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Construction of fused, bridged, and spiro bicyclic skeletons via nickel-catalyzed intramolecular cyclization of cyclic 1,3-dienes and a tethered aldehyde

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Abstract—Nickel-catalyzed intramolecular cyclization of cyclohexa-1,3-dienes and an aldehyde in a chain produced fused, bridged or spiro bicyclic skeletons depending on the length of the tether. This chemistry can be extended to cyclohepta-1,3-dienes and cyclohepta-1,3,5-trienes having an aldehyde moiety on the side chain.

1. Introduction

Metal catalysts provide new opportunities for highly selective cycloaddition reactions since complexation of the metal to an olefin, diene, acetylene, or arene significantly modifies the reactivity of this moiety, opening the way for improved reactivity and novel chemistry. One of the most important consequences of complexation is to temporarily polarize and activate an otherwise unreactive species. In addition to the rate enhancements observed in the presence of the metal catalyst, the opportunity to achieve stereoselective transformations is one of the attractive features of this strategy. Recently, nickel-catalyzed cyclization of 1,3-dienes and multiple bonds has proven to be highly efficient in the construction of complex molecules.[1–9] Among these, nickel-catalyzed cyclization of acyclic 1,3-dienes and an aldehyde in a chain to produce five- to seven-membered ring carbocycles in stereoselective fashion[10–13] prompted us to investigate the intramolecular cyclization of cyclic 1,3-dienes and a tethered aldehyde. In this paper, we report for the first time that fused, bridged and spiro bicyclic ring skeletons can be constructed by nickel-catalyzed intramolecular cyclization of cyclic 1,3-dienes and an aldehyde in a chain.

2. Results and discussion

The starting aldehydes **1a–e** (entries 1–5, Table 1) were prepared starting from addition of the corresponding ester or cyano functionalized zinc–copper reagents RCu(CN)ZnI to the (η^5-cyclohexadienyl)tricarbonyliron cation salt in tetrahydrofuran (THF) according to literature procedures.[14,15] Decomplexation[16] of the resulting complexes with cerium ammonium nitrate (CAN) in methanol followed by reduction with diisobutylaluminum hydride (DIBAL) at −78°C afforded the starting substrates **1a–e** in good yields (Scheme 1). Seven-membered ring substrates **2a–c** (entries 6–8, Table 1) and **3a–c** (entries 9–11, Table 1) were synthesized in the similar fashion starting from addition of the corresponding ester or cyano functionalized zinc–copper reagents to (η^5-cycloheptadienyl)tricarbonyliron (Scheme 1)[17] and (η^7-cycloheptatrienyl)tricarbonylchromium cation salts (Scheme 2),[18] respectively.

Under our optimized reaction conditions, intramolecular cyclization reactions of cyclic dienals using $Ni(COD)_2$ (0.2 equiv.), PPh_3 (0.4 equiv.) and Et_3SiH (5.0 equiv.) in THF were investigated and results are listed in Table 1. Compound **1a** with two methylene units at the chain produced bicyclo[4.3.0]nonenol derivatives **4** and **5** as olefinic isomers in 66% total yield (entry 1, Table 1). The ratio of **4** and **5** was determined to be 2:1 by ^1H NMR spectroscopy of the crude mixture. The relative stereochemistry of **4** and **5** were assigned as all *cis*-relationship on the basis of NOESY experiments. It is important to note that three new contiguous stereogenic centers of bicyclic compounds **4** and **5** are created with extreme diastereoselectivity, however, only the single diastereomer shown was isolated. Formation of regio isomers **4** and **5** is consistent with that of the reaction path proposed by Mori in intramolecular cyclization of acyclic dienes and an aldehyde.[19] The formation of fused bicyclic compound **4** presumably started from oxidative cycloaddition of **1a** to Ni(0) complex to give postulated oxanickel intermediate **6** (path a, Scheme 1). Sigma bond metathesis of triethylsilane and the nickel/oxygen bond of **6** would afford nickel hydride

Keywords: nickel; stereoselectivity; cyclic 1,3-dienes; fused, bridged, and spiro carbobicycles.

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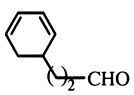
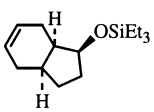
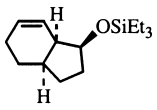
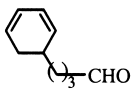
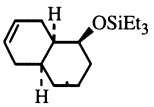
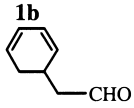
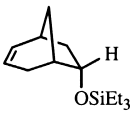
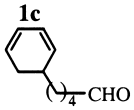
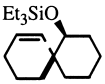
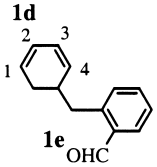
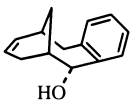
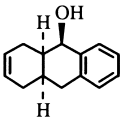
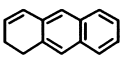
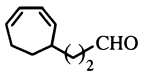
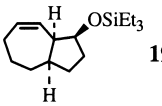
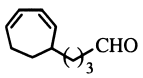
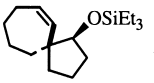
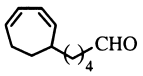
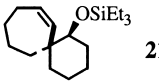
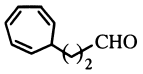
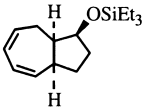
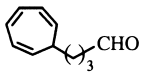
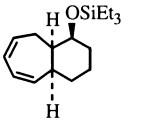
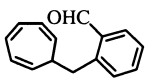
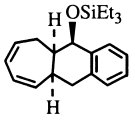
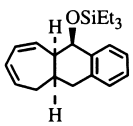
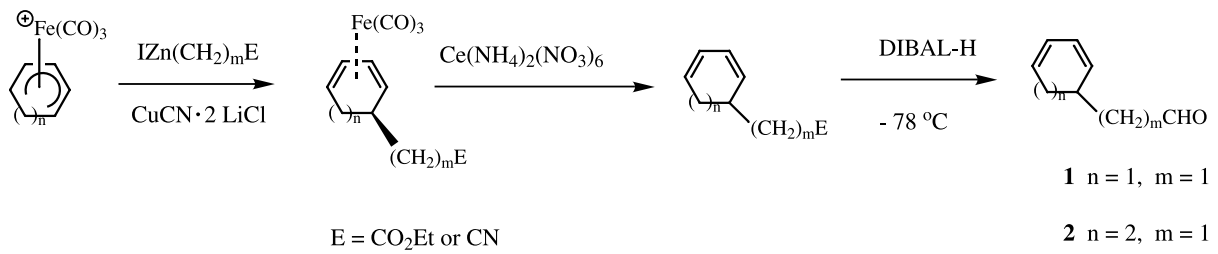
Table 1. Intramolecular cyclization of dienals using $Ni(COD)_2$, Et_3SiH and PPh_3

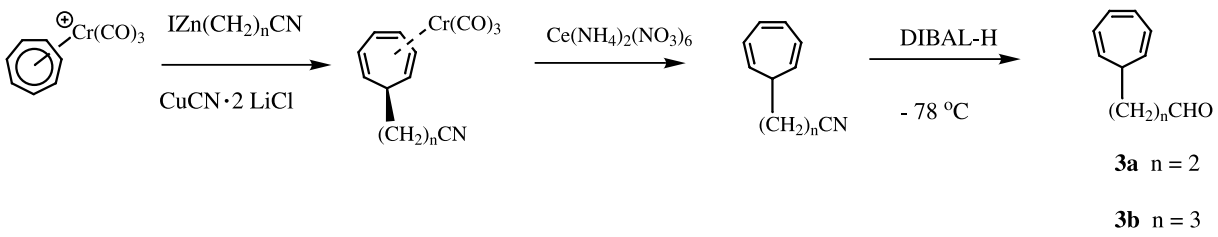
Entry[a]	Dienal	Temperature (°C)	Time (h)	Products
1	 **1a**	30°C	10	 **4** (44%)  **5** (22%)
2	 **1b**	30°C	3	 **10** (60%)
3	 **1c**	55°C	17	 **11a** (13%)[b]
4	 **1d**	55°C	10	 **13** (30%)[b]
5	 **1e**	55°C	8	 **16** (34%)[c]  **17** (17%)[c]  **18** (17%)[c]
6	 **2a**	30°C	4	 **19** (81%)
7	 **2b**	35°C	8	 **20** (36%)[b]
8	 **2c**	45°C	34	 **21** (22%)[b]
9	 **3a**	30°C	2	 **23** (47%)[b]
10	 **3b**	35°C	16	 **24** (30%)[b]
11	 **3c**	35°C	16	 **25** (15%)[b]  **26** (13%)[b]

[a] All cyclizations were carried out in THF using $Ni(COD)_2$ (0.2 equiv.), PPh_3 (0.4 equiv.) and Et_3SiH (5.0 equiv.).
[b] A significant amount of the starting material and polymeric mixtures were obtained after separation of the crude mixture on silica gel.
[c] Desilylation of the crude mixture was performed by using TBAF (5.0 equiv.) in CH_2Cl_2.

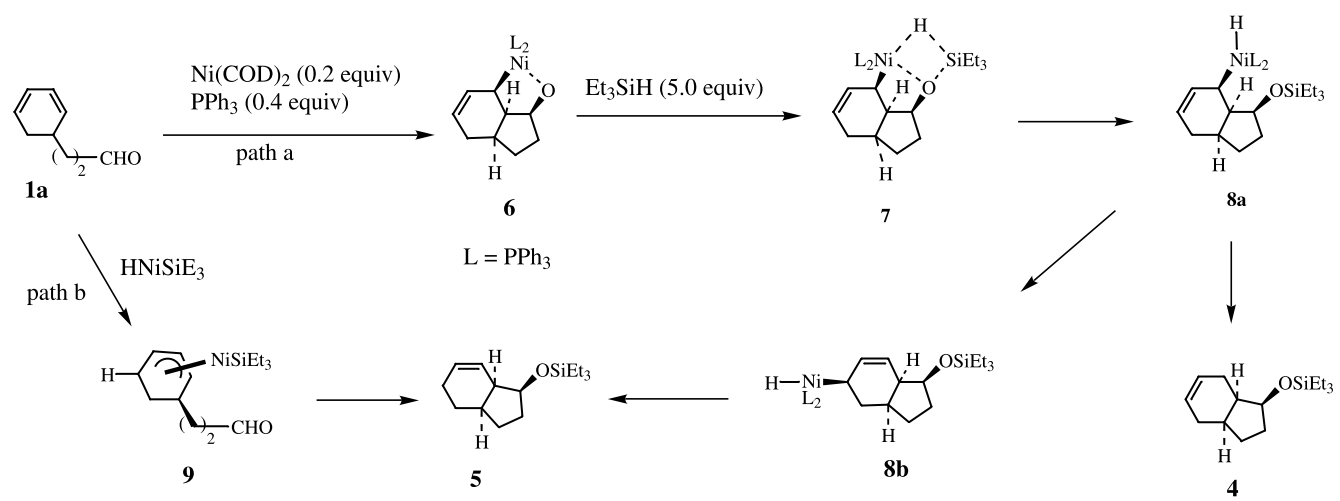
7, which led to allylnickel **8a**. Intermediate **8a** underwent reductive elimination to afford **4**. The formation of **5** could be explained by reaction of **1a** and $HNiSiEt_3$ to give π-allylnickel species **9** (path b, Scheme 3). Addition of the allylnickel to the aldehyde moiety followed by reductive elimination afforded **5**. Alternatively, converting of allylnickel **8a** via a π-allylnickel intermediate would give **8b**. Intermediate **8b** led to **5** after reductive elimination. Increasing the tether length by one with the starting substrate **1b** also allowed intramolecular cyclization to provide bicyclo[4.4.0]decenol derivative **10** as the only regio and diastereo isomer obtained in 60% yield (entry 2, Table 1). The isolation of the single regioisomer **10** may indicate that oxidative cycloaddition of Ni(0) to **1b** may be a



Scheme 1.

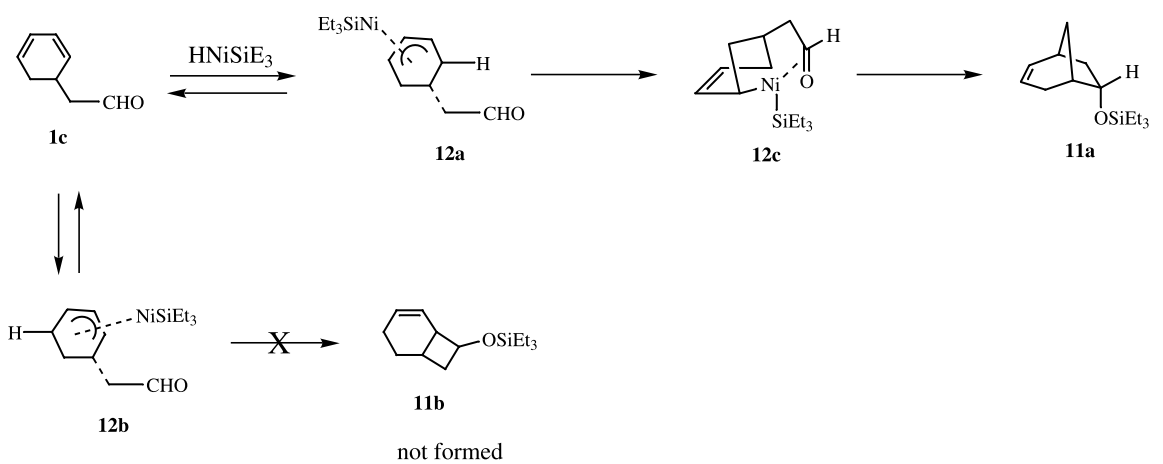


Scheme 2.

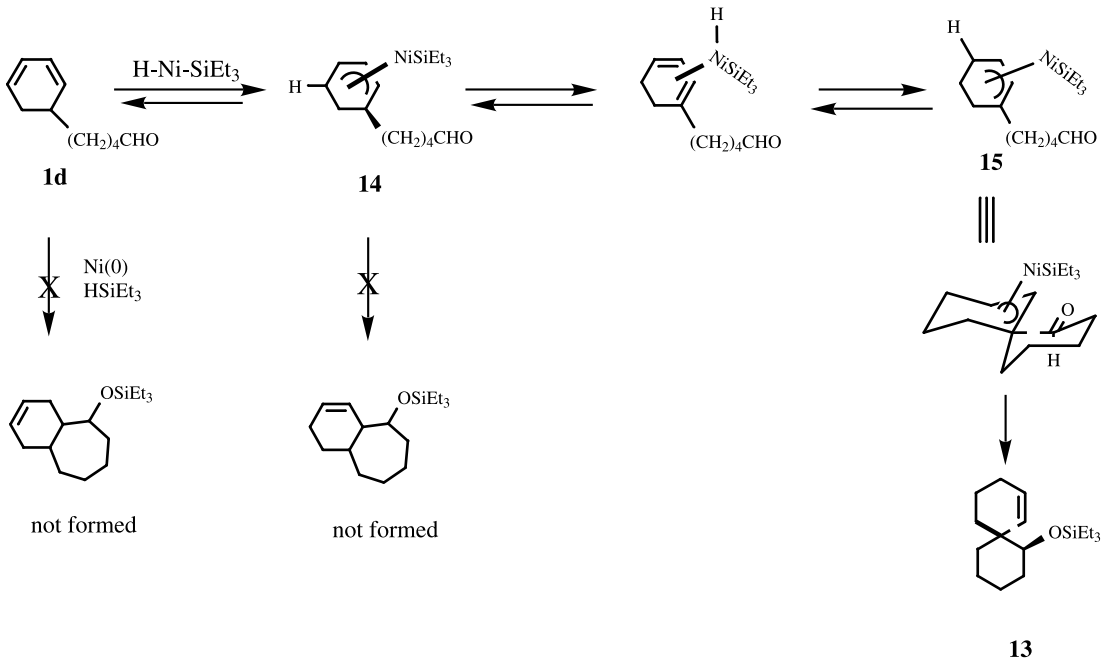


Scheme 3.

favored route (path a) compared to that of addition of $HNiSiEt_3$ to the diene (path b). Interestingly, cyclization of the substrate with one carbon tether, **1c**, gave bicyclo[3.2.1]-octenol derivative **11a** in 13% yield (entry 3, Table 1) together with recovery of the starting dienal **1c** and an identified mixture of polymeric compounds. The generation of bridged bicyclic skeleton **11a** may start with addition of $HNiSiEt_3$ to **1c** to generate π-allylnickel species **12a**,**b** (Scheme 4). Intermediate **12a** led to **11a** and π-allylnickel **12b** would produce the fused bicyclo[4.2.0]cyclooctenol



Scheme 4.

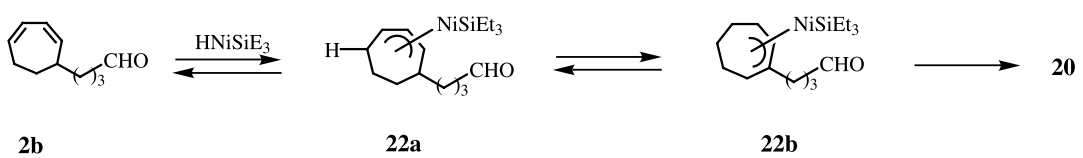


Scheme 5.

derivative **11b**. However, formation of four-membered ring may be difficult. Thus, none of **11b** was obtained. The low yield of the cyclization may be due to a high activation energy required for converting π-allylnickel **12b** to the relative congested σ-allylnickel **12c**, which led to **11a**. Hydride elimination of **12a** would regenerate **1c**. Moreover, intermolecular addition of π-allylnickel **12b** to the aldehyde moiety would produce polymeric compounds. Surprisingly, the substrate with four methylene units and an aldehyde in a chain, **1d**, produced spiro[5,5]undecenol derivative **13** in 30% yield (entry 4, Table 1) together with isolation of the starting dienal **1d** and an identified mixture of polymeric compounds. The generation of the spiro compound **13** is suggested in Scheme 5. It may be due to unfavorable formation of seven-membered ring, bicyclo[5.3.0]decenol derivatives were not generated via either oxidative cycloaddition or $HNiSiEt_3$ addition to the diene. The postulate intermediate **14**, derived from $HNiSiEt_3$ addition to **1d**, underwent β-hydride elimination/readdition to give π-allylnickel **15**, which underwent cyclization presumably via a chair-form transition state to produce the spiro compound **13**. The low yield for the formation of the spiro compound (via infra) may be explained as follows. The energy barrier required for converting disubstituted π-allylnickel **14** to the less stable trisubstituted π-allylnickel species **15** may be high. Intermediate π-allylnickel **14** would lead to the starting dienal **1d** via β-hydride elimination or to polymers via intermolecular addition of π-allylnickel to the aldehyde moiety.

The cyclohexa-1,3-diene with an aromatic aldehyde, **1e**, generated the bridged tricyclic compound **16** (34%), fused tricyclic compounds **17** (17%) and 1,2-dihydroanthracene **18** (17%) after desilylation of the crude product with tetrabuylammonium fluoride (TBAF) and column chromatography of the crude mixture (entry 5, Table 1). The bridged tricyclic compound **16** presumably derived from initial oxidative cycloaddition of the C_1-C_2 double bond of **1e** to Ni(0) after desilylation, while oxidative cycloaddition occurred at the C_3-C_4 double bond of **1e** to generate **17** after desilylation. Alternatively, addition of $HNiSiEt_3$ to the diene followed by desilylation with TBAF and dehydration during aqueous work up afforded dihydroanthracene **18**.

This chemistry can be extended to cyclohepta-1,3-dienes and a tethered aldehyde. Thus, intramolecular cyclization of **2a** furnished fused bicyclo[5.3.0]decenol derivative **19** as the only diastereomer in 81% yield (entry 6, Table 1). Increasing the tether length by one and two with substrates **2b**,**c** produced spiro[6.4]undecenol derivative **20** (36%, from **2b**, entry 7, Table 1) and spiro[6.5]dodecenol derivative **21** (22%, from **4c**, entry 8, Table 1), respectively. It is important to mention that unlike the cyclohexadiene derivative **1b** gave fused product **10**, the corresponding cycloheptadiene derivative **2b** produced spiro compound **20** in low yield. The difference is not clear. It is explained by the rate of allyl migration, for example **22a** to **22b**, is faster than that of π-allylnickel addition to the aldehyde moiety in seven-membered ring (Scheme 6). Intermediate **22b** led to



2b **22a** **22b**

Scheme 6.

the spiro compound **20**. While in the six-membered ring the rate of π-allylnickel addition to the aldehyde is faster than that of allyl migration. Thus, the fused skeleton **10** was formed. The reaction path leading to spiro compounds **21** was presumably similar to that of the spiro compound **13**. Moreover, cyclohepta-1,3,5-triene derivatives **3a**–**c** containing an aldehyde on the side chain also underwent nickel-catalyzed intramolecular cyclization smoothly at room temperature to generate bicyclo[5.3.0]decenol derivative **23** (47% from **3a**, entry 9, Table 1), bicyclo[5.4.0]undecenol **24** (30%, from **3b**, entry 10, Table 1) and tricyclic derivatives **25** (12%, from **3c**, entry 11, Table 1) and **26** (11%, from **3c**, entry 11, Table 1), respectively.

In conclusion, we have found that fused, bridged and spiro bicyclic skeletons containing functional groups can be constructed in diastereoselective fashion using simple organic substrates and catalytic amount of $Ni(COD)_2$. The same strategy can also be applied for the diastereoselective synthesis of tricyclic skeletons using cyclic 1,3-dienes containing a benzaldehyde moiety. This simple organic transformation allowing formation of complicated bicyclic and tricyclic skeletons in diastereoselective fashion may have further applications.

3. Experimental

All reactions were run under an argon atmosphere in oven-dried glassware unless otherwise indicated. Anhydrous solvents or reaction mixtures were transferred via an oven-dried syringe or cannula. THF was dried by passing through two sequential column of activated alumina.[20] Compounds **1a**–**e**,[14] **2a**–**c**[17] and **3a**–**c**[18] were prepared according to literature procedures. Flash column chromatography, following the method of Still, was carried out with E. Merck silica gel (Kieselgel 60, 230–400 mesh) using the indicated solvents.[21] ^{1}H nuclear magnetic resonance (NMR) spectra were obtained with JEOL-EX 400 (400 MHz), and Varian G-200 (200 MHz) spectrometers. The chemical shifts are reported in parts per million with either tetramethylsilane (0.00 ppm) or $CHCl_3$ (7.26 ppm) as internal standard. ^{13}C NMR spectra were recorded with JEOL-EX 400 (100.4 MHz) and Varian G-200 (50 MHz) spectrometers with $CDCl_3$ (77.0 ppm) as the internal standard. Infrared (IR) spectra were recorded with a JASCO IR-700 spectrometer. Mass spectra were acquired on a JEOL JMS-D 100 spectrometer at an ionization potential of 70 eV and are reported as mass/charge (*m*/*e*) with percent relative abundance. High-resolution mass spectra (HRMS) were obtained with an AEI MS-9 double-focusing mass spectrometer and a JEOL JMS-HX 110 spectrometer at the Department of Chemistry, Central Instrument Center, Taichung, Taiwan.

3.1. General procedure for nickel-catalyzed intramolecular cyclization of cyclic 1,3-dienes and a tethered aldehyde

In a typical procedure, to a 100 mL round bottom flask under argon was added PPh_3 (0.36 g, 0.88 mmol) and $Ni(COD)_2$ (0.18 g, 0.44 mmol). The reaction flask was flushed three times with argon. To the reaction mixture at 0°C, THF (9 mL) was added via syringe and was stirred at 0°C for 30 min to give a red brown solution. The reaction was allowed to warm to 30°C and was added Et_3SiH (1.7 mL, 11.0 mmol). The reaction mixture was cooled to 0°C and followed by addition of complex **1a** (0.30 g, 2.2 mmol). The reaction mixture was quenched with 1.0 mL of saturated aqueous ammonium chloride after complex **1a** was no longer appeared on TLC. The reaction mixture was extracted with ether (3×50 mL). The resultant solution was washed with water (50 mL×3) and brine (100 mL×2), dried over anhydrous magnesium sulfate (5.0 g), and concentrated to give the crude mixture.

3.1.1. Triethyl(2,3,3a,4,7,7a-hexahydro-1*H*-inden-1-yloxy)silane 4. Purification of the residue by column chromatography of the crude mixture using hexanes as the eluent gave **4** (0.32 g, 1.2 mmol, 44%) and **5** (0.12 g, 0.5 mmol, 22%), both as colorless oil. Compound **4**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (m, 1H), 5.62 (m, 1H), 4.22 (m, 1H), 2.21 (m, 1H), 2.03 (m, 1H), 1.98 (m, 3H), 1.90 (m, 1H), 1.85 (m, 1H), 1.70–1.45 (m, 3H), 0.95 (t, *J*=7.8 Hz, 9H), 0.58 (q, *J*=7.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.00, 124.97, 76.30, 40.14, 33.93, 31.78, 27.75, 27.54, 20.78, 6.84, 4.84; IR (CH_2Cl_2) 3379, 3060, 2981, 2304, 1615, 1421, 1085 cm^{-1}; EIMS *m*/*z* 251.2 (M^+-1), HRMS calcd for $C_{15}H_{28}OSi$: 252.1909. Found 252.1923.

3.1.2. Triethyl(1-methyl-2,3,3a,4,5,7a-hexahydro-1*H*-inden-1-yloxy)silane 5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 (m, 1H), 5.74 (m, 1H), 2.19 (m, 1H), 2.02 (m, 1H), 1.96 (m, 1H), 1.89 (m, 1H), 1.86 (m, 2H), 1.74 (m, 2H), 1.65 (m, 1H), 1.54 (m, 1H), 1.34 (s, 3H), 0.93 (q, *J*=7.8 Hz, 9H), 0.55 (t, *J*=7.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.11, 126.56, 82.34, 49.83, 40.57, 35.27, 28.36, 27.52, 26.96, 23.42, 7.10, 6.72; IR (CH_2Cl_2) 3375, 3050, 2982, 2305, 1634, 1431, 1079 cm^{-1}; EIMS *m*/*z* 266.1 (M^+), HRMS calcd for $C_{16}H_{30}OSi$: 266.2066. Found 266.2050.

3.1.3. Triethyl(1,2,3,4,4a,5,8,8a-octahydronaphthalen-1-yloxy)silane 10. The general procedure was employed with **1b** (0.30 g, 2.00 mmol) to afford **10** (0.32 g, 1.2 mmol, 60%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.64 (m, 1H), 5.56 (m, 1H), 3.71 (m, 1H), 2.27 (m, 1H), 2.03 (m, 3H), 1.81 (dd, *J*=17.8, 4.9 Hz, 1H), 1.60–1.74 (m, 2H), 1.52–1.58 (m, 2H), 1.35–1.15 (m, 3H), 0.95 (t, *J*=7.8 Hz, 9H), 0.58 (q, *J*=7.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.39, 124.67, 73.56, 39.20, 34.03, 31.60, 29.56, 26.09, 24.24, 20.33, 6.92, 4.93; IR (CH_2Cl_2) 3379, 3058, 2987, 2305, 1616, 1421, 1085 cm^{-1}; EIMS *m*/*z* 266.2 (M^+), HRMS calcd for $C_{16}H_{30}OSi$: 266.2066. Found 266.2038.

3.1.4. Triethyl(bicyclo[3.2.1]oct-3-en-6-yloxy)silane 11a. The general procedure was employed with **1c** (0.50 g, 4.10 mmol) to afford **11a** (0.13 g, 1.5 mmol, 13%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (m, 1H), 5.58 (m, 1H), 4.36 (dt, *J*=8.9, 5.4 Hz, 1H), 2.39 (m, 1H), 2.31 (m, 1H), 2.17 (m, 2H), 1.92 (m, 1H), 1.54 (m, 2H), 1.24 (dd, *J*=12.0, 6.4 Hz, 1H), 0.95 (t, *J*=7.8 Hz, 9H), 0.56 (q, *J*=7.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.19, 125.35, 81.07, 40.66, 39.44, 37.90, 32.56, 32.30, 6.80, 4.74; IR (CH_2Cl_2) 3383, 3060, 2984, 2307, 1626, 1428, 1084 cm^{-1}; EIMS *m*/*z* 238.2 (M^+), HRMS calcd for $C_{14}H_{26}OSi$: 238.1753. Found 238.1729.

3.1.5. Triethyl(spiro[5.5]undec-7-en-1-yloxy)silane 13. The general procedure was employed with **1d** (0.40 g, 2.40 mmol) to afford **13** (0.20 g, 0.72 mmol, 30%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 (dt, J=10.1, 3.8 Hz, 1H), 5.43 (d, J=10.1 Hz, 1H), 3.43 (dd, J=8.7, 3.6 Hz, 1H), 1.93 (m, 2H), 1.8–1.1 (m, 12H), 0.95 (t, J=7.8 Hz, 9H), 0.56 (q, J=7.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.95, 127.31, 75.96, 40.10, 34.70, 30.45, 26.59, 25.60, 23.38, 20.80, 18.85, 6.97, 5.19; IR (CH_2Cl_2) 3380, 3061, 2982, 2305, 1634, 1424, 1084 cm^{-1}; EIMS m/z 279.1 (M^+-1), HRMS calcd for $C_{17}H_{32}OSi$: 280.2222. Found 280.2225.

3.1.6. Tricyclo[8.3.1.0]tetradeca-3(8),4,6,11-tetraen-2-ol (16). The general procedure was employed with **1d** (0.70 g, 3.50 mmol) to afford a crude mixture. Addition of molecular sieves (5.00 g) and tetrabutyl ammonium fluoride (5.00 mL) to the crude mixture followed by regular aqueous workup to produce **16** (0.24 g, 1.19 mmol, 34%), **17** (0.12 g, 17%, 0.60 mmol) and dihydroanthracene **18** (0.11 g, 17%, 0.59 mmol). Compound **16** a white solid (mp 102–104°C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J=7.0 Hz, 1H), 7.22 (m, 2H), 7.12 (d, J=7.0 Hz, 1H), 5.71 (m, 1H), 5.65 (m, 1H), 4.98 (d, J=4.0 Hz, 1H), 2.92 (dd, J=17.0, 8.0 Hz, 1H), 2.79 (dd, J=17.0, 7.0 Hz, 1H), 2.62 (m, 1H), 2.20 (m, 3H), 1.90 (br, OH), 1.78 (dd, J=13.2, 12.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.86, 136.49, 131.35, 128.49, 127.72, 127.49, 125.85, 125.75, 71.00, 39.94, 32.69, 29.66, 27.91, 23.85; IR (CH_2Cl_2) 3369, 3054, 2987, 2305, 1622, 1422, 1086 cm^{-1}; EIMS m/z 200.1 (M^+), HRMS calcd for $C_{14}H_{16}O$: 200.1201. Found 200.1204.

3.1.7. 1,4,4a,9,9a,10-Hexahydroanthracen-9-ol (17). A white solid (mp 99–101°C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J=7.5 Hz, 1H), 7.18 (m, 2H), 7.12 (d, J=7.0 Hz, 1H), 5.99 (m, 1H), 5.75 (m, 1H), 4.97 (d, J=5.4 Hz, 1H), 2.83 (dd, J=17.2, 11.7 Hz, 1H), 2.60 (dd, J=17.2, 5.8 Hz, 1H), 2.42 (m, 2H), 2.30 (m, 1H), 2.10 (d, J=18.6 Hz, 1H), 1.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.53, 135.99, 128.64, 127.05, 126.65, 126.13, 125.78, 124.79, 72.36, 37.75, 31.14, 30.34, 30.09, 20.69; IR (CH_2Cl_2) 3375, 3057, 2990, 2305, 1622, 1420, 1086 cm^{-1}; EIMS m/z 200.1 (M^+), HRMS calcd for $C_{14}H_{16}O$: 200.1201. Found 200.1196.

3.1.8. 1,2-Dihydroanthracene (18). Compound **18** was obtained as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (m, 2H), 7.51 (s, 1H), 7.43 (s, 1H), 7.37 (m, 2H), 6.64 (d, J=8.8 Hz, 1H), 6.13 (m, 1H), 2.97 (t, J=8.0 Hz, 1H), 2.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.39, 132.98, 132.87, 132.69, 129.91, 128.02, 127.57, 127.11, 125.44, 125.25, 123.99, 28.09, 23.64. The analytical data for **18** is identical to that reported in the literature.[22]

3.1.9. Triethyl(1,2,3,3a,4,5,8,8a-octahydroazulen-1-yloxy)silane (19). The general procedure was employed with **2a** (0.49 g, 3.26 mmol) to afford **19** (0.70 g, 2.63 mmol, 81%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) 5.72–5.63 (m, 2H), 4.21–4.14 (m, 1H), 2.73–2.66 (m, 1H), 2.22–1.95 (m, 3H), 1.78–1.43 (m, 8H), 0.95 (t, J=8.2 Hz, 9H), 0.57 (q, J=8.2 Hz, 6H); ^{13}C NMR (50.2 MHz, $CDCl_3$) δ 128.67, 128.45, 76.18, 48.02, 39.39, 33.84, 32.44, 30.13, 28.41, 23.94, 6.80, 4.86; IR (CH_2Cl_2): 3372, 3061, 3020, 2982, 2955, 2875, 1605, 1458, 1273 cm^{-1}; EIMS m/z 266 (M^+, 1), HRMS calcd for $C_{16}H_{30}OSi$: 266.2066. Found 266.2066.

3.1.10. Triethyl(spiro[4.6]undec-6-en-1-yloxy)silane (20). The general procedure was employed with **2b** (0.23 g, 1.40 mmol) to afford **20** (0.14 g, 0.50 mmol, 36%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (d, J=11.8 Hz, 1H), 5.71 (dt, J=11.8, 5.6 Hz, 1H), 3.70 (t, J=6.0 Hz, 1H), 2.16–2.08 (m, 2H), 1.93–1.26 (m, 12H), 0.95 (t, J=8.0 Hz, 9H), 0.59 (q, J=8.0 Hz, 6H); ^{13}C NMR (50.2 MHz, $CDCl_3$) δ 136.69, 129.62, 81.95, 51.75, 36.58, 34.49, 32.90, 28.18, 27.80, 26.55, 19.73, 6.80, 4.92; IR (CH_2Cl_2) 3373, 3057, 3018, 2956, 2875, 1605, 1422, 1272 cm^{-1}; EIMS m/z 280 (M^+, 3), HRMS calcd for $C_{17}H_{32}OSi$: 280.2222. Found 280.2223.

3.1.11. Triethyl(spiro[5.6]dodec-7-en-1-yloxy)silane (21). The general procedure was employed with **2c** (0.25 g, 1.41 mmol) to afford **21** (0.09 g, 0.30 mmol, 22%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.65 (dt, J=11.8, 6.0 Hz, 1H), 5.45 (d, J=11.8 Hz, 1H), 3.67–3.62 (m, 1H), 2.14–2.04 (m, 2H), 1.74–1.10 (m, 14H), 0.96 (t, J=8.1 Hz, 9H), 0.58 (q, J=8.1 Hz, 6H); ^{13}C NMR (50.2 MHz, $CDCl_3$) δ 140.40, 129.41, 75.26, 44.85, 32.77, 30.59, 27.97, 27.96, 24.20, 22.40, 21.11, 21.10, 6.94, 5.27; IR (CH_2Cl_2) 3368, 3066, 3045, 2987, 2932, 1651, 1615, 1558, 1426 cm^{-1}; MS m/z % 294 (M^+, 2), HRMS calcd for $C_{18}H_{34}OSi$: 294.2379. Found 294.2373.

3.1.12. Triethyl(1,2,3,3a,8,8a-hexahydroazulen-1-yloxy)-silane (23). The general procedure was employed with **3a** (0.15 g, 1.00 mmol) to afford **23** (0.12 g, 0.47 mmol, 47%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (td, J=9.7, 4.5 Hz, 1H), 5.87 (m, 1H), 5.80 (m, 1H), 5.76 (m, 1H), 4.24 (td, J=7.5, 5.6 Hz, 1H), 2.58 (m, 1H), 2.44 (dd, J=14.4, 8.6 Hz, 1H), 2.08 (m, 1H), 1.93 (m, 1H), 1.87 (m, 1H), 1.74 (m, 1H), 1.60 (m, 1H), 1.51 (m, 1H), 0.96 (t, J=6.4 Hz, 9H), 0.59 (q, J=6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.92, 133.81, 126.76, 123.41, 75.80, 49.83, 42.47, 30.47, 29.87, 24.02, 6.83, 4.80; IR (CH_2Cl_2) 3943, 3685, 3382, 2985, 2826, 2682, 2518, 2407, 2302, 1989, 1605, 1419, 1361, 1318, 1084 cm^{-1}; EIMS m/z 264 (M^+), HRMS calcd for $C_{16}H_{28}OSi$: 264.1909. Found 264.1906.

3.1.13. Triethyl(2,3,4,4a,9,9a-hexahydro-1*H*-benzocyclohepten-1-yloxy)silane (24). The general procedure was employed with **3b** (0.16 g, 1.00 mmol) to afford **24** (0.08 g, 0.30 mmol, 30%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (m, 1H), 5.74 (m, 2H), 5.64 (m, 1H), 3.77 (dt, J=7.0, 4.1 Hz, 1H), 2.55 (m, 1H), 2.33 (m, 1H), 2.05 (m, 1H), 2.04 (m, 1H), 1.68 (m, 1H), 1.54 (m, 1H), 1.38 (m, 1H), 1.31 (m, 1H), 1.28 (m, 1H), 0.95 (t, J=7.4 Hz, 9H), 0.57 (q, J=7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.79, 133.84, 125.16, 123.26, 72.38, 44.81, 44.12, 30.48, 29.40, 24.08, 6.87, 4.91; IR (CH_2Cl_2): 3942, 3363, 2983, 2682, 2407, 2302, 2122, 1615, 1420, 1096 cm^{-1}; EIMS m/z 278 (M^+), HRMS calcd for $C_{17}H_{30}OSi$: 278.2066. Found 278.2072.

3.1.14. Triethyl(5a,6,10a,11-tetrahydro-5*H*-cyclohepta-[*b*]naphthalene-5-yloxy)silane (25). The general procedure

was employed with **3c** (0.20 g, 1.00 mmol) to afford **25** (0.046 g, 0.15 mmol, 15%) and **26** (0.042 g, 0.13 mmol, 13%) both as colorless oils: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J=7.1 Hz, 1H), 7.18 (m, 2H), 7.02 (d, J=7.0 Hz), 5.82 (m, 4H), 5.00 (d, J=4.8 Hz, 1H), 2.89 (m, 2H), 2.67 (dd, J=18.6, 13.8 Hz, 1H), 2.57 (dddd, J=18.7, 7.1, 2.3, 2.2 Hz), 2.29 (m, 1H), 1.99 (dddd, J=18.6, 11.7, 2.9, 2.8 Hz, 1H), 1.02 (t, J=8.5 Hz, 9H), 0.72 (q, J=8.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.58, 134.49, 133.31, 132.69, 128.41, 127.00, 126.33, 126.12, 124.33, 124.27, 72.32, 40.81, 39.59, 32.37, 24.44, 6.97, 5.06; IR (CH_2Cl_2) 3946, 3758, 3687, 3378, 2983, 2683, 2409, 2304, 2123, 2055, 1993, 1604, 1314, 1090 cm^{-1}; MS m/z 326 (M^+), HRMS calcd for $C_{21}H_{30}OSi$ 326.2066. Found 326.2062.

3.1.15. Triethyl(5a,10,10a,11-tetrahydro-5*H*-cyclohepta-[*b*]naphthalen-5-yloxy)silane (26). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J=7.2 Hz, 1H), 7.15 (m, 2H), 7.01 (d, J=7.0 Hz, 1H), 5.74 (m, 4H), 5.00 (d, J=5 Hz, 1H), 2.98 (m, 2H), 2.74 (m, 1H), 2.47 (m, 3H), 1.05 (t, J=7.6 Hz, 9H), 0.73 (q, J=7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.11, 136.25, 130.36, 129.77, 128.46, 126.78, 125.79, 125.56, 125.07, 72.82, 46.80, 36.65, 33.77, 31.17, 7.00, 5.16; IR (CH_2Cl_2) 3944, 3687, 3380, 2683, 2305, 1605, 1317, 1091 cm^{-1}; EIMS m/z 326 (M^+), HRMS calcd for $C_{21}H_{30}OSi$: 326.2066. Found 326.2065.

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