Supporting Information

In situ generation of formaldehyde and triphenylphosphine from (hydroxymethyl)triphenylphosphonium and its application in Wittig olefination

Wenhua Huang* and Jie Xu

Department of Chemistry, Tianjin University, 92 Weijin Road, Tianjin 300072, P. R.
China.

Email: huangwh@tju.edu.cn.

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EXPERIMENTAL

Tricyclohexyl(hydroxymethyl)phosphonium tetrafluoroborate (**1d**)

A solution of HBF₄ in water (40 w%, 11.152 g, 0.05 mol) was added dropwise to a mixture of tricyclohexylphosphine (5.609 g, 0.02 mmol), paraformaldehyde (0.601 g, 0.02 mol) and ether (20 mL) in a round-bottom flask (100 mL). After stirred at rt for 16 h, the reaction mixture was evaporated to remove ether, diluted with water (30 mL), and then extracted with CH₂Cl₂ (30 mL x 2). The combined extracts were dried over anhydrous MgSO₄, evaporated to dryness, and then treated with *tert*-buty methylether. The resulting precipitates were collected by filtration, and dried in vacuo to afford **1d** (4.334 g, 54%). A white solid, mp 134-137 °C; ¹H-NMR (400 MHz, CDCl₃) δ 1.25-1.50 (m, 9 H), 1.55-1.70 (m, 6 H), 1.77-1.83 (m, 3 H), 1.90-2.04 (m, 12 H), 2.40-2.53 (m, 3 H), 4.32 (brs, 1 H), 4.62 (s, 2 H). ¹³C-NMR (100 MHz, CDCl₃) δ 50.8 (d, *J*_{C-P} = 59.0 Hz), 28.7 (d, *J*_{C-P} = 38.5 Hz), 26.6 (d, *J*_{C-P} = 4.0 Hz), 26.5 (d, *J*_{C-P} = 11.7 Hz), 25.3. ³¹P-NMR (162 MHz, CDCl₃) δ 28.78. HRMS-ESI (positive) *m/z*: calcd for C₁₉H₃₆OP⁺ (**1d**-cation), 311.2498; found, 311.2499.

2-Vinylnaphthalene (**3a**)

A white solid, yield: 66.8 mg, 87%; *R*_f = 0.53 (PE); mp 62-64 (lit.¹ 64-66); ¹H-NMR (600 MHz, CDCl₃) δ 5.32 (d, *J* = 10.9 Hz, 1 H), 5.85 (d, *J* = 17.6 Hz, 1 H), 6.86 (dd, *J* = 10.9, 17.6 Hz, 1 H), 7.39-7.45 (m, 2 H), 7.62 (d, *J* = 8.5 Hz, 1 H), 7.72 (s, 1 H), 7.75-7.79 (m, 3 H). ¹³C-NMR (151 MHz, CDCl₃) δ 137.0, 135.0, 133.6, 133.2, 128.2, 128.1, 127.7, 126.4, 126.3, 125.9, 123.2, 114.2.

1-Methoxy-4-vinylbenzene (**3b**)²

A colorless oil, yield: 46.8 mg, 73%; *R*_f = 0.66 (CCl₄); ¹H-NMR (600 MHz, CDCl₃) δ 3.80 (s, 3 H), 5.12 (d, 1 H, *J* = 10.9 Hz), 5.61 (d, 1 H, *J* = 17.5 Hz), 6.66 (dd, 1 H, *J* = 10.9, 17.5 Hz), 6.86 (d, 2 H, *J* = 8.0 Hz), 7.34 (d, 2 H, *J* = 8.0 Hz). ¹³C-NMR (151 MHz, CDCl₃) δ 159.3, 136.2, 130.4, 127.4, 113.9, 111.6, 55.3.

1-Methyl-4-vinylbenzene (**3c**)¹

A colorless oil, yield: 46.8 mg, 79%; *R*_f = 0.77 (PE); ¹H-NMR (400 MHz, CDCl₃) δ 2.39 (s, 3 H), 5.23 (d, 1 H, *J* = 10.9 Hz), 5.75 (d, 1 H, *J* = 17.6 Hz), 6.74 (dd, 1 H, *J* = 10.9, 17.6 Hz), 7.18 (d, 2 H, *J* = 7.9 Hz), 7.36 (d, 2 H, *J* = 8.0 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 137.6, 136.7, 134.8, 129.2, 126.1, 112.7, 21.2.

1-(*tert*-Butyl)-4-vinylbenzene (**3d**)³

A colorless oil, yield: 63.0 mg, 79%; *R*_f = 0.55 (PE); ¹H-NMR (600 MHz, CDCl₃) δ 1.31 (s, 9 H), 5.19 (d, 1 H, *J* = 10.9 Hz), 5.70 (d, 1 H, *J* = 17.6 Hz), 6.69 (dd, 1 H, *J* = 10.9, 17.6 Hz), 7.35 (s, 4 H). ¹³C-NMR (151 MHz, CDCl₃) δ 150.9, 136.6, 134.8, 125.9, 125.4, 113.0, 34.6, 31.3.

1,4-Divinylbenzene (**3e**)³

In this case, **1a** (1.0 mmol) and K₂CO₃ (2.0 mmol) was used. A pale yellow semi-

solid, yield: 45.1 mg, 69%; $R_f = 0.54$ (PE); $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 5.23 (d, 2 H, $J = 10.9$ Hz), 5.74 (d, 2 H, $J = 17.6$ Hz), 6.70 (dd, 2 H, $J = 10.9, 17.6$ Hz), 7.37 (s, 4 H). $^{13}\text{C-NMR}$ (151 MHz, CDCl_3) δ 137.1, 136.4, 126.4, 113.7.

(*E*)-Buta-1,3-dien-1-ylbenzene (3f)¹

A pale yellow oil, yield: 53.1 mg, 82%; $R_f = 0.58$ (PE); $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 5.25 (d, 1 H, $J = 10.1$ Hz), 5.41 (d, 1 H, $J = 16.9$ Hz), 6.53-6.68 (m, 2 H), 6.87 (dd, 1 H, $J = 10.5, 15.6$ Hz), 7.30 (t, 1 H, $J = 7.3$ Hz), 7.36-7.42 (m, 2 H), 7.48 (d, 2 H, $J = 7.4$ Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 137.17, 137.15, 132.8, 129.6, 128.6, 127.6, 126.4, 117.5.

Buta-1,3-dien-2-ylbenzene (3g)⁴

A pale yellow oil, yield: 40.0 mg, 61%; $R_f = 0.61$ (PE); $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 5.19-5.27 (m, 3 H), 5.34 (s, 1 H), 6.66 (dd, 1 H, $J = 10.9, 17.3$ Hz), 7.31-7.41 (m, 5 H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 148.2, 139.7, 138.1, 128.2, 128.1, 127.4, 117.1, 116.8.

1-Bromo-4-vinylbenzene (3h)³

A pale yellow oil, yield: 80.2 mg, 88%; $R_f = 0.54$ (PE); $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 5.26 (d, 1 H, $J = 10.9$ Hz), 5.73 (d, 1 H, $J = 17.6$ Hz), 6.64 (dd, 1 H, $J = 10.9, 17.6$ Hz), 7.25 (d, 2 H, $J = 8.4$ Hz), 7.43 (d, 2 H, $J = 8.4$ Hz). $^{13}\text{C-NMR}$ (151 MHz, CDCl_3) δ 136.4, 135.7, 131.6, 127.7, 121.6, 114.6.

1-Chloro-4-vinylbenzene (3i)¹

A colorless oil, yield: 55.9 mg, 81%; $R_f = 0.70$ (PE); $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 5.30 (d, 1 H, $J = 10.9$ Hz), 5.76 (d, 1 H, $J = 17.5$ Hz), 6.70 (dd, 1 H, $J = 10.9, 17.5$ Hz), 7.31-7.38 (m, 4 H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 136.0, 135.6, 133.4, 128.6, 127.4, 114.4.

Methyl 4-vinylbenzoate (3j)¹

A white semi-solid, yield: 69.2 mg, 85%; $R_f = 0.30$ (PE: EtOAc 25:1); $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 3.91 (s, 3 H), 5.38 (d, 1 H, $J = 10.9$ Hz), 5.86 (d, 1 H, $J = 17.6$ Hz), 6.75 (dd, 1 H, $J = 10.9, 17.6$ Hz), 7.46 (d, 2 H, $J = 8.3$ Hz), 8.00 (d, 2 H, $J = 8.3$ Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 166.8, 141.9, 136.0, 129.8, 129.2, 126.1, 116.4, 52.0.

4-Vinylbenzonitrile (3k)¹

A colorless oil, yield: 55.0 mg, 85%; $R_f = 0.24$ (PE: EtOAc 25:1); $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 5.45 (d, 1 H, $J = 10.9$ Hz), 5.88 (d, 1 H, $J = 17.6$ Hz), 6.73 (dd, 1 H, $J = 10.9, 17.6$ Hz), 7.49 (d, 2 H, $J = 8.2$ Hz), 7.62 (d, 2 H, $J = 8.2$ Hz). $^{13}\text{C-NMR}$ (151 MHz, CDCl_3) δ 141.9, 135.3, 132.4, 126.7, 118.9, 117.7, 111.1.

2-Vinylbenzonitrile (3l)¹

A colorless oil, yield: 55.9 mg, 87%; $R_f = 0.48$ (PE: EtOAc 25:1); $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 5.53 (d, 1 H, $J = 11.0$ Hz), 5.95 (d, 1 H, $J = 17.4$ Hz), 7.07 (dd, 1 H, $J = 10.9, 17.4$ Hz), 7.31-7.38 (m, 4 H).

= 11.0, 17.4 Hz), 7.34 (t, 1 H, $J = 7.7$ Hz), 7.56 (t, 1 H, $J = 7.7$ Hz), 7.62 (d, 1 H, $J = 7.7$ Hz), 7.67 (d, 1 H, $J = 7.7$ Hz). ^{13}C -NMR (151 MHz, CDCl_3) δ 140.6, 132.9, 132.8, 132.7, 127.9, 125.4, 118.9, 117.7, 111.1.

1-Nitro-4-vinylbenzene (3m)¹

A yellow oil, yield: 65.3 mg, 88%; $R_f = 0.33$ (PE: EtOAc 25:1); ^1H -NMR (600 MHz, CDCl_3) δ 5.41 (d, 1 H, $J = 10.9$ Hz), 5.84 (d, 1 H, $J = 17.6$ Hz), 6.69 (dd, 1 H, $J = 10.9$, 17.6 Hz), 7.44 (d, 2 H, $J = 8.8$ Hz), 8.09 (d, 2 H, $J = 8.8$ Hz). ^{13}C -NMR (151 MHz, CDCl_3) δ 147.1, 143.8, 134.9, 126.8, 123.9, 118.6,

1-Nitro-2-vinylbenzene (3n)⁵

A yellow oil, yield: 66.1 mg, 89%; $R_f = 0.31$ (PE: EtOAc 25:1); ^1H -NMR (600 MHz, CDCl_3) δ 5.48 (d, 1 H, $J = 11.0$ Hz), 5.75 (d, 1 H, $J = 17.3$ Hz), 7.17 (dd, 1 H, $J = 11.0$, 17.3 Hz), 7.38-7.45 (m, 1 H), 7.56-7.60 (m, 1 H), 7.63 (d, 1 H, $J = 7.8$ Hz), 7.92 (d, 1 H, $J = 8.2$ Hz). ^{13}C -NMR (151 MHz, CDCl_3) δ 147.8, 133.3, 133.1, 132.4, 128.5, 128.3, 124.4, 118.9.

1-Nitro-3-vinylbenzene (3o)⁶

A yellow oil, yield: 65.4 mg, 88%; $R_f = 0.10$ (PE); ^1H -NMR (600 MHz, CDCl_3) δ 5.44 (d, 1 H, $J = 10.9$ Hz), 5.90 (d, 1 H, $J = 17.6$ Hz), 6.76 (dd, 1 H, $J = 10.9$, 17.6 Hz), 7.49 (t, 1 H, $J = 7.9$ Hz), 7.71 (d, 1 H, $J = 7.9$ Hz), 8.10 (d, 1 H, $J = 7.9$ Hz), 8.24 (s, 1 H). ^{13}C -NMR (151 MHz, CDCl_3) δ 148.5, 139.2, 134.7, 132.1, 129.4, 122.4, 120.8, 117.0.

Phenyl(4-vinylphenyl)methanone (3p)⁷

A pale yellow oil, yield: 91.0 mg, 87%; $R_f = 0.12$ (PE: EtOAc 25:1); ^1H -NMR (600 MHz, CDCl_3) δ 5.38 (d, 1 H, $J = 10.9$ Hz), 5.87 (d, 1 H, $J = 17.6$ Hz), 6.76 (dd, 1 H, $J = 10.9$, 17.6 Hz), 7.44-7.51 (m, 4 H), 7.54-7.59 (m, 1 H), 7.76-7.80 (m, 4 H). ^{13}C -NMR (151 MHz, CDCl_3) δ 196.1, 141.5, 137.7, 136.6, 136.0, 132.3, 130.5, 129.9, 128.3, 126.0, 116.6.

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¹H-NMR (400 MHz, CDCl₃)

¹³C-NMR (100 MHz, CDCl₃)

1d

28.781

³¹P-NMR (162 MHz, CDCl₃)

1d

7.350
7.336
6.862
6.849
6.681
6.663
6.652
6.634
5.621
5.591
5.128
5.110
3.800

¹H-NMR (600 MHz, CDCl₃)

66.1
26.1
26.0
00.1
26.0
16.2

¹H-NMR (400 MHz, CDCl₃)

¹H-NMR (600 MHz, CDCl₃)

3d

¹³C-NMR (151 MHz, CDCl₃)

3d

8.012
7.991
7.468
7.447
6.784
6.757
6.740
6.713
5.884
5.840
5.393
5.366

¹H-NMR (400 MHz, CDCl₃)

1.96
2.00
0.97
1.00
1.00
3.05

¹H-NMR (CDCl₃, 600 MHz)

¹H-NMR (600 MHz, CDCl₃)

31

8.095
8.080

7.449
7.435

6.712
6.694
6.683
6.665

5.855
5.826

5.419
5.401

¹H-NMR (600 MHz, CDCl₃)

¹H-NMR (600 MHz, CDCl₃)

3p

196.1

141.6

137.8

136.7

136.0

132.4

130.6

130.0

128.3

126.1

116.6

77.4

77.1

76.9

¹³C-NMR (151 MHz, CDCl₃)

3p