

## New Approaches to Olefin Cross-Metathesis

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### Supporting Material

**Experimental procedures and characterization (<sup>1</sup>H and <sup>13</sup>C NMR, HRMS/elemental analysis, m.p., [ $\alpha$ ]<sub>D</sub>) employed in the preparation of cross- and self-metathesis products. <sup>1</sup>H NMR spectra for 4, 5, 7, 8, 10, 12-16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 38, 40, 42, 44, 46-49, 51-55, 57, 59, 61, 73, 74, 76, 78, 85, 89, 91 (71 pages).**

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**Compound 4.** 9-Decen-1-yl benzoate (**3**)<sup>1</sup> (349 mg, 1.34 mmol) and **1** (3.5 mg, 4  $\mu$ mol, 0.3 mol %) were combined in a 1 dram vial. A magnetic stir bar was added to the vial, which was placed inside a vacuum chamber and held under vacuum (60-100 mtorr) accompanied by stirring for 36 hours at room temperature. The thick burgundy-colored oil was observed to steadily produce gas during the course of the reaction. The reaction mixture was dissolved in 1.0 mL CH<sub>2</sub>Cl<sub>2</sub> and applied to a silica gel column (2x10 cm, eluting with CH<sub>2</sub>Cl<sub>2</sub> (375 mL). Pure fractions were concentrated to give a clear, colorless, viscous oil which formed a white solid over time (312 mg, 94% yield, 3.8:1 *trans/cis* as determined by integration of peaks at 5.38 and 5.35 ppm in the <sup>1</sup>H NMR spectrum). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.03 (4H, d,  $J = 7.2$  Hz), 7.53 (2H, t,  $J = 7.3$  Hz), 7.42 (4H, t,  $J = 7.2$  Hz), 5.38 (2H, m), 4.30 (4H, t,  $J = 6.7$  Hz), 2.10-1.90 (4H, m), 1.75 (4H, quint,  $J = 7.2$  Hz), 1.50-1.20 (20H, m). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  166.3, 132.5, 130.4, 130.2, 129.7, 129.4, 128.1, 64.9, 32.4, 29.6, 29.4, 29.2, 29.1, 28.9, 28.6, 27.0, 25.9.  $R_f = 0.50$  (9:1 hexane/ethyl acetate); HRMS (FAB) calcd for C<sub>32</sub>H<sub>44</sub>O<sub>4</sub> [M+H]<sup>+</sup> 493.3239, found 493.3318.

**Compound 5.** 9-Decen-1-yl benzoate (**3**) (69  $\mu$ l, 0.25 mmol) was added *via* syringe to a stirring solution of *cis*-1,4-bis-(acetyloxy)but-2-ene (79  $\mu$ l, 0.5 mmol) and **1** (21 mg, 0.025 mmol, 10 mol %) in CH<sub>2</sub>Cl<sub>2</sub> (2.5 mL). The flask was fitted with a condenser and refluxed under nitrogen for 3 hours. The reaction mixture was then reduced in volume to 0.5 mL and purified directly on a silica gel column (2x10 cm), eluting with 9:1, 4:1, and 2:1 hexane/ethyl acetate (100 mL aliquots). A pale yellow oil was obtained (68 mg, 82% yield, 5:1 *trans/cis* as determined by integration of peaks at 4.50 and 4.61 ppm in the <sup>1</sup>H NMR spectrum). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.03 (2H, d,  $J = 7.2$  Hz), 7.53 (1H, t,  $J = 7.4$  Hz), 7.42 (2H, t,  $J = 7.8$  Hz), 5.78-5.72 (1H, broad m), 5.57-5.50 (1H, broad m), 4.50 (2H, d,  $J = 6.4$  Hz), 4.30 (2H, t,  $J = 6.7$  Hz), 2.06-2.02 (2H, broad m), 2.03 (3H, s), 1.75 (2H, m), 1.44-1.31 (10H, broad m). <sup>13</sup>C NMR (125

(1) Prepared according to a general literature procedure: Schlessinger, R. H.; Lopes, A. J. *Org. Chem.* **1981**, *46*, 5252-5253.

MHz, CDCl<sub>3</sub>, ppm):  $\delta$  170.7, 166.5, 150.5, 136.4, 135.2, 132.6, 130.5, 129.4, 128.2, 123.7, 123.3, 65.1, 64.9, 60.2, 32.1, 29.2, 29.1, 28.9, 28.7, 28.6, 27.4, 25.9, 20.9.  $R_f$  = 0.36 (9:1 hexane/ethyl acetate); HRMS (FAB) calcd for C<sub>20</sub>H<sub>28</sub>O<sub>4</sub> [M-H]<sup>+</sup> 333.2066, found 333.2067.

**Compound 6.** 9-Decen-1-yl benzoate (**3**) (69  $\mu$ l, 0.25 mmol) was added *via* syringe to a stirring solution of *cis*-1,4-bis-(trifluoroacetyloxy)but-2-ene<sup>2</sup> (188  $\mu$ l, 1.0 mmol) and **1** (11 mg, 0.013 mmol, 5 mol %) in CH<sub>2</sub>Cl<sub>2</sub> (2.5 mL). The flask was fitted with a condenser and refluxed under nitrogen for 16 hours. The reaction mixture was then reduced in volume to a thick brown oil and redissolved in 2 mL methanol to which 1 mL of NEt<sub>3</sub> was added to effect cleavage of the trifluoroacetate moiety.<sup>2</sup> The mixture was stirred for two hours at room temperature until TLC analysis indicated that deprotection was complete. The solution of alcohols (**7**) was concentrated and purified directly on a silica gel column (2x10 cm), eluting with 9:1, 4:1, 2:1 and 1:1 hexane/ethyl acetate (100 mL aliquots). A pale yellow, viscous oil was obtained that exhibited spectral properties identical to alcohol **7** (45 mg, 63% yield over two steps, 2.8:1 *trans/cis* as determined by integration of peaks at 4.07 and 4.18 ppm in the <sup>1</sup>H NMR spectrum).

**Compound 7.** 9-Decen-1-yl benzoate (**3**) (130 mg, 0.5 mmol) was added *via* syringe to a stirring solution of 1,4-butanediol (95% *cis*, 88 mg, 1.0 mmol) and **1** (21 mg, 0.026 mmol, 5 mol %) in CH<sub>2</sub>Cl<sub>2</sub> (5.0 mL). The reaction was stirred at room temperature under a nitrogen atmosphere for 12 hours. The reaction mixture was then reduced in volume to 1.0 mL and applied to a silica gel column (2x10 cm), eluting with CH<sub>2</sub>Cl<sub>2</sub> (100 mL) followed by 4:1 CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate (150 mL). A clear, colorless, viscous oil was obtained (80 mg, 56% yield, 5:1 *trans/cis* as determined by integration of peaks at 4.07 and 4.18 ppm in the <sup>1</sup>H NMR spectrum). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.03 (2H, app d,  $J$  = 7.0 Hz), 7.53 (1H, tt,  $J$  = 7.4, 1.4 Hz), 7.41 (2H, t,  $J$  = 8.0 Hz), 5.70-5.50 (2H, m), 4.30 (2H, t,  $J$  = 6.7 Hz), 4.07 (2H, dd,  $J$

(2) Prepared according to a standard literature procedure: Lardon, A.; Reichstein, T. *Helv. Chim. Acta.* **1954**, *37*, 443-450.

= 0.7, 5.5 Hz), 2.02 (2H, q, 6.8 Hz), 1.78 (1H, s), 1.77 (2H, quint,  $J = 7.9$  Hz), 1.45-1.28 (10H, m).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  166.6, 133.2, 132.9, 132.7, 130.5, 129.5, 128.9, 128.5, 128.2, 65.0, 63.7, 58.5, 32.1, 29.5, 29.3, 29.1, 29.0, 28.99, 28.7, 27.3, 25.9.  $R_f = 0.23$  (3:1 hexane/ethyl acetate); HRMS (EI) calcd for  $\text{C}_{18}\text{H}_{26}\text{O}_3$   $[\text{M}-\text{H}]^+$  290.1882, found 289.1804.

**Compound 8.** 9-Decen-1-yl benzoate (3) (130 mg, 0.5 mmol) was added *via* syringe to a stirring solution of *cis*-1,4-bis-(*tert*-butoxy)but-2-ene<sup>3</sup> (200 mg, 1.0 mmol) and 1 (21 mg, 0.026 mmol, 5 mol %) in  $\text{CH}_2\text{Cl}_2$  (5.0 mL). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 1.0 mL and applied to a silica gel column (2x8 cm), eluting with  $\text{CH}_2\text{Cl}_2$  (300 mL). Fractions containing the desired product were concentrated to an oil (164 mg, 94% yield, 7:1 *trans/cis* as determined by integration of peaks at 3.80 and 3.93 ppm in the  $^1\text{H}$  NMR spectrum).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  8.03 (2H, app d,  $J = 7.0$  Hz), 7.52 (1H, tt,  $J = 7.4, 1.4$  Hz), 7.40 (2H, t,  $J = 8.0$  Hz), 5.7-5.6 (1H, m), 5.57-5.47 (1H, m), 3.80 (2H, d,  $J = 5.9$  Hz), 2.10 (2H, m), 1.74 (2H, quint,  $J = 7.0$  Hz), 1.45-1.25 (10H, m), 1.19 (9H, s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  166.5, 133.0, 132.6, 132.0, 130.5, 130.2, 129.4, 128.2, 127.6, 72.8, 64.9, 62.8, 57.6, 32.4, 32.2, 29.5, 29.4, 29.2, 29.1, 29.0, 28.9, 28.6, 27.5, 27.4, 25.9.  $R_f = 0.46$  (9:1 hexane/ethyl acetate); HRMS (FAB) calcd for  $\text{C}_{22}\text{H}_{34}\text{O}_3$   $[\text{M}+\text{H}]^+$  347.2508, found 347.2586.

**Compound 9.** 9-Decen-1-yl benzoate (3) (66 mg, 0.25 mmol) was added *via* syringe to a stirring solution of *cis*-1,4-bis-(*O*-trityl)but-2-ene<sup>4</sup> (285 mg, 0.5 mmol) and 1 (11 mg, 0.013 mmol, 5 mol %) in  $\text{CH}_2\text{Cl}_2$  (2.5 mL). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 1.0 mL and applied to a silica gel column (2x10 cm), eluting with  $\text{CH}_2\text{Cl}_2$  (250 mL). Fractions containing the

(3) Prepared using a general method: Alexakis, A.; Gardette, M.; Colin, S. *Tetrahedron Lett.* **1988**, 29, 2951-2954.

(4) Prepared using a general method: Chaudary, S. K.; Hernandez, O. *Tetrahedron Lett.* **1979**, 2, 95-98.

desired product and homodimer were concentrated to an oil which was dissolved in  $\text{CH}_2\text{Cl}_2$  (8 mL) and treated with 98% formic acid (2.0 mL, 53 mmol) at room temperature for one hour.<sup>5</sup> The reaction was quenched by dilution with ethyl acetate (40 mL) followed by slow addition of aqueous sodium bicarbonate solution (7 g  $\text{NaHCO}_3$  in 40 mL  $\text{H}_2\text{O}$ ). The biphasic mixture was allowed to stir for two hours, after which the organic layer was removed, washed with brine and dried with sodium sulfate. This brown solution was concentrated, redissolved in 2.0 mL  $\text{CH}_2\text{Cl}_2$  and applied to a silica gel column (2x10 cm), eluting with 9:1 hexane/ethyl acetate (100 mL) followed by 1:1 hexane/ethyl acetate (100 mL). A clear, colorless, viscous oil was obtained with spectral properties identical to alcohol **7** (55 mg, 75% yield over 2 steps, 8:1 *trans/cis* as determined by integration of peaks at 4.07 and 4.18 ppm in the  $^1\text{H}$  NMR spectrum).

**Compound 10.** 9-Decen-1-yl benzoate (**3**) (130 mg, 0.5 mmol) was added *via* syringe to a stirring solution of *cis*-1,4-bis-(benzyloxy)but-2-ene<sup>6</sup> (270 mg, 1.0 mmol) and **1** (21 mg, 0.026 mmol, 5 mol %) in  $\text{CH}_2\text{Cl}_2$  (5.0 mL). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 1.0 mL and applied to a silica gel column (2x10 cm), eluting with  $\text{CH}_2\text{Cl}_2$  (300 mL). Fractions containing the desired product and unreacted terminal alkene were concentrated to an oil which was dissolved in ethyl acetate (15 mL) and hydrogenated (1 atm  $\text{H}_2$  balloon) over 10% Pd-C (20 mg) for 6 hours.<sup>7</sup> The reaction mixture was filtered through a glass frit and concentrated to an oil. The alcohol product (**11**) was isolated by silica gel chromatography (2x10 cm), eluting with 9:1 hexane/ethyl acetate (100 mL) followed by 1:1 hexane/ethyl acetate (100 mL). A clear, colorless, viscous oil (**11**) was obtained (104 mg, 71% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):

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- (5) For a reference to this cleavage protocol, see: Bessodes, M.; Komiotis, D.; Antonakis, K. *Tetrahedron Lett.* **1986**, *5*, 579-580.
  - (6) Prepared by a general procedure: Forster, R. C.; Owen, L. N. *J. Chem. Soc., Perkin Trans. I* **1978**, 822-829.
  - (7) For details of the cleavage protocol, see: Heathcock, C. H.; Ratcliffe, R. *J. Org. Chem.* **1971**, *93*, 1746-1757.

$\delta$  8.03 (2H, m), 7.53 (1H, tt,  $J = 7.4, 1.4$  Hz), 7.42 (2H, t,  $J = 7.4$  Hz), 4.29 (2H, t,  $J = 6.7$  Hz), 3.6 (2H, t,  $J = 6.7$  Hz), 2.03 (1H, br s), 1.75 (2H, quint,  $J = 6.8$  Hz), 1.54 (2H, quint,  $J = 6.6$  Hz), 1.4 (2H, m), 1.38-1.22 (12H, m).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  166.6, 132.7, 130.4, 129.4, 128.2, 65.0, 62.8, 32.7, 29.4, 29.4, 29.3, 29.1, 28.6, 25.9, 25.7.  $R_f = 0.34$  (3:1 hexane/ethyl acetate); HRMS (EI) calcd for  $\text{C}_{18}\text{H}_{28}\text{O}_3$ ,  $[\text{M}+\text{H}]^+$  293.2038, found 293.2113.

**Compound 11.** 9-Decen-1-yl benzoate (**3**) (130 mg, 0.5 mmol) was added *via* syringe to a stirring solution of *cis*-1,4-bis-(tert-butyldimethylsilyloxy)but-2-ene<sup>8</sup> (317 mg, 1.0 mmol) and **1** (21 mg, 0.026 mmol, 5 mol %) in  $\text{CH}_2\text{Cl}_2$  (5 mL). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.75 mL and applied to a silica gel column (2x10 cm), eluting with  $\text{CH}_2\text{Cl}_2$  (300 mL). Fractions containing the desired product and unreacted terminal alkene were concentrated to an oil which was dissolved in THF (5 mL) and treated with TBAF (1.6 mL of a 1.0M THF solution) at room temperature for 2 hours.<sup>8</sup> The reaction mixture was concentrated, redissolved in 2.0 mL  $\text{CH}_2\text{Cl}_2$  and applied to a silica gel column (2x10 cm), eluting with 9:1 hexane/ethyl acetate (100 mL) followed by 1:1 hexane/ethyl acetate (100 mL). A clear, colorless, viscous oil was obtained that exhibited spectral properties identical to alcohol **7** (113 mg, 77% yield over 2 steps, 10:1 *trans/cis* as determined by integration of peaks at 4.07 and 4.18 ppm in the  $^1\text{H}$  NMR spectrum).

**Compound 12.** 9-Decen-1-yl benzoate (**3**) (130 mg, 0.5 mmol) was added *via* syringe to a stirring solution of *cis*-3-hexene (84 mg, 1 mmol) and **1** (21 mg, 0.026 mmol, 5 mol %) in  $\text{CH}_2\text{Cl}_2$  (5.0 mL). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 1.0 mL and applied to a silica gel column (2x10 cm), eluting with  $\text{CH}_2\text{Cl}_2$  (300 mL). Fractions containing the desired product were concentrated to an oil (104 mg, 72% yield, 3:1 *trans/cis* as determined by analysis of methyl

(8) Prepared using a general method: Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* 1972, 94, 6190-6191.

intensities at 0.97 and 0.96 ppm in the  $^1\text{H}$  NMR spectrum).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  8.03 (2H, app d,  $J = 7.0$  Hz), 7.52 (1H, tt,  $J = 7.4, 1.4$  Hz), 7.40 (2H, t,  $J = 8.0$  Hz), 5.50-5.30 (2H, m), 4.32 (2H, t,  $J = 6.7$  Hz), 2.10-1.90 (4H, m), 1.75 (2H, quint,  $J = 7.2$  Hz), 1.43 (2H, m), 1.40-1.25 (10H, m), 0.97 (3H, t,  $J = 7.4$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  166.5, 132.7, 131.9, 131.5, 130.6, 129.2, 129.16, 128.2, 65.0, 32.5, 29.7, 29.5, 29.3, 29.2, 29.1, 29.0, 28.7, 27.0, 26.0, 25.5, 20.4, 14.3, 13.92.  $R_f = 0.63$  (9:1 hexane/ethyl acetate); HRMS (EI) calcd for  $\text{C}_{19}\text{H}_{28}\text{O}_2$   $[\text{M}+\text{H}]^+$  289.2167, found 289.2171.

**Compound 13.** 9-Decen-1-yl benzoate (**3**) (69  $\mu\text{l}$ , 0.25 mmol) was added *via* syringe to a stirring solution of *cis*-1,4-bis-(*N*-Boc)but-2-ene<sup>9</sup> (286 mg, 1.0 mmol) and **1** (11 mg, 0.013 mmol, 5 mol %) in  $\text{CH}_2\text{Cl}_2$  (2.5 mL). The flask was fitted with a condenser and refluxed under nitrogen for 16 hours. The reaction mixture was then reduced in volume to 0.5 mL and purified directly on a silica gel column (2x10 cm), eluting with 9:1, 4:1, 2:1 and 1:1 hexane/ethyl acetate (100 mL aliquots). A pale yellow, viscous oil was obtained (70 mg, 71% yield, 2.9:1 *trans/cis* as determined by integration of peaks at 3.64 and 3.73 ppm in the  $^1\text{H}$  NMR spectrum).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  8.01 (2H, d,  $J = 7.2$  Hz), 7.52 (1H, t,  $J = 7.3$  Hz), 7.40 (2H, t,  $J = 7.7$  Hz), 5.56-5.52 (1H, broad m), 5.41-5.37 (1H, broad m), 4.58 (1H, m), 4.28 (2H, t,  $J = 6.6$  Hz), 3.64 (2H, app s), 1.97 (2H, m), 1.73 (2H, quint,  $J = 6.7$  Hz), 1.41 (9H, s), 1.47-1.27 (10H, broad m).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  166.8, 155.9, 133.2, 133.16, 132.9, 131.0, 129.7, 128.5, 127.7, 126.6, 126.3, 79.3, 65.2, 62.4, 43.0, 38.1, 32.3, 29.7, 29.5, 29.4, 29.33, 29.29, 29.2, 29.0, 28.6, 28.5, 27.5, 26.2.  $R_f = 0.30$  (9:1 hexane/ethyl acetate); HRMS (FAB) calcd for  $\text{C}_{23}\text{H}_{35}\text{NO}_4$   $[\text{M}-\text{H}]^+$  390.2644, found 390.2635.

(9) Prepared according to a modified literature procedure. See: Zuwen, H.; Nadkarni, D. V.; Sayre, L. M.; Greenaway, F. T. *Biochim. Biophys. Acta* **1995**, *1253*, 117-127.

**Compound 14.** 9-Decen-1-yl benzoate (**3**) (130 mg, 0.5 mmol) was added *via* syringe to a stirring solution of dimethyl trans-3-hexene-1,6-dioate<sup>10</sup> (84 mg, 1.0 mmol) and **1** (21 mg, 0.026 mmol, 5 mol %) in CH<sub>2</sub>Cl<sub>2</sub> (5.0 mL). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 1.0 mL and applied to a silica gel column (2x10 cm), eluting with CH<sub>2</sub>Cl<sub>2</sub> (300 mL). Fractions containing the desired product were concentrated to an oil (124 mg, 74% yield, 3:1 *trans/cis* as determined by integration of peaks at 3.00 and 3.07 ppm in the <sup>1</sup>H NMR spectrum). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 8.03 (2H, app d, *J* = 7.0 Hz), 7.52 (1H, tt, *J* = 7.4, 1.4 Hz), 7.40 (2H, t, *J* = 8.0 Hz), 5.50-5.30 (2H, m), 4.32 (2H, t, *J* = 6.7 Hz), 3.63 (3H, s), 3.00 (2H, d, *J* = 5.5 Hz), 1.98 (2H, q, *J* = 7.1 Hz), 1.74 (2H, quint, *J* = 6.8 Hz), 1.45-1.20 (10H, m). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm): δ 172.4, 166.5, 131.7, 133.4, 132.7, 130.5, 129.4, 128.2, 121.4, 120.7, 65.0, 51.6, 51.5, 37.8, 32.7, 32.3, 29.2, 29.1, 29.0, 28.9, 28.7, 27.3, 25.9. *R*<sub>f</sub> = 0.38 (9:1 hexane/ethyl acetate); HRMS (FAB) calcd for C<sub>20</sub>H<sub>28</sub>O<sub>4</sub> [M+H]<sup>+</sup> 333.2066, found 333.2059.

**Compound 15.** 9-Decen-1-yl benzoate (**3**) (69 μL, 0.25 mmol) was added *via* syringe to a stirring solution of trans-1,4-bis-(methyl(methoxy)amido)hex-3-ene<sup>11</sup> (230 mg, 1.0 mmol) and **1** (11 mg, 0.013 mmol, 5 mol %) in CH<sub>2</sub>Cl<sub>2</sub> (2.5 mL). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 mL and purified directly on a silica gel column (2x10 cm), eluting with 9:1, 5:1, and 1:1 hexane/ethyl acetate (100 mL aliquots). A clear, viscous oil was obtained (15 mg, 17% yield, 1.9:1 *trans/cis* as determined by the relative intensities of peaks at 65.35 and 65.33 ppm in the <sup>13</sup>C NMR spectrum). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 8.03 (2H, d, *J* = 7.3 Hz), 7.54 (1H, t, *J* = 7.4 Hz), 7.43 (2H, t, *J* = 7.8 Hz), 5.56 (2H, m), 4.30 (2H, t, *J* = 6.6 Hz), 3.67 (3H, s), 3.20 (2H, m), 3.16 (3H, s), 2.06-2.02 (2H, broad m), 1.75 (2H, quint, *J* = 6.7 Hz), 1.42-1.24 (10H, broad

(10) Prepared according to a literature procedure: Gassman, P. G.; Bonser, S. M.; Mlinaric-Majerski, K. *J. Am. Chem. Soc.* **1989**, *111*, 2652-2662.

(11) Prepared *via* a DCC coupling between muconic acid and *N,O*-dimethyl-hydroxylamine hydrochloride. See: Nahm, S.; Weinreb, S. M. *Tetrahedron Lett.* **1981**, *22*, 3815-3818.



m).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  134.6, 133.2, 132.9, 129.8, 128.5, 122.7, 121.9, 65.35, 65.33, 61.5, 36.4, 32.7, 31.4, 29.62, 29.58, 29.47, 29.46, 29.3, 29.0, 27.8, 26.3.  $R_f = 0.09$  (9:1 hexane/ethyl acetate); HRMS (FAB) calcd for  $\text{C}_{21}\text{H}_{31}\text{NO}_4$   $[\text{M}]^+$  362.2331, found 362.2337.

**Compound 16.** 9-Decen-1-yl benzoate (145  $\mu\text{l}$ , 0.52 mmol) was added *via* syringe to a stirring solution of trans-1,6-bis-(*tert*-butyldimethylsilyloxy)hex-3-ene<sup>12</sup> (400  $\mu\text{l}$ , 1.16 mmol) and **1** (11 mg, 0.013 mmol, 2.6 mol %) in  $\text{CH}_2\text{Cl}_2$  (2.5 mL). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 mL and purified directly on a silica gel column (2x10 cm), eluting with 9:1 hexane/ethyl acetate. Fractions containing the desired product and unreacted alkene were concentrated to an oil which was redissolved in THF (8 mL) and treated with TBAF (2 mL of a 1.0M THF solution) at room temperature for 2 hours.<sup>76</sup> The reaction mixture was concentrated, redissolved in 2.0 mL  $\text{CH}_2\text{Cl}_2$  and applied to a silica gel column (2x10 cm), eluting with 4:1 hexanes/ethyl acetate. A clear oil was obtained (79 mg, 49% yield, 2.8:1 *trans/cis* as determined by relative intensities of  $^{13}\text{C}$  peaks at 125.6 and 126.4 ppm).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  8.03 (2H, app d,  $J = 7.2$  Hz), 7.55 (1H, m), 7.43 (2H, t,  $J = 6.8$  Hz), 5.53 (1H, m), 5.36 (1H, m), 4.30 (2H, t,  $J = 6.6$  Hz), 3.61 (2H, m), 2.28 (2H, m), 2.03 (2H, m) 1.76 (2H, m), 1.60 (1H, unresolved s), 1.45-1.20 (10H, broad m).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  167.3, 134.7, 133.4, 130.1, 128.9, 126.4, 125.6, 65.7, 62.6, 36.5, 33.2, 30.2, 29.9, 29.8, 29.6, 29.3, 27.9, 26.6, 20.8.  $R_f = 0.23$  (4:1 hexane/ethyl acetate); HRMS (FAB) calcd for  $\text{C}_{19}\text{H}_{29}\text{O}_3$   $[\text{M} + \text{H}]^+$  305.2117, found 305.2116.

**Compound 18.** 9-Decen-1-ol (**17**) (1.14 mL, 6.4 mmol) and **1** (15.8 mg, 0.019 mmol, 0.3 mol %) were combined in a 5 mL one-neck round-bottom flask. A magnetic stir bar was added to the flask and it was equipped with a vacuum adapter. The flask was held under vacuum (60-100 mtorr) accompanied by stirring for 36 hours at room temperature. The thick burgundy-colored

(12) Prepared according to a general literature procedure: Zhdanov, R. I.; Zhenodarova, S. M. *Synthesis* **1975**, 222-245.

oil steadily produced gas during the course of reaction, and after 24 hours a white solid was visible. The reaction mixture was then dissolved in 1.0 mL  $\text{CH}_2\text{Cl}_2$  and purified directly on a silica gel column (5x25 cm), eluting with 9:1, 4:1, and 3:1  $\text{CH}_2\text{Cl}_2$ /ethyl acetate (250 mL aliquots). A fluffy white, crystalline solid was obtained (494 mg, 54% yield, 1.7:1 *trans/cis* as determined by integration of peaks at 5.36 and 5.33 ppm in the  $^1\text{H}$  NMR spectrum).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  5.36 (2H, m), 3.61 (4H, t,  $J = 6.6$  Hz), 2.00-1.94 (4H, br m), 1.54 (4H, quint,  $J = 6.5$  Hz), 1.30-1.27 (20H, br m).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  130.6, 130.1, 63.3, 33.0, 32.8, 29.9, 29.8, 29.68, 29.66, 29.6, 29.4, 29.3, 27.4, 25.9.  $R_f = 0.18$  (9:1  $\text{CH}_2\text{Cl}_2$ /ethyl acetate); HRMS (EI) calcd for  $\text{C}_{18}\text{H}_{36}\text{O}_2$   $[\text{M}]^+$  284.2715, found 284.2713.

**Compound 20.** 9-Decen-1-yl acetate (**19**) (1.0 g, 5.0 mmol) and **1** (13 mg, 0.015 mmol, 0.3 mol %) were combined in a 1 dram vial. A magnetic stir bar was added to the vial, which was placed inside a vacuum chamber and held under vacuum (60-100 mtorr) accompanied by stirring for 16 hours at room temperature. The thick burgundy-colored oil steadily produced gas during the course of reaction, which subsided as the product began to crystallize. The reaction mixture was then purified directly on a silica gel column (2x15 cm), eluting with 9:1, 2:1, and 1:1 hexane/ethyl acetate (200 mL aliquots). A pale yellow, viscous oil that crystallized over time was obtained (878 mg, 95% yield, 4.4:1 *trans/cis* as determined by the relative intensities of peaks at 130.2 and 129.6 ppm in the  $^{13}\text{C}$  NMR spectrum).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  5.17 (2H, m), 3.85 (4H, t,  $J = 6.8$  Hz), 1.83 (6H, s), 1.85-1.78 (4H, broad m), 1.43 (4H, m), 1.11 (20H, m).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  170.3, 130.2, 129.6, 61.2, 32.4, 29.6, 29.4, 29.2, 29.1, 29.0, 28.9, 28.6, 27.0, 25.8, 20.5.  $R_f = 0.29$  (9:1 hexane/ethyl acetate); HRMS (FAB) calcd for  $\text{C}_{22}\text{H}_{40}\text{O}_4$   $[\text{M}-\text{H}]^+$  369.3005, found 369.2993.

**Compound 22.** Methyl 10-undecylenate (**21**) (2.26 g, 11.4 mmol) and **1** (46 mg, 0.06 mmol, 0.5 mol %) were combined in a round-bottom flask. A magnetic stir bar was added to the flask, and the flask was equipped with a vacuum adapter. The flask was held under vacuum (100-200

mtorr) and stirred for 36 hours at room temperature. The thick burgundy-colored oil was observed to steadily produce gas during the course of reaction, and after two hours a thick precipitate formed. The solidified reaction mixture was melted by warming the flask with a heat-gun. This procedure was repeated three times over a three hour period. The reaction mixture was dissolved in 3 mL  $\text{CH}_2\text{Cl}_2$  and applied to a silica gel column (10x10 cm), eluting with  $\text{CH}_2\text{Cl}_2$  (700 mL). Pure fractions were concentrated to give a white solid upon standing (1.9 g, 90% yield, 5:1 *trans/cis* as determined by integration of olefinic peaks while decoupling allylic protons at 2.24 ppm in the  $^1\text{H}$  NMR spectrum).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  5.31 (2H, m), 3.58 (6H, s), 2.24 (4H, t,  $J = 7.5$  Hz), 1.90 (4H, m), 1.55 (4H, quint,  $J = 7.2$  Hz), 1.30-1.15 (20H, m).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  174.0, 130.2, 129.7, 51.2, 33.9, 32.4, 29.6, 29.5, 29.2, 29.1, 29.0, 28.9, 27.1, 24.8.  $R_f = 0.66$  (3:1 hexane/ethyl acetate); HRMS (EI) calcd for  $\text{C}_{32}\text{H}_{44}\text{O}_4$   $[\text{M}+\text{H}]^+$  368.2928, found 368.2927.

**Compound 24.** 9-Decen-1-yl *N*-Boc-glycinate (**23**)<sup>13</sup> (173 mg, 0.55 mmol) and **1** (1.4 mg, 2.0  $\mu\text{mol}$ , 0.3 mol %) were combined in a 1 dram vial. A magnetic stir bar was added to the vial, which was placed inside a vacuum chamber and held under vacuum (60-100 mtorr) accompanied by stirring for 36 hours at room temperature. The thick burgundy-colored oil steadily produced gas during the course of reaction. The reaction mixture was then purified directly on a silica gel column (2x10 cm), eluting with 9:1, 4:1, and 2:1 hexane/ethyl acetate (100 mL aliquots). A clear, colorless viscous oil was obtained (153 mg, 93% yield, 3.9:1 *trans/cis* as determined by the relative intensities of peaks at 130.5 and 130.0 ppm in the  $^{13}\text{C}$  NMR spectrum).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  5.33 (2H, m), 5.07 (2H, m), 4.09 (4H, t,  $J = 6.7$  Hz), 3.85 (4H, d,  $J = 5.0$  Hz), 1.92 (4H, m), 1.58 (4H, m), 1.53-1.24 (20H, m).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  170.5, 155.8, 130.5, 130.0, 80.1, 65.6, 42.9, 32.7, 29.9, 29.8, 29.52, 29.48, 29.3, 29.2, 28.8, 28.5,

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(13) Prepared *via* a DCC coupling between *N*-Boc-L-glycine-OH and 9-decen-1-ol.

27.4, 26.0.  $R_f = 0.31$  (3:1 hexane/ethyl acetate); HRMS (FAB) calcd for  $C_{32}H_{58}N_2O_8$   $[M-H]^+$  599.4271, found 599.4271.

**Compound 26.** Undecylenic aldehyde acetal (**25**) (661 mg, 3.0 mmol) was added *via* syringe to a flask containing **1** (18 mg, 0.021 mmol, 0.7 mol %). The flask was fitted with a vacuum adapter and placed under vacuum (100 mtorr) for 12 hours. The reaction mixture was then purified directly on a silica gel column (2x10 cm), eluting with 15:1 hexane/ethyl acetate (300 mL). A white solid was obtained (511 mg, 83% yield, 4:1 *trans/cis* as determined by integration of peaks at 5.45 and 5.28 ppm in the  $^1H$  spectrum).  $^1H$  NMR (300 MHz,  $CDCl_3$ , ppm):  $\delta$  5.45-5.28 (2H, m), 4.30 (2H, t,  $J = 6.6$  Hz), 4.05-3.83 (8H, m), 1.97 (4H, broad m), 1.60 (4H, broad m), 1.50-1.25 (24H, broad m).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ , ppm):  $\delta$  130.8, 105.2, 65.3, 34.4, 33.1, 30.1, 30.0, 29.8, 29.7, 29.6, 24.6.  $R_f = 0.19$  (15:1 hexane/ethyl acetate); HRMS (FAB) calcd for  $C_{24}H_{43}O_4$   $[M-H]^+$  395.3161, found 395.3164.

**Compound 28.** Allyl benzene (**27**) (1.0 g, 8.5 mmol) and **1** (15.8 mg, 0.019 mmol, 0.3 mol %) were combined in a 1 dram vial. A magnetic stir bar was added to the vial, which was placed inside a vacuum chamber and held under vacuum (60-100 mtorr) accompanied by stirring for 24 hours at room temperature. The thick burgundy-colored oil steadily produced gas during the course of reaction, and after 24 hours the reaction mixture became a pale brown, crystalline mass. The crude reaction mixture was then purified directly by Kugel-Rohr distillation (140°C, 60 mtorr). A clear, viscous oil was obtained which slowly crystallized over time (664 mg, 75% yield, 8.3:1 *trans/cis* as determined by the relative intensities of peaks at 39.1 and 33.7 ppm in the  $^{13}C$  NMR spectrum). This product could not be characterized by TLC.  $^1H$  NMR (500 MHz,  $CDCl_3$ , ppm):  $\delta$  7.31 (5H, m), 7.21 (5H, m), 5.68 (2H, m), 3.37 (4H, m).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ , ppm):  $\delta$  141.0, 140.9, 130.6, 129.3, 128.7, 128.67, 128.6, 126.2, 39.1, 33.7. HRMS (EI) calcd for  $C_{16}H_{16}$   $[M]^+$  208.1252, found 208.1250.

**Compound 30.** Allyl pentafluorobenzene (**29**) (147  $\mu$ l, 0.96 mmol) was added *via* syringe to a stirring solution of **1** (40 mg, 0.048 mmol, 5 mol %) in  $\text{CH}_2\text{Cl}_2$  (9.6 mL). The flask was fitted with a condenser and refluxed under nitrogen for 16 hours during which time the reaction was monitored by  $^1\text{H}$  NMR. The reaction mixture was reduced in volume to 0.5 mL and purified directly by addition of 10 equivalents of  $\text{P}(\text{CH}_2\text{OH})_3\text{H}^+\text{Cl}$  and  $\text{NEt}_3$ , respectively, in 3.0 mL  $\text{CH}_2\text{Cl}_2$  to effect removal of the ruthenium catalyst **1** and/or catalyst decomposition products.<sup>14</sup> The brown homogenous solution was stirred at room temperature for 30 minutes. The solution gradually became clear light yellow over this time period. The organic layer was then washed with 10 mL of brine, 10 mL of 10% citric acid solution, and 10 mL of deionized water to remove the water soluble phosphine derivative complexed to any residual catalyst and/or catalyst decomposition products. The colorless organic layer was dried over  $\text{MgSO}_4$  and concentrated to give an off-white crystalline solid (155 mg, 83% yield, 16:1 *trans/cis*).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  5.57 (2H, app br s), 3.37 (4H, app br s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  146.1, 144.2, 141.1, 139.1, 138.7, 136.7, 127.7, 113.3, 113.1, 25.2.  $R_f$  = 0.60 (9:1 hexane/ethyl acetate); HRMS (EI) calcd for  $\text{C}_{16}\text{H}_6\text{F}_{10}$   $[\text{M}]^+$  388.0310, found 388.0315.

**Compound 32.** Eugenol (**31**) (1.0 mL, 6.5 mmol) and **1** (16 mg, 0.02 mmol, 0.3 mol %) were combined in a 1 dram vial. A magnetic stir bar was added to the vial, which was placed inside a vacuum chamber and held under vacuum (60-100 mtorr) accompanied by stirring for 24 hours at room temperature. The thick burgundy-colored oil steadily produced gas during the course of reaction, gradually turning into a pale brown, crystalline mass. The reaction mixture was then purified directly by on a silica gel column, eluting with 9:1, 4:1, 3:1, and 1:1 hexane/ethyl acetate. A cream-colored, crystalline solid was obtained which slowly turned maroon in color over time (697 mg, 71% yield, 5.9:1 *trans/cis* as determined by integration of peaks at 3.29 and 3.44 ppm in the  $^1\text{H}$  NMR spectrum).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  6.83 (2H, d,  $J$  = 7.9

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(14) Maynard, H. D.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 4137-4140.

Hz), 6.69 (2H, masked d,  $J = 7.7$  Hz), 6.68 (2H, s), 5.63 (2H, m), 5.49 (2H, s), 3.84 (6H, s), 3.29 (4H, d,  $J = 5.0$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  146.6, 144.0, 132.9, 130.8, 129.4, 121.2, 121.1, 114.5, 114.4, 111.3, 111.28, 111.2, 56.0, 38.8, 33.2.  $R_f = 0.21$  (3:1 hexane/ethyl acetate); HRMS (EI) calcd for  $\text{C}_{18}\text{H}_{20}\text{O}_4$   $[\text{M}]^+$  300.1362, found 300.1364.

**Compound 34.** 1-Ferrocene methanol *O*-allyl ether (**33**)<sup>15</sup> (200 mg, 0.78 mmol) was added to a stirring solution of **1** (32 mg, 0.039 mmol, 5 mol %) in  $\text{CH}_2\text{Cl}_2$  (7.8 mL). The flask was fitted with a condenser and refluxed under nitrogen for 14 hours. The reaction mixture was then reduced in volume to 0.5 mL and purified directly on a silica gel column (2x15 cm), eluting with 9:1, 7:1, 4:1, and 3:1 hexane/ethyl acetate (100 mL aliquots). An orange crystalline solid was obtained (145 mg, 77% yield, 7.8:1 *trans/cis* as determined by the relative intensities of peaks at 129.73 and 129.69 ppm in the  $^{13}\text{C}$  NMR spectrum).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  5.78 (2H, app br s), 4.27 (4H, app br s), 4.23 (4H, app br s), 4.15 (4H, app s obscured), 4.13 (10H, app s), 3.82 (4H, d,  $J = 7.2$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  129.73, 129.69, 83.6, 70.0, 69.6, 68.7, 68.6.  $R_f = 0.57$  (3:1 hexane/ethyl acetate); HRMS (FAB) calcd for  $\text{C}_{26}\text{H}_{28}\text{Fe}_2\text{O}_2$   $[\text{M}]^+$  484.0788, found 484.0802.

**Compound 36.** Allyl phenyl sulfone (1.09 g, 6.0 mmol) was added *via* syringe to a flask containing **1** (51 mg, 0.062 mmol, 1.0 mol %). The flask was fitted with a vacuum adapter and placed under vacuum (100 mtorr) for 12 hours. The reaction mixture was then purified directly on a silica gel column (2x10 cm), eluting with 2:1 hexane/ethyl acetate (400 mL). A white solid was obtained (373 mg, 37% yield, 8:1 *trans/cis* as determined integration of peaks at 5.77 and 5.61 ppm in the  $^1\text{H}$  NMR spectrum).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm): 7.84-7.80 (4H, m), 7.69-7.52 (6H, m), 5.61-5.57 (2H, m), 3.76 (4H, dd,  $J = 1.9$  Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm): 138.8, 134.6, 129.9, 129.6, 129.0, 128.9, 126.9, 60.1.  $R_f = 0.20$  (2:1 hexane/ethyl acetate);

(15) The allyl ether was introduced into 1-ferrocene methanol using a standard literature procedure: Corey, E. J.; Suggs, J. W. *J. Org. Chem.* **1973**, *38*, 3224.

HRMS (FAB) calcd for  $C_{22}H_{32}O_2$   $[M+H]^+$  337.0576, found 337.0568. Elemental analysis calcd: C: 57.12, H: 4.79; found: C: 56.88, H: 4.95.

**Compound 38.** *N*-Boc-*L*-serine(*O*-Allyl) methyl ester (**37**)<sup>16</sup> (160 mg, 0.62 mmol) and **1** (2.0 mg, 2  $\mu$ mol, 0.3 mol %) were combined in a 1 dram vial. A magnetic stir bar was added to the vial, which was placed inside a vacuum chamber and held under vacuum (60-100 mtorr) accompanied by stirring for 48 hours at room temperature. The thick burgundy-colored oil steadily produced gas during the course of reaction. The reaction mixture was then dissolved in 0.5 mL  $CH_2Cl_2$  and purified directly on a silica gel column (2x10 cm), eluting with 4:1, 2:1, and 1:1 hexane/ethyl acetate (100 mL aliquots). A clear, viscous oil was obtained (110 mg, 73% yield, 2.6:1 *trans/cis* as determined by the relative intensities of peaks at 129.3 and 129.2 ppm in the  $^{13}C$  NMR spectrum).  $^1H$  NMR (500 MHz,  $CDCl_3$ , ppm):  $\delta$  5.59 (2H, m), 5.34 (2H, d,  $J = 8.3$  Hz), 4.33 (2H, m), 3.93-3.81 (4H, broad m), 3.74 (2H, m), 3.64 (6H, s), 3.53 (2H, m), 1.36 (18H, s).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ , ppm):  $\delta$  171.1, 155.4, 129.3, 129.2, 80.0, 71.3, 70.5, 70.4, 67.3, 54.7, 52.1, 28.5.  $R_f = 0.21$  (2:1 hexane/ethyl acetate);  $[\alpha]_D^{25} = +16.11$  ( $CH_2Cl_2$ ,  $c = 0.36$ ); HRMS (FAB) calcd for  $C_{22}H_{38}N_2O_{10}$   $[M-H]^+$  491.2605, found 491.2605.

**Compound 40.** *N*-Boc-*L*-homoserine(*O*-Allyl) methyl ester (**39**)<sup>16</sup> (223 mg, 0.82 mmol) and **1** (2.0 mg, 2.0  $\mu$ mol, 0.3 mol %) were combined in a 1 dram vial. A magnetic stir bar was added to the vial, which was placed inside a vacuum chamber and held under vacuum (60-100 mtorr) accompanied by stirring for 48 hours at room temperature. The thick burgundy-colored oil steadily produced gas during the course of reaction. The reaction mixture was then dissolved in 0.5 mL  $CH_2Cl_2$  and purified directly on a silica gel column (2x10 cm), eluting with 4:1, 2:1, and 1:1 hexane/ethyl acetate (100 mL aliquots). A clear, viscous oil that slowly crystallized over

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(16) For the allylation procedure, see: Sugano, H.; Miyoshi, M. *J. Org. Chem.* **1976**, *41*, 2352-2353. For the methyl ester formation, see: Hirai, Y.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1989**, *111*, 3062-3063.

time was obtained (159 mg, 75% yield, 2.7:1 *trans/cis* as determined by the relative intensities of peaks at 129.4 and 129.3 ppm in the  $^{13}\text{C}$  NMR spectrum).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  5.65 (2H, m), 5.39 (2H, broad s), 4.29 (2H, m), 3.84 (4H, app s), 3.60 (6H, s), 3.44-3.38 (4H, broad m), 1.98-1.90 (4H, broad m), 1.34 (18H, broad s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  172.9, 155.4, 129.4, 129.3, 79.8, 71.0, 66.8, 66.6, 52.1, 32.3, 28.4.  $R_f = 0.12$  (2:1 hexane/ethyl acetate);  $[\alpha]_D = +2.14$  ( $\text{CH}_2\text{Cl}_2$ ,  $c = 0.35$ ); HRMS (FAB) calcd for  $\text{C}_{24}\text{H}_{42}\text{N}_2\text{O}_{10}$   $[\text{M}-\text{H}]^+$  519.2918, found 519.2921.

**Compound 42.** *N*-Boc-L-tyrosine(*O*-Allyl) methyl ester (**41**)<sup>16</sup> (115 mg, 0.34 mmol) was added to a stirring solution of **1** (14 mg, 0.017 mmol, 5 mol %) in  $\text{CH}_2\text{Cl}_2$  (3.3 mL). The flask was fitted with a condenser and refluxed under nitrogen for 14 hours. The reaction mixture was then reduced in volume to 0.5 mL and purified directly on a silica gel column (2x12 cm), eluting with 8:1, 4:1, 2:1, and 1:1 hexane/ethyl acetate (100 mL aliquots). A clear, viscous oil was obtained which slowly crystallized over time (78.2 mg, 71% yield, 3:1 *trans/cis* as determined by integration of peaks at 6.04 and 5.89 ppm in the  $^1\text{H}$  NMR spectrum).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.01 (4H, d,  $J = 8.2$  Hz), 6.81 (4H, d,  $J = 8.5$  Hz), 6.04 (2H, app br s), 4.99 (2H, d,  $J = 7.7$  Hz), 4.51 (6H, app br s), 3.68 (6H, s), 2.99 (4H, m), 1.39 (9H, br s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  172.5, 157.8, 157.6, 155.2, 130.5, 130.4, 128.7, 128.51, 128.47, 114.9, 101.8, 80.0, 67.8, 64.3, 62.2, 54.7, 52.3, 37.6, 28.4.  $R_f = 0.31$  (2:1 hexane/ethyl acetate);  $[\alpha]_D = +49.16$  ( $\text{CH}_2\text{Cl}_2$ ,  $c = 0.52$ ); HRMS (FAB) calcd for  $\text{C}_{34}\text{H}_{46}\text{N}_2\text{O}_{10}$   $[\text{M}+\text{H}]^+$  643.3231, found 643.3220.

**Compound 44.** 2,3,4,6-tetra-*O*-benzyl-1- $\alpha$ -*C*-allylglucoside (**43**)<sup>17</sup> (133 mg, 0.24 mmol) was added to a stirring solution of **1** (9.7 mg, 0.012 mmol, 5 mol %) in  $\text{CH}_2\text{Cl}_2$  (2.4 mL). The flask was fitted with a condenser and refluxed under nitrogen for 16 hours. The reaction mixture was

(17) For the synthesis of *C*-allylglucoside **43**, see: Lewis, M. D.; Cha, J. K.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4976-4978.



then reduced in volume to 0.5 mL and purified directly on a silica gel column (2x15 cm), eluting with 9:1, 5:1, 4:1, and 2:1 hexane/ethyl acetate (100 mL aliquots). A pale yellow, crystalline solid was obtained (121 mg, 93% yield, 2.5:1 *trans/cis* as determined by the relative intensities of peaks at 82.6 and 82.5 ppm in the  $^{13}\text{C}$  NMR spectrum).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.60-7.21 (40 H, br m), 5.61 (2H, m), 5.02 (2H, m), 4.89 (4H, m), 4.73 (6H, m), 4.54 (4H, m), 4.17 (2H, m), 3.84-3.70 (12H, br m), 2.52 (4H, m).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  138.9, 138.4, 138.3, 138.2, 128.55, 128.51, 128.1, 128.03, 127.99, 127.91, 127.87, 127.82, 127.76, 127.7, 127.5, 82.6, 82.5, 80.2, 80.1, 78.2, 75.6, 75.5, 75.2, 74.3, 74.2, 73.6, 73.2, 73.1, 71.5, 71.3, 69.0, 29.8, 28.8, 23.8.  $R_f$  = 0.59 (3:1 hexane/ethyl acetate);  $[\alpha]_D = +58.85$  ( $\text{CH}_2\text{Cl}_2$ ,  $c = 0.53$ ); LRMS (FAB) calcd for  $\text{C}_{72}\text{H}_{76}\text{O}_{10}$   $[\text{M}-\text{H}]^+$  1101.5, found 1102.0.

**Compound 46.** Pentapeptide **45** (100 mg, 0.10 mmol) was added to a stirring solution of **1** (1.2 mg, 1.0  $\mu\text{mol}$ , 1 mol %) in  $\text{CH}_2\text{Cl}_2$  (0.5 mL). The flask was fitted with a condenser and refluxed under nitrogen for 20 hours. The reaction mixture was then reduced in volume to 0.25 mL and purified directly on a silica gel column (2x10 cm), eluting with 3:1, 5:1 and 9:1 ethyl acetate/hexane (100 mL aliquots), and finally with 100% ethyl acetate (200 mL). An off-white crystalline solid was obtained (61 mg, 62% yield, 2.8:1 *trans/cis* as determined by the relative intensities of peaks at 129.1 and 129.0 ppm in the  $^{13}\text{C}$  NMR spectrum).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.47 (2H, d,  $J = 6.6$  Hz), 7.27 (2H, d,  $J = 9.1$  Hz), 7.11 (2H, d,  $J = 6.3$  Hz), 6.83 (2H, s), 5.66 (2H, m), 5.37 (2H, m), 4.66 (2H, m), 4.54 (2H, m), 4.24 (2H, m), 4.05-3.93 (6H, br m), 3.81 (2H, m), 3.70 (8H, s), 2.42 (2H, m), 1.70-1.59 (12H, br m), 1.46 (30H, m), 0.99-0.89 (36H, br m).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  175.7, 175.6, 173.6, 173.5, 172.9, 171.7, 170.4, 170.3, 156.6, 129.1, 129.0, 80.8, 71.1, 69.7, 66.8, 60.4, 57.0, 55.0, 54.1, 52.3, 51.1, 40.7, 40.3, 29.8, 29.3, 28.4, 27.1, 24.8, 24.6, 24.0, 23.0, 22.97, 22.0, 21.8, 19.4, 17.3.  $R_f$  = 0.08 (3:1 ethyl acetate/hexane);  $[\alpha]_D = -13.67$  ( $\text{CH}_2\text{Cl}_2$ ,  $c = 0.34$ ); LRMS (FAB) calcd for  $\text{C}_{64}\text{H}_{114}\text{N}_{10}\text{O}_{18}$   $[(\text{M})-\text{Boc}]^+$  1211.8, found 1211.9.

**Compound 47.** 9-Decen-1-yl benzoate (**3**) (75  $\mu$ L, 0.27 mmol) was added *via* syringe to a stirring solution of allyl benzene homodimer **28** (114 mg, 0.55 mmol) and **1** (11.3 mg, 0.014 mmol, 5 mol %) in  $\text{CH}_2\text{Cl}_2$  (2.7 mL). The flask was fitted with a condenser and refluxed under nitrogen for 20 hours. The reaction mixture was then reduced in volume to 0.5 mL and purified directly on a silica gel column (2x10 cm), eluting with 99:1, 49:1, and 20:1 hexane/ethyl acetate (100 mL aliquots). A clear, colorless oil was obtained (64.7 mg, 68% yield, 3.7:1 *trans/cis* as determined by integration of peaks at 3.33 and 3.40 ppm in the  $^1\text{H}$  NMR spectrum).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  8.06 (2H, d,  $J = 7.1$  Hz), 7.55 (1H, t,  $J = 7.4$  Hz), 7.44 (2H, t,  $J = 7.8$  Hz), 7.28 (3H, m), 7.19 (2H, apparent d,  $J = 2.6$  Hz), 5.59-5.49 (2H, br m), 4.32 (2H, t,  $J = 6.7$  Hz), 3.33 (2H, d,  $J = 6.1$  Hz), 2.02 (2H, m), 1.76 (2H, m), 1.43-1.26 (10H, br m).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  166.8, 141.3, 132.9, 132.2, 131.1, 130.7, 129.7, 128.9, 128.63, 128.55, 128.5, 128.2, 126.1, 126.02, 125.98, 112.3, 65.3, 39.2, 33.7, 32.7, 29.9, 29.8, 29.6, 29.5, 29.4, 29.3, 28.9, 27.4, 26.2.  $R_f = 0.57$  (9:1 hexane/ethyl acetate); HRMS (EI) calcd for  $\text{C}_{24}\text{H}_{30}\text{O}_2$   $[\text{M}]^+$  350.2246, found 350.2246.

**Compound 48.** Allyl benzene (**27**) (55  $\mu$ L, 0.50 mmol) was added *via* syringe to a stirring solution of *cis*-1,4-bis-(acetyloxy)but-2-ene (160  $\mu$ L, 1.0 mmol) and **1** (11 mg, 0.013 mmol, 2.7 mol %) in  $\text{CH}_2\text{Cl}_2$  (2.5 mL). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 mL and purified directly on a silica gel column (2x10 cm), eluting with 9:1 hexane/ethyl acetate (300 mL). A pale oil was obtained (76 mg, 80% yield, 3:1 *trans/cis* as determined by integration of peaks at 4.47 and 4.55 ppm in the  $^1\text{H}$  NMR spectrum).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.34-7.17 (5H, m), 5.92 (1H, m), 5.65 (1H, m), 4.54 (2H, m), 3.41 (2H, d,  $J = 3.3$  Hz), 2.06 (3H, br s).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  171.4, 135.1, 134.0, 129.2, 129.1, 126.8, 125.8, 65.5, 60.8, 39.2, 21.6.  $R_f = 0.53$  (9:1 hexane/ethyl acetate); HRMS (EI) calcd for  $\text{C}_{12}\text{H}_{14}\text{O}_2$   $[\text{M}-\text{H}]^+$  189.0916, found 189.0916.

**Compound 49.** 9-Decen-1-yl *N*-Boc-glycinate (**23**) (61.7 mg, 0.20 mmol) was added to a stirring solution of bis-acetate **20** (147 mg, 0.40 mmol) and **1** (7.9 mg, 0.010 mmol, 5 mol %) in CH<sub>2</sub>Cl<sub>2</sub> (1.9 mL). The flask was fitted with a condenser and refluxed under nitrogen for 16 hours. The reaction mixture was then reduced in volume to 0.5 mL and purified directly on a silica gel column (2x10 cm), eluting with 9:1, 4:1 and 2:1 hexane/ethyl acetate (100 mL aliquots). A clear, viscous oil was obtained (68.2 mg, 72% yield, 3.5:1 *trans/cis* as determined by the relative intensities of peaks at 130.46 and 129.99 in the <sup>13</sup>C NMR spectrum). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 5.33 (2H, m), 5.04 (1H, br s), 4.10, (2H, t, *J* = 6.7 Hz), 4.01 (2H, t, *J* = 6.8 Hz), 3.86 (2H, d, *J* = 5.2 Hz), 2.02 (3H, masked s), 2.04-1.93 (4H, br m), 1.56 (4H, m), 1.45 (9H, masked s), 1.35-1.25 (20H, br m). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm): δ 171.3, 170.6, 155.9, 130.48, 130.46, 130.01, 129.99, 80.0, 65.6, 64.8, 42.6, 32.7, 29.9, 29.73, 29.66, 29.55, 29.53, 29.5, 29.48, 29.4, 29.34, 29.32, 29.2, 28.8, 28.7, 28.5, 27.3, 26.2, 26.0, 25.96, 21.1. *R*<sub>f</sub> = 0.23 (9:1 hexane/ethyl acetate); HRMS (FAB) calcd for C<sub>27</sub>H<sub>49</sub>NO<sub>6</sub> [(M-H)-Boc]<sup>+</sup> 384.3114, found 384.3114.

**Compound 50.** Allyl phenyl sulfone (**36**) (155 μL, 1.0 mmol) and 9-decen-1-yl benzoate (**3**) (145 μL, 0.5 mmol) were simultaneously added *via* syringe to a stirring solution of **1** (12 mg, 0.014 mmol, 2.7 mol %) in CH<sub>2</sub>Cl<sub>2</sub> (2.5 mL). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 mL and purified directly on a silica gel column (2x10 cm), eluting with 2:1 hexane/ethyl acetate (200 mL). A clear oil was obtained (196 mg, 90% yield, 8:1 *trans/cis* as determined by integration of peaks at 5.60 and 5.46 in the <sup>1</sup>H NMR spectrum). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): 8.03 (2H, d, *J* = 7.3 Hz), 7.83 (2H, d, *J* = 7.3 Hz), 7.63-7.41 (6H, m), 5.50-5.34 (2H, m), 4.30 (2H, t, *J* = 6.6 Hz), 3.72 (2H, t, *J* = 6.9 Hz), 1.95 (2H, m), 1.72 (2H, m), 1.43-1.08 (10H, broad m). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm): 167.2, 142.3, 134.1, 133.4, 130.0, 129.6, 129.5, 129.1, 128.9, 116.4, 115.7, 65.6, 60.7, 55.8, 33.0, 29.8, 29.7, 29.6, 29.4, 29.3, 29.2, 27.8, 26.6. *R*<sub>f</sub> = 0.42 (2:1

hexane/ethyl acetate); HRMS (EI) calcd for  $C_{22}H_{32}O_2$   $[M+H]^+$  415.1943, found 415.1953. Elemental analysis calcd: C: 69.54, H: 7.29; found: C: 69.72, H: 6.95.

**Compound 51.** *N*-Boc-serine(*O*-Allyl) methyl ester (**37**)<sup>16</sup> (100 mg, 0.39 mmol) was added to a stirring solution of bis-acetate **20** (284 mg, 0.77 mmol) and **1** (16 mg, 0.019 mmol, 5 mol %) in  $CH_2Cl_2$  (3.9 mL). The flask was fitted with a condenser and refluxed under nitrogen for 16 hours. The reaction mixture was then reduced in volume to 0.5 mL and purified directly on a silica gel column (2x10 cm), eluting with 4:1, 2:1 and 1:1 hexane/ethyl acetate (100 mL aliquots). A pale yellow, viscous oil was obtained (142 mg, 86% yield, 6:1 *trans/cis* as determined by the relative intensities of peaks at 135.0 and 134.1 ppm in the  $^{13}C$  NMR spectrum).  $^1H$  NMR (500 MHz,  $CDCl_3$ , ppm):  $\delta$  5.58-5.52 (1H, broad m), 5.39-5.32 (1H, broad m), 5.34 (1H, d), 4.31 (1H, m), 3.95 (2H, t,  $J = 6.7$  Hz), 3.82 (2H, m), 3.70 (1H, m), 3.65 (3H, s), 3.52 (1H, m), 1.94 (3H, s), 1.97-1.92 (2H, broad m), 1.53-1.48 (2H, broad m), 1.35 (9H, broad s), 1.38-1.20 (10H, broad m).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ , ppm):  $\delta$  171.2, 170.8, 155.5, 135.0, 134.1, 125.9, 125.6, 79.8, 72.1, 69.9, 69.7, 67.0, 64.5, 62.3, 54.4, 52.2, 32.8, 32.2, 29.5, 29.3, 29.2, 29.1, 28.7, 28.4, 27.6, 26.0, 20.8.  $R_f = 0.12$  (9:1 hexane/ethyl acetate);  $[\alpha]_D = +7.59$  ( $CH_2Cl_2$ ,  $c = 0.34$ ); HRMS (FAB) calcd for  $C_{22}H_{39}NO_7$   $[M-H]^+$  430.2805, found 430.2810.

**Compound 52.** 2,3,4,6-tetra-*O*-benzyl-1- $\alpha$ -*C*-allylglucoside (**43**)<sup>17</sup> (75 mg, 0.13 mmol) was added to a stirring solution of bis-acetate **20** (96 mg, 0.26 mmol) and **1** (5.4 mg, 6.6  $\mu$ mol, 5 mol %) in  $CH_2Cl_2$  (1.5 mL). The flask was fitted with a condenser and refluxed under nitrogen for 6 hours. The reaction mixture was then reduced in volume to 0.25 mL and purified directly on a silica gel column (2x10 cm), eluting with 9:1, 4:1 and 2:1 hexane/ethyl acetate (100 mL aliquots). A clear, viscous oil was obtained (72 mg, 73% yield, 2.8:1 *trans/cis* as determined by analysis of methyl intensities at 2.04 and 2.03 ppm in the  $^1H$  NMR spectrum).  $^1H$  NMR (500 MHz,  $CDCl_3$ , ppm):  $\delta$  7.52-7.22 (18H, br m), 7.14 (2H, m), 5.56-5.37 (2H, br m), 4.94 (1H, m), 4.81 (2H, m), 4.70-4.61 (3H, br m), 4.49-4.46 (2H, br m), 4.11-4.03 (3H, br m), 3.82-3.69 (3H,

br m), 3.67-3.60 (3H, br m), 2.45-2.41 (2H, br m), 2.04 (3H, masked s), 1.98 (2H, apparent masked q,  $J = 6.4$  Hz), 1.62 (2H, quint,  $J = 6.7$  Hz), 1.32-1.28 (10H, br m).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  171.4, 139.1, 138.6, 138.5, 138.4, 133.2, 132.1, 128.6, 128.5, 128.2, 128.1, 128.0, 127.93, 127.90, 127.8, 126.0, 125.5, 82.7, 82.67, 80.5, 78.5, 75.7, 75.6, 75.3, 74.6, 74.3, 73.7, 73.4, 73.2, 71.6, 71.3, 69.3, 64.8, 32.9, 29.9, 29.7, 29.6, 29.5, 29.3, 28.9, 27.9, 26.2, 23.5, 21.2.  $R_f = 0.14$  (9:1 hexane/ethyl acetate); HRMS (FAB) calcd for  $\text{C}_{47}\text{H}_{58}\text{O}_7$   $[\text{M}+\text{H}]^+$  735.4261, found 735.4242.

**Compound 53.** 2,3,4,6-tetra-*O*-benzyl-1- $\alpha$ -*C*-allylglucoside (**43**) (58 mg, 0.01 mmol) was added to a stirring solution of *N*-Boc-L-serine(*O*-Allyl)-OMe dimer **38** (100 mg, 0.02 mmol) and **1** (4.2 mg, 5  $\mu\text{mol}$ , 5 mol %) in  $\text{CH}_2\text{Cl}_2$  (1.0 mL). The flask was fitted with a condenser and refluxed under nitrogen for 16 hours. The reaction mixture was then reduced in volume to 0.25 mL and purified directly on a silica gel column (2x10 cm), eluting with 9:1, 4:1 and 2:1 hexane/ethyl acetate (100 mL aliquots). A clear, viscous oil was obtained (30.1 mg, 37% yield, 5:1 *trans/cis* as determined by the relative intensities of peaks at 28.8 and 28.6 ppm in the  $^{13}\text{C}$  NMR spectrum).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.32-7.25 (18H, broad m), 7.11 (2H, m), 5.64 (1H, m), 5.55 (1H, m), 5.34 (1H, d,  $J = 8.4$  Hz), 4.92 (1H, d,  $J = 10.9$  Hz), 4.79 (2H, d,  $J = 10.7$  Hz), 4.69 (1H, d,  $J = 11.6$  Hz), 4.60 (2H, d,  $J = 11.1$  Hz), 4.46 (1H, d,  $J = 4.0$  Hz), 4.44 (1H, d,  $J = 2.2$  Hz), 4.39 (1H, m), 4.07 (1H, m), 3.88 (2H, app d,  $J = 5.8$  Hz), 3.73 (3H, s), 3.79-3.69 (4H, broad m), 3.68-3.56 (4H, broad m), 2.46 (2H, m), 1.44 (9H, s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  171.4, 159.8, 139.2, 138.8, 138.6, 130.9, 128.6, 128.53, 128.47, 128.1, 128.02, 127.97, 127.81, 127.76, 127.7, 82.6, 80.4, 78.7, 75.4, 75.1, 74.4, 74.1, 73.8, 73.6, 73.4, 72.2, 71.9, 70.0, 69.7, 67.5, 54.6, 52.4, 28.8, 28.6, 27.2.  $R_f = 0.50$  (2:1 hexane/ethyl acetate);  $[\alpha]_D = +39.95$  ( $\text{CH}_2\text{Cl}_2$ ,  $c = 0.33$ ); HRMS (FAB) calcd for  $\text{C}_{47}\text{H}_{57}\text{NO}_{10}$   $[\text{M}-\text{H}]^+$  796.4061, found 796.4059.

**Compound 54.** 2,3,4,6-tetra-O-benzyl- $\alpha$ -C-allyl glucoside (**43**)<sup>17</sup> (100 mg, 0.18 mmol) was added to a stirring solution of *cis*-1,4-bis-(tert-butyltrimethylsilyloxy)but-2-ene (130  $\mu$ L, 0.36 mmol) and **1** (7.2 mg, 0.0087 mmol, 5 mol %) in CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 1.0 mL and applied to a silica gel column (2x10 cm), eluting with CH<sub>2</sub>Cl<sub>2</sub>, followed by 4:1 CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate (100 mL aliquots). Fractions containing the desired product were pooled and evaporated to yield a clear, colorless, viscous oil (89 mg, 70% yield, 9:1 *trans/cis* as determined by integration of peaks at 4.07 and 4.18 ppm in the <sup>1</sup>H NMR spectrum). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.03 (2H, app d,  $J = 7.0$  Hz), 7.53 (1H, tt,  $J = 7.4, 1.4$  Hz), 7.41 (2H, t,  $J = 8.0$  Hz), 5.70-5.50 (2H, m), 4.30 (2H, t,  $J = 6.7$  Hz), 4.07 (2H, dd,  $J = 0.7, 5.5$  Hz), 2.02 (2H, q,  $J = 6.8$  Hz), 1.78 (1H, s), 1.77 (2H, quint,  $J = 7.9$  Hz), 1.45-1.28 (10H, m). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  166.6, 133.2, 132.9, 132.7, 130.5, 129.5, 128.9, 128.5, 128.2, 65.0, 63.7, 58.5, 32.1, 29.5, 29.3, 29.1, 29.0, 28.99, 28.7, 27.3, 25.9.  $R_f = 0.64$  (3:1 hexane/ethyl acetate); HRMS (EI) calcd for C<sub>18</sub>H<sub>26</sub>O<sub>3</sub> [M-H]<sup>+</sup> 290.1882, found 289.1804.

**Compound 55.** Pentapeptide **45** (50 mg, 0.075 mmol) was added to a stirring solution of 9-decen-1-yl *N*-Boc-glycinate dimer **24** (89 mg, 0.149 mmol) and **1** (3.1 mg, 0.037 mmol, 5 mol %) in CH<sub>2</sub>Cl<sub>2</sub> (0.75 mL). The flask was fitted with a condenser and refluxed under nitrogen for 16 hours. The reaction mixture was then reduced in volume to 0.25 mL and purified directly on a silica gel column (2x8 cm), eluting with 3:1, 2:1, 1:1, and 1:2 hexane/ethyl acetate (100 mL aliquots), and finally flushing with 100% ethyl acetate (200 mL). A pale yellow oil was obtained (46.9 mg, 66% yield, 5.5:1 *trans/cis* as determined by the relative intensities of peaks at 134.7 and 133.4 in the <sup>13</sup>C NMR spectrum). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.45 (1H, d,  $J = 5.7$  Hz), 7.23 (1H, d,  $J = 8.6$  Hz), 7.07 (1H, d,  $J = 5.9$  Hz), 6.85 (1H, s), 5.58 (1H, m), 5.44 (1H, m), 5.32 (1H, br s), 5.05 (1H, br s), 4.64 (1H, m), 4.53 (1H, m), 4.18 (1H, m), 4.09 (2H, m), 4.03 (1H, m), 3.88 (4H, m), 3.77 (1H, m), 3.69 (1H, m), 3.67 (3H, masked s), 2.64 (1H, m), 1.94 (2H, m), 1.63-1.55 (6H, br m), 1.47-1.42 (26 H, br m), 1.35-1.21 (10H, br m), 0.98-0.86 (18H, br m). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  174.8, 173.3, 172.9, 171.5, 170.5, 170.2, 156.4, 134.7,

133.4, 126.4, 80.98, 71.9, 69.5, 69.3, 67.0, 65.6, 60.1, 57.6, 54.6, 53.4, 52.1, 51.3, 42.9, 41.3, 40.8, 32.4, 29.8, 29.7, 29.5, 29.3, 29.29, 28.8, 28.6, 28.5, 27.8, 26.6, 26.0, 25.2, 25.0, 24.8, 23.1.  $R_f = 0.42$  (3:1 ethyl acetate/hexane);  $[\alpha]_D = -13.72$  ( $\text{CH}_2\text{Cl}_2$ ,  $c = 0.38$ ); HRMS (FAB) calcd for  $\text{C}_{48}\text{H}_{86}\text{N}_6\text{O}_{13}$  [(M-H)-Boc]<sup>+</sup> 855.5807, found 855.5800.

**Compound 57.** 3-Buten-2-yl benzoate (**56**)<sup>1</sup> (80  $\mu\text{l}$ , 0.49 mmol) was added *via* syringe to a stirring solution of *cis*-1,4-bis-(acetyloxy)but-2-ene (155  $\mu\text{l}$ , 0.98 mmol) and **1** (20 mg, 0.025 mmol, 5 mol %) in  $\text{CH}_2\text{Cl}_2$  (4.9 mL). The flask was fitted with a condenser and refluxed under nitrogen for 15 hours. The reaction mixture was then reduced in volume to 0.5 mL and purified directly on a silica gel column (2x12 cm), eluting with 9:1, 7:1, 4:1, and 3:1 hexane/ethyl acetate (100 mL aliquots). A clear, colorless oil was obtained (36.5 mg, 30% yield, 16:1 *trans/cis* as determined by the relative intensities of peaks at 70.6 and 67.7 ppm in the  $^{13}\text{C}$  NMR spectrum).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  8.04 (2H, d,  $J = 7.9$  Hz), 7.54 (1H, t,  $J = 7.3$  Hz), 7.43 (2H, t,  $J = 7.8$  Hz), 5.87 (2H, m), 5.63 (1H, m), 4.57 (2H, d,  $J = 3.6$  Hz), 2.06 (3H, s), 1.44 (3H, d,  $J = 6.5$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  170.9, 165.9, 133.8, 133.1, 130.6, 129.8, 128.5, 126.3, 125.9, 70.6, 67.7, 64.2, 60.9, 29.8, 21.1, 21.0, 20.4.  $R_f = 0.29$  (9:1 hexane/ethyl acetate); HRMS (EI) calcd for  $\text{C}_{14}\text{H}_{16}\text{O}_4$  [M]<sup>+</sup> 248.1049, found 248.1041.

**Compound 59.** 3-Buten-2-yl benzoate (**56**) (80  $\mu\text{l}$ , 0.49 mmol) was added *via* syringe to a stirring solution of *cis*-1,4-bis-(tert-butyldimethylsilyloxy)but-2-ene (361  $\mu\text{l}$ , 0.98 mmol) and **1** (20 mg, 0.025 mmol, 5 mol %) in  $\text{CH}_2\text{Cl}_2$  (4.9 mL). The flask was fitted with a condenser and refluxed under nitrogen for 24 hours. The crude reaction mixture was then reduced in volume to 0.5 mL and applied directly to a silica gel column (2x12 cm), eluting with 9:1, 7:1, 4:1, and 3:1 hexane/ethyl acetate (100 mL aliquots). A pale brown, viscous oil was obtained, which was directly treated with TBAF (0.98 mL of a 1M solution in THF) to effect cleavage of the TBDMS group. The solution was stirred for one hour at 25° C until TLC analysis indicated that the deprotection was complete. The reaction mixture was reduced in volume to 0.3 mL and purified directly on a silica gel column (2x10 cm), eluting with 9:1, 3:1, 2:1, and 1:1 hexane/ethyl acetate.

A clear, viscous oil (**59**) was isolated (55 mg, 54% yield over 2 steps, 47:1 *trans/cis* as determined by the relative intensities of the peaks at 20.5 and 20.9 ppm in the  $^{13}\text{C}$  NMR spectrum).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  8.02 (2H, d,  $J = 8.4$  Hz), 7.52 (1H, t,  $J = 7.5$  Hz), 7.40 (2H, t,  $J = 7.8$  Hz), 5.92 (1H, m), 5.81 (1H, m), 5.59 (1H, quint,  $J = 6.1$  Hz), 4.14 (2H, d,  $J = 4.9$  Hz), 2.31 (1H, br s), 1.43 (3H, d,  $J = 6.5$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  166.1, 133.1, 132.7, 132.3, 131.9, 131.2, 130.7, 130.67, 130.1, 129.7, 128.5, 128.2, 127.8, 127.7, 127.5, 127.3, 124.4, 121.7, 115.0, 71.1, 62.8, 55.6, 29.8, 20.9, 20.5.  $R_f = 0.24$  (3:1 hexane/ethyl acetate); HRMS (EI) calcd for  $\text{C}_{12}\text{H}_{14}\text{O}_3$   $[\text{M}]^+$  206.0943, found 206.0939.

**Compound 61.** 3-Buten-2-*O*-tert-butyldiphenylsilyl ether (**60**)<sup>18</sup> (80 mg, 0.258 mmol) was added *via* syringe to a stirring solution of *cis*-1,4-bis-(acetyloxy)but-2-ene (81  $\mu\text{L}$ , 0.516 mmol) and **1** (10.6 mg, 0.013 mmol, 5 mol %) in  $\text{CH}_2\text{Cl}_2$  (2.58 mL). The flask was fitted with a condenser and refluxed under nitrogen for 20 hours. The reaction mixture was then reduced in volume to 0.5 mL and purified directly on a silica gel column (2x12 cm), eluting with 9:1, 4:1, and 2:1 hexane/ethyl acetate (100 mL aliquots). A clear, viscous oil was obtained (23 mg, 23% yield, 7.5:1 *trans/cis* as determined by the relative intensities of peaks at 69.6 and 66.1 ppm in the  $^{13}\text{C}$  NMR spectrum).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.67-7.62 (4H, br m), 7.41-7.33 (6H, br m), 5.73 (1H, m), 5.56 (1H, m), 4.45 (2H, d,  $J = 6.0$  Hz), 4.43 (1H, m), 2.04 (3H, s), 1.14 (3H, d,  $J = 6.3$  Hz), 1.05 (9H, s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  170.9, 139.0, 138.9, 136.1, 136.06, 136.0, 134.6, 134.2, 129.8, 129.76, 129.7, 127.8, 127.7, 127.66, 122.8, 122.0, 112.9, 69.9, 66.1, 64.7, 60.5, 29.9, 27.2, 27.1, 24.6, 24.2, 21.2, 19.4.  $R_f = 0.49$  (9:1 hexane/ethyl acetate); HRMS (EI) calcd for  $\text{C}_{23}\text{H}_{30}\text{O}_3\text{Si}$   $[\text{M}-\text{H}]^+$  381.1886, found 381.1883.

**Compound 69.** 9-Decen-1-yl benzoate (**3**) (140  $\mu\text{L}$ , 0.50 mmol) and acrolein diethyl acetal (**67**) (153  $\mu\text{L}$ , 1.0 mmol) were added *via* syringe to a stirring solution of **1** (10.4 mg, 0.013 mmol, 2.5 mol %) in  $\text{CH}_2\text{Cl}_2$  (2.5 mL). The flask was fitted with a condenser and refluxed under nitrogen

(18) Prepared according to a literature procedure: Hanessian, S.; Lavalley, P. *Can. J. Chem.* **1975**, *53*, 2975-2977.



for 12 hours. The reaction mixture was allowed to come to room temperature and excess 98% formic acid (0.5 mL, 13 mmol) was added. The orange brown solution was allowed to stir for 1.5 hrs until TLC analysis indicated complete cleavage of the acetal group.<sup>19</sup> The reaction mixture was then reduced in volume to 0.75 mL and purified directly on a silica gel column (2x15 cm), eluting first with CH<sub>2</sub>Cl<sub>2</sub> (90 mL), and then 9:1 and 4:1 CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate (100 mL aliquots). A clear yellow liquid **69** was obtained (120.5 mg, 82% yield). Aldehyde **69** (110 mg, 0.38 mmol) was dissolved in 2:1 EtOH/H<sub>2</sub>O (7.5 mL) at room temperature. CeCl<sub>3</sub>·7H<sub>2</sub>O (142 mg, 0.38 mmol) was added and the solution was stirred for 10 minutes to effect dissolution. The solution was then cooled to 0 °C and NaBH<sub>4</sub> (25 mg, 0.66 mmol) was added slowly in portions. The reaction mixture was allowed to stir at 0 °C for 30 minutes after which TLC analysis showed complete reduction of aldehyde **69** to allylic alcohol **7**. The reaction was quenched by dilution with Et<sub>2</sub>O (10 mL), followed by slow addition of a saturated aqueous NaHCO<sub>3</sub> solution (10 mL). The biphasic mixture was allowed to stir for two hours, after which the organic layer was removed, washed with brine, dried over MgSO<sub>4</sub>, and concentrated to yield a light yellow oil. The oil was diluted to 0.5 mL in CH<sub>2</sub>Cl<sub>2</sub> and purified directly on a silica gel column (2x15 cm), eluting with 2:1 CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate (300 mL). A clear, colorless oil was obtained that exhibited spectral properties identical to alcohol **7** (107 mg, 80% yield over 2 steps, 26:1 *trans/cis* as determined by integration of peaks at 4.07 and 4.18 ppm in the <sup>1</sup>H NMR spectrum).

**Compound 73.** 9-Decen-1-yl benzoate (**3**) (140 mL, 0.50 mmol) and 2-vinyl-1,3-dioxolane (**72**) (100 mL, 1.0 mmol) were added *via* syringe to a stirring solution of **1** (10.4 mg, 0.013 mmol, 2.5 mol %) in CH<sub>2</sub>Cl<sub>2</sub> (2.5 mL). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.75 mL and purified directly on a silica gel column (2x15 cm), eluting first with CH<sub>2</sub>Cl<sub>2</sub> (90 mL), and then 9:1 and 4:1 CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate (100 mL aliquots). A clear yellow liquid was obtained (156.4 mg, 93% yield, 8.6:1 *trans/cis* as determined by integration of peaks at 1.91 and 2.12 ppm in the <sup>1</sup>H NMR

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(19) Barbot, F.; Miginiac, P. *Synthesis* **1983**, 651-654.

spectrum).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  8.19 (2H, m), 7.16-7.06 (3H, br m), 5.87 (1H, m), 5.71 (1H, m), 5.27 (1H, d,  $J = 6.1$  Hz), 4.21 (2H, t,  $J = 6.1$  Hz), 3.60 (2H, m), 3.43 (2H, m), 1.91 (2H, m), 1.51 (2H, quint,  $J = 6.8$  Hz), 1.40-1.02 (10H, br m).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  166.3, 136.5, 132.7, 131.3, 129.8, 128.5, 128.2, 128.0, 127.8, 127.4, 104.5, 99.7, 65.0, 64.8, 32.2, 29.7, 29.6, 29.4, 29.3, 29.2, 29.0, 28.9, 28.1, 26.2.  $R_f = 0.35$  (9:1 hexane/ethyl acetate); HRMS (EI) calcd for  $\text{C}_{20}\text{H}_{28}\text{O}_4$   $[\text{M}]^+$  332.1988, found 332.1982.

**Compound 74.** 2-Vinyl-1,3-dioxolane (**72**) (1.0 g, 9.99 mmol) was added *via* syringe to a stirring solution of **1** (205 mg, 0.25 mmol, 2.5 mol %) in  $\text{CH}_2\text{Cl}_2$  (49 mL). The flask was fitted with a condenser and refluxed under nitrogen for 16 hours. The reaction mixture was then reduced in volume to 0.5 mL and purified directly on a silica gel column (4x20 cm), eluting with 4:1, 2:1 and 1:1 hexane/ethyl acetate (250 mL aliquots). An off-white crystalline solid was obtained (451 mg, 52% yield, 9.2:1 *trans/cis* as determined by the relative intensities of peaks at 131.5 and 124.1 ppm in the  $^{13}\text{C}$  NMR spectrum).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  5.89 (2H, m), 5.32 (2H, m), 4.01-3.85 (8H, br m).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  131.5, 124.1, 102.4, 72.8, 65.2, 65.1, 47.1.  $R_f = 0.08$  (9:1 hexane/ethyl acetate); HRMS (EI) calcd for  $\text{C}_8\text{H}_{14}\text{O}_4$   $[\text{M}-\text{H}]^+$  171.0657, found 171.0659.

**Compound 76.** 3-Butenal diethyl acetal (**75**) (450  $\mu\text{L}$ , 2.65 mmol) was added to a stirring solution of **1** (60.7 mg, 0.074 mmol, 2.8 mol %) in  $\text{CH}_2\text{Cl}_2$  (14.8 mL). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 mL and purified directly on a silica gel column (2x15 cm), eluting with 19:1, 9:1, and 4:1 hexane/ethyl acetate (100 mL aliquots, ca. 2 mL of  $\text{NEt}_3$  added to each aliquot to prevent deprotection of the acetal on the column). A pale yellow oil was obtained (127 mg, 37% yield, 1.1:1 *trans/cis* as determined by integration of peaks at 2.28 and 2.32 ppm in the  $^1\text{H}$  NMR spectrum).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  5.44 (2H, m), 4.42 (2H, m), 3.46-3.40 (8H, br m), 2.28 (4H, t,  $J = 3.9$  Hz), 1.13 (12H, t,  $J = 7.0$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  127.8, 126.4, 102.7, 102.6, 61.4, 61.2, 37.4, 32.4, 29.8, 15.4.  $R_f = 0.30$  (9:1 hexane/ethyl

acetate); HRMS (EI) calcd for  $C_{14}H_{28}O_4$   $[M-H]^+$  259.1909, found 259.1904.

**Compound 78.** 9-Decen-1-yl benzoate (**3**) (140  $\mu$ L, 0.50 mmol) was added *via* syringe to a stirring solution of 3-butenal diethyl acetal (**75**) (171  $\mu$ L, 1.0 mmol) and **1** (10.4 mg, 0.013 mmol, 2.5 mol %) in  $CH_2Cl_2$  (2.5 mL). The flask was fitted with a condenser and refluxed under nitrogen for 16 hours. The reaction mixture was then allowed to come to room temperature, after which excess 98% formic acid (340  $\mu$ L, 5.0 mmol) was added to effect cleavage of the diethyl acetal. The reaction was stirred at room temperature for 2 hours until the reaction was judged complete by TLC. The reaction was quenched by dilution with  $CH_2Cl_2$  (10 mL), followed by slow addition of a saturated aqueous  $NaHCO_3$  solution (10 mL). The biphasic mixture was allowed to stir for two hours, after which the organic layer was removed, washed with brine, dried over  $MgSO_4$ , and concentrated to yield a light brown oil. The reaction mixture was then diluted to 0.5 mL with  $CH_2Cl_2$  and purified directly on a silica gel column (2x12 cm), eluting with 19:1, 9:1, 6:1, and 4:1 hexane/ethyl acetate (100 mL aliquots). A clear viscous oil (**79**) was obtained (28 mg, 18% yield over 2 steps, 1.3:1 *trans/cis* as determined by integration of peaks at 3.10 and 3.17 ppm in the  $^1H$  NMR spectrum), which gradually isomerized to the  $\alpha,\beta$ -unsaturated aldehyde over time.  $^1H$  NMR (500 MHz,  $CDCl_3$ , ppm):  $\delta$  9.64 (1H, t,  $J = 2.1$  Hz), 8.03 (2H, d,  $J = 7.1$  Hz), 7.54 (1H, t,  $J = 7.4$  Hz), 7.43 (2H, t,  $J = 7.8$  Hz), 5.62-5.45 (2H, br m), 4.31 (2H, t,  $J = 7.0$  Hz), 3.10 (2H, d,  $J = 6.0$  Hz), 2.04 (2H, quint,  $J = 6.6$  Hz), 1.75 (2H, quint,  $J = 6.8$  Hz), 1.43-1.24 (10H, br m).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ , ppm):  $\delta$  166.9, 137.1, 135.7, 133.0, 129.8, 128.5, 119.3, 118.3, 65.3, 47.5, 42.8, 32.9, 29.6, 29.5, 29.4, 29.36, 29.3, 29.2, 28.9, 27.8, 26.2.  $R_f = 0.33$  (9:1 hexane/ethyl acetate); HRMS (EI) calcd for  $C_{19}H_{26}O_3$   $[M]^+$  302.1882, found 302.1874.

**Compound 83.** Dimethyl vinylidene-L-tartrate<sup>20</sup> (**82**) (215  $\mu$ L, 1.0 mmol) and 9-decen-1(*tert*-butyldimethylsilane)-yl (165  $\mu$ L, 0.5 mmol) were simultaneously added *via* syringe to a stirring solution of **1** (12 mg, 0.014 mmol, 2.9 mol %) in  $CH_2Cl_2$  (2.5 mL). The flask was fitted with a

(20) Tsuzuki, T.; Koyama, M.; Tanabe, K. *Bull. Chem. Soc. Japan* **1967**, *40*, 1008-1013.

condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 mL and purified directly on a silica gel column (2x10 cm), eluting with 5:1 hexane/ethyl acetate (200 mL). A clear oil was obtained (214 mg, 94% yield, 9:1 *trans/cis* as determined by the relative intensities of peaks at 125.3 and 124.8 ppm in the  $^{13}\text{C}$  NMR spectrum).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm): 6.00 (1H, m), 5.55 (2H, m), 4.82 (1H, d,  $J = 3.7$  Hz), 4.73 (1H, d,  $J = 3.7$  Hz), 3.80 (6H, s), 3.57 (2H, t,  $J = 6.6$  Hz), 2.07 (2H, m), 1.50-1.21 (12H, m), 0.87 (9H, s), 0.02 (6H, s).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm): 170.6, 170.2, 141.1, 125.3, 124.8, 108.1, 102.7, 63.8, 53.4, 53.3, 33.4, 32.6, 30.0, 29.9, 29.7, 29.0, 26.5, 26.3, 18.9, 14.8.  $R_f = 0.23$  (9:1 hexane/ethyl acetate); HRMS (FAB) calcd for  $\text{C}_{23}\text{H}_{42}\text{O}_7\text{Si}$   $[\text{M}+\text{H}]^+$  459.2778, found 459.2776. Elemental analysis calcd: C: 60.23, H: 9.23; found: C: 59.98, H: 9.15.

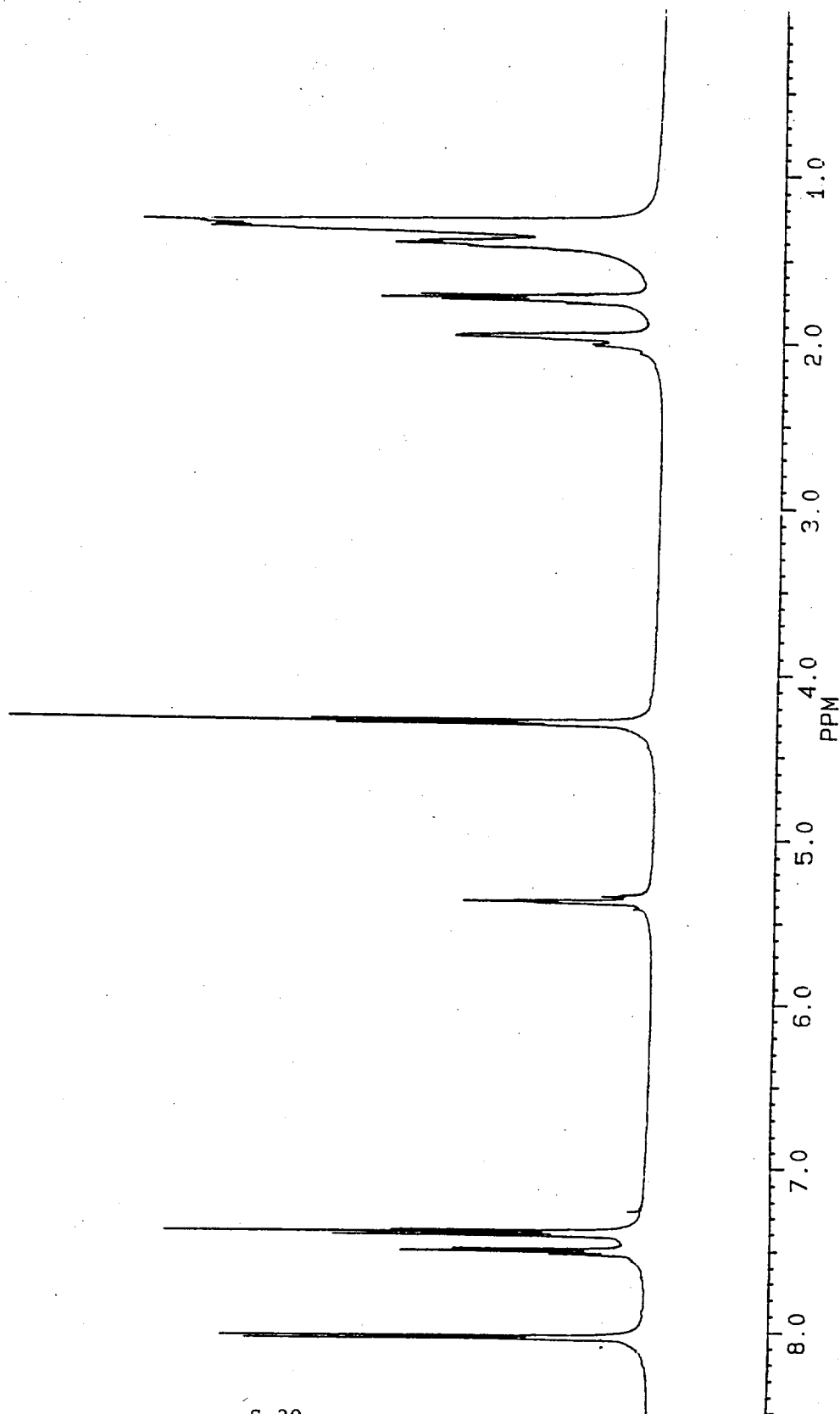
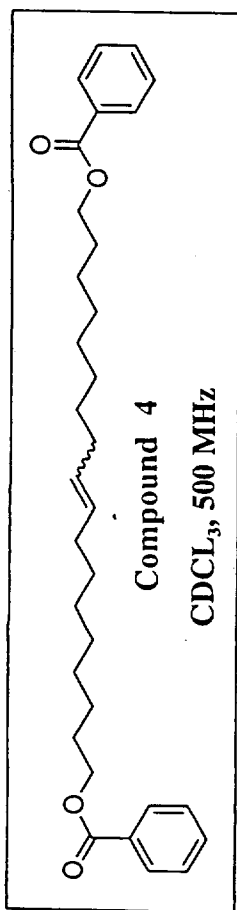
**Compound 85.** Vinylcyclopentane (**84**) (140  $\mu\text{L}$ , 1.0 mmol) and 9-decen-1-yl benzoate (**3**) (140  $\mu\text{L}$ , 0.5 mmol) were simultaneously added *via* syringe to a stirring solution of **1** (11 mg, 0.013 mmol, 2.5 mol %) in  $\text{CH}_2\text{Cl}_2$  (2.5 mL). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 mL and purified directly on a silica gel column (2x10 cm), eluting with 10:1 hexane/ethyl acetate (200 mL). A clear oil was obtained (110 mg, 66% yield, 7:1 *trans/cis* as determined by integration of peaks at 5.38 and 5.34 in the  $^1\text{H}$  NMR spectrum).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm): 8.05 (2H, d,  $J = 7.3$  Hz), 7.54 (2H, m), 7.44 (2H, t,  $J = 7.5$  Hz), 5.38 (2H, m), 4.32 (2H, t,  $J = 6.7$  Hz), 2.48-2.32 (1H, m), 1.98-1.21 (22H, broad m).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm): 167.2, 135.9, 135.6, 133.3, 130.1, 129.0, 128.9, 65.7, 43.9, 34.4, 33.8, 33.1, 30.2, 30.0, 29.8, 29.6, 29.3, 26.6, 25.7.  $R_f = 0.61$  (10:1 hexane/ethyl acetate); HRMS (FAB) calcd for  $\text{C}_{22}\text{H}_{32}\text{O}_2$   $[\text{M}]^+$  328.2402, found 328.2400.

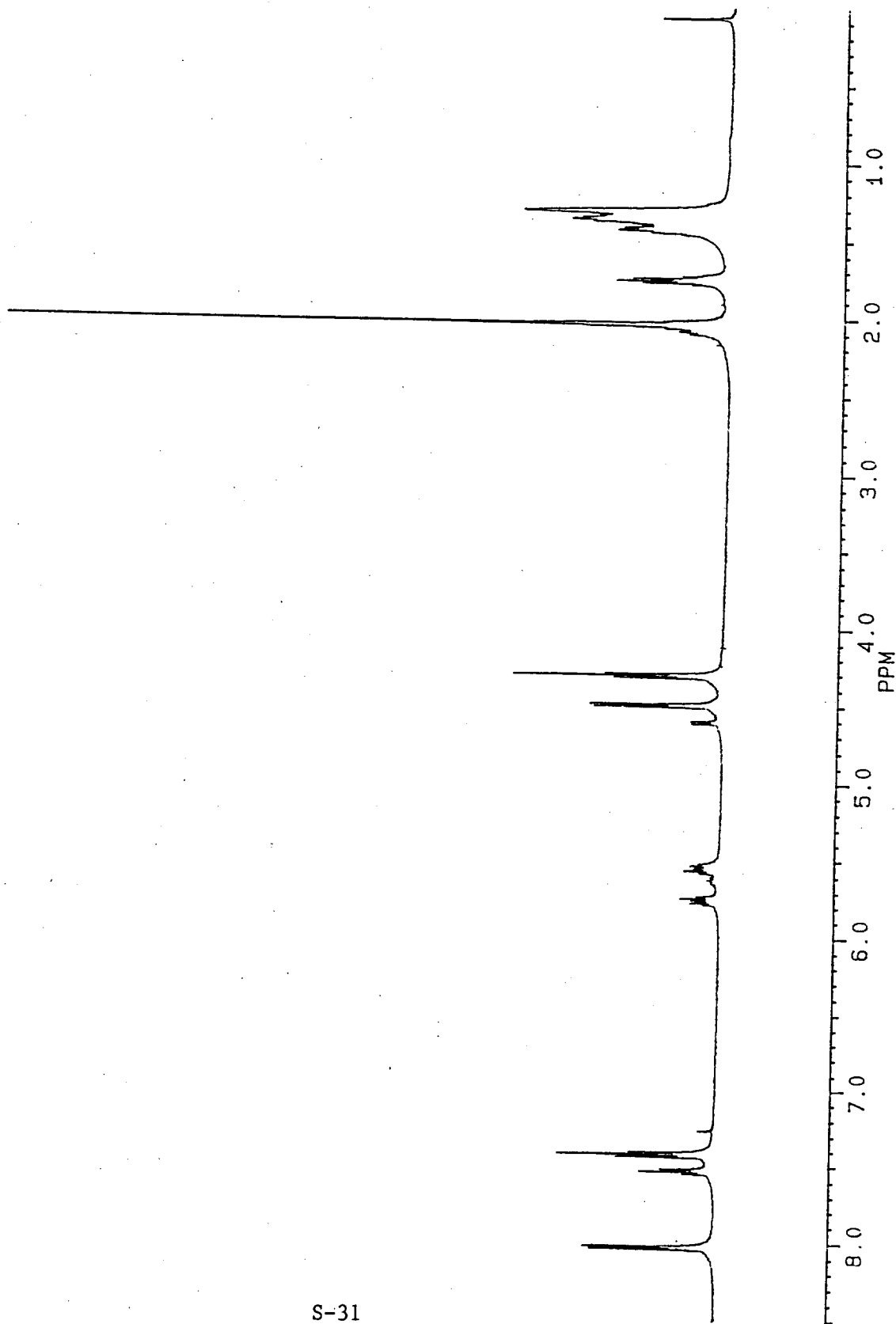
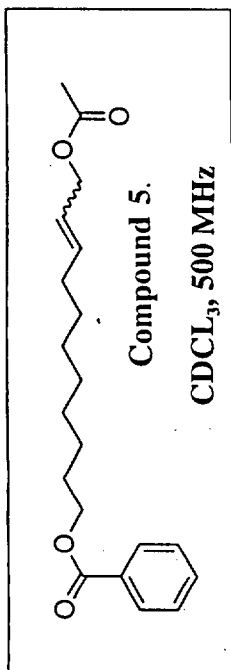
**Compound 89.** Allyl glycidyl ether (**88**) (120  $\mu\text{L}$ , 1.0 mmol) and 9-decen-1-yl benzoate (**3**) (130  $\mu\text{L}$ , 0.5 mmol) were added in succession *via* syringe to a stirring solution of **1** (27.2 mg, 0.033 mmol, 7.0 mol %) in  $\text{CH}_2\text{Cl}_2$  (2.5 mL). The flask was fitted with a condenser and refluxed

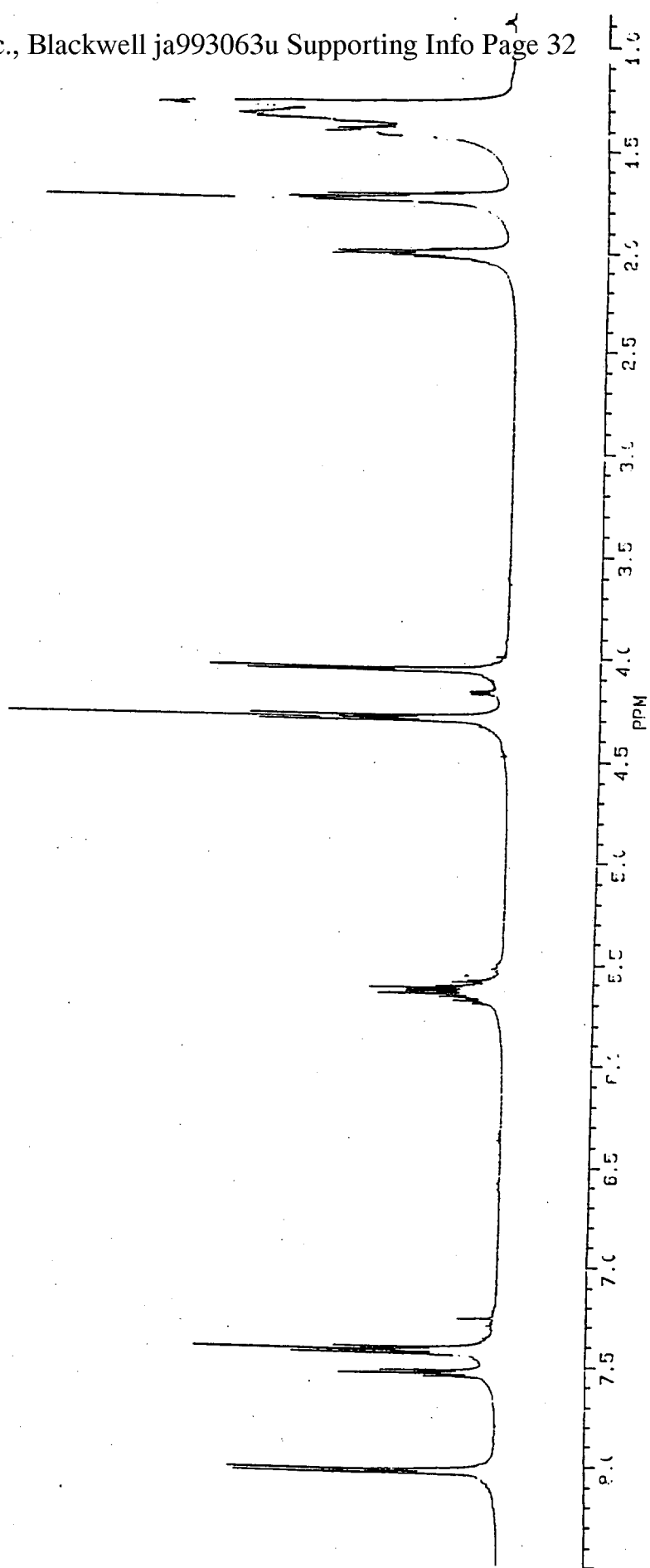
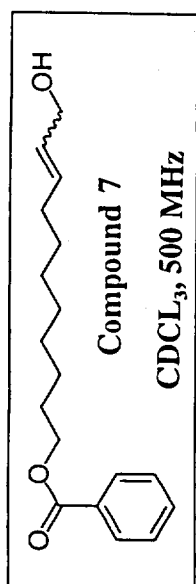
under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 mL and purified directly on a silica gel column (2x15 cm), eluting with 9:1 CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate (200 mL). A clear oil was obtained (100.3 mg, 62% yield, 3:1 *cis/trans* as determined by integration of peaks at 3.98 and 4.11 in the <sup>1</sup>H NMR spectrum). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm): 8.07 (2H, d, *J* = 8.0 Hz), 7.61 (1H, t, *J* = 7.5 Hz), 7.49 (2H, t, *J* = 7.6 Hz), 5.74 (1H, m), 5.51-5.66 (1H, m), 4.33 (2H, t, *J* = 6.6 Hz), 4.11 and 3.98 (2H, m), 3.72 (1H, m), 3.33 (1H, m), 3.13 (1H, m), 2.78 (1H, t, *J* = 4.6 Hz), 2.58 (1H, m), 2.09 (2H, m), 1.80 (2H, m), 1.50-1.37 (10H, broad m). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm): 166.8, 135.3, 134.1, 133.1, 131.1, 129.8, 128.7, 126.5, 126.3, 72.3, 71.3, 71.1, 67.2, 65.5, 51.1, 51.1, 44.4, 44.4, 32.6, 29.9, 29.8, 29.6, 29.5, 29.5, 29.1, 27.9, 26.4. *R*<sub>f</sub> = 0.27 (9:1 hexane/ethyl acetate); HRMS (FAB) calcd for C<sub>21</sub>H<sub>30</sub>O<sub>4</sub> [M+H]<sup>+</sup> 347.2222, found 346.2210.

**Compound 91.** 2-Ethenyl-4,5-tetramethyl-1,3,2-dioxaborolane<sup>21</sup> (**90**) (130 μL, 1.0 mmol) and 9-decen-1-yl benzoate (**3**) (145 μL, 0.5 mmol) were simultaneously added *via* syringe to a stirring solution of **1** (11 mg, 0.013 mmol, 2.5 mol %) in CH<sub>2</sub>Cl<sub>2</sub> (2.5 mL). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 mL and purified directly on a silica gel column (2x10 cm), eluting with 20:1 hexane/ethyl acetate (200 mL). A pale yellow oil was obtained (127 mg, 67% yield, only *trans* isomer detected in <sup>1</sup>H-NMR spectra). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): δ 8.03 (2H, d, *J* = 6.9 Hz), 7.54 (1H, t, *J* = 7.4 Hz), 7.43 (2H, t, *J* = 7.6 Hz), 6.62 (1H, dt, *J* = 6.9, 6.4 Hz) 5.39-5.28 (1H, broad m), 4.30 (2H, t, *J* = 6.7 Hz), 2.14 (2H, m), 1.75 (2H, q, *J* = 6.8 Hz), 1.50-1.05 (22H, broad m). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm): δ 167.2, 155.3, 133.3, 130.1, 128.9, 83.5, 65.7, 36.4, 29.9, 29.7, 29.3, 28.7, 26.6, 25.3. *R*<sub>f</sub> = 0.26 (20:1 hexane/ethyl acetate); HRMS (FAB) calcd for C<sub>23</sub>H<sub>35</sub>BO<sub>4</sub> [M+H]<sup>+</sup> 387.2711, found 387.2699.

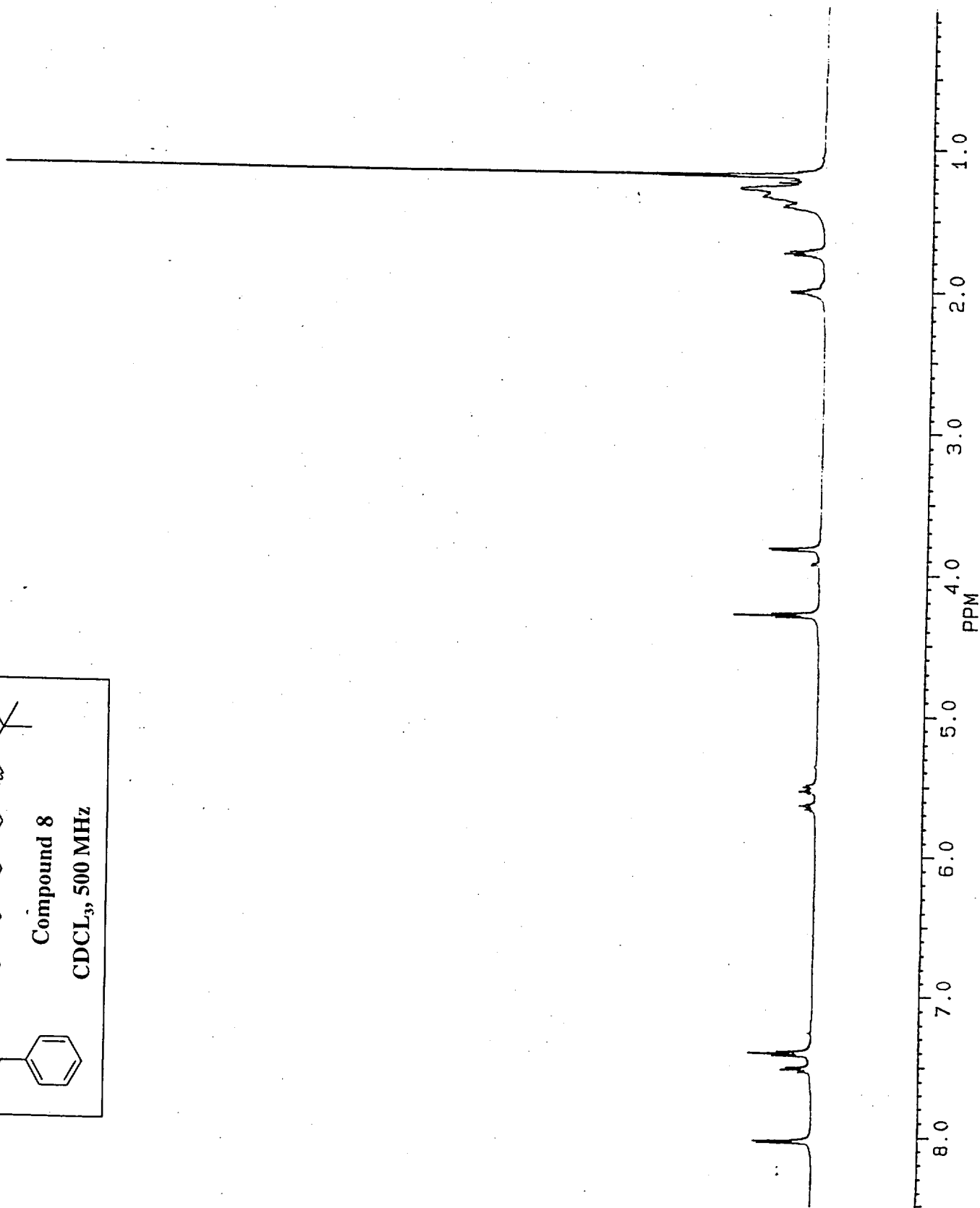
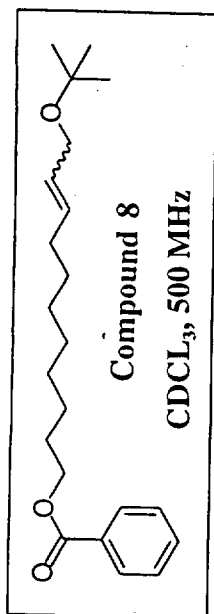
(21) Prepared according to a literature procedure: Hunt, A. R.; Stewart, S. K.; Whiting, A. *Tetrahedron Lett.* **1993**, *34*, 3599-3602.

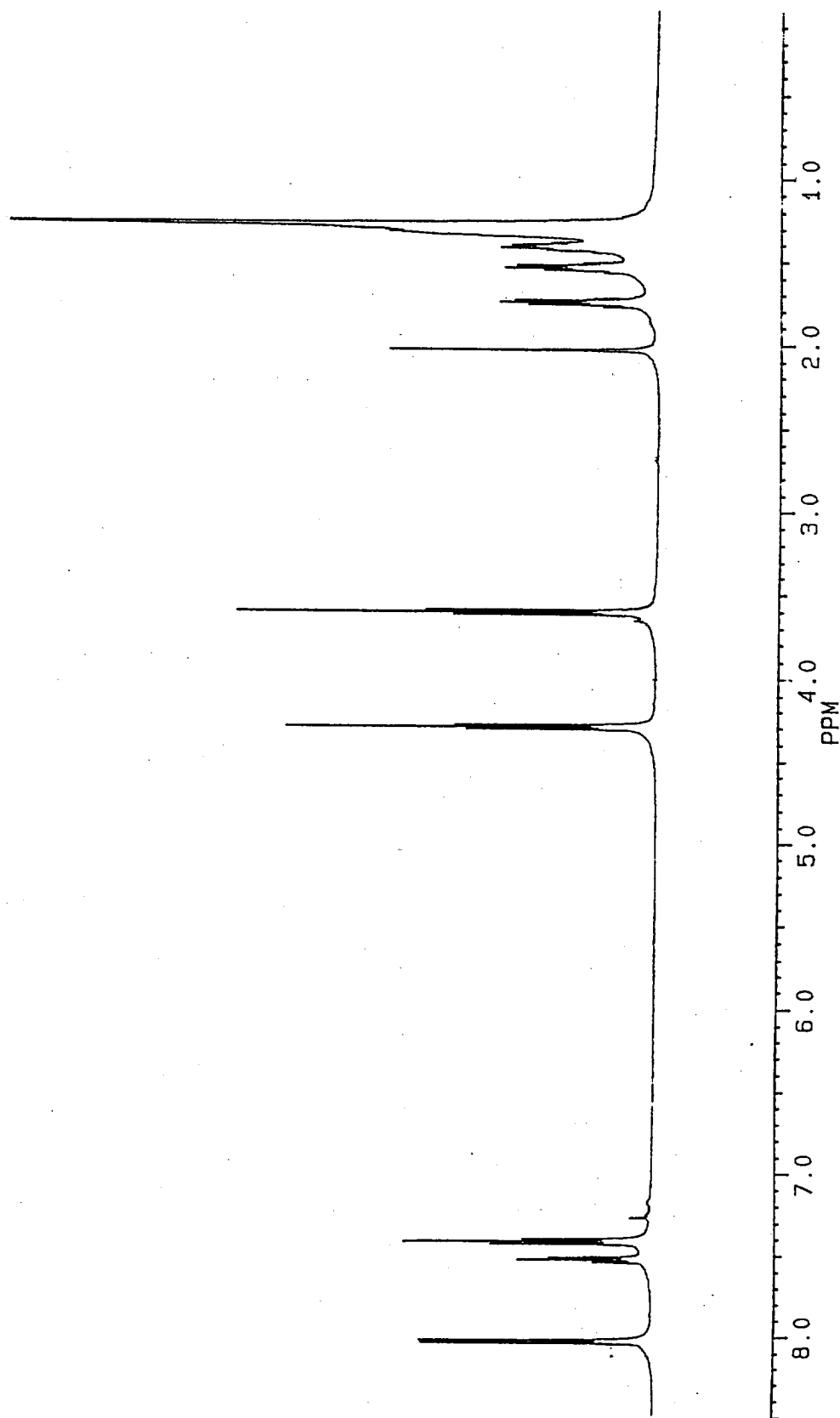
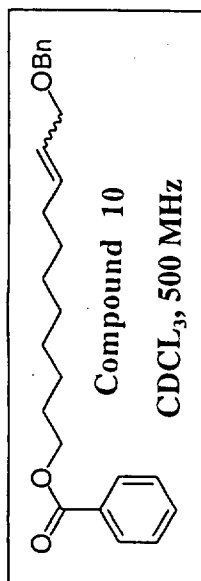


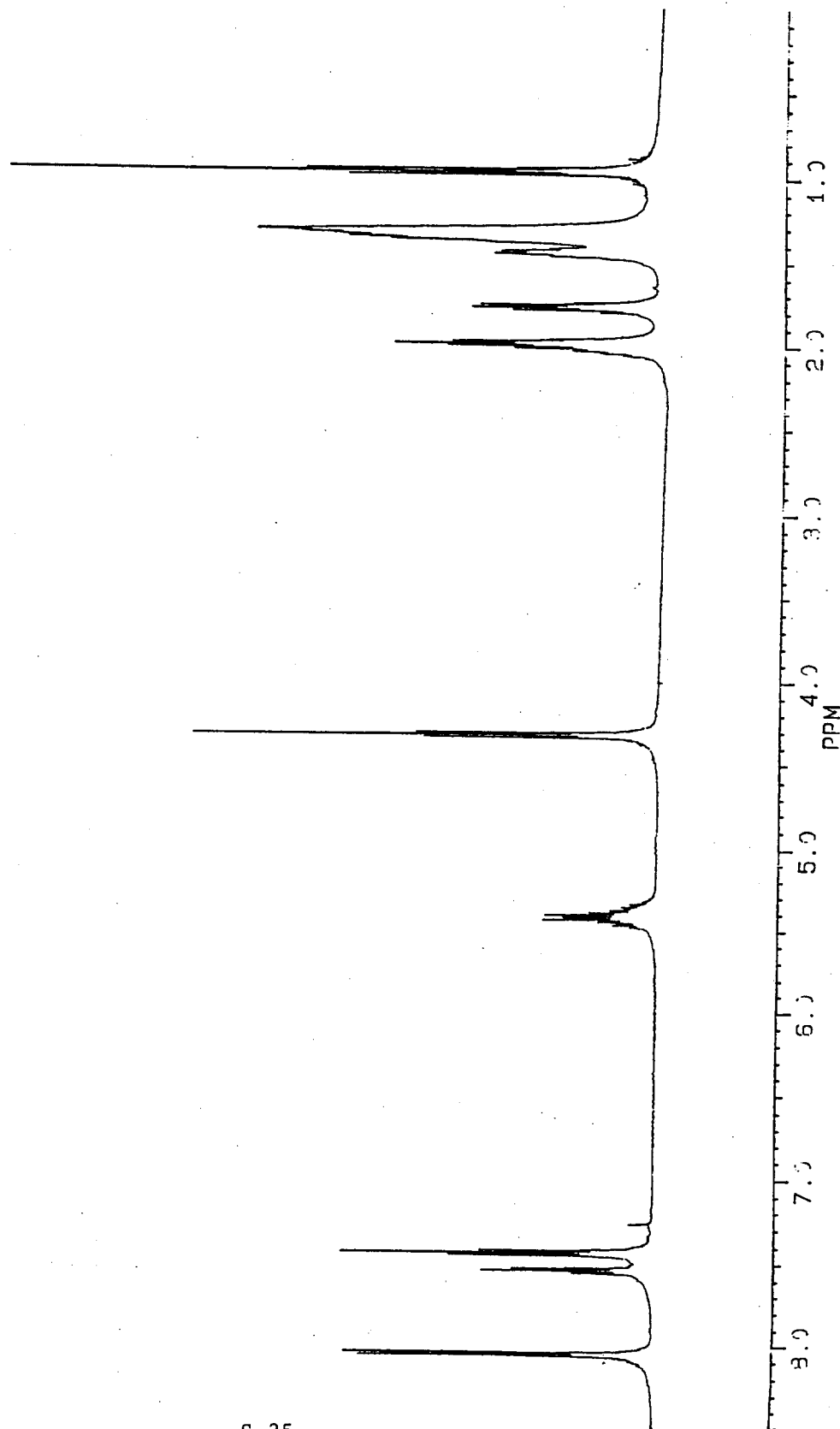
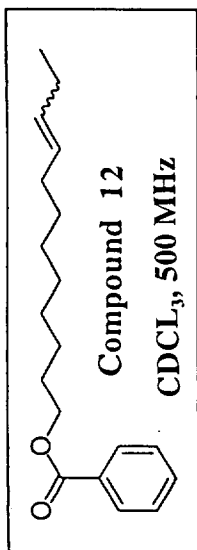


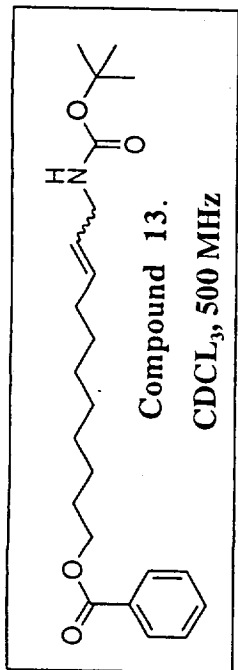




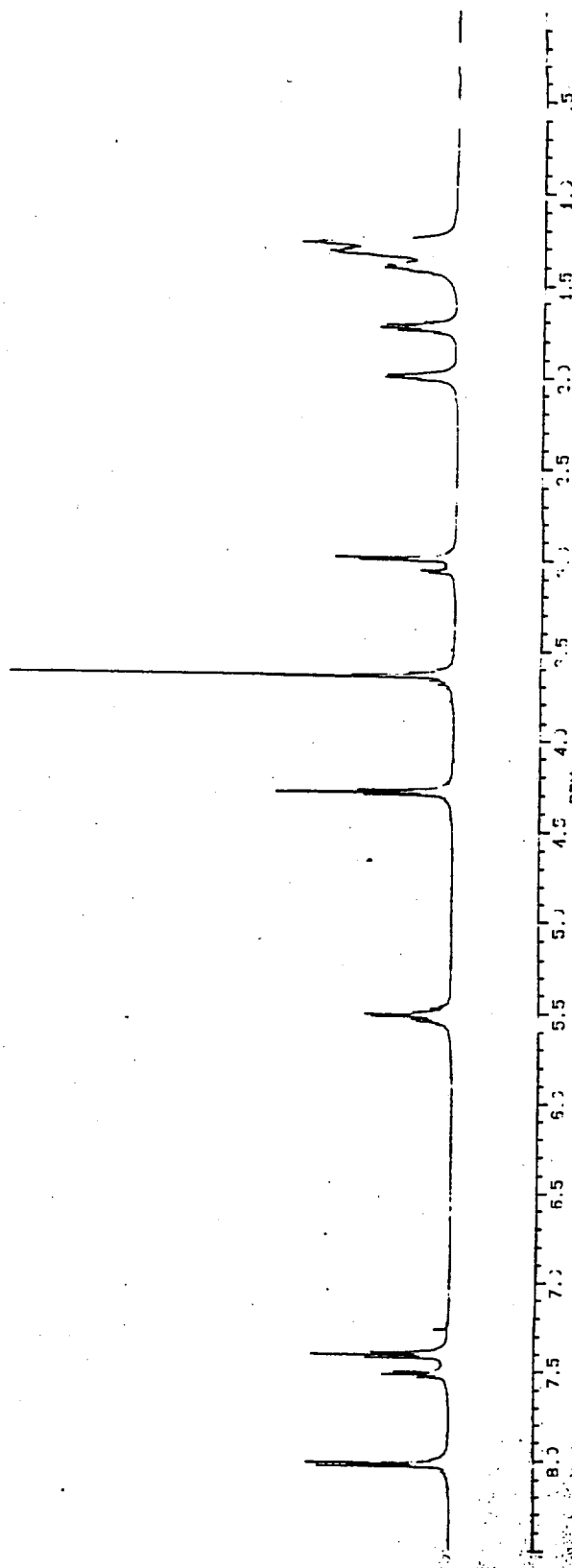
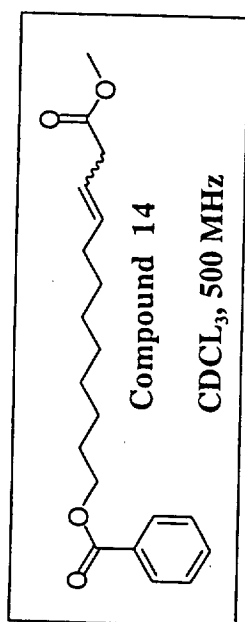




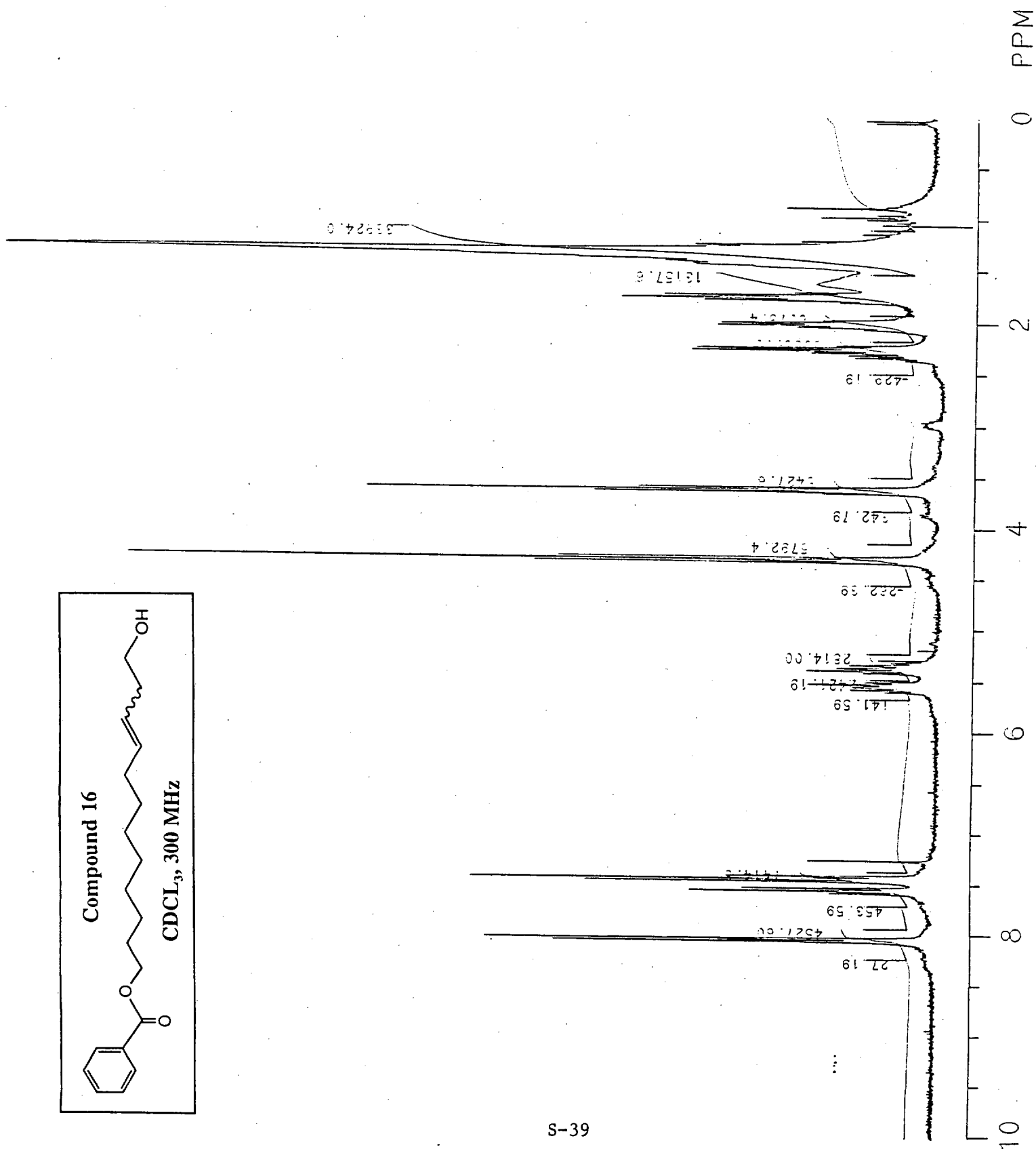
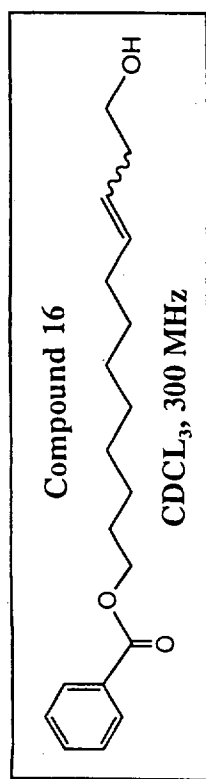




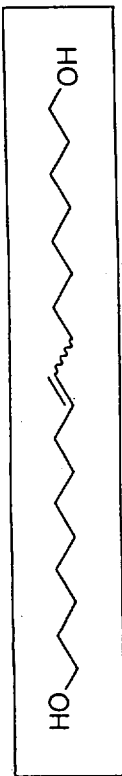
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Compound 18.



CDCL<sub>3</sub>, 500 MHz

