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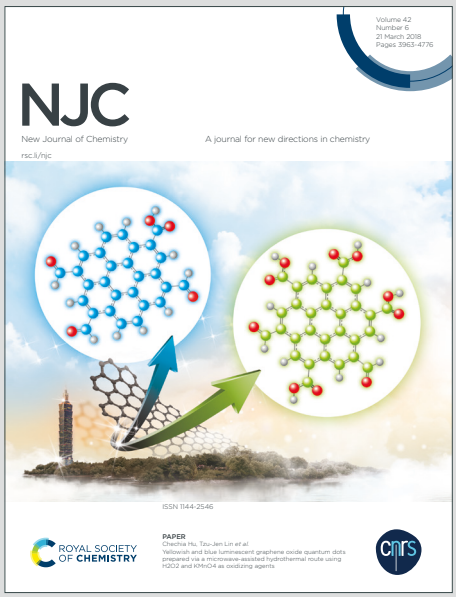

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ARTICLE

Quantitative NaH catalytic hydroboration of aldimines

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The Catalytic hydroboration of aldimines was demonstrated, with only 3 mol% NaH required for the quantitative production of secondary amines under minimal solvent conditions. In addition, chemoselective hydroboration in the presence of other reducible functional groups was achieved. DFT calculations were then used to propose a reaction mechanism for imine hydroboration.

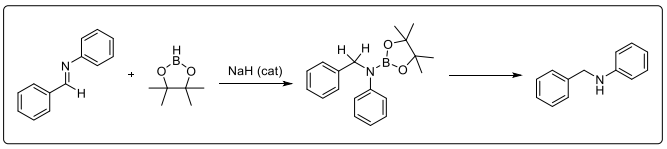
Introduction

Amines are ubiquitous and important functional groups in many natural products, pharmaceuticals, agrochemicals, and polymers.[1] Although, the preparation of amines *via* imine reduction is simple, straight-forward, and standard synthetic methods, it suffer from distinct disadvantages. For example, traditional imine hydrogenation requires high pressure and temperature, and hydride-mediated reduction necessitates the use of stoichiometric or excess quantities of reducing agents that effects the conversion of product by forming by-products.[2] Recently, catalytic hydroboration was found to be superior for the reduction of C=X (X = C, O, and N) bonds, as it uses weaker and more selective reducing agents (CatBH, HBpin) that are relatively stable in air.[3-7] Extensive studies on the catalytic hydroboration of carbonyl compounds have already been reported. Several catalytic systems have been developed for the catalytic hydroboration of imines using transition metals (Ni, Ru, Ti, Co, Cu etc.),[3] main group metals (Li, Na, Mg, Al, etc.),[6] rare earth metal complexes (Er, Y, Dy, Gd),[4] actinium group metal (Th),[5] and non-metals (P, B)[7] as catalyst. In addition, commercial bases (NaOH/C_6D_6,[6a] *n*-BuLi[6b]) and frustrated Lewis pairs (FLPs)[8] have been investigated as alternative to the toxic and less-selective metal catalysts.

Continuing our efforts towards the development of partial reducing agents, we have demonstrated methods for the catalytic hydroboration (reduction) of carbonyls, alkene, alkyne and imines with readily available reagents.[9] During the preparation of this manuscript, Pandey et al.[10] reported catalyst-free hydroboration of imines with pinacolborane. This method afforded corresponding amines in good to reasonable yields. However, to minimize industrial waste and by–products, systems are still needed quantitative conversion of imines to amines.

Building off our recent findings that NaH can function as an effective catalyst for the hydroboration of carbonyls (aldehydes and ketones),[9a] we now report an industrially feasible, quantitative, catalytic hydroboration of aldimines using only trace quantities of NaH as catalyst (scheme 1).

Scheme 1 Catalytic hydroboration of aldimine with NaH



Results and discussion

The reaction was optimized by varying the catalyst load, mole ratio, and reaction time (Table 1). In the absence of catalyst, only 20% yield was achieved in 24 h using 1.5 equiv of pinacolborane (HBpin) in THF (entry 1 in table 1). Even when the reducing agent was increased to 3 equiv, only moderate conversion was obtained (entry 2 in table 1). However, the addition of even a small quantity of NaH (3 mol%) in the presence of 1.2 equiv of HBpin greatly improved the conversion, affording 86% of the desired product (entry 3). A 99% of conversion was achieved using 1.5 equiv of HBpin (entry 5).

The reaction was further optimized by investigating alternative solvent systems, including hexane, toluene, ether and dichloromethane. Only dichloromethane afforded a reasonable conversion (entry 9 in Table 1). In an attempt to reduce the reaction time, the reduction was performed with 5 mol% catalyst; however, unreacted aldimine remained (entries 10-12). Consequently, 3 mol% of NaH and 1.5 equiv of HBpin in THF were determined to be suitable conditions for the quantitative reductions (entry 5).

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† Footnotes relating to the title and/or authors should appear here.
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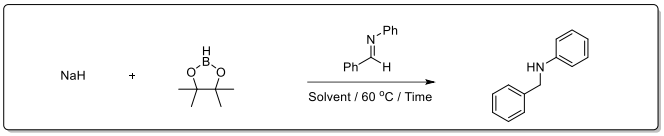
Table 1 Optimization of reaction conditions for aldimine reduction

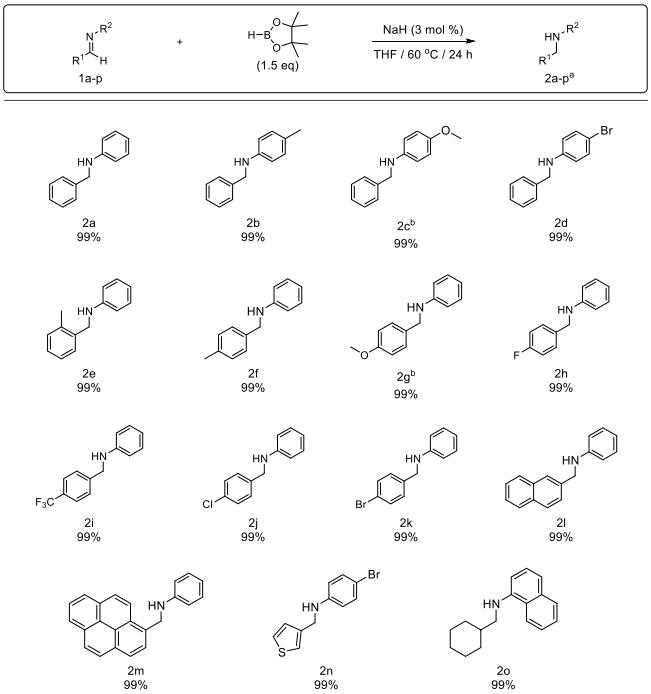


Entry	NaH	Pinacolborane	Solvent (1ml)	Time (h)	Yield[a] (%) (S.M / Product)
1	none	1.5 eq	THF	24	70 / 20 (14)
2	none	3.0 eq	THF	24	37 / 52 (9)
3	3 mol%	1.2 eq	THF	24	1 / 86 (1)
4	3 mol%	1.5 eq	THF	12	37 / 52 (9)
5	3 mol%	1.5 eq	THF	24	0 / 99
6	3 mol%	1.5 eq	Hexane	24	71 / 28
7	3 mol%	1.5 eq	Toluene	24	64 / 30
8	3 mol%	1.5 eq	Ether	24	70 / 28
9	3 mol%	1.5 eq	MC	24	29 / 71
10	5 mol%	1.2 eq	THF	12	1 / 86 (1)
11	5 mol%	1.5 eq	THF	3	14 / 73 (4)
12	5 mol%	1.5 eq	THF	6	0 / 87

[a] Yields were determined by GC. The values in parenthesis are yield for aldehyde.

Having obtained the optimal conditions for the quantitative conversion of an aldimine to an amine, the substrate scope was explored using various aldimines (Table 2).

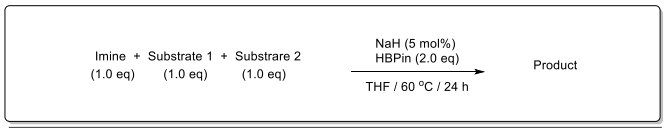
Table 2 Catalytic hydroboration of aldimines

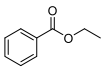
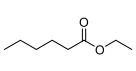
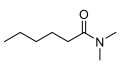
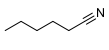
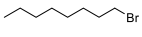


[a]Isolated yield after silica gel column chromatography. [b]The reaction was conducted for 48 h.

Irrespective of the electron-donating and electron-withdrawing substitutions, the reduction of the aldimines proceeded smoothly to afford the corresponding amines in quantitative yields, although the substrates with a strong electron-donating methoxy group (2c and 2g) required a longer reaction time. Moreover, regardless of the position of the substitution (ortho- and para-), the reaction afforded the desired amines (**2b-2k**), a longer reaction time was required (48 h). Notably, the heteroaryl imine (**2n**) was converted in excellent yield, which improves upon the method recently reported by Pandey et at.[10] Polyaromatic and aliphatic aldimines were also suitable for the reaction, producing the corresponding amine (**2l-m**, **o**) in excellent yields.

Table 3 Chemoselective catalytic hydroboration of aldimine in the presence of various functional groups

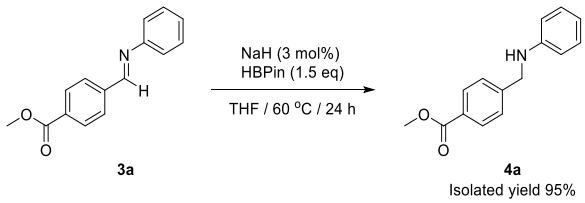


Entry	Imine	Substrate 1	Substrate 2	Yield (%)[a] Imine S.M. / prod.	Substrate 1 S.M. / prod.	Substrate 2 S.M. / prod.
1				9 / 91	95 / 0	92 / 0
2				6 / 91	95 / 0	95 / 0
3				1 / 99	92 / 0	90 / 0
4				4 / 96	96 / 0	98 / 0

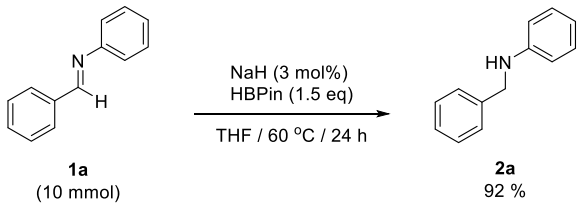
[a]Yields were determined by GC.

To assess the chemoselectivity of this system, the reaction was conducted with *N*-benzylideneaniline in the presence of other reducible functionalities, including esters, amides, nitriles, alkyl halides, and epoxides (Table 3). *N*-benzylideneaniline was quantitatively and selectively converted regardless of the additional substrates. In addition, hydroboration of methyl (*E*)-4-((phenylimino)methyl)benzoate (3a) afforded the desired amine in 95% isolated yield without reduction of the intramolecular ester group (Scheme 2).

Scheme 2 Chemoselective catalytic hydroboration of aldimine containing intramolecular ester group



Scheme 3. Scale-up reaction of catalytic hydroboration using NaH and pinacolborane



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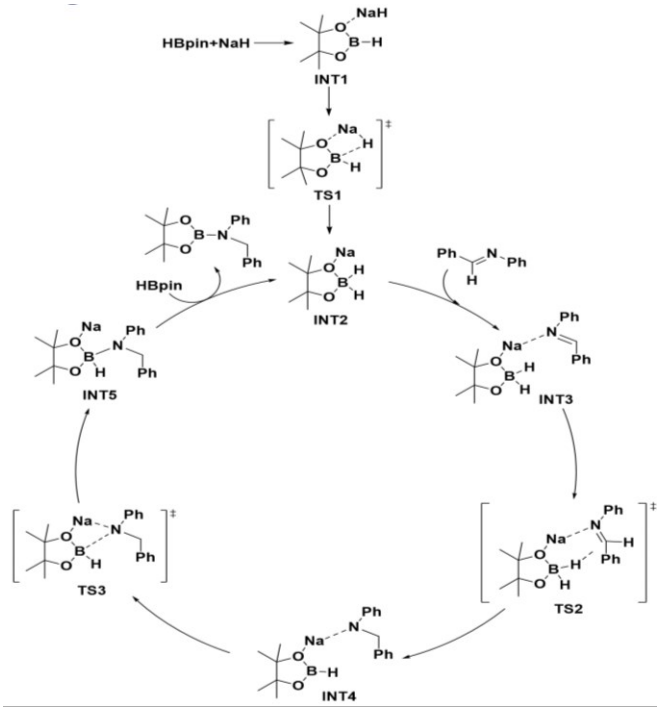
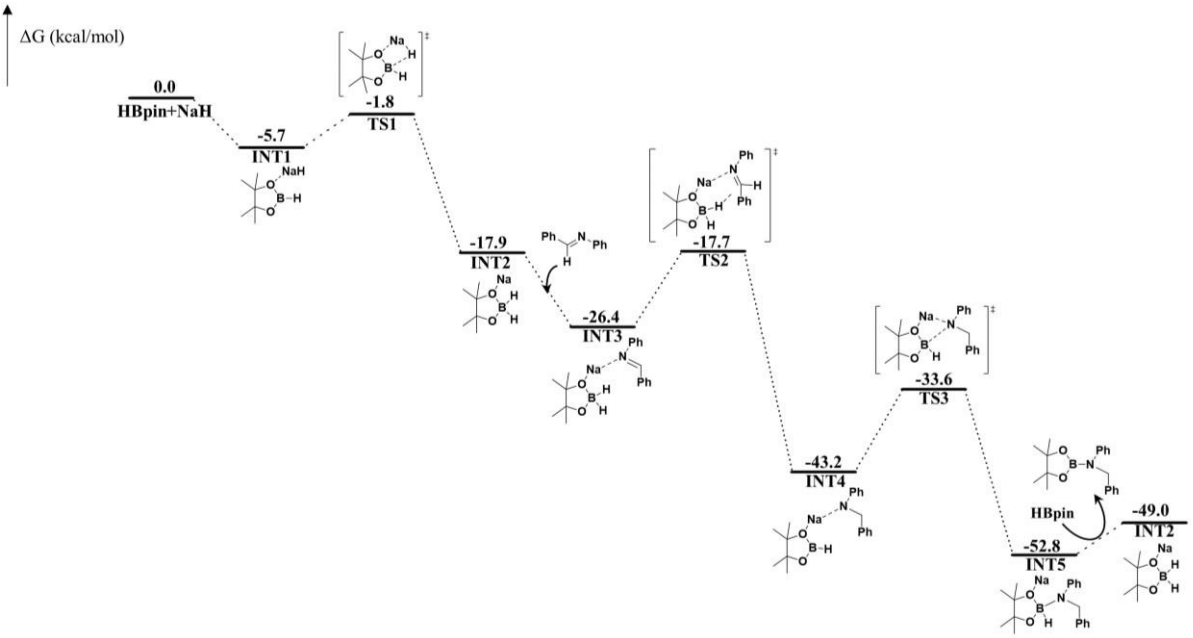
Next, the potential scalability of the present protocol was evaluated. Benzylidenaniline (10 mmol) was treated with 3.0 mol % of NaH and HBpin. *N*-benzylaniline was obtained in 92% yield (Scheme 3).

Finally, the reaction pathway for the NaH-catalyzed hydroboration of an aldimine (PhHCNPh) was investigated 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 which NaH initially binds to HBpin to generate the intermediate INT1 (Scheme 4). An intramolecular rearrangement occurs within INT1 where the sodium-bound hydrogen atom migrates to boron through a cyclic transition state TS1, leading to INT2. Next, the catalytic cycle begins with the reaction of INT2 with the imine to produce intermediate INT3. The subsequent reaction of INT3 via a six-membered ring transition state TS2 yields intermediate INT4, which is converted into intermediate INT5 via a four-membered ring transition state TS3. The catalytic cycle is completed when INT5 reacts with a second HBpin to regenerate INT2 and produce the dioxolan amine by ligand exchange. Based on the free energy profile, a plausible mechanism is proposed (Scheme 5).

Scheme 4. Plausible reaction mechanism for NaH-catalyzed hydroboration of an imine



Scheme 5. Free energy profile (in kcal/mol) for NaH-catalyzed hydroboration of an imine



Conclusions

We have demonstrated a practical and industrially viable method for the large-scale synthesis of amines via the catalytic hydroboration of aldimines. Only 3 mol% NaH required for the quantitative conversion of aldimines to amines under minimal solvent condition. NaH is a readily available and easy to handle catalyst. Furthermore, this protocol allows the chemoselective reduction of aldimines in the presence of other reducible groups, including esters, amides, nitriles, alkyl halides, and epoxide groups.

Experimental section

General Information

All glassware was thoroughly dried in an oven, assembled hot, and cooled under a stream of dry nitrogen prior to use. All reactions and

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manipulations of air- and moisture-sensitive materials were performed using standardized techniques for their proper handling. All chemicals were commercial products of the highest purity and were further purified using standard methods prior to use. Sodium hydride (60 % dispersion in mineral oil), HBpin, aldehydes and amines were purchased from Sigma-Aldrich Co., Alfa Aesar, and Tokyo Chemical Industry Company (TCI). Imines were synthesized from amines, aldehyde. ^{1}H NMR spectra were measured at 400 MHz using $CDCl_3$ 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 6500GC FID chromatography, using an HP-5 capillary column (30m). All GC yields were determined with the use of naphthalene as the internal standard and the authentic sample.

Catalytic hydroboration of aldimines (Table 2)

The following experimental procedure for the synthesis of N-benzylaniline is representative. A dry and argon-flushed flask, equipped with a magnetic stirring bar was charged with sodium hydride (0.0013 g, 3 mol%), *N*-Benzylidenaniline (0.1812 g, 1.0 mmol) and 1 mL of THF at room temperature. To this, pinacolborane (0.22 mL, 1.5 mmol) was added dropwise under nitrogen atmosphere at the same temperature. Reaction mixture was brought to 60 °C and stirred for 24 h. After this time, reaction mixture was cooled to room temperature, unreacted substrates were quenched by the addition of 2 drops of water. The crude mixture was extracted with ethyl acetate and combined organic layers were dried over $MgSO_4$. Solvents (volatiles) were evaporated under reduced presser, residue mixture was subjected to column chromatography using silica gel. Isolated compounds were analyzed by NMR spectroscopy.

Chemoselective catalytic hydroboration of aldimine in the presence of various functional groups (Table 3)

The following procedure for the reaction of *N*-Benzylidenaniline in the presence of ester is representative. A dry and argon-flushed flask, equipped with a magnetic stirring bar was charged with sodium hydride (0.0022 g, 5 mol%), *N*-Benzylidenaniline (0.1812 g, 1.0 mmol), ethyl benzoate (0.14 ml, 1.0 mmol), ethyl hexanoate (0.17 ml, 1.0 mmol) and 1 mL of THF at room temperature. To this, pinacolborane (0.29 mL, 2.0 mmol) was added dropwise under nitrogen atmosphere at the same temperature. Reaction mixture was brought to 60 °C and stirred for 24 h. After this time, reaction mixture was cooled to room temperature, unreacted substrates were quenched by the addition of 2 drops of water. All products in Table 3 were confirmed through comparison with GC data of the authentic sample.

Procedure for the gram scale synthesis of *N*-benzylaniline (2a)

A dry and argon-flushed flask, equipped with a magnetic stirring bar was charged with sodium hydride (0.0131 g, 3 mol%), *N*-Benzylidenaniline (1.8124 g, 10.0 mmol) and 10 mL of THF at room temperature. To this, pinacolborane (2.2 mL, 15.0 mmol) was added dropwise under nitrogen atmosphere at the same temperature. Reaction mixture was brought to 60 °C and stirred for 24 h. After this time, reaction mixture was cooled to room temperature, unreacted substrates were quenched by the addition of 10 drops of water. The crude mixture was extracted with ethyl acetate and combined organic layers were dried over $MgSO_4$. Solvents (volatiles) were evaporated under reduced presser, residue mixture was subjected to column chromatography using silica gel. Isolated compounds were analyzed by NMR spectroscopy.

Spectroscopic data for isolated products.

***N*-benzylaniline (2a)[11]** Colorless soild. Yield. 181 mg (99%). ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 4H), 7.31 – 7.25 (m, 1H), 7.22 – 7.14 (m, 2H), 6.73 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.68 – 6.59 (m, 2H), 4.34 (s, 2H), 4.03 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.25, 139.53, 129.37, 128.74, 127.61, 127.33, 117.66, 112.93, 48.42 ppm.

***N*-benzyl-4-methylaniline (2b)[11]** Pale yellow oil. Yield. 195 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.25 (m, 5H), 6.98 (dd, *J* = 8.3, 0.9 Hz, 2H), 6.64 – 6.47 (m, 2H), 4.30 (s, 2H), 3.90 (bs, 1H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.00, 139.73, 129.83, 128.69, 127.59, 127.24, 126.85, 113.08, 48.73, 20.49 ppm.

***N*-benzyl-4-methoxyaniline (2c)[11]** Pale yellow solid. Yield. 211 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.25 (m, 5H), 6.81 – 6.73 (m, 2H), 6.63 – 6.57 (m, 2H), 4.28 (s, 2H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.27, 142.52, 139.75, 128.68, 127.64, 127.26, 114.98, 114.19, 55.91, 49.34 ppm.

***N*-benzyl-4-bromoaniline (2d)[11]** Pale yellow solid. Yield. 259 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 4.5 Hz, 4H), 7.31 – 7.25 (m, 1H), 7.25 – 7.21 (m, 2H), 6.53 – 6.46 (m, 2H), 4.29 (s, 2H), 4.07 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.13, 138.94, 132.02, 128.80, 127.47, 127.46, 114.49, 109.21, 48.32. ppm.

***N*-(2-methylbenzyl)aniline (2e)[12]** Pale yellow solid. Yield. 195 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 6.8 Hz, 1H), 7.24 – 7.15 (m, 5H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.7 Hz, 2H), 4.28 (s, 2H), 3.85 (bs, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.39, 137.09, 136.46, 130.52, 129.39, 128.36, 127.54, 126.27, 117.55, 112.77, 46.47, 19.06 ppm.

***N*-(4-methylbenzyl)aniline (2f)[11]** Pale yellow solid. Yield. 195 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.10 (m, 4H), 6.71 (td, *J* = 7.4, 1.0 Hz, 1H), 6.67 – 6.58 (m, 2H), 4.28 (s, 2H), 3.97 (bs, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.31, 136.97, 136.44, 129.40, 129.34, 127.61, 117.57, 112.91, 48.17, 21.20 ppm.

***N*-(4-methoxybenzyl)aniline (2g)[11]** Pale yellow solid. Yield. 211 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.3 Hz, 2H), 7.22 – 7.14 (m, 2H), 6.89 (d, *J* = 8.2 Hz, 2H), 6.72 (td, *J* = 7.3, 0.9 Hz, 1H), 6.66 – 6.61 (m, 2H), 4.26 (s, 2H), 3.94 (bs, 1H), 3.81 (s,

3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.96, 148.31, 131.51, 129.35, 128.91, 117.59, 114.12, 112.93, 55.40, 47.89 ppm.

***N*-(4-fluorobenzyl)aniline (2h)[13]** Pale yellow oil. Yield. 199 mg (99%). ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 8.3, 5.5 Hz, 2H), 7.18 (t, *J* = 7.7 Hz, 2H), 7.02 (t, *J* = 8.6 Hz, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 8.5 Hz, 2H), 4.30 (s, 2H), 4.02 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.12, (d, J_{C-F} = 246.44 Hz), 148.01, 135.17 (d, J_{C-F} = 3.03 Hz), 129.40, 129.10 (d, J_{C-F} = 8.08 Hz), 117.82, 115.55 (d, J_{C-F} = 21.21 Hz), 112.94, 47.68 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.52 ppm.

***N*-(4-(trifluoromethyl)benzyl)aniline (2i)[14]** Pale yellow oil. Yield. 248 mg (99%). ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.19 (tt, *J* = 7.6, 2.2 Hz, 2H), 6.79 – 6.69 (m, 1H), 6.61 (d, *J* = 7.6 Hz, 2H), 4.42 (s, 2H), 4.15 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.76, 143.84, 129.45, 127.53, 125.67 (q, *J* = 4.04 Hz), 118.05, 112.98, 47.86 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.27ppm

***N*-(4-chlorobenzyl)aniline (2j)[11]** Pale yellow solid. Yield. 216 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 4H), 7.20 – 7.14 (m, 2H), 6.72 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.63 – 6.58 (m, 2H), 4.31 (s, 2H), 4.05 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.90, 138.07, 132.95, 129.40, 128.84, 128.78, 117.89, 112.96, 47.69 ppm.

***N*-(4-bromobenzyl)aniline (2k)[11]** Pale yellow soild. Yield. 260 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.37 (m, 2H), 7.29 – 7.21 (m, 2H), 7.21 – 7.12 (m, 2H), 6.72 (tt, *J* = 7.4, 1.0 Hz, 1H), 6.65 – 6.55 (m, 2H), 4.29 (s, 2H), 4.06 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.87, 138.62, 131.79, 129.40, 129.14, 121.01, 117.90, 112.96, 47.73 ppm.

***N*-(naphthalen-2-ylmethyl)aniline (2l)[11]** Pale yellow solid. Yield. 231 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.76 (m, 4H), 7.58 – 7.40 (m, 3H), 7.19 (t, *J* = 7.5 Hz, 2H), 6.74 (t, *J* = 6.9 Hz, 1H), 6.69 (d, *J* = 8.5 Hz, 2H), 4.50 (s, 2H), 4.14 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.27, 137.05, 133.60, 132.87, 129.40, 128.48, 127.86, 127.81, 126.26, 126.02, 125.84, 117.74, 113.05, 48.61 ppm.

***N*-(pyren-1-ylmethyl)aniline (2m)[15]** Yellow solid. Yield. 306 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 9.2 Hz, 1H), 8.23 – 8.17 (m, 2H), 8.17 – 8.10 (m, 2H), 8.10 – 8.04 (m, 3H), 8.02 (t, *J* = 8.0 Hz, 1H), 7.26 – 7.20 (m, 2H), 6.82 – 6.70 (m, 3H), 4.99 (s, 2H), 4.10 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.36, 132.19, 131.38, 131.10, 130.88, 129.47, 129.07, 128.03, 127.53, 127.44, 126.81, 126.13, 125.40, 125.33, 125.13, 124.93, 124.88, 123.09, 117.79, 112.90, 46.85 ppm

4-bromo-*N*-(thiophen-3-ylmethyl)aniline (2n) Pale yellow solid. Yield. 265 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.27 – 7.22 (m, 2H), 7.17 (dt, *J* = 2.1, 1.1 Hz, 1H), 7.05 (dd, *J* = 4.9, 1.1 Hz, 1H), 6.56 – 6.45 (m, 2H), 4.30 (s, 2H), 4.01 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.03, 139.99, 132.04, 127.09, 126.44, 121.92, 114.56, 109.35, 43.80 ppm. HRMS(EI-MS) Calcd for $C_{11}H_{10}BrNS$: 266.9717, Found: 266.9719.

***N*-(cyclohexylmethyl)naphthalen-1-amine (2o)** Pale yellow liquid. Yield. 237 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (td, *J* = 6.6, 2.1 Hz, 2H), 7.49 – 7.39 (m, 2H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 1H), 6.59 (d, *J* = 7.5 Hz, 1H), 4.42 (bs, 1H), 3.13 (d, *J* = 6.7 Hz, 2H), 2.02 – 1.87 (m, 2H), 1.82 – 1.69 (m, 4H), 1.36 – 1.16 (m, 3H), 1.08 (qd, *J* = 12.2, 3.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.78, 134.43, 128.79, 126.78, 125.73, 124.64, 123.40, 119.84, 116.92, 104.17, 50.90, 37.54, 31.66, 26.71, 26.13 ppm. HRMS(EI-MS) Calcd for $C_{17}H_{21}N$: 239.1674, Found: 239.1673.

Methyl 4-((phenylamino)methyl)benzoate (4a)[16] Pale yellow solid. Yield. 229 mg (95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.16 (t, *J* = 8.6 Hz, 2H), 6.72 (tt, *J* = 7.4, 1.0 Hz, 1H), 6.60 (dd, *J* = 8.6, 1.0 Hz, 2H), 4.40 (s, 2H), 4.14 (bs, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.07, 147.85, 145.07, 130.06, 129.42, 129.16, 127.24, 117.94, 112.98, 52.21, 48.07 ppm.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Experimental details, spectroscopic data for all compounds, (PDF)

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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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