

**Supplementary data**

**Phosphazene base-promoted halogen-zinc exchange reaction of aryl iodides using diethylzinc**

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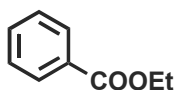
**General comment**

<sup>1</sup>H-NMR spectra were recorded on a JEOL AL-400 using tetramethylsilane as an internal standard. Chemical shifts are expressed in  $\delta$ (ppm) values, and coupling constants are expressed in Hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, m = multiplet, t = triplet, brs = broad singlet, dd = double-doublet, dt = double-triplet and ddd = double-doublet-doublet. Mass spectra were recorded on JEOL JMS-DX303 or JEOL JMS-AX500 spectrometer. IR spectra were measured with

SensIR ATR FT-IR. All the reactions dealing with air or moisture sensitive compounds were carried out in a dry reaction vessel under argon atmosphere unless otherwise noted. Flash column chromatography was carried out using Kanto Chemical Silica gel 60N (70-230 mesh). Dry THF, dry dimethylformamide (DMF) and diethylzinc 1.0 M solution in *n*-hexane were purchased from Kanto Chemical Company and used as supplied. *tert*-Butyl P4 base 1.0 M solution in *n*-hexane was purchased from Fulka Chemie and used as supplied.

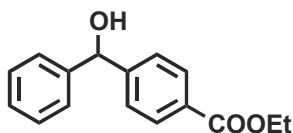
### Procedures and Characterization:

#### Ethyl benzoate **2**



A mixture of ethyl 4-iodobenzoate **1** (69 mg, 0.25 mmol), diethylzinc 1.0 M solution in hexane (0.60 mL, 0.60 mmol) and dry THF (0.5 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*-Bu-P4 base 1.0 M solution in *n*-hexane (0.075 mL, 0.075 mmol) was added to the solution at ambient temperature and the mixture was stirred for 11 h. The mixture was treated with saturated aq. NH<sub>4</sub>Cl and H<sub>2</sub>O and the mixture was extracted with CHCl<sub>3</sub>. The extract was washed with brine and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure and afforded the crude ethyl benzoate **2**. The yield of ethyl benzoate **2** was quantitatively determined by <sup>1</sup>H-NMR using 1,1,2-trichloroethane as an internal standard.

#### Ethyl (4-hydroxyphenylmethyl)benzoate **3**

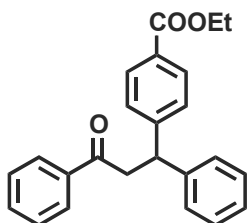


A mixture of ethyl 4-iodobenzoate **1** (69 mg, 0.25 mmol), diethylzinc 1.0 M solution in hexane (0.60 mL, 0.60 mmol) and dry THF (0.5 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base 1.0 M solution in *n*-hexane (0.075 mL, 0.075 mmol) was added to the solution at ambient temperature and the mixture was stirred for 5 h. Benzaldehyde (64 mg, 0.60 mmol) was added to the reaction mixture at -40 °C after which it was allowed to reach ambient temperature gradually. After stirring for 17 h, the mixture was treated with saturated aq. NH<sub>4</sub>Cl and H<sub>2</sub>O and then was extracted with CHCl<sub>3</sub>. The extract was washed with brine and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure and the crude material was purified by SiO<sub>2</sub> column chromatography (10% AcOEt-hexane) to afford 60 mg of a mixture of compound **3** and 1-phenylpropanol. The yield of compound **3** was 78% determined by <sup>1</sup>H-NMR.

<sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>)δ(ppm): 0.92 (t, *J* = 7.4 Hz, 3 H), 4.35 (q, *J* = 7.4 Hz, 2 H), 5.89 (s, 1 H), 7.26-7.38 (m, 5 H), 7.46 (d, *J* = 8.0 Hz, 2 H), 8.00 (d, *J* = 8.0 Hz, 2 H); IR(neat) 3475, 2981, 1715,

1661, 1270, 1175, 1102, 1019, 766, 708; LRMS (EI)  $m/z$  256( $M^+$ ); HRMS calcd for  $C_{16}H_{16}O_3$  256.1099, found 256.1106.

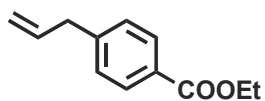
Ethyl 4-(3-oxo-1,3-diphenylpropyl)benzoate **4**



A mixture of ethyl 4-iodobenzoate **1** (69 mg, 0.25 mmol), diethylzinc 1.0 *M* solution in hexane (0.60 mL, 0.60 mmol) and dry THF (0.5 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*-Bu-P4 base 1.0 *M* solution in *n*-hexane (0.075 mL, 0.075 mmol) was added to the solution at ambient temperature and the mixture was stirred for 5 h. *trans*-Chalcone (125 mg, 0.60 mmol) was added to the reaction mixture in an ice bath, after which it was stirred for 10 h at ambient temperature. The mixture was treated with saturated aq.  $NH_4Cl$  and  $H_2O$  and the mixture was extracted with EtOAc. The extract was washed with brine and dried over  $MgSO_4$ . The solvent was removed under reduced pressure and the crude material was purified by  $SiO_2$  column chromatography (hexane to 10% AcOEt-hexane) to afford 63 mg (y. 71%) of compound **4** as a colorless oil.

$^1H$ -NMR (400MHz,  $CDCl_3$ ) $\delta$ (ppm): 1.35 (t,  $J = 7.1$  Hz, 3 H), 3.70-3.80 (m, 2 H), 4.33 (q,  $J = 7.1$  Hz, 2 H), 4.88 (t,  $J = 7.4$  Hz, 1 H), 7.15-7.35 (m, 7 H), 7.44 (t,  $J = 7.8$  Hz, 2 H) 7.51 (t,  $J = 7.8$  Hz, 1 H), 7.90-7.97 (m, 4 H); IR(neat) 3060, 1711, 1684, 1447, 1273, 1102, 1021, 752, 689; LRMS (EI)  $m/z$  358( $M^+$ ); HRMS calcd for  $C_{24}H_{22}O_3$  358.1569, found 358.1585.

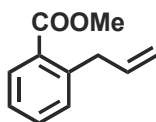
Ethyl 4-allylbenzoate **5**



A mixture of ethyl 4-iodobenzoate **1** (138 mg, 0.50 mmol), diethylzinc 1.0 *M* solution in hexane (0.60 mL, 0.60 mmol) and dry DMF (0.5 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*-Bu-P4 base 1.0 *M* solution in *n*-hexane (0.025 mL, 0.025 mmol) was added to the solution at ambient temperature and the mixture was stirred for 5 h. Allylbromide was added to the reaction mixture and stirred for 20 h. The mixture was treated with saturated aq.  $NH_4Cl$  and  $H_2O$  and then was extracted with EtOAc. The extract was washed with brine and dried over  $MgSO_4$ . The solvent was removed under reduced pressure and obtained as the crude material was purified by  $SiO_2$  column chromatography (2% AcOEt-hexane) to afford 94 mg (99%) of compound **5** as a colorless oil.

$^1\text{H-NMR}$  (400MHz,  $\text{CDCl}_3$ ) $\delta$ (ppm): 1.39 (t,  $J = 7.0$  Hz, 3 H), 3.43 (d,  $J = 6.4$  Hz, 2 H), 4.36 (q,  $J = 7.0$  Hz, 2 H), 5.05-5.12 (m, 2 H), 5.90-6.01 (m, 1 H), 7.24 (d,  $J = 8.4$  Hz, 2 H), 7.96 (d,  $J = 8.4$  Hz, 2 H); IR(neat) 2981, 1715, 1611, 1270, 1177, 1102, 1021, 916, 756; LRMS (EI)  $m/z$  190 ( $\text{M}^+$ ); HRMS calcd for  $\text{C}_{12}\text{H}_{14}\text{O}_2$  190.0994, found 190.0977.

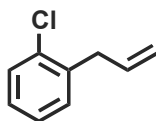
#### Methyl 2-allylbenzoate **6**



Yield: 85%, colorless oil.

$^1\text{H-NMR}$  (400MHz,  $\text{CDCl}_3$ ) $\delta$ (ppm): 3.75 (d,  $J = 6.4$  Hz, 2 H), 3.88 (s, 3 H), 4.98-5.06 (m, 2 H), 5.95-6.06 (m, 1 H), 7.25-7.30 (m, 2 H), 7.44 (dt,  $J = 2.0$  Hz, 7.6 Hz, 1 H), 7.87 (dd,  $J = 2.0$  Hz, 7.6 Hz, 1 H); IR(neat) 2950, 1717, 1434, 1254, 1131, 1098, 1073, 915, 747; LRMS (EI)  $m/z$  : 176( $\text{M}^+$ ); HRMS calcd for  $\text{C}_{11}\text{H}_{12}\text{O}_2$  176.0837, found 176.0821.

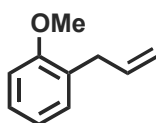
#### 2-Chloroallylbenzene **7**



Yield: 89%, colorless oil.

$^1\text{H-NMR}$  (400MHz,  $\text{CDCl}_3$ ) $\delta$ (ppm): 3.50 (d,  $J = 6.4$  Hz, 2 H), 5.04-5.13 (m, 2 H), 5.92-6.03 (m, 1 H), 7.13-7.25 (m, 3 H), 7.35 (dd,  $J = 1.2$  Hz, 7.6 Hz, 1 H); IR(neat) 2923, 1638, 1472, 1443, 1052, 994, 916, 749; LRMS (EI)  $m/z$  152( $\text{M}^+$ ); HRMS calcd for  $\text{C}_9\text{H}_9\text{Cl}$  152.0393, found 152.0377.

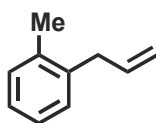
#### 2-Allylanisole **8**



Yield: 95 %, colorless oil.

$^1\text{H-NMR}$  (400MHz,  $\text{CDCl}_3$ ) $\delta$ (ppm): 3.38 (d,  $J = 6.0$  Hz, 2 H), 3.82 (s, 3 H), 5.01-5.08 (m, 2 H), 5.94-6.05 (m, 1 H), 6.85 (d,  $J = 8.0$  Hz, 1 H), 6.89 (t,  $J = 8.0$  Hz, 1 H), 7.13 (d,  $J = 8.0$  Hz, 1 H), 7.19 (t,  $J = 8.0$  Hz, 1 H); IR(neat) 2977, 1600, 1492, 1465, 1241, 1030, 910, 749; LRMS (EI)  $m/z$  148( $\text{M}^+$ ); HRMS calcd for  $\text{C}_{10}\text{H}_{12}\text{O}$  148.0888, found 148.0878.

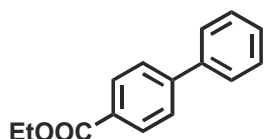
#### 2-Methylallylbenzene **9**



Yield: 76 %, colorless oil.

$^1\text{H-NMR}$  (400MHz,  $\text{CDCl}_3$ ) $\delta$ (ppm): 2.29 (s, 3 H), 3.36 (td,  $J = 1.4$  Hz, 6.4 Hz, 2 H), 4.96-5.07 (m, 2 H), 5.89-6.00 (m, 1 H), 7.13 (s, 4 H); IR(neat) 3078, 2923, 1638, 1474, 1015, 994, 913, 739; LRMS (EI)  $m/z$  132( $\text{M}^+$ ); HRMS calcd for  $\text{C}_{10}\text{H}_{12}$  132.0939, found 132.0923.

Ethyl 4-biphenylcarboxylate **10**



A mixture of ethyl 4-iodobenzoate **1** (138 mg, 0.50 mmol), diethylzinc 1.0 *M* solution in hexane (0.60 mL, 0.60 mmol) and dry DMF (0.5 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*-Bu-P4 base 1.0 *M* solution in *n*-hexane (0.025 mL, 0.025 mmol) was added to the solution at ambient temperature and the mixture was stirred for 5 h. iodobenzene (122 mg, 0.60 mmol) and  $\text{Pd}(\text{Ph}_3\text{P})_4$  (17 mg, 0.015 mmol) was added to the reaction mixture in an ice bath. The mixture was stirred for 7 h at ambient temperature, was then treated with saturated aq. $\text{NH}_4\text{Cl}$  and  $\text{H}_2\text{O}$  and the resulting mixture was extracted with EtOAc. The extract was washed with brine and dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure and the crude material was purified by  $\text{SiO}_2$  column chromatography (hexane to 10% AcOEt-hexane) to afford 86 mg of a mixture of compound **10** and ethyl 4-ethylbenzoate. This product included ethyl 4-ethylbenzoate. The yield of compound **10** was 53% determined by  $^1\text{H}$  -NMR.

$^1\text{H-NMR}$  (400MHz,  $\text{CDCl}_3$ ) $\delta$ (ppm): 1.38 (t,  $J = 7.2$  Hz, 3 H), 4.39 (q,  $J = 7.2$  Hz, 2 H), 7.38-7.44 (m, 3 H), 7.60-7.68 (m, 4 H), 8.11 (d,  $J = 8.8$  Hz, 2 H); IR(neat) 2981, 1708, 1607, 1405, 1268, 1177, 1102, 1023, 856, 745; LRMS (EI)  $m/z$  226( $\text{M}^+$ ); HRMS calcd for  $\text{C}_{15}\text{H}_{14}\text{O}_2$  226.0994, found 226.0975.