# **ORGANOMETALLICS**

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### **Supporting Information**

General Procedure for the Reaction of N, N-bis(2-alkynyl)benzylamine with Manganese(II) chloride (189 mg, 1.5 mmol) was sonicated in THF under Triallylmanganate. argon atmosphere for 10 min. Allylmagnesium chloride (0.77 M THF solution, 5.84 mL, 4.5 mmol) was added to the suspension of MnCl2 at 0 °C. The mixture turned into a clear brown solution. After being stirred for 20 min, a solution of N,N-bis(2-nonyny)benzylamine (1a, 0.35) g, 1.0 mmol) in THF (2 mL) was added at 0 °C. The mixture was stirred at 0 °C for 3 h, quenched with MeOH (1 mL), and poured into water, and extracted with ethyl acetate (20 mL x 3). Concentration of dried organic layer provided a residual oil. The ratio (46:54) of products 2a and 3a was determined by the examination of <sup>1</sup>H NMR of crude product. Silica gel column chromatography purification afforded 9-aza-9-benzyl-(2,6-dihexyl)bicyclo[5.3.0]deca-1(7),2-diene (2a,  $R_f = 0.45$  (hex/AcOEt = 5/1), 180 mg, contaminated by unidentified by products) and bicyclo[5.3.0]deca-1(7), 3-diene (3a,  $R_f = 0.35$  (hex/AcOEt = 10/1), 138 mg, 35% isolated 9-aza-9-benzyl-2,6-dihexylbicyclo[5.3.0]deca-1(7),3-diene (3a): IR (neat) 2950, 2922, 2852, 2782, 2748, 1467, 1454, 726, 697 cm $^{-1}$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.86 (t, J=6Hz, 6H), 1.10-1.50 (m, 20H), 2.15 (m, 2H), 2.30 (m, 1H), 2.88 (m, 1H), 3.43 (m, 4H), 5.53 (dd, J = 4.5, 11.4 Hz, 1H), 5.65 (m, 1H), 7.23-7.36 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  14.00 (2C), 22.55, 22.58, 26.79, 27.32, 29.45, 29.49, 30.18, 31.75 (2C), 33.73, 34.40, 37.00, 39.58, 60.64, 64.58, 65.12, 126.95, 127.47, 128.36, 128.84, 132.02, 133.83, 137.99, 139.72. Found: C, 85.21; H, 10.98%. Calcd for C<sub>28</sub>H<sub>43</sub>N: C, 85.43; H, 11.01%. An analytically pure sample of 2a could not be obtained because of the contamination by unidentified by products. Thus the yield (30%) of 2a was calculated from the ratio (2a:3a = 46:54) determined by  ${}^{1}H$  NMR of crude product.

9-aza-9-benzyl-2,6-dimethylbicyclo[5.3.0]deca-1(7),3-diene (3b, 67:23 diastereomeric mixture): IR (neat) 2958, 2922, 2866, 2778, 2748, 1454, 742, 696 cm<sup>-1</sup>;  $^{1}$ H NMR (CDCl<sub>3</sub>)  $\delta$  1.01 (d, J = 7.2 Hz, 2.33H), 1.02 (d, J = 6.9 Hz, 0.67H), 1.12 (d, J = 7.5 Hz,

2.33H), 1.13 (d, J = 7.5 Hz, 0.67H), 2.12 (m, 1H), 2.36 (m, 2H), 2.85 (m, 0.23H), 3.00 (m, 0.67H), 3.40 (m, 2H), 3.53 (m, 2H), 3.75 (s, 2H), 5.55 (dd, J = 4.5, 11.1 Hz, 1H), 5.67 (m, 1H), 7.24–7.38 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) for a major product  $\delta$  19.72, 19.91, 31.65, 33.39 (2C), 60.55, 63.99, 64.16, 126.98, 127.37, 128.37, 128.85, 133.63, 136.06, 137.27, 139.68. The conpound **3b** was not stable enough to prepare a sample for elemental analysis and easily oxidized to give 9-aza-9-benzyl-2,6-dimethyl-bicyclo[5.3.0]deca-1(10),3,7-triene (**3b'**) (C<sub>18</sub>H<sub>21</sub>N) standing at 25 °C for 1 d. HRMS 251.1671 Calcd for C<sub>18</sub>H<sub>21</sub>N: M+ 251.1674.

General **Procedure** for the Reaction of N, N-(3-trimethylsilyl-2propynyl) benzylamine (1c) with trially lmanganate. Manganese(II) chloride (189 mg, 1.5 mmol) was sonicated in THF (5.0 mL) under argon atmosphere for 10 min. Allylmagnesium chloride (0.77 M THF solution, 5.84 mL, 4.5 mmol) was added at 0 °C. The mixture turned into a clear brown solution and then, after being stirred for 20 min at 0 °C, a solution of 1c (327 mg, 1.0 mmol) in THF (2 mL) was added at 0 °C. The whole was stirred at 0 °C for 3 h. Deuterium oxide ( 10 mmol) was added and the mixture was stirred for another 30 min at 25 °C. The mixture was poured into water extracted with ethyl acetate (3 x 20 mL). Purification of the products by silica gel column chromatography using hex/AcOEt = 10/1-5/1 as an eluant gave 6c ( $R_f = 0.50$  (hex/AcOEt = 10/1), 146 mg, 38% yield) and 4c ( $R_f = 0.35$  (hex/AcOEt = 5/1), 38 mg, 10% yield), and 5c $(R_f = 0.30 \text{ (hex/AcOEt} = 5/1), 38 \text{ mg}, 10\% \text{ yield)}$ . Physical data for 4c, 5c, and 6c are as follows. An examination of <sup>1</sup>H NMR of crude product containing dibenzyl ether as an internal standard revealed that the yields and ratio of products were 4c (16%), 5c (16%), and 6c (43%) (4c:5c:6c = 21:21:58), respectively.

### 9-aza-9-benzyl-[2,6-bis(trimethylsilyl)]-4-deuterio-5-

methylbicyclo[5.3.0]deca-1(7),2-diene (4c):  $^{1}$ H NMR (CDCl<sub>3</sub>)  $\delta$  -0.04 (s, 9H), 0.06 (s, 9H), 0.91 (d, J = 6.6 Hz, 3H), 1.27 (d, J = 5.1 Hz, 1H), 2.04 (dd, J = 2.7, 7.8 Hz, 1H), 2.25 (m, 1H), 3.33-3.72 (m, 4H), 3.73 (d, J = 13.5 Hz, 1H), 3.78 (d, J = 13.5 Hz, 1H), 6.14 (d, J = 7.2 Hz, 1H), 7.20-7.37 (m, 5H);  $^{13}$ C NMR (CDCl<sub>3</sub>)  $\delta$  -1.55, -0.61, 26.46, 37.85, 38.41 (t,

*d* = 18.9 Hz), 43.70, 60.72, 64.18, 66.44, 126.86, 128.31, 128.68, 130.23, 138.40, 139.79, 139.90, 141.33.

### 9-aza-9-benzyl-[2,6-bis(trimethylsilyl)]-2-deuterio-5-

methylbicyclo[5.3.0]deca-1(7),3-diene (5c): IR (neat) 2948, 2892, 2866, 2782, 1453, 1248, 836, 740, 696 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ –0.01 (s, 9H), 0.08 (s, 9H), 1.09 (d, J = 6.6 Hz, 3H), 1.50 (s, 1H), 2.50 (dq, J = 8.1, 8.1 Hz, 1H), 3.24–3.52 (m, 4H), 3.70 (d, J = 13.5 Hz, 1H), 3.76 (d, J = 13.5 Hz, 1H), 5.28 (d, J = 12 Hz, 1H), 5.70 (dd, J = 8.1, 12 Hz, 1H), 7.19–7.36 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ –0.75, 0.26, 24.03, 33.90, 37.51, 60.81, 66.37, 68.35, 126.13, 126.82, 127.73, 128.30, 128.62, 131.04, 133.07, 139.98. Elemental analysis was performed for a mixture of **4c** and **5c**. Found: C, 71.55; H, 9.35%. Calcd for C<sub>23</sub>H<sub>36</sub>DSi<sub>2</sub>N: C, 71.81; H, 9.43%.

### 8-aza-8-benzyl-2,5-bis(trimethylsilyl)-3-deuteriomethyl-4-

methylbicyclo[4.3.0]nona-1,5-diene (6c): IR (neat) 2950, 2916, 2892, 2784, 2754, 1455, 1334, 1250, 1163, 1146, 1061, 835, 753, 698, 634 cm<sup>-1</sup>;  $^{1}$ H NMR (CDCl<sub>3</sub>) δ 0.06 (s, 18H), 0.79–0.83 (m, 5H), 2.10 (q, J = 6.6 Hz, 2H), 3.26 (d, J = 13.2 Hz, 2H), 3.31 (d, J = 13.2 Hz, 2H), 3.66 (d, J = 12.9 Hz, 1H), 3.72 (d, J = 12.9 Hz, 1H), 7.24–7.33 (m, 5H);  $^{13}$ C NMR (CDCl<sub>3</sub>) δ 1.14, 18.43 (t, J = 18.9 Hz), 18.72, 22.55, 31.50, 37.00, 37.03, 57.49, 60.88, 127.09, 128.34, 129.04, 130.51, 138.59. Found: C, 71.74; H, 9.34%. Calcd for C<sub>23</sub>H<sub>36</sub>NSi<sub>2</sub>: C, 71.81; H, 9.34%.

9-aza-9-benzyl-2,6-bis(trimethylsilyl)bicyclo[5.3.0]deca-1(7),3-diene (5a): IR (neat) 3014, 2946, 2894, 2858, 2780, 1453, 1375, 1342, 1248, 1156, 1113, 1064, 940, 916, 837, 792, 750, 729 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  -0.01 (s, 9H), 0.06 (s, 9H), 1.68 (s, 1H), 2.05-2.13 (m, 1H), 2.30-2.40 (m, 2H), 3.21-3.41 (m, 4H), 3.70 (s, 2H), 5.61-5.74 (m, 2H), 7.24-7.31 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  -1.27, -0.66, 26.70, 28.29, 35.06, 60.58, 66.32, 66.72, 126.90, 128.31, 128.60, 128.74, 129.54, 131.96, 132.56, 139.69. The compound **5a** was easily oxidized to deca-1(10), 3,7-triene (**5a**'): IR (neat) 2950, 2894, 1519, 1455, 1378, 1356, 1247, 1153, 837,

797, 777, 731, 694, 651, 623 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.04 (s, 9H), 0.05 (s, 9H), 2.24 (m, 3H), 3.03 (m, 1H), 4.93 (s, 2H), 5.74 (m, 2H), 6.26 (d, J = 1.8 Hz, 2H), 6.37 (d, J = 1.8 Hz, 1H), 7.02 (m, 2H), 7.28 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  -1.68, -1.52, 24.03, 28.87, 28.94, 52.94, 117.63, 118.33, 122.21, 124.53, 126.70, 127.36, 128.62, 130.31, 130.33, 139.05. HRMS: 367.2142. Calcd for C<sub>22</sub>H<sub>33</sub>NSi<sub>2</sub> M<sup>+</sup> 367.2151.

## 8-aza-8-benzyl-2,5-bis(trimethylsilyl)-3-methylbicyclo[4.3.0]nona-1,5-diene

(6a): IR (neat) 2948, 2896, 2782, 2752, 1453, 1333, 1248, 1162, 1145, 1048, 962, 913, 896, 832, 748 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.04 (s, 9H), 0.07 (s, 9H), 0.79 (t, J = 6.9 Hz, 3H), 2.06–2.31 (m, 3H), 3.27–2.30 (m, 4H), 3.66 (d, J = 12.9 Hz, 1H), 3.71 (d, J = 12.9 Hz, 1H), 7.24–7.32 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  –1.58, 0.73, 17.98, 28.72, 33.20, 57.52, 57.59, 60.85, 124.68, 127.08, 128.33, 128.99, 132.87, 138.62, 143.37, 143.56. Found: C, 71.42; H, 9.60%. Calcd for C<sub>22</sub>H<sub>35</sub>NSi<sub>2</sub>: C, 71.47; H, 9.54%.

## 9-aza-9-benzyl-[2,6-bis(trimethylsilyl)]-5-methylbicyclo[5.3.0]deca-1(7),3-

**diene** (**5b**): IR (neat) 2950, 2918, 2892, 2862, 2782, 2730, 1454, 1376, 1248, 1076, 987, 875, 837, 779, 732, 696, 622 cm<sup>-1</sup>;  $^{1}$ H NMR (CDCl<sub>3</sub>) d 0.00 (s, 9H), 0.08 (s, 9H), 1.10 (d, J = 6.9 Hz, 3H), 1.51 (s, 1H), 2.48–2.54 (m, 2H), 3.24–3.53 (m, 4H), 3.71 (d, J = 12.9 Hz, 1H), 3.77 (d, J = 12.9 Hz, 1H), 5.29 (dd, J = 3.3, 12 Hz, 1H), 5.71 (m, 1H), 7.22–7.36 (m, 5H);  $^{13}$ C NMR (CDCl<sub>3</sub>)  $\delta$  –0.74, –0.23, 23.98, 33.91, 34.79, 37.53, 60.81, 66.38, 68.33, 126.17, 126.83, 127.72, 128.30, 128.64, 131.04, 133.03, 139.94. The compound **5b** was also unstable like **5a** to prepare a fine sample for elemental analysis.

### 8-aza-8-benzyl-3,4-dimethyl-[2,5-bis(trimethylsilyl)]bicyclo[4.3.0]nona-1,5-

**diene** (**6b**): IR (neat) 2948, 2916, 2892, 2864, 2787, 2752, 1454, 1368, 1333, 1248, 1163, 1145, 1123, 1072, 1027, 938, 893, 832, 746, 698, 634 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.05 (s, 18H), 0.81 (d, J = 6.9 Hz, 6H), 2.10 (q, J = 7.2 Hz, 2H), 3.25 (d, J = 12.9 Hz, 2H), 3.30 (d, J = 12.9 Hz, 2H), 3.66 (d, J = 12.6 Hz, 1H), 3.72 (d, J = 12.6 Hz, 1H), 7.24–7.32 (m, 5H); <sup>13</sup>C

NMR (CDCl<sub>3</sub>) δ 1.14, 18.72, 37.06, 57.49, 60.88, 127.08, 128.33, 129.03, 130.49, 138.60, 142.46. Found: C, 72.04; H, 9.81%. Calcd for C<sub>23</sub>H<sub>37</sub>NSi<sub>2</sub>: C, 71.99; H, 9.72%.

### 9-aza-9-benzyl-[2,5-bis(trimethylsilyl)]-5-decylbicyclo[5.3.0]deca-1(7),3-

**diene** (**5d**): IR (neat) 2918, 2850, 2780, 2732, 1466, 1454, 1376, 1247, 1070, 830, 732, 696, 623 cm<sup>-1</sup>;  ${}^{1}$ H NMR (CDCl<sub>3</sub>)  $\delta$  –0.02 (s, 9H), 0.08 (s, 9H), 0.86 (t, J = 7.2 Hz, 3H), 1.43–1.46 (m, 18H), 1.62 (s, 1H), 2.25 (m, 1H), 2.51 (s, 1H), 3.23–3.52 (m, 4H), 3.70 (d, J = 13.2 Hz, 1H), 3.76 (d, J = 13.2 Hz, 1H), 5.35 (dd, J = 3.3, 12.3 Hz, 1H), 5.71 (m, 1H), 7.22–7.35 (m, 5H);  ${}^{13}$ C NMR (CDCl<sub>3</sub>)  $\delta$  –0.69, –0.23, 14.00, 22.59, 28.33, 29.27, 29.56, 29.59, 29.61, 29.63, 31.85, 34.37, 34.79, 37.69, 39.17, 60.82, 66.34, 68.15, 126.31, 126.83, 127.72, 128.31, 128.63, 131.20, 132.51, 139.00. Found: C, 75.28; H, 11.08%. Calcd for C<sub>32</sub>H<sub>55</sub>NSi<sub>2</sub>: C, 75.37; H, 10.87%.  ${}^{1}$ H NMR and  ${}^{13}$ C NMR data were for major diastereomer (diastereomeric ratio was 7:1).

### 8-aza-8-benzyl-[2,5-bis(trimethylsilyl)]-3-decyl-4-methylbicyclo[4.3.0]nona-

**1,5-diene** (**6d**): IR (neat) 2916, 2850, 2780, 2750, 1454, 1334, 1248, 1159, 1145, 895, 832, 751, 697, 634 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.05 (s, 9H), 0.054 (s, 9H), 0.82 (d, J = 6.9 Hz, 3H), 0.86 (t, J = 6.3 Hz, 3H), 1.06–1.34 (m, 18H), 1.93 (m, 1H), 2.31 (q, J = 7.2 Hz, 1H), 3.22–3.33 (m, 4H), 3.66 (d, J = 13.2 Hz, 1H), 3.72 (d, J = 13.2 Hz, 1H), 7.24–7.33 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  –1.11, –0.95, 14.00, 18.70, 22.58, 26.82, 27.42, 29.26, 29.53, 29.76, 31.17, 31.50, 31.83, 32.39, 42.72, 57.44, 57.47, 60.87, 127.08, 128.34, 129.04, 130.16, 130.82, 138.59, 142.71, 143.03. Found: C, 75.28; H, 11.08%. Calcd for C<sub>32</sub>H<sub>55</sub>NSi<sub>2</sub>: C, 75.37; H, 10.87%.

**N-3-phenyl-2-propynyl-3,4-diphenylmethylenepyrrolidine** (**8**): white needle solid, mp 108–109 °C;  $^{1}$ H NMR (CDCl<sub>3</sub>)  $\delta$  3.85 (s, 2H), 3.91 (s, 2H), 3.92 (s, 2H), 7.02 (s, 2H), 7.23–7.50 (m, 15H);  $^{13}$ C NMR (CDCl<sub>3</sub>)  $\delta$  43.24, 55.97, 83.97, 86.09, 118.99, 123.02, 126.96, 128.27, 128.37, 128.55, 128.76, 131.88, 137.55, 139.71. Found: C, 88.43; H, 6.04%. Calcd

General Precedure for the Reaction of Enyne and Diene with Triallylmanganate.

The reaction of N,N-diallylbenzylamine (12a) with triallylmanganate is representative. A solution of 12a (187 mg, 1.0 mmol) in THF (2 mL) was added to a solution of triallylmanganate, generated from MnCl<sub>2</sub> (189 mg, 1.5 mmol) and allylmagnesium chloride (0.77 M THF solution, 5.84 mL, 4.5 mmol) in THF at 0 °C. The resulting mixture was stirred for 1 h at 0 °C, and then for 20 h at 25 °C. The reaction was quenched with methanol and the product was extracted with ethyl acetate (20 mL x 3). The combined organic layers were washed with water, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. Silica gel column chromatography gave N-benzyl-cis-3,4-dimethylpyrrolidine (13a, 132 mg) in 70% yield: IR (neat) 3024, 2956, 2910, 2870, 2780, 1496, 1476, 1454, 1375, 1129, 1071, 1029, 736, 697 cm<sup>-1</sup>;  $^{1}$ H NMR (CDCl<sub>3</sub>)  $\delta$  0.89 (d, J = 6.9 Hz, 6H), 1.94 (dd, J = 7.5, 9.3 Hz, 2H), 2.29 (m, 2H), 3.01 (dd, J = 6.9, 9.3 Hz, 2H), 7.24–7.32 (m, 5H);  $^{13}$ C NMR (CDCl<sub>3</sub>)  $\delta$  14.30, 34.29, 61.03, 62.26, 126.84, 128.23, 128.90, 139.61.

N-benzyl-3-methyl-4-trimethylsilylmethylidenepyrrolidine (10a): IR (neat) 2952, 2924, 2868, 2780, 1635, 1454, 1248, 865, 840, 744, 697 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.04 (s, 9H), 1.04 (d, J = 6.9 Hz, 3H), 1.96 (dd, J = 8.7, 8.7 Hz, 1H), 2.62 (m, 1H), 2.92 (d, J = 8.7 Hz, 1H), 2.99 (d, J = 16.5 Hz, 1H), 3.51 (d, J = 16.5 Hz, 1H), 3.55 (d, J = 12.6 Hz, 1H), 3.64 (d, J = 12.6 Hz, 1H), 5.27 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  0.59, 17.24, 40.25, 59.41, 60.77, 61.23, 116.74, 127.02, 128.32, 128.90, 138.94, 162.85.

N-allyl-3-methyl-4-trimethylsilylmethylidenepyrrolidine (10b): IR (neat) 2952, 2868, 2766, 1633, 1248, 918, 865, 839, 689 cm<sup>-1</sup>;  $^{1}$ H NMR (CDCl<sub>3</sub>)  $\delta$  0.04 (s, 9H), 1.05 (d, J = 6.9 Hz, 3H), 1.92 (dd, J = 8.7, 8.7 Hz, 1H), 2.63 (m, 1H), 2.91 (d, J = 14.4 Hz, 1H), 2.89 (dd, J = 8.7, 8.7 Hz, 1H), 3.08 (d, J = 6.6 Hz, 2H), 3.50 (d, J = 14.4 Hz, 1H), 5.20 (m, 2H), 5.27 (m, 1H), 5.92 (m, 1H);  $^{13}$ C NMR (CDCl<sub>3</sub>)  $\delta$  -0.61, 17.24, 40.13, 59.12, 59.44, 61.37, 116.86, 117.07, 135.78, 162.63. Found: C, 68.55; H, 11.06%. Calcd for C<sub>12</sub>H<sub>23</sub>NSi: C, 68.83; H, 11.07%.

N-allyl-3-methyl-4-heptylidenepyrrolidine (10c): IR (neat) 2954, 2922, 2852, 2768, 1468, 1458, 1340, 1141, 994, 917, 881 cm<sup>-1</sup>;  $^{1}$ H NMR (CDCl<sub>3</sub>)  $^{5}$  0.83 (t, J = 6.6 Hz, 3H), 1.04 (d, J = 6.9 Hz, 3H), 1.18–1.36 (m, 8H), 1.88 (m, 2H), 1.95 (dd, J = 8.7, 8.7 Hz, 1H), 2.64 (m, 1H), 2.86 (d, J = 13.8 Hz, 1H), 2.98 (dd, J = 8.7, 8.7 Hz, 1H), 3.09 (m, 2H), 3.45 (d, J = 13.8 Hz, 1H), 5.16 (m, 3H), 5.92 (m, 1H);  $^{13}$ C NMR (CDCl<sub>3</sub>)  $^{5}$  13.99, 17.51, 22.54, 28.88, 29.35, 29.42, 31.70, 37.14, 56.60, 59.53, 62.23, 116.91, 120.02, 136.04, 143.71. Found: C, 81.24; H, 12.49%. Calcd for C<sub>15</sub>H<sub>27</sub>N: C, 81.38; H, 12.29%.

N-allyl-3-methyl-4-(2-allyl-heptylidene)pyrrolidine (11): IR (neat) 2954, 2924, 2854, 2766, 1456, 1342, 1132, 993, 914 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.85 (t, J = 6.6 Hz, 3H), 1.09 (d, J = 6.9 Hz, 3H), 1.18–1.36 (m, 8H), 1.86 (t, J = 8.1 Hz, 2H), 2.42 (d, J = 3.3, 9.0 Hz, 1H), 2.57 (d, J = 6.6, 9.0 Hz, 1H), 2.76 (d, J = 6.3 Hz, 2H), 2.94 (d, J = 13.2 Hz, 1H), 3.06 (m, 2H), 3.33 (d, J = 13.2 Hz, 1H), 5.06 (m, 4H), 5.73 (m, 1H), 5.91 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  13.98, 20.29, 22.52, 27.61, 29.26, 31.69, 32.37, 35.33, 36.21, 57.23, 59.54, 62.25, 115.40, 116.70, 128.52, 136.16, 136.99, 139.05. Found: C, 82.70; H, 12.02%. Calcd for C<sub>18</sub>H<sub>31</sub>N: C, 82.69; H, 11.95%.

N-cyclohexyl-cis-3,4-dimethylpyrrolidine (13c): IR (neat) 2906, 2852, 2766, 1474, 1464, 1449, 1375, 1181, 1138, 891 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.85 (d, J = 6.6 Hz, 6H), 1.07–1.24 (m, 5H), 1.55–1.58 (m, 1H), 1.68–1.72 (m, 2H), 1.83–1.91 (m, 5H), 2.23 (m, 2H), 3.14 (dd, J = 7.2, 9.6 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  14.36, 25.08, 26.02, 31.84, 33.91, 59.63, 63.91. Found: C, 79.52; H, 13.08%. Calcd for C<sub>12</sub>H<sub>23</sub>N: C, 79.49; H, 12.79%.

N-benzyl-cis-3,4-dideuteriomethylpyrrolidine (14): IR (neat) 2950, 2922, 2778, 1453, 736, 697 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.87 (m, 4H), 1.94 (dd, J = 7.8, 9.6 Hz, 2H), 2.28 (m, 2H), 3.00 (dd, J = 7.2, 9.6 Hz, 2H), 3.58 (s, 2H), 7.23–7.34 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  14.01 (t, J = 18.9 Hz), 34.20, 61.03, 62.23, 126.84, 128.23, 128.90, 139.62.

N-benzyl-*cis*-3,4-diiodomethylpyrrolidine (15): IR (neat) 2950, 2906, 2786, 1494, 1452, 1181, 1152, 737, 697 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.42 (dd, J = 6.0, 9.6 Hz, 2H), 2.69 (m, 2H), 3.01 (dd, J = 6.6, 9.6 Hz, 2H), 3.13 (dd, J = 9.6, 9.6 Hz, 2H), 3.30 (dd, J = 5.4, 9.6 Hz, 2H), 3.60 (s, 2H), 7.24–7.33 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  4.97, 44.30, 59.88, 60.90, 127.13, 128.40, 128.62, 138.78.