Supporting information

Proline/Pipecolinic Acid-Promoted Copper-Catalyzed *P*-Arylation

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Table of contents

General experimental methods	S2
The characterization data of compounds 3a-m	S2
References	S6
The ³¹ P, ¹ H and ¹³ C NMR spectra of compounds (3a-m)	S7

General experimental procedures

All reactions were carried out under nitrogen atmosphere. DMF was freshly distilled from CaH_2 . Toluene was freshly distilled from Na. Proton and carbon magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded with tetramethylsilane or solvent resonance as the internal standard (^1H NMR: TMS at 0.00 ppm, CDCl_3 at 7.24 ppm, DMSO at 2.50 ppm; ^{13}C NMR: CDCl_3 at 77.0 ppm). 85% H_3PO_4 was used as the external reference of ^{31}P NMR spectra.

The yields of compounds **3a-m** are shown in Table 1 in text, and the characterization data are from the compounds prepared under the catalysis of CuI /proline.

Diisopropyl phenylphosphonate (3a).¹ Oil. ^{31}P NMR (CDCl_3 , 121 MHz) δ 17.14. ^1H NMR (CDCl_3 , 300 MHz) δ 7.72-7.76 (q, 2H), 7.30-7.46 (m, 3H), 4.55-4.67 (m, 2H), 1.14 (d, J = 6.18 Hz, 6H), 1.28 (d, J = 6.18 Hz, 6H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 131.8, 131.6, 129.6 (J = 182.32 Hz), 128.2, 128.0, 70.5., 23.9, 23.7. HR-EI-MS M^+ m/z Calcd for $\text{C}_{12}\text{H}_{19}\text{O}_3\text{P}$: 242.1072. Found: 242.1066.

(4-Nitro-phenyl)-phosphonic acid diisopropyl ester (3b). Oil. ^{31}P NMR (CDCl_3 , 300 MHz) δ 13.30. ^1H NMR (CDCl_3 , 300 MHz) δ 8.27-8.30 (m, 2H), 7.98-8.04 (m, 2H), 4.73-4.79 (m, 2H), 1.40 (d, 6H, J = 6.18 Hz), 1.25 (d, 6H, J = 6.18 Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ 150.1, 135.7 (J = 79.59 Hz), 133.0, 132.8, 123.4, 123.2, 71.9 (J = 5.74 Hz), 23.9 (J = 3.99 Hz). HR-EI-MS M^+ m/z Calcd for $\text{C}_{12}\text{H}_{18}\text{NO}_5\text{P}$: 287.0923. Found: 287.0929.

Diethyl phenylphosphonate (3c).¹ Oil. ^{31}P NMR (CDCl_3 , 121 MHz) δ 19.41. ^1H

NMR (CDCl₃, 300 MHz) δ 7.81-7.85 (q, 2H), 7.42-7.58 (m, 3H), 4.10-4.14 (m, 4H), 1.32 (t, J = 6.87 Hz, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ 132.2, 131.7, 131.6, 128.5, 128.3, 128.3 (J = 181.26 Hz), 62.0, 16.2. HR-EI-MS M^+ m/z Calcd for C₁₀H₁₅O₃P: 214.0759. Found: 214.0755.

Diethyl (4-methylphenyl)phosphonate (3d).¹ Oil. ³¹P NMR (CDCl₃, 121 MHz) δ 20.11. ¹H NMR (CDCl₃, 300 MHz) δ 7.67-7.74 (q, 2H), 7.25-7.29 (m, 2H), 4.02-4.17 (m, 4H), 2.40 (s, 3H), 1.29-1.34 (m, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ 143.0, 132.0, 131.8, 129.4, 129.2, 123.9, 62.1 (J = 5.03 Hz), 21.8, 16.4 (J = 6.46 Hz). HR-EI-MS M^+ m/z Calcd for C₁₁H₁₇O₃P: 228.0915. Found: 228.0922.

Diethyl (4-bromophenyl)phosphonate (3e).² Oil. ³¹P NMR (CDCl₃, 121 MHz) δ 18.33. ¹H NMR (CDCl₃, 300 MHz) δ 7.60-7.72 (m, 4H), 4.10-4.20 (m, 4H), 1.32 (t, J = 7.2 Hz, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ 133.4, 133.3, 132.0, 131.8, 127.7 (J = 188.59 Hz), 127.6, 62.4 (J = 5.02 Hz), 16.3 (J = 6.46 Hz). HR-EI-MS M^+ m/z Calcd for C₁₀H₁₄BrO₃P: 291.9864. Found: 291.9872.

Ethyl diphenylphosphinate (3f).³ Oil. ³¹P NMR (CDCl₃, 121 MHz) δ 25.01. ¹H NMR (CDCl₃, 300 MHz) δ 7.64-7.66 (m, 4H), 7.47 (d, J = 7.56 Hz, 4H), 4.16 (m, 2H), 1.38 (m, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ 139.9, 132.8, 130.0, 128.7, 58.9, 16.3. HR-EI-MS M^+ m/z Calcd for C₁₄H₁₅O₂P: 246.0810. Found: 246.0814.

Ethyl (4-methylphenyl)phenylphosphinate (3g).⁴ Oil. ³¹P NMR (CDCl₃, 121 MHz) δ 24.97. ¹H NMR (CDCl₃, 300 MHz) δ 7.66 (d, J = 7.23, 2H), 7.48-7.51 (m, 3H), 7.39-7.45 (m, 1H), 6.96-6.99 (m, 4H), 4.15 (m, 2H), 2.18 (s, 3H), 1.28 (t, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ 141.7, 133.3, 131.7, 129.7, 128.9, 126.3, 61.3 (J = 5.74 Hz), 61.1, 23.0, 16.3, 16.1. HR-EI-MS M⁺ m/z Calcd for C₁₅H₁₇O₂P: 260.0966. Found: 260.0970.

Ethyl (4-bromophenyl)phenylphosphinate (3h). Oil. ³¹P NMR (CDCl₃, 121 MHz) δ 28.87. ¹H NMR (CDCl₃, 300 MHz) δ 7.45-7.81 (m, 9H), 4.09-4.16 (m, 2H), 1.37 (t, J = 7.20 Hz, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ 133.3, 133.2, 131.9, 131.7, 131.6, 128.7, 127.4, 61.6 (J = 5.74 Hz), 16.6 (J = 6.46 Hz). HR-EI-MS M⁺ m/z Calcd for C₁₀H₁₄NO₅P: 323.9915. Found: 323.9919.

Phosphoryl triphenyl (3i). White solid, mp 119-123 °C. ³¹P NMR (CDCl₃, 121 MHz) δ 29.11. ¹H NMR (CDCl₃, 300 MHz) δ 7.63-7.67 (m, 6H), 7.38-7.56 (m, 9H). ¹³C NMR (CDCl₃, 75 MHz) δ 131.9, 131.6 (J = 61.67 Hz), 128.5, 128.3. HR-EI-MS M⁺ m/z Calcd for C₁₈H₁₅OP: 278.0861. Found: 278.0862.

1-(Diphenyl-phosphinoyl)-4-methyl-benzene (3j).⁵ White solid, mp 130-131 °C. ³¹P NMR (CDCl₃, 121 MHz) δ 29.98. ¹H NMR (CDCl₃, 300 MHz) δ 7.43-7.67 (m, 12H), 7.26–7.44 (m, 2H), 2.40 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ 132.1, 132.0, 129.4, 128.5 (J = 12.2 Hz), 21.6. HR-EI-MS M⁺ m/z Calcd for C₁₉H₁₇OP: 292.1017. Found: 292.1025.

1-Chloro-4-(diphenyl-phosphinoyl)-benzene (3k).⁶ Brown solid, mp 141-142 °C. ³¹P NMR (CDCl₃, 121 MHz) δ 28.82. ¹H NMR (CDCl₃, 300 MHz) δ 7.45-7.66 (m, 14H). ¹³C NMR (CDCl₃, 75 MHz) δ 133.6, 132.3, 132.1, 128.8, 128.7. HR-EI-MS M⁺ m/z Calcd for C₁₈H₁₄ClOP: 312.0471. Found: 312.0465.

Phenylphosphinic acid (3l).⁷ Oil. ³¹P NMR (CDCl₃, 121 MHz) δ 20.03. ¹H NMR (CDCl₃, 300 MHz) δ 7.46-7.850 (m, 5H), 6.16 (d, J = 564.78 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ 133.0 (J = 3.7 Hz), 132.0 (J = 3.6 Hz), 128.5, 128.3. HR-ESI-MS [M+H]⁺ m/z Calcd for C₆H₈O₂P: 143.0262. Found: 143.0251

Diphenylphosphinic acid (3m).⁸ White solid, mp 129-132 °C. ³¹P NMR (CDCl₃, 121 MHz) δ 22.44. ¹H NMR (CDCl₃, 300 MHz) δ 9.73 (br, s, 1H), 7.32-7.66 (m, 10H). ¹³C NMR (CDCl₃, 75 MHz) δ 133.3, 131.8, 131.6, 131.0, 128.5, 127.5. HR-ESI-MS [M+H]⁺ m/z Calcd for C₁₂H₁₂O₂P: 219.0575. Found: 219.0570.

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X : parts per Million : 31P

X : parts per Million : 1H

1a

13.2994

X : parts per Million : 31 P

13.5234

X : parts per Million : 31P

2
 1.11462
 1.93066

4.04252

6.14642

7.8506
 7.8277
 7.8059
 7.7831
 7.4946
 7.4809
 7.4683
 7.4546

4.1365
 4.1216
 4.1124
 4.0975

1.3472
 1.3231
 1.3002

0.0000

X : parts per Million : 1H

X : parts per Million : 1H

20.1653

X : parts per Million : 31P

X : parts per Million : 1H

X : parts per Million : ^{31}P

18.3272

X : parts per Million : 31P

1.91852

2.0

3.08688

7.6970
7.6684
7.6272
7.6169
7.6032
7.5883
7.2575

4.1180
4.1031
4.0939
4.0768

1.3298
1.3069
1.2829

-0.0151

X : parts per Million : MHz

X : parts per Million : ^{31}P

25.1623

X : parts per Million : 31P

X : parts per Million : 31P

X : parts per Million : ^{31}P

9.24696

6

7.6720
 7.6663
 7.6320
 7.6262
 7.4603
 7.4454
 7.4397
 7.4351

X : parts per Million : 1H

0.0000

28.5179

X : parts per Million : 31P

X : parts per Million : 13C

X : parts per Million : 1H

X : parts per Million : 31P

N : parts per Million : 31P

26.5176

X : parts per Million : 31P

20.9617

X : parts per Million : 31P

22.4360

X : parts per Million : 31P