Electronic Supplementary Information

Fluoride-Triggered Indium-Mediated Synthesis of (Hetero)biaryls

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**General methods.** All $^1$H and $^{13}$C NMR spectra were recorded on a 300 MHz instrument in CDCl$_3$, unless otherwise stated. All reactions were carried out in dried glassware. Tetrahydrofuran (THF) was dried by distillation from sodium and benzophenone. 3-Iodopyridine, iodobenzene, 2-iodothiophene, 4-bromobenzaldehyde, 4-iodoacetophenone, triethoxyphenylsilane, 2-(triethoxysilyl)thiophene, tetrabutylammonium fluoride (TBAF), $N,N$-diisopropylethylamine, indium (III) chloride, 1-methyl-2-pyrrolidinone (NMP), tetrakis(triphenylphosphine) palladium (0) and [1,1’-bis(diphenylphosphino)ferrocene] dichloropalladium(II) complex with dichloromethane are commercially available and were used as received. 4-(Triethoxysilyl)acetophenone was prepared according to described procedures.1

Synthesis of 3-(triethoxysilyl)pyridine (3). 3-iodopyridine (1.025 g, 5 mmol) and i-Pr₂NEt (2.6 mL, 15 mmol) were added to a stirring solution of Pd(dppf)Cl₂·CH₂Cl₂ (122 mg, 0.15 mmol) in 20 mL of NMP under an atmosphere of argon. Triethoxysilane (1.385 mL, 7.5 mmol) was added. The reaction was heated at 80 °C (12 h). After cooling at room temperature, the reaction mixture was extracted with pentane (3 x 25 mL). The combined extracts were washed with water to remove NMP, dried over MgSO₄, filtered, and concentrated. The resulting oil was purified by distillation (125 °C, 0.5 mmHg) to give 651 mg (54% yield) of a colorless oil.

¹H NMR δ 1.17 (t, 9 H, J = 6.9 Hz), 3.81 (q, 6 H, J = 6.9 Hz), 7.18-7.24 (m, 1 H), 7.86 (d, 1 H, J = 6.0 Hz), 8.56 (d, 1 H, J = 6.0 Hz), 8.75 (s, 1 H); ¹³C NMR δ 18.0, 58.7, 123.1, 126.5, 142.3, 151.0, 154.9

**1H- and 13C-NMR data of already known compounds**

2-Phenylthiophene (1a). $^1$H NMR δ 7.05-7.08 (m, 1 H), 7.25-7.39 (m, 5 H), 7.59-7.62 (m, 2 H); $^{13}$C NMR δ 123.0, 124.8, 125.9, 127.4, 127.9, 128.8, 134.4, 144.4

[2,2']-Bithieryl (2a). $^1$H NMR δ 7.15-7.20 (m, 4 H), 7.98-7.01 (m, 2 H); $^{13}$C NMR δ 123.7, 124.3, 127.7, 137.4

3-(2-Thienyl)pyridine (3a). $^1$H NMR δ 7.10-7.37 (m, 4 H), 7.85-7.89 (m, 1 H), 8.56 (d, 1 H, $J = 6.0$ Hz), 8.89 (s, 1 H); $^{13}$C NMR δ 123.4, 123.9, 125.8, 128.0, 130.2, 132.8, 140.0, 146.7, 148.1

p-Phenylbenzaldehyde (1b). $^1$H NMR δ 7.44-7.48 (m, 3 H), 7.61-7.65 (m, 2 H), 7.73 (d, 2 H, $J = 9.0$ Hz), 7.94 (d, 2 H, $J = 9.0$ Hz), 10.05 (s, 1 H); $^{13}$C NMR δ 127.2, 127.5, 128.3, 128.9, 130.1, 135.0, 139.5, 146.9, 191.7

p-Thienylacetophenone (2c). $^1$H NMR δ 2.60 (s, 1 H), 7.11 (dd, 1 H, $J_1 = 5.1$ Hz, $J_2 = 3.6$ Hz), 7.35 (d, 1 H, $J = 5.1$ Hz), 7.41 (d, 1 H, $J = 3.6$ Hz), 7.68 (d, 2 H, $J = 8.3$ Hz), 7.95 (d, 2 H, $J = 8.3$ Hz); $^{13}$C NMR δ 26.5, 124.5, 125.6, 126.4, 128.3, 129.0, 135.7, 138.7, 142.9, 197.2

Isolation and NMR characterization of the intermediate species

A solution of TBAF (1 M in THF, 1 mmol) was added to a stirring solution of InCl₃ (0.33 mmol) and 2-(triethoxysilyl)thiophene (1 mmol) in THF (20 mL). After 1 hour at room temperature, the solution was concentrated and ¹H-NMR spectrum in CDCl₃ (spectrum B, pages S6, S7 and S8) or ¹³C-NMR spectrum in THF-d₈ (spectrum B, pages S9, S10 and S11) was performed to the residue.

A solution of thienyllithium (1 M in THF, 1 mmol) was added to a stirring solution of InCl₃ (0.33 mmol) in THF (20 mL). After 1 hour at room temperature, the solution was concentrated and ¹H-NMR spectrum in CDCl₃ (spectrum C, pages S7 and S8) or ¹³C-NMR spectrum in THF-d₈ (spectrum C, pages S10 and S11) was performed to the residue.

¹H-NMR spectrum in CDCl₃ (spectrum A, pages S6 and S8) and ¹³C-NMR spectrum in THF-d₈ (spectrum A, S9 and S11) of commercially available 2-(triethoxysilyl)thiophene are also provided for comparison.
$^1$H- and $^{13}$C-NMR spectra

$$\text{Si} \quad \text{OCH$_2$CH$_3$}$$

$$\text{OCH$_2$CH$_3$}$$

(3)
(2c)