Supporting Information

Transition Metal-Free Cross-Coupling of Indium Organometallics with Chromene and Isochroman Acetals Mediated by BF$_3$•OEt$_2$

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General Methods.
All reactions were carried out in flame-dried glassware, under argon using standard gas-tight syringes, cannulae and septa. THF was dried by distillation from sodium benzophenone ketyl. Reaction temperatures refer to external bath temperatures. Commercially available reagents were used as received without further purification. Organolithium reagents were titrated prior to use. Reactions were monitored by TLC using pre-coated silica gel plates (Alugram Xtra SIL G/UV<sub>254</sub>, 0.20 mm thick), UV light as the visualizing agent and ethanolic phosphomolybdic acid as the developing agent. Flash column chromatography was performed with 230-400 mesh silica gel. <sup>1</sup>H and <sup>13</sup>C NMR were recorded in CDCl<sub>3</sub> at 300 MHz for <sup>1</sup>H and 75 MHz for <sup>13</sup>C, at 300 K, and calibrated to the solvent peak. DEPT data were used to assign carbon types. Mass spectra were obtained with EI ionization at 70 eV.

Triorganoindium Reagents.
Triorganoindium compounds were prepared according to previously published methods<sup>1</sup> by treatment of the corresponding organolithium reagent (3 equiv, ~0.5 M in THF) with a solution of InCl<sub>3</sub> (1 equiv, 0.45 M in THF) at −78 ºC and warming to room temperature. Phenylacetylene, ethynyltrimethylsilane, and thiophene were lithiated by treatment with n-BuLi (1 equiv) at −78 ºC and warming to room temperature. Organolithium reagents derived from 2-bromonaphtalene, β-bromostyrene, and cyclopropylbromide were prepared by metal-halogen exchange reaction with t-BuLi (2 equiv) at −78 ºC.

2-Ethoxy-2H-chromene (1).<sup>2</sup>
To a solution of coumarin (2 g, 13.7 mmol) in 40 mL of CH<sub>2</sub>Cl<sub>2</sub>, DIBAL-H (15 mL, 14.4 mmol, 1.0 M) was added drop wise for 1.5 h at −78 ºC. The reaction was stirred for 2 h, warmed to 0 ºC, and then allowed to reach rt. The reaction was diluted with EtOAc (100 mL) and water (100 mL). After filtration through Celite, the aqueous layer was extracted with EtOAc (2 × 50 mL) and the combined organic layer were washed with brine (100 mL), dried (MgSO<sub>4</sub>), filtered, and concentrated to yield a viscous yellow oil. The crude was redissolved in absolute EtOH (50 mL) and trifluoroacetic acid (40 µL, 0.54 mmol) was added. After 12 h stirring at room temperature, K<sub>2</sub>CO<sub>3</sub> (100 mg, 0.72 mmol) was added. The mixture was filtered and the solvent evaporated under reduced pressure. The crude was purified by flash chromatography with silica gel (EtOAc/hexane 5:95, 3% Et<sub>3</sub>N) to afford 1.642 g of 1 (68 %) as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.25–7.18 (m, 1H), 7.14 (dd, <i>J</i> = 7.2, 1.2 Hz, 1H), 6.96 (t, <i>J</i> = 7.2 Hz, 2H), 6.73 (d, <i>J</i> = 9.7 Hz, 1H), 5.86 (dd, <i>J</i> = 9.7, 3.7 Hz, 1H), 5.71 (d, <i>J</i> = 3.7 Hz, 1H), 4.00-3.90 (m, 1H), 3.73-3.63 (m, 1H), 1.22 (t, <i>J</i> = 7.1 Hz, 3H); <sup>13</sup>C<sup>1</sup>H
NMR (CDCl₃, 75 MHz) δ 151.5 (C), 129.3 (CH), 127.1 (CH), 126.5 (CH), 121.4 (C), 120.8 (CH), 120.0 (CH), 116.5 (CH), 95.0 (CH), 63.5 (CH₂), 15.3 (CH₃); MS (EI) m/z 176 [M⁺] (18), 131 [M – C₂H₅O⁺] (100); HRMS (EI-magnetic sector) calcd for C₁₁H₁₂O₂ [M⁺] 176.0832, found 176.0828.

1-Methoxy-isochroman (14).³

To a solution of DDQ (4.03 g, 17.9 mmol) in CH₂Cl₂ (140 mL), MeOH (0.8 mL, 19.4 mmol) and isochroman (1.9 mL, 14.9 mmol) were successively added. The mixture was stirred at room temperature for 24 h, quenched with of satd aq NaHCO₃ (100 mL) and filtered through Celite. The aqueous layer was extracted with CH₂Cl₂ (2 × 60 mL), and then the combined organic layers were washed with brine (50 mL), dried (MgSO₄), filtered, and concentrated in vacuo. The crude was purified by flash chromatography with silica gel (EtOAc/hexane 5:95, 3% Et₃N) to afford 2.127 g of 14 (87%) as a yellow oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.27–7.23 (m, 3H), 7.15–7.13 (m, 1H), 5.47 (s, 1H), 4.15 (dt, J = 11.3, 3.4 Hz, 1H), 3.93 (dd, J = 11.3, 6.1 Hz, 1H), 3.57 (s, 3H), 3.05 (m, 1H); ¹³C{¹H} NMR (CDCl₃, 75 MHz) δ 134.1 (C), 134.0 (C), 128.4 (CH), 128.1 (CH), 127.4 (CH), 126.3 (CH), 97.8 (CH), 57.8 (CH₂), 55.3 (CH₃), 28.0 (CH₂); MS (EI) m/z 164 [M⁺] (17), 163 [M – H]⁺ (42), 133 [M – CH₃O]⁺ (100); HRMS (EI-magnetic sector) calcd for C₁₀H₁₁O₂ [M⁺] 164.0754, found 164.0750.

General Procedure for the Reaction of R₃In with 1 and 14.

To a solution of 1 or 14 (0.60 mmol) in dry THF (5 mL) at 0 ºC, BF₃•OEt₂ (0.091 mL, 0.72 mmol) was added. After 10 min stirring, a solution of R₃In (0.30 mmol, ~0.05 M) was added via cannula and the resulting mixture refluxed for 12 h. Reaction progress was monitored by TLC. The crude was concentrated in vacuo, and Et₂O (30 mL) was added. The organic phase was successively washed with water (2 × 50 mL) and brine (30 mL), dried (MgSO₄), filtered, and concentrated in vacuo. The residue was purified by flash chromatography to afford, after concentration and high vacuum-drying, the corresponding products.

2-Phenyl-2H-chromene (2).⁴

Following the General Procedure, the reaction of 1 (106 mg, 0.60 mmol) with triphenylindium (6 mL, 0.05 M in THF, 0.30 mmol) and BF₃•OEt₂ (0.091 mL, 0.72 mmol) for 12 h at 80 ºC afforded, after purification by flash chromatography (EtOAc/hexane 5:95, 3% Et₃N), 114 mg of 2 (91%) as a colorless oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.50–7.44 (m, 2H), 7.43–7.33 (m, 3H), 7.13 (td, J = 7.8, 1.8 Hz, 1H), 7.03 (dd, J = 7.5, 1.7 Hz, 1H), 6.89 (td,
\[ J = 7.4, 1.2 \text{ Hz}, 1\text{H} \], 6.82 (dd, \( J = 8.0, 1.2 \text{ Hz}, 1\text{H} \)), 6.56 (dd, \( J = 9.8, 1.9 \text{ Hz}, 1\text{H} \)), 5.94 (dd, \( J = 3.4, 1.9 \text{ Hz}, 1\text{H} \)), 5.82 (dd, \( J = 9.8, 3.4 \text{ Hz}, 1\text{H} \)); \[ ^{13}C\{^1H\} \text{ NMR} \text{ (CDCl}_3, 75 \text{ MHz}) \delta 153.2 \text{ (C)}, 140.9 \text{ (C)}, 129.5 \text{ (CH)}, 128.6 \text{ (2 × CH)}, 128.3 \text{ (CH)}, 127.0 \text{ (2 × CH)}, 126.6 \text{ (CH)}, 124.8 \text{ (CH)}, 124.0 \text{ (CH)}, 121.3 \text{ (C)}, 121.2 \text{ (CH)}, 116.0 \text{ (CH)}, 77.2 \text{ (CH)}; \text{ MS (EI)} \text{ m/z 208 [M]}^+ \text{ (77)} 207 [M – H]^- \text{ (100)}, 131 [M – C}_6H_5]^+ \text{ (47)}; \text{ HRMS (EI-magnetic sector) calcd for C}_{15}H_{12}O [M]^+ 208.0883, found 208.0877.

2-(4-Methylphenyl)-2H-chromene (3).\(^5\)

Following the General Procedure, the reaction of 1 (106 mg, 0.60 mmol) with tri-p-tolylindium (6 mL, 0.05 M in THF, 0.30 mmol) and BF\(_3\)•O\(_2\)Et (0.091 mL, 0.72 mmol) for 6 h at 23 °C afforded, after purification by flash chromatography (EtOAc/hexane 3:97, 3% Et\(_3\)N), 118 mg of 3 (88%) as a yellow oil. \(^1\)H NMR (CDCl\(_3\), 300 MHz) \( \delta 7.35 \text{ (d, } J = 8.1 \text{ Hz, } 1\text{H}), 7.18 \text{ (d, } J = 7.8 \text{ Hz, } 2\text{H}), 7.10 \text{ (td, } J = 7.6, 1.5 \text{ Hz, } 1\text{H}), 7.01 \text{ (dd, } J = 7.5, 1.5 \text{ Hz, } 1\text{H}), 6.86 \text{ (td, } J = 7.5, 1.2 \text{ Hz, } 1\text{H}), 6.77 \text{ (d, } J = 8.1 \text{ Hz, } 1\text{H}), 6.53 \text{ (dd, } J = 9.9, 1.5 \text{ Hz, } 1\text{H}), 5.91-5.87 \text{ (m, } 1 \text{H}), 5.79 \text{ (dd, } J = 9.8, 3.4 \text{ Hz, } 1\text{H}), 2.35 \text{ (s, } 1\text{H}); \[ ^{13}C\{^1H\} \text{ NMR} \text{ (CDCl}_3, 75 \text{ MHz}) \delta 153.2 \text{ (C)}, 138.2 \text{ (C)}, 137.9 \text{ (C)}, 129.4 \text{ (C)}, 129.3 \text{ (2 × CH)}, 127.1 \text{ (2 × CH)}, 126.5 \text{ (CH)}, 125.0 \text{ (CH)}, 123.9 \text{ (CH)}, 121.3 \text{ (C)}, 121.1 \text{ (CH)}, 116.0 \text{ (CH)}, 77.0 \text{ (CH)}, 21.2 \text{ (CH)}; \text{ MS (EI)} \text{ m/z 222 [M]}^+ \text{ (85)}, 221 [M – H]^+ \text{ (100)}, 207 [M – CH}_3]^+ \text{ (42)}; \text{ HRMS (EI-magnetic sector) calcd for C}_{16}H_{14}O [M]^+ 222.1039, found 222.1030.

2-(4-Methoxyphenyl)-2H-chromene (4).\(^5\)

Following the General Procedure, the reaction of 1 (106 mg, 0.60 mmol) with tri-(4-methoxyphenyl)indium (10 mL, 0.030 M in THF, 0.30 mmol) and BF\(_3\)•O\(_2\)Et (0.091 mL, 0.72 mmol) for 3 h at 23 °C afforded, after purification by flash chromatography (EtOAc/hexane 3:97, 3% Et\(_3\)N) 120 mg of 4 (84 %) as a colorless oil. \(^1\)H NMR (CDCl\(_3\), 300 MHz) \( \delta 7.43–7.37 \text{ (m, } 2\text{H}), 7.12 \text{ (td, } J = 7.8, 1.5 \text{ Hz, } 1\text{H}), 7.03 \text{ (dd, } J = 7.5, 1.5 \text{ Hz, } 1\text{H}), 6.94–6.90 \text{ (m, } 2\text{H}), 6.88 \text{ (t, } J = 7.5 \text{ Hz, } 1\text{H}), 6.8 \text{ (d, } J = 8.1 \text{ Hz, } 1\text{H}), 6.57 \text{ (dd, } J = 9.9, 1.8 \text{ Hz, } 1\text{H}), 5.89 \text{ (m, } 1\text{H}), 5.81 \text{ (dd, } J = 9.9, 3.6 \text{ Hz, } 1\text{H}), 3.82 \text{ (s, } 3\text{H}); \[ ^{13}C\{^1H\} \text{ NMR} \text{ (CDCl}_3, 75 \text{ MHz}) \delta 159.8 \text{ (C)}, 153.12 \text{ (C)}, 133.0 \text{ (C)}, 129.4 \text{ (CH)}, 128.6 \text{ (2 × CH)}, 126.5 \text{ (CH)}, 124.9 \text{ (CH)}, 124.0 \text{ (CH)}, 121.3 \text{ (C)}, 121.0 \text{ (CH)}, 116.0 \text{ (CH)}, 114 \text{ (2 × CH)}, 76.8 \text{ (CH)}, 55.3 \text{ (CH)}; \text{ MS (EI)} \text{ m/z 238 [M]}^+ \text{ (85)}, 237 [M – H]^+ \text{ (100)}; \text{ HRMS (EI-magnetic sector) calcd for C}_{16}H_{14}O_2 [M]^+ 238.0988, found 238.0983.

2-(Naphthalen-2-yl)-2H-chromene (5). Following the General Procedure, the reaction of 1 (106 mg, 0.60 mmol) with trinaphthylindium (12 mL, 0.025 M in THF, 0.30 mmol) and BF$_3$•OEt$_2$ (0.091 mL, 0.72 mmol) for 12 h at 80 °C afforded, after purification by flash chromatography (EtOAc/hexane 1:99, 3% Et$_3$N), 104 mg of 5 (67%) as white crystals. mp 80–81 °C (hexane); $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.62 (dd, $J = 7.4$, 1.8 Hz, 1H), 7.47 (m, 2H), 7.14 (td, $J = 7.8$, 1.5 Hz, 1H), 7.06 (dd, $J = 7.5$, 1.8 Hz, 1H), 6.90 (t, $J = 7.5$ Hz, 1H), 6.83 (d, $J = 8.1$ Hz, 1H), 6.60 (dd, $J = 9.8$, 1.8 Hz, 1H), 6.10 (m, 1H), 5.89 (dd, $J = 9.8$, 3.4 Hz, 1H); $^{13}$C {$^1$H} NMR (CDCl$_3$, 75 MHz) δ 153.2 (C), 143.7 (C), 133.3 (C), 133.2 (C), 129.5 (CH), 128.6 (CH), 128.2 (CH), 127.7 (CH), 126.6 (CH), 126.2 (CH), 126.0 (CH), 124.9 (CH), 124.7 (CH), 124.2 (CH), 121.3 (C), 121.2 (CH), 116.0 (CH), 77.3 (CH); MS (EI) m/z 258 [M]$^+$ (100), 257 [M – H]$^+$ (79); HRMS (EI-magnetic sector) calcd for C$_{19}$H$_{14}$O [M]$^+$ 258.1039, found 258.1030.

2-(4-Fluorophenyl)-2H-chromene (6). Following the General Procedure, the reaction of 1 (106 mg, 0.60 mmol) with tri-(4-fluorophenyl)indium (6 mL, 0.05 M in THF, 0.30 mmol) and BF$_3$•OEt$_2$ (0.091 mL, 0.72 mmol) for 12 h at 80 °C afforded, after purification by flash chromatography (EtOAc/hexane 5:95, 3% Et$_3$N), 115 mg of 6 (85%) as a colorless oil. $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.48–7.41 (m, 2H), 7.13 (td, $J = 7.8$, 1.5 Hz, 1H), 7.09–7.04 (m, 2H), 7.04–7.01 (m, 1H), 6.88 (td, $J = 7.4$, 1.1 Hz, 1H), 6.79 (d, $J = 8.1$ Hz, 1H), 6.56 (dd, $J = 9.9$, 1.5 Hz, 1H), 5.94–5.89 (m, 1H), 5.78 (dd, $J = 9.9$, 3.6 Hz, 1H); $^{13}$C {$^1$H} NMR (CDCl$_3$, 75 MHz) δ 163.7 (d, $J = 245.3$ Hz, C), 152.9 (C), 136.6 (d, $J = 3Hz$, C), 129.6 (CH), 129.0 (d, $J = 8.3$ Hz, 2 × CH), 126.6 (CH), 124.5 (CH), 124.3 (CH), 121.3 (CH), 121.2 (C), 116.0 (CH), 115.5 (d, $J = 21.8$ Hz, 2 × CH), 76.4 (CH); MS (EI) m/z 226 [M]$^+$ (68), 225 [M – H]$^+$ (100), 131 [M – C$_8$H$_4$F]$^+$ (73); HRMS (EI-magnetic sector) calcd for C$_{15}$H$_{11}$OF [M]$^+$ 226.0783, found 226.0783.

2-(Thiophen-2-yl)-2H-chromene (7). Following the General Procedure, the reaction of 1 (106 mg, 0.60 mmol) with tri(tiophen-2-yl)indium (8 mL, 0.0375 M in THF, 0.30 mmol) and BF$_3$•OEt$_2$ (0.091 mL, 0.72 mmol) for 12 h at 80 °C afforded, after purification by flash chromatography (EtOAc/hexane 2:98, 3% Et$_3$N) 95 mg of 7 (74%) as a colorless oil. $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.29 (dd, $J = 5.0$, 1.8 Hz, 1H), 7.15–7.07 (m, 2H), 7.04 (dd, $J = 7.8$, 1.8 Hz, 1H), 6.97 (dd, $J = 5.0$, 3.5 Hz, 1H), 6.88 (t, $J = 7.8$ Hz, 1H), 6.79 (d, $J = 8.1$ Hz, 1H), 6.6 (d, $J = 9.9$ Hz, 1H), 6.12 (d, $J = 3.9$ Hz, 1H), 5.93 (dd, $J = 9.9$, 3.9 Hz, 1H); $^{13}$C {$^1$H} NMR (CDCl$_3$, 75 MHz) δ 152.5 (C), 143.7 (C), 129.5 (CH), 126.7 (CH), 126.6 (CH), 126.3 (CH), 126.1 (CH), 124.6 (CH), 123.9 (CH), 121.2 (CH), 116.0 (CH), 77.3 (CH); MS (EI) m/z 258 [M]$^+$ (100), 257 [M – H]$^+$ (79); HRMS (EI-magnetic sector) calcd for C$_{15}$H$_{11}$OF [M]$^+$ 226.0783, found 226.0783.

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121.42 (CH), 121.38 (C), 116.41 (CH), 71.69 (CH); MS (EI) m/z 214 [M]+ (85), 213 [M – H]+ (100); HRMS (EI-magnetic sector) calcd for C_{13}H_{10}OS [M]+ 214.0447, found 214.0437.

2-(Trimethylsilylethynyl)-2H-chromene (8).
Following the General Procedure, the reaction of 1 (106 mg, 0.60 mmol) with tris(trimethylsilylethynyl)indium (8 mL, 0.0375 M in THF, 0.30 mmol) and BF$_3$•OEt$_2$ (0.091 mL, 0.72 mmol) for 12 h at 80 °C afforded, after purification by flash chromatography (EtOAc/hexane 2:98, 3% Et$_3$N) 116 mg of 8 (85%) as a yellow oil. $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.15 (td, J = 7.5, 1.8 Hz, 1H), 7.01 (dd, J = 7.4, 1.8 Hz, 1H), 6.92 (dd, J = 7.5, 1.2 Hz, 1H), 6.90–6.86 (m, 1H), 6.47 (dd, J = 9.6, 1.8 Hz, 1H), 5.75 (dd, J = 9.6, 3.6 Hz, 1H), 5.59 (dd, J = 3.6, 1.8 Hz, 1H) 0.18 (s, 9H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 75 MHz) δ 152.5 (C), 129.4 (CH), 126.7 (CH), 124.6 (CH), 122.2 (CH), 121.7 (CH), 121.3 (C), 116.4 (CH), 102.0 (C), 90.1 (C), 65.2 (CH), −0.3 (3 × CH$_3$); MS (EI) m/z 228 [M]+ (92), 227 [M – H]+ (85), 213 [M – CH$_3$]+ (100); HRMS (EI-magnetic sector) calcd for C$_{14}$H$_{16}$OSi [M]+ 228.0965, found 228.0962.

2-(Phenylethynyl)-2H-chromene (9). Following the General Procedure, the reaction of 1 (106 mg, 0.60 mmol) with tri(phenylethynyl)indium (8 mL, 0.0375 M in THF, 0.30 mmol) and BF$_3$•OEt$_2$ (0.091 mL, 0.72 mmol) for 12 h at 80 °C afforded, after purification by flash chromatography (EtOAc/hexane 2:98, 3% Et$_3$N) 124 mg of 9 (89%) as a colorless oil. $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.45–7.40 (m, 2H), 7.32–7.27 (m, 3H), 7.20 (td, J = 7.8, 1.8 Hz, 1H), 7.07 (dd, J = 8.0, 1.8 Hz, 1H), 6.96 (m, 2H), 6.65 (dd, J = 9.3 Hz, 1H), 5.87 (dd, J = 9.3, 3.9 Hz, 1H), 5.84 (d, J = 3.9Hz, 1H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 75 MHz) δ 152.5 (C), 131.9 (2 × CH), 129.5 (CH), 128.6 (CH), 128.2 (2 × CH), 126.8 (CH), 124.6 (CH), 122.2 (C), 122.1 (CH), 121.8 (CH), 121.4 (C), 116.5 (CH), 86.0 (C), 85.7 (C), 65.1 (CH); MS (EI) m/z 233 [M + H]+ (19), 232 [M]+ (100); HRMS (EI-magnetic sector) calcd for C$_{17}$H$_{12}$O [M]+ 232.0883, found 232.0877.

2-Styryl-2H-chromene (10). Following the general procedure A, the reaction of 1 (106 mg, 0.60 mmol) with tri(2-styryl)indium (16 mL, 0.038 M in THF, 0.60 mmol, prepared from β-bromostyrene, E/Z 88:12) and BF$_3$•OEt$_2$ (0.091 mL, 0.72 mmol) for 12 h at 80 °C afforded, after purification by flash chromatography (EtOAc/hexane 5:95, 3% Et$_3$N) 129 mg of 10 (92%, E/Z 87:13) as a yellow oil. $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.43–7.36 (m, 2H), 7.34–7.24 (m, 3H), 7.13 (td, J = 7.5, 1.5 Hz, 1H), 7.00 (dd, J = 7.2, 1.2 Hz, 1H), 6.94–6.86 (m, 1H), 6.84 (d, J = 7.8 Hz, 1H), 6.54 (dd, J = 2.1 Hz, 1H).

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6.68 (d, $J$ = 15.8 Hz, 1H), 6.50 (d, $J$ = 9.6 Hz, 1H), 6.37 (dd, $J$ = 15.8, 6.9 Hz, 1H), 5.80–5.89 (m, 0.26 H) 5.75 (dd, $J$ = 9.6, 3.6 Hz, 1H), 5.51–5.46 (m, 1H); 153.0 (C), 136.3 (C), 132.0 (CH), 129.3 (CH), 128.5 (2 × CH), 128.0 (CH), 127.2 (CH), 126.7 (2 × CH), 126.6 (CH), 124.2 (CH), 123.8 (CH), 121.6 (C), 121.2 (CH), 116.1 (CH), 75.6 (CH); MS (EI) m/z 234 [M$^+$] (100), 233 [M – H$^-$] (84); HRMS (EI-magnetic sector) calcd for C$_{17}$H$_{14}$O [M$^+$] 234.1039, found 234.1028.

2-n-Butyl-2H-chromene (11).$^9$

Following the General Procedure, the reaction of 1 (106 mg, 0.60 mmol) with tributylindium (6 mL, 0.05 M in THF, 0.30 mmol) and BF$_3$•OEt$_2$ (0.091 mL, 0.72 mmol) for 12 h at 80 ºC afforded, after purification by flash chromatography (EtOAc/hexane 1:99, 3% Et$_3$N), 47 mg of 11 (42%) as a colorless oil. $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.11 (td, $J$ = 7.5, 1.8 Hz, 1H), 6.97 (dd, $J$ = 7.5, 1.8 Hz, 1H), 6.85 (td, $J$ = 7.5, 1.2 Hz, 1H), 6.80 (d, $J$ = 7.5 Hz, 1H), 6.40 (d, $J$ = 9.9 Hz, 1H), 5.70 (dd, $J$ = 9.9, 3.3 Hz, 1H), 4.91–4.82 (m, 1H), 1.89–1.62 (m, 2H), 1.55–1.30 (m, 4H), 0.94 (t, $J$ = 7.2 Hz, 3H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 75 MHz) δ 153.6 (C), 129.0 (CH), 126.4 (CH), 126.0 (CH), 123.9 (CH), 122.0 (C), 120.9 (CH), 115.9 (CH), 75.2 (CH), 35.1 (CH$_2$), 27.0 (CH$_2$), 22.6 (CH$_2$), 14.0 (CH$_2$); MS (EI) m/z 188 [M$^+$] (7), 131 [M – C$_4$H$_9$]$^+$ (100); HRMS (EI-magnetic sector) calcd for C$_{13}$H$_{16}$O [M$^+$] 188.1196, found 188.1193.

2-Methyl-2H-chromene (12).$^{10}$

Following the General Procedure, the reaction of 1 (106 mg, 0.60 mmol) with trimethylindium (6 mL, 0.05 M in THF, 0.30 mmol) and BF$_3$•OEt$_2$ (0.091 mL, 0.72 mmol) for 12 h at 80 ºC afforded, after purification by flash chromatography (EtOAc/hexane 1:99, 3% Et$_3$N), 35 mg of 12 (40%) as a colorless oil. $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.10 (td, $J$ = 7.8, 1.8 Hz, 1H), 6.96 (dd, $J$ = 7.4, 1.8 Hz, 1H), 6.84 (td, $J$ = 7.4, 1.2 Hz, 1H), 6.78 (d, $J$ = 7.8 Hz, 1H), 6.38 (dd, $J$ = 9.8, 1.8 Hz, 1H), 5.65 (dd, $J$ = 9.8, 3.1 Hz), 5.06–4.96 (m, 1H), 1.45 (d, $J$ = 6.6 Hz, 3H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 75 MHz) δ 153.5 (C), 129.1 (CH), 126.9 (CH), 126.4 (CH), 123.7 (CH), 121.8 (C), 121.0 (CH), 115.9 (CH), 71.4 (CH), 21.3 (CH$_3$); MS (EI) m/z 146 [M$^+$] (13), 131 [M – CH$_3$]$^+$ (100); HRMS (EI-magnetic sector) calcd for C$_{10}$H$_{10}$O [M$^+$] 146.0726, found 146.0726.

2-Cyclopropyl-2H-chromene (13).

Following the General Procedure, the reaction of 1 (106 mg, 0.60 mmol) with tricyclopropylindium (8 mL, 0.0375 M in THF, 0.30 mmol) and BF$_3$•OEt$_2$ (0.091 mL, 0.72 mmol) for 12 h at 80 ºC afforded, after purification by flash chromatography (EtOAc/hexane

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0.5:99.5, 3% Et<sub>3</sub>N), 87 mg of 13 (84%) as a colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.12 (td, J = 7.8, 1.5 Hz, 1H), 6.97 (dd, J = 7.5, 1.8 Hz, 1H), 6.84 (t, J = 7.8 Hz, 2H), 6.43 (d, J = 9.9 Hz, 1H), 5.74 (dd, J = 9.9, 3.3 Hz, 1H), 4.24 (d, J = 8.4 Hz, 1H), 1.35–1.21 (m, 1H), 0.68–0.45 (m, 3H), 0.39–0.30 (m, 1H); <sup>13</sup>C<sup>{1}H</sup>NMR (CDCl<sub>3</sub>, 75 MHz) δ 153.7 (C), 129.1 (CH), 126.4 (CH), 124.6 (CH), 124.2 (CH), 121.9 (C), 120.9 (CH), 115.9 (CH), 79.5 (CH), 15.8 (CH), 3.1 (CH<sub>2</sub>), 1.3 (CH<sub>2</sub>); MS (EI) m/z 172 [M]+ (40), 131 [M – C<sub>3</sub>H<sub>5</sub>]+ (100); HRMS (EI-magnetic sector) calcd for C<sub>12</sub>H<sub>12</sub>O [M]+ 172.0888, found 172.0883.

### 1-Phenyl-isochroman (15)<sup>11</sup>

Following the General Procedure, the reaction of 14 (100 mg, 0.61 mmol) with triphenylindium (6 mL, 0.052 M in THF, 0.31 mmol) and BF<sub>3</sub>•OEt<sub>2</sub> (0.092 mL, 0.73 mmol) for 12 h at 80 ºC afforded, after purification by flash chromatography (EtOAc/hexane 5:95, 3% Et<sub>3</sub>N), 118 mg of 15 (92%) as a colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.12 (td, J = 7.8, 1.5 Hz, 1H), 6.97 (dd, J = 7.5, 1.8 Hz, 1H), 6.84 (t, J = 7.8 Hz, 2H), 6.43 (d, J = 9.9 Hz, 1H), 5.74 (dd, J = 9.9, 3.3 Hz, 1H), 4.24 (d, J = 8.4 Hz, 1H), 1.35–1.21 (m, 1H), 0.68–0.45 (m, 3H), 0.39–0.30 (m, 1H); <sup>13</sup>C<sup>{1}H</sup>NMR (CDCl<sub>3</sub>, 75 MHz) δ 153.7 (C), 129.1 (CH), 126.4 (CH), 124.6 (CH), 124.2 (CH), 121.9 (C), 120.9 (CH), 115.9 (CH), 79.5 (CH), 15.8 (CH), 3.1 (CH<sub>2</sub>), 1.3 (CH<sub>2</sub>); MS (EI) m/z 210 [M]+ (100), 209 [M – H]+ (49); HRMS (EI-magnetic sector) calcd for C<sub>15</sub>H<sub>14</sub>O [M]+ 210.1039, found 210.1034.

### 1-(4-Methylphenyl)-isochroman (16)<sup>12</sup>

Following the General Procedure, the reaction of 14 (100 mg, 0.61 mmol) with tri-p-tolylindium (6 mL, 0.052 M in THF, 0.31 mmol) and BF<sub>3</sub>•OEt<sub>2</sub> (0.092 mL, 0.73 mmol) for 12 h at 80 ºC afforded, after purification by flash chromatography (EtOAc/hexane 2:98, 3% Et<sub>3</sub>N), 123 mg of 16 (90%) as a colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.23–7.18 (m, 2H), 7.14–7.07 (m, 1H), 6.79 (d, J = 7.9 Hz, 1H), 5.77 (s, 1H), 4.27–4.20 (m, 1H), 4.01–3.93 (m, 1H), 3.23–3.13 (m, 1H), 2.83 (dt, J = 16.7, 4.2 Hz, 1H); <sup>13</sup>C<sup>{1}H</sup>NMR (CDCl<sub>3</sub>, 75 MHz) δ 142.3 (C), 137.4 (C), 133.9 (C), 128.9 (2×CH), 128.7 (CH), 128.4 (2×CH), 128.1 (CH), 126.9 (CH), 126.6 (CH), 125.9 (CH), 79.7 (CH), 63.9 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>); MS (EI) m/z 224 [M]+ (100), 209 [M – H]+ (49); HRMS (EI-magnetic sector) calcd for C<sub>16</sub>H<sub>16</sub>O [M]+ 224.1139, found 224.1139.

### 1-(4-Methoxyphenyl)-isochroman (17)<sup>13</sup>

Following the General Procedure, the reaction of 14 (100 mg, 0.61 mmol) with tri-(4-methoxyphenyl)indium (10 mL, 0.031 M in THF, 0.31 mmol) and BF<sub>3</sub>•OEt<sub>2</sub> (0.092 mL, 0.73

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mmol) for 12 h at 80 °C afforded, after purification by flash chromatography (EtOAc/hexane 2:98, 3% Et3N), 123 mg of 17 (84%) as a yellow oil. 1H NMR (CDCl3, 300 MHz) δ 7.28–7.22 (m, 2H), 7.21–7.16 (m, 2H), 7.13–7.06 (m, 1H), 6.93–6.86 (m, 2H), 6.78 (d, J = 7.5 Hz, 1H), 5.72 (s, 1H), 4.24–4.16 (m, 1H), 3.99–3.90 (m, 1H), 3.81 (s, 3H), 3.21–3.08 (m, 1H), 2.83 (dt, J = 16.5, 3.9 Hz, 1H); 13C{1H} NMR (CDCl3, 75 MHz) δ 159.4 (C), 137.7 (C), 134.6 (C), 133.9 (C), 130.1 (2×CH), 128.7 (CH), 127.0 (CH), 126.6 (CH), 125.9 (CH), 126.3 (CH2), 55.3 (CH3), 28.9 (CH2); MS (EI) m/z 240 [M]+ (100), 239 [M–H]+ (68), 209 [CH3O]+ (81); HRMS (EI–magnetic sector) calcd for C16H16O2 [M]+ 240.1145, found 240.1140.

1-(4-Fluorophenyl)-isochroman (18).12

Following the General Procedure, the reaction of 14 (100 mg, 0.61 mmol) with tri-(4-fluorophenyl)indium (6 mL, 0.052 M in THF, 0.31 mmol) and BF3•OEt2 (0.092 mL, 0.73 mmol) for 12 h at 80 °C afforded, after purification by flash chromatography (EtOAc/hexane 5:95, 3% Et3N), 123 mg of 18 (88%) as a colorless oil. 1H NMR (CDCl3, 300 MHz) δ 7.34–7.27 (m, 2H), 7.22–7.16 (m, 2H), 7.13–7.08 (m, 1H), 7.04 (t, J = 8.7 Hz, 2H), 6.74 (d, J = 7.5 Hz, 1H), 5.73 (s, 1H), 4.25–4.15 (m, 1H), 3.99–3.90 (m, 1H), 3.22–3.10 (m, 1H), 2.82 (dt, J = 16.2, 3.6 Hz, 1H); 13C{1H} NMR (CDCl3, 75 MHz) δ 162.5 (d, J = 244.9 Hz, C), 138.1 (d, J = 3.2 Hz, C), 137.2 (C), 133.8 (C), 130.6 (d, J = 8.2 Hz, 2×CH), 128.8 (CH), 126.8 (CH), 126.7 (CH), 126.0 (CH), 115.3 (d, J = 21.3 Hz, 2×CH), 78.9 (CH), 63.9 (CH2), 28.8 (CH2); MS (EI) m/z 228 [M]+ (16), 83 [M–C10H9O]+ (100); HRMS (EI–magnetic sector) calcd for C15H13OF [M]+ 228.0945, found 228.0940.

1-(Thiophen-2-yl)-isochroman (19).14

Following the General Procedure, the reaction of 14 (100 mg, 0.61 mmol) with tri(thiophen-2-yl)indium (8.2 mL, 0.038 M in THF, 0.31 mmol) and BF3•OEt2 (0.092 mL, 0.73 mmol) for 12 h at 80 °C afforded, after purification by flash chromatography (EtOAc/hexane 3:97, 3% Et3N), 98 mg of 19 (71%) as a colorless oil. 1H NMR (CDCl3, 300 MHz) δ 7.32–7.29 (m, 1H), 7.23–7.12 (m, 3H), 7.02–6.96 (m, 3H), 6.06 (s, 1H), 4.18–4.10 (m, 1H), 4.00–3.90 (m, 1H), 3.01–2.87 (m, 2H); 13C{1H} NMR (CDCl3, 75 MHz) δ 146.0 (C), 136.3 (C), 133.5 (C), 128.8 (CH), 127.2 (CH), 127.0 (CH), 126.8 (CH), 126.2 (CH), 126.1 (CH), 125.9 (CH), 73.9 (CH), 62.4 (CH2), 28.5 (CH2); MS (EI) m/z 216 [M]+ (100), 215 [M–H]+ (37); HRMS (EI–magnetic sector) calcd for C13H12OS [M]+ 216.0603, found 216.0599.

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1-Phenylethynyl-isochroman (20).\(^{15}\)
Following the General Procedure, the reaction of 14 (100 mg, 0.61 mmol) with tri(phenylethynyl)indium (8.2 mL, 0.038 M in THF, 0.31 mmol) and BF\(_3\)•OEt\(_2\) (0.092 mL, 0.73 mmol) for 12 h at 80 °C afforded, after purification by flash chromatography (EtOAc/hexane 2:98, 3% Et\(_3\)N), 117 mg of 20 (82%) as a yellow oil. \(^1\)H NMR (CDCl\(_3\), 300 MHz) δ 7.49–7.43 (m, 2H), 7.38–7.33 (m, 1H), 7.33–7.28 (m, 3H), 7.25–7.20 (m, 2H), 7.17–7.12 (m, 1H), 5.78 (s, 1H), 4.37–4.26 (m, 1H), 4.08–3.98 (m, 1H), 2.96–2.89 (m, 2H); \(^{13}\)C\{\(^1\)H\} NMR (CDCl\(_3\), 75 MHz) δ 134.9 (C), 132.8 (C), 131.8 (2×CH), 129.0 (CH), 128.4 (CH), 128.2 (2×CH), 127.2 (CH), 126.4 (CH), 126.0 (CH), 122.6 (C), 88.1 (C), 85.7 (C), 67.3 (CH), 62.7 (CH\(_2\)), 28.0 (CH\(_2\)); MS (EI) m/z 234 [M\(^+\)] (92), 233 [M–H\(^+\)] (77); HRMS (EI-magnetic sector) calcd for C\(_{17}\)H\(_{14}\)O [M\(^+\)] 234.1039, found 234.1032.

1-Trimethylsilylethynyl-isochroman (21).\(^{16}\)
Following the General Procedure, the reaction of 14 (100 mg, 0.61 mmol) with tris(trimethylsilylethynyl)indium (8.4 mL, 0.037 M in THF, 0.31 mmol) and BF\(_3\)•OEt\(_2\) (0.092 mL, 0.73 mmol) for 12 h at 80 °C afforded, after purification by flash chromatography (EtOAc/hexane 3:97, 3% Et\(_3\)N), 97 mg of 21 (70%) as a yellow oil. \(^1\)H NMR (CDCl\(_3\), 300 MHz) δ 7.33–7.27 (m, 1H), 7.25–7.17 (m, 2H), 7.16–7.07 (m, 1H), 5.54 (s, 1H), 4.30–4.20 (m, 1H), 4.00–3.90 (m, 1H), 2.88 (t, \(J = 5.9\) Hz, 2H), 0.19 (s, 9H); \(^{13}\)C\{\(^1\)H\} NMR (CDCl\(_3\), 75 MHz) δ 134.7 (C), 132.7 (C), 128.9 (CH), 127.2 (CH), 126.3 (CH), 126.0 (CH), 104.1 (C), 90.4 (C), 67.4 (CH), 62.8 (CH\(_2\)), 28.0 (CH\(_2\)), −0.2 (3×CH\(_3\)); MS (EI) m/z 230 [M\(^+\)] (40), 229 [M−H\(^+\)] (34), 73 [M−C\(_{11}\)H\(_9\)O]\(^+\) (100); HRMS (EI-magnetic sector) calcd for C\(_{14}\)H\(_{18}\)OSi [M\(^+\)] 230.1121, found 230.1113.

\((2\xi)-2-((1S)-1-phenylethoxy)-2H-chromene (22a and 22b).\)
To a solution of coumarin (650 mg, 4.44 mmol) in CH\(_2\)Cl\(_2\) (15 mL), DIBAL-H (4.66 mL, 4.66 mmol, 1.0 M) was added drop wise for 1.5 h at −78 °C. The reaction was stirred for 2 h, warmed to 0 °C, and then allowed to reach rt. The mixture was diluted with EtOAc (30 mL) and water (30 mL). After filtration through Celite, the aqueous layer was extracted with EtOAc (2×20 mL) and the resulting organic layer was washed with brine (30 mL), dried (MgSO\(_4\)), filtered, and concentrated to yield a viscous yellow oil. The crude was dissolved in dry THF (20 mL) and (R)-1-phenylethanol (0.8 ml, 6.65 mmol) and trifluoroacetic acid (15 µL, 0.20 mmol) were added. After 12 h stirring at rt, K\(_2\)CO\(_3\) (30 mg, 0.22 mmol) was added. The mixture was filtered and the solvent evaporated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 3:97, 3% Et\(_3\)N) to afford, after high vacuum

\(^{15}\) Correia, C.A.; Li, C.-J.; \textit{Heterocycles} \textbf{2010}, 82, 555–562.
drying, 490 mg of 22a (44%) and 181 mg of 22b (6%) as yellow oils (the absolute stereochemistry of diastereomers of 22 was not determined).

22a: $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.44–7.29 (m, 5H), 7.24 (td, $J = 7.6$ Hz, 1.8 Hz, 1H), 7.15 (dd, $J = 7.5$ Hz, 1.5 Hz, 1H), 7.05–6.93 (m, 2H), 6.74 (d, $J = 9.6$ Hz, 1H), 5.78 (dd, $J = 9.6$ Hz, 3.9 Hz, 1H), 5.52 (d, $J = 3.6$ Hz, 1H), 5.11 (q, $J = 6.6$ Hz, 1H), 1.41 (d, $J = 6.6$ Hz, 3H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 75 MHz) δ 151.4 (C), 143.1 (C), 129.3 (CH), 128.6 (2×CH), 127.7 (CH), 127.1 (CH), 126.53 (2×CH), 126.48 (CH), 121.4 (CH), 120.9 (C), 120.2 (CH), 116.6 (CH), 92.3 (CH), 74.3 (CH) 24.2 (CH$_3$). MS (EI) $m/z$ 252 [M]$^+$ (3), 105 [M–C$_{10}$H$_{11}$O]$^+$ (100); HRMS (EI-magnetic sector) calcd for C$_{17}$H$_{16}$O$_2$ [M]$^+$ 252.1145, found 252.1147.

22b: $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.31–7.20 (m, 5H), 7.14–7.04 (m, 2H), 6.93 (td, $J = 7.5$ Hz, 1.2 Hz, 1H), 6.74 (d, $J = 9.3$ Hz, 1H), 6.41 (d, $J = 8.1$ Hz, 1H), 5.96–5.87 (m, 2H), 4.96 (q, $J = 6.6$ Hz, 1H), 1.53 (d, $J = 6.6$ Hz, 3H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 75 MHz) δ 151.1 (C), 144.3 (C), 129.0 (CH), 128.1 (2×CH), 127.0 (CH), 126.7 (CH), 126.6 (CH), 126.1 (2×CH), 121.2 (CH), 120.6 (C), 119.9 (CH), 116.7 (CH), 94.6 (CH), 76.8 (CH), 23.2 (CH$_3$). MS (EI) $m/z$ 252 [M]$^+$ (3), 105 [M–C$_{10}$H$_{11}$O]$^+$ (100); HRMS (EI-magnetic sector) calcd for C$_{17}$H$_{16}$O$_2$ [M]$^+$ 252.1149, found 252.1149.

**Reaction of Ph$_3$In with 22a and 22b.**

Following the General Procedure, the reaction of 22a (100 mg, 0.40 mmol) with triphenylindium (8 mL, 0.05 M in THF, 0.40 mmol) and BF$_3$•OEt$_2$ (0.061 mL, 0.48 mmol) for 6 h at rt afforded, after purification by flash chromatography (EtOAc/hexane 5:95, 3% Et$_3$N), 77 mg of 2 (92%, er 48:52) as a colorless oil. Enantiomers were discriminated by HPLC analysis using a chiral stationary phase (Chiralcel OJ-H) eluent 2-propanol/hexane 1:99, flow rate = 0.7 mL/min, $\lambda = 280$ nm, $t_1 = 28$ min, $t_2 = 32$ min.

Following the General Procedure, the reaction of 22b (100 mg, 0.40 mmol) with triphenylindium (8 mL, 0.05 M in THF, 0.40 mmol) and BF$_3$•OEt$_2$ (0.061 mL, 0.48 mmol) for 6 h at rt afforded, after purification by flash chromatography (EtOAc/hexane 5:95, 3% Et$_3$N), 79 mg of 2 (94%, er 50:50) as a colorless oil. Enantiomers were discriminated by HPLC analysis using a chiral stationary phase (Chiralcel OJ-H) eluent 2-propanol/hexane 1:99, flow rate = 0.7 mL/min, $\lambda = 280$ nm, $t_1 = 30$ min, $t_2 = 34$ min.
300 MHz $^1$H NMR Spectrum of Compound 1 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of Compound 1 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of Compound 2 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of Compound 2 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of Compound 3 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of Compound 3 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of Compound 4 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of Compound 4 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of Compound 5 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of Compound 5 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of Compound 6 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of Compound 6 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of Compound 7 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of Compound 7 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of Compound 8 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of Compound 8 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of Compound 9 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of Compound 9 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of Compound 10 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of Compound 10 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of Compound 11 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of Compound 11 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of Compound 12 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of Compound 12 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of Compound 13 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of Compound 13 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of Compound 14 (CDCl$_3$, 300 K)

![300 MHz $^1$H NMR Spectrum of Compound 14 (CDCl$_3$, 300 K)](image1)

75 MHz $^{13}$C NMR Spectrum of Compound 14 (CDCl$_3$, 300 K)

![75 MHz $^{13}$C NMR Spectrum of Compound 14 (CDCl$_3$, 300 K)](image2)
300 MHz $^1$H NMR Spectrum of Compound 15 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of Compound 15 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of Compound 16 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of Compound 16 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of Compound 17 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of Compound 17 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of Compound 18 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of Compound 18 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of Compound 19 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of Compound 19 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of Compound 20 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of Compound 20 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of Compound 21 (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of Compound 21 (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of Compound 22a (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of Compound 22a (CDCl$_3$, 300 K)
300 MHz $^1$H NMR Spectrum of Compound 22b (CDCl$_3$, 300 K)

75 MHz $^{13}$C NMR Spectrum of Compound 22b (CDCl$_3$, 300 K)
HPLC: Chiralcel OJ-H, eluent 2-propanol/hexane 1:99, flow rate = 0.7 mL/min, $\lambda = 280$ nm

Chromatogram of 2 from reaction of acetal 22a
er = 48:52

Chromatogram of 2 from reaction of acetal 22b
er = 50:50