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Copper-catalyzed cross-coupling of 1-haloalkyl-*o*-carboranes with Grignard reagents: an efficient route to monosubstituted *o*-carborane derivatives

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ABSTRACT

A convenient and efficient copper-catalyzed reaction has been developed for the synthesis of functionalized *o*-carborane derivatives by using a Cu/phosphine catalytic system. Cross-coupling of readily available 1-haloalkyl-*o*-carboranes with Grignard reagents proceeds efficiently under mild conditions, and the corresponding monosubstituted *o*-carboranes were obtained in good to excellent yields.

1. Introduction

The field of icosahedral *ortho*-carboranes has been developed extensively since the first publication almost 50 years ago,[1] and the monosubstituted *o*-carboranes have found application in a wide range of fields, such as catalysis,[2] materials science,[3] supramolecular chemistry,[4] and medicine.[5] The *nido*-shaped $[C_2B_9H_{11}]^{2-}$ or $[C_2B_9H_{12}]^{1-}$ anionic residues, which are obtained by the deboronation of *o*-carboranes,[6] can strongly bind metal ions to their open C_2B_3 faces, and are useful for metal-extraction[7] and catalytic applications.[8] Their potential role in boron neutron capture therapy (BNCT) is further enhanced by their amphiphilic nature, ensuring solubility and interaction with both hydrophilic and lipophilic systems.[9]

The unique structure and properties of the *o*-carborane scaffold has long attracted the attention of organic chemists. Numerous synthetic methodologies for the synthesis of substituted *o*-carboranes have been developed in the past decades, such as, two traditional methods leading to *o*-carboranes were used in the early years: (a) alkyne insertion reaction of substituted acetylenes with decaborane,[10] and (b) substitution on *o*-carboranyllithium.[11] Among the methodologies described in the literature, the *o*-carboranyl alkyl-alkyl cross-coupling is a promising strategy to prepare these compounds. As nucleophilic coupling partner, *o*-carboranyl alkyl Grignard reagents are most often utilized in the cross-coupling reactions. For instance, Fein's group showed that *o*-carboranyl alkyl magnesium bromides could be coupled to alkyl bromide.[12] Chen and co-workers revealed the reaction of *o*-carboranyl methyl Grignard reagent and allyl bromide in the presence of Cu catalysts.[13] However, *o*-carboranyl methyl magnesium bromide can isomerize to 1-methyl-2-carboranyl magnesium bromide, which often results in mixtures of substituted derivatives. Therefore, the development of new and more efficient methods for the construction of substituted *o*-carboranes is of considerable interest.

Recently, there has been increased interest in the use of 1-haloalkyl-*o*-carboranes as electrophilic coupling partners for the cross-coupling reaction. For example, our group reported that nickel-catalyzed cross-coupling reaction of sterically hindered 1-bromomethyl-*o*-carborane with Grignard reagents in the presence of *N*-methylpyrrolidone (NMP) (Scheme 1a).[14] Herein, we report the cross-coupling of 1-haloalkyl-*o*-carboranes with alkyl and aryl Grignard reagents under Cu catalysis, which is an efficient route to monosubstituted *o*-carborane derivatives (Scheme 1b).

2. Results and discussion

1-Haloalkyl-*o*-carboranes are among the most useful starting materials for the synthesis of substituted *o*-carboranes, which were

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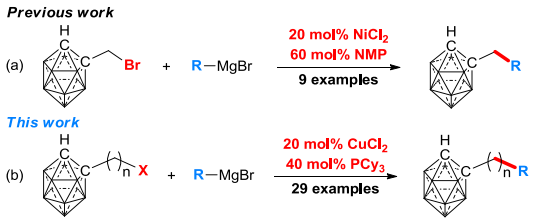
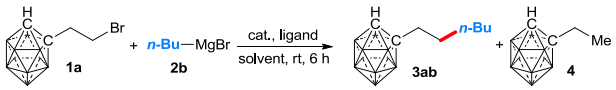


Scheme 1. Cross-coupling of 1-haloalkyl-*o*-carboranes with Grignard reagents.

prepared following the reaction of terminal alkynes with a complex of $B_{10}H_{12}(Et_2S)_2$.[10c] Inspired by the recent advances in Cu-catalyzed Grignard cross-coupling reactions of alkyl halides and organomagnesium reagents,[15] we initially investigated reaction conditions using 1-(2-bromoethyl)-*o*-carborane (**1a**) and *n*-BuMgBr (**2b**) as a model substrate (Table 1). As employing 20 mol % $CuCl_2$ as catalyst, 40 mol % NMP as ligand, tetrahydrofuran (THF) as the solvent at 25 °C for 6 h, the coupling product 1-(*n*-hexyl)-*o*-carborane (**3ab**) was obtained in 67% yield accompanied by a 10% yield of 1-ethyl-*o*-carborane (**4**), which was formed by the dehalogenation of **1a** (entry 1). No target product was observed in the absence of copper catalyst (entry 2). Besides, the effect of ligand on the reaction was investigated. Several ligands, including π-carbon ligands and convenient phosphine ligands, were screened (entries 3–10), and tricyclohexyl phosphine (PCy_3) showed the highest activity (entry 6). In the absence of any ligand, a poor yield was obtained (48%, entry 11). We next optimized the reaction conditions using PCy_3 as ligand. **3ab** was obtained in good yields (90–94%) by the use of Cu(I) salts in combination with PCy_3 (entries 12–14). CuCl and $CuCl_2$ showed almost the same catalytic activity for cross-coupling. The effect of catalyst loading was also explored (entries 6, 15–19). A similar formation of the coupling product was obtained using 10 mol % of Cu salt (93%, entry 15). When the catalyst loading was reduced to 5 mol %, the yield of product decreased to 83% (entry 18). Using 20 mol % $CuCl_2$ and 40 mol % PCy_3 as the catalytic system, the reaction afforded the highest yield (entry 6). When Et_2O was used as solvent, dehalogenation product **4** was the major product (entry 20). Therefore, the optimal conditions for the Cu-catalyzed synthesis of monosubstituted *o*-carboranes are as follows: 20 mol % $CuCl_2$ as the catalyst, 40 mol % PCy_3 as the ligand, 2.0 equiv of Grignard reagents as the coupling partners of 1-haloalkyl-*o*-carboranes, and the reactions were performed at 25 °C under N_2.

Table 1
Optimization of reaction conditions[a]



Entry	Cat. (mol %)	Ligand (mol %)	**3ab** (%)[b]	**4** (%)[b]
1	$CuCl_2$ (20)	NMP (40)	67	10
2	—	NMP (40)	0	Trace
3	$CuCl_2$ (20)	1-Phenylpropyne (40)	35	43
4	$CuCl_2$ (20)	2-Methyl-1,3-butadiene (40)	30	Trace
5	$CuCl_2$ (20)	PPh_3 (40)	84	8
6	**$CuCl_2$ (20)**	**PCy_3 (40)**	**96 (93[c])**	**Trace**
7	$CuCl_2$ (20)	*t*-Bu_3P (40)	83	10
8	$CuCl_2$ (20)	(R)-BINAP (40)	67	9
9	$CuCl_2$ (20)	dppe (40)	87	8
10	$CuCl_2$ (20)	Xantphos (40)	88	5
11	$CuCl_2$ (20)	—	48	34
12	CuCl (20)	PCy_3 (40)	94	Trace
13	CuBr (20)	PCy_3 (40)	93	Trace
14	CuI (20)	PCy_3 (40)	90	Trace
15	$CuCl_2$ (10)	PCy_3 (40)	93	Trace
16	$CuCl_2$ (10)	PCy_3 (20)	91	Trace
17	$CuCl_2$ (10)	PCy_3 (10)	72	Trace
18	$CuCl_2$ (5)	PCy_3 (40)	83	Trace
19	$CuCl_2$ (5)	PCy_3 (10)	68	Trace
20[d]	$CuCl_2$ (20)	PCy_3 (40)	19	35

[a] Reaction conditions: **1a** (0.5 mmol), **2c** (1.0 mmol), catalyst (0.1 mmol), ligand (0.2 mmol), THF (2 mL), at 25 °C under N_2 for 6 h; NMP=*N*-methylpyrrolidone; (R)-BINAP=(R)-(+)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl; dppe=1,2-bis(diphenylphosphino)ethane; Xantphos=dimethylbisdiphenylphosphinoxanthene.
[b] Determined by GC analysis.
[c] Isolated yield.
[d] Et_2O was employed as solvent.

After having optimized the model reaction, we were interested in extending the scope of the coupling reaction, and various *o*-carborane derivatives were prepared in good to excellent yields by using this copper-based procedure. As illustrated in Table 2, the cross-coupling of **1a** with unbranched or branched primary-alkyl Grignard reagents afforded the target products in 80–95% yields (entries 1–10). The yield of **3aa** prepared from EtMgBr increased by 19% over that from the conventional *o*-carboranyllithium route (entry 1, 89% vs 70%).[11c] With the ionic liquid route, the yield of **3ab** was 91%,[10f] while with $CuCl_2/PCy_3$, the yield increased further to 93% (entry 2). The $CuCl_2$ route also worked effectively with *n*-PentylMgBr where the yield of **3ac** increased by 20% over that from the *o*-carboranyllithium route employing a *tert*-butyldimethylsilyl protecting group (entry 4, 93% vs 73%).[16]

Likewise, the nucleophilic partners were not limited to *n*-butylMgCl (entry 3) and *n*-pentylMgCl (entry 5). Substituents at the *beta*-position of the Grignard reagent had a slight effect on the yield (entry 7). Interestingly, satisfactory results were obtained with various functionalized Grignard reagents. For instance, phenyl- and vinyl-alkylcarboranes were readily produced (entries 9–11). The same trend was also observed for allylmagnesium bromide, with a protecting group the yield of **3ai** was 50%,[17] while with $CuCl_2$ as the catalyst, the yield increased further to 64% (entry 11). Notably, not only primary-alkyl Grignard reagents, but also secondary-alkyl Grignard reagent could be coupled under similar conditions. As expected, both acyclic (**3aj** and **3ak**) and cyclic (**3al**, **3am** and **3an**) alkyl Grignard reagents smoothly coupled with **1a** in 81–97% yields (entries 12–16). More importantly, tertiary-alkyl Grignard reagents can also be employed successfully. As an example, 1-(3,3-dimethyl-1-butyl)-*o*-carborane (**3ao**) was obtained in 93% yield from *t*-BuMgCl (entry 17).

Fortunately, the use of more sterically hindered 1-bromomethyl-*o*-carborane (**1b**) that contains no *beta*-hydrogens, coupled with alkyl Grignard reagents to give compound **3ab** in a moderate yield with 40 mol % NMP as ligand at 40 °C (62%, entry 18). Encouraged by the above results, we had tried to extend the reaction to the cross-coupling of 1-(3-chloropropyl)-*o*-carborane (**1c**), which may suffer from a fast *beta*-hydride elimination. Additional information on the influence of catalyst, ligand, and temperature can be found in Table S1 in the Supplementary data. It is noteworthy that, the use of $CuCl_2$ in combination with PPh_3 gave the satisfactory yields. A substrate containing a phenyl group was coupled in an acceptable yield (63%, entry 19). Under similar conditions, yields were still more impressive with secondary, as well as with tertiary-alkyl Grignard reagents (entries 20 and 21). It is assumed that the use of PPh_3 ligand is the key to promote the cross-coupling reaction of *o*-carboranylalkyl chloride as mentioned above.

Notably, not only primary, secondary and tertiary-alkyl Grignard reagents, but also aryl Grignard reagents can be coupled in high yields under the same conditions as described above. As shown in Table 3, the coupling reactions of **1a** with different phenyl, tolyl, and 4-fluorophenyl Grignard reagents proceeded as well without troubles (81–91%; entries 1–3). Introduction of methyl groups onto the *ortho*, *meta*, and *para* positions of the phenyl Grignard reagents resulted in high yields of the corresponding compounds **6ad**, **6ae**, and **6af** (entries 4–6). It is noteworthy that naphthyl Grignard

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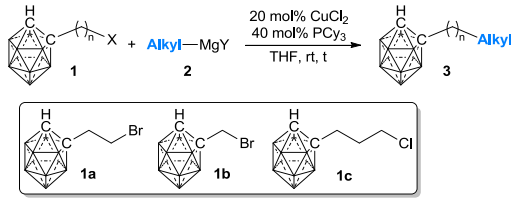
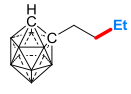
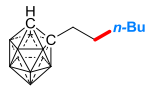
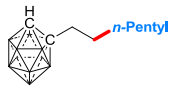
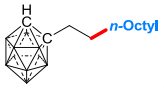
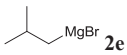
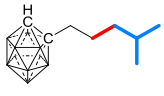
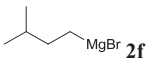
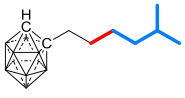
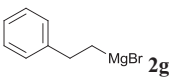
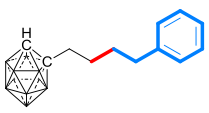
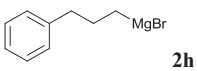
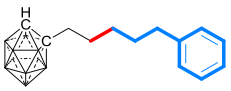
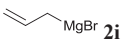
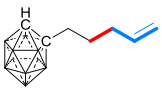
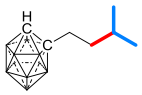
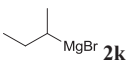
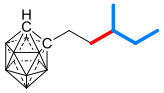
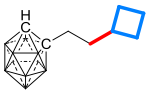
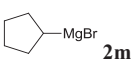
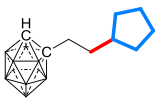
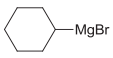
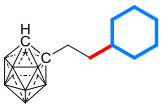
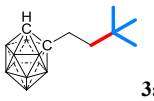
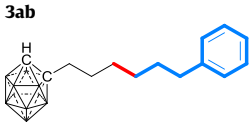
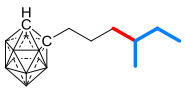
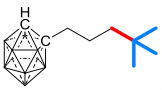
Table 2
Cu-catalyzed cross-coupling of 1-haloalkyl-*o*-carboranes with alkyl Grignard reagents[a]



Entry	Alkyl—MgY (**2**)	**3**	t (h)	Yield (%)[b]
1	EtMgBr **2a**	 **3aa**	6	89
2	*n*-BuMgBr **2b**	 **3ab**	6	93
3	*n*-BuMgCl **2b′**	**3ab**	12	91
4	*n*-PentylMgBr **2c**	 **3ac**	6	93
5	*n*-PentylMgCl **2c′**	**3ac**	12	90
6	*n*-OctylMgBr **2d**	 **3ad**	10	88
7	 **2e**	 **3ae**	8	94
8	 **2f**	 **3af**	8	95
9	 **2g**	 **3ag**	12	80
10	 **2h**	 **3ah**	12	86
11	 **2i**	 **3ai**	12	64
12	 **2j**	 **3aj**	8	95
13	 **2k**	 **3ak**	8	97
14	 **2l**	 **3al**	10	92
15	 **2m**	 **3am**	10	81

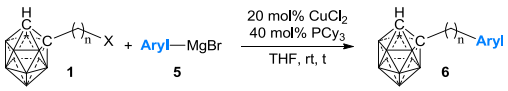
(*continued on next page*)

Table 2 (*continued*)

Entry	Alkyl—MgY (**2**)	**3**	t (h)	Yield (%)[b]
16	 **2n**	 **3an**	10	83
17	*t*-BuMgCl **2o**	 **3ao**	12	93
18[c]	**2c**	**3ab**	18	62
19[d]	**2h**	 **3ch**	15	63
20[d]	**2k**	 **3ck**	15	66
21[d]	**2o**	 **3co**	15	72

[a] Reaction conditions: **1** (0.5 mmol), **2** (1.0 mmol), $CuCl_2$ (0.1 mmol), PCy_3 (0.2 mmol), THF (2 mL), at 25 °C under N_2.
[b] Isolated yield.
[c] **1b** (0.5 mmol), 40 mol % NMP, 40 °C.
[d] **1c** (0.5 mmol), 40 mol % PPh_3, 25 °C.

Table 3
Cu-catalyzed cross-coupling of 1-haloalkyl-*o*-carboranes with aryl Grignard reagents[a]



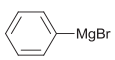
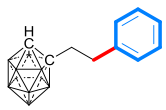
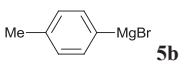
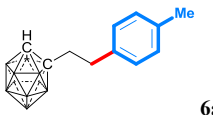
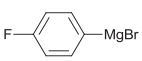
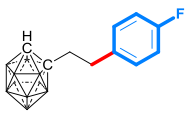
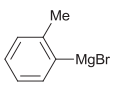
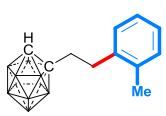
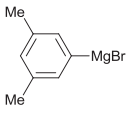
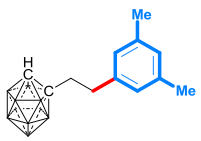
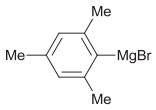
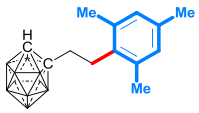
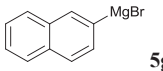
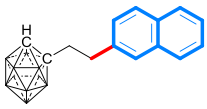
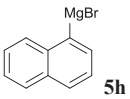
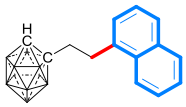
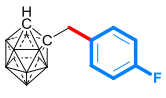
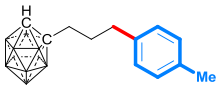
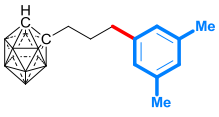
Entry	Aryl—MgBr (**5**)	**6**	t (h)	Yield (%)[b]
1	 **5a**	 **6aa**	8	89
2	 **5b**	 **6ab**	8	91
3	 **5c**	 **6ac**	8	81
4	 **5d**	 **6ad**	8	90
5	 **5e**	 **6ae**	8	85

Table 3 (*continued*)

Entry	Aryl–MgBr (**5**)	**6**	t (h)	Yield (%)[b]
6	 **5f**	 **6af**	8	83
7	 **5g**	 **6ag**	8	75
8	 **5h**	 **6ah**	10	73
9[c]	**5c**	 **6bc**	15	56
10[d]	**5b**	 **6cb**	12	65
11[d]	**5e**	 **6ce**	12	63

[a] Reaction conditions: **1** (0.5 mmol), **2** (1.0 mmol), $CuCl_2$ (0.1 mmol), PCy_3 (0.2 mmol), THF (2 mL), at 25 °C under N_2.
[b] Isolated yield.
[c] **1b** (0.5 mmol), 40 mol % NMP, 40 °C.
[d] **1c** (0.5 mmol), 40 mol % PPh_3, 25 °C.

reagent is a good coupling partner as well as the aryl Grignard reagents in this Cu-catalyzed reaction (entries 7 and 8). **1b** and **1c** provided the coupling products in around 60% yields for reactions with aryl Grignard reagents (entries 9–11).

Compounds **3** and **6** were fully characterized by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy as well as Infrared spectra, Mass spectra, and Elemental analysis. The molecular structure of **3ag** was further confirmed by single-crystal X-ray analyses. Fig. 1 shows the representative structure of **3ag**. The C(11)-C(10) distance of 1.529(5) Å is significantly shorter than the C(11)-C(12) distance of 1.664(5) Å. X-ray analyses confirmed that **3ag** is molecular compound without any significant intermolecular interactions. Crystal data and details of data collection and structure refinements are given in the Supplementary data (Table S2, ESI).

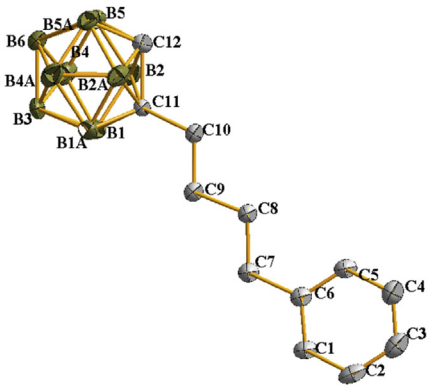
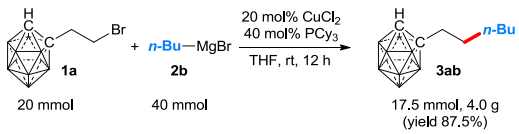


Fig. 1. Structure of compound **3ag** determined by X-ray diffraction. Thermal ellipsoids are drawn at the 30% probability level.

We also attempted scaling up the cross-coupling reaction of **1a** with *n*-butylmagnesium bromide in preparation of **3ab**, and 87.5% yield was achieved (Scheme 2). Therefore, 1-haloalkyl-*o*-carboranes are good building blocks for synthesis of functionalized boron cluster compounds under copper catalysis.

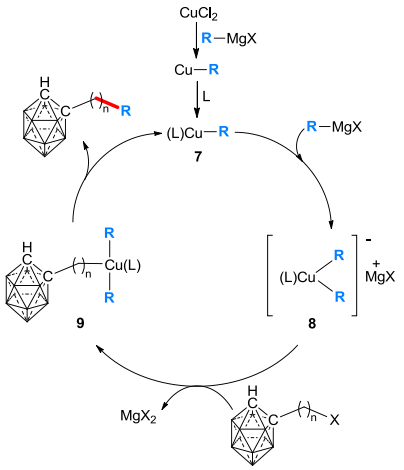


Scheme 2. Scale-up synthesis of **3ab**.

A plausible catalytic pathway is depicted in Scheme 3. First, an organocopper(I) **7**, generated from the copper salt and the Grignard reagents, reacts with the Grignard reagents to form cuprate **8**, which undergoes nucleophilic substitution with 1-haloalkyl-*o*-carboranes to give the complex **9**, which undergoes reductive elimination to afford the desired coupling products along with **7** to complete the catalytic cycle.[15h–l]

3. Conclusion

In conclusion, we have developed an efficient method for the preparation of functionalized *o*-carborane derivatives via copper-catalyzed Grignard cross-coupling reactions under mild conditions. The protocol uses 20 mol % $CuCl_2$ as catalyst, 40 mol % PCy_3,



Scheme 3. Proposed catalytic cycle of cross-coupling.

NMP or PPh_3 as ligand, readily available 1-haloalkyl-*o*-carboranes as electrophiles, various alkyl and aryl Grignard reagents as nucleophiles, and the corresponding monosubstituted *o*-carboranes were obtained in good to excellent yields. The wide substrate scope makes this copper-based strategy remarkably practical for the synthesis of functional boron cluster compounds. We believe this general method will attract much attention and have broad applications in academic and industrial research.

4. Experimental section

4.1. General information

Unless otherwise stated, all chemical reagents were purchased and used as received from Energy Chemical Industrial Inc. without further purification. Solvents were purchased from Guangdong Guanghua Sci-Tech Co., Ltd. 1-Haloalkyl-*o*-carboranes were synthesized according to literature procedures. Reactions were monitored using thin layer chromatography (TLC) plates. The *o*-carborane-containing species were visualized with 0.2% $PdCl_2$ in hydrochloric acid (3.0 M) which, upon heating, gave dark brown spots. Column chromatography was accomplished with ultrapure silica gel (Yucheng Chemical Co, Ltd.).

The ^1H, ^{13}C, and ^{11}B NMR spectra were recorded on a Bruker AV500 spectrometer. ^1H chemical shifts are reported in ppm relative to the residual proton signal of the NMR solvents. Coupling constants (*J*) are reported in Hertz (Hz). The ^1H NMR spectra of *o*-carboranes typically exhibit a broad signal between 3.00 and −0.75 ppm arising from the protons attached to the boron atoms of the cage, which were not reported separately in the ensuing assignments. ^{13}C chemical shifts are reported in ppm relative to the carbon signal of the NMR solvents. ^{11}B chemical shifts are reported in ppm relative to an external standard of $BF_3 \cdot Et_2O$. Low resolution mass spectra were obtained on a Thermo ITQ700 instrument using electron impact ionization. Infrared spectra were obtained on a Bruker Tensor 27 spectrometer using KBr pellets. Melting points were obtained on a standard melting point apparatus and are uncorrected. Gas chromatograph were obtained on a Shimadzu GC-2014C.

4.2. General synthetic procedure

1-Haloalkylcarborane (**1**) (0.5 mmol), $CuCl_2$ (13 mg, 0.1 mmol) and ligand (0.2 mmol) were added to a 25-mL Schlenk flask charged with a magnetic stirrer. The flask was evacuated and backfilled with nitrogen, and then dry THF (2 mL) and freshly prepared Grignard reagent (**2**) (1.0 mmol) were added to the flask under a stream of nitrogen. After completion of the reaction, the resulting solution was cooled to room temperature, and the reaction was quenched with a saturated aqueous solution of NH_4Cl (5 mL), and the product was extracted with diethyl ether (8 mL×3). The organic layer was dried over $MgSO_4$. The solvent was removed with the aid of a rotary evaporator, and the residue was purified by column chromatography on silica gel using *n*-hexane as eluent to provide the desired product.

*4.2.1. 1-(n-Heptyl)-1,2-dicarba-closo-dodecaborane (**3ac**).*[16] Eluent: hexane. Yield 93% (113 mg). Colorless liquid. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 3.55 (s, 1H), 2.18 (t, 2H, *J*=8.6 Hz, cluster−CH_2−), 1.47−1.41 (m, 2H, −CH_2−), 1.30−1.20 (m, 8H, −$(CH_2)_4$−), 0.88 (t, 3H, *J*=6.8 Hz, −CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 75.5, 60.9, 38.1, 31.5, 29.2, 28.9, 28.8, 22.5, 14.0. ^{11}B NMR ($CDCl_3$, 160 MHz, ppm): δ −2.4 (d, *J*=148.9 Hz, 1B), −5.9 (d, *J*=146.1 Hz, 1B), −8.8−(−13.6) (m, 8B). FTIR (KBr, cm^{-1}): ν 3066, 2956, 2929, 2858, 2593, 1464, 1378, 723. EIMS $[M+H]^+$ *m*/*z* 245.3. Anal. Calcd for $C_9H_{26}B_{10}$: C, 44.62; H, 10.74. Found: C, 44.86; H, 11.00.

*4.2.2. 1-(n-Decyl)-1,2-dicarba-closo-dodecaborane (**3ad**).* Eluent: hexane. Yield 88% (125 mg). Colorless liquid. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 3.54 (s, 1H, $C_{cluster}$−H), 2.19−2.16 (m, 2H, cluster−CH_2−), 1.48−1.42 (m, 2H, −CH_2−), 1.31−1.24 (m, 14H, −$(CH_2)_7$−), 0.87 (t, 3H, *J*=6.8 Hz, −CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 75.5, 60.9, 38.1, 31.8, 29.4, 29.3, 29.2, 29.1, 29.0, 28.9, 22.6, 14.1. ^{11}B NMR ($CDCl_3$, 160 MHz, ppm): δ −2.3 (d, *J*=149.1 Hz, 1B), −5.8 (d, *J*=143.0 Hz, 1B), −8.8−(−13.6) (m, 8B). FTIR (KBr, cm^{-1}): ν 3066, 2955, 2927, 2855, 2594, 1465, 1377, 722. EIMS $[M+H]^+$ *m*/*z* 287.3. Anal. Calcd for $C_{12}H_{32}B_{10}$: C, 50.35; H, 11.19. Found: C, 51.29; H, 11.24.

*4.2.3. 1-(5-Methyl-1-hexyl)-1,2-dicarba-closo-dodecaborane (**3af**).* Eluent: hexane. Yield 95% (115 mg). Colorless liquid. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 3.55 (s, 1H), 2.19 (t, 2H, *J*=8.5 Hz, cluster−CH_2−), 1.54−1.48 (m, 1H, −CH−), 1.46−1.40 (m, 2H, −CH_2−), 1.27−1.22 (m, 2H, −CH_2−), 1.16−1.12 (m, 2H, −CH_2−), 0.86 (d, 6H, *J*=6.6 Hz, −$(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 75.5, 60.9, 38.3, 38.1, 29.4, 27.8, 26.7, 22.5. ^{11}B NMR ($CDCl_3$, 160 MHz, ppm): δ −2.4 (d, *J*=148.6 Hz, 1B), −5.9 (d, *J*=146.4 Hz, 1B), −8.8−(−13.6) (m, 8B). FTIR (KBr, cm^{-1}): ν 3066, 2955, 2933, 2868, 2593, 1465, 1385, 1367, 723. EIMS $[M+H]^+$ *m*/*z* 245.3. Anal. Calcd for $C_9H_{26}B_{10}$: C, 44.62; H, 10.74. Found: C, 45.05; H, 10.92.

*4.2.4. 1-(4-Phenyl-1-butyl)-1,2-dicarba-closo-dodecaborane (**3ag**).* Eluent: hexane. Yield 80% (110 mg). White solid, mp=65−66 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.26 (t, *J*=7.4 Hz, 2H), 7.18 (dd, *J*=9.0, 5.7 Hz, 1H), 7.12 (d, *J*=7.9 Hz, 2H), 3.45 (s, 1H), 2.57 (t, *J*=7.5 Hz, 2H), 2.20−2.14 (m, 2H), 1.56 (dt, *J*=15.1, 7.4 Hz, 2H), 1.47 (ddd, *J*=15.9, 9.1, 6.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 141.61, 128.55, 128.41, 126.12, 75.41, 61.09, 37.93, 35.41, 30.67, 28.79. ^{11}B NMR (160 MHz, $CDCl_3$): δ −2.30 (d, *J*=148.0 Hz, 1B), −5.78 (d, *J*=144.2 Hz, 1B), −8.02 to −15.11 (m, 8B). FTIR (KBr, cm^{-1}): ν 3040, 2996, 2944, 2873, 2654, 2601, 1550, 1460, 1375, 723. EIMS $[M+H]^+$ *m*/*z* 279.2. Anal. Calcd for $C_{12}H_{24}B_{10}$: C, 52.14; H, 8.75. Found: C, 52.55; H, 8.92.

*4.2.5. 1-(5-Phenyl-1-pentyl)-1,2-dicarba-closo-dodecaborane (**3ah**).* Eluent: hexane. Yield 86% (125 mg). White solid, mp=50−51 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.27 (t, *J*=7.4 Hz, 2H), 7.17 (dd, *J*=21.2, 7.6 Hz, 3H), 3.50 (s, 1H), 2.58 (t, *J*=7.6 Hz, 2H), 2.19−2.13 (m, 2H), 1.60 (dt, *J*=15.4, 7.7 Hz, 2H), 1.45 (dt, *J*=11.7, 8.0 Hz, 2H), 1.29−1.25 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 142.14, 128.44, 128.42, 125.90, 75.39, 61.01, 38.01, 35.71, 30.94, 29.16, 28.51.

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^{11}B NMR (160 MHz, $CDCl_3$): δ −2.38 (d, *J*=148.4 Hz, 1B), −5.85 (d, *J*=144.4 Hz, 1B), −8.03 to −21.98 (m, 8B). FTIR (KBr, cm^{-1}): ν 3066, 2975, 2930, 2860, 2660, 2596, 1510, 1444, 1398, 722. EIMS $[M+H]^+$ *m*/*z* 293.3. Anal. Calcd for $C_{13}H_{26}B_{10}$: C, 53.76; H, 9.02. Found: C, 54.07; H, 9.48.

*4.2.6. 1-(3-Methyl-1-butyl)-1,2-dicarba-closo-dodecaborane (**3aj**).*[10a] Eluent: hexane. Yield 95% (102 mg). Colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 3.49 (s, 1H), 2.13 (t, 2H, *J*=8.5 Hz, cluster−CH_2−), 1.46−1.38 (m, 1H, −CH−), 1.28−1.24 (m, 2H, −CH_2−), 0.80 (d, 6H, *J*=6.6 Hz, −$(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 62.1, 47.4, 24.4, 22.6, 18.1, 14.2, 8.7. ^{11}B NMR ($CDCl_3$, 160 MHz, ppm): δ −2.4 (d, *J*=148.3 Hz, 1B), −5.9 (d, *J*=147.8 Hz, 1B), −8.8−(−13.6) (m, 8B). FTIR (KBr, cm^{-1}): ν 3066, 2960, 2933, 2873, 2593, 1468, 1388, 1369, 723. EIMS $[M+H]^+$ *m*/*z* 217.2. Anal. Calcd for $C_7H_{22}B_{10}$: C, 39.22; H, 10.34. Found: C, 39.88; H, 10.24.

*4.2.7. 1-(3-Methyl-1-pentyl)-1,2-dicarba-closo-dodecaborane (**3ak**).* Eluent: hexane. Yield 97% (111 mg). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.57 (s, 1H), 2.24−2.15 (m, 2H), 1.50−1.41 (m, 1H), 1.28 (dt, *J*=15.0, 6.1 Hz, 3H), 1.19−1.07 (m, 1H), 0.89−0.81 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 75.72, 60.97, 35.83, 35.68, 33.89, 29.01, 18.89, 11.14. ^{11}B NMR (160 MHz, $CDCl_3$): δ −2.44 (d, *J*=149.0 Hz, 1B), −5.92 (d, *J*=147.2 Hz, 1B), (−8.25)−(−14.62) (m, 8B). FTIR (KBr, cm^{-1}): ν 3060, 2955, 2920, 2883, 2590, 1466, 1390, 1370, 722. EIMS $[M+H]^+$ *m*/*z* 231.2. Anal. Calcd for $C_8H_{24}B_{10}$: C, 42.07; H, 10.59. Found: C, 42.36; H, 10.84.

*4.2.8. 1-(2-Cyclobutyl-1-ethyl)-1,2-dicarba-closo-dodecaborane (**3al**).* Eluent: hexane. Yield 92% (104 mg). Colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 3.54 (s, 1H, $C_{cluster}$−H), 2.16−2.13 (m, 1H), 2.08−2.00 (m, 5H), 1.86−1.81 (m, 2H), 1.57−1.51 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 75.3, 60.9, 36.2, 35.7, 34.9, 27.8, 18.2. ^{11}B NMR ($CDCl_3$, 160 MHz, ppm): δ −2.3 (d, *J*=148.7 Hz, 1B), −5.9 (d, *J*=149.3 Hz, 1B), −8.8−(−13.6) (m, 8B). FTIR (KBr, cm^{-1}): ν 3066, 2955, 2931, 2861, 2593, 1454, 1441, 1369, 723. EIMS $[M+H]^+$ *m*/*z* 229.2. Anal. Calcd for $C_8H_{22}B_{10}$: C, 42.45; H, 9.80. Found: C, 42.60; H, 9.96.

*4.2.9. 1-(2-Cyclopentyl-1-ethyl)-1,2-dicarba-closo-dodecaborane (**3am**).* Eluent: hexane. Yield 81% (97 mg). Colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 3.56 (s, 1H, $C_{cluster}$−H), 2.21−2.18 (m, 2H, cluster−CH_2−), 1.75−1.69 (m, 2H), 1.66−1.63 (m, 1H), 1.61−1.58 (m, 2H), 1.53−1.49 (m, 2H), 1.47−1.42 (m, 2H), 1.05−1.01 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 75.5, 60.9, 39.3, 37.4, 35.5, 32.4, 25.0. ^{11}B NMR ($CDCl_3$, 160 MHz, ppm): δ −2.3 (d, *J*=148.7 Hz, 1B), −5.9 (d, *J*=145.7 Hz, 1B), −8.8−(−13.6) (m, 8B). FTIR (KBr, cm^{-1}): ν 3065, 2952, 2865, 2592, 1454, 1370, 723. EIMS $[M+H]^+$ *m*/*z* 243.2. Anal. Calcd for $C_9H_{24}B_{10}$: C, 44.97; H, 10.06. Found: C, 45.20; H, 10.42.

*4.2.10. 1-(2-Cyclohexyl-1-ethyl)-1,2-dicarba-closo-dodecaborane (**3an**).* Eluent: hexane. Yield 83% (105 mg). Colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 3.55 (s, 1H, $C_{cluster}$−H), 2.22−2.19 (m, 2H, cluster−CH_2−), 1.70−1.62 (m, 5H), 1.35−1.30 (m, 2H), 1.20−1.11 (m, 4H), 0.90−0.83 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 75.7, 60.8, 37.1, 36.5, 35.7, 32.9, 26.3, 26.0. ^{11}B NMR ($CDCl_3$, 160 MHz, ppm): δ −2.4 (d, *J*=147.2 Hz, 1B), −5.9 (d, *J*=140.3 Hz, 1B), −8.8−(−13.6) (m, 8B). FTIR (KBr, cm^{-1}): ν 3065, 2925, 2853, 2592, 1449, 1373, 723. EIMS $[M+H]^+$ *m*/*z* 257.3. Anal. Calcd for $C_{10}H_{26}B_{10}$: C, 47.21; H, 10.30. Found: C, 47.70; H, 10.58.

*4.2.11. 1-(3,3-Dimethyl-1-butyl)-1,2-dicarba-closo-dodecaborane (**3ao**).* Eluent: hexane. Yield 93% (106 mg). White solid, mp=75−76 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.57 (s, 1H), 2.20−2.15 (m, 2H), 1.36−1.30 (m, 2H), 0.86 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 75.76, 60.96, 42.78, 33.58, 30.09, 29.01. ^{11}B NMR (160 MHz, $CDCl_3$): δ −2.42 (d, *J*=148.8 Hz, 1B), −5.89 (d, *J*=149.9 Hz, 1B), −7.79 to −18.64 (m, 8B). FTIR (KBr, cm^{-1}): ν 3059, 2960, 2940, 2862, 2589, 1444, 1398, 1350, 722. EIMS $[M+H]^+$ *m*/*z* 231.2. Anal. Calcd for $C_8H_{24}B_{10}$: C, 42.07; H, 10.59. Found: C, 42.70; H, 10.85.

*4.2.12. 1-(6-Phenyl-1-hexyl)-1,2-dicarba-closo-dodecaborane (**3ch**).* Eluent: hexane. Yield 45% (68 mg). White solid, mp=35−36 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (t, *J*=7.6 Hz, 2H), 7.17 (dd, *J*=14.1, 7.3 Hz, 3H), 3.51 (s, 1H), 2.61−2.56 (m, 2H), 2.18−2.13 (m, 2H), 1.59 (dt, *J*=15.2, 7.6 Hz, 2H), 1.47−1.39 (m, 2H), 1.29 (ddd, *J*=15.4, 10.1, 3.9 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 142.45, 128.41, 128.34, 125.77, 75.44, 60.98, 38.09, 35.82, 31.18, 29.12, 28.83, 28.71. ^{11}B NMR (160 MHz, $CDCl_3$): δ −2.38 (d, *J*=148.6 Hz, 1B), −5.86 (d, *J*=145.9 Hz, 1B), −8.15 to −17.09 (m, 8B). FTIR (KBr, cm^{-1}): ν 3068, 2990, 2908, 2850, 2612, 2555, 1605, 1456, 1380, 722. EIMS $[M+H]^+$ *m*/*z* 307.3. Anal. Calcd for $C_{14}H_{28}B_{10}$: C, 55.22; H, 9.27. Found: C, 55.63; H, 9.48.

*4.2.13. 1-(4-Methyl-1-hexyl)-1,2-dicarba-closo-dodecaborane (**3ck**).* Eluent: hexane. Yield 62% (75 mg). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.56 (s, 1H), 2.17 (ddd, *J*=10.9, 5.9, 4.7 Hz, 2H), 1.53−1.36 (m, 2H), 1.35−1.20 (m, 3H), 1.18−1.01 (m, 2H), 0.85 (t, *J*=6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 75.54, 60.97, 38.39, 35.75, 34.05, 29.32, 26.87, 19.01, 11.32. ^{11}B NMR (160 MHz, $CDCl_3$): δ −2.41 (d, *J*=149.3 Hz, 1B), −6.43 (t, *J*=161.3 Hz, 1B), −8.86 to −13.67 (m, 8B). FTIR (KBr, cm^{-1}): ν 3058, 2958, 2925, 2894, 2605, 1455, 1390, 1366, 723. EIMS $[M+H]^+$ *m*/*z* 245.3. Anal. Calcd for $C_9H_{26}B_{10}$: C, 44.59; H, 10.81. Found: C, 44.82; H, 11.14.

*4.2.14. 1-(4,4-Dimethyl-1-pentyl)-1,2-dicarba-closo-dodecaborane (**3co**).* Eluent: hexane. Yield 72% (87 mg). White solid, mp=52−53 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.56 (s, 1H), 2.18−2.13 (m, 2H), 1.45−1.37 (m, 2H), 1.14−1.08 (m, 2H), 0.87 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 75.59, 61.03, 43.17, 38.87, 30.32, 29.24, 24.60. ^{11}B NMR (160 MHz, $CDCl_3$): δ −2.36 (d, *J*=148.7 Hz, 1B), −5.86 (d, *J*=146.6 Hz, 1B), −8.13 to −14.22 (m, 8B). FTIR (KBr, cm^{-1}): ν 3055, 2942, 2945, 2901, 2595, 1460, 1401, 1350, 722. EIMS $[M+H]^+$ *m*/*z* 245.3. Anal. Calcd for $C_9H_{26}B_{10}$: C, 44.59; H, 10.81. Found: C, 44.91; H, 11.25.

*4.2.15. 1-(2-Phenyl-1-ethyl)-1,2-dicarba-closo-dodecaborane (**6aa**).* Eluent: hexane. Yield 89% (110 mg). White solid, mp=80−81 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (t, *J*=7.4 Hz, 2H), 7.21 (dd, *J*=8.1, 6.6 Hz, 1H), 7.10 (d, *J*=7.2 Hz, 2H), 3.56 (s, 1H), 2.78−2.72 (m, 2H), 2.49−2.44 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 138.62, 128.75, 128.10, 126.80, 74.63, 61.16, 39.68, 35.26. ^{11}B NMR (160 MHz, $CDCl_3$): δ −2.19 (d, *J*=148.7 Hz, 1B), −5.62 (d, *J*=144.7 Hz, 1B), −7.77 to −15.44 (m, 8B). FTIR (KBr, cm^{-1}): ν 3050, 2980, 2915, 2845, 2625, 2540, 1615, 1460, 1384, 723. EIMS $[M+H]^+$ *m*/*z* 251.2. Anal. Calcd for $C_{10}H_{20}B_{10}$: C, 48.36; H, 8.12. Found: C, 48.70; H, 8.53.

*4.2.16. 1-[2-(4-Methylphenyl)-1-ethyl]-1,2-dicarba-closo-dodecaborane (**6ab**).* Eluent: hexane. Yield 91% (119 mg). White solid, mp=91−92 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14 (d, *J*=7.7 Hz, 2H), 7.04 (d, *J*=7.8 Hz, 2H), 3.59 (s, 1H), 2.78−2.73 (m, 2H), 2.52−2.47 (m, 2H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 136.52, 135.66, 129.52, 128.05, 74.82, 61.20, 39.91, 34.92, 21.06. ^{11}B NMR (160 MHz, $CDCl_3$): δ −2.15 (d, *J*=149.0 Hz, 1B), −5.59 (d, *J*=145.1 Hz, 1B), −6.72 to −15.87 (m, 8B). FTIR (KBr, cm^{-1}): ν 3066, 2985, 2920, 2855, 2610, 2560, 2550, 1610, 1465, 1377, 722. EIMS $[M+H]^+$ *m*/*z* 265.2. Anal. Calcd for $C_{11}H_{22}B_{10}$: C, 50.35; H, 8.45. Found: C, 50.66; H, 8.80.

*4.2.17. 1-[2-(4-Fluorophenyl)-1-ethyl]-1,2-dicarba-closo-dodecaborane (**6ac**).* Eluent: hexane. Yield 81% (108 mg). White solid, mp=52−53 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.11 (dd, *J*=8.4, 5.4 Hz,

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2H), 7.00 (t, J=8.6 Hz, 2H), 3.62 (s, 1H), 2.80–2.74 (m, 2H), 2.51–2.46 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.75 (d, J=245.1 Hz), 134.42 (d, J=3.2 Hz), 129.73, 129.66, 115.72, 115.55, 74.57, 61.35, 39.85, 34.55. ^{11}B NMR (160 MHz, $CDCl_3$): δ −2.18 (d, J=149.2 Hz, 1B), −5.59 (d, J=145.6 Hz, 1B), −7.77 to −16.39 (m, 8B). FTIR (KBr, cm^{-1}): ν 3065, 2945, 2869, 2610, 2590, 1605, 1501, 723. EIMS $[M+H]^+$ m/z 269.2. Anal. Calcd for $C_{10}H_{19}B_{10}F$: C, 45.09; H, 7.19. Found: C, 45.33; H, 7.56.

*4.2.18. 1-[2-(2-Methylphenyl)-1-ethyl]-1,2-dicarba-closo-dodecaborane (**6ad**).* Eluent: hexane. Yield 90% (118 mg). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.08–6.99 (m, 3H), 6.97–6.91 (m, 1H), 3.50 (s, 1H), 2.68–2.63 (m, 2H), 2.31–2.27 (m, 2H), 2.18 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 136.96, 135.69, 130.71, 128.67, 127.10, 126.50, 74.83, 61.41, 38.65, 32.93, 19.01. ^{11}B NMR (160 MHz, $CDCl_3$): δ −2.18 (d, J=148.1 Hz, 1B), −5.54 (d, J=153.1 Hz, 1B), −8.65 to −13.45 (m, 8B). FTIR (KBr, cm^{-1}): ν 3064, 2958, 2920, 2865, 2585, 1450, 1366, 723. EIMS $[M+H]^+$ m/z 265.2. Anal. Calcd for $C_{11}H_{22}B_{10}$: C, 50.35; H, 8.45. Found: C, 50.71; H, 8.60.

*4.2.19. 1-[2-(3,5-Dimethylphenyl)-1-ethyl]-1,2-dicarba-closo-dodecaborane (**6ae**).* Eluent: hexane. Yield 85% (117 mg). White solid, mp=82–83 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.89 (s, 1H), 6.75 (s, 2H), 3.60 (s, 1H), 2.70 (dd, J=10.9, 6.8 Hz, 2H), 2.50–2.45 (m, 2H), 2.30 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 138.65, 138.41, 128.45, 125.96, 74.82, 61.19, 39.91, 35.20, 21.23. ^{11}B NMR (160 MHz, $CDCl_3$): δ −2.19 (d, J=150.5 Hz, 1B), −5.64 (d, J=145.2 Hz, 1B), −7.85 to −14.96 (m, 8B). FTIR (KBr, cm^{-1}): ν 3066, 2955, 2925, 2872, 2590, 1460, 1386, 1368, 722. EIMS $[M+H]^+$ m/z 279.2. Anal. Calcd for $C_{12}H_{24}B_{10}$: C, 52.14; H, 8.75. Found: C, 52.58; H, 8.95.

*4.2.20. 1-[2-(2,4,6-Trimethylphenyl)-1-ethyl]-1,2-dicarba-closo-dodecaborane (**6af**).* Eluent: hexane. Yield 83% (120 mg). White solid, mp=112–113 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.88 (s, 2H), 3.64 (s, 1H), 2.81–2.76 (m, 2H), 2.33–2.30 (m, 2H), 2.28 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 136.34, 135.80, 132.29, 129.37, 127.04, 74.90, 61.45, 37.07, 29.05, 20.91, 19.45. ^{11}B NMR (160 MHz, $CDCl_3$): δ −2.18 (d, J=148.9 Hz, 1B), −5.68 (d, J=145.8 Hz, 1B), −8.03 to −14.31 (m, 8B). FTIR (KBr, cm^{-1}): ν 3064, 3005, 2970, 2919, 2858, 2621, 2578, 2565, 2549, 1613, 1581, 1482, 1464, 1446, 1376, 821. EIMS $[M+H]^+$ m/z 293.3. Anal. Calcd for $C_{13}H_{26}B_{10}$: C, 53.76; H, 9.02. Found: C, 53.94; H, 9.45.

*4.2.21. 1-[2-(2-Naphthyl)-1-ethyl]-1,2-dicarba-closo-dodecaborane (**6ag**).* Eluent: hexane. Yield 75% (112 mg). White solid, mp=75–77 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83–7.76 (m, 3H), 7.58 (s, 1H), 7.47 (pd, J=6.9, 1.5 Hz, 2H), 7.24 (dd, J=8.4, 1.6 Hz, 1H), 3.62 (s, 1H), 2.97–2.92 (m, 2H), 2.61–2.56 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 136.27, 133.66, 132.44, 128.68, 127.83, 127.58, 126.66, 126.56, 126.53, 125.95, 74.78, 61.38, 39.83, 35.61. ^{11}B NMR (160 MHz, $CDCl_3$): δ −2.09 (d, J=152.2 Hz, 1B), −5.52 (d, J=144.0 Hz, 1B), −7.60 to −14.51 (m, 8B). FTIR (KBr, cm^{-1}): ν 3075, 2960, 2930, 2860, 2614, 2571, 2550, 1611, 1455, 1370, 723. EIMS $[M+H]^+$ m/z 301.2. Anal. Calcd for $C_{14}H_{22}B_{10}$: C, 56.34; H, 7.43. Found: C, 56.47; H, 7.59.

*4.2.22. 1-[2-(1-Naphthyl)-1-ethyl]-1,2-dicarba-closo-dodecaborane (**6ah**).* Eluent: hexane. Yield 73% (109 mg). White solid, mp=82–83 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (t, J=9.2 Hz, 2H), 7.74 (d, J=8.2 Hz, 1H), 7.54 (t, J=7.3 Hz, 1H), 7.49 (t, J=7.3 Hz, 1H), 7.38 (t, J=7.6 Hz, 1H), 7.24 (d, J=3.4 Hz, 1H), 3.63 (s, 1H), 3.25–3.18 (m, 2H), 2.58–2.53 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.8, 134.0, 131.3, 129.2, 127.8, 126.7, 126.3, 126.0, 125.7, 122.6, 74.8, 61.6, 39.1, 32.7. ^{11}B NMR (160 MHz, $CDCl_3$) δ −2.14 (d, J=149.1 Hz, 1B), −5.59 (d, J=146.4 Hz, 1B), −9.10 (d, J=151.6 Hz, 2B), −10.32 to −18.09 (m, 6B). FTIR (KBr, cm^{-1}): ν 3066, 2958, 2933, 2861, 2615, 2570, 2550, 1614, 1460, 1388, 722. EIMS $[M+H]^+$ m/z 301.2. Anal. Calcd for $C_{14}H_{22}B_{10}$: C, 56.34; H, 7.43. Found: C, 56.54; H, 7.55.

*4.2.23. 1-[3-(4-Methylphenyl)-1-propyl]-1,2-dicarba-closo-dodecaborane (**6cb**).* Eluent: hexane. Yield 65% (90 mg). White solid, mp=64–66 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10 (d, J=7.8 Hz, 2H), 7.01 (d, J=7.9 Hz, 2H), 3.51 (s, 1H), 2.55 (t, J=7.4 Hz, 2H), 2.32 (s, 3H), 2.20 (dd, J=10.2, 7.0 Hz, 2H), 1.78 (dt, J=19.4, 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 137.38, 136.04, 129.43, 128.24, 75.30, 61.27, 37.62, 34.63, 30.94, 21.14. ^{11}B NMR (160 MHz, $CDCl_3$): δ −2.38 (d, J=150.9 Hz, 1B), −5.86 (d, J=141.9 Hz, 1B), −8.32 to −14.35 (m, 8B). FTIR (KBr, cm^{-1}): ν 3058, 2965, 2905, 2845, 2620, 2552, 1605, 1450, 1384, 722. EIMS $[M+H]^+$ m/z 279.2. Anal. Calcd for $C_{12}H_{24}B_{10}$: C, 52.14; H, 8.75. Found: C, 52.60; H, 8.92.

*4.2.24. 1-[3-(3,5-Dimethylphenyl)-1-propyl]-1,2-dicarba-closo-dodecaborane (**6ce**).* Eluent: hexane. Yield 63% (91 mg). White solid, mp=54–55 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.86 (s, 1H), 6.75 (s, 2H), 3.53 (s, 1H), 2.52 (t, J=7.5 Hz, 2H), 2.30 (s, 6H), 2.22 (dd, J=10.2, 7.0 Hz, 2H), 1.78 (dt, J=19.7, 7.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 140.44, 138.25, 128.12, 126.19, 75.34, 61.24, 37.74, 34.97, 30.92, 21.40. ^{11}B NMR (160 MHz, $CDCl_3$): δ −2.28 (d, J=150.3 Hz, 1B), −5.71 (d, J=149.0 Hz, 1B), −6.99 to −16.46 (m, 8B). FTIR (KBr, cm^{-1}): ν 3068, 2943, 2895, 2831, 2610, 2550, 1620, 1453, 1375, 723. EIMS $[M+H]^+$ m/z 293.3. Anal. Calcd for $C_{13}H_{26}B_{10}$: C, 53.76; H, 9.02. Found: C, 53.98; H, 9.55.

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Supplementary data

Supplementary data (Text files giving additional experimental and characterization data. Copies of the ^{1}H, ^{13}C and ^{11}B NMR spectra of the products produced in this study) associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.11.019.

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