

## Skeletal Reorganization of Enynes to 1-Vinylcycloalkenes Catalyzed by GaCl<sub>3</sub>

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**General Information.** <sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded on a JEOL JMN-270 spectrometer in CDCl<sub>3</sub> with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, c = complex, and m = multiplet), coupling constant (Hz), integration, and interpretation. Infrared spectra (IR) were obtained on a Hitachi 270-50 spectrometer; absorptions are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained on a Shimadzu GCMS-QP 5000 instrument with ionization voltages of 70 eV. Elemental analyses were performed by the Elemental Analysis Section of Osaka University. High resolution mass spectra (HRMS) were obtained on a JEOL JMS-DX303. Analytical GC was carried out on a Shimadzu GC-14A gas chromatography, equipped with a flame ionization detector. Column chromatography was performed with SiO<sub>2</sub> (Merck Silica gel 60).

**Materials.** Toluene and methylcyclohexane were distilled over CaH<sub>2</sub>. GaCl<sub>3</sub>, purchased from Aldrich Chemical Co., at a concentration of 1 M in methylcyclohexane was used as the catalyst. Compounds **11** and **12** were known compounds (Fürstner, A.; Stelzer, F.; Szillat, H. *J. Am. Chem. Soc.* **2001**, *123*, 11863).

### Typical procedure for GaCl<sub>3</sub>-Catalyzed Skeletal Reorganization

To a solution of (2-propynyl)-(3-methyl-2-butenyl)propanedioic acid diethyl ester (**1**) (134.3 mg, 0.50 mmol) in methylcyclohexane (2.5 mL) at 0 °C was added GaCl<sub>3</sub> (1.0 M in methylcyclohexane, 0.05 mL, 0.05 mmol) in one portion. After stirring at 0 °C for 3 h, Et<sub>2</sub>NH (5 mL) was added and the resulting mixture was filtered and concentrated *in vacuo*. The residue was subjected to flash column chromatography on silica gel (hexane/EtOAc = 5/1, *R<sub>f</sub>* = 0.46) to afford 109 mg of 3-(2-methylpropenyl)-3-cyclopentene-1, 1-dicarboxylic acid diethyl ester (**2**) (81 %) as colorless liquid.

**3-(2-methylpropenyl)-3-cyclopentene-1,1-dicarboxylic acid diethyl ester (2).** Colorless oil; bp 70-75 °C/1.5 mmHg; *R<sub>f</sub>* 0.43 (hexane/EtOAc = 5/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.25 (t, *J* = 7.1 Hz, 6 H, CH<sub>2</sub>CH<sub>3</sub>), 1.78 (s, 3 H, *Me*), 1.82 (s, 3 H, *Me*), 3.04 (s, 2 H, 5-H), 3.18 (d, *J* = 2.0 Hz, 2 H, 2-H), 4.20 (q, *J* = 7.1 Hz, 4 H, CH<sub>2</sub>CH<sub>3</sub>), 5.38 (s, 1 H, 4-H), 5.73 (s, 1 H, CH=CMe<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 14.0 (CH<sub>2</sub>CH<sub>3</sub>), 19.8 (*Me*), 27.2 (*Me*), 40.2 (5-C), 43.1 (2-C), 59.3 (1-C), 61.4 (CH<sub>2</sub>CH<sub>3</sub>), 120.5 (CH=CMe<sub>2</sub>), 124.3 (4-C), 135.3 (3-C or C=CMe<sub>2</sub>), 138.5 (3-C or C=CMe<sub>2</sub>), 171.9 (C=O); IR (neat) 2982 m, 2936 m, 1734 s, 1654 w, 1448 m, 1387 m, 1366 m, 1249 s, 1182 s, 1157 s, 1096 m, 1070 m, 1054 m, 1015 m, 862 m, 784 w, 508 w; MS, *m/z* (relative intensity, %) 266 (M<sup>+</sup>, 19), 193 (39), 192 (88), 177 (46), 149 (14), 148 (11), 147 (55), 146 (28), 120 (18), 119 (100), 118 (23), 117 (22), 105 (52), 103 (12), 93 (13), 92 (11), 91

(60), 79 (27), 78 (12), 77 (34), 65 (14), 55 (17), 53 (13), 51 (13). Anal. Calcd for C<sub>15</sub>H<sub>22</sub>O<sub>4</sub>: C, 67.64; H 8.33. Found: C, 67.87; H 8.56.

**(3-Methyl-2-heptenyl)-(2-propynyl)propanedioic acid diethyl ester (3).** Colorless liquid; *R<sub>f</sub>* 0.37 (hexane/Et<sub>2</sub>O = 5/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.88 (t, *J* = 7.1 Hz, 3 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.19-1.41 (m, 4 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.25 (t, *J* = 7.3 Hz, 6 H, CH<sub>3</sub>), 1.64 (s, 3 H, Me), 1.97 (t, *J* = 7.6 Hz, 2 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.99 (t, *J* = 2.6 Hz, 1 H, CCH), 2.77 (d, *J* = 2.6 Hz, 2 H, CH<sub>2</sub>CCH), 2.77-2.80 (d, *J* = 7.6 Hz, 2 H, CH<sub>2</sub>CH=), 4.11-4.28 (m, 4 H, CH<sub>2</sub>), 4.92 (dt, *J* = 1.3, 7.6 Hz, 1 H, CH=); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 13.90 (CH<sub>3</sub>), 13.99 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 16.15 (Me), 22.21 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> or CH<sub>2</sub>CCH or CH<sub>2</sub>CH=), 22.38 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> or CH<sub>2</sub>CCH or CH<sub>2</sub>CH=), 30.04 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 30.41 (CH<sub>2</sub>CCH or CH<sub>2</sub>CH=), 39.63 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 57.01 [C(CO<sub>2</sub>Et)<sub>2</sub>], 61.46 (CH<sub>2</sub>), 71.04 (CCH), 79.42 (CCH), 116.75 (CH=), 140.60 (C=CH), 170.02 (C=O); IR (neat) 3292 m, 2962 s, 2934 s, 2876 m, 1737 s, 1469 m, 1449 m, 1390 m, 1368 m, 1286 s, 1219 s, 1193 s, 1094 m, 1069 m, 1038 m, 1014 m, 954 w, 859 m, 644 m; MS, *m/z* (relative intensity, %) 308 (M<sup>+</sup>, 9), 269 (44), 263 (30), 235 (100), 234 (80), 223 (76), 205 (22), 198 (90), 192 (47), 177 (77), 161 (68), 153 (30), 137 (17), 119 (18), 111 (26), 105 (21), 96 (18), 79 (12), 69 (38), 55 (34). exact mass calcd for C<sub>18</sub>H<sub>28</sub>O<sub>4</sub> 308.1988, found 308.1992.

**3-(2-Methylhexenyl)-3-cyclopentene-1,1-dicarboxylic acid diethyl ester (4).** Colorless oil; bp 80-90 °C/3 mmHg; *R<sub>f</sub>* 0.4 (hexane/Et<sub>2</sub>O = 5/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.90 (t, *J* = 7.3 Hz, 3 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.25 (t, *J* = 7.1 Hz, 6 H, CH<sub>3</sub>), 1.30-1.46 (m, 4 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.81 (s, 3 H, CH=CMeBu), 2.03 (t, *J* = 7.1 Hz, 2 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 3.04 (s, 2 H, 2-H, 5-H), 3.19 (d, *J* = 2.0 Hz, 2 H, 2-H, 5-H), 4.20 (q, *J* = 7.1 Hz, 4 H, CH<sub>2</sub>), 5.39 (s, 1 H, 4-H), 5.72 (s, 1 H, CH=CMeBu); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 13.99 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 14.03 (Me), 18.16 (CH=CMeBu), 22.39 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 30.19 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 40.26 (2-C or 5-C), 40.78 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 43.35 (2-C or 5-C), 59.27 (1-C), 61.40 (CH<sub>2</sub>), 120.04 (CH=CMeBu), 124.33 (4-C), 138.56 (CH=CMeBu), 139.30 (3-C), 171.91 (C=O); IR (neat) 2964 m, 2936 m, 2864 w, 1736 s, 1459 m, 1389 w, 1367 m, 1250 s, 1180 m, 1095 m, 1070 m, 1015 w, 863 w; MS, *m/z* (relative intensity, %) 308 (M<sup>+</sup>, 22), 235 (48), 234 (86), 205 (14), 192 (11), 189 (14), 178 (10), 177 (50), 163 (11), 162 (11), 161 (70), 160 (13), 159 (15), 147 (10), 146 (20), 145 (13), 134 (16), 133 (20), 132 (10), 131 (61), 119 (59), 118 (16), 117 (47), 115 (14), 107 (10), 106 (10), 105 (57), 103 (13), 93 (23), 92 (12), 91 (83), 83 (19), 81 (13), 79 (48), 78 (15), 77 (43), 69 (13), 67 (16), 65 (19), 55 (100), 53 (20), 51 (12). Anal. Calcd for C<sub>18</sub>H<sub>28</sub>O<sub>4</sub>: C, 70.10; H 9.15. Found: C, 70.01; H 9.13.

**(3-Butynyl)-(3-methyl-2-butenyl)propanedioic acid diethyl ester (5).** Colorless oil; bp 70-75 °C/1.5 mmHg; *R<sub>f</sub>* 0.49 (hexane/EtOAc = 5/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.25 (t, *J* = 7.1 Hz, 6 H, CH<sub>2</sub>CH<sub>3</sub>), 1.62 (s, 3 H, Me<sub>2</sub>), 1.69 (s, 3 H, Me<sub>2</sub>), 1.95 (t, *J* = 1.6 Hz, 1 H, CCH), 2.15 (s, 4 H, CH<sub>2</sub>CH<sub>2</sub>), 2.61 (d, *J* = 7.3 Hz, 2 H, CH<sub>2</sub>CH=), 4.18 (q, *J* = 7.1 Hz, 4 H, CH<sub>2</sub>CH<sub>3</sub>), 4.95 (m, 1 H, CH=); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 14.00 (CH<sub>2</sub>CH<sub>2</sub>), 14.08 (CH<sub>2</sub>CH<sub>3</sub>), 17.97 (Me<sub>2</sub>), 26.03 (Me<sub>2</sub>), 31.33 (CH<sub>2</sub>CH<sub>2</sub> or CH<sub>2</sub>CH=), 31.39 (CH<sub>2</sub>CH<sub>2</sub> or CH<sub>2</sub>CH=), 56.97 (1-C), 61.22 (CH<sub>2</sub>CH<sub>3</sub>), 68.52 (CCH), 83.37 (CCH), 117.24 (CH<sub>2</sub>CH=), 135.60 (=CMe<sub>2</sub>), 170.80 (C=O); IR (neat) 3290 w, 2984 m, 2936 w, 1732 s, 1451 m, 1368 m, 1272 m, 1241 s, 1215 s, 1190 s, 1082 m, 1026 m, 862 w, 654 w; MS, *m/z* (relative intensity, %) 280 (M<sup>+</sup>, 1), 207 (26), 206 (68), 191 (16), 173 (80), 167 (100), 161 (12), 133 (27), 127 (38), 121 (21), 99 (12), 93 (40), 79 (10), 69 (53), 55 (11). exact mass calcd for C<sub>16</sub>H<sub>24</sub>O<sub>4</sub> 280.1682, found 280.1665. Anal. Calcd for C<sub>16</sub>H<sub>24</sub>O<sub>4</sub>: C, 68.54; H 8.63. Found: C, 68.27; H 8.68.

**4-(2-Methylpropenyl)-3-cyclohexen-1,1-dicarboxylic acid diethyl ester (6).** Colorless oil; bp 115-125 °C/0.7 mmHg; *R<sub>f</sub>* 0.46 (hexane/EtOAc = 5/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.24 (t, *J* = 7.1 Hz, 6 H, CH<sub>2</sub>CH<sub>3</sub>), 1.73 (s, 6 H, Me), 2.14-2.15 (c, 4 H, 5-H, 6-H), 2.64 (s, 2 H, 2-H), 4.18 (q, *J* = 7.1 Hz, 4 H, CH<sub>2</sub>CH<sub>3</sub>), 5.45 (s, 1 H, 4-H or CH=CMe<sub>2</sub>), 5.50 (s, 1 H, 4-H, CH=CMe<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 14.1

(CH<sub>2</sub>CH<sub>3</sub>), 19.5 (*Me*), 26.4 (5-C or 6-C), 26.7 (*Me*), 27.9 (5-C or 6-C), 30.9 (2-C), 52.8 (1-C), 61.2 (CH<sub>2</sub>CH<sub>3</sub>), 121.6 (4-C or CH=CMe<sub>2</sub>), 126.4 (4-C or CH=CMe<sub>2</sub>), 133.2 (3-C or CH=CMe<sub>2</sub>), 134.4 (3-C or CH=CMe<sub>2</sub>) 171.4 (C=O); IR (neat) 2982 w, 2938 w, 2358 w, 1735 s, 1453 m, 1367 w, 1323 w, 1294 m, 1248 s, 1176 m, 1083 m, 1069 m, 1056 m, 1030 m, 895 w, 854 w, 654 w, 300 w; MS, *m/z* (relative intensity, %) 280 (M<sup>+</sup>, 11), 207 (19), 206 (85), 205 (14), 177 (14), 133 (25), 119 (11), 117 (12), 105 (21), 93 (14), 92 (10), 91 (100), 79 (16), 77 (21), 55 (26), 53 (13). exact mass calcd for C<sub>16</sub>H<sub>24</sub>O<sub>4</sub> 280.1682, found 280.1671. Anal. Calcd for C<sub>16</sub>H<sub>24</sub>O<sub>4</sub>: C, 68.54; H 8.63. Found: C, 68.90; H 8.94.

**(*E*)-(2-Hexenyl)-(2-propynyl)propanedioic acid diethyl ester (7E).** Colorless liquid; bp 60 –70 °C / 1 mmHg; R<sub>f</sub> 0.35 (hexane/Et<sub>2</sub>O = 5/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.81 (t, *J* = 7.3 Hz, 3 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 1.19 (t, *J* = 7.0 Hz, 6 H, CH<sub>3</sub>), 1.29 (q, *J* = 7.3 Hz, 2 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 1.90 (q, *J* = 7.3 Hz, 2 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 1.95 (brs, 1 H, CCH), 2.66-2.78 (c, 4 H, CH<sub>2</sub>CCH and CH<sub>2</sub>CH=), 4.13 (q, *J* = 7.0 Hz, 4 H, CH<sub>2</sub>), 5.15 (dt, *J* = 7.4, 15.2 Hz, 1 H, CH<sub>2</sub>CH=), 5.51 (dt, *J* = 7.1 Hz, 1 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 13.49 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 14.01 (CH<sub>3</sub>), 22.38 [CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH= and (CH<sub>2</sub>CCH or CH<sub>2</sub>CH=)], 34.56 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 35.05 (CH<sub>2</sub>CCH or CH<sub>2</sub>CH=), 56.75 (2-C), 61.36 (CH<sub>2</sub>), 71.11 (CCH), 78.88 (CCH), 122.70 (CH<sub>2</sub>CH=), 135.68 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 169.48 (C=O); IR (neat) 3470 w, 3284 s, 2970 w, 2874 s, 2396 w, 2122 w, 1739 s, 1467 s, 1368 s, 1283 s, 1204 s, 1141 s, 1093 s, 1054 s, 1030 s, 972 s, 950 m, 910 w, 858 s, 809 w, 755 w, 645 m, 515 w, 460 w, 343 w, 258 w; MS, *m/z* (relative intensity, %) 280 (M<sup>+</sup>, 0), 241 (16, M<sup>+</sup>-CH<sub>2</sub>CCH), 207 (10), 206 (26), 198 (16), 195 (56), 189 (10), 179 (12), 177 (11), 163 (28), 161 (11), 149 (33), 135 (21), 133 (43), 132 (12), 131 (12), 125 (16), 124 (24), 123 (66), 121 (17), 107 (19), 105 (41), 103 (13), 97 (12), 96 (48), 95 (34), 93 (23), 92 (13), 91 (79), 82 (11), 81 (18), 79 (46), 78 (13), 77 (43), 69 (12), 68 (12), 67 (32), 65 (29), 57 (18): Anal. Calcd for C<sub>16</sub>H<sub>24</sub>O<sub>4</sub>: C, 68.54; H 8.63. Found: C, 68.57; H 8.63.

**(*E*)-3-(1-pentenyl)-3-cyclopentene-1,1-dicarboxylic acid diethyl ester (8E).** Yellow oil; bp 100-110 °C / 0.5 mmHg; R<sub>f</sub> 0.26 (hexane/Et<sub>2</sub>O = 10/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.91 (t, *J* = 7.3 Hz, 3 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 1.26 (t, *J* = 7.1 Hz, 6 H, CH<sub>3</sub>), 1.43 (tq, *J* = 7.3, 7.3 Hz, 2 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 2.08 (dt, *J* = 7.3, 6.9 Hz, 2 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 3.08 (s, 1 H, 2-H or 5-H), 3.10 (s, 1 H, 2-H or 5-H), 4.21 (q, *J* = 7.1 Hz, 2 H, CH<sub>2</sub>), 5.43 (s, 1 H, 4-H), 5.60 (dt, *J* = 6.9, 15.8 Hz, 1 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 6.18 (d, *J* = 15.8 Hz, 1 H, CH=); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 13.78 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 14.10 (CH<sub>3</sub>), 22.52 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 34.95 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 39.78 (2-C or 5-C), 40.68 (2-C or 5-C), 58.83 (1-C), 61.52 (CH<sub>2</sub>), 123.75 (4-C), 125.82 (CH=), 132.21 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 139.54 (3-C), 171.96 (C=O); IR (neat) 3472 w, 2968 s, 2940 s, 2876 s, 1930 w, 1744 s, 1616 w, 1468 s, 1452 s, 1392 m, 1370 s, 1340 m, 1262 s, 1180 s, 1158 s, 1096 s, 1070 s, 1014 s, 966 s, 898 w, 862 s, 828 m, 778 m, 524 w, 468 w, 366 w; MS, *m/z* (relative intensity, %) 280 (M<sup>+</sup>, 22), 207 (35), 206 (93), 177 (19), 164 (14), 163 (50), 135 (11), 134 (16), 133 (100), 132 (32), 131 (20), 123 (10), 119 (12), 117 (22), 106 (17), 105 (77), 104 (12), 103 (38), 101 (11), 93 (19), 92 (20), 91 (90), 79 (55), 78 (18), 77 (51), 67 (11), 65 (21). Exact mass calcd for C<sub>16</sub>H<sub>24</sub>O<sub>4</sub> 280.1675, found 280.1676.

**(*Z*)-(2-Hexenyl)-(2-propynyl)propanedioic acid diethyl ester (7Z).** Colorless oil; bp 90 –100 °C / 2 mmHg; R<sub>f</sub> 0.53 (hexane/Et<sub>2</sub>O = 2/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.83 (t, *J* = 7.3 Hz, 3 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 1.18 (t, *J* = 7.1 Hz, 6 H, CH<sub>3</sub>), 1.30 (tq, *J* = 7.3 Hz, 2 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 1.94 (t, *J* = 2.6 Hz, 1 H, CCH), 2.00 (q, *J* = 7.9 Hz, 2 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 2.70 (d, *J* = 2.6 Hz, 2 H, CH<sub>2</sub>CCH), 2.75 (d, *J* = 7.9 Hz, 2 H, CH<sub>2</sub>CH=), 4.07-4.21 (m, 4 H, CH<sub>2</sub>), 5.03-5.13 (m, 1 H, CH<sub>2</sub>CH=), 5.44-5.54 (m, 1 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 13.54 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 13.83 (CH<sub>3</sub>), 22.19 (CH<sub>2</sub>CH=), 22.57 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 29.20 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 29.46 (CH<sub>2</sub>CCH), 56.53 (2-C), 61.37 (CH<sub>2</sub>), 71.07 (CCH), 78.95 (CCH), 121.90 (CH<sub>2</sub>CH=), 134.61 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 169.66 (C=O); IR (neat) 3474 w, 3206 m, 2964 s, 2936 s, 2874 m, 2122 w, 1738 s, 1468 s, 1449 s, 1391 m, 1368 s, 1290 s, 1243 s, 1187 s,

1136 s, 1095 s, 1071 s, 1056 s, 1024 s, 960 w, 858 m, 809 w, 683 m, 579 w, 464 w, 341 w; ; MS, *m/z* (relative intensity, %) 280 ( $M^+$ , 24), 241 (42), 235 (15), 207 (56), 206 (100), 198 (31), 196 (15), 195 (93), 189 (14), 179 (21), 178 (14), 177 (35), 164 (20), 163 (46), 161 (27), 152 (11), 151 (16), 149 (43), 137 (10), 135 (24), 134 (14), 133 (76), 132 (20), 131 (16), 125 (14), 124 (21), 123 (46), 121 (14), 119 (11), 117 (11), 107 (13), 105 (42), 103 (16), 96 (27), 95 (16), 93 (18), 92 (11), 91 (50), 81 (11), 79 (25), 77 (21), 67 (14), 65 (11), 55 (25); Anal. Calcd for  $C_{16}H_{24}O_4$ : C, 68.54; H 8.63. Found: C, 68.45; H 8.55.

**(Z)-3-(1-Pentenyl)-3-cyclopentene-1,1-dicarboxylic acid diethyl ester (8Z).** Colorless oil; bp 100–105 °C / 2 mmHg;  $R_f$  0.26 (hexane/Et<sub>2</sub>O = 10/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.93 (t,  $J$  = 7.4 Hz, 3 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 1.26 (t,  $J$  = 7.1 Hz, 6 H, CH<sub>3</sub>), 1.42 (tq,  $J$  = 7.4, 7.4 Hz, 2 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 2.23 (dt,  $J$  = 7.4, 7.4 Hz, 2 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 3.04 (s, 2 H, 2-H or 5-H), 3.22 (s, 2 H, 2-H or 5-H), 4.20 (q,  $J$  = 7.1 Hz, 4 H, CH<sub>2</sub>), 5.40 (dt,  $J$  = 7.4, 11.5 Hz, 1 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 5.49 (s, 1 H, 4-H), 5.92 (d,  $J$  = 11.5 Hz, 1 H, CH=); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 13.85 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 14.13 (CH<sub>3</sub>), 23.27 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 31.11 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 40.10 (2-C or 5-C), 42.96 (2-C or 5-C), 59.63 (1-C), 61.59 (CH<sub>2</sub>), 124.03 (CH=), 126.79 (4-C), 132.38 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 138.55 (3-C), 171.95 (C=O); IR (neat) 3464 w, 2968 m, 1736 s, 1644 w, 1466 m, 1452 m, 1390 w, 1370 m, 1254 s, 1182 s, 1162 s, 1094 m, 1070 s, 1014 m, 862 m, 724 m, 514 w; MS, *m/z* (relative intensity, %) 280 ( $M^+$ , 26), 207 (21), 206 (68), 178 (22), 163 (46), 134 (19), 133 (99), 131 (18), 117 (32), 106 (20), 105 (82), 103 (38), 101 (15), 93 (24), 92 (29), 91 (100), 79 (63), 78 (20), 77 (51), 69 (11), 67 (12), 65 (32), 55 (54), 53 (23), 52 (10), 51 (19). Exact mass calcd for  $C_{16}H_{24}O_4$  280.1675, found 280.1676.

**(E)-2-[[4-Methylphenyl)sulfonyl]-2-hexenylamino]-4-pentynoic acid ethyl ester (9E).** Yellow oil; bp 130–140 °C / 3 mmHg;  $R_f$  0.28 (hexane/EtOAc = 5/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.86 (t,  $J$  = 7.3 Hz, 3 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 1.19 (t,  $J$  = 7.1 Hz, 3 H, CH<sub>3</sub>), 1.27–1.41 (m, 2 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 1.94 (dt,  $J$  = 6.9, 7.3 Hz, 2 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 1.98 (t,  $J$  = 2.6 Hz, 1 H, 5-H), 2.42 (s, 3 H, MePh), 2.71 (ddd,  $J$  = 2.6, 8.9, 17.1 Hz, 3-H), 2.90 (ddd,  $J$  = 2.6, 6.3, 17.1 Hz, 3-H), 3.71–3.93 (c, 2 H, NCH<sub>2</sub>CH=), 4.08 (q,  $J$  = 7.1 Hz, 2 H, CH<sub>2</sub>), 4.70 (dd,  $J$  = 6.3, 8.9 Hz, 2-H), 5.40 (dt,  $J$  = 6.6, 15.5 Hz, NCH<sub>2</sub>CH=), 5.58 (dt,  $J$  = 6.9, 15.5 Hz, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 7.27 (d,  $J$  = 6.6 Hz, Ar), 7.77 (d,  $J$  = 8.2 Hz, Ar); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 13.52 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 13.75 (CH<sub>3</sub>), 20.74 (3-C), 21.28 (MePh), 21.81 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 33.97 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 48.07 (NCH<sub>2</sub>CH=), 58.08 (2-C), 61.31 (CH<sub>2</sub>), 71.01 (5-C), 79.45 (4-C), 125.42 (NCH<sub>2</sub>CH=), 127.33 (Ar), 128.94 (Ar), 134.74 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 137.18 (Ar), 142.90 (Ar), 169.04 (C=O); IR (neat) 3278 m, 2962 s, 2932 s, 2874 m, 2124 w, 1737 s, 1669 w, 1600 m, 1498 m, 1449 s, 1344 s, 1305 s, 1273 s, 1237 s, 1185 s, 1163 s, 1091 s, 1032 s, 974 s, 950 m, 881 m, 858 m, 814 s, 782 m, 726 s, 703 m, 659 s, 571 s, 550 s, 337 w; MS, *m/z* (relative intensity, %) 377 ( $M^+$ , 0.3), 304 (16), 256 (25), 223 (20), 222 (100), 157 (17), 155 (67), 91 (42), 83 (23), 82 (12), 79 (11), 55 (21), 41 (12); Anal. Calcd for  $C_{20}H_{27}NO_4S$ : C, 63.63; H 7.21; N 3.71; S 8.49. Found: C, 63.54; H 6.84; N 4.10; S 8.56.

**(E)-4-(1-Pentenyl)-1,2,3,6-tetrahydro-1-[(4-methylphenyl)sulfonyl]-2-pyridinecarboxylic acid ethyl ester (10E).** Colorless oil; bp 110–120 °C / 0.2 mmHg;  $R_f$  0.27 (hexane/Et<sub>2</sub>O = 2/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.88 (t,  $J$  = 7.3 Hz, 3 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 1.06 (t,  $J$  = 7.1 Hz, 3 H, CH<sub>3</sub>), 1.40 (tq,  $J$  = 7.3 Hz, 2 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 2.05 (dt,  $J$  = 6.9, 7.3 Hz, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 2.41 (s, 3 H, MeAr), 2.52 (m, 1 H, 3-H), 2.79 (d,  $J$  = 16.5 Hz, 3-H), 3.94 (c, 3 H, 6-H, CH<sub>2</sub>), 4.16 (d,  $J$  = 17.5 Hz, 1 H, 6-H), 4.93 (dd,  $J$  = 1.5, 6.8 Hz, 1 H, 2-H), 5.49 (brt,  $J$  = 1.7 Hz, 1 H, 5-H), 5.59 (dt,  $J$  = 6.9 Hz, 15.8 Hz, 1 H, CH=), 5.98 (d,  $J$  = 15.8 Hz, 1 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 7.28 (d,  $J$  = 8.1 Hz, 1 H, Ar), 7.69 (d,  $J$  = 8.1 Hz, 1 H, Ar); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 13.61 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 13.84 (CH<sub>3</sub>), 21.45 (MeAr), 22.41 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 27.56 (3-C), 34.72 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=), 42.28 (6-C), 52.92 (2-C), 61.16 (CH<sub>2</sub>), 120.31 (5-C), 129.35 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH= or Ar), 129.39 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH= or Ar), 130.94 (CH=), 131.60 (4-C or Ar), 136.34 (4-C or Ar), 143.24 (4-C or Ar), 170.19 (C=O); IR (neat) 3288 w, 2968 s, 2932 m,

2872 m, 1742 s, 1658 w, 1602 m, 1498 m, 1456 m, 1344 s, 1286 s, 1250 m, 1196 s, 1162 s, 1096 s, 1034 s, 966 m, 936 s, 882 m, 860 m, 816 m, 742 m, 712 m, 660 s, 578 m, 552 s; MS, *m/z* (relative intensity, %) 377 ( $M^+$ , 1), 304 (25), 223 (21), 222 (100), 155 (13), 148 (35), 91 (25), 43 (10). Anal. Calcd for  $C_{20}H_{27}NO_4S$ : C, 63.63; H 7.21; N 3.71. Found: C, 63.50; H 7.19; N 3.77.

**(Z)-2-[(4-Methylphenyl)sulfonyl]-2-hexenylamino]-4-pentynoic acid ethyl ester (9Z).** Yellow oil; bp 120–130 °C / 3 mmHg;  $R_f$  0.27 (hexane/EtOAc = 5/1);  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.88 (t,  $J$  = 7.3 Hz, 3 H,  $CH_3CH_2CH_2CH=$ ), 1.20 (t,  $J$  = 7.1 Hz, 3 H,  $CH_3$ ), 1.30-1.43 (m, 2 H,  $CH_3CH_2CH_2CH=$ ), 1.90-2.03 (c, 3 H, 5-H,  $CH_3CH_2CH_2CH=$ ), 2.42 (s, 3 H, *MePh*), 2.70 (ddd,  $J$  = 2.6, 8.9, 17.1 Hz, 1 H, 3-H), 2.89 (ddd,  $J$  = 2.3, 6.3, 17.1 Hz, 1 H, 3-H), 3.71-4.02 (c, 2 H,  $NCH_2CH=$ ), 4.10 (q,  $J$  = 7.1 Hz, 2 H,  $CH_2$ ), 4.70 (dd,  $J$  = 6.3, 8.9 Hz, 1 H, 2-H), 5.34-5.52 (c, 2 H,  $CH=CH$ ), 7.28 (d,  $J$  = 8.2 Hz, Ar), 7.78 (d,  $J$  = 8.2 Hz, Ar);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  13.69 ( $CH_3CH_2CH_2CH=$ ), 13.87 ( $CH_3$ ), 20.90 (3-C), 21.42 (*MePh*), 22.42 ( $CH_3CH_2CH_2CH=$ ), 29.13 ( $CH_3CH_2CH_2CH=$ ), 42.98 ( $NCH_2CH=$ ), 58.32 (2-C), 61.48 ( $CH_2$ ), 71.15 (5-C), 79.51 (4-C), 125.40 ( $CH=CH$ ), 127.44 (Ar), 129.08 (Ar), 133.01 ( $CH=CH$ ), 137.18 (Ar), 143.08 (Ar), 169.16 (C=O); IR (neat) 3286 m, 2964 s, 2934 s, 2876 m, 2124 w, 1739 s, 1655 w, 1600 m, 1498 m, 1458 m, 1344 s, 1305 s, 1235 s, 1185 s, 1163 s, 1092 s, 1018 s, 954 m, 883 m, 815 s, 706 m, 660 s, 571 m, 550 s, 336 w; MS, *m/z* (relative intensity, %) 377 ( $M^+$ , 0.2), 304 (18), 256 (22), 223 (21), 222 (100), 155 (56), 91 (35), 83 (14), 79 (10), 55 (11); Anal. Calcd for  $C_{20}H_{27}NO_4S$ : C, 63.63; H 7.21; N 3.71; S 8.49. Found: C, 63.54; H 6.84; N 4.10; S 8.56.

**(Z)-4-(1-Pentenyl)-1,2,3,6-tetrahydro-1-[(4-methylphenyl)sulfonyl]-2-pyridinecarboxylic acid ethyl ester (10Z).** Yellow oil; bp 125–135 °C / 2 mmHg;  $R_f$  0.41 (hexane/Et<sub>2</sub>O = 5/1);  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.88 (t,  $J$  = 7.4 Hz, 3 H,  $CH_3CH_2CH_2CH=$ ), 1.08 (t,  $J$  = 7.3 Hz, 3 H,  $CH_3$ ), 1.30-1.44 (m, 2 H,  $CH_3CH_2CH_2CH=$ ), 2.06-2.13 (m, 2 H,  $CH_3CH_2CH_2CH=$ ), 2.42 (s, 3 H, *MeAr*), 2.65 (s, 2 H, 3-H), 3.86-4.03 (c, 3 H,  $CH_2$  and 6-H), 4.16 (d,  $J$  = 1.6 Hz, 1 H, 6-H), 4.88 (t,  $J$  = 4.3 Hz, 1 H, 2-H), 5.38 (dt,  $J$  = 7.4, 11.5 Hz, 1 H,  $CH=CHPr$ ), 5.49 (brs, 1 H, 5-H), 5.67 (d,  $J$  = 11.5 Hz,  $CH=CHPr$ ), 7.28 (d,  $J$  = 8.7 Hz, 2 H), 7.69 (d,  $J$  = 8.7 Hz, 2 H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  13.72 ( $CH_3CH_2CH_2CH=$ ), 13.89 ( $CH_3$ ), 21.51 (*MeAr*), 23.14 ( $CH_3CH_2CH_2CH=$ ), 30.77 ( $CH_3CH_2CH_2CH=$ ), 31.68 (3-C), 42.27 (6-C), 53.05 (2-C), 61.20 ( $CH_2$ ), 121.08 (5-C), 127.29 (Ar), 129.07 ( $CH=CHPr$ ), 129.31 (Ar), 131.16 (4-C or Ar), 132.23 ( $CH=CHPr$ ), 136.28 (4-C or Ar), 143.30 (4-C or Ar), 170.16 (C=O); IR (neat) 3564 w, 3448 w, 3280 w, 2964 s, 2868 s, 2500 w, 2260 m, 2052 w, 1920 m, 1746 s, 1654 m, 1602 s, 1498 s, 1456 s, 1348 s, 1286 s, 1248 s, 1168 s, 1094 s, 1034 s, 966 s, 936 s, 880 m, 860 m, 816 s, 734 s, 712 s, 660 s, 604 m, 552 s, 482 w, 430 w, 356 w, 326 w; MS, *m/z* (relative intensity, %) 377 ( $M^+$ , 0.4), 304 (26), 223 (100), 148 (34), 91 (19). Anal. Calcd for  $C_{20}H_{27}NO_4S$ : C, 63.63; H 7.21; N 3.71; S 8.49. Found: C, 63.46; H 7.15; N 3.65; S 8.20.

**(4aa, 10a, 10aa)-2,3,4a,5,6,7,8,9,10,10a-decahydro-4 H-10,1-methanobenzocyclooctene-4,4-dicarboxylic acid diethyl ester (14).** Colorless oil; bp 150-160 °C/8 mmHg;  $R_f$  0.39 (hexane/Et<sub>2</sub>O = 5/1);  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  1.25 (t,  $J$  = 7.1 Hz, 3 H,  $CH_2CH_3$ ), 1.28 (t,  $J$  = 7.1 Hz, 3 H,  $CH_2CH_3$ ), 1.21-1.31 (m, 1 H,  $CH_2$ ), 1.37-1.48 (m, 5 H,  $CH_2$ ), 1.52-1.57 (m, 2 H,  $CH_2$ ), 1.65-1.68 (m, 1 H, 8-H), 1.77 (dt,  $J$  = 5.1, 13.1 Hz, 1 H, 3-H), 1.86 (ddd,  $J$  = 2.6, 11.5, 22.7 Hz, 1 H, 5-H), 1.96 (dt,  $J$  = 2.6, 11.5 Hz, 1 H, 4a-H), 2.02-2.07 (m, 1 H, 2-H), 2.18 (ddd,  $J$  = 2.0, 4.3, 14.1 Hz, 1 H, 2-H), 2.43 (ddd,  $J$  = 2.0, 5.1, 13.0 Hz, 1 H, 3-H), 2.62 (dd,  $J$  = 3.7, 11.5 Hz, 1 H, 10a-H), 2.73 (ddd,  $J$  = 3.7, 6.8, 11.5 Hz, 1 H, 10-H), 4.16 (q,  $J$  = 7.1 Hz, 2 H,  $CH_2CH_3$ ), 4.21 (q,  $J$  = 7.1 Hz, 2 H,  $CH_2CH_3$ ), 5.54 (d,  $J$  = 2.2 Hz, 1 H, 11-H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  14.12 ( $CH_3$ ), 14.16 ( $CH_3$ ), 23.95 (2-C), 25.68 (6-C), 26.41 (7-C), 27.03 (8-C), 29.97 (9-C), 33.16 (5-C), 35.35 (3-C), 44.96 (4a-C), 45.10 (10a-C), 45.65 (10-C), 59.31 (4-C), 60.50 ( $CH_2$ ), 61.04 ( $CH_2$ ), 126.98 (11-C), 148.98 (1-C), 170.33 (C=O), 172.47 (C=O); IR (neat) 3452 w, 3036 m, 2928 s, 2860 s, 2692 s, 1744 s, 1654 m, 1448 s, 1392 m, 1370 s, 1330 m, 1244 s, 1184 s, 1132 s,

1086 s, 1060 s, 1040 s, 952 w, 930 w, 902 w, 850 m, 826 m, 758 w, 734 w, 630 m, 552 w, 516 w, 456 w, 412 w; MS,  $m/z$  (relative intensity, %) 320 ( $M^+$ , 8), 247 (23), 246 (48), 174 (14), 173 (100), 160 (10), 131 (15), 127 (25), 117 (15), 105 (14), 91 (24), 84 (10), 79 (10). Anal. Calcd for  $C_{19}H_{28}O_4$ : C, 71.22; H 8.81. Found: C, 71.15; H 8.79. The stereochemistry of **14** was determined by NOE enhancement and the long range  $^1H$ - $^{13}C$  cosy measurements.