# Supporting Information Experimental Procedures and Characterization Data 



9
$\xrightarrow[\substack{\text { 2. Nal, Acetone } \\ 66 \% \text { 2 steps }}]{\text { 1. } \mathrm{Et}_{3} \mathrm{~N}, \mathrm{MsCl}}$
66\% 2 steps


## 1-Iodo-5-methylhex-3-yne (8)

To a solution of 5-methylhex-3-yn-1-ol ( $\mathbf{9}, 714 \mathrm{mg}, 6.38 \mathrm{mmol})$ in $30 \mathrm{mLCH} \mathrm{Cl}_{2}$ and $\mathrm{Et}_{3} \mathrm{~N}(1.25 \mathrm{~mL}, 8.93 \mathrm{mmol})$ was added $\mathrm{MsCl}(0.59 \mathrm{~mL}, 7.66 \mathrm{mmol})$ dropwise at $-20^{\circ} \mathrm{C}$. After 30 min at $-20^{\circ} \mathrm{C}$, the mixture was diluted with pentane and filtered through a pad of celite and pad was washed with pentane. The pentane was washed with sat'd $\mathrm{NaHCO}_{3}$, brine and dried over $\mathrm{MgSO}_{4}$. The solvent was removed in vacuo and the residue was dissolved in 40 mL acetone and $\mathrm{NaI}(1.91 \mathrm{~g}, 12.8 \mathrm{mmol})$ was added in one portion. The reaction was heated at $55^{\circ} \mathrm{C}$. After 12 h , the reaction was cooled to rt and filtered through a pad of celite and pad was washed with pentane. The pentane was washed with sat'd $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ and brine, dried over $\mathrm{MgSO}_{4}$. The solvent was removed in vacuo and the residue was purified by chromatography on silica gel eluting with pure pentane to yield 0.93 g ( $66 \%$ ) of compound $\mathbf{8}$ as a colorless oil.
${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \square 3.19(\mathrm{t}, J=7.4 \mathrm{~Hz}, 2 \mathrm{H}), 2.71(\mathrm{dt}, J=2.1,7.4 \mathrm{~Hz}, 2 \mathrm{H})$, $2.50(\mathrm{t}$ of sep, $J=2.1,6.9 \mathrm{~Hz}, 1 \mathrm{H}), 1.14(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ —88.1, 78.0, 24.0, 23.1, 20.5, 2.64; IR (neat) 2968, 2931, $2870 \mathrm{~cm}^{-1}$.


6-Methyl-6-(5-methylhex-3-ynyl)-4,6,7,8-tetrahydrobenzo[1,3]dioxin-5-one (11).
To a solution of lithium diisopropylamide [prepared from diisopropylamine ( 0.64 mL , 4.52 mmol ) in 5 mL of THF and $n$-butyllithium ( 2.63 mL of a 1.6 M hexanes solution, 4.45 mmol ) at $-78^{\circ} \mathrm{C}$ ] was added a solution of 6-methyl-4,6,7,8-tetrahydro-benzo[1,3]dioxin-5-one ( $6,0.47 \mathrm{~g}, 2.77 \mathrm{mmol}$ ) and HMPA ( $2.4 \mathrm{~mL}, 13.9 \mathrm{mmol}$ ) in 5 mL of THF over 30 min . After an additional 1.5 h at $-78^{\circ} \mathrm{C}$, 1-iodo-5-methylhex-3-yne ( $\mathbf{8}$, $1.23 \mathrm{~g}, 5.54 \mathrm{mmol}$ ) was added. The reaction was gradually warmed to rt and after 24 h quenched with sat'd $\mathrm{NH}_{4} \mathrm{Cl}$ solution. The aqueous layer was separated and extracted with pentane. The combined organic layers were washed with brine and dried over $\mathrm{MgSO}_{4}$.

The solvent was removed in vacuo and the residue was purified by chromatography on silica gel eluting with $20: 80 \mathrm{EtOAc}$ : hexanes to yield $0.26 \mathrm{~g}(36 \%)$ of compound $\mathbf{1 1}$ as a yellow oil.
${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\square 5.14\left({ }^{1} /{ }_{2} \mathrm{AB} \mathrm{q}, J=5.5 \mathrm{~Hz}, 1 \mathrm{H}\right), 5.10\left({ }^{1} /{ }_{2} \mathrm{AB} \mathrm{q}, J=5.5 \mathrm{~Hz}\right.$, $1 \mathrm{H}), 4.43(\mathrm{dt}, J=14.6,2.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.36(\mathrm{dt}, J=14.6,2.0 \mathrm{~Hz}, 1 \mathrm{H}), 2.56-2.36(\mathrm{~m}, 3 \mathrm{H})$, 2.18-1.93 (m, 3H), 1.83-1.64 (m, 3H), 1.11 (d, $J=6.9 \mathrm{~Hz}, 6 \mathrm{H}), 1.09(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \square 200.2,168.3,110.1,91.5,86.3,79.2,63.3,43.2,36.4,31.6,24.7$, 23.5, 22.1, 20.6, 14.1; IR (neat) 2966, 2932, 2871, $1637 \mathrm{~cm}^{-1}$; HRMS calcd for $\mathrm{C}_{16} \mathrm{H}_{22} \mathrm{O}_{3}$ 262.1569 , found 262.1560 .


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3-Ethynyl-2-hydroxymethyl-4-methyl-4-(5-methylhex-3-ynyl)cyclohex-2-enone (12).

To a mixture of lithium acetylide ethylenediamine ( $0.65 \mathrm{~g}, 7.1 \mathrm{mmol}$ ) in 30 mL of THF was added a solution of 6-methyl-6-(5-methylhex-3-ynyl)-4,6,7,8-tetrahydro-benzo[1,3]dioxin-5-one ( $\mathbf{1 1}, 0.19 \mathrm{~g}, 0.71 \mathrm{mmol}$ ) in 5 mL of THF dropwise at $-78^{\circ} \mathrm{C}$. The reaction was gradually warmed to rt overnight and quenched with a sat'd $\mathrm{NH}_{4} \mathrm{Cl}$ solution. The aqueous layer was separated and extracted with $\mathrm{Et}_{2} \mathrm{O}$. The combined organic layers were washed with $\mathrm{H}_{2} \mathrm{O}$, brine and dried over $\mathrm{MgSO}_{4}$. The solvent was removed in vacuo and the residue was dissolved in 3 mL of THF. Then 0.1 mL of 3 M HCl was added. After 30 min , sat'd $\mathrm{NaHCO}_{3}$ was added, the aqueous layer was separated and extracted with $\mathrm{Et}_{2} \mathrm{O}$. The combined organic layers were washed with brine and dried over $\mathrm{MgSO}_{4}$. The solvent was removed in vacuo and the residue was purified by chromatography on silica gel eluting with $20: 80 \mathrm{EtOAc}$ : hexanes to yield 0.16 g ( $65 \%$ yield for two steps) of compound $\mathbf{1 2}$ as a yellow oil.
${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\square 4.47(\mathrm{~s}, 2 \mathrm{H}), 3.85(\mathrm{~s}, 1 \mathrm{H}), 2.52-2.46(\mathrm{~m}, 2 \mathrm{H}), 2.17-1.73$ $(\mathrm{m}, 7 \mathrm{H}), 1.23(\mathrm{~s}, 3 \mathrm{H}), 1.09(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\square 199.4$, $146.3,141.4,93.8,86.6,78.8,78.6,60.4,38.8,38.3,34.0,31.9,25.0,23.3,20.5,14.1$; IR (neat) $3444,2932,2871,2086,1660 \mathrm{~cm}^{-1}$; HRMS calcd for $\mathrm{C}_{17} \mathrm{H}_{22} \mathrm{O}_{2} 258.1620$, found 258.1615.


2-(tert-Butyldimethylsiloxymethyl)-3-ethynyl-4-methyl-4-(5-methylhex-3-ynyl)-cyclo-hex-2-enone (13).

To a solution of 3-ethynyl-2-hydroxymethyl-4-methyl-4-(5-methylhex-3-ynyl)-cyclohex-2-enone ( $\mathbf{1 2}, 120 \mathrm{mg}, 0.47 \mathrm{mmol}$ ) in 1.0 mL DMF were added imidazole ( 89 $\mathrm{mg}, 1.3 \mathrm{mmol})$ and $\mathrm{TBSCl}(98 \mathrm{mg}, 0.65 \mathrm{mmol})$ at rt . After 30 min , the reaction was complete and the solution was directly loaded to a column eluting with $30: 70 \mathrm{EtOAc}$ : hexanes to yield 848 mg ( $<95 \%$, the NMR is contaminated with extra silyl peaks) $\mathbf{1 3}$ as a yellow oil.
${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\square 4.41$ (s, 2H), 3.78 (s, 1H), 2.46-2.41 (m, 3H), 2.12-1.69 $(\mathrm{m}, 6 \mathrm{H}), 1.20(\mathrm{~s}, 3 \mathrm{H}), 1.06(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H}), 0.81(\mathrm{~s}, 9 \mathrm{H}), 0.10(\mathrm{~s}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (75 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \square 196.8,146.7,142.5,93.0,86.6,79.7,79.0,58.7,39.3,38.6,34.3,32.3$, 26.2, 26.0, 25.3, 23.6, 20.7, 18.7, 14.3, -4.9.


## 2-(tert-Butyldimethylsiloxymethyl)-3-ethynyl-4-methyl-4-(5-methylhex-3-

 ynyl)-cyclohex-2-enol (14).To a solution of 2-(tert-butyldimethylsiloxymethyl)-3-ethynyl-4-methyl-4-(5-methylhex-3-ynyl)cyclohex-2-enone ( $\mathbf{1 3}, 65 \mathrm{mg}, 0.17 \mathrm{mmol}$ ) dissolved in 0.5 mL of methanolic $0.4 \mathrm{M} \mathrm{CeCl}_{3} \cdot 7 \mathrm{H}_{2} \mathrm{O}$ solution was added sodium borohydride ( $8 \mathrm{mg}, 0.19$ mmol ) in one portion at $-30^{\circ} \mathrm{C}$. After 30 min , the reaction was quenched with 3 mL of $\mathrm{H}_{2} \mathrm{O}$ and diluted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. The aqueous layer was separated and extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. The combined organic layers were dried over $\mathrm{MgSO}_{4}$. The solvent was removed in vacuo and the residue was purified by chromatography on silica gel eluting with 20 : 80 EtOAc : hexanes to yield $59 \mathrm{mg}(91 \%)$ of compound 14 as two diastereomers ( $3: 1$ ) as a yellow oil. HRMS calcd for $\mathrm{C}_{23} \mathrm{H}_{38} \mathrm{O}_{2} \mathrm{Si} 374.2641$, found 374.2646
Major diastereomer: $\mathrm{R}_{\mathrm{f}} 0.4$ (EtOAc: hexanes $1: 9$ ); ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\square 4.75$ $\left({ }^{1} / 2 \mathrm{AB} \mathrm{q}, J=12.6 \mathrm{~Hz}, 1 \mathrm{H}\right), 4.37\left({ }^{1} / 2 \mathrm{AB}\right.$ q $\left., J=12.6 \mathrm{~Hz}, 1 \mathrm{H}\right), 4.28(\mathrm{t}, J=4.0 \mathrm{~Hz}, 1 \mathrm{H})$, $3.28(\mathrm{bs}, 1 \mathrm{H}), 3.23(\mathrm{~s}, 1 \mathrm{H}), 2.51$ (t of sep, $J=2.1,6.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.24-2.03(\mathrm{~m}, 2 \mathrm{H}), 1.98-$ $1.62(\mathrm{~m}, 5 \mathrm{H}), 1.30-1.23(\mathrm{~m}, 1 \mathrm{H}), 1.13(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H}), 1.06(\mathrm{~s}, 3 \mathrm{H}), 0.91(\mathrm{~s}, 9 \mathrm{H}), 0.12$
$(\mathrm{s}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \square 144.9,125.9,85.8,84.6,79.8,66.1,65.7,40.3$, 37.4, 28.1, 26.2, 26.0, 25.5, 23.6, 20.7, 18.3, 14.1, -5.2, -5.3; IR (neat) 3461, 3311, 2957, 2931, 2858, $1463 \mathrm{~cm}^{-1}$.
Minor diastereomer: $\mathrm{R}_{\mathrm{f}} 0.3$ (EtOAc: hexanes $1: 9$ ); ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\square 4.72$ $\left({ }^{1} /{ }_{2} \mathrm{AB} \mathrm{q}, J=13.0 \mathrm{~Hz}, 1 \mathrm{H}\right), 4.50\left({ }^{1} /{ }_{2} \mathrm{AB}\right.$ q $\left., J=13.1 \mathrm{~Hz}, 1 \mathrm{H}\right), 4.33(\mathrm{t}, J=5.3 \mathrm{~Hz}, 1 \mathrm{H})$, $3.60(\mathrm{bs}, 1 \mathrm{H}), 3.22(\mathrm{~s}, 1 \mathrm{H}), 2.51(\mathrm{t}$ of sep, $J=2.1,6.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.19-2.01(\mathrm{~m}, 2 \mathrm{H}), 1.94-$ $1.50(\mathrm{~m}, 6 \mathrm{H}), 1.14(\mathrm{~s}, 3 \mathrm{H}), 1.13(\mathrm{~d}, J=6.7 \mathrm{~Hz}, 6 \mathrm{H}), 0.92(\mathrm{~s}, 9 \mathrm{H}), 0.12(\mathrm{~s}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \square 145.6,125.2,85.9,84.3,79.6,79.4,66.9,65.4,39.1,37.3,29.3,26.6$, $26.1,25.8,23.3,20.6,18.1,14.0,-5.4,-5.5$; IR (neat) $3472,3311,2932,2858,1463 \mathrm{~cm}^{-1}$.


14


15

6-(tert-Butyldimethylsiloxymethyl)-1-(tert-butyldimethylsiloxymethyl)-2-ethy-nyl-3-methyl-3-(5-methylhex-3-ynyl)cyclohexene (15).

The same procedure used for the conversion of $\mathbf{1 2}$ to $\mathbf{1 3}$ was used for the conversion of $\mathbf{1 4}$ to $\mathbf{1 5}$ to give a $95 \%$ yield of compound $\mathbf{1 5}$ as a $3: 1$ mixture of two diastereomers. Prepared from compound 14 ( $890 \mathrm{mg}, 2.38 \mathrm{mmol}$ ), imidazole ( $453 \mathrm{mg}, 6.67 \mathrm{mmol}$ ), TBSCl ( $502 \mathrm{mg}, 3.33 \mathrm{mmol}$ ) and DMF ( 1 mL ).
${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ), (mixture of two diastereomers, * denotes minor diastereomer) $\square * 4.66(1 / 2 \mathrm{AB} \mathrm{q}, J=12.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.63(1 / 2 \mathrm{AB} \mathrm{q}, J=11.5 \mathrm{~Hz}, 1 \mathrm{H}), 4.42-$ $4.38(\mathrm{~m}, 1 \mathrm{H}$, diastereomer overlap), $4.28(1 / 2 \mathrm{AB} \mathrm{q}, J=11.6 \mathrm{~Hz}, 1 \mathrm{H}), * 4.17(1 / 2 \mathrm{AB}$ q,$J=$ $12.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.13(\mathrm{~s}, 1 \mathrm{H}), 2.52(\mathrm{t}$ of sep, $J=1.9,6.9 \mathrm{~Hz}, 1 \mathrm{H}), 2.18-2.02(\mathrm{~m}, 2 \mathrm{H}), 1.94-$ $1.50(\mathrm{~m}, 6 \mathrm{H}), 1.14(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H}),{ }^{*} 1.13(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H}), 1.12(\mathrm{~s}, 3 \mathrm{H}), * 1.07(\mathrm{~s}$, $3 \mathrm{H}), 0.90(\mathrm{~s}, 9 \mathrm{H}), 0.89(\mathrm{~s}, 9 \mathrm{H}), 0.11$ (s, 3H), *0.09 (s, 3H), *0.08 (s, 3H), 0.07 (s, 3H), $0.05(\mathrm{~s}, 3 \mathrm{H}),{ }^{* 0.02}(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\square 147.9,126.2,86.0$, *85.8, 83.0, 81.1, 80.0, 64.6, 62.1, 41.0, 39.2, *37.4, 37.2, 29.3, 28.7, *28.0, 26.3, 26.2, 23.7, 20.8, $18.5,18.4,14.2,-4.3,-4.5,-4.6,-4.9$.


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16

3-[3-(tert-Butyldimethylsiloxy)-2-(tert-butyldimethylsiloxymethyl)-6-methyl-6-(5-methyl-hex-3-ynyl)cyclohex-1-enyl]prop-2-yn-1-ol (16).

To a solution of 6-(tert-butyldimethylsiloxy)-1-(tert-butyldimethylsiloxymethyl)-2-ethynyl-3-methyl-3-(5-methylhex-3-ynyl)cyclohexene (15, 3: 1 mixture of two diastereomers, $114 \mathrm{mg}, 0.23 \mathrm{mmol}$ ) in 1.0 mL of THF was added $n$-butyllithium ( 0.22 mL of a 1.6 M hexanes solution, 0.35 mmol ) at $-78^{\circ} \mathrm{C}$. After 30 min , paraformaldehyde powder ( $35 \mathrm{mg}, 1.2 \mathrm{mmol}$ ) was added in one portion. The reaction was allowed to gradually warm to rt and after 24 h was quenched with sat'd $\mathrm{NH}_{4} \mathrm{Cl}$ solution. The aqueous layer was separated and extracted with $\mathrm{Et}_{2} \mathrm{O}$. The combined organic layers were washed with brine and dried over $\mathrm{MgSO}_{4}$. The solvent was removed in vacuo and the residue was purified by chromatography on silica gel eluting with $20: 80 \mathrm{EtOAc}$ : hexanes to yield $88 \mathrm{mg}(74 \%)$ of compound $\mathbf{1 6}$ as a mixture of two diastereomers ( $3: 1$ ) as a yellow oil.
${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ), (mixture of two diastereomers, * denotes minor diastereomer) $\square^{*} 4.60\left({ }^{1} / 2 \mathrm{AB}\right.$ q $\left., J=11.9 \mathrm{~Hz}, 1 \mathrm{H}\right), 4.58\left({ }^{1} / 2 \mathrm{AB}\right.$ q $\left., J=11.4 \mathrm{~Hz}, 1 \mathrm{H}\right), 4.43$ $(\mathrm{s}, 2 \mathrm{H}), 4.43-4.37(\mathrm{~m}, 3 \mathrm{H}), 4.27(1 / 2 \mathrm{AB}$ q $, J=11.5 \mathrm{~Hz}, 1 \mathrm{H}), * 4.16\left({ }^{1} / 2 \mathrm{AB}\right.$ q,$J=11.9 \mathrm{~Hz}$, $1 \mathrm{H}), 2.52(\mathrm{t}$ of sep, $J=1.8,6.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.16-2.00(\mathrm{~m}, 2 \mathrm{H}), 1.91-1.45(\mathrm{~m}, 6 \mathrm{H}), 1.14(\mathrm{~d}, J$ $=6.9 \mathrm{~Hz}, 6 \mathrm{H}),{ }^{*} 1.13(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 6 \mathrm{H}), 1.10(\mathrm{~s}, 3 \mathrm{H}), 1.05(\mathrm{~s}, 3 \mathrm{H}), 0.89(\mathrm{~s}, 9 \mathrm{H}), 0.88(\mathrm{~s}$, 9H), *0.87 (s, 9H), $0.10(\mathrm{~s}, 3 \mathrm{H}), 0.08(\mathrm{~s}, 6 \mathrm{H}), 0.05(\mathrm{~s}, 3 \mathrm{H}),{ }^{*} 0.02(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (75 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \square 146.6, * 146.2,126.3,92.7,85.9,83.2,79.9,64.6,62.0,51.8,39.1,37.3$, $29.2,28.5,26.5,26.1,26.0,23.5,20.7,18.4,18.2,14.1,-4.4,-4.6,-4.8,-5.0$; IR (neat) 3431, 2930, 2857, 2214, $1727 \mathrm{~cm}^{-1}$; HRMS calcd for $\mathrm{C}_{30} \mathrm{H}_{54} \mathrm{O}_{3} \mathrm{Si}_{2}$ 518.3612, found 518.3627.


16


17
(\{1-[3-(tert-Butyldimethylsiloxy)-2-(tert-butyldimethylsiloxymethyl)-6-methyl-ethylhex-3-ynyl)cyclohex-1-enyl]propa-1,2-dienyl\}dimethylsilanyl)benzene (17).

To a solution of 3-[3-(tert-butyldimethylsiloxy)-2-(tert-butyldimethylsiloxy-methyl)-6- methyl-6-(5-methylhex-3-ynyl)cyclohex-1-enyl]prop-2-yn-1-ol (16, 3: 1 mixture of two diastereomers), ( $126 \mathrm{mg}, 0.24 \mathrm{mmol}$ ) in 2 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ were added $\mathrm{Et}_{3} \mathrm{~N}(69 \mu \mathrm{~L}$, $0.49 \mathrm{mmol})$ and $\mathrm{MsCl}(28 \mu \mathrm{~L}, 0.37 \mathrm{mmol})$ dropwise at $-20^{\circ} \mathrm{C}$. After 30 min at $-20^{\circ} \mathrm{C}$, the mixture was diluted with pentane and filtered through a pad of celite and pad was washed
with pentane. The pentane was washed with sat'd $\mathrm{NaHCO}_{3}$, brine and dried over $\mathrm{MgSO}_{4}$. The solvent was removed in vacuo and the residue (propargyl mesylate) was used without purification.

To a mixture of $\mathrm{Li}\left(17 \mathrm{mg}, 2.4 \mathrm{mmol}\right.$, washed with hexanes and dried with $\left.\mathrm{N}_{2}\right)$ in 2 mL of THF was added dropwise dimethylphenylsilyl chloride ( $83 \mathrm{mg}, 0.49 \mathrm{mmol}$ ) at 0 ${ }^{\circ} \mathrm{C}$, and the mixture was warmed to rt . After 24 h , the red solution was added dropwise to a suspension of $\mathrm{CuCN}(24 \mathrm{mg}, 0.27 \mathrm{mmol})$ in 4 mL of THF at $0^{\circ} \mathrm{C}$, and the mixture was stirred for 30 min . A solution of propargyl mesylate in 1.0 mL of THF was added dropwise to the mixture at $-85^{\circ} \mathrm{C}$. After 30 min , the reaction was complete and poured into 10 mL of saturated aqueous $\mathrm{NH}_{4} \mathrm{Cl}$ solution. The mixture was stirred for 2 h during this time the aqueous layer became cobalt blue. The aqueous layer was separated and extracted with $\mathrm{Et}_{2} \mathrm{O}$. The combined organic layers were washed with brine, dried over $\mathrm{MgSO}_{4}$, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel, eluting with $20: 80 \mathrm{EtOAc}$ : hexanes to produce 139 mg in $90 \%$ yield of compound $\mathbf{1 7}$ as a mixture of two diastereomers ( $3: 1$ ) as a yellow oil.
${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ), (mixture of two diastereomers, * denotes minor diastereomer) $\square 7.67-7.61(\mathrm{~m}, 2 \mathrm{H}), 7.39-7.35(\mathrm{M}, 3 \mathrm{H}), * 4.55\left({ }^{1} / 2 \mathrm{AB} \mathrm{q}, J=11.5 \mathrm{~Hz}, 1 \mathrm{H}\right)$, $4.46\left({ }^{1} / 2 \mathrm{AB} \mathrm{q}, J=11.6 \mathrm{~Hz}, 1 \mathrm{H}\right), 4.48-4.44(\mathrm{~m}, 2 \mathrm{H}), 4.19-4.08(\mathrm{~m}, 1 \mathrm{H}), 4.09(1 / 2 \mathrm{AB}$ q, $J$ $=10.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.54(\mathrm{t}$ of sep, $J=1.9,6.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.08(\mathrm{bs}, 2 \mathrm{H}), 1.77-1.49(\mathrm{~m}, 6 \mathrm{H})$, *1.19 (d, $J=6.6 \mathrm{~Hz}, 3 \mathrm{H}), ~ * 1.18(\mathrm{~d}, J=6.7 \mathrm{~Hz}, 3 \mathrm{H}), 1.17(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 6 \mathrm{H}), 1.10(\mathrm{~s}$, $3 \mathrm{H}), 0.95(\mathrm{~s}, 18 \mathrm{H}), * 0.94(\mathrm{~s}, 18 \mathrm{H}), 0.89(\mathrm{~s}, 3 \mathrm{H}), * 0.86(3,3 \mathrm{H}), 0.44(\mathrm{~s}, 3 \mathrm{H}), 0.42(\mathrm{~s}, 3 \mathrm{H})$, $0.14(\mathrm{~s}, 3 \mathrm{H}), 0.12(\mathrm{~s}, 3 \mathrm{H}),{ }^{*}-0.03(\mathrm{~s}, 3 \mathrm{H}),{ }^{*}-0.04(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\square$ 208.2, 138.8, 137.9, 134.7, 134.5, 134.3, 134.2, *133.9, 129.3, *128.7, *128.2, *128.1, 128.0, 94.1, 85.8, 80.3, 68.6, 64.0, 62.5, 41.3, 39.4, 39.1, 37.9, 28.9, 28.4, 27.0, 26.3, $26.2,23.8,20.9,18.4,18.3,14.4, *-2.05, *-2.23, *-3.59,-4.1,-4.7,-5.0$; IR (neat) 2955, 1922, $1463 \mathrm{~cm}^{-1}$; HRMS calcd for $\mathrm{C}_{36} \mathrm{H}_{64} \mathrm{O}_{2} \mathrm{Si}_{3} 636.4214$, found 636.4221.


6-(tert-Butyldimethylsiloxy)-5-(tert-butyldimethylsiloxymethyl)-4-(dimethyl-phenylsil)-1-isopropyl-8a-methyl-6, 7, 8, 8a, 9, 10-hexahydro-3H-benzo[f]azulen-2one (18).

To a flame-dried test tube ( $16 \times 100 \mathrm{~mm}$ ) equipped with a magnetic stir bar was added (\{1-[3-(tert-butyldimethylsiloxy)-2-(tert-butyldimethylsiloxymethyl)-6-methyl-6-(5-methylhex-3-ynyl)cyclohex-1-enyl]prop-1,2-dienyl\}dimethylsil)benzene (17, $3: 1$ mixture of two diastereomers), ( $93 \mathrm{mg}, 0.15 \mathrm{mmol}$ ) in toluene ( 1.5 mL ). The test tube was evacuated and charged with CO three times, then $\left[\mathrm{Rh}(\mathrm{CO})_{2} \mathrm{Cl}\right]_{2}(5.7 \mathrm{mg}, 0.015$ mmol ) was added. The mixture was heated at $80^{\circ} \mathrm{C}$ under CO balloon ( 1 atm ) for 5 h ,
during this time the solution changed from light yellow to brown. By TLC, the starting material had been consumed and the mixture was taken out of the oil bath and cooled to rt. Most of the solvent was evaporated in vacuo and the residue was filtered through a pad of celite and the pad was washed with ether. The ether was removed in vacuo and the residue was purified by chromatography on silica gel eluting with $5: 95 \mathrm{EtOAc}$ : hexanes to yield $61 \mathrm{mg}(65 \%)$ of compound $\mathbf{1 8}$ as a mixture of two diastereomers (3:1) as a yellow oil. IR (neat) 2930, 2857, $1698 \mathrm{~cm}^{-1}$; HRMS calcd for $\mathrm{C}_{39} \mathrm{H}_{64} \mathrm{O}_{3} \mathrm{Si}_{3} 664.4163$, found 664.4200. The diastereomers were separated using HPLC (Microsorb silica gel column, $5 \square, 100 \AA$ ) eluting with $5: 95 \mathrm{EtOAc}$ : hexanes.

Major diastereomer: $\mathrm{R}_{\mathrm{f}} 0.4$ (EtOAc: hexanes $1: 9$ ); ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\square 7.59$ $7.56(\mathrm{~m}, 2 \mathrm{H}), 7.35-7.33(\mathrm{~m}, 3 \mathrm{H}), 4.50(\mathrm{bs}, 1 \mathrm{H}), 4.15\left({ }^{1} / 2 \mathrm{AB} \mathrm{q}, J=11.5 \mathrm{~Hz}, 1 \mathrm{H}\right), 4.04\left({ }^{1} / 2\right.$ AB q, $J=11.6 \mathrm{~Hz}, 1 \mathrm{H}), 2.90(\mathrm{~d}, J=20.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.80(\mathrm{q}, J=6.9 \mathrm{~Hz}, 1 \mathrm{H}), 2.79(\mathrm{~d}, J=$ $20.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.67$ (dd, $J=15.8,6.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.43(\mathrm{dd}, J=15.7,11.4 \mathrm{~Hz}, 1 \mathrm{H}) 2.11(\mathrm{dt}, J$ $=2.8,13.5 \mathrm{~Hz}, 1 \mathrm{H}), 1.78-1.57(\mathrm{~m}, 3 \mathrm{H}), 1.44-1.24(\mathrm{~m}, 2 \mathrm{H}), 1.18(\mathrm{~d}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H}), 1.16$ $(\mathrm{d}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H}), 1.07(\mathrm{~s}, 3 \mathrm{H}), 0.90(\mathrm{~s}, 9 \mathrm{H}), 0.89(\mathrm{~s}, 9 \mathrm{H}), 0.57(\mathrm{~s}, 3 \mathrm{H}), 0.38(\mathrm{~s}, 3 \mathrm{H})$, $0.12(\mathrm{~s}, 3 \mathrm{H}), 0.11(\mathrm{~s}, 3 \mathrm{H}), 0.086(\mathrm{~s}, 3 \mathrm{H}), 0.016(\mathrm{~s}, 3 \mathrm{H}),{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \square$ 204.5, 170.2, 148.3, 146.7, 141.5, 138.3, 136.8, 135.3, 134.4, 128.9, 127.9, 63.5, 60.6, $41.8,40.6,40.1,31.2,28.1,26.9,26.0,25.9,24.7,24.0,20.4,20.3,18.2,18.1,-0.53$, -$0.61,-3.74,-4.60,-4.67,-4.98$. Minor diastereomer: $\mathrm{R}_{\mathrm{f}} 0.35$ (EtOAc: hexanes $1: 9$ ); ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\square 7.61-7.56(\mathrm{~m}, 2 \mathrm{H}), 7.38-7.34(\mathrm{~m}, 3 \mathrm{H}), 4.44(\mathrm{t}, J=5.9 \mathrm{~Hz}$, $1 \mathrm{H}), 4.21\left(\frac{1}{2} \mathrm{AB}\right.$ q $\left., J=9.8 \mathrm{~Hz}, 1 \mathrm{H}\right), 4.14(1 / 2 \mathrm{AB}$ q $, J=9.7 \mathrm{~Hz}, 1 \mathrm{H}), 2.86(\mathrm{~s}, 2 \mathrm{H}), 2.83-$ $2.67(\mathrm{~m}, 2 \mathrm{H}), 2.36(\mathrm{t}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.93-1.83(\mathrm{~m}, 1 \mathrm{H}), 1.73-1.48(\mathrm{~m}, 4 \mathrm{H}), 1.36(\mathrm{t}, J=$ $12.9 \mathrm{~Hz}, 1 \mathrm{H}), 1.16(\mathrm{~d}, J=7.0 \mathrm{~Hz}, 6 \mathrm{H}), 1.13(\mathrm{~s}, 3 \mathrm{H}), 0.92(\mathrm{~s}, 9 \mathrm{H}), 0.76(\mathrm{~s}, 9 \mathrm{H}), 0.48(\mathrm{~s}$, $3 \mathrm{H}), 0.36(\mathrm{~s}, 3 \mathrm{H}), 0.11(\mathrm{~s}, 3 \mathrm{H}), 0.10(\mathrm{~s}, 3 \mathrm{H}),-0.10(\mathrm{~s}, 3 \mathrm{H}),-0.20(\mathrm{~s}, 3 \mathrm{H}),{ }^{13} \mathrm{C}$ NMR (75 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \square 204.5,169.2,147.1,146.6,141.3,138.4,137.5,136.0,134.6,129.1$, $128.0,65.9,61.8,41.0,40.4,39.5,34.8,29.2,28.6,25.9,25.8,24.8,24.8,20.5,20.3$, 18.2, 18.1, -0.92, -0.99, -4.10, -5.00, -5.15, -5.48.

