Supplementary Information

Sila-spirocyclization Involving Unstrained C(sp<sup>3</sup>)–Si Bond Cleavage

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1. Supplementary Notes

Unless otherwise noted, all reactions were set up on a Schlenk vacuum line or in a glovebox using oven-dried glassware and were stirred with Teflon-coated magnetic stirring bars under a N₂ atmosphere with dry solvents. Et₂O and toluene were distilled with Na before using. Other dry solvents or commercially available chemicals were obtained from Adamas-beta, Alfa Aesar, J&K, Sigma-Aldrich, Energy Chemical, Bide Pharmatech, Sinocompound, TCI, Sinocompound and used as received unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on SANPONT SGF254 glass plates. TLC plates were visualized by exposure to short wave ultraviolet light (254 nm, 365 nm) and/or iodine. Column chromatography was performed using GENERAL-REAGENT silica gel (200-300 mesh).

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV 400 spectrometer at 400 MHz for ¹H NMR, 100 MHz for ¹³C NMR, 376 MHz for ¹⁹F NMR using CDCl₃ as solvent. ¹H and ¹³C NMR are reported (ppm) relative to the CDCl₃ peak (δ_H = 7.26 ppm, δ_C = 77.16 ppm). All coupling constants (J values) were reported in Hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), triplet of doublets (td) and multiplet (m).

GC-MS analysis were performed on a GC-MS with an EI mode (Thermo Scientific Trace 300/GC-System and ISQ/QD). High-resolution mass spectra (HRMS) were performed on a Q Exactive GC-Orbitrap MS (EI). The residues of the catalytic reactions were purified on C18(ODS) column (5µm, 21.2x250 mm) with CH₃CN by preparative RP-HPLC with an Bonna-Agela CHEETAH HP series.
2. Supplementary Methods

Synthesis of Starting Materials

Procedure A:

**Step I:** 1-(2-Bromophenyl) ethan-1-one derivatives were prepared following a previously reported procedure\[1\]. To a solution of 2-bromobenzaldehyde derivatives (commercially available chemicals; 20 mmol) in THF (20 mL) was added MeMgBr (commercially available chemicals; 24 mmol) dropwise at 0 °C under N\(_2\), and stirred at the same temperature. Upon completion, the reaction was quenched with saturated NH\(_4\)Cl solution and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na\(_2\)SO\(_4\), filtered, and concentrated to deliver the corresponding secondary benzylic alcohols, which were directly used for the next
without further purification. To a solution of 1-(2-bromophenyl) ethan-1-ol derivatives (15 mmol) in DCM was added a mixture of PCC (45.0 mmol) and silica gel [PCC/silica gel = 1/1 (w/w)]. The resulted reaction mixture was stirred at room temperature. Upon completion, the reaction mixture was then filtered through a pad of silica gel with EtOAc as eluent. The resulting solution was concentrated, and the residue was purified by silica gel chromatography column to yield the desired 1-(2-bromophenyl) ethan-1-one derivatives.

Step II: Following a modified literature procedure\[^2\], to the mixture of methyl triphenylphosphonium bromide (40 mmol, 2 equiv.) and tBuOK (50.0 mmol, 2.5 equiv.) was added anhydrous THF (50.0 mL) and stirred at rt. for 20 min. under argon, then the solution of ketone (20 mmol, 1.0 equiv.) in THF (50.0 mL) was added slowly, the resulting solution was allowed to stir at rt. overnight. To the mixture was added sat. NH₄Cl, then THF was removed and the mixture was extracted with EtOAc (3 x 30 mL), the combined EtOAc solution was washed with brine, dried over anhydrous Na₂SO₄. After removing the solvent, the residue was purified by flash chromatography on silica gel to yield 1-bromo-2-(prop-1-en-2-yl) benzene derivatives.

Step III: Following a modified literature procedure\[^3\], a solution of ^n^BuLi in hexane (11 mmol, 1.1 equiv., 2.5 M in hexane) was added dropwise to a solution of 1-bromo-2-(prop-1-en-2-yl) benzene derivatives (10 mmol, 1.0 equiv.) in anhydrous THF (20 mL) at -78 °C. After the reaction mixture was stirred at this temperature for 0.5 hour, chlorosilane (12 mmol, 1.2 equiv.) was added via a syringe. Then, the mixture was warmed to room temperature. The solvent was removed in vacuo, and evaporated under reduced pressure to give trimethyl(2-(prop-1-en-2-yl) phenyl) silane derivatives, which was used for the next step without purification.

Step IV: Following a modified literature procedure\[^2\], in an oven dried flask trimethyl (2-(prop-1-en-2-yl) phenyl) silane derivatives (8 mmol, 1.0 equiv.) was dissolved in anhydrous THF (3.0 mL/mmol). To the resulting solution N-Bromosuccinimide (NBS, 8.4mmol, 1.05 equiv.) and TsOH (0.8 mmol, 0.1 equiv.) was added and the solution was
refluxed at 80 °C for 4 h. Reaction mixture was cooled to rt and the reaction mixture was taken in petroleum ether (15 mL/mmol), washed with H2O (15 mL × 3). Organic phase was dried over anh. Na2SO4, concentrated under reduced pressure to afford the corresponding compounds.

**Step V:** Following a modified literature procedure[4], to a solution of 2-iodophenol (5 mmol, 1.0 equiv.) and K2CO3 (7.5 mmol, 1.5 equiv.) in DMF (10 mL) was added allyl halide (6 mmol, 1.2 equiv). The reaction mixture was allowed to warm at 70 °C and stirred overnight. The reaction was quenched with water (10 mL), and extracted with ethyl acetate (3 ×10 mL), wash with brine, dried over anhydrous Na2SO4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give the products 1.

**Procedure B:**

(2-(3-Bromoprop-1-en-2-yl) phenyl) trimethylsilane was prepared following **Procedure A.**

Following a modified literature procedure[5], to a suspension of NaH (60% in oil, 6 mmol, 1.2 equiv.) in DMF (10 mL) were added (2-iodophenyl) methanol (5 mmol, 1.0 equiv.) in DMF (5 mL) at 0 °C under Ar atmosphere. When the evolution of H2 has ceased, (2-(3-bromoprop-1-en-2-yl) phenyl) trimethylsilane (5.5 mmol, 1.0 equiv.) was added. The reaction mixture was heated to 80 °C overnight. The reaction mixture was quenched with water and extracted with Et2O. The organic phase was dried over MgSO4 and concentrated in vacuo. The residue was purified by column chromatography (PE: EA = 40:1) to afford compound 1ca.
Procedure C:

Trimethyl(2-(prop-1-en-2-yl) phenyl) silane was prepared following Procedure A.

Step I: Following a modified literature procedure,[6] to a stirred suspension of SeO$_2$ (15 mmol, 1.5 equiv.) in CH$_2$Cl$_2$ (10 mL) at R.T. was added a solution of tert-butyl hydroperoxide (70% in water, 15 mmol, 1.5 equiv.). After 10 min a solution of trimethyl(2-(prop-1-en-2-yl) phenyl) silane (10.0 mmol, 1.0 equiv.) in CH$_2$Cl$_2$ (5 mL) was added and the mixture stirred at ambient temperature for 4 h. Saturated aqueous NaHCO$_3$ (10 mL) was added and the mixture was extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic phases were washed with water and brine, dried (MgSO$_4$) and evaporated. Flash chromatography (PE: EA = 5:1) afforded 2-(2-(trimethylsilyl) phenyl) prop-2-en-1-ol as a clear colorless oil (yield = 50%).

Step II: Following a modified literature procedure,[7], to a flame-dried flask were added PPh$_3$ (15 mmol, 1.5 equiv.), aryl iodide (10.05 mmol, 1.05 equiv.), allylic alcohol (10 mmol, 1.0 equiv.) and anhydrous THF (40 mL) sequentially under Ar atmosphere at room temperature. A solution of DIAD (15 mmol, 1.5 equiv.) in 10 mL of anhydrous THF was added dropwise via addition funnel at 0°C. The resulting mixture was allowed to warm to room temperature naturally with stirring. After the reaction was complete as monitored by TLC, the reaction mixture was concentrated on a rotary evaporator and the residue was purified by chromatography on silica gel to afford the desired product.
Characterization of Products 1

(2-(3-(2-Iodophenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1aa)

Following the procedure A, 1aa was obtained as a colorless oil (Rf = 0.3, petroleum ether) in 50% yield (2 g, 5 mmol). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.80 (m, 1H), 7.58 (m, 1H), 7.39 – 7.28 (m, 2H), 7.28 – 7.24 (m, 2H), 6.79 (m, 1H), 6.72 (m, 1H), 5.88 (q, J = 1.8 Hz, 1H), 5.24 (d, J = 1.8 Hz, 1H), 4.67 (d, J = 1.8 Hz, 2H), 0.30 (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 156.13, 145.02, 144.66, 138.65, 137.73, 134.17, 128.52, 127.73, 125.98, 121.82, 115.19, 111.24, 85.67, 70.92, 52.55, -0.00. MS (EI) calcd. for C\(_{18}\)H\(_{21}\)IOSi [M]+: 408.04. Found: 408.15.

(2-(3-(2-Iodo-4-methylphenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1ab)

Following the procedure A, 1ab was obtained as a colorless oil (Rf = 0.3, petroleum ether) in 57% yield (2.4 g, 5.7 mmol). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.63 (m, 1H), 7.61 – 7.56 (m, 1H), 7.41 – 7.28 (m, 2H), 7.27 – 7.23 (m, 1H), 7.07 (m, 1H), 6.68 (m, 1H), 5.86 (d, J = 1.8 Hz, 1H), 5.22 (q, J = 1.8 Hz, 1H), 4.63 (t, J = 1.8 Hz, 2H), 2.26 (s, 3H), 0.30 (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 154.18, 145.16, 144.84, 139.03, 137.82, 134.22, 131.42, 129.00, 127.77, 127.70, 125.99, 115.08, 111.05, 85.49, 71.09, 19.16, -0.00. MS (EI) calcd. for C\(_{19}\)H\(_{23}\)IOSi [M]+: 422.06. Found: 422.15.
(2-(3-(4-Fluoro-2-iodophenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1ac)

Following the procedure A, 1ac was obtained as a white solid ($R_f = 0.25$, petroleum ether) in 42% yield (1.8 g, 4.2 mmol). $^1$H NMR (400 MHz, CDCl₃) δ 7.64 (m, 1H), 7.56 (m, 1H), 7.40 – 7.36 (m, 2H), 7.30 – 7.28 (m, 1H), 7.09 – 6.98 (m, 1H), 6.76 (m, 1H), 5.89 (p, $J = 1.5$ Hz, 1H), 5.28 (t, $J = 1.5$ Hz, 1H), 4.67 (t, $J = 1.5$ Hz, 2H), 0.35 (s, 9H). $^{13}$C NMR (101 MHz, CDCl₃) δ 156.00 (d, $J = 243.7$ Hz), 152.92 (d, $J = 2.4$ Hz), 144.92, 144.63, 137.76, 134.23, 127.71, 126.04, 125.48, 125.23, 115.27, 114.68 (d, $J = 22.8$ Hz), 111.39 (d, $J = 8.1$ Hz), 85.08 (d, $J = 8.7$ Hz), 71.73, -0.00. $^{19}$F NMR (376 MHz, CDCl₃) δ -121.76. MS (EI) calcd. for C₁₈H₂₀FIO₂Si [M]⁺: 426.03. Found: 426.13.

(2-(3-(4-(tert-Butyl)-2-iodophenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1ad)

Following the procedure A, 1ad was obtained as a colorless oil ($R_f = 0.3$, petroleum ether) in 44% yield (2.0 g, 4.4 mmol). $^1$H NMR (400 MHz, CDCl₃) δ 7.79 (m, 1H), 7.59 (m, 1H), 7.42 – 7.22 (m, 4H), 6.72 (m, 1H), 5.86 (s, 1H), 5.22 (s, 1H), 4.65 (m, 2H), 1.28 (s, 9H), 0.30 (s, 9H). $^{13}$C NMR (101 MHz, CDCl₃) δ 154.01, 145.17, 144.90, 144.84, 137.80, 135.77, 134.19, 127.75, 127.67, 125.96, 125.37, 115.08, 110.71, 85.57, 71.03, 33.18, 30.55, 0.00. MS (EI) calcd. for C₂₂H₂₉IO₂Si [M]⁺: 464.10. Found: 464.25.
(2-(3-(4-Chloro-2-iodophenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1ae)

Following the procedure A, 1ae was obtained as a colorless oil (Rf = 0.3, petroleum ether) in 40% yield (1.77 g, 4.0 mmol). H NMR (400 MHz, CDCl3) δ 7.77 (m, 1H), 7.59 (m, 1H), 7.40 – 7.28 (m, 2H), 7.27 – 7.22 (m, 2H), 6.70 (m, 1H), 5.83 (q, J = 1.8 Hz, 1H), 5.24 (d, J = 1.8 Hz, 1H), 4.64 (d, J = 1.8 Hz, 2H), 0.29 (s, 9H). C NMR (101 MHz, CDCl3) δ 155.19, 144.86, 144.45, 137.88, 137.83, 134.29, 134.29, 128.33, 127.76, 126.12, 125.80, 115.43, 111.72, 85.84, 71.43, 0.00. MS (EI) calcd. for C18H20ClIOSi [M]+: 442.00. Found: 441.95

(2-(3-(2-Iodo-4-(trifluoromethyl)phenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1af)

Following the procedure A, 1af was obtained as a yellow liquid (Rf = 0.3, petroleum ether) in 46% yield (2.2 g, 4.6 mmol). H NMR (400 MHz, CDCl3) δ 8.05 (m, 1H), 7.58 (m, 2H), 7.35 (m, 2H), 7.25 – 7.16 (m, 1H), 6.83 (m, 1H), 5.85 (q, J = 1.8 Hz, 1H), 5.27 (d, J = 1.8 Hz, 1H), 4.72 (t, J = 1.8 Hz, 2H), 0.30 (s, 9H). C NMR (101 MHz, CDCl3) δ 158.73, 144.66, 144.13, 137.85, 135.86 (q, J = 3.7 Hz), 134.35, 127.81, 127.78, 126.22, 126.09 (q, J = 3.7 Hz), 123.76 (q, J = 30.4 Hz), 122.42 (q, J = 269.3 Hz), 115.66, 110.54, 85.31, 71.30, -0.00. F NMR (376 MHz, CDCl3) δ -61.62. MS (EI) calcd. for C19H20F3IOSi [M]+: 476.03. Found: 476.35.
(2-(3-Iodo-[1,1'-biphenyl]-4-yl)oxy)prop-1-en-2-yl)phenyl)trimethylsilane (1ag)

Following the procedure B, 1ag was obtained as a colorless oil ($R_f = 0.3$, petroleum ether) in 42% yield (2.0 g, 4.2 mmol). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.06 (m, 1H), 7.65 – 7.59 (m, 1H), 7.53 (m, 3H), 7.43 (s, 2H), 7.40 – 7.27 (m, 4H), 6.87 (m, 1H), 5.91 (q, $J = 1.8$ Hz, 1H), 5.27 (q, $J = 1.8$ Hz, 1H), 4.73 (t, $J = 1.8$ Hz, 2H), 0.33 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 155.60, 144.96, 144.59, 138.34, 137.74, 137.15, 135.05, 134.19, 127.91, 127.72, 127.69, 127.12, 126.27, 126.01, 125.82, 115.23, 111.20, 86.09, 71.07, 0.00. MS (EI) calcd. for C$_{24}$H$_{25}$IOSi [M]$^+$: 484.07. Found: 483.87.

3-Iodo-4-((2-(2-(trimethylsilyl)phenyl)allyl)oxy)benzonitrile (1ah)

Following the procedure A, 1ah was obtained as a colorless oil ($R_f = 0.3$, petroleum ether) in 52% yield (2.3 g, 5.2 mmol). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.08 (m, 1H), 7.61 (m, 2H), 7.35 (m, 2H), 7.24 (m, 1H), 6.82 (m, 1H), 5.82 (q, $J = 1.7$ Hz, 1H), 5.28 (q, $J = 1.7$ Hz, 1H), 4.73 (d, $J = 1.7$ Hz, 2H), 0.30 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.65, 144.41, 143.78, 142.07, 137.84, 134.39, 133.14, 127.84, 127.76, 126.29, 116.68, 115.94, 110.94, 105.33, 85.64, 71.43, 0.00. MS (EI) calcd. for C$_{19}$H$_{20}$NOSi [M]$^+$: 433.04. Found: 433.03.
1-(2-(1-(4-Ethylphenyl)vinyl)phenyl)-1-methylsiletane (1ai)

Following the procedure A, 1ai was obtained as a colorless oil (Rf = 0.3, petroleum ether) in 42% yield (1.8 g, 4.2 mmol). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.65 (m, 1H), 7.62 – 7.56 (m, 1H), 7.34 (m, 2H), 7.27 (m, 1H), 6.40 (s, 1H), 6.34 (m, 1H), 5.87 (d, J = 1.8 Hz, 1H), 5.24 (d, J = 1.8 Hz, 1H), 4.64 (t, J = 1.8 Hz, 2H), 3.77 (s, 3H), 0.30 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 160.44, 156.99, 145.07, 144.60, 138.39, 137.86, 134.25, 127.82, 127.73, 126.05, 115.31, 106.70, 99.35, 74.41, 70.96, 54.68, 0.00. MS (EI) calcd. for C$_{19}$H$_{23}$IO$_2$Si [M]$^+$: 438.05. Found: 438.10.

(2-(3-(5-(tert-Butyl)-2-iodophenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1aj)

Following the procedure A, 1aj was obtained as a colorless oil (Rf = 0.3, petroleum ether) in 56% yield (2.6 g, 5.6 mmol). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.70 (m, 1H), 7.61 (m, 1H), 7.42 – 7.29 (m, 2H), 7.27 (m, 1H), 6.82 (m, 1H), 6.78 (m, 1H), 5.91 (d, J = 1.9 Hz, 1H), 5.24 (d, J = 1.9 Hz, 1H), 4.69 (t, J = 1.9 Hz, 2H), 1.29 (s, 9H), 0.32 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 155.94, 152.53, 145.20, 144.82, 137.93, 137.89, 134.23, 127.82, 127.73, 126.02, 119.24, 109.09, 115.06, 81.96, 70.86, 34.03, 30.39, 0.00. MS (EI) calcd. for C$_{22}$H$_{29}$IOSi [M]$^+$: 464.10. Found: 464.19.
Following the procedure A, 1ak was obtained as a colorless oil (RF = 0.3, petroleum ether) in 46% yield (2.0 g, 4.6 mmol). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.60 (m, 2H), 7.34 (m, 2H), 7.19 (m, 1H), 6.73 (m, 1H), 6.59 (m, 1H), 5.59 (q, \(J = 1.7\) Hz, 1H), 5.19 (q, \(J = 1.7\) Hz, 1H), 4.63 (t, \(J = 1.7\) Hz, 2H), 0.29 (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 163.01 (d, \(J = 247.1\) Hz), 157.17, 144.74, 144.19, 138.76 (d, \(J = 9.9\) Hz), 137.81, 134.29, 127.77, 126.13, 115.56, 108.71 (d, \(J = 21.8\) Hz), 100.03, 99.77, 78.46, 71.20, -0.00. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -92.06. MS (EI) calcd. for C\(_{18}\)H\(_{20}\)FIOSi [M]\(^+\): 426.03. Found: 426.25.

Following the procedure A, 1al was obtained as a colorless liquid (RF = 0.3, petroleum ether) in 55% yield (2.4 g, 5.5 mmol). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.60 (m, 1H), 7.39 – 7.29 (m, 2H), 7.28 – 7.24 (m, 1H), 6.74 (d, \(J = 1.8\) Hz, 1H), 6.43 (d, \(J = 1.8\) Hz, 1H), 5.94 (t, \(J = 1.8\) Hz, 1H), 5.24 (q, \(J = 1.8\) Hz, 1H), 4.65 (t, \(J = 1.8\) Hz, 2H), 2.45 (s, 3H), 2.27 (s, 3H), 0.30 (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 156.06, 145.23, 144.87, 142.15, 137.95, 137.83, 134.20, 127.75, 127.68, 125.96, 122.68, 115.01, 109.40, 88.58, 71.06, 27.68, 20.36, 0.00. MS (EI) calcd. for C\(_{20}\)H\(_{25}\)IOSi [M]\(^+\): 436.07. Found: 436.00.
(2-(3-(2-Iodo-4,6-dimethylenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1am)

Following the procedure A, 1am was obtained as a pale yellow liquid (R_f = 0.6, petroleum ether) in 49% yield (2.2 g, 4.9 mmol). ^1H NMR (400 MHz, CDCl_3) δ 7.62 – 7.56 (m, 1H), 7.49 – 7.42 (m, 1H), 7.37 – 7.26 (m, 2H), 7.27 – 7.21 (m, 1H), 6.99 – 6.91 (m, 1H), 5.84 (d, J = 1.8 Hz, 1H), 5.22 (q, J = 1.8 Hz, 1H), 4.49 (t, J = 1.8 Hz, 2H), 2.26 (s, 3H), 2.23 (s, 3H), 0.33 (s, 9H). ^13C NMR (101 MHz, CDCl_3) δ 153.37, 145.41, 145.24, 137.36, 136.29, 134.55, 133.84, 131.17, 130.69, 127.49, 127.24, 125.50, 114.50, 90.57, 73.73, 19.06, 15.84, 0.00. MS (EI) calcd. for C_{20}H_{25}IOSi [M]^{+}: 436.07 Found: 436.09.

(2-(3-(2,4-Difluoro-6-iodophenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1an)

Following the procedure A, 1an was obtained as a colorless oil (R_f = 0.4, petroleum ether) in 57% yield (2.5 g, 5.7 mmol). ^1H NMR (400 MHz, CDCl_3) δ 7.60 – 7.55 (m, 1H), 7.34 – 7.27 (m, 3H), 7.23 (m, 1H), 6.88 (m, 1H), 5.84 (q, J = 1.8 Hz, 1H), 5.23 (q, J = 1.8 Hz, 1H), 4.68 (q, J = 1.8 Hz, 2H), 0.32 (s, 9H). ^13C NMR (101 MHz, CDCl_3) δ 158.41 (dd, J = 249.3, 11.7 Hz), 153.16 (dd, J = 254.3, 12.7 Hz), 145.11, 144.90, 141.57 (dd, J = 12.8, 4.2 Hz), 137.65, 134.07, 127.65, 127.49, 125.80, 120.20 (dd, J = 24.6, 3.8 Hz), 115.11, 104.70 (dd, J = 26.7, 23.4 Hz), 90.26 (dd, J = 10.2, 2.6 Hz), 75.29, 0.00. ^19F NMR (376 MHz, CDCl_3) δ -115.36, -122.12. MS (EI) calcd. for C_{18}H_{19}F_{2}OSi [M]^{+}: 444.02. Found: 444.09.
(2-(3-(5-Chloro-2-iodo-4-methylphenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1ao)

Following the procedure A, 1ao was obtained as a yellow liquid (Rf = 0.3, petroleum ether) in 50% yield (2.3 g, 5.0 mmol). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.65 (m, 1H), 7.62 – 7.52 (m, 1H), 7.34 (m, 2H), 7.26 – 7.22 (m, 1H), 6.78 (s, 1H), 5.83 (d, J = 1.8 Hz, 1H), 5.24 (d, J = 1.8 Hz, 1H), 4.62 (t, J = 1.8 Hz, 2H), 2.27 (s, 3H), 0.30 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 154.94, 144.84, 144.43, 139.74, 137.80, 134.26, 133.97, 129.40, 127.74, 126.08, 115.31, 112.20, 107.85, 82.85, 71.33, 17.93, 0.00. MS (EI) calcd. for C$_{19}$H$_{22}$ClIOSi [M]$^+$: 456.02. Found: 456.13

(2-(3-((3-Iodonaphthalen-2-yl)oxy)prop-1-en-2-yl)phenyl)trimethylsilane (1ap)

Following the procedure A, 1ao was obtained as a colorless oil (Rf = 0.3, petroleum ether) in 38% yield (1.7 g, 3.8 mmol). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.38 (s, 1H), 7.73 – 7.63 (m, 3H), 7.49 – 7.43 (m, 1H), 7.43 – 7.33 (m, 4H), 7.08 (s, 1H), 6.01 (q, J = 1.8 Hz, 1H), 5.32 (q, J = 1.8 Hz, 1H), 4.82 (t, J = 1.8 Hz, 2H), 0.36 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 153.08, 145.08, 144.59, 138.40, 137.84, 134.24, 133.25, 129.53, 127.81, 127.73, 126.06, 126.03, 125.76, 125.71, 123.50, 115.21, 105.73, 87.59, 70.97, 0.00. MS (EI) calcd. for C$_{22}$H$_{23}$IOSi [M]$^+$: 458.06. Found: 458.03.
(2-(3-((2-Iodothiophen-3-yl)oxy)prop-1-en-2-yl)phenyl)trimethylsilane (1aq)

Following the procedure A, 1aq was obtained as a colorless oil ($R_f = 0.5$, petroleum ether) in 39% yield (1.6 g, 3.9 mmol). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.65 – 7.56 (m, 1H), 7.43 (m, 1H), 7.39 – 7.28 (m, 2H), 7.24 (m, 1H), 6.68 (m, 1H), 5.74 (q, $J = 1.8$ Hz, 1H), 5.22 (q, $J = 1.8$ Hz, 1H), 4.71 (t, $J = 1.8$ Hz, 2H), 0.33 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.72, 145.13, 144.93, 137.66, 134.15, 129.05, 127.63, 127.61, 125.91, 115.77, 115.00, 73.71, 54.11, 0.00. MS (EI) calcd. for $C_{16}H_{19}$IOSSi $[M]^+$: 414.00. Found: 414.15.

(5-Fluoro-2-(3-(2-iodophenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1ba)

Following the procedure A, 1ba was obtained as a blue liquid ($R_f = 0.3$, petroleum ether) in 24% yield (1.0 g, 2.4 mmol). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (m, 1H), 7.33 – 7.27 (m, 1H), 7.23 (m, 2H), 7.03 (m, 1H), 6.79 (m, 1H), 6.73 (m, 1H), 5.87 (d, $J = 1.8$ Hz, 1H), 5.23 (q, $J = 1.8$ Hz, 1H), 4.63 (t, $J = 1.8$ Hz, 2H), 0.30 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.18 (d, $J = 248.5$ Hz), 156.37, 144.12, 141.26 (d, $J = 3.4$ Hz), 141.01 (d, $J = 3.3$ Hz), 138.98, 129.93 (d, $J = 7.5$ Hz), 128.80, 122.18, 120.64 (d, $J = 18.6$ Hz), 116.34, 114.68 (d, $J = 20.9$ Hz), 111.53, 85.89, 71.29, -0.00. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -115.62. MS (EI) calcd. for $C_{18}H_{20}$FIOSi $[M]^+$: 426.03. Found: 425.88.
(2-(3-(2-Iodophenoxy)prop-1-en-2-yl)-5-methylphenyl)trimethylsilane (1bb)

Following the **procedure A**, 1bb was obtained as a pale yellow solid (R$_f$ = 0.4, petroleum ether) in 48% yield (2.0 g, 4.8 mmol). **1H NMR (400 MHz, CDCl$_3$)** δ 7.82 (m, 1H), 7.42 (s, 1H), 7.30 (m, 1H), 7.22 – 7.15 (m, 2H), 6.81 (m, 1H), 6.74 (m, 1H), 5.89 (t, J = 1.7 Hz, 1H), 5.24 (q, J = 1.7 Hz, 1H), 4.68 (m, 2H), 2.39 (s, 3H), 0.32 (s, 9H). **13C NMR (101 MHz, CDCl$_3$)** δ 156.20, 144.55, 142.16, 138.68, 137.61, 135.40, 134.88, 128.54, 128.44, 127.76, 121.80, 115.11, 111.26, 85.66, 71.00, 20.44, 0.00. **MS (EI)** calcd. for C$_{19}$H$_{23}$IO$_2$Si [M]$^+$: 422.06. Found: 422.22.

(2-(3-(2-Iodophenoxy)prop-1-en-2-yl)-5-(trifluoromethyl)phenyl)trimethylsilane (1bc)

Following the **procedure A**, 1bc was obtained as a colorless oil (R$_f$ = 0.3, petroleum ether) in 33% yield (1.6 g, 3.3 mmol). **1H NMR (400 MHz, CDCl$_3$)** δ 7.83 – 7.78 (m, 2H), 7.59 (m, 1H), 7.40 (m, 1H), 7.29 (m, 1H), 6.79 (m, 1H), 6.77 – 6.71 (m, 1H), 5.92 (q, J = 1.8 Hz, 1H), 5.27 (q, J = 1.8 Hz, 1H), 4.79 – 4.50 (q, J = 1.8 Hz, 2H), 0.33 (s, 9H). **13C NMR (101 MHz, CDCl$_3$)** δ 160.61, 160.52, 141.57, 137.61, 129.97 (q, J = 31.8 Hz), 129.22 (q, J = 3.6 Hz), 128.09 (q, J = 3.5 Hz), 126.63, 124.05, 122.55 (q, J = 271 Hz), 122.29, 110.68, 87.45, 78.00, 58.43, 29.24, -0.77. **19F NMR (376 MHz, CDCl$_3$)** δ -62.49. **MS (EI)** calcd. for C$_{19}$H$_{20}$F$_3$IO$_2$Si [M]$^+$: 476.03. Found: 476.22.
(4-Fluoro-2-(3-(2-iodophenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1bd)

![Chemical Structure](image)

Following the procedure A, 1bd was obtained as a colorless oil (R_f = 0.5, petroleum ether) in 42% yield (1.8 g, 4.2 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.81 (m, 1H), 7.61 – 7.51 (m, 1H), 7.38 – 7.27 (m, 1H), 7.08 – 6.98 (m, 2H), 6.81 (m, 1H), 6.74 (m, 1H), 5.89 (q, J = 1.7 Hz, 1H), 5.28 (q, J = 1.7 Hz, 1H), 4.66 (t, J = 1.7 Hz, 2H), 0.30 (s, 9H). **^13C NMR (101 MHz, CDCl_3)** δ 163.57 (d, J = 249.3 Hz), 156.06, 147.38 (d, J = 7.0 Hz), 143.67, 138.73, 136.10, 133.28, 133.25, 128.57, 121.97, 115.02, (d, J = 19.9 Hz), 113.00 (d, J = 19.0 Hz), 111.21, 85.61, 70.75, 0.02. **^19F NMR (376 MHz, CDCl_3)** δ -112.96. **MS (EI)** calcd. for C_{18}H_{20}F_{18}O_{10}Si [M]^+: 426.03. Found: 426.34.

(4-Chloro-2-(3-(2-iodophenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1be)

![Chemical Structure](image)

Following the procedure A, 1be was obtained as a colorless liquid (R_f = 0.3, petroleum ether) in 43% yield (1.9 g, 4.3 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.81 (m, 1H), 7.51 (m, 1H), 7.35 – 7.26 (m, 3H), 6.81 (m, 1H), 6.75 (m, 1H), 5.96 – 5.74 (m, 1H), 5.39 – 5.14 (m, 1H), 4.70 – 4.60 (m, 2H), 0.30 (s, 9H). **^13C NMR (101 MHz, CDCl_3)** δ 156.15, 146.79, 143.72, 138.84, 136.20, 135.61, 133.94, 128.65, 128.05, 126.19, 122.07, 116.49, 111.32, 85.71, 79.91, 0.00. **MS (EI)** calcd. for C_{18}H_{20}Cl_{10}O_{10}Si [M]^+: 442.00. Found: 441.97.
(2-(3-(2-Iodophenoxy)prop-1-en-2-yl)-4-methylphenyl)trimethylsilane (1bf)

Following the procedure A, 1bf was obtained as a yellow oil (R$_f$ = 0.5, petroleum ether) in 40% yield (1.7 g, 4.0 mmol). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.81 (m, 1H), 7.49 (m, 1H), 7.32 – 7.26 (m, 1H), 7.15 (m, 1H), 7.12 (m, 1H), 6.81 (m, 1H), 6.74 (m, 1H), 5.86 (q, $J$ = 1.8 Hz, 1H), 5.24 (q, $J$ = 1.8 Hz, 1H), 4.67 (t, $J$ = 1.8 Hz, 2H), 2.37 (s, 3H), 0.29 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 156.23, 145.13, 144.71, 138.70, 137.59, 134.30, 134.12, 128.66, 128.54, 126.86, 121.81, 115.19, 111.26, 85.64, 71.03, 20.35, 0.00. MS (EI) calcd. For C$_{19}$H$_{23}$IOSi [M]$^+$: 422.06. Found: 422.32

(2-(3-(2-Iodophenoxy)prop-1-en-2-yl)-4-methoxyphenyl)trimethylsilane (1bg)

Following the procedure A, 1bg was obtained as a yellow oil (R$_f$ = 0.3, petroleum ether) in 52% yield (2.3 g, 5.2 mmol). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.81 (m, 1H), 7.51 (d, $J$ = 8.3 Hz, 1H), 7.28 (m, 1H), 6.88 (dd, $J$ = 8.3, 2.4 Hz, 1H), 6.84 – 6.76 (m, 2H), 6.73 (d, $J$ = 2.4 Hz, 1H), 5.87 (q, $J$ = 1.8 Hz, 1H), 5.26 (q, $J$ = 1.8 Hz, 1H), 4.67 (t, $J$ = 1.8 Hz, 2H), 3.83 (s, 3H), 0.27 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 158.89, 156.13, 146.71, 144.42, 138.63, 135.61, 128.61, 128.48, 121.79, 115.25, 113.65, 111.55, 111.21, 85.58, 70.87, 54.24, -0.00. MS (EI) calcd. for C$_{19}$H$_{23}$O$_2$Si [M]$^+$: 438.05. Found: 437.95.
(2-(3-(2-iodophenoxy)prop-1-en-2-yl)-4,5-dimethoxyphenyl)trimethylsilane (1bh)

Following the procedure A, 1bh was obtained as a yellow oil ($R_f = 0.4$, petroleum ether) in 45% yield (2.1 g, 4.5 mmol). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 (m, 1H), 7.29 (m, 1H), 7.04 (s, 1H), 6.84 – 6.79 (m, 2H), 6.77 – 6.67 (m, 1H), 5.87 (t, $J = 1.7$ Hz, 1H), 5.27 (d, $J = 1.7$ Hz, 1H), 4.66 (t, $J = 1.7$ Hz, 2H), 3.91 (s, 3H), 3.89 (s, 3H), 0.29 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 156.10, 148.13, 146.64, 144.32, 138.61, 138.52, 128.73, 128.48, 121.77, 116.40, 115.87, 111.35, 111.17, 85.56, 71.10, 54.97, 54.93, -0.00. MS (EI) calcd. for C$_{20}$H$_{25}$IO$_3$Si [M]$^+$: 468.06. Found: 468.00.

(6-(3-(2-Iodophenoxy)prop-1-en-2-yl)benzo[d][1,3]dioxol-5-yl)trimethylsilane (1bi)

Following the procedure A, 1bi was obtained as a colorless oil ($R_f = 0.4$, petroleum ether) in 54% yield (2.3 g, 5.5 mmol). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.81 (m, 1H), 7.33 – 7.26 (m, 1H), 7.04 (s, 1H), 6.85 – 6.77 (m, 2H), 6.74 (m, 1H), 5.96 (s, 2H), 5.85 (t, $J = 1.8$ Hz, 1H), 5.24 (t, $J = 1.8$ Hz, 1H), 4.63 (d, $J = 1.8$ Hz, 2H), 0.28 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 156.00, 146.84, 145.68, 143.98, 139.33, 138.56, 130.49, 128.42, 121.73, 115.78, 113.01, 111.07, 108.71, 99.92, 85.49, 70.88, 0.00. MS (EI) calcd. for C$_{19}$H$_{21}$IO$_3$Si [M]$^+$: 452.03. Found: 451.88.
(2-(3-(2-Iodophenoxo)prop-1-en-2-yl)-6-methylphenyl)trimethylsilane (1bj)

Following the procedure A, 1bj was obtained as a colorless oil (Rf = 0.3, petroleum ether) in 37% yield (1.6 g, 3.7 mmol). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 (m, 1H), 7.39 (s, 1H), 7.32 – 7.27 (m, 1H), 7.17 (s, 2H), 6.79 (m, 1H), 6.73 (m, 1H), 5.86 (d, $J$ = 1.8 Hz, 1H), 5.22 (d, $J$ = 1.8 Hz, 1H), 4.65 (t, $J$ = 1.8 Hz, 2H), 2.37 (s, 3H), 0.29 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 156.22, 144.55, 142.18, 138.69, 137.63, 135.41, 134.89, 128.55, 128.45, 127.76, 121.81, 115.11, 111.28, 85.67, 71.02, 20.43, -0.02. MS (EI) calcd. for C$_{19}$H$_{23}$IO$_3$Si [M]$^+$: 422.06. Found: 422.00.

(2-(3-(2-Iodobenzyl)oxy)prop-1-en-2-yl)phenyl)trimethylsilane (1ca)

Following the procedure B, 1ca was obtained as a colorless oil (Rf = 0.3, petroleum ether) in 44% yield (1.9 g, 4.4 mmol). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.60 (m, 1H), 7.34 (m, 1H), 7.28 (m, 1H), 7.19 – 7.00 (m, 3H), 6.95 (m, 1H), 6.77 (m, 1H), 5.36 (p, $J$ = 1.7 Hz, 1H), 4.90 (p, $J$ = 1.7 Hz, 1H), 4.40 (d, $J$ = 1.7 Hz, 2H), 4.03 (q, $J$ = 1.7 Hz, 2H), 0.06 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 146.73, 145.85, 139.58, 138.16, 137.39, 134.02, 128.18, 127.65, 127.53, 127.49, 127.29, 125.62, 113.86, 96.55, 75.57, 73.12, 0.00. MS (EI) calcd. For C$_{19}$H$_{23}$IOSi [M]$^+$: 422.06. Found: 422.26.
Following the procedure C, 1da was obtained as a yellow solid (R_f = 0.4, petroleum ether/ethyl acetate = 20:1) in 46% yield (2.4 g, 4.6 mmol). 

**1H NMR (400 MHz, CDCl_3)**

\( \delta \) 7.84 (m, 1H), 7.58 – 7.53 (m, 2H), 7.50 – 7.45 (m, 1H), 7.28 (m, 2H), 7.23 (m, 4H), 7.08 – 6.88 (m, 2H), 5.66 (q, J = 1.5 Hz, 1H), 5.12 (q, J = 1.5 Hz, 1H), 4.68 (dt, J = 17.5, 1.5 Hz, 1H), 4.35 (dt, J = 17.5, 1.5 Hz, 1H), 2.42 (s, 3H), 0.09 (s, 9H).

**13C NMR (101 MHz, CDCl_3)**

\( \delta \) 146.22, 145.33, 142.99, 140.88, 140.14, 137.40, 136.06, 134.29, 132.22, 129.03, 128.81, 128.04, 127.91, 127.44, 125.93, 116.71, 99.94, 57.13, 20.93, -0.00.

**MS (EI)** calcd. For C_{25}H_{28}INO_2SSi [M]^+: 561.07. Found: 560.95.

Following the procedure C, 1db was obtained as a yellow solid (R_f = 0.4, petroleum ether/ethyl acetate = 20:1r) in 46% yield (1.6 g, 4.6 mmol). 

**1H NMR (400 MHz, CDCl_3)**

\( \delta \) 7.93 (m, 1H), 7.50 (m, 1H), 7.46 (m, 1H), 7.36 (m, 1H), 7.33 – 7.19 (m, 2H), 7.13 – 7.01 (m, 2H), 5.66 (q, J = 1.7 Hz, 1H), 5.17 (q, J = 1.3 Hz, 1H), 4.83 (dt, J = 17.7, 1.7 Hz, 1H), 4.30 (dt, J = 17.7, 1.3 Hz, 1H), 3.02 (s, 3H), 0.10 (s, 9H).

**13C NMR (101 MHz, CDCl_3)**

\( \delta \) 146.11, 145.79, 140.53, 140.14, 137.40, 136.06, 134.47, 133.24, 129.43, 128.43, 128.25, 128.00, 126.12, 116.46, 98.95, 57.28, 40.83, 0.00. **MS (EI)** calcd. For C_{19}H_{24}INO_2SSi [M]^+: 485.03. Found: 485.01.
N-(2-iodophenyl)-N-(2-(2-(trimethylsilyl)phenyl)allyl)acetamide (1dc)

Following the procedure C, 1dc was obtained as a yellow solid (R_f = 0.4, petroleum ether/ethyl acetate = 20:1 in 37% yield (1.7 g, 3.7 mmol). 1H NMR (400 MHz, CDCl3) δ 7.94 (m, 1H), 7.52 (m, 1H), 7.34 (m, 1H), 7.31 – 7.23 (m, 2H), 7.14 (m, 1H), 7.10 – 7.03 (m, 2H), 5.41 (q, J = 1.7 Hz, 1H), 5.24 (dt, J = 16.9, 1.7 Hz, 1H), 5.13 (q, J = 1.4 Hz, 1H), 3.58 (dt, J = 16.9, 1.4 Hz, 1H), 1.85 (s, 3H), 0.17 (s, 9H).

13C NMR (101 MHz, CDCl3) δ 169.62, 146.49, 145.04, 144.92, 139.64, 137.38, 134.18, 129.64, 129.09, 128.57, 127.87, 127.76, 125.77, 114.34, 99.32, 54.78, 22.06, -0.00. MS (EI) calcd. For C20H24INOSi [M]+: 449.07. Found: 449.02.

N-(4-fluoro-2-iodophenyl)-4-methyl-N-(2-(2-(trimethylsilyl)phenyl)allyl)benzenesulfonamide (1dd)

Following the procedure C, 1dd was obtained as a yellow solid (R_f = 0.4, petroleum ether/ethyl acetate = 20:1) in 41% yield (2.4 g, 4.1 mmol). 1H NMR (400 MHz, CDCl3) δ 7.55 (m, 3H), 7.52 – 7.45 (m, 1H), 7.26 – 7.21 (m, 4H), 7.14 (m, 1H), 6.99 (m, 2H), 5.62 (q, J = 1.5 Hz, 1H), 5.13 (d, J = 1.5 Hz, 1H), 4.68 (dt, J = 17.3, 1.5 Hz, 1H), 4.32 (dt, J = 17.3, 1.5 Hz, 1H), 2.42 (s, 3H), 0.11 (s, 9H). 13C NMR (101 MHz, CDCl3) δ 160.44 (d, J = 254.1 Hz), 146.09, 145.32, 143.14, 143.14, 137.40, 137.40, 137.25 (d, J = 3.5 Hz), 135.93, 134.36, 133.00 (d, J = 9.0 Hz), 128.88, 128.88 (d, J = 13.7 Hz), 127.44, 126.93, 126.68, 125.99, 116.82, 114.90 (d, J = 22.0 Hz), 99.86 (d, J = 8.5 Hz), 57.29, 20.92, 0.00. 19F NMR (376 MHz, CDCl3) δ -111.42. MS (EI) calcd. For C25H27FINO2SSi [M]+: 579.06. Found: 578.92.

S22
N-(2-ido-4-(trifluoromethyl)phenyl)-4-methyl-N-(2-(2-(trimethylsilyl)phenyl)allyl)benzenesulfonamide (1de)

Following the procedure C, 1de was obtained as a yellow solid (R_f = 0.4, petroleum ether/ethyl acetate = 20:1) in 43% yield (1.8 g, 4.3 mmol). ¹H NMR (400 MHz, CDCl₃) δ 8.07 (m, 1H), 7.57 (s, 1H), 7.55 (s, 1H), 7.54 – 7.50 (m, 1H), 7.48 (m, 1H), 7.25 (m, 5H), 6.92 (m, 1H), 5.61 (m, 1H), 5.17 – 5.10 (m, 1H), 4.67 (d, J = 17.2 Hz, 1H), 4.40 (d, J = 17.2 Hz, 1H), 2.43 (s, 3H), 0.09 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 145.81, 145.11, 144.50, 143.46, 137.42, 137.06 (q, J = 3.7 Hz), 135.78, 134.45, 132.31, 130.73 (q, J = 33.2 Hz), 129.12, 128.08, 127.98, 127.42, 126.12, 124.85 (q, J = 3.7 Hz), 121.89 (q, J = 273.1 Hz), 117.12, 99.90, 56.99, 20.96, 0.00. ¹⁹F NMR (376 MHz, CDCl₃) δ -61.58. MS (EI) calcd. For C₂₆H₂₇F₃INO₂SSi [M]⁺: 629.05. Found: 629.00.

N-(2-ido-4-methylphenyl)-4-methyl-N-(2-(2-(trimethylsilyl)phenyl)allyl)benzene -sulfonamide (1df)

Following the procedure C, 1df was obtained as a yellow solid (R_f = 0.4, petroleum ether/ethyl acetate = 20:1) in 39% yield (2.2 g, 3.9 mmol). ¹H NMR (400 MHz, CDCl₃) δ 7.67 (m, 1H), 7.56 (m, 2H), 7.51 – 7.45 (m, 1H), 7.26 – 7.22 (m, 3H), 7.22 – 7.20 (m, 1H), 7.09 (m, 2H), 6.99 – 6.94 (m, 1H), 5.65 (q, J = 1.4 Hz, 1H), 5.11 (d, J = 1.4 Hz, 1H), 4.65 (dt, J = 17.3 Hz, 1.4 Hz, 1H), 4.33 (dt, J = 17.3, 1.4 Hz, 1H), 2.41 (s, 3H), 2.30 (s, 3H), 0.11 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 146.32, 145.29, 142.84, 140.50, 139.35, 138.14, 137.43, 136.14, 134.26, 131.63, 128.75, 128.69, 128.59.
128.01, 127.86, 127.44, 125.87, 116.64, 99.64, 57.11, 20.91, 19.82, 0.00. **MS (EI)** calcd. For C_{26}H_{30}INO_{2}SSi [M]^{+}: 575.08. Found: 575.02

*N-(2-iodo-4-methoxyphenyl)-4-methyl-N-(2-(trimethylsilyl)phenyl)allylbenzenesulfonamide (1dg)*

![1dg Structure](image)

Following the **procedure C**, 1dg was obtained as a yellow solid (R_f = 0.4, petroleum ether/ethyl acetate = 20:1) in 34% yield (2.0 g, 3.4 mmol). **^1H NMR (400 MHz, CDCl$_3$)** δ 7.56 (m, 1H), 7.54 (m, 1H), 7.51 – 7.44 (m, 1H), 7.34 (m, 1H), 7.23 (m, 4H), 7.10 (m, 1H), 7.01 – 6.94 (m, 1H), 6.81 (m, 1H), 5.64 (d, J = 1.4 Hz, 1H), 5.12 (q, J = 1.4 Hz, 1H), 4.66 (dt, J = 17.4, 1.4 Hz, 1H), 4.31 (dt, J = 17.4, 1.4 Hz, 1H), 3.79 (s, 3H), 2.42 (s, 3H), 0.12 (s, 9H). **^13C NMR (101 MHz, CDCl$_3$)** δ 158.49, 146.35, 145.39, 142.81, 137.42, 136.13, 134.26, 133.51, 132.39, 128.75, 128.02, 127.86, 127.44, 125.86, 124.80, 116.62, 113.54, 100.23, 57.31, 54.98, 20.90, 0.00. **MS (EI)** calcd. For C_{26}H_{30}INO_{2}SSi [M]^{+}: 591.08. Found: 591.03.

*N-(5-chloro-2-iodophenyl)-4-methyl-N-(2-(trimethylsilyl)phenyl)allylbenzenesulfonamide (1dh)*

![1dh Structure](image)

Following the **procedure C**, 1dh was obtained as a yellow solid (R_f = 0.4, petroleum ether/ethyl acetate = 20:1) in 42% yield (2.5 g, 4.2 mmol). **^1H NMR (400 MHz, CDCl$_3$)** δ 7.73 (m, 1H), 7.57 (m, 2H), 7.48 (m, 1H), 7.25 (m, 4H), 7.03 (m, 1H), 6.99 (m, 1H), 6.94 – 6.90 (m, 1H), 5.60 (s, 1H), 5.14 (s, 1H), 4.64 (d, J = 17.1 Hz, 1H), 4.33 (d, J = 17.1 Hz, 1H), 2.43 (s, 3H), 0.10 (s, 9H). **^13C NMR (101 MHz, CDCl$_3$)** δ 145.81, 145.13, 143.30, 142.20, 140.50, 137.33, 135.76, 134.36, 133.63, 132.30,
129.25, 128.91, 128.09, 127.93, 127.43, 126.11, 117.10, 97.36, 57.10, 20.94, 0.00. **MS (EI)** calcd. For C_{25}H_{27}ClINO_{2}SSi [M]^+ : 595.03. Found: 594.99.

**Benzyl(2-(3-(2-iodophenoxy)prop-1-en-2-yl)phenyl)dimethylsilane (1ea)**

Following the **procedure A**, 1ea was obtained as a yellow oil (R_f = 0.3, petroleum ether) in 49% yield (2.4 g, 4.9 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.79 (m, 1H), 7.55 (m, 1H), 7.42 – 7.22 (m, 4H), 7.16 (m, 2H), 7.09 – 7.02 (m, 1H), 6.97 – 6.88 (m, 2H), 6.73 (m, 2H), 5.89 (q, J = 1.8 Hz, 1H), 5.20 (q, J = 1.8 Hz, 1H), 4.60 (t, J = 1.8 Hz, 2H), 2.36 (s, 2H), 0.25 (s, 6H). **^13C NMR (101 MHz, CDCl_3)** δ 158.38, 147.46, 147.01, 141.20, 140.94, 138.30, 136.85, 130.79, 130.21, 130.16, 129.80, 129.50, 128.23, 125.51, 124.15, 117.62, 113.61, 87.94, 73.24, 28.54, 0.00. **MS (EI)** calcd. for C_{24}H_{25}IOSi [M]^+ : 484.07. Found: 484.06.

**Ethyl(2-(3-(2-iodophenoxy)prop-1-en-2-yl)phenyl)dimethylsilane (1eb)**

Following the **procedure A**, 1eb was obtained as a yellow solid (R_f = 0.3, petroleum ether) in 37% yield (1.6 g, 3.7 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.88 (m, 1H), 7.74 – 7.60 (m, 1H), 7.42 (m, 2H), 7.39 – 7.31 (m, 2H), 6.88 (m, 1H), 6.80 (m, 1H), 5.98 (d, J = 1.8 Hz, 1H), 5.33 (d, J = 1.8 Hz, 1H), 4.76 (t, J = 1.8 Hz, 2H), 1.11 – 0.95 (m, 3H), 0.95 – 0.76 (m, 2H), 0.39 (s, 6H). **^13C NMR (101 MHz, CDCl_3)** δ 158.56, 147.59, 147.09, 141.07, 139.09, 136.91, 130.93, 130.23, 130.04, 128.31, 124.23,
117.48, 113.67, 88.11, 73.34, 10.19, 9.25, 0.00. **MS (EI)** calcd. for C_{19}H_{23}OSi [M]^+: 422.06. Found: 422.04.

1-(4,5-Dimethoxy-2-(1-(4-methoxyphenyl)vinyl)phenyl)-1-methylsiletane (1ec)

Following the **procedure A**, **1ec** was obtained as a colorless oil (R_f = 0.3, petroleum ether) in 46% yield (2.2 g, 4.6 mmol). **1H NMR (400 MHz, CDCl_3)** δ 7.76 (m, 1H), 7.66 – 7.59 (m, 1H), 7.49 – 7.43 (m, 2H), 7.41 – 7.29 (m, 2H), 7.28 – 7.11 (m, 5H), 6.68 (m, 1H), 6.37 (m, 1H), 5.75 (d, J = 1.8 Hz, 1H), 5.09 (q, J = 1.8 Hz, 1H), 4.10 (t, J = 1.8 Hz, 2H), 0.59 (s, 6H). **13C NMR (101 MHz, CDCl_3)** δ 157.45, 147.08, 145.92, 139.91, 139.70, 137.33, 136.34, 134.78, 133.59, 129.80, 129.59, 129.40, 128.27, 127.39, 123.01, 117.28, 112.62, 86.96, 71.77, 0.00. **MS (EI)** calcd. for C_{23}H_{23}OSi [M]^+: 470.06. Found: 470.04.

Triethyl(2-(3-(2-iodophenoxy)prop-1-en-2-yl)phenyl)silane (1ed)

Following the **procedure A**, **1ed** was obtained as a colorless oil (R_f = 0.3, petroleum ether) in 40% yield (1.8 g, 4.0 mmol). **1H NMR (400 MHz, CDCl_3)** δ 7.73 (m, 1H), 7.47 (m, 1H), 7.33 – 7.12 (m, 4H), 6.73 (m, 1H), 6.66 (m, 1H), 5.77 (q, J = 1.8 Hz, 1H), 5.12 (q, J = 1.8 Hz, 1H), 4.59 (t, J = 1.8 Hz, 2H), 0.91 – 0.80 (m, 9H), 0.81 – 0.71 (m, 6H). **13C NMR (101 MHz, CDCl_3)** δ 157.13, 146.49, 145.62, 139.59, 136.12, 135.34, 129.45, 128.92, 128.42, 126.64, 122.75, 115.69, 112.24, 86.62, 71.82, 7.66, 4.42. **MS (EI)** calcd. for C_{21}H_{27}OSi [M]^+: 450.09. Found: 450.04.
### Pd-Catalyzed Spirocyclization Reaction of 1

#### Condition Screening

**Supplementary Table S1.** Optimization of reaction conditions \(^a\)

| Entry | [Pd] Source | Ligand | Base | Additive (X eq.) | Solvent | 2aa [%] \(^b\) | 3aa [%] \(^b\) |
|-------|-------------|--------|------|------------------|---------|----------------|---------------|
| 1     | [Pd(allyl)Cl] \(_2\) | PBU \(_3\) | LiO\(_{Bu}\) | p-NO\(_2\) PhCHO (1) | PhMe | 10 | 28 |
| 2     | [Pd(allyl)Cl] \(_2\) | PBU \(_3\) | LiO\(_{Bu}\) | KBr (2) | PhMe | 34 | 20 |
| 3     | [Pd(allyl)Cl] \(_2\) | PBU \(_3\) | LiO\(_{Bu}\) | AgBr (2) | PhMe | 45 | Trace |
| 4     | [Pd(allyl)Cl] \(_2\) | PBU \(_3\) | LiO\(_{Bu}\) | NaBr (2) | PhMe | 20 | 25 |
| 5     | Pd(PBU \(_3\)) | - | LiO\(_{Bu}\) | AgBr (2) | PhMe | Trace | 40 |
| 6     | Pd(dpdpfCl) | - | LiO\(_{Bu}\) | AgBr (2) | PhMe | 47 | 34 |
| 7     | [Pd]-1 | - | LiO\(_{Bu}\) | AgBr (2) | PhMe | 38 | Trace |
| 8     | [Pd]-1 | - | LiO\(_{Bu}\) | Ag\(_3\) PO\(_4\) (2) | PhMe | 57 | 12 |
| 9     | [Pd]-1 | - | LiO\(_{Bu}\) | Ag\(_3\) CO\(_3\) (2) | PhMe | 20 | Trace |
| 10    | [Pd]-1 | - | LiO\(_{Bu}\) | AgOAc (2) | PhMe | 67 | 28 |
| 11    | [Pd]-1 | - | LiO\(_{Bu}\) | TcCu (1) | PhMe | 40 | N.D. |
| 12    | [Pd]-1 | - | LiO\(_{Bu}\) | - | PhMe | 20 | 10 |
| 13    | [Pd]-1 | - | LiO\(_{Bu}\) | AgOAc(2)+TcCu (1) | PhMe | 72 | Trace |
| 14    | [Pd]-1 | - | LiO\(_{Bu}\) | AgOAc(2)+TcCu (1) | Dioxane | 40 | Trace |
| 15    | [Pd]-1 | - | LiO\(_{Bu}\) | AgOAc(2)+TcCu (1) | PhCl | 65 | Trace |
| 16    | [Pd]-1 | - | LiO\(_{Bu}\) | AgOAc(2)+TcCu (1) | DCE | 68 | Trace |
| 17    | [Pd]-1 | - | LiO\(_{Bu}\) | AgOAc(2)+TcCu (1) | Cy | 72 | Trace |
| 18    | [Pd]-1 | - | LiO\(_{Bu}\) | AgOAc(2)+TcCu (0.5) | Cy | 84 | Trace |
| 19    | [Pd]-1 | - | LiO\(_{Bu}\) | AgOAc(2)+TcCu (0.2) | Cy | 90 | Trace |
| 20    | [Pd]-1 | - | LiO\(_{Bu}\) | AgOAc(2)+TcCu (0.5) | PhMe | 85 | 10 |
| 21    | [Pd]-1 | - | NaO\(_{Bu}\) | AgOAc(2)+TcCu (0.2) | Cy | N.R. | - |
| 22    | [Pd]-1 | - | KO\(_{Bu}\) | AgOAc(2)+TcCu (0.2) | Cy | N.R. | - |
Reactions were carried out by using [Pd]-1 catalyst (5 mol%), ligand (10 mol%), base (0.6 mmol, 3.0 equiv.), 1aa (0.2 mmol) in solvent (0.4 M) for 12 h at 125 °C under an N₂ atmosphere. *Yield was determined by NMR analysis of the mixture. **Isolated Yield. N.D.: No Detected. N.R.: No Reaction.

General procedure

In a nitrogen-filled glovebox, an oven-dried 15 mL screw capped sealed tube was charged with a magnetic stir bar, 1 (0.20 mmol), [Pd]-1 (5 mol%), AgOAc (2 equiv), LiO^t^Bu (3 equiv), additive and cyclohexane or PhMe (0.5 mL). The tube was sealed, then removed from the glovebox, and the formed mixture was stirred at 125 °C under N₂ for 12 h. After being cooled to room temperature, Saturated aqueous NH₄Cl (5 mL) was added and the mixture was extracted with EA (3 × 5 mL). The combined organic phases were washed with water and brine, dried (MgSO₄) and evaporated. The crude product was purified by preparative RP-HPLC on reversed phase column (C18(ODS)) (eluent: CH₃CN) to afford the corresponding product.

Characterization of Products 2

1',1'-Dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]silole (2aa)

Following the general procedure, the reaction was carried out with 1aa (81.6 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^t^Bu (48 mg,
0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (47.9 mg, 0.180 mmol, 90% yield). Rf (petroleum ether/dichloromethane = 20:1) = 0.3. 1H NMR (400 MHz, CDCl3) δ 7.56 (m, 1H), 7.38 – 7.27 (m, 2H), 7.17 (m, 1H), 7.08 – 7.04 (m, 1H), 6.98 – 6.75 (m, 3H), 4.43 (m, 1H), 4.40 (m, 1H), 1.53 (d, J = 15.2 Hz, 1H), 1.35 (d, J = 15.2 Hz, 1H), 0.43 (s, 3H), 0.36 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 160.40, 156.56, 140.40, 138.25, 132.24, 130.98, 128.68, 127.48, 126.18, 124.99, 110.26, 87.70, 58.25, 29.33, -0.80. HRMS (EI) calcd. for C17H18OSi [M]+: 266.1127. Found: 266.1129.

1',1',5-Trimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]silole] (2ab)

Following the general procedure, the reaction was carried out with 1ab (84.4 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (14.7 mg, 0.1 mmol) in PhMe (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (47 mg, 0.166 mmol, 83% yield). Rf (petroleum ether/dichloromethane = 20:1) = 0.3. 1H NMR (400 MHz, CDCl3) δ 7.56 (m, 1H), 7.38 – 7.27 (m, 2H), 7.07 (m, 1H), 6.97 (m, 1H), 6.79 (m, 1H), 6.71 – 6.66 (m, 1H), 4.42 (d, J = 8.4 Hz, 1H), 4.38 (d, J = 8.4 Hz, 1H), 2.25 (s, 3H), 1.52 (d, J = 15.1 Hz, 1H), 1.34 (d, J = 15.1 Hz, 1H), 0.44 (s, 3H), 0.36 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 158.32, 156.57, 140.42, 138.17, 132.20, 131.19, 130.92, 129.09, 127.43, 126.22, 124.44, 109.75, 87.74, 58.31, 29.16, 21.49, -0.81, -0.88. HRMS (EI) calcd. for C18H20OSi [M]+: 280.1283. Found: 280.1277.

5-Fluoro-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]silole] (2ac)

S29
Following the general procedure, the reaction was carried out with 1ac (85.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (46 mg, 0.160 mmol, 80% yield). Rf (petroleum ether/dichloromethane = 20:1) = 0.3. 1H NMR (400 MHz, CDCl3) δ 7.64 – 7.53 (m, 1H), 7.38 – 7.27 (m, 2H), 7.08 (m, 1H), 6.89 – 6.77 (m, 2H), 6.63 (m, 1H), 4.45 (d, J = 8.5 Hz, 1H), 4.41 (d, J = 8.5 Hz, 1H), 1.55 (d, J = 15.2 Hz, 1H), 1.30 (d, J = 15.2 Hz, 1H), 0.44 (s, 3H), 0.36 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 158.70 (d, J = 237.6 Hz), 156.30, 155.69, 140.45, 139.67 (d, J = 7.5 Hz), 132.35, 131.07, 127.72, 126.08, 114.90 (d, J = 24.3 Hz), 111.01 (d, J = 24.5 Hz), 110.47 (d, J = 8.6 Hz), 88.17, 58.60, 29.09, -0.00, -0.81. 19F NMR (376 MHz, CDCl3) δ -123.14. HRMS (EI) calcd. for C17H17FOSi [M]+: 284.1033. Found: 284.1028.

5-(tert-Butyl)-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]-silole] (2ad)

Following the general procedure, the reaction was carried out with 1ad (92.8 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (61.2 mg, 0.190 mmol, 95% yield). Rf (petroleum ether/dichloromethane = 20:1) = 0.3. 1H NMR (400 MHz, CDCl3) δ 7.62 – 7.54 (m, 1H), 7.37 – 7.26 (m, 2H), 7.20 (m, 1H), 7.07 (m, 1H), 6.97 (m, 1H), 6.82 (m,
1H), 4.41 (d, J = 8.3 Hz, 1H), 4.36 (d, J = 8.3 Hz, 1H), 1.53 (d, J = 15.1 Hz, 1H), 1.35 (d, J = 15.1 Hz, 1H), 1.25 (s, 9H), 0.45 (s, 3H), 0.37 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 158.23, 156.64, 145.00, 140.44, 137.49, 132.23, 130.93, 127.38, 126.13, 125.47, 120.80, 109.28, 87.71, 58.51, 35.08, 32.35, 29.23, 0.00, -0.86. HRMS (EI) calcd. for C$_{21}$H$_{26}$OSi [M]$^+$: 322.1753. Found: 322.1750.

5-Chloro-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]silole] (2ae)

Following the general procedure, the reaction was carried out with 1ae (88.4 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TeCu (14.7 mg, 0.1 mmol) in PhMe (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white soild (44 mg, 0.146 mmol, 73% yield). RF (petroleum ether/dichloromethane = 20:1) = 0.3. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.60 – 7.54 (m, 1H), 7.34 (m, 1H), 7.30 (m, 1H), 7.11 (m, 1H), 7.05 (m, 1H), 6.87 (m, 1H), 6.81 (m, 1H), 4.45 (d, J = 8.5 Hz, 1H), 4.41 (d, J = 8.5 Hz, 1H), 1.54 (d, J = 15.1 Hz, 1H), 1.30 (d, J = 15.1 Hz, 1H), 0.44 (s, 3H), 0.35 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.10, 155.65, 140.49, 140.23, 132.38, 131.14, 128.62, 127.78, 126.53, 126.14, 124.23, 111.31, 88.21, 58.43, 29.36, 0.00, -0.82. HRMS (EI) calcd. for C$_{17}$H$_{17}$ClOSi [M]$^+$: 300.0737. Found: 300.0729.

1',1'-Dimethyl-5-((trifluoromethyl)-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo [b]silole] (2af)
Following the general procedure, the reaction was carried out with 1af (95.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO’Bu (48 mg, 0.6 mmol), and TcCu (14.7 mg, 0.1 mmol) in PhMe (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (32 mg, 0.096 mmol, 48% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.2. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.61 – 7.54 (m, 1H), 7.48 – 7.42 (m, 1H), 7.39 – 7.28 (m, 2H), 7.18 (m, 1H), 7.01 (m, 1H), 6.95 (m, 1H), 4.51 (d, \(J = 8.5\) Hz, 1H), 4.46 (d, \(J = 8.5\) Hz, 1H), 1.56 (d, \(J = 15.1\) Hz, 1H), 1.32 (d, \(J = 15.1\) Hz, 1H), 0.45 (s, 3H), 0.37 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 163.05, 155.50, 140.54, 139.07, 132.47, 131.23, 127.87, 126.71 (q, \(J = 3.8\) Hz), 125.17 (q, \(J = 272.7\) Hz), 126.04, 124.36 (q, \(J = 32.3\) Hz), 121.49 (q, \(J = 3.5\) Hz), 110.38, 88.41, 57.95, 29.76, 0.00, -0.91. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -60.92. HRMS (EI) calcd. for C\(_{18}\)H\(_{17}\)F\(_3\)OSi [M\(^+\)]: 334.1001. Found: 334.1028.

1',1'-Dimethyl-5-phenyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]silole] (2ag)

Following the general procedure, the reaction was carried out with 1ag (95.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO’Bu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (50.6 mg, 0.148 mmol, 74% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.63 – 7.56 (m, 1H), 7.52 – 7.45 (m, 2H), 7.43 (m, 1H), 7.39 – 7.23 (m, 5H), 7.17 (m, 1H), 7.15 – 7.10 (m, 1H), 6.97 (m, 1H), 4.49 (d, \(J = 8.5\) Hz, 1H), 4.45 (d, \(J = 8.5\) Hz, 1H), 1.58 (d, \(J = 15.2\) Hz, 1H), 1.40 (d, \(J = 15.2\) Hz, 1H), 0.46 (s, 3H), 0.38 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 159.55, 155.67, 141.23, 139.94, 138.32, 134.83, 131.69,
Following the general procedure, the reaction was carried out with 1ah (86.6 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (35 mg, 0.120 mmol, 60% yield). \( R_f \) (petroleum ether/dichloromethane = 20:1) = 0.2. \( ^1H \) NMR (400 MHz, CDCl₃) \( \delta \) 7.58 (m, 1H), 7.49 (m, 1H), 7.38 – 7.28 (m, 2H), 7.20 (m, 1H), 6.98 (m, 1H), 6.94 (m, 1H), 4.54 (d, \( J = 8.8 \) Hz, 1H), 4.49 (d, \( J = 8.8 \) Hz, 1H), 1.55 (d, \( J = 15.1 \) Hz, 1H), 1.29 (d, \( J = 15.1 \) Hz, 1H), 0.46 (s, 3H), 0.37 (s, 3H). \( ^{13}C \) NMR (101 MHz, CDCl₃) \( \delta \) 161.45, 152.55, 138.00, 137.60, 131.59, 130.07, 128.82, 125.89, 125.56, 123.41, 117.62, 108.83, 102.63, 86.14, 55.29, 27.43, -2.51, -3.34. HRMS (EI) calcd. for C₁₈H₁₇NOSi [M]⁺: 291.1079. Found: 291.1059.

6-Methoxy-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]silole] (2ai)

Following the general procedure, the reaction was carried out with 1ai (87.6 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (35 mg, 0.120 mmol, 60% yield). \( R_f \) (petroleum ether/dichloromethane = 20:1) = 0.2. \( ^1H \) NMR (400 MHz, CDCl₃) \( \delta \) 7.58 (m, 1H), 7.49 (m, 1H), 7.38 – 7.28 (m, 2H), 7.20 (m, 1H), 6.98 (m, 1H), 6.94 (m, 1H), 4.54 (d, \( J = 8.8 \) Hz, 1H), 4.49 (d, \( J = 8.8 \) Hz, 1H), 1.55 (d, \( J = 15.1 \) Hz, 1H), 1.29 (d, \( J = 15.1 \) Hz, 1H), 0.46 (s, 3H), 0.37 (s, 3H). \( ^{13}C \) NMR (101 MHz, CDCl₃) \( \delta \) 161.45, 152.55, 138.00, 137.60, 131.59, 130.07, 128.82, 125.89, 125.56, 123.41, 117.62, 108.83, 102.63, 86.14, 55.29, 27.43, -2.51, -3.34. HRMS (EI) calcd. for C₁₈H₁₇NOSi [M]⁺: 291.1079. Found: 291.1059.
Following the general procedure, the reaction was carried out with \textbf{1aj} (92.8 mg, 0.2 mmol), \textbf{[Pd]-1} (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (51.5 mg, 0.160 mmol, 80% yield). R\textsubscript{f} (petroleum ether/dichloromethane = 20:1) = 0.3. \textbf{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})} \( \delta \) 7.57 (m, 1H), 7.40 – 7.26 (m, 2H), 7.10 – 6.90 (m, 2H), 6.86 (m, 1H), 4.45 (d, \( J = 8.4 \) Hz, 1H), 4.41 (d, \( J = 8.4 \) Hz, 1H), 1.53 (d, \( J = 15.0 \) Hz, 1H), 1.38 (d, \( J = 15.0 \) Hz, 1H), 1.34 (s, 9H), 0.44 (s, 3H), 0.37 (s, 3H). \textbf{\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3})} \( \delta \) 161.30, 157.58, 153.30, 141.15, 135.88, 132.99, 131.70, 128.19, 126.99, 123.93, 119.72, 108.27, 88.70, 58.85, 36.26, 32.95, 30.03, 0.81, -0.00. \textbf{HRMS (EI)} calcd. for \( C_{21}H_{26}OSi [M]^+ \): 322.1753. Found: 322.1740.
Following the general procedure, the reaction was carried out with 1ak (85.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (14.7 mg, 0.2 mmol) in PhMe (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (40.5 mg, 0.142 mmol, 71% yield). Rf (petroleum ether/dichloromethane = 20:1) = 0.3. 1H NMR (400 MHz, CDCl3) δ 7.56 (m, 1H), 7.32 (m, 2H), 7.04 (d, J = 7.6 Hz, 1H), 6.83 (m, 1H), 6.68 – 6.50 (m, 2H), 4.48 (d, J = 8.5 Hz, 1H), 4.44 (d, J = 8.5 Hz, 1H), 1.52 (d, J = 15.1 Hz, 1H), 1.30 (d, J = 15.1 Hz, 1H), 0.43 (s, 3H), 0.35 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 163.73 (d, J = 243.3 Hz), 161.52 (d, J = 12.9 Hz), 156.28, 140.41, 134.99 (d, J = 2.7 Hz), 132.36, 131.08, 127.64, 126.06, 124.35 (d, J = 10.2 Hz), 108.51 (d, J = 22.8 Hz), 98.67 (d, J = 26.6 Hz), 88.82, 57.70, 29.57, -0.00, -0.80. 19F NMR (376 MHz, CDCl3) δ -114.37. HRMS (EI) calcd. for C17H17FOSi [M]+: 284.1033. Found: 284.1030.

Following the general procedure, the reaction was carried out with 1al (87.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (14.7 mg, 0.1 mmol) in PhMe (0.5 mL) at 125 °C for 4 h. The title compound was obtained as a white solid (43 mg, 0.146 mmol, 73% yield). Rf (petroleum ether/dichloromethane = 20:1) = 0.3. 1H NMR (400 MHz, CDCl3) δ 7.58
Following the general procedure, the reaction was carried out with 1am (87.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (40.5 mg, 0.138 mmol, 69% yield). Rf (petroleum ether/dichloromethane = 20:1) = 0.3. 1H NMR (400 MHz, CDCl3) δ 7.61 – 7.49 (m, 1H), 7.40 – 7.22 (m, 2H), 7.08 (m, 1H), 6.81 (s, 1H), 6.56 (s, 1H), 4.42 (d, J = 8.4 Hz, 1H), 4.36 (d, J = 8.4 Hz, 1H), 2.26 (s, 3H), 2.21 (s, 3H), 1.51 (d, J = 15.1 Hz, 1H), 1.31 (d, J = 15.1 Hz, 1H), 0.42 (s, 3H), 0.35 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 157.47, 141.24, 138.29, 134.38, 132.94, 131.86, 131.66, 131.31, 128.16, 127.06, 122.47, 120.59, 88.30, 59.43, 29.96, 22.22, 16.56, 0.81, -0.00. HRMS (EI) calcd. For C19H22OSi [M]+: 294.1440. Found: 294.1429.
5,7-Difluoro-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]-silole] (2an)

Following the general procedure, the reaction was carried out with 1an (87.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (35.0 mg, 0.116 mmol, 58% yield). Rf (petroleum ether/dichloromethane = 20:1) = 0.2. 1H NMR (400 MHz, CDCl3) δ 7.61 – 7.55 (m, 1H), 7.33 (m, 2H), 7.07 (m, 1H), 6.72 (m, 1H), 6.44 (m, 1H), 4.53 (d, J = 8.6 Hz, 1H), 4.48 (d, J = 8.6 Hz, 1H), 1.57 (d, J = 15.1 Hz, 1H), 1.29 (d, J = 15.1 Hz, 1H), 0.44 (s, 3H), 0.36 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 158.60 (dd, J = 241.1, 8.8 Hz), 148.00 (dd, J = 249.2, 12.6 Hz), 144.06 (dd, J = 10.7, 2.7 Hz), 143.05 (dd, J = 8.7, 3.6 Hz), 141.33, 133.28, 133.26, 132.02, 128.78, 126.86, 107.22 (dd, J = 24.3, 3.8 Hz), 104.79 (dd, J = 28.1, 20.9 Hz), 89.78, 59.95, 29.83, 0.79, -0.00. 19F NMR (376 MHz, CDCl3) δ -119.48, -135.12. HRMS (EI) calcd. For C17H16F2Si [M]+: 302.0938. Found: 302.0935.

5,7-Difluoro-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]-silole] (2ao)

Following the general procedure, the reaction was carried out with 1ao (91.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6
mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (41 mg, 0.130 mmol, 65% yield). Rf (petroleum ether/dichloromethane = 20:1) = 0.3. 1H NMR (400 MHz, CDCl3) δ 7.61 – 7.51 (m, 1H), 7.38 – 7.26 (m, 2H), 7.05 (m, 1H), 6.90 (s, 1H), 6.76 (s, 1H), 4.43 (d, J = 8.5 Hz, 1H), 4.39 (d, J = 8.5 Hz, 1H), 2.25 (s, 3H), 1.52 (d, J = 15.2 Hz, 1H), 1.30 (d, J = 15.2 Hz, 1H), 0.44 (s, 3H), 0.35 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 159.24, 156.05, 140.47, 137.20, 133.66, 132.34, 131.07, 129.06, 127.65, 126.14, 125.65, 111.01, 88.26, 58.04, 29.36, 20.33, 0.01, -0.80. HRMS (EI) calcd. For C18H19ClOSi [M]+: 314.0894. Found: 314.0893.

1,1-Dimethyl-1,2-dihydro-2'H-spiro[benzo[b]silole-3,3'-naphtho[2,3-b]furan] (2ap)

Following the general procedure, the reaction was carried out with 1ap (91.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (50 mg, 0.158 mmol, 79% yield). Rf (petroleum ether/dichloromethane = 20:1) = 0.3. 1H NMR (400 MHz, CDCl3) δ 7.74 (d, J = 8.2 Hz, 1H), 7.65 (d, J = 8.2 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.43 – 7.34 (m, 2H), 7.32 – 7.28 (m, 2H), 7.26 (m, 1H), 7.21 (s, 1H), 7.13 – 7.05 (m, 1H), 4.51 (d, J = 8.4 Hz, 1H), 4.47 (d, J = 8.4 Hz, 1H), 1.64 (d, J = 15.1 Hz, 1H), 1.42 (d, J = 15.1 Hz, 1H), 0.48 (s, 3H), 0.39 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 160.03, 156.74, 142.20, 141.37, 135.75, 133.05, 131.75, 131.46, 129.19, 128.37, 128.18, 127.13, 127.02, 124.60, 123.45, 105.33, 88.51, 58.67, 30.56, 0.76, 0.00. HRMS (EI) calcd. For C21H20OSi [M]+: 316.1283. Found: 316.1275.
1,1-dimethyl-1,2-dihydro-2'H-spiro[benzo[b]silole-3,3'-thieno[3,2-b]furan] (2aq)

Following the general procedure, the reaction was carried out with 1aq (82.8 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (14.7 mg, 0.1 mmol) in PhMe (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (38 mg, 0.140 mmol, 70% yield). Rf (petroleum ether/dichloromethane = 20:1) = 0.3. \(^1\)H NMR (400 MHz, CDCl3) δ 7.57 – 7.50 (m, 1H), 7.37 (m, 1H), 7.31 – 7.28 (m, 1H), 7.27 (m, 1H), 7.10 (d, J = 5.1 Hz, 1H), 6.63 (d, J = 5.1 Hz, 1H), 4.76 (s, 2H), 1.55 (d, J = 15.1 Hz, 1H), 1.42 (d, J = 15.1 Hz, 1H), 0.41 (s, 3H), 0.34 (s, 3H). \(^1\)^13C NMR (101 MHz, CDCl3) δ 162.54, 156.71, 139.88, 132.52, 131.39, 128.85, 128.08, 127.97, 125.95, 112.59, 94.18, 58.52, 29.03, -0.00, -0.69. HRMS (EI) calcd. For C\(_{15}\)H\(_{16}\)OSSi \([M]\): 272.0691. Found: 272.0686.

6'-Fluoro-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]silole] (2ba)

Following the general procedure, the reaction was carried out with 1ba (85.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (49.5 mg, 0.174 mmol, 87% yield). Rf (petroleum ether/dichloromethane = 20:1) = 0.3. \(^1\)H NMR (400 MHz, CDCl3) δ 7.22 – 7.13 (m, 2H), 6.99 (m, 2H), 6.93 – 6.86 (m, 3H), 4.43 (d, J = 8.5 Hz, 1H), 4.35 (d, J
= 8.5 Hz, 1H), 1.55 (d, J = 15.2 Hz, 1H), 1.37 (d, J = 15.2 Hz, 1H), 0.44 (s, 3H), 0.36 (s, 3H). **13C NMR (101 MHz, CDCl3)** δ 163.78 (d, J = 247.8 Hz), 161.26, 152.90, 144.12 (d, J = 4.9 Hz), 138.96, 129.80, 128.80 (d, J = 7.5 Hz), 124.80, 122.94, 119.10 (d, J = 22.5 Hz), 118.84 (d, J = 18.9 Hz), 111.33, 88.51, 58.60, 30.59, 0.77, 0.00. **19F NMR (376 MHz, CDCl3)** δ -116.92. **HRMS (EI)** calcd. For C_{17}H_{17}FOSi [M]+: 284.1033. Found: 284.1028.

1',1',6'-Trimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]silole] (2bb)

Following the general procedure, the reaction was carried out with 1bb (84.4 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TeCu (14.7 mg, 0.04 mmol) in PhMe (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (51.5 mg, 0.184 mmol, 92% yield). **Rf** (petroleum ether/dichloromethane = 20:1) = 0.3. **1H NMR (400 MHz, CDCl3)** δ 7.39 – 7.34 (m, 1H), 7.16 (m, 2H), 6.99 – 6.80 (m, 4H), 4.43 (d, J = 8.4 Hz, 1H), 4.38 (d, J = 8.4 Hz, 1H), 2.36 (s, 3H), 1.52 (d, J = 15.1 Hz, 1H), 1.33 (d, J = 15.1 Hz, 1H), 0.43 (s, 3H), 0.35 (s, 3H). **13C NMR (101 MHz, CDCl3)** δ160.32, 153.67, 140.49, 138.34, 136.95, 132.66, 131.97, 128.57, 125.96, 123.91, 121.83, 110.19, 87.71, 57.82, 29.50, 21.67, -0.00, -0.81. **HRMS (EI)** calcd. For C_{18}H_{20}O Si [M]+: 280.1283. Found: 280.1278.

1',1',6'-Trimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]silole] (2bc)
Following the general procedure, the reaction was carried out with 1bc (95.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (48 mg, 0.144 mmol, 72% yield). Rf (petroleum ether/dichloromethane = 20:1) = 0.3. \( ^1H \text{ NMR (400 MHz, CDCl}_3 \) \( \delta \) 7.91 – 7.72 (m, 1H), 7.54 (m, 1H), 7.20 (m, 1H), 7.14 (m, 1H), 6.97 – 6.86 (m, 3H), 4.45 (d, \( J = 8.6 \) Hz, 1H), 4.38 (d, \( J = 8.6 \) Hz, 1H), 1.57 (d, \( J = 15.3 \) Hz, 1H), 1.41 (d, \( J = 15.3 \) Hz, 1H), 0.48 (s, 3H), 0.39 (s, 3H). \( ^{13}C \text{ NMR (101 MHz, CDCl}_3 \) \( \delta \) 160.61, 160.52, 141.57, 137.61, 129.97 (q, \( J = 31.7 \) Hz), 129.27, 129.22 (q, \( J = 3.5 \) Hz), 128.09 (q, \( J = 3.4 \) Hz), 126.63, 125.27 (q, \( J = 273.7 \) Hz), 124.05, 122.29, 110.68, 87.45, 58.43, 29.24, -0.00, -0.77. \( ^{19}F \text{ NMR (376 MHz, CDCl}_3 \) \( \delta \) -62.17. \( \text{HRMS (EI) calcd. For C}_{18}\text{H}_{17}\text{F}_3\text{OSi [M]}}^+ \text{: } 334.1001. \text{Found: } 334.0084.

5'-Fluoro-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]silole] (2bd)

Following the general procedure, the reaction was carried out with 1bd (85.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (35 mg, 0.122 mmol, 61% yield). Rf (petroleum ether/dichloromethane = 20:1) = 0.3. \( ^1H \text{ NMR (400 MHz, CDCl}_3 \) \( \delta \) 7.50 (m, 1H), 7.22 – 7.15 (m, 1H), 7.02 – 6.88 (m, 4H), 6.72 (m, 1H), 4.44 (d, \( J = 8.5 \) Hz, 1H), 4.38 (d, \( J = 8.5 \) Hz, 1H), 1.54 (d, \( J = 15.2 \) Hz, 1H), 1.39 (d, \( J = 15.2 \) Hz, 1H), 0.43 (s, 3H), 0.35 (s, 3H). \( ^{13}C \text{ NMR (101 MHz, CDCl}_3 \) \( \delta \) 164.96 (d, \( J = 248.6 \) Hz), 159.72, 159.02, 136.85, 134.94 (d, \( J = 3.0 \) Hz), 133.26 (d, \( J = 8.5 \) Hz), 128.38, 123.32, 121.42, 114.60 (d, \( J = 21.1 \) Hz), 112.40 (d, \( J = 20.6 \) Hz), 109.83, 86.72, 57.53, 28.87, -0.55, -
1.32. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -110.72. HRMS (EI) calcd. For C$_{17}$H$_{17}$FOSi [M]$^+$: 284.1033. Found: 284.1025.

5'-Chloro-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]silole] (2be)

![Image of compound 2be]

Following the general procedure, the reaction was carried out with 1be (88.4 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (14.7 mg, 0.1 mmol) in PhMe (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (52 mg, 0.174 mmol, 87% yield). $R_f$ (petroleum ether/dichloromethane = 20:1) = 0.3. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 (m, 1H), 7.26 – 7.23 (m, 1H), 7.20 (m, 1H), 7.02 (m, 1H), 6.91 (m, 3H), 4.43 (d, $J$ = 8.6 Hz, 1H), 4.38 (d, $J$ = 8.6 Hz, 1H), 1.54 (d, $J$ = 15.2 Hz, 1H), 1.37 (d, $J$ = 15.2 Hz, 1H), 0.44 (s, 3H), 0.36 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.41, 158.77, 138.69, 137.46, 137.40, 133.51, 129.08, 128.02, 126.35, 124.00, 122.15, 110.54, 87.42, 58.26, 29.46, -0.00, -0.77. HRMS (EI) calcd. For C$_{17}$H$_{17}$FOSi [M]$^+$: 300.0737. Found: 300.0733.

1',1',5'-Trimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]silole] (2bf)

![Image of compound 2bf]

Following the general procedure, the reaction was carried out with 1bf (84.4 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (14.7 mg, 0.1 mmol) in PhMe (0.5 mL) at 125 °C for 12 h. The title
compound was obtained as a white solid (34 mg, 0.122 mmol, 61% yield). Rf (petroleum ether/dichloromethane = 20:1) = 0.3. $^1\text{H NMR (400 MHz, CDCl}_3\text{) }\delta 7.46$ (m, 1H), 7.22 – 7.15 (m, 1H), 7.11 (m, 1H), 6.98 – 6.84 (m, 4H), 4.43 (d, $J = 8.5$ Hz, 1H), 4.40 (d, $J = 8.5$ Hz, 1H), 2.27 (s, 3H), 1.52 (d, $J = 15.1$ Hz, 1H), 1.33 (d, $J = 15.1$ Hz, 1H), 0.42 (s, 3H), 0.34 (s, 3H). $^{13}\text{C NMR (101 MHz, CDCl}_3\text{) }\delta 159.77, 156.28, 140.49, 137.69, 136.36, 131.54, 128.08, 128.00, 126.11, 123.44, 121.26, 109.62, 87.14, 57.52, 29.01, 21.62, -0.50, -1.29. \text{HRMS (EI) calcd. For C}_{18}\text{H}_{20}\text{O}_{2}\text{Si [M]$^+$: 280.1283. Found: 280.1277.}$

5'-Methoxy-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]silole] (2bg)

Following the general procedure, the reaction was carried out with 1bg (87.6 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO′Bu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (35.5 mg, 0.120 mmol, 60% yield). Rf (petroleum ether/dichloromethane = 20:1) = 0.3. $^1\text{H NMR (400 MHz, CDCl}_3\text{) }\delta 7.47$ (m, 1H), 7.21 – 7.13 (m, 1H), 7.01 – 6.76 (m, 4H), 6.57 (m, 1H), 4.44 (d, $J = 8.5$ Hz, 1H), 4.40 (d, $J = 8.5$ Hz, 1H), 3.71 (s, 3H), 1.53 (d, $J = 15.1$ Hz, 1H), 1.34 (d, $J = 15.1$ Hz, 1H), 0.41 (s, 3H), 0.34 (s, 3H). $^{13}\text{C NMR (101 MHz, CDCl}_3\text{) }\delta 162.20, 160.13, 158.57, 137.72, 133.11, 131.20, 128.45, 123.78, 121.66, 114.03, 110.91, 110.01, 87.31, 58.04, 55.51, 29.54, 0.00, -0.81. \text{HRMS (EI) calcd. For C}_{18}\text{H}_{20}\text{O}_{2}\text{Si [M]$^+$: 296.1233. Found: 296.1220.}$
5',6'-Dimethoxy-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]-silole] (2bh)

Following the general procedure, the reaction was carried out with 1bh (93.6 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (28 mg, 0.086mmol, 43% yield). Rf (petroleum ether/dichloromethane = 20:1) = 0.3. 1H NMR (400 MHz, CDCl₃) δ 7.17 (m, 1H), 6.98 – 6.92 (m, 2H), 6.89 (m, 2H), 6.55 (s, 1H), 4.41 (d, J = 8.5 Hz, 1H), 4.39 (d, J = 8.5 Hz, 1H), 3.92 (s, 3H), 3.71 (s, 3H), 1.53 (d, J = 15.1 Hz, 1H), 1.30 (d, J = 15.1 Hz, 1H), 0.42 (s, 3H), 0.35 (s, 3H). 13C NMR (101 MHz, CDCl₃) δ 160.75, 152.40, 149.82, 149.72, 138.75, 131.92, 129.12, 124.39, 122.41, 113.58, 110.73, 109.26, 87.97, 58.57, 57.02, 56.87, 30.33, 0.74, 0.00. HRMS (EI) calcd. For C₁₉H₂₂O₃Si [M]+: 326.1338. Found: 326.1326.

5',6'-Dimethoxy-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]-silole] (2bi)

Following the general procedure, the reaction was carried out with 1bi (90.4 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 4 h. The title compound was obtained as a white solid (34.1 mg, 0.11 mmol, 55% yield). Rf
(petroleum ether/dichloromethane = 20:1) = 0.3. \( ^1H \text{ NMR (400 MHz, CDCl}_3 \) \( \delta 7.21 - 7.10 \) (m, 1H), 6.99 – 6.79 (m, 4H), 6.51 (s, 1H), 5.92 (d, 2H), 4.40 (d, \( J = 8.5 \) Hz, 1H), 4.36 (d, \( J = 8.5 \) Hz, 1H), 1.52 (d, \( J = 15.1 \) Hz, 1H), 1.34 (d, \( J = 15.1 \) Hz, 1H), 0.40 (s, 3H), 0.32 (s, 3H). \( ^{13}C \text{ NMR (101 MHz, CDCl}_3 \) \( \delta 160.09, 150.81, 150.56, 147.77, 137.90, 132.60, 128.55, 123.72, 121.73, 110.15, 110.04, 106.71, 101.50, 87.29, 57.80, 29.57, 0.00, -0.77. HRMS (EI) calcd. For \( C_{18}H_{18}O_3Si \ [M]^+ \): 310.1025. Found: 310.1018.

\( 1',1',7'-\text{Trimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[\text{b}]silole]} \) (2bj)

\[
\begin{align*}
\text{2bj}
\end{align*}
\]

Following the general procedure, the reaction was carried out with \( 1bj \) (84.4 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 4 h. The title compound was obtained as a white solid (37.5 mg, 0.134 mmol, 67% yield). \( R_f \) (petroleum ether/dichloromethane = 20:1) = 0.3. \( ^1H \text{ NMR (400 MHz, CDCl}_3 \) \( \delta 7.38 \) (s, 1H), 7.16 (m, 2H), 7.03 – 6.84 (m, 4H), 4.42 (m, 1H), 4.38 (m, 1H), 2.36 (s, 3H), 1.53 (d, \( J = 15.1 \) Hz, 1H), 1.33 (d, \( J = 15.1 \) Hz, 1H), 0.43 (s, 3H), 0.35 (s, 3H). \( ^{13}C \text{ NMR (101 MHz, CDCl}_3 \) \( \delta 160.32, 153.67, 140.49, 138.34, 136.96, 132.66, 131.97, 128.57, 125.96, 123.91, 121.83, 110.19, 87.72, 57.82, 29.50, 21.67, -0.00, -0.81. HRMS (EI) calcd. For \( C_{18}H_{20}O_3Si \ [M]^+ \): 280.1283. Found: 280.1277.
1,1-Dimethyl-1,2-dihydropyrido[benzo[b]silole-3,4'-isochromane] (2ca)

Following the general procedure, the reaction was carried out with 1ca (84.4 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (38.2 mg, 0.2 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (25.2 mg, 0.090 mmol, 45% yield). Rf (petroleum ether/dichloromethane = 20:1) = 0.3. $^1$H NMR (400 MHz, CDCl₃) δ 7.63 – 7.55 (m, 1H), 7.33 – 7.21 (m, 2H), 7.21 – 7.08 (m, 2H), 7.04 – 6.99 (m, 1H), 6.96 – 6.89 (m, 1H), 6.85 (m, 1H), 4.94 (m, 2H), 3.72 (m, 2H), 1.84 (d, $J = 15.6$ Hz, 1H), 1.16 (d, $J = 15.6$ Hz, 1H), 0.41 (s, 3H), 0.38 (s, 3H). $^{13}$C NMR (101 MHz, CDCl₃) δ 157.04, 145.42, 142.16, 134.56, 132.62, 130.50, 129.01, 127.89, 127.72, 127.53, 126.62, 124.48, 78.70, 69.70, 52.33, 29.16, 0.75, 0.00. HRMS (EI) calcd. For C₁₈H₂₀OSi [M]⁺: 280.1283. Found: 280.1281.

1,1-dimethyl-1'-tosyl-1,2-dihydropyrido[benzo[b]silole-3,3'-indoline] (2da)

Following the general procedure, the reaction was carried out with 1da (112.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (38.2 mg, 0.2 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (25.2 mg, 0.090 mmol, 47% yield).
Following the general procedure, the reaction was carried out with 1db (89.8 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TeCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (34.3 mg, 0.100 mmol, 50% yield). Rf (petroleum ether/ethyl acetate = 10:1) = 0.5. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.58 (m, 1H), 7.31 (m, 2H), 7.28 – 7.22 (m, 1H), 7.05 (m, 1H), 7.00 – 6.89 (m, 2H), 3.95 (d, $J = 9.9$ Hz, 1H), 3.82 (d, $J = 9.9$ Hz, 1H), 2.94 (s, 3H), 1.58 (d, $J = 15.1$ Hz, 1H), 1.27 (d, $J = 15.1$ Hz, 1H), 0.43 (s, 3H), 0.39 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 156.01, 142.07, 141.92, 140.69, 132.51, 130.99, 128.81, 127.83, 125.98, 124.91, 124.71, 113.70, 67.84, 56.21, 35.13, 30.03, -0.00, -0.86. HRMS (EI) calcd. For C$_{18}$H$_{21}$NO$_2$Si [M]$^+$: 343.1062. Found: 343.1055.
1-(1,1-Dimethyl-1,2-dihydrospiro[benzo[b]silole-3,3'-indolin]-1'-yl)ethan-1-one (2dc)

Following the general procedure, the reaction was carried out with 1dc (89.8 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO’Bu (48 mg, 0.6 mmol), and TcCu (38.2 mg, 0.2 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (31.3 mg, 0.102 mmol, 51% yield). Rf (petroleum ether/ethyl acetate = 10:1) = 0.5. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.27 (m, 1H), 7.64 – 7.50 (m, 1H), 7.36 – 7.26 (m, 2H), 7.25 – 7.22 (m, 1H), 7.04 (m, 1H), 6.92 (m, 2H), 4.01 (d, $J$ = 10.1 Hz, 1H), 3.99 (d, $J$ = 10.1 Hz, 1H), 2.18 (s, 3H), 1.48 (d, $J$ = 15.2 Hz, 1H), 1.38 (d, $J$ = 15.2 Hz, 1H), 0.44 (s, 3H), 0.40 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.03, 157.88, 143.73, 142.96, 140.95, 133.22, 131.99, 129.28, 128.52, 126.85, 125.88, 124.63, 118.26, 68.37, 57.14, 31.49, 25.68, 1.00, 0.00. HRMS (EI) calcd. For C$_{19}$H$_{21}$NOSi [M$^+$]: 307.1392. Found: 307.1383.

5'-Fluoro-1,1-dimethyl-1'-tosyl-1,2-dihydrospiro[benzo[b]silole-3,3'-indoline] (2dd)

Following the general procedure, the reaction was carried out with 1dd (115.8 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO’Bu (48 mg, 0.6 mmol), and TcCu (7.64 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (50.7 mg, 0.116 mmol, 58% yield).
RF (petroleum ether/ethyl acetate = 10:1) = 0.4. 1H NMR (400 MHz, CDCl3) δ 7.68 (m, 3H), 7.56 – 7.49 (m, 1H), 7.25 (m, 3H), 7.15 (m, 1H), 6.92 (m, 1H), 6.57 – 6.43 (m, 2H), 3.92 (d, J = 10.4 Hz, 1H), 3.73 (d, J = 10.4 Hz, 1H), 2.42 (s, 3H), 1.22 (d, J = 15.1 Hz, 1H), 1.02 (d, J = 15.1 Hz, 1H), 0.36 (s, 3H), 0.35 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 160.78 (d, J = 242.6 Hz), 155.71, 144.93, 144.44 (d, J = 7.5 Hz), 140.60, 138.12, 134.25, 132.38, 130.99, 130.36, 128.15, 127.80, 125.94, 115.98 (d, J = 8.6 Hz), 115.19 (d, J = 23.6 Hz), 111.62 (d, J = 24.0 Hz), 67.61, 56.27, 30.40, 22.21, 0.00, -0.95.

19F NMR (376 MHz, CDCl3) δ -118.63. HRMS (EI) calcd. For C24H24FNO2Si [M]+: 437.1281. Found: 437.1273.

5’-Fluoro-1,1-dimethyl-1’-tosyl-1,2-dihydrospiro[benzo[b]silole-3,3’-indoline]
(2de)

Following the general procedure, the reaction was carried out with 1de (125.8 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO’Bu (48 mg, 0.6 mmol), and TcCu (14.7 mg, 0.1 mmol) in PhMe (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (39.0 mg, 0.080 mmol, 40% yield). RF (petroleum ether/ethyl acetate = 10:1) = 0.4. 1H NMR (400 MHz, CDCl3) δ 7.80 (m, 1H), 7.73 (m, 2H), 7.53 (m, 2H), 7.33 – 7.24 (m, 3H), 7.18 (m, 1H), 7.05 (m, 1H), 6.53 (m, 1H), 3.98 (d, J = 10.2, 1H), 3.78 (d, J = 10.2 Hz, 1H), 2.42 (s, 3H), 1.33 (d, J = 15.1, 1H), 1.10 (d, J = 15.1 Hz, 1H), 0.40 (s, 3H), 0.38 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 156.42, 146.30, 146.00, 143.89, 141.67, 135.35, 133.54, 132.13, 131.54, 129.01, 128.96, 127.90 (q, J = 32.6 Hz), 127.24 (q, J = 3.7 Hz), 126.87, 125.85 (q, J = 273.1 Hz), 122.71 (q, J = 3.3 Hz), 115.41, 68.51, 57.02, 31.59, 23.24, 1.03, 0.00. 19F NMR (376 MHz, CDCl3) δ -63.85. HRMS (EI) calcd. For C25H24F3NO2SSi [M]+: 487.1249. Found: 487.1223.
1,1,5'-Trimethyl-1'-tosyl-1,2-dihydrospiro[benzo[b]silole-3,3'-indoline] (2df)

Following the general procedure, the reaction was carried out with 1df (120.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (7.64 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (55.4 mg, 0.128 mmol, 64% yield). 

Rf (petroleum ether/ethyl acetate = 10:1) = 0.5. 1H NMR (400 MHz, CDCl3) δ 7.70 (m, 2H), 7.61 (m, 1H), 7.51 (m, 1H), 7.21 (m, 3H), 7.14 (m, 1H), 7.03 (m, 1H), 6.59 (s, 1H), 6.52 (m, 1H), 3.89 (d, J = 10.2 Hz, 1H), 3.69 (d, J = 10.2 Hz, 1H), 2.40 (s, 3H), 2.21 (s, 3H), 1.23 (d, J = 15.2 Hz, 1H), 1.07 (d, J = 15.2 Hz, 1H), 0.36 (s, 3H), 0.35 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 157.48, 145.53, 143.26, 141.51, 140.70, 135.48, 135.35, 133.15, 131.74, 131.18, 130.09, 129.08, 128.43, 127.04, 125.89, 115.57, 68.34, 57.11, 31.28, 23.12, 22.51, 0.95, 0.00. HRMS (EI) calcd. For C25H27NO2SSi [M]+: 433.1532. Found: 433.1523.

5'-Methoxy-1,1-dimethyl-1'-tosyl-1,2-dihydrospiro[benzo[b]silole-3,3'-indoline] (2dg)

Following the general procedure, the reaction was carried out with 1dg (118.2 mg, 0.2 mmol), [Pd]-1(5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (7.64 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (62.9 mg, 0.140 mmol, 70% yield).
Rf (petroleum ether/ethyl acetate = 10:1) = 0.5. 1H NMR (400 MHz, CDCl3) δ 7.67 (m, 3H), 7.51 (m, 1H), 7.25 – 7.19 (m, 3H), 7.14 (m, 1H), 6.78 (m, 1H), 6.58 – 6.45 (m, 1H), 6.31 (m, 1H), 3.89 (d, J = 10.4 Hz, 1H), 3.70 (d, J = 10.4 Hz, 1H), 3.68 (s, 3H), 2.40 (s, 3H), 1.18 (d, J = 15.1 Hz, 1H), 1.04 (d, J = 15.1 Hz, 1H), 0.36 (s, 3H), 0.35 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 157.76, 156.28, 144.60, 143.83, 140.59, 135.68, 134.33, 132.25, 130.89, 130.24, 128.22, 127.57, 126.08, 115.98, 113.96, 109.92, 67.52, 56.50, 56.22, 30.34, 22.19, 0.00, -0.94. HRMS (EI) calcd. For C25H27NO3SSi [M]+: 449.1481. Found: 449.1474.

6'-Chloro-1,1-dimethyl-1'-tosyl-1,2-dihydrospiro[benzo[b]silole-3,3'-indoline] (2dh)

Following the general procedure, the reaction was carried out with 1dh (119.0 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO′Bu (48 mg, 0.6 mmol), and TcCu (7.64 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (47.1 mg, 0.104 mmol, 52% yield). Rf (petroleum ether/ethyl acetate = 10:1) = 0.5. 1H NMR (400 MHz, CDCl3) δ 7.79 – 7.64 (m, 3H), 7.52 (m, 1H), 7.34 – 7.27 (m, 2H), 7.25 – 7.20 (m, 1H), 7.15 (m, 1H), 6.94 (m, 1H), 6.70 (m, 1H), 6.52 (m, 1H), 3.93 (d, J = 10.2 Hz, 1H), 3.73 (d, J = 10.2 Hz, 1H), 2.42 (s, 3H), 1.26 (d, J = 15.1 Hz, 1H), 1.05 (d, J = 15.1 Hz, 1H), 0.37 (s, 3H), 0.35 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 156.80, 146.03, 144.12, 141.80, 141.51, 135.29, 135.19, 133.32, 131.91, 131.41, 129.01, 128.70, 126.83, 126.25, 125.83, 115.97, 68.56, 56.76, 31.41, 23.17, 0.93, 0.00. HRMS (EI) calcd. For C24H24ClNO3SSi [M]+: 453.0986. Found: 453.0979.
Following the general procedure, the reaction was carried out with 1ea (96.8 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (7.64 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (26 mg, 0.076 mmol, 38% yield, dr = 1:1). Rf (petroleum ether/dichloromethane = 20:1) = 0.3. For the first diastereoisomer: 

\[ \text{H NMR (400 MHz, CDCl}_3] \delta 7.45 (m, 1H), 7.32 (m, 1H), 7.25 – 7.17 (m, 3H), 7.17 – 7.07 (m, 2H), 7.03 (m, 3H), 6.88 (m, 1H), 6.84 (m, 1H), 6.64 (m, 1H), 4.39 (d, J = 8.7 Hz, 1H), 4.37 (d, J = 8.7 Hz, 1H), 2.52 (d, J = 13.9 Hz, 1H), 2.45 (d, J = 13.9 Hz, 1H), 1.46 (d, J = 15.4 Hz, 1H), 1.36 (d, J = 15.4 Hz, 1H), 0.35 (s, 3H). \]

\[ \text{C NMR (101 MHz, CDCl}_3] \delta 159.63, 156.24, 138.68, 130.65, 137.66, 132.11, 130.62, 128.44, 128.35, 128.06, 126.84, 125.74, 124.53, 123.31, 121.32, 109.58, 87.45, 57.35, 26.63, 25.30, -2.53. \]

For the second diastereoisomer: 

\[ \text{H NMR (400 MHz, CDCl}_3] \delta 7.50 – 7.44 (m, 1H), 7.36 – 7.26 (m, 2H), 7.19 (m, 2H), 7.16 – 7.12 (m, 1H), 7.12 – 7.06 (m, 1H), 6.98 (m, 1H), 6.94 (m, 2H), 6.89 – 6.81 (m, 3H), 3.98 (d, J = 8.7 Hz, 1H), 3.83 (d, J = 8.7 Hz, 1H), 2.45 (d, J = 13.8 Hz, 1H), 2.35 (d, J = 13.8 Hz, 1H), 1.54 (d, J = 15.5 Hz, 1H), 1.26 (d, J = 15.5 Hz, 1H), 0.41 (s, 3H). \]

\[ \text{C NMR (101 MHz, CDCl}_3] \delta 159.70, 156.45, 138.80, 137.81, 137.79, 132.06, 130.63, 128.45, 128.27, 128.08, 126.87, 125.73, 124.64, 123.26, 121.27, 109.56, 86.87, 57.51, 26.48, 25.73, -2.93. \] HRMS (EI) calcd. For C\(_{23}\)H\(_{22}\)OSi [M\(^+\)]: 342.1440. Found: 342.1435.
1'-Ethyl-1'-methyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]silole] (2eb)

Following the general procedure, the reaction was carried out with 1eb (84.4 mg, 0.2 mmol), [Pd]-1(5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO’Bu (48 mg, 0.6 mmol), and TcCu (7.64 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (38.1 mg, 0.136 mmol, 68% yield, dr = 1:1). Rf (petroleum ether/dichloromethane = 20:1) = 0.3. 1H NMR (400 MHz, CDCl3) δ 7.56 (m, 2H), 7.54 – 7.41 (m, 1H), 7.31 (m, 4H), 7.17 (m, 2H), 7.09 – 7.03 (m, 2H), 6.98 – 6.84 (m, 5H), 4.49 – 4.41 (m, 3H), 4.41 – 4.35 (m, 1H), 1.55 (d, J = 15.3 Hz, 1H), 1.48 (d, J = 15.3 Hz, 1H), 1.35 (d, J = 17.0 Hz, 1H), 1.28 (d, J = 17.0 Hz, 1H), 1.14 – 1.01 (m, 6H), 0.99 – 0.87 (m, 4H), 0.41 (s, 3H), 0.35 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 159.82, 159.72, 156.26, 156.21, 159.77, 139.07, 138.95, 137.80, 131.97, 131.90, 130.38, 130.35, 128.06, 126.79, 126.77, 125.70, 125.67, 123.82, 123.37, 123.32, 121.90, 121.30, 121.28, 119.73, 111.22, 109.63, 87.39, 87.33, 57.59, 27.11, 26.70, 10.29, 7.70, 7.61, 7.57, 7.29, 6.97, 6.79, -2.81, -3.71. HRMS (EI) calcd.

For C18H20OSi [M]+: 280.1283. Found: 280.1275.

1'-Methyl-1'-phenyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]-silole] (2ec)

Following the general procedure, the reaction was carried out with 1ec (94.0 mg, 0.2 mmol), [Pd]-1(5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO’Bu (48 mg, 0.6 mmol), and TcCu (7.64 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h.
The title compound was obtained as a white solid (14.4 mg, 0.044 mmol, 22% yield, dr = 1:1). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. \textbf{1H NMR (400 MHz, CDCl}_3) \delta 7.71 – 7.65 (m, 1H), 7.60 (m, 3H), 7.50 (m, 2H), 7.45 – 7.26 (m, 10H), 7.22 – 7.09 (m, 4H), 6.99 (m, 1H), 6.94 – 6.80 (m, 5H), 4.53 (d, J = 8.5 Hz, 1H), 4.49 (d, J = 8.5 Hz, 1H), 4.29 (m, 2H), 1.79 (d, J = 15.3 Hz, 1H), 1.70 (d, J = 15.3 Hz, 1H), 1.63 (d, J = 15.3 Hz, 1H), 1.50 (d, J = 15.3 Hz, 1H), 0.70 (s, 3H), 0.67 (s, 3H). \textbf{13C NMR (101 MHz, CDCl}_3) \delta 162.29, 162.13, 159.25, 140.17, 139.90, 139.84, 139.51, 138.75, 136.74, 136.56, 134.84, 133.21, 132.19, 132.03, 130.57, 130.50, 129.58, 129.52, 128.20, 128.16, 125.92, 125.75, 123.75, 112.12, 112.09, 89.62, 89.20, 60.25, 59.99, 30.84, 30.71, -0.00, -0.16. \textbf{HRMS (EI)} calcd. For C_{22}H_{20}OSi [M]+: 328.1283. Found: 328.1275.

1',1'-diethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]silole] (2ed)

Following the general procedure, the reaction was carried out with 1ed (90.0 mg, 0.2 mmol), [Pd]-1(5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and TcCu (7.64 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (35.2 mg, 0.120 mmol, 60% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. \textbf{1H NMR (400 MHz, CDCl}_3) \delta 7.55 (dd, J = 7.3, 1.6 Hz, 1H), 7.32 (dd, J = 7.3, 1.6 Hz, 1H), 7.28 (m, 1H), 7.17 (m, 1H), 7.05 (m, 1H), 6.94 – 6.82 (m, 3H), 4.43 (d, J = 8.5 Hz, 1H), 4.39 (d, J = 8.5 Hz, 1H), 1.48 (d, J = 15.4 Hz, 1H), 1.31 (d, J = 15.4 Hz, 1H), 1.04 (m, 6H), 0.95 – 0.87 (m, 2H), 0.86 – 0.76 (m, 2H). \textbf{13C NMR (101 MHz, CDCl}_3) \delta 159.71, 156.55, 138.10, 138.03, 132.20, 130.34, 128.02, 126.66, 125.80, 123.28, 121.30, 109.58, 87.69, 57.54, 24.90.
7.79, 7.63, 5.77, 4.92. **HRMS (EI)** calcd. For C$_{19}$H$_{22}$O Si [M]$^+$: 294.1440. Found: 294.1434.

**Removal of the Protecting Group (-Ts) in Spirosilacycle 2dd**

**General Procedure**

The compound 5 was prepared according to the literature with modification.$^{[8]}$

**Preparation of SmI$_2$ in THF**

Diiodoethane (13 mmol, 3.65 g) was added to THF (100 ml). To this was added samarium metal (19 mmol, 2.85 g, powder). The mixture was allowed to stir at room temperature under a nitrogen atmosphere for one hour. This yields a deep-blue 0.13 M solution of SmI$_2$.

**Experiment:**

To a solution of SmI$_2$ (13 mL, 0.13 M, 1 mmol) in THF was added the sulfonamide (0.1 mmol) followed by water (60 µL, 0.3 mmol) and pyrrolidine (173 µL, 2 mmol) under a nitrogen atmosphere. The reaction mixture immediately turned white upon addition of amine. The resulting mixture was diluted with diethyl ether (16 mL) and treated with a solution of potassium sodium tartrate and potassium carbonate (10% w/v each). The aqueous phase was extracted with two portions of diethyl ether. The organic extracts was pooled, dried and evaporated to yield the crude amine. The crude product was purified by preparative RP-HPLC on reversed phase column (C18(ODS)) (eluent: CH$_3$CN) to afford the corresponding product 5 (27mg, 0.095 mmol, 95% yield).
Characterization of Product 5

5'-Fluoro-1,1-dimethyl-1,2-dihydrospiro[benzo[b]silole-3,3'-indoline]. (5)

Compound 5 was obtained as colorless oil (R_f = 0.3, petroleum ether: ethyl acetate = 5:1) in 95% yield. 

_H NMR (400 MHz, CDCl_3) δ 7.51 – 7.41 (m, 1H), 7.22 (m, 1H), 7.19 – 7.13 (m, 1H), 7.00 (m, 1H), 6.66 (m, 1H), 6.55 (m, 1H), 6.45 (m, 1H), 3.45 (d, J = 8.9 Hz, 1H), 3.39 (d, J = 8.9 Hz, 1H), 1.51 (d, J = 15.1 Hz, 1H), 1.05 (d, J = 15.1 Hz, 1H), 0.30 (s, 3H), 0.25 (s, 3H). 

_C NMR (101 MHz, CDCl_3) δ 159.01 (d, J = 241.0 Hz), 148.11, 142.64, 141.33, 133.02, 131.43, 128.12, 127.06, 115.01, 114.77, 111.86 (d, J = 23.5 Hz), 111.56 (d, J = 8.3 Hz), 66.91, 59.36, 29.13, 0.88, 0.01. 

_F NMR (376 MHz, CDCl_3) δ -125.05.

HRMS (EI) calcd. For C_{17}H_{18}FNSi [M]^+: 283.1193. Found: 283.1188.

3. Supplementary Discussion

Experimental Mechanistic Study

GC Analyse of the Gas Composition of the Reactions

_Experiment_: Under the protection of nitrogen, the reaction was carried out with _1aa_ (81.6 mg, 0.2 mmol), [Pd]-OAc (0.2 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO'Bu (48 mg, 0.6 mmol), and CuTc (7.64 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for
12 h. Then, the crude product was analyzed by GC-MS.

**Supplementary Figure 1.** GC analyses of the reaction of 1aa in the presence of stoichiometric amount of [Pd]-OAc complex

**X-ray Photoelectron Spectroscopy Analysis of Palladium Catalysts**

![Chemical structure](image)

In a nitrogen-filled glovebox, an oven-dried 15 mL screw capped sealed tube was charged with a magnetic stir bar, [Pd]-1 (55.2 mg, 0.1 mmol, 1.0 equiv), AgOAc (66.8 mg, 0.4 mmol, 4.0 equiv), LiO'Bu (48 mg, 0.6 mmol, 6.0 equiv), additive and cyclohexane (1.0 mL). The tube was sealed, then removed from the glovebox, and the formed mixture was stirred at 125 °C under N₂ for 12 h. After being cooled to room temperature, the organic phases were evaporated and the residues obtained for XPS test.
Supplementary Figure 2. XPS analysis of reaction residue to identify Pd(0) species

To gain information about the oxidation state of the Pd species, analysis of Pd 3d by X-ray photoelectron spectroscopy (XPS) was performed. All measurements were performed on a Thermo Scientific ESCALAB 250Xi spectrometer equipped with a monochromatic Al Kα X-ray source. The pressure throughout the analysis chamber was less than 10⁻⁷ mbar. Samples were finely ground in a glovebox and pressed into aluminum foil before being placed on a sample holder and transferred to the XPS instrument in a sealed container to avoid exposure to air during transport. All results were analyzed with use of the Avantage software package. Charge correction was calibrated with C 1s (284.8 eV) as reference.

The spectra showed that the electron binding energies of Pd 3d₃/2 and 3d₅/2 in black residue were 340.3 eV and 335.1 eV (see Supplementary Figure 2), respectively, which is consistent with the position for metallic Pd. Further analysis showed that the electron binding energy (342.5 eV and 337.4 eV) were very close to the corresponding electron binding energy in PdO reported in the literature. In summary, we deduced that the palladium complex for this Pd-catalyzed sila-spirocyclization of 1aa can produce Pd(0).
Computational Studies

Quantum Mechanical Studies

Method. Density functional theory calculations were carried out in Gaussian 16.\textsuperscript{[12]} Geometry optimization and frequency calculation employed the M06-L functional\textsuperscript{[13]} and the def2-SV(P) basis set.\textsuperscript{[14]} Single-point energies were then computed with the PBE0-D3 hybrid functional,\textsuperscript{[15]} the def2-TZVP basis set,\textsuperscript{[14]} and the SMD implicit solvation model\textsuperscript{[16]} for cyclohexane. Free energies were calculated using the GoodVibes code applying quasi-harmonic corrections.\textsuperscript{[17]} We assumed a concentration of 1 mol/L and a temperature of 398.15 K in all calculations.

Ligand Exchange. Possible ligation modes were evaluated on IM1\textsuperscript{II}. Supplementary Figure 3 presents calculated energies of ligand exchanges involving ‘BuO\textsuperscript{-}, AcO\textsuperscript{-} and I\textsuperscript{-}. The calculations show that IM1\textsuperscript{II} with the ligation of ‘BuO\textsuperscript{-} is of the lowest-energy in the scope of our investigation.

Supplementary Figure 3. Possible coordination modes of IM1\textsuperscript{II}. Relative free energies are shown in kcal/mol. Considered ligand exchanges involve AgI/AgOAc, LiO’Bu/LiOAc and NR\textsubscript{3}.

To further evaluate the influence of I-/BuO\textsuperscript{-} exchange, Supplementary Figure 4 compares the free-energy profiles with the ligations of these two anions. Our calculations show that the ‘BuO\textsuperscript{-}-coordinated species are substantially lower in energy than the I\textsuperscript{-}-coordinated counterparts. The result again supports the favorability of the ligand exchange.
Supplementary Figure 4. Effect of I’/BuO⁻ exchange on the free-energy profile (unit: kcal/mol).

Reductive Elimination. In addition, several possibly competing reductive elimination pathways were also considered. The results in Supplementary Figure 5 suggest that the following two pathways are kinetically less likely due to elevated activation barrier: (1) formation of Ar–Me bond from reductive elimination (TS5<sub>RE</sub> ArMe), (2) reductive elimination with I⁻ substituting one 'BuO⁻ (TS5'<sub>RE</sub> and TS5''<sub>RE</sub>).

Supplementary Figure 5. Relative free energies of possible reductive-elimination pathways (unit: kcal/mol).

Energies and Coordinates of Calculated Structures

Supplementary Table 2. Energies, enthalpies, and free energies of all calculated structures.

|                | E (a.u.)    | H (a.u.)    | G (a.u.)    | v<sub>imag</sub> (cm⁻¹) |
|----------------|-------------|-------------|-------------|-------------------------|
| 1aa            | -1360.310142| -1359.938274| -1360.048278|                         |

S60
|     |         |         |         |
|-----|---------|---------|---------|
| 2aa | -1022.742602 | -1022.412805 | -1022.504362 |
| AgI | -444.764425   | -444.758747   | -444.796127   |
| AgOAc | -375.331716  | -375.271678  | -375.322048  |
| LiOAc | -235.915152   | -235.854215   | -235.899226   |
| LiO' Bu | -240.436963  | -240.298866  | -240.352587  |
| MeO' Bu | -272.761065   | -272.584109   | -272.639251   |
| NR3 | -174.328517   | -174.198890   | -174.243829   |
| IM1'H | -1423.387087  | -1422.880765  | -1423.012122  |
| IM1'H-S1 | -1597.738929  | -1597.100026  | -1597.249585  |
| IM1'H-S2 | -1418.853391  | -1418.423836  | -1418.547932  |
| IM1'H-S3 | -1593.212452  | -1592.650868  | -1592.795610  |
| IM1'H-S4 | -1488.269266  | -1487.895407  | -1488.011492  |
| IM1'H-S5 | -1662.626090  | -1662.120973  | -1662.259735  |
| IM2'H | -1597.771892  | -1597.132380  | -1597.282322  |
| IM3'IV | -1423.409621  | -1422.902375  | -1423.031677  |
| IM4'H | -575.018218    | -574.710387   | -574.797999   |
| IM5'IV | -1870.474403  | -1869.660372  | -1869.842037  |
| IM2'H-I | -1662.662102   | -1662.154915  | -1662.296747  |
| IM3'IV-I | -1488.295490  | -1487.919887  | -1488.033147  |
| IM4'H-I | -639.902817   | -639.726959   | -639.798496   |
| IM5'IV-I | -1760.991662  | -1760.442971  | -1760.591549  |
| TS1_Mi | -1597.730456  | -1597.092329  | -1597.239357  | -230.48 |
| TS1'Mi | -1423.363221  | -1422.857303  | -1422.984901  | -313.26 |
| TS2_OA | -1423.393699  | -1422.887285  | -1423.012112  | -90.73 |
| TS3_RE | -1423.405440  | -1422.899493  | -1423.026906  | -44.62 |
| TS4_OA | -1760.974869  | -1760.427900  | -1760.575767  | -61.82 |
| TS5_RE | -1870.435138  | -1869.622279  | -1869.802512  | -387.89 |
| TS5' RE | -1935.323831  | -1934.644489  | -1934.810646  | -223.73 |
| TS5'' RE | -1935.319587  | -1934.639725  | -1934.805603  | -374.44 |
| TS5'REArMe | -1870.434382  | -1869.620620  | -1869.800535  | -363.62 |
| TS6_RE | -574.955397   | -574.648758   | -574.734828   | -511.46 |
4. Supplementary Figures

NMR Spectra

Supplementary Figure 6. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1aa

Supplementary Figure 7. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1aa
Supplementary Figure 8. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1ab

Supplementary Figure 9. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1ab
Supplementary Figure 10. \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) spectra of 1ac

Supplementary Figure 11. \( ^{13} \)C NMR (101 MHz, CDCl\(_3\)) spectra of 1ac
Supplementary Figure 12. $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of 1ac
Supplementary Figure 13. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1ad

Supplementary Figure 14. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1ad
Supplementary Figure 15. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1ae

Supplementary Figure 16. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1ae
Supplementary Figure 17. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1af

Supplementary Figure 18. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1af
Supplementary Figure 19. $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of 1af
Supplementary Figure 20. \(^1\)H NMR (400 MHz, CDCl\(_3\)) spectra of 1ag

Supplementary Figure 21. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) spectra of 1ag
Supplementary Figure 22. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1ah

Supplementary Figure 23. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1ah
Supplementary Figure 24. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1ai

Supplementary Figure 25. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1ai
Supplementary Figure 26. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1aj

Supplementary Figure 27. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1aj
Supplementary Figure 28. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1ak

Supplementary Figure 29. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1ak
Supplementary Figure 30. $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of 1ak
Supplementary Figure 31. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1al

Supplementary Figure 32. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1al
Supplementary Figure 33. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1am

Supplementary Figure 34. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1am
Supplementary Figure 35. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1an

Supplementary Figure 36. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1an
Supplementary Figure 37. $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of 1an
Supplementary Figure 38. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1ao

Supplementary Figure 39. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1ao
Supplementary Figure 40. H NMR (400 MHz, CDCl₃) spectra of 1ap

Supplementary Figure 41. ¹³C NMR (101 MHz, CDCl₃) spectra of 1ap
Supplementary Figure 42. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1aq

Supplementary Figure 43. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1aq
Supplementary Figure 44. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1ba

Supplementary Figure 45. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1ba
Supplementary Figure 46. $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of 1ba
Supplementary Figure 47. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1bb

Supplementary Figure 48. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1bb
Supplementary Figure 49. ^1^H NMR (400 MHz, CDCl$_3$) spectra of 1bc

Supplementary Figure 50. ^13^C NMR (101 MHz, CDCl$_3$) spectra of 1bc
Supplementary Figure 51. $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of 1bc
Supplementary Figure 52. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1bd

Supplementary Figure 53. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1bd
Supplementary Figure 54. $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of 1bd
Supplementary Figure 55. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1be

Supplementary Figure 56. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1be
Supplementary Figure 57. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1bf

Supplementary Figure 58. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1bf
Supplementary Figure 59. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1bg

Supplementary Figure 60. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1bg
Supplementary Figure 61. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1bh

Supplementary Figure 62. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1bh
Supplementary Figure 63. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1bi

Supplementary Figure 64. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1bi
Supplementary Figure 65. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1bj

Supplementary Figure 66. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1bj
Supplementary Figure 67. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1ca

Supplementary Figure 68. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1ca
Supplementary Figure 69. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1da

Supplementary Figure 70. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1da
Supplementary Figure 71. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1db

Supplementary Figure 72. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1db
Supplementary Figure 73. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1dc

Supplementary Figure 74. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1dc
Supplementary Figure 75. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1dd

Supplementary Figure 76. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1dd
Supplementary Figure 77. $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of 1dd
Supplementary Figure 78. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1de

Supplementary Figure 79. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1de
Supplementary Figure 80. $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of 1de
Supplementary Figure 81. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1df

Supplementary Figure 82. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1df
Supplementary Figure 83. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1dg

Supplementary Figure 84. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1dg
Supplementary Figure 85. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1dh

Supplementary Figure 86. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1dh
Supplementary Figure 87. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1ea

Supplementary Figure 88. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1ea
Supplementary Figure 89. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1eb

Supplementary Figure 90. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1eb
Supplementary Figure 91. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1ec

Supplementary Figure 92. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1ec
Supplementary Figure 93. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 1ed

Supplementary Figure 94. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1ed
Supplementary Figure 95. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2aa

Supplementary Figure 96. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2aa
**Supplementary Figure 97.** $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2ab

**Supplementary Figure 98.** $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2ab
Supplementary Figure 99. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2ac

Supplementary Figure 100. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2ac
Supplementary Figure 101. $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of 2ac
Supplementary Figure 102. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2ad

Supplementary Figure 103. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2ad
Supplementary Figure 104. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2ae

Supplementary Figure 105. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2ae
Supplementary Figure 106. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2af

Supplementary Figure 107. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2af
Supplementary Figure 108. $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of 2af
Supplementary Figure 109. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2ag

Supplementary Figure 110. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2ag
Supplementary Figure 111. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2ah

Supplementary Figure 112. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2ah
Supplementary Figure 113. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2ai

Supplementary Figure 114. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2ai
Supplementary Figure 115. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2aj

Supplementary Figure 116. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2aj
Supplementary Figure 117. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2ak

Supplementary Figure 118. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2aj
Supplementary Figure 119. $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of 2ak
Supplementary Figure 120. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2al

Supplementary Figure 121. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2al
Supplementary Figure 122. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2am

Supplementary Figure 123. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2am
Supplementary Figure 124. ^1^H NMR (400 MHz, CDCl$_3$) spectra of 2an

Supplementary Figure 125. ^13^C NMR (101 MHz, CDCl$_3$) spectra of 2an
Supplementary Figure 126. $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of 2an
Supplementary Figure 127. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2ao

Supplementary Figure 128. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2ao
Supplementary Figure 129. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2ap

Supplementary Figure 130. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2ap
Supplementary Figure 131. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2aq

Supplementary Figure 132. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2aq
Supplementary Figure 133. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2ba

Supplementary Figure 134. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2ba
Supplementary Figure 135. $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of 2ba
Supplementary Figure 136. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2bb

Supplementary Figure 137. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2bb
Supplementary Figure 138. $^1$H NMR (400 MHz, CDCl₃) spectra of 2bc

Supplementary Figure 139. $^{13}$C NMR (101 MHz, CDCl₃) spectra of 2bc
Supplementary Figure 140. $^{19}$F NMR (376 MHz, CDCl₃) spectra of 2bc
Supplementary Figure 141. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2bd

Supplementary Figure 142. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2bd
Supplementary Figure 143. $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of 2bd
Supplementary Figure 144. \(^1\)H NMR (400 MHz, CDCl\(_3\)) spectra of 2be

Supplementary Figure 145. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) spectra of 2be
Supplementary Figure 146. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2bf

Supplementary Figure 147. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2bf
Supplementary Figure 148. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2bg

Supplementary Figure 149. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2bg
Supplementary Figure 150. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2bh

Supplementary Figure 151. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2bh
Supplementary Figure 152. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2bi

Supplementary Figure 153. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2bi
Supplementary Figure 154. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2bj

Supplementary Figure 155. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2bj
Supplementary Figure 156. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2ca

Supplementary Figure 157. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2ca
Supplementary Figure 158. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2da

Supplementary Figure 159. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2da
Supplementary Figure 160. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2db

Supplementary Figure 161. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2db
Supplementary Figure 162. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2dc

Supplementary Figure 163. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2dc
Supplementary Figure 164. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2dd

Supplementary Figure 165. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2dd
Supplementary Figure 166. $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of 2dd
Supplementary Figure 167. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2de

Supplementary Figure 168. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2de
Supplementary Figure 169. $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of 2de
Supplementary Figure 170. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2df

Supplementary Figure 171. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2df
Supplementary Figure 172. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2dg

Supplementary Figure 173. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2dg
Supplementary Figure 174. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2dh

Supplementary Figure 175. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2dh
Supplementary Figure 178. $^1$H NMR (400 MHz, CDCl$_3$) spectra of the first diastereoisomer 2ea

Supplementary Figure 177. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of the first diastereoisomer 2ea
Supplementary Figure 178. $^1$H NMR (400 MHz, CDCl$_3$) spectra of the second diastereoisomer 2ea

Supplementary Figure 179. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of the second diastereoisomer 2ea
Supplementary Figure 180. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2eb

Supplementary Figure 181. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2eb
Supplementary Figure 182. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2ec

Supplementary Figure 183. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2ec
Supplementary Figure 184. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2ed

Supplementary Figure 185. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 2ed
Supplementary Figure 186. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 5

Supplementary Figure 187. $^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 5
Supplementary Figure 188. $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of 5
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