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Supporting Information

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((Catalytic amide-mediated methyl transfer from silanes to alkenes in Fujiwara-Moritani oxidative coupling))

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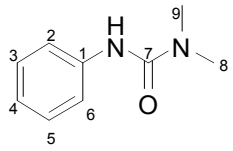
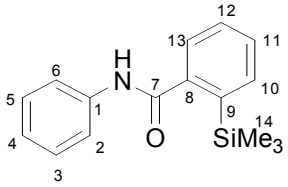
Electronic Supplementary Information

1,1-dimethyl-3-phenylurea[1]:



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 (s, N-H), 3018 (s, C-H[aromatic]), 1667 (s, C=O) ;^{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, $CDCl_3$) δppm 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.

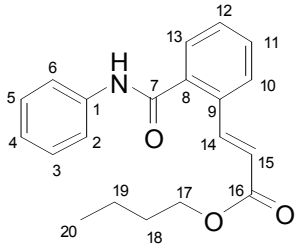
N-phenyl-2-(trimethylsilyl)benzamide (5)[2]:



A solution of benzanilide (985 mg, 5 mmol)) in THF (30 mL) was cooled to -78 ˚C and Bu^{t}Li (1.7 M in pentane) (5.9 mL, 10 mmol) was added dropwise while stirring the mixture vigorously. After 2 h Me_3SiCl (4 mL, 30 mmol) was added dropwise keeping the reaction mixture at 78 ˚C followed by stirring for 2 h. Then the mixture was warmed slowly to room temperature and stirred overnight. The reaction was quenched by adding saturated NH_4Cl (10 mL) and the organic layer was extracted, dried with magnesium sulphate, saturated *in vacuo* and purified by column chromatography (ether/pentane, 1:2) to get the product (1.2 g, 90%); m.p 128-130 °C; ν_{max} ($CHCl_3$) 3445 (s, N-H), 3109 (s, C-H[aromatic]), 1680 (s, C=O), 1437 (m, C-Si [aromatic]), 1215 (s, C-Si [aliphatic]);^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.71 (1 H, dd, *J* = 7.3, 0.9 Hz, C(13)*H*), 7.70 (1 H, N*H*), 7.63 (2 H, d, *J* = 7.9 Hz, 2 x C(2)*H*), 7.55 (1 H, d, *J* = 7.4 Hz, C(10)*H*), 7.48 (1 H, dt, *J* = 7.4, 1.4 Hz, C(11)*H*), 7.44-7.38 (1 H, m, C(12)*H*), 7.38 (2 H, t, *J* = 7.9 Hz, 2 x C(3)*H*), 7.20-7.15 (1 H, m, C(4)*H*), 0.36 (9 H, s, 3 x C(14)H_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 169.38

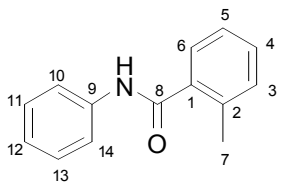
(*C*(7)), 142.70 (*C*(1)), 139.78 (*C*(9)), 138.11 (*C*(8)), 135.58 (*C*(13)), 129.78 (*C*(10)), 129.23 (*C*(11)), 128.96 (2 x *C*(3)), 126.12 (*C*(10)), 124.60 (*C*(4)), 120.07 (2 x *C*(2)), 0.17 (3 x *C*(14)); HRMS (ESI) *m/z*: calc for $C_{16}H_{20}NOSi$ [M+H]: 270.1314, Found 270.1315.

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



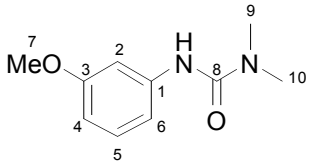
N-phenyl-2-(trimethylsilyl)benzamide **5** (80.7 mg, 0.3 mmol), benzoquinone (37.8 mg, 0.35 mmol) and $Pd(OAc)_2$ (3.36 mg, 5mol%) were taken in a flask and butyl acrylate (44.8 mg, 0.35 mmol) dissolved in AcOH (0.7 mL) was added to the mixture followed by stirring at 70 ˚C for 2 h. Then the mixture was diluted with ether (2 mL) and washed with 0.1N NaOH (3 x 2 mL), water (3 x 2 mL) and saturated NaCl (3 x 2 mL) and dried over $MgSO_4$. After filtration and concentration *in vacuo* the residue was subjected to column chromatography (ether/pentane, 1:1) to yield the product (53 mg, 55%); m.p. 130-134 ˚C; ν_{max} ($CHCl_3$) 3410, 3300, 3020, 2963, 2401, 1707, 1600, 1522, 1439, 1318, 1216, 1073, 767; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.05 (1 H, d, *J* = 15.9 Hz, C(14)*H*), 7.68-7.57 (5 H, m, C(2, 6, 11, 13)*H,* N*H*), 7.52-7.41 (2 H, m, C(10, 12)*H*), 7.37 (2 H, t, *J* = 7.5 Hz, 2 x C(3)*H*), 7.17 (1 H, t, *J* = 7.3 Hz, C(4)*H*), 6.40 (1 H, d, *J* = 15.9 Hz, C(15)*H*), 4.21-4.13 (2 H, m, C(17)H_2), 1.68-1.60 (2 H, m, C(18)H_2), 1.42-1.33 (2 H, m, C(19)H_2), 0.91 (3 H, t, *J* = 7.4 Hz, C(20)H_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 172.8 (*C*(16)), 166.50 (*C*(16)), 141.55 (*C*(14)), 137.72 (*C*(1)), 133.18 (*C*(9)), 130.80 (*C*(11)), 129.93 (2 x *C*(3)), 129.15 (*C*(10)), 128.84 (*C*(4)), 127.70 (*C*(12)), 127.49 (*C*(8)),124.94 (*C*(13)), 121.46 (2 x *C*(2)), 120.19 (*C*(15)), 64.64 (*C*(17)), 30.74 (*C*(18)), 19.22 (*C*(19)), 13.77 (*C*(20)); HRMS (ESI) *m/z*: calc for $C_{20}H_{21}NO_3$ [M+Na]: 346.1414, Found 346.1428.

2-methyl-N-phenylbenzamide (7)[3]:



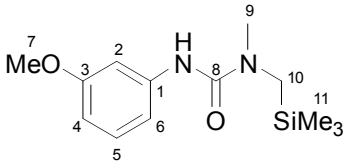
The compound **7** was isolated by column chromatography (ether/pentane, 1:1) as white solid (18 mg, 30%) from the reaction above for the preparation of **6**; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.63 (2 H, d, *J* = 7.8 Hz, 2 x C(10)*H*), 7.53 (1 H, s, N*H*), 7.49 (1 H, d, *J* = 7.6 Hz, C(6)*H*), 7.42-7.34 (3 H, m, 2 x C(11)*H*, C(4)*H*), 7.30-7.24 (2 H, m, 2 x C(3)*H*), 7.17 (1 H, t, *J* = 7.4 Hz, C(12)*H*), 2.52 (3 H, s, C(7)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 168.48 (*C*(8)), 137.98 (*C*(9)), 136.47 (*C*(1)), 134.30 (*C*(2)),131.30 (*C*(3)), 130.32 (*C*(4)), 129.14 (2 x *C*(11)), 126.61 (*C*(6)), 125.93 (*C*(5)), 124.57 (*C*(12)), 119.86 (2 x *C*(10)), 19.85 (*C*(7)); HRMS (ESI) *m/z*: calc for $C_{14}H_{13}NO$ [M+Na]: 234.0889, Found 234.0905.

3-(3-methoxyphenyl)-1,1-dimethylurea (8)[4]:



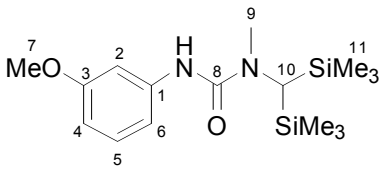
The solution of dimethylamine (2M in methanol), (10 mmol, 5 mL) was added to 3-methoxyphenyl isocyanate (10 mmol, 1.5 g) dissolved in toluene (50 mL) at 75 ˚C. After 4 h stirring the reaction was concentrated *in vacuo* and precipitated urea was washed with toluene followed by concentration to get (1.9 g, 90%) of the product as white solid; m.p 140-142 °C; ν_{max} ($CHCl_3$) 3324 (s, N-H), 3019 (s, C-H[aromatic]), 2400, 1666, 1606, 1365, 1216, 1040, 961, 844, 757, 689, 668;1H 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); 13C NMR (101 MHz, $CDCl_3$) δppm 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.

3-(3-methoxyphenyl)-1-methyl-1-((trimethylsilyl)methyl)urea (9a):



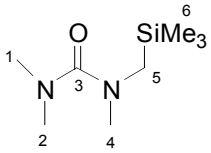
3-(3-methoxyphenyl)-1,1-dimethylurea **8** (1.17 g, 6 mmol) was dissolved in THF (60 mL) and cooled to -78 ˚C. Bu^{t}Li (1.7M in pentane) (10.6 mL, 18 mmol) was added to the urea dropwise and stirred for 2 h at -78 ˚C followed by the addition of Me_3SiCl (4 mL, 30 mmol) and stirring for further 4 h. The reaction mixture was warmed slowly and stirred for 12 h at room temperature. The reaction was quenched by adding saturated NH_4Cl (10 mL) and the organic layer was extracted, dried over $MgSO_4$ and saturated *in vacuo.* The purification by column chromatography (ether/pentane, 2:1) gave the product (280 mg, 15%) as a white solid; mp 105-109˚ C; ν_{max} ($CHCl_3$) 3454, 3307 (s, N-H), 3108 (s, C-H[aromatic]), 2966 (s, C-H[aliphatic]), 1655 (s, C=O), 1253 (s, C-Si); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.18 (1 H, t, *J* = 2.2 Hz, C(2)*H*), 7.14 (1 H, t, *J* = 8.13 Hz, C(5)*H*), 6.84-6.79 (1 H, m, C(6)*H*), 6.58-6.53 (1 H, m, C(4)*H*), 6.31 (1 H, s, N*H*), 3.78 (3 H, s, C(7)H_3), 3.01 (3 H, s, C(9)H_3), 2.90 (2 H, s, C(10)H_2), 0.13 (9 H, s, 3 x C(11)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δppm 160.17 (*C*(3)), 155.11 (*C*(8)), 140.74 (*C*(1)), 129.42 (*C*(5)), 111.50 (*C*(6)), 108.66 (*C*(4)), 104.92 (*C*(2)), 55.25 (*C*(7)), 40.81 (*C*(9)), 36.94 (*C*(10)), -1.56 (3 x *C*(11)); HRMS (ESI) *m/z*: calc for $C_{13}H_{23}N_2O_2Si$ [M+H]: 267.1529, Found 267.1523.

1-(bis(trimethylsilyl)methyl)-3-(3-methoxyphenyl)-1-methylurea (9b):



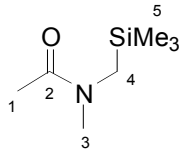
The compound **9b** (509mg, 25%) was isolated by column chromatography (ether/pentane, 2:1) from the reaction above; ν_{max} ($CHCl_3$) 3455, 3308 (s, N-H), 3109 (s, C-H[aromatic]), 2956 (s, C-H[aliphatic]), 1656 (s, C=O), 1253 (s, C-Si); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.18 (1 H, s, C(2)*H*), 7.13 (1 H, t, *J* = 8.1 Hz, C(5)*H*), 6.85 (1 H, d, *J* = 7.8 Hz, C(6)*H*), 6.54 (1 H, d, *J* = 8.1 Hz, C(4)*H*), 6.45 (1 H, s, N*H*), 3.76 (3 H, d, *J* = 2.4 Hz, C(7)H_3), 3.02 (3 H, s, C(9)H_3), 2.81 (1 H, s, C(10)*H*), 0.13 (18 H, s, 6 x C(11)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δppm 160.16 (*C*(3)), 155.04 (*C*(8)), 140.96 (*C*(1)), 129.40 (*C*(5)), 111.60 (*C*(4)), 108.39 (*C*(6)), 105.04 (*C*(2)), 55.20 (*C*(7)), 54.10 (*C*(10)), 35.62 (*C*(9)), 1.22 (6 x *C*(11));HRMS (ESI) *m/z*: calc for $C_{16}H_{30}N_2O_2Si_2$ [M+H]: 339.1924, Found 339.1919.

1,1,3-trimethyl-3-((trimethylsilyl)methyl)urea (10):



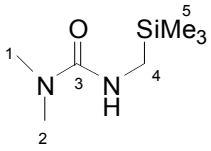
A solution of tetramethylurea (1.05 g, 9 mmol) in THF (50 mL) was cooled to -78 ˚C and Bu^{t}Li (1.7 M in pentane) (5.9 mL, 10 mmol) was added dropwise while stirring the mixture vigorously. After 4 h CH_3SiCl (10 mL, 75 mmol) was added dropwise keeping the reaction mixture at 78 ˚C followed by stirring for further 4 h. Then the mixture was warmed slowly to room temperature and stirred for 5 h. The reaction was quenched by adding saturated NH_4Cl (10 mL) and the organic layer was extracted, dried over $MgSO_4$ and saturated *in vacuo.* The purification by column chromatography (ether/pentane, 3:1) gave the product (90 mg, 5%) as light orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.84 (3 H, s, C(4)H_3), 2.75 (6 H, s, 2 x C(1)H_3), 2.72 (2 H, s, C(5)H_2), 0.08 (9 H, s, 3 x C(6)H_3).

N-methyl-N-((trimethylsilyl)methyl)acetamide (11)[5]:



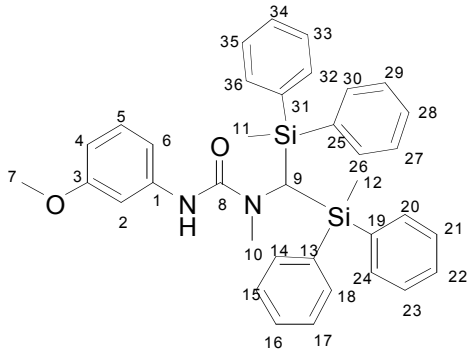
A mixture of N-methylacetamide (2.0 g, 27 mmol) and 60% sodium hydride (1.1 g, 27 mmol) (washed with hexane) in THF (30 mL) was stirred at reflux for 3 h. Me_3SiI (4.2 mL, 28 mmol) was added to the reaction mixture and reflux was continued for 12 h. The mixture was filtered and washed with saturated KI (3 x 5 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The column chromatography (EtOAc) gave the product (1 g, 25%) as yellow oil; ν_{max} (neat) 3440, 2953, 1625, 1416, 1248, 1021, 968, 854; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.94, 2.93 (3 H, s, C(3)H_3), 2.79 , 2.85 (2 H, s, C(4)H_2), 2.00, 1.97 (3 H, s, C(1)H_3) , 0.04, -0.01 (9 H, s, 3 x C(5)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.72, 169.97 (*C*(2)), 42.52, 39.99 (*C*(4)), 35.63 , 35.16 (*C*(3)), 21.60, 21.42 (*C*(1)), -1.54, -1.72 (3 x *C*(5)); HRMS (ESI) *m/z*: calc for $C_7H_{17}NOSi$ [M+Na]: 182.0972, Found 182.0968.

1,1-dimethyl-3-((trimethylsilyl)methyl)urea:



A solution of trimethylurea (1.53 g, 15 mmol) in THF (50 mL) was cooled to -78 ˚C for 4 h and Bu^{t}Li (1.7 M in pentane) (22 mL, 37 mmol) was added dropwise while stirring the mixture vigorously. After 4 hr CH_3SiCl (10 mL, 75 mmol) was added dropwise keeping the reaction mixture at 78˚ C followed by stirring for 4 hr. 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 over $MgSO_4$ and saturated *in vacuo*. The purification by column chromatography (ether/pentane, 1:3) gave the product (120 mg, 5%) as light yellow oil. ν_{max} (neat) 3347, 2954, 2228, 1627, 1543, 1412, 1373, 1287, 1249, 1153, 1086, 856, 764, 733; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 4.39 (1 H, s, N*H*), 2.86 (3 H, s, C(1)*H*$_3$), 2.76 (2 H, s, C(4)*H*$_2$), 2.75 (3 H, s, C(2)*H*$_3$), 0.06, 0.05 (9 H, s, 3 x C(5)*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 158.94 (*C*(3)), 40.39 (*C*(1)), 36.59 (*C*(2)), 27.79 (*C*(4)), -1.57 (*C*(5)); HRMS (ESI) *m/z*: calc for $C_7H_{18}N_2OSi$ [M+Na]: 197.1081, Found 197.1077.

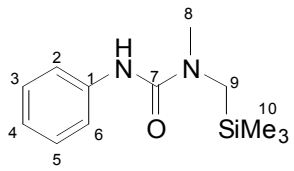
1-(bis(methyldiphenylsilyl)methyl)-3-(3-methoxyphenyl)-1-methylurea (14):



3-(3-methoxyphenyl)-1,1-dimethylurea **8** (1.17 g, 6 mmol) was dissolved in THF (60 mL) and cooled to -78 ˚C. Bu^{t}Li solution (1.7M in pentane) (11.8 mL, 20 mmol) was added to the urea dropwise and stirred for 3 h at -78 ˚C followed by the addition of chlorodiphenylmethylsilane (4 g, 20 mmol) and stirring for further 3 h. The reaction mixture was warmed slowly and stirred for 12 h at room temperature. The reaction was quenched by adding saturated NH_4Cl (10 mL) and the organic layer was extracted, dried over $MgSO_4$ and saturated *in vacuo*. The purification by column chromatography (ether/pentane, 1:2) gave the product (1.23 g, 35%) as a white solid; m.p. 159-

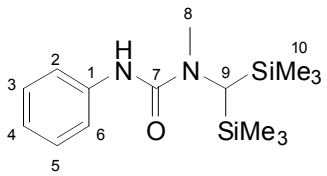
161 ˚C; ν_{max} ($CHCl_3$) 3335 (s, N-H), 3071, 3011 (s, C-H[aromatic]), 2926, 2850 (s, C-H[aliphatic]), 1645, 1604 (s, C=O), 1214 (s, C-Si); 1H NMR (400 MHz, $CDCl_3$) δ ppm 7.80-7.07 (23 H, m, 23 x Ar*H*), 6.63 (1 H, d, *J* = 6.9 Hz, C(6)*H*), 5.86 (1 H, s, N*H*), 3.84 (3 H, s, C(7)H_3), 2.80 (1 H, s, C(9)H_3), 2.70 (3 H, s, C(10)H_3), 0.68 (1 H, s, 2 x C(11)H_3); 13C NMR (101 MHz, $CDCl_3$) δ ppm 160.06 (*C*(3)), 155.42 (*C*(8)), 137.65 (*C*(1)), 135.54 (3 x *C*(13)), 134.99-134.64 (m, 3 x *C*(14)), 134.07 (*C*(5)), 129.77-129.11 (m, 6 x *C*(15)), 128.07-127.61 (m, 3 x *C*(16)), 112.53 (*C*(4)), 108.61 (*C*(6)), 105.95 (*C*(2)), 55.33 (*C*(7)), 36.22 (*C*(10)), 27.02 (*C*(9)), -0.44 (2 x *C*(11)), -2.69 (2 x *C*(11)); HRMS (ESI) *m/z*: calc for $C_{36}H_{38}N_2O_2Si_2$ [M+Na]: 609.2364, Found 609.2360.

1-methyl-3-phenyl-1-((trimethylsilyl)methyl)urea:



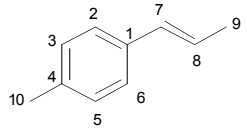
1,1-dimethyl-3-phenylurea (1.15 g, 7 mmol) was dissolved in THF (120 mL) and cooled to -78 ˚C. Bu^{t}Li solution (1.7M in pentane) (13.2 mL, 22.4 mmol) was added to the urea dropwise and stirred for 4 h at -78 ˚C followed by the addition of Me_3SiCl (2.5 g, 23.1 mmol) and stirring for further 4 h. The reaction mixture was warmed slowly and stirred for 12 h at room temperature. The reaction was quenched by adding saturated NH_4Cl (10 mL) and the organic layer was extracted, dried over $MgSO_4$ and saturated *in vacuo*. The purification by column chromatography (ether/pentane, 1:2) gave the product (250 mg, 15%) as a white solid; m.p. 138-140 ˚C; ν_{max} ($CHCl_3$) 3455, 3345, 3018, 2956, 1651, 1595, 1523, 1439, 1375, 1307, 1250, 1216, 855, 756, 693, 668; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.37 (2 H, d, *J* = 7.9 Hz, 2 x C(2)*H*), 7.27 (1 H, t, *J* = 7.9 Hz, 2 x C(3)*H*), 7.00 (1 H, t, *J* = 7.3 Hz, C(4)*H*), 6.35 (1 H, s, N*H*), 3.01 (3 H, s, C(8)H_3), 2.91 (2 H, s, C(9)H_2), 0.14 (9 H, s, 3 x C(10)H_3); ^{13}C NMR (101MHz, $CDCl_3$) δ ppm 155.29 (*C*(7)), 139.42 (*C*(1)), 128.82 (2x*C*(3)), 122.67 (*C*(4)), 119.64 (2 x *C*(2)), 40.82 (*C*(9)), 36.96 (*C*(8)), -1.54 (3 x *C*(10)); HRMS (ESI) *m/z*: calc for $C_{15}H_{28}N_2OSi_2$ [M+Na]: 259.1237, Found 259.1237.

1-(bis(trimethylsilyl)methyl)-1-methyl-3-phenylurea (15):



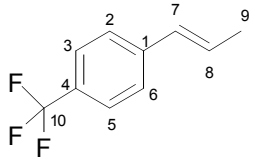
The compound **15** was isolated as a white solid (0.98 g, 45%) from the reaction above by column chromatography (ether/pentane, 1:2); m.p. 104-106 ˚C*;* ν_{max} ($CHCl_3$) 3457, 3348 (s, N-H), 3017 (s, C-H[aromatic]), 2955 (s, C-H[aliphatic]), 1651 (s, C=O), 1253 (s, C-Si); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.38 (2 H, d, *J* = 7.7 Hz, 2 x C(2)*H*), 7.27 (2 H, t, *J* = 7.8 Hz, 2 x C(3)*H*), 7.00 (1 H, t, *J* = 7.2 Hz, C(4)*H*), 6.29 (1 H, s, N*H*), 3.06 (3 H, s, C(8)H_3), 2.81 (1 H, s, C(9)*H*), 0.15 (18 H, s, 6x C(10)H_3); ^{13}C NMR (101MHz, $CDCl_3$) δ ppm 154.79 (*C*(7)),139.60 (*C*(1)), 128.84 (*C*(3)), 122.53 (*C*(4)), 119.53 (*C*(2)), 38.23 (*C*(9)), 30.95 (*C*(8)), 0.12 (6 x *C*(10)); HRMS (ESI) *m/z*: calc for $C_{15}H_{28}N_2OSi_2$ [M+Na]: 331.1638, Found 331.1648.

(E)-1-methyl-4-(prop-1-enyl)benzene (18)[6]:



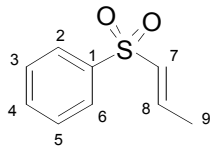
1-(bis(trimethylsilyl)methyl)-1-methyl-3-phenylurea **15** (78 mg, 0.25 mmol), benzoquinone (55 mg, 0.5 mmol) and $Pd(OAc)_2$ (5.6 mg, 5 mol%) were placed in a flask and 1-methyl-4-vinylbenzene (59 mg, 0.5 mmol) in AcOH (0.7 mL) was added. The mixture was stirred at room temperature for 24 h. The AcOH was removed and pentane was added to the residue which was then filtered and concentrated *in vacuo.* GC/MS analysis of the raw mixture showed 95% conversion. The purification by column chromatography (ether:penatane 1:3) gave the product (56 mg, 85%) as colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.27 (2 H, d, *J* = 8.0 Hz, 2 x C(2)*H*), 7.14 (2 H, d, *J* = 8.0 Hz, 2 x C(3)*H*), 6.41 (1 H, dd, *J* = 15.7, 1.5 Hz, C(7)*H*), 6.22 (1 H, dq, *J* = 15.7 , 6.6 Hz, C(8)*H*), 2.36 (3 H, s, C(10)*H*), 1.91 (3 H, dd, *J* = 6.6, 1.5 Hz, C(9)*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 136.41 (*C*(4)), 135.18 (*C*(1)), 130.87 (*C*(7)), 129.19 (2 x *C*(3)), 125.73 (*C*(2)), 124.63 (*C*(8)), 21.16 (*C*(10)), 18.50 (*C*(9)). HRMS (CI) *m/z*: calc for $C_{10}H_{12}$ M^+: 132.0939, Found 132.0912.

(E)-1-(prop-1-enyl)-4-(trifluoromethyl)benzene (19)[7]:



1-(bis(trimethylsilyl)methyl)-1-methyl-3-phenylurea **15** (34 mg, 0.11 mmol), benzoquinone (22 mg, 0.2 mmol) and $Pd(OAc)_2$ (2.24 mg, 5 mol%) were placed in a flask and 1-(trifluoromethyl)-4-vinylbenzene (34.4 mg, 0.2 mmol) in AcOH (0.6 mL) was added. The mixture was stirred at room temperature. The reaction was stopped after 12h when palladium black appeared along the walls of the flask. The AcOH was removed and pentane was added to the residue which was then filtered and concentrated *in vacuo.* GC/MS analysis of the raw mixture showed 99% conversion. The purification by column chromatography (ether:penatane 2:3) gave the product as a light yellow oil (32 mg, 86%). ν_{max} (neat) 2920, 1659, 1448, 1337, 1165, 1127, 1072, 962, 900, 779, 697; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.60-7.37 (4 H, m, 4 x C(2)*H*), 6.44 (1 H, dd, *J* = 15.8, 1.3 Hz, C(7)*H*), 6.33 (1 H, qd, *J* = 15.8, 6.4 Hz, C(8)*H*), 1.92 (3 H, dd, *J* = 6.4, 1.3 Hz, C(9)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 138.65 (*C*(1)), 129.78 (*C*(7)), 128.95 (*C*(4)), 128.87 (2 x *C*(2)), 127.86 (2 x *C*(3)), 123.26 *C*(8)), 122.46 (*C*(10)), 18.49 (*C*(9)); ^{19}F NMR (377 MHz, $CDCl_3$) δ ppm -62.73; HRMS (CI) *m/z*: calc for $C_{10}H_9F_3$ M^+: 186.0656, Found 186.0655.

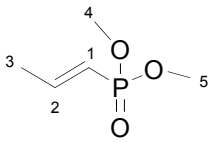
(E)-(prop-1-enylsulfonyl)benzene (20)[8]:



1-(bis(trimethylsilyl)methyl)-1-methyl-3-phenylurea **15** (17 mg, 0.05 mmol), benzoquinone (11 mg, 0.1 mmol) and $Pd(OAc)_2$ (1.12 mg, 5 mol%) were placed in a flask and vinylsulfonylbenzene (17 mg, 0.2 mmol) in AcOH (0.6 mL) was added. The mixture was stirred at room temperature for 16 h. The AcOH was removed and ether was added to the residue which was then filtered and concentrated *in vacuo.* GC/MS analysis of the raw mixture showed 97% conversion. The purification by column chromatography (ether:pentane 2:3) gave the product (14.6 mg, 80%) as a light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.88 (2 H, d, *J* = 7.5 Hz, 2 x C(2)*H*), 7.61 (1 H, t, *J* = 7.2 Hz, C(4)*H*), 7.53 (1 H, t, *J* = 7.3 Hz, 2 x C(3)*H*), 7.03-6.94 (1 H, m, C(7)*H*), 6.35 (1 H, d, *J* = 15.0 Hz, C(8)*H*), 1.93 (3 H, d, *J* = 6.7 Hz, C(9)H_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 142.98

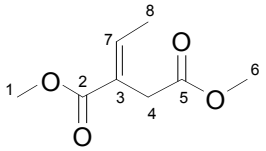
(*C*(7)), 141.13 (*C*(1)), 133.70 (*C*(4)), 132.28 (*C*(8)), 129.69 (2 x *C*(3)), 128.04 (2 x *C*(2)), 17.79 (*C*(9)); HRMS (ESI) *m/z*: calc for $C_9H_{10}O_2S$ [M+Na]: 205.0294, Found 205.0288.

(E)-dimethyl prop-1-enylphosphonate (21)[9]:



1-(bis(trimethylsilyl)methyl)-1-methyl-3-phenylurea **15** (108 mg, 0.35 mmol), benzoquinone (77 mg, 0.7 mmol) and $Pd(OAc)_2$ (7.84mg, 5 mol%) were placed in a flask and dimethyl vinylphosphonate (95.2 mg, 0.7 mmol) in AcOH (0.6 mL) was added. The mixture was stirred at 50˚ C for 3 h. The reaction mixture was cooled to room temperature, diluted with ether and the product was extracted in water (3 x 5 mL). The aqueous phase was concentrated *in vacuo* and the raw mixture was distilled (125 ˚C, 40 mmHg) to get the product as colourless oil (84 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 6.82 (1 H, dddd, *J* = 21.9, 17.1, 13.2, 6.6 Hz, C(2)*H*), 5.63 (1 H, qdd, *J* = 21.90, 17.1, 1.7 Hz, C(1)*H*), 3.70 (6 H, d, *J* = 11.1 Hz, 2 x C(4)H_3), 1.92 (3 H, td, *J* = 6.6, 1.9 Hz, C(3)H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 150.77 (*C*(2)), 116.47 (d, *J* = 188.61 Hz, *C*(1)), 52.46 (d, *J* = 5.57 Hz, (2 x *C*(4)), 20.26 (d, *J* = 24.24 Hz, (*C*(3)); ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 21.57; HRMS (CI) *m/z*: calc for C5H11O3P $[M+H]^+$: 151.0524, Found 151.0524.

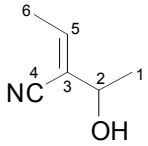
(E)-dimethyl 2-ethylidenesuccinate (22):



1-(bis(trimethylsilyl)methyl)-1-methyl-3-phenylurea **15** (160 mg, 0.52 mmol), benzoquinone (110 mg, 1 mmol) and $Pd(OAc)_2$ (11.2 mg, 5 mol%) were placed in a flask and dimethyl itaconate (160 mg, 0.1 mmol) in AcOH (0.6 mL) was added. The mixture was stirred at room temperature for 22h. The reaction mixture was diluted with ether and washed with 0.1 N NaOH (3 x 3 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuo. GC/MS analysis of raw mixture showed 95% conversion consisting 99% of E isomer. The purification by column chromatography (diethyl ether/pentane, 2:3) gave the product (156 mg, 90%) as colourless oil. ν_{max} ($CHCl_3$) 3002 (m, C-H[olefinic]), 2955 s, 2848 w (C-H[aliphatic]), 1741, 1721 (s, C=O), 1656 (m, C=C), 1437,

1362, 199, 1021; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.05 (1 H, q, *J* = 7.2 Hz, C(7)*H*), 3.73 (3 H, s, C(1)H_3), 3.67 (3 H, s, C(6)H_3), 3.35 (2 H, s, C(4)H_2), 1.81 (3 H, d, *J* = 7.2 Hz, C(8)H_3); ^{13}C NMR (101MHz, $CDCl_3$) δ ppm 171.23 (*C*(5)), 167.27 (*C*(2)), 140.84 (*C*(7)), 126.36 (*C*(3)), 52.01 (*C*(1)), 51.94 (*C*(6)), 31.77 (*C*(4)), 14.60 (*C*(8)); HRMS (ESI) *m/z*: calc for $C_8H_{12}O_4$ [M+Na]: 195.0628, Found 195.0627.

(Z)-2-(1-hydroxyethyl)but-2-enenitrile (23):



1-(bis(trimethylsilyl)methyl)-1-methyl-3-phenylurea **15** (68 mg, 0.22 mmol), benzoquinone (88 mg, 0.8 mmol) and $Pd(OAc)_2$ (9 mg, 10 mol%) were placed in a flask and 3-hydroxy-2-methylenebutanenitrile (40 mg, 0.4 mmol) in AcOH (0.6 mL) was added. The mixture was stirred at 40 ˚C for 8 h and then at 70 ˚C for 16 h. The reaction mixture was cooled to room temperature, diluted with ether and washed with 0.1 N NaOH (3 x 3 mL). The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The purification by column chromatography (diethyl ether/pentane, 2:3) gave the product (36.5 mg, 80%) as colourless oil; ν_{max} (neat) 3423, 3020, 2990, 2223, 1447, 1217, 1079, 757; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.55 (1 H, q, *J* = 6.9 Hz, C(5)*H*), 4.48-4.42 (1 H, m, C(2)*H*), 2.07 (3 H, d, *J* = 6.9 Hz, C(6)H_3), 1.48 (3 H, d, *J* = 6.4 Hz, C(1)H_3), C(5)*H* has strong NOE with C(2)*H*; 13C NMR (126 MHz, $CDCl_3$) δ ppm 142.73 (*C*(5)), 117.45 (*C*(4)), 116.33 (*C*(3)), 68.74 (*C*(2)), 22.89 (*C*(1)), 17.31 (*C*(6)); HRMS (CI) *m/z*: calc for C_6H_9NO $[M+NH_4]^+$: 129.1028, Found 129.1030.

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