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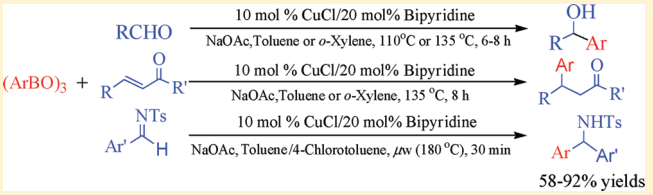
CuCl/Bipyridine-Catalyzed Addition Reactions of Arylboroxines with Aldehydes, α,β-Unsaturated Ketones, and *N*-Tosyl Aldimines

Yuan-Xi Liao and Qiao-Sheng Hu*

Department of Chemistry, College of Staten Island and the Graduate Center of the City University of New York, Staten Island, New York 10314, United States

Supporting Information

ABSTRACT: CuCl/bipyridine-catalyzed addition reactions of arylboroxines with aldehydes and α,β-unsaturated ketones at elevated temperatures were described. By using the microwave energy, CuCl/bipyridine-catalyzed addition reactions of arylboroxines with aldimines were also realized.



Over the past decade, transition-metal-catalyzed addition reactions of arylboron reagents with aldehydes have emerged as useful transformations in organic synthesis.[1−9] Transition metal catalysts including Rh(I)/(II),[2] Pd(II),[3] Ni(0)/(II),[4] Cu(I)/(II),[5] Fe(III)[6] complexes, and more recently Ru(II)[7] and Co(II)[8] complexes have been reported to catalyze this type of addition reaction. Although enormous success, including promising enantioselectivity, has been achieved, most of the transition metal catalysts are expensive and/or require air-free handling operation. The search for operationally convenient and cost-effective catalysts for this type of addition reaction continues.

In our laboratory, we are interested in employing readily available transition metal complexes as catalysts for this type of addition reaction. In this context, we have recently documented air/moisture-stable anionic four-electron donor-based (type I) metalacycles (Figure 1),[10] a large family of cyclic organometallic compounds, as catalysts for the addition reactions of arylboronic acids with aldehydes, α,β-unsaturated ketones, α-keto esters, and aldimines.[11,12] We have also reported $[Rh(COD)Cl]_2$ and $Ni(COD)_2$/4-$RCOC_6H_4Cl$-catalyzed addition reactions of arylborons with aldehydes.[13] During our study, we became interested in using Cu(I)/Cu(II) complexes as catalysts for this type of addition reaction because Cu(I) or Cu(II) salts such as CuCl or $CuCl_2$ are inexpensive. So far, two Cu catalysts have been reported for addition reactions. CuF_2/(*R*)-5,5′-bis[di(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-4,4′-bi-1,3-benzodioxole with tetrabutylammonium difluorotriphenylsilicate (TBAT) as additive was reported for the addition reaction of arylborates with aldehydes.[5a] Recently, the $Cu(OAc)_2$/dppf complex was also reported as the catalyst for the addition reaction of arylboronic acids with activated aromatic aldehydes.[5b] While these protocols are useful, there are drawbacks associated with them, such as the requirement of additives and/or limited substrate scope. In our early study, we found low conversions (<5%) were observed for the addition reaction of phenylboronic acid with benzaldehyde (Scheme 1), presumably because of the decomposition of the catalyst under the reaction condition.

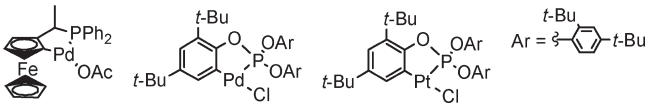
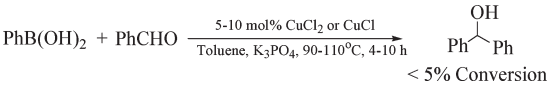


Figure 1. Type I metalacycles.

Scheme 1



During our study of using type I palladacycles as addition reaction catalysts, we discovered that addition reactions can efficiently occur under anhydrous conditions and the palladacycle catalysts were very stable under such anhydrous conditions.[11d] We thus surmised that Cu(I)/(II) catalysts might also be long-lived under the anhydrous condition and might be able to function as efficient catalysts for the addition reactions. Herein, we report our study on such addition reactions with simple Cu(I)/(II) complexes as catalysts, specifically, CuCl/bipyridine-catalyzed addition reactions of arylboroxines with aldehydes, α,β-unsaturated ketones, and *N*-tosyl aldimines.

Our study began with the testing of several copper(I)/(II) complexes as catalysts for the addition reaction of phenylboron compounds with benzaldehyde under anhydrous conditions. By using dry K_3PO_4, toluene, and dry phenylboronic acid (phenylboroxine), we found that although low efficiency was observed by using $CuCl_2$, CuCl, $CuCl_2$/dppf, $CuCl_2$/4,7-diphenyl-1,10-phenanthroline, $CuCl_2$/tetramethylethane-1,2-diamine, or $CuCl_2$/pyridine complex (Table 1, entries 1−6), $CuCl_2$/bipyridine exhibited moderate catalytic activity (Table 1, entry

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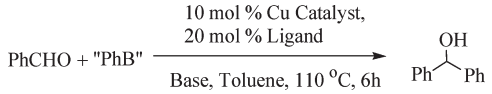
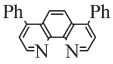
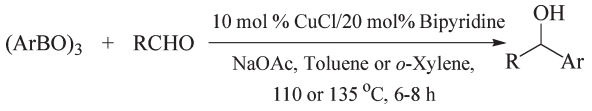
Table 1. Copper(I)/Cu(II)-Catalyzed Addition Reaction of Phenylboron Reagents with Benzaldehyde [a]

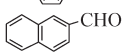
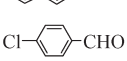
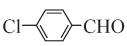
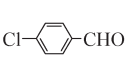
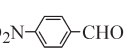
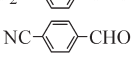
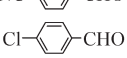
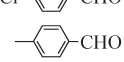


entry	catalyst	ligand	"PhB"	base	conv.(%)[b]
1	$CuCl_2$	-	$(PhBO)_3$	K_3PO_4	<1
2	CuCl	-	$(PhBO)_3$	K_3PO_4	<1
3	$CuCl_2$	DPPF	$(PhBO)_3$	K_3PO_4	7
4	$CuCl_2$		$(PhBO)_3$	K_3PO_4	7
5	$CuCl_2$		$(PhBO)_3$	K_3PO_4	3
6	$CuCl_2$		$(PhBO)_3$	K_3PO_4	<1
7	$CuCl_2$		$(PhBO)_3$	K_3PO_4	25
8	$CuCl_2$		$(PhBO)_3$	K_2CO_3	18
9	$CuCl_2$		$(PhBO)_3$	Cs_2CO_3	8
10	$CuCl_2$		$(PhBO)_3$	KOAc	59
11	$CuCl_2$		$(PhBO)_3$	NaOAc	66
12	$CuCl_2$		$(PhBO)_3$	KF	67
13	CuCl		$(PhBO)_3$	NaOAc	78
14	CuCl		$(PhBO)_3$	KF	63
15	$Cu(OAc)_2$		$(PhBO)_3$	NaOAc	40
16	CuCl		$(PhBO)_3$	NaOAc	96 [c]
17	CuCl		$PhB(OH)_2$	NaOAc	<1
18	CuCl			NaOAc	<1
19	CuCl			NaOAc	<1
20	CuCl		$PhBF_3K$	NaOAc	<1

[a] Reaction conditions: benzaldehyde (0.25 mmol), phenylboron reagent (2.0 equiv), base (3.0 equiv), 10 mol % of Cu catalyst, 20 mol % of ligand, 110 °C, 6 h. [b] Based on ^1H NMR analysis. [c] *o*-Xylene was used as solvent at 135 °C.

Table 2. CuCl/Bipyridine-Catalyzed Addition Reactions of Arylboroxines with Aldehydes [a]



Entry	$(ArBO)_3$	RCHO	Condition	Yield(%)[b]
1			A	86
2			A	85
3			A	83
4			A	85
5			A	86
6			B	87
7			B	85
8			B	88
9			C	87
10			C	83
11			C	80
12			C	83
13			C	88
14			C	81
15			C	62
16			A	92 [c]
17			A	83 [c]
18			A	81 [c]
19			A	80 [c]

[a] Reaction conditions: aldehydes (1.0 equiv), arylboroxine (0.66 equiv). **A**: 10 mol % of CuCl, 20 mol % of bipyridine, *o*-xylene, 135 °C, 6−8 h. **B**: 10 mol % of CuCl, 20 mol % of bipyridine, toluene, 110 °C, 6 h. **C**: 20 mol % of CuCl, 40 mol % of bipyridine, *o*-xylene, 135 °C, 6 h. [b] Isolated yields. [c] 3-Substituted phthalides as the products.

7). Further study revealed that CuCl/bipyridine was the most active complex and NaOAc was the best base (Table 1, entries 7−15). The CuCl/bipyridine catalyst system showed higher activity at higher temperature with *o*-xylene as the solvent (Table 1, entry 16). We also examined other phenylboron reagents and found that only phenylboroxine showed reactivity (Table 1, entries 17−20).

With 10 mol % of CuCl/20 mol % of bipyridine as the catalyst, NaOAc as the base, and *o*-xylene as solvent, different arylboroxines and aldehydes for the addition reactions were examined, and our results are listed in Table 2. As shown in Table 2, arylboroxines with electron-donating and electron-withdrawing substituents smoothly react with different aldehydes to give corresponding diarylmethanols in good yields. Our study showed that aromatic aldehydes bearing electron-withdrawing groups were more reactive than aromatic aldehydes bearing electron-donating groups and aliphatic aldehydes. With aromatic aldehydes bearing electron-withdrawing groups as substrates, the addition reaction could occur at lower temperature (Table 2, entries 6−8). With aromatic aldehydes bearing electron-donating groups and aliphatic aldehyde as substrates, good yields were obtained by using 20 mol % of CuCl/40 mol % of bipyridine as the catalyst (Table 2, entries 9−15).

Recently, we reported Pd(II)-, Pt(II)-, and Rh(I)-catalyzed addition reactions of arylboronic acids with alkyl 2-formylbenzoates followed by lactonization to access 3-substituted phthalides.[14] After establishing that CuCl/bipyridine could catalyze addition

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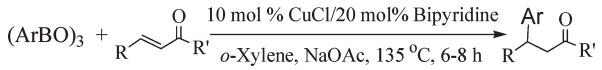
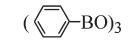
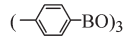
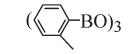
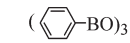
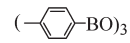
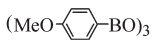
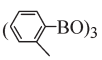
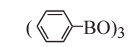
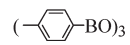
Table 3. CuCl/Bipyridine-Catalyzed Addition Reactions of Arylboroxines with α,β-Unsaturated Ketones[a]



Entry	$(ArBO)_3$	R	R'	Yield(%)[b]
1		Ph	Ph	89
2		Ph	Ph	82
3		Ph	Ph	80
4		Ph	CH_3	85
5		Ph	CH_3	83
6		Ph	CH_3	82
7		Ph	CH_3	81
8		n-C_4H_9	CH_3	85
9		n-C_4H_9	CH_3	84

[a] Reaction conditions: ketone (1.0 equiv), arylboroxine (0.66 equiv), 10 mol % of CuCl, 20 mol % of bipyridine, *o*-xylene, 135 °C, 6−8 h. [b] Isolated yields.

reactions of aldehydes with arylboroxines, it was necessary to determine whether or not this catalyst system might be useful for addition reactions of arylboroxines with methyl 2-formylbenzoates to access 3-substituted phthalides. Our study showed that CuCl/bipyridine-catalyzed addition reactions of arylboroxines with methyl 2-formylbenzoates occurred smoothly and 3-substituted phthalides were obtained in good to excellent yields (Table 2, entries 16−19).

Our success of using CuCl/bipyridine as the catalyst for addition reactions of arylboroxines with aldehydes prompted us to examine other types of substrates for the addition reactions. We next examined α,β-unsaturated ketones as substrates for 1,4-addition reactions of arylboroxines.[1,15] We found that CuCl/bipyridine was also an efficient catalyst for the 1,4-addition reaction of arylboroxines with α,β-unsaturated ketones. Complete conversions and high yields were obtained for all tested substrates. Our study represents the first examples of Cu-catalyzed 1,4-addition reactions of arylborons with α,β-unsaturated ketones.[16]

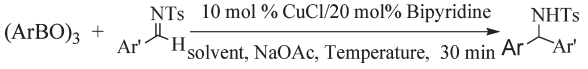
We also examined the addition reaction of arylboroxines with *N*-tosyl aldimines.[17] We found that the addition reaction of arylboroxines with *N*-tosyl benzaldimine occurred slower and up to 84% conversion was observed with toluene/4-chlorotoluene as cosolvents (Table 4, entries 1−3). Complete conversions and good yields were achieved with the assistance of microwave energy (Table 4, entries 4−9). To our knowledge, this represents the first example of Cu-complex-catalyzed addition reactions of organoborons with aldimines.

In summary, on the basis of the consideration that Cu(I) or Cu(II) catalysts could be more stable under the anhydrous conditions than in the presence of water, we demonstrated that readily available CuCl/bipyridine complex was a good catalyst for the addition reactions of arylboroxines with aldehydes and α,β-unsaturated ketones by using dry base and solvent. With the assistance of microwave energy, the CuCl/bipyridine complex also catalyzed the addition reactions of arylboroxines with *N*-tosyl aldimines. Our study provided an inexpensive transition metal catalyst for the addition reactions of arylboroxines with aldehydes, α,β-unsaturated ketones, and *N*-tosyl aldimines. Our future work will be directed toward the elucidation of the detailed mechanism for such CuCl/bipyridine-catalyzed addition reactions and to further examine the effect of water on the longevity of other transition metal catalysts.

EXPERIMENTAL SECTION

General. NMR spectra were recorded on 300 or 600 MHz spectrometers (300 or 600 MHz for ^{1}H NMR, 150 MHz for ^{13}C NMR, and 287 MHz for ^{19}F NMR) with $CDCl_3$ as the solvent. The microwave-assisted reactions were conducted in 10 mL sealed pressure reaction vessels, with a CEM Discover S-class microwave reactor that is equipped with an infrared temperature detector. The temperatures were controlled within less than ±1−2 °C in the temperature-controlled microwave-assisted reactions. Arylboroxines were prepared by azeotropic distillation of arylboronic acids with dry toluene for 6 h. The bases were dried by baking well-ground base powder at 140 °C under vacuum for 6 h. Other chemicals were used directly as received from commercial sources.

Table 4. Microwave-Assisted, CuCl/Bipyridine-Catalyzed Addition Reactions of Arylboroxines with *N*-Tosyl Aldimine[a]



entry	Ar	Ar′	solvent	temp (°C)	yield (%)[b]
1	Ph	Ph	toluene	110[c]	50[d]
2	Ph	Ph	*o*-xylene	135[c]	52[d]
3	Ph	Ph	toluene/4-chlorotoluene	135[c]	84[d]
4	Ph	Ph	toluene/4-chlorotoluene	180 (μw)	70
5	4-$CH_3C_6H_4$	Ph	toluene/4-chlorotoluene	180 (μw)	61
6	2-$CH_3C_6H_4$	Ph	toluene/4-chlorotoluene	180 (μw)	65
7	4-$CH_3OC_6H_4$	Ph	toluene/4-chlorotoluene	180 (μw)	62
8	Ph	4-$CH_3C_6H_4$	toluene/4-chlorotoluene	180 (μw)	58
9	Ph	4-ClC_6H_4	toluene/4-chlorotoluene	180 (μw)	69

[a] Reaction conditions: aldehydes (1.0 equiv), arylboroxine (0.66 equiv), 10 mol % of CuCl, 20 mol % of bipyridine, NaOAc (3.0 equiv), oil bath heating, 6 h or microwave heating at 180 °C for 30 min. [b] Isolated yields. [c] Conventional heating by oil bath for 6 h. [d] Conversion based on ^{1}H NMR analysis.

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General Procedure for CuCl/Bipyridine-Catalyzed Addition Reactions of Arylboroxines with Aldehydes. To a vial containing aldehyde (0.25 mmol), arylboroxine (0.168 mmol), base (NaOAc, 0.75 mmol), and CuCl/bipyridine (conditions A, B, or D: 0.025 mmol/0.05 mmol; condition C: 0.05 mmol/0.1 mmol) was added solvent (1.0 mL, condition A or C: *o*-xylene; condition B: toluene). After the mixture was stirred at 110 °C (condition B) or 135 °C (condition A or C) for 6−8 h, the reaction was quenched by 4 N HCl (2 mL) aqueous solution. The mixture was extracted with CH_2Cl_2 (3 × 15 mL). The organic layers were combined. After evaporation of the organic solvents, the residue was subjected to column chromatography [silica gel, ethyl acetate/hexane (v/v = 1:10) as eluent] to afford the products.

Diphenylmethanol[13a] *(Table 2, entry 1):* ^{1}H NMR δ 7.33−7.28 (m, 8H), 7.23 (t, J = 7.2 Hz, 2H), 5.74 (s, 1H), 2.45 (s, 1H); ^{13}C NMR δ 143.7, 128.4, 127.5, 126.5, 76.1.

Naphthalen-2-yl(phenyl)methanol[11c] *(Table 2, entry 2):* ^{1}H NMR δ 7.80 (s, 1H), 7.77−7.75 (m, 2H), 7.72 (d, J = 8.4 Hz, 1H), 7.44−7.41 (m, 2H), 7.36−7.33 (m, 3H), 7.27 (t, J = 7.8 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 5.86 (d, J = 3.0 Hz, 1H), 2.61 (s, 1H); ^{13}C NMR δ 143.5, 141.0, 133.2, 132.8, 128.4, 128.2, 128.0, 127.6, 127.5, 126.6, 126.1, 125.9, 124.9, 124.7, 76.2.

(4-Chlorophenyl)(2-(trifluoromethyl)phenyl)methanol[11d] *(Table 2, entry 3):* ^{1}H NMR δ 7.67 (d, J = 8.4 Hz,1H), 7.57−7.52 (m, 2H), 7.39 (t, J = 7.2 Hz, 1H), 7.28 (s, 4H), 6.25 (s, 1H), 2.46 (d, J = 3.6 Hz, 1H); ^{13}C NMR δ 141.9, 141.2, 133.3, 132.4, 129.4, 128.5, 128.0, 127.8, 127.6 (q, J = 29.7 Hz), 125.6 (q, J = 5.6 Hz), 124.3 (q, J = 272.3 Hz), 70.7 (q, J = 2.3 Hz).

(4-Chlorophenyl)(4-fluorophenyl)methanol[18] *(Table 2, entry 4):* ^{1}H NMR δ 7.30−7.25 (m, 6H), 7.01 (t, J = 9.0 Hz, 2H), 5.75 (s, 1H), 2.42 (d, J = 2.4 Hz, 1H); ^{13}C NMR δ 162.3 (d, J = 245.4 Hz), 142.0, 139.2 (d, J = 2.9 Hz), 133.4, 128.7, 128.2 (d, J = 7.8 Hz), 127.8, 115.5 (d, J = 21.2 Hz), 74.9.

(2,4-Bis(trifluoromethyl)phenyl)(4-chlorophenyl)methanol (Table 2, entry 5): Light yellow oil; ^{1}H NMR δ 7.92 (s, 1H), 7.81−7.77 (m, 2H), 7.46 (d, J = 7.8 Hz, 1H), 7.19 (d, J = 7.8 Hz, 1H), 6.27 (s, 1H), 2.67 (d, J = 3.6 Hz, 1H); ^{13}C NMR δ 145.8, 140.3, 133.9, 130.5 (q, J = 33.5 Hz, 1C), 130.3, 129.2, 128.8, 128.3 (q, J = 30.6 Hz), 127.8, 123.5 (q, J = 272.7 Hz), 123.2 (q, J = 272.7 Hz), 123.0 (q, J = 3.9 Hz), 70.0; ^{19}F NMR δ −58.9, −63.7 ppm; IR 3325(br), 1491(s), 1345(m), 1300(s), 1124(s); HR-MS (-ESI) calcd for $C_{16}H_{10}ClF_6O_3$ [M + HCOO]$^-$ 399.0228, found 399.0231.

(4-Nitrophenyl)(phenyl)methanol[11c] *(Table 2, entry 6):* ^{1}H NMR δ 8.19 (d, J = 7.2 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.38−7.30 (m, 5H), 5.92 (d, J = 3.0 Hz, 1H), 2.40 (d, J = 3.0 Hz, 1H); ^{13}C NMR δ 150.7, 147.2, 142.7, 129.0, 128.4, 127.0, 126.7, 123.7, 75.5.

4-(Hydroxyphenylmethyl)benzonitrile[11a] *(Table 2, entry 7):* ^{1}H NMR δ 7.58 (d, J = 8.4 Hz, 2H), 7.48 (t, J = 8.4 Hz, 2H), 7.35−7.28 (m, 5H), 5.75 (d, J = 3.0 Hz, 1H), 2.70 (d, J = 3.6 Hz, 1H); ^{13}C NMR δ 148.8, 142.7, 132.2, 128.8, 128.2, 126.9, 126.6, 118.8, 110.9, 75.5.

(4-Chlorophenyl)(phenyl)methanol[11c] *(Table 2, entry 8):* ^{1}H NMR δ 7.33−7.30 (m, 4H), 7.28−7.25 (m, 5H), 5.74 (d, J = 2.4 Hz, 1H), 2.49 (d, J = 2.4 Hz, 1H); ^{13}C NMR δ 143.3, 142.1, 133.2, 128.6, 128.5, 127.8, 127.7, 126.5, 75.5.

Phenyl(p-tolyl)methanol[11c] *(Table 2, entry 9):* ^{1}H NMR δ 7.34 (d, J = 7.2 Hz, 2H), 7.30 (t, J = 7.8 Hz, 2H), 7.24−7.22 (m, 3H), 7.12 (d, J = 7.8 Hz, 2H), 5.75 (s, 1H), 2.36 (br, 1H), 2.31 (s, 3H); ^{13}C NMR δ 143.9, 140.9, 137.2, 129.1, 128.4, 127.4, 126.5, 126.4, 76.0, 21.1.

Di(p-tolyl)methanol[11c] *(Table 2, entry 10):* ^{1}H NMR δ 7.22 (d, J = 7.2 Hz, 4H), 7.11 (d, J = 7.8 Hz, 4H), 5.72 (s, 1H), 2.31 (s, 6H), 2.27 (s, 1H); ^{13}C NMR δ 141.1, 137.0, 129.1, 126.4, 75.8, 21.0.

Phenyl(o-tolyl)methanol[11c] *(Table 2, entry 11):* ^{1}H NMR δ 7.50 (d, J = 7.8 Hz, 1H), 7.31−7.30 (4 m, H), 7.27−7.22 (m, 2H), 7.19 (t, J = 7.8 Hz, 1H), 7.13 (d, J = 7.2 Hz, 1H), 5.98 (d, J = 3.6 Hz, 1H), 2.23 (s, 3H), 2.17 (d, J = 4.2 Hz, 1H); ^{13}C NMR δ 142.8, 141.4, 135.3, 130.5, 128.4, 127.5(2C), 127.1, 126.2, 126.1, 73.3, 19.4.

o-Tolyl(p-tolyl)methanol[11d] *(Table 2, entries 12 and 13):* ^{1}H NMR δ 7.51 (d, J = 7.2 Hz, 1H), 7.25−7.17 (m, 3H), 7.11−7.10 (m, 4H), 5.91 (s, 1H), 2.31 (s, 3H), 2.22 (s, 1H), 2.20 (s, 3H); ^{13}C NMR δ 141.5, 139.9, 137.2, 135.2, 130.4, 129.1, 127.3, 127.0, 126.0, 73.1, 21.1, 19.3.

(4-Methoxyphenyl)(p-tolyl)methanol[11d] *(Table 2, entry 14):* ^{1}H NMR δ 7.24 (d, J = 9.0 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 5.72 (s, 1H), 3.75 (s, 3H), 2.31 (s, 4H); ^{13}C NMR δ 158.9, 141.1, 137.0, 136.3, 129.0, 127.7, 126.3, 113.7, 75.5, 55.2, 21.0.

Cyclohexyl(phenyl)methanol[11a] *(Table 2, entry 15):* ^{1}H NMR δ 7.32 (t, J = 7.2 Hz, 2H), 7.28−7.24 (m, 3H), 4.27 (dd, J = 3.0, 7.2 Hz, 1H), 1.98−1.96 (m, 1H), 1.93 (d, J = 3.0 Hz, 2H), 1.77−1.74 (m, 1H), 1.66−1.57 (m, 3H), 1.37−1.35 (m, 1H), 1.25−1.00 (m, 4H), 0.95−0.89 (m, 1H); ^{13}C NMR δ 143.6, 128.1, 127.3, 126.6, 79.3, 44.9, 29.2, 28.8, 26.4, 26.0, 25.9.

3-Phenylisobenzofuran-1(3H)-one[14] *(Table 2, entry 16):* ^{1}H NMR δ 7.95 (d, J = 7.2 Hz, 1H), 7.64 (t, J = 7.2 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H), 7.38−7.26 (m, 6H), 6.40 (s, 1H); ^{13}C NMR δ 170.5, 149.6, 136.3, 134.3, 129.3, 129.2, 128.9, 126.9, 125.5, 125.5, 122.8, 82.6.

3-p-Tolylisobenzofuran-1(3H)-one[14] *(Table 2, entry 17):* ^{1}H NMR δ 7.95 (d, J = 8.4 Hz, 1H), 7.63 (t, J = 7.8 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.32 (t, J = 7.8 Hz, 1H), 7.18−7.14 (m, 4H), 6.37 (s, 1H), 2.34 (s, 3H); ^{13}C NMR δ 170.5, 149.7, 139.2, 134.2, 133.3, 129.5, 129.2, 127.0, 125.6, 125.5, 122.8, 21.1.

3-o-Tolylisobenzofuran-1(3H)-one[14] *(Table 2, entry 18):* ^{1}H NMR δ 7.97 (d, J = 7.8 Hz, 1H), 7.66 (t, J = 7.2 Hz, 1H), 7.56 (t, J = 7.2 Hz, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.28−7.24 (m, 2H), 7.12 (t, J = 7.8 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 6.67 (s, 1H), 2.49 (s, 3H); ^{13}C NMR δ 170.5, 149.2, 137.1, 134.1, 134.0, 131.0, 129.3, 129.2, 127.1, 126.3, 126.3, 125.6, 123.0, 80.4, 19.2.

3-(4-Methoxyphenyl)isobenzofuran-1(3H)-one[14] *(Table 2, entry 19):* ^{1}H NMR δ 7.95 (d, J = 7.8 Hz, 1H), 7.64 (t, J = 7.2 Hz, 1H), 7.55 (t, J = 7.2 Hz, 1H), 7.31 (d, J = 7.8 Hz, 1H), 7.17 (d, J = 7.8 Hz, 1H), 6.88 (d, J = 8.4 Hz, 1H), 6.37 (s, 1H), 3.80 (s, 3H); ^{13}C NMR δ 170.5, 163.4, 149.7, 134.2, 129.3, 128.8, 128.3, 125.9, 125.5, 122.9, 114.3, 82.7, 55.3, 21.1.

General Procedure for CuCl/Bipyridine-Catalyzed Addition Reactions of Arylboroxines with α,β-Unsaturated Ketones. To a vial containing α,β-unsaturated ketone (0.25 mmol), arylboroxine (0.168 mmol), base (NaOAc, 0.75 mmol), and CuCl/bipyridine (0.025 mmol/0.05 mmol) was added *o*-xylene (1.0 mL). After the mixture was stirred at 135 °C for 6−8 h, the reaction was quenched by 4 N HCl (2 mL) aqueous solution. The mixture was extracted with CH_2Cl_2 (3 × 15 mL). The organic layers were combined. After evaporation of the organic solvents, the residue was subjected to column chromatography [silica gel, ethyl acetate/hexane (v/v = 1:20) as eluent] to afford the products.

1,3,3-Triphenylpropan-1-one[11c] *(Table 3, entry 1):* ^{1}H NMR δ 7.92 (d, J = 6.6 Hz, 2H), 7.51 (t, J = 6.6 Hz, 1H), 7.40 (d, J = 7.2 Hz, 2H), 7.26−7.25 (m, 8H), 7.17−7.14 (m, 2H), 4.83 (t, J = 7.2 Hz, 1H), 3.72 (d, J = 7.2 Hz, 2H); ^{13}C NMR δ 197.9, 144.1, 137.0, 133.0, 128.5, 128.4, 128.0, 127.8, 126.3, 45.9, 44.7.

1,3-Diphenyl-3-p-tolylpropan-1-one[11c] *(Table 3, entry 2):* ^{1}H NMR δ 7.93 (d, J = 7.2 Hz, 2H), 7.54 (t, J = 6.6 Hz, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.26 (t, J = 4.8 Hz, 2H), 7.17−7.15 (m, 3H), 7.07 (d, J = 7.8 Hz, 2H), 4.79 (t, J = 7.2 Hz, 1H), 3.72 (d, J = 7.8 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR δ 198.0, 144.4, 141.1, 137.1, 135.9, 133.0, 129.2, 128.6, 128.5, 128.0, 127.8, 127.6, 126.3, 45.5, 44.8, 21.0.

1,3-Diphenyl-3-o-tolylpropan-1-one[11a] *(Table 3, entry 3):* ^{1}H NMR δ 7.92 (d, J = 7.8 Hz, 2H), 7.53 (t, J = 7.8 Hz, 1H), 7.42 (t, J = 7.8 Hz, 2H), 7.25 (t, J = 8.4 Hz, 2H), 7.23−7.20 (m, 3H), 7.17−7.09 (m, 4H), 5.02 (t, J = 7.2 Hz, 1H), 3.71 (m, 2H), 2.32 (s, 3H); ^{13}C NMR δ 198.0,

143.7, 141.8, 137.0, 136.4, 133.0, 130.7, 128.6, 128.4, 128.0, 127.9, 126.3, 126.2, 126.0, 45.0, 41.8, 19.9.

4,4-Diphenylbutan-2-one[11e] *(Table 3, entry 4):* ^{1}H NMR δ 7.27 (t, J = 7.8 Hz, 4H), 7.24 (d, J = 7.2 Hz, 4H), 7.17 (t, J = 7.2 Hz, 2H), 4.59 (t, J = 7.2 Hz, 1H), 3.18 (d, J = 7.8 Hz, 2H), 2.08 (s, 3H); ^{13}C NMR δ 206.9, 143.8, 128.6, 127.7, 126.4, 49.7, 46.0, 30.6.

4-Phenyl-4-p-tolylbutan-2-one[11e] *(Table 3, entry 5):* ^{1}H NMR δ 7.25 (t, J = 7.2 Hz, 2H), 7.21 (d, J = 7.2 Hz, 2H), 7.16 (t, J = 7.2 Hz, 1H), 7.11−7.07 (m, 4H), 4.54 (t, J = 7.2 Hz, 1H), 3.15 (d, J = 7.2 Hz, 2H), 2.28 (s, 3H), 2.06 (s, 3H); ^{13}C NMR δ 206.9, 144.0 140.7, 135.9, 129.2, 128.5, 127.5, 127.4, 126.3, 49.7, 45.6, 30.6, 20.9.

4-(4-Methoxyphenyl)-4-phenylbutan-2-one[11e] *(Table 3, entry 6):* ^{1}H NMR δ 7.26 (t, J = 7.2 Hz, 4H), 7.21−7.19 (m, 2H), 7.16 (t, J = 7.2 Hz, 2H), 7.13 (d, J = 7.2 Hz, 2H), 6.81 (d, J = 7.2 Hz, 2H), 4.53 (t, J = 7.2 Hz, 1H), 3.75 (s, 3H,), 3.14 (d, J = 7.8 Hz, 2H), 2.06 (s, 3H); ^{13}C NMR δ 207.0, 158.0, 144.2, 135.9, 128.6, 128.5, 127.5, 126.3, 113.9, 55.1, 49.8, 45.2, 30.6.

4-Phenyl-4-o-tolylbutan-2-one[11e] *(Table 3, entry 7):* ^{1}H NMR δ 7.25−7.22 (m, 3H), 7.19−7.09 (m, 6H), 4.78 (t, J = 7.2 Hz, 1H), 3.14 (d, J = 7.2 Hz, 2H), 2.29 (s, 3H), 2.06 (s, 3H); ^{13}C NMR δ 206.9, 143.4, 141.5, 136.3, 130.7, 128.4, 127.9, 126.40, 126.2 (2C), 126.0, 50.0, 41.9, 30.6, 19.8.

4-Phenyloctan-2-one[11c] *(Table 3, entry 8):* ^{1}H NMR δ 7.28 (t, J = 7.8 Hz, 2H), 7.20−7.16 (m, 3H), 3.10 (m, 1H), 2.75−2.67 (m, 2H), 2.01 (s, 3H), 1.65−1.52 (m, 2H), 1.31−1.18 (m, 2H), 1.17−1.05 (m, 2H), 0.82 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 208.0, 144.6, 128.4, 127.4, 126.3, 50.9, 41.3, 36.2, 30.6, 29.5, 25.6, 22.6, 13.9.

4-p-Tolyloctan-2-one[11c] *(Table 3, entry 9):* ^{1}H NMR δ 7.09 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 7.8 Hz, 2H), 3.07−3.05 (m, 1H), 2.72−2.67 (m, 2H), 2.30 (s, 3H), 2.00 (s, 3H), 1.61−1.51 (m, 2H), 1.28−1.20 (m, 2H), 1.16−1.07 (m, 2H), 0.82 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 208.2, 141.5, 135.7, 129.1, 127.3, 51.1, 40.9, 36.2, 30.6, 29.6, 22.6, 21.0, 13.9.

General Procedure for CuCl/Bipyridine-Catalyzed Addition Reactions of Arylboroxines with *N*-Tosyl Aldimine. To a 10 mL pressure vial containing *N*-tosyl aldimine (0.25 mmol), arylboroxine (0.168 mmol), base (NaOAC, 0.75 mmol), and CuCl/bipyridine (0.025 mmol/0.05 mmol) was added toluene/4-chlorotoluene (total 1.0 mL, 1:1 ratio). The vial was then sealed with a rubber septum and placed in the microwave reactor. After the mixture in the sealed vial was irradiated by microwave at 180 °C for 30 min, the reaction was quenched by adding 4 N HCl (2 mL) aqueous solution. The mixture was extracted with CH_2Cl_2 (3 × 15 mL). The organic layers were combined. After evaporation of the organic solvents, the residue was subjected to column chromatography [silica gel, ethyl acetate/hexane (v/v = 1:20) as eluent] to afford the products.

N-Tosyldiphenylmethylamine[17c] *(Table 4, entry 4):* ^{1}H NMR δ 7.56 (d, J = 8.4 Hz, 2H), 7.21−7.09 (m, 12H), 5.57 (d, J = 7.8 Hz, 1H), 5.18 (d, J = 7.2 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR δ 143.2, 140.5, 137.3, 129.3, 128.5, 127.5, 127.3, 127.2, 61.3, 21.5.

N-Tosylphenyl-(p-tolyl)methylamine[17d] *(Table 4, entries 5 and 8):* ^{1}H NMR δ 7.56 (d, J = 8.4 Hz, 2H), 7.21−7.20 (m, 3H), 7.14−7.10 (m, 4H), 7.02−6.96 (m, 4H), 5.52 (d, J = 7.8 Hz, 1H), 5.10 (d, J = 7.2 Hz, 1H), 2.38 (s, 3H), 2.28 (s, 3H); ^{13}C NMR δ 143.2, 140.5, 137.3, 129.3, 128.5, 127.5, 127.3, 127.2, 61.3, 21.5, 21.0.

N-Tosylphenyl-(o-tolyl)methylamine[17d] *(Table 4, entry 6):* ^{1}H NMR δ 7.55 (d, J = 7.8 Hz, 2H), 7.21−7.19 (m, 3H), 7.13−7.10 (m, 4H), 7.06−7.05 (m, 4H), 5.80 (d, J = 7.2 Hz, 1H), 5.10 (d, J = 6.6 Hz, 1H), 2.37 (s, 3H), 2.16 (s, 3H); ^{13}C NMR δ 143.2, 140.0, 138.2, 137.4, 135.5, 130.6, 129.3, 128.5, 127.6, 127.5, 127.2, 127.1, 126.1, 58.1, 21.5, 19.3.

N-Tosyl-(4-methoxyphenyl)-phenylmethylamine[17d] *(Table 4, entry 7):* ^{1}H NMR δ 7.56 (d, J = 7.8 Hz, 2H), 7.22−7.17 (m, 3H), 7.14−7.10 (m, 4H), 7.00 (d, J = 8.4 Hz, 2H), 6.73 (d, J = 8.4 Hz, 2H), 5.52 (d, J = 6.6 Hz, 1H), 5.09 (d, J = 7.2 Hz, 1H), 3.75 (s, 3H), 2.38 (s, 3H); ^{13}C NMR δ 160.0, 143.1, 140.7, 137.4, 132.7, 129.3, 128.6, 128.5, 127.4, 127.3, 127.2, 60.8, 55.2, 21.5.

N-Tosyl-(4-chlorophenyl)phenylmethylamine[17d] *(Table 4, entry 9):* ^{1}H NMR δ 7.54 (d, J = 8.4 Hz, 2H), 7.20−7.19 (m, 3H), 7.17−7.12 (m, 4H), 7.06−7.04 (m, 4H), 5.53 (d, J = 7.2 Hz, 1H), 5.41 (d, J = 7.2 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR δ 143.4, 140.0, 139.0, 137.2, 133.4, 129.4, 128.8, 128.7, 128.6, 127.8, 127.2, 127.1, 60.7, 21.5.

■ ASSOCIATED CONTENT

Supporting Information. NMR spectra of CuCl/bipyridine-catalyzed addition reaction products. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: qiaosheng.hu@csi.cuny.edu.

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