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Lithium diisobutyl-*tert*-butoxyaluminum hydride (LDBBA) catalyzed hydroboration of alkynes and imines with pinacolborane†

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Lithium diisobutyl-*tert*-butoxyaluminum hydride (LDBBA)-catalyzed hydroboration of alkynes with pinacolborane (HBpin) was demonstrated. The hydroboration proceeded more efficiently with LDBBA than with other aluminum hydrides and afforded alkenyl boronates in moderate to good yields. In addition, high-yielding LDBBA-catalyzed hydroboration of imines was achieved. The coordination of anionic aluminate with lithium enables effective hydride transfer for hydroboration.

Introduction

Because of their versatile nature, organoboron compounds are valuable synthetic synthons for various chemical transformations and cross-coupling reactions in organic synthesis.[1] For instance, the C–B bond in organoborons can be readily transformed to C–X bonds (X = C, N, O, P, or a halogen), thus triggering much interest in the preparation of the corresponding boron precursors.[2]

Hydroboration is a straightforward and atom-economic method to synthesize boron precursors from unsaturated hydrocarbons. Hydroboration of unsaturated (C–C) bonds was first reported with sodium borohydride–aluminum chloride by the Nobel laureate Prof. H. C. Brown.[3] Subsequently, several related methods for this transformation have been developed, mainly using transition metal complexes as catalysts.[4] Recently, the focus had shifted to the use of main-group metals as alternative to expensive and sensitive transition-metal and precious-metal complexes (Fig. 1).[5]

Group 13 hydrides have been widely studied because of their ability to store hydrogen, participate in various organic transformations, and mediate the reduction of unsaturated substrates.[6] In particular, aluminum derived mono-hydrides and dihydrides have been investigated for the hydroboration of carbonyl and acetylene compounds. Yang *et al.* reported the aluminum dihydride $LAlH_2$ (L = HC(CMeNAr)$_2$, Ar = 2,6-Et$_2$C$_6$H$_3$)-catalyzed hydroboration of terminal alkynes and dehydrocoupling of boranes with amines, phenols, and thiols under deuterated solvent.[5f] More recently,

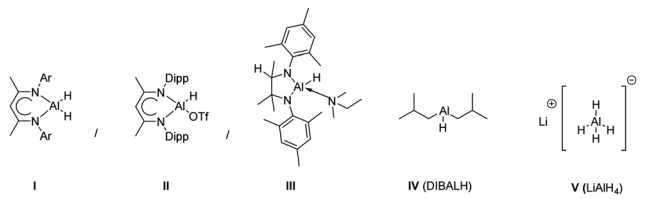
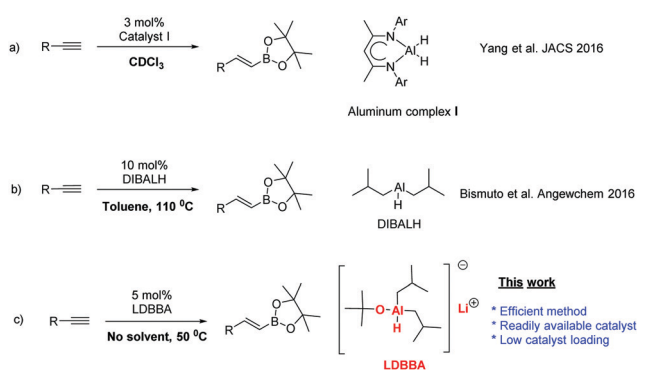


Fig. 1 Reported aluminum hydrides for catalytic hydroboration of C=O and C=C bonds.

Bismuto *et al.*[7] reported the hydroboration of alkynes catalyzed by the commercially available aluminum hydride (DIBALH) and/or Et_3Al·DABCO (10 mol%) (Scheme 1). However, the reported methods require high temperature or involve the preparation of an aluminum complex, which may hinder their practical utility.

In continuation of our research for selective and partial hydride reagents, we attempted to establish a robust practical method for the catalytic hydroboration of unsaturated hydrocarbons. Lithium



Scheme 1 (a and b) Aluminum hydride catalyzed hydroboration and (c) the present work.

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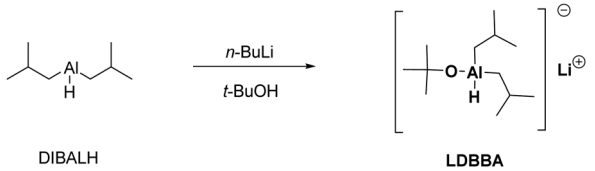


Scheme 2 Preparation of LDBBA from DIBALH.

diisobutyl-*tert*-butoxyaluminum hydride (LDBBA) is known for the selective and partial reduction of carbonyl compounds, especially esters.[8] Here LDBBA prepared from the reaction of commercial DIBALH with lithium *tert*-butoxide was applied for catalytic hydroboration of alkynes and imines (Scheme 2).

Results and discussion

We started our investigation with the hydroboration of phenyl acetylene using 10 mol% LDBBA and pinacolborane (HBpin) at room temperature, in order to understand the effect of our catalyst on the success of the reaction. To our delight, the starting material was almost completely converted into the corresponding alkenyl boronate with high regioselectivity in 38 h (entry 1 in Table 1). Next, we increased the reaction temperature to 50 °C in an attempt to reduce the reaction time; 90% product conversion was achieved in 6 h (entry 2), and quantitative conversion to the product was achieved within 12 h (entry 3). Reducing the catalyst loading to 5 mol% gave the same conversion as that with 10 mol% catalyst (entry 4), but further reducing the loading to 1 mol% resulted in only 43% conversion (entry 6). When the reaction was performed in the absence of the catalyst, only a trace amount (~5%) of the hydroboration product was formed (entry 7). Moreover, the product conversion decreased when the number of equivalents of HBpin was decreased from 1.5 to 1.2 (entry 5). Therefore, the optimal conditions for the best results were 5 mol% catalyst load, 1.5 equivalents HBpin at 50 °C for 12 h reaction time under neat conditions (entry 4).

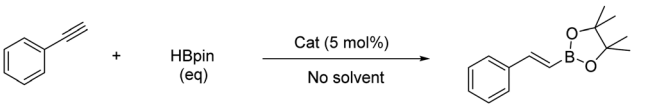
We next compared the results of our hydroboration protocol with those obtained with another hydride (Table 2). DIBALH and

Table 1 Optimization of the reaction conditions for LDBBA-catalyzed hydroboration of alkynes

Entry	HBpin (eq.)	LDBBA (mol%)	Temp. (°C)	Time (h)	Conversion[a] (%)
1	1.5	10	25	38	74
2	1.5	10	50	6	90
3	1.5	10	50	12	99
4	1.5	5	50	12	99 (98)[b]
5	1.2	5	50	12	86
6	1.5	1	50	24	43
7	1.5	—	50	12	Trace

[a] GC area ratio based on starting material consumption. [b] Isolated yield after silica column chromatography.

Table 2 Comparative study of LDBBA-catalyzed hydroboration of alkynes



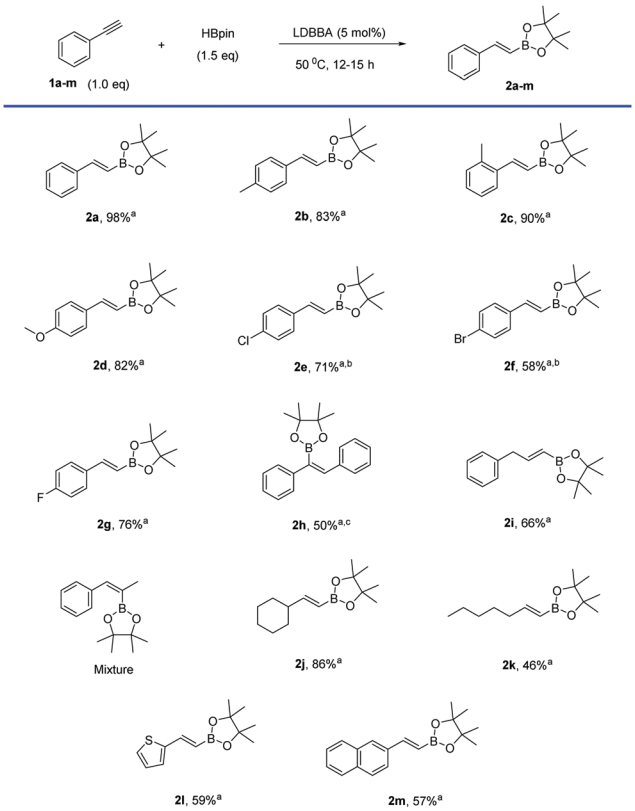
Entry	HBpin (eq.)	Catalyst	(mol%)	Temp. (°C)	Time (h)	Conversion[a] (%)
1	1.5	LDBBA	5	50	12	99 (98)[b]
2	1.5	DIBALH	5	50	12	65
3	1.5	Red-Al	5	50	12	71
4	1.5	$NaBH_4$	5	50	12	<10
5	1.5	PDBBA	5	50	12	53
6	1.5	SDBBA	5	50	12	55

[a] GC area ratio based on starting material consumption. [b] Isolated yield after silica column chromatography, PDBBA (potassium diisobutyl-*tert*-butoxyaluminum hydride); SDBBA (sodium diisobutyl-*tert*-butoxyaluminum hydride).

Red-Al mediated the catalytic hydroboration to give moderate product conversion (entries 2 and 3 in Table 2). However, less than 10% conversion was obtained with $NaBH_4$ (entry 4). Other alkoxy derivatives of DIBALH [SDBBA (sodium diisobutyl-*tert*-butoxyaluminum hydride) and PDBBA (potasium diisobutyl-*tert*-butoxyaluminum hydride)] were also investigated for use in this catalytic hydroboration, but only moderate conversion was achieved (entries 5 and 6).

With the optimized conditions in hand, we next extended the catalytic hydroboration to various alkyne substrates (Scheme 3). Accordingly, aromatic and aliphatic alkynes were subjected to the catalytic hydroboration in the presence of 5 mol% LDBBA. Electron-rich alkynes with methyl and methoxy substituents produced the corresponding alkenyl boronates in good yields. In contrast, electron-deficient substrates with bromo, chloro, and fluoro substituents gave moderate conversion to the products. The reaction with an internal alkyne diphenylethyne required a high temperature to result in moderate conversion to the corresponding boronate. The aliphatic cyclic alkyne ethynylcyclohexane smoothly underwent the catalytic hydroboration to afford the corresponding boronate in good yield. The alkyl chain substrate 1-heptyne produced the corresponding boronate ester in moderate yield. The heteroaromatic substrate 2-ethynylthiophene and polyaromatic substrate 2-ethynylnaphthalene produced corresponding boronate in good yield. However, the other heteroaromatic substrate 2-ethynylpyridine decomposed during the reaction.

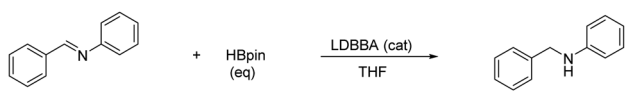
After obtaining successful results for alkyne hydroboration, we turned our attention toward the reduction of imine substrates *via* this catalytic hydroboration and established the conditions for this reaction. The results are presented in Table 3. Benzylideneaniline was used as a model substrate to optimize the reaction conditions. Quantitative conversion of the corresponding secondary amine was achieved with 5 mol% LDBBA (entry 3). The conversion decreased when the catalyst loading or number of equivalents of HBpin was decreased (entries 4 and 5). The reaction in the absence of the catalyst produced <10% of the desired product even with a high eq. value of HBpin (entry 6). From the results, the optimized conditions were 5 mol% LDBBA, 1.5 eq. of pinacolborane at 50 °C for 24 h (entry 3).



Reaction condition: alkyne (1 mmol), HBpin (1.5 mmol), LDBBA (5 mol%), 50 °C, 12-15 h. [a]Isolated yields after silica column chromatography. [b]Reaction time is 15 h. [c]Reaction temperature is 110 °C, and reaction time is 12 h.

Scheme 3 Substrate scope for LDBBA catalyzed hydroboration of alkynes.

Table 3 Optimization of the reaction conditions for LDBBA-catalyzed reduction of imines

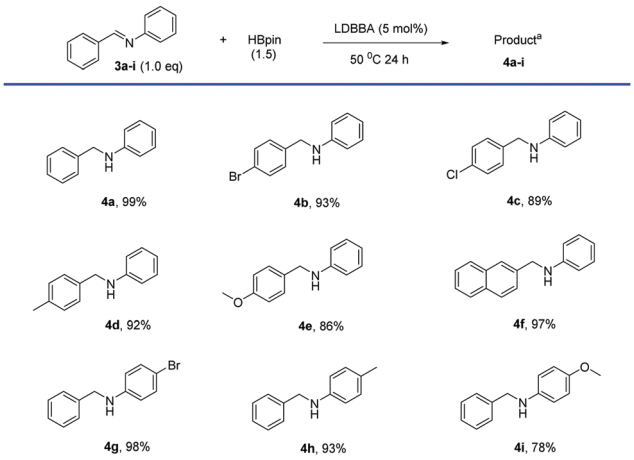


Entry	HBpin (eq.)	LDBBA (mol%)	Temp. (°C)	Time (h)	Conversion[a] (%)
1	2	5	25	24	80
2	1.5	5	50	12	78
3	1.5	5	50	24	99 (99)[b]
4	1.2	5	50	24	90
5	1.5	1	50	24	84
6	3	—	50	24	<10

[a] Conversions were determined by the GC area ratio based on starting material consumption. [b] Isolated yields after silica column chromatography.

Using the optimized conditions, we examined the substrate scope for the LDBBA-catalyzed hydroboration (reduction) of imines (Scheme 4). Accordingly, electron-donating or electron-withdrawing imines as well as a polyaromatic imine were treated with pinacolborane; the reaction proceeded smoothly to afford the corresponding secondary amines in good to excellent yields.

In addition, the catalytic activity of LDBBA was demonstrated from NBO calculations. Accordingly, the hydrides of



Reaction condition: imine (1 mmol), HBpin (1.5 mmol), LDBBA (5 mol%), 50 °C 24 h. [a]Isolated yields after silica column chromatography.

Scheme 4 Substrate scope for LDBBA catalyzed hydroboration (reduction) of imines.

tert-butoxy-diisobutyl derivatives (LDBBA, SDBBA and PDBBA) were analysed in terms of their NBO charges and Al–H bond lengths (Fig. 2).

Calculations of natural bond orbital (NBO) charges and Al–H bond lengths at the M06-2X/6-31G(d,p) level of theory strongly support the higher catalytic activity of LDBBA over SDBBA or PDBBA (Fig. 2). The more negatively charged hydrogen and longer bond length of Al–H in LDBBA indicate that LDBBA possesses a stronger hydride character and a higher reactivity due to a weaker Al–H bond, compared to SDBBA or PDBBA.

The reaction pathway for LDBBA catalyzed hydroboration of phenylacetylene (PhCCH) was explored using density functional theory (DFT) calculations at the M06-2X/6-31G(d,p) level of theory. A free energy profile for the reaction pathway is presented in Scheme 5 where LDBBA initially reacts with PhCCH to generate the intermediate INT1 and a hydrogen molecule through a cyclic transition state TS1. INT1, which acts as a reactive species, initiates the cyclic reaction. As the first step in the catalytic cycle, the intermediate INT1 reacts with HBpin to yield INT2 through another cyclic transition state TS2. The subsequent reaction of the intermediate INT2 with another PhCCH completes the cyclic reaction by reproducing the intermediate INT1 along with the hydroboration product PD through the final cyclic transition

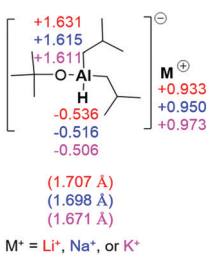
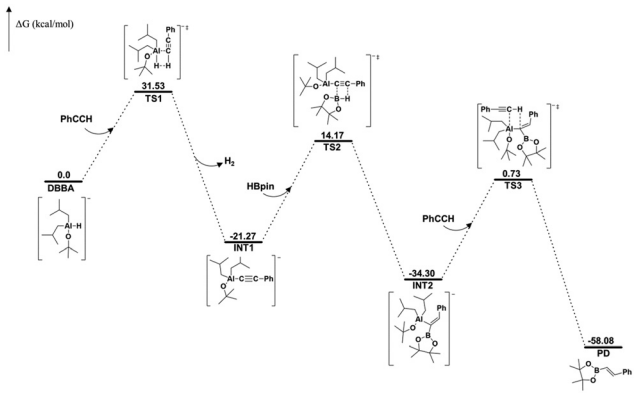
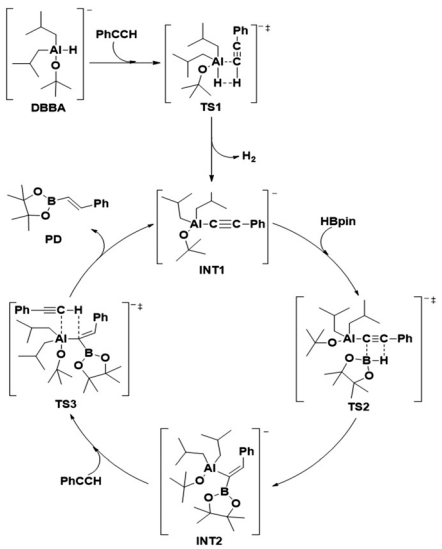


Fig. 2 NBO charge and bond length analysis of LDBBA, SDBBA, and PDBBA. NBO charges for Al, H and M are given in atomic units. Al–H bond lengths are given in parentheses.



Scheme 5 Free energy profile (in kcal mol^{-1}) for LDBBA catalysed hydroboration of phenylacetylene. (Note: To avoid complications in the calculations, the effect of the Li atom on the energy profile was not taken into account, LDBBA is mentioned as DBBA).



Scheme 6 A plausible mechanism based on the free energy profiles shown in Scheme 5.

state TS3. Based on the free energy profile in Scheme 5, a plausible mechanism is presented in Scheme 6.

Conclusions

In summary, we have identified an efficient protocol for the catalytic hydroboration of alkynes and imines. The reaction proceeded smoothly with 5 mol% LDBBA (readily prepared from DIBALH) producing the corresponding alkenyl boronates and secondary amines in moderate to good yields. Further, LDBBA was superior among the other aluminum hydrides tested. The NBO calculations demonstrated the significant activity of the catalyst (Al–H character). In addition, the coordination of anionic aluminate with lithium enables effective hydride transfer for hydroboration in the present catalytic system. The high regioselectivity and low catalyst loading make this method more useful than hydroborations catalyzed by expensive transition and precious-metal complexes. The further extension of LDBBA catalyzed hydroborations with other functional groups is in progress and will be reported in due course.

Experimetal section

General information

All glassware used was dried thoroughly in an oven, assembled hot, and cooled under a stream of dry nitrogen prior to use. All chemicals were commercial products of the highest purity. HBpin, alkynes, and imines were purchased from the Aldrich Chemical Company. ^{1}H NMR spectra were measured at 400 MHz with $CDCl_3$ as a solvent at ambient temperature unless otherwise indicated and the chemical shifts were recorded in parts per million downfield from tetramethylsilane (δ = 0 ppm) or based on residual $CDCl_3$ (δ = 7.26 ppm) as the internal standard. ^{13}C NMR spectra were recorded at 100 MHz with $CDCl_3$ as a solvent and referenced to the central line of the solvent (δ = 77.0 ppm). The coupling constants (J) are reported in hertz. Analytical thin-layer chromatography (TLC) was performed on glass precoated with silica gel (Merck, silica gel 60 F254). Column chromatography was carried out using 70–230 mesh silica gel (Merck) at normal pressure. GC analyses were performed on a Younglin Acme 6100M and a 6500 GC FID chromatograph, using an HP-5 capillary column (30 m). All GC yields were determined with the use of naphthalene as the internal standard and the authentic sample.

General procedure for the hydroboration of alkynes (2a–m)

A 20 mL test tube was charged with phenylacetylene (1.0 mmol, 0.11 mL) and pinacolborane (1.5 mmol, 0.22 mL) at room temperature. To this LDBBA (5 mol%, 0.45 M, 0.11 mL) was added under a nitrogen atmosphere at the same temperature, and the reaction mixture was brought to 50 °C and stirred for 12 h. After this time, the reaction mixture was cooled to room temperature, and the unreacted substrates were quenched by the addition of 1 mL of water. The crude mixture was extracted with ethyl acetate and the combined organic layers were dried over $MgSO_4$ (conversions were determined by gas chromatography). Solvents (volatiles) were evaporated under reduced pressure, and the residue mixture was subjected to column chromatography using silica gel. The isolated compounds were analyzed using spectroscopic data.

General procedure for the hydroboration of imines (4a–i)

A 20 mL test tube was charged with the corresponding imine (0.5 mmol), pinacolborane (0.75 mmol, 0.11 mL) and THF (2 mL) at room temperature. To this LDBBA (5 mol%, 0.45 M, 0.05 mL) was added under a nitrogen atmosphere at the same temperature, and the reaction mixture was brought to 50 °C and stirred for 24 h. After this time, the reaction mixture was cooled to room temperature, and the unreacted substrates were quenched by the addition of 1 mL of water. The crude mixture was extracted with ethyl acetate and the combined organic layers were dried over $MgSO_4$ (conversions were determined by gas chromatography). Solvents (volatiles) were evaporated under reduced pressure, and the residue mixture was subjected

to column chromatography using silica gel. The isolated compounds were analyzed using spectroscopic data.

Spectroscopic data for the isolated products

(*E*)-4,4,5,5-Tetramethyl-2-styryl-1,3,2-dioxaborolane (2a)[7]. Colorless oil. Yield. 225 mg (98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, J = 7.8, 1.6 Hz, 2H), 7.40 (d, J = 18.5 Hz, 1H), 7.31 (ddd, J = 12.9, 7.9, 6.3 Hz, 3H), 6.17 (d, J = 18.5 Hz, 1H), 1.31 (d, J = 1.3 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.63, 137.58, 129.00, 128.67, 127.16, 83.44, 24.91 ppm.

(*E*)-4,4,5,5-Tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (2b)[9]. Colorless oil. Yield. 202 mg (83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.33 (m, 3H), 7.13 (d, J = 7.8 Hz, 2H), 6.10 (d, J = 18.5 Hz, 1H), 2.33 (s, 3H), 1.30 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 49.60, 139.14, 134.79, 129.43, 127.14, 83.41, 24.93, 21.50 ppm.

(*E*)-4,4,5,5-Tetramethyl-2-(2-methylstyryl)-1,3,2-dioxaborolane (2c)[9]. Colorless oil. Yield. 219 mg (90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 18.3 Hz, 1H), 7.58–7.52 (m, 1H), 7.19–7.11 (m, 3H), 6.07 (d, J = 18.3 Hz, 1H), 2.41 (s, 3H), 1.31 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.20, 136.72, 136.46, 130.53, 128.73, 126.23, 125.83, 83.43, 24.93, 20.01 ppm.

(*E*)-2-(4-Methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d)[7]. Colorless oil. Yield. 213 mg (82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.40 (m, 2H), 7.34 (d, J = 18.4 Hz, 1H), 6.88–6.81 (m, 2H), 6.00 (d, J = 18.4 Hz, 1H), 3.79 (s, 3H), 1.29 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.35, 149.19, 130.38, 128.59, 114.04, 83.33, 55.38, 24.92 ppm.

(*E*)-2-(4-Chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e)[10]. Colorless oil. Yield. 187 mg (71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 –7.37 (m, 2H), 7.36–7.26 (m, 3H), 6.12 (d, J = 18.4 Hz, 1H), 1.30 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.14, 135.94, 134.70, 128.91, 128.34, 83.58, 24.91 ppm.

(*E*)-2-(4-Bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f)[11]. Colorless oil. Yield. 208 mg (58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.41 (m, 2H), 7.35–7.27 (m, 3H), 6.14 (dd, J = 18.4, 0.6 Hz, 1H), 1.30 (d, J = 0.7 Hz, 12H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.19, 136.41, 131.86, 128.63, 123.03, 83.59, 24.91 ppm.

(*E*)-2-(4-Fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2g)[7]. Colorless oil. Yield. 188 mg (76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, J = 8.6, 5.6 Hz, 2H), 7.33 (d, J = 18.4 Hz, 1H), 7.01 (t, J = 8.7 Hz, 2H), 6.06 (d, J = 18.4 Hz, 1H), 1.30 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.23 (d, J = 248.0 Hz), 148.29, 133.74 (d, J = 3.3 Hz), 128.82 (d, J = 8.3 Hz), 115.69 (d, J = 21.7 Hz), 83.51, 24.91 ppm.

(*E*)-2-(1,2-Diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2h)[7]. Colorless oil. Yield. 153 mg (50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.28–7.23 (m, 2H), 7.22–7.13 (m, 3H), 7.13–7.07 (m, 3H), 7.06–7.01 (m, 2H), 1.30 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.29, 140.48, 137.03, 130.07, 128.95, 128.37, 127.96, 127.70, 126.39, 83.90, 24.89 ppm.

(*E*)-4,4,5,5-Tetramethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (2i)[9]. Colorless oil. Yield. 160 mg (66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.24 (m, 2H), 7.24–7.12 (m, 3H), 6.75 (dt, J = 17.9, 6.3 Hz, 1H), 5.43 (dt, J = 17.8, 1.7 Hz, 1H), 3.47 (dd, J = 6.3, 1.6 Hz, 2H), 1.24 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.66, 139.14, 129.06, 128.56, 126.28, 83.23, 42.40, 24.90 ppm.

(*E*)-2-(2-Cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2j)[11]. Colorless oil. Yield. 203 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61–6.48 (m, 1H), 5.35 (dt, J = 18.2, 1.2 Hz, 1H), 2.04–1.95 (m, 1H), 1.76–1.57 (m, 6H), 1.24 (s, 12H), 1.19–1.00 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.03, 83.08, 43.37, 31.98, 26.24, 26.05, 24.88 ppm.

(*E*)-2-(Hept-1-*en*-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)[12]. Colorless oil. Yield. 104 mg (46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.62 (dt, J = 18.0, 6.5 Hz, 1H), 5.40 (dt, J = 18.0, 1.5 Hz, 1H), 2.17–2.08 (m, 2H), 1.45–1.34 (m, 2H), 1.25 (m, 4H), 1.25 (s, 12H), 0.85–0.83 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.04, 83.08, 35.92, 31.51, 27.99, 24.88, 22.64, 14.14 ppm.

(*E*)-4,4,5,5-Tetramethyl-2-(2-(thiophen-2-yl)vinyl)-1,3,2-dioxaborolane (2l)[13]. Pale yellow liquid. Yield. 139 mg (59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 18.1 Hz, 1H), 7.23–7.24 (m, 1H), 7.07–7.08 (m, 1H), 6.9–6.99 (m, 1H), 5.91 (d, J = 18.1 Hz, 1H), 1.30 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.92, 141.82, 127.68, 127.63, 126.31, 83.38, 24.81 ppm.

(*E*)-4,4,5,5-Tetramethyl-2-(2-(naphthalen-2-yl)vinyl)-1,3,2-dioxaborolane (2m)[14]. Pale yellow liquid. Yield. 159 mg (57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.80 (m, 4H), 7.71 (d, J = 8.6 Hz, 1H), 7.59 (d, J = 18.4 Hz, 1H), 7.48–7.46 (m, 2H), 6.31 (d, J = 18.4 Hz, 1H), 1.35 (s, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 135.1, 133.9, 133.6, 128.5, 128.4, 128.1, 127.8, 126.5, 126.4, 123.5, 83.5, 25.0 ppm.

***N*-Benzylaniline (4a)**[15]. Colorless liquid. Yield. 91 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.26 (m, 5H), 7.22–7.15 (m, 2H), 6.73 (tt, J = 7.3, 1.1 Hz, 1H), 6.67–6.62 (m, 2H), 4.34 (s, 2H), 4.04 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 139.5, 129.5, 128.8, 127.7, 127.4, 117.7, 113.0, 48.4 ppm.

***N*-(4-Bromobenzyl)aniline (4b)**[16]. Pale yellow liquid. Yield. 121 mg (93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.43 (m, 2H), 7.27–7.23 (m, 2H), 7.21–7.15 (m, 2H), 6.74 (tt, J = 7.3, 1.1 Hz, 1H), 6.64–6.57 (m, 2H), 4.29 (s, 2H), 4.08 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 138.6, 131.8, 129.4, 129.1, 121.0, 117.9, 112.9, 47.7 ppm.

N-(4-Chloroobenzyl)aniline (4c)[16]. Pale yellow solid. Yield. 96 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.29 (m, 4H), 7.23–7.13 (m, 2H), 6.75 (tt, J = 7.3, 1.1 Hz, 1H), 6.65–6.57 (m, 2H), 4.31 (s, 2H), 4.07 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 138.1, 132.9, 129.4, 128.89, 128.83, 117.8, 112.9, 47.6 ppm.

***N*-(4-Methylbenzyl)aniline (4d)**[16]. Pale yellow liquid. Yield. 91 mg (92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 7.8 Hz, 2H), 7.22–7.13 (m, 4H), 6.72 (td, J = 7.3, 1.1 Hz, 1H), 6.67–6.61 (m, 2H), 4.28 (s, 2H), 3.99 (bs, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 137.0, 136.4, 129.5, 129.4, 127.7, 117.6, 112.9, 48.1, 21.3 ppm.

N-(4-Methoxybenzyl)aniline (4e)[16]. Pale yellow liquid. Yield. 91 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, J = 8.6, 2.4 Hz, 2H), 7.18 (dddd, J = 8.5, 7.4, 2.9, 1.2 Hz, 2H), 6.93–6.84 (m, 2H), 6.72 (tdd, J = 7.3, 3.0, 1.3 Hz, 1H), 6.64 (ddt, J = 8.6, 2.2, 1.1 Hz, 2H), 4.25 (s, 2H), 3.96 (bs, 1H), 3.81 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 148.2, 131.4, 129.4, 128.9, 117.5, 114.0, 112.9, 55.4, 47.8 ppm.

***N*-(Naphthalen-2-ylmethyl)aniline (4f)**[16,17]. Pale yellow solid. Yield. 113 mg (97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.76 (m, 4H), 7.52–7.41 (m, 3H), 7.22–7.13 (m, 2H), 6.72 (tt, J = 7.4, 1.1 Hz, 1H),

6.69–6.63 (m, 2H), 4.49 (s, 2H), 4.15 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.25, 137.03, 133.57, 132.84, 129.43, 128.50, 127.88, 127.83, 126.29, 126.02, 125.86, 117.73, 113.01, 48.58 ppm.

***N*-Benzyl-4-bromoaniline (4g)[16].** Pale yellow solid. Yield. 257 mg (98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.34 (m, 4H), 7.31–7.28 (m, 1H), 7.27–7.22 (m, 2H), 6.54–6.48 (m, 2H), 4.31 (s, 2H), 4.09 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 138.9, 132.0, 128.8, 127.5, 127.4, 114.5, 109.2, 48.3 ppm.

***N*-Benzyl-4-methylaniline (4h)[16].** Pale yellow oil. Yield. 183 mg (93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.35 (m, 4H), 7.32–7.27(m, 1H), 7.02 (d, J = 8.1 Hz, 2H), 6.64–6.52 (m, 2H), 4.34 (s, 2H), 3.92 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.05, 139.79, 129.86, 128.71, 127.61, 127.26, 126.85, 113.11, 48.76, 20.52 ppm.

N-Benzyl-4-methoxyaniline (4i)[16]. Pale yellow solid. Yield. 166 mg (78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.35 (m, 4H), 7.33–7.30 (m, 1H), 6.87–6.78 (m, 2H), 6.67–6.61 (m, 2H), 4.32 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.25, 142.55, 139.79, 128.67, 127.62, 127.24, 114.99, 114.18, 55.8, 49.30 ppm.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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