Supporting Information
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Supporting Information; Synlett Submission

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Pages 1 – 9 Experimental descriptions

Page 11 ff 1H and 13C Spectra of compounds described

All reactions were conducted in oven- or flame-dried glassware. Reactions involving air- and water-sensitive reagents were performed under a dry argon atmosphere using standard vacuum line and Schlenk techniques. Reaction temperatures reported refer to external bath temperatures. Solvents used in chromatography were BDH AnalaR or GPR grade and were used without further purification. Solvents used for reactions either were distilled prior to use: CH2Cl2 (from CaH2); Toluene, THF and Et2O (from benzophenone and sodium) or dried over an alumina Grubb’s column. All other solvents or reagents were used as commercially supplied and were used without further purification except when otherwise noted. Analytical thin layer chromatography (TLC) was performed on Merck aluminium-backed silica plates coated with a 200 µm layer of 60 F254 silica. Visualization was accomplished using the quenching of UV fluorescence (λmax 254 nm), and by staining with potassium permanganate solution followed by heat. Flash chromatography utilised Silica gel 60 (Flurochem; 40-63 µm; 550 m2g-1). All solvents were evaporated at or below 50 °C under reduced pressure using a rotary evaporator.

Melting points were recorded using a Reichert-Koffler block apparatus and are uncorrected.

Nuclear Magnetic Resonance (NMR) spectra were recorded using a Bruker AV400 spectrometer, Bruker DPX400, Bruker AVB500 or Bruker DRX500. Chemical shifts (δ) are quoted in parts per million (ppm) and are referenced to the residual solvent peak. Coupling constants (J) were recorded in Hertz (Hz) and are reported to the nearest 0.1 Hz. The abbreviations br, d, m, q, s, t and dd refer to broad, doublet, multiplet, quartet, singlet, triplet and doublet of doublets respectively. Fourier Transform Infrared (FTIR) spectra were recorded as thin films on a KBr disc using a Perkin-Elmer Paragon 1000 FTIR spectrometer. Signal intensities and ranges are denoted in parentheses. The abbreviations br, m, s and w refer to broad, medium, strong and weak respectively. Mass Spectra (MS) were recorded by the author and Mr. R. Proctor using a Micromass GCT (Chemical Ionisation) or a V.G. Autospec spectrometer (EI and CI). Exact masses were measured on a Waters 2790-Micromass LCT spectrometer or a V.G. Autospec spectrometer using electrospray and chemical ionisation. Mass-to-charge (m/z) values are quoted in Daltons.

All substituted N-phenylbenzamides were synthesized from their respective benzoyl chlorides following literature procedures.7

N-methyl-2-(trimethylsilyl)benzamide (2b):
A solution of \( N \)-methylbenzamide (1.35 g, 10 mmol) in THF (30 mL) was cooled to -78 °C and Bu'Li (1.7 M in pentane) (11.8 mL, 20 mmol) was added dropwise while stirring the mixture vigorously. After 1 h Me\(_2\)SiCl (4 mL, 30 mmol) was added dropwise keeping the reaction mixture at -78 °C followed by stirring for 2 h. Then the mixture was warmed slowly to room temperature and stirred overnight. The reaction was quenched by adding saturated NH\(_4\)Cl (10 mL) and the organic layer was extracted, dried with magnesium sulphate, saturated in vacuo and purified by column chromatography (ethyl acetate/pentane, 3:1) to give the product (1.55 g, 75 %); m.p. 85 °C; \( \text{[M+Na]}^{+} \): calc for C\(_{16}\)H\(_{19}\)NOSi [M+Na]+: 346.1438, Found 346.1428.

\( (E)\)-butyl 3-(2-(phenylcarbamoyl)phenyl)acrylate (3):

2-(tert-butyldimethylsilyl)-\( N \)-phenylbenzamide 6a (311 mg, 1 mmol), \( p \)-toluenesulfonic acid monohydrate (228 mg, 1.2 mmol), \( p \)-benzoquinone (119 mg, 1.1 mmol) and Pd(OAc)\(_2\) (11.2 mg, 0.05 mmol) were dissolved in acetone (4 mL). n-butylacrylate (140 mg, 1.1 mmol) in acetone (1 mL) was added in the above mixture and stirred at room temperature for 24 h. The reaction mixture was concentrated in vacuo and dissolved in ether (20 mL). The solution was washed with water (2 x 20 mL) and dried over MgSO\(_4\). After filtration and concentration in vacuo the residue was subjected to column chromatography (ethyl acetate / hexane, 1:2) to yield the product (266 mg, 77 %); m.p. 136-138 °C; \( \nu_{\text{max}} \) (CHCl\(_3\)) 2253, 1707, 1600, 1521, 1439, 1317, 1182; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) ppm 8.03 (1H, d, \( J = 16.2 \) Hz, C(14)H), 7.77 (1H, br. s., NH), 7.55 - 7.67 (4H, \( m \), C(4)H, C(6)H, 2 x C(9)H), 7.40 - 7.52 (2H, \( m \), C(3)H, C(5)H), 7.36 (2H, \( t \), \( J = 7.8 \) Hz, 2 x C(10)H), 7.13 - 7.20 (1H, \( m \), C(11)H), 6.38 (1H, d, \( J = 16.2 \) Hz, C(15)H), 4.16 (2H, \( t \), \( J = 6.7 \) Hz, C(17)H), 1.59 - 1.68 (2H, \( m \), C(18)H), 1.38 (2H, sxt, \( J = 7.5 \) Hz, C(19)H), 0.92 (3H, \( t \), C(20)H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) ppm 166.7 (C(7)), 166.5 (C(16)), 141.6 (C(14)), 137.7 (C(8)), 137.0 (C(2)), 133.1 (C(5)), 130.7 (C(3)), 129.9 (C(1)), 129.1 (2 x C(10)), 127.6 (C(4)), 127.4 (C(6)), 124.8 (C(11)), 121.2 (C(15)), 120.1 (2 x C(9)), 64.6 (C(17)), 30.7 (C(18)), 19.2 (C(19)), 13.7 (C(20)); HRMS (ESI) \( m/z \): calc for C\(_{18}\)H\(_{23}\)NOSi [M+Na]+: 346.1438, Found 346.1428.

2-(dimethyl(2-phenylpropan-2-yl)silyl)-\( N \)-phenylbenzamide (5):

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A solution of N-phenylbenzamide<sup>3</sup> 1a (985 mg, 5 mmol) in THF (50 mL) was cooled to -78 °C and Bu'Li (1.7 M in pentane) (6.5 mL, 11 mmol) was added drop wise while stirring the mixture vigorously. After 1.5 h PhMe<sub>3</sub>SiCl (3.5 g, 23 mmol) was added drop wise keeping the reaction mixture at -78 °C followed by stirring for 2 h. Then the mixture was warmed slowly to room temperature and was stirred overnight. The reaction was quenched by adding sat. NH<sub>4</sub>Cl (20 mL). The organic layer was extracted with ether (50 mL), dried with MgSO<sub>4</sub>, and purified by column chromatography (ether / pentane, 1:4) to get the product (1.24 g, 75 %); m.p. 104-106 °C; v<sub>max</sub> (CHCl<sub>3</sub>) 3396, 3016, 1670, 1600, 1523, 1439, 1319, 1254, 1216, 1110, 890, 817, 757, 702, 668; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ ppm 7.67 - 7.71 (1H, m, C(6)H), 7.60 - 7.64 (1H, m, C(3)H), 7.53 (2H, dd, J = 1.6 and 7.7 Hz, 2 x C(16)H), 7.46 - 7.51 (2H, m, C(4)H, C(5)H), 7.43 (1H, s, NH), 7.32 - 7.39 (3H, m, 2 x C(17)H, C(18)H), 7.25 - 7.30 (2H, m, 2 x C(9)H), 7.19 - 7.24 (2H, m, 2 x C(10)H), 7.09 - 7.14 (1H, m, C(11)H), 0.64 (6H, m, 2 x C(14)H<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ ppm 169.0 (C(7)), 143.3 (C(1)), 139.0 (C(15)), 137.7 (C(8)), 136.4 (C(6)), 136.3 (C(2)) 134.1 (2 x C(16)), 129.7 (C(5)), 129.5 (2 x C(10)), 129.2 (C(4)), 128.9 (2 x C(17)), 128.1 (C(18)), 127.2 (C(3)), 124.4 (C(11)), 119.8 (2 x C(9)), -1.3 (2 x C(14)); HRMS (ESI) m/z: calc for C<sub>2</sub>H<sub>2</sub>NOSi[M+Na]<sup>+</sup>: 354.1290, Found 354.1280.

2-(*tert-butyldimethylsilyl)-N-phenylbenzamide (6a):

A solution of N-phenylbenzamide 1a (1.97 g, 10 mmol) in THF (80 mL) was cooled to -78 °C and Bu'Li (1.7 M in pentane) (12.9 mL, 22 mmol) was added drop wise while stirring the mixture vigorously. After 1.5 h Bu'Me<sub>2</sub>SiCl (3.5 g, 23 mmol) was added drop wise keeping the reaction mixture at -78 °C followed by stirring for 2 h. Then the mixture was warmed slowly to room temperature and was stirred overnight. The reaction was quenched by adding sat. NH<sub>4</sub>Cl (30 mL). The organic layer was extracted with ether (50 mL), dried with MgSO<sub>4</sub>, and purified by column chromatography (ether / pentane, 1:3) to get the product (2.8 g, 90 %); m.p. 123-125 °C; m.p. 123-125 °C; v<sub>max</sub> (CHCl<sub>3</sub>) 3300, 3019, 2956, 1650, 1598, 1519, 1469, 1438, 1320, 1252, 1216, 1117, 1063, 888, 823, 756, 692, 669; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ ppm 7.66 (1H, br. s, NH), 7.50 (1H, br. s; NH ), 7.40 - 7.48 (3H, m, C(3)H, C(4)H, C(5)H), 7.37 (2H, t, J = 7.8 Hz, C(10)H), 7.13 - 7.19 (1H, m, C(11)H), 0.98 (9H, s, 3 x C(16)H<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ ppm 169.7 (C(7)), 144.0 (C(2)), 138.1 (C(1)), 136.8 (C(6)), 135.6 (C(8)), 129.2 (2 x C(10)), 128.8 (C(4)), 128.5 (C(3)), 126.4 (C(5)), 124.5 (C(11)), 119.7 (2 x C(9)), 27.3 (3 x C(16)), 17.7 (C(15)), -3.9 (2 x C(14)); HRMS (ESI) m/z: calc for C<sub>16</sub>H<sub>21</sub>NOSi[M+Na]<sup>+</sup>: 334.1598, Found 334.1592.

2-(*tert-butyldimethylsilyl)-3-methoxy-N-phenylbenzamide (6b):

![Diagram of molecule 6b](image)
A solution of 3-methoxy-N-phenylbenzamide$^3$ 1b (2.28 g, 10 mmol) in THF (70 mL) was cooled to -78 °C and Bu'Li (1.7 M in pentane) (12.9 mL, 22 mmol) was added drop wise while stirring the mixture vigorously. After 1.5 h Bu'Me$_2$SiCl (3.5 g, 23 mmol) was added drop wise keeping the reaction mixture at -78 °C followed by stirring for 2 h. Then the mixture was warmed slowly to room temperature and was stirred overnight. The reaction was quenched by adding sat. NH$_4$Cl (30 mL). The organic layer was extracted, dried with MgSO$_4$, saturated in vacuo and purified by column chromatography (ether / pentane, 1:3) to get the product (1.7 g, 50 %): m.p. 182-184 °C; $\nu$ max (CHCl$_3$) 3425, 3019, 2930, 2856, 2401, 1683, 1599, 1564, 1519, 1433, 1316, 1250, 1216, 1061, 926, 825, 755, 669; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ ppm 7.60 (2H, d, $J = 7.9$ Hz, 2 x C(9)H), 7.32 - 7.42 (4H, m, 2 x C(10)H, C(S)H, NH), 7.11 - 7.18 (1H, m, C(11)H), 7.04 (1H, d, $J = 7.6$ Hz, C(6)H), 6.91 (1H, d, $J = 8.2$ Hz, C(4)H), 3.80 (3H, s, C(17)H$_3$), 0.98 (9H, s, 3 x C(16)H$_3$), 0.26 (6H, s, 2 x C(14)H$_2$); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ ppm 170.0 (C(7)), 165.2 (C(3)), 146.6 (C(1)), 138.5 (C(8)), 131.3 (C(5)), 129.6 (2 x C(10)), 124.8 (C(11)), 123.8 (C(2)), 119.9 (2 x C(9), C(6)), 111.3 (C(4)), 55.2 (C(17)), 28.6 (3 x C(16)), 18.9 (C(15)), -1.9 (2 x C(14)); HRMS (ESI) m/z: calc for C$_{28}$H$_{37}$NO$_2$Si [M+Na]$^+$: 364.1703, Found 364.1695.

2-(tert-butyldimethylsilyl)-4-methoxy-N-phenylbenzamide (6c):

A solution of 4-methoxy-N-phenylbenzamide$^4$ (1.14 g, 5 mmol) in THF (60 mL) was cooled to -78 °C and Bu'Li (1.7 M in pentane) (6.5 mL, 11 mmol) was added drop wise while stirring the mixture vigorously. After 1 h Bu'Me$_2$SiCl (1.8 g, 11.5 mmol) was added drop wise keeping the reaction mixture at -78 °C followed by stirring for 2 h. Then the mixture was warmed slowly to room temperature and was stirred overnight. The reaction was quenched by adding sat. NH$_4$Cl (30 mL). The organic layer was extracted, dried with MgSO$_4$, saturated in vacuo and purified by column chromatography (ether / pentane, 1:5) to get the product (765 mg, 45 %): m.p.: calc for C$_{28}$H$_{37}$NO$_2$Si [M+Na]$^+$: 364.1703, Found 364.1695.

2-(tert-butyldimethylsilyl)-4-methyl-N-phenylbenzamide (6d):

A solution of 4-methyl-N-phenylbenzamide$^5$ (1.33 g, 6.3 mmol) in THF (60 mL) was cooled to -78 °C and Bu'Li (1.7 M in pentane) (7.7 mL, 13 mmol) was added drop wise while stirring the mixture vigorously. After 1.5 h Bu'Me$_2$SiCl (2.1 g, 14 mmol) was added drop wise keeping the reaction mixture at -78 °C followed by stirring for 2 h. Then the mixture was warmed slowly to room temperature and was stirred overnight. The
reaction was quenched by adding sat. NH₄Cl (30 mL). The organic layer was extracted, dried with MgSO₄, saturated in vacuo and purified by column chromatography (ether / pentane, 1:3) to get the product (1.43 g, 70 %); m.p. 174-176 °C; \( \bar{v}_{\text{max}} \) (CHCl₃) 3304, 3019, 2954, 1596, 1519, 1499, 1348, 1329, 1257, 1216, 1130, 1064, 898, 756, 692, 668; ¹H NMR (CDCl₃): 6 ppm 7.61 (2H, d, J = 7.8 Hz, 2 x C(9)H), 7.34 - 7.45 (5H, m, C(3)H, C(6)H, 2 x C(10)H, NH), 7.23 (1H, d, J = 7.8 Hz, C(5)H), 7.12 - 7.18 (1H, m, C(11)H), 2.41 (3H, s, C(17)H₃), 0.95 - 1.01 (9H, m, 3 x C(16)H₃), 0.29 (6H, s, 2 x C(14)H₂); ¹³C NMR (CDCl₃): 6 ppm 169.7 (C(7)), 141.2 (C(4)), 138.2 (C(2)), 138.1 (C(8)), 137.5 (C(3)), 135.6 (C(1)), 129.4 (C(5)), 129.2 (2 x C(10)), 126.4 (C(6)), 124.3 (C(11)), 119.6 (2 x C(9)), 27.3 (3 x C(16)), 21.6 (C(17)), 17.7 (C(15)), -3.9 (2 x C(14)); HRMS (ESI) m/z: calc for C₂₇H₂₅NOSi[M+Na]⁺: 348.1754, Found 348.1745.

2-(tert-butyldimethylsilyl)-3-methyl-N-phenylbenzamide (6e):

A solution of 5-methyl-N-phenylbenzamide (2.1 g, 10 mmol) in THF (70 mL) was cooled to -78 °C and Bu’Li (1.7 M in pentane) (12.9 mL, 22 mmol) was added drop wise while stirring the mixture vigorously. After 1.5 h Bu’Me₃SiCl (3.5 g, 23 mmol) was added drop wise keeping the reaction mixture at -78 °C followed by stirring for 2 h. Then the mixture was warmed slowly to room temperature and was stirred overnight. The reaction was quenched by adding sat. NH₄Cl (30 mL). The organic layer was extracted, dried with MgSO₄, saturated in vacuo and purified by column chromatography (ether / pentane, 1:3) to get the product (3.0 g, 94 %); m.p. 163 - 165 °C; \( \bar{v}_{\text{max}} \) (CHCl₃) 3425, 3019, 2957, 1684, 1599, 1518, 1437, 1316, 1216, 824, 759, 669; ¹H NMR (CDCl₃): 6 ppm 7.61 (2H, d, J = 6.3 Hz, 2 x C(9)H), 7.54 (1H, dt, J = 2.1 and 7.6 Hz, C(4)H), 7.33 - 7.43 (3H, m, C(6)H, 2 x C(10)H), 7.31 (1H, br, s; NH), 7.23 - 7.29 (1H, m, C(3)H), 7.11 - 7.20 (1H, m, C(11)H), 2.39 (3H, s, C(17)H₃), 0.96 (9H, m, 3 x C(16)H₃), 0.25 - 0.31 (6H, s, 2 x C(14)H₂); ¹³C NMR (CDCl₃): 6 ppm 169.8 (C(7)), 144.1 (C(5)), 138.9 (C(1)), 138.1 (C(8)), 136.9 (C(4)), 131.8 (C(2)), 129.3 (C(3)), 129.2 (2 x C(10)), 127.1 (C(6)), 124.4 (C(11)), 119.6 (2 x C(9)), 27.2 (C(17)), 21.2 (3 x C(16)), 17.7 (C(15)), -4.0 (2 x C(14)); HRMS (ESI) m/z: calc for C₂₀H₂₇NOSi[M+Na]⁺: 348.1754, Found 348.1744.

2-(tert-butyldimethylsilyl)-3-fluoro-N-phenylbenzamide (6g):

A solution of 3-fluoro-N-phenylbenzamide (2.15 g, 10 mmol) in THF (70 mL) was cooled to -78 °C and Bu’Li (1.7 M in pentane) (12.9 mL, 22 mmol) was added drop wise while stirring the mixture vigorously. After 1.5 h Bu’Me₃SiCl (3.5 g, 23 mmol) was added drop wise keeping the reaction mixture at -78 °C followed by stirring for 2 h. Then the mixture was warmed slowly to room temperature and was stirred overnight. The reaction was quenched by adding sat. NH₄Cl (30 mL). The organic layer was extracted with ether (50 mL), dried with MgSO₄, saturated in vacuo and purified by column chromatography (ether / hexane, 1:5) to get the product (650
mg, 20 %); m.p. 118-120 °C; νmax (CHCl3) 3424, 3019, 1866, 1598, 1520, 1500, 1317, 1216, 757, 669; 1H NMR (CDCl3, 400MHz): δ ppm 7.60 (2H, d, J = 7.8 Hz, 2 x C(9)H), 7.50 (1H, br. s., NH), 7.34 - 7.44 (3H, m, C(5)H), 7.32 (2 x C(10)H), 7.23 (1H, d, J = 7.1 Hz, C(6)H), 7.14 - 7.20 (1H, m, C(11)H), 7.09 (1H, t, J = 8.7 Hz, C(4)H), 1.01 (9H, s, 3 x C(16)H3), 0.31 (6H, d, 2 x C(14)H3); 13C NMR (CDCl3, 400MHz): δ ppm 168.5 (C(7)), 167.5 (C(3)), 146.0 (C(1)), 137.8 (C(8)), 131.4 (C(5)), 129.2 (2 x C(10)), 124.6 (C(11)), 122.0 (d, J = 69 Hz, C(2)), 119.6 (2 x C(9)), 116.5 (d, J = 28 Hz, C(4)), 27.4 (3 x C(16)), 18.1 (C(15)), -3.3 (d, J = 5 Hz, 2 x C(14)); 19F NMR (CDCl3, 376MHz): δ ppm -90.2; HRMS (ESI) m/z: calc for C19H24FNOSi [M+Na]+: 352.1503, Found 352.1502.

2-(tert-butyldimethylsilyl)-4-chloro-N-phenylbenzamide (6g):

A solution of 4-chloro-N-phenylbenzamide6 Ig (1.7 g, 7.5 mmol) in THF (70 mL) was cooled to -78 °C and BuLi (1.7 M in pentane) (8.8 mL, 15 mmol) was added drop wise while stirring the mixture vigorously. After 1.5 h BuMe2SiCl (2.4 g, 16 mmol) was added drop wise keeping the reaction mixture at -78 °C followed by stirring for 2 h. Then the mixture was warmed slowly to room temperature and was stirred overnight. The reaction was quenched by adding sat. NH4Cl (30 mL). The organic layer was extracted, dried with MgSO4, saturated in vacuo and purified by column chromatography (ether / pentane, 1:3) to get the product (1.55 g, 36 %); m.p. 138-140 °C; 1H NMR (CDCl3, 400MHz): δ ppm 7.60 (2H, d, J = 7.8 Hz, 2 x C(9)H), 7.57 (1H, d, J = 2.3 Hz, C(3)H), 7.35 - 7.45 (5H, m, C(5)H, C(6)H, 2 x C(10)H), 7.14 - 7.21 (1H, m, C(11)H), 0.97 (9H, s, 3 x C(16)H3), 0.29 (6H, s, 2 x C(14)H3); 13C NMR (CDCl3, 101MHz): δ ppm 168.6 (C(7)), 142.1(C(2)), 138.8(C(8)), 137.8(C(4)), 136.4(C(3)), 135.1(C(1)), 129.2(2 x C(10)), 128.8(C(6)), 127.9(C(5)), 124.7(C(11)), 119.7(2 x C(9)), 27.2(C(16)), 17.7(C(15)), -4.0(C(14)); HRMS (ESI) m/z: calc for C19H24FNOSi [M+Na]+: 368.1208, Found 368.1206.

Palladacycle Complex(7a)

A mixture of 2-(tert-butyldimethylsilyl)-N-phenylbenzamide 6a (78 mg, 0.25 mmol) and Pd(OAc)2 (56 mg, 0.25 mmol) was dissolved in toluene (2 mL). A solution of p-TsOH (48 mg, 0.25 mmol) in acetone (0.2 mL) was added to this mixture and stirred at room temperature for 1 h. The settled greenish yellow precipitate in the
reaction mixture was filtered, washed with toluene and dried under vacuum to get the pure product (109 mg, 92 %); \( \nu_{\text{max}} \) (CHCl\(_3\)) 3319, 3020, 1622, 1595, 1535, 1499, 1446, 1431, 1360, 1220, 1157, 1121, 1036, 1010, 817, 753, 691, 670, 568; \( ^1 \)H NMR (400 MHz, DMSO-d\(_6\)): \( \delta \) ppm 11.52 (1H, s, NH), 8.04 (1H, d, \( J = 7.3 \) Hz, C(6)H), 7.59 - 7.72 (3H, m, C(3)H, 2 x C(9)H), 7.52 (2H, d, \( J = 8.1 \) Hz, 2 x C(16)H), 7.45 (2H, t, \( J = 7.8 \) Hz, 2 x C(10)H), 7.36 (1H, t, \( J = 7.2 \) Hz, C(4)H), 7.20 - 7.32 (2H, m, C(5)H, C(11)H), 7.09 (2H, d, \( J = 8.1 \) Hz, 2 x C(15)H), 2.25 (3H, s, C(20)H); \( ^{13} \)C NMR (400 MHz, DMSO-d\(_6\)): \( \delta \) ppm 177.1 (C(7)), 148.0 (C(2)), 146.0 (C(1)), 141.8 (C(14)), 138.9 (C(8)), 136.3 (C(17)), 133.8 (C(4)), 132.7 (C(3)), 129.8 (2 x C(10)), 129.1 (2 x C(16)), 128.5 (C(6)), 127.6 (C(5)), 126.9 (C(11)), 126.4 (2 x C(15)), 124.4 (2 x C(9)), 21.7 (C(20)); HRMS (ESI) m/z: calc for C\(_{13}\)H\(_{12}\)N\(_2\)O\(_2\)Pd [Monomer-TsO+CH\(_2\)CN]: 343.0063, Found 343.0066.

2-(\textit{tert}-butyldimethylsilyl)-N-phenylfuran-3-carboxamide (8):

A solution of N-phenylfuran-3-carboxamide\(^\text{8} \) 1i (1.38 g, 7.4 mmol) in THF (50 mL) was cooled to -78 °C and BuLi (1.7 M in pentane) (8.8 mL, 15 mmol) was added drop wise while stirring the mixture vigorously. After 1.5 h Bu'\textit{Me}_2SiCl (2.4 g, 16 mmol) was added drop wise keeping the reaction mixture at -78 °C followed by stirring for 2 h. Then the mixture was warmed slowly to room temperature and was stirred overnight. The reaction was quenched by adding sat. NH\(_4\)Cl (30 mL). The organic layer was extracted with ether (50 mL), dried with MgSO\(_4\), saturated in vacuo and purified by column chromatography (ether / pentane, 1:3) to get the product (1.9 g, 86 %); m.p. 198-202 °C; \( ^1 \)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) ppm 7.67 (1H, d, \( J = 1.8 \) Hz, C(4)H), 7.58 (2H, d, \( J = 8.6 \) Hz, 2 x C(7)H), 7.44 (1H, br. s, NH), 7.36 (2H, t, \( J = 8.0 \) Hz, 2 x C(8)H), 7.10 - 7.18 (1H, m, C(9)H), 6.64 (1H, d, C(3)H), 0.98 (9H, s, 3 x C(14)H), 0.37 (6H, s, 2 x C(12)H); \( ^{13} \)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) ppm 162.6 (C(5)), 162.4 (C(1)), 146.6 (C(4)), 137.8 (C(6)), 132.8 (C(2)), 129.1 (2 x C(8)), 124.4 (C(9)), 120.1 (2 x C(7)), 108.7 (C(3)), 26.7 (3 x C(14)), 17.8 (C(13)), -5.6 (2 x C(12)); HRMS (ESI) m/z: calc for C\(_{13}\)H\(_{12}\)N\(_2\)O\(_2\)Si [M+Na]: 324.1390, Found 324.1391.

\((E)\)-butyl 3-(2-methoxy-6-(phenylcarbamoyl)phenyl)acrylate 9b:

2-(\textit{tert}-butyldimethylsilyl)-3-methoxy-N-phenylbenzamide 6b (34.1 mg, 0.1 mmol), \textit{p}-toluenesulfonic acid monohydrate (22.8 mg, 0.12 mmol), \textit{p}-benzoquinone (12 mg, .11 mmol) and Pd(OAc\(_2\)) (2.2 mg, 0.01 mmol) were dissolved in acetone (0.4 mL), \textit{n}-butyllacrylate (14 mg, 0.11 mmol) in acetone (0.1 mL) was added in the above mixture and stirred at room temperature for 36 h. The reaction mixture was concentrated in vacuo and dissolved in ether (5 mL). The solution was washed with water (2 x 5 mL) and dried over MgSO\(_4\). After filtration and concentration in vacuo the residue was subjected to column chromatography (ethyl acetate / hexane, 1:2) to yield the product (27 mg, 72 %); m.p. 108-112 °C; \( \nu_{\text{max}} \) (CHCl\(_3\)) 3308, 3019, 2962, 1674, 1599, 1522, 1438, 1323, 1274, 1216, 1189, 1060, 985, 873, 756, 692; \( ^1 \)H NMR (CDCl\(_3\)): \( \delta \) ppm 7.91 (1H, d, \( J = 16.2 \) Hz, C(14)H), 7.55 - 7.61 (3H, m, 2 x C(9)H, NH), 7.32 - 7.41 (3H, m, 2 x C(10)H, C(5)H), 7.13 - 7.19 (2H, m, C(11)H, C(6)H), 7.02 (1H, d, \( J = 8.3 \) Hz, C(4)H), 6.68 (1H, d, \( J = 16.2 \) Hz, C(15)H), 4.12 (2H, t, \( J = 6.7 \) Hz, 2-H), 4.04 - 4.08 (2-H, t, \( J = 6.7 \) Hz, 3-H), 3.83 (3-H, t, \( J = 6.7 \) Hz, 4-H), 3.78 (3-H, t, \( J = 6.7 \) Hz, 4-H), 3.72 - 3.78 (2-H, m, 2 x C(12)H), 3.27 (1-H, s, N), 3.15 - 3.19 (1-H, s, N), 2.22 (3-H, s, C(20)H).
C(17)H₂₃NO₄, calc for C₂₃H₂₃NO₄[M+Na⁺]: 376.1519, Found 376.1513.

(E)-butyl 3-(4-methoxy-2-(phenylcarbamoyl)phenyl)acrylate (9c):

2-(tert-butyldimethylsilyl)-4-methoxy-N-phenylbenzamide 6c (171 mg, 0.5 mmol), p-toluenesulfonic acid monohydrate (114 mg, 0.6 mmol), p-benzoquinone (60 mg, 0.55 mmol) and Pd(OAc)₂ (5.6 mg, 0.025 mmol) were dissolved in acetone (2 mL). n-butylacrylate (14 mg, 0.11 mmol) in acetone (0.5 mL) was added in the above mixture and stirred at room temperature for 24 h. The reaction mixture was concentrated in vacuo and dissolved in ether (10 mL). The solution was washed with water (2 x 10 mL) and dried over MgSO₄. After filtration and concentration in vacuo the residue was subjected to column chromatography (ethyl acetate / hexane, 1:2) to yield the product (98 mg, 52 %); m.p. 188 ˚C; νmax (CHCl₃) 3020, 1641, 1605, 1501, 1439, 1325, 755, 669; ¹H NMR (CDCl₃, 400MHz): δ ppm 8.09 (1H, d, J = 15.9 Hz, C(14)H), 7.54 - 7.66 (4H, m, C(6)H, 2 x C(9)H, NH), 7.36 (2H, t, J = 8.0 Hz, 2 x C(10)H), 7.12 - 7.19 (1H, m, C(11)H), 7.10 (1H, d, J = 2.5 Hz, C(3)H), 6.95 (1H, dd, J = 2.5 and 8.6 Hz, C(5)H), 6.37 (1H, d, J = 15.9 Hz, C(15)H), 4.17 (2H, t, J = 6.7 Hz, C(17)H), 3.87 (3H, s, C(21)H₃), 1.65 (2H, t, J = 7.6 Hz, C(18)H₂), 1.32 - 1.45 (2H, m, C(19)H₂), 0.92 (3H, t, J = 7.3 Hz, C(20)H₃); ¹³C NMR (CDCl₃, 101MHz): δ ppm 166.4 (C(7)), 166.3 (C(16)), 161.2 (C(4)), 142.0 (C(14)), 137.9 (C(8)), 135.3 (C(2)), 129.6 (C(1)), 129.4 (C(6)), 129.1 (2 x C(10)), 124.7 (C(11)), 121.4 (C(15)), 120.1 (2 x C(9)), 115.3 (C(5)), 112.4 (C(3)), 64.6 (C(17)), 55.5 (C(21)), 30.7 (C(18)), 19.2 (C(19)), 13.7 (C(20)); HRMS (ESI) m/z: calc for C₂₁H₂₃NO₄[M+Na⁺]: 376.1519, Found 376.1514.

(E)-butyl 3-(5-methyl-2-(phenylcarbamoyl)phenyl)acrylate (9d):

2-(tert-butyldimethylsilyl)-4-methyl-N-phenylbenzamide 6d (67.8 mg, 0.2 mmol), p-toluenesulfonic acid monohydrate (42 mg, 0.22 mmol), p-benzoquinone (24 mg, 0.22 mmol) and Pd(OAc)₂ (2.2 mg, 0.01 mmol) were dissolved in acetone (0.7 mL). n-butylacrylate (28 mg, 0.22 mmol) in acetone (0.3 mL) was added in the above mixture and stirred at room temperature for 24 h. The reaction mixture was concentrated in vacuo and dissolved in ether (10 mL). The solution was washed with water (2 x 10 mL) and dried over MgSO₄. After filtration and concentration in vacuo the residue was subjected to column chromatography (ethyl acetate / hexane, 1:10) to yield the product (97 mg, 51 %); m.p. 192 ˚C; νmax (CHCl₃) 3044, 1632, 1607, 1506, 1441, 1330, 1292, 1214, 1123; ¹H NMR (CDCl₃, 400MHz): δ ppm 8.09 (1H, t, J = 7.6 Hz, C(18)H), 7.66 (4H, m, C(9)H, C(10)H, C(12)H, C(13)H), 7.10 - 7.19 (1H, m, C(11)H), 7.05 (1H, d, J = 7.6 Hz, C(17)H), 4.24 (2H, t, J = 6.7 Hz, C(20)H), 3.87 (3H, s, C(21)H₃), 1.61 (2H, t, J = 7.6 Hz, C(18)H₂), 1.28 - 1.38 (2H, m, C(19)H₂), 0.89 (3H, t, J = 7.3 Hz, C(20)H₃); ¹³C NMR (CDCl₃, 101MHz): δ ppm 166.7 (C(7)), 166.4 (C(16)), 161.2 (C(4)), 141.9 (C(14)), 137.9 (C(8)), 135.3 (C(2)), 129.6 (C(1)), 129.4 (C(6)), 129.1 (2 x C(10)), 124.5 (C(11)), 121.4 (C(15)), 120.1 (2 x C(9)), 115.4 (C(5)), 112.4 (C(3)), 64.6 (C(17)), 55.5 (C(21)), 30.7 (C(18)), 19.2 (C(19)), 13.7 (C(20)); HRMS (ESI) m/z: calc for C₂₁H₂₃NO₄[M+Na⁺]: 376.1519, Found 376.1514.
hexane, 1:2) to yield the product (49 mg, 73 %); m.p. 104-108 °C, δC; ν<sub>max</sub> (CHCl<sub>3</sub>) 3304, 3019, 2962, 1704, 1658, 1600, 1538, 1441, 1319, 1279, 1216, 1180, 1072, 1028, 977, 758, 692, 668; ¹H NMR (CDCl<sub>3</sub>, 400MHz): δ ppm 8.02 (1H, d, J = 16.2 Hz, C(14)H), 7.87 (1H, s, NH), 7.61 (2H, d, J = 7.8 Hz, 2 x C(9)H), 7.47 (1H, d, J = 7.8 Hz, C(6)H), 7.40 (1H, s, C(3)H), 7.34 (2H, t, J = 7.8 Hz, 2 x C(10)H), 7.20 (1H, d, J = 7.8 Hz, C(5)H), 7.11 - 7.18 (1H, m, C(11)H), 6.34 (1H, d, J = 16.2 Hz, C(15)H), 4.14 (2H, t, J = 6.6 Hz), 2.40 (3H, s, C(21)H<sub>3</sub>), 1.57 - 1.69 (2H, m, C(18)H<sub>2</sub>), 1.38 (2H, sext, J = 7.4 Hz, C(19)H<sub>2</sub>), 0.90 - 0.94 (3H, t, C(20)H<sub>2</sub>); ¹³C NMR (CDCl<sub>3</sub>, 400MHz): δ ppm 166.8 (C(7)), 160.0, 1538, 1441, 1319, 1279, 1216, 1180, 1072, 1028, 977, 758, 692, 668; 2-(tert-butyl dimethylsilyl)-4-methyl-N-phenylbenzamide 6e (170 mg, 0.5 mmol), p-toluenesulfonic acid monohydrate (95 mg, 0.5 mmol), p-benzoquinone (55 mg, 0.5 mmol) and Pd(OAc)<sub>2</sub> (5.6 mg, 0.025 mmol) were dissolved in aceton (2 mL). α-butyralcylate (65 mg, 0.5 mmol) in acetone (0.5 mL) was added in the above mixture and stirred at room temperature for 20 h. The reaction mixture was concentrated in vacuo and dissolved in ether (20 mL). The solution was washed with water (2 x 10 mL) and dried over MgSO<sub>4</sub>. After filtration and concentration in vacuo the residue was subjected to column chromatography (ethyl acetate / hexane, 1:3) to yield the product (130 mg, 77 %); m.p. 137-139 °C; ν<sub>max</sub> (CHCl<sub>3</sub>) 3280, 2955, 2869, 2290, 1713, 1647, 1598, 1528, 1444, 1387, 1325, 1270, 1178, 1064, 1028, 976, 908, 821, 733, 693, 649; ¹H NMR (400 MHz, CDCl<sub>3</sub>): δ ppm 8.25 (1H, s, NH), 7.90 (1H, d, J = 15.9 Hz, C(14)H), 7.60 (2H, d, J = 7.8 Hz, 2 x C(9)H), 7.43 (1H, d, J = 8.1 Hz, C(3)H), 7.27 - 7.34 (3H, m, C(6)H<sub>2</sub>, 2 x C(10)H), 7.21 (1H, d, J = 8.1 Hz, C(4)H), 7.09 - 7.16 (1H, m, C(11)H), 6.22 (1H, d, J = 15.9 Hz, C(15)H), 4.10 (2H, t, J = 6.7 Hz, C(17)H<sub>2</sub>), 2.32 (3H, s, C(21)H<sub>3</sub>), 1.56 - 1.66 (2H, m, C(18)H<sub>2</sub>), 1.31 - 1.42 (2H, m, C(19)H<sub>2</sub>), 0.91 (3H, t, C(20)H<sub>2</sub>); ¹³C NMR (400 MHz, CDCl<sub>3</sub>): δ ppm 167.0 (C(7)), 166.8 (C(16)), 141.6 (C(14)), 140.3 (C(8)), 137.9 (C(5)), 137.1 (C(3)), 131.2 (C(4)), 130.0 (C(6)), 129.0 (2 x C(10)), 128.3 (C(1)), 127.1 (C(3)), 124.6 (C(11)), 120.2 (2 x C(9)), 119.6 (C(15)), 64.5 (C(17)), 30.7 (C(18)), 21.3 (C(21)), 19.2 (C(19)), 13.8 (C(20)); HRMS (ESI) m/z: calc for C<sub>21</sub>H<sub>23</sub>N<sub>3</sub>O<sub>3</sub>[M+Na]<sup>+</sup>: 360.1570, Found 360.1568.

(E)-butyl 3-(2-methyl-6-(phenylcarbamoyl)phenyl)acrylate (9e):

(E)-butyl 3-(5-chloro-2-(phenylcarbamoyl)phenyl)acrylate (9g):
2-(tert-butyldimethylsilyl)-4-chloro-N-phenylbenzamide 6g (69 mg, 0.2 mmol), \( p \)-toluenesulfonic acid monohydrate (42 mg, 0.22 mmol), \( p \)-benzoquinone (24 mg, 0.22 mmol) and \( \text{Pd(OAc)}_2 \) (4.5 mg, 0.02 mmol) were dissolved in acetone (0.7 mL). \( n \)-butylacrylate (28 mg, 0.22 mmol) in acetone (0.3 mL) was added in the above mixture and stirred at room temperature for 24 h. The reaction mixture was concentrated \textit{in vacuo} and dissolved in ether (10 mL). The solution was washed with water (2 x 10 mL) and dried over \( \text{MgSO}_4 \). After filtration and concentration \textit{in vacuo} the residue was subjected to column chromatography (ethyl acetate / hexane, 1:3) to yield the product (33 mg, 46 %); m.p. 164-166 °C; \( \nu_{\text{max}} \) (500 MHz, \( \text{CDCl}_3 \)) 3310, 3020, 2962, 1710, 1600, 1523, 1440, 1316, 1215, 920, 755, 669; \( ^1\text{H NMR} \) (\( \text{CDCl}_3 \), 500MHz): \( \delta \) ppm 8.05 (1H, \( d \), \( J = 15.8 \) Hz, C(14)H), 7.54 - 7.76 (5H, \( m \), 2 x C(9)H, C(5)H, C(6)H, NH), 7.38 - 7.54 (3H, \( m \), 2 x C(10)H, C(3)H), 7.18 - 7.29 (1H, \( m \), C(11)H), 6.47 (1H, \( d \), \( J = 15.8 \) Hz, C(15)H), 4.23 (2H, \( t \), \( J = 6.5 \) Hz, C(17)H), 1.70 (2H, \( dt \), \( J = 6.9 \) and 14.3 Hz, C(18)H), 1.36 - 1.52 (2H, \( m \), C(19)H), 0.98 (3H, \( t \), \( J = 7.3 \) Hz, C(20)H); \( ^{13}\text{C NMR} \) (\( \text{CDCl}_3 \), 125MHz): \( \delta \) ppm 166.1 (C(7)), 165.7 (C(16)), 140.2 (C(14)), 137.5 (C(8)), 137.0 (C(4)), 135.1 (C(2)), 129.8 (2 x C(10)), 129.2 (C(6)), 129.1 (C(5)), 127.5 (C(3)), 125.2 (C(11)), 125.1 (C(1)), 122.7 (C(15)), 120.2 (2 x C(9)), 64.8 (C(17)), 30.7 (C(18)), 19.2 (C(19)), 13.8 (C(20)); HRMS (ESI) \( m/z \): calc for C\(_{20}\)H\(_{20}\)ClNO\(_3\) [M+Na]\(^+\): 380.1024, Found 380.1018.

$^{13}$C NMR, CDCl$_3$
\(^1\text{H NMR, CDCl}_3\)
$^{13}$C NMR, CDCl$_3$
1H NMR, CDCl3

6a
13-C NMR, CDCl₃
$^1$H NMR, CDCl$_3$
$\text{\textsuperscript{13}C NMR, CDCl}_3$
$^1$H NMR, CDCl$_3$
$^{13}$C NMR, CDCl$_3$
$^{13}$C NMR, CDCl$_3$
$^1$H NMR, CDCl$_3$
$^{13}$C NMR, CDCl$_3$
$^{13}$C NMR, CDCl$_3$
$^{13}$C NMR, DMSO-d$_6$
\[ f_1 \text{ (ppm)} \]

\[ ^1\text{H NMR, CDCl}_3 \]
$^1$H NMR, CDCl$_3$
$^{13}$C NMR, CDCl$_3$
$^{13}$C NMR, CDCl$_3$
$^1$H NMR, CDCl$_3$
$^{13}$C NMR, CDCl$_3$
$^{1}$H NMR, CDCl$_3$
$^1\text{H} \text{NMR, CDCl}_3$