JOC The Journal of Organic Chemistry

Article

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“Naked” Lithium Cation: Strongly Activated Metal Cations Facilitated by Carborane Anions

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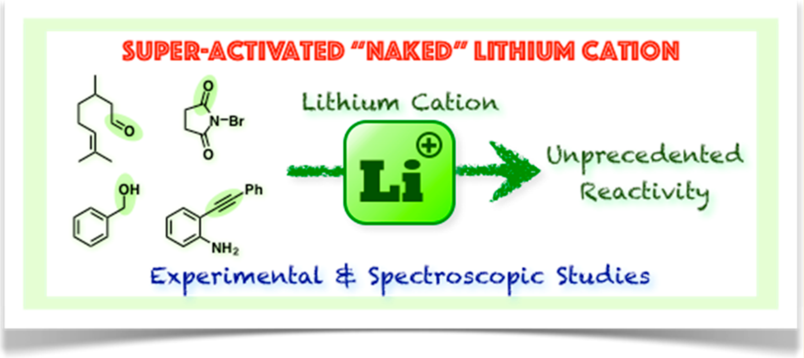
Supporting Information



ABSTRACT: Experimental and spectroscopic studies revealed unprecedented reactivity of a “naked” lithium cation with very weakly coordinating anions, including carborane anions. The superactivated lithium cation has greatly enhanced Lewis acidic character and mediates various organic reactions such as carbonyl-ene reaction, NBS-bromination of unactivated aromatics, and Friedel−Crafts alkylation, which are not promoted by conventional lithium salts. Chemical robustness of the counteranion also plays an important role in the chemistry of the strongly activated lithium cation.

INTRODUCTION

Hydrogen and lithium are vertically adjacent elements in the periodic table and are categorized as congeneric elements. However, they differ in many respects, including electronegativity (H 2.2 vs Li 1.0). This dissimilarity is reflected in their acid chemistry: for instance, trifluoromethanesulfonic acid (CF_3SO_3H: TfO^-H^+) and fluorosulfonic acid ($FSO_3^-H^+$) have been traditionally employed as superacids (super Brønsted acids), enabling a range of superacid-promoted synthetic transformations,[1] whereas Li^+OTf^- and $Li^+OSO_2F^-$ are essentially ineffective in most of these reactions because the potent electropositivity of the lithium cation prevents complete dissociation of the counteranion. Indeed, the chemistry of “naked” metal cations (i.e., superactivation of metal cations) has not been well developed in general. Given that a wide variety of elements can be used in Lewis acid/metal cation chemistry, the development of superactivated metal cations should open up tremendous possibilities for enhanced or unprecedented reactivity. Here, we report a systematic study designed to generate “naked” Li^+. The key to success proved to be appropriate design/choice of counteranions. The formation of superactivated Li^+ was confirmed by ^7Li NMR and UV−vis spectroscopies. We found that the superactivated lithium cation, which has greatly enhanced Lewis acidic character, mediates various reactions such as the carbonyl-ene reaction, NBS-bromination of unactivated aromatics, and Friedel−Crafts alkylation, which are not promoted by conventional lithium salts.

RESULTS AND DISCUSSION

To screen suitable counteranions to maximize the intrinsic character of Li^+, we systematically examined various anions, including traditional weakly coordinating anions (WCAs: OTf^-, NTf_2^-, BF_4^-, and ClO_4^-),[2] borate-based anions ($BARF^-$ and $TFPB^-$),[3,4] and carborane anions ($CB_{11}H_{12}^-$ and $CB_{11}H_6Br_6^-$)[5] (Figure 1). Carborane anion is an icosahedral cluster molecule composed of 1 carbon and 11 boron atoms with exceptionally low basicity/nucleophilicity.[6] In addition, it can be flexibly functionalized,[5b,7] enabling precise tuning of its characteristics.

Received: November 5, 2016
Published: January 19, 2017

DOI: 10.1021/acs.joc.6b02677
J. Org. Chem. 2017, 82, 1931−1935

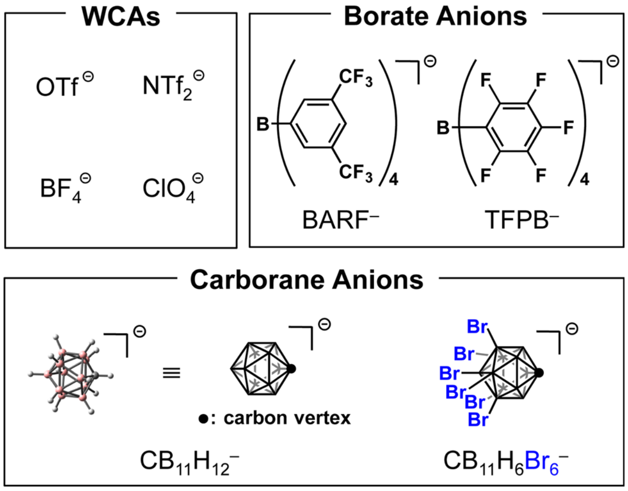


Figure 1. Counteranions investigated in this work with weak coordinating ability.

First, we measured the ^{7}Li NMR spectra of the lithium salts in liquid SO_2 as a solvent[8] (Table 1). Although Brønsted acidity can be easily assessed using parameters such as the acid dissociation constant (pK_a) and Hammett acidity function (H_0), evaluation of the Lewis acidity of metal cations is difficult due to the lack of a similar index. The ^{7}Li signals of Li^+OTf^- and $Li^+NTf_2^-$ were observed as sharp singlets at −1.56 and −1.50 ppm, respectively, under the conditions given in Table 1 (entries 1 and 2), while signals of $Li^+BF_4^-$ and $Li^+ClO_4^-$ could not be recorded because these salts did not dissolve under the NMR conditions. On the other hand, lithium salts of borate and carborane anions showed lower-field shifts to the observation limit (ca. −1.28 ppm),[9] which indicates that they have lower electron density (entries 5−8).

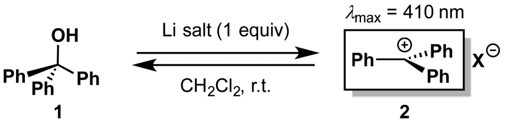
We then performed a UV−vis spectral study to evaluate the generation of trityl cation (**2**) (at 410 nm) via Lewis acidic activation of trityl alcohol (**1**), as reported by Kobayashi and co-workers.[10] The lithium salts of borate and carborane anions, Li^+TFPB^-, Li^+BARF^-, $Li^+CB_{11}H_{12}^-$, and $Li^+CB_{11}H_6Br_6^-$ were sufficiently reactive to generate **2** (Table 2, entries 5−8), whereas Li^+OTf^-, $Li^+NTf_2^-$, $Li^+BF_4^-$, and $Li^+ClO_4^-$ produced no spectral change (entries 1−4). This indicates that there is a distinct difference of Lewis/metal acidity between them, which is in accordance with the ^{7}Li NMR results. Note that in the cases of Li^+BARF^- and $Li^+CB_{11}H_{12}^-$, the absorbance of **2** diminished during the course of measurements, implying that side reactions or decomposition of **2** occur in the presence of these counteranions.[11] These results suggest that not only counteranion stability (i.e., extremely low nucleophilicity) but also chemical robustness, that is, tolerance to side reactions/decomposition, would be necessary to enable superactivation of the Li^+ center.

Table 1. ^{7}Li NMR Data of the Lithium Salts[a]

	Li salt	Δδ (^{7}Li)		Li salt	Δδ (^{7}Li)
1	LiOTf	−1.56 ± 0.03	5	LiTFPB	−1.28 ± 0.02
2	$LiNTf_2$	−1.50 ± 0.02	6	LiBARF	−1.27 ± 0.04
3	$LiBF_4$	*b*	7	$LiCB_{11}H_{12}$	−1.28 ± 0.01
4	$LiClO_4$	*b*	8	$LiCB_{11}H_6Br_6$	−1.28 ± 0.02

[a] All spectra were recorded in liquid SO_2 at −20 °C and referenced to external LiCl in acetone-d_6 (see the Supporting Information for details). [b] These Δδ (^{7}Li) values were not determined because $LiBF_4$ and $LiClO_4$ were only sparingly soluble in liquid SO_2.

Table 2. Effects of Counteranions on the Lewis Acidity of Lithium Cation in Trityl Cation (2) Formation

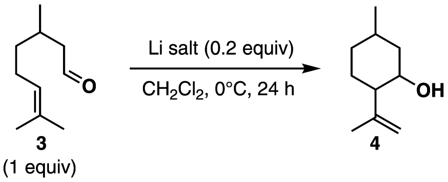


	Li salt	abs (λ = 410 nm)		Li salt	abs (λ = 410 nm)
1	LiOTf	no data	5	LiTFPB	1.14
2	$LiNTf_2$	no data	6	LiBARF	0.28[a]
3	$LiBF_4$	no data	7	$LiCB_{11}H_{12}$	0.16[a]
4	$LiClO_4$	no data	8	$LiCB_{11}H_6Br_6$	1.24

[a] Decrease in the peak intensity at 410 nm was observed during the course of measurement.

With the spectroscopic results in hand, we next examined whether superactivated lithium could promote various fundamental reactions that do not proceed in the presence of ordinary lithium salts. Carbonyl activation is a key step for organic transformation. For example, carbonyl-ene reaction generally requires strong Lewis acids to activate the carbonyl group.[12] When Li^+OTf^-, $Li^+NTf_2^-$, $Li^+BF_4^-$, or $Li^+ClO_4^-$ was employed for the carbonyl-ene reaction of citronellal (**3**) in dichloromethane at 0 °C, the desired product **4** was not obtained at all, and only the starting **3** was recovered (Table 3, entries 1−4). In contrast, the desired cyclization proceeded under the same conditions in the presence of a catalytic amount of Li^+TFPB^-, Li^+BARF^-, $Li^+CB_{11}H_{12}^-$, or $Li^+CB_{11}H_6Br_6^-$ (entries 5−8).

Table 3. Carbonyl-ene Reaction of Citronellal (3)

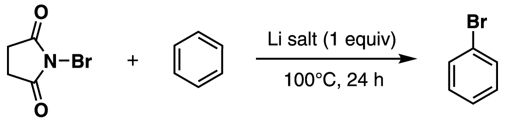


	Li salt	yield (%)[a]		Li salt	yield (%)[a]
1	LiOTf	0	5	LiTFPB	75
2	$LiNTf_2$	0	6	LiBARF	60
3	$LiBF_4$	0	7	$LiCB_{11}H_{12}$	63
4	$LiClO_4$	0	8	$LiCB_{11}H_6Br_6$	69

[a] Yields were determined by GC analysis using tridecane as an internal standard.

Inspired by the success of the first carbonyl-ene reaction catalyzed by lithium salts (i.e., intramolecular C−C bond formation via carbonyl activation), we then examined the bromination of benzene (**6**) by activation of *N*-bromosuccinimide (NBS) (**5**) (Table 4). With nonactivated benzenes, this reaction requires superelectrophilic reagents such as (multiple) protonated NBS reagents in superacid.[13] Again, ordinary lithium salts such as Li^+OTf^-, $Li^+NTf_2^-$, $Li^+BF_4^-$, or $Li^+ClO_4^-$ did not mediate the bromination reaction at all (entries 1−4). On the other hand, the combination of NBS with 1 equiv of $Li^+CB_{11}H_6Br_6^-$ successfully brominated benzene (**7**) in 84% yield at 100 °C for 24 h (entry 8). Moreover, even bromobenzene (**7**), a deactivated benzene substrate, could be brominated in the presence of 1.5 equiv of $Li^+CB_{11}H_6Br_6^-$ to

Table 4. Bromination of Benzene (6) with NBS (5)

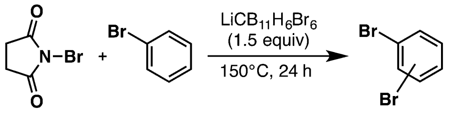


5 (1 equiv) 6 (excess) 7

	Li salt	yield (%)[a]		Li salt	yield (%)[a]
1	LiOTf	0	5	LiTFPB	35
2	LiNTf_2	0	6	LiBARF	34
3	LiBF_4	0	7	$\text{LiCB}_{11}\text{H}_{12}$	0
4	LiClO_4	0	8	$\text{LiCB}_{11}\text{H}_6\text{Br}_6$	84

[a]Yields were determined by GC analysis using tridecane as an internal standard.

give the product **8** in 50% yield (eq 1). With Li^+TFPB^-, Li^+BARF^-, or $\text{Li}^+\text{CB}_{11}\text{H}_{12}{}^-$, the reaction was sluggish, and bromination of the carborane anion or decomposition of the borate scaffold occurred preferentially (entries 5−7).[14] These results indicate that the reaction requires (1) an extremely acidic lithium cation that strongly activates NBS to give superelectrophilic brominating reagents and (2) a robust anion skeleton compatible with the generated superelectrophilic species.

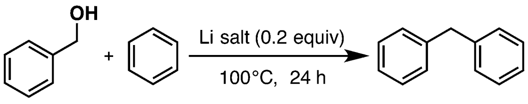


(1)

5 (1 equiv) 7 (excess) 8 (50%) (*o*- : 3%, *p*- : 47%)

Intermolecular Friedel−Crafts (FC) alkylation reaction of benzene was next investigated (Table 5). For the success of FC reactions using alcohols (OH is a poor leaving group) as the electrophile, the use of a superacid or strong Lewis acid is generally required.[15] Indeed, no reaction of **9** took place in the presence of Li^+OTf^-, $\text{Li}^+\text{NTf}_2{}^-$, $\text{Li}^+\text{BF}_4{}^-$, or $\text{Li}^+\text{ClO}_4{}^-$. However, we found that the use of Li^+TFPB^- or $\text{Li}^+\text{CB}_{11}\text{H}_6\text{Br}_6{}^-$ gave the desired FC product **10** in 95 or 94% yield, respectively (entries 5 and 8). On the other hand, decomposition/side reactions of the anion moiety prior to the FC reaction were observed when Li^+BARF^- or $\text{Li}^+\text{CB}_{11}\text{H}_{12}{}^-$ was employed.

Table 5. Friedel-Crafts Alkylation of Benzene (6) with Benzyl Alcohol (9)



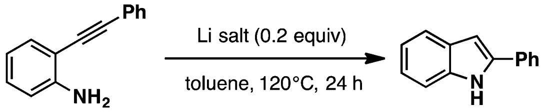
9 (1 equiv) 6 (excess) 10

	Li salt	yield (%)[a]		Li salt	yield (%)[a]
1	LiOTf	0	5	LiTFPB	95
2	LiNTf_2	0	6	LiBARF	trace
3	LiBF_4	0	7	$\text{LiCB}_{11}\text{H}_{12}$	0
4	LiClO_4	0	8	$\text{LiCB}_{11}\text{H}_6\text{Br}_6$	94

[a]Yields were determined by GC analysis using tridecane as an internal standard.

Finally, to characterize the behavior of lithium cation compared with that of normal superacids such as TfO^-H^+, we focused on activation of a less-polar alkyne triple bond. Indole synthesis from *o*-alkynylanilines (Table 6) was selected because "soft" metals are generally required to activate the C−C π-bond,[16] and superacids are ineffective for the annulation, presumably due to preferential protonation of the aniline nitrogen in superacid media.[17] When ordinary lithium salt, Li^+OTf^-, $\text{Li}^+\text{NTf}_2{}^-$, $\text{Li}^+\text{BF}_4{}^-$, or $\text{Li}^+\text{ClO}_4{}^-$ was employed, the desired indole annulation proceeded, albeit in low yield, probably due to the low acidity (entries 1−4). In sharp contrast, the use of $\text{Li}^+\text{CB}_{11}\text{H}_{12}{}^-$ promoted the desired annulation reaction to give **12** in 84% yield. Other lithium salts with borate anions and $\text{Li}^+\text{CB}_{11}\text{H}_6\text{Br}_6{}^-$ seemed to favor strong coordination to nitrogen, which disturbed the indole cyclization.

Table 6. Intramolecular Cyclization of 2-Phenylethynylaniline (11) to Afford 2-Phenylindole (12)



11 12

	Li salt	yield (%)[a]		Li salt	yield (%)[a]
1	LiOTf	5	5	LiTFPB	25
2	LiNTf_2	9	6	LiBARF	7
3	LiBF_4	6	7	$\text{LiCB}_{11}\text{H}_{12}$	84
4	LiClO_4	19	8	$\text{LiCB}_{11}\text{H}_6\text{Br}_6$	50

[a]Yields were determined by GC analysis using tridecane as an internal standard.

In summary, combined spectroscopic and experimental studies demonstrated that the Lewis acidity and character of the lithium cation can be finely tuned by means of an appropriate choice of counteranion. In particular, carborane anions strongly activated lithium cations to achieve unprecedented reactivity, and the superactivated lithium cation mediated various reactions (carbonyl-ene reaction, NBS-bromination of unactivated aromatics, Friedel−Crafts alkylation) that are not promoted by conventional lithium salts. Counteranion stability and chemical robustness are both crucial to prevent side reactions. Given that the carborane anion is readily customizable,[5b] including carborane-based multivalent anions,[7a] we anticipate that carborane anions will be an excellent platform for the flexible design of superactivated metal centers in periodic table-wide chemistry. We believe the concept/methods described herein offer a toolkit that will be of general use for exploration of a range of superactivated metal cations.

■ EXPERIMENTAL SECTION

General Remarks. $\text{Me}_3\text{NHCB}_{11}\text{H}_{12}$ and $\text{CsCB}_{11}\text{H}_{12}$ were purchased from commercial suppliers. Bromobenzene, citronellal, *N*-bromosuccinimide, and benzyl alcohol were used after appropriate purification (distillation or recrystallization). 2-Phenylethynylaniline was prepared as described previously.[18] Lithium tetrakis(3,5-trifluoromethyl)phenylborate (LiBARF) was prepared as described previously.[19] Lithium trifluoromethanesulfonate, lithium bis(trifluoromethanesulfonimide), lithium tetrafluoroborate, and lithium perchlorate were used after being dried under vacuum (1.0 × 10^{-1} hPa/80 °C overnight). All other chemicals were of reagent grade and used as received. Air- and moisture-sensitive manipulations were performed with standard Schlenk techniques or in a glovebox under argon atmosphere. Normal-phase column chromatography was performed with silica gel 60 (230−400 mesh), and thin-layer chromatography was carried out on 0.25 mm silica gel plates. The NMR spectral measurements were performed on a 500 MHz spectrometer. Chemical shifts are expressed in δ (ppm) values, and coupling constants are expressed in hertz (Hz). ^{1}H and ^{13}C NMR spectra were referenced to tetramethylsilane as an internal standard. The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and bs = broad singlet.

Synthesis of Trimethylammonium-7,8,9,10,11,12-hexabromo-1-carba-closo-dodecaborate, $(NMe_3H)CB_{11}H_6Br_6$ [CAS Registry no. 442549-75-9]. $CsCB_{11}H_6Br_6$ (2.5 g, 3.35 mmol) was dissolved in an aqueous solution of HCl (10%, 100 mL) and extracted with Et_2O three times. The combined Et_2O extracts were evaporated to dryness. The solid residue was treated with water. The product was precipitated by addition of $NHMe_3Cl$ (960 mg, 10.05 mmol). The white solid was filtered off, washed with water, and dried under vacuum (1.0×10^{-1} hPa/100 °C, overnight) to give the title compound as white powder in 85% yield (1900 mg). This compound was previously reported.[20a,b] ^{1}H{^{11}B} NMR (500 MHz, acetone-d_6): 2.33 (bs, 5H), 3.04 (bs, 1H), 3.23 (s, 9H); HRMS (ESI-TOF) m/z calcd for $CH_6B_{11}Br_6$ ($[M]^-$): 616.6605, found: 616.6601.

Synthesis of Lithium-7,8,9,10,11,12-hexabromo-1-carba-closo-dodecaborate, $LiCB_{11}H_6Br_6$ [CAS Registry no. 225797-12-6]. Typical procedure A: To the aqueous solution (200 mL) of (NMe_3H)-$CB_{11}H_6Br_6$ (2.0 g, 2.97 mmol) was added $LiOH{\cdot}H_2O$ (374 mg, 8.92 mmol). This solution was stirred for 60 min at room temperature and then evaporated to dryness. The solid was treated with water again and extracted with Et_2O three times. The Et_2O fractions were washed with an aqueous solution of LiOH (10%), LiCl (20%), and water and were then dried with activated molecular sieves (powdered, 4 Å). The sieves were filtered off and washed with dry Et_2O. The combined Et_2O extracts were stirred with LiH (1.0 g) for 24 h under an argon atmosphere at room temperature, filtered to remove any residual LiOH and LiH, and evaporated under reduced pressure to afford brown oil. The oil was dissolved in acetonitrile (100 mL), and the solution was stirred overnight with activated charcoal (200 mg). The charcoal was filtered off through Celite pad and washed with acetonitrile. Combined filtrates were evaporated, and the product was dried under reduced pressure (1.0×10^{-1} hPa/130 °C, 7 days) to give the title compound as white powder in 68% yield (1958 mg). This compound was previously reported.[21] ^{1}H{^{11}B} NMR (500 MHz, acetone-d_6): 2.33 (bs, 5H), 3.03 (bs, 1H); HRMS (ESI-TOF) m/z calcd for $CH_6B_{11}Br_6$ ($[M]^-$): 616.6605, found: 616.6604.

Synthesis of Lithium-1-carba-closo-dodecaborate, $LiCB_{11}H_{12}$ [CAS Registry no. 92468-37-6]. According to the typical procedure A, using $NMe_3HCB_{11}H_{12}$ (2.0 g, 9.84 mmol) and $LiOH{\cdot}H_2O$ (4958 mg, 29.5 mmol), the title compound was obtained as white powder in 74% yield (1092 mg). This compound was previously reported.[22] ^{1}H{^{11}B} NMR (500 MHz, acetone-d_6): 1.57 (bs, 5H), 1.66 (bs, 5H), 1.73 (bs, 1H), 2.23 (bs, 1H); HRMS (ESI-TOF) m/z calcd for $CH_{12}B_{11}$ ($[M]^-$): 143.2035, found: 143.2038.

*General Procedure for Carbonyl-ene Reaction of Citronellal (**3**).* $LiCB_{11}H_6Br_6$ (13.7 mg, 0.022 mmol) and dichloromethane (5.0 mL) were charged in a dried Schlenk tube in a glovebox. To the mixture was added citronellal (17.1 mg, 0.11 mmol). The mixture was stirred at 0 °C for 24 h, and then the reaction was quenched by brine. The generation of the desired compound (**4**: mixture of two isomer) (69%) was confirmed by comparison of the ^{1}H NMR spectrum and GC−MS traces of the authentic sample.[12d] Chemical yield was determined by GC analysis using tridecane as an internal standard.

*Major Isomer of **4**: Isopulegol [CAS Registry no. 7786-67-6].* ^{1}H NMR data are consistent with those previously reported.[12d]

*General Procedure for Bromination of Benzene (**6**) with NBS (**5**).* Benzene (3.0 mL), $LiCB_{11}H_6Br_6$ (62.3 mg, 0.1 mmol), and *N*-bromosuccinimide (**5**, 17.2 mg, 0.1 mmol) were charged in a dried Schlenk tube in a glovebox. The mixture was stirred at 100 °C for 24 h in the dark, and the reaction was quenched by brine. The generation of the desired compound **7** (84%) was confirmed by comparison of ^{1}H NMR spectrum and GC−MS trace of the commercially available authentic sample. Chemical yield was determined by GC analysis using tridecane as an internal standard.

*Bromobenzene (**7**): [CAS Registry no. 7786-67-6].* ^{1}H NMR data are consistent with a commercially available authentic sample.

*Major Isomer of **8**: 1,4-Dibromobenzene [CAS Registry no. 106-37-6].* 1,4-Dibromobenzene (47%) was obtained by using $LiCB_{11}H_6Br_6$, NBS (**5**), and bromobenzene (**7**) at 150 °C. Chemical yield was determined by GC analysis using tridecane as an internal standard. ^{1}H NMR data are consistent with a commercially available authentic sample.

General Procedure for Friedel−Crafts Alkylation. Benzene (1.0 mL) and $LiCB_{11}H_6Br_6$ (12.0 mg, 0.02 mmol) were charged in a dried Schlenk tube in a glovebox. To the mixture was added benzyl alcohol (**9**, 10.4 mg, 0.1 mmol). The mixture was stirred at 100 °C for 24 h, and then the reaction was quenched by brine. The generation of the desired compound **10** (94%) was confirmed by comparison of the ^{1}H NMR spectrum and GC−MS trace of the authentic sample.[23] Chemical yield was determined by GC analysis using tridecane as an internal standard.

*1,1-Diphenylmethane (**10**): [CAS Registry no. 612-00-0].* ^{1}H NMR data are consistent with a commercially available authentic sample.[23]

*General Procedure for Indole Cyclization of 2-Phenylethynylaniline (**11**).* Toluene (27 mL), $LiCB_{11}H_6Br_6$ (19.3 mg, 0.031 mmol), and 2-phenylethynylaniline (**11**, 30 mg, 0.155 mmol) were charged in a dried Schlenk tube in a glovebox. The mixture was stirred at 120 °C for 24 h, and the reaction was quenched by brine. The generation of the desired compound **12** (50%) was confirmed by comparison of ^{1}H NMR spectrum and GC−MS trace of the authentic sample.[24] Chemical yield was determined by GC analysis using tridecane as an internal standard.

*2-Phenyl-1H-indole (**13**): [CAS Registry no. 948-65-2].* ^{1}H NMR data are consistent with those previously reported.[24]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02677.

> UV−vis absorption spectra, representative ^{7}Li NMR spectra, and copies of ^{1}H NMR spectra of known compounds for purity (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by JSPS KAKENHI (S) (Grant 24229011), The Asahi Glass Foundation, Foundation NAGASE Science Technology Development, the Sumitomo Foundation (to M.U.), and a JSPS Grant-in-Aid for Young Scientists (A) (Grant 25713001, to R.T.). Y.K. thanks RIKEN Junior Research Associate program (until March 2015) and the JSPS Research Fellowship for Young Scientists (from April 2015).

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NOTE ADDED AFTER ASAP PUBLICATION

Equation 1 and the Table 5 scheme were corrected on January 30, 2017.