Rhodium-Catalyzed Hydroformylation of Alkynes Employing a Self-Assembling Ligand System

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Supporting Information

I General

All reactions were carried out in oven-dried glassware under an atmosphere of argon (argon 5.0 from Sauerstoffwerke Friedrichshafen). [Rh(CO)\textsubscript{2}acac] was a gift from BASF. All solvents were dried and distilled by standard procedures. Chromatographic purification of products was accomplished using flash chromatography\textsuperscript{[1]} on Macherey-Nagel silica gel 60\textsuperscript{®} (230-400 mesh). Hydroformylation reactions at 50-55 °C were performed in an Endeavor parallel autoclave with 8 reaction vessels from Argonaut Technologies. Gases: Carbon monoxide 3.7, hydrogen 4.3 (1:1, Messer-Griesheim).

Melting points were measured on a Büchi melting point apparatus using open glass capillaries, and the values are uncorrected.

Nuclear magnetic resonance spectra were acquired on a Bruker DRX 500 spectrometer, a Bruker Avance 400 spectrometer, a Bruker Avance DRX 250 spectrometer and on a Varian Mercury 300 spectrometer. NMR-spectra are referenced internally according to TMS [0.00 ppm (\textsuperscript{1}H)] or residual protio solvent signals [CDCl\textsubscript{3}: 77.10 ppm (\textsuperscript{13}C)].\textsuperscript{[2]} Data for \textsuperscript{1}H-NMR are reported as follows: chemical shift (δ in ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; mc, symmetrical multiplet; br, broad signal; p, pseudo), coupling constant (Hz), integration. Data for \textsuperscript{13}C-NMR are reported in terms of chemical shift, integration.
II Experimental procedures and characterizations

Synthesis of ligands

PPh$_3$ and Biphephos are commercially available. The 6-DPPon ligand (L1) was prepared applying a methodology developed in our group.$^{[3]}$

General procedure A: Synthesis of L2-4

![Chemical Structure]

To a solution of 2-bromo-6-( tert-butoxy)pyridine (1.0 equiv.) in Et$_2$O was added slowly at 0 °C nBuLi (1.1 equiv.). The reaction mixture was stirred for 60 min, then bisarylchlorophosphine (1.15 equiv.) was added and the reaction mixture was stirred for further 60 min at room temperature. The reaction was quenched with H$_2$O (1.15 equiv.) and the solution concentrated in vacuo. The resulting oil was directly dissolved in degased formic acid and was stirred at room temperature for 60 min. Afterwards the mixture was diluted with H$_2$O and extracted with Et$_2$O three times. The combined organic layers were washed with brine, dried over MgSO$_4$ and concentrated in vacuo. Flash chromatography (CH$_2$Cl$_2$/EtOAc) and subsequently trituration in pentane yielded the desired compounds L2-4.

Synthesis of 6-bis-(4-fluorophenyl)-phosphino-pyridin-2(1H)-one (L2)

Following the general procedure A the title compound was isolated by flash chromatography (SiO$_2$, CH$_2$Cl$_2$:EtOAc = 10:1, R$_f$ = 0.5) as a colorless solid in 75% (0.64 g, 2.03 mmol) yield. Mp = 185 °C.
**1H-NMR (400.130 MHz, CDCl3):** δ (ppm) = 6.06 (dd, 3J = 6.1 Hz, 3J = 5.1 Hz, 1H, ArH), 6.46 (d, 3J = 9.2 Hz, 1H, ArH), 7.10 (dd, 3J = 8.4 Hz, 4J = 8.4 Hz, 1H, ArH), 7.30 (m, 4H ArH), 7.35 (m, 4H ArH), 9.63 (bs, 1H, NH).

**13C{1H}-NMR (125.692 MHz, CDCl3):** δ (ppm) = 113.3 (d, 2J_C-P = 17.0 Hz), 116.7 (dd, 2J_C-F = 21.2 Hz, 3J_C-P = 8.3 Hz, 4C), 121.0 (b), 128.2 (dd, 1J_C-P = 9.6 Hz, 4J_C-F = 3.5 Hz, 2C), 136.1 (dd, 2J_C-P = 22.1 Hz, 3J_C-F = 8.3 Hz, 4C), 140.3 (d, 3J_C-P = 5.7 Hz), 146.6 (d, 1J_C-P = 23.2 Hz), 164.2 (d, 1J_C-F = 251.8 Hz, 2C), 164.2 (b).

**31P{1H}-NMR (121.468 MHz, C6D6):** δ (ppm) = −10.9 (t, 2J_P-F = 4.2 Hz).

**CHN:** Calcd. C: 64.77, H: 3.84, N: 4.44; Found C: 64.58, H: 3.90, N: 4.53.

**Synthesis of 6-bis-([4-trifluoromethyl]phenyl)-phosphino-pyridin-2(1H)-one (L3)**

Following the general procedure A the title compound was isolated by flash chromatography (SiO2, CH2Cl2:EtOAc = 10:1, Rf = 0.6) as a colorless solid in 62% (1.19 g, 2.87 mmol) yield. Mp =166-169 °C.

**1H-NMR (400.130 MHz, CDCl3, (CD3)2SO):** δ (ppm) = 5.59 (dd, 3J = 6.7 Hz, 2J = 2.7 Hz, 1H, ArH), 6.18 (d, 3J = 9.3 Hz, 1H, ArH), 7.01 (dd, 3J = 8.1 Hz, 3J = 8.1 Hz, 1H, ArH), 7.18 (m, 4H ArH), 7.35 (m, 4H ArH), 7.75 (bs, 1H, NH).

**13C{1H}-NMR (100.613 MHz, CDCl3, (CD3)2SO):** δ (ppm) = 112.9 (d, 2J_C-P = 10.7 Hz), 120.0 (bs), 123.1 (q, 1J_C-F = 271.6 Hz, 2C), 125.0 (dq, 3J_C-F = 7.4 Hz, 4J_C-F = 3.6 Hz, 4C), 131.0 (q, 2J_C-F = 32.6 Hz, 2C), 132.0 (d, 1J_C-P = 10.0 Hz, 2C), 133.7 (d, 2J_C-P = 20.5 Hz, 4C), 137.4 (d, 3J_C-P = 12.6 Hz), 139.4 (d, 3J_C-P = 3.9 Hz), 163.4 (d, 3J_C-P = 4.9 Hz).

**19F-NMR (235.357 MHz, CDCl3, (CD3)2SO):** δ (ppm) = −57.95 (s).

**31P{1H}-NMR (161.976 MHz, CDCl3, (CD3)2SO):** δ (ppm) = −5.5 (s).

**MS (APCI, C19H13F6NOP, M = 415.27 g/mol):** m/z (%) = 432.0 (12), 416.1 (100), 395.1 (1), 353.1 (1).

Synthesis of 6-bis-(3,5-bis-(trifluoromethyl)-phenyl)-phosphino-pyridin-2(1H)-one (L4)

Following the general procedure A the title compound was isolated by flash chromatography (SiO\textsubscript{2}, CH\textsubscript{2}Cl\textsubscript{2}:EtOAc = 10:1, R\textsubscript{f} = 0.3) as a colorless solid in 61% (584 mg, 1.06 mmol) yield.

\[ \text{Mp} = 213 \, ^{\circ}\text{C} \]

\[ ^{1}\text{H}-\text{NMR} \, (300.066 \text{ MHz, CDCl}_{3}): \delta (\text{ppm}) = 6.27 \, (d, \, ^{3}J = 9.2 \, \text{Hz, 1H, ArH}), \, 6.45 \, (dd, \, ^{3}J = 7.5 \, \text{Hz, }^{3}J = 7.5 \, \text{Hz, 1H, ArH}), \, 7.37 \, (ddd, \, ^{3}J = 8.8 \, \text{Hz, }^{3}J = 7.0 \, \text{Hz, }^{3}J = 1.8 \, \text{Hz, 1H, ArH}), \, 7.91 \, (bs, \, 4\text{H, ArH}), \, 7.94 \, (bs, \, 2\text{H, ArH}), \, 11.00 \, (bs, \, 1\text{H, NH}). \]

\[ ^{13}\text{C}\{^{1}\text{H}\}-\text{NMR} \, (100.613 \text{ MHz, CDCl}_{3}): \delta (\text{ppm}) = 116.8 \, (d, \, ^{2}J_{C:P} = 31.2 \, \text{Hz}), \, 122.9, \, 123.0 \, (q, \, ^{1}J_{C:F} = 273.3 \, \text{Hz, 4C}), \, 123.9-124.3 \, (m, \, 2C), \, 132.5 \, (qd, \, ^{2}J_{C:F} = 33.7 \, \text{Hz, }^{3}J_{C:P} = 6.8 \, \text{Hz, 4C}), \, 133.7 \, (m, \, 4C), \, 136.1 \, (d, \, ^{1}J_{C:P} = 15.0 \, \text{Hz, 2C}), \, 140.4 \, (d, \, ^{3}J_{C:P} = 11.1 \, \text{Hz}), \, 142.7 \, (d, \, ^{1}J_{C:P} = 25.4 \, \text{Hz}), \, 165.3 \, (d, \, ^{4}J_{C:P} = 1.4 \, \text{Hz}). \]

\[ ^{31}\text{P}\{^{1}\text{H}\}-\text{NMR} \, (161.976 \text{ MHz, CDCl}_{3}): \delta (\text{ppm}) = -5.7 \, (s). \]

HRMS (EI, [M\textsuperscript{+}]): Calcd.: 551.030802; Found: 551.030056.

Synthesis of substrates

Alkynes 1a-d, 4a, 7a-b are commercially available. Alkynes 4b-n were prepared in accordance with a literature procedure developed by P. A. Grieco.\[^{[4]}\]

General procedure B: Synthesis of 2 and 8

An oven dried glass inlet was purged with argon and charged with [Rh(CO)\textsubscript{2}acac] (3.0 mg, 11.6 μmol, 1.0 mol%), L4 (19.2 mg, 34.8 μmol, 3.0 mol%) and 1 or 7 (1.16 mmol, 100 mol%). Toluene (2 ml) was added via syringe and the glass inlet was transferred into the autoclave. The autoclave was sealed and purged three times with 5 bar of the CO/H\textsubscript{2} gas-mixture (1:1). Then it was pressurized with 5 bar of CO/H\textsubscript{2} (1:1), heated to 55 °C and stirred for 20 h. Subsequently, the autoclave was cooled to room temperature, the CO/H\textsubscript{2} gas was released and the reaction mixture was analyzed and purified.
General procedure C: Synthesis of 5
An oven dried glass inlet was purged with argon and charged with [Rh(CO)$_2$acac] (1.5 mg, 5.8 μmol, 0.5 mol%), L4 (9.6 mg, 17.4 μmol, 1.5 mol%) and 4 (1.16 mmol, 100 mol%). Toluene (2 ml) was added via syringe and the glass inlet was transferred into the autoclave. The autoclave was sealed and purged three times with 5 bar of the CO/H$_2$ gas-mixture (1:1). Then it was pressurized with 5 bar of CO/H$_2$ (1:1), heated to 55 °C and stirred for 20 h. Subsequently, the autoclave was cooled to room temperature, the CO/H$_2$ gas was released and the reaction mixture was analyzed and purified.

Synthesis of (E)-2-propylhex-2-enal (2a)

Following the general procedure B the title compound was isolated by flash chromatography (SiO$_2$, pentane:CH$_2$Cl$_2$ = 1.5:1, R$_f$ = 0.3) as a colorless oil in 92% (150 mg, 1.068 mmol) yield. The analytical data are in agreement with those reported previously.[5]

$^1$H-NMR (400.130 MHz, CDCl$_3$): $\delta$ (ppm) = 0.89 (t, $^3J = 7.4$ Hz, 3H), 0.98 (t, $^3J = 7.4$ Hz, 3H), 1.38 (qt, $^3J = 7.4$ Hz, $^3J = 7.4$ Hz, 2H), 1.54 (qt, $^3J = 7.4$ Hz, $^3J = 7.4$ Hz, 2H), 2.22 (t, $^3J = 7.4$ Hz, 2H), 2.34 (dt, $^3J = 7.4$ Hz, $^3J = 7.4$ Hz, 2H), 6.45 (t, $^3J = 7.4$ Hz, 1H), 9.37 (s, 1H, CHO).

$^{13}$C-NMR (100.613 MHz, CDCl$_3$): $\delta$ (ppm) = 14.0, 14.2, 22.0, 22.1, 26.0, 31.0, 143.9, 155.3, 195.5 (CHO).

Synthesis of tiglic aldehyde (2b)

Following the general procedure B the title compound was isolated by flash chromatography (SiO$_2$, pentane:Et$_2$O = 5:1, R$_f$ = 0.5) as a colorless oil in 78% (76 mg, 0.903 mmol) yield. The analytical data are in agreement with those reported previously.[6]

$^1$H-NMR (400.130 MHz, CDCl$_3$): $\delta$ (ppm) = 1.74 (d, $^4J = 1.0$ Hz, 3H), 1.97 (d, $^3J = 7.0$ Hz, 3H), 6.59 (qq, $^3J = 7.0$ Hz, $^4J = 1.3$ Hz, 1H), 9.37 (s, 1H, CHO).

$^{13}$C-NMR (100.613 MHz, CDCl$_3$): $\delta$ (ppm) = 8.9, 14.8, 140.9, 149.4, 194.7 (CHO).
Synthesis of (E)-2-butylhept-2-enal (2c)

Following the general procedure B the title compound was isolated by flash chromatography (SiO₂, pentane:Et₂O = 5:1, R_f = 0.3) as a colorless oil in 86% (168 mg, 0.998 mmol) yield. The analytical data are in agreement with those reported previously.[7]

¹H-NMR (400.130 MHz, CDCl₃): δ (ppm) = 0.90 (t, 3J = 7.0 Hz, 3H), 0.95 (t, 3J = 7.2 Hz, 3H), 1.26-1.55 (m, 8H), 2.24 (t, 3J = 7.4 Hz, 2H), 2.36 (dt, 3J = 7.4 Hz, 3J = 7.4 Hz, 2H), 6.44 (t, 3J = 7.4 Hz, 1H), 9.36 (s, 1H, CHO).

¹³C-NMR (100.613 MHz, CDCl₃): δ (ppm) = 14.0, 14.2, 20.5, 22.1, 22.8, 28.5, 28.9, 31.3, 146.3, 156.9, 194.0 (CHO).

Synthesis of (E)-2-pentyloct-2-enal (2d)

Following the general procedure B the title compound was isolated by flash chromatography (SiO₂, pentane:Et₂O = 5:1, R_f = 0.3) as a colorless oil in 97% (220 mg, 1.125 mg) yield. The analytical data are in agreement with those reported previously.[7]

¹H-NMR (400.130 MHz, CDCl₃): δ (ppm) = 0.88 (t, 3J = 7.1 Hz, 3H), 0.92 (t, 3J = 7.1 Hz, 3H), 1.24-1.39 (m, 10H), 1.45-1.57 (m, 2H), 2.23 (t, 3J = 7.4 Hz, 2H), 2.35 (dt, 3J = 7.4 Hz, 3J = 7.4 Hz, 2H), 6.44 (t, 3J = 7.4 Hz, 1H), 9.36 (s, 1H, CHO).

¹³C-NMR (100.613 MHz, CDCl₃): δ (ppm) = 14.0, 14.2, 20.9, 22.8 (2C), 26.7, 29.4 (2C), 31.1, 31.9, 144.8, 156.4, 195.1 (CHO).

Synthesis of (E)-2,3-diphenylacrylaldehyde (5a)

Following the general procedure C the title compound was isolated by flash chromatography (SiO₂, PE:EtOAc = 5:1, R_f = 0.26) as a colorless solid in 92% (223 mg, 1.071 mmol) yield. The analytical data are in agreement with those reported previously.[8]

Mp = 92-94 °C.
1H-NMR (400.130 MHz, CDCl₃): δ (ppm) = 7.19-7.26 (m, 6H, ArH), 7.28-7.32 (m, 1H, ArH), 7.36-7.45 (m, 3H, ArH), 7.40 (s, 1H, CH=C), 9.78 (s, 1H, CHO).

13C-NMR (100.612 MHz, CDCl₃): δ (ppm) = 128.4 (2C), 128.6 (2C), 128.9 (2C), 129.4 (2C), 130.3, 130.8, 133.4, 134.1, 141.9, 150.1, 193.9 (CHO).

MS (EI, C₁₅H₁₂O, M = 208.09 g/mol): m/z (%) = 208.2 (49), 178.1 (100), 165.1 (33), 105.1 (8), 102.1 (22).

HRMS (EI): Calcd. for C₁₅H₁₂O: 208.08882; Found: 208.08860.

**Synthesis of (E)-2,3-di-p-tolylacrylaldehyde (5b)**

Following the general procedure C the title compound was isolated by flash chromatography (SiO₂, PE:EtOAc = 10:1, Rᵣ = 0.26) as a pale yellow solid in 93% (255 mg, 1.078 mmol) yield.

Mp = 104-106 °C.

1H-NMR (400.130 MHz, CDCl₃): δ (ppm) = 2.32 (s, 3H, CH₃), 2.40 (s, 3H, CH₃), 7.03-7.07 (m, 2H, ArH), 7.08-7.11 (m, 2H, ArH), 7.12-7.16 (m, 2H, ArH), 7.21-7.24 (m, 2H, ArH), 7.33 (s, 1H, CH=C), 9.74 (s, 1H, CHO).

13C-NMR (100.612 MHz, CDCl₃): δ (ppm) = 21.4 (CH₃), 21.5 (CH₃), 129.2 (2C), 129.3 (2C), 129.7 (2C), 130.6, 130.9 (2C), 131.5, 138.1, 140.8, 141.1, 150.2 (CH=C), 194.2 (CHO).

MS (APCI, C₁₇H₁₆O, M = 236.31 g/mol): m/z (%) = 251.1 (4), 238.1 (22), 237.1 (100) 219.1 (5).


**Synthesis of (E)-2,3-di-m-tolylacrylaldehyde (5c)**

Following the general procedure C the title compound was isolated by flash chromatography (SiO₂, PE:EtOAc = 10:1, Rᵣ = 0.35) as a colorless oil in 86% (236 mg, 1.000 mmol) yield.
$^1$H-NMR (400.130 MHz, CDCl$_3$): $\delta$ (ppm) = 2.24 (s, 3H, CH$_3$), 2.36 (s, 3H, CH$_3$), 6.96-7.00 (m, 2H, ArH), 7.02 (m, 1H, ArH), 7.06 (m, 1H, ArH), 7.08-7.13 (m, 2H, ArH), 7.18-7.22 (m, 1H, ArH), 7.30 (dd, 1H, $^3$J = 7.6 Hz, $^3$J = 7.6 Hz, ArH), 7.34 (s, 1H, CH=O).

$^{13}$C-NMR (100.612 MHz, CDCl$_3$): $\delta$ (ppm) = 21.3 (CH$_3$), 21.5 (CH$_3$), 126.4, 127.8, 128.4, 128.8, 129.1, 129.8, 131.1, 131.9, 133.5, 134.1, 138.1, 138.5, 142.0, 150.3 (CH=C), 194.2 (CH=O).

MS (APCI, C$_{17}$H$_{16}$O, M = 236.31 g/mol): m/z (%) = 237.1 (100).

HRMS (APCI): Calcd. for C$_{17}$H$_{17}$O$^+$: 237.12794; Found: 237.12800.

Synthesis of (E)-2,3-dio-tolylacrylaldehyde (5d)

Following the general procedure C the title compound was isolated by flash chromatography (SiO$_2$, PE:EtOAc = 10:1, Rf = 0.34) as a pale yellow oil in 93% (255 mg, 1.081 mmol) yield.

$^1$H-NMR (400.130 MHz, CDCl$_3$): $\delta$ (ppm) = 2.05 (s, 3H, CH$_3$), 2.51 (s, 3H, CH$_3$), 6.71 (dd, $^3$J = 7.8 Hz, $^4$J = 1.0 Hz, 1H, ArH), 6.88 (dddd, $^3$J = 7.5 Hz, $^3$J = 7.5 Hz, $^4$J = 0.6 Hz, $^4$J = 0.6 Hz, 1H, ArH), 7.00 (dd, $^3$J = 7.5 Hz, $^4$J = 1.4 Hz, 1H, ArH) 7.15-7.29 (m, 5H, ArH), 7.74 (s, 1H, CH=C), 9.84 (s, 1H, CH=O).

$^{13}$C-NMR (100.612 MHz, CDCl$_3$): $\delta$ (ppm) = 19.7 (CH$_3$), 20.1 (CH$_3$), 125.9, 126.2, 128.4, 129.1, 129.7, 130.0, 130.5, 130.6, 133.1, 133.2, 136.3, 138.1, 142.4, 148.1 (CH=C), 193.9 (CH=O).

MS (APCI, C$_{17}$H$_{16}$O, M = 236.31 g/mol): m/z (%) = 269.1 (11), 251.1 (4), 237.1 (100), 214.1 (3).

HRMS (APCI): Calcd. for C$_{17}$H$_{17}$O$^+$: 237.12794; Found: 237.12800.
Synthesis of (E)-2,3-bis(4-methoxyphenyl)acrylaldehyde (5e)

Following the general procedure C the title compound was isolated by flash chromatography (SiO\textsubscript{2}, PE:EtOAc = 10:1, R\textsubscript{f} = 0.12) as a pale yellow solid in 92% (286 mg, 1.066 mmol) yield.

Mp = 96-98 °C.

\textsuperscript{1}H-NMR (400.130 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) = 3.79 (s, 3H, OCH\textsubscript{3}), 3.85 (s, 3H, OCH\textsubscript{3}), 6.74-6.78 (m, 2H, ArH), 6.94-6.98 (m, 2H, ArH), 7.12-7.16 (m, 2H, ArH), 7.19-7.23 (m, 2H, ArH), 7.29 (s, 1H, CH=CH), 9.70 (s, 1H, CH=O).

\textsuperscript{13}C-NMR (100.612 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) = 55.3 (OCH\textsubscript{3}), 55.4 (OCH\textsubscript{3}), 114.1 (2C), 114.5 (2C), 125.8, 127.0, 130.7 (2C), 132.7 (2C), 139.6, 150.0 (CH=CH), 159.6, 161.3, 194.3 (CHO).

MS (APCI, C\textsubscript{17}H\textsubscript{16}O\textsubscript{3}, M = 268.31 g/mol): m/z (%) = 270.1 (26), 269.1 (100).

HRMS (APCI): Calcd. for C\textsubscript{17}H\textsubscript{17}O\textsubscript{3}[M+H\textsuperscript{+}]: 269.11777; Found: 269.11770.

Synthesis of (E)-2,3-bis(3-methoxyphenyl)acrylaldehyde (5f)

Following the general procedure C the title compound was isolated by flash chromatography (SiO\textsubscript{2}, PE:EtOAc = 10:1, R\textsubscript{f} = 0.13) as a colorless solid in 90% (280 mg, 1.044 mmol) yield.

Mp = 50-53 °C.

\textsuperscript{1}H-NMR (400.130 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) = 3.54 (s, 3H, OCH\textsubscript{3}), 3.77 (s, 3H, OCH\textsubscript{3}), 6.72 (dd, \(^4J = 2.6\) Hz, \(^5J = 1.5\) Hz, 1H, ArH), 6.75 (dd, \(^4J = 2.6\) Hz, \(^5J = 1.5\) Hz, 1H, ArH), 6.79 (ddd, \(^3J = 7.6\) Hz, \(^4J = 1.5\) Hz, \(^4J = 1.0\) Hz, 1H, ArH), 6.86 (ddd, \(^3J = 8.2\) Hz, \(^4J = 2.6\) Hz, \(^4J = 1.0\) Hz, 1H, ArH), 6.93 (dd, \(^3J = 8.2\) Hz, \(^4J = 2.6\) Hz, \(^4J = 1.0\) Hz, 1H, ArH), 7.18 (dd, \(^3J = 8.0\) Hz, \(^3J = 8.0\) Hz, 1H, ArH), 7.34 (dd, \(^3J = 8.0\) Hz, \(^3J = 2.0\) Hz, 1H, ArH), 7.36 (s, 1H, CH=CH), 9.76 (s, 1H, CH=O).

\textsuperscript{13}C-NMR (100.612 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) = 55.0, 55.3, 55.4, 124.0, 129.6, 130.1, 135.0, 135.2, 141.9, 149.9 (CH=CH), 159.4, 160.1, 193.8 (CH=O).

MS (APCI, C\textsubscript{17}H\textsubscript{16}O\textsubscript{3}, M = 268.31 g/mol): m/z (%) = 269.1 (100).
HRMS (APCI): Calcd. for C_{17}H_{17}O_{3}[M+H]^+: 269.11777; Found: 269.11767.

**Synthesis of (E)-2,3-bis(2-methoxyphenyl)acrylaldehyde (5g)**

Following the **general procedure C** the title compound was isolated by flash chromatography (SiO_2, PE:EtOAc = 10:1, R_f = 0.17) as a pale yellow solid in 78% (243 mg, 0.905 mmol) yield.

Mp = 116-119 °C.

^1^H-NMR (400.130 MHz, CDCl_3): \( \delta \) (ppm) = 3.69 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 6.65 (dddd, \( ^3J = 7.6 \) Hz, \( ^3J = 7.6 \) Hz, \( ^4J = 0.5 \) Hz, \( ^4J = 0.5 \) Hz, 1H, ArH), 6.89 (dd, \( ^3J = 8.5 \) Hz, \( ^4J = 0.8 \) Hz, 1H, ArH), 6.93 (dd, \( ^3J = 7.7 \) Hz, \( ^4J = 1.7 \) Hz, 1H, ArH), 7.26 (dddd, \( ^3J = 7.6 \) Hz, \( ^3J = 7.6 \) Hz, \( ^4J = 1.7 \) Hz, 1H, ArH), 7.35 (dddd, \( ^3J = 7.6 \) Hz, \( ^3J = 7.6 \) Hz, \( ^4J = 1.8 \) Hz, 1H, ArH), 7.93 (s, 1H, CH=C), 9.77 (s, 1H, CH=O).

^13^C-NMR (100.612 MHz, CDCl_3): \( \delta \) (ppm) = 55.67 (OCH_3), 55.69 (OCH_3), 110.7, 111.5, 120.3, 121.1, 123.3, 123.6, 129.8, 129.9, 130.8, 131.5, 138.8, 144.4 (CH=C), 157.2, 158.1, 193.9 (CH=O).

**MS** (APCI, C_{17}H_{16}O_3, M = 268.31 g/mol): m/z (%) = 283.1 (7), 270.1 (19), 269.1 (100), 241.1 (4), 237.1 (3).

**HRMS** (APCI): Calcd. for C_{17}H_{17}O_{3}[M+H]^+: 269.11777; Found: 269.11770.

**Synthesis of (E)-2,3-bis(3,4,5-trimethoxyphenyl)acrylaldehyde (5h)**

Following the **general procedure C** the title compound was isolated by flash chromatography (SiO_2, PE:EtOAc = 1:1, R_f = 0.36) as a yellow solid in 61% (276 mg, 0.710 mmol) yield.

Mp = 71-74 °C.
1H-NMR (400.130 MHz, CDCl₃): δ (ppm) = 3.62 (s, 6H, 2×OCH₃), 3.80 (s, 6H, 2×OCH₃), 3.84 (s, 3H, OCH₃), 3.85 (s, 3H, OCH₃), 6.43 (s, 2H, ArH), 6.52 (s, 2H, ArH), 7.28 (s, 1H, CH=C), 9.73 (s, 1H, CHO).

13C-NMR (100.612 MHz, CDCl₃): δ (ppm) = 55.9 (2C, 2×OCH₃), 56.3 (2C, 2×OCH₃), 60.8 (OCH₃), 61.0 (OCH₃), 106.4 (2C), 108.5 (2C), 129.0, 129.3, 138.0, 140.3, 141.2, 150.2 (CH=C), 152.9 (2C), 154.0 (2C), 193.7 (CHO).

HRMS: Calcd. for C₂₁H₂₄O₇: 388.15220; Found: 388.15200.

MS (EI, C₂₁H₂₄O₇, M = 388.41 g/mol): m/z (%) = 388.2 (100), 373.2 (19), 360.2 (16), 345.2 (60).

HRMS (EI): Calcd. for C₂₁H₂₄O₇: 388.15220; Found: 388.15200.

Synthesis of (E)-2,3-bis(4-fluorophenyl)acrylaldehyde (5i)

Following the general procedure C the title compound was isolated by flash chromatography (SiO₂, PE:EtOAc = 10:1, Rf = 0.18) as a colorless solid in 90% (255 mg, 1.046 mmol) yield.

Mp = 109-111 °C.

1H-NMR (400.130 MHz, CDCl₃): δ (ppm) = 6.92-6.98 (m, 2H, ArH), 7.08-7.14 (m, 2H, ArH), 7.15-7.23 (m, 4H, ArH), 7.36 (s, 1H, CH=C), 9.74 (s, 1H, CHO).

13C-NMR (100.612 MHz, CDCl₃): δ (ppm) = 116.0 (d, ²J = 21.8 Hz, 2C), 116.2 (d, ²J = 21.6 Hz, 2C), 128.9 (d, ⁴J = 3.5 Hz), 130.2 (d, ⁴J = 3.5 Hz), 131.3 (d, ³J = 8.1 Hz, 2C), 132.8 (d, ³J = 8.6 Hz, 2C), 140.6 (d, ⁵J = 1.9 Hz), 149.2 (CH=C), 162.0 (d, ¹J = 80.5 Hz), 164.5 (d, ¹J = 85.5 Hz), 193.6 (CHO).

19F-NMR (235.357 MHz, CDCl₃): δ (ppm) = -108.4 (m, 2F), -112.9 (m, 2F).

MS (APCI, C₁₅H₁₀F₂O, M = 244.24 g/mol): m/z (%) = 262.1 (6), 245.1 (100), 214.1 (3).

Synthesis of (E)-2,3-bis(4-chlorophenyl)acrylaldehyde (5j)

Following the general procedure C the title compound was isolated by flash chromatography (SiO₂, PE:EtOAc = 10:1, Rf = 0.12) as a colorless solid in 78% (251 mg, 0.904 mmol) yield. 
Mp = 108-110 °C.

1H-NMR (400.130 MHz, CDCl₃): δ (ppm) = 7.11-7.13 (m, 2H, ArH), 7.14-7.16 (m, 2H, ArH), 7.22-7.26 (m, 2H, ArH), 7.35 (s, 1H, CH=C), 7.38-7.41 (m, 2H, ArH), 9.74 (s, 1H, CHO).

13C-NMR (100.612 MHz, CDCl₃): δ (ppm) = 129.1 (2C), 129.4 (2C), 130.9 (2C), 131.3, 131.8 (2C), 132.3, 134.7, 136.6, 141.0, 148.9 (CH=C), 193.2 (CHO).

MS (APCI, C₁₅H₁₀Cl₂O, M = 276.01 g/mol): m/z (%) = 277.0 (100), 214.1 (21).


Synthesis of (E)-2,3-bis(4-bromophenyl)acrylaldehyde (5k)

Following the general procedure C the title compound was isolated by flash chromatography (SiO₂, PE:EtOAc = 10:1, Rf = 0.19) as a colorless solid in 78% (332 mg, 0.908 mmol) yield. 
Mp = 108-110 °C.

1H-NMR (400.130 MHz, CDCl₃): δ (ppm) = 7.04-7.06 (m, 2H, ArH), 7.07-7.09 (m, 2H, ArH), 7.33 (s, 1H, CH=C), 7.38-7.42 (m, 2H, ArH), 7.53-7.56 (m, 2H, ArH), 9.74 (s, 1H, CHO).

13C-NMR (100.612 MHz, CDCl₃): δ (ppm) = 123.0, 125.0, 131.1 (2H), 131.8, 132.0 (2C), 132.1 (2C), 132.3 (2C), 132.7, 141.1, 149.0 (CH=C), 193.1 (CHO).

MS (APCI, C₁₅H₁₀Br₂O, M = 366.05 g/mol): m/z (%) = 419.3 (8), 383.9 (10), 366.9 (100), 214.1 (12), 101.1 (32), 87.1 (28).

Synthesis of \((E)\)-2,3-bis(4-((trifluoromethyl)phenyl)acrylaldehyde (5l)

\[
\begin{array}{c}
\text{F}_3\text{C} \\
\text{CF}_3
\end{array}
\]

Following the general procedure C the title compound was isolated by flash chromatography (SiO\(_2\), PE:EtOAc = 10:1, R\(_f\) = 0.36) as a pale yellow solid in 33% (133 mg, 0.385 mmol) yield.

Mp = 56-60 °C.

\(^1\text{H-NMR}\ (400.130 \text{ MHz, CDCl}_3): \delta \ (\text{ppm}) = 7.27-7.34 \ (\text{m, 4H, ArH}), 7.50 \ (\text{s, 1H, CH=C}), 7.51-7.55 \ (\text{m, 2H, ArH}), 7.67-7.70 \ (\text{m, 4H, ArH}), 9.81 \ (\text{s, 1H, CHO}).

\(^{13}\text{C-NMR}\ (100.612 \text{ MHz, CDCl}_3): \delta \ (\text{ppm}) = 123.7 \ (\text{q, } {^1\text{J}} = 272.1 \text{ Hz}), 124.0 \ (\text{q, } {^1\text{J}} = 272.1 \text{ Hz}), 125.7 \ (\text{q, } {^3\text{J}} = 3.8 \text{ Hz, 2C}), 126.0 \ (\text{q, } {^3\text{J}} = 3.8 \text{ Hz, 2C}), 130.0 \ (2\text{C}), 130.7 \ (2\text{C}), 131.0 \ (\text{q, } {^2\text{J}} = 32.6 \text{ Hz}), 132.0 \ (\text{q, } {^2\text{J}} = 32.9 \text{ Hz}), 136.4, 136.9, 142.3, 148.6 \ (\text{CH=C}), 192.7 \ (\text{CHO}).

\(^{19}\text{F-NMR}\ (235.357 \text{ MHz, CDCl}_3): \delta \ (\text{ppm}) = −62.7 \ (\text{m, 3F}), −63.1 \ (\text{m, 3F}).

\text{MS\ (APCI, C}_{17}\text{H}_{10}\text{FO}_6\text{, M} = 344.25 \text{ g/mol): m/z (%)} = 345.1 \ (100), 327.1 \ (23), 288.0 \ (14), 207.0 \ (8), 173.0 \ (11), 77.0 \ (8).

\text{HRMS\ (APCI): Calcd. for C}_{17}\text{H}_{11}\text{OF}_6[\text{M+H}]^+: 345.07141; \text{Found: 345.07140.}

Synthesis of \((Z)\)-2,3-di(thiophen-2-yl)acrylaldehyde (5m)

\[
\begin{array}{c}
\text{S} \\
\text{S}
\end{array}
\]

Following the general procedure C the title compound was isolated by flash chromatography (SiO\(_2\), PE:EtOAc = 10:1, R\(_f\) = 0.15) as a pale brown solid in 82% (210 mg, 0.955 mmol) yield.

Mp = 72-74 °C.

\(^1\text{H-NMR}\ (400.130 \text{ MHz, CDCl}_3): \delta \ (\text{ppm}) = 7.04-7.07 \ (\text{m, 2H, ArH}), 7.18 \ (\text{dd, } {^3\text{J}} = 5.1 \text{ Hz, } {^3\text{J}} = 5.1 \text{ Hz, 1H, ArH}), 7.38 \ (\text{d, } {^3\text{J}} = 3.5 \text{ Hz, 1H, ArH}), 7.44 \ (\text{d, } {^3\text{J}} = 5.1 \text{ Hz, 1H, ArH}), 7.56 \ (\text{dd, } {^3\text{J}} = 5.1 \text{ Hz, } {^4\text{J}} = 1.1 \text{ Hz, 1H, ArH}), 7.72 \ (\text{s, 1H, CH=C}), 9.70 \ (\text{s, 1H, CHO}).

\(^{13}\text{C-NMR}\ (100.612 \text{ MHz, CDCl}_3): \delta \ (\text{ppm}) = 127.3, 127.8, 128.5, 129.1, 132.0, 132.3, 133.0, 135.2, 137.8, 144.1 \ (\text{CH=C}), 191.9 \ (\text{CHO}).

\text{MS\ (APCI, C}_{11}\text{H}_{8}\text{OS}_2, M = 220.31 \text{ g/mol): m/z (%)} = 235.0 \ (2), 221.0 \ (100), 193.1 \ (2).
**HRMS (APCI):** Calcd. for C\textsubscript{11}H\textsubscript{9}O\textsubscript{2}[M+H]\textsuperscript{+}: 221.00948; Found: 221.00940.

**Synthesis of (E)-2,3-di(thiophen-3-yl)acrylaldehyde (5n)**

Following the **general procedure C** the title compound was isolated by flash chromatography (Si\textsubscript{2}, PE:EtOAc = 10:1, \( R_f = 0.21 \)) as a pale brown solid in 91% (233 mg, 1.056 mmol) yield.

\( \text{Mp} = 72-74 \^\circ \text{C} \).

\(^1\text{H}-\text{NMR (400.130 MHz, CDCl}_3)\): \( \delta \) (ppm) = 6.82 (ddd, \( ^3J = 5.1 \text{ Hz}, \ ^4J = 1.3 \text{ Hz}, \ ^5J = 0.4 \text{ Hz}, 1\text{H, Ar}H \)), 6.98 (dd, \( ^3J = 4.9 \text{ Hz}, \ ^4J = 1.3 \text{ Hz}, 1\text{H, Ar}H \)), 7.21 (ddd, \( ^3J = 5.1 \text{ Hz}, \ ^4J = 3.0 \text{ Hz}, \ ^4J = 0.6 \text{ Hz}, 1\text{H, Ar}H \)), 7.31 (dd, \( ^4J = 2.9 \text{ Hz}, \ ^4J = 1.2 \text{ Hz}, 1\text{H, Ar}H \)), 7.41 (dd, \( ^3J = 4.9 \text{ Hz}, \ ^4J = 3.0 \text{ Hz}, \ ^4J = 0.6 \text{ Hz}, 1\text{H, Ar}H \)), 7.41 (d, \( ^4J = 0.6 \text{ Hz}, 1\text{H, CH=C} \)), 7.43 (ddd, \( ^4J = 3.0 \text{ Hz}, \ ^4J = 1.3 \text{ Hz}, \ ^5J = 0.4 \text{ Hz}, 1\text{H, Ar}H \)), 9.70 (s, 1H, CHO).

\(^{13}\text{C}-\text{NMR (100.612 MHz, CDCl}_3)\): \( \delta \) (ppm) = 125.3, 126.0, 126.2, 128.1, 128.4, 130.7, 133.0, 135.5, 136.5, 143.7 (CH=C), 193.4 (CHO).

**MS (APCI, C\textsubscript{11}H\textsubscript{9}O\textsubscript{2}, M = 220.31 g/mol):** m/z (%) = 238.0 (5), 229.0 (4), 221.0 (100).

**HRMS (APCI):** Calcd. for C\textsubscript{11}H\textsubscript{9}O\textsubscript{2}[M+H]\textsuperscript{+}: 221.00948; Found: 221.00940.

**Synthesis of cinnamaldehyde (8a)**

Following the **general procedure B** the title compound was isolated by flash chromatography (Si\textsubscript{2}, PE:EtOAc = 11:1, \( R_f = 0.31 \)) as a colorless oil in 39% (59.8 mg, 0.453 mmol) yield.

The analytical data are in agreement with those reported previously.\[^9\]

\(^1\text{H}-\text{NMR (400.130 MHz, CDCl}_3)\): \( \delta \) (ppm) = 6.73 (dd, \( ^3J = 15.9 \text{ Hz}, \ ^3J = 7.6 \text{ Hz}, 1\text{H})\)), 7.39-7.46 (m, 3H, Ar-H), 7.48 (d, \( ^3J = 15.9 \text{ Hz}, 1\text{H})\)), 7.54-7.60 (m, 2H, Ar-H), 9.71 (d, \( ^3J = 7.6 \text{ Hz}, 1\text{H, CHO} \)).

\(^{13}\text{C}-\text{NMR (100.612 MHz, CDCl}_3)\): \( \delta \) (ppm) = 128.6, 128.7 (2C), 129.2 (2C), 131.4, 134.1, 152.8, 193.8 (CHO).

**Synthesis of (E)-3-(4-methoxyphenyl)acrylaldehyde (8b)**
Following the **general procedure B** the title compound was isolated by flash chromatography (SiO₂, PE:EtOAc = 10:1, R_f = 0.29) as a colorless oil in 45% (84.5 mg, 0.522 mmol) yield. The analytical data are in agreement with those reported previously.[10]

**1H-NMR (400.130 MHz, CDCl₃):** δ (ppm) = 3.86 (s, 3H, OCH₃), 6.60 (dd, 3_J = 16.0 Hz, 3_J = 7.6 Hz, 1H), 6.94 (m, 2H, ArH), 7.42 (d, 3_J = 16.0 Hz, 1H), 7.52 (m, 2H, ArH), 9.64 (d, 3_J = 7.6 Hz, 1H, CHO).

**13C-NMR (100.612 MHz, CDCl₃):** δ (ppm) = 55.5 (OCH₃), 114.5 (2C), 126.5, 128.7, 130.3 (2C), 152.7, 162.2, 193.7 (CHO).

**Synthesis of (E)-3-(3,4,5-trimethoxyphenyl)acrylaldehyde (8c)**

Following the **general procedure B** the title compound was isolated by flash chromatography (SiO₂, PE:EtOAc = 1:1, R_f = 0.42) as a pale yellow solid in 62% (161.1 mg, 0.725 mmol) yield. The analytical data are in agreement with those reported previously.[11]

Mp = 108-110 °C.

**1H-NMR (400.130 MHz, CDCl₃):** δ (ppm) = 3.89 (s, 9H, 3×OCH₃), 6.63 (dd, 3_J = 15.9 Hz, 3_J = 7.7 Hz, 1H), 6.79 (s, 2H, ArH), 7.39 (d, 3_J = 15.9 Hz, 1H), 9.67 (d, 3_J = 7.7 Hz, 1H, CHO).

**13C-NMR (100 MHz, CDCl₃):** δ (ppm) = 56.3 (2C, OCH₃), 61.1 (OCH₃), 105.8 (2C), 128.0, 129.5, 141.1, 152.7, 153.6 (2C), 193.4 (CHO).

**MS (EI, C₁₂H₁₄O₄, M = 222.24 g/mol):** m/z (%) = 222.2 (100), 207.1 (8), 191.1 (29), 180.1 (8), 179.1 (77), 151.1 (26), 136.1 (13), 121.1 (9), 91.1 (8).

**HRMS (EI):** Calcd. for C₁₂H₁₄O₄: 222.08921; Found: 222.08920.
Synthesis of Trimethyl((3,4,5-trimethoxyphenyl)ethynyl)silane (10)

\[
\begin{array}{c}
\text{MeO} \\
\text{MeO} \\
\text{MeO} \\
\text{TMS} \\
\text{OMe}
\end{array}
\]

To a solution of 5-iodo-1,2,3-trimethoxybenzene (9) (5.00 g, 17.00 mmol, 1.0 equiv.) in THF (75 ml) PdCl\(_2\)(PPh\(_3\))\(_2\) (119.3 mg, 0.170 mmol, 0.01 equiv.) and dry HN\(^\text{t}^\text{i}\)Pr\(_2\) (7.2 ml, 5.16 g, 51.00 mmol, 3.0 equiv.) were added. The reaction flask was then packed in aluminum foil and ice-chilled trimethylsilylacetylene (2.6 ml, 1.84 g, 18.70 mmol, 1.05 equiv.) was added by syringe. After stirring for 1 h at room temperature the reaction mixture was quenched by addition of 5%-aqueous disodium EDTA solution (40 ml) and 'BuOMe (40 ml). The aqueous phase was extracted with 'BuOMe (2 × 40 ml) and the combined organic layers were washed with brine (40 ml), dried over Na\(_2\)SO\(_4\) and concentrated in vacuo. Flash chromatography (PE/EtOAc, 10:1, \(R_f = 0.25\)) yielded the desired compound 10 (4.14 g, 15.65 mmol, 92%) as a pale brown solid.

\(^1\text{H}-\text{NMR}\) (400.130 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 0.25 (s, 9H, (Si\(\text{C} \text{H}_3\))), 3.83 (s, 3H, O\(\text{C} \text{H}_3\)), 3.84 (s, 6H, 2\(\times\)O\(\text{C} \text{H}_3\)), 6.70 (s, 2H, Ar\(\text{H}\)).

\(^{13}\text{C}-\text{NMR}\) (100 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 0.1 (3C, Si(CH\(_3\))), 56.2 (2C, O\(\text{C} \text{H}_3\)), 61.0 (O\(\text{C} \text{H}_3\)), 93.2, 105.2, 109.3 (2C), 118.1, 139.2, 153.0 (2C).

The analytical data are in agreement with those reported previously.\(^{[12]}\)

Synthesis of 5-ethynyl-1,2,3-trimethoxybenzene (7c)

\[
\begin{array}{c}
\text{MeO} \\
\text{MeO} \\
\text{OMe} \\
\text{OMe}
\end{array}
\]

To a solution of trimethyl((3,4,5-trimethoxyphenyl)ethynyl)silane (10) (3.96 g, 14.98 mmol, 1.0 equiv.) in MeOH (50 ml), K\(_2\)CO\(_3\) (7.46 g, 53.96 mmol, 3.6 equiv.) was added and the reaction mixture was stirred for 3 h (TLC-control) at room temperature. Subsequently, water (40 ml) was added and the mixture was stirred for further 10 min. After dilution of the reaction mixture with 'BuOMe (40 ml) the aqueous phase was separated and extracted with 'BuOMe (3 × 30 ml). The combined organic layers were washed with brine (30 ml), dried over Na\(_2\)SO\(_4\) and concentrated in vacuo. Flash chromatography (PE/EtOAc, 10:1, \(R_f = 0.23\)) yielded the desired compound 7c (2.57 g, 14.50 mmol, 97%) as a pale yellow solid.
Mp = 70-71 °C.

$^1$H-NMR (400.130 MHz, CDCl$_3$): \( \delta \) (ppm) = 3.01 (s, 1H, CCH), 3.83 (s, 3H, OCH$_3$), 3.84 (s, 6H, 2×OCH$_3$), 6.71 (s, 2H, ArH).

$^{13}$C-NMR (100 MHz, CDCl$_3$): \( \delta \) (ppm) = 56.2 (2C, OCH$_3$), 61.0 (OCH$_3$), 76.0, 83.6, 109.3 (2C), 117.1, 139.2, 153.7 (2C).

The analytical data are in agreement with those reported previously.$^{[13]}$

**Synthesis of (E)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-ol (11)**

A solution of (E)-3-(3,4,5-trimethoxyphenyl)acrylaldehyde (8c) (100 mg, 0.450 mmol, 1.0 equiv.) in MeOH (3.5 ml) and CH$_2$Cl$_2$ (1.5 ml) was cooled to 0 °C followed by successive addition of CeCl$_3$•7H$_2$O (83.8 mg, 0.225 mmol, 0.5 equiv.) and NaBH$_4$ (30.6 mg, 0.810 mmol, 1.8 equiv.). The reaction mixture was stirred at 0 °C for 1.5 h, subsequently quenched by addition of saturated aqueous NH$_4$Cl solution (3 ml) and diluted with CH$_2$Cl$_2$ (3 ml). The aqueous phase was separated and extracted with CH$_2$Cl$_2$ (3 × 3 ml). The combined organic layers were washed with brine (5 ml), dried over Na$_2$SO$_4$ and concentrated in vacuo. Filtration through a plug of silica gel yielded desired compound 11 (87.7 mg, 0.391 mmol, 87%) as a pale yellow oil.

$^1$H-NMR (300 MHz, CDCl$_3$): \( \delta \) (ppm) = 3.85 (s, 3H, OCH$_3$), 3.87 (s, 6H, 3×OCH$_3$), 4.32 (dd, \( ^3 J = 5.6 \) Hz, \( ^4 J = 1.5 \) Hz, 2H, H1) 5.29 (s, 1H, OH), 6.28 (dt, \( ^3 J = 16.0 \) Hz, \( ^3 J = 5.6 \) Hz, 1H, H2), 6.55 (d, \( ^3 J = 16.0 \) Hz, 1H), 6.62 (s, 2H, ArH).

The analytical data are in agreement with those reported previously.$^{[14]}$
Synthesis of (E)-1,2,3-trimethoxy-5-(3-methoxyprop-1-en-1-yl)benzene (Boropinol B)

The solution of (E)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-ol (11) (80 mg, 0.357 mmol 1.0 equiv.) in THF (2.5 ml) was cooled to 0 °C and NaH (10.3 mg, 0.428 mmol, 1.2 equiv.) was added. The reaction mixture was stirred at 0 °C for 1 h before adding MeI (29 μl, 65.8 mg, 0.463 mmol, 1.3 eq). The reaction mixture was allowed to warm to room temperature and stirred at this temperature for further 4 h. H₂O (3 ml) was added, and the solution was extracted with 'BuOMe (3 × 3 ml). Combined organic layers were washed with brine (4 ml), dried over Na₂SO₄ and concentrated in vacuo. Flash chromatography (PE/EtOAc, 5:1, Rf = 0.3) yielded the desired compound Boropinol B (78.2 mg, 0.328 mmol, 92%) as a pale yellow oil.

The analytical data are identical to those reported for Boropinol B isolated from natural sources.[15]

¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 3.38 (s, 3H, OCH₃), 3.83 (s, 3H, ArOH), 3.86 (s, 6H, 2×ArOCH₃), 4.07 (dd, ³J = 6.0 Hz, ⁴J = 1.4 Hz, 2H) 6.19 (dt, ³J = 15.9 Hz, ³J = 6.0 Hz, 1H), 6.53 (dt, ³J = 15.9 Hz, ⁴J = 1.4 Hz, 1H), 6.61 (s, 2H, ArH).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm) = 56.1 (2C, ArOCH₃), 58.1 (OCH₃), 60.9 (ArOCH₃), 73.0, 103.6 (2C), 125.6, 132.4, 138.0, 153.4 (2C).
Product ratios in the hydroformylation of terminal alkynes\(^{[a]}\)

\[
\text{R} \xrightarrow{\text{CO}/\text{H}_2 (1:1) 5 \text{ bar}, [\text{Rh(CO)}_2 \text{acac}] (1.0 \text{ mol\%}), \text{L}_4 (3.0 \text{ mol\%})} \text{toluene, 55 °C, 20 h}} \\
7a-c \quad 8a-c \quad 12a-c \quad 13a-c \quad 14a-c \quad 15a-c
\]

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<td>3</td>
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<td>100</td>
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</tr>
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</table>

\(^{[a]}\) Reaction conditions: CO/H\(_2\) (1:1) 5 bar, [Rh(CO)\(_2\)acac]/L\(_4\)/7a-c = 1/3/100 in 2 ml toluene, c\(_0\)(7a-c) = 0.6 M, 20 h at 55 °C.

\[^{[b]}\] The conversion and product ratio were determined by GC and \(^1\)H-NMR spectroscopy.


Appendix I

L2

\[ \text{Chemical Shift (ppm)} \]

\[ \text{Normalized Intensity} \]
Electronic Supplementary Material (ESI) for Chemical Science
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\(^{13}\)C-NMR

\(^{31}\)P-NMR
L3

\[
\begin{align*}
\text{O} & \quad \text{P} \\
\text{N} & \quad \text{CF}_3 \\
\text{N} & \quad \text{P} \\
\text{O} & \quad \text{CF}_3
\end{align*}
\]

$^1$H-NMR

![Graph showing H-NMR spectrum with chemical shifts and normalized intensity]
$^{13}$C-NMR

$^{31}$P-NMR
\[19^F\text{-NMR}\]
L4

\[ \text{Chemical Shift (ppm)} \]

\[ \text{Normalized Intensity} \]

Electronic Supplementary Material (ESI) for Chemical Science

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**5b**

![Chemical Structure](Image)

**$^1$H-NMR**

![NMR Spectrogram](Image)

**$^{13}$C-NMR**

![NMR Spectrogram](Image)
5c

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\end{align*}
\]

$^1$H-NMR

$^{13}$C-NMR
5d

Electronic Supplementary Material (ESI) for Chemical Science
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$^{1}H$-NMR

$^{13}C$-NMR
$^{1}$H-NMR

$^{13}$C-NMR
$^1$H-NMR

$^{13}$C-NMR
Electronic Supplementary Material (ESI) for Chemical Science
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5h

$^1$H-NMR

$^{13}$C-NMR
$^{1}H$-NMR

$^{13}C$-NMR
$5k$

$\text{\textsuperscript{1}H-NMR}$

$\text{\textsuperscript{13}C-NMR}$
$^{1}H$-NMR

$^{13}C$-NMR
5m

$^1$H-NMR

$^{13}$C-NMR
5n

$^{1}H$-NMR

$^{13}C$-NMR
Appendix II (Crystallographic Data to 5a and 5i)

The following crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number **CCDC 923424**.

![Chemical Structure](image)
### Table 1. Crystal data and structure refinement 5a

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<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C15 H12 O</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>208.25</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>173(2) K</td>
</tr>
<tr>
<td><strong>Wavelength</strong></td>
<td>0.71073 Å</td>
</tr>
<tr>
<td><strong>Crystal system, space group</strong></td>
<td>Monoclinic, P 21/c</td>
</tr>
</tbody>
</table>
| **Unit cell dimensions**| \(a = 5.8262(2) \text{ Å} \), \(\alpha = 90 \text{ deg.}\)  
                          | \(b = 21.4617(13) \text{ Å} \), \(\beta = 95.017(3) \text{ deg.}\) 
                          | \(c = 9.2279(4) \text{ Å} \), \(\gamma = 90 \text{ deg.}\) |
| **Volume**              | 1149.44(9) Å³ |
| **Z, Calculated density**| 4, 1.203 Mg/Å³ |
| **Absorption coefficient** | 0.074 mm⁻¹   |
| **F(000)**              | 440           |
| **Crystal size**        | 0.30 x 0.25 x 0.04 mm |
| **Theta range for data collection** | 1.90 to 27.46 deg. |
| **Limiting indices**    | -7 ≤ h ≤ 7, -27 ≤ k ≤ 26, -10 ≤ l ≤ 11 |
| **Reflections collected / unique** | 9998 / 2625 [R(int) = 0.0400] |
| **Completeness to theta = 27.46** | 99.8 % |
| **Absorption correction** | Semi-empirical from equivalents |
| **Max. and min. transmission** | 0.998 and 0.942 |
| **Refinement method**   | Full-matrix least-squares on F² |
| **Data / restraints / parameters** | 2625 / 0 / 193 |
| **Goodness-of-fit on F²** | 1.025 |
| **Final R indices [I>2sigma(I)]** | R₁ = 0.0417, wR₂ = 0.0969 |
| **R indices (all data)** | R₁ = 0.0703, wR₂ = 0.1105 |
| **Largest diff. peak and hole** | 0.139 and -0.168 e.Å⁻³ |
The following crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number **CCDC 923423**.

![Crystal Structure Diagram]
Table 1. Crystal data and structure refinement for $^{5}$i

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>mk473blp21c</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C15 H10 F2 O</td>
</tr>
<tr>
<td>Formula weight</td>
<td>244.23</td>
</tr>
<tr>
<td>Temperature</td>
<td>173(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, P 21/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 6.6609(2) Å, alpha = 90 deg.</td>
</tr>
<tr>
<td></td>
<td>b = 9.7886(5) Å, beta = 106.893(3) deg.</td>
</tr>
<tr>
<td></td>
<td>c = 18.8033(8) Å, gamma = 90 deg.</td>
</tr>
<tr>
<td>Volume</td>
<td>1173.09(9) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>4, 1.383 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.107 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>504</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.30 x 0.20 x 0.10 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.26 to 27.89 deg.</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-8 &lt;= h &lt;= 8, -11 &lt;= k &lt;= 12, -19 &lt;= l &lt;= 23</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>8538 / 2798 [R(int) = 0.0280]</td>
</tr>
<tr>
<td>Completeness to theta</td>
<td>27.89 99.8 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.990 and 0.913</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on $F^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>2798 / 0 / 203</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.033</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0389, wR2 = 0.0976</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0536, wR2 = 0.1070</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.127 and -0.194 e Å⁻³</td>
</tr>
</tbody>
</table>