有机化学 DOI: 10.6023/cjoc202301027 研究论文
Chinese Journal of Organic Chemistry ARTICLE

铜催化芳基重氮乙酸酯与双[(频哪醇)硼基]甲烷的偶联反应

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摘要 报道铜催化下重氮苯乙酸酯作为卡宾前体与双[(频哪醇)硼基]甲烷的交叉偶联反应, 实现 sp^3-杂化碳碳键的构筑. 条件筛选表明亚磷酰胺配体 monophos 对该反应的成功尤为关键. 原位氧化使得硼酯产物以醇的形式被分离, 反应具有高效率以及良好的官能团兼容性. 该两步反应是芳基重氮酯类化合物形式上的羟甲基化.
关键词 铜催化; sp^3-杂化碳碳键构筑; 重氮化合物; 双[(频哪醇)硼基]甲烷

Copper-Catalyzed Cross-Coupling of Aryldiazoacetates with Bis[(pinacolato)boryl]methane

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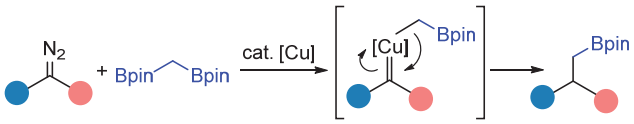
Abstract The copper-catalyzed cross-coupling reaction of 1,1-bis[(pinacolato)boryl]methane with *α*-diazophenylacetate as carbene precursor was reported, leading to the construction of $C(sp^3)$—$C(sp^3)$ bond. Reaction optimization experiments showed that Monophos ligand was critical for the success of this reaction. *In situ* oxidation afforded the corresponding primary alcohols instead of the relatively unstable boronates. The reaction has high efficiency and good functional group compatibility. The two-step transformation represents a formal hydroxymethylation of diazoacetates.
Keywords copper catalysis; $C(sp^3)$—$C(sp^3)$ bond formation; diazo compounds; bis[(pinacolato)boryl]methane

1 Introduction

Transition-metal-catalyzed cross-coupling reaction involving metal carbene species has become a practical method for the construction of carbon-carbon bonds or carbon-heteroatom bonds.[1] A series of transition-metal catalysts, such as Pd, Rh, Cu, have been utilized to promote such coupling reactions. The copper catalysts are important among them due to their unique reactivity. Redox neutral condition throughout the catalytic cycle is the characteristic of carbene coupling reactions with copper catalysis. The copper-catalyzed cross-coupling reactions so far developed can be divided into two categories according to the formation of organocopper species. One type of such reactions is those utilizing the substrates bearing acidic C—H bonds, such as terminal alkynes.[2] The other type is those using nucleophilic reagents that are able to undergo transmetalation.[3] After the migratory insertion of the copper carbene species, the newly formed organocopper species is terminated with protonation in most cases. On the other hand, 1,1-diboronates have recently been established as versatile building blocks for a variety of transformations,[4] such as cross-coupling reactions, nucleophilic addition reactions and radical reactions. We have developed a convenient method for synthesizing *gem*-diboronates[5] and have further explored the chemistry of *gem*-diboronates.[6] Along with our interests in both carbene and 1,1-diborylalkanes, we have conceived to explore the copper-catalyzed diazo compounds with bis[(pinacolato)boryl]methane. This reaction is expected to involve copper carbene migratory insertion into Bpin-CH_2—Cu bond, which has not been explored previously (Scheme 1).



Scheme 1 Cu(I) carbene migratory insertion with $BpinCH_2$

2 Results and discussion

To test our hypothesis, *tert*-butyl 2-diazo-2-phenylacetate **1a** was chosen as the model substrate to react with di-

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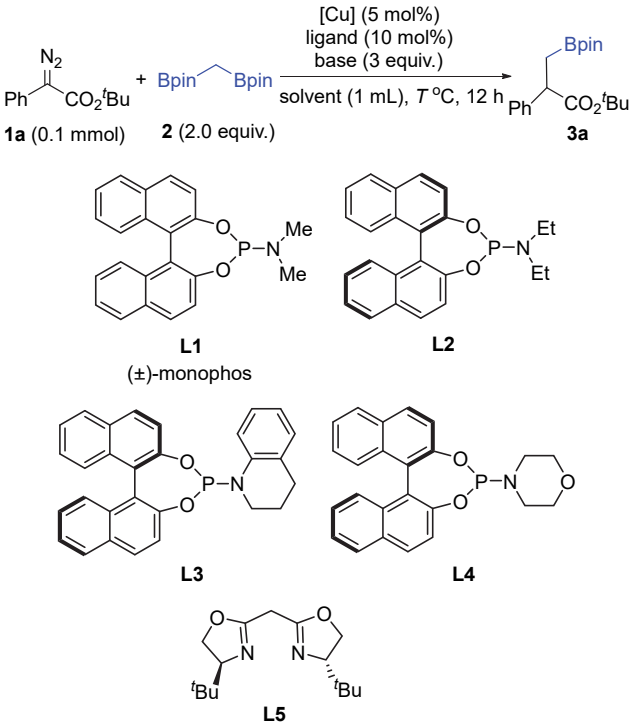
Received January 31, 2023; revised March 12, 2023; published online March 23, 2023.
Project supported by the National Natural Science Foundation of China (No. 21871010).
国家自然科学基金(No. 21871010)资助项目.

borylmethane **2**. Initial investigation using CuCl as the catalyst showed that a series of monodentate/bidentate phosphine or nitrogen-containing ligands were not effective (Table 1, Entry 1). When the ligand was turned to the phosphoramidite ligand (±)-monophos **L1**, the expected product **3a** could be generated with 16% yield (^{1}H NMR) (Table 1, Entry 2). However, further examination of other related ligands **L2**～**L5** showed no reactivity (Table 1, Entry 3). Thus, with (±)-monophos **L1** as the ligand, the effect of bases was screened (Table 1, Entry 4), however, the results showed that only lithium *tert*-butoxide was effective. Besides, other non-aromatic solvents of tetrahydrofuran (THF) and 1,2-dichloroethane (DCE) did not afford **3a** (Table 1, Entries 6 and 7). Toluene was proved to be the effective solvent (Table 1, Entries 7～9). Increasing the loading of catalyst and ligand was found to improve the yield of **3a** (Table 1, Entries 10～11). Under the otherwise identical conditions, other copper catalysts provide inferior yields (Table 1, Entries 12～16). Finally, considering that the dimerization of diazo substrate was the main side reaction, the concentration of diazo substrate for minimizing this side reaction was decreased. Thus, the diazo substrate was divided into two parts, and the addition of the second part was two hours later. This procedure offered the optimal yield of 74% (Table 1, Entry 18). Decreasing the amount of ligand to 30 mol% would not affect the reaction efficiency remarkably (Entry 19).

With the optimized reaction conditions in hand, the substrate scope of the reaction was investigated. However, when the isolation of boronates was attempted, decomposing in the silica gel occurred, and this caused a significant decrease of the yields. Due to the instability of the boronate products, the purified products still contained some impurities in some cases. Through repeated and careful purification, three examples were given in the form of boronates (Scheme 2).

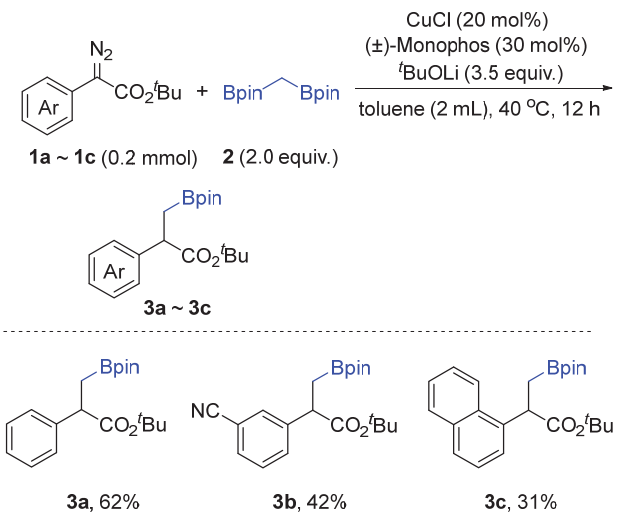
To avoid the problem of the instability of the boronate products, the crude cross-coupling products were subjected to oxidation after simple filtration and change of solvents. The corresponding *β*-hydroxy esters **4a**～**4p** were obtained upon purification (Scheme 3). A series of aryldiazoacetates were used as the substrates in this transformation, it was found that different substituents could be well tolerated. For weak electron-withdrawing substituents in the *para* position, such as fluorine and chlorine, high yields would be obtained (**4b** and **4c**). However, when it was turned to electron-donating groups, such as methyl and methoxyl, moderate yields were observed (**4d** and **4e**). Substituents in the *meta* position did not affect the reaction. A series of aryldiazoacetates bearing halo groups, methyl, trifluoromethyl and methoxy in the *meta* position could be transformed into the corresponding products with high yields (**4f**～**4m**). The aryldiazoacetate bearing *ortho*-methoxy group **1n** and naphthyldiazoacetate **1o** were also examined in the reaction, affording the corresponding products **4n** and **4o** in moderate yields. However, when the *tert*-butyl ester was replaced by methyl ester, a significant decrease

Table 1 Optimization of the reaction conditions[a]



Entry	[Cu]	Ligand	Base	Solvent	Yield[b]/%
1	CuCl	Ligand[c]	LiO^{t}Bu	Toluene	0
2	CuCl	**L1**	LiO^{t}Bu	Toluene	24
3	CuCl	**L2**～**L5**	LiO^{t}Bu	Toluene	0
4	CuCl	**L1**	Base[d]	Toluene	0
5	CuCl	**L1**	LiO^{t}Bu	THF	0
6	CuCl	**L1**	LiO^{t}Bu	DCE	0
7	CuCl	**L1**	LiO^{t}Bu	*m*-Xylene	18
8	CuCl	**L1**	LiO^{t}Bu	Chlorobenzene	14
9	CuCl	**L1**	LiO^{t}Bu	Trifluorotoluene	8
10[e]	CuCl	**L1**	LiO^{t}Bu	Toluene	38
11[f]	CuCl	**L1**	LiO^{t}Bu	Toluene	52
12	CuBr	**L1**	LiO^{t}Bu	Toluene	30
13	CuI	**L1**	LiO^{t}Bu	Toluene	24
14	CuTC	**L1**	LiO^{t}Bu	Toluene	38
15	$Cu(MeCN)_4PF_6$	**L1**	LiO^{t}Bu	Toluene	48
16	$CuCl_2$	**L1**	LiO^{t}Bu	Toluene	48
17[g]	CuCl	**L1**	LiO^{t}Bu	Toluene	54
18[h]	CuCl	**L1**	LiO^{t}Bu	Toluene	74

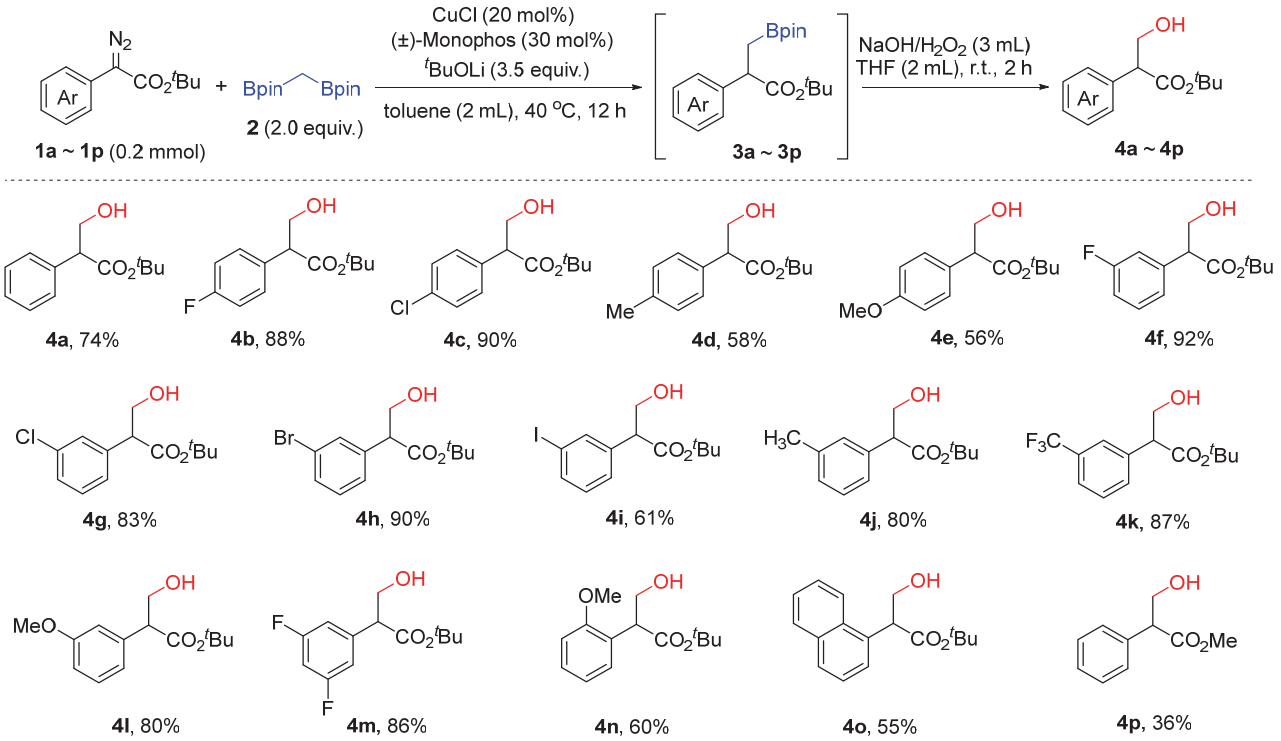
[a] If no otherwise noted, the reaction conditions are as following: *tert*-butyl 2-diazo-2-phenylacetate **1a** (0.1 mmol), diboronates **2** (2.0 equiv.), catalyst (0.005 mmol, 5 mol%), ligand (0.01 mmol, 10 mol%) and base (0.3 mmol, 3 equiv.) in toluene (1 mL) under 40 ℃ for 12 h. [b] Yields were determined by ^{1}H NMR (400 MHz) spectra of the crude products using CH_2Br_2 as the internal standard. [c] The ligands examined included: PPh_3, PCy_3•HBF_4, dppe, bpy, phen. [d] The bases examined included: MeOLi, MeONa, KOH, NaOH, CsF, KF, Cs_2CO_3, Ag_2O. [e] 10 mol% CuCl and 20 mol% **L1** were used. [f] 20 mol% CuCl and 40 mol% **L1** were used. [g] Adding the second part of **1a** one hour later. [h] Adding of the second part two hours later. [h] 30 mol% of **L1** was used.



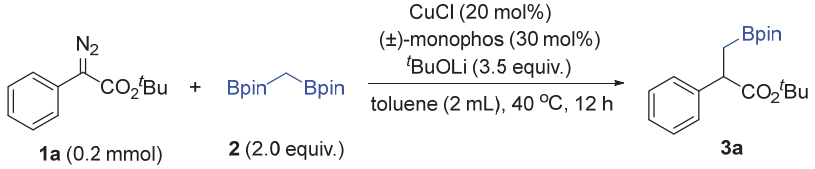
Scheme 2 Substrate scope of the Cu(I)-catalyzed reaction of diazoester with bis[(pinacolato)boryl]methane

in the yield was observed (**4p**). It was reasoned that the steric bulk of the ester group, which inhibited the dimerization of diazoacetates, might be attributed to low yield for methyl ester. The substituted *gem*-diboronates were also examined. However, no expected products were observed and protodeboronation of diboronates was detected by GC-MS. It was reasoned that the steric hindrance might inhibit the organocopper species to react with diazo compounds for the formation of copper carbene intermediate.

Further experiments were carried out for investigating the reaction mechanism (Scheme 4). When H_2O (1 equiv.) was added to the reaction system, neither the coupling products nor diboronates could be detected. It was speculated that methyl boronate was generated due to direct protodeboronation of bis[(pinacolato)boryl]methane **2**. However, because of the low boiling point of methyl boronate, it could not be detected by GC-MS.[7] When ethanol was added as the additive, the yield of **3a** was diminished as the loading of ethanol was increased. Adding molecular sieves as the additive led to the failure of the **3a** formation. These experiments indicated that the protonation in the termina-



Scheme 3 Substrate scope of the cross-coupling reaction/oxidation

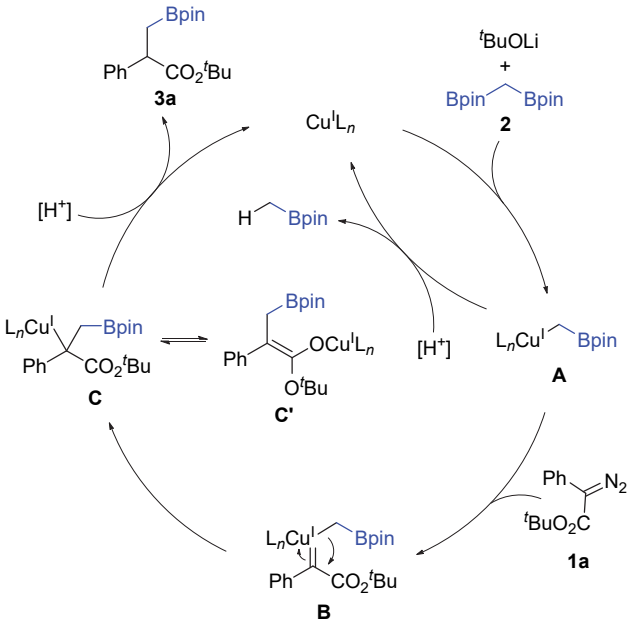


Additive: H_2O (1 equiv.), 0% yield of **3a** (^{1}H NMR)
Additive: EtOH (0.3 equiv.), 50% yield of **3a** (^{1}H NMR)
Additive: EtOH (1 equiv.), 30% yield of **3a** (^{1}H NMR)
Additive: 4 Å MS (100 mg), 0% yield of **3a** (^{1}H NMR)

Scheme 4 Effect of additives on the reaction

ting step of the catalytic cycle was caused by trace amounts of water from solvents and reagents. However, if an additional proton source was added, even in small amounts, the organocopper species formed by transmetalation would undergo protonation directly.

Considering the general reaction mechanism of the diazo compounds-involved coupling reaction,[1] it was proposed the catalytic cycle of the current reaction as following (Scheme 5). First, the catalyst undergoes transmetalation with diborylmethane **2** to form organocopper species **A** in the presence of LiO^{t}Bu. If other additive proton sources were added to the reaction system, direct protonation might occur readily. Thus, an unproductive catalytic cycle exists which leads to the consumption of diborylmethane **2**. Otherwise, it could react with diazo compounds to generate carbene species **B**, followed by migratory insertion to the Cu—CH_2Bpin bond, leading to a C(sp^3)—C(sp^3) bond formation. The α-ester copper intermediate **C** can be generated, which may be in equilibrium with copper enolate complex **C'**.[8] Finally, protonation of copper complexes **C** and **C'** affords the product **3a**.



Scheme 5 Proposed reaction mechanism

3 Conclusions

In conclusion, the cross-coupling reaction between aryldiazoacetates and bis[(pinacolato)boryl]methane for the construction of C(sp^3)—C(sp^3) bond has been developed. This is the first example to demonstrate Cu(I) carbene migratory insertion of borylmethyl group. Detailed condition optimization has revealed that the reaction is markedly affected by solvents, bases and ligands. Moreover, the presence of proton sources also affects the reaction. Oxidation of the coupling products without isolation affords the hydroxymethylated products. Further utilization of the enolate complex as nucleophiles to realize a three-components reaction as well as asymmetric catalysis is underway in our laboratory.

4 Experimental section

4.1 Instrument and reagents

^{1}H NMR spectra were recorded on a Bruker ARX 400 (400 MHz); ^{13}C NMR spectra were recorded on a Bruker ARX 400 (101 MHz). The data for NMR spectra were reported using tetramethylsilane as internal standard when using $CDCl_3$ as solvent. IR spectra were recorded on a Nicolet 5MX-S infrared spectrometer and were reported in terms of frequency of absorption (cm^{-1}). HRMS were obtained on a Bruker APEX IV FTMS. All reactions were performed under nitrogen atmosphere in an oven-dried reaction tube. Solvents were distilled under nitrogen atmosphere prior to use. Toluene, dioxane, and THF were dried over Na with benzophenoneketyl intermediate as indicator. MeCN was dried over CaH_2. The boiling point of petroleum ether is between 60 ℃ and 70 ℃. Unless otherwise noted, commercially available reagents were used as received. For chromatography, 200～300 mesh silica gel (Qingdao, China) was used.

4.2 General procedure for the copper-catalyzed coupling reaction

An oven-dried 10 mL Schlenk flask with magnetic stir bar was charged with bis[(pinacolato)boryl]methane **2** (0.4 mmol, 2 equiv.), CuCl (20 mol%), (±)-monophos (30 mol%) and ^{t}BuOLi (3.5 equiv.). The reaction flask was sealed with a rubber stopper, evacuated and filled with nitrogen for three times, followed by the addition of toluene (2 mL) and diazo substrate (0.05 mmol). The reaction mixture was stirred at 40 ℃ for 2 h. Then, the second part of diazo substrate (0.05 mmol) was added and stirring was continued for another 10 h. Upon completion of the reaction, the mixture was cooled to room temperature and filtered through a short plug of silica gel, rinsed with ethyl acetate. The filtrate was evaporated by rotary evaporation and purified by silica gel column chromatography to afford the pure product [V(petroleum ether)∶V(ethyl acetate)=15∶1].

4.3 General procedure for the coupling reaction/oxidation

An oven-dried 10 mL Schlenk flask with magnetic stir bar was charged with *gem*-diboronates **2** (0.4 mmol, 2 equiv.), CuCl (20 mol%), (±)-monophos (30 mol%) and ^{t}BuOLi (3.5 equiv.). The flask was sealed with a rubber stopper, evacuated and filled with nitrogen for three times, followed by the addition of toluene (2 mL) and diazo substrate (0.05 mmol). The reaction mixture was stirred at 40 ℃ for 2 h. Then, the second part of diazo substrate (0.05 mmol) was added and stirring was continued for another 10 h. Upon completion of the reaction, the mixture was cooled to room temperature and filtered through a short plug of silica gel, rinsed with ethyl acetate. The filtrate was evaporated by rotary evaporation and the crude product was

diluted with 2 mL of THF. The pre-prepared NaOH/H_2O_2 (2 mol/L, V∶V=2∶1, 3 mL) was added at 0 ℃. The reaction mixture was stirred for 2 h at room temperature. Upon completion of the reaction, the mixture was filtered through a short plug of silica gel, rinsed with ethyl acetate and purified by silica gel column chromatography to afford the pure product [V(petroleum ether)∶V(ethyl acetate)=2∶1].

4.4 Characterization of products

tert-Butyl 2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (**3a**): 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21～7.19 (m, 5H), 3.66 (dd, J=9.8, 6.8 Hz, 1H), 1.50～1.34 (m, 2H), 1.29 (s, 9H), 1.10 (d, J= 5.6 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.0, 141.8, 128.3, 127.6, 126.6, 83.2, 80.2, 48.0, 27.9, 24.7, 24.7; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 33.3; HRMS (ESI) calcd for $C_{19}H_{30}BO_4$ $[M+H]^+$ 333.2237, found 333.2228.

tert-Butyl 2-(*m*-cyanophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (**3b**): 42% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53～7.52 (m, 1H), 7.49～7.43 (m, 2H), 7.35～7.31 (m, 1H), 3.69 (dd, J=9.0, 7.4 Hz, 1H), 1.44 (dd, J=16.0, 9.0 Hz, 1H), 1.30 (s, 9H), 1.10 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.9, 143.1, 132.2, 131.6, 130.5, 129.1, 112.3, 83.4, 83.0, 47.6, 27.9, 24.7; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 33.6; HRMS (ESI) calcd for $C_{20}H_{29}BNO_4$ $[M+H]^+$ 358.2190, found 358.2179.

tert-Butyl 2-(naphthalen-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (**3c**): 31% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11～8.09 (m, 1H), 7.78～7.76 (m, 1H), 7.69～7.61 (m, 1H), 7.47～7.31 (m, 4H), 4.46 (dd, J=10.0, 6.4 Hz, 1H), 1.58 (dd, J=15.9, 10.0 Hz, 1H), 1.26 (s, 9H), 1.10 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.5, 138.4, 133.9, 131.4, 128.7, 127.2, 125.8, 125.5, 125.3, 123.9, 83.2, 27.9, 24.8, 24.6; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 33.7; HRMS (ESI) calcd for $C_{23}H_{32}BO_4$ $[M+H]^+$ 383.2394, found 383.2377.

tert-Butyl 3-hydroxy-2-phenylpropanoate (**4a**): 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41～7.27 (m, 4H), 7.25～7.23 (m, 1H), 4.13～4.00 (m, 1H), 3.84～3.69 (m, 2H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.5, 136.3, 131.4, 128.7, 128.1, 127.4, 124.2, 124.0, 117.8, 81.5, 64.8, 54.8, 28.0; HRMS (ESI) calcd for $C_{13}H_{19}O_3$ $[M+H]^+$ 223.1334, found 223.1326.

tert-Butyl 2-(*p*-fluorophenyl)-3-hydroxypropanoate (**4b**): 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27～7.20 (m, 2H), 7.06～6.98 (m, 2H), 4.03 (dd, J=10.8, 8.1 Hz, 1H), 3.81～3.65 (m, 2H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.3, 163.4, 160.9, 132.1, 132.1, 129.7, 129.6, 115.7, 115.5, 81.7, 64.6, 53.9, 27.9; HRMS (ESI) calcd for $C_{13}H_{18}FO_3$ $[M+H]^+$ 241.1240, found 241.1232.

tert-Butyl 2-(*p*-chlorophenyl)-3-hydroxypropanoate (**4c**): 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34～7.28 (m, 2H), 7.23～7.17 (m, 2H), 4.03 (dd, J=11.0, 8.3 Hz, 1H), 3.82～3.66 (m, 2H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.1, 134.8, 133.4, 129.4, 128.9, 81.8, 64.5, 54.0, 27.9; HRMS (ESI) calcd for $C_{13}H_{18}ClO_3$ $[M+H]^+$ 257.0944, found 257.0938.

tert-Butyl 3-hydroxy-2-(*p*-tolyl)propanoate (**4d**): 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.13 (s, 4H), 4.04 (dd, J=10.7, 8.1 Hz, 1H), 3.81～3.63 (m, 2H), 2.33 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.6, 137.1, 133.2, 129.4, 128.1, 127.9, 81.4, 64.9, 54.4, 28.0, 21.1; HRMS (ESI) calcd for $C_{14}H_{21}O_3$ $[M+H]^+$ 237.1491, found 237.1483.

tert-Butyl 3-hydroxy-2-(*p*-methoxyphenyl)propanoate (**4e**): 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21～7.14 (m, 2H), 6.89～6.83 (m, 2H), 4.03 (dd, J=11.0, 8.5 Hz, 1H), 3.79 (s, 3H), 3.77～3.66 (m, 2H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.7, 158.9, 129.1, 128.3, 114.1, 81.4, 64.8, 55.2, 53.9, 28.0; HRMS (ESI) calcd for $C_{14}H_{21}O_4$ $[M+H]^+$ 253.1440, found 253.1431.

tert-Butyl 2-(*m*-fluorophenyl)-3-hydroxypropanoate (**4f**): 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33～7.25 (m, 1H), 7.05～7.02 (m, 1H), 7.01~6.95 (m, 2H), 4.05 (dd, J=11.0, 8.3 Hz, 1H), 3.83～3.70 (m, 2H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.9, 164.1, 161.6, 138.7, 138.6, 130.2, 130.1, 123.8, 123.8, 115.2, 115.0, 114.5, 114.3, 81.9, 64.5, 54.4, 54.4, 27.9; HRMS (ESI) calcd for $C_{13}H_{18}FO_3$ $[M+H]^+$ 241.1240, found 241.1233.

tert-Butyl 2-(*m*-chlorophenyl)-3-hydroxypropanoate (**4g**): 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33～7.23 (m, 3H), 7.17～7.12 (m, 1H), 4.04 (dd, J=11.1, 8.4 Hz, 1H), 3.83～3.66 (m, 2H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.8, 138.2, 134.4, 129.9, 128.3, 127.7, 126.2, 81.9, 64.5, 54.3, 27.9; HRMS (ESI) calcd for $C_{13}H_{18}ClO_3$ $[M+H]^+$ 257.0944, found 257.0939.

tert-Butyl 2-(*m*-bromophenyl)-3-hydroxypropanoate (**4h**): 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45～7.39 (m, 2H), 7.22～7.16 (m, 2H), 4.03 (dd, J=11.2, 8.4 Hz, 1H), 3.83～3.61 (m, 2H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.8, 138.5, 131.2, 130.6, 130.2, 126.7, 122.6, 81.9, 64.5, 54.3, 27.9; HRMS (ESI) calcd for $C_{13}H_{18}BrO_3$ $[M+H]^+$ 301.0439, found 301.0436.

tert-Butyl 3-hydroxy-2-(*m*-iodophenyl)propanoate (**4i**): 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63～7.60 (m, 2H), 7.27～7.21 (m, 1H), 7.09～7.05 (m, 1H), 4.02 (dd, J=11.2, 8.4 Hz, 1H), 3.77 (dd, J=11.2, 5.2 Hz, 1H), 3.66 (dd, J=8.4, 5.1 Hz, 1H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.8, 138.6, 137.2, 136.5, 130.4, 127.3, 94.5, 81.92, 64.5, 54.2, 27.9; HRMS (ESI) calcd for $C_{13}H_{18}IO_3$ $[M+H]^+$ 349.0301, found 349.0288.

tert-Butyl 3-hydroxy-2-(*m*-tolyl)propanoate (**4j**): 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29～7.17 (m, 1H), 7.09～7.04 (m, 3H), 4.05 (dd, J=10.9, 8.4 Hz, 1H), 3.81～3.62 (m, 2H), 2.34 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.6, 138.3, 136.1, 128.8, 128.5, 128.2, 125.0, 81.4, 64.8, 54.7, 28.0, 21.4; HRMS (ESI) calcd for $C_{14}H_{21}O_3$ $[M+H]^+$ 237.1491, found 237.1481.

tert-Butyl 3-hydroxy-2-(*m*-(trifluoromethyl)phenyl)propanoate (**4k**): 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57～7.50 (m, 2H), 7.48～7.45 (m, 2H), 4.11～4.02 (m, 1H), 3.86～3.77 (m, 2H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.8, 137.4, 131.5, 129.1, 125.0, 124.3, 124.3,

82.1, 64.5, 54.4, 27.9; HRMS (ESI) calcd for $C_{14}H_{18}F_3O_3$ $[M+H]^+$ 291.1208, found 291.1202.

tert-Butyl 3-hydroxy-2-(*m*-methoxyphenyl)propanoate (**4l**): 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28～7.21 (m, 1H), 6.86～6.77 (m, 3H), 4.06 (dd, J=10.9, 8.4 Hz, 1H), 3.80 (s, 3H), 3.79～3.68 (m, 2H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.3, 159.7, 137.7, 129.7, 120.4, 113.8, 112.8, 81.5, 64.7, 55.2, 54.8, 28.0; HRMS (ESI) calcd for $C_{14}H_{21}O_4$ $[M+H]^+$ 253.1440, found 253.1431.

tert-Butyl 2-(3,5-difluorophenyl)-3-hydroxypropanoate (**4m**): 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.86～6.78 (m, 2H), 6.76～6.71 (m, 1H), 4.03 (dd, J=11.2, 8.1 Hz, 1H), 3.81 (dd, J=11.2, 5.1 Hz, 1H), 3.70 (dd, J=8.1, 5.1 Hz, 1H), 1.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.3, 161.8, 140.0, 111.3, 111.2, 111.1, 103.3, 103.0, 82.2, 74.8, 64.3, 54.2, 27.9; HRMS (ESI) calcd for $C_{13}H_{17}F_2O_3$ $[M+H]^+$ 259.1146, found 259.1144.

tert-Butyl 3-hydroxy-2-(2-methoxyphenyl)propanoate (**4n**): 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26～7.21 (m, 1H), 7.17～7.13 (m, 1H), 6.94～6.90 (m, 1H), 6.89～6.86 (m, 1H), 4.09～4.00 (m, 2H), 3.81 (s, 3H), 3.69 (dd, J=9.3, 2.8 Hz, 1H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.4, 156.9, 129.2, 128.5, 125.2, 120.6, 110.6, 81.2, 63.5, 55.3, 49.1, 28.0; HRMS (ESI) calcd for $C_{14}H_{21}O_4$ $[M+H]^+$ 253.1440, found 253.1436.

tert-Butyl 3-hydroxy-2-(naphthalen-1-yl)propanoate (**4o**): 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12～8.10 (m, 1H), 7.90～7.85 (m, 1H), 7.80～7.77 (m, 1H), 7.57～7.48 (m, 2H), 7.45～7.41 (m, 1H), 7.39～7.37 (m, 1H), 4.57 (dd, J=9.1, 4.6 Hz, 1H), 4.23 (dd, J=11.4, 9.1 Hz, 1H), 3.86 (dd, J=11.4, 4.6 Hz, 1H), 1.40 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.2, 134.0, 132.5, 131.5, 129.0, 128.0, 126.4, 125.7, 125.4, 125.2, 123.1, 81.7, 64.3, 50.6, 27.9; HRMS (ESI) calcd for $C_{17}H_{21}O_3$ $[M+H]^+$ 273.1491, found 273.1480.

Methyl 3-hydroxy-2-phenylpropanoate (**4p**): 36% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37～7.27 (m, 3H), 7.24 (s, 1H), 4.11～4.03 (m, 1H), 3.81～3.72 (m, 2H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 128.7, 128.1, 127.4, 81.5, 64.8, 54.8, 28.0; HRMS (ESI) calcd for $C_{10}H_{13}O_3$ $[M+H]^+$ 181.0865, found 181.0857.

Supporting Information Experimental procedure for the synthesis of α-diazophenylacetates, details of the optimization experiments for the coupling reaction, ^{1}H NMR and ^{13}C NMR spectra of **3a**～**3c** and **4a**～**4p**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

References

[1] For selected reviews, see:
(a) Liu, Z.; Zhang, Y.; Wang, J. *Chin. J. Org. Chem.* **2013**, *33*, 687 (in Chinese).
(刘振兴, 张艳, 王剑波, 有机化学, **2013**, *33*, 687.)
(b) Xia, Y.; Qiu, D.; Wang, J. *Chem. Rev.* **2017**, *117*, 13810.
(c) Liu, Z.; Sivaguru, P.; Zanoni, G.; Bi, X. *Acc. Chem. Res.* **2022**, *55*, 1763.
For selected recent examples, see:
(d) Xu, Z.-W.; Zhang, W.; Lin, J.-H.; Jin, C.-M.; Xiao, J.-C. *Chin. J. Chem.* **2020**, *38*, 1647.
(e) Liu, B.; Xu, M.-H. *Chin. J. Chem.* **2021**, *39*, 1911.
(f) Li, F.; Lu, B.; Liu, Y.; Wang, X. *Chin. J. Org. Chem.* **2022**, *42*, 3390 (in Chinese).
(李芳洁, 卢斌, 刘阳, 王晓明, 有机化学, **2022**, *42*, 3390.)
(g) Li, S.; Zhou, L. *Chin. J. Org. Chem.* **2022**, *42*, 3944.
(h) Shang, M.; Zhang, L.; Chen, M.; Hu, W.; He, X.; Lu, H. *Chin. J. Org. Chem.* **2022**, *42*, 3816 (in Chinese).
(商铭洲, 张兰兰, 陈淼淼, 胡汪成, 何心伟, 陆红健, 有机化学, **2022**, *42*, 3816.)
(i) Xia, J.; Gu, Z. *Chin. J. Chem.* **2020**, *38*, 1081.

[2] For selected examples of alkynes, see:
(a) Xiao, Q.; Xia, Y.; Li, H.; Zhang, Y.; Wang, J. *Angew. Chem., Int. Ed.* **2011**, *50*, 1114.
(b) Ye, F.; Ma, X.; Xiao, Q.; Li, H.; Zhang, Y.; Wang, J. *J. Am. Chem. Soc.* **2012**, *134*, 5742.
(c) Hossain, M. L.; Ye, F.; Zhang, Y.; Wang, J. *J. Org. Chem.* **2013**, *78*, 1236.
(d) Ye, F.; Hossain, M. L.; Xu, Y.; Ma, X.; Xiao, Q.; Zhang, Y.; Wang, J. *Chem.-Asian J.* **2013**, *8*, 1404.
(e) Ye, F.; Wang, C.; Ma, X.; Hossain, M. L.; Xia, Y.; Zhang, Y.; Wang, J. *J. Org. Chem.* **2015**, *80*, 647.
(f) Poh, J.-S.; Tran, D. N.; Battilocchio, C.; Hawkins, J. M.; Ley, S. V. *Angew. Chem., Int. Ed.* **2015**, *54*, 7920.
(g) Tang, Y.; Chen, Q.; Liu, X.; Wang, G.; Lin, L.; Feng, X. *Angew. Chem., Int. Ed.* **2015**, *54*, 9512.
(h) Chu, W.-D.; Zhang, L.; Zhang, Z.; Zhou, Q.; Mo, F.; Zhang, Y.; Wang, J. *J. Am. Chem. Soc.* **2016**, *138*, 14558.
For selected examples of arenes, see:
(i) Zhao, X.; Wu, G.; Zhang, Y.; Wang, J. *J. Am. Chem. Soc.* **2011**, *133*, 3296.
(j) Xiao, Q.; Ling, L.; Ye, F.; Tan, R.; Tian, L.; Zhang, Y.; Li, Y.; Wang, J. *J. Org. Chem.* **2013**, *78*, 3879.
(k) Xu, S.; Wu, G.; Ye, F.; Wang, X.; Li, H.; Zhao, X.; Zhang, Y.; Wang, J. *Angew. Chem., Int. Ed.* **2015**, *54*, 4669.

[3] For selected examples, see:
(a) Hu, M.; Ni, C.; Hu, J. *J. Am. Chem. Soc.* **2012**, *134*, 15257.
(b) Hu, M.; He, Z.; Gao, B.; Li, L.; Ni, C.; Hu, J. *J. Am. Chem. Soc.* **2013**, *135*, 17302.
(c) Wang, X.; Zhou, Y.; Ji, G.; Wu, G.; Li, M.; Zhang, Y.; Wang, J. *Eur. J. Org. Chem.* **2014**, 3093.
(d) Das, A.; Wang, D.; Belhomme, M. C.; Szabó, K. J. *Org. Lett.* **2015**, *17*, 4754.
(e) Xu, S.; Gao, Y.; Chen, R.; Wang, K.; Zhang, Y.; Wang, J. *Chem. Commun.* **2016**, *52*, 4478.
(f) Zhang, H.; Wu, G.; Yi, H.; Sun, T.; Wang, B.; Zhang, Y.; Dong, G.; Wang, J. *Angew. Chem., Int. Ed.* **2017**, *56*, 3945.

[4] For selected reviews, see:
(a) Paul, S.; Das, K. K.; Aich, D.; Manna, S.; Panda, S. *Org. Chem. Front.* **2022**, *9*, 838.
(b) Lee, Y.; Han, S.; Cho, S. H. *Acc. Chem. Res.* **2021**, *54*, 3917.
(c) Nallagonda, R.; Padala, K.; Masarwa, A. *Org. Biomol. Chem.* **2018**, *16*, 1050.
(d) Miralles, N.; Maza, R. J.; Fernández, E. *Adv. Synth. Catal.* **2018**, *360*, 1306.
(e) Wu, C.; Wang, J. *Tetrahedron Lett.* **2018**, *59*, 2128.
(f) Jo, W.; Lee, J. H.; Cho, S. H. *Chem. Commun.* **2021**, *57*, 4346.
(g) Xu, L.; Zhang, S.; Li, P. *Chem. Soc. Rev.* **2015**, *44*, 8848.

[5] Li, H.; Shangguan, X.; Zhang, Z.; Huang, S.; Zhang, Y.; Wang, J.

Org. Lett. **2014**, *16*, 448.
[6] For selected examples, see:
(a) Wu, C.; Bao, Z.; Dou, B.; Wang, J. *Chem.-Eur. J.* **2021**, *27*, 2294.
(b) Bao, Z.; Wu, C.; Wang, J. *Eur. J. Org. Chem.* **2022**, e202201264.
(c) Bao, Z.; Huang, M.; Xu, Y.; Zhang, X.; Wu, Y.-D.; Wang, J. *Angew. Chem.*, *Int. Ed.* **2023**, *62*, e202216356.
[7] Walton, J. C.; McCarroll, A. J.; Chen, Q.; Carboni, B.; Nziengui, R. *J. Am. Chem. Soc.* **2000**, *122*, 5455.
[8] Huang, Z.; Hartwig, J. F. *Angew. Chem.*, *Int. Ed.* **2012**, *51*, 1028.

(Cheng, F.)

