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Rh(I)-Catalyzed Arylation of α-Diazo Phosphonates with Aryl Boronic Acids: Synthesis of Diarylmethylphosphonates

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An efficient synthetic method for diarylmethylphosphonates is presented. A series of phosphonate derivatives with diverse functional groups can be accessed *via* a rhodium catalyzed cross−coupling reaction between α-diazo phosphonates and aryl boronic acids. Migratory insertion of rhodium carbene intermediates is postulated to be the critical step in this transformation.

Keywords Rh(I)-catalysis, metal carbene, migratory insertion, α-diazo phosphonates, aryl boronic acids

Introduction

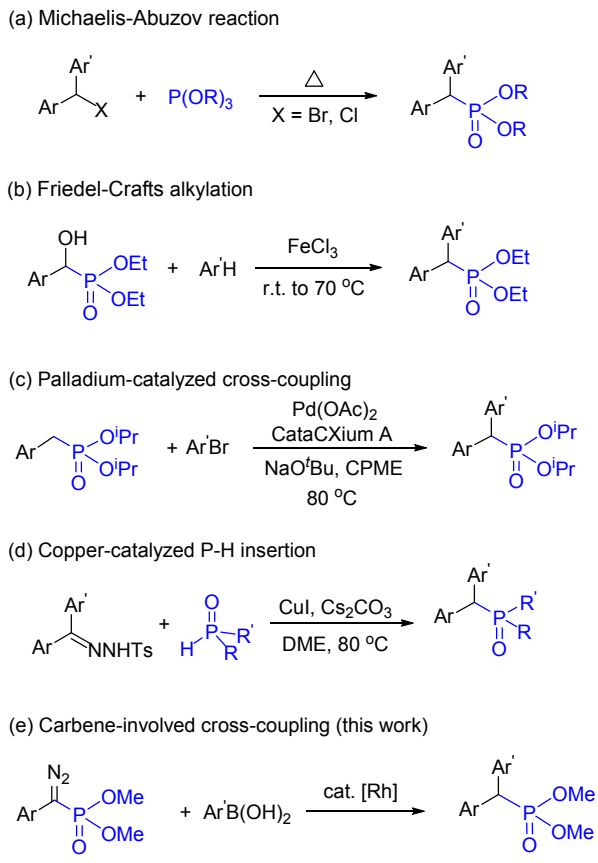
Organophosphorus compounds are of great importance because of their widespread applications in chemistry, biology and life sciences.[1] Especially, diarylmethylphosphonates are routinely found as structural elements in many natural products and bioactive molecules.[2] They can also be used as crucial building blocks in Horner-Wadsworth-Emmons olefination reactions.[3] Therefore, many efforts have been devoted to pursuing the efficient methods for the synthesis of this scaffold (Scheme 1).

One of the most commonly utilized methods is Michaelis-Arbuzov reaction by employing the alkyl halides and phosphites as the starting materials (Scheme 1a).[4] However, the inconvenient access of diarylmethyl halides and harsh reaction conditions prevent this transformation from becoming a practical synthetic method.

In 2013, a Friedel-Crafts type reaction was demonstrated to afford diarylmethylphosphonate compounds in relatively good yields (Scheme 1b).[5] However, the reaction suffered from several drawbacks such as limited arene scope and the formation of regioisomers. Subsequently, Walsh and co-workers disclosed a palladium-catalyzed α-arylation procedure to obtain the phosphonate derivatives (Scheme 1c).[6] In this case, a series of aryl bromides and benzylic phosphonates could be converted to the desired products in high yields with good functional group compatibility.

Additionally, several examples concerning the P-H insertion reaction of metal carbene intermediates have been described as complementary strategies for the synthesis of phosphonate molecules (Scheme 1d).[7] However, to the best of our knowledge, diaryl substi-

Scheme 1 Synthetic methods for diarylmethylphosphonates



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tuted hydrazones were not effective starting substrates in this transformation due to the steric hindrance. As a result, diarylmethylphosphonates cannot be generally accessed through this protocol. Considering the high importance of phosphorus functionality and limited synthetic methods currently available, further development of efficient and general approaches for the construction of diarylmethylphosphonate motifs is still highly desirable.

For the past decade, transition-metal-catalyzed carbene involved cross-coupling reactions have become an effective method for the C—C bond formations.[8] In particular, the Suzuki-type coupling of diazo compounds is frequently employed because organoboron reagents are usually non-toxic and stable, and many of them are commercially available.[9] On the other hand, we have recently disclosed several transformations of α-diazo phosphonates,[10] which have proved to be good substrates for the introduction of phosphonate moiety to the target molecules. As a continuation of our interest in carbene coupling reactions, we report herein a rhodium-catalyzed cross-coupling reaction between α-diazo phosphonates and aryl boronic acids. This reaction represents an efficient access toward diarylmethylphosphonates with diverse substituents.

Experimental

General procedure for the preparation of aryldiazophosphonates 1a—1g[11]

The diazo compounds **1a**—**1g** were prepared according to our previously reported method of palladium-catalyzed cross-coupling of dimethyl (1-diazo-2-oxopropyl)phosphonate with aryl iodide. The dimethyl (1-diazo-2-oxopropyl)phosphonate was prepared following a literature procedure.[12] A solution of dimethyl 2-oxopropylphosphonate (3.32 g, 20.0 mmol) in toluene (85 mL) and THF (18 mL) was stirred and cooled to 0 ℃ by ice-water bath for 30 min, and sodium hydride (60% in oil, 0.88 g, 22.0 mmol) was slowly added into the flask. The mixture was stirred at 0 ℃ under N_2 for 1 h, and *p*-ABSA (5.28 g, 22.0 mmol) was then added. The reaction was warmed to room temperature and stirring was continued overnight under N_2. The mixture was filtered through a *Celite* pad, and the filtrate was evaporated *in vacuo* to remove the volatile materials. The crude residue was purified by chromatography (silica gel, petroleum ether∶EtOAc=1∶1) to give the product as a yellow oil (2.38 g, 62%).

$Pd(PPh_3)_4$ (116 mg, 5 mol%), K_2CO_3 (552 mg, 4.0 mmol) and aryl iodide (2.0 mmol) were suspended in methanol (5 mL) and toluene (5 mL) in a 25 mL flask under ambient atmosphere. Dimethyl (1-diazo-2-oxopropyl)phosphonate (499 mg, 1.3 equiv.) was then added, and the resulting solution was stirred at room temperature for 5 h. The mixture was filtered through a short path of silica gel, eluting with ethyl acetate, and the filtrate was evaporated *in vacuo* to remove the volatile materials. The crude residue was purified by column chromatography (silica gel, petroleum ether∶EtOAc=1∶1) to afford the final products.

Dimethyl (diazo(phenyl)methyl)phosphonate (1a)[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34—7.38 (m, 2H), 7.13—7.17 (m, 3H), 3.81 (d, J=11.9 Hz, 6H).

Dimethyl (diazo(*p*-tolyl)methyl)phosphonate (1b)[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.17 (d, J=8.4 Hz, 2H), 7.06 (d, J=8.4 Hz, 2H), 3.80 (d, J=11.6 Hz, 6H), 2.33 (s, 3H).

Dimethyl ((4-chlorophenyl)(diazo)methyl)phosphonate (1c)[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31—7.34 (m, 2H), 7.08—7.11 (m, 2H), 3.82 (d, J=12.0 Hz, 6H).

Dimethyl ((4-bromophenyl)(diazo)methyl)phosphonate (1d)[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (d, J=8.6 Hz, 2H), 7.04 (d, J=8.6 Hz, 2H), 3.81 (d, J=11.9 Hz, 6H).

Dimethyl (diazo(4-methoxyphenyl)methyl)phosphonate (1e)[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.09—7.12 (m, 2H), 6.92—6.94 (m, 2H), 3.81 (d, J=12.0 Hz, 6H), 3.80 (s, 3H).

Methyl 4-(diazo(dimethoxyphosphoryl)methyl)-benzoate (1f)[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, J=8.5 Hz, 2H), 7.21 (d, J=8.5 Hz, 2H), 3.91 (s, 3H), 3.84 (d, J=12.0 Hz, 6H).

Dimethyl ((3-chlorophenyl)(diazo)methyl) phosphonate (1g) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (t, J=8.0 Hz, 1H), 7.11—7.14 (m, 2H), 7.04 (d, J=8.0 Hz, 1H), 3.83 (d, J=12.0 Hz, 6H).

Experimental procedure for the Rh(I)-catalyzed arylation reaction

A 10 mL Schlenk tube was charged with $[Rh(COD)Cl]_2$ (1 mg, 1 mol%), KO^{t}Bu (25 mg, 0.22 mmol, 1.1 equiv.) and aryl boronic acid (0.22 mmol, 1.1 equiv.). The tube was sealed and then evacuated and backfilled with N_2 three times. Then a solution of α-diazo phosphonate in methyl *tert*-butyl ether (MTBE) (0.20 mmol, 1.0 mL) was added, and the mixture was allowed to stir at 40 ℃ for 12 h. The mixture was filtered through a short path of silica gel, eluting with ethyl acetate, and the filtrate was evaporated *in vacuo* to remove the volatile materials. The crude residue was purified *via* column chromatography (silica gel, petroleum ether∶EtOAc=1∶1) to give the final products.

Dimethyl benzhydrylphosphonate (3a)[14] White solid, yield 92% (51 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52—7.54 (m, 4H), 7.32 (d, J=7.6 Hz, 4H), 7.23—7.278 (m, 2H), 4.46 (d, J=25.2 Hz, 1H), 3.56 (d, J=10.8 Hz, 6H).

Dimethyl ((4-chlorophenyl)(phenyl)methyl)phosphonate (3b) Colorless oil, yield 95% (60 mg), R_f=0.40 (petroleum ether∶EtOAc=1∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44—7.49 (m, 4H), 7.24—7.35 (m, 5H), 4.43 (d, J=25.2 Hz, 1H), 3.59 (d, J=10.8 Hz, 3H), 3.55 (d, J=10.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.9 (d, J=5.1 Hz), 135.0 (d, J=5.2 Hz), 133.2 (d, J=

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2.6 Hz), 130.6 (d, J=8.0 Hz), 129.2 (d, J=7.9 Hz), 128.8 (d, J=1.0 Hz), 128.8 (d, J=1.1 Hz), 127.5 (d, J=2.0 Hz), 53.5 (d, J=7.1 Hz), 53.4 (d, J=7.2 Hz), 50.0 (d, J=138.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 26.86; IR (film) v: 1490, 1251, 1055, 1030, 1016, 826, 755, 730, 699 cm^{-1}; EI-MS (m/z, relative intensity): 310 (28), 201 (100), 165 (64); HRMS (ESI) calcd for $C_{15}H_{17}ClO_3P$ $(M+H)^+$ 311.0598, found 311.0592.

Dimethyl ((4-methoxyphenyl)(phenyl)methyl)-phosphonate (3c) Colorless solid, yield 96% (59 mg), R_f=0.30 (petroleum ether∶EtOAc=1∶1), m.p. 91−93 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49−7.51 (m, 2H), 7.43−7.45 (m, 2H), 7.31 (t, J=7.6 Hz, 2H), 7.22−7.26 (m, 1H), 6.85−6.87 (m, 2H), 4.41 (d, J=25.2 Hz, 1H), 3.77 (s, 3H), 3.55 (d, J=10.8 Hz, 3H), 3.54 (d, J=10.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.7 (d, J=2.0 Hz), 136.8 (d, J=4.9 Hz), 130.4 (d, J=8.0 Hz), 129.2 (d, J=8.0 Hz), 128.6 (d, J=0.9 Hz), 128.4 (d, J=5.3 Hz), 127.1 (d, J=1.9 Hz), 114.0 (d, J=0.9 Hz), 55.1, 53.3 (d, J=7.1 Hz), 53.3 (d, J=6.9 Hz), 49.8 (d, J=137.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 27.68; IR (film) v: 1511, 1252, 1181, 1055, 1028, 822, 770, 734, 700 cm^{-1}; EI-MS (m/z, relative intensity): 306 (12), 197 (100), 153(12); HRMS (ESI) calcd for $C_{16}H_{20}O_4P$ $(M+H)^+$ 307.1094, found 307.1090.

Dimethyl ([1,1'-biphenyl]-4-yl(phenyl)methyl)-phosphonate (3d) White solid, yield 68% (48 mg), R_f=0.35 (petroleum ether∶EtOAc=1∶1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54−7.61 (m, 8H), 7.39−7.43 (m, 2H), 7.30−7.36 (m, 3H), 7.24−7.28 (m, 1H), 4.50 (d, J=25.2 Hz, 1H), 3.59 (t, J=10.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.5, 140.1 (d, J=2.3 Hz), 136.4 (d, J=5.3 Hz), 135.5 (d, J=5.6 Hz), 129.7 (d, J=7.9 Hz), 129.4 (d, J=8.0 Hz), 128.7, 127.3 (d, J=1.1 Hz), 127.3, 127.3, 127.0, 53.4 (t, J=7.6 Hz), 50.5 (d, J=137.5 Hz) (One peak is missing because of overlap); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 27.33; IR (film) v: 1488, 1250, 1055, 1030, 823, 762, 731, 698 cm^{-1}; EI-MS (m/z, relative intensity): 352 (23), 243 (100), 228 (8), 165 (14); HRMS (ESI) calcd for $C_{21}H_{22}O_3P$ [$(M+H)^+$] 353.1301, found 353.1296.

Dimethyl ((3-bromophenyl)(phenyl)methyl)phosphonate (3e) Colorless oil, yield 97% (69 mg), R_f=0.40 (petroleum ether∶EtOAc=1∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62−7.63 (m, 1H), 7.50−7.53 (m, 3H), 7.32−7.39 (m, 3H), 7.25−7.29 (m, 1H), 7.20 (t, J=8.0 Hz, 1H), 4.41 (d, J=25.2 Hz, 1H), 3.60 (d, J=10.8 Hz, 3H), 3.55 (d, J=10.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.8 (d, J=5.0 Hz), 135.7 (d, J=5.2 Hz), 132.3 (d, J=8.6 Hz), 130.4 (d, J=1.8 Hz), 130.1 (d, J=1.2 Hz), 129.3 (d, J=7.7 Hz), 128.8, 127.9 (d, J=7.6 Hz), 127.5 (d, J=2.0 Hz), 122.6, 53.5 (d, J=6.8 Hz), 53.3 (d, J=7.0 Hz), 50.3 (d, J=138.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 26.55; IR (film) v: 1251, 1055, 1029, 826, 762, 729, 704 cm^{-1}; EI-MS (m/z, relative intensity): 354 (26), 245 (100), 165 (96); HRMS (ESI) calcd for $C_{15}H_{17}BrO_3P$ [$(M+H)^+$] 355.0093, found 355.0089.

Dimethyl ((3-methoxyphenyl)(phenyl)methyl)-phosphonate (3f) Colorless oil, yield 79% (48 mg), R_f=0.30 (petroleum ether∶EtOAc=1∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51−7.53 (m, 2H), 7.32 (t, J=8.0 Hz, 2H), 7.21−7.26 (m, 2H), 7.08−7.13 (m, 2H), 7.78−7.81 (m, 1H), 4.43 (d, J=24.8 Hz, 1H), 3.78 (s, 3H), 3.58 (d, J=10.8 Hz, 3H), 3.56 (d, J=10.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.6, 137.8 (d, J=5.1 Hz), 136.3 (d, J=5.6 Hz), 129.6, 129.3 (d, J=7.9 Hz), 128.6, 127.2 (d, J=2.1 Hz), 121.7 (d, J=7.9 Hz), 115.2 (d, J=8.3 Hz), 112.6 (d, J=2.1 Hz), 55.1, 53.4 (d, J=7.1 Hz), 53.4 (d, J=7.1 Hz), 50.7 (d, J=137.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 27.30; IR (film) v: 1597, 1490, 1252, 1030, 829, 732, 703 cm^{-1}; EI-MS (m/z, relative intensity): 306 (35), 197 (100), 182 (18), 165 (19), 153 (6); HRMS (ESI) calcd for $C_{16}H_{20}O_4P$ [$(M+H)^+$] 307.1094, found 307.1092.

Dimethyl (phenyl(3-(trifluoromethoxy)phenyl)-methyl)phosphonate (3g) Colorless oil, yield 88% (63 mg), R_f=0.60 (petroleum ether∶EtOAc=1∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45−7.51 (m, 3H), 7.40 (s, 1H), 7.34 (t, J=7.6 Hz, 3H), 7.26−7.30 (m, 1H), 7.11−7.13 (m, 1H), 4.47 (d, J=25.2 Hz, 1H), 3.59 (d, J=10.8 Hz, 3H), 3.55 (d, J=10.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.2, 138.8 (d, J=5.2 Hz), 135.6 (d, J=5.4 Hz), 129.9, 129.3 (d, J=7.8 Hz), 128.8 (d, J=1.1 Hz), 127.7 (d, J=7.8 Hz), 127.6 (d, J=2.0 Hz), 122.0 (d, J=7.9 Hz), 120.4 (q, J=255.6 Hz), 119.6, 53.5 (d, J=7.0 Hz), 53.3 (d, J=6.9 Hz), 50.4 (d, J=138.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 26.41; IR (film) v: 1258, 1215, 1166, 1031, 832, 736, 703 cm^{-1}; EI-MS (m/z, relative intensity): 360 (32), 251 (100), 165 (40); HRMS (ESI) calcd for $C_{16}H_{17}F_3O_4P$ [$(M+H)^+$] 361.0811, found 361.0806.

Dimethyl ((3,5-dimethylphenyl)(phenyl)methyl)-phosphonate (3h) Colorless oil, yield 90% (55 mg), R_f=0.40 (petroleum ether∶EtOAc=1∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51−7.52 (m, 2H), 7.31 (t, J=7.6 Hz, 2H), 7.23−7.25 (m, 1H), 7.13 (s, 2H), 6.88 (s, 1H), 4.38 (d, J=25.2 Hz, 1H), 3.57 (d, J=10.8 Hz, 3H), 3.54 (d, J=10.8 Hz, 3H), 2.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.1, 136.7 (d, J=5.4 Hz), 136.2 (d, J=5.1 Hz), 129.3 (d, J=8.0 Hz), 129.0 (d, J=1.9 Hz), 128.6 (d, J=1.1 Hz), 127.1 (d, J=2.2 Hz), 127.0 (d, J=8.5 Hz), 53.3 (d, J=7.2 Hz), 53.3 (d, J=7.1 Hz), 50.7 (d, J=137.2 Hz), 21.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 27.64; IR (film) v: 1251, 1056, 1030, 827, 711, 696 cm^{-1}; EI-MS (m/z, relative intensity): 304 (34), 195 (100), 180 (31), 165 (35); HRMS (ESI) calcd for $C_{17}H_{22}O_3P$ [$(M+H)^+$] 305.1301, found 305.1299.

Dimethyl (phenyl(*o*-tolyl)methyl)phosphonate (3i) Colorless oil, yield 95% (55 mg), R_f=0.40 (petroleum ether∶EtOAc=1∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, J=7.6 Hz, 1H), 7.46 (d, J=7.6 Hz, 2H), 7.20−7.29 (m, 4H), 7.14−7.18 (m, 2H), 4.70 (d, J=26.0 Hz, 1H), 3.55 (d, J=10.8 Hz, 3H), 3.55 (d, J=10.8 Hz, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.3 (d, J=11.9 Hz), 135.9 (d, J=5.8 Hz), 134.9 (d, J=3.8 Hz),

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130.7, 129.6 (d, J=7.4 Hz), 129.3 (d, J=5.4 Hz), 128.5 (d, J=1.4 Hz), 127.2 (d, J=1.2 Hz), 127.1 (d, J=2.4 Hz), 126.2 (d, J=1.4 Hz), 53.3 (d, J=7.1 Hz), 53.2 (d, J=6.9 Hz), 46.2 (d, J=138.7 Hz), 19.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 28.27; IR (film) ν: 1495, 1453, 1252, 1054, 1028, 823, 737, 699 cm^{-1}; EI-MS (m/z, relative intensity): 290 (42), 181 (100), 165 (51); HRMS (ESI) calcd for $C_{16}H_{20}O_3P$ [$(M+H)^+$] 291.1145, found 291.1149.

Dimethyl (naphthalen-2-yl(phenyl)methyl)phosphonate (3j) Colorless oil, yield 97% (63 mg), R_f=0.35 (petroleum ether∶EtOAc=1∶1), m.p. 69−71 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.02 (s, 1H), 7.77−7.84 (m, 3H), 7.57−7.63 (m, 3H), 7.41−7.48 (m, 2H), 7.33 (t, J=7.6 Hz, 2H), 7.22−7.26 (m, 1H), 4.63 (d, J=25.2 Hz, 1H), 3.58 (d, J=10.8 Hz, 3H), 3.55 (d, J=10.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.4 (d, J=5.3 Hz), 134.0 (d, J=5.4 Hz), 133.3 (d, J=1.2 Hz), 132.4 (d, J=1.2 Hz), 129.4 (d, J=8.0 Hz), 128.7 (d, J=1.0 Hz), 128.3, 128.1 (d, J=8.8 Hz), 128.0, 127.5, 127.4 (d, J=7.8 Hz), 127.3 (d, J=2.0 Hz), 126.1, 126.0, 53.4 (d, J=7.1 Hz), 50.8 (d, J=137.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 27.31; IR (film) ν: 1250, 1056, 1030, 828, 730, 699 cm^{-1}; EI-MS (m/z, relative intensity): 326 (23), 277 (16), 236 (19), 217 (100), 202 (25); HRMS (ESI) calcd for $C_{19}H_{20}O_3P$ [$(M+H)^+$] 327.1145, found 327.1137.

Methyl 4-((dimethoxyphosphoryl)(phenyl)methyl)-benzoate (3k) Colorless oil, yield 45% (30 mg), R_f=0.30 (petroleum ether∶EtOAc=1∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (d, J=8.4 Hz, 2H), 7.61 (dd, J=8.4, 1.6 Hz, 2H), 7.50−7.52 (m, 2H), 7.34 (t, J=7.6 Hz, 2H), 7.27−7.30 (m, 1H), 4.52 (d, J=25.2 Hz, 1H), 3.89 (s, 3H), 3.58 (d, J=10.8 Hz, 3H), 3.56 (d, J=10.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.7, 141.7 (d, J=5.2 Hz), 135.7 (d, J=5.6 Hz), 129.9, 129.4 (d, J=7.8 Hz), 129.3 (d, J=7.8 Hz), 129.1 (d, J=1.8 Hz), 128.8, 127.5 (d, J=2.0 Hz), 53.6 (d, J=6.8 Hz), 53.4 (d, J=7.2 Hz), 52.1, 50.8 (d, J=137.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 26.40; IR (film) ν: 1722, 1282, 1253, 1109, 1056, 1030, 757, 733, 709 cm^{-1}; EI-MS (m/z, relative intensity): 334 (18), 225 (100), 207 (15), 165 (42); HRMS (ESI) calcd for $C_{17}H_{20}O_5P$ [$(M+H)^+$] 335.1043, found 335.1054.

Dimethyl (phenyl(*p*-tolyl)methyl)phosphonate (4a) White solid, yield 93% (54 mg), R_f=0.40 (petroleum ether∶EtOAc=1∶1); m.p. 63−65 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 (d, J=7.6 Hz, 2H), 7.41 (d, J=6.8 Hz, 2H), 7.31 (t, J=7.6 Hz, 2H), 7.21−7.25 (m, 1H), 7.13 (d, J=7.6 Hz, 2H), 4.41 (d, J=25.2 Hz, 1H), 3.56 (d, J=10.8 Hz, 3H), 3.54 (d, J=10.8 Hz, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.8 (d, J=2.2 Hz), 136.7 (d, J=5.1 Hz), 133.5 (d, J=5.2 Hz), 129.3 (d, J=1.1 Hz), 129.2 (d, J=8.2 Hz), 129.1 (d, J=8.1 Hz), 128.7 (d, J=1.0 Hz), 127.1 (d, J=2.1 Hz), 53.3 (d, J=7.2 Hz), 53.3 (d, J=6.7 Hz), 50.4 (d, J=137.4 Hz), 21.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 27.65; IR (film) ν: 1513, 1495, 1453, 1252, 1057, 1030, 824, 732, 699 cm^{-1}; EI-MS (m/z, relative intensity): 290 (14), 181 (100), 165 (31); HRMS (ESI) calcd for $C_{16}H_{20}O_3P$ [$(M+H)^+$] 291.1145, found 291.1153.

Dimethyl (di-*p*-tolylmethyl)phosphonate (4b) Colorless oil, yield 89% (54 mg), R_f=0.40 (petroleum ether∶EtOAc=1∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (dd, J=8.0, 1.6 Hz, 4H), 7.11 (d, J=8.0 Hz, 4H), 4.39 (d, J=24.8 Hz, 1H), 3.57 (d, J=10.8 Hz, 6H), 2.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.8 (d, J=2.3 Hz), 133.6 (d, J=5.2 Hz), 129.3, 129.1 (d, J=8.1 Hz), 53.3 (d, J=6.9 Hz), 49.9 (d, J=137.6 Hz), 21.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 27.87; IR (film) ν: 1521, 1253, 1056, 1031, 864, 826, 750, 730 cm^{-1}; EI-MS (m/z, relative intensity): 304 (22), 195 (100), 180 (34), 165 (44); HRMS (ESI) calcd for $C_{17}H_{22}O_3P$ [$(M+H)^+$] 305.1301, found 305.1297.

Dimethyl ((4-chlorophenyl)(*p*-tolyl)methyl)phosphonate (4c) Colorless oil, yield 77% (50 mg), R_f=0.40 (petroleum ether∶EtOAc=1∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (dd, J=8.4, 2.0 Hz, 2H), 7.37 (dd, J=8.0, 2.0 Hz, 2H), 7.28 (d, J=8.4 Hz, 2H), 7.13 (d, J=8.0 Hz, 2H), 4.39 (d, J=25.2 Hz, 1H), 3.57 (t, J=10.4 Hz, 6H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.2 (d, J=2.1 Hz), 135.3 (d, J=5.2 Hz), 133.1 (d, J=2.5 Hz), 132.9 (d, J=5.3 Hz), 130.6 (d, J=7.9 Hz), 129.5, 129.1 (d, J=8.0 Hz), 128.8 (d, J=1.1 Hz), 53.5 (d, J=7.1 Hz), 53.3 (d, J=7.2 Hz), 49.6 (d, J=138.0 Hz), 21.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 27.07; IR (film) ν: 1489, 1252, 1056, 1031, 827, 756, 730 cm^{-1}; EI-MS (m/z, relative intensity): 324 (18), 215 (100), 180 (35), 165 (46), 109 (8); HRMS (ESI) calcd for $C_{16}H_{19}ClO_3P$ [$(M+H)^+$] 325.0755, found 325.0759.

Dimethyl ((4-bromophenyl)(*p*-tolyl)methyl)phosphonate (4d) Colorless oil, yield 63% (46 mg), R_f=0.40 (petroleum ether∶EtOAc=1∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (d, J=8.4 Hz, 2H), 7.35−7.40 (m, 4H), 7.13 (d, J=8.0 Hz, 2H), 4.38 (d, J=25.2 Hz, 1H), 3.57 (t, J=10.8 Hz, 6H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.2 (d, J=2.2 Hz), 135.9 (d, J=5.1 Hz), 132.8 (d, J=5.2 Hz), 131.7, 131.0 (d, J=7.9 Hz), 129.5 (d, J=1.0 Hz), 129.1 (d, J=7.9 Hz), 121.3 (d, J=2.9 Hz), 53.5 (d, J=6.9 Hz), 53.3 (d, J=7.2 Hz), 49.7 (d, J=138.4 Hz), 21.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 26.92; IR (film) ν: 1486, 1251, 1054, 1032, 826, 754, 731 cm^{-1}; EI-MS (m/z, relative intensity): 368 (16), 259 (100), 180 (28), 165 (65); HRMS (ESI) calcd for $C_{16}H_{19}BrO_3P$ [$(M+H)^+$] 369.0250, found 369.0255.

Dimethyl ((4-methoxyphenyl)(*p*-tolyl)methyl)-phosphonate (4e) Colorless oil, yield 84% (54 mg), R_f=0.30 (petroleum ether∶EtOAc=1∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38−7.43 (m, 4H), 7.12 (d, J=8.0 Hz, 2H), 6.85 (d, J=8.4 Hz, 2H), 4.37 (d, J=25.6 Hz, 1H), 3.76 (s, 3H), 3.56 (d, J=10.8 Hz, 6H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.6 (d, J=2.1 Hz), 136.8 (d, J=2.3 Hz), 133.8 (d, J=4.8 Hz), 130.3 (d, J=8.0 Hz), 129.3 (d, J=1.0 Hz), 129.1 (d, J=8.0 Hz), 128.7 (d, J=5.3 Hz), 114.0 (d, J=1.1 Hz), 55.1, 53.3 (d, J=7.0 Hz), 53.3 (d, J=7.2 Hz), 49.4 (d, J=137.9 Hz), 21.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 27.92; IR (film) ν:

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1511, 1252, 1181, 1057, 1030, 823, 754, 729 cm^{-1}; EI-MS (*m*/*z*, relative intensity): 320 (9), 211 (100), 165 (5); HRMS (ESI) calcd for $C_{17}H_{22}O_4P$ [$(M+H)^+$] 321.1250, found 321.1250.

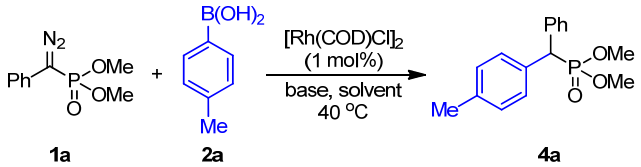
Methyl 4-((dimethoxyphosphoryl)(*p*-tolyl)methyl) benzoate (4f) Colorless solid, yield 95% (66 mg), R_f = 0.30 (petroleum ether : EtOAc = 1 : 1); m.p. 99—102 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99 (d, J=8.0 Hz, 2H), 7.59 (dd, J=8.0, 1.6 Hz, 2H), 7.31 (dd, J=8.0, 1.6 Hz, 2H), 7.14 (d, J=8.0 Hz, 2H), 4.49 (d, J=25.2 Hz, 1H), 3.89 (s, 3H), 3.57 (d, J=10.8 Hz, 3H), 3.57 (d, J=10.8 Hz, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.7, 141.9 (d, J=5.0 Hz), 137.2 (d, J=2.2 Hz), 132.6 (d, J=5.6 Hz), 129.8 (d, J=0.9 Hz), 129.5 (d, J=1.0 Hz), 129.3 (d, J=7.8 Hz), 129.1 (d, J=8.0 Hz), 128.9 (d, J=2.1 Hz), 53.5 (d, J=7.1 Hz), 53.3 (d, J=7.2 Hz), 50.3 (d, J=137.7 Hz), 20.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 26.71; IR (film) v: 1722, 1609, 1436, 1281, 1253, 1189, 1112, 1031, 1022, 824, 745 cm^{-1}; EI-MS (*m*/*z*, relative intensity): 348 (10), 239 (100), 180 (11), 165 (18); HRMS (ESI) calcd for $C_{18}H_{22}O_5P$ [$(M+H)^+$] 349.1199, found 349.1195.

Dimethyl ((3-chlorophenyl)(*p*-tolyl)methyl)phosphonate (4g) Colorless oil, yield 86% (56 mg), R_f= 0.40 (petroleum ether : EtOAc = 1 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43—7.47 (m, 2H), 7.38 (dd, J=8.0, 1.6 Hz, 2H), 7.20—7.27 (m, 2H), 7.14 (d, J=8.4 Hz, 2H), 4.39 (d, J=25.2 Hz, 1H), 3.60 (d, J=10.8 Hz, 3H), 3.56 (d, J=10.8 Hz, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.7 (d, J=5.0 Hz), 137.2 (d, J=2.1 Hz), 134.3, 132.7 (d, J=5.4 Hz), 129.8 (d, J=1.2 Hz), 129.5, 129.3 (d, J=8.4 Hz), 129.2 (d, J=7.9 Hz), 127.5, 127.4, 53.6 (d, J=6.9 Hz), 53.3 (d, J=7.2 Hz), 50.0 (d, J=138.4 Hz), 21.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 26.83; IR (film) v: 1252, 1056, 1031, 906, 830, 753, 729, 692 cm^{-1}; EI-MS (*m*/*z*, relative intensity): 324 (20), 215 (100), 180 (28), 165 (30); HRMS (ESI) calcd for $C_{16}H_{19}ClO_3P$ [$(M+H)^+$] 325.0755, found 325.0747.

Results and Discussion

We initiated our investigation by examining the cross coupling reactions between diazo compound **1a** and boronic acid **2a** under conditions similar to those previously developed for the carboxylic acid ester analogues (Table 1).[9e] When toluene was employed as the solvent, only trace amount of coupling product was detected by GC-MS analysis (Entry 1). Then several solvents were screened (Entries 2—5). To our delight, although most solvents tested were ineffective to promote the reaction, methyl *tert*-butyl ether (MTBE) afforded the desired diarylmethylphosphonate in excellent yield (Entry 5). Further decreasing the substrate ratio to 1 : 1 resulted in a slightly diminished yield (Entry 6), but 1.1 equivalents of boronic acid led to the full conversion of diazo compound, giving the final product in 93% isolated yield (Entry 7). Replacing the KO^{t}Bu with weak base K_3PO_4 has little influence on the reaction efficiency (88% isolated yield), but it caused complicated problems for isolation of the product (Entry 8).[15]

Table 1 Optimization of reaction conditions[a]



1a **2a** **4a**

Entry	Solvent	Base (equiv)	**1a** : **2a**	Yield[b]/%
1	toluene	KO^{t}Bu (2.0)	1 : 2	*trace*
2	DMF	KO^{t}Bu (2.0)	1 : 2	*trace*
3	1,4-dioxane	KO^{t}Bu (2.0)	1 : 2	*trace*
4	DCE	KO^{t}Bu (2.0)	1 : 2	*trace*
5	MTBE	KO^{t}Bu (2.0)	1 : 2	90
6	MTBE	KO^{t}Bu (1.0)	1 : 1	85
7	MTBE	KO^{t}Bu (1.1)	1 : 1.1	93
8	MTBE	K_3PO_4 (1.1)	1 : 1.1	88

[a] If not otherwise noted, all the reactions were carried out with 0.20 mmol scale in the corresponding solvent (0.20 mol•L^{-1}) under N_2 atmosphere for 12 h. [b] Isolated yield.

With the optimized reaction conditions in hand, we set out to explore the substrate scope of this protocol (Scheme 2). A variety of readily accessible boronic acids were subjected to the standard conditions. Although phenyl boronic acid afforded the coupling product in excellent yield, the conversion of **1a** is low when *para*-chloro substrate was used. We postulated that the transmetallation process was probably the turnover-limiting step of this reaction, and electron-deficient boronic acids usually result in a slower transmetallation compared to their electron-rich counterparts. To overcome the problems associated with this key process, the reaction was carried out at a higher temperature in some cases. Gratifyingly, substrates with weak electron-withdrawing groups (**3b**, **3e**, **3f**) and sterically hindered substituents (**3i**) underwent the reaction smoothly, generating the corresponding diarylmethylphosphonate scaffolds with satisfying results. However, switching the substrate to 4-methoxycarbonylphenylboronic acid, the yield decreased dramatically. The desired product was only afforded in 45% isolated yield albeit 2 mol% rhodium catalyst and 2 equivalents of boronic acid were employed (**3k**).

In efforts to extend the cross coupling procedure to heteroaryl and alkenyl boronic acids, we found that only trace amount of desired products were generated (Scheme 3). The unsuccessful transformation may be due to the deactivation of catalysts by the basic heteroatoms or carbon-carbon double bond. Alkyl boronic acids, which are more reluctant to undergo the transmetallation and prone to undergo side reactions, were also unsuitable for this protocol.

Subsequently, we turned our attention to the scope of α-diazo phosphonate derivatives (Scheme 4). The diazo

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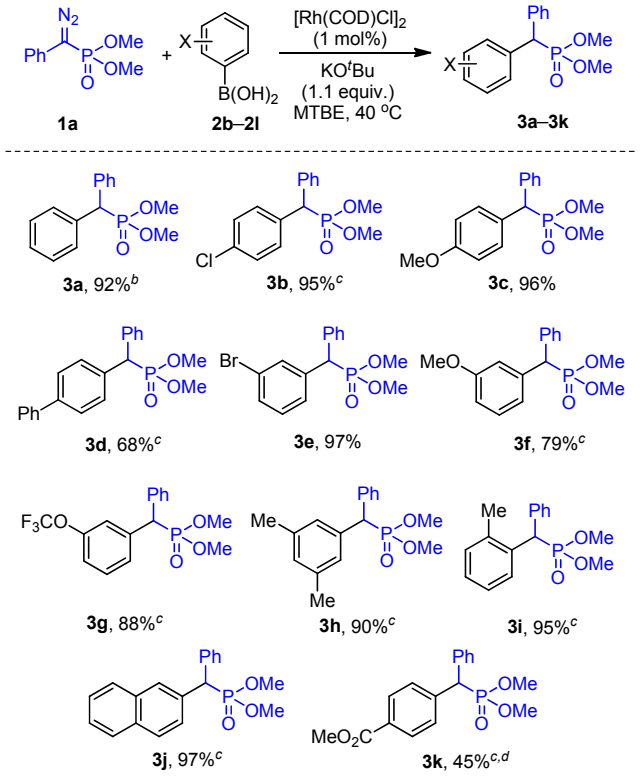
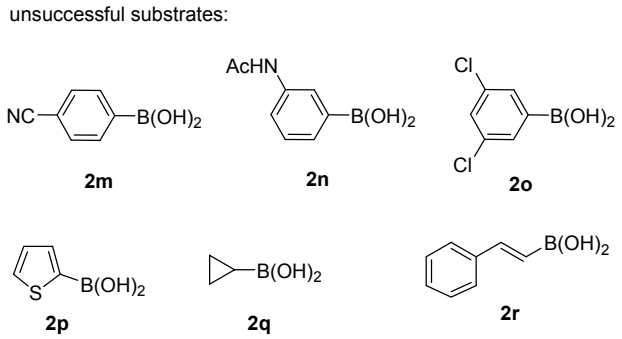
Scheme 2 Substrate scope of boronic acids[a]



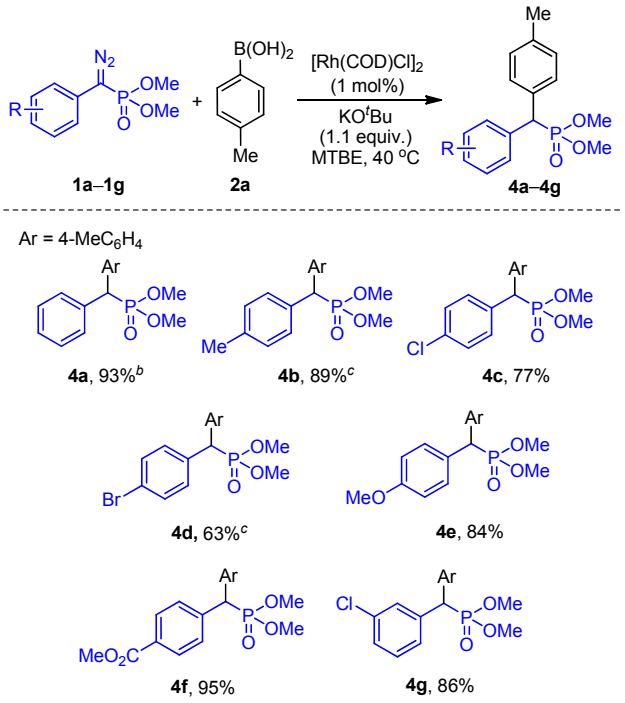
[a] If not otherwise noted, all the reactions were carried out with **1a** (0.20 mmol), **2b**—**2k** (0.22 mmol), $[Rh(COD)Cl]_2$ (1 mol%), KO^{t}Bu (0.22 mmol) in MTBE (1.0 mL) under N_2 atmosphere at 40 ℃ for 12 h. [b] Isolated yield. [c] The reaction was carried out at 60 ℃. [d] $[Rh(COD)Cl]_2$ (2 mol%), **2l** (0.40 mmol), KO^{t}Bu (0.40 mmol) were used.

Scheme 3 Scope limitation of boronic acids



compounds bearing both electron-donating and electron-withdrawing substituents are efficient coupling partners in this reaction, furnishing the desired products in good to excellent yields. As mentioned before, boronic acids with electron-withdrawing groups show undesirable reactivity in this transformation. If we need to synthesize a diarylmethylphosphonate with one electron-deficient aryl ring and one electron-rich aryl ring, we can improve the efficiency by reasonably choosing the starting substrates. Additionally, halogen atoms and ester functionality were well tolerated under current catalytic system.

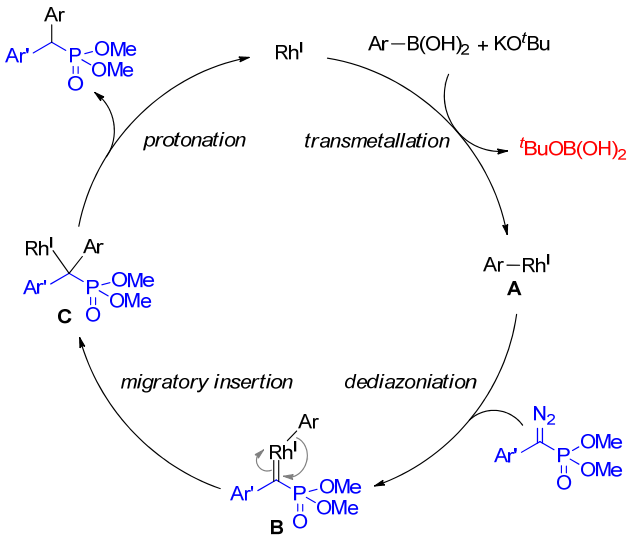
Scheme 4 Substrate scope of α-diazo phosphonates[a]



[a] If not otherwise noted, all the reactions were carried out with **1** (0.20 mmol), **2a** (0.22 mmol), $[Rh(COD)Cl]_2$ (1 mol%), KO^{t}Bu (0.22 mmol) in MTBE (1.0 mL) under N_2 atmosphere at 40 ℃ for 12 h. [b] Isolated yield. [c] The reaction was carried out at 60 ℃.

According to the previous study on Rh(I)-catalyzed cross-coupling reaction with Rh(I) carbene intermediate,[8] we propose the following reaction mechanism (Scheme 5). Firstly, aryl rhodium species **A** is generated through transmetallation. The aryl rhodium species then reacts with α-diazo phosphonate to afford the Rh(I) carbene intermediate **B**, which is followed by migratory insertion to generate intermediate **C**. Finally, protonation of intermediate **C** delivers the coupling product and regenerates Rh(I) catalyst.

Scheme 5 Proposed reaction mechanism



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Conclusions

In conclusion, we have reported an efficient rhodium catalyzed cross coupling reactions of α-diazo phosphonates[16] and boronic acids. Generally, a class of diarylmethylphosphonates with diverse functionality can be readily accessed under the mild reaction conditions. Further efforts concerning the expansion of organoboron reagent scope and the development of asymmetric version of this coupling reaction are underway in our group.

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