# Synthesis of Diarylmethanes via Metal-Free Reductive Cross-Coupling of Diarylborinic Acids with Tosyl Hydrazones

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S Supporting Information

ABSTRACT: This paper describes a practical and efficient procedure that takes advantage of diarylborinic acids as a cost-effective alternative to arylboronic acids for synthesis of diarylmethanes through metal-free reductive cross-coupling with _N_-tosylhydrazones of aromatic aldehydes and ketones. The procedure tolerates hydroxyl, halide, amine, and allyl functionality, complementary to the transition-metal catalyzed cross-coupling techniques.

31 examples including heterocyclics, up to 94% yield
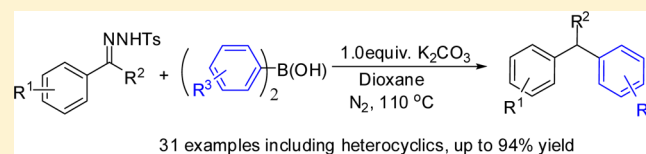
Diarylmethanes have attracted intensive attention because of the presence of their structural motif in supramolecular architectures,[1] pharmaceuticals, and biologically active compounds,[2] such as piritrexim, papaverine, beclobrate, and dimetindene (Figure 1).
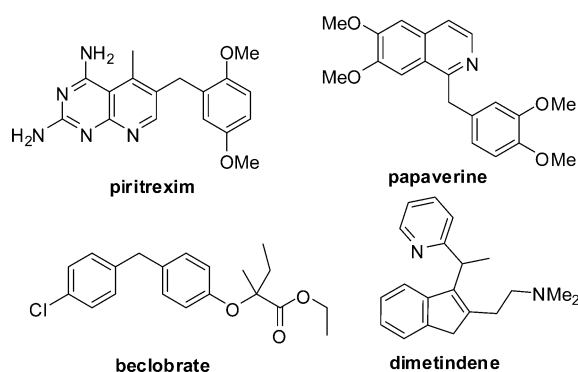
Figure 1. Selected biologically active diarylmethanes.

The direct method for synthesis of diarylmethanes is Friedel−Crafts benzylation. Although there have been many modifications to the traditional Friedel−Crafts benzylation using new catalysts and benzyl sources,[2a,3] the intrinsic problems of regioselectivity and oversubstitution, except for the presence of strong directing effects, often decrease the effectiveness of Friedel−Crafts benzylation in the synthesis of diarylmethanes. To overcome the drawbacks of Friedel−Crafts benzylation, transition-metal-catalyzed cross-coupling reactions have been extensively explored for synthesis of diarylmethanes[4] using organoboronic acids (Suzuki coupling),[4b−d] organomagnesium reagents (Kumada coupling), and zinc reagents (Negishi coupling),[4e−j] among which Suzuki coupling is particularly attractive due to the friendly properties of organoboronic acids, e.g., nontoxicity, air/moisture stability, and tolerance of a variety of functional groups. Although the transition-metal-catalyzed cross-coupling approaches have

proven highly effective in the synthesis of symmetrical and unsymmetrical diarylmethanes, metal-free cross-coupling procedures are still advantageous considering the possible toxicity, cost, and metal residual in final products of transition-metal catalysts. Generally, only highly reactive substrates, such as aryl iodides[5] and allyl bromides,[6] could be used in metal-free Suzuki coupling unless unconventional conditions were applied.[7] However, Barluenga and Valdés reported a novel metal-free reductive carbon−carbon cross-coupling between _N_-tosylhydrazones and organoboronic acids under mild conditions in 2009,[8] inspiring great interest in exploring _N_-tosylhydrazones in metal-free cross-coupling reactions.[9]

Compared with arylboronic acids, high-order arylborons, e.g., diarylborinic acids ($Ar_2B(OH)$), triarylboranes (Ar_3B), and tetraarylborates ($[Ar_4B]^-$), have higher atom economy as aryl reagents and could be more economically prepared from aryl halides, boronates, and magnesium under noncryogenic conditions.[10] However, high-order arylborons have been rarely applied as aryl sources in cross-coupling.[11] We have recently found that diarylborinic acids, which have properties closest to arylboronic acids among the high-order arylborons, could take part in Suzuki coupling as efficient as arylboronic acids under proper conditions.[10c] As part of our ongoing efforts to use diarylborinic acids as a cost-effective alternative to arylboronic acids, we report herein a general and practical synthesis of symmetrical and unsymmetrical diarylmethanes through a metal-free reductive cross-coupling of tosylhydrazones with diarylborinic acids or anhydrides.

It has been well established from the elegant work by Aggarwal et al. that the key to using _N_-tosylhydrazones as a safe and effective source of active diazo compounds lies in their controllable decomposition.[12] Therefore, reaction of _N_-tosylhydrazone (**1a**) of acetophenone with bis(4-methoxyphenyl)borinic acid (**2a**) was chosen as model reaction to screen conditions for the metal-free reductive cross-coupling

considering both of the substrates could be readily monitored by TLC (Table 1).

Table 1. Reductive Coupling of N-Tosylhydrazone 1a with Diarylborinic Acid 2a[a]
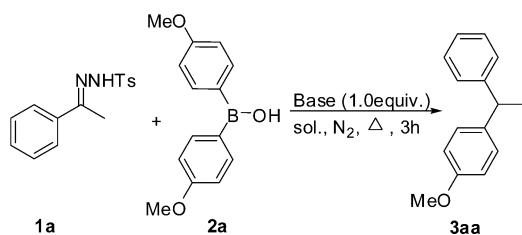
entry	base	solvent	T (°C)	time (h)	yield (%)[b]
1	K$_3$PO$_4$·3H$_2$O	dioxane	reflux	3	65
2	K$_2$CO$_3$	dioxane	reflux	3	92
3	Na$_2$CO$_3$	dioxane	reflux	3	26
4	NaOAc	dioxane	reflux	12	trace
5	Ba(OH)$_2$·8H$_2$O	dioxane	reflux	3	trace
6	KOH	dioxane	reflux	3	trace
7[c]	K$_2$CO$_3$	dioxane	reflux	6	53
8	K$_2$CO$_3$	dioxane	80	12	38[d]
9[e]	K$_2$CO$_3$	dioxane	reflux	3	92
10[f]	K$_2$CO$_3$	dioxane	reflux	6	81
11[g]	K$_2$CO$_3$	dioxane	reflux	3	94
12	K$_2$CO$_3$	pyridine	reflux	12	50[h]
13	K$_2$CO$_3$	DMF	110	6	24
14	K$_2$CO$_3$	n-BuOH	reflux	6	59
15	K$_2$CO$_3$	PEG-400	110	6	43
16	K$_2$CO$_3$	CH$_3$CN	reflux	12	15
17	K$_2$CO$_3$	THF	reflux	12	20

[a]Reaction conditions: **1a**, 1.0 mmol; **2a**, 0.6 mmol (1.2 equiv); solvent, 5 mL. [b]Isolated yield. [c]In air. [d]32% of **1a** was recovered. [e]2.0 equiv of K$_2$CO$_3$ was used. [f]1.0 equiv of **2a** was used. [g]1.5 equiv of **2a** (0.75 mmol) was used. [h]1,2-Bis(1-phenylethylidene)hydrazine was isolated as the major byproduct.

The model reaction proceeded smoothly to offer the desired product **3aa** in 65%, 92%, and 26% yields with a slight excess of borinic acid **2a** (1.2 equiv) after refluxing for 3 h under nitrogen in dioxane in the presence of 1.0 equiv of K$_3$PO$_4$, K$_2$CO$_3$, and Na$_2$CO$_3$, respectively, while either weaker or stronger bases, e.g., NaOAc, Ba(OH)$_2$, and KOH, failed (Table 1, entries 1−6). When the reaction was run in air, the yield of **3aa** decreased to 53% (Table 1, entry 7). Increasing the stoichiometry of bis(4-methoxyphenyl)borinic acid (**2a**) or K$_2$CO$_3$ showed no remarkable influence on the reaction while a significant decrease of **3aa** yields from 92% to 81% was observed with a loading of 1.0 equiv of **2a**, possibly due to the common side reaction of organoborons, proton deboronation (Table 1, entries 9−11).

The reaction appeared to strongly depend on solvents (Table 1, entries 12−17). Product **3aa** was isolated in low yields, and byproducts acetophenone from hydrolysis of N-tosylhydrazone (**1a**) and 1,2-bis(1-phenylethylidene)hydrazine from trapping the corresponding carbene by phenyldiazoethane were also isolated when the model reaction was conducted in DMF and pyridine, respectively. When the reaction was run in n-butanol **3aa** was isolated in 59% yield due to the formation of some 1-methylbenzyl butyl ether.[13] A metal-free cross-coupling of aryl iodides with arylboronic acids was reported to occur to afford biaryls in PEG preferably over conventional organic solvents.[5a]

Therefore, we tested the model reaction in PEG-400 under otherwise identical conditions, but the coupling product **3aa** was isolated in only 43% yield. The poor performance of THF and CH$_3$CN in the model reaction could, at least partly, be attributed to their low boiling points considering a slow reaction observed at low temperature (80 °C) in dioxane (Table 1, entries 8, 16, and 17).

Generality of the synthesis of diarylmethanes via the metal-free reductive cross-coupling of N-tosylhydrazones with diarylborinic acids was investigated (Table 2). Because of the

Table 2. Scope of Cross-Coupling of N-Tosylhydrazones with Diarylborinic Acids[a]

| entry	R^1/R^2 (1)	R^3 (2)	3	time (h)	yield[b] (%)
1	H/Me (**1a**)	H (**2b**)	**3ab**	2	78
2	H/Et (**1b**)	H (**2b**)	**3bb**	2.5	82
3	4-Br/Me (**1c**)	H (**2b**)	**3cb**	2	93
4	4-OH/Me (**1d**)	H (**2b**)	**3db**	2.5	85
5	4-NO$_2$/Me (**1e**)	H (**2b**)	**3eb**	2.5	35
6	4-NH$_2$/Me (**1f**)	H (**2b**)	**3fb**	2.5	72
7	4-MeO/H (**1g**)	H (**2b**)	**3gb**	1	92
8	4-CN/H (**1h**)	H (**2b**)	**3hb**	1	94
9	4-OH/H (**1i**)	H (**2b**)	**3ib**	1	93
10	2-OH/H (**1j**)	H (**2b**)	**3jb**	1	79
11	2-OAllyl/H (**1k**)	H (**2b**)	**3kb**	1.5	75
12	2,4-(Cl)$_2$/H (**1l**)	H (**2b**)	**3lb**	1	86
13	4-Br/Me (**1c**)	4-OMe (**2a**)	**3ca**	3	89
14	4-NO$_2$/Me (**1e**)	4-OMe (**2a**)	**3ea**	2	14
15	4-CN/H (**1h**)	4-OMe (**2a**)	**3ha**	1	83
16	4-OH/H (**1i**)	4-OMe (**2a**)	**3ia**	1.5	92
17	H/Me (**1a**)	4-F (**2c**)	**3ac**	2	75
18	H/Et (**1b**)	4-F (**2c**)	**3bc**	3	93
19	4-Br/Me (**1c**)	4-F (**2c**)	**3cc**	2.5	88
20	4-NO$_2$/Me (**1e**)	4-F (**2c**)	**3ec**	3	37
21	4-MeO/H (**1g**)	4-F (**2c**)	**3gc**	1	91
22	4-CN/H (**1h**)	4-F (**2c**)	**3hc**	1	84
23	2,4-(Cl)$_2$/H (**1l**)	4-F (**2c**)	**3lc**	1	80
24	2-OH/H (**1j**)	4-F (**2c**)	**3jc**	1.5	80
25	H/Me (**1a**)	2-Me (**2e**)	**3ae**	2.5	79
26	H/Et (**1b**)	2-Me (**2e**)	**3be**	2.5	70
27	4-Br/Me (**1c**)	4-Me (**2d**)	**3cd**	2.5	90
28	4-Br/Me (**1c**)	2-Me (**2e**)	**3ce**	2.5	71

[a]Reaction run on 1.0 mmol scale of **1** with 0.6 mmol of **2a**, **2c**−**e** or 0.3 mmol of **2b** in anhydride form in 5 mL of dioxane. [b]Isolated yield.

ready dehydration, diphenylborinic acid was used in anhydride form for convenient stoichiometry. A variety of symmetrical and unsymmetrical diarylmethanes with a wide range of functional groups, such as CN, OH, NH$_2$, halide, and allyl groups, could be readily obtained in good to excellent yields, while the presence of a NO$_2$ group in N-tosylhydrazones appeared to be deleterious, leading to complicated reactions and low yields (14−37%) of the desired coupling products (Table 2, entries 5, 14, and 20). The tolerance of halide and allyl groups make the metal-free method complementary to

transition-metal-catalyzed techniques, which generally destroy C−X (X ≠ F) and allyl groups. Generally, N-tosylhydrazones of aryl alkyl ketones required longer reaction time to give comparable results than aryl aldehydes. No reaction was observed for N-tosylhydrazone of diphenylketone. A small steric effect was observed in the reaction with respect to both N-tosylhydrazones and diarylborinic acids. For example, although N-tosylhydrazones of propiophenone and acetophenone reacted similarly to provide the desired diarylmethanes **3ab** and **3bb** in comparable yields (78% and 82%), reaction of N-tosylhydrazones of 2-hydroxybenzaldehyde and 2-allyloxybenzaldehyde with diphenylborinic anhydride **2b** gave products **3jb** and **3kb** in lower yields (75 and 79%) than that of 4-hydroxybenzaldehyde (93%) (Table 2, entries 9−11). Similarly, yields of diarylmethanes from ortho-substituted diarylborinic acids, such as di(2-methylphenyl)borinic acid, were lower than those from para- or nonsubstituted ones (Table 2, entries 1, 2, and 25−28).

Electronic effects of substituents at aryl moieties of both N-tosylhydrazones and diarylborinic acids appeared to be negligible except for NO$_2$-containing N-tosylhydrazones that seemed to competitively decompose under the reaction conditions. For example, reaction of diphenylborinic anhydride (**2b**) with N-tosylhydrazones bearing both electron-donating (OH, OMe and NH$_2$) and -withdrawing (CN and Cl) groups at the para-position of the benzene ring proceeded similarly with respect to rate and yields (Table 2, entries 4, 6, 7, 8, and 12). p-Methoxy- (**2a**) and p-fluoro-substituted (**2c**) diarylborinic acids also showed little difference from diphenylborinic anhydride (**2b**) in the reaction. It is worth pointing out that, in all of the cases investigated, hydroxyl and amino groups on aromatic rings of N-tosylhydrazones survived, and no aryl ether or amine product was detected in our experiments although that oxygen and sulfur ethers could be synthesized from reaction of N-tosylhydrazones with phenols and arylthiols, respectively, under similar conditions.[13] Reaction of N-tosylhydrazones of heterocyclic carbonyls, such as 2-fufural (**1m**) and 4-acetylpyridine (**1n**), with **2a** also afforded the desired products **3ma** and **3na** in 56% and 70% yields, respectively (Scheme 1).

Scheme 1. Synthesis of Pyridyl/Furylarylmethanes
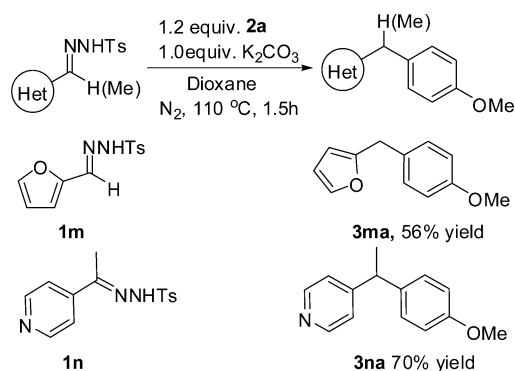
In conclusion, metal-free reductive cross-coupling of N-tosylhydrazones of aromatic aldehydes and aryl alkyl ketones with diarylborinic acids or anhydrides was shown to be a practical and efficient protocol for synthesis of diarylmethanes under mild conditions in good yields. The higher process and atom economies of diarylborinic acids over arylboronic acids promise a more cost-effective synthesis of diarylmethanes. The

other features of this procedure include elimination of possible toxicity, cost, and metal residual of transition-metal catalysts, and tolerance of hydroxyl, halide, amine, and allyl functionality, thus complementary to the transition-metal catalyzed cross-coupling techniques.

■ EXPERIMENTAL SECTION

General Information. All reactions were carried out under a nitrogen atmosphere unless otherwise stated. Commercially available chemicals were used as received. N-Tosylhydrazones[14] and diarylborinic acids[10c] were prepared according to previously reported procedures. ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ at ambient temperature. Chemical shifts in NMR were reported in ppm (δ), relative to the internal standard of tetramethylsilane (TMS). The signals observed were described as s (singlet), d (doublet), t (triplet), dd(double doublet), m (multiplets), br (board). The number of protons (n) for a given resonance was indicated as nH. Coupling constants were reported as J in hertz. The high-resolution mass spectra (HRMS) were performed on an electron ionization mass spectrometer with a quadrupole analyzer.

General Procedure for Reductive Coupling Reaction. Under a N$_2$ atmosphere, to a 10 mL flask were added N-tosylhydrazone (1.0 mmol), diarylborinic acid (0.6 mmol) or anhydride (0.3 mmol), K$_2$CO$_3$ (1.0 mmol), and dioxane (5 mL). The mixture was stirred at 110 °C and monitored by TLC until N-tosylhydrazone was completely consumed. The reaction mixture was diluted with CH$_2$Cl$_2$ (20 mL), followed by washing twice with H$_2$O (2 × 20 mL). The organic layer was dried over Na$_2$SO$_4$, filtered, and evaporated under reduced pressure to give crude product diarylmethane, which was purified by column chromatography on silica gel with EtOAc/petroleum ether.

1-Methoxy-4-(1-phenylethyl)benzene (3aa):[15] colorless liquid (0.195 g, 92%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.27−7.12 (m, 7H), 6.82 (d, J = 8.4 Hz, 2H), 4.10 (q, J = 7.2 Hz, 1H), 3.76 (s, 3H), 1.61 (d, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 156.8, 145.7, 137.5, 127.4, 127.3, 126.5, 124.9, 112.7, 54.1, 42.9, 21.0.

Ethane-1,1-diyldibenzene (3ab):[3a] colorless liquid (0.142 g, 78%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.29−7.15 (m, 10H), 4.14 (q, J = 7.2 Hz, 1H), 1.63 (d, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 146.5, 128.5, 127.7, 126.1, 44.9, 22.0.

Propane-1,1-diyldibenzene (3bb):[16] colorless liquid (0.161 g, 82%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.27−7.21 (m, 8H), 7.16−7.12 (m, 2H), 3.77 (t, J = 8.0 Hz, 1H), 2.10−2.02 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 145.3, 128.5, 128.1, 126.2, 53.4, 28.7, 12.9.

1-Bromo-4-(1-phenylethyl)benzene (3cb):[3a] light yellow liquid (0.243 g, 93%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.39 (d, J = 8.4 Hz, 2H), 7.30−7.26 (m, 2H), 7.20−7.17 (m, 3H), 7.08 (d, J = 8.4 Hz, 2H), 4.10 (q, J = 7.2 Hz, 1H), 1.61 (d, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 145.8, 145.5, 131.5, 129.5, 128.6, 127.6, 126.4, 119.9, 44.3, 21.9.

4-(1-Phenylethyl)phenol (3db):[17] light yellow liquid (0.168 g, 85%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.26 (t, J = 7.2 Hz, 2H), 7.19−7.14 (m, 3H), 7.05 (d, J = 8.4 Hz, 2H), 6.71 (d, J = 7.6 Hz, 2H), 5.37 (br. s, 1H), 4.06 (q, J = 7.2 Hz, 1H), 1.58 (d, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 153.7, 147.0, 138.9, 128.9, 128.6, 127.7, 126.2, 115.5, 44.1, 22.2.

1-Nitro-4-(1-phenylethyl)benzene (3eb):[18] yellow liquid (0.079 g, 35%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.05 (dd, J = 2.0, 6.8 Hz, 2H), 7.30−7.21 (m, 4H), 7.17−7.10 (m, 3H), 4.17 (q, J = 7.2 Hz, 1H), 1.59 (d, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 154.1, 146.4, 144.6, 128.7, 128.5, 127.6, 126.7, 123.7, 44.8, 21.5.

4-(1-Phenylethyl)aniline (3fb):[19] yellow liquid (0.142 g, 72%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.26−7.15 (m, 5H), 7.00 (d, J = 8.4 Hz, 2H), 6.59 (d, J = 8.4 Hz, 2H), 4.04 (q, J = 7.2 Hz, 1H), 3.51 (br. s, 2H), 1.58 (d, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 147.3, 144.6, 136.6, 128.5, 128.4, 127.7, 126.0, 115.3, 44.0, 22.2.

1-Benzyl-4-methoxybenzene (3gb):[20] light yellow liquid (0.182 g, 92%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.29−7.25 (m, 2H), 7.22−7.15 (m, 3H), 7.10 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 3.92 (s,

2H), 3.77 (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 156.9, 140.5, 132.2, 128.8, 127.7, 127.4, 124.9, 112.8, 54.1, 40.0.

4-Benzylbenzonitrile (3hb):[15] colorless liquid (0.182 g, 94%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.55 (d, J = 8.0 Hz, 2H), 7.36−7.21 (m, 5H), 7.15 (d, J = 7.2 Hz, 2H), 4.02 (s, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 146.8, 139.4, 132.3, 129.7, 129.0, 128.8, 126.7, 119.1, 110.0, 42.0.

4-Benzylphenol (3ib):[15] white solid (0.171 g, 93%); mp 83−84 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.18−7.15 (m, 2H), 7.10−7.05 (m, 3H), 6.93−6.91 (m, 2H), 6.64−6.61 (m, 2H), 5.35 (br. s, 1H), 3.79 (s, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 153.7, 141.6, 133.6, 130.2, 128.9, 128.6, 126.1, 115.5, 41.1.

2-Benzylphenol (3jb):[21] yellow liquid (0.145 g, 79%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.30−7.27 (m, 3H), 7.23−7.18 (m), 7.14−7.10 (m, 2H), 6.88 (t, J = 7.2 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 4.78 (br. s, 1H), 3.99 (s, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 153.8, 140.1, 131.1, 128.8, 128.7, 127.9, 127.2, 126.4, 121.0, 115.8, 36.4.

1-(Allyloxy)-2-benzylbenzene (3kb):[22] colorless liquid (0.168 g, 75%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.27−7.07 (m, 7H), 6.89−6.82 (m, 2H), 6.05−5.95 (m, 1H), 5.36 (dd, J = 1.6, 17.2 Hz, 1H), 5.23 (dd, J = 1.6, 10.4 Hz, 1H), 4.51 (d, J = 4.8 Hz, 2H), 4.00 (s, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 156.4, 141.2, 133.6, 130.6, 130.2, 129.1, 128.3, 127.5, 125.9, 120.8, 117.1, 111.8, 68.8, 36.2.

1-Benzyl-2,4-dichlorobenzene (3lb):[23] light yellow liquid (0.204 g, 86%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.39 (d, J = 2.4 Hz, 1H), 7.31−7.14 (m, 6H), 7.05 (d, J = 8.4 Hz, 1H), 4.06 (s, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 139.0, 137.4, 134.9, 132.7, 131.8, 129.4, 129.0, 128.7, 127.2, 126.6, 38.7.

1-Bromo-4-(1-(4-methoxyphenyl)ethyl)benzene (3ca):[17] colorless liquid (0.259 g, 89%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.30 (d, J = 8.4 Hz, 2H), 7.03−6.98 (m, 4H), 6.75 (d, J = 8.8 Hz, 2H), 3.98 (q, J = 7.2 Hz, 1H), 3.70 (s, 3H), 1.50 (d, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 156.9, 144.7, 136.7, 130.3, 128.3, 127.4, 118.6, 112.8, 54.1, 42.3, 20.9.

1-Methoxy-4-(1-(4-nitrophenyl)ethyl)benzene (3ea):[18] yellow liquid (0.036 g, 14%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.04 (d, J = 8.8 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 8.4 Hz, 2H), 6.77 (d, J = 8.4 Hz, 2H), 4.12 (q, J = 7.2 Hz, 1H), 3.70 (s, 3H), 1.56 (d, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 158.3, 154.5, 146.3, 136.7, 128.5, 128.4, 123.7, 114.1, 55.3, 44.0, 21.7.

4-(4-Methoxybenzyl)benzonitrile (3ha):[8] white solid (0.185 g, 83%); mp 48−49 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.55 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 3.96 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 158.4, 147.3, 132.3, 131.5, 130.0, 129.6, 119.1, 114.2, 109.9, 55.3, 41.1.

4-(4-Methoxybenzyl)phenol (3ia):[15] light yellow solid (0.197 g, 92%); mp 81−82 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.06 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 6.71 (d, J = 8.4 Hz, 2H), 5.75 (br. s, 1H), 3.82 (s, 2H), 3.75 (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 157.8, 153.9, 134.0, 133.8, 130.0, 129.9, 115.4, 114.0, 55.4, 40.2.

1-Fluoro-4-(1-phenylethyl)benzene (3ac):[3a] light yellow liquid (0.150 g, 75%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.30−7.26 (m, 2H), 7.20−7.14 (m, 5H), 6.98−6.93 (m, 2H), 4.13 (q, J = 7.2 Hz, 1H), 1.61 (d, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 161.4 (d, J = 242.4 Hz), 146.3, 142.1 (d, J = 3.1 Hz), 129.1 (d, J = 7.7 Hz), 128.5, 127.6, 126.3, 115.2 (d, J = 20.9 Hz), 44.1, 22.1.

1-Fluoro-4-(1-phenylpropyl)benzene (3bc): light yellow liquid (0.199 g, 93%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.29−7.16 (m, 7H), 6.95 (t, J = 8.8 Hz, 2H), 3.77 (t, J = 8.0 Hz, 1H), 2.08−2.00 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 161.3 (d, J = 242.3 Hz), 145.0, 140.9 (d, J = 3.0 Hz), 129.3 (d, J = 7.7 Hz), 128.5, 127.9, 126.2, 115.1 (d, J = 21.0 Hz), 52.5, 28.8, 12.8; HRMS (EI) m/z (M$^+$) calcd for C$_{15}$H$_{15}$F 214.1158, found 214.1163.

1-Bromo-4-(1-(4-fluorophenyl)ethyl)benzene (3cc):[3a] light yellow liquid (0.245 g, 88%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.39 (d, J = 8.4 Hz, 2H), 7.15−7.11 (m, 2H), 7.05 (d, J = 8.4 Hz, 2H), 6.98−6.94 (m, 2H), 4.08 (q, J = 7.2 Hz, 1H), 1.59 (d, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 161.4 (d, J = 242.9 Hz), 145.3, 141.5 (d, J = 3.1

Hz), 131.6, 129.4, 129.0 (d, J = 7.6 Hz), 120.0, 115.3 (d, J = 21.1 Hz), 43.6, 22.0.

1-Fluoro-4-(1-(4-nitrophenyl)ethyl)benzene (3ec): yellow liquid (0.091 g, 37%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.04 (d, J = 8.8 Hz, 2H), 7.26 (d, J = 8.8 Hz, 2H), 7.08−7.05 (m, 2H), 6.92−6.88 (m, 2H), 4.15 (q, J = 7.2 Hz, 1H), 1.57 (d, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 160.5 (d, J = 243.7 Hz), 152.8, 145.4, 139.2 (d, J = 3.1 Hz), 128.0 (d, J = 7.8 Hz), 127.3, 122.7, 114.4 (d, J = 21.1 Hz), 43.0, 20.6; HRMS (EI) m/z (M$^+$) calcd for C$_{14}$H$_{12}$FNO$_2$ 245.0852, found 245.0855.

1-Fluoro-4-(4-methoxybenzyl)benzene (3gc):[24] colorless liquid (0.197 g, 91%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.05−6.98 (m, 4H), 6.89−6.84 (m, 2H), 6.75 (d, J = 8.8 Hz, 2H), 3.80 (s, 2H), 3.69 (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 160.3 (d, J = 242.2 Hz), 157.0, 136.2 (d, J = 3.1 Hz), 132.0, 129.1 (d, J = 7.7 Hz), 128.7, 114.1 (d, J = 21.1 Hz), 112.9, 54.1, 39.1.

4-(4-Fluorobenzyl)benzonitrile (3hc):[25] light yellow liquid (0.177 g, 84%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.45 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.01 (dd, J = 5.6, 12.4 Hz, 2H), 7.00−6.86 (m, 2H), 4.00 (s, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 160.6 (d, J = 243.5 Hz), 145.5, 134.1 (d, J = 3.3 Hz), 131.3, 129.4 (d, J = 7.9 Hz), 128.5, 117.9, 114.5 (d, J = 21.1 Hz), 109.1, 40.0.

2,4-Dichloro-1-(4-fluorobenzyl)benzene (3lc): light yellow liquid (0.204 g, 80%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.39 (s, 1H), 7.18−6.95 (m, 6H), 4.02 (s, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 161.6 (d, J = 243.3 Hz), 137.2, 134.8, 134.6 (d, J = 3.2 Hz), 132.9, 131.7, 130.3 (d, J = 7.9 Hz), 129.4, 127.2, 115.4 (d, J = 21.2 Hz), 37.9. HRMS (EI) m/z (M$^+$) calcd for C$_{13}$H$_9$Cl$_2$F 254.0065, found 254.0061.

2-(4-Fluorobenzyl)phenol (3jc):[2d] Light yellow liquid (0.162 g, 80%), ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.21−7.06 (m, 4H), 6.96−6.86 (m, 3H), 6.73 (d, J = 7.6 Hz, 1H), 4.93 (br. s, 1H), 3.93 (s, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 161.5 (d, J = 242.3 Hz), 153.6, 135.8, 130.9, 130.2 (d, J = 7.8 Hz), 127.9, 127.1, 121.1, 115.7, 115.3 (d, J = 21.1 Hz), 35.4.

1-Methyl-2-(1-phenylethyl)benzene (3ae):[3c] colorless liquid (0.155 g, 79%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.28−7.11 (m, 9H), 4.31 (q, J = 7.2 Hz, 1H), 2.22 (s, 3H), 1.60 (d, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 146.4, 144.0, 136.2, 130.5, 128.4, 127.8, 126.8, 126.2, 126.1, 125.9, 41.1, 22.3, 19.9.

1-Methyl-2-(1-phenylpropyl)benzene (3be):[26] colorless liquid (0.147 g, 70%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.33−7.09 (m, 9H), 3.97 (t, J = 7.6 Hz, 1H), 2.25 (s, 3H), 2.05 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 144.9, 143.0, 136.5, 130.6, 128.4, 128.3, 126.7, 126.1, 126.0, 125.9, 48.9, 29.2, 20.1, 13.0.

1-Bromo-4-(1-p-tolylethyl)benzene (3cd): light yellow liquid (0.248 g, 90%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.39−7.36 (m, 2H), 7.10−7.06 (m, 6H), 4.06 (q, J = 7.2 Hz, 1H), 2.30 (s, 3H), 1.59 (d, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 145.8, 142.9, 135.9, 131.5, 129.5, 129.3, 127.5, 119.9, 44.0, 22.0, 21.2; HRMS (EI) m/z (M$^+$) calcd for C$_{15}$H$_{15}$Br 274.0357, found 274.0359.

1-(1-(4-Bromophenyl)ethyl)-2-methylbenzene (3ce): light yellow liquid (0.195 g, 71%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.36 (d, J = 8.4 Hz, 2H), 7.24−7.11 (m, 4H), 7.01 (d, J = 8.4 Hz, 2H), 4.26 (q, J = 7.2 Hz, 1H), 2.20 (s, 3H), 1.57 (d, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 145.4, 143.3, 136.1, 131.5, 130.6, 129.6, 126.7, 126.5, 126.3, 119.7, 40.6, 22.1, 19.8; HRMS (EI) m/z (M$^+$) calcd for C$_{15}$H$_{15}$Br 274.0357, found 274.0359.

2-(4-Methoxybenzyl)furan (3ma):[27] colorless liquid (0.105 g, 56%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.22 (d, J = 1.2 Hz, 1H), 7.06 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 8.4 Hz, 2H), 6.19 (dd, J = 2.8, 1.6 Hz, 1H), 5.88 (d, J = 2.8 Hz, 1H), 3.81 (s, 2H), 3.68 (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 158.3, 155.1, 141.4, 130.2, 129.7, 113.9, 110.3, 106.0, 55.3, 33.6.

4-(1-(4-Methoxyphenyl)ethyl)pyridine (3na):[8] light yellow liquid (0.149 g, 70%); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.50 (br s, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 8.0 Hz, 2H), 4.07 (q, J = 7.8 Hz, 1H), 3.78 (s, 3H), 1.61 (d, J = 8.0 Hz, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 158.3, 156.3, 136.3, 128.6, 123.2, 114.0, 55.3, 43.5, 21.2.

ASSOCIATED CONTENT

⑤ Supporting Information

^{1}H and ^{13}C NMR spectra for all compounds and HRMS for new compounds reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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