**Syntheses and Characterization of Molecular Weight Enlarged**

**Olefin Metathesis Pre-Catalysts**

Adel Keraani,[a,b] Ghassan Nasser,[a] Saurabh Shahane,[c] Thierry Renouard,[a] Christian Bruneau,[c] Murielle Rabiller-Baudry,[a]\* Cédric Fischmeister [c]\*

**Supporting information**

**General remarks**: All reactions were carried out under an inert atmosphere of dry argon using standard Schlenk tube techniques. Toluene and THF were freshly distilled over Na/benzophenone before use. NMR data were recorded on Bruker DPX 200, Bruker avance 300, 400 and 500 MHZ spectrometers. Chemical shifts (δ ppm) are reported *vs* tetramethyl silane and calibrated *vs* residual non-deuterated solvent. Gas chromatography were recorded on Shimadzu 2014 gas chromatograph (FID, column Supelco Equity 5, 30x0.25x0.25). **1**, **6**, **11**, **16, 20** and diethyl-diallylmalonate (DEDAM) were purchased from commercial sources and used as received. **2,**[[1]](#footnote-1) **3**[[2]](#footnote-2) and **12**[[3]](#footnote-3) were prepared according to reported procedures. Ruthenium complexes were purchased from Sigma-Aldrich and stored under argon.

- Synthesis of 4-isopropoxy-2'-methyl-[1,1'-biphenyl]-3-carbaldehyde **4**



A Schlenk tube was loaded with **2** (0.5 g, 2.29 mmol, 1 equiv), 5-bromo-2-isopropoxybenzaldehyde **3** (0.612 g, 2.52 mmol, 1.1 equiv), and [Pd(PPh3)4] (26.4 mg, 2.2 mol %). 3 mL of dioxane and 3 mL of 1M solution of K2CO3 were added, and the reaction mixture was heated at 100 °C for 16 h. The organic products were extracted with diethyl ether, and the resulting organic phase was washed with water (310 mL). Purification by column chromatography on silica gel using diethyl ether/petroleum ether (10:90 v/v) as the eluant afforded **4** as a colouress oil (0.83 g, 76%).

1H NMR (200.12 MHz, CDCl3, 25°C, TMS): *δ (ppm)*: 1.45 (d, *J*3 = 6.1 Hz, 6H, C*H*3); 2.31 (s, 3H, C*H*3); 4.75 (sept, *J*3 = 6.1 Hz, 1H, C*H*(CH3)2); 7.05 (d, *J*3 = 8.6 Hz, 1H, C*H*); 7.25 (m, 3H, C*H*); 7.55 (dd, *J*3=8.7 Hz, *J*4 = 2.1 Hz, 2H, C*H*), 7.87 (d, *J3* = 2.3 Hz, 1H, C*H*); 10.62 (s, 1H, C*H*O).

13C NMR (50.33 MHz, CDCl3): *δ (ppm)*: 19.4, 22.0, 71.2, 113.6, 125.1, 125.8, 127.4, 128.7, 129.7, 130.4, 134.1, 135.3, 136.4, 140.5, 159.5, 190.1

HRMS (ESI): m/z: M+. calculated for C17H18O2: 254.13068; found: 254.1310 (1 ppm)

- Synthesis of 4'-isopropoxy-2-methyl-3'-vinyl-1,1'-biphenyl **5**



In a Schlenk tube maintained under an argon atmosphere, Ph3P+CH3I- (0.72 g, 1.77 mmol, 1.5 equiv) was slowly added at room temperature to a suspension of NaH (42.5 mg, 1.77 mmol, 1.5 equiv) in THF (15 mL), and the reaction mixture was heated at 60°C for 2 h. After cooling to room temperature, the resulting solution was added to **4** (0.3 g, 1.18 mmol, 1 equiv) dissolved in diethyl ether (15 mL). After stirring for 16 h at 30 °C, the reaction was quenched by the slow addition of water (15 mL) and the organic products were extracted with diethyl ether (10 mL). Purification by column chromatography on silica gel using CH2Cl2/pentane (10:90 v/v) as the eluant afforded **5** as a colouress oil (0.26 g, 87%).

1H NMR (200.12 MHz, CDCl3, 25°C, TMS): *δ (ppm)*: 1.45 (d, *J*3 = 6.1 Hz, 6H, C*H*3); 2.35 (s, 3H, C*H3*); 4.75 (sept, *J*3 = 6.05 Hz, 1H, C*H*(CH3)2); 5.26 (d, *J*3= 11.2 Hz, 1H, C*H*), 5.89 (dd, *J*3=17.8 Hz, 1H; C*H*), 7.05 (d, *J*3 = 8.4 Hz, 1H, C*H*); 7.10-7.35 (m, 6H, C*H*); 7.52 (d, *J*3 = 1.6 Hz, 1H, C*H*).

13C NMR (50.33 MHz, CDCl3): *δ (ppm)*: 20.5, 22.3, 70.77, 113.5, 114.1, 125.7, 126.9, 127.2, 127.3, 129.4, 129.8, 130.2, 131.9, 134.1, 135.5, 141.6, 154.1

HRMS (ESI) m/z: M+. calculated for C18H20O: 252.15142; found: 252.1513 (0 ppm).

E.A: elemental analysis (%) calculated for C18H20O: C 85.67, H 7.99; found: C 86.00, H 7.91.

- Synthesis of 5-bromo-2-butoxy-1,3-di-tert-butylbenzene **7**



In a Schlenk tube maintained under an argon atmosphere, 4-Bromo-2,6-di-tert-butylphenol **6** (2 g, 7.01 mmol, 1 equiv) was dissolved in dry DMF (15 mL) and NaH (176 mg, 7.36 mmol, 1.05 equiv) was then added in several portions at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. 1-bromobutane (1.00 g, 7.36 mmol, 1.05 equiv) dissolved in THF (5 mL) was added, and the reaction mixture was stirred at 80 °C for 15 h. The reaction was quenched by slow addition of water (10 mL), and the organic products were extracted with CH2Cl2 (2×10 mL). Purification of the residue by column chromatography on silica gel using CH2Cl2/petroleum ether (70:30 v/v) as the eluant afforded **7** as a colourless oil (29 %).

1H NMR (200.12 MHz, CDCl3, 25°C, TMS): *δ (ppm)*: 1.10 (t, *J*3 = 6.8 Hz, 3H, C*H3*), 1.30 (m, 2H, C*H2*); 1.50 (s, 18H, C*H3*); 1.90 (m, 2H, C*H2*); 3.75 (t, *J*3 = 6.5 Hz, 2H, C*H2*); 7.40 (s, 2H, C*H*).

13C NMR (50.33 MHz, CDCl3): *δ (ppm)*: 14.3, 19.2, 31.3, 31.6, 32.1, 71.5, 115.3, 126.4, 135.6, 144.1

HRMS (ESI): m/z: [M+Na]+. calculated for C20H33OBrNa: 391.16125; found: 391.1615. ppm).

- Synthesis 2-(4-butoxy-3,5-di-tert-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **8**



Compound **7** (1.0 g, 2.93 mmol, 1 equiv) was dissolved in THF (15 mL), and the solution was cooled to -80 °C before *n*BuLi (1.3 mL, 2.5 M in hexane; 3.22 mmol, 1.1 equiv) was introduced dropwise. After 1 h at -80 °C, the reaction mixture was added dropwise to a cooled solution (-80°C) of B(OMe)3 (0.98 mL, 8.79 mmol, 3 equiv) in THF (5 mL). The reaction was allowed to warm to room temperature and stirred for 15 h. Water (10 mL) was slowly added, and the organic product was extracted with dichloromethane. Pinacol (0.41 g, 3.5 mmol, 1.2 equiv) was added at room temperature to the organic fraction in CH2Cl2 (20 mL), and the reaction was stirred for 15 h. The crude mixture was washed with water, and the solvent was evaporated. Purification by column chromatography on silica gel using CH2Cl2/petroleum ether (75/35 v/v) as the eluant afforded **8** as a colouress solid (77%).

1H NMR (200.12 MHz, CDCl3, 25°C, TMS): *δ (ppm)*: 0.90 (t, *J*3 = 6.8 Hz, 3H, C*H3*), 1.25 (s, 12H, C*H3*); 1.30 (m, 2H, C*H2*); 1.45 (s, 18H, C*H3*); 1.95 (m, 2H, C*H2*); 3.75 (t, *J*3 = 6.3 Hz, 2H, C*H2*); 7.75 (s, 2H, C*H*).

13C NMR (50.33 MHz, CDCl3): *δ (ppm)*: 14.1, 18.8, 24.1, 31.5, 31.8, 32.4, 71.5, 84.3, 115.6, 126.7, 135.9, 144.8.

HRMS (ESI): m/z: [M+Na]+. calculated for C26H45O3BNa: 439.33595; found: 439.3358.

- Synthesis of 4'-butoxy-3',5'-di-tert-butyl-4-isopropoxy-[1,1'-biphenyl]-3-carbaldehyde **9**



A Schlenk tube was loaded with **8** (0.75 g, 1.93 mmol, 1 equiv.), 5-bromo-2-isopropoxybenzaldehyde **3** (0.515 g, 2.12 mmol, 1.1 equiv), and [Pd(PPh3)4] (24.4 mg, 2.2 mol %). Dioxane (3 mL) and 3 mL aqueous 1M solution of K2CO3 were added, and the reaction mixture was heated at 100 °C for 16 h. The organic products were extracted with diethyl ether, and the resulting organic phase was washed with water. Purification by column chromatography on silica gel using diethyl ether/petroleum ether (80:20 v/v) as the eluant afforded **9** as a colouress oil (73%).

1H NMR (200.12 MHz, CDCl3, 25°C, TMS): *δ (ppm)*: 1.10 (t, *J*3 = 6.7 Hz, 3H, C*H3*), 1.30 (m, 2H, CH2); 1.25 (s, 18H, CH3); 1,45 (d, *J*3 = 6.1 Hz, 6H, C*H3*); 2.00 (m, 2H, C*H2*); 3.75 (t, *J*3 = 6.5 Hz, 2H, C*H2*); 4.75 (sept, *J*3 = 6.1 Hz, 1H, C*H*); 7.10 (d, *J*3= 8.4 Hz, 1H, C*H*); 7.45 (s, 2H, CH); 7.75 (dd, *J*3=8.4 Hz, *J*4= 2.5 Hz, 1H, C*H*); 8.10 (d, *J*4= 2.5 Hz, 1H, C*H*); 10.5 (s, 1H, C*H*O).

13C NMR (50.33 MHz, CDCl3): *δ (ppm)*: 14.6, 19.5, 22.5, 32.2, 32.5, 36.4, 71.8, 76.9, 114.8, 125.6, 126.1, 126.7, 134.1, 134.8, 144.4, 158.2, 160.1, 190.7

HRMS (ESI) m/z: [M+.]calculated for C28H40O3: 424.29775; found: 424.2986.

Elemental analysis (%) calculated for C28H40O3: C 79.20, H 9.50; found: C 78.99, H 9.76.

Synthesis of 4-butoxy-3,5-di-tert-butyl-4'-isopropoxy-3'-vinyl-1,1'-biphenyl **10**



In a Schlenk tube maintained under an argon atmosphere, Ph3P+CH3I- (0.573 g, 1.77 mmol, 1.5 equiv) was slowly added at room temperature to a suspension of NaH (33.85 mg, 1.41 mmol, 1.5 equiv) in THF (15 mL), and the reaction mixture was heated at 60°C for 2 h. After cooling to room temperature, the resulting solution was added to **9** (0.4 g, 0.94 mmol, 1 equiv) dissolved in diethyl ether (15 mL). After stirring for 16 h at 30°C, the reaction was quenched by the slow addition of water (15 mL) and the organic products were extracted with diethyl ether (10 mL). Purification by column chromatography on silica gel using CH2Cl2/pentane (15:85 v/v) as the eluant afforded **10** as a colouress solid (0.32 g, 82%).

1H NMR (200.12 MHz, CDCl3, 25°C, TMS): *δ (ppm)*: 1.10 (t, *J*3 = 6.8 Hz, 3H, C*H3*), 1.30 (m, 2H, C*H2*); 1.25 (s, 18H, C*H3*); 1,45 (d, *J*3 = 6.1 Hz, 6H, C*H3*); 2.00 (m, 2H, C*H2*); 3.85 (t, *J*3 = 7.5 Hz, 2H, C*H2*); 4.65 (sept, *J*3 = 6.1 Hz, 1H, C*H*); 5.40 (d, *J*3= 11.3 Hz, 1H, C*H*), 5.92 (d, *J*3=17.7 Hz, 1H, C*H*), 7.00 (d, *J*3= 8.5 Hz, 1H, C*H*); 7.35 (s, 2H, C*H*); 7.40–7.60 (m, 4H; C*H*), 7.80 (d, *J*3= 1.4 Hz, 1H, C*H*).

13C NMR (50.33 MHz, CDCl3): *δ (ppm)*: 14.5, 22.5, 23.0, 32.2, 32.6, 36.4, 71.4, 77.1, 114.7, 125.8, 127.8, 128.3, 132.5, 134.9, 135.4, 144.1, 154.7, 160.1, 190.7

HRMS (ESI): m/z: [M+Na]+. calculated for C31H46O2Na: 473.33955; found: 473.3398.

- Synthesis of 2,2'-(5'-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-[1,1':3',1''-terphenyl]-4,4''-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **13**



In a Schlenk tube maintained under an argon atmosphere, **12** (2.5 g, 4.6 mmol, 1 equiv) was dissolved in THF (20 mL), and the solution was cooled to -80 °C before *t*-BuLi (18.2 mL, 1.6 M in hexane; 28.98 mmol, 6.3 equiv) was introduced dropwise. After 1 h at -80 °C, the reaction mixture was added dropwise to a cooled solution (-80 °C) of B(OMe)3 (4.62 mL, 41.4 mmol, 9 equiv) in THF (7 mL). The reaction was allowed to warm to room temperature and stirred overnight. Water (15 mL) was slowly added, and the organic product was extracted with dichloromethane. Pinacol (1.78 g, 15.18 mmol, 3.3 equiv) was added at room temperature to the organic fraction in CH2Cl2 (30 mL) and Et2O (20 mL), and the reaction was stirred overnight at room temperature. The crude mixture was washed with water, and the solvent was evaporated. Purification by column chromatography on silica gel using CH2Cl2/petroleum ether (75/25 v/v) as the eluant afforded **13** as white powder (2.14 g, 68%).

1H NMR (200.12 MHz, CDCl3, 25°C, TMS): *δ (ppm)*: 1.42 (s, 36H, C*H3*), 7.75 (d, *J*3 = 8.0 Hz, 6H, C*H*); 7.84 (s, 3H, C*H*); 7.94 (d, *J*3 = 8.0 Hz, 6*H*).

13C NMR (50.33 MHz, CDCl3): *δ (ppm)*:24.9, 83.9, 125.6, 126.7, 128.1, 135.4, 142.3, 143.7

Elemental analysis (%) calculated for C42H51O6B3: C 73.72, H 7.51; found: C 73.89, H 7.51.

- Synthesis of 5''-(3'-formyl-4'-isopropoxy-[1,1'-biphenyl]-4-yl)-4,4''''-diisopropoxy-[1,1':4',1'':3'',1''':4''',1''''-quinquephenyl]-3,3''''-dicarbaldehyde **14**



A Schlenk tube was loaded with **13** (1.5 g, 2.2 mmol, 1 equiv), 5- bromo-2-isopropoxybenzaldehyde (1.76 g, 7.26 mmol, 3.3 equiv), and [Pd(PPh3)4] (62.64 mg, 3.3 mol %). Dioxane (4 mL) and 4 mL aqueous solution of K2CO3 (3 mL) were added, and the reaction mixture was heated overnight at 100°C. The organic products were extracted with diethyl ether, and the resulting organic phase was washed with water. Purification by column chromatography on silica gel using CH2Cl2/petroleum ether (80:20 v/v) as the eluant afforded **14** as white powder (1.07 g, 61%).

1H NMR (200.12 MHz, CDCl3, 25°C, TMS): *δ (ppm)*: 1.45 (d, *J*3 = 6.0 Hz, 6H, C*H3*); 4.79 (sept, *J*3 = 6.05 Hz, 3H, C*H*); 7.12 (d, *J*3 = 8.8 Hz, 3H, C*H*); 7.25 (m, 4H, C*H*); 7.55 (dd, *J*3=8.7 Hz, *J*4=2.1 Hz, 2H, C*H*), 7.78 (d, *J*3 = 7.9 Hz, 6H, C*H*); 7.85 (s, 3H, CH); 8.21 (d, *J* = 2.3 Hz, 3H, C*H*); 10.57 (s, 3H, C*H*O).

13C NMR (50.33 MHz, CDCl3): *δ (ppm)*: 22.1, 71.4, 114.5, 125.0, 126.5, 127.1, 130.1, 132.9, 134.1, 139.9, 141.9, 160.2, 190.1

HRMS (ESI): m/z: [M+Na]+ calculated for C54H48O6Na: 815.33486; found: 815.3364 (2 ppm).

Elemental analysis (%) calculated for C54H48O6: C 81.49, H 6.10; found: C 80.91, H 6.21.

- Synthesis of 4,4''''-diisopropoxy-5''-(4'-isopropoxy-3'-vinyl-[1,1'-biphenyl]-4-yl)-3,3''''-divinyl-1,1':4',1'':3'',1''':4''',1''''-quinquephenyl **15**



In a Schlenk tube maintained under an argon atmosphere, Ph3P+CH3I- (2.10 g, 5.04 mmol, 4.0 equiv) was slowly added at room temperature to a suspension of NaH (121.0 mg, 5.04 mmol, 4.0 equiv) in dry THF (20 mL), and the reaction mixture was heated at 60 °C for 2 h. After cooling to room temperature, the resulting solution was added to **14** (1.0 g, 1.26 mmol, 1 equiv) dissolved in diethyl ether (15 mL). After stirring for 16 h at 30°C, the reaction was quenched by the slow addition of water and the organic products were extracted with diethyl ether. Purification by column chromatography on silica gel using CH2Cl2/pentane (60:40 v/v) as the eluent afforded **15** as a white solid (0.783 g, 79 %).

1H NMR (200.12 MHz, CDCl3, 25°C, TMS): *δ (ppm)*: 1.45 (d, *J*3 = 6.0 Hz, 18H, C*H3*); 4.80 (sept, *J*3 = 6.0 Hz, 3H, C*H*); 5.41 (d, *J*3= 11.2 Hz, 3H, C*H*), 5.91 (d, *J*3=17.6 Hz, 3H, C*H*), 7.05 (d, *J*3 = 8.6 Hz, 3H, C*H*); 7.15 (dd, *J*3=8.7 Hz, *J*3=2.1 Hz, 3H, C*H*), 7.52 (d, *J* = 8.0 Hz, 3H, C*H*); 7.85 (m, 15H, C*H*), 7.95 (s, 3H, C*H*).

13C NMR (50.33 MHz, CDCl3): *δ (ppm)*: 21.1, 69.8, 113.3, 113.4, 123.7, 124.2, 126.6, 127.0, 131.0, 131.9, 134,4, 138.4, 139.1, 141.0, 153.8

HRMS (ESI): m/z: [M+Na+CH3OH]+ calculated for C58H58O4Na: 841.42328; found: 841.4214 (2 ppm).

- Synthesis of isobutylboronic acid **17**



A 2.5 M stock solution of isobutylmagnesium bromide in THF was prepared from commercially available isobutyl bromide **16** and standardized according to protocols described in literature.[[4]](#footnote-4)

Trimethyl borate (1.5 g, 15 mmol, 6.0 equiv.) was placed in an oven dried Schlenk flask under argon and cooled to -20 °C. To this was added drop-wise, isobutylmagnesium bromide in THF (1.0 mL, 2.5 mmol, 1.0 equiv.) and the reaction was stirred overnight. The reaction was again cooled to 0 °C and 5 mL of 10% aq. H2SO4 solution was added and the reaction stirred for 2 hours. The reaction was diluted with 10 mL of water the THF evaporated on a rotary evaporator. The resulting solution was extracted with 3×50 mL of EtOAc. The combined organic phases were washed with a dilute solution of NaHCO3 and brine and dried over anhydrous MgSO4 to give white powder. The boronic acid (165 mg, 65% yield) was found sufficiently pure and was used as such for the next step. The product characteristics are in agreement with previously reported literature.[[5]](#footnote-5)

1H NMR (300 MHz, CD3CDO): δ 1.88 (m, 1 H, C*H*), 0.91 (d, *J* = 6.6 Hz, 6 H, C*H3*), 0.68 (d, *J* = 6.6 Hz, 2 H, C*H2*).

* Synthesis of 5-isobutyl-2-isopropoxybenzaldehyde **18**



Isobutylboronic acid **17** (150 mg, 1.47 mmol, 3.0 equiv.), 5-bromo-2-isopropoxybenzaldehyde **3** (120 mg, 0.49 mmol, 1.0 equiv.), K2CO3 (170 mg, 1.22 mmol, 2.5 equiv.) and PdCl2. dppf (10 mg, 0.014 mmol, 3.0 mol%) were suspended in a Schlenk flask containing 2.0 mL of xylenes under argon. The reaction was heated for 20 hours at 140 °C and cooled to room temperature. The contents of the flask were poured onto 5.0 mL of water and the resulting suspension was extracted with EtOAc and evaporated. The resulting semisolid was suspended in 5 mL of pentane and passed from a Pasteur pipette containing a cotton plug to remove solids. The resulting solution was evaporated and chromatographed on a silica column for purification using a 1/19 mixture of diethyl ether/petroleum ether to yield **18** as a colourless oil (70 mg, 65% yield).

1H NMR (200 MHz, CDCl3): δ 0.90 (d, *J* = 6.6 Hz, C*H3*), 1.43-1.40 (d, *J* = 6.1 Hz, 6 H, C*H3*), 2.45 (d, *J* = 7.2 Hz, 2 H, C*H2*), 4.69-4.63 (m, 1 H, CH), 6.92 (d, *J* = 8.5 Hz, 1 H, C*H*), 7.32 (dd, *J* = 8.5 Hz, 2.5 Hz, 1 H, C*H*), 7.62 (d, *J* = 2.5 Hz, 1 H, C*H*), 10.49 (s, 1 H, C*H*O).

13C NMR (100 MHz, CDCl3): δ 19.0, 22.0, 29.0, 44.8, 76.0, 115.0, 130.1, 131.4, 132.3, 137.6, 154.0, 191.4.

HRMS (ESI) [M+H] + (C14H21O2): calc. 221.1492, found 221.1490.

Elemental analysis C14H20O2 (220.31) calc. C 76.33, H 9.15, O 14.52 found C 76.29, H 9.14, O 14.56.

- Synthesis of 4-isobutyl-1-isopropoxy-2-vinylbenzene **19**



Ph3P+CH3I- (275 mg, 0.68 mmol, 2.5 equiv.) was slowly added at room temperature to a suspension of NaH (60% in mineral oil, 28 mg, 0.68 mmol, 2.5 equiv.) in 5.0 mL THF in an oven dried Schlenk flask and the reaction mixture was heated to 60 °C for 2 hours, during which the colourless reaction mixture became lemon yellow coloured. After cooling to room temperature, the resulting solution was added to the aldehyde **18** (60 mg, 0.27 mmol, 1.0 equiv.) dissolved in 5.0 mL of dry, distilled diethyl ether and the resulting solution was stirred overnight at 30 °C. 5.0 mL of water was then added to it and the content extracted with 3×10 mL of EtOAc, washed with 50 mL brine dried over anhydrous MgSO4 and the organic phase evaporated to yield a cream coloured semisolid. This was purified by column chromatography using a 1/19 mixture of diethyl ether/petroleum ether to yield **19** a colourless oil (49 mg, 83% yield).

1H NMR (500 MHz, CDCl3): δ 0.93 (d, *J* = 6.0 Hz, 6 H, C*H3*), 1.36 (d, *J* = 6.0 Hz, 6 H, C*H3*), 1.85 (septet, 1 H, C*H*), 2.43 (d, *J* = 7.1 Hz, 2 H, C*H2*), 4.55-4.48 (septet, 1 H, C*H*), 5.23 (dd, *J* = 11.1 Hz, 1.6 Hz, 1 H, C*H* vinyl), 5.74 (dd, *J* = 17.8 Hz, 1.6 Hz, 1 H, C*H* vinyl), 6.82 (d, *J* = 8.2 Hz, 1 H, C*H*), 6.99 (dd, *J* = 8.3 Hz, 2.2 Hz, 1 H, C*H*), 7.10-7.04 (m, 1 H, C*H* vinyl), 7.27 (d, *J* = 2.2 Hz, 1 H, C*H*).

13C NMR (125 MHz, CDCl3): δ 151.2, 134.2, 132.0, 128.9, 127.0, 115.7, 114.3, 114.1, 75.5, 45.0, 29.0, 22.0, 21.0.

HRMS (ESI) [M+H] + (C15H23O): calc. 219.1671 found 219.1670.

Elemental analysis C15H22O (218.33) calc. C 82.52, H 10.16, O 7.33 found C 82.49, H 10.15, O 7.32.

- Synthesis (4-bromo-2,6-dimethylphenoxy) (tert-butyl) dimethylsilane **21**



4-bromo-2,6-dimethylphenol **20** (200 mg, 0.94 mmol, 1.0 equiv.), *N*-Methylimidazole (0.8 mL, 9.94 mmol, 2.0 equiv.) and sublimed *t*-BuMe2SiCl (824 mg, 5.46 mmol, 1.1 equiv.) were mixed together in a 100 mL round bottom flask and heated to 60 °C for 5 hours. The reaction was cooled, and the contents filtered using cotton wool to remove unreacted silyl ether to give a clear colourless liquid. This was then purified by column chromatography using a 1/19 mixture of EtOAc /petroleum ether as eluents to yield a colourless oil (237 mg, 80% yield). The product characteristics are in agreement with previously reported data.[[6]](#footnote-6)

1H NMR (200 MHz, CDCl3): δ 0.20 (s, 6 H, SiC*H3*), 1.04 (s, 9 H, *t*-BuC*H3*), 2.19 (s, 6 H, CH3), 7.11 (s, 2 H, CH).

- Synthesis of tert-butyl(2,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3-dioxaborolan-2 yl)phenoxy)dimethylsilane **22**



(4-bromo-2,6-dimethylphenoxy) (tert-butyl) dimethylsilane **21**, (500 mg, 1.58 mmol, 1.0 equiv.) was dissolved in 5 mL of THF in an oven dried Schlenk flask and the solution cooled to -80 °C using a EtOH/liquid N2 bath. *t*BuLi (1.6 M in pentane stock solution, 2.07 mL, 3.3 mmol, 2.1 equiv.) was introduced into this solution drop-wise and the reaction was stirred for one hour. This was then canulated into a dry Schlenk flask containing a solution of B(OMe)3 (1.05 mL, 9.48 mmol, 6 equiv.) in 5 mL THF cooled to – 80 °C. The reaction was then allowed to warm to room temperature, stirred overnight and quenched with 10 mL of distilled water. The organic products were extracted with 2×20 mL of DCM and pinacol (392 mg, 3.31 mmol, 2.1 equiv.) was added to the organic fraction at room temperature and the reaction stirred overnight. This crude mixture was washed with 2×50 mL of water and the DCM evaporated over a rotary evaporator. The resulting solid was chromatographed on a silica column using a 1/9 mixture of diethyl ether/petroleum ether (Rf = 0.46) to give a white coloured crystalline solid (303 mg, 53% yield).

1H NMR (200 MHz, CDCl3): δ 0.20 (s, 6 H, C*H3*), 1.04 (s, 9 H, C*H3*), 1.35 (s, 12 H, C*H3*), 2.23 (s, 6 H, C*H3*), 7.46 (s, 2 H, C*H*).

13C NMR (125 MHz, CDCl3): δ 155.3, 135.7, 128.2, 83.6, 26.2, 25.0, 18.2, 17.7, -2.7.

HRMS (ESI) [M+H] + (C20H36O3BSi): calc. 363.2521, found 363.2518.

Elemental analysis C20H35O3BSi (362.39) calc. C 66.29, H 9.74 found, C 65.95, H 9.73.

- Synthesis of 4'-(tert-butyldimethylsilyloxy)-4-isopropoxy-3'-methylbiphenyl-3-carbaldehyde **23**



An oven dried Schlenk flask was charged with the pinacol-borane **22** (1.08 g, 2.98 mmol, 1.2 equiv.), 5-bromo-2-hydroxybenzaldehyde **3** (500 mg, 2.48 mmol, 1.0 equiv.), and Pd(PPh3)4 (115 mg, 0.1 mmol, 4.0 mol%) and to this was introduced 3.0 mL of degased 1,4-dioxane and 3.0 mL of a 2M aq. solution of K2CO3. The reaction mixture was heated at 100 °C for 18 hours and cooled to room temperature. The organic products were extracted with 10×2 mL of diethyl ether and the combined organic phases were washed with 2×10 mL of distilled water. The resulting yellow oil was then purified by column chromatography using first a 1/19 mixture of diethyl ether/petroleum ether and then a 1/9 mixture of diethyl ether/petroleum ether (Rf = 0.47) to yield a faint yellow coloured oil (743 mg, 70% yield).

1H NMR (200 MHz, CDCl3): δ 0.24 (s, 6 H, C*H3*), 1.07 (s, 9 H, C*H3*), 1.43 (s, 3 H, C*H3*), 1.46 (s, 3 H, C*H3*), 2.28 (s, 6 H, C*H3*), 4.67-4.79 (m, 1 H, C*H*), 7.04 (d, *J* = 8.6 Hz, 1 H, C*H*), 7.22 (s, 2 H, C*H*), 7.74 (dd, *J* = 8.6 Hz, 2.5 Hz, 1 H, C*H*), 10.54 (s, 1 H, C*H*O), 8.04 (d, *J* = 2.5 Hz, 1 H, C*H*).

13C NMR (125 MHz, CDCl3): δ 190.3, 159.5, 151.8, 133.8, 133.4, 132.3, 129.0, 126.9, 126.0 (d), 125.7, 114.4, 71.3, 26.1, 22.0, 18.8, 17.9, -2.87.

HRMS (ESI) [M+Na] + (C24H34O3NaSi) calc. 421.2169 found 421.2171.

- Synthesis of tert-butyl(4'-isopropoxy-3,5-dimethyl-3'-vinylbiphenyl-4-yloxy)dimethylsilane **24**



Ph3P+CH3I- (760 mg, 1.8 mmol, 2.5 equiv.) was slowly added at room temperature to a suspension of NaH (60% in mineral oil, 70 mg, 1.8 mmol, 2.5 equiv.) in 5.0 mL THF in an oven dried Schlenk flask and the reaction mixture was heated to 60 °C for 2 hours, during which the colourless reaction mixture became lemon yellow coloured. After cooling to room temperature, the resulting solution was added to the aldehyde **23** (300 mg, 0.75 mmol, 1.0 equiv.) dissolved in 5.0 mL of dry, distilled diethyl ether and the resulting solution was stirred overnight at 30 °C. 5.0 mL of water was then added to it and the content extracted with 3×10 mL of EtOAc, washed with 50 mL brine dried over anhydrous MgSO4 and the organic phase evaporated to yield a cream coloured semisolid. This was purified by column chromatography using a 1/19 mixture of diethyl ether/petroleum (Rf = 0.8) ether to yield white crystals (250 mg, 85% yield).

1H NMR (200 MHz, CDCl3): δ 0.24 (s, 6 H, C*H3*), 1.07 (s, 9 H, C*H3*), 1.40 (d, *J* = 6 Hz, 6 H, C*H3*), 2.29 (s, 6 H, C*H3*), 4.52-4.64 (m, 1 H, C*H*), 5.30 (d, *J* = 12 Hz, C*H*), 5.83, (d, *J* = 17.4 Hz, C*H*), 6.93 (d, *J* = 8.5 Hz, 1 H, C*H*), 7.05-7.13 (m, 1 H, vinyl C*H*), 7.20 (s, 2 H, C*H*), 7.42 (dd, *J* = 8.5 Hz, 1.8 Hz, 1 H, C*H*), 7.67 (d, *J* = 1.8 Hz, 1 H, C*H*).

13C NMR (125 MHz, CDCl3): δ 154.2, 151.3, 133.8, 133.6, 132.1, 128.7, 127.9, 127.1, 127.0, 124.9, 114.5, 114.1, 71.0, 26.1, 22.2, 18.8, 18.0, -2.8.

HRMS (ESI) [M+Na] + (C25H36O2NaSi) calc. 419.2376, found 419.2375.

C25H36O2Si (396.64) calc. C 75.70, H 9.15, found C 75.62, H 9.07.

- Synthesis of pre-catalyst **IIa**



In a Schlenk tube maintained under an argon atmosphere, **GII** complex (109 mg, 0.13 mmol, 1 equiv) and CuCl (12.8 mg, 0.13 mmol, 1 equiv) were dissolved in 3 mL of dry and degassed CH2Cl2. **5** (32.5 mg, 0.13 mmol, 1 equiv) dissolved in 3 mL of dry and degassed CH2Cl2 was then added to the stirred solution. The reaction was stirred at 40°C for 2 h. The solvent was evaporated, and the crude residue was dissolved in a mixture of pentane and CH2Cl2 (1 mL:1 mL). The insoluble phosphine-copper adduct was filtered, and the complex was purified by column chromatography on silica gel using CH2Cl2/pentane (30:70 v/v) as the eluent to afford **IIa** as a green powder (70 mg, 75%).

1H NMR (200.12 MHz, CDCl3, 25°C, TMS): *δ (ppm)*: 1.34 (d, *J*3=6.2 Hz, 6H, C*H3*); 2.29 (s, 3H, C*H3*); 2.38 (s, 6H, C*H3*); 2.51 (s, 12H, C*H3*); 4.21 (s, 4H, C*H2*); 4.99 (sept, *J*3=6.2 Hz, 1H, C*H*); 6.85 (d, *J*3=8.6 Hz, 1H, C*H*); 6.94 (m, 1H, CH); 7.08 (s, 4H, C*H*), 7.15–7.35 (m, 4H, C*H*); 7.48 (dd, *J*3=8.6 Hz, *J*4=2 Hz, 1H, CH); 16.58 (s, 1H, Ru=C*H*).

13C NMR (50.33 MHz, CDCl3): *δ (ppm)*: 19.6, 20.6, 21.2, 21.3, 51.9, 75.8, 113.0, 123.1, 126.3, 127.7, 129.7, 130.5, 130.6, 130.8, 136.0, 136.5, 139.3, 139.4, 140.7, 145.2, 151.4, 210.9 (N*C*N), 295.4 (Ru=*C*)

HRMS (LSIMS): m/z: [M]+. calculated for C38H44N2OCl2Ru: 716.118742; found: 716.1891 (2 ppm).

Elemental analysis (%) calculated for C38H44N2OCl2Ru: C 63.68, H 6.19, N 3.91; found: C 63.69, H 7.16, N 3.02.

- Synthesis of pre-catalyst **IIb**:



In a Schlenk tube maintained under an argon atmosphere, **GII** complex (100 mg, 0.118 mmol, 1.1 equiv) and CuCl (11.7 mg, 0.118 mmol, 1.1 equiv) were dissolved in 3 mL of dry and degassed CH2Cl2. **10** (45.2 mg, 0.108 mmol, 1 equiv) dissolved in 4 mL of dry and degassed CH2Cl2 was then added to the stirred solution. The reaction was stirred at 40 °C for 2 h. The solvent was evaporated, and the crude residue was dissolved in a mixture of pentane and CH2Cl2 (1 mL:1 mL). The insoluble phosphine-copper adduct was filtered, and the complex was purified by column chromatography on silica gel using CH2Cl2/pentane (30:70 v/v) as the eluant to afford **IIb** as a green powder (77 mg, 80%).

1H NMR (200.12 MHz, CDCl3, 25°C, TMS): *δ (ppm)*: 1.02 (t, *J*3 = 8.0 Hz, 3H, CH3), 1.32 (d, *J*3 = 6.0 Hz, 6H, CH3), 1.50 (s, 18H, CH3), 1.80-2.05 (m, 4H, CH2), 2.3-2.65 (m, 18H; CH3), 3.79 (t, *J*3 = 7.6 Hz, 2H, CH2), 4.21 (s, 4H, CH2), 4.85-5.05 (m, 1H, CH), 6.86 (d, *J*3 = 6.0Hz, 1H, CH), 7.11 (s, 4H, H), 7.20-7.35 (s, 3H, CH), 7.69 (bs, 1H, CH), 16.56 (s, 1H, CH).

13C NMR (75.48 MHz, CD2Cl2, 25°C, TMS): *δ (ppm)*:15.8, 21.0, 22.8, 33.6, 33.7, 33.8, 37.8, 77.2, 78.5, 114.9, 122.4, 127.5, 129.7, 131.2, 135.7, 138.2, 140.7, 145.9, 147.2, 153.1, 164.3, 212.6, 297.3

MS (ESI) m/z: M+. calculated for C49H66N2O2Cl2Ru: 886.35448; found: 886.3532 (1 ppm).

- Synthesis of pre-catalyst **IIc**



In a Schlenk tube maintained under an argon atmosphere, **15** (30.0 mg, 0.038 mmol, 1 equiv) in dry and degassed CH2Cl2 (4 mL) was added to **GII** complex (90.3 mg, 0.118 mmol, 3.1 equiv) and CuCl (11.69 mg, 0.118 mmol, 3.1 equiv) in dry and degassed CH2Cl2 (4 mL), and the reaction was stirred at 40 °C for 2 h. The solvent was evaporated, and the crude residue was dissolved in a mixture of pentane and CH2Cl2 (1 mL:1 mL). The insoluble phosphine-copper adduct was filtered, and the complex was purified by column chromatography on silica gel using CH2Cl2/pentane (30:70 v/v) as the eluant to afford **IIc** as a green powder (0.71 g, 67%).

1H-NMR (200.12 MHz, CDCl3, 25°C, TMS): *δ (ppm)*: 1.41 (d, *J*3=6.9 Hz, 18H, CH3), 2.50 (m, 54H, CH3), 4.21 (s, 12H, N-CH2), 4.95 (sept, *J*3=6.9 Hz, 3H, CH), 7.05 (d, *J*3=8.9 Hz, 3H, CH); 7.21 (bs, 12H, CH), 7.75 (m, 18H, CH); 8.05 (s, 3H, CH); 16.55 (s, 3H, CH).

- Syntheses (1,3-dimesityl-4,5-dihydro-1H-imidazol-3-ine)dichloro(5-isobutyl-2-isopropoxybenzylidene) ruthenium(II) (**IId**)



An oven dried Schlenk flask containing 5.0 mL of dry dichloromethane was charged with **GII** complex (50 mg, 0.058mmol, 1.1 equiv.) and CuCl (104 mg, 1.06 mmol, 2 equiv.) and ligand **19** (12 mg, 0.052 mmol, 1.0 equiv.), dissolved in 5.0 mL of dichloromethane was canulated into it and the reaction was heated at 40 °C for 2 hours. The reaction was cooled, solvent evaporated over a rotary evaporator and its contents were suspended in a 2 mL of a 1/1 mixture of pentane/CH2Cl2. A Pasteur pipette was separately prepared with a plug of cotton wool and the suspension was passed through it, thereby removing an insoluble phosphine-copper adduct and unreacted CuCl. The resulting green solution was evaporated and purified by column chromatography using silica gel and a 1/1 mixture of pentane/CH2Cl2 as eluents to afford **IId** as a green powder after evaporation (32 mg, 88%).

1H NMR (500 MHz, CDCl3): δ 16.44 (s, 1 H), 7.39 (dd, *J* = 8.3 Hz, 2.0 Hz, 1 H, CH), 7.11 (s, 4 H, CH), 6.77 (d, *J* = 8.3 Hz, 1 H, CH), 6.75 (d, *J* = 2.0 Hz, 1 H, CH), 4,84-4.91 (septet, 1 H, CH), 4.20 (s, 4 H, CH2), 2.53 (d, *J* = 7 Hz, 2 H, CH2), 2.48 (br, s, 12 H, CH3), 2.45 (s, 6 H, CH3), 1.89-1.81 (m, 1 H, CH), 1.26 (d, *J* = 6.6 Hz, 6 H, CH3), 0.95 (d, *J* = 6.6 Hz, 6 H, CH3).

13C NMR (125 MHz, CDCl3): δ 296.8, 211.1, 150.2, 144.9, 138.8, 135.5, 129.9, 129.2, 122.4, 112.4, 74.8, 43.9, 30.3, 22.0, 20.9, 20.7, 19.0 (br), 14.0.

HRMS (ESI) [M+**.**] (C35H46N2OCl2Ru) calc. for 682.2030, found 682.2036.

Elemental analysis (C35H46Cl2N2ORu) (682.74) calc. C 61.57, H 6.79, N 4.10 found C 61.31, H 7.04, N 3.94.

- Synthesis of (1,3-dimesityl-4,5-dihydro-1H-imidazol-3-ine)dichloro-((4'-(tert-butyldimethylsilyloxy)-4-isopropoxy-3',5'-dimethylbiphenyl-3-yl)methylene)ruthenium **IIe**



An oven dried Schlenk flask containing 5.0 mL of dry dichloromethane was charged with **G2** (50 mg, 0.05mmol, 1.1 equiv.) and CuCl (104 mg, 1.06 mmol, 2 equiv.). Ligand **24** (23 mg, 0.58 mmol, 1.1 equiv.), dissolved in 5.0 mL of dichloromethane was then canulated into and the reaction was heated at 40 °C for 2 hours. The reaction was cooled to room temperature, the solvent evaporated over a rotary evaporator and the resulting solid was suspended in a 2 mL of a 1/1 mixture of pentane/CH2Cl2. A Pasteur pipette was separately prepared with a plug of cotton wool and the suspension was passed through, thereby removing an insoluble phosphine-copper adduct and unreacted CuCl. The resulting green solution was evaporated and purified by column chromatography using silica gel and a 1/1 mixture of pentane/CH2Cl2 as eluents to afford **IId** as a green powder after evaporation (45 mg, 89%).

1H NMR (200 MHz, CDCl3): δ 16.47 (s, 1 H), 7.68 (dd, *J* = 8.6 Hz, 1.9 Hz, 1 H, CH), 7.11-7.08 (m, 7 H, CH), 6.83 (d, *J* = 8.6 Hz, 1 H, CH), 4.99-4.86 (m, 1 H, CH), 4.22 (s, 4 H, CH2), 2.51 (br, 12 H, CH3), 2.43 (s, 6 H, CH3), 2.28 (s, 6 H, CH3), 1.31 (d, *J* = 6.0 Hz, 6 H, CH3), 1.08 (s, 9 H, CH3), 0.25 (s, 6 H, CH3).

13C NMR (125 MHz, CDCl3): δ 154.6, 151.0, 143.6, 133.6, 132.3, 129.1, 128.8, 128.4, 127.8, 127.3, 127.1, 126.2, 124.7, 114.2, 71.3, 56.2, 26.2, 22.3, 22.1, 18.2, 18.6, 18.1, -2.7.

HRMS (EI) [M+**.**] (C45H60Cl2N2O2SiRu) calc. for 860.2844, found 860.2856.

Elemental analysis (C45H60Cl2N2O2SiRu) (861.03) calc. C 62.77, H 7.02, N 3.25 found C 62.77, H 7.14, N 3.11.

### General procedure for RCM reactions of diethyl diallyl malonate (DEDAM)

12 L of substrate was introduced into a dry NMR tube under argon via a dry micro-syringe. To this was introduced 0.5-0.6 mL of dry, CD2Cl2 (containing 0.1 mol% catalyst) from 1.5 M stock solutions of catalysts. The tubes were sealed with an air-tight septum and quickly introduced into NMR probes and acquisitions were made at regular intervals. The conversions were calculated from 1H NMR by comparing peak integrations at δ = 4.93 ppm (diethyl cyclopent-3-ene-1, 1-dicarboxylate, ethylenic H peaks) and at δ = 4.55 ppm (diethyl diallyl malonate, allyl H peaks) and at δ = 5. 18 ppm (Diethyl 3-methylcyclopent-3-en-1,1-dicarboxylate, ethylinic 1H peak) and δ = 5.64-5.75 (Diethyl 2-allyl-2-(2-methylallyl) malonate, unsubstituted allyl 1H peak) using a 500 MHz spectrometer.

**General procedure for the Nanofiltration of complexes I and IIe**

The membrane used was a Starmem 122 provided by MET (UK). NF of the pure complexes 0.5.10-3 mM in toluene were performed at 25 °C with a transmembrane pressure of 40 bar and a cross-flow velocity of 0.1 m. s-1. The retentate was continuously recycled in the feed tank whereas the permeate was continuously extracted up to reach a volume reduction ratio VRR= 2 (concentration mode, with VRR = initial feed volume/ final feed volume). All given retentions correspond to those reached at VRR=2, after a slight concentration of the feed solution depending on the solute retention.

1. M. Melaini, C. Thoumazet, L. Ricard, P. Le Floch, *J. Organomet. Chem*., **2004**, *689*, 2988. [↑](#footnote-ref-1)
2. Andrushko, V.; Schwinn, D.; Tzschucke, C. C.; Michalek, F.; Horn, J.; Mossner, C.; Bannwarth, W. *Helv. Chim. Acta* **2005**, *88*, 936. [↑](#footnote-ref-2)
3. J. Brunel, O. Mongin, A. Jutand, I. Ledoux, J. Zyss, M. Blanchard-Desce, *Chem Mater.*, **2003**, *15*, 4139 [↑](#footnote-ref-3)
4. (a) Furniss, B.S., Hannaford, A.J., Smith, P.W.G., Tatchell, A.R. in *Vogel’s Textbook of practical Organic Chemistry* Fifth Edn., Longman Scientific and Technical, **1989**, 534. (b) Watson, S.C. and Eastham, J.F. *J. Organometal. Chem.* 9, **1967**, 165. [↑](#footnote-ref-4)
5. Molander, G. A.; Cavalcanti, L. N.; Canturk, B.; Pan, P.-S.; Kennedy, L. E. *J. Org. Chem.* **2009**, *74*, 7364-7369. [↑](#footnote-ref-5)
6. Caldwell, S. T.; Quin, C.; Edge, R.; Hartley, R. C. *Org. Lett.* **2007**, *9*, 3499-3502. [↑](#footnote-ref-6)