



Supporting Information

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# Two Novel Manifolds For Metal Catalyzed Intramolecular Diels-Alder Reactions of Unactivated Alkynes

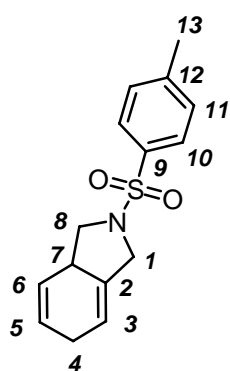
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**General.** NMR spectra were recorded with a Bruker DPX 300, AV 400, or DMX 600 spectrometer in the solvents indicated; chemical shifts ( $\delta$ ) are given in ppm relative to TMS, coupling constants ( $J$ ) in Hertz. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl<sub>3</sub>:  $\delta_C$  = 77.0 ppm; residual CHCl<sub>3</sub> in CDCl<sub>3</sub>:  $\delta_H$  = 7.24 ppm; CD<sub>2</sub>Cl<sub>2</sub>:  $\delta_C$  = 53.8 ppm; residual CH<sub>2</sub>Cl<sub>2</sub> in CD<sub>2</sub>Cl<sub>2</sub>:  $\delta_H$  = 5.32 ppm). **Where indicated, the signal assignments are unambiguous; the numbering scheme is arbitrary and is shown in the inserts. The assignments are based upon 1D and 2D spectra recorded using the following pulse sequences from the Bruker standard pulse program library: DEPT; COSY (*cosygs* and *cosydgtp*); HSQC (*invietgssi*) optimized for  $^1J(C,H) = 145$  Hz; HMBC (*inv4gslprnd*) for correlations via  $^nJ(C,H)$ ; HSQC-TOCSY (*invietgsml*) using an MLEV17 mixing time of 120 ms.** IR: Nicolet FT-7199 spectrometer, wavenumbers ( $\tilde{\nu}$ ) in cm<sup>-1</sup>. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Finnigan MAT 95, accurate mass determination: Bruker APEX III FT-MS (7 T magnet). Melting points: Büchi melting point apparatus B-540 (corrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr.

**1,3,3a,6-Tetrahydro-indene-2,2-dicarboxylic acid diethyl ester (2a, X = C(COOEt)<sub>2</sub>).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 5.80-5.72 (m, 2H), 5.50 (m, 1H), 4.23-4.14 (m, 4H), 2.97-2.88 (m, 3H), 2.67-2.61 (m, 3H), 1.81 (virt. t,  $J = 12$  Hz, 1H), 1.27-1.21 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 172.5, 171.9, 138.7, 126.5, 125.2, 115.8, 61.5, 57.3, 40.1, 38.4, 38.2, 27.1, 14.0; IR (film):  $\tilde{\nu} = 3432, 3073, 3025, 2937, 2822, 1732, 1641, 1606, 1462, 1446, 1367, 1280, 1249, 1189, 1158, 1096, 1071, 1053, 1026, 861, 757$  cm<sup>-1</sup>; MS (ESI):  $m/z$  (%): 285 (100) [ $M^+ + Na - H_2$ ]; HRMS (ESI):  $m/z$ : calcd for C<sub>15</sub>H<sub>20</sub>O<sub>4</sub>: 285.1097 [ $M^+ + Na - H_2$ ]; found: 285.1097.

**2-(Toluene-4-sulfonyl)-2,3,3a,6-tetrahydro-1H-isoindole (2b, X = NTs).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):



$\delta = 7.68$  (d,  $J = 8.3$  Hz, 2H, H-10),  $7.28$  (d,  $J = 8.3$  Hz, 2H, H-11),  $5.74$  (dddd,  $J = 10.0, 3.5, 2.7, 1.2$  Hz, 1H, H-5),  $5.63$  (ddq,  $J = 10.0, 2.1, < 1$  Hz, 1H, H-6),  $5.52$  (m, 1H, H-3),  $3.98$  (ddt,  $J = 13.2, 2.6, 1.7$  Hz, 1H, H-1a),  $3.80$  (ddd,  $J = 8.8, 8.0, < 1$  Hz, 1H, H-8a),  $3.69$  (dq,  $J = 13.2, 1.6$  Hz, 1H, H-1b),  $2.94$  (m, 1H, H-7),  $2.63$  (dd,  $J = 11.4, 8.8$  Hz, 1H, H-8b),  $2.59$  (m, 2H, H-4),  $2.39$  (s, 3H, H-13); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 143.4$  (C-12),  $134.8$  (C-9),  $133.7$  (C-2),  $129.6$  (C-11),  $127.5$  (C-10),  $126.7$  (C-5),  $123.1$  (C-6),  $117.1$  (C-3),  $52.8$  (C-8),  $50.7$  (C-1),  $37.8$  (C-7),  $26.6$  (C-4),  $21.5$  (C-13); IR (film):  $\tilde{\nu} = 3029, 2920, 2861, 1639, 1597, 1493, 1459, 1344, 1306, 1163, 1095, 1048, 1017, 816, 750, 705, 664, 591, 551$  cm<sup>-1</sup>; MS (EI):  $m/z$  (%): 275

(11) [ $M^+$ ], 155 (8), 120 (24), 91 (100), 65 (9), 42 (12); HRMS (ESI):  $m/z$ : calcd for C<sub>15</sub>H<sub>17</sub>NO<sub>2</sub>+Na: 298.0872 [ $M^+$ +Na]; found: 298.0872; elemental analysis calcd (%) for C<sub>15</sub>H<sub>17</sub>NO<sub>2</sub>: C 65.43, H 6.22, N 5.09; found: C 65.37, H 6.14, N 4.96.

**2,2-Bis(phenylsulfonyl)-2,3,3a,6-tetrahydro-1H-indene (2c, X = C(SO<sub>2</sub>Ph)<sub>2</sub>).** m.p. = 157–158 °C, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.11$  (dm,  $J = 7$  Hz, 2H),  $7.92$  (dm,  $J = 7$  Hz, 2H),  $7.71$  (tm,  $J = 7$  Hz, 1H),  $7.66$ – $7.58$  (m, 3H),  $7.52$  (t,  $J = 7$  Hz, 2H),  $5.66$  (m, 2H),  $5.16$  (m, 1H),  $3.23$  (dm,  $J = 17$  Hz, 1H),  $3.04$ – $2.90$  (m, 3H),  $2.51$  (m, 1H),  $2.33$  (m, 1H),  $2.21$  (dd,  $J = 14, 11$  Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 136.5, 136.2, 135.0, 135.0, 134.3, 131.3, 131.1, 128.7, 128.6, 124.9, 124.8, 117.1, 89.8, 37.9, 37.6, 36.9, 26.7$ ; IR (film):  $\tilde{\nu} = 3066, 3028, 2887, 2818, 2257, 1584, 1448, 1330, 1311, 1146, 1079, 999, 912, 732, 688, 619, 578, 554, 529$  cm<sup>-1</sup>; MS (ESI):  $m/z$  (%): 258 (68), 143 (29), 125 (22), 115 (100), 91 (20), 77 (29); HRMS (ESI):  $m/z$ : calcd for C<sub>21</sub>H<sub>20</sub>O<sub>4</sub>S<sub>2</sub>+Na: 423.0695 [ $M^+$ +Na]; found: 423.0694.

**4-Methyl-1,3,3a,6-tetrahydro-indene-2,2-dicarboxylic acid diethyl ester (5, E = COOEt).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 5.48$  (m, 1H),  $5.40$  (m, 1H),  $4.22$ – $4.15$  (m, 4H),  $2.99$ – $2.92$  (m, 2H),  $2.82$  (m, 1H),  $2.71$ – $2.63$  (m, 3H),  $1.81$  (dd,  $J = 12, 12$  Hz, 1H),  $1.72$  (s, 3H),  $1.27$ – $1.21$  (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta = 172.7, 172.0, 138.5, 133.3, 119.6, 116.1, 61.7, 61.6, 56.9, 42.3, 39.3, 38.3, 28.2, 21.3, 14.2$ ; IR (film):  $\tilde{\nu} = 3460, 2981, 2935, 2820, 1733, 1602, 1465, 1446, 1366, 1280, 1250, 1179, 1160, 1096, 1070, 1029, 860, 792$  cm<sup>-1</sup>; MS (ESI):  $m/z$  (%): 278 (30) [ $M^+$ +Na], 204 (50), 175 (10), 158 (10), 131 (100), 91 (20); HRMS (ESI):  $m/z$ : calcd for C<sub>16</sub>H<sub>22</sub>O<sub>4</sub>+Na: 301.1410 [ $M^+$ +Na]; found: 301.1410.

**6-Methyl-1,3,3a,6-tetrahydro-indene-2,2-dicarboxylic acid diethyl ester (7, E = COOEt).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 5.71$  (d,  $J = 10$  Hz, 1H),  $5.56$  (d,  $J = 10$  Hz, 1H),  $5.30$  (s, 1H),  $4.18$  (m, 4H),  $2.99$  (d,  $J = 17$  Hz, 1H),  $2.87$  (d,  $J = 17$  Hz, 1H),  $2.84$  (m, 1H),  $2.74$  (m, 1H),  $2.60$  (dd,  $J = 12, 7$  Hz, 1H),  $1.76$  (virt. t,  $J = 12$  Hz, 1H),  $1.24$  (m, 6H),  $1.05$  (d,  $J = 7$  Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta = 172.4, 171.8, 137.9, 131.9, 125.2, 122.4, 61.5, 61.4, 57.8, 39.9, 38.6, 37.8, 31.3, 21.9, 14.0$ ; IR (film):  $\tilde{\nu} = 3460, 3018, 2980, 2962, 2872, 2828, 1732, 1639, 1447, 1367, 1298, 1252, 1186, 1159, 2096, 1070, 1057, 861, 700$  cm<sup>-1</sup>; MS (ESI):  $m/z$  (%): 276 (30) [ $M^+$ +Na-H<sub>2</sub>], 263 (10), 202 (100), 175 (30), 157 (15), 143 (20), 131 (80), 115 (30), 91 (25).

**7-Tributylstannanyl-1,3,3a,6-tetrahydro-indene-2,2-dicarboxylic acid diethyl ester (9a, R = SnBu<sub>3</sub>).**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 5.78$ – $5.75$  (m, 2H),  $4.21$ – $4.15$  (m, 4H),  $2.96$  (m, 1H),  $2.90$ – $2.74$  (m, 4H),

2.61 (m, 1H), 1.85 (dd,  $J = 12$ , 12 Hz, 1H), 1.52-1.44 (m, 6H), 1.33-1.21 (m, 12H), 0.95-0.86 (m, 15H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 172.4, 171.8, 147.5, 128.1, 126.9, 126.0, 61.5, 57.4, 40.4, 40.0, 39.2, 33.7, 29.2, 27.4, 14.0, 13.7, 9.4$ ; IR (film):  $\tilde{\nu} = 3023, 2957, 2927, 2871, 2853, 2813, 1734, 1666, 1631, 1464, 1366, 1297, 1253, 1184, 1156, 1095, 1071, 1031, 960, 862, 693, 667\text{ cm}^{-1}$ ; MS (ESI):  $m/z$  (%): 553 (16) [ $M^+$ ], 497 (100), 441 (6), 165 (9), 117 (8); HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{27}\text{H}_{46}\text{O}_4\text{Sn}+\text{Na}$ : 577.2310 [ $M^++\text{Na}$ ]; found: 577.2304.

**7-Acetoxymethyl-1,3,3a,6-tetrahydro-indene-2,2-dicarboxylic acid diethyl ester (9b, R =  $\text{CH}_2\text{OAc}$ ).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 5.87$  (s, 2H), 4.67 (s, 2H), 4.32-4.26 (m, 4H), 3.37-3.04 (m, 3H), 2.76-2.72 (m, 3H), 2.13 (s, 3H), 1.89 (virt. t,  $J = 12$  Hz, 1H), 1.37-1.31 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 171.4, 171.2, 170.7, 137.7, 125.8, 124.8, 121.3, 64.0, 61.3, 57.3, 39.6, 38.9, 35.3, 28.3, 20.6, 13.7$ ; IR (film):  $\tilde{\nu} = 3416, 2982, 2939, 2906, 1734, 1602, 1464, 1381, 1249, 1193, 1180, 1160, 1097, 1026, 861, 781\text{ cm}^{-1}$ ; MS (EI):  $m/z$  (%): 334 (16) [ $M^+-\text{H}_2$ ], 274 (75), 201 (100), 173 (20), 129 (50); HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{18}\text{H}_{24}\text{O}_6$ : 357.1309 [ $M^++\text{Na}-\text{H}_2$ ]; found: 357.1305.

**3-(2-Tosyl-2,3,5,7a-tetrahydro-1H-isoindol-5-yl)propan-1-ol (12).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.72$  (d,  $J = 8$  Hz, 2H), 7.32 (d,  $J = 8$  Hz, 2H), 5.65 (m, 2H), 5.41 (br. s, 1H), 4.00 (d,  $J = 13$  Hz, 1H), 3.82 (virt. t,  $J = 8$  Hz, 1H), 3.72 (d,  $J = 13$  Hz, 1H), 3.59 (m, 2H), 2.95 (m, 1H), 2.74 (m, 1H), 2.64 (dd,  $J = 11, 9$  Hz, 1H), 2.42 (s, 3H), 1.51-1.37 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 143.4, 135.0, 134.1, 131.7, 129.7, 127.5, 122.9, 121.8, 62.9, 52.8, 50.7, 38.3, 35.6, 31.3, 29.3, 21.5$ ; IR (film):  $\tilde{\nu} = 3552, 2936, 2862, 1597, 1453, 1341, 1161, 1094, 1049, 816, 665\text{ cm}^{-1}$ ; MS (EI):  $m/z$  (%): 274 (28), 178 (19), 149 (12), 118 (13), 105 (27), 91 (100); HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{18}\text{H}_{23}\text{NO}_3\text{S}+\text{Na}$ : 356.1291 [ $M^++\text{Na}$ ]; found: 356.1293.

**3-Methylene-4-(2-(tetrahydrofuran-2-yl)vinyl)-1-tosylpyrrolidine (13).**  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 7.67$  (d,  $J = 8$  Hz, 2H), 7.35 (d,  $J = 8$  Hz, 2H), 5.54 (m, 1H), 5.34 (m, 1H), 4.95 (m, 1H), 4.82 (m, 1H), 4.20 (m, 1H), 3.96 (m, 1H), 3.80 (m, 1H), 3.72-3.66 (m, 2H), 3.57 (m, 1H), 3.21 (m, 1H), 2.82 (m, 1H), 2.43 (s, 3H), 1.99 (m, 1H), 1.94-1.82 (m, 2H), 1.54 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 146.7, 143.5, 134.6, 129.5, 128.4, 128.0, 127.5, 108.0, 78.9, 67.9, 53.4, 51.7, 46.0, 32.1, 25.6, 21.3$ ; IR (film):  $\tilde{\nu} = 2864, 1347, 1162, 1094, 1050, 815, 663\text{ cm}^{-1}$ ; MS (EI):  $m/z$  (%): 333 (5) [ $M^+$ ], 262 (15), 178 (84), 150 (20), 91 (58), 79 (28), 71 (100); HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{18}\text{H}_{23}\text{NO}_3\text{S}+\text{Na}$ : 356.1291 [ $M^++\text{Na}$ ]; found: 356.1287.

**7-Phenyl-1,3,3a,6-tetrahydro-indene-2,2-dicarboxylic acid diethyl ester (16, E =  $\text{COOEt}$ ).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.36$ -7.14 (m, 5H), 5.82-5.75 (m, 2H), 4.16-3.98 (m, 4H), 3.07-2.95 (m, 3H), 2.88-2.78 (m, 2H), 2.59 (dd,  $J = 12, 7$  Hz, 1H), 1.81 (virt. t,  $J = 12$  Hz, 1H), 1.19 (t,  $J = 7$  Hz, 3H), 1.10 (t,  $J = 7$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 172.4, 171.8, 141.5, 134.5, 128.5, 128.1, 127.9, 126.7, 126.5, 125.5, 61.6, 61.4, 57.6, 40.2, 39.5, 37.1, 32.2, 14.0, 13.9$ ; IR (film):  $\tilde{\nu} = 3026, 2980, 2936, 2816, 1730, 1600, 1575, 1541, 1493, 1465, 1444, 1387, 1366, 1254, 1183, 1155, 1095, 1072, 1031, 860, 760, 701\text{ cm}^{-1}$ ; MS (ESI):  $m/z$  (%): 340 (40) [ $M^+$ ], 266 (87), 193 (100), 192 (77), 191 (32), 178 (38), 165 (23); HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{21}\text{H}_{24}\text{O}_4+\text{Na}$ : 363.1567 [ $M^++\text{Na}$ ]; found: 363.1570.

**4-Vinyl-1,3,3a,4-tetrahydro-cyclopenta[b]naphthalene-2,2-dicarboxylic acid diethyl ester (18, E = COOEt).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.17-7.10 (m, 3H), 7.04-7.02 (m, 1H), 6.34 (s, 1H), 5.89 (m, 1H), 5.34 (dd, *J* = 10, 2 Hz, 1H), 5.24 (dd, *J* = 17, 2 Hz, 1H), 4.22-4.17 (m, 4H), 3.29 (d, *J* = 18 Hz, 1H), 3.21 (m, 1H), 3.10 (d, *J* = 18 Hz, 1H), 2.66-2.62 (m, 2H), 2.02 (m, 1H), 1.28-1.22 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 171.3, 143.8, 138.4, 135.7, 134.6, 126.5, 126.1, 125.8, 125.4, 119.3, 118.1, 61.3, 61.2, 58.8, 50.0, 42.8, 39.4, 38.4, 13.7; IR (film):  $\tilde{\nu}$  = 3459, 3063, 2980, 2936, 2907, 2849, 1731, 1665, 1599, 1478, 1450, 1367, 1280 1246, 1187, 1157, 1067, 999, 921, 864, 755 cm<sup>-1</sup>; MS (ESI): *m/z* (%): 340 (28) [*M*<sup>+</sup>], 295 (10), 266 (100), 193 (76), 173 (70) 165 (28), 153 (16), 128 (19); HRMS (ESI): *m/z*: calcd for C<sub>21</sub>H<sub>24</sub>O<sub>4</sub>+Na: 363.1567 [*M*<sup>+</sup>+Na]; found: 363.1567.

**Diethyl 6-methyl-5,7a-dihydro-1H-indene-2,2(3H)-dicarboxylate (20).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 5.48 (m, 2H), 4.19 (q, *J* = 7 Hz, 2H), 4.16 (q, *J* = 7 Hz, 2H), 3.00-2.85 (m, 3H), 2.63-2.47 (m, 3H), 1.75 (virt. t, *J* = 12 Hz, 1H), 1.70 (s, 3H), 1.25 (t, *J* = 7 Hz, 3H), 1.22 (t, *J* = 7 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 172.5, 172.0, 138.8, 132.7, 120.9, 115.7, 61.5, 61.4, 57.7, 40.3, 39.7, 37.9, 32.1, 22.9, 14.1; IR (film):  $\tilde{\nu}$  = 2980, 1731, 1446, 1366, 1250, 1176, 1067, 1023 cm<sup>-1</sup>; MS (EI): *m/z* (%): 278 (9) [*M*<sup>+</sup>], 239 (40), 193 (100), 175 (21), 159 (12), 147 (15), 131 (65), 115 (17), 91 (41), 81 (45); HRMS (ESI): *m/z*: calcd for C<sub>16</sub>H<sub>22</sub>O<sub>4</sub>+Na: 301.1410 [*M*<sup>+</sup>+Na]; found: 301.1409; elemental analysis calcd (%) for C<sub>16</sub>H<sub>22</sub>O<sub>4</sub>: C 68.93, H 8.06, found: C 69.04, H 7.97.

**6-(3-(*tert*-Butyldimethylsilyloxy)propyl)-2-tosyl-2,3,3a,6-tetrahydro-1H-isoindole (22b, X = OSiMe<sub>2</sub>tBu).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.71 (d, *J* = 8 Hz, 2H), 7.31 (d, *J* = 8 Hz, 2H), 5.84 (m, 2H), 5.41 (m, 1H), 4.00 (d, *J* = 13 Hz, 1H), 3.83 (virt t, *J* = 8 Hz, 1H), 3.74 (d, *J* = 13 Hz, 1H), 3.56 (m, 2H), 2.94 (m, 1H), 2.72 (m, 1H), 2.65 (dd, *J* = 11, 9 Hz, 1H), 2.42 (s, 3H), 1.43 (m, 4H), 0.88 (s, 9H), 0.02 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 143.4, 134.9, 134.2, 132.0, 129.7, 127.5, 122.8, 122.1, 63.1, 52.8, 50.7, 38.4, 35.6, 31.5, 29.5, 26.0, 21.5, 18.3, -5.3; IR (film):  $\tilde{\nu}$  = 2928, 2856, 1598, 1471, 1346, 1161, 1093, 1051, 833, 774, 708, 662 cm<sup>-1</sup>; MS (EI): *m/z* (%): 390 (100), 292 (52), 274 (18), 207 (43), 131 (24), 105 (20), 91 (69); HRMS (ESI): *m/z*: calcd for C<sub>24</sub>H<sub>37</sub>NO<sub>2</sub>SSi+Na: 470.2156 [*M*<sup>+</sup>+Na]; found: 470.2160; elemental analysis calcd (%) for C<sub>24</sub>H<sub>37</sub>NO<sub>2</sub>SSi: C 64.39, H 8.53, N 3.13; found: C 64.26, H 8.28, N 3.18.

**6-(3-Iodopropyl)-2-tosyl-2,3,3a,6-tetrahydro-1H-isoindole (22c, X = I).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.71 (d, *J* = 8 Hz, 2H), 7.31 (d, *J* = 8 Hz, 2H), 5.68 (d, *J* = 10 Hz, 1H), 5.63 (d, *J* = 10 Hz, 1H), 5.38 (s, 1H), 4.02 (d, *J* = 13 Hz, 1H), 3.83 (dd, *J* = 8, 7.5 Hz, 1H), 3.74 (d, *J* = 13 Hz, 1H), 3.11 (t, *J* = 7 Hz, 2H), 2.95 (m, 1H), 2.76 (m, 1H), 2.64 (dd, *J* = 11, 9 Hz, 1H), 2.43 (s, 3H), 1.69 (m, 2H), 1.52 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 143.4, 135.4, 134.1, 131.2, 129.7, 127.5, 123.3, 121.4, 52.8, 50.7, 38.3, 35.8, 35.1, 30.1, 21.6, 6.7; IR (film):  $\tilde{\nu}$  = 2921, 2856, 1597, 1455, 1343, 1217, 1161, 1094, 1054, 816, 761, 707, 663 cm<sup>-1</sup>; MS (EI): *m/z* (%): 443 (<5) [*M*<sup>+</sup>], 274 (74), 259 (15), 118 (12), 91 (100); HRMS (ESI): *m/z*: calcd for C<sub>18</sub>H<sub>22</sub>NO<sub>2</sub>SI+Na: 466.0308 [*M*<sup>+</sup>+Na]; found: 466.0319; elemental analysis calcd (%) for C<sub>18</sub>H<sub>22</sub>NO<sub>2</sub>SI: C 48.77, H 5.00, N 3.16; found: C 48.70, H 4.92, N 3.22.

**2-(Toluene-4-sulfonyl)-1,2,3,7a-tetrahydro-pyrano[3,4-c]pyrrole (24a, R = H).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.71 (d, *J* = 8 Hz, 2H), 7.32 (d, *J* = 8 Hz, 2H), 6.30 (m, 2H), 4.77 (dd, *J* = 6, 2 Hz, 1H), 3.89

(d,  $J = 13$  Hz, 1H), 3.86 (d,  $J = 13$  Hz, 1H), 3.75 (dd,  $J = 9, 7$  Hz, 1H), 3.10 (m, 1H), 2.93 (dd,  $J = 10, 9$  Hz, 1H), 2.43 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 143.6, 141.7, 134.9, 134.0, 129.8, 127.5, 112.8, 100.0, 54.4, 47.9, 32.4, 21.5$ ; IR (film):  $\tilde{\nu} = 3451, 3062, 2923, 2866, 1729, 1673, 1597, 1453, 1343, 1291, 1266, 1162, 1093, 1064, 815, 668, 548\text{ cm}^{-1}$ ; MS (EI):  $m/z$  (%): 277 (<5) [ $M^+$ ], 155 (30), 122 (100), 91 (90), 65 (40); HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{14}\text{H}_{15}\text{O}_3\text{NS}+\text{Na}$ : 300.0665 [ $M^++\text{Na}$ ]; found: 300.0666.

**6-Methyl-2-(toluene-4-sulfonyl)-1,2,3,7a-tetrahydro-pyrano[3,4-c]pyrrole (24b, R = Me).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.69$  (d,  $J = 8$  Hz, 2H), 7.31 (d,  $J = 8$  Hz, 2H), 6.30 (s, 1H), 4.49 (s, 1H), 3.89 (d,  $J = 12$  Hz, 1H), 3.79 (d,  $J = 12$  Hz, 1H), 3.71 (dd,  $J = 9, 8$  Hz, 1H), 3.10 (m, 1H), 2.79 (dd,  $J = 9, 9$  Hz, 1H), 2.41 (s, 3H), 1.71 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 148.6, 142.5, 134.0, 133.1, 128.7, 126.5, 111.5, 94.3, 53.7, 46.9, 33.0, 20.5, 17.8$ ; IR (film):  $\tilde{\nu} = 3452, 3064, 2958, 2923, 2868, 1923, 1719, 1617, 1597, 1343, 1162, 1094, 1063, 816, 667, 708, 667, 607, 548\text{ cm}^{-1}$ ; MS (EI):  $m/z$  (%): 291 (<5) [ $M^+$ ], 136 (100), 108 (29), 91 (12).

**6-Phenyl-2-(toluene-4-sulfonyl)-1,2,3,7a-tetrahydro-pyrano[3,4-c]pyrrole (24c, R = Ph).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.71$  (d,  $J = 8$  Hz, 2H), 7.48 (m, 3H), 7.33-7.30 (m, 4H), 6.51 (s, 1H), 5.27 (s, 1H), 4.00 (d,  $J = 13$  Hz, 1H), 3.90 (d,  $J = 13$  Hz, 1H), 3.85 (d,  $J = 8$  Hz, 1H), 3.34 (m, 1H), 2.88 (virt. t,  $J = 9$  Hz, 1H), 2.41 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 150.3, 143.6, 135.2, 133.8, 133.4, 129.8, 128.8, 128.3, 127.5, 124.7, 112.8, 95.4, 54.6, 47.8, 34.2, 21.5$ ; IR (film):  $\tilde{\nu} = 3428, 3061, 2949, 2862, 1715, 1672, 1597, 1494, 1449, 1343, 1267, 1162, 1136, 1095, 1060, 879, 815, 764, 736, 666, 566, 548\text{ cm}^{-1}$ ; MS (EI):  $m/z$  (%): 353 (<5) [ $M^+$ ], 198 (100), 170 (22), 141 (14); HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{20}\text{H}_{19}\text{O}_3\text{NS}+\text{Na}$ : 376.0978 [ $M^++\text{Na}$ ]; found: 376.0979.

**3,7a-Dihydro-1H-furo[3,4-c]pyran (26).**  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 6.40$ -6.36 (m, 2H), 4.85 (dd,  $J = 6, 2$  Hz, 1H), 4.28 (d,  $J = 11$  Hz, 1H), 4.20 (dm,  $J = 11$  Hz, 1H), 4.06 (dd,  $J = 7, 7$  Hz, 1H), 3.30 (dd,  $J = 10, 7$  Hz, 1H), 3.20 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta = 142.4, 134.3, 116.7, 101.0, 74.1, 67.3, 34.2$ ; IR (film):  $\tilde{\nu} = 3410, 2977, 2674, 2481, 1717, 1681, 1392, 1359, 1289, 1240, 1158, 1065, 1030, 836, 807\text{ cm}^{-1}$ ; MS (EI):  $m/z$  (%): 124 (10), 94 (100), 66 (47), 39 (34); HRMS (ESI):  $m/z$ : calcd for  $\text{C}_7\text{H}_8\text{O}_2$ : 124.0524 [ $M^+$ ]; found: 124.0522.

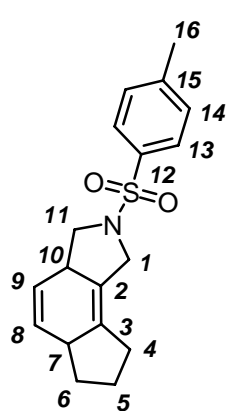
**Diethyl 4a,5-dihydrocyclopenta[c]pyran-6,6(7H)-dicarboxylate (28a, R = H, E = COOEt).**  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 6.31$  (dd,  $J = 6, 2$  Hz, 1H), 6.25 (m, 1H), 4.85 (dd,  $J = 6, 2$  Hz, 1H), 4.18-4.10 (m, 4H), 3.00 (m, 1H), 2.94 (d,  $J = 16$  Hz, 1H), 2.78 (dt,  $J = 16, 2$  Hz, 1H), 2.57 (dd,  $J = 13, 7$  Hz, 1H), 1.92 (dd,  $J = 13, 11$  Hz, 1H), 1.23-1.18 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta = 172.6, 172.0, 141.1, 134.2, 117.2, 103.4, 62.2, 62.1, 56.9, 42.8, 35.7, 33.4, 14.4$ ; IR (film):  $\tilde{\nu} = 2983, 1726, 1632, 1446, 1367, 1252, 1180, 1064, 939, 856, 747\text{ cm}^{-1}$ .

**Diethyl 3-phenyl-4a,5-dihydrocyclopenta[c]pyran-6,6(7H)-dicarboxylate (28b, R = Ph, E = COOEt).**  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 7.54$ -7.52 (m, 2H), 7.34-7.28 (m, 3H), 6.48 (s, 1H), 5.40 (s, 1H), 4.21-4.11 (m, 4H), 3.23 (m, 1H), 3.03 (d,  $J = 16$  Hz, 1H), 2.90 (m, 1H), 2.68 (dd,  $J = 13, 7$  Hz, 1H), 2.01 (dd,  $J = 13, 11$  Hz, 1H), 1.26-1.19 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta = 172.6, 172.0, 149.8, 134.9, 134.6, 128.9, 128.8, 125.2, 117.2, 99.3, 62.3, 62.2, 57.4, 42.8, 35.4, 35.3, 14.4$ ; IR (film):  $\tilde{\nu} = 2982, 1726, 1447, 1366, 1250, 1181, 1066, 1011, 859, 761, 691\text{ cm}^{-1}$ ; MS (EI):  $m/z$  (%): 280 (<5) [ $M^+$ ], 342 (50), 313 (16),

297 (16), 269 (56), 239 (20), 223 (21), 195 (100), 170 (35), 105 (84), 77 (23); HRMS (ESI):  $m/z$ : calcd for  $C_{20}H_{22}O_5+Na$ : 365.1359 [ $M^++Na$ ]; found: 365.1358.

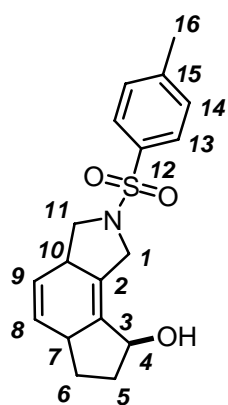
**2-Tosyl-2,3,3a,5a,6,7-hexahydro-1H-cyclobuta[e]isoindole (34).**  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.73 (d,  $J$  = 8 Hz, 2H), 7.31 (d,  $J$  = 8 Hz, 2H), 5.74 (dm,  $J$  = 9 Hz, 1H), 5.61 (dm,  $J$  = 9 Hz, 1H), 3.86-3.89 (m, 2H), 3.73 (dm,  $J$  = 14 Hz, 1H), 3.33 (m, 1H), 2.95 (m, 1H), 2.72 (m, 1H), 2.63 (dd,  $J$  = 10, 9 Hz, 1H), 2.42 (s, 3H), 2.35 (m, 1H), 2.19 (m, 1H), 1.60 (m, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  = 143.4, 134.3, 133.7, 129.7, 129.5, 127.7, 125.9, 122.2, 52.9, 47.8, 43.8, 37.9, 29.8, 28.0, 21.5; IR (film):  $\tilde{\nu}$  = 2944, 2857, 1597, 1457, 1345, 1161, 1097, 1027, 816, 659  $cm^{-1}$ ; MS (EI):  $m/z$  (%) 301 (<5) [ $M^+$ ], 197 (11), 146 (100), 130 (26), 117 (91), 91 (52); HRMS (ESI):  $m/z$ : calcd for  $C_{17}H_{19}NO_2S+Na$ : 324.1029 [ $M^++Na$ ]; found: 324.1029.

**2-Tosyl-1,2,3,3a,5a,6,7,8-octahydrocyclopenta[e]isoindole (35).**  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.70



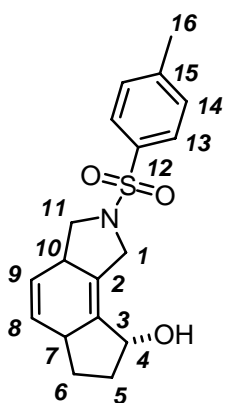
(d,  $J$  = 8.2 Hz, 2H, H-13), 7.29 (d,  $J$  = 8.2 Hz, 2H, H-14), 5.84 (dt,  $J$  = 9.6, 2.3 Hz, 1H, H-9), 5.61 (ddd,  $J$  = 9.6, 2.8, 1.9 Hz, 1H, H-8), 3.92 (dddt,  $J$  = 13.8, 3.6, 2.2, 1.8 Hz, 1H, H-1a), 3.85 (dd,  $J$  = 9.0, 8.2 Hz, 1H, H-11a), 3.62 (ddm,  $J$  = 13.8, 1.8 Hz, 1H, H-1b), 3.03 (dddt, 1H,  $J$  = 11.2, 8.0, 3.0, 1.6 Hz, H-10), 2.69 (m, 1H, H-7), 2.53 (dd,  $J$  = 11.2, 9.0 Hz, 1H, H-11b), 2.40 (s, 3H, H-16), 2.17 (dddd,  $J$  = 16.6, 10.0, 2.6, 2.4 Hz, 1H, H-4a), 2.08 (dddm,  $J$  = 16.4, 9.2, 8.8 Hz, 1H, H-4b), 2.01 (dtm,  $J$  = 11.8, 6.9 Hz, 1H, H-6a), 1.76 (dddd,  $J$  = 12.7, 8.8, 7.1, 2.8, 1.5 Hz, 1H, H-5a), 1.64 (dddd,  $J$  = 12.9, 11.7, 10.0, 9.2, 6.6 Hz, 1H, H-5b), 1.03 (dq,  $J$  = 12.0, 7.4 Hz, 1H, H-6b);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  = 143.4 (C-15), 135.2 (C-3\*), 133.9 (C-12), 130.5 (C-9), 129.6 (C-14), 127.6 (C-13), 124.7 (C-2\*), 124.1 (C-8), 52.6 (C-11), 49.0 (C-1), 42.0 (C-7), 39.6 (C-10), 32.2 (C-6), 27.4 (C-4), 24.0 (C-5), 21.5 (C-16) (signals marked \* may be interchanged); IR (film):  $\tilde{\nu}$  = 3023, 2951, 2864, 1597, 1344, 1160, 1093, 1040, 903, 815, 743, 663  $cm^{-1}$ ; MS (EI):  $m/z$  (%) 315 (12) [ $M^+$ ], 160 (36), 131 (100), 117 (51), 91 (44), 42 (32); HRMS (ESI):  $m/z$ : calcd for  $C_{18}H_{21}NO_2S+Na$ : 338.1185 [ $M^++Na$ ]; found: 338.1183.

**2-Tosyl-1,2,3,3a,5a,6,7,8-octahydrocyclopenta[e]isoindol-8-ol (37).** Mixture of isomers (dr = 3:2).



**Major isomer:**  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.70 (d,  $J$  = 8.3 Hz, 2H, H-13), 7.28 (d,  $J$  = 8.3 Hz, 2H, H-14), 5.85 (ddd,  $J$  = 9.6, 2.8, 1.8 Hz, 1H, H-9), 5.63 (ddd,  $J$  = 9.6, 3.0, 1.8 Hz, 1H, H-8), 4.67 (ddm,  $J$  = 6.8, 4.8 Hz, 1H, H-4), 4.14 (ddt,  $J$  = 14.6, 3.4, 1.8 Hz, 1H, H-1a), 4.06 (ddt,  $J$  = 14.6, 3.5, 1.6 Hz, 1H, H-1b), 3.90 (dd,  $J$  = 8.8, 8.0 Hz, 1H, H-11a), 3.10 (m, 1H, H-10), 2.67 (dddt,  $J$  = 11.3, 8.4, 3.0, 1.8 Hz, 1H, H-7), 2.53 (dd,  $J$  = 11.3, 8.9 Hz, 1H, H-11b), 2.39 (s, 3H, H-16), 1.95 (dddt,  $J$  = 12.0, 7.0, 1.4, 0.7, 1H, H-6a), 1.87 (ddt,  $J$  = 13.6, 12.0, 6.8 Hz, 1H, H-5a), 1.71 (ddt,  $J$  = 13.7, 6.8, 1.5 Hz, 1H, H-5b), 1.36 (dq,  $J$  = 12.0, 7.0 Hz, 1H, H-6b), 1.16 (br. s, 1H, -OH);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  = 143.5 (C-15), 137.1 (C-3), 133.4 (C-12), 131.1 (C-2), 130.9 (C-9), 129.7 (C-14), 127.8 (C-13), 124.5 (C-8), 71.5 (C-4), 52.1 (C-11), 48.3 (C-1), 42.0 (C-7), 40.5 (C-10), 35.7 (C-5), 29.0 (C-6), 21.5 (C-16).

**Minor isomer:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.71 (d,  $J$  = 8.3 Hz, 2H, H-13), 7.30 (d,  $J$  = 8.3 Hz, 2H, H-14), 5.81 (ddd,  $J$  = 9.6, 2.6, 1.8 Hz, 1H, H-9), 5.60 (ddd,  $J$  = 9.6, 2.8, 1.8 Hz, 1H, H-8), 4.46 (tdt,  $J$  = 7.0, 1.5, < 1 Hz, 1H, H-4), 4.11 (ddt,  $J$  = 14.4, 3.5, 1.6 Hz, 1H, H-1a), 3.89 (dd,  $J$  = 9.0, 8.3 Hz, 1H, H-11a), 3.79 (ddd,  $J$  = 14.4, 2.7, 2.0 Hz, 1H, H-1b), 3.07 (dddt,  $J$  = 10.7, 9.4, 2.8, 1.8 Hz, 1H, H-10), 2.97 (m, 1H, H-7), 2.57 (dd,  $J$  = 10.7, 9.3 Hz, 1H, H-11b), 2.41 (s, 3H, H-16), 2.20 (ddt,  $J$  = 13.3, 7.3, 1.7 Hz, 1H, H-5a), 2.09 (ddt,  $J$  = 12.3, 7.2, 1.5 Hz, 1H, H-6a), 1.58 (ddt,  $J$  = 13.2, 12.0, 7.0 Hz, 1H, H-5b), 1.53 (br. s, 1H, -OH), 1.03 (dq,  $J$  = 11.8, 7.2 Hz, 1H, H-6b);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 143.5 (C-15), 136.8 (C-3), 133.7 (C-12), 130.6 (C-2), 130.5 (C-9), 129.7 (C-14), 127.7 (C-13), 123.8 (C-8), 71.4 (C-4), 52.1 (C-11), 48.4 (C-1), 40.0 (C-7), 39.7 (C-10), 35.4 (C-5), 29.7 (C-6), 21.5 (C-16); IR (film):  $\tilde{\nu}$  = 3458, 3027, 2927, 2853, 1733, 1597, 1457, 1346, 1155, 1091, 1043, 1010, 866, 816, 736, 660  $\text{cm}^{-1}$ ; MS (EI):  $m/z$  (%): 184 (15), 158 (17), 155 (16), 147 (15), 130 (100), 105 (21), 91 (35); HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{18}\text{H}_{21}\text{NO}_3\text{S}+\text{Na}$ : 354.1134 [ $M^++\text{Na}$ ]; found: 354.1138.



**Ethyl 2-(2-tosyl-1,2,3,3a,5a,6,7,8-octahydrocyclopenta[e]isoindol-8-yl)acetate (39).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.73 (d,  $J$  = 8.3 Hz, 2H, H-13), 7.33 (d,  $J$  = 8.3 Hz, 2H, H-14), 5.80 (ddd,  $J$  = 9.7, 2.8, 2.0 Hz, 1H, H-9), 5.59 (ddd,  $J$  = 9.6, 2.8, 2.0 Hz, 1H, H-8), 4.12 (q,  $J$  = 7.2 Hz, 2H, H-19), 3.97 (ddt,  $J$  = 13.8, 3.5, 1.8 Hz, 1H, H-1a), 3.84 (dd,  $J$  = 9.0, 8.2 Hz, 1H, H-11a), 3.66 (dt,  $J$  = 13.8, 2.0 Hz, 1H, H-1b), 3.05 (dt,  $J$  = 11.2, 8.0 Hz, 1H, H-10), 2.75-2.85 (m, 2H, H-4, H-7), 2.51 (dd,  $J$  = 11.0, 9.0 Hz, 1H, H-11b), 2.44 (dd,  $J$  = 15.4, 5.0 Hz, 1H, H-17a), 2.41 (s, 3H, H-16), 2.22 (dd,  $J$  = 15.4, 9.6 Hz, 1H, H-17b), 2.02 (m, 2H, H-5), 1.40 (dddd,  $J$  = 13.0, 12.0, 8.2, 6.8 Hz, 1H, H-6a), 1.25 (t,  $J$  = 7.1 Hz, 3H, H-20), 1.04 (dq,  $J$  = 12.0, 7.6 Hz, 1H, H-6b);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 172.1 (C-18), 143.5 (C-15), 137.6 (C-2), 133.8 (C-12), 130.2 (C-9), 129.7 (C-14), 127.6 (C-13), 126.1 (C-3), 123.7 (C-8), 60.4 (C-19), 52.3 (C-11), 48.5 (C-1), 41.3 (C-7), 39.8 (C-10), 39.8 (C-17), 37.0 (C-4), 31.7 (C-5), 31.4 (C-6), 21.5 (C-16), 14.3 (C-20); IR (film):  $\tilde{\nu}$  = 2926, 1731, 1652, 1598, 1447, 1346, 1265, 1161, 1094, 1042, 815, 753  $\text{cm}^{-1}$ ; MS (EI):  $m/z$  (%): 401 (17), 246 (67), 217 (24), 197 (17), 172 (18), 156 (27), 143 (38), 131 (100), 117 (20), 91 (82); HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{22}\text{H}_{27}\text{NO}_4\text{S}+\text{Na}$ : 424.1553 [ $M^++\text{Na}$ ]; found: 424.1557.

