C-Lithiation/Alkylation of Trimethylamine Cyanoborane

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Summary: C-lithiation of trimethylamine cyanoborane readily occurs with 1.5 equiv of s-BuLi. The C-lithiated complex ***1*** *reacts with various electrophiles such as alkyl iodides, aldehydes, ketones, allyl bromide, and bromotrimethylsilane to give the corresponding products* ***2*****−*****14****, in excellent conversion and in good yields. This is the first example of C-lithiation/alkylation of an amine cyanoborane and allows the preparation of amine cyanoboranes not readily available before.*

Introduction

Amine cyanoboranes are interesting compounds that were first reported in 1970.[1] In 1974 Bratt reported the preparation of amine cyanoboranes by the reaction of cyanide and amine iodoboranes.[2] Reaction of $NaBH_3CN$ with X_2 and conversion of the oligomer with amines was reported in 1978 by Martin.[3] In the same year, Spielvogel[4] developed a general method for the synthesis of amine−cyanoboranes based on amine boranes[5] and $NaBH_3CN$. In 1984 Geanangel prepared a quinuclidine derivative by amine exchange.[6] In 1990 Todd devised a protocol for synthesizing amine alkyl cyanoboranes from alkyl trihydroborates and mercuric cyanide.[7] Györi has reported the use of oligomeric $NaBH_3CN$ in the presence of SMe_2.[8] More recently, he reported the synthesis of amine dicyanoboranes.[9] Amine cyanoboranes can be converted to amine carboxyboranes, isoelectronic analogues of amino acids.[10] Both amine carboxyboranes and amine cyanoboranes have been shown to possess considerable biological activity.[10,11]

Amine boranes and other Lewis acid complexed boranes can be C-lithiated.[12−17] In the case of tetrahydroisoquinolines, C-lithiation of the complexed amine occurs on C1 and not on C4 as in the uncomplexed case.[13] Thus, interesting differences in reactivity can be anticipated between complexed and uncomplexed amines. C-lithiation of amine cyanoboranes would offer a new route to more complex amine cyanoboranes not readily attainable by other methods.

Results and Discussion

C-lithiation of Trimethylamine Cyanoborane and Reaction with Alkyl Halides. C-lithiated trimethylamine cyanoborane, $Li^+[CH_2N(Me)_2BH_2CN]^-$ (**1**)**,** was obtained in situ from trimethylamine cyanoborane, Me_3NBH_2CN, using 1.5 equiv of *s*-BuLi as the deprotonation reagent. *n*-BuLi was less effective.[14,16,17] Metalation using 1.5 equiv of *s*-BuLi in THF at −78 to +25 °C, recooling the reaction to −78 °C, adding the electrophile, and warming the reaction mixture to 25 °C gave the highest yields. Metalation at −78 °C gave back only starting material. The use of fewer than 1.5 equiv resulted in reduced conversion to product. Raising the amount of *s*-BuLi to 3 equiv did not increase the yield, except in the case of MeI. The need to use an approximately 50% excess of *s*-BuLi reagent may be due to the known instability of organolithium reagents in THF.[18] Adventitious water may also be involved.[17] The reaction proceeds with alkyl iodides, allyl bromide, and bromotrimethylsilane to provide compounds **2**−**6** (Scheme 1, Table 1). The desired compounds were obtained with excellent conversion. Attempted purification of the amine cyanoboranes on silica resulted in decomposition. However, after extensive investigation, products **2**−**6** could be separated from the starting material by multiple extractions in benzene/water, where Me_3NBH_2CN has higher solubility in water. Using this selective extraction technique, products **2**−**6** were obtained in high purity. However, this caused a partial decrease in the isolated yield, mainly of **2**, due to loss of the product in the aqueous layer (Table 1).

Reaction of the C-lithiated Trimethylamine Cyanoborane with Ketones and Aldehydes. The same

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Scheme 1. Synthesis of Amine Cyanoboranes 2−14 from Trimethylamine Cyanoborane

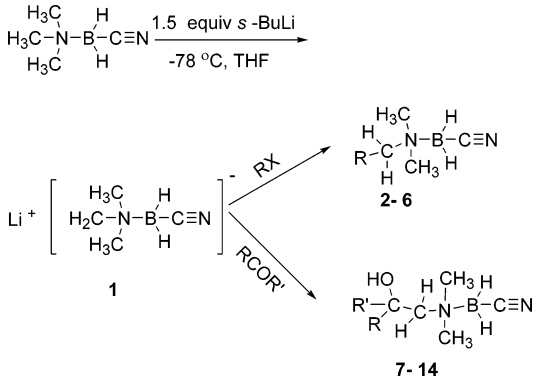


Table 1. Amine Cyanoboranes 2−14 Prepared from Me_3NBH_2CN

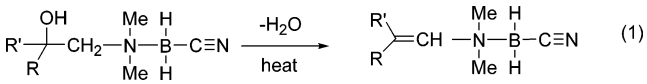
compd	R	R′	X	yield (%)[a]
2	Me		I	80
3	*n*-Pr		I	86
4	*n*-Bu		I	84
5	allyl		Br	87
6	Me_3Si		Cl	94
7	Me	Me		83
8	Me	H		85
9	Ph	H		88
10	anisyl	H		87
11	styryl	H		87
12	furan-2-yl	H		84
13	*p*-tolyl	H		87
14	*o*-tolyl	H		85

[a] Isolated yield.

reaction conditions were then used with different ketones and aldehydes such as acetone, acetaldehyde, benzaldehyde, cinnamaldehyde, furaldehyde, anisaldehyde, *p*-tolualdehyde, and *o*-tolualdehyde, to give the hydroxyl-containing amine cyanoboranes **7**−**14** (Scheme 1). The excesses of nonvolatile or non-water-soluble aldehydes were removed from the crude product using concentrated aqueous sodium bisulfite solution, to give the so-called sodium bisulfite addition compounds, which produced a precipitate that was separated by filtration.[19] For compounds **7**−**14**, unreacted Me_3NBH_2CN was removed by several extractions in CH_2Cl_2/water. Compounds **7**−**14** were obtained in good isolated yields and in high purity (Scheme 1, Table 1).

Spectroscopic Analysis. Compounds **2**−**14** were fully characterized by ^1H, ^{13}C, and ^{11}B NMR, GC/MS, LC/MS, FT-IR and elemental analysis. The ^1H and ^{13}C NMR spectra for compounds **2**−**6** contain new peaks due to the N−CH_2R group with the expected multiplicity in the ^1H NMR: a triplet for **2**, doublets for **3**−**5**, and a singlet for **6**. In the ^{13}C NMR spectra of all compounds, no peaks due to cyano carbon atoms were found, due to the rapid relaxation of the boron-bonding carbon.[20] In all cases, negative boron chemical shifts were observed which are typically associated with tetracoordinate boron. An upfield shift of the ^{11}B resonances is expected, due to the significant donation from the nitrogen atom into the vacant p orbital on the boron.[21] In view of this, the downfield shift of compound **6** can possibly be attributed to the β-effect of the CH_2SiMe_3 group,[22] which may reduce the charge density localized on the boron atom. In addition to the appearance of the signals attributable to the N−CH_2R group in the ^1H and ^{13}C NMR spectra for compounds **7**−**14**, a peak due to H−C−OH with the expected multiplicity appeared downfield between 4.2 and 6.5 ppm in the ^1H NMR spectra, and between 68 and 71 ppm in ^{13}C NMR spectra. This is expected due to the deshielding effect of the two adjacent electron-withdrawing groups (hydroxyl and amine groups). The methylene hydrogens (N−C*H*$_2$CH(OH)R) of complexes **8**−**14** are now diastereotopic and in most cases showed different peaks for each hydrogen. The *N*-methyl groups (NMe_2) are also diastereotopic, and peaks for each group were evident in both the ^1H and ^{13}C NMR spectra (see Experimental Section). In the ^{11}B NMR spectra, comparison of the chemical shifts reveals a downfield shift of approximately 2 ppm in compounds **7**−**14** compared to compounds **2**−**6**. This is attributed to the presence of the OH group, which reduces the charge density on the boron atom. B−H (2894−2939 cm^{-1}), C≡N (2337−2361 cm^{-1}), and B−N (428−461 cm^{-1}) bands in the IR spectra were present in all compounds and are consistent with the assigned structures. In the hydroxyl-containing compounds **7**−**14**, broad bands due to O−H also appeared in the range of 3367−3422 cm^{-1}.

Particularly interesting were the mass spectra results. For LC-MS spectra, compounds **7**−**14** were dissolved in water; it was evident that they have a high affinity for complexation with water and form a number of water complexes. All mass spectra of **7**−**14** showed a molecular peak of $(M + 2n) \times 18$. Fragmentation peaks due to successive loss of molecules of water were also prominent. In addition, a peak at M − 18 also appeared for **7**−**14**, due to water loss (eq 1).



(1)

Conclusion

A series of alkylamine cyanoboranes and hydroxyl-containing amine cyanoboranes were prepared by a simple method involving C-lithiation of trimethylamine cyanoborane with *s*-BuLi, to produce **1**. Subsequent reactions with alkyl halides gave compounds **2**−**6** in high purity and yield. Reaction of **1** with aldehydes and ketones provided **7**−**14**. Many of these compounds were not previously available or could only be synthesized in multiple steps and low yields.

Experimental Section

General Comments. ^1H, ^{13}C, and ^{11}B NMR spectra were recorded in $CDCl_3$ solution on a Varian Unity spectrometer (300, 75, 96 MHz) using Me_4Si as an internal standard for ^1H and ^{13}C NMR and $Et_2O{\cdot}BF_3$ as an external standard for ^{11}B NMR. Infrared spectra were run for samples as neat films for liquids and in KBr disks for solids on a Bruker Vector 22 FT-

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IR spectrophotometer. GC-MS analyses were performed on an HP GCMS instrument (Model HP6890 GC /HP5971 MSD) with an electron impact detector and 30 m methyl silicon column. LC-MS analyses were performed on a Finnigan LCQDUO Thermo Quad, with electron spray detector. Elemental analyses were performed in house at the Hebrew University Microaanalysis laboratory. Melting points were measured on a Fisher Scientific melting point apparatus.

Me_3NBH_2CN was prepared from $Me_3N{\cdot}HCl$ and $NaBH_3CN$ using the literature method.[4] All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried by the usual methods and distilled before use. All other chemicals were obtained from Sigma-Aldrich and used as received without any further purification.

General Procedure.[4] A 0.098 g (1 mmol) amount of Me_3NBH_2CN (**1**) was dissolved in 10 mL of dry THF, the solution was cooled to −78 °C, and 1.15 mL (1.5 mmol) of 1.3 M *s*-BuLi/cyclohexane solution was added dropwise. The reaction mixture was warmed gradually to room temperature over a period of 1 h and then recooled to −78 °C, and 1.5 mmol of the appropriate electrophile was added in one portion. After 5 min the cooling bath was removed, and the reaction mixture was stirred for 0.5 h. Then 10 mL of saturated aqueous $NaHCO_3$ solution was added to the reaction mixture. The organic layer was separated, washed with brine, dried over sodium sulfate, filtered, and concentrated under vacuum. A yellowish liquid, which contains the desired product, in addition to the unreacted starting materials was obtained.

Purification. Crude **2**−**6** were dissolved in 5 mL of benzene and washed with distilled water (7 × 5 mL). The benzene layer was dried over sodium sulfate, filtered, and concentrated under vacuum. Crude **7**−**14** were dissolved in 5 mL of ether, and these solutions were stirred for 3 h with 10 mL of saturated aqueous sodium bisulfite solution. The precipitate was filtered out and discarded. The ether layer was dried over sodium sulfate, filtered, and concentrated under vacuum.[19] The crude product was then dissolved in 5 mL of CH_2Cl_2, and this solution was washed with distilled water (7 × 5 mL). The organic layer was extracted, dried over sodium sulfate, filtered, and concentrated under vacuum.

Ethyldimethylamine Cyanoborane (2). Yellow oil, 80% (0.09 g) yield. ^{1}H NMR ($CDCl_3$): δ 1.28 (t, 3H, J = 7.2 Hz), 2.63 (s, 6H), 2.99 (q, 2H, J = 7.2 Hz); HB cannot be detected.^{13}C{^{1}H} NMR ($CDCl_3$): δ 9.05, 49.41, 58.21; CB cannot be detected. ^{11}B NMR ($CDCl_3$): δ −15.98 (t, J_{B-H} = 102.6 Hz). IR (neat, cm^{-1}): 2894 (B−H), 2361 (C≡N), 1459 (C−N), 430 (B−N). MS (EI): *m*/*z* (%) 112 (M$^+$, 1), 111 (15), 84 (25), 83 (100), 73 (14), 58 (100), 43 (8), 29 (20). Anal. Calcd for $C_5H_{13}BN_2$: C, 53.63; H, 11.70; N, 25.02. Found: C, 53.36; H, 11.47; N, 23.83.

***n*-Butyldimethylamine Cyanoborane (3).** Yellow oil, 86% (0.12 g) yield. ^{1}H NMR ($CDCl_3$): δ 0.84 (t, 3H, J = 7.2 Hz), 1.22 (sex, 2H, J = 7.2 Hz), 1.54 (m, 2H), 2.52 (s, 6H), 2.73 (t, 2H, J = 7.2 Hz); HB cannot be detected. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 13.86, 20.31, 25.40, 49.99, 63.45; CB cannot be detected. ^{11}B NMR ($CDCl_3$): δ −15.98 (t, J_{B-H} = 104.4 Hz). IR (neat, cm^{-1}): 2894 (B−H), 2360 (C≡N), 1464 (C−N), 430 (B−N). MS (EI): *m*/*z* (%) 140 (M$^+$, 10), 139 (15), 137 (15), 112 (20), 101 (12), 86 (10), 83 (100), 82 (30), 81 (15), 71 (5), 58 (100), 57 (22), 56 (75). Anal. Calcd for $C_7H_{17}BN_2$: C, 60.04; H, 12.24; N, 20.00. Found: C, 59.74; H, 11.99; N, 19.05.

Dimethyl-*n*-pentylamine Cyanoborane (4). Yellow oil, 84% (0.14 g) yield. ^{1}H NMR ($CDCl_3$): δ 0.82 (t, 3H, J = 7.5 Hz), 1.23 (m, 4H), 1.59 (m, 2H), 2.55 (s, 6H), 2.76 (t, 2H, J = 7.2 Hz); HB cannot be detected. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 14.04, 22.43, 23.09, 29.12, 50.01, 63.687; CB cannot be detected. ^{11}B NMR ($CDCl_3$): δ −15.93 (t, J_{B-H} = 104.4 Hz). IR (neat, cm^{-1}): 2894 (B−H), 2360 (C≡N), 1459 (C−N), 449 (B−N). MS (EI): *m*/*z* (%) 154 (M$^+$, 1), 153 (10), 151 (20), 126 (27), 115 (12), 98 (7), 85 (2), 83 (100), 82 (36), 71 (6), 70 (11), 58 (87), 56 (61), 55 (25), 54 (7), 52 (7). Anal. Calcd for $C_8H_{19}BN_2$: C, 62.37; H, 12.43; N, 18.18. Found: C, 62.06; H, 12.19; N, 19.14.

But-3-enyldimethylamine Cyanoborane (5). Yellow oil, 87% (0.12 g) yield. ^{1}H NMR ($CDCl_3$): δ 2.46 (m, 2H), 2.66 (s, 6H), 2.91 (t, 2H, J = 7.2 Hz), 5.13 (m, 2H), 5.69 (m, 1H); BH cannot be detected. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 23.21, 50.30, 62.74, 118.54, 133.11; CB cannot be detected. ^{11}B NMR ($CDCl_3$): δ −15.87 (t, J_{B-H} = 104.5 Hz). IR (neat, cm^{-1}): 2909 (B−H), 2360 (C≡N), 1645 (C═C), 1470 (C−N), 443 (B−N). MS (EI): *m*/*z* (%) 138 (M$^+$, 1), 137 (15), 110 (25), 96 (23), 84 (15), 83 (58), 69 (8), 58 (100), 56 (58), 55 (58), 54 (60), 53 (15), 52 (10), 51 (7). Anal. Calcd for $C_7H_{15}BN_2$: C, 60.92; H, 10.95; N, 20.30. Found: C, 60.61; H, 10.73; N, 21.40.

Dimethyl((trimethylsilyl)methyl)amine Cyanoborane (6). Yellow oil, 94% (0.16 g) yield. ^{1}H NMR ($CDCl_3$): δ 0.21 (s, 9H), 2.58 (s, 2H), 2.74 (s, 6H); BH cannot be detected. ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 0.05, 54.58, 58.46; CB cannot be detected. ^{11}B NMR ($CDCl_3$): δ −14.94 (t, J_{B-H} = 100.9 Hz). IR (neat, cm^{-1}): 2917 (B−H), 2337 (C≡N), 1466 (C−N), 446 (B−N). MS (EI): *m*/*z* (%) 170 (M$^+$, 17), 169 (7), 155 (10), 142 (17), 131 (13), 116 (58), 101 (17), 87 (17), 83 (12), 73 (25), 70 (20), 58 (100), 56 (17). Anal. Calcd for $C_7H_{19}BN_2Si$: C, 49.42; H, 11.26; N, 16.47. Found: C, 49.17; H, 11.04; N, 17.34.

Dimethyl(2-methyl-2-hydroxypropyl)amine Cyanoborane (7). Yellow oil, 83% (0.13 g) yield. ^{1}H NMR ($CDCl_3$): δ 1.38 (s, 6H), 2.88 (s, 6H), 3.00 (s, 2H); BH cannot be detected. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 30.83, 50.50, 61.89, 69.35; BC cannot be detected. ^{11}B NMR ($CDCl_3$): δ −13.55 (t, J_{B-H} = 106.2 Hz). IR (neat, cm^{-1}): 3422 (O−H), 2939 (B−H), 2361 (C≡N), 1467 (C−N), 433 (B−N). MS (ES): *m*/*z* (%) 157 (M + 1, 35), 138 (10), 179 (20), 174 (94), 192 (15), 228 (18), 264 (90), 300 (95). Anal. Calcd for $C_7H_{17}BN_2O$: C, 53.88; H, 10.98; N, 17.95. Found: C, 53.61; H, 10.76; N, 17.59.

Dimethyl(2-hydroxypropyl)amine Cyanoborane (8). Red oil, 85% (0.12 g) yield. ^{1}H NMR ($CDCl_3$): δ 1.23 (d, 3H, J = 6.3 Hz), 2.87 (s, 3H), 2.75 (s, 3H), 2.87 (d, 1H, J = 12.9 Hz), 2.88 (d, 1H, J = 7.2 Hz), 4.40 (m, 1H); BH cannot be detected. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 23.21, 49.41, 52.57, 63.49, 69.25; CB cannot be detected. ^{11}B NMR ($CDCl_3$): δ −10.56 (t, J_{B-H} = 91.1 Hz). IR (neat, cm^{-1}): 3365 (O−H), 2917 (B−H), 2359 (C≡N), 1456 (C−N), 433 (B−N). MS (ES): *m*/*z* (%) 143 (M + 1, 74), 124 (6), 165 (22), 178 (50), 214 (100), 286 (64). Anal. Calcd for $C_6H_{15}BN_2O$: C, 50.75; H, 10.65; N, 19.73. Found: C, 50.34; H, 10.44; N, 19.34.

Dimethyl(2-phenyl-2-hydroxyethyl)amine Cyanoborane (9). Yield 88% (0.18 g), mp 119 °C. ^{1}H NMR ($CDCl_3$): δ 2.82 (s, 3H), 2.88 (s, 3H), 3.04 (d, 1H, J = 3.9 Hz), 3.05 (d, 1H, J = 7.5 Hz), 5.38 (dd, 1H, J = 4.2, 4.2 Hz), 7.39 (m, 5H); BH cannot be detected. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 50.07, 53.36, 69.61, 70.53, 125.99, 128.86, 129.22, 141.60; BC cannot be detected. ^{11}B NMR ($CDCl_3$): δ −13.62 (t, J_{B-H} = 104.5 Hz). IR (KBr, cm^{-1}): 3374 (O−H), 2894 (B−H), 2360 (C≡N), 1462 (C−N), 430 (B−N). MS (ES): *m*/*z* (%) 205 (M + 1, 65), 227 (29), 222 (10), 276 (40), 348 (100). Anal. Calcd for $C_{11}H_{17}BN_2O$: C, 64.74; H, 8.40; N, 13.73. Found: C, 64.22; H, 8.38; N, 14.45.

Dimethyl(2-(4-methoxyphenyl)-2-hydroxyethyl)amine Cyanoborane (10). Yellow oil, 87% (0.20 g) yield. ^{1}H NMR ($CDCl_3$): 2.80 (s, 3H), 2.85 (s, 3H), 3.02 (d, 2H, J = 6.0 Hz), 4.59 (s, 3H), 5.30 (t, 1H, J = 6.0 Hz), 6.87 (d, 1H, J = 1.5 Hz), 6.89 (d, 1H, J = 2.1 Hz), 7.26 (d, 1H, J = 3.3 Hz), 7.29 (d, 1H, J = 2.4 Hz); BH cannot be detected. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 29.93, 49.94, 53.24, 69.58, 70.04, 114.15, 114.50, 127.28, 128.91; BC cannot be detected. ^{11}B NMR ($CDCl_3$): δ −13.20 (t, J_{B-H} = 104.5 Hz). IR (neat, cm^{-1}): 3378 (O−H), 2902 (B−H), 2360 (C≡N), 1461 (C−N), 444 (B−N). MS (ES): *m*/*z* (%) 235 (M + 1, 5), 216 (35), 257 (45), 252 (5), 270 (8), 306 (100), 342 (40), 378 (6). Anal. Calcd for $C_{12}H_{19}BN_2O_2$: C, 61.57; H, 8.18; N, 11.97. Found: C, 61.26; H, 8.01; N, 14.31.

Dimethyl(4-phenyl-2-hydroxybut-3-enyl)amine Cyanoborane (11). Yellow oil, 87% (0.02 g) yield. ^{1}H NMR

($CDCl_3$): δ 2.71 (s, 3H), 2.82 (s, 3H), 2.97 (d, 1H, J = 9.3 Hz), 3.05 (d, 1H, J = 2.1), 6.14 (dd, 1H, J = 6.6, 6.6 Hz), 6.37 (dt, 1H, J = 5.7, 6.6 Hz), 6.71 (d, 1H, J = 15.9 Hz), 7.25 (m, 5H); BH cannot be detected. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 29.95, 49.95, 63.96, 67.68, 68.95, 126.70, 126.90, 128.83, 128.98; CB cannot be detected. ^{11}B NMR ($CDCl_3$): δ −13.13 (t, J_{B-H} = 100.8 Hz). IR (neat, cm^{-1}): 3382 (O−H), 2917 (B−H), 2360 (C≡N), 1455 (C−N), 427 (B−N). MS (ES): *m*/*z* (%) 231 (M + 1, 15), 212 (12), 253 (43), 302 (100), 338 (6). Anal. Calcd for $C_{13}H_{19}BN_2O$: C, 67.85; H, 8.32; N, 12.17. Found: C, 67.58; H, 8.29; N, 11.93.

(2-(Furan-2-yl)-2-hydroxyethyl)dimethylamine Cyanoborane (12). Orange oil, 84% (0.16 g) yield. ^1H NMR ($CDCl_3$): δ 2.67 (s, 3H), 2.77 (s, 3H), 3.20 (d, 2H, J = 6.3 Hz), 5.36 (t, 1H, J = 6.6 Hz), 6.29 (dd, 1H, J = 5.4, 4.2 Hz), 6.58 (d, 1H, J = 5.4 Hz), 7.23 (d, 1H, J = 4.2 Hz); BH cannot be detected. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 49.89, 52.35, 69.52, 70.61, 104.59, 110.15, 141.36, 153.51; BC cannot be detected. ^{11}B NMR ($CDCl_3$): δ −13.20 (t, J_{B-H} = 108.2 Hz). IR (neat, cm^{-1}): 3367 (O−H), 2902 (B−H), 2360 (C≡N), 1460 (C−N), 461 (B−N). MS (ES): *m*/*z* (%) 195 (M + 1, 30), 176 (10), 217 (40), 212 (25), 230 (100), 266 (32). Anal. Calcd for $C_9H_{15}BN_2O_2$: C, 55.71; H, 7.79; N, 14.44. Found: C, 55.27; H, 7.61; N, 13.98.

Dimethyl(2-*p*-tolyl-2-hydroxyethyl)amine Cyanoborane (13). Yellow oil, 87% (0.19 g). ^1H NMR ($CDCl_3$): δ 2.34 (s, 3H), 2.80 (s, 3H), 3.85 (s, 3H), 3.02 (d, 2H, J = 5.7 Hz), 5.29 (t, 1H, J = 5.7 Hz), 7.17 (m, 4H); BH cannot be detected. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.38, 49.86, 65.36, 69.59, 70.18, 125.93, 127.34, 129.44, 129.79; BC cannot be detected. ^{11}B NMR ($CDCl_3$): δ −13.30 (t, J_{B-H} = 105.5 Hz). IR (neat, cm^{-1}): 3407 (O−H), 2917 (B−H), 2356 (C≡N), 1457 (C−N), 428 (B−N). MS (ES): *m*/*z* (%) 219 (M + 1, 50), 200 (5), 241 (12), 236 (4), 254 (4), 290 (80), 326 (90), 362 (5). Anal. Calcd for $C_{12}H_{19}BN_2O$: C, 66.08; H, 8.78; N, 12.84. Found: C, 65.75; H, 8.61; N, 12.71.

Dimethyl(2-*o*-tolyl-2-hydroxyethyl)amine Cyanoborane (14). Yellow oil, 85% (0.19 g) yield. ^1H NMR ($CDCl_3$): δ 2.38 (s, 3H), 2.81 (s, 3H), 2.90 (s, 3H), 2.93 (dd, 2H, J = 5.7, 8.1 Hz), 5.52 (dd, 1H, J = 3.3, 7.5 Hz), 7.25 (m, 4H); BH cannot be detected. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.87, 49.79, 53.32, 66.60, 68.48, 125.90, 126.24, 126.86, 127.69, 130.49, 130.98; BC cannot be detected. ^{11}B NMR ($CDCl_3$): δ −13.20 (t, J_{B-H} = 104.5 Hz). IR (neat, cm^{-1}): 3396 (O−H), 2939 (B−H), 2349 (C≡N), 1464 (C−N), 435 (B−N). MS (ES): *m*/*z* (%) 219 (M + 1, 22), 241 (4), 236 (4), 254 (12), 290 (64), 326 (100), 362 (4). Anal. Calcd for $C_{12}H_{19}BN_2O$: C, 66.08; H, 8.78; N, 12.84. Found: C, 65.67; H, 8.68; N, 12.55.

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