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## ACS Publications

## Supporting Information

General Procedure for the Reaction of $\boldsymbol{N}, \boldsymbol{N}$-bis(2-alkynyl)benzylamine with Triallylmanganate. Manganese(II) chloride ( $189 \mathrm{mg}, 1.5 \mathrm{mmol}$ ) was sonicated in THF under argon atmosphere for 10 min . Allylmagnesium chloride ( 0.77 M THF solution, $5.84 \mathrm{~mL}, 4.5$ mmol) was added to the suspension of $\mathrm{MnCl}_{2}$ at $0^{\circ} \mathrm{C}$. 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 $\mathrm{g}, 1.0 \mathrm{mmol})$ in THF ( 2 mL ) was added at $0^{\circ} \mathrm{C}$. The mixture was stirred at $0^{\circ} \mathrm{C}$ for 3 h , quenched with $\mathrm{MeOH}(1 \mathrm{~mL})$, and poured into water, and extracted with ethyl acetate ( $20 \mathrm{~mL} \times 3$ ). Concentration of dried organic layer provided a residual oil. The ratio (46:54) of products $\mathbf{2 a}$ and $\mathbf{3 a}$ was determined by the examination of $1_{\mathrm{H}}$ 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 $/ \mathrm{AcOEt}=10 / 1$ ), $138 \mathrm{mg}, 35 \%$ isolated yield). 9-aza-9-benzyl-2,6-dihexylbicyclo[5.3.0]deca-1(7),3-diene (3a): IR (neat) $2950,2922,2852,2782,2748,1467,1454,726,697 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right) \delta 0.86(\mathrm{t}, J=6$ $\mathrm{Hz}, 6 \mathrm{H}), 1.10-1.50(\mathrm{~m}, 20 \mathrm{H}), 2.15(\mathrm{~m}, 2 \mathrm{H}), 2.30(\mathrm{~m}, 1 \mathrm{H}), 2.88(\mathrm{~m}, 1 \mathrm{H}), 3.43(\mathrm{~m}, 4 \mathrm{H}), 5.53$ $(\mathrm{dd}, J=4.5,11.4 \mathrm{~Hz}, 1 \mathrm{H}), 5.65(\mathrm{~m}, 1 \mathrm{H}), 7.23-7.36(\mathrm{~m}, 5 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right) \delta 14.00(2 \mathrm{C})$, $22.55,22.58,26.79,27.32,29.45,29.49,30.18,31.75$ (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, $85.21 ; \mathrm{H}, 10.98 \%$. Calcd for $\mathrm{C}_{28} \mathrm{H}_{43} \mathrm{~N}: \mathrm{C}, 85.43 ; \mathrm{H}, 11.01 \%$. An analytically pure sample of 2 a could not be obtained because of the contamination by unidentified by products. Thus the yield $(30 \%)$ of $\mathbf{2 a}$ was calculated from the ratio $(\mathbf{2 a}: 3 \mathrm{a}=46: 54)$ determined by ${ }^{1} \mathrm{H}$ NMR of crude product.
$2.33 \mathrm{H}), 1.13(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 0.67 \mathrm{H}), 2.12(\mathrm{~m}, 1 \mathrm{H}), 2.36(\mathrm{~m}, 2 \mathrm{H}), 2.85(\mathrm{~m}, 0.23 \mathrm{H}), 3.00(\mathrm{~m}$, $0.67 \mathrm{H}), 3.40(\mathrm{~m}, 2 \mathrm{H}), 3.53(\mathrm{~m}, 2 \mathrm{H}), 3.75(\mathrm{~s}, 2 \mathrm{H}), 5.55(\mathrm{dd}, J=4.5,11.1 \mathrm{~Hz}, 1 \mathrm{H}), 5.67(\mathrm{~m}$, $1 \mathrm{H}), 7.24-7.38(\mathrm{~m}, 5 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}\right)$ 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') ( $\mathrm{C}_{18} \mathrm{H}_{21} \mathrm{~N}$ ) standing at $25^{\circ} \mathrm{C}$ for 1 d . HRMS 251.1671 Calcd for $\mathrm{C}_{18} \mathrm{H}_{21} \mathrm{~N}$ : M+251.1674.

General Procedure for the Reaction of $N, N$-(3-trimethylsilyl-2propynyl)benzylamine (1c) with triallylmanganate. 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, $5.84 \mathrm{~mL}, 4.5 \mathrm{mmol}$ ) was added at $0^{\circ} \mathrm{C}$. The mixture turned into a clear brown solution and then, after being stirred for 20 min at $0^{\circ} \mathrm{C}$, a solution of $\mathbf{1 c}(327 \mathrm{mg}, 1.0$ mmol ) in THF ( 2 mL ) was added at $0^{\circ} \mathrm{C}$. The whole was stirred at $0^{\circ} \mathrm{C}$ for 3 h . Deuterium oxide ( 10 mmol ) was added and the mixture was stirred for another 30 min at $25^{\circ} \mathrm{C}$. The mixture was poured into water extracted with ethyl acetate $(3 \times 20 \mathrm{~mL})$. Purification of the products by silica gel column chromatography using hex/ $\mathrm{AcOEt}=10 / 1-5 / 1$ as an eluant gave $6 \mathrm{c}\left(R_{f}=0.50\right.$ (hex/ AcOEt $=10 / 1), 146 \mathrm{mg}, 38 \%$ yield $)$ and $\mathbf{4 c}\left(R_{f}=0.35\right.$ (hex/AcOEt $\left.=5 / 1\right), 38 \mathrm{mg}, 10 \%$ yield), and $\mathbf{5 c}$ $\left(R_{f}=0.30(\right.$ hex $/ \mathrm{AcOEt}=5 / 1), 38 \mathrm{mg}, 10 \%$ yield $)$. Physical data for $\mathbf{4 c}, 5 \mathbf{c}$, and $\mathbf{6 c}$ are as follows. An examination of ${ }^{1} \mathrm{H}$ NMR of crude product containing dibenzyl ether as an internal standard revealed that the yields and ratio of products were $\mathbf{4 c}(16 \%), 5 \mathrm{c}(16 \%)$, and $\mathbf{6 c}(43 \%)$ $(4 c: 5 c: 6 c=21: 21: 58)$, respectively .

9-aza-9-benzyl-[2,6-bis(trimethylsilyl)]-4-deuterio-5-
methylbicyclo[5.3.0]deca-1 (7), 2-diene (4c): ${ }^{1} \mathrm{H}$ NMR ( $\mathrm{CDCl}_{3}$ ) $\delta \mathbf{- 0 . 0 4}$ ( $\mathrm{s}, 9 \mathrm{H}$ ), 0.06 (s, $9 \mathrm{H}), 0.91(\mathrm{~d}, J=6.6 \mathrm{~Hz}, 3 \mathrm{H}), 1.27(\mathrm{~d}, J=5.1 \mathrm{~Hz}, 1 \mathrm{H}), 2.04(\mathrm{dd}, J=2.7,7.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.25$ $(\mathrm{m}, 1 \mathrm{H}), 3.33-3.72(\mathrm{~m}, 4 \mathrm{H}), 3.73(\mathrm{~d}, J=13.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.78(\mathrm{~d}, J=13.5 \mathrm{~Hz}, 1 \mathrm{H}), 6.14(\mathrm{~d}, J$ $=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.20-7.37(\mathrm{~m}, 5 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}\right) \delta-1.55,-0.61,26.46,37.85,38.41(\mathrm{t}$,
$d=18.9 \mathrm{~Hz}), 43.70,60.72,64.18,66.44,126.86,128.31,128.68,130.23,138.40,139.79$, 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, $1248,836,740,696 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right) \delta-0.01(\mathrm{~s}, 9 \mathrm{H}), 0.08(\mathrm{~s}, 9 \mathrm{H}), 1.09(\mathrm{~d}, J=6.6$ $\mathrm{Hz}, 3 \mathrm{H}), 1.50(\mathrm{~s}, 1 \mathrm{H}), 2.50(\mathrm{dq}, J=8.1,8.1 \mathrm{~Hz}, 1 \mathrm{H}), 3.24-3.52(\mathrm{~m}, 4 \mathrm{H}), 3.70(\mathrm{~d}, J=13.5$ $\mathrm{Hz}, 1 \mathrm{H}), 3.76(\mathrm{~d}, J=13.5 \mathrm{~Hz}, 1 \mathrm{H}), 5.28(\mathrm{~d}, J=12 \mathrm{~Hz}, 1 \mathrm{H}), 5.70(\mathrm{dd}, J=8.1,12 \mathrm{~Hz}, 1 \mathrm{H})$, 7.19-7.36 (m, 5H); ${ }^{13} \mathrm{C} \mathrm{NMR}_{\left(\mathrm{CDCl}_{3}\right)} \delta-0.75,0.26,24.03,33.90,37.51,60.81,66.37$, $68.35,126.13,126.82,127.73,128.30,128.62,131.04,133.07,139.98$. Elemental analysis was performed for a mixture of $\mathbf{4 c}$ and $\mathbf{5 c}$. Found: $\mathrm{C}, 71.55 ; \mathrm{H}, 9.35 \%$. Calcd for $\mathrm{C}_{23} \mathrm{H}_{36} \mathrm{DSi}_{2} \mathrm{~N}: \mathrm{C}$, $71.81 ; \mathrm{H}, 9.43 \%$.
## 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, $634 \mathrm{~cm}^{-1}$; ${ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right) \delta 0.06(\mathrm{~s}, 18 \mathrm{H})$, $0.79-0.83(\mathrm{~m}, 5 \mathrm{H}), 2.10(\mathrm{q}, J=6.6 \mathrm{~Hz}, 2 \mathrm{H}), 3.26(\mathrm{~d}, J=13.2 \mathrm{~Hz}, 2 \mathrm{H}), 3.31(\mathrm{~d}, J=13.2 \mathrm{~Hz}$, $2 \mathrm{H}), 3.66(\mathrm{~d}, J=12.9 \mathrm{~Hz}, 1 \mathrm{H}), 3.72(\mathrm{~d}, J=12.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.24-7.33(\mathrm{~m}, 5 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.14,18.43(\mathrm{t}, J=18.9 \mathrm{~Hz}), 18.72,22.55,31.50,37.00,37.03,57.49,60.88$, $127.09,128.34,129.04,130.51,138.59$. Found: $\mathrm{C}, 71.74 ; \mathrm{H}, 9.34 \%$. Calcd for $\mathrm{C}_{23} \mathrm{H}_{36} \mathrm{NSi}_{2}$ : C, $71.81 ; \mathrm{H}, 9.34 \%$.

9-aza-9-benzyl-2,6-bis(trimethylsilyl)bicyclo[5.3.0]deca-1(7),3-diene (5a): IR (neat) $3014,2946,2894,2858,2780,1453,1375,1342,1248,1156,1113,1064,940,916,837$, $792,750,729 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta-0.01(\mathrm{~s}, 9 \mathrm{H}), 0.06(\mathrm{~s}, 9 \mathrm{H}), 1.68(\mathrm{~s}, 1 \mathrm{H}), 2.05-2.13$ $(\mathrm{m}, 1 \mathrm{H}), 2.30-2.40(\mathrm{~m}, 2 \mathrm{H}), 3.21-3.41(\mathrm{~m}, 4 \mathrm{H}), 3.70(\mathrm{~s}, 2 \mathrm{H}), 5.61-5.74(\mathrm{~m}, 2 \mathrm{H}), 7.24-7.31$ $(\mathrm{m}, 5 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}\right) \delta-1.27,-0.66,26.70,28.29,35.06,60.58,66.32,66.72,126.90$, $128.31,128.60,128.74,129.54,131.96,132.56,139.69$. The compound $\mathbf{5 a}$ 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, $623 \mathrm{~cm}^{-1}$; ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 0.04(\mathrm{~s}, 9 \mathrm{H}), 0.05(\mathrm{~s}, 9 \mathrm{H}), 2.24(\mathrm{~m}$, $3 \mathrm{H}), 3.03(\mathrm{~m}, 1 \mathrm{H}), 4.93(\mathrm{~s}, 2 \mathrm{H}), 5.74(\mathrm{~m}, 2 \mathrm{H}), 6.26(\mathrm{~d}, J=1.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.37(\mathrm{~d}, J=1.8 \mathrm{~Hz}$, $1 \mathrm{H}), 7.02(\mathrm{~m}, 2 \mathrm{H}), 7.28(\mathrm{~m}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}\right) \delta-1.68,-1.52,24.03,28.87,28.94$, $52.94,117.63,118.33,122.21,124.53,126.70,127.36,128.62,130.31,130.33,139.05$. HRMS: 367.2142. Calcd for $\mathrm{C}_{22} \mathrm{H}_{33} \mathrm{NSi}_{2} \mathrm{M}^{+}$367.2151.

8-aza-8-benzyl-2,5-bis(trimethylsilyl)-3-methylbicyclo[4.3.0]nona-1,5-diene (6a): IR (neat) $2948,2896,2782,2752,1453,1333,1248,1162,1145,1048,962,913,896$, $832,748 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{CDCl}_{3}\right) \delta 0.04(\mathrm{~s}, 9 \mathrm{H}), 0.07(\mathrm{~s}, 9 \mathrm{H}), 0.79(\mathrm{t}, J=6.9 \mathrm{~Hz}, 3 \mathrm{H})$, $2.06-2.31(\mathrm{~m}, 3 \mathrm{H}), 3.27-2.30(\mathrm{~m}, 4 \mathrm{H}), 3.66(\mathrm{~d}, J=12.9 \mathrm{~Hz}, 1 \mathrm{H}), 3.71(\mathrm{~d}, J=12.9 \mathrm{~Hz}, 1 \mathrm{H})$, 7.24-7.32 (m, 5H); $\left.{ }^{13} \mathrm{C} \mathrm{NMR} \mathrm{(CDCl} 3\right) ~ \delta-1.58, ~ 0.73,17.98,28.72,33.20,57.52,57.59$, $60.85,124.68,127.08,128.33,128.99,132.87,138.62,143.37,143.56$. Found: C, 71.42; H, $9.60 \%$. Calcd for $\mathrm{C}_{22} \mathrm{H}_{35} \mathrm{NSi}_{2}$ : $\mathrm{C}, 71.47 ; \mathrm{H}, 9.54 \%$.

## 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, $837,779,732,696,622 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right) \mathrm{d} 0.00(\mathrm{~s}, 9 \mathrm{H}), 0.08(\mathrm{~s}, 9 \mathrm{H}), 1.10(\mathrm{~d}, J=6.9$ $\mathrm{Hz}, 3 \mathrm{H}), 1.51(\mathrm{~s}, 1 \mathrm{H}), 2.48-2.54(\mathrm{~m}, 2 \mathrm{H}), 3.24-3.53(\mathrm{~m}, 4 \mathrm{H}), 3.71(\mathrm{~d}, J=12.9 \mathrm{~Hz}, 1 \mathrm{H}), 3.77$ $(\mathrm{d}, J=12.9 \mathrm{~Hz}, 1 \mathrm{H}), 5.29(\mathrm{dd}, J=3.3,12 \mathrm{~Hz}, 1 \mathrm{H}), 5.71(\mathrm{~m}, 1 \mathrm{H}), 7.22-7.36(\mathrm{~m}, 5 \mathrm{H}) ;{ }^{13} \mathrm{C}$ $\operatorname{NMR}\left(\mathrm{CDCl}_{3}\right) \delta-0.74,-0.23,23.98,33.91,34.79,37.53,60.81,66.38,68.33,126.17,126.83$, $127.72,128.30,128.64,131.04,133.03,139.94$. The compound $\mathbf{5 b}$ was also unstable like $\mathbf{5 a}$ 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, $1145,1123,1072,1027,938,893,832,746,698,634 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right) \delta 0.05(\mathrm{~s}, 18 \mathrm{H})$, $0.81(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H}), 2.10(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 3.25(\mathrm{~d}, J=12.9 \mathrm{~Hz}, 2 \mathrm{H}), 3.30(\mathrm{~d}, J=$ $12.9 \mathrm{~Hz}, 2 \mathrm{H}), 3.66(\mathrm{~d}, J=12.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.72(\mathrm{~d}, J=12.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.24-7.32(\mathrm{~m}, 5 \mathrm{H}) ;{ }^{13} \mathrm{C}$$\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right) \delta 1.14,18.72,37.06,57.49,60.88,127.08,128.33,129.03,130.49,138.60$, 142.46. Found: $\mathrm{C}, 72.04 ; \mathrm{H}, 9.81 \%$. Calcd for $\mathrm{C}_{23} \mathrm{H}_{37} \mathrm{NSi}_{2}: \mathrm{C}, 71.99 ; \mathrm{H}, 9.72 \%$.

## 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, $623 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta-0.02(\mathrm{~s}, 9 \mathrm{H}), 0.08(\mathrm{~s}, 9 \mathrm{H}), 0.86(\mathrm{t}, J=7.2 \mathrm{~Hz}, 3 \mathrm{H}), 1.43-1.46$ $(\mathrm{m}, 18 \mathrm{H}), 1.62(\mathrm{~s}, 1 \mathrm{H}), 2.25(\mathrm{~m}, 1 \mathrm{H}), 2.51(\mathrm{~s}, 1 \mathrm{H}), 3.23-3.52(\mathrm{~m}, 4 \mathrm{H}), 3.70(\mathrm{~d}, J=13.2 \mathrm{~Hz}$, $1 \mathrm{H}), 3.76(\mathrm{~d}, J=13.2 \mathrm{~Hz}, 1 \mathrm{H}), 5.35(\mathrm{dd}, J=3.3,12.3 \mathrm{~Hz}, 1 \mathrm{H}), 5.71(\mathrm{~m}, 1 \mathrm{H}), 7.22-7.35(\mathrm{~m}$, $5 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}\right) \delta-0.69,-0.23,14.00,22.59,28.33,29.27,29.56,29.59,29.61$, $29.63,31.85,34.37,34.79,37.69,39.17,60.82,66.34,68.15,126.31,126.83,127.72,128.31$, $128.63,131.20,132.51,139.00$. Found: C, $75.28 ; \mathrm{H}, 11.08 \%$. Calcd for $\mathrm{C}_{32} \mathrm{H}_{55} \mathrm{NSi}_{2}: \mathrm{C}$, $75.37 ; \mathrm{H}, 10.87 \% .{ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ 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, $751,697,634 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{CDCl}_{3}\right) \delta 0.05(\mathrm{~s}, 9 \mathrm{H}), 0.054(\mathrm{~s}, 9 \mathrm{H}), 0.82(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 3 \mathrm{H})$, $0.86(\mathrm{t}, J=6.3 \mathrm{~Hz}, 3 \mathrm{H}), 1.06-1.34(\mathrm{~m}, 18 \mathrm{H}), 1.93(\mathrm{~m}, 1 \mathrm{H}), 2.31(\mathrm{q}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H})$, $3.22-3.33(\mathrm{~m}, 4 \mathrm{H}), 3.66(\mathrm{~d}, J=13.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.72(\mathrm{~d}, J=13.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.24-7.33(\mathrm{~m}, 5 \mathrm{H})$; ${ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}\right) \delta-1.11,-0.95,14.00,18.70,22.58,26.82,27.42,29.26,29.53,29.76$, $31.17,31.50,31.83,32.39,42.72,57.44,57.47,60.87,127.08,128.34,129.04,130.16$, $130.82,138.59,142.71,143.03$. Found: C, $75.28 ; \mathrm{H}, 11.08 \%$. Calcd for $\mathrm{C}_{32} \mathrm{H}_{55} \mathrm{NSi}_{2}: \mathrm{C}$, 75.37 ; H, $10.87 \%$.

N-3-phenyl-2-propynyl-3,4-diphenylmethylenepyrrolidine (8): white needle solid, mp 108-109 ${ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right) \delta 3.85(\mathrm{~s}, 2 \mathrm{H}), 3.91(\mathrm{~s}, 2 \mathrm{H}), 3.92(\mathrm{~s}, 2 \mathrm{H}), 7.02(\mathrm{~s}, 2 \mathrm{H})$, $7.23-7.50(\mathrm{~m}, 15 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}\right) \delta 43.24,55.97,83.97,86.09,118.99,123.02,126.96$, $128.27,128.37,128.55,128.76,131.88,137.55,139.71$. Found: C, $88.43 ; H, 6.04 \%$. Calcd
for $\mathrm{C}_{27} \mathrm{H}_{23} \mathrm{~N}: \mathrm{C}, 89.71 ; \mathrm{H}, 6.41 \%$.

## 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 $\mathbf{1 2 a}(187 \mathrm{mg}, 1.0 \mathrm{mmol})$ in THF ( 2 mL ) was added to a solution of triallylmanganate, generated from $\mathrm{MnCl}_{2}(189 \mathrm{mg}, 1.5 \mathrm{mmol})$ and allylmagnesium chloride ( 0.77 M THF solution, $5.84 \mathrm{~mL}, 4.5$ mmol ) in THF at $0^{\circ} \mathrm{C}$. The resulting mixture was stirred for 1 h at $0^{\circ} \mathrm{C}$, and then for 20 h at $25^{\circ} \mathrm{C}$. 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 $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated. Silica gel column chromatography gave $N$-benzyl-cis-3,4-dimethylpyrrolidine ( $\mathbf{1 3 a}, 132 \mathrm{mg}$ ) in $70 \%$ yield: IR (neat) $3024,2956,2910,2870,2780,1496,1476,1454,1375,1129,1071,1029$, $736,697 \mathrm{~cm}^{-1}$; ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 0.89(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H}), 1.94(\mathrm{dd}, J=7.5,9.3 \mathrm{~Hz}, 2 \mathrm{H})$, $2.29(\mathrm{~m}, 2 \mathrm{H}), 3.01(\mathrm{dd}, J=6.9,9.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.24-7.32(\mathrm{~m}, 5 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}\right) \delta 14.30$, $34.29,61.03,62.26,126.84,128.23,128.90,139.61$.N-benzyl-3-methyl-4-trimethylsilylmethylidenepyrrolidine (10a): IR (neat) 2952, 2924, 2868, 2780, 1635, 1454, 1248, 865, 840, 744, $697 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right) \delta 0.04(\mathrm{~s}$, $9 \mathrm{H}), 1.04(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 3 \mathrm{H}), 1.96(\mathrm{dd}, J=8.7,8.7 \mathrm{~Hz}, 1 \mathrm{H}), 2.62(\mathrm{~m}, 1 \mathrm{H}), 2.92(\mathrm{~d}, J=8.7$ $\mathrm{Hz}, 1 \mathrm{H}), 2.99(\mathrm{~d}, J=16.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.51(\mathrm{~d}, J=16.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.55(\mathrm{~d}, J=12.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.64$ $(\mathrm{d}, J=12.6 \mathrm{~Hz}, 1 \mathrm{H}), 5.27(\mathrm{~m}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}\right) \delta 0.59,17.24,40.25,59.41,60.77$, $61.23,116.74,127.02,128.32,128.90,138.94,162.85$.

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

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

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

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

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

N-benzyl-cis-3,4-diiodomethylpyrrolidine (15): IR (neat) 2950, 2906, 2786, 1494, 1452, 1181, 1152, 737, $697 \mathrm{~cm}^{-1}$; ${ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right) \delta 2.42(\mathrm{dd}, J=6.0,9.6 \mathrm{~Hz}, 2 \mathrm{H}), 2.69(\mathrm{~m}$, $2 \mathrm{H}), 3.01(\mathrm{dd}, J=6.6,9.6 \mathrm{~Hz}, 2 \mathrm{H}), 3.13(\mathrm{dd}, J=9.6,9.6 \mathrm{~Hz}, 2 \mathrm{H}), 3.30(\mathrm{dd}, J=5.4,9.6 \mathrm{~Hz}$, $2 \mathrm{H}), 3.60(\mathrm{~s}, 2 \mathrm{H}), 7.24-7.33(\mathrm{~m}, 5 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}\right) \delta 4.97,44.30,59.88,60.90,127.13$, $128.40,128.62,138.78$.

