4a**, they are 174.54, 74.68 and 18.12,

while for **3a**, they are 173.65, 72.67, 17.21. The *trans* isomer **4a** always have larger chemical shifts for these three carbons than those of *cis* one. See: (a) Heathcock, C. H.; Pirrung, M. C.; Sohn, J. E. *J. Org. Chem.* **1979**, *44*, 4294–4299. (b) Bouvier, B.; Jung, G.; Liu, Z.; Guerin, B.; Guindon, Y. *Org. Lett.* **2001**, *3*, 1391–1394.

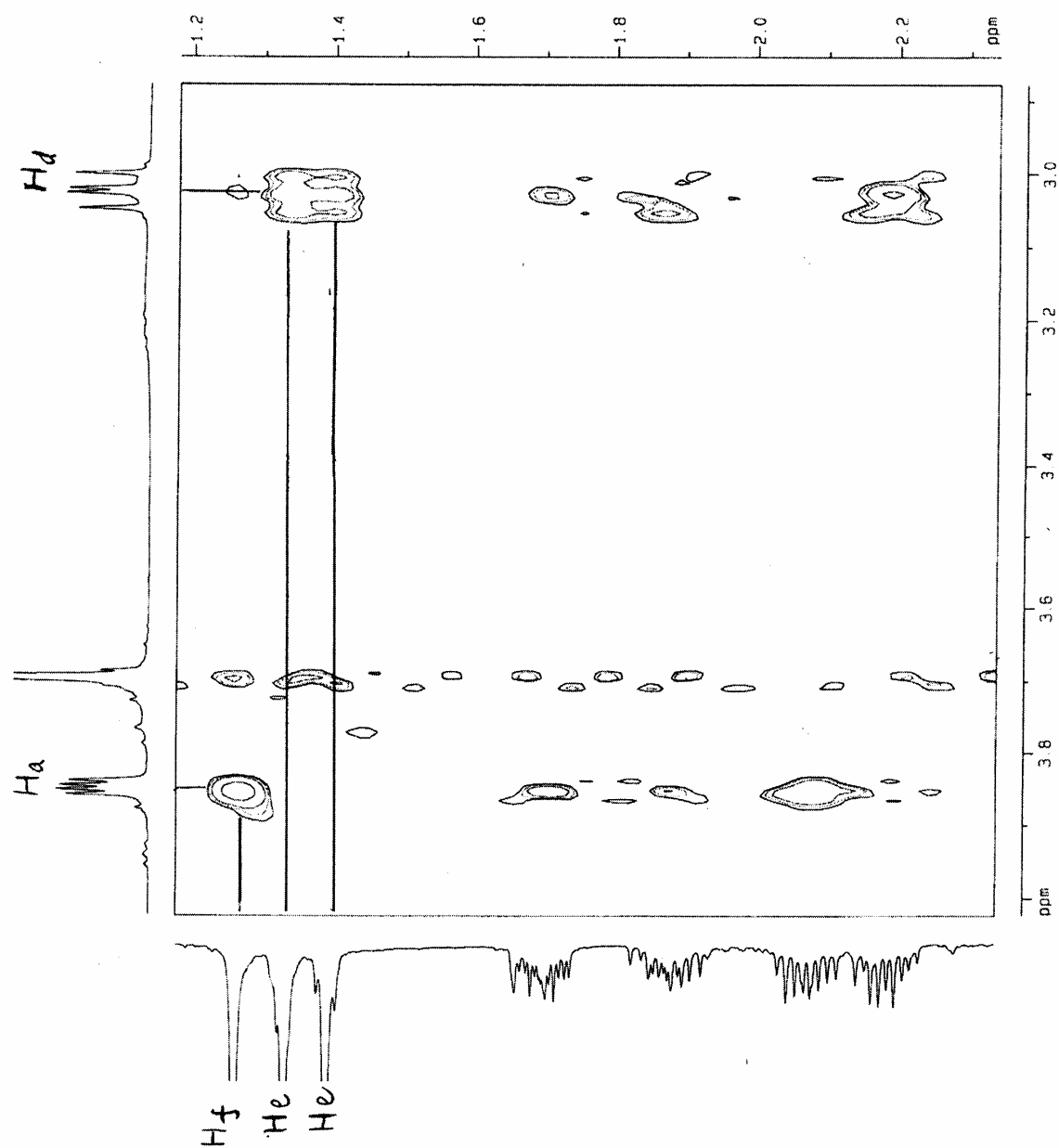
5. Greck, C.; Ferreira, F.; Genet, J. P. *Tetrahedron Lett* **1996**, *37*, 2031–2034.
6. The absolute configuration of **(-)-8b** was determined by converting it to **(+)-8c** in two steps, and the CD spectra of **(+)-8c** was the same as the known compound. See: Yang, D. Xu, M. *Org. Lett.* **2001**, *3*, 1785–1788.

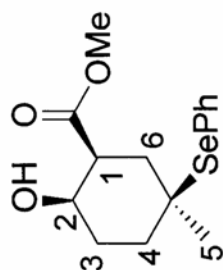




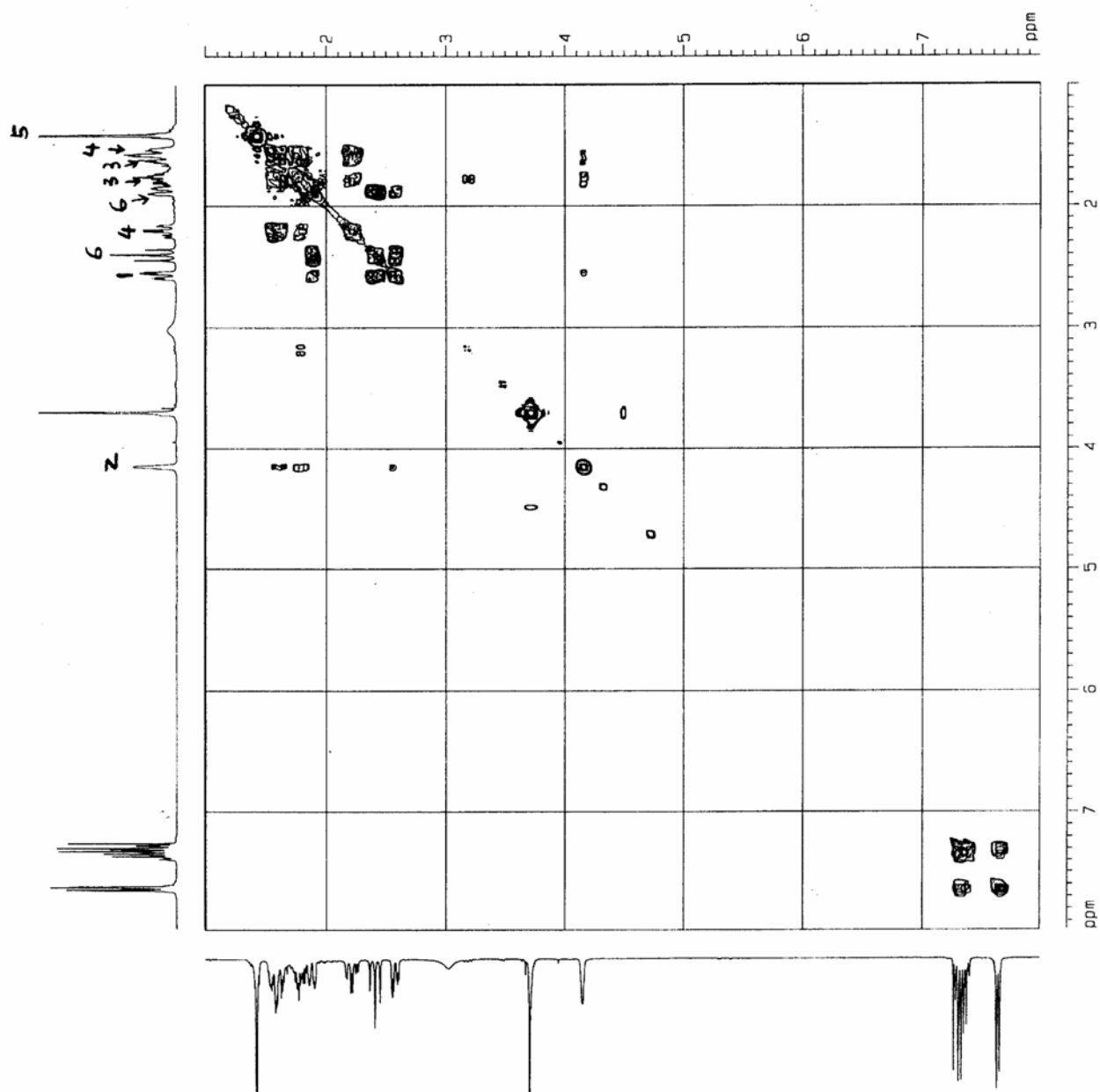


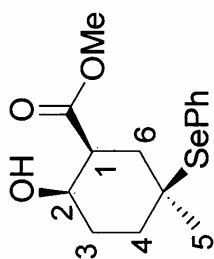
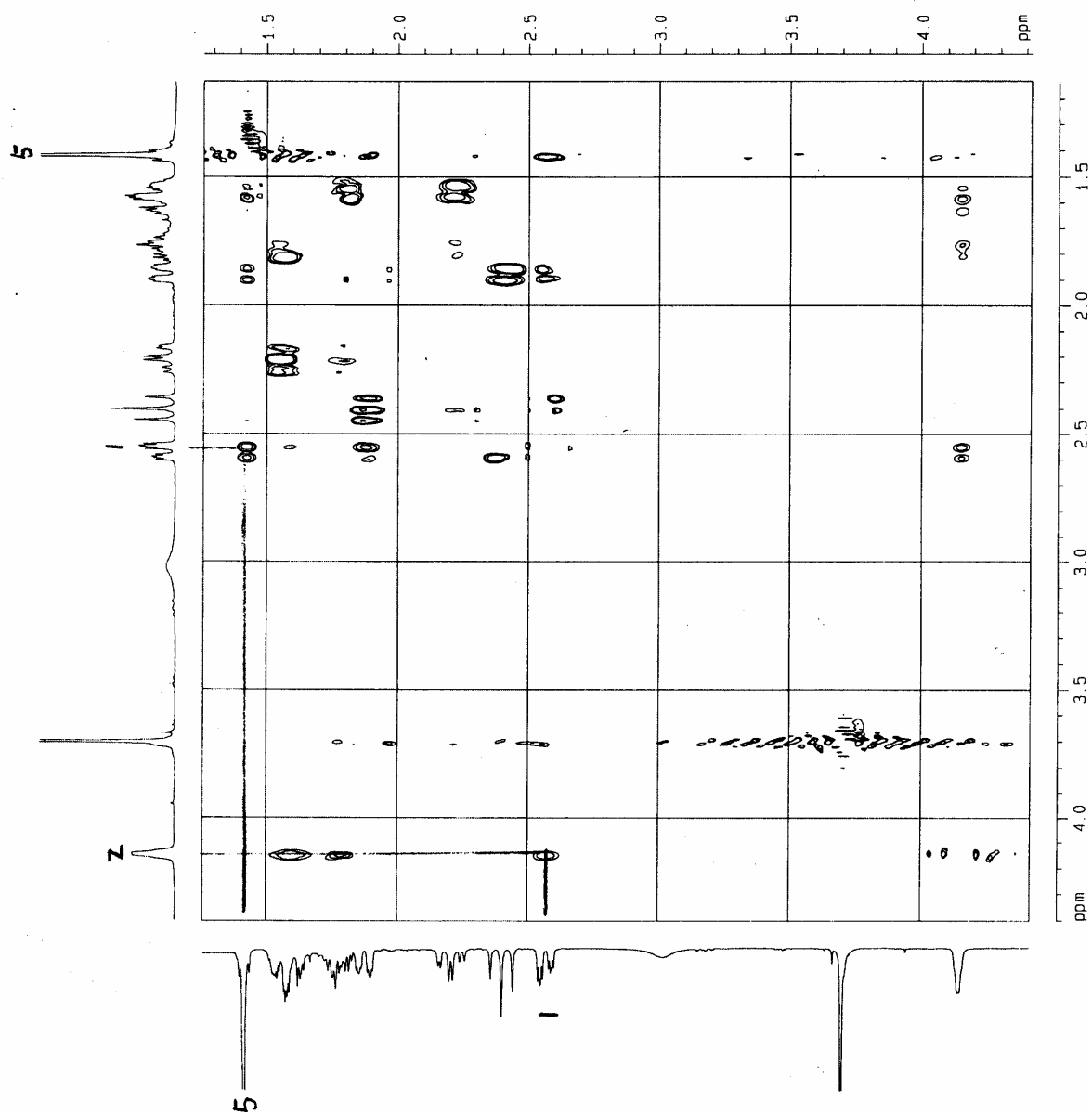
**3f**  $^1\text{H}$ - $^1\text{H}$  Noesy



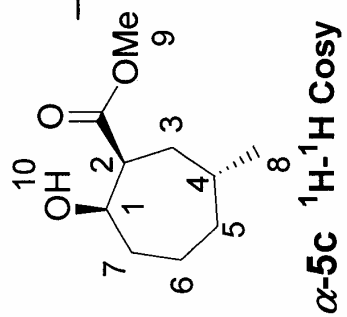
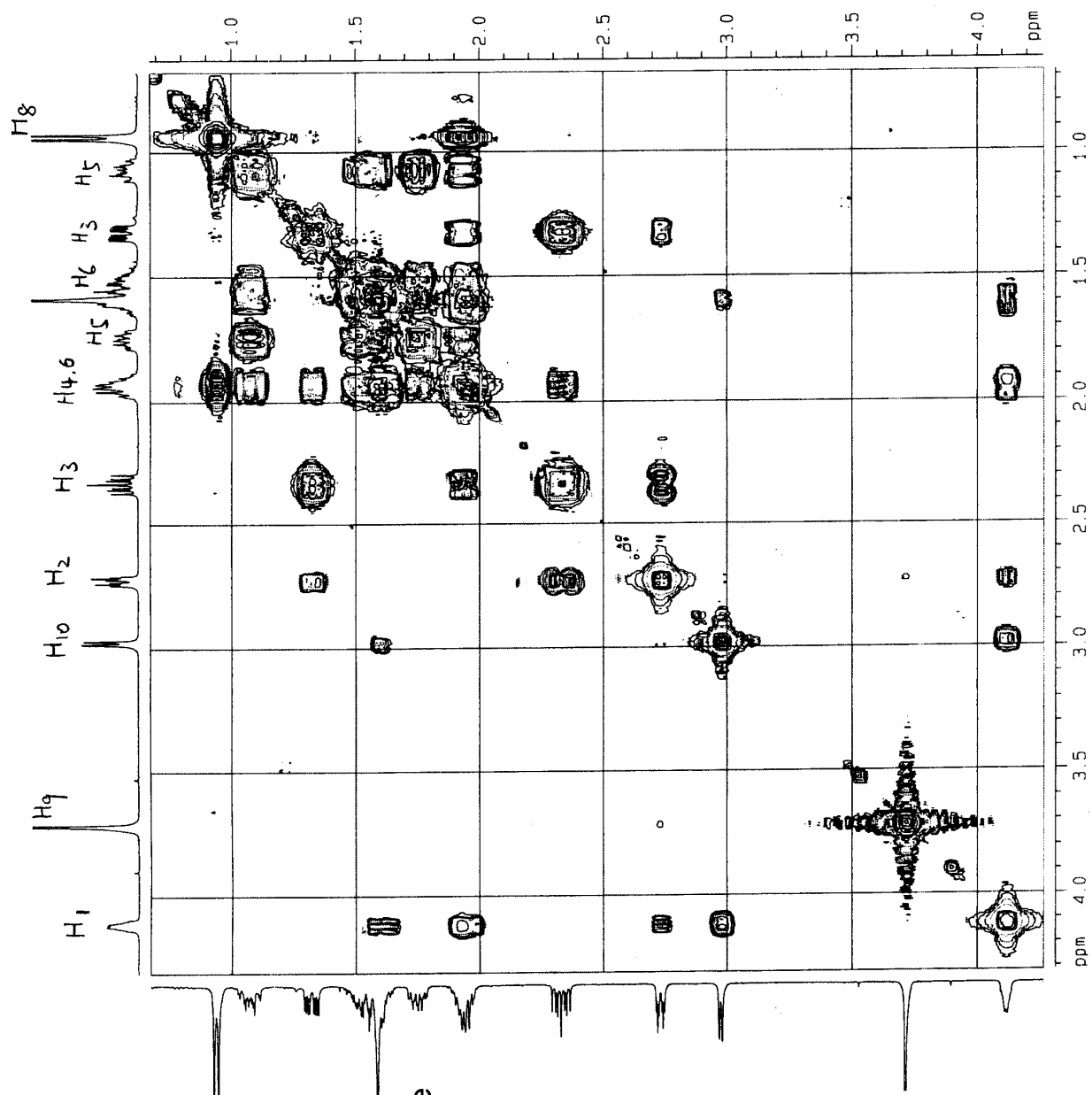


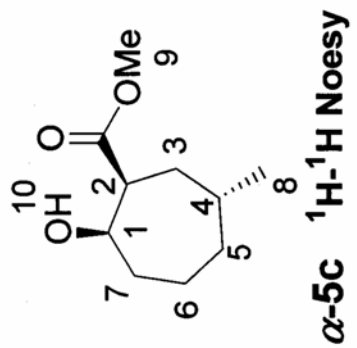
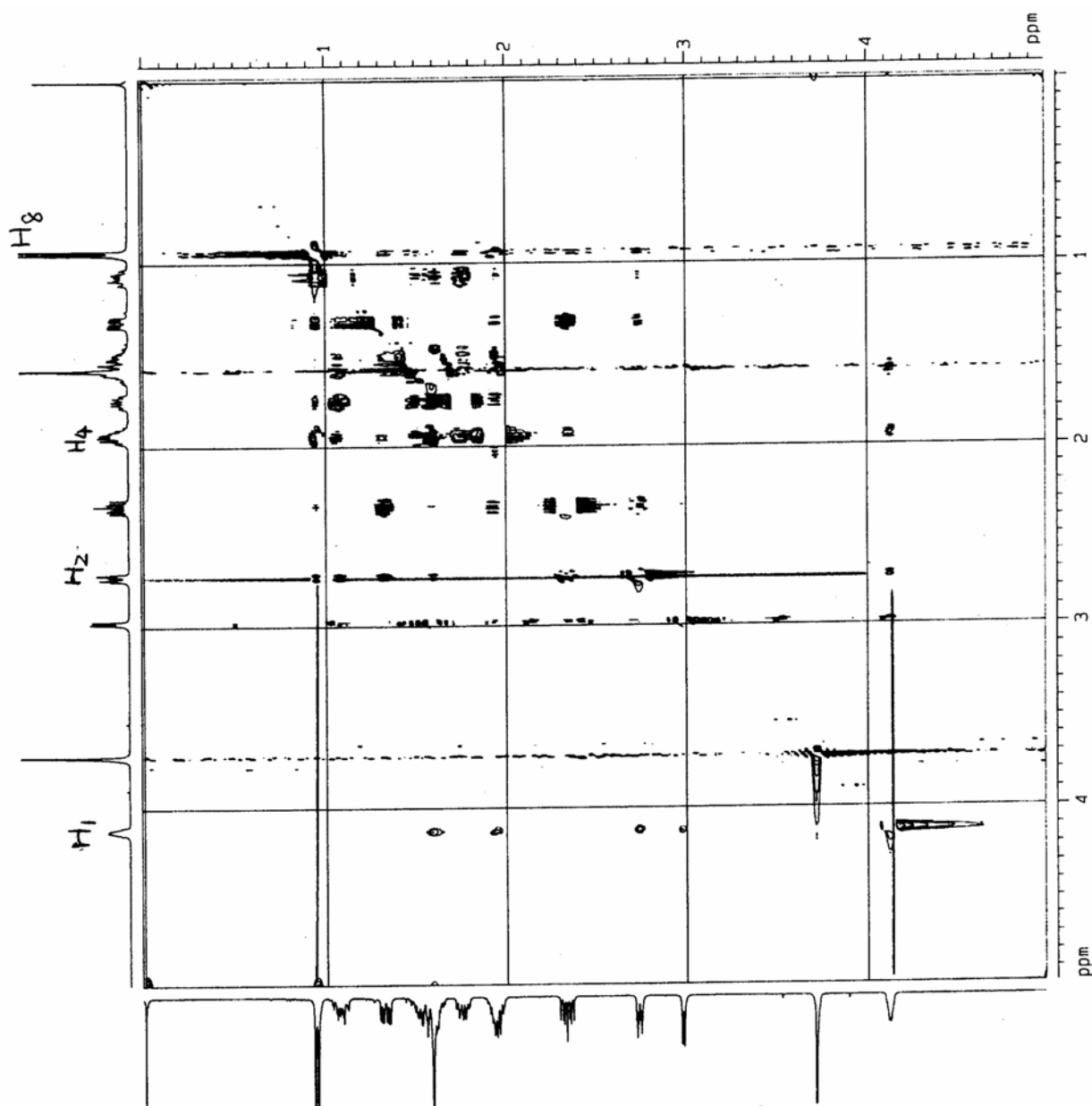
**3b**  $^1\text{H}$ - $^1\text{H}$  Cosy

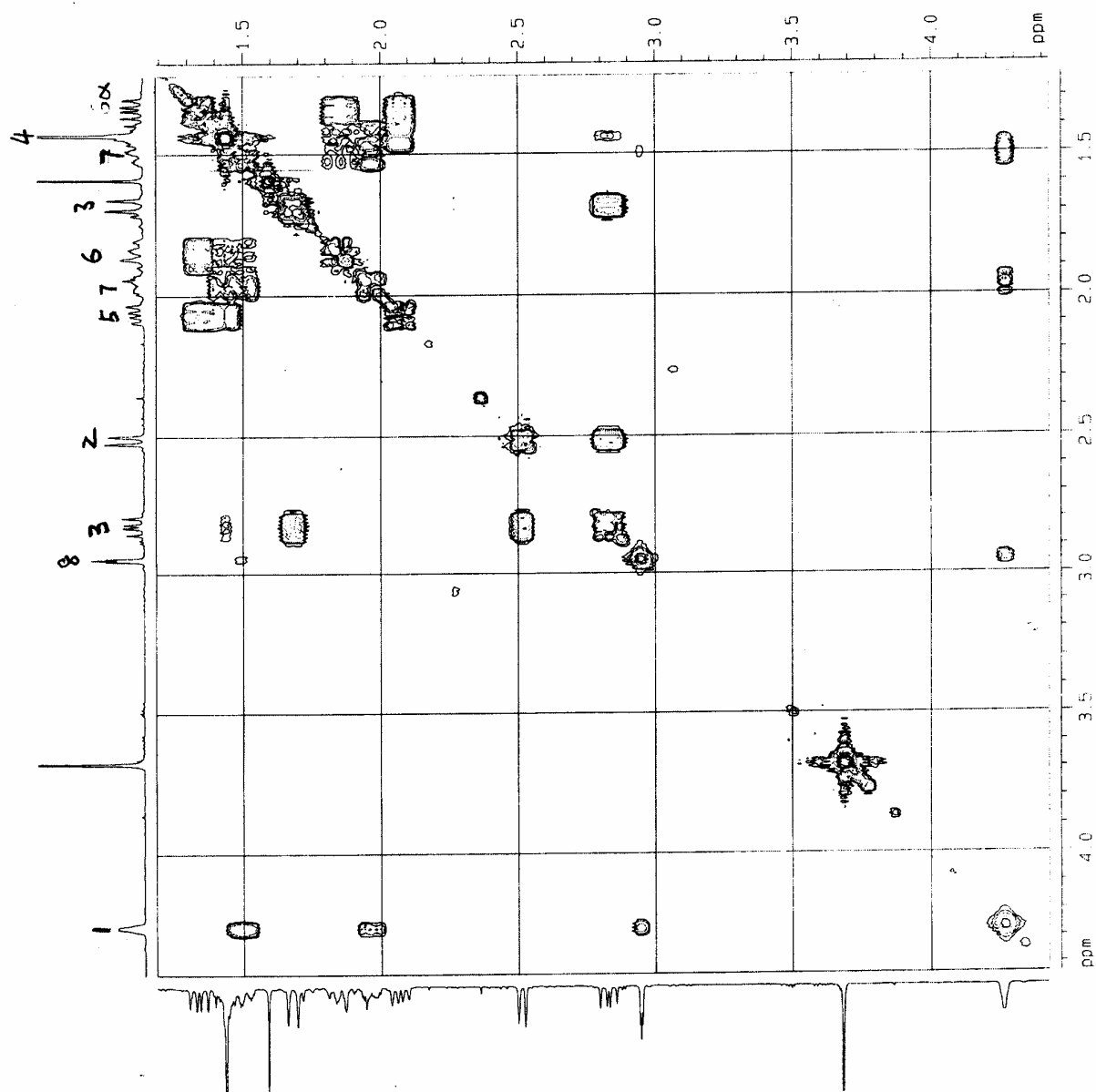
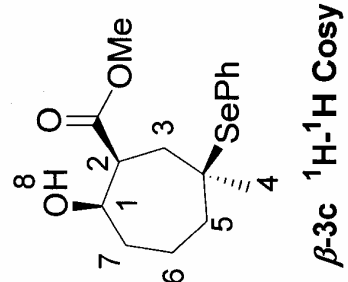


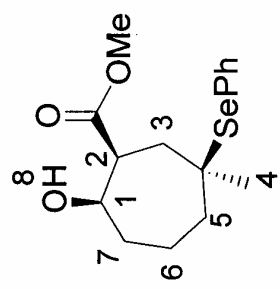


**3b**  $^1\text{H}$ - $^1\text{H}$  Noesy

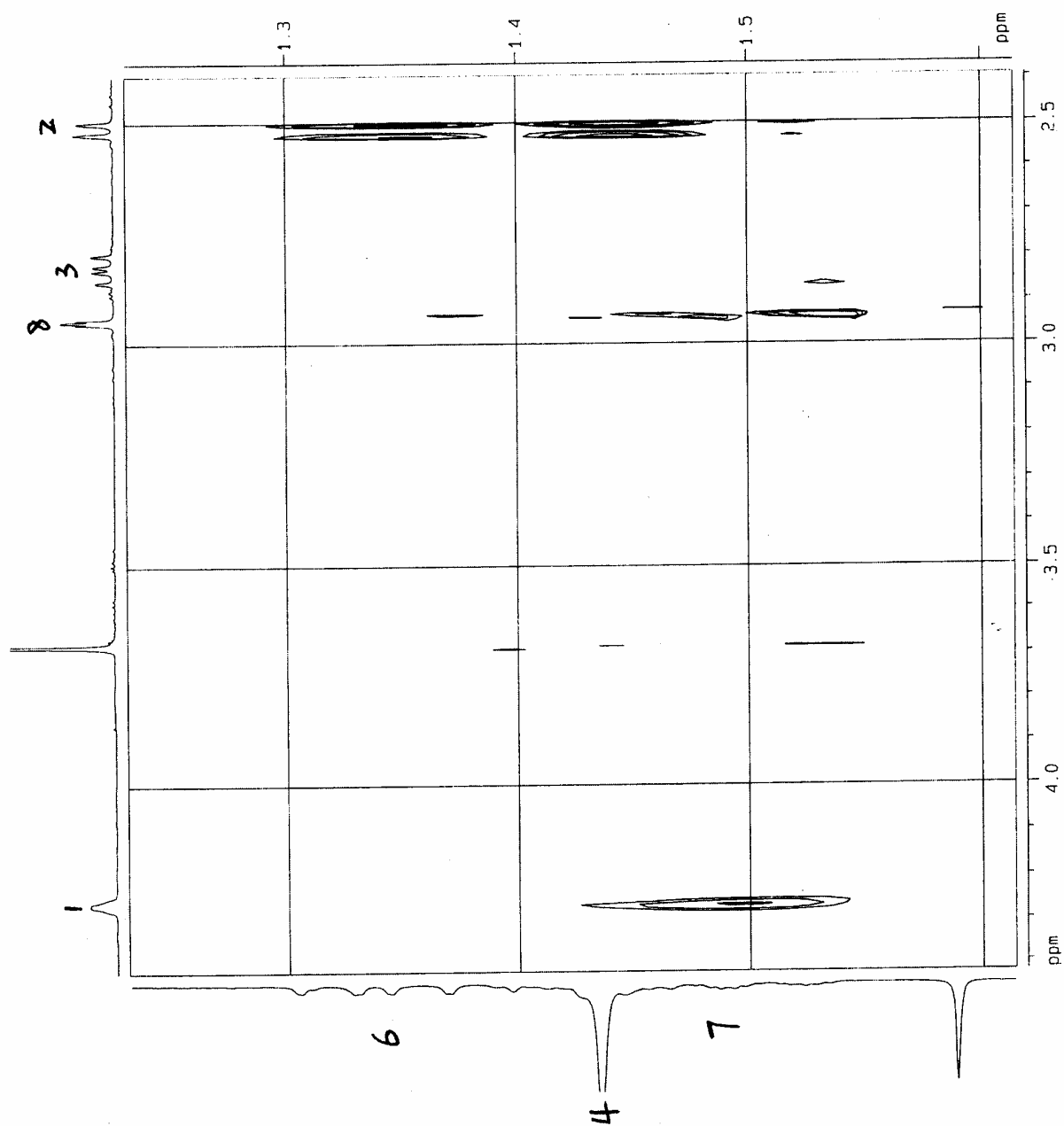


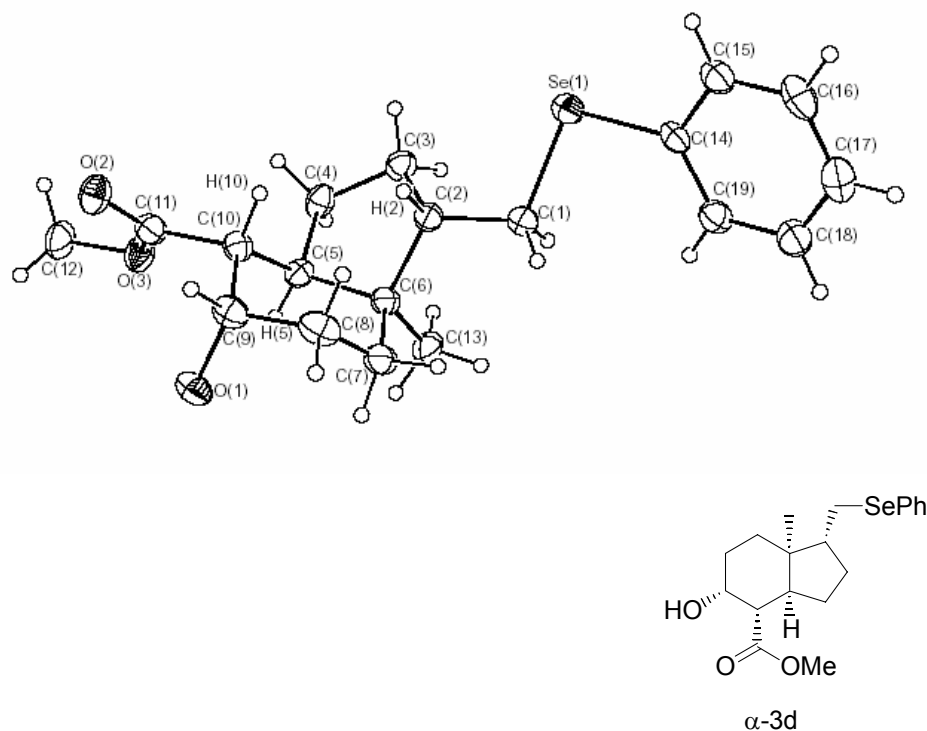






**3c**  $^1\text{H}$ - $^1\text{H}$  NMR





**Crystal data:** [C<sub>19</sub> H<sub>25</sub> O<sub>3</sub> Se] ; formula weight = 380.35, Monoclinic, P 2<sub>1</sub>/n, a = 6.235(1) Å, b = 20.458(4) Å, c = 14.051(3) Å,  $\beta$  = 91.57(3)°, V = 1791.6(6) Å<sup>3</sup>, Z = 4, D<sub>c</sub> = 1.410 g cm<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 2.108 mm<sup>-1</sup>, F(000) = 788, T = 253 K.

**Data collection:** A crystal of dimensions 0.3 x 0.2 x 0.1 mm mounted in a glass capillary was used for data collection at -20°C on a MAR diffractometer with a 300 mm image plate detector using graphite monochromatized Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Data collection was made with 3° oscillation step of  $\phi$ , 300 seconds exposure time and scanner distance at 120 mm. 60 images were collected.

**Data reduction:** The images were interpreted and intensities integrated using program DENZO<sup>1</sup>.

**Structure solution:** The structure was solved by direct methods employing SIR-97 program<sup>2</sup> on PC. Se and many non-H atoms were located according to the direct methods and the successive least-square Fourier cycles. Positions of other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using program SHELXL-97<sup>3</sup> on PC.

**Structure refinement:** According to the SHELXL-97 program<sup>3</sup>, all 2758 independent reflections ( $R_{\text{int}}$ <sup>4</sup> equal to 0.0693, 1765 reflections larger than  $4\sigma(F_o)$ ) from a total 8409 reflections were participated in the full-matrix least-square refinement against  $F^2$ . These reflections were in the range  $-7 \leq h \leq 7$ ,  $-24 \leq k \leq 24$ ,  $-13 \leq l \leq 16$  with  $2\theta_{\text{max}}$  equal to 50.72°.

<sup>1</sup> Otwinowski, Z. and Minor, W., "Processing of X-ray Diffraction Data Collected in Oscillation Mode", Methods in Enzymology, Volume 276: Macromolecular Crystallography, part A, p. 307-326, 1997. Carter C. W., Sweet Jr. & R. M., Eds., Academic Press.

<sup>2</sup> A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna. *Sir97: a new tool for crystal structure determination and refinement*. *J. Appl. Cryst.*, **1998**, 32, 115-119.

<sup>3</sup> SHELXL97, Sheldrick, G. M. (1997). SHELX97. Programs for Crystal Structure Analysis (Release 97-2). University of Goettingen, Germany.

<sup>4</sup>  $R_{\text{int}} = \sum |F_o^2 - F_o^2(\text{mean})| / \sum [F_o^2]$



One crystallographic asymmetric unit consists of one formula unit. In the final stage of least-squares refinement, all non-hydrogen atoms were refined anisotropically. H atoms were generated by program SHELXL-97. The positions of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final R-indices<sup>5</sup>.

Convergence ( $(\Delta/\sigma)_{\max} = 0.001$ , av. 0.001) for 210 variable parameters by full-matrix least-squares refinement on  $F^2$  reaches to  $R_1 = 0.0350$  and  $wR_2 = 0.0739$  with a goodness-of-fit of 0.785, the parameters a and b for weighting scheme are 0.0 and 0. The final difference Fourier map shows maximum rest peaks and holes of 0.354 and -0.375  $e\text{\AA}^{-3}$  respectively.

**Drawing:** The ORTEP<sup>6</sup> drawing of the molecule was made with thermal ellipsoids at the 30 % probability level. Screen drawing is provided for reference. Drawing with high quality can be provided upon request.

**Tables:** Table (1) of Crystallographic and refinement data, table (3) of full bond lengths and bond angles and this report<sup>7</sup> are provided. The other supplementary materials, such as table (2) of atomic coordinates, table of anisotropic displacement parameters, table of hydrogen coordinates and/or other tables and/or CIF, RES-files, can be provided under request by notifying the identification code.

Table 1. Crystal data and structure refinement for mar996.

Identification code	mar996	
Empirical formula	$C_{19}H_{25}O_3Se$	
Formula weight	380.35	
Temperature	253(2) K	
Wavelength	0.71073 $\text{\AA}$	
Crystal system	Monoclinic	
Space group	$P 2_1/n$	
Unit cell dimensions	$a = 6.235(1) \text{\AA}$	$\alpha = 90^\circ$ .
	$b = 20.458(4) \text{\AA}$	$\beta = 91.57(3)^\circ$ .
	$c = 14.051(3) \text{\AA}$	$\gamma = 90^\circ$ .
Volume	$1791.6(6) \text{\AA}^3$	
Z	4	
Density (calculated)	$1.410 \text{ Mg/m}^3$	
Absorption coefficient	$2.108 \text{ mm}^{-1}$	
$F(000)$	788	
Crystal size	$0.3 \times 0.2 \times 0.1 \text{ mm}^3$	

<sup>5</sup> Since the structure refinements are against  $F^2$ , R-indices based on  $F^2$  are larger than (more than double) those based on  $F$ . For comparison with older refinements based on  $F$  and an OMIT threshold, a conventional index  $R_1$  based on observed  $F$  values larger than  $4\sigma(F_o)$  is also given (corresponding to  $\text{Intensity} \geq 2\sigma(I)$ ).  $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ ,  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ , The Goodness of Fit is always based on  $F^2$ :  $\text{GooF} = S = \{ \sum [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$ , where  $n$  is the number of reflections and  $p$  is the total number of parameters refined. The weighting scheme is:  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ , where  $P$  is  $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$ .

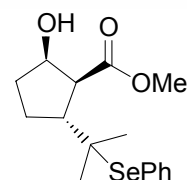
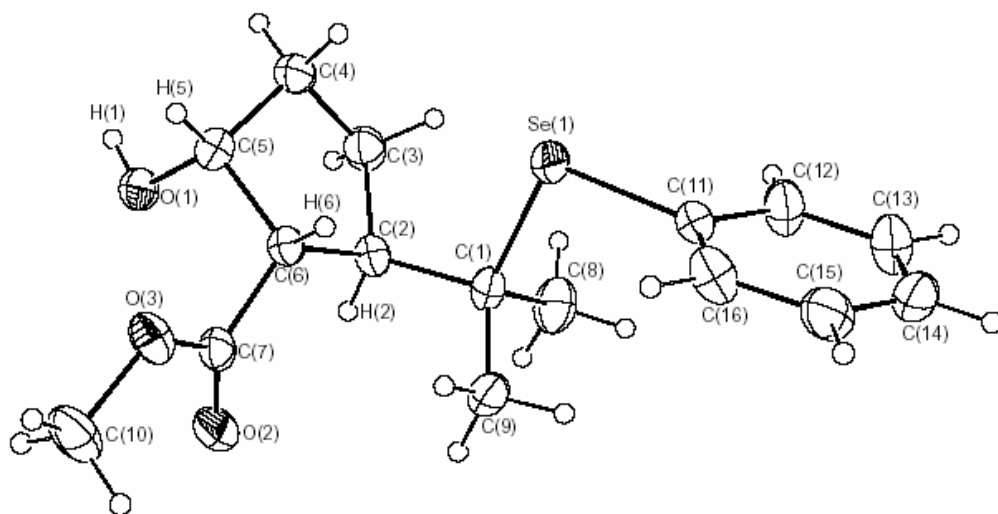
<sup>6</sup> ORTEP3 for Windows - Farrugia, L. J. (1997) J. Appl. Cryst. 30, 565.

<sup>7</sup> Crystallographic data summarized in this report are abstracted from tables of crystallographic data and data collection record.

Theta range for data collection	1.76 to 25.36°.
Index ranges	-7<= <i>h</i> <=7, -24<= <i>k</i> <=24, -13<= <i>l</i> <=16
Reflections collected	8409
Independent reflections	2758 [R(int) = 0.0693]
Completeness to theta = 25.36°	83.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2758 / 0 / 210
Goodness-of-fit on F <sup>2</sup>	0.785
Final R indices [I>2sigma(I)]	R1 = 0.0350, wR2 = 0.0739
R indices (all data)	R1 = 0.0604, wR2 = 0.0782
Largest diff. peak and hole	0.354 and -0.375 e.Å <sup>-3</sup>

Table 3. Bond lengths [Å] and angles [°] for mar996.

Se(1)-C(14)	1.903(4)	C(13)-C(6)-C(5)	108.8(2)
Se(1)-C(1)	1.955(3)	C(7)-C(6)-C(5)	112.4(3)
O(1)-C(9)	1.434(4)	C(2)-C(6)-C(5)	102.0(2)
O(2)-C(11)	1.211(4)	C(8)-C(7)-C(6)	114.4(3)
O(3)-C(11)	1.333(4)	C(9)-C(8)-C(7)	111.0(3)
O(3)-C(12)	1.447(4)	O(1)-C(9)-C(8)	111.8(3)
C(1)-C(2)	1.515(4)	O(1)-C(9)-C(10)	108.7(3)
C(2)-C(6)	1.541(4)	C(8)-C(9)-C(10)	110.0(3)
C(2)-C(3)	1.549(4)	C(11)-C(10)-C(5)	114.4(3)
C(3)-C(4)	1.535(4)	C(11)-C(10)-C(9)	107.5(3)
C(4)-C(5)	1.540(4)	C(5)-C(10)-C(9)	112.9(3)
C(5)-C(10)	1.535(4)	O(2)-C(11)-O(3)	122.4(3)
C(5)-C(6)	1.552(4)	O(2)-C(11)-C(10)	123.3(3)
C(6)-C(13)	1.534(4)	O(3)-C(11)-C(10)	114.4(3)
C(6)-C(7)	1.540(4)	C(15)-C(14)-C(19)	117.9(3)
C(7)-C(8)	1.518(4)	C(15)-C(14)-Se(1)	119.1(3)
C(8)-C(9)	1.512(5)	C(19)-C(14)-Se(1)	123.0(3)
C(9)-C(10)	1.539(4)	C(16)-C(15)-C(14)	120.4(3)
C(10)-C(11)	1.510(5)	C(17)-C(16)-C(15)	121.0(3)
C(14)-C(15)	1.385(4)	C(18)-C(17)-C(16)	118.8(4)
C(14)-C(19)	1.401(4)	C(19)-C(18)-C(17)	120.6(4)
C(15)-C(16)	1.383(5)	C(18)-C(19)-C(14)	121.2(3)
C(16)-C(17)	1.382(5)		
C(17)-C(18)	1.378(5)		
C(18)-C(19)	1.371(5)		
Symmetry transformations used to generate equivalent atoms:			
C(14)-Se(1)-C(1)	100.47(13)		
C(11)-O(3)-C(12)	115.9(3)		
C(2)-C(1)-Se(1)	110.1(2)		
C(1)-C(2)-C(6)	115.4(2)		
C(1)-C(2)-C(3)	115.0(3)		
C(6)-C(2)-C(3)	103.1(2)		
C(4)-C(3)-C(2)	106.2(2)		
C(3)-C(4)-C(5)	106.5(3)		
C(10)-C(5)-C(4)	110.8(2)		
C(10)-C(5)-C(6)	113.2(2)		
C(4)-C(5)-C(6)	103.2(2)		
C(13)-C(6)-C(7)	108.5(3)		
C(13)-C(6)-C(2)	111.7(3)		
C(7)-C(6)-C(2)	113.3(3)		



**(-)-3a**

**Crystal data:** [C<sub>16</sub> H<sub>22</sub> O<sub>3</sub> Se] ; formula weight = 341.30, Orthorhombic, P 2<sub>1</sub> 2<sub>1</sub> 2<sub>1</sub>, a = 6.280(1) Å, b = 10.367(2) Å, c = 24.434(5) Å, V = 1590.8(5) Å<sup>3</sup>, Z = 4, D<sub>c</sub> = 1.425 g cm<sup>-3</sup>, μ(Mo-Kα) = 2.365 mm<sup>-1</sup>, F(000) = 704, T = 253 K.

**Data collection:** A crystal of dimensions 0.4 x 0.3 x 0.2 mm mounted in a glass capillary was used for data collection at -20°C on a MAR diffractometer with a 300 mm image plate detector using graphite monochromatized Mo-K<sub>α</sub> radiation (λ = 0.71073 Å). Data collection was made with 2° oscillation step of φ, 300 seconds exposure time and scanner distance at 120 mm. 90 images were collected.

**Data reduction:** The images were interpreted and intensities integrated using program DENZO<sup>8</sup>.

**Structure solution:** The structure was solved by direct methods employing SIR-97 program<sup>9</sup> on PC. Se and many non-H atoms were located according to the direct methods and the successive least-square Fourier cycles. Positions of other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using program SHELXL-97<sup>10</sup> on PC. The absolute structure was proved by the Flack absolute structure parameter, which is equal to -0.007(14).

<sup>8</sup> Otwinowski, Z. and Minor, W., "Processing of X-ray Diffraction Data Collected in Oscillation Mode", Methods in Enzymology, Volume 276: Macromolecular Crystallography, part A, p. 307-326, 1997. Carter C. W., Sweet Jr. & R. M., Eds., Academic Press.

<sup>9</sup> A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna. *Sir97: a new tool for crystal structure determination and refinement*. *J. Appl. Cryst.*, **1998**, 32, 115-119.

<sup>10</sup> SHELXL97, Sheldrick, G. M. (1997). SHELX97. Programs for Crystal Structure Analysis (Release 97-2). University of Goettingen, Germany.

**Structure refinement:** According to the SHELXL-97 program<sup>3</sup>, all 2500 independent reflections ( $R_{\text{int}}^{11}$  equal to 0.0435, 2069 reflections larger than  $4\sigma(F_o)$ ) from a total 9128 reflections were participated in the full-matrix least-square refinement against  $F^2$ . These reflections were in the range  $-6 \leq h \leq 6$ ,  $-12 \leq k \leq 12$ ,  $-29 \leq l \leq 29$  with  $2\theta_{\text{max}}$  equal to  $50.66^\circ$ .

One crystallographic asymmetric unit consists of one formula unit. In the final stage of least-squares refinement, all non-hydrogen atoms were refined anisotropically. H atoms were generated by program SHELXL-97. The positions of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final R-indices<sup>12</sup>.

Convergence ( $(\Delta/\sigma)_{\text{max}} = 0.001$ , av. 0.001) for 185 variable parameters by full-matrix least-squares refinement on  $F^2$  reaches to  $R_1 = 0.0305$  and  $wR_2 = 0.0754$  with a goodness-of-fit of 1.069, the parameters a and b for weighting scheme are 0.0496 and 0. The final difference Fourier map shows maximum rest peaks and holes of 0.284 and  $-0.555 \text{ e}\text{\AA}^{-3}$  respectively.

**Drawing:** The ORTEP<sup>13</sup> drawing of the molecule was made with thermal ellipsoids at the 30 % probability level. Screen drawing is provided for reference. Drawing with high quality can be provided upon request.

**Tables:** Table (1) of Crystallographic and refinement data, table (3) of full bond lengths and bond angles and this report<sup>14</sup> are provided. The other supplementary materials, such as table (2) of atomic coordinates, table of anisotropic displacement parameters, table of hydrogen coordinates and/or other tables and/or CIF, RES-files, can be provided under request by notifying the identification code.

Table 1. Crystal data and structure refinement for mar1000.

Identification code	mar1000	
Empirical formula	$\text{C}_{16} \text{H}_{22} \text{O}_3 \text{Se}$	
Formula weight	341.30	
Temperature	253(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P 2_1 2_1 2_1$	
Unit cell dimensions	$a = 6.280(1) \text{ Å}$	$\alpha = 90^\circ$ .
	$b = 10.367(2) \text{ Å}$	$\beta = 90^\circ$ .
	$c = 24.434(5) \text{ Å}$	$\gamma = 90^\circ$ .
Volume	$1590.8(5) \text{ Å}^3$	
Z	4	
Density (calculated)	$1.425 \text{ Mg/m}^3$	

<sup>11</sup>  $R_{\text{int}} = \sum |F_o^2 - F_o^2(\text{mean})| / \sum [F_o^2]$

<sup>12</sup> Since the structure refinements are against  $F^2$ , R-indices based on  $F^2$  are larger than (more than double) those based on F. For comparison with older refinements based on F and an OMIT threshold, a conventional index  $R_1$  based on observed F values larger than  $4\sigma(F_o)$  is also given (corresponding to  $\text{Intensity} \geq 2\sigma(I)$ ).  $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ ,  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ , The Goodness of Fit is always based on  $F^2$ :  $\text{Goof} = S = \{ \sum [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$ , where n is the number of reflections and p is the total number of parameters refined. The weighting scheme is:  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ , where P is  $[2 F_c^2 + \text{Max}(F_o^2, 0)]/3$ .

<sup>13</sup> ORTEP3 for Windows - Farrugia, L. J. (1997) J. Appl. Cryst. 30, 565.

<sup>14</sup> Crystallographic data summarized in this report are abstracted from tables of crystallographic data and data collection record.

Absorption coefficient	2.365 mm <sup>-1</sup>
F(000)	704
Crystal size	0.4 x 0.3 x 0.2 mm <sup>3</sup>
Theta range for data collection	1.67 to 25.33°.
Index ranges	-6<= <i>h</i> <=6, -12<= <i>k</i> <=12, -29<= <i>l</i> <=29
Reflections collected	9128
Independent reflections	2500 [R(int) = 0.0435]
Completeness to theta = 25.33°	88.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2500 / 0 / 185
Goodness-of-fit on F <sup>2</sup>	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0305, wR2 = 0.0754
R indices (all data)	R1 = 0.0393, wR2 = 0.0966
Absolute structure parameter	-0.007(14)
Largest diff. peak and hole	0.284 and -0.555 e.Å <sup>-3</sup>

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for mar1000.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	$U(\text{eq})$
Se(1)	249(1)	1255(1)	270(1)	63(1)
O(1)	-90(7)	759(3)	2438(1)	62(1)
O(2)	1000(5)	-1994(3)	1896(1)	59(1)
O(3)	3971(4)	-812(3)	1964(1)	55(1)
C(1)	-999(7)	-286(4)	649(2)	47(1)
C(2)	-1109(6)	43(4)	1266(2)	41(1)
C(3)	-2304(6)	1308(5)	1414(2)	54(1)
C(4)	-635(6)	2192(4)	1664(2)	50(1)
C(5)	842(6)	1285(4)	1953(2)	49(1)
C(6)	1092(6)	187(4)	1545(2)	39(1)
C(7)	1937(6)	-1009(4)	1815(1)	43(1)
C(8)	-3267(7)	-543(6)	435(2)	71(2)
C(9)	357(8)	-1458(4)	541(2)	57(1)
C(10)	5075(9)	-1861(5)	2230(2)	72(1)
C(11)	466(7)	630(4)	-468(2)	49(1)
C(12)	-1210(8)	798(5)	-831(2)	62(1)
C(13)	-963(8)	429(6)	-1372(2)	68(2)
C(14)	896(9)	-91(5)	-1552(2)	67(1)
C(15)	2542(9)	-258(5)	-1199(2)	69(2)
C(16)	2344(8)	102(5)	-655(2)	62(1)

Table 3. Bond lengths [Å] and angles [°] for mar1000.

Se(1)-C(11)	1.922(4)	C(5)-C(4)-C(3)	103.7(3)
Se(1)-C(1)	2.005(4)	O(1)-C(5)-C(4)	112.1(3)
O(1)-C(5)	1.430(5)	O(1)-C(5)-C(6)	107.5(3)
O(2)-C(7)	1.195(5)	C(4)-C(5)-C(6)	103.0(3)
O(3)-C(7)	1.344(5)	C(7)-C(6)-C(5)	111.5(3)
O(3)-C(10)	1.444(5)	C(7)-C(6)-C(2)	115.4(3)
C(1)-C(9)	1.507(6)	C(5)-C(6)-C(2)	105.6(3)
C(1)-C(8)	1.540(6)	O(2)-C(7)-O(3)	123.6(4)
C(1)-C(2)	1.548(6)	O(2)-C(7)-C(6)	127.2(4)
C(2)-C(6)	1.548(5)	O(3)-C(7)-C(6)	109.2(3)
C(2)-C(3)	1.553(6)	C(16)-C(11)-C(12)	119.3(4)
C(3)-C(4)	1.521(6)	C(16)-C(11)-Se(1)	120.3(3)
C(4)-C(5)	1.498(5)	C(12)-C(11)-Se(1)	120.2(3)
C(5)-C(6)	1.520(6)	C(13)-C(12)-C(11)	119.4(4)
C(6)-C(7)	1.503(6)	C(14)-C(13)-C(12)	120.9(4)
C(11)-C(16)	1.377(6)	C(15)-C(14)-C(13)	120.0(4)
C(11)-C(12)	1.386(6)	C(14)-C(15)-C(16)	120.4(5)
C(12)-C(13)	1.385(6)	C(11)-C(16)-C(15)	120.0(4)
C(13)-C(14)	1.360(7)		
C(14)-C(15)	1.356(7)		
C(15)-C(16)	1.389(7)		
		Symmetry transformations used to generate equivalent atoms:	
C(11)-Se(1)-C(1)	101.08(17)		
C(7)-O(3)-C(10)	117.6(4)		
C(9)-C(1)-C(8)	108.9(4)		
C(9)-C(1)-C(2)	111.9(3)		
C(8)-C(1)-C(2)	109.1(3)		
C(9)-C(1)-Se(1)	109.9(3)		
C(8)-C(1)-Se(1)	110.0(3)		
C(2)-C(1)-Se(1)	106.9(3)		
C(6)-C(2)-C(1)	114.2(3)		
C(6)-C(2)-C(3)	104.3(3)		
C(1)-C(2)-C(3)	115.7(3)		
C(4)-C(3)-C(2)	105.6(3)		



Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for mar1000. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
Se(1)	111(1)	45(1)	33(1)	2(1)	-2(1)	-9(1)
O(1)	104(2)	50(2)	31(1)	-1(1)	4(2)	9(2)
O(2)	75(2)	48(2)	55(2)	14(2)	-6(2)	-4(2)
O(3)	48(2)	63(2)	54(2)	13(2)	-7(1)	11(1)
C(1)	57(2)	51(3)	33(2)	-4(2)	-7(2)	-3(2)
C(2)	42(2)	46(3)	34(2)	4(2)	-1(2)	-1(2)
C(3)	57(2)	56(3)	47(2)	0(2)	1(2)	13(2)
C(4)	65(3)	41(2)	45(2)	1(2)	2(2)	7(2)
C(5)	57(2)	46(2)	43(2)	-5(2)	-8(2)	-1(2)
C(6)	44(2)	39(2)	33(2)	2(2)	1(2)	0(2)
C(7)	50(2)	47(3)	31(2)	2(2)	1(2)	3(2)
C(8)	62(3)	89(4)	62(3)	-7(3)	-23(2)	-9(3)
C(9)	85(3)	47(3)	40(2)	-6(2)	1(2)	-7(3)
C(10)	74(3)	79(3)	63(3)	18(3)	4(3)	37(3)
C(11)	69(3)	42(2)	36(2)	5(2)	-1(2)	0(2)
C(12)	63(3)	82(4)	41(3)	1(2)	-3(2)	22(2)
C(13)	72(3)	89(4)	42(3)	5(3)	-4(2)	4(3)
C(14)	96(4)	57(3)	46(3)	-7(2)	9(3)	-7(3)
C(15)	87(4)	64(4)	58(3)	8(3)	22(3)	15(3)
C(16)	59(3)	74(4)	54(3)	18(3)	1(2)	6(2)

Table 5. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for mar1000.

	x	y	z	U(eq)
H(1)	-529	1348	2632	92
H(2)	-1853	-668	1448	49
H(3A)	-2918	1696	1089	64
H(3B)	-3436	1136	1674	64
H(4A)	110	2674	1383	60
H(4B)	-1278	2793	1919	60
H(5)	2214	1696	2031	58
H(6)	2120	458	1266	47
H(8A)	-3204	-777	55	107
H(8B)	-4113	222	476	107
H(8C)	-3898	-1234	640	107
H(9A)	-236	-2188	729	86
H(9B)	1777	-1305	671	86
H(9C)	393	-1629	155	86
H(10A)	4402	-2046	2574	108
H(10B)	6532	-1621	2292	108
H(10C)	5025	-2613	2001	108
H(12)	-2487	1155	-712	74
H(13)	-2086	540	-1616	81
H(14)	1040	-333	-1917	80
H(15)	3811	-617	-1324	83
H(16)	3479	-12	-415	75