Electronic Supporting Information

Alkene as Hydrogen Trapper to Control the *Regio*-Selective Ruthenium(II) Catalyzed *ortho* C-H Silylation of Amides and Anilides

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General remarks

All reagents were obtained from commercial sources and used as received. Technical grade petroleum ether (40-60°C bp.) and ethyl acetate were used for chromatography column.

¹H NMR spectra were recorded in CDCl₃ at ambient temperature on Bruker AVANCE I 300, 400, 500 or 600 spectrometers at 300.1, 400.1, 500.1 or 600.1 MHz, using the solvent as internal standard (7.26 ppm). ¹³C NMR spectra were obtained at 75, 100, 125 or 151 MHz and referenced to the internal solvent signals (central peak is 77.2 ppm). Chemical shift (δ) and coupling constants (*J*) are given in ppm and in Hz, respectively. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and br. for broad.

GC analyses were performed with GC-7890A (Agilent) equipped with a 30-m capillary column (HP-5ms, fused silica capillary column, 30 M*0.25 mm*0.25 mm film thickness), was used with N₂/air as vector gas. GCMS were measured by GCMS-7890A-5975C (Agilent) with GC-7890A equipped with a 30-m capillary column (HP-5ms, fused silica capillary column, 30 M*0.25 mm*0.25 mm film thickness), was used with helium as vector gas. HRMS were measured by MAT 95XP (Termol) (LCMS-IT-TOF).

Compounds 2m were collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu K α radiation. Data reduction was carried out with the diffractometer's software.

The following GC conditions were used: initial temperature 80 °C, for 2 minutes, then rate 20 °C/min. until 260 °C and 260°C for 20 minutes.

<u>General procedure for RuHCl(CO)(PPh₃)₃ catalyzed selective C-H mono-silylation</u> of amide derivatives with hydrosilane

Ru(PPh₃)₃(CO)HCl (0.025 mmol, 23.8 mg), amide (0.5 mmol), triethylsilane (2.0 mmol), KOAc (0.25 mmol, 25 mg), norbornylene (2.0 mmol, 188 mg) and toluene (2 mL) were introduced in a tube under N_2 , equipped with magnetic stirring bar and was stirred at 120 °C. After 20 or 36 h, the conversion of the reaction was analyzed by gas chromatography. The solvent was then evaporated under vacuum and the desired product was purified by using a silica gel chromatography column and a mixture of petrol ether/ethyl acetate as eluent.

<u>General procedure for RuHCl(CO)(PPh₃)₃ catalyzed selective C-H mono-silylation</u> of anilide derivatives with hydrosilane

Ru(PPh₃)₃(CO)HCl (0.0125 mmol, 11.9 mg), anilide (0.25 mmol), triethylsilane (1.0 mmol), KOAc (0.125 mmol, 12.5 mg), MSE (1.0 mmol, 130 μ L) and NMP (1 mL) were introduced in a tube under N₂, equipped with magnetic stirring bar and was stirred at 120 °C. After 20 h, the conversion of the reaction was analyzed by gas chromatography. The solvent was then evaporated under vacuum and the desired product was purified by using a silica gel chromatography column and a mixture of petrol ether/ethyl acetate as eluent.

Table 1. Optimization of Ru(II)-catalyzed ortho C-H silylation of anilide 3a

, H		RuHCI(CO)(PPh ₃) ₃ (5 mol%) SiE	H
B		NMP, KOAc, <mark>Alkene</mark> 130 °C, 20 h, Ar	B	
3a				4a
ontry	Allena	additive	solvent	GC viald
entry	Aikelie	additive	solvent	(%)
1	NBE	KOAc	NMP	9
2	TBE	KOAc	NMP	29
3	DTBP	KOAc	NMP	9
4	TMBE	KOAc	NMP	14
5	NBD	KOAc	NMP	5
6	MSE	KOAc	NMP	53
7	MSE	KOAc	NMP	60 ^b (57 ^c)
8	MSE	KOPiv	NMP	51
9	MSE	KOPiv	Heptane	5
10	MSE	KOAc	DCE	0
11	MSE	KOAc	1,4-dioxane	0
12	MSE	KOAc	toluene	8

^{*a*}anilide **3a** (0.25 mmol), Et₃SiH (1.0 mmol), RuHCl(CO)(PPh₃)₃ (5 mol%), KOAc (0.125 mmol), alkene (1.0 mmol), NMP (0.5 mL), at 130 °C for 20 h, under N₂. ^{*b*} NMP (1 mL), 120 °C. ^{*c*} Isolated yield of **4a**.



Scheme S1. Ruthenium catalyzed reduction of amide 1a.

N,4-dimethyl-N-phenyl-2-(triethylsilyl)benzamide (2a)



Green oil, yield = 78%, 132 mg, ¹H NMR (500 MHz, CDCl₃): δ = 7.36-6.88 (m, 8H), 3.47 (s, 3H), 2.30 (s, 3H), 1.03-0.94 (m, 15H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 172.2, 139.6, 137.5, 136.7, 129.1, 129.0, 128.9, 128.4, 127.4, 126.5, 126.2, 38.5, 21.6, 7.8, 3.9. HRMS (EI): *m/z* calcd for C₂₁H₃₀NOSi [M+H]⁺ 340.2091, found 340.2094.

4-ethoxy-N-methyl-N-phenyl-2-(triethylsilyl)benzamide (2b)



Brown oil, yield = 72%, 133 mg, ¹H NMR (500 MHz, CDCl₃): δ = 7.28-7.24 (m, 2H), 7.15-7.08 (m, 4H), 6.90 (brs, 1H), 6.55 (brs, 1H), 4.00-3.96 (m, 2H), 3.47 (s, 3H), 1.40 (t, 3H, *J* = 7.0 Hz), 1.03-0.94 (m, 15H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 172.0, 158.3, 145.0, 139.4, 134.5, 129.9, 129.1, 126.6, 126.2, 122.6, 112.5, 63.3, 38.8, 14.9, 7.9, 3.9. HRMS (EI): *m/z* calcd for C₂₂H₃₂NO₂Si [M+H]⁺ 370.2197, found 370.2199.

4-fluoro-N-methyl-N-phenyl-2-(triethylsilyl)benzamide (2c)



Brown oil, yield = 52%, 89 mg, ¹H NMR (500 MHz, CDCl₃): δ = 7.34-6.71 (m, 8H), 3.48 (s, 3H), 1.03-0.95 (m, 15H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 171.2, 163.1, 161.1, 144.5, 141.2, 138.4, 130.2, 129.3, 126.6 (J_{CF} = 8.8 Hz), 122.6 (J_{CF} = 18.9 Hz), 114.6, 38.3, 7.8, 3.8. ¹⁹F NMR (470 MHz, CDCl₃): δ = 112.8 Hz. HRMS (EI): *m/z* calcd for C₂₀H₂₇NOFSi [M+H]⁺ 344.1840, found 344.1841.

N,N-diethyl-5-methyl-2-(triethylsilyl)benzamide (2d)



Light yellow oil, yield = 70%, 107 mg, ¹H NMR (500 MHz, CDCl₃): δ = 7.46 (d, 1H, *J* = 7.5 Hz), 7.17 (d, 1H, *J* = 7.5 Hz), 7.03 (s, 1H), 3.56 (d, 2H, *J* = 7.0 Hz), 3.18 (d, 2H, *J* = 7.0 Hz), 2.35 (s, 3H), 1.29 (t, 3H, *J* = 7.0 Hz), 1.12 (t, 3H, *J* = 7.0 Hz), 0.93 (t, 9H, *J* = 8.0 Hz), 0.84-0.79 (m, 6H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 172.6, 143.6, 138.4, 136.2, 130.9, 128.6, 126.6, 43.6, 39.0, 21.4, 13.9, 12.8, 7.6, 3.6. HRMS (EI): *m/z* calcd for C₁₈H₃₂NOSi [M+H]⁺ 306.2248, found 306.2249.

N,N-dicyclohexyl-2-(triethylsilyl)benzamide (2e)



Light yellow oil, yield = 60%, 121 mg, ¹H NMR (400 MHz, CDCl₃): δ = 7.58-7.56 (m, 1H), 7.33-7.28 (m, 2H), 7.16-7.14 (m, 1H), 3.27 (t, 1H, *J* = 11.6 Hz), 3.02 (t, 1H, *J* = 12.0 Hz), 2.78-2.61 (m, 2H), 1.85-1.45 (m, 12H), 1.31-1.28 (m, 4H), 1.09-0.86 (m, 17H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 172.7, 145.2, 136.2, 135.0, 128.2, 127.4, 125.3, 59.9, 56.3, 31.3, 26.9, 25.8, 25.5, 7.7, 3.9. HRMS (EI): *m/z* calcd for C₂₅H₄₂NOSi [M+H]⁺ 400.3036, found 400.3010.

pyrrolidin-1-yl(2-(triethylsilyl)phenyl)methanone (2f)



Colorless oil, yield = 52%, 75 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.59-7.56 (m, 1H), 7.36-7.24 (m, 3H), 3.63 (t, 2H, *J* = 6.6 Hz), 3.23 (t, 2H, *J* = 6.6 Hz), 1.99-1.83 (m, 4H), 0.97-0.81 (m, 15H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 171.1, 144.2, 136.1, 134.8, 128.5, 127.9, 126.1, 49.5, 45.8, 26.2, 24.7, 7.6, 3.6. HRMS (EI): *m/z* calcd for C₂₇H₂₈NOSi [M+H]⁺ 290.1940, found 290.1921.

piperidin-1-yl(2-(triethylsilyl)phenyl)methanone (2g)



Colorless oil, yield = 67%, 102 mg, ¹H NMR (600 MHz, CDCl₃): δ = 7.57-7.55 (m, 1H), 7.34-7.32 (m, 2H), 7.18-7.17 (m, 1H), 1.67-1.63 (m, 6H), 1.53-1.44 (m, 2H), 1.28-1.19 (m, 2H), 0.92 (t, 9H, *J* = 7.8 Hz), 0.89-0.82 (m, 6H). ¹³C {¹H} NMR (150 MHz, CDCl₃): δ = 171.4, 143.1, 136.2, 135.3, 128.5, 127.8, 126.0, 48.7, 42.6, 26.3, 25.7, 24.8, 7.7, 3.7. HRMS (EI): *m/z* calcd for C₁₈H₃₀NOSi [M+H]⁺ 304.2091, found 304.2093.

(4-methyl-2-(triethylsilyl)phenyl)(morpholino)methanone (2h)



White solid, yield = 78%, 124 mg, ¹H NMR (500 MHz, CDCl₃): δ = 7.38 (s, 1H), 7.18-7.16 (m, 1H), 7.09 (d, 1H, *J* = 7.5 Hz), 3.88-3.71 (m, 4H), 3.62 (t, 2H, *J* = 4.5 Hz), 3.44-3.24 (m, 2H), 2.38 (s, 3H), 0.95 (t, 9H, *J* = 8.0 Hz), 0.86-0.82 (m, 6H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 171.8, 138.9, 137.8, 137.1, 135.7, 129.1, 126.3, 66.9, 66.7, 48.1, 42.1, 21.6, 7.7, 3.7. HRMS (EI): *m*/*z* calcd for C₁₈H₃₀NO₂Si [M+H]⁺ 320.2040, found 320.2042.

N-methyl-N-phenyl-3-(triethylsilyl)furan-2-carboxamide (2i)



Green solid, yield = 83%, 131 mg, ¹H NMR (600 MHz, CDCl₃): δ = 7.30-7.28 (m, 2H), 7.21-7.18 (m, 1H), 7.08-7.03 (m, 3H), 6.31 (s, 1H), 3.43 (s, 3H), 0.97 (t, 9H, *J* = 7.8 Hz), 0.90-0.86 (m, 6H). ¹³C{¹H} NMR (150 MHz, CDCl₃): δ = 161.3, 152.2, 144.8, 142.4, 129.1, 126.5, 126.1, 123.2, 116.7, 38.5, 7.7, 3.5. HRMS (EI): *m/z* calcd for C₁₈H₂₆NO₂Si [M+H]⁺ 316.1727, found 316.1729.

N,N-dibenzyl-3-(triethylsilyl)furan-2-carboxamide (2j)



Colorless oil, yield = 88%, 178 mg, ¹H NMR (500 MHz, CDCl₃): δ = 7.44-7.34 (m, 11H), 6.52 (d, 1H, *J* = 1.5 Hz), 4.66 (s, 2H), 4.60 (s, 2H), 0.96-0.91 (m, 15H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 162.5, 152.3, 142.3, 137.0, 128.8, 128.7, 127.8, 127.7, 127.6, 122.9, 117.1, 50.9, 47.8, 7.7, 3.5. HRMS (EI): *m/z* calcd for C₂₅H₃₂NO₂Si [M+H]⁺ 406.2202, found 406.2199.

morpholino(3-(triethylsilyl)furan-2-yl)methanone (2k)



Red oil, yield = 85%, 125 mg, ¹H NMR (500 MHz, CDCl₃): δ = 7.45 (d, 1H, *J* = 1.5 Hz), 8.45 (d, 1H, *J* = 1.5 Hz), 3.72-3.63 (m, 8H), 0.93 (t, 9H, *J* = 8.5 Hz), 0.84-0.79 (m, 6H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 161.0, 151.8, 142.2, 122.2, 116.8, 67.2, 47.5, 43.1, 7.6, 3.5. HRMS (EI): *m*/*z* calcd for C₁₅H₂₆NO₃Si [M+H]⁺ 296.1676, found 296.1678.

4-ethoxy-N-propyl-2-(triethylsilyl)benzamide (2l)



H₃CH₂CO

F₃C

Light yellow solid, yield = 77%, 124 mg, ¹H NMR (500 MHz, CDCl₃): δ = 7.40 (d, 1H, J = 8.0 Hz), 7.12 (d, 1H, J = 2.5 Hz), 6.83-6.81 (m, 1H), 5.89 (s, 1H), 4.09-4.04 (m, 2H), 3.39-3.35 (m, 2H), 1.66-1.62 (m, 2H), 1.45 (t, 3H, J = 7.0 Hz), 0.99 (t, 3H, J = 7.5 Hz), 0.96-0.87 (m, 15H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 171.1, 159.5, 139.0, 135.6, 128.0, 123.4, 113.1, 63.5, 42.0, 23.0, 14.9, 11.6, 7.9, 4.0. HRMS (EI): *m/z* calcd for C₁₈H₃₁NO₂NaSi [M+Na]⁺ 344.2016, found 344.2018.

N-propyl-2-(triethylsilyl)-4-(trifluoromethyl)benzamide (2m)



Dark green solid, yield = 67%, 115 mg, ¹H NMR (600 MHz, CDCl₃): δ = 7.79 (s, 1H), 7.60 (d, 1H, J = 7.8 Hz), 7.50 (d, 1H, J = 7.8 Hz), 5.91 (s, 1H), 3.41-3.38 (m, 2H), 1.68-1.62 (m, 2H), 0.99 (t, 3H, J = 7.2 Hz), 0.95-0.88 (m, 15H). ¹³C{¹H} NMR (150

MHz, CDCl₃): δ = 170.4, 146.8, 138.3, 132.9 (q, J_{CF} = 3.6 Hz), 130.9 (q, J_{CF} = 32.0 Hz), 126.6, 125.7 (q, J_{CF} = 3.5 Hz), 125.1 (q, J_{CF} = 271.1 Hz), 42.1, 22.9, 11.6, 7.8, 3.8. HRMS (EI): m/z calcd for C₁₇H₂₆NOF₃NaSi [M+Na]⁺ 368.1628, found 368.1630.

5-methyl-N-propyl-2-(triethylsilyl)benzamide (2n)



Colorless oil, yield = 55%, 80 mg, ¹H NMR (500 MHz, CDCl₃): δ = 7.39 (d, 1H, *J* = 1.5 Hz), 7.34 (d, 1H, *J* = 7.5 Hz), 7.19-7.17 (m, 1H), 5.85 (s, 1H), 3.42-3.38 (m, 2H), 2.39 (s, 3H), 1.68-1.63 (m, 2H), 1.00 (t, 3H, *J* = 7.5 Hz), 0.96-0.87 (m, 15H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 171.6, 140.7, 139.0, 137.4, 136.5, 129.3, 126.4, 42.0, 23.0, 21.7, 11.7, 8.0, 4.0. HRMS (EI): *m*/*z* calcd for C₁₇H₂₉NONaSi [M+Na]⁺ 314.1910, found 314.1913.

methyl 4-(propylcarbamoyl)-3-(triethylsilyl)benzoate (20)



Colorless oil, yield = 75%, 125 mg, ¹H NMR (500 MHz, CDCl₃): δ = 8.24 (d, 1H, *J* = 1.5 Hz), 8.01-7.99 (m, 1H), 7.47 (d, 1H, *J* = 8.0 Hz), 6.00 (s, 1H), 3.94 (s, 3H), 3.42-3.38 (m, 2H), 1.68-1.64 (m, 2H), 1.01 (t, 3H, *J* = 7.5 Hz), 0.95-0.90 (m, 15H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 170.8, 167.0, 147.5, 137.5, 137.1, 130.3, 130.0, 126.4, 52.5, 42.0, 22.9, 11.6, 7.8, 3.8. HRMS (EI): *m*/*z* calcd for C₁₈H₂₉NO₃NaSi [M+Na]⁺ 358.1809, found 358.1810.

N-(tert-butyl)-4-methyl-2-(triethylsilyl)benzamide (2p)



Colorless oil, yield = 68%, 104 mg, ¹H NMR (600 MHz, CDCl₃): δ = 7.35 (s, 1H), 7.28 (d, 1H, *J* = 7.8 Hz), 7.13 (d, 1H, *J* = 7.8 Hz), 5.63 (s, 1H), 2.36 (s, 3H), 1.46 (s, 9H), 0.94-0.89 (m, 15H). ¹³C{¹H} NMR (150 MHz, CDCl₃): δ = 171.2, 142.0, 138.7, 137.3, 136.3, 129.1, 126.6, 51.7, 29.0, 21.7, 8.0, 4.1. HRMS (EI): *m/z* calcd for C₁₈H₃₂NOSi [M+H]⁺ 306.2248, found 306.2249.

N-cyclohexyl-4-methyl-2-(triethylsilyl)benzamide (2q)



Light yellow solid, yield = 78%, 129 mg, ¹H NMR (600 MHz, CDCl₃): δ = 7.37 (s, 1H), 7.29 (d, 1H, *J* = 7.8 Hz), 7.13 (d, 1H, *J* = 7.8 Hz), 5.70 (s, 1H), 3.95-3.90 (m, 1H), 2.36 (s, 3H), 2.04-2.02 (m, 2H), 1.75-1.73 (m, 2H), 1.44-1.42 (m, 2H), 1.26-1.21 (m, 4H), 0.92-0.89 (m, 15H). ¹³C{¹H} NMR (150 MHz, CDCl₃): δ = 170.7, 140.9, 138.9, 137.3,

136.4, 129.2, 126.4, 48.7, 33.3, 25.7, 25.0, 21.7, 8.0, 4.1. HRMS (EI): m/z calcd for C₂₀H₃₄NOSi [M+H]⁺ 332.2404, found 332.2405.

N-cyclohexyl-3-(triethylsilyl)furan-2-carboxamide (2r)



Yellow oil, yield = 82%, 126 mg, ¹H NMR (600 MHz, CDCl₃): δ = 7.33 (d, 1H, *J* = 0.6 Hz), 6.39 (d, 1H, *J* = 1.2 Hz), 6.25 (s, 1H), 3.87-3.81 (m, 1H), 1.93-1.91 (m, 2H), 1.68-1.65 (m, 2H), 1.35-1.29 (m, 2H), 1.18-1.10 (m, 4H), 0.93-0.79 (m, 15H). ¹³C{¹H} NMR (150 MHz, CDCl₃): δ = 158.2, 151.8, 142.5, 121.9, 118.0, 47.9, 33.5, 25.7, 25.1, 7.7, 3.4. HRMS (EI): *m/z* calcd for C₁₇H₃₀NO₂Si [M+H]⁺ 308.2040, found 308.2043.

N-propyl-3-(triethylsilyl)furan-2-carboxamide (2s)



Brown oil, yield = 62%, 83 mg, ¹H NMR (500 MHz, CDCl₃): δ = 7.42 (d, 1H, *J* = 2.0 Hz), 6.47 (d, 1H, *J* = 1.5 Hz), 6.46 (s, 1H), 3.39-3.35 (m, 2H), 1.65-1.58 (m, 2H), 0.97-0.88 (m, 18H). ¹³C{¹H} NMR (150 MHz, CDCl₃): δ = 159.1, 151.8, 142.6, 122.1, 118.0, 41.0, 23.2, 11.5, 7.7, 3.4. HRMS (EI): *m*/*z* calcd for C₁₅H₂₆NO₂Si [M+H]⁺ 268.1727, found 268.1728.

N-isobutyl-3-(triethylsilyl)furan-2-carboxamide (2t)



Orange oil, yield = 82%, 115 mg, ¹H NMR (500 MHz, CDCl₃): δ = 7.44 (d, 1H, *J* = 1.5 Hz), 6.52 (s, 1H), 6.49 (d, 1H, *J* = 1.5 Hz), 3.25 (t, 2H, *J* = 6.5 Hz), 1.90-1.85 (m, 1H), 0.98 (s, 3H), 0.97 (s, 3H), 0.95-0.88 (m, 15H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 159.1, 151.7, 142.6, 122.0, 118.0, 46.5, 28.9, 20.3, 7.7, 3.4. HRMS (EI): *m/z* calcd for C₁₅H₂₈NO₂Si [M+H]⁺ 282.1884, found 282.1885.

N-(tert-butyl)-3-(triethylsilyl)furan-2-carboxamide (2u)



Orange oil, yield = 65%, 91 mg, ¹H NMR (500 MHz, CDCl₃): δ = 7.41 (d, 1H, *J* = 1.0 Hz), 6.46 (d, 1H, *J* = 1.5 Hz), 6.28 (s, 1H), 1.46 (s, 9H), 0.96-0.89 (m, 15H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 158.5, 152.6, 142.1, 120.9, 117.9, 51.3, 29.1, 7.8, 3.4. HRMS (EI): *m/z* calcd for C₁₅H₂₈NO₂Si [M+H]⁺ 282.1884, found 282.1886.

N-phenyl-2-(triethylsilyl)benzamide (2v)



Colorless oil, yield = 40%, 62 mg, ¹H NMR (500 MHz, CDCl₃): δ = 7.67-7.39 (m, 8H), 7.19 (t, 1H, *J* = 7.5 Hz), 1.01-0.88 (m, 15H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 169.6, 143.6, 138.2, 136.7, 136.5, 129.6, 129.3, 128.9, 126.4, 124.7, 120.1, 7.8, 4.0. HRMS (EI): *m/z* calcd for C₁₉H₂₆NOSi [M+H]⁺ 312.1784, found 312.1771.

N,N-dibenzyl-3-(dimethyl(phenyl)silyl)furan-2-carboxamide (2w)



Colorless oil, yield = 64%, 136 mg, ¹H NMR (500 MHz, CDCl₃): δ = 7.73-7.71 (m, 1H), 7.48-7.22 (m, 15H), 6.43 (d, 1H, *J* = 1.5 Hz), 4.65 (s, 4H), 0.74 (s, 6H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 161.8, 152.6, 142.4, 138.4, 134.3, 129.1, 128.8, 128.7, 128.5, 127.8, 127.7, 117.3, 50.7, 48.0, 1.9. HRMS (EI): *m/z* calcd for C₂₇H₂₈NO₂Si [M+H]⁺ 426.1889, found 426.1890.

N-(2-(triethylsilyl)phenyl)pivalamide (4a)



Colorless solid, yield = 57%, 42 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.91 (d, 1H, *J* = 8.1 Hz), 7.45-7.37 (m, 3H), 7.19-7.13 (m, 1H), 1.35 (s, 9H), 1.03-0.86 (m, 15H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 176.6, 142.9, 135.8, 130.2, 127.9, 124.7, 124.1, 39.7, 27.8, 7.6, 4.1. HRMS (EI): *m/z* calcd for C₁₇H₃₀NOSi [M+H]⁺ 292.2097, found 292.2088.

N-(2-(triethylsilyl)phenyl)butyramide (4b)



Yellow solid, yield = 40%, 28 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.94 (d, 1H, *J* = 8.1 Hz), 7.44-7.37 (m, 2H), 7.18-7.13 (m, 2H), 2.34 (t, 2H, *J* = 7.5 Hz), 1.84-1.74 (m, 2H), 1.07-0.84 (m, 18H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 171.1, 142.7, 135.8, 130.3, 127.6, 124.7, 123.5, 40.0, 19.2, 14.0, 7.6, 4.3. HRMS (EI): *m/z* calcd for C₁₆H₂₇NONaSi [M+Na]⁺ 300.1760, found 300.1756.

N-(2-(triethylsilyl)phenyl)isobutyramide (4c)

. SiEt₃ H Ô

Colorless solid, yield = 39%, 27 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.98 (d, 1H, *J* = 7.8 Hz), 7.44-7.37 (m, 2H), 7.22-7.13 (m, 2H), 2.54-2.45 (m, 1H), 1.29 (d, 6H, *J* = 6.9 H), 1.03-0.97 (m, 9H), 0.93-0.84 (m, 6H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 175.0, 142.9, 135.8, 130.3, 124.6, 123.4, 37.2, 19.8, 7.6, 4.3. HRMS (EI): *m/z* calcd for C₁₆H₂₈NOSi [M+H]⁺ 278.1940, found 278.1934.

N-(2-(triethylsilyl)phenyl)acetamide (4d)



Colorless solid, yield = 37%, 23 mg, ¹H NMR (400 MHz, CDCl₃): δ = 7.86 (d, 1H, *J* = 8.0 Hz), 7.45-7.39 (m, 2H), 7.20-7.16 (m, 2H), 2.19 (s, 3H), 1.00 (t, 9H, *J* = 7.6 Hz), 0.91-0.85 (m, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 168.2, 142.6, 135.8, 130.3, 128.2, 125.0, 124.0, 24.6, 7.6, 4.3. HRMS (EI): *m*/*z* calcd for C₁₄H₂₄NOSi [M+H]⁺ 250.1627, found 250.1620.

N-(2-(triethylsilyl)phenyl)cyclohexanecarboxamide (4e)



White solid, yield = 42%, 33 mg, ¹H NMR (500 MHz, CDCl₃): δ = 7.95 (d, 1H, *J* = 8.0 Hz), 7.46-7.38 (m, 2H), 7.19-7.14 (m, 2H), 2.25-2.19 (m, 1H), 2.02-1.99 (m, 2H), 1.90-1.87 (m, 2H), 1.61-1.54 (m, 3H), 1.34-1.28 (m, 3H), 1.04-0.97 (m, 9H), 0.91-0.86 (m, 6H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 174.2, 142.9, 135.8, 130.3, 129.2, 124.7, 123.6, 47.1, 29.9, 25.95, 25.93, 25.88, 7.7, 4.3. HRMS (EI): *m/z* calcd for C₁₉H₃₁NONaSi [M+Na]⁺ 340.2073, found 340.2071.

N-(2-(triethylsilyl)phenyl)dodecanamide (4f)



Light yellow oil, yield = 35%, 34 mg, ¹H NMR (400 MHz, CDCl₃): δ = 7.95 (d, 1H, *J* = 8.0 Hz), 7.44-7.38 (m, 2H), 7.18-7.14 (m, 2H), 2.36 (t, 2H, *J* = 7.6 Hz), 1.78-1.73 (m, 2H), 145-1.28 (m, 16H), 0.99 (t, 9H, *J* = 7.6 Hz), 0.92-0.85 (m, 9H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 171.3, 142.8, 135.8, 130.3, 127.5, 124.7, 123.4, 38.1, 32.1, 29.8, 29.7, 29.6, 29.5, 25.8, 22.9, 14.3, 7.7, 4.3. HRMS (EI): *m*/*z* calcd for C₂₄H₄₄NOSi [M+H]⁺ 390.3192, found 390.3181.

N-(4-methoxy-2-(triethylsilyl)phenyl)pivalamide (4g)



MeO

Light yellow solid, yield = 52%, 42 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.66 (d, 1H, J = 8.7 Hz), 7.20 (brs, 1H), 6.98-6.89 (m, 2H), 3.81 (s, 3H), 1.34 (s, 9H), 1.01-0.95 (m, 9H), 0.90-0.85 (m, 6H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 176.8, 156.6, 135.7, 131.1, 126.6, 121.6, 114.4, 55.5, 39.5, 27.9, 7.6, 4.0. HRMS (EI): *m/z* calcd for C₁₈H₃₂NO₂Si [M+H]⁺ 322.2202, found 322.2199.

N-(4-methyl-2-(triethylsilyl)phenyl)pivalamide (4h)



Colorless oil, yield = 52%, 40 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.72 (d, 1H, *J* = 8.1 Hz), 7.28 (s, 1H), 7.21-7.18 (m, 2H), 2.34 (s, 3H), 1.34 (s, 9H), 1.02-0.86 (m, 15H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 176.7, 140.4, 136.3, 134.1, 130.8, 128.3, 124.5, 39.6, 27.9, 21.2, 7.7, 4.1. HRMS (EI): *m*/*z* calcd for C₁₈H₃₂NOSi [M+H]⁺ 306.2253, found 306.2244.

N-(4-(benzyloxy)-2-(triethylsilyl)phenyl)pivalamide (4i)



Colorless oil, yield = 58%, 58 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.67 (d, 1H, *J* = 8.7 Hz), 7.48-7.34 (m, 5H), 7.22 (brs, 1H), 7.04-6.98 (m, 2H), 5.07 (s, 2H), 1.34 (s, 9H), 1.01-0.84 (m, 15H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 176.8, 155.8, 137.2, 135.9, 131.1, 128.7, 128.1, 127.7, 126.5, 122.5, 115.7, 70.4, 39.5, 27.9, 7.6, 4.0. HRMS (EI): *m/z* calcd for C₂₄H₃₆NO₂Si [M+H]⁺ 398.2515, found 398.2510.

N-(4-(dimethylamino)-2-(triethylsilyl)phenyl)pivalamide (4j)



Colorless solid, yield = 44%, 37 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.54 (d, 1H, *J* = 8.7 Hz), 7.15 (brs, 1H), 6.83-6.77 (m, 2H), 2.95 (s, 3H), 1.34 (s, 9H), 1.03-0.85 (m, 15H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 176.8, 148.0, 130.3, 126.5, 119.8, 114.5, 41.1, 39.4, 27.9, 7.7, 4.2. HRMS (EI): *m*/*z* calcd for C₁₉H₃₅N₂OSi [M+H]⁺ 335.2519, found 335.1516.

N-(2,4-dimethyl-6-(triethylsilyl)phenyl)pivalamide (4k)



Colorless oil, yield = 41%, 33 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.11 (s, 1H), 7.09 (s, 1H), 7.03 (brs, 1H), 2.33 (s, 3H), 2.15 (s, 3H), 1.36 (s, 9H), 1.00-0.94 (m, 9H), 0.86-0.81 (m, 6H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 176.4, 138.1, 136.3, 136.1, 134.4, 134.3, 133.1, 39.4, 28.0, 21.2, 18.6, 7.7, 4.1. HRMS (EI): *m/z* calcd for C₁₉H₃₄NOSi [M+H]⁺ 320.2410, found 320.2407.

N-(4,5-dimethyl-2-(triethylsilyl)phenyl)pivalamide (4l)



Colorless solid, yield = 48%, 38 mg, ¹H NMR (400 MHz, CDCl₃): δ = 7.67 (s, 1H), 7.26 (brs, 1H), 7.16 (s, 1H), 2.27 (s, 3H), 2.25 (s, 3H), 1.35 (s, 9H), 1.01-0.97 (m, 9H), 0.90-0.86 (m, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 176.6, 140.8, 138.8, 136.7, 133.0, 125.6, 125.1, 39.6, 27.9, 20.0, 19.5, 7.7, 4.2. HRMS (EI): *m/z* calcd for C₁₉H₃₄NOSi [M+H]⁺ 320.2410, found 320.2400.

N-(6-(triethylsilyl)benzo[d][1,3]dioxol-5-yl)pivalamide (4m)



Light yellow solid, yield = 45%, 38 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.32 (s, 1H), 7.23 (brs, 1H), 6.85 (s, 1H), 5.96 (s, 2H), 1.33 (s, 9H), 1.00-0.94 (m, 9H), 0.88-0.82 (m, 6H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 176.7, 149.1, 145.2, 137.5, 121.2, 113.7, 107.2, 101.4, 39.6, 27.9, 7.6, 4.1. HRMS (EI): *m/z* calcd for C₁₈H₃₀NO₃Si [M+H]⁺ 336.1995, found 336.1996.

N-(4-fluoro-2-(triethylsilyl)phenyl)pivalamide (4n)



White solid, yield = 56%, 43 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.79-7.75 (m, 1H), 7.26 (brs, 1H), 7.12-7.02 (m, 2H), 1.34 (s, 9H), 1.02-0.86 (m, 15H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 176.8, 158.3 (J_{CF} = 244.7 Hz), 138.6 (J_{CF} = 2.6 Hz), 131.8 (J_{CF} = 4.0 Hz), 126.7 (J_{CF} = 7.2 Hz), 121.6 (J_{CF} = 20.3 Hz), 116.6 (J_{CF} = 22.2 Hz), 39.6, 27.8, 7.5, 3.9. ¹⁹F NMR (376 MHz, CDCl₃): δ = 118.1 Hz. HRMS (EI): m/z calcd for C₁₇H₂₉NOFSi [M+H]⁺ 310.2003, found 310.1991.

ethyl 4-pivalamido-3-(triethylsilyl)benzoate (40)



Light yellow oil, yield = 77%, 70 mg, ¹H NMR (400 MHz, CDCl₃): δ = 8.21 (d, 1H, *J* = 8.8 Hz), 8.12 (d, 1H, *J* = 2.0 Hz), 8.06-8.03 (m, 1H), 7.52 (brs, 1H), 4.40-4.35 (m, 2H), 1.40 (t, 3H, *J* = 6.8 Hz), 1.35 (s, 9H), 1.01-0.92 (m, 15H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 176.9, 166.6, 147.3, 137.5, 131.8, 126.4, 125.9, 122.0, 60.9, 40.0, 27.8, 14.5, 7.5, 4.0. HRMS (EI): *m/z* calcd for C₂₀H₃₄NO₃Si [M+H]⁺ 364.2308, found 364.2295.

N-(3-(triethylsilyl)pyridin-4-yl)pivalamide (4p)



Orange solid, yield = 80%, 58 mg, ¹H NMR (400 MHz, CDCl₃): δ = 8.54-8.50 (m, 2H), 8.25 (d, 1H, *J* = 5.6 Hz), 7.49 (brs, 1H), 1.34 (s, 9H), 1.03-0.92 (m, 15H). ¹³C{¹H}

NMR (100 MHz, CDCl₃): δ = 177.1, 156.1, 151.8, 150.6, 119.1, 115.1, 40.2, 27.7, 7.4, 4.0. HRMS (EI): *m*/*z* calcd for C₁₆H₂₈N₂ONaSi [M+H]⁺ 315.1869, found 315.1859.

N-methyl-N-(4-methylbenzyl)aniline (1a')¹



Colorless oil, yield = 85%, 90 mg, ¹H NMR (500 MHz, CDCl₃): δ = 7.34-7.23 (m, 6H), 6.87-6.81 (m, 3H), 4.60 (s, 2H), 3.10 (s, 3H), 2.44 (s, 3H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 149.9, 136.6, 136.0, 129.4, 129.3, 126.9, 116.6, 112.5, 56.5, 38.6, 21.2.

Reference [1] Das, S.; Karmakar, H.; Bhattacharjee, J.; Panda, T. K. *Dalton Trans.* **2019**, *48*, 11978.

Table of crystallographic data for 2m (CCDC 1940358)



Complex	2m
Empirical formula	C17 H25 F3 N O Si
Formula weight	344.47
Temperature/K	120.00(10)
Crystal system	orthorhombic
Space group	$P2_{1}2_{1}2_{1}$
a/Å	8.2994(4)
b/Å	11.9792(9)
c/Å	18.8409(10)
$\alpha/^{\circ}$	90
β/°	90
$\gamma/^{\circ}$	90
Volume/A ³	1873.17(19)
Z	4
$\rho_{calc}g/cm^3$	1.221
μ/mm^{-1}	0.155
F(000)	/32.0
Crystal size/mm ³	$0.15 \times 0.14 \times 0.12$
Radiation	MoKα ($\lambda = 0.71073$)
2Θ range for data collection/°	4.03 to 49.992
Index ranges	$-9 \le h \le 9, -11 \le k \le 14, -22 \le l \le 20$
Reflections collected	11626
Independent reflections	$3298 \ [R_{int} = 0.0406, R_{sigma} = 0.0452]$
Data/restraints/parameters	3298/0/222
Goodness-of-fit on F ²	1.017
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0535, wR_2 = 0.1225$
Final R indexes [all data]	$R_1 = 0.0651, wR_2 = 0.1303$



N,4-dimethyl-N-phenyl-2-(triethylsilyl)benzamide (2a)



S16

4-ethoxy-N-methyl-N-phenyl-2-(triethylsilyl)benzamide (2b)



4-fluoro-N-methyl-N-phenyl-2-(triethylsilyl)benzamide (2c)



N,N-diethyl-5-methyl-2-(triethylsilyl)benzamide (2d)









N,N-dicyclohexyl-2-(triethylsilyl)benzamide (2e)



S20

pyrrolidin-1-yl(2-(triethylsilyl)phenyl)methanone (2f)







piperidin-1-yl(2-(triethylsilyl)phenyl)methanone (2g)



(4-methyl-2-(triethylsilyl)phenyl)(morpholino)methanone (2h)







N,N-dibenzyl-3-(triethylsilyl)furan-2-carboxamide (2j)

morpholino(3-(triethylsilyl)furan-2-yl)methanone (2k)





S27



N-propyl-2-(triethylsilyl)-4-(trifluoromethyl)benzamide (2m)

5-methyl-N-propyl-2-(triethylsilyl)benzamide (2n)





methyl 4-(propylcarbamoyl)-3-(triethylsilyl)benzoate (20)

N-(tert-butyl)-4-methyl-2-(triethylsilyl)benzamide (2p)



N-cyclohexyl-4-methyl-2-(triethylsilyl)benzamide (2q)





	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Solvent	CDC13
3	Temperature	296.9
4	Pulse Sequence	zg30
5	Number of Scans	16
6	Receiver Gain	31
7	Relaxation Delay	1.0000
8	Pulse Width	10.0000
9	Spectrometer Frequency	600.13
10	Spectral Width	12019.2
11	Lowest Frequency	-2316.4
12	Nucleus	1H
13	Acquired Size	32768
14	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Solvent	CDC13
3	Temperature	297.5
4	Pulse Sequence	zgpg30
5	Number of Scans	1024
6	Receiver Gain	200
7	Relaxation Delay	2.0000
8	Pulse Width	12.0000
9	Spectrometer Frequency	150.90
10	Spectral Width	36231.9
11	Lowest Frequency	-3003.0
12	Nucleus	130
13	Acquired Size	32768
14	Spectral Size	65536







	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Solvent	CDC13
3	Temperature	296.6
4	Pulse Sequence	zg30
5	Number of Scans	16
6	Receiver Gain	14
7	Relaxation Delay	1.0000
8	Pulse Width	10.0000
9	Spectrometer Frequency	600.13
10	Spectral Width	12019.2
11	Lowest Frequency	-2353.2
12	Nucleus	1H
13	Acquired Size	32768
14	Spectral Size	65536













N-isobutyl-3-(triethylsilyl)furan-2-carboxamide (2t)



N-(tert-butyl)-3-(triethylsilyl)furan-2-carboxamide (2u)

N-phenyl-2-(triethylsilyl)benzamide (2v)



N,N-dibenzyl-3-(dimethyl(phenyl)silyl)furan-2-carboxamide (2w)





N-(2-(triethylsilyl)phenyl)pivalamide (4a)





N-(2-(triethylsilyl)phenyl)butyramide (4b)





N-(2-(triethylsilyl)phenyl)isobutyramide (4c)



N-(2-(triethylsilyl)phenyl)acetamide (4d)





N-(2-(triethylsilyl)phenyl)cyclohexanecarboxamide (4e)



N-(2-(triethylsilyl)phenyl)dodecanamide (4f)







N-(4-methyl-2-(triethylsilyl)phenyl)pivalamide (4h)



N-(4-(benzyloxy)-2-(triethylsilyl)phenyl)pivalamide (4i)



N-(4-(dimethylamino)-2-(triethylsilyl)phenyl)pivalamide (4j)



N-(2,4-dimethyl-6-(triethylsilyl)phenyl)pivalamide (4k)



230

210

190

170

150

130

110 fl (ppm)



-500

0

--500

90 80 70 60 50 40 30 20 10 0 -10

N-(4,5-dimethyl-2-(triethylsilyl)phenyl)pivalamide (4l)





N-(6-(triethylsilyl)benzo[d][1,3]dioxol-5-yl)pivalamide (4m)



N-(4-fluoro-2-(triethylsilyl)phenyl)pivalamide (4n)







ethyl 4-pivalamido-3-(triethylsilyl)benzoate (40)



N-(3-(triethylsilyl)pyridin-4-yl)pivalamide (4p)



S55

N-methyl-N-(4-methylbenzyl)aniline (1a')

