ESI for :

Comparative Catalytic C-H vs. C-Si Activation of Arenes with Pd Complexes Directed by Urea or Amide Groups

Waqar Rauf, Amber L. Thompson and John M. Brown

Supplementary Information:

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: CH_2Cl_2 (from CaH_2); Toluene, THF and Et_2O (from benzophenone and sodium) or dried over an alumina Grubb's column.[1] 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 F_{254} silica. Visualization was accomplished using the quenching of UV fluorescence (λ_{max} 254 nm), and by staining with potassium permanganate solution followed by heat. Flash chromatography utilised Silica gel 60 (Flurochem; 40-63 μm; 550 m^2g^{-1}). All solvents were evaporated at or below 50 °C under reduced pressure using a rotary evaporator.

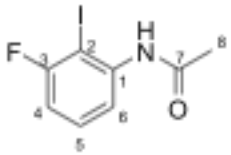
Melting points were recorded using a Reichert-Koffler block apparatus and are uncorrected.

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.

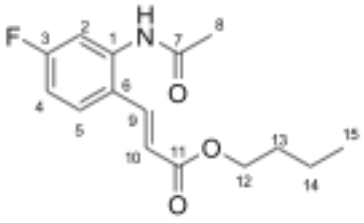
Mass Spectra (MS) were recorded by the author and Mr. R. Proctor using a Micromass GCT (Chemical Ionisation) or a V.G. Autospec spectrometer (EI and CI). Exact masses were measured on a Waters 2790-Micromass LCT spectrometer or a V.G. Autospec spectrometer using electrospray and chemical ionisation. Mass-to-charge (*m/z*) values are quoted in Daltons.

***N*-(3-fluoro-2-iodophenyl)acetamide (1c):**



A solution of 3-fluoro-2-iodoaniline (142.2 mg, 0.6 mmol) in benzene (0.7 mL) was cooled in an ice bath and acetic anhydride (102 mg, 1 mmol) solution in benzene (0.7 mL) was added dropwise to it. The mixture was refluxed for 1 h and then cooled to room temperature. The mixture was washed with water (3 x 5 mL) and aqueous layer was extracted once with benzene (10 mL). The combined organic phase was washed with dil. HCl (3 x 10 mL), sat. $NaHCO_3$ (3 x 10 mL), water (3 x 10 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Recrystallization from CH_2Cl_2 / pentane gave the product (88.9 mg, 54 %). m.p. 130-133 ˚C; ν_{max} ($CHCl_3$) 3390, 3020, 1683, 1521, 1464, 1413, 1216, 929; ^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 8.06 (1 H, d, *J* = 8.21 Hz, C(6)*H*), 7.53 (1 H, s, N*H*), 7.37-7.27 (1 H, m, C(5)*H*), 6.89-6.79 (1H, m, C(4)*H*), 2.26 (3 H, s, C(8)H_3); ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm 168.80 (*C*(7)), 162.05 (d, *J* = 243.81 Hz, *C*(3)), 140.34 (d, *J* = 3.05 Hz, *C*(1)), 130.82 (d, *J* = 9.05 Hz, *C*(5)), 117.46 (d, *J* = 2.08 Hz, *C*(6)), 111.50 (d, *J* = 23.70 Hz, *C*(4)), 77.68 (*C*(2)), 25.35 (*C*(8)); HRMS (ESI) *m/z*: calc for C_8H_7FINO [M+Na]: 301.9449, Found 301.9456.

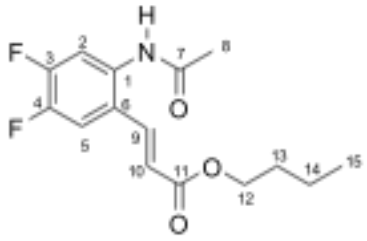
***(E)*-butyl 3-(2-acetamido-4-fluorophenyl)acrylate (2a):**



N-(3-fluorophenyl)acetamide **1a** (306 mg, 2.0 mmol), *p*-toluenesulfonic acid monohydrate (190 mg, 1.0 mmol), *p*-benzoquinone (217 mg, 2.0 mmol) and $Pd(OAc)_2$ (13.4 mg, 0.06 mmol) were dissolved in acetic acid (4 mL). *n*-butyl acrylate (281 mg, 2.2 mmol) in toluene (2 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 0.1 N NaOH (3 x 10 mL), water (3 x 10 mL) and saturated NaCl (1 x 5 mL) and dried over $MgSO_4$. After filtration and concentration *in vacuo* the residue was subjected to column chromatography (ethyl acetate / pentane, 3:1) to yield the product (480 mg, 83 %); m.p. 132-135 ˚C; ν_{max} ($CHCl_3$) 3319, 3019, 2963, 1698, 1634, 1521, 1433, 1321, 1216, 1185; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.96 (1 H, s, N*H*), 7.74 (1 H, d, *J* = 15.8 Hz, C(9)*H*), 7.61 (1 H, d, *J* = 10.2 Hz, C(2)*H*), 7.47 (1 H, dd, *J* = 8.1, 6.7 Hz, C(5)*H*), 6.85 (1 H, t, *J* = 7.2 Hz, C(4)*H*), 6.29 (1 H, d, *J* = 15.8 Hz, C(10)*H*), 4.15 (2 H, t, *J* = 6.7 Hz, C(12)H_2), 2.20 (3 H, s, C(8)H_3), 1.69-1.58 (2 H, m, C(13)H_2), 1.44-1.33 (2 H, m, C(14)H_2), 0.92 (3 H, t, *J* = 7.4 Hz, C(15)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 169.19 (*C*(7)), 167.03 (*C*(11)), 163.75 (d, *J* = 250.0 Hz, *C*(3)), 149.69 (*C*(1)), 138.41 (*C*(9)), 128.57 (d, *J* = 9.6 Hz, *C*(5)), 122.76 (*C*(6)), 120.01 (*C*(10)), 112.82 (d, *J* = 21.7 Hz, *C*(4)), 111.69 (d, *J* = 24.6 Hz, *C*(2)), 64.76 (*C*(12)), 30.66 (*C*(13)), 24.17 (*C*(8)), 19.15 (*C*(14)), 13.71 (*C*(15)); HRMS (ESI) *m/z*: calc for $C_{15}H_{18}FNO_3$ [M+Na]: 302.1163, Found 302.1159.

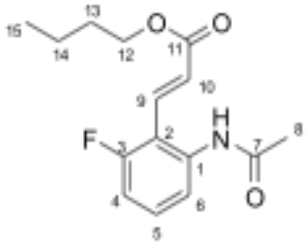
***(E)*-butyl 3-(2-acetamido-4,5-difluorophenyl)acrylate (2b):**



N-(3,4-difluorophenyl)acetamide **1b** (154 mg, 0.9 mmol), *p*-toluenesulfonic acid monohydrate (172 mg, 0.9 mmol), *p*-benzoquinone (99 mg, 0.9 mmol) and palladium acetate (10.08 mg, 0.045 mmol) were dissolved in acetic acid (2.4 mL). *n*-butyl acrylate (115.2 mg, 0.9 mmol) in toluene (1.2 mL) was added in the above mixture and stirred at room temperature. After 24 h the reaction mixture was diluted in ether (5 mL) and carefully neutralized with 2.5 M NaOH. After extraction of the aqueous phase with 10 mL of ether, the combined organic phases were washed with water (10 mL), dried over anhydrous magnesium sulphate and concentrated under reduced pressure. The resulting solid was

purified by flash chromatography (ethyl acetate/pentane, 3:1) to yield the product (160 mg, 60 %). ν_{max} ($CHCl_3$) 3222 (s, N-H), 1706 (s, C=O), 1510, 1190 (C-F), ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.76 (1 H, bs, N*H*), 7.69 (1 H, d, *J* = 15.8 Hz, C(9)*H*), 7.63 (1 H, dd, *J* = 11.5, 7.7 Hz, ArC*H*), 7.32 (1 H, dd, *J* = 10.4, 8.5 Hz, ArC*H*), 6.30 (1 H, d, *J* = 15.8 Hz, C(10)*H*), 4.19 (1 H, t, *J* = 6.7 Hz, C(12)H_2), 2.18 (1 H, s, C(8)H_2), 1.70-1.62 (1 H, m, C(13)H_2), 1.46-1.35 (1 H, m, C(14)H_2), 0.95 (1 H, t, *J* = 7.4 Hz, C(15)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 169.05 (*C*(11)), 166.70 (*C*(7)), 151.1 (dd, *J* = 253.4, 13.5 Hz, *C*(3)), 148.1 (dd, *J* = 248.5, 13.2 Hz, *C*(4)), 137.20 (*C*(9)), 132.51 (d, *J* = 1.7 Hz, *C*(1)), 123.95-123.72 (m, *C*(6)), 64.97 (*C*(12)), 30.64 (*C*(13)), 24.09 (*C*(8)), 19.15 (*C*(14)), 13.71 (*C*(15)); ^{19}F NMR (377 MHz, CD_3Cl) δ ppm -131.58 (ddd, *J* = 21.1, 11.5, 8.5 Hz), -139.37 (ddd, *J* = 21.1, 10.4, 7.7 Hz); HRMS (ESI) *m/z*: calc for $C_{15}H_{16}F_2NO_3$ [M-H]: 296.1098, Found 296.1093.

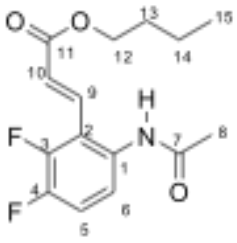
***(E)*-butyl 3-(2-acetamido-6-fluorophenyl)acrylate (3a):**



N-(3-fluoro-2-iodophenyl)acetamide **1c** (25 mg, 0.09 mmol), Na_2HPO_4 (30 mg), NBu_4Cl (20 mg), and $Pd(OAc)_2$ (1.2 mg, 0.01 mmol) were taken in a schlenk tube filled with argon. Degassed anhydrous DMF (0.7 mL) was added to the schlenk tube and the mixture was stirred at room temperature for 15 min. The solution of butyl acrylate (18 mg, 0.014 mmol) in DMF (0.3 mL) was added to the above mixture and the reaction mixture was stirred for 8 h at room temperature under argon. Water (5 mL) was added to the reaction mixture and the product was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with water (3 x 5 mL), dried over $MgSO_4$, filtered, concentrated *in vacuo* and the residue was subjected to column chromatography (ethyl acetate / pentane, 3:1) to yield the product (38

mg, 60 %); ν_{max} ($CHCl_3$) 3320, 3020, 2960, 1699, 1513, 1466, 1216; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.71-7.47 (3 H, m, C(6)*H*, C(9)*H*, N*H*), 7.31 (1 H, dd, *J* = 14.4, 8.2 Hz, C(5)*H*), 6.93 (1 H, t, *J* = 9.3 Hz, C(4)*H*), 6.58 (1 H, d, *J* = 16.3 Hz, C(10)*H*), 4.20 (2 H, t, *J* = 6.7 Hz, C(12)*H*), 2.22 (3 H, s, C(8)*H*), 1.72-1.63 (2 H, m, C(13)*H*), 1.47-1.36 (1 H, m, C(14)*H*), 0.95 (1 H, t, *J* = 7.4 Hz, C(15)*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 168.84 (*C*(7)), 167.12 (*C*(11)), 157.21 (d, *J* = 247.6, *C*(3)), 138.04 (*C*(1)), 137.31 (*C*(2)), 133.34 (*C*(9)), 130.81 (d, *J* = 10.5 Hz, (*C*(5)), 124.89 (d, *J* = 12.9 Hz, (*C*(10)), 120.42 (*C*(6)), 112.81 (d, *J* = 22.0 Hz, *C*(4)), 64.82 (*C*(12)), 53.44 (*C*(13)), 30.68 (*C*(14)), 19.18 (*C*(15)), 13.73 (*C*(16)); HRMS (ESI) *m/z*: calc for $C_{15}H_{18}FNO_3$ [M+Na]: 302.1163, Found 302.1165.

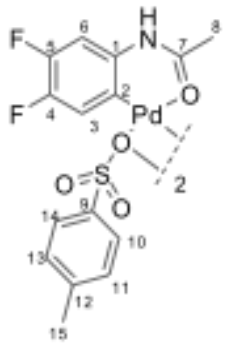
***(E)*-butyl 3-(6-acetamido-2,3-difluorophenyl)acrylate (3b):**



N-(3,4-difluoro-2-(trimethylsilyl)phenyl)acetamide **6** (122 mg, 0.5 mmol), *p*-toluenesulfonic acid monohydrate (95 mg, 0.5 mmol), *p*-benzoquinone (54 mg, 0.5 mmol) and palladium acetate (11.2 mg, 0.05 mmol) were dissolved in acetone (1.2 mL). *n*-butylacrylate (64 mg, 0.5 mmol) in acetone (0.2 mL) was added in the above mixture and stirred at room temperature. After 40 h the reaction mixture was concentrated under reduced pressure and the residue was dissolved in ether (3 mL) and washed with sat. $NaHCO_3$ (3 x 5 mL), and finally with water. The ether layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The product (126 mg, 85 %) was obtained after flash chromatography (ethyl acetate / pentane, 3:1); m.p. 142-146 °C; ν_{max} ($CHCl_3$) 3295, 3020, 2963, 2876, 1698, 1636, 1494, 1436, 1372, 1320, 1216, 1029, 984, 872, 819; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.55 (1 H, d, *J* = 16.3 Hz, C(9)*H*), 7.49-7.46 (1 H, m, C(6)*H*), 7.45 (1 H, s, N*H*), 7.16 (1

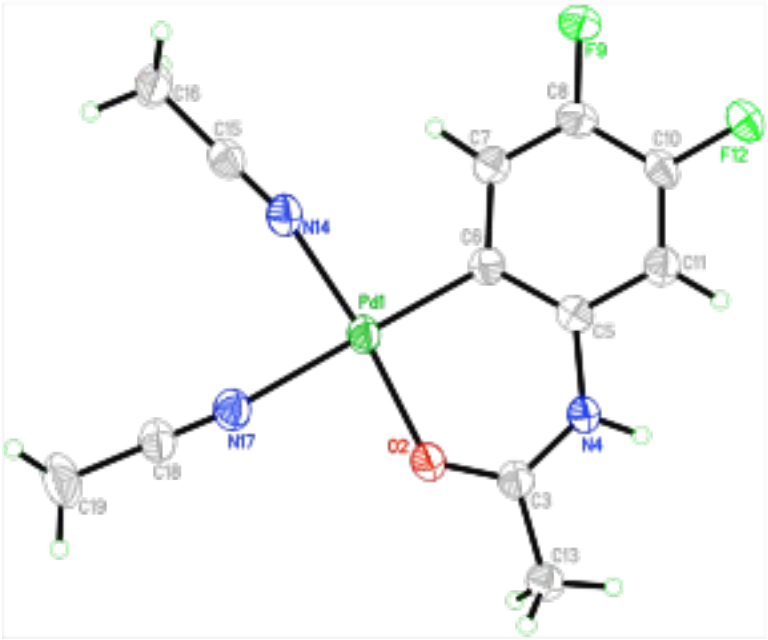
H, m, C(5)*H*), 6.63 (1 H, d, *J* = 16.3 Hz, C(10)*H*), 4.22 (2 H, t, *J* = 6.7 Hz, C(12)H_2), 2.22 (3 H, s, C(8)H_3), 1.74-1.64 (2 H, m, C(13)H_2), 1.47-1.36 (2 H, m, C(14)H_2),0.97 (3 H, t, *J* = 7.4 Hz, C(15)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 169.06 (*C*(11)), 166.75 (*C*(7)), 149.24 (dd, *J* = 253.4, 13.8 Hz, *C*(3)), 148.47 (dd, *J* = 247.6, 13.4 Hz, *C*(4)), 132.69 (d, *J* = 2.3 Hz, *C*(9)), 132.25 (d, *J* = 3.2 Hz, *C*(1)), 125.92 (d, *J* = 13.1 Hz, *C*(10)), 121.25 (dd, *J* = 5.9, 3.8 Hz, *C*(6)), 118.89 (d, *J* = 9.5 Hz, *C*(2)), 117.88 (d, *J* = 18.0 Hz, *C*(5)), 64.97 (*C*(12)), 30.64 (*C*(13)), 23.97 (*C*(8)), 19.17 (*C*(14)), 13.72 (*C*(15)); ^{19}F NMR (377 MHz, $CDCl_3$) δ ppm -135.62 (dd, *J* = 20.6, 8.4 Hz, C(3)*F*), -139.57 (ddd, *J* = 20.6, 9.4, 4.3 Hz, C(4)*F*); HRMS (ESI) *m/z*: calc for $C_{15}H_{16}F_2NO_3$ [M-H]: 296.1098, Found 296.1094.

Di-μ-*p*-toluenesulfonatobis(2-acetamino-4,5-difluorophenyl-C,O)dipalladium(II) (4):

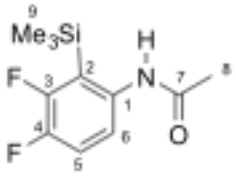


A mixture of *N*-(3,4-difluorophenyl)acetamide **1b** (85.5 mg, 0.5 mmol) and $Pd(OAc)_2$ (112 mg, 0.5 mmol) was dissolved in toluene (10 mL). A solution of *p*-TsOH (86 mg, 0.5 mmol) in acetone (0.5-1 mL) was added to this mixture and stirred at room temperature for 4 h. The settled yellow precipitates in the reaction mixture were filtered, washed with toluene and dried under vacuum to get the pure product (216 mg, 85 %); m.p. 186 °C (dec.); ^{1}H NMR (500 MHz, DMSO-d_6) δ ppm 12.13 (1 H, s, *N*H), 7.64-7.55 (1 H, m, C(3)*H*), 7.50 (2 H, d, *J* = 7.8 Hz, 2 x C(10)*H*), 7.17-7.06 (3 H, m, C(6)*H*, 2 x C(11)*H*); 2.37 (3 H, s, C(8)H_3), 2.27 (3 H, s, C(15)H_3); ^{13}C NMR (126 MHz, DMSO-d_6) δ ppm 169.80 (*C*(7)), 148.66 (dd, *J* = 245.4, 16.2 Hz, *C*(4)), 146.07 (C(9)), 145.49 (dd, *J* = 249.0, 14.2 Hz, C(5)), 138.85 (C(12)), 129.55-129.37 (m, C(1)), 129.05 (2 x C(11)), 126.36 (s, 2 x C(10)), 122.28 (d, *J* = 16.2 Hz, C(3)),

115.92-115.72 (m, C(2)*H*), 106.55 (dd, *J* = 16.8, 2.6 Hz, C(6)), 22.11 (C(8)), 21.66 (C(15)); ^{19}F NMR (377 MHz, DMSO-d_6) δ ppm -141.92. An acetonitrile derivative **5** of the compound **4** was crystallised from CH_3CN and the crystal structure of the cation is shown below with thermal ellipsoids drawn at 50% probability. Crystallographic details are given in the relevant section at the end and in the CIF.



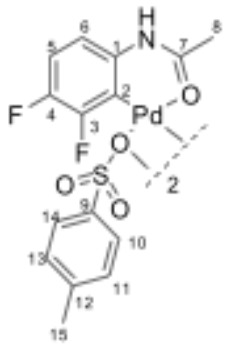
***N*-(3,4-difluoro-2-(trimethylsilyl)phenyl)acetamide (6):**



3,4-difluoro-2-(trimethylsilyl)aniline (101 mg, 0.5 mmol) was dissolved in benzene (0.5 mL) and cooled to 0 °C. Acetic Anhydride (90 mg, 0.9 mmol) in benzene (0.5 mL) was added drop wise. The reaction mixture was brought to reflux for 1 h and then cooled to room temperature. Water (2 mL) was added and the two layers were separated. The aqueous layer was extracted with benzene (1 mL) and the combined benzene layers were washed with dil. HCl (3 x 5 mL), sat. $NaHCO_3$ (3 x 5 mL) and finally water (2 x 5 mL). The benzene

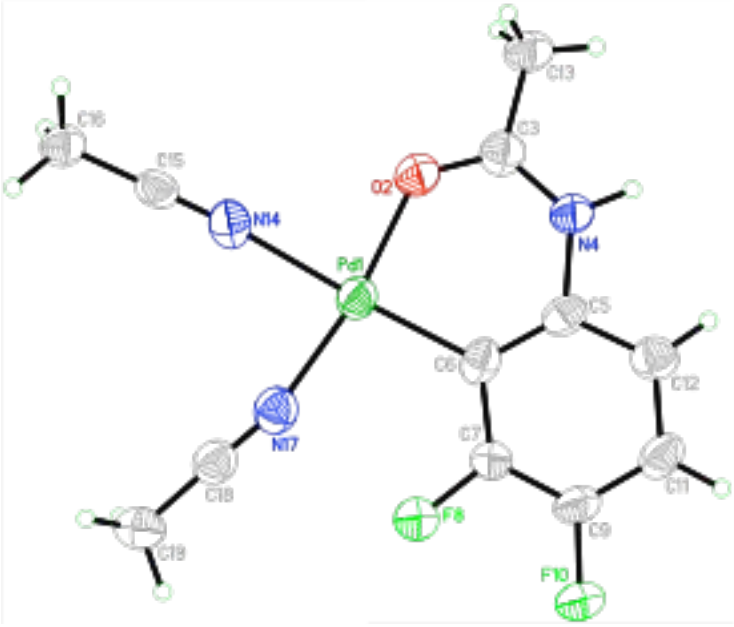
layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure giving 106 mg of the solid. Recrystallization from dichloromethane / pentane gave the product (102 mg, 83 %) as a white crystalline solid; m.p 114-118 °C; ν_{max} ($CHCl_3$) 3251, 3022, 2951, 1673, 1524, 1369, 1253, 1178; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.43 (1 H, s, N*H*), 7.28 (1 H, ddd, *J* = 8.9, 3.9, 1.4 Hz, C(6)*H*), 7.08 (1 H, m, C(5)*H*), 2.09 (3 H, s, C(8)H_3), 0.37 (9 H, d, *J* = 1.8 Hz, 3 x C(9)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 168.97 (*C*(7)), 154.20 (dd, *J* = 241.2, 12.0 Hz, *C*-F), 148.15 (dd, *J* = 248.44, 17.82 Hz, *C*-F), 136.97 (dd, *J* = 11.0, 3.5 Hz, *C*(1)), 122.87 (dd, *J* = 26.3, 1.2 Hz, *C*(2)), 122.09 (dd, *J* = 5.1, 3.5 Hz, *C*(6)), 118.16 (dd, *J* = 18.0, 1.4 Hz, *C*(5)), 23.98 (*C*(8)), 0.67 (d, *J* = 3.5 Hz, 3 x *C*(9)); ^{19}F NMR (377 MHz, $CDCl_3$) δ ppm -122.82 (ddd, *J* = 23.7, 7.4, 1.4 Hz, C(3)*F*), -141.02 (ddd, *J* = 23.7, 9.6, 3.9 Hz, C(4)*F*); HRMS (ESI) *m/z*: calc for $C_{11}H_{16}F_2NOSi$ [M+H]: 244.0969, Found 244.0964.

Di-μ-*p*-toluenesulfonatobis(2-acetamino-5,6-difluorophenyl-C,O)dipalladium(II) (7):

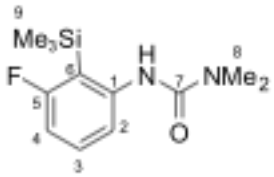


A mixture of *N*-(3,4-difluoro-2-(trimethylsilyl)phenyl)acetamide **6** (48.6 mg, 0.2 mmol) and $Pd(OAc)_2$ (56 mg, 0.25 mmol) was dissolved in toluene (3 mL). A solution of *p*-TsOH (38 mg, 0.2 mmol) in acetone (0.3 mL) was added to this mixture and stirred at room temperature for 1 h. The precipitation started very quickly and these yellow precipitates in the reaction mixture were filtered off, washed with toluene and dried under vacuum to get the pure product (85 mg, 95 %); m.p. 183 °C (dec.); ν_{max} (KBr) 1605, 1472, 1410, 1219, 1155, 1118, 1035, 1008, 807, 683; ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 12.16 (1 H, s, *N*H),

7.49 (1 H, d, *J* = 8.0 Hz, 2 x C(10)*H*), 7.22 (1 H, dd, *J* = 18.4, 8.7 Hz, C(5)*H*), 7.12 (1 H, d, *J* = 7.8 Hz, 2 x C(11)*H*), 6.86 (1 H, ddd, *J* = 8.6, 4.0, 1.6 Hz, C(6)*H*), 2.38 (3 H, s, C(8)H_3), 2.28 (3 H, s, C(15)H_3); ^{13}C NMR (126 MHz, DMSO-d$_6$) δ ppm 172.13 (*C*(7)), 153.80 (dd, *J* = 231.8, 11.8 Hz, *C*(3)), 148.04 (dd, *J* = 247.8, 18.6 Hz, *C*(4)), 146.33 (*C*(9)), 138.69 (*C*(12)), 132.19-131.49 (*C*(1)), 129.00 (2 x *C*(11)), 126.38 (2 x *C*(10)), 116.07 (d, *J* = 19.1 Hz, *C*(5)), 114.27 (d, *J* = 37.07 Hz, *C*(2)), 113.23 (d, *J* = 5.08 Hz, *C*(6)), 22.23 (*C*(8)), 21.67 (*C*(15)); ^{19}F NMR (377 MHz, DMSO-d$_6$) δ ppm -114.82, -140.38. An acetonitrile derivative **8** of the complex **7** was crystallised from CH_3CN and the crystal structure of the cation is shown below with thermal ellipsoids drawn at 50% probability. Crystallographic details are given in the relevant section at the end and in the CIF.



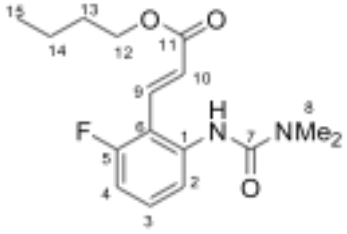
3-(3-fluoro-2-(trimethylsilyl)phenyl)-1,1-dimethylurea (9):



A solution of 1-(3-fluorophenyl)-1,3,3-trimethylurea **13g** (364 mg, 2 mmol) in THF (20 mL) was cooled to -78 ˚C and *t*-BuLi (1.7 M in pentane) (3.5 mL, 6.0 mmol) was added drop wise

while stirring the mixture vigorously. After 1 h Me_3SiCl (1.3 mL, 10 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_4Cl (10 mL). The organic layer was extracted, dried with $MgSO_4$, saturated *in vacuo* and purified by column chromatography (ethyl acetate / pentane, 3:1) to get the product (320 mg, 63 %); m.p. 148-152 ˚C; ν_{max} ($CHCl_3$) 3200, 2954, 1979, 1632, 1375, 1217, 1110, 1056, 975, 912, 844, 761; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.32-7.22 (2 H, m, C(2)*H* and C(3)*H*), 6.74 (1 H, t, *J* = 7.7 Hz, C(4)*H*), 6.40 (1 H, N*H*), 3.00 (6 H, s, 2 x C(8)*H*), 0.38 (9 H, d, *J* = 1.6 Hz, 3 x C(9)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 167.45 (d, *J* = 239.2 Hz, *C*(5)), 156.27 (*C*(7)), 144.50 (d, *J* = 12.9 Hz, *C*(1)), 131.13 (d, *J* = 10.6 Hz, *C*(3)), 120.66 (d, *J* = 2.6 Hz, *C*(2)), 118.37 (d, *J* = 30.2 Hz, *C*(6)), 110.90 (d, *J* = 27.1 Hz, *C*(4)), 36.52 (s, *C*(8)), 1.06 (d, *J* = 3.9 Hz, 3 x *C*(9)); HRMS (ESI) *m/z*: calc for $C_{12}H_{19}N_2FOSi$ [M+Na]: 277.1143, Found 277.1152.

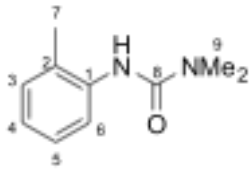
***(E)*-butyl 3-(2-(3,3-dimethylureido)-6-fluorophenyl)acrylate (10):**



3-(3-fluoro-2-(trimethylsilyl)phenyl)-1,1-dimethylurea **9** (51 mg, 0.2 mmol), *p*-toluenesulfonic acid monohydrate (38 mg, 0.2 mmol), *p*-benzoquinone (22 mg, 0.2 mmol) and $Pd(OAc)_2$ (4.48 mg, 0.02 mmol) were dissolved in acetone (0.5 mL). *n*-butyl acrylate (26 mg, 0.2 mmol) in acetone (0.2 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 (5 mL). The solution was washed with 0.1 N NaOH (3 x 5 mL), water (5 mL) and saturated NaCl (1 x 5 mL) and dried over $MgSO_4$. After filtration and concentration *in vacuo* the residue was subjected to column chromatography (ethyl acetate / pentane, 3:1) to yield the colorless oil

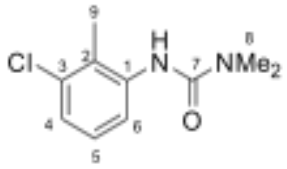
(25 mg, 40 %); ν_{max} ($CHCl_3$) 3316, 3019, 2962, 1707, 1578, 1518, 1469, 1366, 1316, 1216; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.64 (1 H, d, *J* = 16.3 Hz, C(9)*H*), 7.58 (1 H, d, *J* = 8.2 Hz, C(2)*H*), 7.28 (1 H, dd, *J* = 14.8, 7.5 Hz, C(3)*H*), 6.86 (1 H, t, *J* = 9.4 Hz, C(4)*H*), 6.58 (1 H, d, *J* = 16.3 Hz, C(10)*H*), 6.41 (1 H, s, N*H*), 4.21 (2 H, t, *J* = 6.6 Hz, C(12)H_2), 3.05 (6 H, s, 2 x C(8)H_3), 1.72-1.65 (2 H, m, C(13)H_2), 1.48-1.38 (2 H, m, C(14)H_2), 0.96 (3 H, t, *J* = 7.3 Hz, C(15)H_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 167.38 (*C*(11)), 161.77 (d, *J* = 251.5 Hz, *C*(5)), 155.84 (*C*(7)), 139.43 (d, *J* = 5.1 Hz, *C*(1)), 134.29 (*C*(9)), 131.15 (d, *J* = 10.6 Hz, *C*(3)), 124.98 (d, *J* = 10.9 Hz, *C*(6)), 119.96 (d, *J* = 2.9 Hz, *C*(2)), 115.89 (d, *J* = 14.0 Hz, *C*(10)), 111.72 (d, *J* = 22.5 Hz, *C*(4)), 65.14 (*C*(12)), 37.04 (*C*(13)), 31.16 (*C*(14)), 19.65 (*C*(15)), 14.19 (*C*(16)); ^{19}F NMR (377 MHz, $CDCl_3$) δ ppm -111.06; HRMS (ESI) *m/z*: calc for $C_{16}H_{21}FN_2O_3$ [M+Na]: 331.1428, Found 331.1425.

1,1-dimethyl-3-*o*-tolylurea (13a):[2]



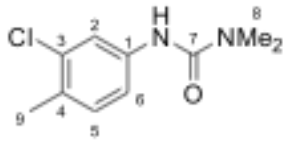
The 40 % aqueous solution of dimethylamine (1.15 mL, 10 mmol) was added to 1-isocyanato-2-methylbenzene (1.33 g, 10 mmol) dissolved in toluene (40 mL) at 75 ˚C. After 4 h stirring the reaction was concentrated *in vacuo* and precipitated urea was washed with toluene followed by concentration to get the product (1.6 g, 90 %) as white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.63 (1 H, d, *J* = 8.0 Hz, C(3)*H*), 7.18-7.09 (2 H, m, C(4)*H*, C(6)*H*), 6.98 (1 H, t, *J* = 7.4 Hz, C(5)*H*), 6.21 (1 H, s, N*H*), 2.96 (6 H, s, C(9)*H*), 2.20 (3 H, s, C(7)*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 156.02 (*C*(8)), 137.26 (*C*(1)), 130.22 (*C*(4)), 128.89 (*C*(2)), 126.59 (*C*(6)), 123.84 (*C*(5)), 122.86 (*C*(3)), 36.41 (*C*(9)), 17.80 (*C*(7)); HRMS (ESI) *m/z*: calc for $C_{10}H_{14}N_2O$ [M+Na]: 201.0998, Found 291.0994.

3-(3-chloro-2-methylphenyl)-1,1-dimethylurea (13b):[3]



The 40 % aqueous solution of dimethylamine (0.85 mL, 7 mmol) was added to 1-chloro-3-isocyanato-2-methylbenzene (960 mg, 5.75 mmol) dissolved in toluene (30 mL) at 75 ˚C. After 4 h stirring the reaction was concentrated *in vacuo* and precipitated urea was washed with toluene followed by concentration to get the product (1.1 g, 91 %) as white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.47 (1 H, d, *J* = 7.8 Hz, C(6)*H*), 7.13 (1 H, d, *J* = 7.9 Hz, C(4)*H*), 7.07 (1 H, t, *J* = 8.0 Hz, C(5)*H*), 6.27 (1 H, s, N*H*), 3.00 (6 H, s, 2 x C(8)H_3), 2.27 (3 H, s, C(9)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 155.89 (*C*(7)), 138.44 (*C*(1)), 134.56 (*C*(3)), 128.25 (*C*(2)), 126.69 (*C*(5)), 125.13 (*C*(4)), 122.23 (*C*(6)), 36.46 (2 x *C*(8)), 14.67 (*C*(9)).

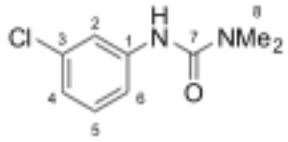
3-(3-chloro-4-methylphenyl)-1,1-dimethylurea (13c):[4]



The 40 % aqueous solution of dimethylamine (1.2 mL, 10 mmol) was added to 1-chloro-4-isocyanatobenzene (1.67 g, 10 mmol) dissolved in toluene (30 mL) at 75 ˚C. After 2 h stirring the reaction was concentrated *in vacuo* and precipitated urea was washed with toluene followed by concentration to get the product (1.7 g, 88 %) as white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.43 (1 H, d, *J* = 2.2 Hz, C(2)*H*), 7.14 (1 H, dd, *J* = 8.3, 2.2 Hz, C(6)*H*), 7.08 (1 H, d, *J* = 8.3 Hz, C(5)*H*), 6.43 (1 H, s, N*H*), 2.99 (6 H, s, 2 x C(8)H_3), 2.29 (3 H, s, C(9)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 155.59 (*C*(7)), 138.04 (*C*(1)), 134.16

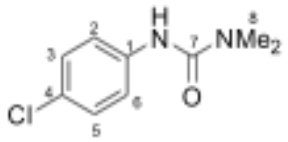
(*C*(3)), 130.75 (*C*(5)), 130.24 (*C*(4)), 120.53 (*C*(2)), 118.34 (*C*(6)), 36.44 (2 x *C*(8)), 19.31 (*C*(9)).

3-(3-chlorophenyl)-1,1-dimethylurea (13d):[5]



The 40 % aqueous solution of dimethylamine (1.15 mL, 10 mmol) was added to 1-chloro-3-isocyanatobenzene (1.53 g, 10 mmol) dissolved in toluene (40 mL) at 75 ˚C. After 4 h stirring the reaction was concentrated *in vacuo* and precipitated urea was washed with toluene followed by concentration to get the product (1.7 g, 88%) as white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.47 (1 H, t, *J* = 2.0 Hz, C(2)*H*), 7.21 (1 H, ddd, *J* = 8.2, 2.0, 1.0 Hz, C(6)*H*), 7.14 (1 H, t, *J* = 8.0 Hz, C(5)*H*), 6.96 (1 H, ddd, *J* = 7.8, 2.0, 1.0 Hz, C(4)*H*), 6.69 (1 H, s, N*H*), 2.98 (6 H, s, 2 x C(8)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 155.54 (*C*(7)), 140.57 (*C*(1)), 134.25 (*C*(3)), 129.67 (*C*(5)), 122.77 (*C*(4)), 119.98 (*C*(2)), 117.97 (*C*(6)), 36.45 (*C*(9)).

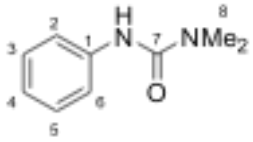
3-(4-chlorophenyl)-1,1-dimethylurea (13e):[4]



The 40 % aqueous solution of dimethylamine (1.2 mL, 10 mmol) was added to 1-chloro-4-isocyanatobenzene (1.53 g, 10 mmol) dissolved in toluene (30 mL) at 75 ˚C. After 2 h stirring the reaction was concentrated *in vacuo* and precipitated urea was washed with toluene followed by concentration to get the product (1.8 g, 90 %) as white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.35-7.31 (2 H, m, 2 x C(2)*H*), 7.25-7.20 (2 H, m, 2 x C(3)*H*), 6.43

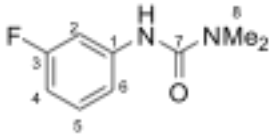
(1 H, s, N*H*), 3.01 (3 H, s, 2 x C(8)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 155.50 (*C*(7)), 137.83 (*C*(1)), 128.76 (2 x *C*(2)), 127.82 (*C*(4)), 121.09 (2 x *C*(3)), 36.47 (2 x *C*(8)).

1,1-dimethyl-3-phenylurea (13f):[4]



The 40 % aqueous solution of dimethylamine (3.8 mL, 22 mmol) was added to phenyl isocyanate (2.4 g, 20 mmol) dissolved in toluene (150 mL) at 75 ˚C. After 4 h stirring the reaction was concentrated *in vacuo* and precipitated urea was washed with toluene followed by concentration to get the product (3.1 g, 95 %) as white solid; m.p. 132-134 ˚C; ν_{max} ($CHCl_3$) 3457, 3348, 3018, 1667;^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.38 (2 H, d, *J* = 8.0 Hz, 2 x C(2)*H*), 7.27 (2 H, t, *J* = 7.7 Hz, 2 x C(3)*H*), 7.02 (1 H, t, *J* = 7.3 Hz, C(4)*H*), 6.46 (1 H, bs, N*H*), 3.00 (6 H, s, 2 x C(8)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 155.79 (*C*(7)), 139.24 (*C*(1)), 128.78 (2 x *C*(3)), 122.88 (*C*(4)), 119.92 (2 x *C*(2)), 36.43 (2 x *C*(8)); HRMS (ESI) *m/z*: calc for $C_9H_{12}N_2O$ [M+Na]: 187.0842, Found 187.0846.

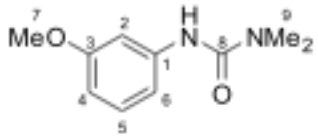
1-(3-fluorophenyl)-1,3,3-trimethylurea (13g):[6]



The 40 % aqueous solution of dimethylamine (1 mL, 8 mmol) was added to 1-fluoro-3-isocyanatobenzene (686 mg, 5 mmol) dissolved in toluene (20 mL) at 75 ˚C.[4] After 4 h stirring the reaction was concentrated *in vacuo* and precipitated urea was washed with toluene followed by concentration to get the product (800 mg, 87 %) as white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.32 (1 H, td, *J* = 11.4, 2.3 Hz, C(2)*H*), 7.17 (1 H, dt, *J* = 8.2, 6.6

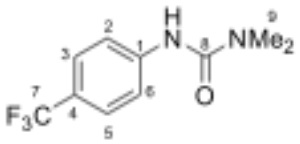
Hz, C(5)*H*), 7.01 (1 H, dd, *J* = 8.2, 2.0 Hz, C(6)*H*), 6.69 (1 H, ddt, *J* = 8.4, 2.5, 0.8 Hz, C(4)*H*), 6.59 (1 H, s, N*H*), 2.99 (6 H, s, C(8)*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 163.06 (d, *J* = 243.5 Hz, *C*(3)), 155.42 (*C*(7)), 140.97 (d, *J* = 11.06 Hz, *C*(1)), 129.73 (d, *J* = 9.57 Hz, *C*(5)), 114.94 (d, *J* = 2.64 Hz, *C*(6)), 109.40 (d, *J* = 21.41 Hz, *C*(4)), 107.08 (d, *J* = 26.28 Hz, *C*(2)), 36.44 (*C*(8)).

3-(3-methoxyphenyl)-1,1-dimethylurea (13h):[7]



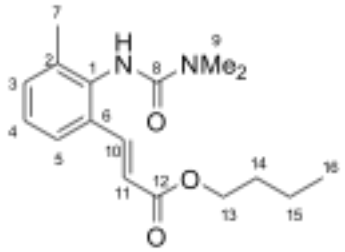
The solution of dimethylamine (2 M in methanol), (10 mmol, 5 mL) was added to 3-methoxyphenyl isocyanate (10 mmol, 1.5 g) dissolved in toluene (50 mL) at 75 ˚C. After 4 h stirring the reaction was concentrated *in vacuo* and precipitated urea was washed with toluene followed by concentration to get (1.9 g, 90 %) of the product as white solid; m.p 140-142 °C; ν_{max} ($CHCl_3$) 3324, 3019, 2400, 1666, 1606, 1365, 1216, 1040, 961, 844, 757, 689, 668; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.18 (1 H, t, *J* = 2.1 Hz, C(6)*H*), 7.15 (1 H, t, *J* = 8.15 Hz, C(3)*H*), 6.82-6.86 (1 H, m, C(2)*H*), 6.60-6.55 (1 H, m, C(4)*H*), 6.44 (1 H, bs, N*H*), 3.78 (3 H, s, C(7)H_3), 3.01 (6 H, s, 2 x C(9)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 160.13 (*C*(5)), 155.65 (*C*(8)), 140.54 (*C*(1)), 129.41 (*C*(3)), 111.80 (*C*(4)), 108.96 (*C*(2)), 105.19 (*C*(6)), 55.25 (*C*(7)), 36.46 (2 x *C*(9)); HRMS (ESI) *m/z*: calc for $C_{10}H_{14}N_2O_2$ [M+Na]: 217.0947, Found 217.0944.

1,1-dimethyl-3-(4-(trifluoromethyl)phenyl)urea (13i):[8]



The 40 % aqueous solution of dimethylamine (0.6 mL, 5 mmol) was added to 1-isocyanato-4-(trifluoromethyl)benzene (935 mg, 5 mmol) dissolved in toluene (40 mL) at 75 ˚C. After 3 h stirring the reaction was concentrated *in vacuo* and precipitated urea was washed with toluene followed by concentration to get the product (1.0 g, 87 %) as white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.50 (4 H, s, 4 x C(2)*H*), 6.56 (1 H, s, N*H*), 3.04 (6 H, s, 2 x C(9)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 155.10 (*C*(8)), 142.39 (*C*(1)), 126.09 (q, *J* = 3.7 Hz, 2 x *C*(3)), 118.95 (2 x *C*(2)), 36.50 (2 x *C*(9)); ^{19}F NMR (377 MHz, $CDCl_3$) δ ppm -61.85; HRMS (ESI) *m/z*: calc for $C_{10}H_{11}F_3N_2O$ [M+Na]: 255.0716, Found 255.0710.

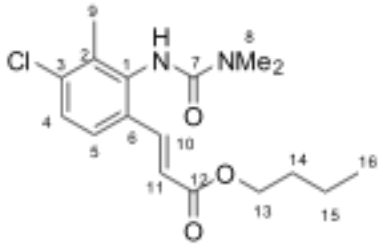
***(E)*-butyl 3-(2-(3,3-dimethylureido)-3-methylphenyl)acrylate (14a):**



1,1-dimethyl-3-*o*-tolylurea **13a** (178 mg, 1.0 mmol), *p*-toluenesulfonic acid monohydrate (190 mg, 1 mmol), *p*-benzoquinone (110 mg, 1.0 mmol) and $Pd(OAc)_2$ (4.48 mg, 0.02 mmol) were dissolved in acetone (1.5 mL). *n*-butyl acrylate (128 mg, 1.0 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 EtOAc (10 mL). The solution was washed with 0.1 N NaOH (3 x 10 mL), water (10 mL) and saturated NaCl (10 mL) and dried over $MgSO_4$. After filtration and concentration *in vacuo* the residue was subjected to column chromatography (EtOAc) to yield the product (155 mg, 50 %); m.p. 89-92 ˚C; ν_{max} ($CHCl_3$) 3293, 2961, 1703, 1636, 1590, 1510, 1467, 1370, 1316, 1264, 1216, 1181, 1065, 1026, 983, 756, 666; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.85 (1 H, d, *J* = 16.0 Hz, C(10)*H*), 7.48-7.41 (1 H, m, C(3)*H*), 7.23 (1 H, d, *J* = 7.4 Hz, C(5)*H*), 7.15 (1 H, t, *J* = 7.6 Hz, C(4)*H*), 6.34 (1 H, d, *J* = 16.0 Hz, C(11)*H*), 6.14 (1 H, s, N*H*), 4.14 (2 H, t, *J* = 6.6 Hz, C(13)*H*), 3.02 (6 H, s, 2

x C(9)*H*), 2.23 (3 H, s, C(7)*H*), 1.70-1.61 (2 H, m, C(14)*H*), 1.47-1.36 (2 H, m, C(15)*H*), 0.95 (1 H, t, *J* = 7.4 Hz, C(16)*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 167.19 (*C*(12)), 156.34 (*C*(8)), 141.11 (*C*(10)), 136.51 (*C*(1)), 136.19 (*C*(2)), 132.40 (*C*(6)), 132.31 (*C*(5)), 126.68 (*C*(4)), 124.41 (*C*(3)), 119.18 (*C*(11)), 64.30 (*C*(13)), 36.58 (*C*(9)), 30.74 (*C*(14)), 19.22 (*C*(15)), 18.33 (*C*(7)), 13.78 (*C*(16)); HRMS (ESI) *m/z*: calc for $C_{17}H_{24}N_2O_3$ [M+Na]: 327.1679, Found 327.1673.

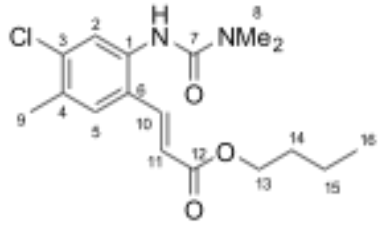
***(E)*-butyl 3-(4-chloro-2-(3,3-dimethylureido)-3-methylphenyl)acrylate (14b):**



3-(3-chloro-2-methylphenyl)-1,1-dimethylurea **13b** (212 mg, 1.0 mmol), *p*-toluenesulfonic acid monohydrate (190 mg, 1 mmol), *p*-benzoquinone (110 mg, 1.0 mmol) and $Pd(OAc)_2$ (4.48 mg, 0.02 mmol) were dissolved in acetone (1.5 mL). *n*-butyl acrylate (128 mg, 1.0 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 EtOAc (10 mL). The solution was washed with 0.1 N NaOH (3 x 10 mL), water (10 mL) and saturated NaCl (10 mL) and dried over $MgSO_4$. After filtration and concentration *in vacuo* the residue was subjected to column chromatography (EtOAc) to yield the product (112 mg, 33 %) as a light yellow oil; ν_{max} ($CHCl_3$) 3019, 1704, 1663, 1503, 1315, 1215, 1181, 757, 669; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.77 (1 H, d, *J* = 16.0 Hz, C(10)*H*), 7.39 (1 H, d, *J* = 8.5 Hz, C(5)*H*), 7.28 (1 H, d, *J* = 8.5 Hz, C(4)*H*), 6.34 (1 H, d, *J* = 16.0 Hz, C(11)*H*), 6.08 (1 H, s, N*H*), 4.16 (2 H, t, *J* = 6.6 Hz, C(13)H_2), 3.06 (6 H, s, 2 x C(8)H_3), 2.28 (3 H, s, C(9)H_3), 1.71-1.61 (2 H, m, C(14)H_2), 1.47-1.36 (2 H, m, C(15)H_2), 0.95 (3 H, t, *J* = 7.4 Hz, C(16)H_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 167.40 (*C*(12)), 156.48 (*C*(7)), 140.65 (*C*(10)), 137.63 (*C*(1)), 137.21

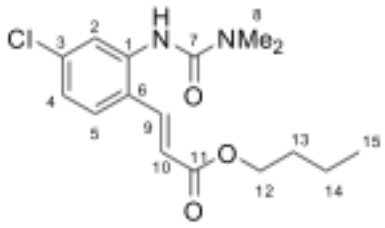
(*C*(2)), 135.58 (*C*(3)), 131.67 (*C*(6)), 128.28 (*C*(5)), 125.04 (*C*(4)), 120.23 (*C*(11)), 64.89 (*C*(13)), 37.07 (2 x *C*(8)), 31.18 (*C*(14)), 19.66 (*C*(15)), 16.12 (*C*(9)), 14.21 (*C*(16)); HRMS (ESI) *m/z*: calc for $C_{17}H_{23}ClN_2O_3$ [M+Na]: 361.1289, Found 361.1284.

***(E)*-butyl 3-(4-chloro-2-(3,3-dimethylureido)-5-methylphenyl)acrylate (14c):**



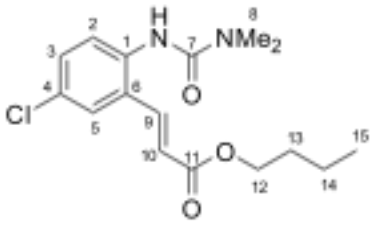
3-(3-chloro-4-methylphenyl)-1,1-dimethylurea **13c** (212 mg, 1.0 mmol), *p*-toluenesulfonic acid monohydrate (190 mg, 1 mmol), *p*-benzoquinone (110 mg, 1.0 mmol) and $Pd(OAc)_2$ (4.48 mg, 0.02 mmol) were dissolved in acetone (1.5 mL). *n*-butyl acrylate (128 mg, 1.0 mmol) in acetone (0.5 mL) was added in the above mixture and stirred at room temperature for 20 h. The reaction mixture was concentrated *in vacuo* and dissolved in EtOAc (10 mL). The solution was washed with 0.1 N NaOH (3 x 10 mL), water (10 mL) and saturated NaCl (10 mL) and dried over $MgSO_4$. After filtration and concentration *in vacuo* the residue was subjected to column chromatography (EtOAc / pentane 4:1) to yield the product (166 mg, 50 %); m.p. 136-138 ˚C; ν_{max} ($CHCl_3$) 3275, 2961, 1705, 1636, 1607, 1567, 1504, 1479, 1317, 1277, 1177, 1065, 1030, 981, 861, 757, 666; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.55 (1 H, d, *J* = 15.9 Hz, C(10)*H*), 7.38 (1 H, s, C(2)*H*), 7.23 (1 H, s, C(5)*H*), 6.78 (1 H, s, N*H*), 6.23 (1 H, d, *J* = 15.9 Hz, C(11)*H*), 4.11 (2 H, t, *J* = 6.6 Hz, C(13)H_2), 2.96 (6 H, s, 2 x C(8)H_3), 2.25 (3 H, s, C(9)H_3), 1.67-1.57 (2 H, m, C(14)H_2), 1.44-1.32 (2 H, m, C(15)H_2), 0.92 (3 H, t, *J* = 7.4 Hz, C(16)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 166.87 (*C*(12)), 155.99 (*C*(7)), 139.20 (*C*(10)), 136.37 (*C*(1)), 136.07 (*C*(3)), 132.36 (*C*(4)), 128.32 (*C*(5)), 126.65 (*C*(6)), 125.99 (*C*(2)), 118.99 (*C*(11)), 64.41 (*C*(13)), 36.42 (2 x *C*(8)), 30.69 (*C*(14)), 19.49 (*C*(15)), 19.18 (*C*(9)), 13.73 (*C*(16)); HRMS (ESI) *m/z*: calc for $C_{17}H_{23}ClN_2O_3$ [M+Na]: 361.1289, Found 361.1288.

***(E)*-butyl 3-(4-chloro-2-(3,3-dimethylureido)phenyl)acrylate (14d):**



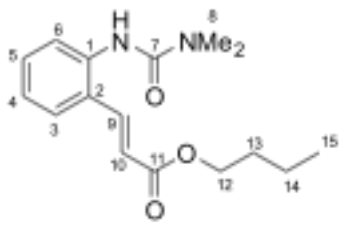
3-(3-chlorophenyl)-1,1-dimethylurea **13d** (198 mg, 1.0 mmol), *p*-toluenesulfonic acid monohydrate (190 mg, 1 mmol), *p*-benzoquinone (110 mg, 1.0 mmol) and $Pd(OAc)_2$ (4.48 mg, 0.02 mmol) were dissolved in acetone (1.5 mL). *n*-butylacrylate (128 mg, 1.0 mmol) in acetone (0.5 mL) was added in the above mixture and stirred at room temperature for 20 h. The reaction mixture was concentrated *in vacuo* and dissolved in EtOAc (10 mL). The solution was washed with 0.1 N NaOH (3 x 10 mL), water (10 mL) and saturated NaCl (10 mL) and dried over $MgSO_4$. After filtration and concentration *in vacuo* the residue was subjected to column chromatography (EtOAc) to yield the product (168 mg, 52 %); m.p. 107-109 ˚C; ν_{max} ($CHCl_3$) 3274, 2960, 1710, 1643, 1596, 1568, 1512, 1414, 1370, 1315, 1255, 1176, 1114, 1089, 1065, 980; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.63 (1 H, d, *J* = 15.9 Hz, C(9)*H*), 7.57 (1 H, d, *J* = 1.8 Hz, C(2)*H*), 7.36 (1 H, d, *J* = 8.4 Hz, C(5)*H*), 7.03 (1 H, dd, *J* = 8.4, 1.8 Hz, C(4)*H*), 6.57 (1 H, s, N*H*), 6.28 (1 H, d, *J* = 15.9 Hz, C(10)*H*), 4.13 (2 H, t, *J* = 6.6 Hz, C(12)H_2), 2.99 (6 H, s, 2 x C(8)H_3), 1.68-1.59 (2 H, m, C(13)H_2), 1.44-1.33 (2 H, m, C(14)H_2), 0.93 (3 H, t, *J* = 7.4 Hz, C(15)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 166.87 (*C*(11)), 155.67 (*C*(7)), 138.84 (*C*(9)), 138.60 (*C*(1)), 136.10 (*C*(3)), 127.79 (*C*(5)), 125.99 (*C*(6)), 125.00 (2), 124.83 (4), 119.88 (*C*(10)), 64.60 (*C*(12)), 36.49 (*C*(8)), 30.67 (*C*(13)), 19.18 (*C*(14)), 13.74 (*C*(15)); HRMS (ESI) *m/z*: calc for $C_{16}H_{21}ClN_2O_3$ [M+Na]: 347.1133, Found 347.1132.

(*E*)-butyl 3-(5-chloro-2-(3,3-dimethylureido)phenyl)acrylate (14e):



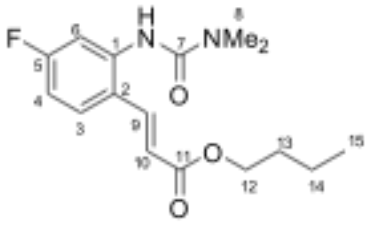
3-(4-chlorophenyl)-1,1-dimethylurea **13e** (199 mg, 1.0 mmol), *p*-toluenesulfonic acid monohydrate (190 mg, 1 mmol), *p*-benzoquinone (110 mg, 1.0 mmol) and $Pd(OAc)_2$ (4.48 mg, 0.02 mmol) were dissolved in acetone (1.5 mL). *n*-butylacrylate (192 mg, 1.5 mmol) in acetone (0.5 mL) was added in the above mixture and stirred at room temperature for 36 h. The reaction mixture was concentrated *in vacuo* and dissolved in EtOAc (10 mL). The solution was washed with 0.1 N NaOH (3 x 10 mL), water (10 mL) and saturated NaCl (10 mL) and dried over $MgSO_4$. After filtration and concentration *in vacuo* the residue was subjected to column chromatography (EtOAc/Hexane, 3:1) to yield the product (129 mg, 40 %); ν_{max} ($CHCl_3$) 3272, 2960, 2239, 1644, 1572, 1506, 1373, 1316, 1176, 1117, 1065, 1026, 979, 915, 861, 814, 734, 678; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.67 (1 H, d, *J*=15.9 Hz, C(9)*H*), 7.46 (1 H, d, *J*=8.8 Hz, C(2)*H*), 7.43 (1 H, d, *J*=2.4 Hz, C(5)*H*), 7.23 (1 H, dd, *J*=8.8, 2.4 Hz, C(3)*H*), 6.56 (1 H, s, N*H*), 6.33 (1 H, d, *J*=15.9 Hz, C(10)*H*), 4.14 (2 H, t, *J*=6.7 Hz, C(12)H_2), 2.99 (6 H, s, 2 X C(8)H_3), 1.58 - 1.69 (2 H, m, C(13)H_2), 1.34 - 1.45 (2 H, m, C(14)H_2), 0.93 ppm (3 H, t, *J*=7.3 Hz, C(15)H_3); ^{13}C NMR ($CDCl_3$,101MHz) δ ppm 166.6, 155.8, 138.6, 136.2, 130.3, 130.1, 129.3, 126.7, 126.5, 120.9, 64.6, 36.5, 30.7, 19.2, 13.7 ppm; HRMS (ESI) *m/z*: calc for $C_{16}H_{21}ClN_2O_3$ [M+Na]: 347.1133, Found 347.1144.

***(E)*-butyl 3-(2-(3,3-dimethylureido)phenyl)acrylate (14f):**



1,1-dimethyl-3-phenylurea **13f** (32.8 mg, 0.2 mmol), *p*-toluenesulfonic acid monohydrate (38 mg, 0.2 mmol), *p*-benzoquinone (22 mg, 0.2 mmol) and $Pd(OAc)_2$ (2.24 mg, 0.01 mmol) were dissolved in acetone (0.5 mL). *n*-butyl acrylate (26 mg, 0.2 mmol) in acetone (0.2 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 (5 mL). The solution was washed with 0.1N NaOH (3 x 5 mL), water (5 mL) and saturated NaCl (1 x 5 mL) and dried over $MgSO_4$. After filtration and concentration *in vacuo* the residue was subjected to column chromatography (ethyl acetate / pentane, 3:1) to yield the product as colourless oil (52 mg, 90 %); ν_{max} ($CHCl_3$) 3292, 2961, 1706, 1635, 1518, 1373, 1318, 1275, 1177, 1066, 1026, 983, 866; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.81 (1 H, d, *J* = 15.9 Hz, C(9)*H*), 7.57 (1 H, d, *J* = 7.5 Hz, C(6)*H*), 7.51 (1 H, d, *J* = 7.8 Hz, C(3)*H*), 7.32 (1 H, t, *J* = 7.8 Hz, C(5)*H*), 7.11 (1 H, t, *J* = 7.5 Hz, C(4)*H*), 6.49 (1 H, N*H*), 6.37 (1 H, d, *J* = 15.7 Hz, C(10)*H*), 4.16 (2 H, t, *J* = 6.6 Hz, C(12)H_2), 3.02 (6 H, s, 2 x C(8)H_3), 1.69-1.62 (2 H, m, C(13)H_2), 1.46-1.36 (2 H, m, C(14)H_2), 0.95 (3 H, t, *J* = 7.4 Hz, C(15)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 166.96 (*C*(11)), 155.94 (*C*(7)), 139.87 (*C*(9)), 137.64 (*C*(1)), 130.63 (*C*(5)), 127.67 (*C*(2)), 126.93 (*C*(3)), 125.12 (*C*(6)), 124.69 (*C*(4)), 119.84 (*C*(10)), 64.45 (*C*(12)), 36.50 (2 x *C*(8)), 30.69 (*C*(13)), 19.17 (*C*(14)), 13.72 (*C*(15)); HRMS (ESI) *m/z*: calc for $C_{16}H_{22}N_2O_3$ [M+H]: 291.1703, Found 291.1694.

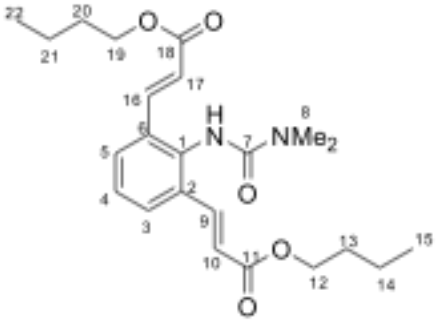
***(E)*-butyl 3-(2-(3,3-dimethylureido)-4-fluorophenyl)acrylate (11):**



1-(3-fluorophenyl)-1,3,3-trimethylurea **13g** (36.4 mg, 0.2 mmol), *p*-toluenesulfonic acid monohydrate (38 mg, 0.2 mmol), *p*-benzoquinone (22 mg, 0.2 mmol) and $Pd(OAc)_2$ (2.24 mg, 0.01 mmol) were dissolved in acetone (0.5 mL). *n*-butyl acrylate (26 mg, 0.2 mmol) in

acetone (0.2 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 (5 mL). The solution was washed with 0.1N NaOH (3 x 5 mL), water (5 mL) and saturated NaCl (1 x 5 mL) and dried over $MgSO_4$. After filtration and concentration *in vacuo* the residue was subjected to column chromatography (ethyl acetate / pentane, 3:1) to yield the product (55 mg, 90 %); ν_{max} ($CHCl_3$) 3289, 3018, 2961, 2875, 1706, 1654, 1609, 1522, 1478, 1435, 1371, 1320, 1291, 1260, 1216, 1179, 1095, 1066, 1027, 981, 907, 858, 810; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.71 (1 H, d, *J* = 15.8 Hz, C(9)*H*), 7.54 (1 H, dd, *J* = 10.9, 2.7 Hz, C(6)*H*), 7.44 (1 H, dd, *J* = 8.7, 6.3 Hz, C(3)*H*), 6.80 (1 H, dt, *J* = 8.3, 2.6 Hz, C(4)*H*), 6.60 (1 H, s, N*H*), 6.31 (1 H, d, *J* = 15.8 Hz, C(10)*H*), 4.16 (2 H, t, *J* = 6.6 Hz, C(12)H_2), 3.02 (6 H, s, 2 x C(8)H_3), 1.69-1.62 (2 H, m, C(13)H_2), 1.46-1.36 (2 H, m, C(14)H_2), 0.95 (3 H, t, *J* = 7.4 Hz, C(15)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 166.79 (*C*(11)), 163.90 (d, *J* = 248.0 Hz, *C*(5)), 155.21 (*C*(7)), 139.34 (d, *J* = 12.0 Hz, *C*(1)), 138.62 (*C*(9)), 128.60 (d, *J* = 10.1 Hz, *C*(3)), 122.41 (*C*(6)), 119.86 (*C*(10)), 111.47 (d, *J* = 22.3 Hz, *C*(4)), 110.92 (d, *J* = 25.1 Hz, *C*(6)), 64.55 (*C*(12)), 36.50 (2 x *C*(8)), 30.69 (*C*(13)), 19.17 (*C*(14)), 13.72 (*C*(15)); ^{19}F -108.32; HRMS (ESI) *m/z*: calc for $C_{16}H_{21}FN_2O_3$ [M+Na]: 331.1428, Found 331.1426.

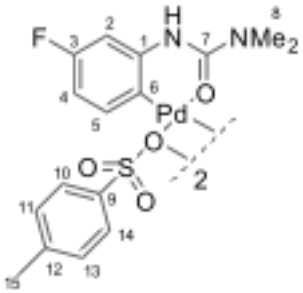
(2*E*,2'*E*)-dibutyl 3,3'-(2-(3,3-dimethylureido)-1,3-phenylene)diacrylate (15):



1,1-dimethyl-3-phenylurea **159** (164 mg, 1 mmol), *p*-toluenesulfonic acid monohydrate (190 mg, 1 mmol), *p*-benzoquinone (220 mg, 2 mmol) and $Pd(OAc)_2$ (22.4 mg, 0.1 mmol) were dissolved in acetone (1.5 mL). *n*-butyl acrylate (256 mg, 2 mmol) in acetone (1 mL) was

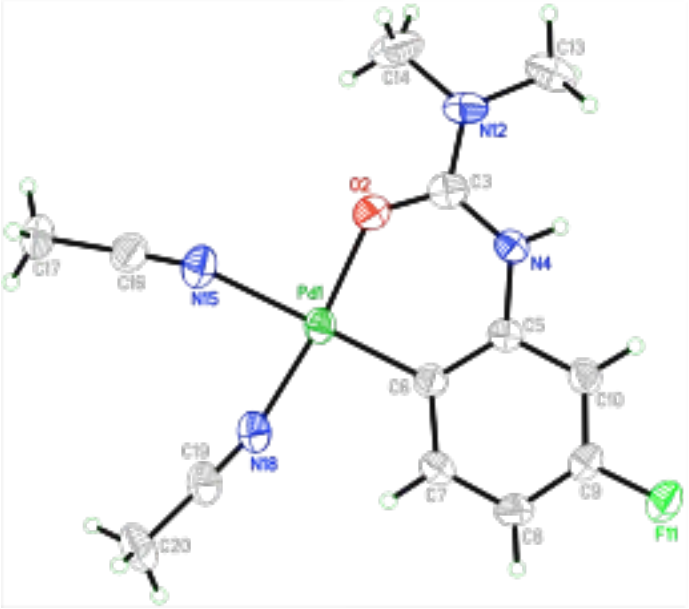
added in the above mixture and stirred at room temperature for 40 h. The reaction mixture was concentrated *in vacuo* and the residue was dissolved in ether (10 mL). The solution was washed with 0.1 N NaOH (3 x 10 mL), water (10 mL) and saturated NaCl (10 mL) and dried over $MgSO_4$. After filtration and concentration *in vacuo* the residue was subjected to column chromatography (ethyl acetate / pentane, 3:1) to yield the product as colourless oil (145 mg, 35 %); ν_{max} ($CHCl_3$) 3373, 3020, 2962, 1707, 1637, 1506, 1464, 1384, 1317, 1216, 1173, 1065, 1027, 984; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.83 (2 H, d, *J* = 16.0 Hz, 2 x C(9)*H*), 7.64 (2 H, d, *J* = 7.8 Hz, 2 x C(3)*H*), 7.29 (1 H, *J* = 7.8 Hz, C(4)*H*), 6.39 (2 H, d, *J* = 16.0 Hz), 6.31 (1 H, s, N*H*), 4.18 (4 H, t, *J* = 6.6 Hz, 2 x C(12)H_2), 3.10 (6 H, s, 2 x C(8)H_3), 1.71-1.63 (4 H, m, C(13)H_2), 1.48-1.38 (4 H, m, C(14)H_2), 0.96 (6 H, t, *J* = 7.4 Hz, 2 x C(15)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 166.87 (2 x *C*(11)), 156.19 (*C*(7)), 140.05 (2 x *C*(9)), 136.38 (*C*(1)), 133.20 (2 x *C*(2)), 128.44 (2 x *C*(3)), 127.03 (*C*(4)), 120.31 (2 x *C*(17)), 64.50 (2 x *C*(12)), 36.68 (2 x *C*(8)), 30.72 (2 x *C*(13)), 19.22 (2 x *C*(14)), 13.77 (2 x *C*(15)); HRMS (ESI) *m/z*: calc for $C_{23}H_{32}N_2O_5$ [M+Na]: 439.2203, Found 439.2200.

Palladacyclic Complex (16):

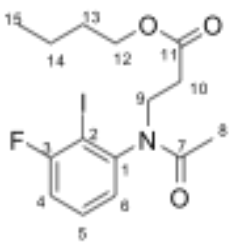


A mixture of 1-(3-fluorophenyl)-1,3,3-trimethylurea **13g** (91 mg, 0.5 mmol) and $Pd(OAc)_2$ (112 mg, 0.5 mmol) was dissolved in toluene (10 mL). A solution of monohydrate *p*-TsOH (95 mg, 0.5 mmol) in acetone (0.5-1 mL) was added to this mixture and stirred at room temperature for 2 h. The settled yellow precipitates in the reaction mixture were filtered, washed with toluene and dried under vacuum to get the complex **16a** (206 mg, 90 %); ν_{max} (neat) 3339, 3020, 1629, 1579, 1528, 1498, 1456, 1412, 1373, 1241, 1215, 1153, 1111,

1030, 1006, 862, 811, 696, 670; ^{1}H NMR (DMSO-d_6 ,400MHz) δ ppm 9.60 (1 H, s, N*H*), 7.50 (2 H, d, *J*=8.0 Hz, 2 X C(10)*H*), 7.37 (1 H, dd, *J*=8.8, 6.8 Hz, C(5)*H*), 7.11 (2 H, d, *J*=8.0 Hz, 2 X C(11)*H*), 6.99 (1 H, dd, *J*=11.1, 3.0 Hz, C(2)*H*), 6.78 (1 H, td, *J*=8.6, 3.0 Hz, C(4)*H*), 3.09 (6 H, s, 2 X C(8)H_3), 2.26 ppm (3 H, s, C(15)H_3); ^{13}C NMR (DMSO-d_6 ,101MHz) δ ppm 162.1, 156.7, 146.2, 138.8, 137.9, 135.8, 129.0, 126.4, 117.1, 110.7, 105.6, 38.4, 21.7 ppm; ^{19}F NMR (DMSO-d_6 ,377MHz) δ ppm -118.76; HRMS (ESI) *m/z*: calc for monomeric complex $[M\text{-}OTs+CH3CN]^+$ $[C_{11}H_{13}FN_3OPd]^+$: 328.0077, Found 328.0072. An acetonitrile derivative **16b** of the complex **16a** was crystallised from CH_3CN and the crystal structure of the cation is shown below with thermal ellipsoids drawn at 50% probability. Crystallographic details are given in the relevant section at the end and in the CIF.

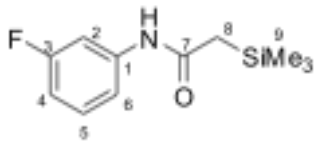


Butyl 3-(*N*-(3-fluoro-2-iodophenyl)acetamido)propanoate:



N-(3-fluoro-2-iodophenyl)acetamide **1c** (42 mg, 0.15 mmol), K_2CO_3 (56 mg, 0.4 mmol), NBu_4Cl (42 mg, 0.15 mmol), PPh_3 (4 mg) and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol) were taken in a schlenk tube filled with argon. Degassed anhydrous DMF (2 mL) was added to the schlenk and the mixture was stirred at room temperature for 15 min. The solution of butyl acrylate (38 mg, 0.3 mmol) in DMF (0.3 mL) was added to the above mixture and the reaction mixture was stirred for 8 h at room temperature under argon. Water (5 mL) was added to the reaction mixture and the product was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with water (3 x 5 mL), dried over $MgSO_4$, filtered, concentrated *in vacuo* and the residue was subjected to column chromatography (ethyl acetate / pentane, 3:1) to yield the product (38 mg, 60 %); ν_{max} ($CHCl_3$) 3019, 2963, 2875, 1729, 1664, 1589, 1570, 1464, 1436, 1392, 1309, 1216, 1185, 1078, 999, ; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.39 (1 H, dt, *J* = 8.2, 6.1 Hz, C(5)*H*), 7.12-7.05 (1 H, m, C(4)*H*, C(6)*H*), 4.40 (1 H, ddd, *J* = 14.5, 8.0, 6.8 Hz, C(9)*H*), 4.01 (1 H, t, *J* = 6.7 Hz, C(12)*H*), 3.44 (1 H, ddd, *J* = 14.5, 8.0, 6.4 Hz), 2.64 (2 H, m, C(10)H_2), 1.78 (3 H, s, C(8)H_3), 1.60-1.51 (2 H, m, C(13)H_2), 1.39-1.28 (2 H, m, C(14)H_2), 0.91 (3 H, t, *J* = 7.4 Hz, C(15)H_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 171.48 (*C*(11)), 170.02 (*C*(7)), 162.93 (d, *J* = 251.0 Hz, *C*(3)), 146.84 (d, *J* = 2.6 Hz, *C*(1)), 130.58 (d, *J* = 9.2 Hz, *C*(5)), 125.85 (d, *J* = 3.0 Hz, *C*(6)), 115.57 (d, *J* = 20.5 Hz, *C*(4)), 88.69 (d, *J* = 24.7 Hz, *C*(2)), 64.60 (*C*(12)), 44.44 (*C*(9)), 32.87 (*C*(12)), 30.52 (*C*(10)), 22.74 (*C*(13)), 19.10 (*C*(14)), 13.69 (*C*(15)); ^{19}F NMR (377 MHz, $CDCl_3$) δ ppm -86.78; HRMS (ESI) *m/z*: calc for $C_{15}H_{19}FINO_3$ [M+Na]: 430.0286, Found 430.0290.

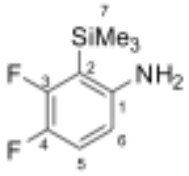
_N_-(3-fluoro-2-iodophenyl)-2-(trimethylsilyl)acetamide:



A solution of *N*-(3-fluoro-2-iodophenyl)acetamide (56 mg, 0.2 mmol) and TMEDA (45 mg, 0.4 mmol) in THF (20 mL) was cooled to -78 ˚C and *t*-BuLi (1.7 M in pentane) (11.8 mL, 20

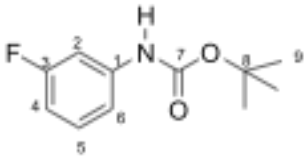
mmol) was added dropwise while stirring the mixture vigorously. After 1 h Me_3SiCl (0.05 mL, 0.4 mmol) was added drop wise keeping the reaction mixture at -78 ˚C followed by stirring for 2 h. Then the mixture was warmed slowly to room temperature and stirred overnight. The reaction was quenched by adding saturated NH_4Cl (10 mL) and the organic layer was extracted, dried with $MgSO_4$, saturated *in vacuo* and purified by column chromatography (ethyl acetate / pentane, 3:1) to get the product (25 mg, 55 %); ν_{max} ($CHCl_3$) 3306, 3018, 2959, 1653, 1608, 1543, 1491, 1441, 1351, 1319, 1253, 1216, 1169, 1136, 1093, 963, 855, 760, 681, 668; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.44 (1 H, d, *J* = 11.0 Hz, C(2)*H*), 7.31 (1 H, s, N*H*), 7.21 (1 H, dt, *J* = 8.1, 6.5 Hz, C(5)*H*), 7.09 (1 H, dd, *J* = 8.1, 1.0 Hz, C(6)*H*), 6.76 (1 H, dt, *J* = 8.3, 1.7 Hz, C(4)*H*), 1.95 (2 H, s, C(8)H_2), 0.16 (9 H, s, 3 x C(9)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.81 (*C*(7)), 162.98 ((d, *J* = 245.4 Hz, *C*(3)), 139.84 (d, *J* = 10.8 Hz, *C*(1)), 129.94 (d, *J* = 9.4 Hz, *C*(5)), 114.93 (d, *J* = 2.3 Hz, *C*(6)), 110.53 (d, *J* = 21.3 Hz, *C*(4)), 107.27 (d, *J* = 26.3 Hz, *C*(2)), 30.66 (*C*(8)), -1.30 (3 x *C*(9)); ^{19}F NMR (235 MHz, $CDCl_3$) δ ppm -111.67; (CI) *m/z*: calc for $C_{11}H_{16}FNOSi$ $[M+Na]^+$: 248.0877, Found 248.0880.

3-fluoro-2-(trimethylsilyl)aniline:[8]



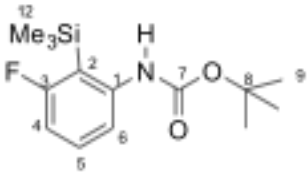
(2-fluoro-6-nitrophenyl)trimethylsilane[8] (1.16 g, 5 mmol) was dissolved in DMF (15 mL) and $SnCl_2.2H_2O$ was added to it. The mixture was stirred for 24 h at room temperature. Water was added to the reaction mixture and the product was extracted with ether (3 x 30 mL). The combined organic phase was washed with water (3 x 50 mL), dried over $MgSO_4$ and concentrated *in vacuo* to get the product[9] (550 mg, 36 %); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 6.92 (1 H, dd, *J* = 18.7, 9.0 Hz, C(5)*H*), 6.29 (1 H, ddd, *J* = 8.7, 3.4, 1.5 Hz, C(6)*H*), 0.42 (1 H, d, *J* = 1.9 Hz, 3 x C(7)H_3); (CI) *m/z*: calc for $C_9H_{13}F_2NSi$ $[M]^+$: 201.08, Found 201.08.

***tert*-butyl 3-fluorophenylcarbamate:**[10]



Di-*tert*-butyl dicarbonate (4.8 g, 22 mmol) was added to 3-fluoroaniline (2.2 g, 20 mmol) in dry THF (25 mL) and the mixture was stirred at room temperature for 12 h. THF was evaporated and the residue was taken up in hexane and filtered. The white solid product (2.8 g, 67 %) was recrystallized from dichlomethane and hexane; m.p. 122-125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.32 (1 H, d, *J* = 11.2 Hz, C(2)*H*), 7.21 (1 H, dt, *J* = 8.2, 6.6 Hz, C(5)*H*), 6.99 (1 H, dd, *J* = 8.2, 1.3 Hz, C(6)*H*), 6.72 (1 H, m, C(4)*H*), 6.66 (1 H, s, N*H*), 1.52 (9 H, s, 3 x C(9)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 163.20 (d, *J* = 244.1 Hz, *C*(3)), 152.48 (*C*(7)), 140.04 (d, *J* = 11.0 Hz, *C*(1)), 129.99 (d, *J* = 9.5 Hz, *C*(5)), 113.70 (d, *J* = 1.8 Hz, *C*(6)), 109.59 (d, *J* = 21.4 Hz, *C*(4)), 105.84 (d, *J* = 26.7 Hz, *C*(2)), 80.95 (*C*(8)), 28.29 (3 x *C*(9)); ^{19}F NMR (377 MHz, $CDCl_3$) δ ppm -111.85.

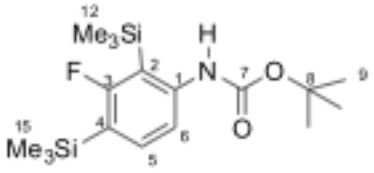
***tert*-butyl 3-fluoro-2-(trimethylsilyl)phenylcarbamate:**



tert-butyl 3-fluorophenylcarbamate (1.85 g, 8.76 mmol) was dissolved in anhydrous THF (100 mL) under argon and cooled to -78 °C. 1.5 M *t*-BuLi in hexane (11.7 mL, 17.5 mmol) was added and the reaction stirred at -78 °C for one hour. Chlorotrimethylsilane (3.9 g, 36 mmol) was added drop wise to the above reaction mixture and stirred at -78 °C for 4 h and was warmed to ambient temperature and stirred for 16 h. The reaction was quenched with sat. NH_4Cl solution (70 mL) and the two layers were separated. The aqueous phase was

extracted with ether (2 x 50 mL). The combined organic phases were washed with brine (2 x 50 ml) before being dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The product was purified by flash column chromatography (ether / pentane, 9:1) yielding the title compound (727 mg, 26 %) as a white solid; mp 74 °C; ν_{max} ($CHCl_3$) 3251 (s, N-H), 2974 (s, C-H), 1697 (s, C=O), 1250 (s, C-Si), 1163 (C-F); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.54 (1 H, d, *J* = 8.1 Hz, C(6)*H*), 7.33-7.26 (1 H, m, C(5)*H*), 6.74 (1 H, dt, *J* = 8.4 Hz, *J* = 0.7 Hz, C(4)*H*), 6.61 (1 H, bs, N*H*), 1.51 (9 H, s, 3 x C(9)H_3), 0.40 (9 H, d, *J* = 1.9 Hz, 3xC(12)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 167.48 (d, *J* = 239.4 Hz, *C*(3)F), 153.14 (*C*(7)), 143.51 (d, *J* = 13.2 Hz, *C*(1)), 131.48 (d, *J* = 10.6 Hz, *C*(5)), 118.16 (*C*(6)), 110.77 (d, *J* = 27.1 Hz, *C*(4)), 80.50 (*C*(8)), 28.35 (s, 3 x *C*(9)), 0.96 (d, *J* = 3.7 Hz, 3 x *C*(12)); ^{19}F NMR (377 MHz, $CDCl_3$) δ ppm -96.74 ; HRMS (ESI) *m/z*: calc for $C_{14}H_{22}FNO_2Si$ [M-H]: 282.1326, Found 282.1320.

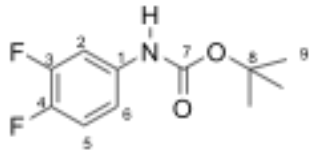
***tert*-butyl 3-fluoro-2,4-bis(trimethylsilyl)phenylcarbamate:**



The compound was isolated by column chromatography (ether / pentane, 9:1) as a white solid (415 mg, 14 %) from the reaction above for the preparation of *tert*-butyl 3-fluoro-2-(trimethylsilyl)phenylcarbamate; m.p. 41-43 °C; ν_{max} ($CHCl_3$) 3467 (s, N-H), 2958 (s, C-H), 1727 (s, C=O), 1251 (s, C-Si), 1157 (C-F); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.57 (1 H, d, *J* = 7.9 Hz, C(6)*H*), 7.38 (1 H, dd, *J* = 7.9, 6.8 Hz, C(5)*H*), 6.69 (1 H, bs, N*H*), 1.53 (9 H, s, 3 x C(9)H_3), 0.43 (1 H, d, *J* = 2.0 Hz, 3 x C(12)H_3), 0.30 (1 H, d, *J* = 1.0 Hz, C(15)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 172.13 (d, *J* = 234.9 Hz, *C*(3)), 153.03 (s, *C*(7)), 145.02 (d, *J* = 13.6 Hz, *C*(1)), 137.05 (d, *J* = 14.4 Hz, *C*(5)), 120.50 (d, *J* = 37.2 Hz, *C*(4)), 117.56 (*C*(6)), 115.30 (d, *J* = 36.3 Hz, *C*(2)), 80.47 (*C*(8)), 28.35 (3 x *C*(9)), 1.12 (d, *J* = 3.9 Hz, 3 x *C*(12)), -

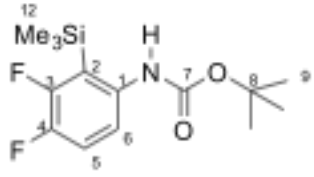
0.93 (d, *J* = 1.6 Hz, 3 x *C*(15)); ^{19}F NMR (377 MHz, $CDCl_3$) δ ppm -82.77; HRMS (ESI) *m/z*: calc for $C_{17}H_{29}FNO_2Si_2$ [M-H]: 354.1721, Found 354.1719.

***tert*-butyl 3,4-difluorophenylcarbamate:**[11]



Di-*tert*-butyl dicarbonate (2.4 g, 11 mmol) was added to 3,4-difluoroaniline (1.3 g, 10 mmol) in dry THF (25 mL) and the mixture was stirred at room temperature for 12 h. THF was evaporated and the residue was taken up in hexane and filtered. The white solid product (1.5 g, 65 %) was recrystallized from dichlomethane and hexane. mp 134-137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.47-7.38 (1 H, m, C(2)*H*), 7.08-6.99 (1 H, m, C(5)*H*), 6.93-6.87 (1 H, m, C(6)*H*), 6.61 (1 H, s, N*H*), 1.50 (9 H, s, 3 x C(9)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 152.59 (s, *C*(7)), 150.20 (dd, *J* = 246.4, 13.2 Hz, *C*(3)), 146.19 (dd, *J* = 243.5, 12.8 Hz, *C*(4)), 134.96 (dd, *J* = 9.0, 2.9 Hz, *C*(1)), 117.09 (dd, *J* = 18.1, 1.2 Hz, *C*(5)), 114.11-113.80 (m, *C*(6)), 108.19 (d, *J* = 21.5 Hz, *C*(2)), 81.08 (*C*(8)), 28.26 (3 x *C*(9)); ^{19}F NMR (377 MHz, $CDCl_3$) δ ppm -136.10, -144.92; ESI *m/z*: calc for $C_{11}H_{12}F_2NO_2$ [M-H]: 228.0836, Found 228.10.

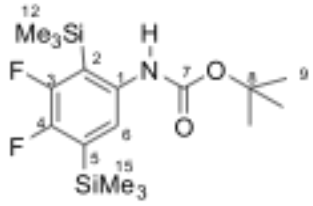
***tert*-butyl 3,4-difluoro-2-(trimethylsilyl)phenylcarbamate:**



tert-butyl 3,4-difluorophenylcarbamate (916 mg, 4 mmol) was dissolved in anhydrous THF (50 mL) under argon and cooled to -78 °C. 1.5 M *t*-BuLi in hexane (6.6 mL, 10 mmol) was added and the reaction stirred at -78 °C for 1 h. Chlorotrimethylsilane (1.1 g, 10 mmol) was

added dropwise to the above reaction mixture and stirred at -78 °C for four hours and was warmed to ambient temperature and stirred for 16 h. The reaction was quenched with sat. NH_4Cl solution (40 mL) and the two layers were separated. The aqueous phase was extracted with ether (2 x 30 mL). The combined organic phases were washed with brine (2 x 30 ml) before being dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The product was purified by flash column chromatography (ether / pentane, 9:1) yielding the title compound (448 mg, 37 %) as a white solid; ν_{max} ($CHCl_3$) 3323 (s, N-H), 2982 (s, C-H), 1704 (s, C=O), 1497 (s, aromatic ring), 1394 (s, C-N), 1254 (s, C-Si), 1160 (C-F); ^{1}H NMR (400 MHz, $CDCl_3$) δppm 7.40-7.29 (1 H, m, C(6)*H*), 7.15-7.05 (1 H, m, C(5)*H*), 6.42 (1 H, s, N*H*), 1.50 (9 H, s, 3 x C(9)H_3), 0.41 (9 H, d, *J* = 1.9 Hz, 3 x C(12)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 154.06 (dd, *J* = 240.9, 12.0 Hz, *C*(3)), 153.57 (*C*(7)), 147.51 (dd, *J* = 247.4, 16.8 Hz, *C*(4)), 137.78 (dd, *J* = 11.4, 3.4 Hz, *C*(1)), 120.90-119.80 (m, *C*(2,5)), 118.12 (dd, *J* = 18.0, 1.7 Hz, *C*(6)), 80.61 (*C*(8)), 28.32 (3 x *C*(9)), 0.66 (d, *J* = 3.7 Hz, 3 x *C*(12)); ^{19}F NMR (377 MHz, $CDCl_3$) δ ppm -123.24 (ddd, *J* = 23.8, 7.3, 1.7 Hz, C(4)*F*), -142.83 (bs, C(3)*F*); HRMS (ESI) *m/z*: calc for $C_{14}H_{21}F_2NO_2SiNa$ [M+Na]: 324.1207, Found 324.1202.

***tert*-butyl 3,4-difluoro-2,5-bis(trimethylsilyl)phenylcarbamate:**



The compound was isolated by column chromatography (ether / pentane, 9:1) as white solid (279 mg, 18 %) from the reaction above for the preparation of *tert*-butyl 3,4-difluoro-2-(trimethylsilyl)phenylcarbamate; ν_{max} ($CHCl_3$) 3290 (s, N-H), 2986 (s, C-H[aromatic]), 2902 (s, C-H[aliphatic]), 1674 (s, C=O), 1503 (s, aromatic ring), 1382 (s, C-N), 1251 (s, C-Si), 1170 (C-F); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.26 (1 H, s, C(6)*H*), 6.29 (1 H, bs, N*H*), 1.49

(9 H, s, 3 x C(9)H_3), 0.39 (9 H, d, J = 1.8 Hz, 3 x C(12) H_3), 0.32 (9 H, s, 3 x C(15) H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 153.79 (*C*(7)), 153.68 (dd, J = 243.9, 16.0 Hz, *C*(3)), 151.63 (dd, J = 241.60, 15.4 Hz, *C*(4)), 137.29 (dd, J = 10.0, 2.7 Hz, *C*(1)), 130.39 (d, J = 27.9 Hz, *C*(5), 126.10-125.23 (m, *C*(6)), 80.46 (*C*(8)), 28.37 (3 x *C*(9)), 0.59 (d, J = 3.6 Hz, 3 x *C*(12)), -1.16 (d, J = 1.2 Hz, 3 x *C*(15)); ^{19}F NMR (377 MHz, $CDCl_3$) δ ppm -124.21 (C(4)*F*), -131.79 (d, J = 21.23 Hz, C(3)*F*); HRMS (ESI) *m/z*: calc for $C_{17}H_{29}F_2NO_2Si_2Na$ [M+Na]: 396.1603, Found 396.1597.

Single Crystal X-ray Structure Analyses:

For each of **5**, **8** and **16** diffraction data were collected using an Enraf-Nonius KappaCCD diffractometer (Mo-Ká radiation (ë = 0.71073 Å) at 150 K with an Oxford Cryosystems Cryostream N2 open-flow cooling device.[12] Data were processed using the DENZO-SMN package, including inter-frame scaling (which was carried out using Scalepack within DENZO-SMN).[13] Structure solution was carried out using SIR92[14] (**5** and **16**) or SHELXS86[15] (**8**) and refined using full-matrix least-squares on F^2 (**5** and **16**) or F (**8**) within the CRYSTALS suite.[16] In general, all non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were visible in the difference map and their positions and isotropic displacement parameters were refined using restraints prior to inclusion into the model using riding constraints.

In the case of compound **8**, the crystal was found to be twinned:

Rotation Angle: -1.911; Laboratory Vector: -0.6274 0.4441 0.6397
Reciprocal Cell Vector: 0.97 -1.08 8.00; Direct Cell Vector: 3.97 -5.07 12.00
H' = +1.005*H -0.021*K +0.001*L
K' = +0.052*H +0.991*K
L' = +0.029*H +0.011*K +0.997*L

ROTAX[17] was used to examine the possibility of this twin and the R-indices improved with the inclusion of a twin component, the scale factor for which refined to 0.236(14).

In the case of **16**, on initial refinement, the tosylate oxygen ADPs were decidedly prolate and a small, but significant amount of residual electron density was visible between the atoms. Examination of the slant Fourier clearly showed the presence of a second orientation for the SO~3~ group, which was modelled with an occupancy of 27.4%, however same distance restraints and SIMU/DELU were used to maintain a sensible geometry and thermal parameters.

Crystallographic data for all eight structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC XXXXXX-XXXXXX. Copies of these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, Organometallics, 1996, **15**, 1518–1520.
2. M. Xian, J. Lu, X. Zhu, L. Mu and J.-P. Cheng, J. Chem. Res., Synop., 1998, 442–443.
3. A. Alcaide, A. M. Municio, A. Ribera and M. D. Stamm, An. R. Soc. Esp. Fis. Quim., Ser. B, 1966, **62**, 1391–1402.
4. R. Laudien and R. Mitzner, J. Chem. Soc. Perkin Trans. 2, 2001, 2226–2229.
5. Y. Mido and C. Furusawa, J. Mol. Struct., 1982, **82**, 23–28.
6. C. W. Todd, (E. I. du Pont de Nemours & Co.). US 2655445, 1953.
7. V. Bekarek, K. Ubik, J. Barborik and J. Socha, Collect. Czech. Chem. Comm., 1977, **42**, 1368–1373.
8. A. H. Katz and C. A. Demerson, (American Home Products Corp., USA), US 4822781, 1989.
9. S. Maiorana, C. Baldoli, E. Licandro, L. Casiraghi, E. de Magistris, A. Paio, S. Provera and P. Seneci, Tetrahedron Lett., 2000, **41**, 7271–7275.
10. R. D. Clark and J. M. Caroon, J. Org. Chem., 1982, **47**, 2804–2806.
11. J. C. Carretero, J. L. Garcia Ruano and M. Vicioso, Tetrahedron, 1992, **48**, 7373–7382.
12. Cosier, J.; Glazer, A. M.; J. Appl. Cryst., 1986, **19**, 105–107.
13. Z. Otwinowski, W. Minor, Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods Enzymol. 1997, 276, Eds C. W. Carter, R. M. Sweet, Academic Press.
14. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori & M. Camalli, J. Appl. Cryst., 1994, **27**, 435.
15. G. M. Sheldrick, Acta Cryst., 2008, **A64**, 112–122.
16 P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout & D. J. Watkin, J. Appl. Cryst., 2003, **36**, 1487.
17. R. I. Cooper, R. O. Gould, S. Parsons & D. J. Watkin, J. Appl. Cryst., 2002, **35**, 168–174.

Methodology

A typical crystal for each sample was mounted in perfluorinated polyether oil and cooled to 150 K[1] where data were collected using a Nonius Kappa-CCD area detector diffractometer (λ = 0.71073 Å). Cell parameters and intensity data were processed using the DENZO-SMN package and reflection intensities were corrected for absorption effects by the multi-scan method.[2] The structures were solved by direct methods[3] and refined by full-matrix least squares on F^2 using the CRYSTALS suite.[4]

CIF data

```
#============================================================
================
data_global
#============================================================
================

_publ_contact_author                'John M. Brown'
_publ_contact_author_email           john.brown@chem.ox.ac.uk

loop_
_publ_author_name
_publ_author_address
 'Rauf, Waqar'
;
Chemistry Research Laboratory,
University of Oxford,
Mansfield Road,
Oxford OX1 3TA. UK.
;
 'Thompson, Amber L.'
;
Chemical Crystallography Department,
Chemistry Research Laboratory,
University of Oxford,
Mansfield Road,
Oxford OX1 3TA. UK.
;
 'Brown, John M.'
;
Chemistry Research Laboratory,
University of Oxford,
Mansfield Road,
Oxford OX1 3TA. UK.
;

_journal_name_full
 'Chemical Communications'
```

```
_journal_volume                   '?'
_journal_page_first               '?'
_journal_page_last                '?'
_journal_year                     '2009'
_ccdc_journal_depnumber           '?'

_publ_section_title
;
Comparative Catalytic C-H vs. C-Si Activation of
Arenes with Pd Complexes Directed by Urea or Amide
Groups
;

_publ_section_abstract
;
Analysis of regiocontrol in Pd-catalysed C-H activation
leads to observations of aryltrimethylsilyl activation
and to superior results with urea-based substrates.
;


#============================================================
================
data_5
#============================================================
================
_audit_creation_date        08-06-13
_audit_creation_method CRYSTALS_ver_12.86

_oxford_structure_analysis_title  '5877'
_chemical_name_systematic         .
_chemical_melting_point           'not measured'

_cell_length_a                    7.2492(2)
_cell_length_b                    8.7969(3)
_cell_length_c                    16.6174(6)
_cell_angle_alpha                 90.7614(17)
_cell_angle_beta                  101.0913(17)
_cell_angle_gamma                 100.9648(19)
_cell_volume                      1019.55(6)

_symmetry_cell_setting            'Triclinic'
_symmetry_space_group_name_H-M    'P -1 '
_symmetry_space_group_name_Hall   '-P 1'
loop_
 _symmetry_equiv_pos_as_xyz
 'x,y,z'
 '-x,-y,-z'

loop_
_atom_type_symbol
_atom_type_scat_dispersion_real
```

```
_atom_type_scat_dispersion_imag
_atom_type_scat_Cromer_Mann_a1
_atom_type_scat_Cromer_Mann_b1
_atom_type_scat_Cromer_Mann_a2
_atom_type_scat_Cromer_Mann_b2
_atom_type_scat_Cromer_Mann_a3
_atom_type_scat_Cromer_Mann_b3
_atom_type_scat_Cromer_Mann_a4
_atom_type_scat_Cromer_Mann_b4
_atom_type_scat_Cromer_Mann_c
_atom_type_scat_source
 C       0.0033   0.0016   2.3100  20.8439   1.0200  10.2075
1.5886   0.5687
   0.8650  51.6512   0.2156 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
 H       0.0000   0.0000   0.4930  10.5109   0.3229  26.1257
0.1402   3.1424
   0.0408  57.7998   0.0030 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
 F       0.0171   0.0103   3.5392  10.2825   2.6412   4.2944
1.5170   0.2615
   1.0243  26.1476   0.2776 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
 N       0.0061   0.0033  12.2126   0.0057   3.1322   9.8933
2.0125  28.9975
   1.1663   0.5826 -11.5290 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
 O       0.0106   0.0060   3.0485  13.2771   2.2868   5.7011
1.5463   0.3239
   0.8670  32.9089   0.2508 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
 Pd     -0.9988   1.0072  19.3319   0.6987  15.5017   7.9893
5.2954  25.2052
   0.6058  76.8986   5.2659 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
 S       0.1246   0.1234   6.9053   1.4679   5.2034  22.2151
1.4379   0.2536
   1.5863  56.1720   0.8669 'International Tables Vol C
4.2.6.8 and 6.1.1.4'


_cell_formula_units_Z                  2

# Given Formula = C17 H16 F2 N2 O4 Pd1 S1
# Dc =      1.59 Fooo =    532.00 Mu =     10.53 M =    488.79
# Found Formula = C19 H19 F2 N3 O4 Pd1 S1
# Dc =      1.73 FOOO =    532.00 Mu =     10.62 M =    529.84

_chemical_formula_sum             'C19 H19 F2 N3 O4 Pd1 S1'
_chemical_formula_moiety          'C12 H12 F2 N3 O Pd, C7 H7
O3 S'
_chemical_compound_source                .
```

```
_chemical_formula_weight            529.84


_cell_measurement_reflns_used         4141
_cell_measurement_theta_min              5
_cell_measurement_theta_max             27
_cell_measurement_temperature          150

_exptl_crystal_description        'needle'
_exptl_crystal_colour             'clear_pale_colourless'
_exptl_crystal_size_min           0.03
_exptl_crystal_size_mid           0.06
_exptl_crystal_size_max           0.18

_exptl_crystal_density_diffrn     1.726
_exptl_crystal_density_meas       'not measured'
_exptl_crystal_density_method     'not measured'
# Non-dispersive F(000):
_exptl_crystal_F_000              532
_exptl_absorpt_coefficient_mu     1.062

# Sheldrick geometric approximatio 0.94 0.97
_exptl_absorpt_correction_type    multi-scan
_exptl_absorpt_process_details    'DENZO/SCALEPACK (Otwinowski
& Minor, 1997)'
_exptl_absorpt_correction_T_min   0.77
_exptl_absorpt_correction_T_max   0.97
# For a Kappa CCD, set Tmin to 1.0 and
# Tmax to the ratio of max:min frame scales in scale_all.log
_diffrn_measurement_device        'Nonius KappaCCD'
_diffrn_measurement_device_type   'Area'
_diffrn_radiation_monochromator   'graphite'
_diffrn_radiation_type            'Mo K\a'
_diffrn_radiation_wavelength          0.71073
_diffrn_measurement_method        \w

# If a reference occurs more than once, delete the author
# and date from subsequent references.
_computing_data_collection        'COLLECT (Nonius, 1997-
2001).'
_computing_cell_refinement        'DENZO/SCALEPACK (Otwinowski
& Minor, 1997)'
_computing_data_reduction         'DENZO/SCALEPACK (Otwinowski
& Minor, 1997)'
_computing_structure_solution     'SIR92 (Altomare et al.,
1994)'
_computing_structure_refinement   'CRYSTALS (Betteridge et
al., 2003)'
_computing_publication_material   'CRYSTALS (Betteridge et
al., 2003)'
_computing_molecular_graphics     'CAMERON (Watkin et al.,
1996)'
```

```
_diffrn_standards_interval_time   .
_diffrn_standards_interval_count  .
_diffrn_standards_number          0
_diffrn_standards_decay_%         .

_diffrn_ambient_temperature        150
_diffrn_reflns_number             14648
_reflns_number_total              4643
_diffrn_reflns_av_R_equivalents   0.043
# Number of reflections with Friedels Law is 4643
# Number of reflections without Friedels Law is 7830
# Theoretical number of reflections is about 4704


_diffrn_reflns_theta_min          5.118
_diffrn_reflns_theta_max          27.542
_diffrn_measured_fraction_theta_max 0.985

_diffrn_reflns_theta_full         25.614
_diffrn_measured_fraction_theta_full 0.991


_diffrn_reflns_limit_h_min        -9
_diffrn_reflns_limit_h_max        8
_diffrn_reflns_limit_k_min        -11
_diffrn_reflns_limit_k_max        10
_diffrn_reflns_limit_l_min        -21
_diffrn_reflns_limit_l_max        21
_reflns_limit_h_min               -9
_reflns_limit_h_max               9
_reflns_limit_k_min               -11
_reflns_limit_k_max               11
_reflns_limit_l_min               0
_reflns_limit_l_max               21

_oxford_diffrn_Wilson_B_factor    2.18
_oxford_diffrn_Wilson_scale       4.77

_atom_sites_solution_primary      direct
#heavy,direct,difmap,geom
# _atom_sites_solution_secondary  difmap
_atom_sites_solution_hydrogens    geom

_refine_diff_density_min          -1.10
_refine_diff_density_max          0.88


# The current dictionary definitions do not cover the
# situation where the reflections used for refinement were
# selected by a user-defined sigma threshold
```

```
# The values actually used during refinement
_oxford_reflns_threshold_expression_ref     I>-3.0\s(I)
_refine_ls_number_reflns          4643
_refine_ls_number_restraints      0
_refine_ls_number_parameters      272
_oxford_refine_ls_R_factor_ref    0.0439
_refine_ls_wR_factor_ref          0.0862
_refine_ls_goodness_of_fit_ref    1.0018
_refine_ls_shift/su_max           0.000343


# The values computed from all data
_oxford_reflns_number_all         4643
_refine_ls_R_factor_all           0.0439
_refine_ls_wR_factor_all          0.0862

# The values computed with a 2 sigma cutoff - a la SHELX
_reflns_threshold_expression      I>2.0\s(I)
_reflns_number_gt                 4061
_refine_ls_R_factor_gt            0.0356
_refine_ls_wR_factor_gt           0.0815

# choose from: rm (reference molecule of known chirality),
# ad (anomolous dispersion - Flack), rmad (rm and ad),
# syn (from synthesis), unk (unknown) or . (not applicable).
_chemical_absolute_configuration  '.'


_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_hydrogen_treatment     constr         # none,
undef, noref, refall,
                                                 # refxyz,
refU, constr or mixed
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
;
 Method= Modified Sheldrick
 w=1/[\s^2^(F^2^) + ( 0.03P)^2^ + 1.39P]
 ,where P=(max(Fo^2^,0) + 2Fc^2^)/3
;
# Insert your own references if required - in alphabetical
order
_publ_section_references
;
Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A.,
Burla, M.C.,
Polidori, G. & Camalli, M. (1994). J. Appl. Cryst. 27, 435.

Betteridge, P.W., Carruthers, J.R., Cooper, R.I.,
Prout, K. & Watkin, D.J. (2003). J. Appl. Cryst. 36, 1487.
```

```
Nonius (1997-2001). COLLECT. Nonius BV, Delft, The
Netherlands.

Otwinowski, Z. & Minor, W. (1997). Methods in Enzymology, Vol.
276,
edited by C. W. Carter Jr & R. M. Sweet, pp. 307--326.
New York: Academic Press.

Watkin, D.J., Prout, C.K. & Pearce, L.J. (1996). CAMERON,
Chemical
Crystallography Laboratory, Oxford, UK.
;

# Uequiv = arithmetic mean of Ui i.e. Ueqiv = (U1+U2+U3)/3

# Replace last . with number of unfound hydrogen atomsattached
to an atom.

# ..._refinement_flags_...
# . no refinement constraints           S special position
constraint on site
# G rigid group refinement of site      R riding atom
# D distance or angle restraint on site T thermal displacement
constraints
# U Uiso or Uij restraint (rigid bond)  P partial occupancy
constraint


loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_occupancy
_atom_site_adp_type
_atom_site_refinement_flags_posn
_atom_site_refinement_flags_adp
_atom_site_refinement_flags_occupancy
_atom_site_disorder_assembly
_atom_site_disorder_group
_oxford_atom_site_special_shape
_atom_site_attached_hydrogens
Pd1 Pd 0.29871(3) 0.03499(3) -0.066304(13) 0.0259 1.0000 Uani
. . . . . . .
O2 O 0.3721(3) 0.2433(2) -0.00695(12) 0.0304 1.0000 Uani . . .
. . . .
C3 C 0.3576(4) 0.2795(3) 0.06463(17) 0.0268 1.0000 Uani . . .
. . . .
```

```
N4 N 0.2902(3) 0.1799(3) 0.11582(14) 0.0257 1.0000 Uani . . .
. . . .
C5 C 0.2193(4) 0.0182(3) 0.10230(17) 0.0239 1.0000 Uani . . .
. . . .
C6 C 0.2104(4) -0.0658(3) 0.02911(17) 0.0249 1.0000 Uani . . .
. . . .
C7 C 0.1288(4) -0.2248(3) 0.02561(18) 0.0290 1.0000 Uani . . .
. . . .
C8 C 0.0634(4) -0.2927(3) 0.09127(19) 0.0306 1.0000 Uani . . .
. . . .
F9 F -0.0173(3) -0.4461(2) 0.08693(12) 0.0439 1.0000 Uani . .
. . . . .
C10 C 0.0787(4) -0.2071(4) 0.16329(18) 0.0292 1.0000 Uani . .
. . . . .
C11 C 0.1555(4) -0.0523(4) 0.16972(18) 0.0287 1.0000 Uani . .
. . . . .
F12 F 0.0153(3) -0.2774(2) 0.22792(11) 0.0407 1.0000 Uani . .
. . . . .
C13 C 0.4191(5) 0.4465(4) 0.0938(2) 0.0348 1.0000 Uani . . . .
. . .
N14 N 0.2296(4) -0.1608(3) -0.13820(15) 0.0304 1.0000 Uani . .
. . . . .
C15 C 0.2001(4) -0.2550(4) -0.18923(18) 0.0294 1.0000 Uani . .
. . . . .
C16 C 0.1633(5) -0.3769(4) -0.2533(2) 0.0349 1.0000 Uani . . .
. . . .
N17 N 0.3850(4) 0.1471(3) -0.16969(16) 0.0317 1.0000 Uani . .
. . . . .
C18 C 0.4253(4) 0.1925(4) -0.22903(19) 0.0313 1.0000 Uani . .
. . . . .
C19 C 0.4793(6) 0.2505(5) -0.3049(2) 0.0487 1.0000 Uani . . .
. . . .
S20 S 0.37636(10) 0.27230(9) 0.34179(4) 0.0288 1.0000 Uani . .
. . . . .
O21 O 0.5338(3) 0.3941(3) 0.38059(14) 0.0392 1.0000 Uani . . .
. . . .
O22 O 0.4274(3) 0.1221(3) 0.33193(14) 0.0366 1.0000 Uani . . .
. . . .
O23 O 0.2726(3) 0.3186(3) 0.26323(12) 0.0346 1.0000 Uani . . .
. . . .
C24 C 0.2044(4) 0.2490(4) 0.40590(17) 0.0273 1.0000 Uani . . .
. . . .
C25 C 0.0389(5) 0.1338(4) 0.3854(2) 0.0360 1.0000 Uani . . . .
. . .
C26 C -0.1018(5) 0.1225(4) 0.4318(2) 0.0398 1.0000 Uani . . .
. . . .
C27 C -0.0809(5) 0.2222(4) 0.4999(2) 0.0348 1.0000 Uani . . .
. . . .
C28 C 0.0859(5) 0.3333(4) 0.5204(2) 0.0371 1.0000 Uani . . . .
. . .
C29 C 0.2280(4) 0.3476(4) 0.47416(19) 0.0330 1.0000 Uani . . .
. . . .
```

```
C30 C -0.2364(5) 0.2108(5) 0.5488(2) 0.0474 1.0000 Uani . . .
. . . .
H71 H 0.1177 -0.2893 -0.0220 0.0350 1.0000 Uiso R . . . . . .
H111 H 0.1664 0.0069 0.2194 0.0343 1.0000 Uiso R . . . . . .
H131 H 0.4001 0.4602 0.1490 0.0542 1.0000 Uiso R . . . . . .
H132 H 0.5523 0.4836 0.0929 0.0541 1.0000 Uiso R . . . . . .
H133 H 0.3412 0.5051 0.0583 0.0538 1.0000 Uiso R . . . . . .
H163 H 0.2207 -0.3405 -0.2983 0.0545 1.0000 Uiso R . . . . . .
H162 H 0.2136 -0.4629 -0.2313 0.0542 1.0000 Uiso R . . . . . .
H161 H 0.0296 -0.4067 -0.2718 0.0545 1.0000 Uiso R . . . . . .
H191 H 0.3665 0.2581 -0.3438 0.0784 1.0000 Uiso R . . . . . .
H192 H 0.5457 0.1792 -0.3259 0.0784 1.0000 Uiso R . . . . . .
H193 H 0.5617 0.3499 -0.2949 0.0783 1.0000 Uiso R . . . . . .
H251 H 0.0216 0.0652 0.3401 0.0429 1.0000 Uiso R . . . . . .
H261 H -0.2142 0.0461 0.4172 0.0480 1.0000 Uiso R . . . . . .
H281 H 0.1033 0.4001 0.5669 0.0461 1.0000 Uiso R . . . . . .
H291 H 0.3397 0.4241 0.4888 0.0399 1.0000 Uiso R . . . . . .
H301 H -0.1927 0.2764 0.5979 0.0765 1.0000 Uiso R . . . . . .
H302 H -0.2741 0.1068 0.5649 0.0762 1.0000 Uiso R . . . . . .
H303 H -0.3472 0.2402 0.5173 0.0764 1.0000 Uiso R . . . . . .
H41 H 0.2868 0.2171 0.1632 0.0321 1.0000 Uiso R . . . . . .
loop_
_atom_site_aniso_label
_atom_site_aniso_U_11
_atom_site_aniso_U_22
_atom_site_aniso_U_33
_atom_site_aniso_U_23
_atom_site_aniso_U_13
_atom_site_aniso_U_12
Pd1 0.02714(14) 0.02868(15) 0.02380(13) 0.00205(8) 0.00901(9)
0.00634(9)
O2 0.0379(11) 0.0282(11) 0.0273(10) 0.0031(8) 0.0129(9)
0.0056(9)
C3 0.0289(14) 0.0278(15) 0.0253(14) 0.0029(11) 0.0071(11)
0.0080(11)
N4 0.0294(12) 0.0262(13) 0.0227(11) 0.0017(9) 0.0090(9)
0.0045(10)
C5 0.0198(12) 0.0252(14) 0.0278(14) 0.0037(11) 0.0054(11)
0.0064(10)
C6 0.0224(13) 0.0274(15) 0.0260(14) 0.0015(11) 0.0062(11)
0.0062(11)
C7 0.0335(15) 0.0270(15) 0.0283(14) 0.0006(12) 0.0099(12)
0.0070(12)
C8 0.0318(15) 0.0241(15) 0.0346(16) 0.0029(12) 0.0077(13)
0.0011(12)
F9 0.0629(13) 0.0259(10) 0.0410(11) 0.0005(8) 0.0204(10) -
0.0058(9)
C10 0.0320(15) 0.0314(16) 0.0264(14) 0.0084(12) 0.0121(12)
0.0048(12)
C11 0.0288(14) 0.0315(16) 0.0260(14) 0.0002(12) 0.0066(12)
0.0053(12)
```

```
F12 0.0544(12) 0.0358(11) 0.0319(10) 0.0074(8) 0.0179(9) -
0.0011(9)
C13 0.0476(18) 0.0256(16) 0.0324(16) 0.0018(12) 0.0147(14)
0.0031(13)
N14 0.0301(13) 0.0355(15) 0.0272(13) 0.0017(11) 0.0095(10)
0.0062(11)
C15 0.0279(14) 0.0328(17) 0.0299(15) 0.0060(13) 0.0108(12)
0.0067(12)
C16 0.0380(17) 0.0363(18) 0.0313(16) -0.0044(13) 0.0114(13)
0.0052(13)
N17 0.0334(13) 0.0339(14) 0.0306(13) 0.0018(11) 0.0107(11)
0.0090(11)
C18 0.0333(16) 0.0351(17) 0.0283(15) 0.0039(13) 0.0096(12)
0.0097(13)
C19 0.062(2) 0.057(2) 0.0336(18) 0.0150(16) 0.0222(17)
0.0147(19)
S20 0.0279(4) 0.0337(4) 0.0247(3) -0.0009(3) 0.0086(3)
0.0027(3)
O21 0.0340(12) 0.0436(14) 0.0359(12) -0.0082(10) 0.0123(10) -
0.0072(10)
O22 0.0358(12) 0.0401(13) 0.0370(12) -0.0010(10) 0.0088(10)
0.0134(10)
O23 0.0401(12) 0.0434(13) 0.0237(10) 0.0042(9) 0.0104(9)
0.0120(10)
C24 0.0280(14) 0.0321(16) 0.0225(13) 0.0030(11) 0.0058(11)
0.0070(12)
C25 0.0389(17) 0.0368(18) 0.0306(16) -0.0025(13) 0.0111(13) -
0.0007(14)
C26 0.0331(16) 0.044(2) 0.0402(18) 0.0075(15) 0.0114(14) -
0.0035(14)
C27 0.0331(16) 0.0446(19) 0.0320(16) 0.0112(14) 0.0135(13)
0.0132(14)
C28 0.0395(17) 0.0448(19) 0.0306(16) -0.0013(14) 0.0118(14)
0.0121(15)
C29 0.0307(15) 0.0385(18) 0.0292(15) -0.0026(13) 0.0075(12)
0.0037(13)
C30 0.0418(19) 0.063(3) 0.044(2) 0.0118(18) 0.0212(16)
0.0138(17)

_refine_ls_extinction_coef 65(8)
_refine_ls_extinction_method
    'Larson (1970), Equation 22'
_oxford_refine_ls_scale 0.4631(8)
loop_
 _geom_bond_atom_site_label_1
 _geom_bond_site_symmetry_1
 _geom_bond_atom_site_label_2
 _geom_bond_site_symmetry_2
 _geom_bond_distance
 _geom_bond_publ_flag
Pd1 . Pd1 2_655 3.4636(4)    yes
Pd1 . O2 . 1.999(2)    yes
```

```
Pd1 . C6 . 1.980(3)    yes
Pd1 . N14 . 2.008(3)    yes
Pd1 . N17 . 2.130(3)    yes
O2 . C3 . 1.256(3)    yes
C3 . N4 . 1.322(4)    yes
C3 . C13 . 1.496(4)    yes
N4 . C5 . 1.417(4)    yes
N4 . H41 . 0.855    no
C5 . C6 . 1.399(4)    yes
C5 . C11 . 1.401(4)    yes
C6 . C7 . 1.407(4)    yes
C7 . C8 . 1.371(4)    yes
C7 . H71 . 0.949    no
C8 . F9 . 1.360(3)    yes
C8 . C10 . 1.380(4)    yes
C10 . C11 . 1.365(4)    yes
C10 . F12 . 1.359(3)    yes
C11 . H111 . 0.952    no
C13 . H131 . 0.962    no
C13 . H132 . 0.962    no
C13 . H133 . 0.961    no
N14 . C15 . 1.138(4)    yes
C15 . C16 . 1.452(4)    yes
C16 . H163 . 0.954    no
C16 . H162 . 0.949    no
C16 . H161 . 0.943    no
N17 . C18 . 1.138(4)    yes
C18 . C19 . 1.460(4)    yes
C19 . H191 . 0.954    no
C19 . H192 . 0.960    no
C19 . H193 . 0.954    no
S20 . O21 . 1.449(2)    yes
S20 . O22 . 1.454(2)    yes
S20 . O23 . 1.480(2)    yes
S20 . C24 . 1.775(3)    yes
C24 . C25 . 1.398(4)    yes
C24 . C29 . 1.382(4)    yes
C25 . C26 . 1.382(4)    yes
C25 . H251 . 0.932    no
C26 . C27 . 1.390(5)    yes
C26 . H261 . 0.941    no
C27 . C28 . 1.384(5)    yes
C27 . C30 . 1.502(4)    yes
C28 . C29 . 1.387(4)    yes
C28 . H281 . 0.939    no
C29 . H291 . 0.939    no
C30 . H301 . 0.958    no
C30 . H302 . 0.960    no
C30 . H303 . 0.952    no
loop_
 _geom_angle_atom_site_label_1
 _geom_angle_site_symmetry_1
```

```
 _geom_angle_atom_site_label_2
 _geom_angle_site_symmetry_2
 _geom_angle_atom_site_label_3
 _geom_angle_site_symmetry_3
 _geom_angle
 _geom_angle_publ_flag
Pd1 2_655 Pd1 . O2 . 83.21(6)    yes
Pd1 2_655 Pd1 . C6 . 72.97(8)    yes
O2 . Pd1 . C6 . 92.26(10)    yes
Pd1 2_655 Pd1 . N14 . 100.05(7)    yes
O2 . Pd1 . N14 . 173.08(9)    yes
C6 . Pd1 . N14 . 94.52(11)    yes
Pd1 2_655 Pd1 . N17 . 108.86(7)    yes
O2 . Pd1 . N17 . 87.12(9)    yes
C6 . Pd1 . N17 . 177.97(10)    yes
N14 . Pd1 . N17 . 86.06(10)    yes
Pd1 . O2 . C3 . 128.70(19)    yes
O2 . C3 . N4 . 124.3(3)    yes
O2 . C3 . C13 . 118.0(3)    yes
N4 . C3 . C13 . 117.7(3)    yes
C3 . N4 . C5 . 128.5(2)    yes
C3 . N4 . H41 . 116.5    no
C5 . N4 . H41 . 115.0    no
N4 . C5 . C6 . 124.4(3)    yes
N4 . C5 . C11 . 113.5(2)    yes
C6 . C5 . C11 . 122.1(3)    yes
C5 . C6 . Pd1 . 121.9(2)    yes
C5 . C6 . C7 . 116.5(3)    yes
Pd1 . C6 . C7 . 121.6(2)    yes
C6 . C7 . C8 . 121.1(3)    yes
C6 . C7 . H71 . 121.4    no
C8 . C7 . H71 . 117.5    no
C7 . C8 . F9 . 120.7(3)    yes
C7 . C8 . C10 . 120.8(3)    yes
F9 . C8 . C10 . 118.5(3)    yes
C8 . C10 . C11 . 120.4(3)    yes
C8 . C10 . F12 . 119.7(3)    yes
C11 . C10 . F12 . 119.9(3)    yes
C5 . C11 . C10 . 119.0(3)    yes
C5 . C11 . H111 . 120.4    no
C10 . C11 . H111 . 120.5    no
C3 . C13 . H131 . 110.5    no
C3 . C13 . H132 . 111.0    no
H131 . C13 . H132 . 108.6    no
C3 . C13 . H133 . 108.1    no
H131 . C13 . H133 . 108.6    no
H132 . C13 . H133 . 110.1    no
Pd1 . N14 . C15 . 167.9(2)    yes
N14 . C15 . C16 . 179.1(3)    yes
C15 . C16 . H163 . 110.4    no
C15 . C16 . H162 . 109.0    no
H163 . C16 . H162 . 110.2    no
```

```
C15 . C16 . H161 . 108.4    no
H163 . C16 . H161 . 109.1    no
H162 . C16 . H161 . 109.6    no
Pd1 . N17 . C18 . 173.0(3)    yes
N17 . C18 . C19 . 179.3(3)    yes
C18 . C19 . H191 . 109.3    no
C18 . C19 . H192 . 108.4    no
H191 . C19 . H192 . 110.0    no
C18 . C19 . H193 . 110.8    no
H191 . C19 . H193 . 109.3    no
H192 . C19 . H193 . 108.9    no
O21 . S20 . O22 . 114.80(14)    yes
O21 . S20 . O23 . 112.02(14)    yes
O22 . S20 . O23 . 111.09(13)    yes
O21 . S20 . C24 . 106.94(13)    yes
O22 . S20 . C24 . 107.15(14)    yes
O23 . S20 . C24 . 104.05(13)    yes
S20 . C24 . C25 . 119.7(2)    yes
S20 . C24 . C29 . 120.9(2)    yes
C25 . C24 . C29 . 119.4(3)    yes
C24 . C25 . C26 . 119.9(3)    yes
C24 . C25 . H251 . 120.5    no
C26 . C25 . H251 . 119.6    no
C25 . C26 . C27 . 121.2(3)    yes
C25 . C26 . H261 . 119.7    no
C27 . C26 . H261 . 119.0    no
C26 . C27 . C28 . 118.1(3)    yes
C26 . C27 . C30 . 120.7(3)    yes
C28 . C27 . C30 . 121.2(3)    yes
C27 . C28 . C29 . 121.6(3)    yes
C27 . C28 . H281 . 119.0    no
C29 . C28 . H281 . 119.3    no
C28 . C29 . C24 . 119.8(3)    yes
C28 . C29 . H291 . 120.4    no
C24 . C29 . H291 . 119.8    no
C27 . C30 . H301 . 110.3    no
C27 . C30 . H302 . 111.5    no
H301 . C30 . H302 . 107.6    no
C27 . C30 . H303 . 110.5    no
H301 . C30 . H303 . 109.2    no
H302 . C30 . H303 . 107.6    no
loop_
 _geom_hbond_atom_site_label_D
 _geom_hbond_site_symmetry_D
 _geom_hbond_atom_site_label_H
 _geom_hbond_site_symmetry_H
 _geom_hbond_atom_site_label_A
 _geom_hbond_site_symmetry_A
 _geom_hbond_angle_DHA
 _geom_hbond_distance_DH
 _geom_hbond_distance_HA
 _geom_hbond_distance_DA
```

```
 _geom_hbond_publ_flag
C11 . H111 . O22 . 136 0.95 2.44 3.194(5)    yes
C13 . H131 . O23 . 143 0.96 2.51 3.332(5)    yes
C16 . H163 . O21 2_655 142 0.95 2.55 3.349(5)    yes
C16 . H161 . O23 2_555 141 0.94 2.49 3.270(5)    yes
C29 . H291 . O21 2_666 131 0.94 2.59 3.275(5)    yes
N4 . H41 . O23 . 174 0.85 1.91 2.758(5)    yes


#============================================================
================
data_8
#============================================================
================
_audit_creation_date        08-06-13
_audit_creation_method CRYSTALS_ver_12.86

_refine_special_details
;
This structure was found to be twinned using DIRAX:

Rotation Angle:  -1.911
Laboratory Vector:   -0.6274 0.4441 0.6397
Reciprocal Cell Vector:   0.97 -1.08 8.00
Direct Cell Vector:   3.97 -5.07 12.00
H' = +1.005*H -0.021*K +0.001*L
K' = +0.052*H +0.991*K
L' = +0.029*H +0.011*K +0.997*L

ROTAX was used to examine the possibility of this twin and the
R-indices
improved with the inclusion of a twin component, the scale
factor
for which refined to 0.236(14).
;

_oxford_structure_analysis_title  '5876'
_chemical_name_systematic         .
_chemical_melting_point           'not measured'

_cell_length_a                    7.5810(2)
_cell_length_b                    12.6494(3)
_cell_length_c                    13.2132(4)
_cell_angle_alpha                 77.4887(11)
_cell_angle_beta                  82.2803(12)
_cell_angle_gamma                 73.9961(12)
_cell_volume                      1185.29(6)

_symmetry_cell_setting            'Triclinic'
_symmetry_space_group_name_H-M    'P -1 '
_symmetry_space_group_name_Hall   '-P 1'
loop_
```

```
 _symmetry_equiv_pos_as_xyz
 'x,y,z'
 '-x,-y,-z'

loop_
_atom_type_symbol
_atom_type_scat_dispersion_real
_atom_type_scat_dispersion_imag
_atom_type_scat_Cromer_Mann_a1
_atom_type_scat_Cromer_Mann_b1
_atom_type_scat_Cromer_Mann_a2
_atom_type_scat_Cromer_Mann_b2
_atom_type_scat_Cromer_Mann_a3
_atom_type_scat_Cromer_Mann_b3
_atom_type_scat_Cromer_Mann_a4
_atom_type_scat_Cromer_Mann_b4
_atom_type_scat_Cromer_Mann_c
_atom_type_scat_source
 C       0.0033   0.0016   2.3100  20.8439   1.0200  10.2075
1.5886   0.5687
   0.8650  51.6512   0.2156 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
 H       0.0000   0.0000   0.4930  10.5109   0.3229  26.1257
0.1402   3.1424
   0.0408  57.7998   0.0030 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
 F       0.0171   0.0103   3.5392  10.2825   2.6412   4.2944
1.5170   0.2615
   1.0243  26.1476   0.2776 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
 N       0.0061   0.0033  12.2126   0.0057   3.1322   9.8933
2.0125  28.9975
   1.1663   0.5826 -11.5290 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
 O       0.0106   0.0060   3.0485  13.2771   2.2868   5.7011
1.5463   0.3239
   0.8670  32.9089   0.2508 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
 Pd     -0.9988   1.0072  19.3319   0.6987  15.5017   7.9893
5.2954  25.2052
   0.6058  76.8986   5.2659 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
 S       0.1246   0.1234   6.9053   1.4679   5.2034  22.2151
1.4379   0.2536
   1.5863  56.1720   0.8669 'International Tables Vol C
4.2.6.8 and 6.1.1.4'


_cell_formula_units_Z                    2

# Given Formula = C17 H16 F2 N2 O4 Pd1 S1
# Dc =      1.37 Fooo =    576.00 Mu =      9.06 M =    488.79
```

```
# Found Formula = C21 H22 F2 N4 O4 Pd1 S1
# Dc =      1.60 FOOO =    576.00 Mu =      9.21 M =    570.89

_chemical_formula_sum             'C21 H22 F2 N4 O4 Pd1 S1'
_chemical_formula_moiety          'C12 H12 F2 N3 O Pd, C7 H7
O3 S, C2 H3 N'
_chemical_compound_source               .
_chemical_formula_weight           570.89


_cell_measurement_reflns_used        4555
_cell_measurement_theta_min             5
_cell_measurement_theta_max            27
_cell_measurement_temperature          150

_exptl_crystal_description        'needle'
_exptl_crystal_colour             'clear_pale_colourless'
_exptl_crystal_size_min           0.06
_exptl_crystal_size_mid           0.09
_exptl_crystal_size_max           0.38

_exptl_crystal_density_diffrn     1.599
_exptl_crystal_density_meas       'not measured'
_exptl_crystal_density_method     'not measured'
# Non-dispersive F(000):
_exptl_crystal_F_000              576
_exptl_absorpt_coefficient_mu     0.921

# Sheldrick geometric approximatio 0.92 0.95
_exptl_absorpt_correction_type    multi-scan
_exptl_absorpt_process_details    'DENZO/SCALEPACK (Otwinowski
& Minor, 1997)'
_exptl_absorpt_correction_T_min   0.73
_exptl_absorpt_correction_T_max   0.95
# For a Kappa CCD, set Tmin to 1.0 and
# Tmax to the ratio of max:min frame scales in scale_all.log
_diffrn_measurement_device        'Nonius KappaCCD'
_diffrn_measurement_device_type   'Area'
_diffrn_radiation_monochromator   'graphite'
_diffrn_radiation_type            'Mo K\a'
_diffrn_radiation_wavelength           0.71073
_diffrn_measurement_method        \w

# If a reference occurs more than once, delete the author
# and date from subsequent references.
_computing_data_collection        'COLLECT (Nonius, 1997-
2001).'
_computing_cell_refinement        'DENZO/SCALEPACK (Otwinowski
& Minor, 1997)'
_computing_data_reduction         'DENZO/SCALEPACK (Otwinowski
& Minor, 1997)'
```

```
_computing_structure_solution     'SHELXS 86 (Sheldrick,
1986)'
_computing_structure_refinement   'CRYSTALS (Betteridge et
al., 2003)'
_computing_publication_material   'CRYSTALS (Betteridge et
al., 2003)'
_computing_molecular_graphics     'CAMERON (Watkin et al.,
1996)'

_diffrn_standards_interval_time   .
_diffrn_standards_interval_count  .
_diffrn_standards_number          0
_diffrn_standards_decay_%         .

_diffrn_ambient_temperature        150
_diffrn_reflns_number             16083
_reflns_number_total              5124
_diffrn_reflns_av_R_equivalents   0.127
# Number of reflections with Friedels Law is 5124
# Number of reflections without Friedels Law is 8464
# Theoretical number of reflections is about 5379


_diffrn_reflns_theta_min          5.122
_diffrn_reflns_theta_max          27.417
_diffrn_measured_fraction_theta_max 0.949

_diffrn_reflns_theta_full         25.224
_diffrn_measured_fraction_theta_full 0.985


_diffrn_reflns_limit_h_min        -9
_diffrn_reflns_limit_h_max        9
_diffrn_reflns_limit_k_min        -16
_diffrn_reflns_limit_k_max        16
_diffrn_reflns_limit_l_min        -17
_diffrn_reflns_limit_l_max        17
_reflns_limit_h_min               -9
_reflns_limit_h_max               9
_reflns_limit_k_min               -15
_reflns_limit_k_max               16
_reflns_limit_l_min               0
_reflns_limit_l_max               17

_oxford_diffrn_Wilson_B_factor    3.10
_oxford_diffrn_Wilson_scale       4.26

_atom_sites_solution_primary      direct
#heavy,direct,difmap,geom
# _atom_sites_solution_secondary  difmap
_atom_sites_solution_hydrogens    geom
```

```
_refine_diff_density_min         -1.48
_refine_diff_density_max         1.92


# The current dictionary definitions do not cover the
# situation where the reflections used for refinement were
# selected by a user-defined sigma threshold


# The values actually used during refinement
_oxford_reflns_threshold_expression_ref     I>2.0\s(I)
_refine_ls_number_reflns         4225
_refine_ls_number_restraints     0
_refine_ls_number_parameters     299
_oxford_refine_ls_R_factor_ref   0.0679
_refine_ls_wR_factor_ref         0.0794
_refine_ls_goodness_of_fit_ref   0.9889
_refine_ls_shift/su_max          0.000313


# The values computed from all data
_oxford_reflns_number_all        5123
_refine_ls_R_factor_all          0.0815
_refine_ls_wR_factor_all         0.1026

# The values computed with a 2 sigma cutoff - a la SHELX
_reflns_threshold_expression     I>2.0\s(I)
_reflns_number_gt                4225
_refine_ls_R_factor_gt           0.0679
_refine_ls_wR_factor_gt          0.0794

# choose from: rm (reference molecule of known chirality),
# ad (anomolous dispersion - Flack), rmad (rm and ad),
# syn (from synthesis), unk (unknown) or . (not applicable).
_chemical_absolute_configuration  '.'


_refine_ls_structure_factor_coef  F
_refine_ls_matrix_type           full
_refine_ls_hydrogen_treatment    constr         # none,
undef, noref, refall,
                                                # refxyz,
refU, constr or mixed
_refine_ls_weighting_scheme      calc
_refine_ls_weighting_details
;
 Method, part 1, Chebychev polynomial, (Watkin, 1994, Prince,
1982)
 [weight] = 1.0/[A~0~*T~0~(x)+A~1~*T~1~(x) ... +A~n-1~]*T~n-
1~(x)]
 where A~i~ are the Chebychev coefficients listed below and x=
Fcalc/Fmax
```

```
 Method = Robust Weighting (Prince, 1982)
 W = [weight] * [1-(deltaF/6*sigmaF)^2^]^2^
 A~i~ are:
 1.41 1.14 0.768
;
# Insert your own references if required - in alphabetical
order
_publ_section_references
;
Betteridge, P.W., Carruthers, J.R., Cooper, R.I.,
Prout, K. & Watkin, D.J. (2003). J. Appl. Cryst. 36, 1487.

Nonius (1997-2001). COLLECT. Nonius BV, Delft, The
Netherlands.

Otwinowski, Z. & Minor, W. (1997). Methods in Enzymology, Vol.
276,
edited by C. W. Carter Jr & R. M. Sweet, pp. 307--326.
New York: Academic Press.

Prince, E.
Mathematical Techniques in Crystallography
and Materials Science
Springer-Verlag, New York, 1982.

Sheldrick, G. M. (2008). Acta Cryst A64, 112-122.

Watkin D.J. (1994).
Acta Cryst, A50, 411-437.

Watkin, D.J., Prout, C.K. & Pearce, L.J. (1996). CAMERON,
Chemical
Crystallography Laboratory, Oxford, UK.
;

# Uequiv = arithmetic mean of Ui i.e. Ueqiv = (U1+U2+U3)/3

# Replace last . with number of unfound hydrogen atomsattached
to an atom.

# ..._refinement_flags_...
# . no refinement constraints          S special position
constraint on site
# G rigid group refinement of site     R riding atom
# D distance or angle restraint on site T thermal displacement
constraints
# U Uiso or Uij restraint (rigid bond)  P partial occupancy
constraint


loop_
_atom_site_label
```

```
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_occupancy
_atom_site_adp_type
_atom_site_refinement_flags_posn
_atom_site_refinement_flags_adp
_atom_site_refinement_flags_occupancy
_atom_site_disorder_assembly
_atom_site_disorder_group
_oxford_atom_site_special_shape
_atom_site_attached_hydrogens
Pd1 Pd 0.20747(5) 0.10306(3) 0.00009(3) 0.0384 1.0000 Uani . .
. . . . .
O2 O 0.3462(6) 0.0880(3) -0.1360(3) 0.0482 1.0000 Uani . . . .
. . .
C3 C 0.4290(7) 0.0005(4) -0.1703(4) 0.0401 1.0000 Uani . . . .
. . .
N4 N 0.4269(6) -0.1019(3) -0.1217(3) 0.0377 1.0000 Uani . . .
. . . .
C5 C 0.3288(6) -0.1353(4) -0.0230(4) 0.0362 1.0000 Uani . . .
. . . .
C6 C 0.2296(7) -0.0607(4) 0.0368(4) 0.0367 1.0000 Uani . . . .
. . .
C7 C 0.1434(7) -0.1125(4) 0.1285(4) 0.0407 1.0000 Uani . . . .
. . .
F8 F 0.0380(6) -0.0533(3) 0.1991(3) 0.0604 1.0000 Uani . . . .
. . .
C9 C 0.1606(8) -0.2253(4) 0.1546(4) 0.0453 1.0000 Uani . . . .
. . .
F10 F 0.0725(6) -0.2669(3) 0.2447(3) 0.0628 1.0000 Uani . . .
. . . .
C11 C 0.2641(8) -0.2984(4) 0.0924(4) 0.0434 1.0000 Uani . . .
. . . .
C12 C 0.3486(7) -0.2515(4) 0.0005(4) 0.0415 1.0000 Uani . . .
. . . .
C13 C 0.5401(9) 0.0126(5) -0.2739(4) 0.0486 1.0000 Uani . . .
. . . .
N14 N 0.2025(6) 0.2739(4) -0.0421(4) 0.0441 1.0000 Uani . . .
. . . .
C15 C 0.2109(6) 0.3648(4) -0.0530(3) 0.0361 1.0000 Uani . . .
. . . .
C16 C 0.2240(7) 0.4788(4) -0.0642(4) 0.0408 1.0000 Uani . . .
. . . .
N17 N 0.0607(6) 0.1458(4) 0.1275(4) 0.0431 1.0000 Uani . . . .
. . .
C18 C -0.0287(7) 0.1929(4) 0.1890(4) 0.0422 1.0000 Uani . . .
. . . .
C19 C -0.1425(9) 0.2502(5) 0.2674(5) 0.0547 1.0000 Uani . . .
. . . .
```

```
S20 S 0.70275(17) 0.62763(10) 0.76233(8) 0.0364 1.0000 Uani .
. . . . . .
O21 O 0.5611(6) 0.5803(3) 0.8263(3) 0.0460 1.0000 Uani . . . .
. . .
O22 O 0.6702(6) 0.7462(3) 0.7631(3) 0.0498 1.0000 Uani . . . .
. . .
O23 O 0.8866(6) 0.5631(4) 0.7866(3) 0.0532 1.0000 Uani . . . .
. . .
C24 C 0.6809(6) 0.6193(4) 0.6321(3) 0.0363 1.0000 Uani . . . .
. . .
C25 C 0.5659(8) 0.7067(5) 0.5700(4) 0.0457 1.0000 Uani . . . .
. . .
C26 C 0.5484(9) 0.6973(6) 0.4687(4) 0.0550 1.0000 Uani . . . .
. . .
C27 C 0.6447(9) 0.6040(6) 0.4290(4) 0.0561 1.0000 Uani . . . .
. . .
C28 C 0.7566(9) 0.5169(6) 0.4927(5) 0.0578 1.0000 Uani . . . .
. . .
C29 C 0.7752(9) 0.5245(5) 0.5945(4) 0.0511 1.0000 Uani . . . .
. . .
C30 C 0.6295(12) 0.5948(9) 0.3168(5) 0.0820 1.0000 Uani . . .
. . . .
N31 N 0.2406(10) -0.0302(6) 0.5333(6) 0.0845 1.0000 Uani . . .
. . . .
C32 C 0.1591(10) 0.0599(6) 0.5363(5) 0.0601 1.0000 Uani . . .
. . . .
C33 C 0.0526(12) 0.1737(6) 0.5367(6) 0.0728 1.0000 Uani . . .
. . . .
H41 H 0.4942 -0.1591 -0.1545 0.0456 1.0000 Uiso R . . . . . .
H111 H 0.2752 -0.3763 0.1115 0.0500 1.0000 Uiso R . . . . . .
H121 H 0.4190 -0.2958 -0.0454 0.0522 1.0000 Uiso R . . . . . .
H132 H 0.5824 -0.0598 -0.2946 0.0730 1.0000 Uiso R . . . . . .
H131 H 0.6441 0.0401 -0.2649 0.0730 1.0000 Uiso R . . . . . .
H133 H 0.4674 0.0670 -0.3246 0.0732 1.0000 Uiso R . . . . . .
H163 H 0.1385 0.5312 -0.1101 0.0600 1.0000 Uiso R . . . . . .
H161 H 0.2026 0.5033 0.0016 0.0600 1.0000 Uiso R . . . . . .
H162 H 0.3468 0.4848 -0.0924 0.0599 1.0000 Uiso R . . . . . .
H191 H -0.0767 0.2973 0.2884 0.0748 1.0000 Uiso R . . . . . .
H192 H -0.1731 0.1966 0.3256 0.0752 1.0000 Uiso R . . . . . .
H193 H -0.2518 0.2978 0.2376 0.0751 1.0000 Uiso R . . . . . .
H251 H 0.5006 0.7722 0.5951 0.0509 1.0000 Uiso R . . . . . .
H261 H 0.4750 0.7584 0.4258 0.0632 1.0000 Uiso R . . . . . .
H281 H 0.8198 0.4506 0.4680 0.0710 1.0000 Uiso R . . . . . .
H291 H 0.8462 0.4638 0.6384 0.0581 1.0000 Uiso R . . . . . .
H301 H 0.7245 0.5319 0.2988 0.1440 1.0000 Uiso R . . . . . .
H303 H 0.6395 0.6633 0.2701 0.1441 1.0000 Uiso R . . . . . .
H302 H 0.5112 0.5807 0.3143 0.1440 1.0000 Uiso R . . . . . .
H332 H 0.0734 0.1969 0.5979 0.1071 1.0000 Uiso R . . . . . .
H331 H -0.0770 0.1805 0.5366 0.1071 1.0000 Uiso R . . . . . .
H333 H 0.0913 0.2239 0.4767 0.1071 1.0000 Uiso R . . . . . .
loop_
_atom_site_aniso_label
```

```
_atom_site_aniso_U_11
_atom_site_aniso_U_22
_atom_site_aniso_U_33
_atom_site_aniso_U_23
_atom_site_aniso_U_13
_atom_site_aniso_U_12
Pd1 0.0466(2) 0.0329(2) 0.0352(2) -0.00451(14) -0.00538(15) -
0.01002(15)
O2 0.064(2) 0.0383(19) 0.0374(19) -0.0013(15) 0.0019(17) -
0.0129(17)
C3 0.045(2) 0.040(2) 0.034(2) -0.0033(19) -0.0091(19) -
0.009(2)
N4 0.045(2) 0.0366(19) 0.0297(19) -0.0021(15) -0.0023(16) -
0.0103(16)
C5 0.041(2) 0.035(2) 0.031(2) 0.0038(17) -0.0107(18) -
0.0109(18)
C6 0.044(2) 0.030(2) 0.038(2) -0.0038(18) -0.0139(19) -
0.0093(18)
C7 0.052(3) 0.035(2) 0.031(2) -0.0048(18) 0.004(2) -0.009(2)
F8 0.093(3) 0.0424(17) 0.0435(18) -0.0096(14) 0.0144(17) -
0.0210(17)
C9 0.064(3) 0.040(3) 0.029(2) 0.0018(19) 0.000(2) -0.017(2)
F10 0.099(3) 0.0450(18) 0.0379(17) -0.0004(13) 0.0143(17) -
0.0230(18)
C11 0.057(3) 0.034(2) 0.037(2) 0.0024(19) -0.012(2) -0.011(2)
C12 0.046(3) 0.046(3) 0.035(2) -0.007(2) -0.005(2) -0.014(2)
C13 0.065(3) 0.046(3) 0.032(2) 0.001(2) 0.003(2) -0.019(2)
N14 0.048(2) 0.039(2) 0.044(2) -0.0121(18) -0.0059(19) -
0.0066(18)
C15 0.043(2) 0.042(3) 0.0220(19) -0.0058(17) -0.0006(17) -
0.0098(19)
C16 0.050(3) 0.039(2) 0.033(2) -0.0017(18) -0.0035(19) -
0.013(2)
N17 0.049(2) 0.039(2) 0.043(2) -0.0071(18) -0.0088(19) -
0.0117(18)
C18 0.049(3) 0.037(2) 0.039(3) -0.002(2) -0.007(2) -0.012(2)
C19 0.065(3) 0.053(3) 0.042(3) -0.006(2) 0.009(3) -0.016(3)
S20 0.0463(6) 0.0372(6) 0.0234(5) -0.0024(4) -0.0010(4) -
0.0103(5)
O21 0.063(2) 0.048(2) 0.0276(16) -0.0030(14) 0.0036(15) -
0.0209(17)
O22 0.073(3) 0.044(2) 0.0351(18) -0.0098(15) 0.0044(17) -
0.0211(18)
O23 0.052(2) 0.064(2) 0.0397(19) -0.0099(18) -0.0086(16) -
0.0058(18)
C24 0.042(2) 0.042(2) 0.0211(19) -0.0007(17) 0.0033(17) -
0.0120(19)
C25 0.050(3) 0.044(3) 0.034(2) 0.000(2) -0.001(2) -0.005(2)
C26 0.060(3) 0.065(4) 0.030(2) 0.010(2) -0.004(2) -0.016(3)
C27 0.069(4) 0.074(4) 0.030(3) -0.004(2) -0.002(2) -0.030(3)
C28 0.072(4) 0.064(4) 0.039(3) -0.023(3) 0.006(3) -0.014(3)
C29 0.063(3) 0.045(3) 0.041(3) -0.008(2) -0.009(2) -0.005(2)
```

```
C30 0.096(6) 0.136(8) 0.027(3) -0.020(4) 0.005(3) -0.053(5)
N31 0.076(4) 0.077(5) 0.094(5) 0.000(4) -0.012(4) -0.017(3)
C32 0.065(4) 0.066(4) 0.049(3) 0.002(3) -0.010(3) -0.023(3)
C33 0.092(5) 0.061(4) 0.063(4) -0.008(3) 0.000(4) -0.023(4)

_refine_ls_extinction_method
    'None'
_oxford_refine_ls_scale 0.555(5)

loop_
    _oxford_twin_element_scale_factors
         0.764(14)
         0.236(14)
loop_
 _geom_bond_atom_site_label_1
 _geom_bond_site_symmetry_1
 _geom_bond_atom_site_label_2
 _geom_bond_site_symmetry_2
 _geom_bond_distance
 _geom_bond_publ_flag
Pd1 . O2 . 1.976(4)    yes
Pd1 . C6 . 1.988(5)    yes
Pd1 . N14 . 2.102(4)    yes
Pd1 . N17 . 1.981(5)    yes
O2 . C3 . 1.257(7)    yes
C3 . N4 . 1.319(6)    yes
C3 . C13 . 1.509(7)    yes
N4 . C5 . 1.451(6)    yes
N4 . H41 . 0.920    no
C5 . C6 . 1.361(8)    yes
C5 . C12 . 1.405(7)    yes
C6 . C7 . 1.416(7)    yes
C7 . F8 . 1.357(6)    yes
C7 . C9 . 1.367(7)    yes
C9 . F10 . 1.360(6)    yes
C9 . C11 . 1.378(8)    yes
C11 . C12 . 1.387(7)    yes
C11 . H111 . 0.947    no
C12 . H121 . 0.928    no
C13 . H132 . 0.969    no
C13 . H131 . 0.975    no
C13 . H133 . 0.957    no
N14 . C15 . 1.146(7)    yes
C15 . C16 . 1.447(7)    yes
C16 . H163 . 0.960    no
C16 . H161 . 0.964    no
C16 . H162 . 0.972    no
N17 . C18 . 1.147(7)    yes
C18 . C19 . 1.443(8)    yes
C19 . H191 . 0.975    no
C19 . H192 . 0.959    no
C19 . H193 . 0.956    no
```

```
S20 . O21 . 1.455(4)    yes
S20 . O22 . 1.453(4)    yes
S20 . O23 . 1.446(4)    yes
S20 . C24 . 1.779(5)    yes
C24 . C25 . 1.387(7)    yes
C24 . C29 . 1.373(8)    yes
C25 . C26 . 1.396(8)    yes
C25 . H251 . 0.944    no
C26 . C27 . 1.375(10)    yes
C26 . H261 . 0.941    no
C27 . C28 . 1.385(9)    yes
C27 . C30 . 1.534(8)    yes
C28 . C29 . 1.397(8)    yes
C28 . H281 . 0.947    no
C29 . H291 . 0.938    no
C30 . H301 . 0.963    no
C30 . H303 . 0.964    no
C30 . H302 . 0.967    no
N31 . C32 . 1.143(10)    yes
C32 . C33 . 1.444(11)    yes
C33 . H332 . 0.964    no
C33 . H331 . 0.963    no
C33 . H333 . 0.969    no
loop_
 _geom_angle_atom_site_label_1
 _geom_angle_site_symmetry_1
 _geom_angle_atom_site_label_2
 _geom_angle_site_symmetry_2
 _geom_angle_atom_site_label_3
 _geom_angle_site_symmetry_3
 _geom_angle
 _geom_angle_publ_flag
O2 . Pd1 . C6 . 91.39(18)    yes
O2 . Pd1 . N14 . 85.99(17)    yes
C6 . Pd1 . N14 . 176.24(18)    yes
O2 . Pd1 . N17 . 170.29(16)    yes
C6 . Pd1 . N17 . 98.2(2)    yes
N14 . Pd1 . N17 . 84.47(18)    yes
Pd1 . O2 . C3 . 129.1(3)    yes
O2 . C3 . N4 . 124.5(5)    yes
O2 . C3 . C13 . 118.2(5)    yes
N4 . C3 . C13 . 117.3(5)    yes
C3 . N4 . C5 . 127.8(4)    yes
C3 . N4 . H41 . 116.3    no
C5 . N4 . H41 . 115.8    no
N4 . C5 . C6 . 122.8(4)    yes
N4 . C5 . C12 . 111.6(4)    yes
C6 . C5 . C12 . 125.6(5)    yes
C5 . C6 . Pd1 . 123.9(4)    yes
C5 . C6 . C7 . 112.6(4)    yes
Pd1 . C6 . C7 . 123.4(4)    yes
C6 . C7 . F8 . 122.2(4)    yes
```

```
C6 . C7 . C9 . 123.5(5)    yes
F8 . C7 . C9 . 114.3(4)    yes
C7 . C9 . F10 . 118.9(5)    yes
C7 . C9 . C11 . 122.2(5)    yes
F10 . C9 . C11 . 118.9(5)    yes
C9 . C11 . C12 . 116.6(5)    yes
C9 . C11 . H111 . 121.3    no
C12 . C11 . H111 . 122.1    no
C5 . C12 . C11 . 119.5(5)    yes
C5 . C12 . H121 . 119.4    no
C11 . C12 . H121 . 121.1    no
C3 . C13 . H132 . 109.0    no
C3 . C13 . H131 . 107.3    no
H132 . C13 . H131 . 110.7    no
C3 . C13 . H133 . 110.0    no
H132 . C13 . H133 . 111.5    no
H131 . C13 . H133 . 108.2    no
Pd1 . N14 . C15 . 170.8(4)    yes
N14 . C15 . C16 . 178.4(5)    yes
C15 . C16 . H163 . 112.7    no
C15 . C16 . H161 . 112.0    no
H163 . C16 . H161 . 107.6    no
C15 . C16 . H162 . 110.3    no
H163 . C16 . H162 . 107.3    no
H161 . C16 . H162 . 106.6    no
Pd1 . N17 . C18 . 165.5(4)    yes
N17 . C18 . C19 . 178.9(6)    yes
C18 . C19 . H191 . 109.2    no
C18 . C19 . H192 . 109.7    no
H191 . C19 . H192 . 111.0    no
C18 . C19 . H193 . 108.5    no
H191 . C19 . H193 . 108.1    no
H192 . C19 . H193 . 110.2    no
O21 . S20 . O22 . 111.8(2)    yes
O21 . S20 . O23 . 112.5(2)    yes
O22 . S20 . O23 . 113.5(3)    yes
O21 . S20 . C24 . 106.2(2)    yes
O22 . S20 . C24 . 105.7(2)    yes
O23 . S20 . C24 . 106.5(2)    yes
S20 . C24 . C25 . 120.2(4)    yes
S20 . C24 . C29 . 119.5(4)    yes
C25 . C24 . C29 . 120.3(5)    yes
C24 . C25 . C26 . 119.2(5)    yes
C24 . C25 . H251 . 120.9    no
C26 . C25 . H251 . 119.9    no
C25 . C26 . C27 . 121.3(5)    yes
C25 . C26 . H261 . 118.7    no
C27 . C26 . H261 . 119.8    no
C26 . C27 . C28 . 118.6(5)    yes
C26 . C27 . C30 . 121.5(6)    yes
C28 . C27 . C30 . 119.9(7)    yes
C27 . C28 . C29 . 120.9(6)    yes
```

```
C27 . C28 . H281 . 120.0    no
C29 . C28 . H281 . 119.1    no
C28 . C29 . C24 . 119.7(5)    yes
C28 . C29 . H291 . 120.4    no
C24 . C29 . H291 . 119.8    no
C27 . C30 . H301 . 109.2    no
C27 . C30 . H303 . 110.0    no
H301 . C30 . H303 . 111.0    no
C27 . C30 . H302 . 107.4    no
H301 . C30 . H302 . 108.5    no
H303 . C30 . H302 . 110.7    no
N31 . C32 . C33 . 177.7(8)    yes
C32 . C33 . H332 . 109.3    no
C32 . C33 . H331 . 111.4    no
H332 . C33 . H331 . 108.7    no
C32 . C33 . H333 . 110.4    no
H332 . C33 . H333 . 107.5    no
H331 . C33 . H333 . 109.3    no
loop_
 _geom_hbond_atom_site_label_D
 _geom_hbond_site_symmetry_D
 _geom_hbond_atom_site_label_H
 _geom_hbond_site_symmetry_H
 _geom_hbond_atom_site_label_A
 _geom_hbond_site_symmetry_A
 _geom_hbond_angle_DHA
 _geom_hbond_distance_DH
 _geom_hbond_distance_HA
 _geom_hbond_distance_DA
 _geom_hbond_publ_flag
N4 . H41 . O22 1_544 166 0.92 1.92 2.824(8)    yes
C11 . H111 . O21 2_656 156 0.95 2.54 3.427(8)    yes
C12 . H121 . O21 1_544 171 0.93 2.49 3.415(8)    yes
C13 . H132 . O22 1_544 146 0.97 2.34 3.186(8)    yes
C16 . H163 . O23 1_454 148 0.96 2.39 3.241(8)    yes
C16 . H162 . O21 1_554 154 0.97 2.30 3.207(8)    yes
C19 . H191 . O23 2_666 142 0.98 2.54 3.357(8)    yes
C19 . H193 . O21 2_566 175 0.96 2.56 3.515(8)    yes


#============================================================
================
data_16
#============================================================
================
_audit_creation_date        09-03-02
_audit_creation_method CRYSTALS_ver_12.87

_refine_special_details
;
On initial refinement, the tosylate oxygen ADPs were prolate
and a small, but significant amount of residual electron
```

```
density was visible between the atoms.  Examination of the
slant Fourier clearly showed the presence of a second
orientation for the SO~3~ group, which was modelled with an
occupancy of 27.4%, however restraints were required to
maintain a sensible geometry and thermal parameters.
;

_oxford_structure_analysis_title  '6066'
_chemical_name_systematic         .
_chemical_melting_point           'not measured'

_cell_length_a                    7.4418(1)
_cell_length_b                    14.5003(2)
_cell_length_c                    20.7460(3)
_cell_angle_alpha                 90
_cell_angle_beta                  96.2239(5)
_cell_angle_gamma                 90
_cell_volume                      2225.47(5)

_symmetry_cell_setting            'Monoclinic'
_symmetry_space_group_name_H-M    'P 1 21/n 1 '
_symmetry_space_group_name_Hall   '-P 2yn'
loop_
 _symmetry_equiv_pos_as_xyz
 'x,y,z'
 '-x,-y,-z'
 '-x+1/2,y+1/2,-z+1/2'
 'x+1/2,-y+1/2,z+1/2'

loop_
_atom_type_symbol
_atom_type_scat_dispersion_real
_atom_type_scat_dispersion_imag
_atom_type_scat_Cromer_Mann_a1
_atom_type_scat_Cromer_Mann_b1
_atom_type_scat_Cromer_Mann_a2
_atom_type_scat_Cromer_Mann_b2
_atom_type_scat_Cromer_Mann_a3
_atom_type_scat_Cromer_Mann_b3
_atom_type_scat_Cromer_Mann_a4
_atom_type_scat_Cromer_Mann_b4
_atom_type_scat_Cromer_Mann_c
_atom_type_scat_source
 C       0.0033   0.0016   2.3100  20.8439   1.0200  10.2075
1.5886   0.5687
   0.8650  51.6512   0.2156 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
 H       0.0000   0.0000   0.4930  10.5109   0.3229  26.1257
0.1402   3.1424
   0.0408  57.7998   0.0030 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
```

```
 F       0.0171   0.0103   3.5392  10.2825   2.6412   4.2944
1.5170   0.2615
   1.0243  26.1476   0.2776 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
 N       0.0061   0.0033  12.2126   0.0057   3.1322   9.8933
2.0125  28.9975
   1.1663   0.5826 -11.5290 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
 O       0.0106   0.0060   3.0485  13.2771   2.2868   5.7011
1.5463   0.3239
   0.8670  32.9089   0.2508 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
 Pd     -0.9988   1.0072  19.3319   0.6987  15.5017   7.9893
5.2954  25.2052
   0.6058  76.8986   5.2659 'International Tables Vol C
4.2.6.8 and 6.1.1.4'
 S       0.1246   0.1234   6.9053   1.4679   5.2034  22.2151
1.4379   0.2536
   1.5863  56.1720   0.8669 'International Tables Vol C
4.2.6.8 and 6.1.1.4'


_cell_formula_units_Z                  4

# Given Formula = C20 H23 F1 N4 O4 Pd1 S1
# Dc =      1.61 Fooo =   1096.00 Mu =      9.70 M =    540.89
# Found Formula = C20 H23 F1 N4 O4 Pd1 S1
# Dc =      1.61 FOOO =   1096.00 Mu =      9.70 M =    540.89

_chemical_formula_sum             'C20 H23 F1 N4 O4 Pd1 S1'
_chemical_formula_moiety          'C13 H16 F N4 O Pd, C7 H7 O3
S'
_chemical_compound_source               .
_chemical_formula_weight          540.89


_cell_measurement_reflns_used       5196
_cell_measurement_theta_min            5
_cell_measurement_theta_max           27
_cell_measurement_temperature        150

_exptl_crystal_description        'needle'
_exptl_crystal_colour             'clear_pale_colourless'
_exptl_crystal_size_min           0.06
_exptl_crystal_size_mid           0.07
_exptl_crystal_size_max           0.59

_exptl_crystal_density_diffrn     1.614
_exptl_crystal_density_meas       'not measured'
_exptl_crystal_density_method     'not measured'
# Non-dispersive F(000):
_exptl_crystal_F_000              1096
```

```
_exptl_absorpt_coefficient_mu     0.970

# Sheldrick geometric approximatio 0.93 0.94
_exptl_absorpt_correction_type    multi-scan
_exptl_absorpt_process_details    'DENZO/SCALEPACK (Otwinowski
& Minor, 1997)'
_exptl_absorpt_correction_T_min   0.77
_exptl_absorpt_correction_T_max   0.94
# For a Kappa CCD, set Tmin to 1.0 and
# Tmax to the ratio of max:min frame scales in scale_all.log
_diffrn_measurement_device        'Nonius KappaCCD'
_diffrn_measurement_device_type   'Area'
_diffrn_radiation_monochromator   'graphite'
_diffrn_radiation_type            'Mo K\a'
_diffrn_radiation_wavelength          0.71073
_diffrn_measurement_method        \w

# If a reference occurs more than once, delete the author
# and date from subsequent references.
_computing_data_collection        'COLLECT (Nonius, 1997-
2001).'
_computing_cell_refinement        'DENZO/SCALEPACK (Otwinowski
& Minor, 1997)'
_computing_data_reduction         'DENZO/SCALEPACK (Otwinowski
& Minor, 1997)'
_computing_structure_solution     'SIR92 (Altomare et al.,
1994)'
_computing_structure_refinement   'CRYSTALS (Betteridge et
al., 2003)'
_computing_publication_material   'CRYSTALS (Betteridge et
al., 2003)'
_computing_molecular_graphics     'CAMERON (Watkin et al.,
1996)'

_diffrn_standards_interval_time   .
_diffrn_standards_interval_count  .
_diffrn_standards_number          0
_diffrn_standards_decay_%         .

_diffrn_ambient_temperature        150
_diffrn_reflns_number             41900
_reflns_number_total              5061
_diffrn_reflns_av_R_equivalents   0.046
# Number of reflections with Friedels Law is 5061
# Number of reflections without Friedels Law is 9872
# Theoretical number of reflections is about 5107


_diffrn_reflns_theta_min          5.106
_diffrn_reflns_theta_max          27.490
_diffrn_measured_fraction_theta_max 0.992
```

```
_diffrn_reflns_theta_full         26.940
_diffrn_measured_fraction_theta_full 0.993


_diffrn_reflns_limit_h_min        -9
_diffrn_reflns_limit_h_max        9
_diffrn_reflns_limit_k_min        -18
_diffrn_reflns_limit_k_max        18
_diffrn_reflns_limit_l_min        -26
_diffrn_reflns_limit_l_max        26
_reflns_limit_h_min               -9
_reflns_limit_h_max               9
_reflns_limit_k_min               0
_reflns_limit_k_max               18
_reflns_limit_l_min               0
_reflns_limit_l_max               26

_oxford_diffrn_Wilson_B_factor    2.37
_oxford_diffrn_Wilson_scale       20.45

_atom_sites_solution_primary      direct
#heavy,direct,difmap,geom
# _atom_sites_solution_secondary  difmap
_atom_sites_solution_hydrogens    geom

_refine_diff_density_min          -0.69
_refine_diff_density_max          0.75


# The current dictionary definitions do not cover the
# situation where the reflections used for refinement were
# selected by a user-defined sigma threshold


# The values actually used during refinement
_oxford_reflns_threshold_expression_ref     I>-3.0\s(I)
_refine_ls_number_reflns          5060
_refine_ls_number_restraints      48
_refine_ls_number_parameters      308
_oxford_refine_ls_R_factor_ref    0.0506
_refine_ls_wR_factor_ref          0.0882
_refine_ls_goodness_of_fit_ref    0.9640
_refine_ls_shift/su_max           0.001100


# The values computed from all data
_oxford_reflns_number_all         5060
_refine_ls_R_factor_all           0.0506
_refine_ls_wR_factor_all          0.0882

# The values computed with a 2 sigma cutoff - a la SHELX
_reflns_threshold_expression      I>2.0\s(I)
```

```
_reflns_number_gt                 3944
_refine_ls_R_factor_gt            0.0330
_refine_ls_wR_factor_gt           0.0727

# choose from: rm (reference molecule of known chirality),
# ad (anomolous dispersion - Flack), rmad (rm and ad),
# syn (from synthesis), unk (unknown) or . (not applicable).
_chemical_absolute_configuration  '.'


_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_hydrogen_treatment     none          # none,
undef, noref, refall,
                                                # refxyz,
refU, constr or mixed
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
;
 Method, part 1, Chebychev polynomial, (Watkin, 1994, Prince,
1982)
 [weight] = 1.0/[A~0~*T~0~(x)+A~1~*T~1~(x) ... +A~n-1~]*T~n-
1~(x)]
 where A~i~ are the Chebychev coefficients listed below and x=
Fcalc/Fmax
 Method = Robust Weighting (Prince, 1982)
 W = [weight] * [1-(deltaF/6*sigmaF)^2^]^2^
 A~i~ are:
 9.72 13.6 6.85 2.05
;
# Insert your own references if required - in alphabetical
order
_publ_section_references
;
Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A.,
Burla, M.C.,
Polidori, G. & Camalli, M. (1994). J. Appl. Cryst. 27, 435.

Betteridge, P.W., Carruthers, J.R., Cooper, R.I.,
Prout, K. & Watkin, D.J. (2003). J. Appl. Cryst. 36, 1487.

Nonius (1997-2001). COLLECT. Nonius BV, Delft, The
Netherlands.

Otwinowski, Z. & Minor, W. (1997). Methods in Enzymology, Vol.
276,
edited by C. W. Carter Jr & R. M. Sweet, pp. 307--326.
New York: Academic Press.

Prince, E.
Mathematical Techniques in Crystallography
and Materials Science
```

```
Springer-Verlag, New York, 1982.

Watkin D.J. (1994).
Acta Cryst, A50, 411-437.

Watkin, D.J., Prout, C.K. & Pearce, L.J. (1996). CAMERON,
Chemical
Crystallography Laboratory, Oxford, UK.
;

# Uequiv = arithmetic mean of Ui i.e. Ueqiv = (U1+U2+U3)/3

# Replace last . with number of unfound hydrogen atomsattached
to an atom.

# ..._refinement_flags_...
# . no refinement constraints           S special position
constraint on site
# G rigid group refinement of site      R riding atom
# D distance or angle restraint on site T thermal displacement
constraints
# U Uiso or Uij restraint (rigid bond)  P partial occupancy
constraint


loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_occupancy
_atom_site_adp_type
_atom_site_refinement_flags_posn
_atom_site_refinement_flags_adp
_atom_site_refinement_flags_occupancy
_atom_site_disorder_assembly
_atom_site_disorder_group
_oxford_atom_site_special_shape
_atom_site_attached_hydrogens
Pd1 Pd 0.33897(3) 0.490852(16) 0.547403(11) 0.0286 1.0000 Uani
. . . . . .
O2 O 0.2008(4) 0.42493(17) 0.47448(12) 0.0394 1.0000 Uani . .
. . . . .
C3 C 0.1220(4) 0.4546(2) 0.42190(17) 0.0314 1.0000 Uani . . .
. . . .
N4 N 0.1135(4) 0.54476(19) 0.40674(13) 0.0304 1.0000 Uani . .
. . . . .
C5 C 0.1846(4) 0.6192(2) 0.44533(15) 0.0267 1.0000 Uani . . .
. . . .
```

```
C6 C 0.2865(4) 0.6114(2) 0.50569(15) 0.0276 1.0000 Uani . . .
. . . .
C7 C 0.3497(5) 0.6934(2) 0.53599(16) 0.0357 1.0000 Uani . . .
. . . .
C8 C 0.3156(5) 0.7796(2) 0.50848(18) 0.0389 1.0000 Uani . . .
. . . .
C9 C 0.2159(5) 0.7827(2) 0.44924(17) 0.0344 1.0000 Uani . . .
. . . .
C10 C 0.1478(4) 0.7063(2) 0.41701(16) 0.0310 1.0000 Uani . . .
. . . .
F11 F 0.1799(3) 0.86678(14) 0.41961(12) 0.0472 1.0000 Uani . .
. . . . .
N12 N 0.0457(4) 0.3930(2) 0.37895(15) 0.0392 1.0000 Uani . . .
. . . .
C13 C -0.0683(5) 0.4184(3) 0.32041(19) 0.0465 1.0000 Uani . .
. . . . .
C14 C 0.0714(7) 0.2943(3) 0.3924(2) 0.0581 1.0000 Uani . . . .
. . .
N15 N 0.3803(4) 0.3615(2) 0.59630(15) 0.0389 1.0000 Uani . . .
. . . .
C16 C 0.4127(5) 0.3052(2) 0.63335(18) 0.0378 1.0000 Uani . . .
. . . .
C17 C 0.4527(6) 0.2349(3) 0.6830(2) 0.0464 1.0000 Uani . . . .
. . .
N18 N 0.4744(4) 0.5430(2) 0.62775(14) 0.0344 1.0000 Uani . . .
. . . .
C19 C 0.5414(5) 0.5570(3) 0.67877(17) 0.0357 1.0000 Uani . . .
. . . .
C20 C 0.6226(6) 0.5719(3) 0.74463(19) 0.0511 1.0000 Uani . . .
. . . .
S21 S -0.00135(15) 0.66750(6) 0.23029(4) 0.0423 1.0000 Uani D
. . . . . .
C25 C -0.0862(5) 0.5889(2) 0.16892(16) 0.0337 1.0000 Uani . .
. . . . .
C26 C 0.0292(5) 0.5465(3) 0.13014(17) 0.0379 1.0000 Uani . . .
. . . .
C27 C -0.0399(5) 0.4846(3) 0.08301(17) 0.0401 1.0000 Uani . .
. . . . .
C28 C -0.2224(6) 0.4635(3) 0.07380(18) 0.0423 1.0000 Uani . .
. . . . .
C29 C -0.3359(6) 0.5078(3) 0.1130(2) 0.0480 1.0000 Uani . . .
. . . .
C30 C -0.2701(5) 0.5697(3) 0.16029(19) 0.0424 1.0000 Uani . .
. . . . .
C31 C -0.2937(7) 0.3949(3) 0.0221(2) 0.0591 1.0000 Uani . . .
. . . .
H71 H 0.4178 0.6907 0.5765 0.0431 1.0000 Uiso R . . . . . .
H81 H 0.3575 0.8330 0.5297 0.0468 1.0000 Uiso R . . . . . .
H101 H 0.0784 0.7117 0.3770 0.0369 1.0000 Uiso R . . . . . .
H132 H -0.1527 0.3694 0.3100 0.0697 1.0000 Uiso R . . . . . .
H131 H -0.1337 0.4746 0.3267 0.0698 1.0000 Uiso R . . . . . .
H133 H 0.0037 0.4262 0.2853 0.0699 1.0000 Uiso R . . . . . .
```

```
H143 H 0.0963 0.2628 0.3540 0.0874 1.0000 Uiso R . . . . . .
H141 H -0.0339 0.2693 0.4075 0.0877 1.0000 Uiso R . . . . . .
H142 H 0.1703 0.2852 0.4249 0.0873 1.0000 Uiso R . . . . . .
H171 H 0.4733 0.1772 0.6627 0.0689 1.0000 Uiso R . . . . . .
H172 H 0.5580 0.2517 0.7110 0.0691 1.0000 Uiso R . . . . . .
H173 H 0.3519 0.2293 0.7075 0.0689 1.0000 Uiso R . . . . . .
H203 H 0.6932 0.6271 0.7468 0.0769 1.0000 Uiso R . . . . . .
H201 H 0.5305 0.5775 0.7728 0.0770 1.0000 Uiso R . . . . . .
H202 H 0.6976 0.5208 0.7580 0.0770 1.0000 Uiso R . . . . . .
H261 H 0.1519 0.5599 0.1358 0.0460 1.0000 Uiso R . . . . . .
H271 H 0.0384 0.4564 0.0572 0.0480 1.0000 Uiso R . . . . . .
H291 H -0.4585 0.4954 0.1075 0.0580 1.0000 Uiso R . . . . . .
H301 H -0.3487 0.5985 0.1865 0.0509 1.0000 Uiso R . . . . . .
H312 H -0.4067 0.4159 0.0004 0.0890 1.0000 Uiso R . . . . . .
H311 H -0.2095 0.3868 -0.0092 0.0893 1.0000 Uiso R . . . . . .
H313 H -0.3128 0.3364 0.0418 0.0891 1.0000 Uiso R . . . . . .
H41 H 0.0676 0.5582 0.3690 0.0361 1.0000 Uiso R . . . . . .
O220 O -0.0766(6) 0.6329(3) 0.28947(17) 0.0520 0.726(6) Uani D
. P . 1 . .
O230 O -0.0976(7) 0.7541(3) 0.2124(2) 0.0585 0.726(6) Uani D .
P . 1 . .
O240 O 0.1846(5) 0.6688(4) 0.2328(2) 0.0613 0.726(6) Uani D .
P . 1 . .
O221 O 0.1320(17) 0.6110(7) 0.2734(5) 0.0616 0.274(6) Uani D .
P . 2 . .
O231 O -0.1259(14) 0.7172(10) 0.2601(7) 0.0654 0.274(6) Uani D
. P . 2 . .
O241 O 0.1306(18) 0.7283(9) 0.1988(6) 0.0658 0.274(6) Uani D .
P . 2 . .
loop_
_atom_site_aniso_label
_atom_site_aniso_U_11
_atom_site_aniso_U_22
_atom_site_aniso_U_33
_atom_site_aniso_U_23
_atom_site_aniso_U_13
_atom_site_aniso_U_12
Pd1 0.03114(13) 0.03009(12) 0.02511(12) 0.00309(10) 0.00610(8)
0.00207(10)
O2 0.0504(15) 0.0302(12) 0.0367(13) 0.0015(10) 0.0010(11) -
0.0056(11)
C3 0.0290(16) 0.0339(16) 0.0332(17) -0.0037(13) 0.0120(13) -
0.0012(13)
N4 0.0341(15) 0.0314(14) 0.0251(13) -0.0020(10) 0.0012(11) -
0.0006(11)
C5 0.0243(15) 0.0283(14) 0.0281(15) -0.0028(12) 0.0051(12) -
0.0008(11)
C6 0.0290(15) 0.0276(14) 0.0263(15) -0.0011(12) 0.0041(12)
0.0009(12)
C7 0.0426(19) 0.0346(17) 0.0281(17) -0.0022(13) -0.0046(14) -
0.0032(15)
```

```
C8 0.053(2) 0.0277(16) 0.0350(18) -0.0045(13) -0.0007(16) -
0.0067(15)
C9 0.0397(18) 0.0254(15) 0.0378(18) 0.0046(13) 0.0031(15)
0.0014(13)
C10 0.0283(16) 0.0342(16) 0.0296(16) 0.0005(13) -0.0010(13)
0.0022(13)
F11 0.0548(14) 0.0290(10) 0.0554(14) 0.0096(9) -0.0046(11)
0.0000(9)
N12 0.0441(17) 0.0354(15) 0.0387(16) -0.0120(13) 0.0074(13) -
0.0095(13)
C13 0.0358(19) 0.061(2) 0.043(2) -0.0201(18) 0.0028(16) -
0.0078(17)
C14 0.076(3) 0.033(2) 0.067(3) -0.0116(19) 0.012(2) -0.012(2)
N15 0.0439(17) 0.0365(16) 0.0375(16) 0.0080(13) 0.0095(13)
0.0039(13)
C16 0.043(2) 0.0329(17) 0.0378(19) 0.0022(14) 0.0071(16) -
0.0005(14)
C17 0.060(3) 0.0383(19) 0.040(2) 0.0111(16) -0.0014(18)
0.0054(17)
N18 0.0319(15) 0.0404(15) 0.0310(15) 0.0054(12) 0.0038(12)
0.0061(12)
C19 0.0307(17) 0.0426(19) 0.0336(18) 0.0067(14) 0.0022(14)
0.0056(14)
C20 0.052(2) 0.066(3) 0.0322(19) 0.0039(18) -0.0088(17)
0.007(2)
S21 0.0608(6) 0.0370(5) 0.0272(4) 0.0008(3) -0.0036(4) -
0.0027(4)
C25 0.046(2) 0.0278(15) 0.0255(16) 0.0049(12) -0.0029(14)
0.0024(14)
C26 0.0363(18) 0.0447(19) 0.0318(17) 0.0047(14) -0.0006(14)
0.0075(15)
C27 0.048(2) 0.0389(18) 0.0329(17) 0.0006(14) 0.0024(15)
0.0111(16)
C28 0.054(2) 0.0375(18) 0.0351(18) -0.0039(15) 0.0047(16) -
0.0027(16)
C29 0.043(2) 0.055(2) 0.046(2) -0.0115(19) 0.0071(16) -
0.0095(18)
C30 0.041(2) 0.045(2) 0.043(2) -0.0078(16) 0.0103(16)
0.0002(16)
C31 0.070(3) 0.054(3) 0.054(3) -0.020(2) 0.009(2) -0.011(2)
O220 0.063(3) 0.065(3) 0.0263(18) 0.0035(17) -0.0031(17) -
0.015(2)
O230 0.084(3) 0.036(2) 0.051(3) -0.0045(18) -0.014(2) 0.003(2)
O240 0.042(2) 0.087(4) 0.054(3) -0.022(3) -0.0050(19) -
0.012(2)
O221 0.097(10) 0.049(6) 0.033(6) -0.002(5) -0.020(6) 0.017(6)
O231 0.055(7) 0.075(9) 0.065(9) -0.034(7) 0.002(6) 0.007(6)
O241 0.095(10) 0.062(8) 0.040(6) -0.002(6) 0.008(6) -0.029(7)

_refine_ls_extinction_method
    'None'
_oxford_refine_ls_scale 0.23036(14)
```

```
loop_
 _geom_bond_atom_site_label_1
 _geom_bond_site_symmetry_1
 _geom_bond_atom_site_label_2
 _geom_bond_site_symmetry_2
 _geom_bond_distance
 _geom_bond_publ_flag
Pd1 . Pd1 2_666 3.2719(5)    yes
Pd1 . O2 . 1.980(2)    yes
Pd1 . C6 . 1.970(3)    yes
Pd1 . N15 . 2.138(3)    yes
Pd1 . N18 . 2.000(3)    yes
O2 . C3 . 1.257(4)    yes
C3 . N4 . 1.345(4)    yes
C3 . N12 . 1.344(4)    yes
N4 . C5 . 1.412(4)    yes
N4 . H41 . 0.842    no
C5 . C6 . 1.397(4)    yes
C5 . C10 . 1.406(4)    yes
C6 . C7 . 1.403(4)    yes
C7 . C8 . 1.386(5)    yes
C7 . H71 . 0.933    no
C8 . C9 . 1.366(5)    yes
C8 . H81 . 0.928    no
C9 . C10 . 1.363(5)    yes
C9 . F11 . 1.379(4)    yes
C10 . H101 . 0.933    no
N12 . C13 . 1.451(5)    yes
N12 . C14 . 1.466(5)    yes
C13 . H132 . 0.958    no
C13 . H131 . 0.966    no
C13 . H133 . 0.957    no
C14 . H143 . 0.954    no
C14 . H141 . 0.946    no
C14 . H142 . 0.952    no
N15 . C16 . 1.130(5)    yes
C16 . C17 . 1.456(5)    yes
C17 . H171 . 0.956    no
C17 . H172 . 0.955    no
C17 . H173 . 0.955    no
N18 . C19 . 1.138(5)    yes
C19 . C20 . 1.449(5)    yes
C20 . H203 . 0.955    no
C20 . H201 . 0.951    no
C20 . H202 . 0.950    no
S21 . C25 . 1.774(3)    yes
S21 . O220 . 1.490(4)    yes
S21 . O230 . 1.474(4)    yes
S21 . O240 . 1.379(4)    yes
C25 . C26 . 1.383(5)    yes
C25 . C30 . 1.389(5)    yes
C26 . C27 . 1.385(5)    yes
```

```
C26 . H261 . 0.929    no
C27 . C28 . 1.384(6)    yes
C27 . H271 . 0.929    no
C28 . C29 . 1.392(6)    yes
C28 . C31 . 1.516(5)    yes
C29 . C30 . 1.379(5)    yes
C29 . H291 . 0.925    no
C30 . H301 . 0.939    no
C31 . H312 . 0.960    no
C31 . H311 . 0.957    no
C31 . H313 . 0.958    no
loop_
 _geom_angle_atom_site_label_1
 _geom_angle_site_symmetry_1
 _geom_angle_atom_site_label_2
 _geom_angle_site_symmetry_2
 _geom_angle_atom_site_label_3
 _geom_angle_site_symmetry_3
 _geom_angle
 _geom_angle_publ_flag
Pd1 2_666 Pd1 . O2 . 86.18(8)    yes
Pd1 2_666 Pd1 . C6 . 77.72(9)    yes
O2 . Pd1 . C6 . 91.76(12)    yes
Pd1 2_666 Pd1 . N15 . 106.21(8)    yes
O2 . Pd1 . N15 . 88.58(11)    yes
C6 . Pd1 . N15 . 176.06(12)    yes
Pd1 2_666 Pd1 . N18 . 97.74(8)    yes
O2 . Pd1 . N18 . 172.68(11)    yes
C6 . Pd1 . N18 . 95.10(13)    yes
N15 . Pd1 . N18 . 84.40(12)    yes
Pd1 . O2 . C3 . 130.7(2)    yes
O2 . C3 . N4 . 122.8(3)    yes
O2 . C3 . N12 . 118.2(3)    yes
N4 . C3 . N12 . 119.0(3)    yes
C3 . N4 . C5 . 127.3(3)    yes
C3 . N4 . H41 . 116.6    no
C5 . N4 . H41 . 116.0    no
N4 . C5 . C6 . 125.4(3)    yes
N4 . C5 . C10 . 113.9(3)    yes
C6 . C5 . C10 . 120.7(3)    yes
C5 . C6 . Pd1 . 121.9(2)    yes
C5 . C6 . C7 . 117.1(3)    yes
Pd1 . C6 . C7 . 121.0(2)    yes
C6 . C7 . C8 . 122.9(3)    yes
C6 . C7 . H71 . 119.4    no
C8 . C7 . H71 . 117.8    no
C7 . C8 . C9 . 117.2(3)    yes
C7 . C8 . H81 . 121.3    no
C9 . C8 . H81 . 121.4    no
C8 . C9 . C10 . 123.5(3)    yes
C8 . C9 . F11 . 119.4(3)    yes
C10 . C9 . F11 . 117.2(3)    yes
```

```
C5 . C10 . C9 . 118.7(3)    yes
C5 . C10 . H101 . 120.8    no
C9 . C10 . H101 . 120.6    no
C3 . N12 . C13 . 123.6(3)    yes
C3 . N12 . C14 . 119.0(3)    yes
C13 . N12 . C14 . 117.4(3)    yes
N12 . C13 . H132 . 108.1    no
N12 . C13 . H131 . 111.0    no
H132 . C13 . H131 . 109.2    no
N12 . C13 . H133 . 110.1    no
H132 . C13 . H133 . 108.9    no
H131 . C13 . H133 . 109.6    no
N12 . C14 . H143 . 110.0    no
N12 . C14 . H141 . 110.0    no
H143 . C14 . H141 . 109.5    no
N12 . C14 . H142 . 110.2    no
H143 . C14 . H142 . 108.7    no
H141 . C14 . H142 . 108.5    no
Pd1 . N15 . C16 . 165.0(3)    yes
N15 . C16 . C17 . 177.9(4)    yes
C16 . C17 . H171 . 109.4    no
C16 . C17 . H172 . 110.0    no
H171 . C17 . H172 . 109.3    no
C16 . C17 . H173 . 108.9    no
H171 . C17 . H173 . 109.4    no
H172 . C17 . H173 . 109.7    no
Pd1 . N18 . C19 . 166.6(3)    yes
N18 . C19 . C20 . 177.8(4)    yes
C19 . C20 . H203 . 109.9    no
C19 . C20 . H201 . 109.7    no
H203 . C20 . H201 . 109.2    no
C19 . C20 . H202 . 109.3    no
H203 . C20 . H202 . 109.7    no
H201 . C20 . H202 . 109.1    no
C25 . S21 . O220 . 103.8(2)    yes
C25 . S21 . O230 . 104.0(2)    yes
O220 . S21 . O230 . 106.2(3)    yes
C25 . S21 . O240 . 108.3(2)    yes
O220 . S21 . O240 . 116.0(3)    yes
O230 . S21 . O240 . 117.2(3)    yes
S21 . C25 . C26 . 120.5(3)    yes
S21 . C25 . C30 . 119.4(3)    yes
C26 . C25 . C30 . 120.1(3)    yes
C25 . C26 . C27 . 119.5(3)    yes
C25 . C26 . H261 . 119.9    no
C27 . C26 . H261 . 120.6    no
C26 . C27 . C28 . 121.6(3)    yes
C26 . C27 . H271 . 119.0    no
C28 . C27 . H271 . 119.4    no
C27 . C28 . C29 . 117.8(3)    yes
C27 . C28 . C31 . 120.3(4)    yes
C29 . C28 . C31 . 121.9(4)    yes
```

```
C28 . C29 . C30 . 121.6(4)    yes
C28 . C29 . H291 . 119.4    no
C30 . C29 . H291 . 119.0    no
C25 . C30 . C29 . 119.4(4)    yes
C25 . C30 . H301 . 120.2    no
C29 . C30 . H301 . 120.4    no
C28 . C31 . H312 . 110.2    no
C28 . C31 . H311 . 110.8    no
H312 . C31 . H311 . 109.0    no
C28 . C31 . H313 . 109.7    no
H312 . C31 . H313 . 108.6    no
H311 . C31 . H313 . 108.6    no
loop_
 _geom_hbond_atom_site_label_D
 _geom_hbond_site_symmetry_D
 _geom_hbond_atom_site_label_H
 _geom_hbond_site_symmetry_H
 _geom_hbond_atom_site_label_A
 _geom_hbond_site_symmetry_A
 _geom_hbond_angle_DHA
 _geom_hbond_distance_DH
 _geom_hbond_distance_HA
 _geom_hbond_distance_DA
 _geom_hbond_publ_flag
C10 . H101 . O220 . 146 0.93 2.34 3.156(5)    yes
C13 . H132 . O230 3_445 173 0.96 2.50 3.457(5)    yes
C13 . H131 . O220 . 129 0.97 2.47 3.176(5)    yes
C14 . H143 . O241 3_545 136 0.95 2.46 3.214(5)    yes
C17 . H172 . O240 2_666 165 0.96 2.42 3.356(5)    yes
C17 . H173 . O231 2_566 151 0.95 2.03 2.901(5)    yes
C20 . H203 . O241 4_565 130 0.96 2.35 3.052(5)    yes
C20 . H202 . O221 2_666 148 0.95 2.42 3.264(5)    yes
N4 . H41 . O220 . 161 0.84 2.16 2.968(5)    yes
N4 . H41 . O221 . 143 0.84 2.23 2.946(5)    yes
```

[1] J. Cosier and A. M. Glazer, *J. Appl. Cryst.*, 1986, **19**, 105-107.
[2] Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods Enzymol.*, 1997, 276, Eds C. W. Carter, R. M. Sweet, Academic Press.
[3] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori & M. Camalli, *J. Appl. Cryst.*, 1994, **27**, 435; G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.
[4] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout, & D. J. Watkin, *J. Appl. Cryst.*, 2003, **36**, 1487; R. I. Cooper, R. O. Gould, S. Parsons & D. J. Watkin, *J. Appl. Cryst.*, 2002, **35**, 168-174.