Skeletal Reorganization of Enynes to 1-Vinylcycloalkenes Catalyzed by GaCl₃

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General Information. ¹H NMR and ¹³C NMR were recorded on a JEOL JMN-270 spectrometer in CDCl₃ 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 SiO₂ (Merck Silica gel 60).

Materials. Toluene and methylcyclohexane were distilled over CaH₂. GaCl₃, 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.; Szilatt, H. *J. Am. Chem. Soc.* **2001**, *123*, 11863).

Typical procedure for GaCl₃-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 GaCl₃ (1.0 M in methylcyclohexane, 0.05 mL, 0.05 mmol) in one portion. After stirring at 0 °C for 3 h, Et₂NH (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_f* = 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_f* 0.43 (hexane/EtOAc = 5/1); ¹H NMR (CDCl₃) δ 1.25 (t, *J* = 7.1 Hz, 6 H, CH₂CH₃), 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, CH₂CH₃), 5.38 (s, 1 H, 4-H), 5.73 (s, 1 H, CH=CMe₂); ¹³C NMR (CDCl₃) δ 14.0 (CH₂CH₃), 19.8 (*Me*), 27.2 (*Me*), 40.2 (5-C), 43.1 (2-C), 59.3 (1-C), 61.4 (CH₂CH₃), 120.5 (CH=CMe₂), 124.3 (4-C), 135.3 (3-C or C=CMe₂), 138.5 (3-C or C=CMe₂), 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⁺, 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 $C_{15}H_{22}O_4$: 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_f 0.37 (hexane/Et₂O = 5/1); 1H NMR (CDCl₃) δ 0.88 (t, J = 7.1 Hz, 3 H, CH₃CH₂CH₂CH₂), 1.19-1.41 (m, 4 H, CH₃CH₂CH₂CH₂), 1.25 (t, J = 7.3 Hz, 6 H, CH₃), 1.64 (s, 3 H, Me), 1.97 (t, J = 7.6 Hz, 2 H, CH₃CH₂CH₂CH₂), 1.99 (t, J = 2.6 Hz, 1 H, CCH), 2.77 (d, J = 2.6 Hz, 2 H, CH₂CCH), 2.77-2.80 (d, J = 7.6 Hz, 2 H, CH₂CH=), 4.11-4.28 (m, 4 H, CH₂), 4.92 (dt, J = 1.3, 7.6 Hz, 1 H, CH=); ^{13}C NMR (CDCl₃) δ 13.90 (CH₃), 13.99 (CH₃CH₂CH₂CH₂), 16.15 (Me), 22.21 (CH₃CH₂CH₂CH₂ or CH₂CCH or CH₂CH=), 22.38 (CH₃CH₂CH₂CH₂ or CH₂CCH or CH₂CH=), 30.04 (CH₃CH₂CH₂CH₂), 30.41 (CH₂CCH or CH₂CH=), 39.63 (CH₃CH₂CH₂CH₂), 57.01 [C(CO₂Et)₂], 61.46 (CH₂), 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⁺, 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 $C_{18}H_{28}O_4$ 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_f 0.4 (hexane/Et₂O = 5/1); 1H NMR (CDCl₃) δ 0.90 (t, J = 7.3 Hz, 3 H, CH₃CH₂CH₂CH₂), 1.25 (t, J = 7.1 Hz, 6 H, CH₃), 1.30-1.46 (m, 4 H, CH₃CH₂CH₂CH₂), 1.81 (s, 3 H, CH=CMeBu), 2.03 (t, J = 7.1 Hz, 2 H, CH₃CH₂CH₂CH₂), 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, CH₂), 5.39 (s, 1 H, 4-H), 5.72 (s, 1 H, CH=CMeBu); ^{13}C NMR (CDCl₃) δ 13.99 (CH₃CH₂CH₂CH₂), 14.03 (Me), 18.16 (CH=CMeBu), 22.39 (CH₃CH₂CH₂CH₂), 30.19 (CH₃CH₂CH₂CH₂), 40.26 (2-C or 5-C), 40.78 (CH₃CH₂CH₂CH₂), 43.35 (2-C or 5-C), 59.27 (1-C), 61.40 (CH₂), 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⁺, 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 $C_{18}H_{28}O_4$: 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_f 0.49 (hexane/EtOAc = 5/1); 1H NMR (CDCl₃) δ 1.25 (t, J = 7.1 Hz, 6 H, CH₂CH₃), 1.62 (s, 3 H, Me₂), 1.69 (s, 3 H, Me₂), 1.95 (t, J = 1.6 Hz, 1 H, CCH), 2.15 (s, 4 H, CH₂CH₂), 2.61 (d, J = 7.3 Hz, 2 H, CH₂CH=), 4.18 (q, J = 7.1 Hz, 4 H, CH₂CH₃), 4.95 (m, 1 H, CH=); ^{13}C NMR (CDCl₃) δ 14.00 (CH₂CH₂), 14.08 (CH₂CH₃), 17.97 (Me₂), 26.03 (Me₂), 31.33 (CH₂CH₂ or CH₂CH=), 31.39 (CH₂CH₂ or CH₂CH=), 56.97 (1-C), 61.22 (CH₂CH₃), 68.52 (CCH), 83.37 (CCH), 117.24 (CH₂CH=), 135.60 (=CMe₂), 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⁺, 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 $C_{16}H_{24}O_4$ 280.1682, found 280.1665. Anal. Calcd for $C_{16}H_{24}O_4$: 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_f 0.46 (hexane/EtOAc = 5/1); 1H NMR (CDCl₃) δ 1.24 (t, J = 7.1 Hz, 6 H, CH₂CH₃), 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, CH₂CH₃), 5.45 (s, 1 H, 4-H or CH=CMe₂), 5.50 (s, 1 H, 4-H, CH=CMe₂); ^{13}C NMR (CDCl₃) δ 14.1

(CH₂CH₃), 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 (CH₂CH₃), 121.6 (4-C or CH=CMe₂), 126.4 (4-C or CH=CMe₂), 133.2 (3-C or CH=CMe₂), 134.4 (3-C or CH=CMe₂) 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⁺, 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 C₁₆H₂₄O₄ 280.1682, found 280.1671. Anal. Calcd for C₁₆H₂₄O₄: C, 68.54; H 8.63. Found: C, 68.90; H 8.94.

(*E*)-(2-Hexenyl)-(2-propynyl)propanedioic acid diethyl ester (7*E*). Colorless liquid; bp 60 –70 °C / 1 mmHg; *R_f* 0.35 (hexane/Et₂O = 5/1); ¹H NMR (CDCl₃) δ 0.81 (t, *J* = 7.3 Hz, 3 H, CH₃CH₂CH₂CH=), 1.19 (t, *J* = 7.0 Hz, 6 H, CH₃), 1.29 (q, *J* = 7.3 Hz, 2 H, CH₃CH₂CH₂CH=), 1.90 (q, *J* = 7.3 Hz, 2 H, CH₃CH₂CH₂CH=), 1.95 (brs, 1 H, CCH), 2.66-2.78 (c, 4 H, CH₂CCH and CH₂CH=), 4.13 (q, *J* = 7.0 Hz, 4 H, CH₂), 5.15 (dt, *J* = 7.4, 15.2 Hz, 1 H, CH₂CH=), 5.51 (dt, *J* = 7.1 Hz, 1 H, CH₃CH₂CH₂CH=); ¹³C NMR (CDCl₃) δ 13.49 (CH₃CH₂CH₂CH=), 14.01 (CH₃), 22.38 [CH₃CH₂CH₂CH= and (CH₂CCH or CH₂CH=)], 34.56 (CH₃CH₂CH₂CH=), 35.05 (CH₂CCH or CH₂CH=), 56.75 (2-C), 61.36 (CH₂), 71.11 (CCH), 78.88 (CCH), 122.70 (CH₂CH=), 135.68 (CH₃CH₂CH₂CH=), 169.48 (C=O); IR (neat) 3470 w, 3284 s, 2970 2, 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⁺, 0), 241 (16, M⁺-CH₂CCH), 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 C₁₆H₂₄O₄: 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 (8*E*). Yellow oil; bp 100-110 °C / 0.5 mmHg; *R_f* 0.26 (hexane/Et₂O = 10/1); ¹H NMR (CDCl₃) δ 0.91 (t, *J* = 7.3 Hz, 3 H, CH₃CH₂CH₂CH=), 1.26 (t, *J* = 7.1 Hz, 6 H, CH₃), 1.43 (tq, *J* = 7.3, 7.3 Hz, 2 H, CH₃CH₂CH₂CH=), 2.08 (dt, *J* = 7.3, 6.9 Hz, 2 H, CH₃CH₂CH₂CH=), 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, CH₂), 5.43 (s, 1 H, 4-H), 5.60 (dt, *J* = 6.9, 15.8 Hz, 1 H, CH₃CH₂CH₂CH=), 6.18 (d, *J* = 15.8 Hz, 1 H, CH=); ¹³C NMR (CDCl₃) δ 13.78 (CH₃CH₂CH₂CH=), 14.10 (CH₃), 22.52 (CH₃CH₂CH₂CH=), 34.95 (CH₃CH₂CH₂CH=), 39.78 (2-C or 5-C), 40.68 (2-C or 5-C), 58.83 (1-C), 61.52 (CH₂), 123.75 (4-C), 125.82 (CH=), 132.21 (CH₃CH₂CH₂CH=), 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⁺, 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 C₁₆H₂₄O₄ 280.1675, found 280.1676.

(*Z*)-(2-Hexenyl)-(2-propynyl)propanedioic acid diethyl ester (7*Z*). Colorless oil; bp 90 –100 °C / 2 mmHg; *R_f* 0.53 (hexane/Et₂O = 2/1); ¹H NMR (CDCl₃) δ 0.83 (t, *J* = 7.3 Hz, 3 H, CH₃CH₂CH₂CH=), 1.18 (t, *J* = 7.1 Hz, 6 H, CH₃), 1.30 (tq, *J* = 7.3 Hz, 2 H, CH₃CH₂CH₂CH=), 1.94 (t, *J* = 2.6 Hz, 1 H, CCH), 2.00 (q, *J* = 7.9 Hz, 2 H, CH₃CH₂CH₂CH=), 2.70 (d, *J* = 2.6 Hz, 2 H, CH₂CCH), 2.75 (d, *J* = 7.9 Hz, 2 H, CH₂CH=), 4.07-4.21 (m, 4 H, CH₂), 5.03-5.13 (m, 1 H, CH₂CH=), 5.44-5.54 (m, 1 H, CH₃CH₂CH₂CH=); ¹³C NMR (CDCl₃) δ 13.54 (CH₃CH₂CH₂CH=), 13.83 (CH₃), 22.19 (CH₂CH=), 22.57 (CH₃CH₂CH₂CH=), 29.20 (CH₃CH₂CH₂CH=), 29.46 (CH₂CCH), 56.53 (2-C), 61.37 (CH₂), 71.07 (CCH), 78.95 (CCH), 121.90 (CH₂CH=), 134.61 (CH₃CH₂CH₂CH=), 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/Et₂O = 10/1); 1H NMR ($CDCl_3$) δ 0.93 (t, J = 7.4 Hz, 3 H, $CH_3CH_2CH_2CH=$), 1.26 (t, J = 7.1 Hz, 6 H, CH_3), 1.42 (tq, J = 7.4, 7.4 Hz, 2 H, $CH_3CH_2CH_2CH=$), 2.23 (dt, J = 7.4, 7.4 Hz, 2 H, $CH_3CH_2CH_2CH=$), 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_2), 5.40 (dt, J = 7.4, 11.5 Hz, 1 H, $CH_3CH_2CH_2CH=$), 5.49 (s, 1 H, 4-H), 5.92 (d, J = 11.5 Hz, 1 H, $CH=$); ^{13}C NMR ($CDCl_3$) δ 13.85 ($CH_3CH_2CH_2CH=$), 14.13 (CH_3), 23.27 ($CH_3CH_2CH_2CH=$), 31.11 ($CH_3CH_2CH_2CH=$), 40.10 (2-C or 5-C), 42.96 (2-C or 5-C), 59.63 (1-C), 61.59 (CH_2), 124.03 ($CH=$), 126.79 (4-C), 132.38 ($CH_3CH_2CH_2CH=$), 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); 1H NMR ($CDCl_3$) δ 0.86 (t, J = 7.3 Hz, 3 H, $CH_3CH_2CH_2CH=$), 1.19 (t, J = 7.1 Hz, 3 H, CH_3), 1.27–1.41 (m, 2 H, $CH_3CH_2CH_2CH=$), 1.94 (dt, J = 6.9, 7.3 Hz, 2 H, $CH_3CH_2CH_2CH=$), 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, $NCH_2CH=$), 4.08 (q, J = 7.1 Hz, 2 H, CH_2), 4.70 (dd, J = 6.3, 8.9 Hz, 2-H), 5.40 (dt, J = 6.6, 15.5 Hz, $NCH_2CH=$), 5.58 (dt, J = 6.9, 15.5 Hz, $CH_3CH_2CH_2CH=$), 7.27 (d, J = 6.6 Hz, Ar), 7.77 (d, J = 8.2 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ 13.52 ($CH_3CH_2CH_2CH=$), 13.75 (CH_3), 20.74 (3-C), 21.28 (*MePh*), 21.81 ($CH_3CH_2CH_2CH=$), 33.97 ($CH_3CH_2CH_2CH=$), 48.07 ($NCH_2CH=$), 58.08 (2-C), 61.31 (CH_2), 71.01 (5-C), 79.45 (4-C), 125.42 ($NCH_2CH=$), 127.33 (Ar), 128.94 (Ar), 134.74 ($CH_3CH_2CH_2CH=$), 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/Et₂O = 2/1); 1H NMR ($CDCl_3$) δ 0.88 (t, J = 7.3 Hz, 3 H, $CH_3CH_2CH_2CH=$), 1.06 (t, J = 7.1 Hz, 3 H, CH_3), 1.40 (tq, J = 7.3 Hz, 2 H, $CH_3CH_2CH_2CH=$), 2.05 (dt, J = 6.9, 7.3 Hz, $CH_3CH_2CH_2CH=$), 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_2), 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, $CH_3CH_2CH_2CH=$), 7.28 (d, J = 8.1 Hz, 1 H, Ar), 7.69 (d, J = 8.1 Hz, 1 H, Ar); ^{13}C NMR ($CDCl_3$) δ 13.61 ($CH_3CH_2CH_2CH=$), 13.84 (CH_3), 21.45 (*MeAr*), 22.41 ($CH_3CH_2CH_2CH=$), 27.56 (3-C), 34.72 ($CH_3CH_2CH_2CH=$), 42.28 (6-C), 52.92 (2-C), 61.16 (CH_2), 120.31 (5-C), 129.35 ($CH_3CH_2CH_2CH=$ or Ar), 129.39 ($CH_3CH_2CH_2CH=$ 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-(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 ($CDCl_3$) δ 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 ($CDCl_3$) δ 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/Et₂O = 5/1); 1H NMR ($CDCl_3$) δ 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 ($CDCl_3$) δ 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/Et₂O = 5/1); 1H NMR (600 MHz, $CDCl_3$) δ 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 ($CDCl_3$) δ 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.