Supporting Information for:

Palladium-catalyzed siloxycarbonylation of alkenes to

synthesize silyl esters

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1. General Information.

Chemicals

Chemicals were commercially purchased from Adamas-beta, Energy Chemical, Aladdin, etc. and directly used without further purification unless otherwise stated. PdCl₂, PdBr₂, PdI₂, Pd(P'Bu₃)₂, 2-diphenylphosphonium-2',4',6'-triisopropylbiphenyl etc. were purchased from Adamas-beta; *tert*-Butyldimethylsilyl chloride, aldehyde, alkenes, etc. were purchased from Energy Chemical.

Chromatography

Analytical thin-layer chromatography (TLC) was carried out with silica gel precoated glass plates (TLC-Silica gel GF254, coating thickness: 0.20-0.25 mm, particle size: 10-40 μ m) purchased from Xinnuo Chemical (Yantai, China). The TLC was visualized with a UV lamp (254 or 365 nm).

Flash Column chromatography was carried out on silica gel (60 Å, 200-300 mesh) purchased from Xinnuo Chemicals (Yantai, China) with technical grade solvents as the eluent. All the yields referred to spectroscopically and chromatographically pure compounds.

Nuclear Magnetic Resonance (NMR) Spectroscopy

¹H NMR spectra were recorded on Bruker AVANCE III-400 instrument (400 MHz spectrometer). The analytical sample was dissolved in an appropriate deuterated solvent. The employed deuterated solvent and the measuring frequency are indicated in each ¹H NMR data. Chemical shifts are reported in parts per million (ppm) with the solvent resonance as the internal reference (CDCl₃ δ 7.26). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. Coupling constants, *J* were reported in Hertz unit (Hz).

¹³C NMR spectra were recorded on Bruker AVANCE III-400 instrument (101 MHz spectrometer). The employed deuterated solvent and the measuring frequency are both indicated in each ¹³C NMR data. Chemical shifts are reported in ppm with the solvent resonance as the internal reference (CDCl₃ δ 77.16).

2. Preparation of Aromatic Alkenes.

2.1 Method A:



To a 25 ml round bottomed flask were added methyl triphenylphosphonium bromide (7.5 mmol, 1.5 equiv) and 'BuOK (7.5 mmol, 1.5 equiv). Adding 10 mL of dry THF, the mixture was stirred at room temperature for 1.0 hour. After that diluted ketones or aldehydes (5.0 mmol, 1.0 equiv) in dry THF (2 mL) was added, then the reaction was stirred at room temperature for overnight. The mixture was diluted with CH_2Cl_2 (25 mL), washed with brine (3 x 15 mL), dried with Na_2SO_4 , filtered and concentrated in vacuo. The crude material was purified by column chromatography (hexanes as the eluent) to afford alkenes.

2.2 Method B:



To a 25 ml round bottomed flask were added 3,4-dihydroxybenzaldehyde (5.0 mmol, 1.0 equiv) and K_2CO_3 (11.0 mmol, 2.2 equiv). Adding 10 mL of DMF, the mixture was stirred at room temperature for 30 mins. After that diluted dibromomethane (5.0 mmol, 1.0 equiv) in DMF (2 mL) was added, then the reaction was stirred at room temperature for overnight. The mixture was diluted with CH_2Cl_2 (25 mL), washed with brine (3 x 15 mL), dried with Na_2SO_4 , filtered and concentrated in vacuo. The crude material was purified by column chromatography to afford piperonyl aldehyde. Subsequently, the Wittig reaction was carried out as shown in Method A to obtain 5-vinylbenzo[d][1,3]dioxole.

2.3 Method C:



To a 25 ml round bottomed flask were added 4-bromo-2-fluoro-1,1'-biphenyl (1.0 mmol, 1.0 equiv), Pd(PPh₃)₄ (0.3 mmol, 0.3 equiv) and K₂CO₃ (3.0 mmol, 3.0 equiv) and dissolved with 5 mL of 1,4-dioxane. Subsequently, pinacol vinylboronate (1.5 mmol, 1.5 equiv) and 0.6 mL of H₂O were added to the reaction mixture. The reflux

condenser was quickly installed and filled three times with nitrogen. The reaction was stirred at reflux overnight and the reaction was measured by TLC. After the reaction was completed, the mixture was diluted with CH₂Cl₂ (25 mL), washed with brine (3 x 15 mL), dried with Na₂SO₄, filtered and concentrated in vacuo. The crude material was purified by column chromatography (hexanes as the eluent) to afford alkenes.

3. Typical Procedure for the Reaction.

3.1 Reaction Conditions for Table 2 in Maintext:

Ar + CO +
$${}^{t}BuMe_{2}SiCl$$

1 2a $[Pd]/PHXPhos, H_{2}O$ Ar O SiMe ${}^{t}Bu$
120 °C, DCE 3

To a dry and stirred glass vessel, alkene **1** (0.2 mmol, 1.0 equiv), PdCl₂ (0.005 mmol, 2.5 mol%), PHXPhos (0.012 mmol, 6.0 mol%) and DCE (0.6 mL) were added. To the above mixture, 'BuMe₂SiCl **2a** (0.4 mmol, 2.0 equiv) and H₂O (0.2 mmol, 1.0 equiv) were added. The glass vessel was then put into an autoclave. The autoclave was evacuated and backfilled with CO for three times in a well-ventilated fume hood and then pressurized to 40 atm of CO. The reaction mixture in autoclave was stirred at 120 °C for 24 h. After the reaction completed, the autoclave was cooled down to room temperature. Then, the CO in autoclave was carefully released in a well-ventilated fume hood. The regioselectivity listed in Table 2 in maintext was directly measured by GC-MS analysis of these crude products and using *n*-hexadecane as the internal standard. The yields listed in Table 2 in maintext were based on the isolated yields of silyl ester by flash column chromatography on silica gel.

3.2 Conditions and Procedure of Silyl Ester Derivatization Experiments:

Ph + CO + ^tBuMe₂SiCl
$$\xrightarrow{1) [Pd]/PHXPhos, H_2O, DCE, 120 \circ C}$$
 Ph \xrightarrow{O}_{Nu}
1a 2a 2a 5a, 3a', 6, 7, 8

The Markovnikov hydrocarbonylation of styrene for the formation of the corresponding branched silyl esters were carried out under the standard conditions as described above in **3.1**.

After the reaction completed, the glass vessel was taken out from autoclave. For **5a**, **3a'**: to the mixture of glass vessel, the solution of NuH (3.0 M in DCM, 0.3 mmol, 1.5 equiv) was added and stirred overnight at room temperature. The reaction mixture was concentrated under reduced pressure. The corresponding ester **3a'** and acid **5a** were purified by flash column chromatography on silica gel. For **6**, **7**, **8**: to the mixture of glass vessel, the solution of NuH (3.0 M in DCM, 0.3 mmol, 1.5 equiv), HBTU (0.4

mmol, 2.0 equiv) and NEt₃ (0.4 mmol, 2.0 equiv) was added and stirred overnight at room temperature. The reaction mixture was concentrated under reduced pressure. The corresponding esters and amides were purified by flash column chromatography on silica gel.

4. Mechanism Studies.

4.1 The Control Experiments by (1-Chloroethyl) benzene as the Substrate.

Ph + CO + ^tBuMe₂SiOH
$$(Pd)/PHXPhos$$
 Ph O SiMe₂^tBu
120 °C, DCE 3a

To a dry and stirred glass vessel, (1-chloroethyl)benzene **9** (0.2 mmol, 1.0 equiv), PdCl₂ (0.005 mmol, 2.5 mol%), PHXPhos (0.012 mmol, 6.0 mol%) and DCE (0.6 mL) were added. To the above mixture, ^{*t*}BuMe₂SiOH (0.3 mmol, 1.5 equiv) was added. The glass vessel was then put into an autoclave. The autoclave was evacuated and backfilled with CO for three times in a well-ventilated fume hood and then pressurized to 40 atm of CO. The reaction mixture in autoclave was stirred at 120 °C for 24 h. After the reaction completed, the autoclave was cooled down to room temperature. Then, the CO in autoclave was carefully released in a well-ventilated fume hood. No any silyl ester **3a** was observed by GC-MS analysis of these crude products.

4.2 The Control Experiments by Silanol as the Substrate.

Ph + CO + ^tBuMe₂SiOH
$$(Pd)/PHXPhos$$
 Ph O SiMe₂^tBu
120 °C, DCE 3a

To a dry and stirred glass vessel, styrene **1a** (0.2 mmol, 1.0 equiv), PdCl₂ (0.005 mmol, 2.5 mol%), PHXPhos (0.012 mmol, 6.0 mol%) and DCE (0.6 mL) were added. To the above mixture, 'BuMe₂SiOH (0.3 mmol, 1.5 equiv) was added. The glass vessel was then put into an autoclave. The autoclave was evacuated and backfilled with CO for three times in a well-ventilated fume hood and then pressurized to 40 atm of CO. The reaction mixture in autoclave was stirred at 120 °C for 24 h. After the reaction completed, the autoclave was cooled down to room temperature. Then, the CO in autoclave was carefully released in a well-ventilated fume hood. The trace of silyl ester **3a** was directly measured by GC-MS analysis of these crude products.

4.3 The Control Experiments by 2-Phenylpropanoic Acid as the Substrate.

$$Ph + CO + {}^{t}BuMe_{2}SiCl \xrightarrow{[Pd]/PHXPhos} Ph + CO + {}^{t}BuMe_{2}SiCl \xrightarrow{120 °C, DCE} Ph + {}^{t}O SiMe_{2}{}^{t}Bu \xrightarrow{5a} 3a$$

To a dry and stirred glass vessel, 2-phenylpropanoic acid **5a** (0.2 mmol, 1.0 equiv), PdCl₂ (0.005 mmol, 2.5 mol%), PHXPhos (0.012 mmol, 6.0 mol%) and DCE (0.6 mL) were added. To the above mixture, 'BuMe₂SiCl (0.3 mmol, 1.5 equiv) was added. The glass vessel was then put into an autoclave. The autoclave was evacuated and backfilled with CO for three times in a well-ventilated fume hood and then pressurized to 40 atm of CO. The reaction mixture in autoclave was stirred at 120 °C for 24 h. After the reaction completed, the autoclave was cooled down to room temperature. Then, the CO in autoclave was carefully released in a well-ventilated fume hood. The yield of silyl ester **3a** (37% yield) was directly measured by GC-MS analysis of these crude products using *n*-hexadecane as the internal standard.

4.4 The Two-chamber Experiment.



In a glove box, to chamber I of a two-chamber reactor was added ^{*i*}BuMe₂SiCl (1 mmol, 5 equiv.), H₂O (1 mmol, 5 equiv.), and DCE (5 mL). To chamber II of a twochamber reactor was added with styrene **1a** (0.2 mmol, 1.0 equiv), PdCl₂ (0.005 mmol, 2.5 mol%), PHXPhos (0.012 mmol, 6.0 mol%) and DCE (0.6 mL). The two-chamber reactor was put into an autoclave. The autoclave was evacuated and backfilled with CO for three times in a well-ventilated fume hood and then pressurized to 40 atm of CO. The reaction mixture in autoclave was stirred at 120 °C for 24 h. After the reaction completed, the autoclave was cooled down to room temperature. Then, the CO in autoclave was carefully released in a well-ventilated fume hood. Take out the two-chamber reactor. ^{*t*}BuMe₂SiOH (0.4 mmol, 2.0 equiv) and Et₃N (0.4 mmol, 2.0 equiv) was added into chamber II, and was stirred for 1h under room temperature. The yield of silyl ester 3a (43% yield) was determined by GC-MS using *n*-hexadecane as the internal standard.

5. Characterization Data of Products.



Tert-butyldimethylsilyl-2-phenylpropanoate (3a): Colorless oil, 93% yield (49.1 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.32-7.27 (m, 4H), 7.24-7.20 (m, 1H), 3.68 (q, *J* = 7.2 Hz, 1H), 1.48 (d, *J* = 7.2 Hz, 3H), 0.81 (s, 9H), 0.21 (s, 3H), 0.17 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.8, 141.0, 128.6, 127.6, 127.0, 47.2, 25.4, 18.2, 17.6, -4.8, -5.1. HRMS calcd. (ESI) m/z for C₁₅H₂₄O₂SiNa [M+Na]⁺: 287.1437, found: 287.1433.



Tert-butyldimethylsilyl-2-(*o*-tolyl)propanoate (3b): Colorless oil, 87% yield (48.4 mg), b/l = 98:2, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.26-7.21 (m, 1H), 7.19-7.11 (m, 3H), 3.93 (q, *J* = 7.2 Hz, 1H), 2.37 (s, 3H), 1.46 (d, *J* = 7.2 Hz, 3H), 0.77 (s, 9H), 0.21 (s, 3H), 0.17 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 175.0, 139.7, 135.8, 130.5, 126.9, 126.5, 126.4, 43.0, 25.4, 19.8, 17.7, 17.6, -4.8, -5.1. HRMS calcd. (ESI) m/z for C₁₆H₂₆O₂SiNa [M+Na]⁺: 301.1594, found: 301.1566.



Tert-butyldimethylsilyl-2-(*m*-tolyl)propanoate (3c): Colorless oil, 89% yield (49.5 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.19 (t, J = 7.6 Hz, 1H), 7.12-7.03 (m, 3H), 3.65 (q, J = 7.2 Hz, 1H), 2.33 (s, 3H), 1.48 (d, J = 7.2 Hz, 3H), 0.83 (s, 9H), 0.22 (s, 3H), 0.18 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 175.0, 140.9, 138.1, 128.5, 128.5, 127.8, 124.7, 47.2, 25.5, 21.5, 18.2, 17.7, -4.8, -5.0. HRMS calcd. (ESI) m/z for C₁₆H₂₆O₂SiH [M+H] ⁺: 279.1774, found: 279.1747.



Tert-butyldimethylsilyl-2-(*p*-tolyl)propanoate (3d): Colorless oil, 92% yield (51.2 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.17 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 3.65 (q, *J* = 7.2 Hz, 1H), 2.32 (s, 3H), 1.46 (d, *J* = 7.2 Hz, 3H), 0.83 (s, 9H), 0.21 (s, 3H), 0.17 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 175.1, 138.0, 136.6, 129.3, 127.5, 46.9, 25.5, 21.2, 18.4, 17.7, -4.8, -5.0. HRMS calcd. (ESI) m/z for C₁₆H₂₆O₂SiNa [M+Na]⁺: 301.1594, found: 301.1591.



Tert-butyldimethylsilyl-2-(4-(tert-butyl)phenyl)propanoate (3e): Colorless oil, 94% yield (60.2 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 3.66 (q, *J* = 7.2 Hz, 1H), 1.47 (d, *J* = 7.2 Hz, 3H), 1.29 (s, 9H), 0.79 (s, 9H), 0.20 (s, 3H), 0.17 (s, 3H); ¹³C NMR (101 MHz, Chloroform*d*) δ 175.1, 149.9, 137.9, 127.3, 125.5, 46.8, 34.5, 31.5, 25.5, 18.2, 17.7, -4.8, -5.0. HRMS calcd. (ESI) m/z for C₁₉H₃₂O₂SiNa [M+Na]⁺: 343.2063, found: 343.2067.



Tert-butyldimethylsilyl-2-(3,5-di-*tert*-butylphenyl)propanoate (3f): Colorless oil, 84% yield (63.2 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.33 (s, 1H), 7.14 (s, 2H), 3.70 (q, *J* = 7.0 Hz, 1H), 1.52 (d, *J* = 7.2 Hz, 3H), 1.34 (s, 18H), 0.78 (s, 9H), 0.24 (s, 3H), 0.19 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 175.2, 150.9, 140.3, 121.8, 121.0, 47.8, 34.9, 31.6, 25.4, 18.2, 17.7, -4.8, -5.1. HRMS calcd. (ESI) m/z for C₂₃H₄₀O₂SiNa [M+Na]⁺: 399.2689, found: 399.2677.



Tert-butyldimethylsilyl-2-([1,1'-biphenyl]-4-yl)propanoate (3g): Colorless oil, 90% yield (61.2 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.60-7.53 (m, 4H), 7.45-7.33 (m, 5H), 3.74 (q, *J* = 7.2 Hz, 1H), 1.53 (d, *J* = 7.6 Hz, 3H), 0.83 (s, 9H), 0.23 (s, 3H), 0.19 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.9, 145.4, 141.0, 140.1, 140.0, 128.9, 128.1, 127.3, 127.2, 47.0, 25.5, 18.3, 17.7, -4.8, -4.9. HRMS calcd. (ESI) m/z for C₂₁H₂₈O₂SiNa [M+Na]⁺: 363.1750, found: 363.1758.



Tert-butyldimethylsilyl-2-(benzo[d][1,3]dioxol-5-yl)propanoate(3h):Colorless oil, 95% yield (58.5 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-d) δ 6.80 (s, 1H), 6.74 (s, 2H), 5.93 (s, 2H), 3.61 (q, J = 7.2 Hz, 1H), 1.44 (d, J = 7.2 Hz,3H), 0.85 (s, 9H), 0.22 (s, 3H), 0.19 (s, 3H); ¹³C NMR (101 MHz, Chloroform-d) δ 174.9, 147.8, 146.6, 134.9, 120.9, 108.3, 108.1, 101.1, 46.9, 25.5, 18.5, 17.7, -4.8, -5.0.HRMS calcd. (ESI) m/z for C₁₆H₂₄O₄SiNa [M+Na]⁺: 331.1336, found: 331.1326.



Tert-butyldimethylsilyl-2-(4-phenoxyphenyl)propanoate (3i): Colorless oil, 78% yield (55.5 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.29 (dt, *J* = 20.4, 8.0 Hz, 3H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 7.00-6.94 (m, 3H), 6.88 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.66 (q, *J* = 7.2 Hz, 1H), 1.46 (d, *J* = 7.6 Hz, 3H), 0.82 (s, 9H), 0.21 (s, 3H), 0.18 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.5, 157.4, 157.3, 143.1, 129.9, 123.3, 122.7, 118.9, 118.4, 117.6, 47.2, 25.5, 18.2, 17.7, -4.8, -5.0. HRMS calcd. (ESI) m/z for C₂₁H₂₈O₃SiNa [M+Na]⁺: 379.1699, found: 379.1692.



Tert-butyldimethylsilyl-2-(2-methoxyphenyl)propanoate (3j): Colorless oil, 89% yield (52.3 mg), b/l = 97:3, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.24-7.16 (m,

2H), 6.91 (t, J = 7.4 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 3.96 (q, J = 7.2 Hz, 1H), 3.80 (s, 3H), 1.45 (d, J = 7.2 Hz, 3H), 0.76 (s, 9H), 0.23 (s, 3H), 0.20 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 175.4, 156.9, 130.1, 128.3, 128.0, 120.6, 110.4, 55.3, 41.4, 25.4, 17.6, 16.9, -4.8, -5.1. HRMS calcd. (ESI) m/z for C₁₆H₂₆O₃SiNa [M+Na]⁺: 317.1543, found: 317.1536.



Tert-butyldimethylsilyl-2-(3-methoxyphenyl)propanoate (3k): Colorless oil, 93% yield (54.7 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.23 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.84 (s, 1H), 6.82-6.74 (m, 1H), 3.80 (s, 3H), 3.67 (q, *J* = 7.2 Hz, 1H), 1.48 (d, *J* = 7.6 Hz, 3H), 0.83 (s, 9H), 0.23 (s, 3H), 0.19 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.7, 159.8, 142.6, 129.6, 120.1, 113.3, 112.6, 55.3, 47.3, 25.5, 18.3, 17.7, -4.8, -5.0. HRMS calcd. (ESI) m/z for C₁₆H₂₆O₃SiNa [M+Na]⁺: 317.1543, found: 317.1540.



Tert-butyldimethylsilyl-2-(4-methoxyphenyl)propanoate (3I): Colorless oil, 91% yield (53.5 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.21 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 3.79 (s, 3H), 3.64 (q, J = 7.2 Hz, 1H), 1.46 (d, J = 7.2 Hz, 3H), 0.83 (s, 9H), 0.21 (s, 3H), 0.17 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 175.2, 158.7, 133.2, 128.7, 114.0, 55.4, 46.4, 25.5, 18.4, 17.7, -4.8, -5.0. HRMS calcd. (ESI) m/z for C₁₆H₂₆O₃SiNa [M+Na]⁺: 317.1543, found: 317.1536.



Tert-butyldimethylsilyl-2-(4-(chloromethyl)phenyl)propanoate(3m):Colorless oil, 85% yield (53.2 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-d) δ 7.34 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 7.6 Hz, 2H), 4.57 (s, 2H), 3.70 (q, J = 7.2 Hz, 1H),

1.48 (d, J = 7.2 Hz, 3H), 0.82 (s, 9H), 0.22 (s, 3H), 0.18 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.6, 141.3, 136.3, 128.9, 128.1, 47.0, 46.1, 25.5, 18.3, 17.7, -4.8, -5.0. HRMS calcd. (ESI) m/z for C₁₆H₂₅ClO₂SiNa [M+Na]⁺: 335.1204, found: 335.1211.



Tert-butyldimethylsilyl-2-(4-fluorophenyl)propanoate (3n): Colorless oil, 76% yield (42.9 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.28-7.22 (m, 2H), 7.04-6.96 (m, 2H), 3.68 (q, *J* = 7.2 Hz, 1H), 1.47 (d, *J* = 6.8 Hz, 3H), 0.82 (s, 9H), 0.21 (s, 3H), 0.17 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.7, 162.0 (d, *J* = 246.4 Hz), 136.7, 129.2 (d, *J* = 9.3 Hz), 115.4 (d, *J* = 22.6 Hz), 46.5, 25.5, 18.3, 17.7, -4.8, -5.0. HRMS calcd. (ESI) m/z for C₁₅H₂₃FO₂SiNa [M+Na]⁺: 305.1343, found: 305.1355.



Tert-butyldimethylsilyl-2-(4-chlorophenyl)propanoate (30): Colorless oil, 81% yield (48.3 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.31-7.26 (m, 2H), 7.24-7.20 (m, 2H), 3.67 (q, J = 7.2 Hz, 1H), 1.47 (d, J = 7.2 Hz, 3H), 0.83 (s, 9H), 0.22 (s, 3H), 0.17 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.4, 139.5, 132.9, 129.1, 128.7, 46.7, 25.5, 18.3, 17.7, -4.8, -5.0. HRMS calcd. (ESI) m/z for C₁₅H₂₃ClO₂SiNa [M+Na]⁺: 321.1048, found: 321.1038.



Tert-butyldimethylsilyl-2-(4-bromophenyl)propanoate (3p): Colorless oil, 84% yield (57.6 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 3.66 (q, *J* = 7.2 Hz, 1H), 1.47 (d, *J* = 7.2 Hz, 3H), 0.83 (s, 9H), 0.22 (s, 3H), 0.18 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.3, 140.0, 131.7, 129.4, 121.0, 46.7, 25.5, 18.2, 17.7, -4.8, -5.0. HRMS calcd. (ESI) m/z for C₁₆H₂₆BrO₂SiNa [M+Na]⁺: 367.0523, found: 367.0596.



Tert-butyldimethylsilyl-2-(3-(trifluoromethyl)phenyl)propanoate(3q):Colorless oil, 70% yield (46.5 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.56-7.43 (m, 4H), 3.76 (q, J = 7.2 Hz, 1H), 1.52 (d, J = 6.8 Hz, 3H), 0.80 (s, 9H), 0.20(d, J = 16.4 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.1, 141.9, 131.1, 130.8,129.1, 125.6, 124.7 (d, J = 4.6 Hz), 124.0 (d, J = 4.8 Hz), 47.1, 25.4, 18.1, 17.6, -4.8, -5.1. HRMS calcd. (ESI) m/z for C₁₆H₂₃F₃O₂SiH [M+H]⁺: 333.1492, found: 333.1486.



Tert-butyldimethylsilyl-2-(4-(trifluoromethyl)phenyl)propanoate(3r):Colorless oil, 72% yield (47.8 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, J = 7.6 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 3.76 (q, J = 7.2 Hz, 1H), 1.51 (d, J =7.2 Hz, 3H), 0.82 (s, 9H), 0.23 (s, 3H), 0.18 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ *d*) δ 174.1, 155.1, 145.0, 128.1, 125.6 (d, J = 3.4 Hz), 47.2, 25.4, 18.2, 17.7, -4.8, -5.0.HRMS calcd. (ESI) m/z for C₁₆H₂₃F₃O₂SiH [M+H]⁺: 333.1492, found: 333.1483.



Methyl-2-(4-nitrophenyl)propanoate (3s'): Colorless oil, 63% yield (26.3 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 3.86 (q, *J* = 7.2 Hz, 1H), 3.69 (s, 3H), 1.55 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 173.8, 147.8, 147.2, 128.7, 124.0, 52.5, 45.4, 18.5.



Methyl-4-(1-((*tert*-butyldimethylsilyl)oxy)-1-oxopropan-2-yl)benzoate (3t): Colorless oil, 76% yield (48.9 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 3.91 (s, 3H), 3.75 (q, J = 7.2 Hz, 1H), 1.51 (d, J = 5.2 Hz, 3H), 0.80 (s, 9H), 0.22 (s, 3H), 0.17 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.1, 167.1, 146.2, 130.0, 129.0, 127.8, 52.2, 47.4, 25.5, 18.1, 17.7, -4.8, -5.0. HRMS calcd. (ESI) m/z for C₁₇H₂₆O₄SiNa [M+Na]⁺: 345.1492, found: 345.1507.



Methyl-2-(4-(methylsulfonyl)phenyl)propanoate (3u'): Colorless oil, 66% yield (31.9 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 3.84 (q, *J* = 7.2 Hz, 1H), 3.69 (s, 3H), 3.06 (s, 3H), 1.54 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.0, 146.8, 139.4, 128.8, 127.9, 52.5, 45.5, 44.6, 18.5.



Tert-butyldimethylsilyl-2-(naphthalen-1-yl)propanoate (3v): White solid, 82% yield (51.5 mg), b/l = 97:3, ¹H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.80-7.73 (m, 1H), 7.56-7.48 (m, 2H), 7.45 (d, *J* = 4.8 Hz, 2H), 4.48 (q, *J* = 7.2 Hz, 1H), 1.68 (d, *J* = 7.2 Hz, 3H), 0.66 (s, 9H), 0.19 (s, 3H), 0.15 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 175.2, 137.4, 134.1, 131.6, 129.0, 127.7, 126.2, 125.6, 125.6, 124.6, 123.6, 43.3, 25.3, 17.9, 17.5, -4.9, -5.1. HRMS calcd. (ESI) m/z for C₁₉H₂₆O₂SiNa [M+Na]⁺: 337.1594, found: 337.1577.



Tert-butyldimethylsilyl-2-(naphthalen-2-yl)propanoate (3w): White solid, 90% yield (56.5 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, J = 8.0 Hz, 3H), 7.73 (s, 1H), 7.48-7.42 (m, 3H), 3.86 (q, J = 7.2 Hz, 1H), 1.58 (d, J = 7.2 Hz, 3H),

0.81 (s, 9H), 0.22 (s, 3H), 0.17 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.8, 138.5, 133.6, 132.6, 128.3, 127.9, 127.7, 126.3, 126.2, 126.1, 125.8, 47.4, 25.5, 18.4, 17.7, -4.8, -5.0. HRMS calcd. (ESI) m/z for C₁₉H₂₆O₂SiNa [M+Na]⁺: 337.1594, found: 337.1561.



Tert-butyldimethylsilyl-2-phenylbutanoate (3x): Colorless oil, 38% yield (21.1 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.33-7.27 (m, 4H), 7.25-7.19 (m, 1H), 3.42 (t, J = 7.6 Hz, 1H), 2.16-2.02 (m, 1H), 1.86-1.72 (m, 1H), 0.91 (d, J = 6.0 Hz, 3H), 0.84 (s, 9H), 0.21 (s, 3H), 0.18 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.3, 139.6, 128.5, 128.1, 127.1, 55.4, 26.4, 25.5, 17.7, 12.3, -4.8, -5.0. HRMS calcd. (ESI) m/z for C₁₆H₂₆O₂SiNa [M+Na]⁺: 301.1594, found: 301.1576.



Tert-butyldimethylsilyl-2-(4-isobutylphenyl)propanoate (3y): Colorless oil, 85% yield (54.4 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.65 (q, *J* = 7.2 Hz, 1H), 2.44 (d, *J* = 7.2 Hz, 2H), 1.90-1.77 (m, 1H), 1.47 (d, *J* = 7.2 Hz, 3H), 0.88 (d, *J* = 6.4 Hz, 6H), 0.79 (s, 9H), 0.20 (s, 3H), 0.16 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 175.1, 140.5, 138.3, 129.3, 127.4, 46.9, 45.2, 30.4, 25.5, 22.4, 18.2, 17.7, -4.8, -5.0. HRMS calcd. (ESI) m/z for C₁₉H₃₂O₂SiNa [M+Na]⁺: 343.2063, found: 343.2067.



Tert-butyldimethylsilyl-2-(6-methoxynaphthalen-2-yl)propanoate (3z): White solid, 78% yield (53.7 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.72-7.66 (m, 3H), 7.42 (d, J = 8.4 Hz, 1H), 7.16-7.10 (m, 2H), 3.90 (s, 3H), 3.84 (q, J = 6.8 Hz,

1H), 1.58 (d, J = 6.8 Hz, 3H), 0.83 (s, 9H), 0.24 (s, 3H), 0.18 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 175.0, 157.6, 136.1, 133.7, 129.3, 129.0, 127.1, 126.5, 126.1, 119.0, 105.6, 55.3, 47.2, 25.5, 18.4, 17.7, -4.8, -5.0. HRMS calcd. (ESI) m/z for C₂₀H₂₈O₃SiNa [M+Na]⁺: 367.1699, found: 367.1713.



Tert-butyldimethylsilyl-2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (3aa): White solid, 75% yield (53.7 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.6 Hz, 2H), 7.45-7.41 (m, 2H), 7.40-7.32 (m, 2H), 7.16-7.08 (m, 2H), 3.73 (q, *J* = 7.2 Hz, 1H), 1.52 (d, *J* = 7.2 Hz, 3H), 0.85 (s, 9H), 0.25 (s, 3H), 0.21 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.3, 161.0, 158.5, 142.4 (d, *J* = 8.0 Hz), 135.7, 130.8 (d, *J* = 4.0 Hz), 129.1 (d, *J* = 3.0 Hz), 128.6, 127.7, 123.8 (d, *J* = 3.5 Hz), 115.4 (d, *J* = 23.3 Hz), 46.8, 25.5, 18.2, 17.7, -4.8, -5.0. HRMS calcd. (ESI) m/z for C₂₁H₂₇FO₂SiNa [M+Na]⁺: 381.1656, found: 381.1634.



Methyl 2-phenylpropanoate (3ab'): Colorless oil, 90% yield (29.5 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.35-7.27 (m, 4H), 7.24 (m, *J* = 8.6, 5.2, 2.0 Hz, 1H), 3.72 (q, *J* = 7.2 Hz, 1H), 3.64 (s, 3H), 1.50 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 175.2, 140.7, 128.8, 127.6, 127.3, 52.2, 45.5, 18.7.



Triethylsilyl-2-phenylpropanoate (3ac): Colorless oil, 86% yield (45.4 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.29 (d, J = 4.4 Hz, 4H), 7.25-7.18 (m, 1H), 3.70 (q, J = 7.2 Hz, 1H), 1.49 (d, J = 7.2 Hz, 3H), 0.87 (t, J = 8.0 Hz, 9H), 0.69 (q, J = 8.0 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 175.0, 141.0, 128.5, 127.6, 127.0,

47.1, 18.3, 6.4, 4.5. HRMS calcd. (ESI) m/z for $C_{15}H_{24}O_2SiNa$ [M+Na]⁺: 287.1437, found: 287.1423.



*Trüsopropylsilyl-2-*phenylpropanoate (3ad): Colorless oil, 76% yield (46.5 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.36-7.27 (m, 4H), 7.26-7.20 (m, 1H), 3.73 (q, *J* = 7.6 Hz, 1H), 1.52 (d, *J* = 7.2 Hz, 3H), 1.27-1.18 (m, 3H), 0.97 (dd, *J* = 8.0, 4.8 Hz, 18H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.5, 141.0, 128.5, 127.8, 127.1, 47.3, 18.1, 17.7, 12.0. HRMS calcd. (ESI) m/z for C₁₈H₃₀O₂SiNa [M+Na]⁺: 287.1437, found: 287.1438.



2-phenylpropanoic acid (5a): Colorless oil, 93% yield (27.9 mg), ¹H NMR (400 MHz, Chloroform-*d*) δ 11.92 (s, 1H), 7.31 (d, *J* = 4.4 Hz, 4H), 7.28-7.23 (m, 1H), 3.72 (q, *J* = 7.2 Hz, 1H), 1.49 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 181.4, 139.8, 128.8, 127.7, 127.5, 45.5, 18.2.



4-methylbenzyl 2-phenylpropanoate (6): Colorless oil, 84% yield (42.7 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.32-7.20 (m, 5H), 7.15-7.08 (m, 4H), 5.11-4.99 (m, 2H), 3.75 (q, *J* = 7.2 Hz, 1H), 2.31 (s, 3H), 1.50 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.5, 140.5, 138.0, 133.1, 129.2, 128.7, 128.1, 127.6, 127.2, 66.5, 45.6, 21.3, 18.6. HRMS calcd. (ESI) m/z for C₁₇H₁₈O₂Na [M+Na]⁺: 277.1199, found: 277.1174.



N-isopropyl-2-phenylpropanamide (7): Colorless oil, 67% yield (25.6 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.38-7.31 (m, 2H), 7.28 (dd, J = 7.2, 3.8 Hz, 3H), 5.17 (s, 1H), 4.03 (dp, J = 13.2, 6.4 Hz, 1H), 3.50 (q, J = 7.2 Hz, 1H), 1.50 (d, J = 7.2 Hz, 3H), 1.05 (dd, J = 20.4, 6.6 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 173.3, 141.7, 129.0, 127.7, 127.2, 47.3, 41.5, 22.7, 22.6, 18.8. HRMS calcd. (ESI) m/z for C₁₂H₁₇NONa [M+Na]⁺: 214.1202, found: 214.1184.



N,2-diphenylpropanamide (8): Colorless oil, 86% yield (38.7 mg), b/l > 99:1, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.44-7.23 (m, 9H), 7.07 (dd, J = 17.0, 9.6 Hz, 2H), 3.72 (q, J = 7.2 Hz, 1H), 1.59 (d, J = 7.6 Hz, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 172.4, 141.0, 138.0, 129.3, 129.0, 127.8, 127.7, 124.4, 119.8, 48.2, 18.7. HRMS calcd. (ESI) m/z for C₁₅H₁₅NONa [M+Na]⁺: 248.1045, found: 248.1039.

6. Copies of ¹H and ¹³C NMR Spectra.

¹H NMR Spectra (400 MHz, CDCl₃) of **3a**



¹³C NMR Spectra (101 MHz, CDCl₃) of **3a**



¹H NMR Spectra (400 MHz, CDCl₃) of **3b**



¹³C NMR Spectra (101 MHz, CDCl₃) of **3b**



¹H NMR Spectra (400 MHz, CDCl₃) of **3c**



¹³C NMR Spectra (101 MHz, CDCl₃) of **3c**



¹H NMR Spectra (400 MHz, CDCl₃) of **3d**



¹³C NMR Spectra (101 MHz, CDCl₃) of **3d**



¹H NMR Spectra (400 MHz, CDCl₃) of **3e**







¹H NMR Spectra (400 MHz, CDCl₃) of **3f**





S32

¹H NMR Spectra (400 MHz, CDCl₃) of **3g**



¹³C NMR Spectra (101 MHz, CDCl₃) of **3g**





¹H NMR Spectra (400 MHz, CDCl₃) of **3h**






¹H NMR Spectra (400 MHz, CDCl₃) of **3i**



¹³C NMR Spectra (101 MHz, CDCl₃) of **3i**





¹H NMR Spectra (400 MHz, CDCl₃) of **3j**







¹H NMR Spectra (400 MHz, CDCl₃) of **3**k



¹³C NMR Spectra (101 MHz, CDCl₃) of **3**k



¹H NMR Spectra (400 MHz, CDCl₃) of **3**l





¹H NMR Spectra (400 MHz, CDCl₃) of **3m**



¹³C NMR Spectra (101 MHz, CDCl₃) of **3m**



¹H NMR Spectra (400 MHz, CDCl₃) of **3n**



¹³C NMR Spectra (101 MHz, CDCl₃) of **3n**



¹H NMR Spectra (400 MHz, CDCl₃) of **30**



¹³C NMR Spectra (101 MHz, CDCl₃) of **30**



¹H NMR Spectra (400 MHz, CDCl₃) of **3p**



¹³C NMR Spectra (101 MHz, CDCl₃) of **3p**



¹H NMR Spectra (400 MHz, CDCl₃) of **3**q



¹³C NMR Spectra (101 MHz, CDCl₃) of **3q**



¹H NMR Spectra (400 MHz, CDCl₃) of **3r**



¹³C NMR Spectra (101 MHz, CDCl₃) of **3r**



¹H NMR Spectra (400 MHz, CDCl₃) of **3s'**



¹³C NMR Spectra (101 MHz, CDCl₃) of **3s'**





¹H NMR Spectra (400 MHz, CDCl₃) of **3t**



¹³C NMR Spectra (101 MHz, CDCl₃) of **3t**



¹H NMR Spectra (400 MHz, CDCl₃) of **3u'**







¹³C NMR Spectra (101 MHz, CDCl₃) of **3u'**



¹H NMR Spectra (400 MHz, CDCl₃) of **3v**



¹³C NMR Spectra (101 MHz, CDCl₃) of **3v**



¹H NMR Spectra (400 MHz, CDCl₃) of **3w**



¹³C NMR Spectra (101 MHz, CDCl₃) of **3w**



¹H NMR Spectra (400 MHz, CDCl₃) of **3**x



¹³C NMR Spectra (101 MHz, CDCl₃) of **3**x





¹H NMR Spectra (400 MHz, CDCl₃) of **3**y



¹³C NMR Spectra (101 MHz, CDCl₃) of **3**y



¹H NMR Spectra (400 MHz, CDCl₃) of **3z**






¹H NMR Spectra (400 MHz, CDCl₃) of **3aa**



¹³C NMR Spectra (101 MHz, CDCl₃) of **3aa**



¹H NMR Spectra (400 MHz, CDCl₃) of **3ab'**



¹³C NMR Spectra (101 MHz, CDCl₃) of **3ab'**





¹H NMR Spectra (400 MHz, CDCl₃) of **3ac**



¹³C NMR Spectra (101 MHz, CDCl₃) of **3ac**



¹H NMR Spectra (400 MHz, CDCl₃) of **3ad**



¹³C NMR Spectra (101 MHz, CDCl₃) of **3ad**





¹³C NMR Spectra (101 MHz, CDCl₃) of **5a**



¹H NMR Spectra (400 MHz, CDCl₃) of 6

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## ¹³C NMR Spectra (101 MHz, CDCl₃) of **6**





### ¹H NMR Spectra (400 MHz, CDCl₃) of 7





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## ¹H NMR Spectra (400 MHz, CDCl₃) of 8



## ¹³C NMR Spectra (101 MHz, CDCl₃) of 8

