Supporting Information

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Preparation of Aryl and Heteroaryl Indium(III) Reagents by the Direct Insertion of Indium in the Presence of LiCl

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General information: All reactions were carried out under an argon atmosphere in dried glassware. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Yields refer to isolated yields of compounds estimated to be > 95 % purity as determined by $^1$H-NMR and capillary-GC. NMR spectra were recorded on solutions in deuterated chloroform ($\text{CDCl}_3$) with residual chloroform (δ 7.24 ppm for $^1$H NMR and δ 77.0 ppm for $^{13}$C NMR). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

Starting Materials: Indium powder was purchased from ChemPur, Germany. Commercial available starting materials were purchased from commercial sources and used without further purification.

General procedure for indium insertion (Table 1): LiCl was placed in an argon-flushed flask and dried additionally 5-10 min at 380 °C (heat gun) on high vacuum (1 mbar). Indium powder was added under argon and the flask was evacuated and refilled with argon three times. After the addition of THF, indium was activated by treatment first with 1,2-dibromoethane (5 mol%) and then with chlorotrimethylsilane (2 mol%).$^{1,2}$ The substrate (along with internal standard) was added as solution in THF at 25 °C and the resulting solution was stirred at the appropriate temperature. The completion of the insertion
reaction was checked by GC analysis of reaction aliquots quenched with a solution of saturated NH₄Cl in water (the conversion was more than 90 %). Yield was determined by GC analysis of the reaction aliquots quenched with iodine solution in anhydrous THF.

Reagent (1a). The general procedure was followed using indium powder (918 mg, 8 mmol), LiCl (340 mg, 8 mmol) in THF (1 mL). 4-idoacetophenone 2a (492 mg, 2 mmol) and tridecane (5 drops) in THF (1 mL). The reaction was carried out at 50 °C for 24 h and provided the indium reagent 1a in 96% yield.

Reagent (1b). The general procedure was followed using indium powder (918 mg, 8 mmol), LiCl (340 mg, 8 mmol) in THF (1 mL). 1-(4-iodophenyl)-2-methyl-1-propanone 2b (550 mg, 2 mmol) and heptadecane (5 drops) in THF (1 mL). The reaction was carried out at 50 °C for 24 h and provided the indium reagent 1b in 93% yield.

Reagent (1c). The general procedure was followed using indium powder (689 mg, 6 mmol), LiCl (254 mg, 6 mmol) in THF (2 mL). 2-idoacetophenone 2c (492 mg, 2 mmol) and tridecane (5 drops) in THF (2 mL). The reaction was carried out at 35 °C for 2 h and provided the indium reagent 1c in 90% yield.


Reagent (1d). The general procedure was followed using indium powder (689 mg, 6 mmol), LiCl (254 mg, 6 mmol) in THF (2 mL).
Ethyl 2-iodobenzoate 2d (563 mg, 2 mmol) and tetradecane (5 drops) in THF (2 mL). The reaction was carried out at 35 °C for 8 h and provided the indium reagent 1d in 86% yield.

Reagent (1e). The general procedure was followed using indium powder (689 mg, 6 mmol), LiCl (254 mg, 6 mmol) in THF (2 mL). 4-((acetyloxy)-3-iodo-5-methoxybenzaldehyde 2e (641 mg, 2 mmol) and heptadecane (5 drops) in THF (2 mL). The reaction was carried out at 35 °C for 4 h and provided the indium reagent 1e in 70% yield.

Reagent (1f). The general procedure was followed using indium powder (689 mg, 6 mmol), LiCl (254 mg, 6 mmol) in THF (2 mL). Methyl 4-[(2,2-dimethylpropanoyloxy)-3-iodobenzoate 2f (724 mg, 2 mmol) and heptadecane (5 drops) in THF (2 mL). The reaction was carried out at 40 °C for 13 h and provided the indium reagent 1f in 70% yield.

Reagent (1g). The general procedure was followed using indium powder (689 mg, 6 mmol), LiCl (254 mg, 6 mmol) in THF (2 mL). Ethyl 3-cyano-5-iodobenzoate 2g (602 mg, 2 mmol) and tetradecane (5 drops) in THF (2 mL). The reaction was carried out at 40 °C for 6 h and provided the indium reagent 1g in 78% yield.

Reagent (1h). The general procedure was followed using indium powder (460 mg, 4 mmol), LiCl (170 mg, 4 mmol) in THF (2 mL). 2-Acetyl-5-iodothiophene 2h (520 mg, 2 mmol) and heptadecane (5 drops) in THF (2 mL). The reaction was carried out at 30 °C for 20 min and provided the indium reagent 1h in 91% yield.

Reagent (1i). The general procedure was followed using indium powder (460 mg, 4 mmol), LiCl (170 mg, 4 mmol) in THF (2 mL). 2, 5-Diiodothiophene 2i (672 mg, 2 mmol) and heptadecane (5
drops) in THF (2 mL). The reaction was carried out at 30 °C for 20 min and provided the indium reagent 1i in 97% yield.

**Reagent (1j).** The general procedure was followed using indium powder (460 mg, 4 mmol), LiCl (170 mg, 4 mmol) in THF (2 mL). 2-Iodo-1-benzothiophene-3-carbaldehyde 2j (576 mg, 2 mmol) and tetradecane (5 drops) in THF (2 mL). The reaction was carried out at 30 °C for 20 min and provided the indium reagent 1j in 78% yield.

**Reagent (1k).** The general procedure was followed using indium powder (689 mg, 6 mmol), LiCl (254 mg, 6 mmol) in THF (3 mL). 3-Iodopyridine 2k (410 mg, 2 mmol) and tetradecane (5 drops) in THF (3 mL). The reaction was carried out at 50 °C for 5 h and provided the indium reagent 1k in 88% yield.

**Reagent (1l).** The general procedure was followed using indium powder (460 mg, 4 mmol), LiCl (170 mg, 4 mmol) in THF (2 mL). 5-Iodo-2-furancarboxaldehyde 2l (448 mg, 2 mmol) and octadecane (5 drops) in THF (2 mL). The reaction was carried out at 30 °C for 20 min and provided the indium reagent 1l in 83% yield.

**Reagent (1m).** The general procedure was followed using indium powder (689 mg, 6 mmol), LiCl (254 mg, 6 mmol) in THF (2 mL). Ethyl 5-bromo-2-furoate 2m (440 mg, 2 mmol) and heptadecane (5 drops) in THF (2 mL). The reaction was carried out at 50 °C for 16 h and provided the indium reagent 1m in 92% yield.


**General procedure A** for cross-coupling (Table 2): The electrophile (1 equiv) and Pd(dppf)Cl₂ (4 mol%) were placed in
an argon-flushed flask. After the addition of NMP, the organoindium solution in THF was carefully transferred to the resulting solution from the rest of indium powder using syringe. Then, the reaction mixture was stirred at the indicated temperature. After the completion of the reaction (checked by GC analysis of reaction aliquots quenched with sat. aqueous NH₄Cl solution and TLC) the reaction mixture was quenched with acetic acid (0.5 mL) and water (2 mL). The aqueous layer was extracted with ethyl acetate or diethyl ether. The combined organic extracts were dried with Na₂SO₄ and concentrated in vacuo. The crude residue was purified by flash column chromatography.

**General procedure B for cross-coupling (Table 1):** The electrophile (1 equiv), Pd(OAc)₂ (4 mol%) and S-Phos (8 mol%) were placed in an argon-flushed flask. After the addition of NMP and THF (0.5 mL), the organoindium solution in THF was carefully transferred to the resulting solution from the rest of indium powder using syringe. Then, the reaction mixture was stirred at the indicated temperature. After the completion of the reaction (checked by GC analysis of reaction aliquots quenched with sat. aqueous NH₄Cl solution and TLC) the reaction mixture was quenched with acetic acid (0.5 mL) and water (2 mL). The aqueous layer was extracted with ethyl acetate or diethyl ether. The combined organic extracts were dried with Na₂SO₄ and concentrated in vacuo. The crude residue was purified by flash column chromatography.

**Ethyl 4′-acetyl-1,1′-biphenyl-4-carboxylate (4a).** The general procedure A was followed using Pd(dppf)Cl₂ (44 mg, 0.06 mmol), ethyl 4-iodobenzoate 3a (414 mg, 1.50 mmol) and NMP (2 mL). The arylindium solution of 1a was diluted with THF (2 mL) and transferred to the reaction mixture. The reaction mixture was stirred at 40 °C for 4 h. The residue was purified by flash chromatography on silica gel (ether/pentane = 1:4) to yield
compound 4a (380 mg, 95%). $^1$H NMR (300 MHz, CDCl$_3$) $d$ 8.20-8.03 (m, 4H), 7.77-7.67 (m, 4H), 4.44 (q, 2H, $J = 7.1$ Hz), 2.67 (s, 3H), 1.44 (t, 3H, $J = 7.1$ Hz); $^{13}$C (75 MHz, CDCl$_3$) $d$ 197.6, 166.3, 144.5, 144.1, 136.5, 130.2, 130.1, 129.0, 127.5, 127.2, 61.1, 26.7, 14.4; HRMS: $m/z$ calcd. for C$_{17}$H$_{16}$O$_3$ (M$^+$) 268.1099, found 268.1083; FT-IR (Diamond-ATR, neat) 2993, 1703, 1678, 1607 cm$^{-1}$, mp (°C) = 106.7-107.7.

5-(4-(Isobutyryl)phenyl)furan-2-carboxaldehyde (4b). The general procedure A was followed using Pd(dppf)Cl$_2$ (44mg, 0.06 mmol), 5-iodo-2-furancarboxaldehyde 21 (344 mg, 1.50 mmol) and NMP (2 mL). The arylindium solution of 1b was diluted with THF (2 mL) and transferred to the reaction mixture. The reaction mixture was stirred at 60 °C for 12 h. The residue was purified by flash chromatography on silica gel (ether/pentane = 1:3) to yield compound 4b (255 mg, 70%). $^1$H NMR (400 MHz, CDCl$_3$) $d$ 9.62 (s, 1H), 7.95 (d, 2H, $J = 12.0$ Hz), 7.83 (d, 2H, $J = 12.0$ Hz), 7.28 (d, 1H, $J = 3.7$ Hz), 6.91 (d, 1H, $J = 3.7$ Hz), 3.49 (m, 1H), 1.16 (d, 6H, $J = 6.9$ Hz); $^{13}$C (100 MHz, CDCl$_3$) $d$ 203.5, 177.4, 157.8, 152.5, 136.4, 132.5, 132.5, 128.9, 125.2, 123.2, 109.4, 35.4, 19.0; HRMS: $m/z$ calcd. for C$_{15}$H$_{14}$O$_3$ (M$^+$) 242.0943, found 242.0929; FT-IR (Diamond-ATR, neat) 2813, 1740, 1664, 1605 cm$^{-1}$, mp (°C) = 74.0-76.7.

5-Formyl-3-methoxy-3’-methylbiphenyl-2-yl acetate (4c). The general procedure B was followed using Pd(OAc)$_2$ (10 mg, 0.04 mmol), S-Phos (33 mg, 0.08 mmol), 3-iodotoluene 3b (197 mg, 0.89 mmol) and NMP (2 mL). The arylindium solution of 1e was transferred to the reaction mixture. It was refluxed for 23 h. The residue was purified by flash chromatography on silica gel (ether/pentane = 1:5) to yield compound 4c (213 mg, 84%). $^1$H NMR (400 MHz, CDCl$_3$) $d$ 9.96 (s, 1H), 7.48 (dd, 2H, $J = 10.6$, 2.0 Hz), 7.34-7.26 (m, 1H), 7.23-7.17 (m, 3H), 3.92 (s, 3H), 2.39 (s, 3H), 2.15 (s, 3H); $^{13}$C (100 MHz, CDCl$_3$) $d$ 191.1, 168.3, 152.4, 142.2, 138.2, 136.9, 136.1, 134.7, 129.4, 128.9,
Methyl 4’-cyano-6-[(2,2-dimethylpropanoyl)oxy]biphenyl-3-carboxylate (4d). The general procedure B was followed using Pd(OAc)$_2$ (10 mg, 0.04 mmol), S-Phos (33 mg, 0.08 mmol), 4-iodobenzonitrile 3c (214 mg, 0.93 mmol) and NMP (2 mL). The arylindium solution of 1f was transferred to the reaction mixture. The reaction mixture was refluxed for 22 h. The residue was purified by flash chromatography on silica gel (ether/pentane = 1:6) to yield compound 4d (210 mg, 68%, mixture of rotamers). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.08 (dd, 1H, $J = 8.4$, 2.2 Hz), 8.03 (d, 1H, $J = 2.2$ Hz), 7.69 (d, 2H, $J = 8.5$ Hz), 7.49 (d, 2H, $J = 8.5$ Hz), 7.18 (d, 1H, $J = 8.4$ Hz), 3.91 (s, 3H), 1.12 (s, 9H); $^{13}$C (100 MHz, CDCl$_3$) $\delta$ 176.1, 165.9, 151.6, 141.3, 133.5, 132.0, 131.9, 130.0, 128.3, 123.3, 118.5, 111.8, 52.3, 39.0, 26.8; HRMS: $m/z$ calcd. for C$_{20}$H$_{19}$NO$_4$ (M$^+$) 337.1314, found 337.1304; FT-IR (Diamond-ATR, neat) 2975, 2229, 1754, 1721 cm$^{-1}$.

Ethyl 4’,5-dicyanobiphenyl-3-carboxylate (4e). The general procedure B was followed using Pd(OAc)$_2$ (11 mg, 0.05 mmol), S-Phos (40 mg, 0.10 mmol), 4-iodoacetophenone 2a (296 mg, 1.20 mmol) and NMP (2 mL). The arylindium solution of 1g was transferred to the reaction mixture. The reaction mixture was refluxed for 16 h. The residue was purified by flash chromatography on silica gel (ether/pentane = 1:3) to yield compound 4e (298 mg, 85%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.47 (s, 1H), 8.30 (s, 1H), 8.10-8.00 (m, 3H), 7.69-7.67 (m, 2H), 4.43 (q, 2H, $J = 8.0$ Hz), 2.63 (s, 3H), 1.42 (t, 3H, $J = 8.0$ Hz); $^{13}$C (100 MHz, CDCl$_3$) $\delta$ 197.3, 164.4, 142.2, 141.6, 137.1, 134.3, 132.5, 132.3, 132.2, 129.2, 127.3, 117.7, 113.7, 62.0, 26.7, 14.2; HRMS: $m/z$ calcd. for C$_{18}$H$_{15}$NO$_3$ (M$^+$) 293.1052, found
1-(5-(3-(Trifluoromethyl)phenyl)thiophene-2-yl)ethanone (4f). The general procedure A was followed using Pd(dppf)Cl₂ (44 mg, 0.06 mmol), 3-iodobenzotrifluoride 3d (416 mg, 1.5 mmol) and NMP (2 mL). The arylindium solution of 1h was transferred to the reaction mixture. The reaction mixture was stirred at 40 °C for 4 h. The residue was purified by flash chromatography on silica gel (ether/pentane = 1:4) to yield compound 4f (386 mg, 95%). ¹H NMR (300 MHz, CDCl₃) δ 7.90 (s, 1H), 7.83 (d, 1H, J = 9.0 Hz), 7.70 (d, 1H, J = 3.9 Hz), 7.67–7.52 (m, 2H), 7.40 (d, 1H, J = 3.9 Hz), 2.60 (s, 3H); ¹³C (75 MHz, CDCl₃) δ 190.5, 150.5, 144.1, 134.2, 133.3, 131.7 (q, J = 32.4 Hz), 129.7, 129.5 (q, J = 1.4 Hz), 125.5 (q, J = 3.8 Hz), 124.9, 123.8 (q, J = 270.9 Hz), 122.9 (q, J = 3.8 Hz), 26.6; HRMS: m/z calcd. for C₁₃H₉F₃OS (M⁺) 270.0326, found 270.0314; FT-IR (Diamond-ATR, neat) 1652, 1614, 1534 cm⁻¹, mp (°C) = 133.6–135.1.

2-Iodo-5-(4-nitrophenoxy)phenyl)thiophene (4g). The general procedure A was followed using Pd(dppf)Cl₂ (57 mg, 0.08 mmol), 1-iodo-4-nitrobenzene 3e (634 mg, 2.52 mmol) and NMP (2 mL). The arylindium solution of 1i was transferred to the reaction mixture. The reaction mixture was stirred at 25 °C for 24 h. The residue was purified by flash chromatography on silica gel (ethyl acetate/pentane = 1:15) to yield compound 4g (466 mg, 73%). ¹H NMR (400 MHz, CDCl₃) δ 8.24–8.19 (m, 2H), 7.65–7.61 (m, 2H), 7.28 (d, 1H, J = 3.8 Hz), 7.11 (d, 1H, J = 3.8 Hz); ¹³C (100 MHz, CDCl₃) δ 147.4, 146.9, 139.4, 138.5, 126.9, 125.9, 124.5, 76.1; HRMS: m/z calcd. for C₁₀H₆INO₂S (M⁺) 330.9164, found 330.9161; FT-IR (Diamond-ATR, neat) 1589, 1530, 1496, 1418, 1325 cm⁻¹, mp (°C) = 100.7–102.4.

4-(3-Formylbenzo[b]thiophen-2-yl)benzonitrile (4h). The general procedure B was followed using Pd(OAc)₂ (10 mg, 0.04
mmol), S-Phos (34 mg, 0.08 mmol), 4-iodobenzonitrile 3c (240 mg, 1.04 mmol) and NMP (2 mL). The solution of the arylindium reagent 1j was transferred to the reaction mixture. It was refluxed for 15 h. The residue was purified by flash chromatography on silica gel (ether/pentane = 1:6) to yield compound 4h (246 mg, 90%). \( ^1H \text{NMR (400 MHz, CDCl}_3 \text{)} \delta 10.01 (s, 1H), 8.75 (d, 1H, J = 7.8 Hz), 7.85 (d, 1H, J = 8.0 Hz), 7.82-7.76 (m, 2H), 7.71-7.65 (m, 2H), 7.55-7.44 (m, 2H); \( ^{13}C \) (100 MHz, CDCl\(_3\)) \delta 185.6, 156.9, 138.2, 136.8, 136.2, 132.5, 131.2, 131.0, 126.7, 126.5, 125.4, 121.7, 117.9, 113.7; HRMS: m/z calcd. for C\(_{16}\)H\(_9\)NO\(_2\) (M\(^+\)) 263.0405, found 263.0383; FT-IR (Diamond-ATR, neat) 2230, 1669, 1603 cm\(^{-1}\), mp (°C) = 164.8-167.7.

**Ethyl 4-(pyridine-3-yl)benzoate (4i).** The general procedure A was followed using Pd(dppf)Cl\(_2\) (48 mg, 0.06 mmol), ethyl 4-iodobenzoate 3a (414 mg, 1.50 mmol) and NMP (3 mL). The solution of the aryl indium reagent 1k was transferred to the reaction mixture. It was refluxed for 17 h. The residue was purified by flash chromatography on silica gel (ether/pentane = 1:1) to yield compound 4i (312 mg, 92%). \( ^1H \text{NMR (400 MHz, CDCl}_3 \text{)} \delta 8.96 (bs, 1H), 8.71 (bs, 1H), 8.15-8.09 (m, 2H), 7.89 (d, 1H, J = 7.8 Hz), 7.65-7.59 (m, 2H), 7.41 (dd, 1H, J = 7.9, 4.6 Hz), 4.38 (q, 2H, J = 7.2 Hz), 1.39 (t, 3H, J = 7.2 Hz); \( ^{13}C \) (100 MHz, CDCl\(_3\)) \delta 166.2, 148.9, 148.0, 142.1, 136.0, 134.5, 130.3, 123.0, 124.1, 61.1, 14.3; HRMS: m/z calcd. for C\(_{14}\)H\(_{13}\)NO\(_2\) (M\(^+\)) 227.0946, found 227.0934; FT-IR (Diamond-ATR, neat) 2984, 1700, 1603 cm\(^{-1}\), mp (°C) = 49.1-50.3.

**Ethyl 4-(5-formylfuran-2-yl)benzoate (4j).** The general procedure A was followed using Pd(dppf)Cl\(_2\) (40 mg, 0.05 mmol), ethyl 4-iodobenzoate 3a (382 mg, 1.38 mmol) and NMP (2 mL). The solution of the arylindium reagent 1l was transferred to the reaction mixture. The reaction mixture was stirred at 25 °C for 1.5 h. The residue was purified by flash chromatography
on silica gel (ether/pentane = 1:4) to yield compound 4j (260 mg, 78%). $^1$H NMR (400 MHz, CDCl$_3$) d 9.68 (s, 1H), 8.11-8.07 (m, 2H), 7.88-7.84 (m, 2H), 7.32 (d, 1H, J = 3.9 Hz), 6.93 (d, 1H, J = 3.9 Hz), 4.38 (q, 2H, J = 7.1 Hz), 1.39 (t, 3H, J = 7.1 Hz); $^{13}$C (100 MHz, CDCl$_3$) d 177.4, 165.9, 158.0, 152.5, 132.7, 131.1, 130.2, 125.0, 123.0, 109.3, 61.2, 14.3; HRMS: m/z calcd. for C$_{14}$H$_{12}$O$_4$ (M$^+$) 244.0736, found 244.0724; FT-IR (Diamond-ATR, neat) 1708, 1658, 1609 cm$^{-1}$, mp (°C) = 127.1-128.6.

5-((E)-oct-1-enyl)furan-2-carboxaldehyde (4k). The general procedure A was followed using Pd(dppf)Cl$_2$ (40 mg, 0.05 mmol), (E)-1-iodooct-1-ene 3f (321 mg, 1.35 mmol) and NMP (2 mL). The solution of the arylindium reagent 1l was transferred to the reaction mixture. It was stirred at 60 °C for 1.5 h. The residue was purified by flash chromatography on silica gel (ether/pentane = 1:8) to yield compound 4k (204 mg, 73%). $^1$H NMR (300 MHz, CDCl$_3$) d 9.55 (s, 1H), 7.21 (d, 1H, J = 3.7 Hz), 6.60 (dt, 1H, J = 15.0, 7.1 Hz), 6.35 (d, 1H, J = 3.7 Hz), 6.28 (dt, 1H, J = 15.0, 1.5 Hz), 2.29-2.19 (m, 2H), 1.56-1.21 (m, 8H), 0.91 (t, 3H, J = 9.0 Hz); $^{13}$C (75 MHz, CDCl$_3$) d 176.9, 159.0, 151.4, 137.7, 123.7, 117.6, 108.6, 33.0, 31.7, 28.8, 28.7, 22.6, 14.1; HRMS: m/z calcd. for C$_{13}$H$_{18}$O$_2$ (M$^+$) 206.1307, found 206.1301; FT-IR (Diamond-ATR, neat) 2925, 1675, 1517 cm$^{-1}$.

1-(2-(1H-indol-5-yl)phenyl)ethanone (4l). The general procedure B was followed using Pd(OAc)$_2$ (11 mg, 0.05 mmol), S-Phos (41 mg, 0.10 mmol), 5-iodoindole 3g (280 mg, 1.13 mmol) and NMP (2 mL). The arylindium solution of 1c was transferred to the reaction mixture. The reaction mixture was refluxed for 27 h. The residue was purified by flash chromatography on silica gel (ethyl acetate/pentane = 1:2) to yield compound 4l (188 mg, 71%). $^1$H NMR (400 MHz, CDCl$_3$) d 8.67 (bs), 7.63 (s, 1H), 7.60-7.57 (m, 1H), 7.55-7.46 (m, 2H), 7.43-7.35 (m, 2H),
7.21 (t, 1H, J = 2.8 Hz), 7.15 (dd, 1H, J = 8.4, 1.8 Hz), 6.59-6.56 (m, 1H), 1.97 (d, 3H, J = 0.8 Hz); $^{13}$C (100 MHz, CDCl$_3$) δ 206.5, 141.9, 141.2, 135.6, 132.3, 130.7, 130.6, 128.2, 127.7, 126.7, 125.4, 123.2, 121.0, 111.4, 102.8, 30.5; HRMS: m/z calcd. for C$_{16}$H$_{13}$NO (M$^+$) 235.0997, found 235.0988; FT-IR (Diamond-ATR, neat) 3340, 1670, 1593 cm$^{-1}$.

**Ethyl 2’-(1-hydroxyethyl)biphenyl-2-carboxylate (4m).** The general procedure A was followed using Pd(dppf)Cl$_2$ (32 mg, 0.04 mmol), 1-(3-iodophenyl)ethanol 3h (248 mg, 1.0 mmol) and NMP (2 mL). The arylindium solution of 1d was transferred to the reaction mixture. It was refluxed for 23 h. The residue was purified by flash chromatography on silica gel (ether/pentane = 1:1) to yield compound 4m (188 mg, 70%). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.84 (dd, 1H, J = 7.6, 1.6 Hz), 7.58-7.49 (m, 1H), 7.44 (dd, 1H, J = 7.6, 1.4 Hz), 7.42-7.31 (m, 4H), 7.23-7.19 (m, 1H), 4.94 (q, 1H, J = 6.4 Hz), 4.10 (q, 2H, J = 7.1 Hz), 2.14 (1H, bs), 1.53 (d, 3H, J = 6.43 Hz), 1.02 (t, 3H, J = 7.1 Hz); $^{13}$C (75 MHz, CDCl$_3$) δ 168.8, 145.7, 142.4, 141.7, 131.3, 131.1, 130.6, 129.7, 128.2, 127.5, 127.2, 125.5, 124.2, 70.3, 60.9, 25.3, 13.7; HRMS: m/z calcd. for C$_{17}$H$_{18}$O$_3$ (M$^+$) 270.1256, found 270.1261; FT-IR (Diamond-ATR, neat) 3418, 2975, 1709, 1598 cm$^{-1}$.

**Ethyl 5-(3-hydroxyphenyl)furan-2-carboxylate (4n).** The general procedure A was followed using Pd(dppf)Cl$_2$ (38 mg, 0.05 mmol), 3-iodophenol 3i (292 mg, 1.31 mmol) and NMP (2 mL). The solution of the arylindium reagent 1m was transferred to the reaction mixture. The reaction mixture was stirred at 40 °C for 4 h. The residue was purified by flash chromatography on silica gel (ether/pentane = 1:2) to yield compound 4n (256 mg, 84%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.31 (dt, 1H, J = 8.0, 1.3 Hz), 7.29-7.23 (m, 2H), 7.21 (d, 1H, J = 3.5 Hz), 6.82 (ddd, 1H, J = 8.0, 2.5, 1.3 Hz), 6.69 (d, 1H, J = 3.5 Hz), 4.37 (q, 2H, J = 7.2 Hz), 1.38 (t, 3H, J = 7.2 Hz); $^{13}$C (100 MHz, CDCl$_3$) δ
159.0, 157.1, 156.1, 143.7, 130.9, 130.1, 119.8, 117.3, 116.0, 111.6, 107.1, 61.0, 14.3; HRMS: m/z calcd. for C_{13}H_{12}O_{4} (M^+) 232.0736, found 232.0722; FT-IR (Diamond-ATR, neat) 3271, 1678, 1591 cm^{-1}, mp (°C) = 144.1-147.1.

**Studying of indium insertion in the presence of LiCl with 2-iodothiophene**

LiCl (0.4 mmol-4 mmol) was placed in an argon-flushed flask and dried additionally 5-10 min at 380 °C (using heat gun) on high vacuum (1 mbar). Indium powder (459 mg, 4 mmol) was added under argon and the flask was evacuated and refilled with argon three times. After the addition of THF (2 mL), indium was activated by treatment first with 1,2-dibromoethane (5 mol%) and then with chlorotrimethylsilane (2 mol%) (gentle heating with heat gun). A solution of 2-iodothiophene (420 mg, 2 mmol) (along with internal standard) in THF (2 mL) was added at 25 °C and the resulting solution was stirred at 25 °C for 8 h. These reactions were followed by GC analysis of reaction aliquots quenched with a solution of saturated NH_{4}Cl in water (Figure 1). The indium powder gave the best results when it was activated by 1,2-dibromoethane and TMSCl. Without the addition of LiCl, a fast aggregation of the indium powder occurs in THF solution. The addition of an equal amount of LiCl prevented the metal to aggregate which decreased the reactivity dramatically.

**Figure 1.**
Preparation of Aryl and Heteroaryl Indium(III)-Reagents by the Direct Insertion of Indium in the Presence of LiCl

$^1$H and $^{13}$C spectra

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Compound 4a
Compound 4c
Compound 4d

\[
\begin{array}{c}
\text{O} \\
\text{MeO}_2\text{C} \\
\text{CN}
\end{array}
\]

2.07 1.97 1.12 3.74 9.50

174.15 145.54 138.60 121.58 109.67 105.67 101.20 76.70 71.74 62.70 26.40 21.32
Compound 4e

\[
\begin{align*}
\text{EtO}_2C & \quad \text{COMe} \\
\text{CN} &
\end{align*}
\]
Compound 4f
Compound 4g
Compound 4h

\[
\begin{aligned}
&\text{CHO} \\
&\text{CN}
\end{aligned}
\]
Compound 4i
Compound 4j

![Chemical Structure](image)

![NMR Spectrogram](image)
Compound 4k

\[
\text{OHC} - \text{Hex}
\]
Compound 41

\[
\begin{align*}
\text{Me} & \\
\text{O} & \\
\text{N} & \\
\text{H} & 
\end{align*}
\]
Compound 4m
Compound 4n

![Chemical Structure](image1)

![NMR Spectrum](image2)

![NMR Spectrum](image3)