JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

Synthesis of Dibenzoheteropines of Group 13−16 Elements via Ring-Closing Metathesis

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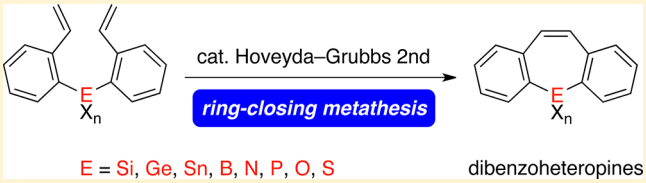
Supporting Information

ABSTRACT: The ring-closing metathesis (RCM) of bis(2-vinylphenyl)silanes in the presence of the second-generation Hoveyda−Grubbs catalyst in toluene at 100 °C afforded dibenzo[*b*,*f*]silepines in excellent yields. Other dibenzoheteropines of group 13−16 elements were also prepared via the RCM of the corresponding heteroatom-tethered dienes.



INTRODUCTION

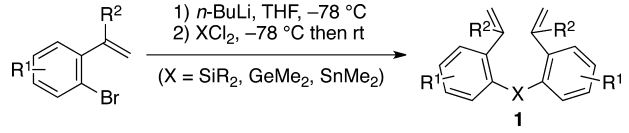
Ring-closing metathesis (RCM) is a straightforward and powerful method for the synthesis of carbo- and heterocyclic alkenes with various ring sizes and has found wide application in organic synthesis.[1] However, examples of the utilization of RCM for the synthesis of fully unsaturated or aromatic compounds are relatively limited.[2] Heteroles (heteroatom-substituted cyclopentadienes) are a unique class of compounds that possess a variety of intriguing properties, and a number of methods for their synthesis have been developed. Thus far, the RCM approach has been employed in the construction of furan,[3] pyrrole,[4] silole,[5] and germole skeletons.[5a] Silepine (silacycloheptatriene) derivatives have recently been reported to exhibit strong blue fluorescence.[6] Given the successful application of RCM in the synthesis of heterole derivatives, we envisioned that a metathesis-based approach to the synthesis of silepines as well as the other heteropine (heteroatom-substituted cycloheptatriene) derivatives would also be feasible. Herein we report the RCM of bis(2-vinylphenyl)silanes, which leads to dibenzo[*b*,*f*]silepines. The RCM strategy was also successfully applied to the synthesis of other dibenzo[*b*,*f*]-heteropines of group 13−16 elements.

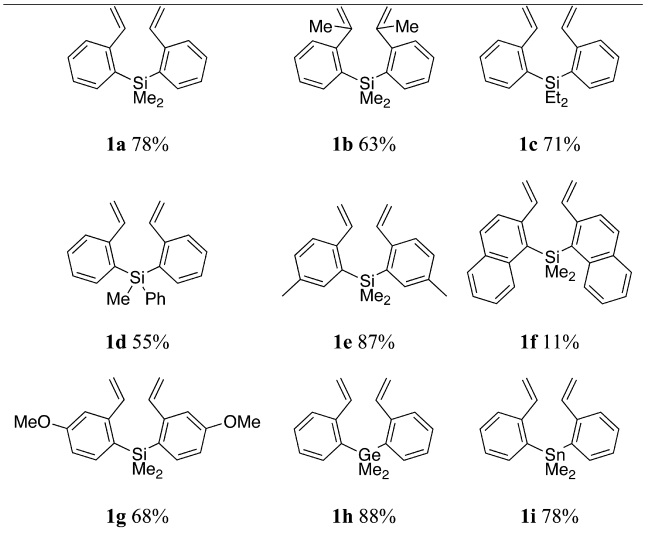
RESULTS AND DISCUSSION

Bis(2-vinylphenyl)silane **1a** was easily prepared through the reaction of dichlorodimethylsilane with 2 equiv of (2-vinylphenyl)lithium, which was generated in situ from 2-bromostyrene[7] and *n*-BuLi (Table 1). Other dienes tethered by group 14 elements were also synthesized analogously.[8]

The RCM of diene **1a** was examined using commercially available catalysts (Table 2). Although no RCM was observed when the first-generation Grubbs catalyst **A** was used as a catalyst in toluene at 120 °C (entry 1), diene **1a** underwent the metathesis in the presence of 5 mol % of the second-generation Grubbs catalyst **B** to give dibenzo[*b*,*f*]silepine **2a** in 72% yield (entry 2).[9] The yield did not increase significantly when the catalyst loading was increased to 15 mol % (entry 3). The second-generation Hoveyda−Grubbs catalyst **C** was found to be an excellent catalyst for the reaction, providing **2a** in 81% yield at 80 °C for 12 h (entry 4). With this catalyst, 94% yield of **2a** was obtained from the RCM of **1a** at 100 °C for 2 h (entry 5).

Table 1. Preparation of Bis(2-vinylphenyl)silanes, -germane, and -stannane 1



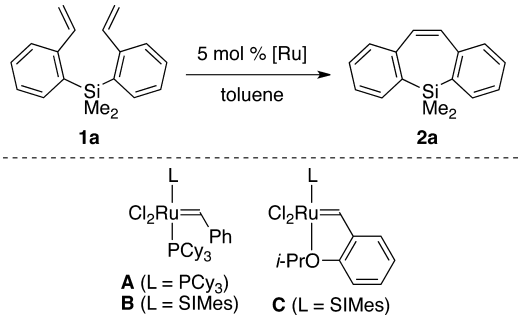


Unfortunately, the RCM of silicon-tethered dienes that have substituted vinyl groups (e.g., **1b** and **1j**) was unsuccessful (eq 1). Thus, our attention was next drawn to variations on the silicon atom and phenyl rings.

Diethylsilylene- and methyl(phenyl)silylene-tethered dienes **1c** and **1d** underwent RCM in toluene at 100 °C in the

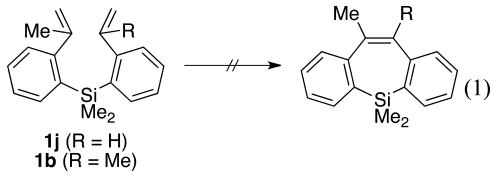
Received: January 31, 2013
Published: March 7, 2013

Table 2. RCM of Diene 1a[a,b]



entry	catalyst [Ru]	conditions	yield[c] (%)
1	Grubbs first (**A**)	toluene, 120 °C, 24 h	no reaction
2	Grubbs second (**B**)	toluene, 120 °C, 24 h	72
3	**B**[d]	toluene, 120 °C, 5 h	80
4	Hoveyda–Grubbs second (**C**)	toluene, 80 °C, 12 h	81
5	**C**	toluene, 100 °C, 2 h	94

[a]PCy_3 = tricyclohexylphosphine, SIMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene. [b]Unless otherwise noted, **1a** was reacted in the presence of 5 mol % Ru catalyst in toluene (0.1 M). [c]Isolated yield. [d]15 mol % catalyst was used.

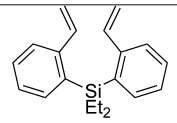
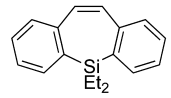
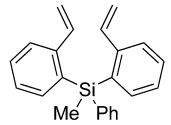
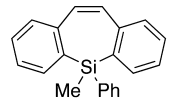
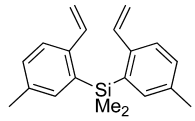
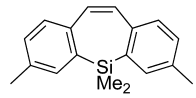
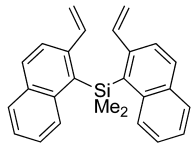
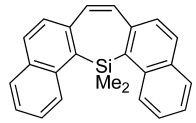


presence of 5 mol % of catalyst **C** to afford dibenzosilepines **2c** and **2d** in excellent yields (Table 3, entries 1 and 2). The RCM of 5-methyl-2-vinylphenyl (**1e**) and 2-vinylnaphthalen-1-yl (**1f**) derivatives also led to the formation of the corresponding silepines (**2e** and **2f**) in 90% and 80% yields, respectively (entries 3 and 4).[10]

When bis(4-methoxy-2-vinylphenyl)silane **1g** was subjected to the standard reaction conditions (toluene, 0.1 M, 5 mol % catalyst **C**, 100 °C), 14-membered disilacycle **3g** was obtained in 40% yield in addition to the desired product **2g** (28%) (Table 4, entry 1).[11] To minimize the formation of self-dimerization product **3g**, the metathesis reaction was performed under dilute conditions (0.002 M). Indeed, self-dimerization was unnoticeable at this concentration, and seven-membered silacycle **2g** was solely isolated in 93% yield (entry 2). Similar results were observed in the RCM of CF_3-substituted diene **1k** (entries 3 and 4). Furthermore, germanium- and tin-tethered dienes (**1h** and **1i**, respectively) were converted into the corresponding dibenzoheteropines **2h** and **2i** (entries 5–8). A high yield of germepine **2h** was obtained at a concentration of 0.002 M (entry 6), whereas suppression of the self-dimer **3i** failed during the RCM of tin derivative **1i** even at 0.002 M (entry 8).

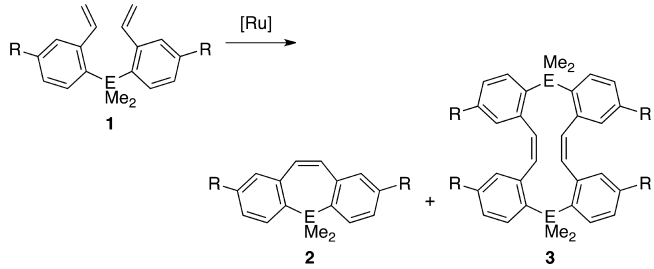
Because the metathesis-based approach for the synthesis of silepines, germepine, and stannepine was found to be quite general, the synthesis of other heteropines of group 13, 15, and 16 elements was subsequently investigated. Dibenzo[*b*,*f*]-borepines with a tricoordinate boron center have attracted much attention as candidates for new organic electronic materials.[12] To the best of our knowledge, however, no examples of dibenzo[*b*,*f*]borepines with a tetracoordinate boron center have been reported. The treatment of tris(2-vinylphenyl)borane, which was prepared from BBr_3 and 3 equiv of (2-vinylphenyl)lithium, using dibenzoylmethane and 8-quinolinol in two separate reactions afforded boron-tethered dienes **1l** (44%) and **1m** (65%), respectively (Scheme 1).[13] The

Table 3. Synthesis of Silepines by RCM of 1c–f[a]

entry	diene **1**	silepine **2**	yield[b]
1	 **1c**	 **2c**	92%
2	 **1d**	 **2d**	88%
3	 **1e**	 **2e**	90%
4	 **1f**	 **2f**	80%

[a]RCM was performed in the presence of 5 mol % **C** at 100 °C in toluene (0.1 M) for 2–3 h. [b]Isolated yield.

Table 4. Synthesis of Group 14 Heteropines by RCM[a]



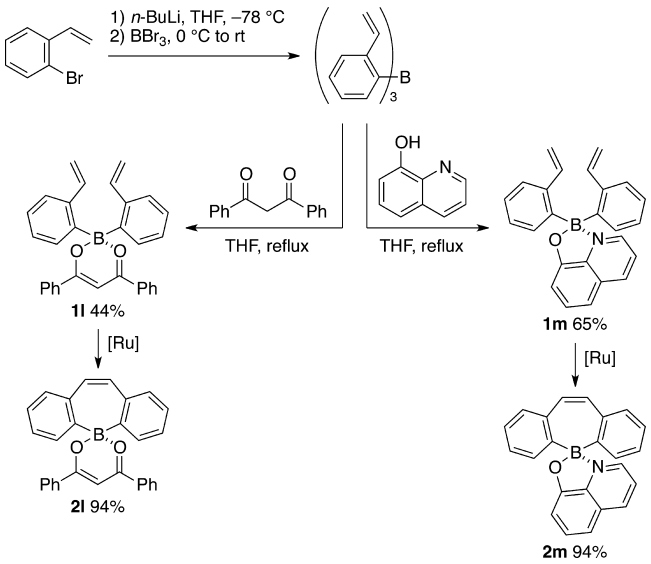
			yield[b] (%)	
entry	**1** (E, R)	conditions	**2**	**3**
1	**1g** (Si, OMe)	0.1 M, 100 °C, 24 h	28	40
2	**1g**	0.002 M, 120 °C, 2 h	93	
3	**1k** (Si, CF_3)	0.1 M, 100 °C, 3 h	44	41
4	**1k**	0.002 M, 120 °C, 4 h	96	
5	**1h** (Ge, H)	0.1 M, 100 °C, 3 h	64	19
6	**1h**	0.002 M, 120 °C, 12 h	89	
7	**1i** (Sn, H)	0.1 M, 100 °C, 24 h	0	39
8[c]	**1i**	0.002 M, 120 °C, 24 h	57	26

[a]Unless otherwise noted, RCM was performed in the presence of 5 mol % of **C** in toluene. [b]Isolated yield. [c]10 mol % catalyst was used.

dx.doi.org/10.1021/jo4001993 | J. Org. Chem. 2013, 78, 3329–3335

RCM of **1l** and **1m** produced spirocyclic tetracoordinate dibenzoborepines **2l** and **2m**, respectively, in high yields.

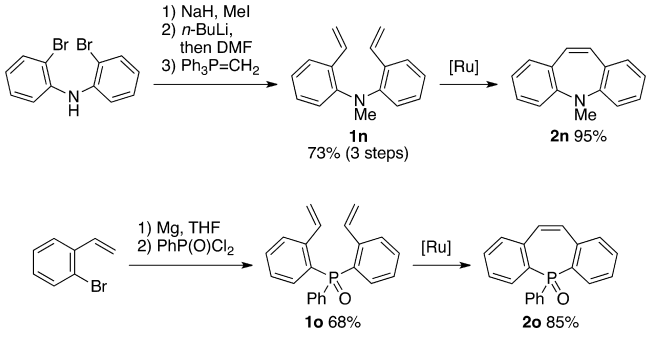
Scheme 1. Synthesis and RCM of Boron-Tethered Dienes 1l and 1m[a]



[a]RCM was performed at 100 °C in toluene (0.1 M) in the presence of 5 mol % **C**.

For group 15 element analogues of dibenzoheteropines, we synthesized the nitrogen and phosphorus derivatives, which can be used in catalysis as ligands.[14] *N*,*N*-Bis(2-vinylphenyl)-methylamine (**1n**) was synthesized in three steps (73%) from bis(2-bromophenyl)amine[15] (Scheme 2). 5-Methyldibenzo-

Scheme 2. Synthesis of Dibenzoheteropines of Group 15 Elements by RCM[a]

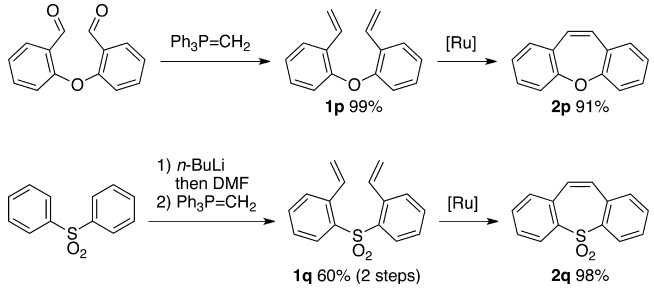


[a]Reaction conditions for **1n**: 5 mol % **C**, toluene, 100 °C, 1 h. Reaction conditions for **1o**: 10 mol % **C**, *p*-xylene, 150 °C, 12 h.

[*b*,*f*]azepine (**2n**) was obtained in 95% yield by means of the RCM reaction of **1n**.[16] The reaction of **2** equiv of (2-vinylphenyl)magnesium bromide and phenylphosphonic dichloride afforded phosphorus-tethered diene **1o**, which underwent RCM under rather forceful conditions to give dibenzo-[*b*,*f*]phosphepine oxide (**2o**) in good yield (Scheme 2).

Recently, dibenzo[*b*,*f*]oxepine/thiepine was prepared via the intramolecular Mizoroki–Heck reaction of 2-bromophenyl 2-vinylphenyl ether/sulfide, where the formation of six-membered products via *exo*-cyclization was inevitable.[17] Bis(2-vinylphenyl) ether **1p**, which was prepared by the Wittig methylenation of commercially available bis(2-formylphenyl) ether, afforded exclusively dibenzo[*b*,*f*]oxepine **2p** in 91% yield via the metathesis approach (Scheme 3). Bis(2-vinylphenyl)

Scheme 3. RCM of Bis(vinylphenyl) Ether 1p and Sulfone 1q[a]



[a]RCM was performed at 100 °C in toluene (0.1 M) in the presence of 5 mol % **C**.

sulfone **1q** was synthesized via *ortho*-formylation of diphenyl sulfone (79%) and subsequent Wittig methylenation (76%). The RCM of **1q** furnished dibenzo[*b*,*f*]thiepine 5,5-dioxide (**2q**) in excellent yield.

CONCLUSION

In summary, we have developed a method for the synthesis of dibenzoheteropines of group 13–16 elements via the RCM of heteroatom-tethered dienes. The second-generation Grubbs–Hoveyda catalyst showed superior activity in forming the desired dibenzoheteropines.

EXPERIMENTAL SECTION

General. All reactions were performed with standard Schlenk techniques under an argon or nitrogen atmosphere. Proton chemical shifts were referenced to the residual $CHCl_3$ signal at 7.26 ppm. Carbon chemical shifts were referenced to the central peak of $CDCl_3$ at 77.0 ppm.

General Procedures for the Preparation of Bis(2-vinylphenyl)silanes, -germane, and -stannane 1. A two-neck flask was charged with 2-bromostyrene (948.4 mg, 5.18 mmol) and THF (12 mL). The flask was cooled to −78 °C, and *n*-BuLi in hexane (1.6 M, 3.2 mL, 5.1 mmol) was added dropwise. After 1 h, Me_2SiCl_2 (319.6 mg, 2.48 mmol) was added dropwise to the mixture, and stirring was continued for 1 h at the same temperature. The flask was allowed to warm to room temperature, and the reaction mixture was diluted with hexane, filtered over a pad of Celite (hexane), and concentrated. The residue was passed through a plug of Florisil (hexane) and concentrated. Purification by column chromatography on silica gel (hexane) afforded dimethylbis(2-vinylphenyl)silane (**1a**, 509.8 mg, 1.93 mmol, 78%): white solid, mp 57–59 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.61 (s, 6H), 5.08 (dd, J = 10.8, 1.2 Hz, 2H), 5.55 (dd, J = 17.4, 1.2 Hz, 2H), 6.82 (dd, J = 17.1, 10.8 Hz, 2H), 7.23–7.30 (m, 2H), 7.34–7.41 (m, 2H), 7.50–7.57 (m, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ −0.3, 114.9, 125.3, 127.0, 129.6, 134.9, 136.8, 138.0, 144.0; HRMS (EI) calcd for $C_{18}H_{20}Si$ $[M]^+$ 264.1329, found 264.1336. Dienes **1b–i** were analogously prepared.

Dimethylbis(2-isopropenylphenyl)silane (1b). Yield: 63% (355.2 mg); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.56 (s, 6H), 1.81 (s, 6H), 4.57 (s, 2H), 4.94 (s, 2H), 7.09 (d, J = 8.5 Hz, 2H), 7.18–7.23 (m, 2H), 7.27–7.32 (m, 2H), 7.51 (d, J = 6.0 Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 1.1, 25.3, 116.0, 125.8, 127.4, 128.5, 135.9, 136.8, 147.3, 150.7; HRMS (EI) calcd for $C_{20}H_{24}Si$ $[M]^+$ 292.1642, found 292.1645.

Diethylbis(2-vinylphenyl)silane (1c). Yield: 71% (514.1 mg); white solid; mp 76–77 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, J =

dx.doi.org/10.1021/jo4001993 | J. Org. Chem. 2013, 78, 3329–3335

8.0 H, 6H), 1.17 (q, J = 7.7 Hz, 4H), 5.00 (d, J = 11.0 Hz, 2H), 5.50 (d, J = 17.0 Hz, 2H), 6.75 (dd, J = 17.0, 11.0 Hz, 2H), 7.23−7.28 (m, 2H), 7.33−7.38 (m, 2H), 7.49−7.55 (m, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ −4.8, 7.5, 114.6, 125.2, 126.9, 129.4, 135.4, 138.0, 144.2; HRMS (EI) calcd for $C_{20}H_{24}Si$ $[M]^+$ 292.1642, found 292.1644.

Methyl(phenyl)bis(2-vinylphenyl)silane (1d). Yield: 55% (430.3 mg); white solid; mp 98−101 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (s, 3H), 5.05 (dd, J = 11.0, 0.7 Hz, 2H), 5.58 (dd, J = 17.1, 0.9 Hz, 2H), 6.81 (dd, J = 17.1, 10.8 Hz, 2H), 7.15−7.23 (m, 2H), 7.25−7.51 (m, 9H), 7.58−7.65 (m, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ −0.5, 114.9, 125.3, 127.0, 127.9, 129.3, 129.9, 134.7, 135.5, 136.6, 136.7, 138.3, 144.3; HRMS (EI) calcd for $C_{23}H_{22}Si$ $[M]^+$ 326.1485, found 326.1493.

Dimethylbis(5-methyl-2-vinylphenyl)silane (1e). Yield: 87% (398.0 mg); white solid; mp 73−75 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.59 (s, 6H), 2.34 (s, 6H), 5.02 (dd, J = 10.8, 1.2 Hz, 2H), 5.51 (dd, J = 17.3, 1.4 Hz, 2H), 6.80 (dd, J = 17.4, 10.8 Hz, 2H), 7.15−7.20 (m, 2H), 7.30−7.33 (m, 2H), 7.45 (d, J = 7.8 Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ −0.1, 21.3, 113.9, 125.2, 130.4, 135.5, 136.4, 136.8, 137.9, 141.2; HRMS (EI) calcd for $C_{20}H_{24}Si$ $[M]^+$ 292.1642, found 292.1648.

Dimethylbis(2-vinylnaphthalen-1-yl)silane (1f). Yield: 11% (67.6 mg); white solid; mp 95−103 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (s, 6H), 5.18 (dd, J = 17.1, 1.5 Hz, 2H), 5.55 (dd, J = 17.1, 1.5 Hz, 2H), 7.18−7.37 (m, 6H), 7.54 (d, J = 8.4 Hz, 2H), 7.72−7.82 (m, 4H), 8.14−8.20 (m, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 7.1, 116.1, 125.0, 125.2, 125.5, 128.2, 128.7, 130.0, 132.9, 136.6, 136.8, 139.5, 142.8; HRMS (EI) calcd for $C_{26}H_{24}Si$ $[M]^+$ 364.1642, found 364.1646.

Bis(4-methoxy-2-vinylphenyl)dimethylsilane (1g). Yield: 68% (691.9 mg); white solid; mp 55−63 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.56 (s, 6H), 3.84 (s, 6H), 5.10 (dd, J = 10.8, 1.2 Hz, 2H), 5.55 (dd, J = 17.1, 1.2 Hz, 2H), 6.77−6.88 (m, 4H), 7.08 (d, J = 2.4 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 0.1, 55.0, 110.9, 112.7, 114.9, 128.4, 136.5, 138.0, 145.6, 160.8; HRMS (ESI) calcd for $C_{20}H_{24}O_2Si$ $[M]^+$ 324.1540, found 324.1545.

Dimethylbis(2-vinylphenyl)germane (1h). Yield: 88% (1.175 g); white solid; mp 39−43 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.73 (s, 6H), 5.14 (dd, J = 10.8, 1.2 Hz, 2H), 5.60 (dd, J = 17.3, 1.0 Hz, 2H), 6.81 (dd, J = 17.1, 10.8 Hz, 2H), 7.20−7.28 (m, 2H), 7.32−7.39 (m, 2H), 7.41−7.46 (m, 2H), 7.55−7.61 (m, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ −0.4, 115.0, 125.2, 127.2, 129.1, 134.2, 137.9, 139.2, 143.3; HRMS (EI) calcd for $C_{18}H_{20}{}^{74}Ge$ $[M]^+$ 310.0771, found 310.0786.

Dimethylbis(2-vinylphenyl)stannane (1i). Yield: 78% (336.0 mg); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.57 (s, 6H), 5.20 (d, J = 11.0 Hz, 2H), 5.63 (d, J = 17.0 Hz, 2H), 6.76 (dd, J = 17.0, 10.0 Hz, 2H), 7.18−7.25 (m, 2H), 7.36−7.46 (m, 4H), 7.56−7.64 (m, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ −7.4, 115.4, 125.1, 127.2, 129.0, 136.7, 139.4, 141.1, 144.8; HRMS (EI) calcd for $C_{17}H_{17}Sn$ $[M - CH_3]^+$ 341.0347, found 341.0346.

Dimethyl(2-isopropenylphenyl)(2-vinylphenyl)silane (1j). To a THF solution of (2-isopropenylphenyl)lithium, which was prepared from 1-bromo-2-isopropenylbenzene (662.2 mg, 3.36 mmol) in THF (7.6 mL) and n-BuLi in hexane (1.6 M, 1.9 mL, 3.0 mmol) at −78 °C, was added dropwise chlorodimethyl(2-vinylphenyl)silane (1.20 g, 6.10 mmol). After stirring for 1 h at −78 °C, the reaction mixture was allowed to warm to room temperature and then was diluted with water and extracted with AcOEt. The combined extracts were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane) to afford the title compound (516.0 mg, 1.85 mmol, 61%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.59 (s, 6H), 1.76 (dd, J = 1.5, 0.9 Hz, 3H), 4.64−4.67 (m, 1H), 4.90−4.95 (m, 1H), 5.05 (dd, J = 10.8, 1.2 Hz, 1H), 5.52 (dd, J = 17.3, 1.4 Hz, 1H), 6.77 (dd, J = 17.1, 10.8 Hz, 1H), 7.09−7.14 (m, 1H), 7.20−7.27 (m, 2H), 7.30−7.38 (m, 2H), 7.48−7.57 (m, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 0.6, 25.1, 114.6, 116.1, 125.0, 126.1, 126.7, 127.5, 128.8, 129.2, 135.1, 135.5, 135.7, 138.0, 138.3, 143.7, 147.2, 151.1; HRMS (EI) calcd for $C_{19}H_{22}Si$ $[M]^+$ 278.1485, found 278.1493.

Dimethylbis[4-(trifluoromethyl)-2-vinylphenyl]silane (1k). A solution of 2-bromo-5-(trifluoromethyl)benzaldehyde (2.512 g, 9.93 mmol), p-TsOH·H_2O (95.1 mg, 0.50 mmol), and ethylene glycol (731.4 g, 11.8 mmol) in toluene (10 mL) was refluxed under a Dean−Stark trap for 1 h. After cooling to room temperature, the mixture was quenched with saturated aqueous $NaHCO_3$ solution and extracted with AcOEt. The combined extracts were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane) to afford 1-bromo-2-(1,3-dioxolan-2-yl)-4-(trifluoromethyl)benzene (1.728 g, 5.82 mmol, 59%).

According to a procedure similar to that described for **1a**, bis[2-(1,3-dioxolan-2-yl)-4-(trifluoromethyl)phenyl]dimethylsilane (930.6 mg, 1.89 mmol, 71%) was prepared from 1-bromo-2-(1,3-dioxolan-2-yl)-4-(trifluoromethyl)benzene (1.603 g, 5.40 mmol), n-BuLi in hexane (1.6 M, 3.7 mL, 5.9 mmol), and Me_2SiCl_2 (343.2 mg, 2.65 mmol).

A solution of bis[2-(1,3-dioxolan-2-yl)-4-(trifluoromethyl)phenyl]-dimethylsilane (1.00 g, 2.03 mmol) and p-TsOH·H_2O (68.3 mg, 0.36 mmol) in acetone−H_2O (1:1, 20 mL) was refluxed for 3 days. The mixture was extracted with AcOEt, and the combined extracts were washed with saturated aqueous $NaHCO_3$ solution and brine. The extracts were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 20:1) to afford bis[2-formyl-4-(trifluoromethyl)phenyl]-dimethylsilane (512.8 mg, 1.27 mmol, 62%).

To a methylenetriphenylphosphorane solution in THF, which was prepared from $MePPh_3I$ (1.142 g, 2.83 mmol) and t-BuOK (305.2 mg, 2.72 mmol) in THF (30 mL) at 0 °C, was added dropwise a solution of bis[2-formyl-4-(trifluoromethyl)phenyl]dimethylsilane (500 mg, 1.24 mmol) in THF (7 mL) at 0 °C, and then the reaction mixture was stirred for 30 min at 0 °C. The reaction was quenched by addition of saturated aqueous NH_4Cl solution, and the resulting mixture was extracted with AcOEt. The combined extracts were dried over Na_2SO_4, filtered, and concentrated. The residue was passed through a plug of Florisil (hexane) and further concentrated. Purification by column chromatography on silica gel (hexane) afforded **1k** (278.3 mg, 0.70 mmol, 56%) as a white solid. Mp 59−60 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.06 (s, 6H), 5.20 (d, J = 11.0 Hz, 2H), 5.62 (d, J = 17.0 Hz, 2H), 6.73 (dd, J = 17.0, 11.0 Hz, 2H), 7.51 (d, J = 7.5 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H), 7.74 (s, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ −0.7, 117.2, 122.1 (q, $^3J_{C-F}$ = 3.8 Hz), 123.4 (q, $^3J_{C-F}$ = 3.8 Hz), 124.1 (q, $^1J_{C-F}$ = 272.2 Hz), 132.1 (q, $^2J_{C-F}$ = 32.4 Hz), 135.2, 136.5, 140.4, 144.7; HRMS (EI) calcd for $C_{20}H_{18}F_6Si$ $[M]^+$ 400.1076, found 400.1079.

(*Z*)-[(3-Oxo-1,3-diphenylprop-1-en-1-yl)oxy]bis(2-vinylphenyl)borane (1l). To a solution of (2-vinylphenyl)lithium, which was prepared from 2-bromostyrene (989.4 mg, 5.41 mmol) in THF and n-BuLi in hexane (1.6 M, 3.4 mL, 5.4 mmol) in THF (27 mL) at −78 °C over a period of 1 h, was added BBr_3 (0.17 mL, 1.79 mmol), and then the mixture was allowed to warm to room temperature. After heating for 12 h at 90 °C, the reaction mixture was treated with a solution of dibenzoylmethane (406.5 mg, 1.81 mmol) in THF (8.2 mL), which was added dropwise. After refluxing the resulting mixture for 6 h, it was concentrated under reduced pressure to remove the volatile materials. The residue was purified by column chromatography on silica gel ($CHCl_3$). Recrystallization from $CHCl_3$−hexane afforded the title compound (350.7 mg, 0.80 mmol, 44%) as a yellow solid. Mp 207−216 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.01 (d, J = 12.5 Hz, 2H), 5.46 (d, J = 18.5 Hz, 2H), 7.0 (s, 1H), 7.14−7.26 (m, 4H), 7.31 (dd, J = 17.0, 11.0 Hz, 2H), 7.49−7.55 (m, 8H), 7.62−7.68 (m, 2H), 8.15 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 93.8, 112.4, 125.4, 126.3, 127.1, 128.7, 128.9, 132.7, 133.1, 134.4, 139.6, 141.9, 182.4 [carbon attached to boron was not observed due to quadrupole broadening caused by the boron nucleus]; HRMS (EI) calcd for $C_{31}H_{25}{}^{11}BO_2$ $[M]^+$ 440.1942, found 440.1946.

(Quinolin-8-yloxy)bis(2-vinylphenyl)borane (1m). According to a procedure similar to that described for **1l**, **1m** (429.9 mg, 1.19 mmol, 66%) was prepared from 2-bromostyrene (1.021 g, 5.58 mmol), n-BuLi in hexane (1.6 M, 3.4 mL, 5.4 mmol), BBr_3 (0.17 mL, 1.79

dx.doi.org/10.1021/jo4001993 | J. Org. Chem. 2013, 78, 3329−3335

mmol), and 8-hydroxyquinoline (266.5 mg, 1.84 mmol). Yellow solid; mp 207−210 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.90 (d, J = 12.0 Hz, 2H), 5.43 (dd, J = 17.0 Hz, 2H), 7.04 (dd, J = 17.7, 10.3 Hz, 2H), 7.09−7.25 (m, 8H), 7.51 (d, J = 7.0 Hz, 2H), 7.59−7.67 (m, 2H), 8.40 (d, J = 7.5 Hz, 1H), 8.65 (d, J = 5.0 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 110.1, 112.2, 113.2, 122.5, 125.8, 126.9, 127.2, 128.4, 131.6, 132.8, 137.6, 138.8, 139.3, 140.9, 141.6, 158.2 [carbon attached to boron was not observed due to quadrupole broadening caused by the boron nucleus]; HRMS (EI) calcd for $C_{25}H_{20}{}^{11}BNO$ $[M]^+$ 361.1632, found 361.1636.

***N,N*-Bis(2-vinylphenyl)methylamine (1n).** A solution of bis(2-bromophenyl)amine (2.199 g, 6.72 mmol) in THF (5.0 mL) was added dropwise to a suspension of NaH (60% in mineral oil, 509.1 mg, 12.7 mmol) in THF (5.0 mL) at 0 °C. After stirring for 30 min at 0 °C, the mixture was treated with MeI (0.79 mL, 12.7 mmol). The reaction mixture was allowed to warm to room temperature and was further stirred for 3 h. The reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane) to afford *N,N*-bis(2-bromophenyl)methylamine (1.964 g, 5.76 mmol, 86%).

To a solution of *N,N*-bis(2-bromophenyl)methylamine (1.921 g, 5.63 mmol) in THF (12 mL) was added *n*-BuLi in hexane (1.6 M, 7.7 mL, 12.3 mmol) at −78 °C. After 1 h, DMF (0.94 mL, 12.2 mmol) was added to the mixture at −78 °C, and then the reaction mixture was allowed to warm to room temperature. The reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 5:1) to afford *N,N*-bis(2-formylphenyl)methylamine (1.152 g, 4.81 mmol, 85%).

According to a procedure similar to that described for **1k**, **1n** (873.6 mg, 3.71 mmol, 87%) was prepared from *N,N*-bis(2-formylphenyl)-methylamine (1.015 g, 4.24 mmol), $MePPh_3I$ (3.812 g, 9.43 mmol), and *t*-BuOK (1.033 g, 9.21 mmol). White solid; mp 98−99 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.1 (s, 3H), 5.08 (d, J = 11.0 Hz, 2H), 5.55 (d, J = 18.5 Hz, 2H), 6.82−6.93 (m, 4H), 7.00−7.06 (m, 2H), 7.14−7.20 (m, 2H), 7.46 (d, J = 7.5 Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 42.4, 113.8, 122.3, 123.2, 127.0, 128.4, 132.4, 134.1, 149.4; HRMS (EI) calcd for $C_{17}H_{17}N$ $[M]^+$ 235.1356, found 235.1362.

Phenylbis(2-vinylphenyl)phosphine Oxide (1o). At 0 °C, phenylphosphonic dichloride (1.546 g, 7.93 mmol) was added to a solution of (2-vinylphenyl)magnesium bromide in THF, which was prepared from 2-bromostyrene (3.01 g, 16.5 mmol), Mg (399.2 mg, 16.4 mmol), and THF (10 mL) at 95 °C over a period of 6 h. After stirring at room temperature for 12 h, the reaction was quenched with 0.1 M H_2SO_4 (30 mL). The mixture was extracted with $CHCl_3$, and the combined extracts were washed with saturated aqueous $NaHCO_3$ solution, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$) to afford the title compound (1.776 g, 5.38 mmol, 68%) as a white solid. Mp 202−208 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.16 (d, J = 11.0 Hz, 2H), 5.62 (d, J = 17.5 Hz, 2H), 7.03−7.10 (m, 2H), 7.16−7.21 (m, 2H), 7.42−7.56 (m, 7H), 7.56−7.63 (m, 2H), 7.68−7.73 (m, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 116.7, 126.7 (d, J_{C-P} = 10.3 Hz), 126.9 (d, J_{C-P} = 13.4 Hz), 128.4 (d, J_{C-P} = 12.4 Hz), 129.9 (d, J_{C-P} = 101.3 Hz), 131.8 (d, J_{C-P} = 3.1 Hz), 132.1 (d, J_{C-P} = 2.1 Hz), 132.27 (d, J_{C-P} = 10.3 Hz), 132.34, 133.2 (d, J_{C-P} = 12.4 Hz), 135.4 (d, J_{C-P} = 6.3 Hz), 142.7 (d, J_{C-P} = 6.2 Hz); HRMS (ESI) calcd for $C_{22}H_{19}OP$ $[M]^+$ 330.1168, found 330.1171.

Bis(2-vinylphenyl) Ether (1p). According to a procedure similar to that described for **1k**, **1p** (98.0 mg, 0.44 mmol, 99%) was prepared from bis(2-formylphenyl) ether (101.1 mg, 0.45 mmol), $MePPh_3I$ (403.1 mg, 1.00 mmol), and *t*-BuOK (109.1 mg, 0.97 mmol). Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.30 (d, J = 10.5 Hz, 2H), 5.82 (d, J = 18.0 Hz, 2H), 6.75 (d, J = 7.5 Hz, 2H), 7.01−7.12 (m, 4H), 7.15−7.22 (m, 2H), 7.61 (d, J = 7.5 Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 115.3, 118.6, 123.5, 126.6, 128.91, 128.95, 131.0, 154.3; HRMS (EI) calcd for $C_{16}H_{14}O$ $[M]^+$ 222.1039, found 222.1046.

Bis(2-vinylphenyl) Sulfone (1q). To a solution of diphenyl sulfone (1.00 g, 4.58 mmol) in THF (46 mL) was added *n*-BuLi in hexane (1.6 M, 6.3 mL, 10.1 mmol) dropwise at −78 °C, and the resulting mixture was stirred for 1 h at −78 °C. To the mixture was added DMF (750.1 mg, 10.3 mmol), and the reaction mixture was allowed to warm to room temperature. The reaction was quenched by addition of AcOH (2.0 mL) and water (50 mL), and the resulting mixture was extracted with AcOEt. The combined extracts were washed with 0.2 M HCl aqueous solution and brine. The extracts were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 2:1) to afford bis(2-formylphenyl) sulfone (987.8 mg, 3.60 mmol, 79%).

According to a procedure similar to that described for **1k**, **1q** (737.9 mg, 2.73 mmol, 76%) was prepared from bis(2-formylphenyl) sulfone (987.8 mg, 3.60 mmol), $MePPh_3I$ (3.281 g, 8.12 mmol), and *t*-BuOK (890.1 mg, 7.93 mmol). White solid; mp 134−138 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.18 (dd, J = 10.9, 1.1 Hz, 2H), 5.45 (dd, J = 17.3, 1.0 Hz, 2H), 7.18−7.30 (m, 2H), 7.40−7.58 (m, 6H), 8.13−8.18 (m, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 118.5, 127.5, 128.1, 129.3, 132.9, 133.5, 137.7, 138.0; HRMS (ESI) calcd for $C_{16}H_{14}NaO_2S^+$ $[M]^+$ 293.0607, found 293.0579.

General Procedure for the Ring-Closing Metathesis of Heteroatom-Tethered Dienes 1. Synthesis of 5,5-Dimethyl-5*H*-dibenzo[*b,f*]silepine (2a). A Schlenk tube equipped with a reflux condenser under Ar was charged with Hoveyda−Grubbs second-generation catalyst **C** (3.2 mg, 5.1 μmol) and diene **1a** (26.8 mg, 0.101 mmol) (liquid substrates were added via syringe after toluene). Toluene (1.0 mL) was added via syringe through the septum. The mixture was heated at 100 °C for 2 h. The reaction mixture was then filtered through a plug of Florisil while washing with hexane−AcOEt (10:1), and the filtrate was concentrated. Purification of the residue by preparative TLC on silica gel (hexane/AcOEt = 50:1) afforded **2a** (22.4 mg, 0.095 mmol, 94%) as a colorless oil. ^{1}H and ^{13}C NMR spectra were identical to those in the literature.[6]

5,5-Diethyl-5*H*-dibenzo[*b,f*]silepine (2c). The general procedure was followed using **1c** (29.3 mg, 0.100 mmol), **C** (3.2 mg, 5.1 μmol), and toluene (1.0 mL); 100 °C, 3 h. Purification by preparative TLC on silica gel (hexane/AcOEt = 50:1) yielded **2c** (24.4 mg, 0.092 mmol, 92%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.02−1.14 (m, 10H), 6.93 (s, 2H), 7.31−7.40 (m, 6H), 7.61 (d, J = 7.0 Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 1.5, 7.7, 127.2, 128.8, 129.8, 133.1, 133.3, 135.4, 141.9; HRMS (EI) calcd for $C_{18}H_{20}Si$ $[M]^+$ 264.1329, found 264.1336.

5-Methyl-5-phenyl-5*H*-dibenzo[*b,f*]silepine (2d). The general procedure was followed using **1d** (32.7 mg, 0.100 mmol), **C** (3.2 mg, 5.1 μmol), and toluene (1.0 mL); 100 °C, 3 h. Purification by preparative TLC on silica gel (hexane/AcOEt = 10:1) yielded **2d** (26.3 mg, 0.088 mmol, 88%) as a white solid. Mp 126−129 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 (s, 3H), 6.86 (s, 2H), 7.25−7.44 (m, 11H), 7.62 (d, J = 7.5 Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ −5.3, 127.3, 127.5, 129.2, 129.3, 129.8, 133.1, 133.9, 134.9, 135.1, 135.3, 141.9; HRMS (EI) calcd for $C_{21}H_{18}Si$ $[M]^+$ 298.1172, found 298.1182.

3,5,5,7-Tetramethyl-5*H*-dibenzo[*b,f*]silepine (2e). The general procedure was followed using **1e** (29.2 mg, 0.100 mmol), **C** (3.1 mg, 4.9 μmol), and toluene (1.0 mL); 100 °C, 2 h. Purification by preparative TLC on silica gel (hexane) yielded **2e** (23.7 mg, 0.090 mmol, 90%) as a white solid. Mp 88−91 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.50 (s, 6H), 2.37 (s, 6H), 6.90 (s, 2H), 7.14−7.20 (m, 2H), 7.24−7.29 (m, 2H), 7.34−7.38 (m, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ −4.6, 21.2, 129.5, 129.7, 132.2, 133.0, 136.8, 137.0, 138.9; HRMS (EI) calcd for $C_{18}H_{20}Si$ $[M]^+$ 264.1329, found 264.1335.

15,15-Dimethyl-15*H*-dinaphtho[1,2-*b*:2′,1′-*f*]silepine (2f). The general procedure was followed using **1f** (36.3 mg, 0.100 mmol), **C** (3.1 mg, 4.9 μmol), and toluene (1.0 mL); 100 °C, 3 h. Purification by preparative TLC on silica gel (hexane/AcOEt = 20:1) yielded **2f** (26.9 mg, 0.080 mmol, 80%) as a white solid. Mp 139−144 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99 (s, 6H), 7.39 (s, 2H), 7.45−7.62 (m, 6H), 7.78−7.86 (m, 4H), 8.79 (d, J = 8.7 Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 4.9, 125.4, 126.0, 127.5, 128.5, 128.6, 129.0,

dx.doi.org/10.1021/jo4001993 | J. Org. Chem. 2013, 78, 3329−3335

133.2, 133.4, 135.4, 136.7, 140.4; HRMS (ESI) calcd for $C_{24}H_{20}Si$ $[M]^+$ 336.1329, found 336.1336.

2,8-Dimethoxy-5,5-dimethyl-5*H*-dibenzo[*b*,*f*]silepine (2g) and 2,8,13,19-Tetramethoxy-5,5,16,16-tetramethyl-5,16-dihydrotetrabenzo[*b*,*f*,*i*,*m*][1,8]disilacyclotetradecine (3g). The general procedure was followed using **1g** (32.3 mg, 0.100 mmol), **C** (3.1 mg, 4.9 μmol), and toluene (1.0 mL); 100 °C, 24 h. Purification by preparative TLC on silica gel (hexane/AcOEt = 8:1) yielded **2g** (8.3 mg, 0.030 mmol, 28%) and **3g** (11.8 mg, 0.020 mmol, 40%).

2g: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.46 (s, 6H), 3.81 (s, 6H), 6.87−6.93 (m, 6H), 7.44−7.50 (m, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ −4.2, 55.1, 113.7, 114.5, 129.4, 133.3, 133.8, 142.8, 160.3; HRMS (ESI) calcd for $C_{18}H_{20}O_2Si$ $[M]^+$ 296.1227, found 296.1231.

3g: white solid; mp 155−159 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.57 (s, 12H), 3.68 (s, 12H), 6.48 (d, J = 2.0 Hz, 4H), 6.63 (s, 4H), 6.79 (dd, J = 8.5, 2.5 Hz, 4H), 7.51 (d, J = 8.5 Hz, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 1.2, 54.8, 109.8, 113.0, 129.5, 133.0, 135.6, 146.1, 160.4; HRMS (EI) calcd for $C_{36}H_{40}O_4Si_2$ $[M]^+$ 592.2460, found 592.2460.

A reaction that was performed using **1g** (32.8 mg, 0.101 mmol), **C** (3.2 mg, 5.1 μmol), and toluene (50 mL) at 120 °C for 2 h afforded **2g** (27.8 mg, 0.094 mmol, 93%), exclusively.

5,5-Dimethyl-2,8-bis(trifluoromethyl)-5*H*-dibenzo[*b*,*f*]silepine (2k) and 5,5,16,16-Tetramethyl-2,8,13,19-tetrakis(trifluoromethyl)-5,16-dihydrotetrabenzo[*b*,*f*,*i*,*m*][1,8]disilacyclotetradecine (3k). The general procedure was followed using **1k** (40.2 mg, 0.100 mmol), **C** (3.2 mg, 5.1 μmol), and toluene (1.0 mL); 100 °C, 3 h. Purification by preparative TLC on silica gel (hexane) yielded **2k** (16.4 mg, 0.044 mmol, 44%) and **3k** (15.2 mg, 0.020 mmol, 41%).

2k: white solid; mp 91−94 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.56 (s, 6H), 7.08 (s, 2H), 7.59 (d, J = 8.5 Hz, 2H), 7.63 (s, 2H), 7.69 (d, J = 7.0 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ −5.1, 123.92 (q, $^3J_{C-F}$ = 3.5 Hz), 123.95 (q, $^1J_{C-F}$ = 271.9 Hz), 125.8 (q, $^3J_{C-F}$ = 3.7 Hz), 131.4 (q, $^2J_{C-F}$ = 32.3 Hz), 133.1, 133.3, 140.9, 141.3; HRMS (EI) calcd for $C_{18}H_{14}F_6Si$ $[M]^+$ 372.0763, found 372.0769.

3k: white solid; mp 250−255 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.64 (s, 12H), 6.54 (s, 4H), 7.06 (br s, 4H), 7.45 (dd, J = 7.8, 1.2 Hz, 4H), 7.71 (d, J = 7.8 Hz, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ −0.1, 120.5 (q), 123.3 (q), 123.6 (q, $^1J_{C-F}$ = 272.1 Hz), 131.7 (q, $^2J_{C-F}$ = 32.5 Hz), 133.3, 134.2, 142.1, 143.6; HRMS (EI) calcd for $C_{36}H_{28}F_{12}Si_2$ $[M]^+$ 744.1532, found 744.1538.

The reaction carried out using **1k** (40.1 mg, 0.100 mmol), **C** (3.2 mg, 5.1 μmol), and toluene (50 mL) at 120 °C for 4 h afforded **2k** (35.7 mg, 0.096 mmol, 96%), exclusively.

5,5-Dimethyl-5*H*-dibenzo[*b*,*f*]germepine[9b,18] (2h) and 5,5,16,16-Tetramethyl-5,16-dihydrotetrabenzo[*b*,*f*,*i*,*m*][1,8]digermacyclotetradecine (3h). The general procedure was followed using **1h** (31.0 mg, 0.100 mmol), **C** (3.2 mg, 5.1 μmol), and toluene (1.0 mL); 100 °C, 3 h. Purification by preparative TLC on silica gel (hexane) yielded **2h** (18.0 mg, 0.064 mmol, 64%) and **3h** (5.3 mg, 0.009 mmol, 19%).

2h: colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.69 (s, 12H), 6.57 (s, 4H), 6.90 (d, J = 8.5 Hz, 4H), 7.01−7.06 (m, 4H), 7.15−7.20 (m, 4H), 7.51 (d, J = 7.5 Hz, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 0.0, 125.0, 126.5, 128.7, 132.7, 133.1, 140.9, 143.7; HRMS (EI) calcd for $C_{16}H_{16}{}^{74}Ge$ $[M]^+$ 282.0458, found 282.0464.

3h: white solid; mp 167−180 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.69 (s, 12H), 6.57 (s, 4H), 6.90 (d, J = 8.5 Hz, 4H), 7.04 (t, J = 6.8 Hz, 4H), 7.18 (t, J = 6.8 Hz, 4H), 7.51 (d, J = 7.5 Hz, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 0.04, 125.0, 126.5, 128.7, 132.7, 133.1, 140.9, 143.7; HRMS (EI) calcd for $C_{32}H_{32}{}^{70}Ge_2$ $[M]^+$ 556.0984, found 556.0988.

The reaction carried out using **1h** (31.4 mg, 0.101 mmol), **C** (3.2 mg, 5.1 μmol), and toluene (50 mL) at 120 °C for 12 h afforded **2h** (25.4 mg, 0.090 mmol, 89%), exclusively.

5,5-Dimethyl-5*H*-dibenzo[*b*,*f*]stannepine (2i) and 5,5,16,16-Tetramethyl-5,16-dihydrotetrabenzo[*b*,*f*,*i*,*m*][1,8]distannacyclotetradecine (3i). The general procedure was followed using **1i** (35.2 mg, 0.099 mmol), **C** (6.3 mg, 10 μmol), and toluene (50 mL); 120 °C, 24 h. Purification by preparative TLC on silica gel (hexane/AcOEt = 50:1) yielded **2i** (18.4 mg, 0.056 mmol, 57%) and **3i** (8.5 mg, 0.013 mmol, 26%).

2i: colorless oil; ^{1}H and ^{13}C NMR spectra were identical to those in the literature.[12a,19] HRMS (EI) calcd for $C_{15}H_{13}{}^{120}Sn$ $[M - CH_3]^+$ 313.0034, found 313.0039.

3i: white solid; mp 172−177 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.55 (s, 12H, $^2J_{Sn-H}$ = 52.5 Hz), 6.56 (s, 4H), 6.94 (d, J = 8.5 Hz, 4H), 7.06 (t, J = 8.0 Hz, 4H), 7.18 (t, J = 7.2 Hz, 4H), 7.50 (d, J = 7.5 Hz, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ −8.1, 125.1, 126.6, 128.8, 133.6, 135.6, 142.7, 145.2; HRMS (EI) calcd for $C_{32}H_{32}{}^{116}Sn_2$ $[M]^+$ 648.0533, found 648.0546.

(*Z*)-5-[(3-Oxo-1,3-diphenylprop-1-en-1-yl)oxy]-5*H*-dibenzo[*b*,*f*]borepine (2l). The general procedure was followed using **1l** (44.0 mg, 0.100 mmol), **C** (3.1 mg, 4.9 μmol), and toluene (1.0 mL); 120 °C, 24 h. Purification by preparative TLC on silica gel ($CHCl_3$/hexane = 3:1) yielded **2l** (38.6 mg, 0.094 mmol, 94%) as a yellow solid. Mp 277−285 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (s, 1H), 7.13 (s, 2H), 7.22−7.30 (m, 4H), 7.42−7.47 (m, 2H), 7.51−7.58 (m, 4H), 7.62−7.68 (m, 4H), 8.14 (d, J = 8.5 Hz, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 93.2, 126.3, 126.7, 128.6, 129.0, 129.2, 129.3, 131.9, 133.4, 134.3, 138.7, 182.7 [carbon attached to boron was not observed due to quadrupole broadening caused by the boron nucleus]; HRMS (EI) calcd for $C_{29}H_{20}{}^{10}BO_2$ $[M - H]^+$ 410.1587, found 410.1600.

5-(Quinolin-8-yloxy)-5*H*-dibenzo[*b*,*f*]borepine (2m). The general procedure was followed using **1m** (36.3 mg, 0.100 mmol), **C** (3.0 mg, 4.8 μmol), and toluene (1.0 mL); 100 °C, 3 h. Purification by preparative TLC on silica gel ($CHCl_3$) yielded **2m** (31.4 mg, 0.094 mmol, 94%) as a yellow solid. Mp 274−276 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (s, 2H), 7.14 (d, J = 8.1 Hz, 1H), 7.22−7.32 (m, 5H), 7.37 (d, J = 7.8 Hz, 1H), 7.39−7.46 (m, 2H), 7.65 (t, J = 8.1 Hz, 1H), 7.91−7.98 (m, 2H), 8.17 (d, J = 8.4 Hz, 1H), 8.96 (d, J = 5.1 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 109.4, 112.6, 122.8, 127.0, 127.7, 128.3, 130.0, 131.1, 132.2, 133.1, 136.0, 137.9, 138.5, 140.9, 158.6 [carbon attached to boron was not observed due to quadrupole broadening caused by the boron nucleus]; HRMS (EI) calcd for $C_{23}H_{15}{}^{10}BNO$ $[M - H]^+$ 333.1278, found 331.1287.

5-Methyl-5*H*-dibenzo[*b*,*f*]azepine (2n). The general procedure was followed using **1n** (23.5 mg, 0.100 mmol), **C** (3.2 mg, 5.1 μmol), and toluene (1.0 mL); 100 °C, 1 h. Purification by preparative TLC on silica gel (hexane) yielded **2n** (19.6 mg, 0.095 mmol, 95%) as a yellow solid. Mp 144−146 °C (lit.[20] 148 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.33 (s, 3H), 6.69 (s, 2H), 6.93−7.05 (m, 6H), 7.21−7.28 (m, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 39.3, 118.8, 123.1, 128.9, 129.2, 132.4, 132.9, 152.3; HRMS (EI) calcd for $C_{15}H_{14}N^+$ $[M]^+$ 208.1121, found 208.1104.

5-Phenyl-5*H*-dibenzo[*b*,*f*]phosphepine 5-oxide (2o). The general procedure was followed using **1o** (33.5 mg, 0.101 mmol), **C** (6.2 mg, 9.9 μmol), and toluene (1.0 mL); 150 °C, 12 h. Purification by preparative TLC on silica gel ($CHCl_3$/MeOH = 10:1) yielded **2o** (26.2 mg, 0.087 mmol, 85%) as a white solid. Mp 225−231 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.78 (s, 2H), 7.06−7.13 (m, 2H), 7.17−7.24 (m, 2H), 7.33−7.39 (m, 1H), 7.39−7.45 (m, 2H), 7.57−7.68 (m, 4H), 8.44−8.52 (m, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 127.9 (d, J_{C-P} = 12.4 Hz), 128.6 (d, J_{C-P} = 10.6 Hz), 129.6 (d, J_{C-P} = 99.4 Hz), 129.7 (d, J_{C-P} = 11.2 Hz), 130.8 (d, J_{C-P} = 11.2 Hz), 131.5 (d, J_{C-P} = 2.5 Hz), 131.7 (d, J_{C-P} = 2.5 Hz), 132.19 (d, J_{C-P} = 2.5 Hz), 132.24 (d, J_{C-P} = 1.3 Hz), 132.3 (d, J_{C-P} = 107.0 Hz), 136.9 (d, J_{C-P} = 10.6 Hz); HRMS (EI) calcd for $C_{20}H_{15}OP$ $[M]^+$ 302.0855, found 302.0863.

Dibenzo[*b*,*f*]oxepine (2p). The general procedure was followed using **1p** (22.1 mg, 0.099 mmol), **C** (3.1 mg, 4.9 μmol), and toluene (1.0 mL); 100 °C, 24 h. Purification by preparative TLC on silica gel (hexane/AcOEt = 50:1) yielded **2p** (17.5 mg, 0.090 mmol, 91%) as a white solid. Mp 110−111 °C (lit.[21] 106−108 °C). ^{1}H and ^{13}C NMR spectra were identical to those in the literature.[21] HRMS (EI) calcd for $C_{14}H_{10}O$ $[M]^+$ 194.0726, found 194.0733.

Dibenzo[*b*,*f*]thiepine 5,5-dioxide (2q). The general procedure was followed using **1q** (27.1 mg, 0.100 mmol), **C** (3.2 mg, 5.1 μmol), and toluene (1.0 mL); 100 °C, 1 h. Purification by preparative TLC on

dx.doi.org/10.1021/jo4001993 | J. Org. Chem. 2013, 78, 3329−3335

silica gel (hexane/AcOEt = 3:2) yielded **2q** (23.8 mg, 0.098 mmol, 98%) as a white solid. Mp 179−182 °C (lit.[22] 171−172 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (s, 2H), 7.57−7.69 (m, 6H), 8.25−8.31 (m, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 126.1, 129.0, 130.6, 132.28, 132.29, 132.6, 133.8, 139.2; HRMS (EI) calcd for $C_{14}H_{10}O_2S$ $[M]^+$ 242.0396, found 242.0405.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for previously unreported compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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