

Supporting Information

Palladium-Catalyzed Catellani-Type Selective C-H Silylation of Aryl-TT salts

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Table of Contents

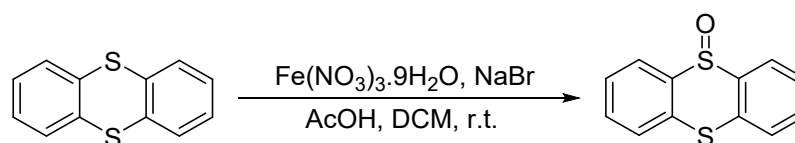
I. General remark	S2
II. Experimental Procedures	S2-S7
III. The data of products	S8-S23
IV. References	S24-S25
V. NMR spectra	S26-S66

I. General remark

NMR spectra of materials and products were recorded on 300 MHz and 75 MHz (VARIAN 300 M), 400 MHz and 100 MHz (BRUKER 400 M or JNM-ECS 400 M), 600 MHz and 150 MHz (BRUKER 600 M). Corresponding solvents were CDCl_3 . All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. All compounds were further characterized by HRMS; copies of ^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra were provided. Products were purified by flash chromatography on 200-300 mesh silica gels. All melting points were determined without correction. All reactions were carried out under air in oven-dried glassware, unless otherwise noted. Commercially available reagents and solvents were used without further purification, unless otherwise noted.

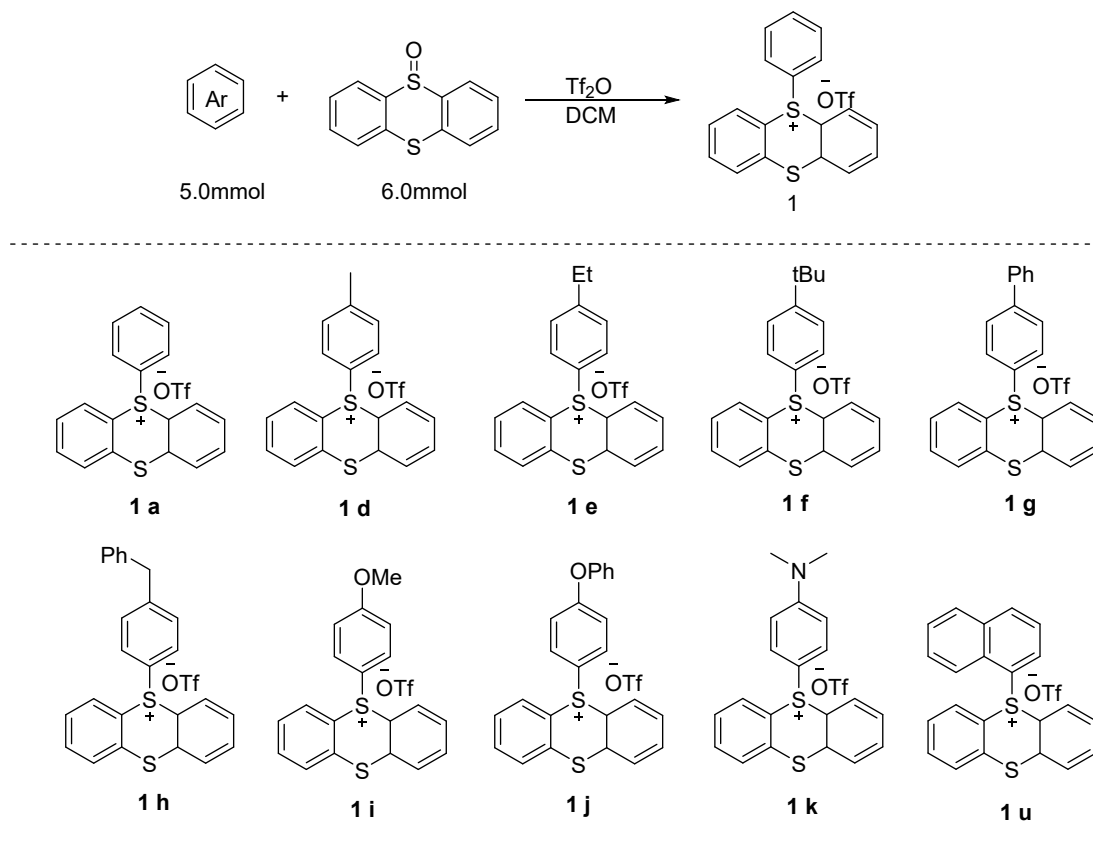
II. Experimental Procedures

General Procedures for the Preparation of thianthrene S-oxide^{1,2,3}



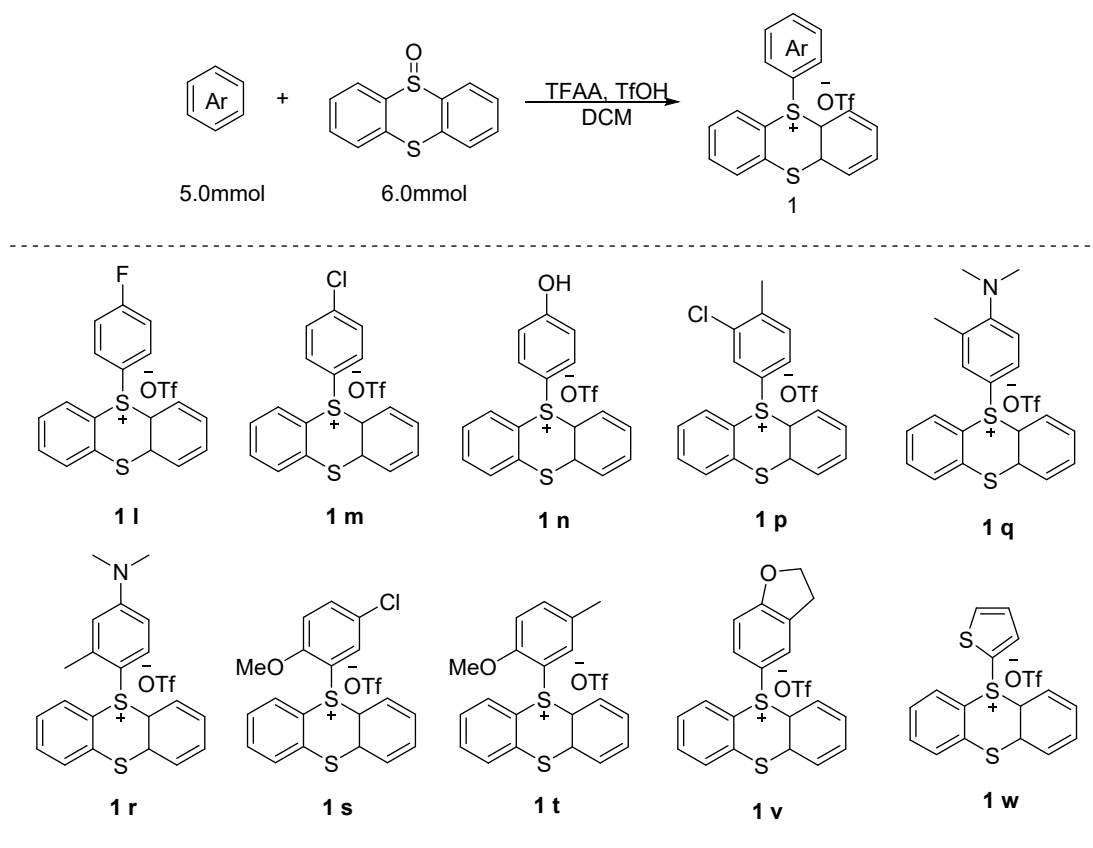
A 100mL round-bottom flask was charged with thianthrene (21.6 g, 100 mmol, 1.0 equiv), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (40.4 g, 100 mmol, 1.0 equiv), NaBr (408 mg, 4 mmol, 4.0 mol%). DCM (200 mL), and AcOH (4.0 mL) were then injected. The reaction mixture was stirred at room temperature and monitored by TLC until thianthrene was consumed. After that, the reaction was dilute with DCM , and then washed with water. The organic phase was dried over anhydrous Na_2SO_4 , filtered and concentrated under vacuum. The grayish-white solid obtained is thianthrene S-oxide.

General Procedures A for the Preparation of Aryl Sulfonium Salts.^{1,2,3}



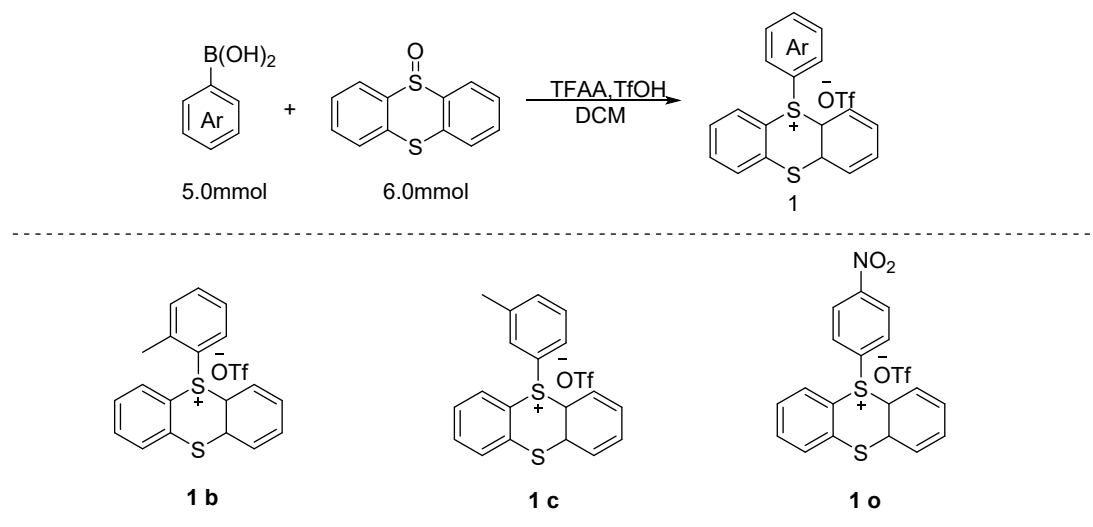
A 50 mL schlenk tube was charged with thianthrene S-oxide (6.0 mmol, 1.2 equiv), DCM (15 mL) and arenes (5.0 mmol, 1.0 equiv) under an argon atmosphere. The reaction mixture was then cooled to $-40\text{ }^{\circ}\text{C}$ and stirred at this temperature. $\text{ Tf}_2\text{O}$ (2.4 mmol, 1.2 equiv) was added dropwise. The reaction mixture was stirred at $-40\text{ }^{\circ}\text{C}$ for 30 min, and then allowed to stir at room temperature for 12 h, neutralized by a saturated aqueous NaHCO_3 solution, and extracted with DCM, and then washed with water. The combined organic layers were dried over anhydrous $\text{ Na}_2\text{SO}_4$ and concentrated to dryness under reduced pressure. The crude product was purified by crystallization from DCM / $\text{ Et}_2\text{O}$ system as a white solid (**1a**, **1d-1k**, **1u**).

General Procedures B for the Preparation of Aryl Sulfonium Salts.^{1,2,3}



A 50 mL schlenk tube was charged with thianthrene S-oxide (6.0 mmol, 1.2 equiv), DCM (15 mL) and arenes (5.0 mmol, 1.0 equiv) under an argon atmosphere. The reaction mixture was then cooled to -40 °C and stirred at this temperature. Trifluoroacetic anhydride (TFAA, 15.0 mmol, 3.0 equiv) and trifluoromethanesulfonic acid (TfOH, 7.5 mmol, 1.5 equiv) were added dropwise. The reaction mixture was stirred at -40 °C for 30 min, and then allowed to stir at room temperature for 12 h, neutralized by a saturated aqueous NaHCO₃ solution, and extracted with DCM. The combined organic layers were washed with aqueous NaOTf solution (3 × 20 mL, 5%(w/w)), dried over anhydrous Na₂SO₄, and concentrated to dryness under reduced pressure. The crude product was purified by crystallization from DCM / Et₂O system as a white solid (**1l-1n**, **1p-1t**, **1v**, **1w**).

General Procedures C for the Preparation of Aryl Sulfonium Salts.⁴



A 50 mL schlenk tube was charged with tolylboronic acid (5 mmol, 1.0 equiv), DCM (15.0 mL) and thianthrene S-oxide (6 mmol, 1.2 equiv), under an argon atmosphere. The reaction mixture was then cooled to -40 °C and stirred at this temperature. Trifluoroacetic anhydride (TFAA, 15.0 mmol, 3.0 equiv) and trifluoromethanesulfonic acid (TfOH, 7.5 mmol, 1.5 equiv) were added dropwise. The reaction mixture was stirred at -40 °C for 30 min, and then allowed to stir at room temperature for 12 h, neutralized by a saturated aqueous NaHCO₃ solution, and extracted with DCM, and then washed with water. The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated to dryness under reduced pressure. The crude product was purified by crystallization from DCM/Et₂O system as a white solid (**1b**, **1c**, **1o**).

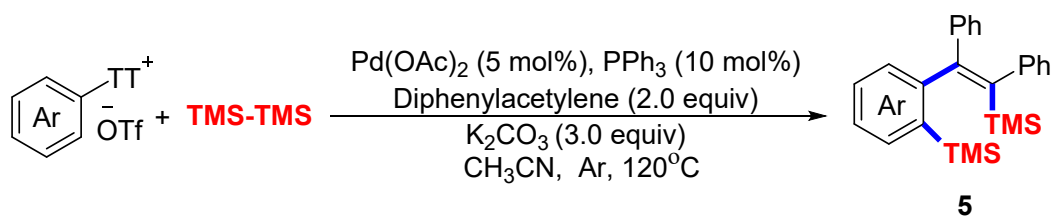
Chemical structures of 15 bis(benzothienyl)sulfonium triflate salts (1a-1w) are shown, each featuring a central sulfonium cation (S⁺) bonded to two benzothienyl groups and a triflate anion (OTf⁻). The substituents on the benzothienyl rings are as follows:

- 1a**: Phenyl
- 1b**: 3-Methylphenyl
- 1c**: 4-Methylphenyl
- 1d**: 4-Methylphenyl
- 1e**: 4-Ethylphenyl
- 1f**: 4-tert-Butylphenyl
- 1g**: 4-Phenylphenyl
- 1i**: 4-Methoxyphenyl
- 1j**: 4-Phenoxypheyl
- 1k**: 4-(Dimethylaminophenyl)
- 1l**: 4-Fluorophenyl
- 1m**: 4-Chlorophenyl
- 1n**: 4-Hydroxyphenyl
- 1o**: 4-Nitrophenyl
- 1p**: 3-Chloro-4-methylphenyl
- 1s**: 3-Chloro-4-methoxyphenyl
- 1t**: 3-Methyl-4-methoxyphenyl
- 1u**: 1-Naphthyl
- 1v**: 2-(2,3-Dihydro-1,4-benzodioxol-5-yl)
- 1w**: 2-(Thiophen-2-yl)

S6

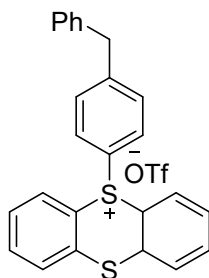
CH₃CN (5 mL). Then, the tube was charged with argon and stirred at 120 °C (oil bath temperature) for the indicated time until complete consumption of starting material, as monitored by TLC analysis. After the completion of the reaction, the reaction mixture was cooled to room temperature, extracted with EtOAc three times, washed with small amounts of water. The combined organic layers were dried with anhydrous Na₂SO₄ and the solvent was removed in vacuo to afford a residue. The residue was purified by column chromatography on silica gel using petroleum ether/EtOAc as eluent to provide the desired compounds **3**.

General Procedures E for the Synthesis of **5a-5i**.



To a Schlenk tube were added aryl-TT salts (0.5 mmol, 1.0 equiv), hexamethyldisilane (1.0 mmol, 2.0 equiv), diphenylacetylene (1.0 mmol, 2.0 equiv), Pd(OAc)₂ (0.025 mmol, 5 mol%), PPh₃ (0.05 mmol, 10mol%), K₂CO₃ (1.5 mmol, 3.0 equiv), and CH₃CN (5 mL). Then, the tube was charged with argon and stirred at 120 °C (oil bath temperature) for the indicated time until complete consumption of starting material, as monitored by TLC analysis. After the completion of the reaction, the reaction mixture was cooled to room temperature, extracted with EtOAc three times, washed with small amounts of water. The combined organic layers were dried with anhydrous Na₂SO₄ and the solvent was removed in vacuo to afford a residue. The residue was purified by column chromatography on silica gel using petroleum ether/EtOAc as eluent to provide the desired compounds **5**.

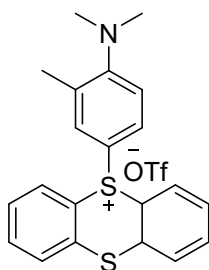
III. The data of products



5-(4-benzylphenyl)-4a,10a-dihydro-5H-thianthren-5-ium trifluoromethanesulfonate (**1h**)

According to general procedure A, **1h** was obtained as a white solid (2.2 g, 82% yield).

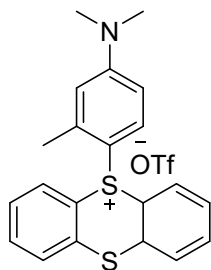
^1H NMR (400 MHz, CDCl_3 , ppm): δ = 8.55(d, J = 7.6 Hz, 2 H), 7.78-7.85(m, 4 H), 7.71-7.75(m, 4 H), 7.22-7.25(m, 4 H), 7.19(d, J = 7.6 Hz, 1 H), 7.07-7.11(m, 4 H), 3.94(s, 1 H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 147.3, 138.6, 136.4, 135.1, 134.9, 131.0, 130.2, 130.1, 128.9, 128.7, 128.1, 126.7, 121.1, 118.6, 41.3. HRMS calcd for $\text{C}_{26}\text{H}_{22}\text{F}_3\text{O}_3\text{S}_3$ $[\text{M}+\text{H}]^+$ 535.0678; found: 535.0664.



5-(4-(dimethylamino)-3-methylphenyl)-4a,10a-dihydro-5H-thianthren-5-ium trifluoromethanesulfonate (**1q**)

According to general procedure B, **1q** was obtained as a white solid (1.9 g, 71% yield).

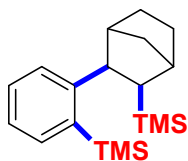
^1H NMR (400 MHz, CDCl_3 , ppm): δ = 8.37(d, J = 7.6 Hz, 2 H), 7.79-7.81(m, 2 H), 7.72-7.76(m, 2 H), 7.68-7.70(m, 2 H), 7.11(s, 1 H), 7.04-7.07(m, 1 H), 6.89(d, J = 8.8 Hz, 1 H), 2.72(s, 6 H), 2.21(s, 3 H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 157.4, 135.6, 134.4, 133.8, 133.5, 133.1, 131.7, 131.2, 130.1, 122.4, 119.7, 111.7, 42.9, 19.8. HRMS calcd for $\text{C}_{22}\text{H}_{23}\text{F}_3\text{NO}_3\text{S}_3$ $[\text{M}+\text{H}]^+$ 502.0787; found: 502.0813.



5-(4-(dimethylamino)-2-methylphenyl)-4a,10a-dihydro-5H-thianthren-5-ium trifluoromethanesulfonate (1r)

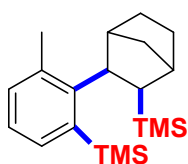
According to general procedure B, **1r** was obtained as a white solid (2.0 g, 75% yield).

^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.85(d, J = 7.6 Hz, 2 H), 7.76(d, J = 8.0 Hz, 2 H), 7.70(d, J = 7.6 Hz, 2 H), 7.66(d, J = 7.6 Hz, 2 H), 7.12(d, J = 8.8 Hz, 1 H), 6.71-6.74 (m, 2 H), 3.11(s, 6 H), 2.62(s, 3 H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 154.4, 144.0, 133.6, 133.3, 130.2, 129.9, 123.9, 119.1, 114.9, 114.8, 112.3, 97.7, 40.1, 20.8. HRMS calcd for $\text{C}_{19}\text{H}_{33}\text{Si}_2$ $[\text{M}+\text{H}]^+$ 317.2116; found: HRMS calcd for $\text{C}_{22}\text{H}_{23}\text{F}_3\text{NO}_3\text{S}_3$ $[\text{M}+\text{H}]^+$ 502.0787; found: 502.0813.



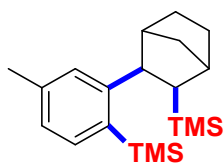
trimethyl(2-((2R,3R)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)phenyl)silane (3a)

Yellow oil (139.1 mg, 88% yield, eluent: petroleum ether). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.39(d, J = 7.6 Hz, 2 H), 7.27-7.31(m, 1 H), 7.11-7.15(m, 1 H), 3.15(d, J = 10.4 Hz, 1 H), 2.32-2.36(m, 1 H), 1.96-1.99(m, 1 H), 1.73-1.78(m, 1 H), 1.57-1.62(m, 1 H), 1.42-1.45(m, 1 H), 1.35-1.38(m, 2 H), 1.25-1.28(m, 1 H), 0.32(s, 9 H), -0.37(s, 9H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 152.8, 138.9, 134.2, 129.3, 126.6, 125.1, 51.2, 44.9, 43.5, 38.9, 38.6, 32.8, 32.2, 1.0, -0.8. HRMS calcd for $\text{C}_{19}\text{H}_{33}\text{Si}_2$ $[\text{M}+\text{H}]^+$ 317.2116; found: 317.2112.



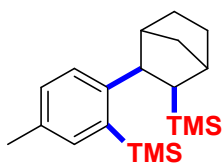
trimethyl(3-methyl-2-((2R,3R)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)phenyl)silane (3b)

Colorless oil (125.4 mg, 76% yield, eluent: petroleum ether). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.31-7.34(m, 1 H), 7.05-7.09(m, 2 H), 3.46(d, J = 11.2 Hz, 1 H), 2.68(s, 1 H), 2.49(s, 3 H), 2.35(d, J = 4.4 Hz, 1 H), 1.96(d, J = 10.0 Hz, 1 H), 1.80-1.84(m, 1 H), 1.55-1.61(m, 1 H), 1.47-1.50(m, 1 H), 1.40-1.43(m, 2 H), 1.31-1.34(m, 1 H), 0.34(s, 9 H), -0.40(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 148.5, 142.1, 135.2, 134.2, 133.1, 125.3, 53.9, 44.9, 41.0, 39.8, 38.9, 33.5, 32.2, 23.1, 2.1, -0.7. HRMS calcd for $\text{C}_{20}\text{H}_{35}\text{Si}_2$ $[\text{M}+\text{H}]^+$ 331.2272; found: 331.2265.



trimethyl(4-methyl-2-((2R,3R)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)phenyl)silane (3c)

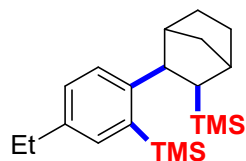
Colorless solid (128.7 mg, 78% yield, eluent: petroleum ether). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.29(d, J = 7.6 Hz, 1 H), 7.20(s, 1 H), 6.95(d, J = 7.6 Hz, 1 H), 3.13(d, J = 10.4 Hz, 1 H), 2.35(d, J = 5.2 Hz, 1 H), 2.29-2.33(m, 4 H), 1.99(d, J = 10.0 Hz, 1 H), 1.72-1.76(m, 1 H), 1.56-1.62(m, 1 H), 1.41-1.44(m, 1 H), 1.35-1.38(m, 2 H), 1.24-1.27(m, 2 H), 0.31(s, 9 H), -0.37(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 152.8, 138.8, 135.3, 134.3, 127.7, 125.9, 51.0, 44.9, 43.6, 39.0, 38.5, 32.8, 32.2, 21.4, 1.0, -0.8. HRMS calcd for $\text{C}_{20}\text{H}_{35}\text{Si}_2$ $[\text{M}+\text{H}]^+$ 331.2272; found: 331.2269.



Trimethyl (5-methyl-2-((3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl)phenyl)silane (3d)

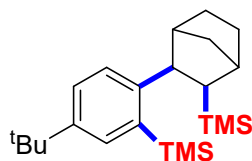
Colorless oil (150.2 mg, 90% yield, eluent: petroleum ether). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.28(d, J = 8.0 Hz, 1 H), 7.18(s, 1 H), 7.95(d, J = 6.0 Hz, 1 H), 3.12(d, J = 10.4 Hz, 1 H), 1.96(d, J = 9.6 Hz, 1 H), 1.71-1.75(m, 1 H), 1.55-1.61(m, 1 H), 1.38-1.43(m, 1 H), 1.32-1.36(m, 2 H), 1.23-1.26(m, 2 H), 0.31(s, 9 H), -0.36(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 149.8, 138.7, 134.9, 134.2, 129.8, 126.5, 50.8, 45.1,

43.6, 38.8, 38.6, 32.8, 32.2, 21.1, 1.0, -0.7. HRMS calcd for $C_{20}H_{35}Si_2$ $[M+H]^+$ 331.2272; found: 331.2264.



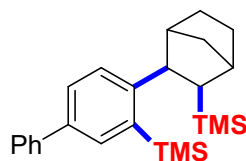
(5-ethyl-2-((2R,3R)-3-(trimethylsilyl) bicyclo[2.2.1] heptan-2-yl) phenyl) trimethylsilane (3e)

Yellow oil (137.6 mg, 80% yield, eluent: petroleum ether). 1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.30(d, J = 8.0 Hz, 1 H), 7.21(s, 1 H), 7.12(d, J = 6.8 Hz, 1 H), 3.13(d, J = 10.4 Hz, 1 H), 2.56-2.62(m, 2 H), 2.30-2.35(m, 2 H), 1.97(d, J = 9.2 Hz, 1 H), 1.71-1.75(m, 1 H), 1.55-1.61(m, 1 H), 1.38-1.44(m, 1 H), 1.34(d, J = 9.6 Hz, 2 H), 1.26(s, 1 H), 1.19-1.23(m, 3 H), 0.32(s, 9 H), -0.37(s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 150.0, 140.6, 138.7, 133.7, 128.7, 126.6, 50.7, 45.0, 43.5, 38.9, 38.6, 32.8, 32.2, 28.5, 15.8, 1.1, -0.7. HRMS calcd for $C_{21}H_{37}Si_2$ $[M+H]^+$ 345.2429; found: 345.2412.



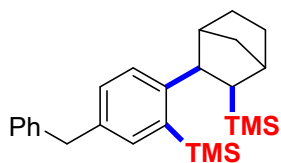
(5-(tert-butyl)-2-((2R,3R)-3-(trimethylsilyl) bicyclo[2.2.1] heptan-2-yl) phenyl) trimethylsilane (3f)

Colorless oil (148.8 mg, 80% yield, eluent: petroleum ether: ethyl acetate= 200:1). 1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.42(s, 1 H), 7.30-7.31(m, 2 H), 3.13(d, J = 10.0 Hz, 1 H), 2.34(s, 2 H), 1.97(d, J = 9.6 Hz, 1 H), 1.72-1.75(m, 1 H), 1.55-1.61(m, 1 H), 1.41-1.42(m, 1 H), 1.35(d, J = 9.2 Hz, 2 H), 1.30(s, 9 H), 1.24(d, J = 10.4 Hz, 1 H), 0.33(s, 1 H), -0.39(s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 149.7, 147.4, 138.1, 130.9, 126.2, 126.1, 50.6, 44.8, 43.6, 38.9, 38.6, 34.4, 32.8, 32.2, 31.5, 1.1, -0.8. HRMS calcd for $C_{23}H_{41}Si_2$ $[M+H]^+$ 373.2742; found: 373.2726.



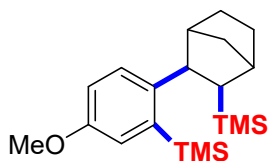
trimethyl((2R,3R)-3-(3-(trimethylsilyl)-[1,1'-biphenyl]-4-yl) bicyclo[2.2.1] heptan-2-yl) silane (3g)

Colorless solid (166.6 mg, 85% yield, eluent: petroleum ether: ethyl acetate= 200:1). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.63(d, *J* = 2.0 Hz, 1 H), 7.59(s, 1 H), 7.57(s, 1 H), 7.52-7.55(m, 1 H), 7.47(d, *J* = 8.0 Hz, 1 H), 7.39-7.43(m, 2 H), 7.28-7.32(m, 1 H), 7.20(d, *J* = 10.4 Hz, 1 H), 2.37(t, *J* = 10.0 Hz, 2 H), 2.00(d, *J* = 10.4 Hz, 1 H), 1.73-1.80(m, 1 H), 1.59-1.65(m, 1 H), 1.44-1.47(m, 1 H), 1.35-1.41(m, 2 H), 1.28-1.31(m, 1 H), 0.37(s, 9 H), -0.34(s, 9 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 152.0, 141.5, 139.5, 137.7, 132.9, 128.7, 127.9, 127.1, 127.0, 126.9, 50.9, 45.0, 43.6, 38.9, 38.6, 32.8, 32.2, 1.0, -0.7. HRMS calcd for C₂₅H₃₇Si₂ [M+H]⁺ 393.2429; found: 393.2433.



(5-benzyl-2-((2R,3R)-3-(trimethylsilyl) bicyclo[2.2.1] heptan-2-yl) phenyl) trimethylsilane (3h)

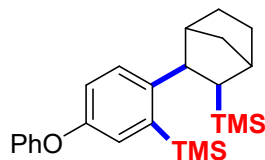
Colorless oil (144.2 mg, 71% yield, eluent: petroleum ether: ethyl acetate= 200:1). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.30(d, *J* = 8.0 Hz, 1 H), 7.22-7.27(m, 3 H), 7.14-7.17(m, 3 H), 7.07-7.09(m, 1 H), 3.93(s, 2 H), 3.13(d, *J* = 10.4 Hz, 1 H), 2.29-2.34(m, 2 H), 1.92-1.96(m, 1 H), 1.70-1.77(m, 1 H), 1.55-1.61(m, 1 H), 1.38-1.43(m, 1 H), 1.33(d, *J* = 9.6 Hz, 2 H), 1.24-1.27(m, 1 H), 0.30(s, 9 H), -0.36(s, 9 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 150.5, 141.5, 138.9, 137.3, 134.9, 129.9, 128.8, 126.7, 125.8, 50.8, 44.9, 43.6, 41.6, 38.9, 38.6, 32.8, 32.2, 1.0, -0.7. HRMS calcd for C₂₆H₃₉Si₂ [M+H]⁺ 407.2585; found: 407.2589.



(5-methoxy-2-((2R,3R)-3-(trimethylsilyl) bicyclo[2.2.1] heptan-2-yl) phenyl) trimethylsilane (3i)

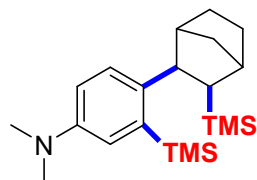
Yellow oil (141.8 mg, 86% yield, eluent: petroleum ether: ethyl acetate= 100:1). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.31(d, *J* = 8.8 Hz, 1 H), 6.96(d, *J* = 2.8 Hz, 1 H), 6.82-6.85(m, 1 H), 3.78(s, 3 H), 3.10(d, *J* = 10.0 Hz, 1 H), 2.34(d, *J* = 4.4 Hz, 1 H), 2.27(d, *J* = 3.2 Hz, 1 H), 1.94(d, *J* = 10.0 Hz, 1 H), 1.72-1.77(m, 1 H), 1.55-1.61(m, 1

H), 1.40-1.43(m, 1 H), 1.34(d, $J = 10.4$ Hz, 2 H), 1.22-1.25(m, 2 H), 0.32(s, 9 H), -0.35(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): $\delta = 156.9, 145.0, 140.1, 127.6, 119.9, 113.8, 55.1, 50.3, 45.1, 43.5, 38.7, 38.5, 32.8, 32.1, 0.9, -0.7$. HRMS calcd for $\text{C}_{20}\text{H}_{35}\text{OSi}_2$ $[\text{M}+\text{H}]^+$ 347.2221; found: 347.2218.



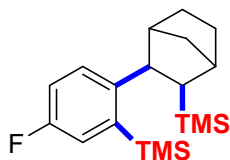
trimethyl(5-phenoxy-2-((2R,3R)-3-(trimethylsilyl) bicyclo[2.2.1] heptan-2-yl) phenyl) silane (3j)

Yellow oil (159.1 mg, 82% yield, eluent: petroleum ether: ethyl acetate= 100:1). ^1H NMR (400 MHz, CDCl_3 , ppm): $\delta = 7.35(\text{d}, J = 8.4$ Hz, 1 H), 7.27-7.31(m, 2 H), 7.10(t, $J = 4.8$ Hz, 1 H), 7.02-7.05(m, 1 H), 6.92-6.97(m, 3 H), 3.15(d, $J = 10.4$ Hz, 1 H), 2.36(s, 1 H), 2.31(s, 1 H), 1.94(d, $J = 10.4$ Hz, 1 H), 1.72-1.78(m, 1 H), 1.57-1.63(m, 1 H), 1.42-1.44(m, 1 H), 1.34-1.39(m, 2 H), 1.27(d, $J = 10.4$ Hz, 1 H), 0.30(s, 9 H), -0.32(s, 9 H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): $\delta = 158.0, 154.0, 148.1, 141.3, 129.6, 127.9, 125.0, 122.5, 119.9, 117.9, 50.5, 45.0, 43.6, 38.8, 38.6, 32.7, 32.2, 0.8, -0.6$. HRMS calcd for $\text{C}_{25}\text{H}_{37}\text{OSi}_2$ $[\text{M}+\text{H}]^+$ 409.2378; found: 409.2363.



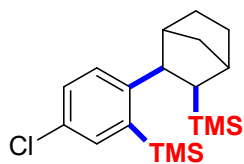
N,N-dimethyl-3-(trimethylsilyl)-4-((2R,3R)-3-(trimethylsilyl) bicyclo[2.2.1] heptan-2-yl) aniline (3k)

Yellow oil (129.2 mg, 72% yield, eluent: petroleum ether: ethyl acetate= 200:1). ^1H NMR (400 MHz, CDCl_3 , ppm): $\delta = 7.26(\text{d}, J = 8.4$ Hz, 1 H), 6.83(d, $J = 2.8$ Hz, 1 H), 6.71-6.74(m, 1 H), 3.07(d, $J = 10.0$ Hz, 1 H), 2.82-2.90(m, 6 H), 1.94(d, $J = 8.8$ Hz, 1 H), 1.70-1.76(m, 1 H), 1.54-1.60(m, 1 H), 1.39-1.42(m, 1 H), 1.32(d, $J = 9.6$ Hz, 2 H), 1.20-1.23(m, 1 H), 0.32(s, 9 H), -0.34(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): $\delta = 148.1, 141.4, 139.2, 127.3, 118.9, 114.1, 50.1, 45.0, 43.5, 41.0, 38.7, 38.5, 32.8, 32.1, 1.0, -0.7$. HRMS calcd for $\text{C}_{21}\text{H}_{38}\text{NSi}_2$ $[\text{M}+\text{H}]^+$ 360.2538; found: 360.2536.



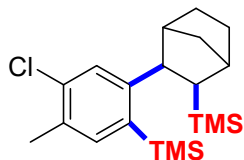
(5-fluoro-2-((2R,3R)-3-(trimethylsilyl) bicyclo[2.2.1] heptan-2-yl) phenyl) trimethylsilane (3l)

Colorless oil (121.9 mg, 77% yield, eluent: petroleum ether). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.33-7.36(m, 1 H), 7.06-7.09(m, 1 H), 6.93-6.98(m, 1 H), 3.13(d, J = 10.4 Hz, 1 H), 2.35(d, J = 2.8 Hz, 1 H), 2.27(d, J = 2.4 Hz, 1 H), 1.91-1.94(m, 1 H), 1.72-1.76(m, 1 H), 1.57-1.62(m, 1 H), 1.40-1.43(m, 1 H), 1.34-1.37(m, 2 H), 1.24-1.27(m, 1 H), 0.32(s, 9 H), -0.35(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 160.8, 148.4, 141.9, 128.1, 120.3, 115.7, 50.5, 45.1, 43.5, 38.7, 38.6, 32.7, 32.2, 0.7, -0.7. ^{19}F NMR (400 MHz, CDCl_3) δ = -118.6. HRMS calcd for $\text{C}_{19}\text{H}_{32}\text{FSi}_2$ $[\text{M}+\text{H}]^+$ 335.2021; found: 335.2018.



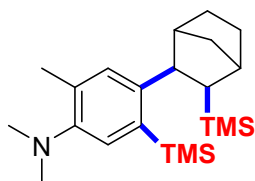
(5-chloro-2-((2R,3R)-3-(trimethylsilyl) bicyclo[2.2.1] heptan-2-yl) phenyl) trimethylsilane (3m)

Yellow oil (126.2 mg, 76% yield, eluent: petroleum ether). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.31-7.33(m, 2 H), 7.23-7.26(m, 1 H), 3.11(d, J = 10.4 Hz, 1 H), 2.35(d, J = 3.6 Hz, 1 H), 2.26(d, J = 2.4 Hz, 1 H), 1.91(d, J = 10.0 Hz, 1 H), 1.72-1.76(m, 1 H), 1.56-1.62(m, 1 H), 1.40-1.43(m, 1 H), 1.34-1.37(m, 2 H), 1.23-1.27(m, 1 H), 0.32(s, 9 H), -0.34(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 151.1, 141.8, 133.7, 131.3, 129.0, 128.1, 50.6, 45.0, 43.5, 38.8, 38.6, 32.7, 32.1, 0.8, -0.7. HRMS calcd for $\text{C}_{19}\text{H}_{32}\text{ClSi}_2$ $[\text{M}+\text{H}]^+$ 351.1726; found: 351.1737.



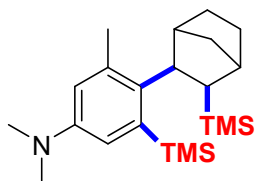
(5-chloro-4-methyl-2-((2R,3R)-3-(trimethylsilyl) bicyclo[2.2.1] heptan-2-yl) phenyl) trimethylsilane(3p)

Colorless solid (143.8 mg, 79% yield, eluent: petroleum ether). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.30(s, 1 H), 7.23(s, 1 H), 3.08(d, J = 10.4 Hz, 1 H), 2.32-2.36(m, 4 H), 2.73(s, 1 H), 1.94(d, J = 9.6 Hz, 1 H), 1.72-1.76(m, 1 H), 1.56-1.62(m, 1 H), 1.40-1.43(m, 1 H), 1.32-1.37(m, 2 H), 1.22-1.26(m, 1 H), 0.31(s, 9 H), -0.35(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 151.2, 138.6, 136.4, 134.3, 131.5, 129.6, 50.5, 45.0, 43.6, 38.8, 38.5, 32.7, 32.1, 20.0, 0.8, -0.7. HRMS calcd for $\text{C}_{20}\text{H}_{34}\text{ClSi}_2$ $[\text{M}+\text{H}]^+$ 365.1882; found: 365.1872.



N,N,2-trimethyl-5-(trimethylsilyl)-4-((2R,3R)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl) aniline (3q)

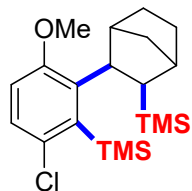
Yellow solid (126.8 mg, 68% yield, eluent: petroleum ether: ethyl acetate=200:1). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.16(s, 1 H), 7.06(s, 1 H), 3.08(d, J = 10.0 Hz, 1 H), 2.67(s, 6 H), 2.34(d, J = 4.0 Hz, 1 H), 2.31(d, J = 3.6 Hz, 1 H), 2.29(s, 3 H), 1.97(d, J = 10.0 Hz, 1 H), 1.70-1.77(m, 1 H), 1.55-1.61(m, 1 H), 1.39-1.42(m, 1 H), 1.32-1.35(m, 2 H), 1.20-1.23(m, 1 H), 0.31(s, 9 H), -0.38(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 149.7, 147.0, 136.3, 132.8, 129.6, 123.8, 50.4, 44.8, 44.4, 43.6, 38.8, 38.5, 32.8, 32.2, 18.2, 1.0, -0.8. HRMS calcd for $\text{C}_{22}\text{H}_{40}\text{NSi}_2$ $[\text{M}+\text{H}]^+$ 374.2694; found: 374.2690.



N,N,3-trimethyl-4-(trimethylsilyl)-5-((2R,3R)-3-(trimethylsilyl)bicyclo[2.2.1]heptan-2-yl) aniline (3r)

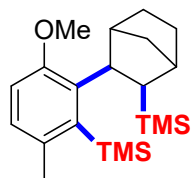
Yellow oil (121.3 mg, 65% yield, eluent: petroleum ether: ethyl acetate= 200:1). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 6.80(d, J =2.8 Hz, 1 H), 6.49(d, J = 2.8 Hz, 1 H), 3.38(d, J = 10.8 Hz, 1 H), 2.88(s, 6 H), 2.61(s, 1 H), 2.46(s, 3 H), 2.33(d, J = 4.8 Hz, 1 H), 1.94-1.97(m, 1 H), 1.78-1.83(m, 1 H), 1.53-1.58(m, 1 H), 1.43-1.48(m, 1 H), 1.39(d, J = 2.0 Hz, 1 H), 1.32-1.36(m, 2 H), 1.29(d, J = 10.4 Hz, 1 H), 0.34(s, 9 H), -0.37(s, 9

H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 148.2, 142.4, 137.4, 135.7, 118.6, 118.6, 52.7, 45.0, 41.4, 41.0, 39.7, 38.9, 33.5, 32.3, 23.6, 2.1, -0.6. HRMS calcd for $\text{C}_{22}\text{H}_{40}\text{NSi}_2$ $[\text{M}+\text{H}]^+$ 374.2694; found: 374.2689.



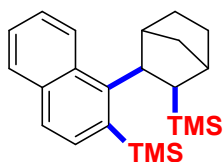
((2R,3R)-3-(6-chloro-3-methoxy-2-(trimethylsilyl)phenyl) bicyclo[2.2.1] heptan-2-yl) trimethylsilane (3s)

Colorless solid (153.9 mg, 81% yield, eluent: petroleum ether: ethyl acetate= 100:1). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.14(d, J = 8.4 Hz, 1 H), 6.71(d, J = 8.8 Hz, 1 H), 3.70(s, 3 H), 3.43(d, J = 10.8 Hz, 1 H), 2.43(s, 1 H), 2.30(d, J = 4.8 Hz, 1 H), 2.12(d, J = 9.2 Hz, 1 H), 1.73-1.80(m, 1 H), 1.45-1.53(m, 1 H), 1.33-1.36(m, 1 H), 1.21-1.26(m, 2 H), 1.16(d, J = 9.2 Hz, 1 H), 0.50(s, 9 H), -0.4(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 156.5, 141.1, 140.4, 132.7, 128.7, 112.8, 54.2, 49.5, 44.5, 42.7, 39.3, 39.2, 33.0, 32.4, 4.2, -0.7. HRMS calcd for $\text{C}_{20}\text{H}_{34}\text{ClOSi}_2$ $[\text{M}+\text{H}]^+$ 381.1831; found: 381.1819.



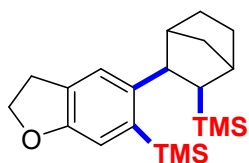
(6-methoxy-3-methyl-2-((2R,3R)-3-(trimethylsilyl) bicyclo[2.2.1] heptan-2-yl) phenyl) trimethylsilane (3t)

Yellow oil (129.6 mg, 72% yield, eluent: petroleum ether: ethyl acetate= 100:1). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 6.94(d, J = 8.4 Hz, 1 H), 6.70(d, J = 8.0 Hz, 1 H), 3.69(s, 3 H), 3.38(d, J = 10.8 Hz, 1 H), 2.43(s, 1 H), 2.38(s, 3 H), 2.29(d, J = 4.8 Hz, 1 H), 2.21(d, J = 9.2 Hz, 1 H), 1.74-1.80(m, 1 H), 1.49-1.54(m, 1 H), 1.36-1.41(m, 1 H), 1.20-1.23(m, 2 H), 1.15(d, J = 9.6 Hz, 1 H), 0.43(s, 9 H), -0.40(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 156.0, 141.0, 139.2, 135.6, 129.6, 111.7, 53.8, 50.1, 44.4, 42.8, 39.3, 39.2, 33.0, 32.6, 24.4, 4.9, -0.8. HRMS calcd for $\text{C}_{21}\text{H}_{37}\text{OSi}_2$ $[\text{M}+\text{H}]^+$ 361.2378; found: 361.2383.



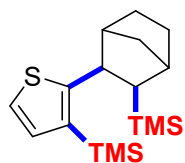
trimethyl(3-((2R,3R)-3-(trimethylsilyl) bicyclo[2.2.1] heptan-2-yl) naphthalen-2-yl) silane (3u)

Yellow solid (131.8 mg, 72% yield, eluent: petroleum ether: ethyl acetate= 100:1). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 9.03(d, J = 9.6 Hz, 1 H), 8.20(d, J = 9.2 Hz, 1 H), 8.08(d, J = 8.4 Hz, 1 H), 7.97(d, J = 8.4 Hz, 1 H), 7.82-7.82(m, 3 H), 4.23(d, J = 10.8 Hz, 1 H), 3.49(s, 1 H), 2.86(s, 1 H), 2.75(d, J = 9.6 Hz, 1 H), 2.30-2.35(m, 1 H), 2.10-2.11(m, 1 H), 2.02-2.05(m, 1 H), 1.98(d, J = 10.4 Hz, 1 H), 1.85-1.88(m, 2 H), 0.84(s, 9 H), -0.30(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 148.4, 139.0, 135.3, 132.2, 131.4, 128.6, 126.7, 126.1, 125.5, 124.4, 54.2, 45.6, 42.7, 40.4, 39.3, 34.0, 32.2, 2.1, -1.0. HRMS calcd for $\text{C}_{23}\text{H}_{35}\text{Si}_2$ $[\text{M}+\text{H}]^+$ 367.2272; found: 367.2263.



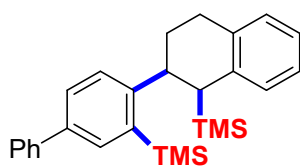
trimethyl((2R,3R)-3-(5-(trimethylsilyl)-2,3-dihydrobenzofuran-6-yl) bicyclo[2.2.1] heptan-2-yl) silane (3v)

Colorless solid (125.3 mg, 70% yield, eluent: petroleum ether: ethyl acetate= 100:1). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.16-7.24(m, 1 H), 6.73-6.85(m, 1 H), 4.43-4.55(m, 2 H), 3.11-3.19(m, 3 H), 2.34(s, 1 H), 2.27(s, 1 H), 1.94(d, J = 10.0 Hz, 1 H), 1.70-1.77(m, 1 H), 1.55-1.61(m, 1 H), 1.40-1.43(m, 1 H), 1.33-1.37(m, 2 H), 1.24(d, J = 9.6 Hz, 1 H), 0.30(s, 9 H), -0.34(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 157.7, 145.1, 138.7, 127.9, 123.4, 114.1, 50.3, 45.0, 43.8, 38.8, 38.5, 32.8, 32.1, 29.9, 1.0, -0.7. HRMS calcd for $\text{C}_{21}\text{H}_{35}\text{OSi}_2$ $[\text{M}+\text{H}]^+$ 359.2221; found: 359.2226.



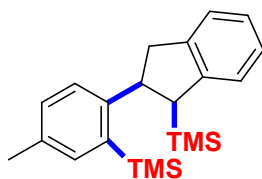
trimethyl(2-((2S,3R)-3-(trimethylsilyl) bicyclo[2.2.1] heptan-2-yl) thiophen-3-yl) silane (3w)

Colorless oil (117.6 mg, 73% yield, eluent: petroleum ether). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.09(d, J = 4.8 Hz, 1 H), 6.88(d, J = 5.2 Hz, 1 H), 3.49(d, J = 10.4 Hz, 1 H), 2.32(d, J = 4.0 Hz, 1 H), 2.28(d, J = 2.8 Hz, 1 H), 1.90(d, J = 10.4 Hz, 1 H), 1.67-1.73(m, 1 H), 1.61-1.66(m, 1 H), 1.35-1.38(m, 1 H), 1.29-1.34(m, 2 H), 1.17-1.20(m, 2 H), 0.28(s, 9 H), -0.24(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 157.9, 135.7, 131.4, 121.9, 48.3, 46.1, 41.9, 39.1, 37.6, 32.7, 31.2, 0.6, -1.1. HRMS calcd for $\text{C}_{17}\text{H}_{40}\text{SSi}_2$ $[\text{M}+\text{H}]^+$ 323.1680; found: 323.1679.



trimethyl(4-((1S,2R)-1-(trimethylsilyl)-1,2,3,4-tetrahydronaphthalen-2-yl)-[1,1'-biphenyl]-3-yl)silane (3x)

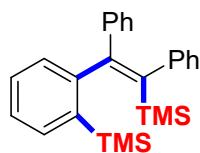
Colorless oil (128.6 mg, 63% yield, eluent: petroleum ether). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.77(d, J = 2.0 Hz, 1 H), 7.61(d, J = 7.6 Hz, 2 H), 7.54-7.56(m, 1 H), 7.41-7.47(m, 3 H), 7.32-7.36(m, 1 H), 7.13(d, J = 6.4 Hz, 1 H), 7.06-7.08(m, 2 H), 6.92-6.94(m, 1 H), 3.55-3.58(m, 1 H), 3.00-3.09(m, 2 H), 2.66(d, J = 2.8 Hz, 1 H), 2.42-2.48(m, 1 H), 2.18-2.22(m, 1 H), 0.33(s, 9 H), -0.23(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 150.3, 141.4, 140.2, 139.7, 138.2, 135.6, 134.1, 129.3, 129.1, 128.7, 127.7, 127.3, 127.0, 124.7, 124.5, 42.4, 40.8, 28.8, 26.9, 1.4, 0.7. HRMS calcd for $\text{C}_{28}\text{H}_{36}\text{Si}_2$ $[\text{M}+\text{H}]^+$ 429.2429; found: 429.2410.



trimethyl(5-methyl-2-((1S,2R)-1-(trimethylsilyl)-2,3-dihydro-1H-inden-2-yl)phenyl)silane (3y)

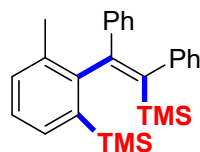
Colorless oil (116.2 mg, 66% yield, eluent: petroleum ether). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.29-7.31(m, 2 H), 7.22-7.24(m, 1 H), 7.14-7.15(m, 2 H), 7.10-7.12(m, 1 H), 7.07-7.09(m, 1 H), 4.12-4.18(m, 1 H), 3.26-3.32(m, 1 H), 3.11-3.17(m, 1 H), 2.90(d, J = 8.8 Hz, 1 H), 0.34(s, 9 H), -0.24(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 ,

ppm): δ = 146.2, 146.2, 142.6, 138.9, 135.8, 135.0, 129.6, 126.5, 125.9, 125.0, 124.4, 123.8, 49.1, 43.3, 40.1, 21.2, 1.2, -0.9. HRMS calcd for $C_{22}H_{32}Si_2$ $[M+H]^+$ 353.2116; found: 353.2108.



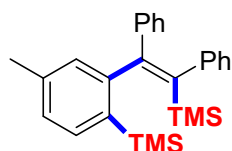
(Z)-(1,2-diphenyl-2-(2-(trimethylsilyl) phenyl) vinyl) trimethylsilane (5a)

Colorless solid (166.1 mg, 83% yield, eluent: petroleum ether: ethyl acetate= 200:1). 1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.67(d, J = 7.2 Hz, 1 H), 7.54-7.56(m, 2 H), 7.22-7.48(m, 6 H), 7.04-7.06(m, 3 H), 6.97-6.99(m, 2 H), 0.12(s, 9 H), -0.15(s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 152.7, 149.7, 144.0, 143.9, 141.4, 138.8, 135.1, 131.8, 131.6, 130.8, 128.3, 128.2, 126.9, 126.6, 126.4, 125.2, 0.1, 0.0. HRMS calcd for $C_{26}H_{33}Si_2$ $[M+H]^+$ 401.2116; found: 401.2116.



(Z)-(2-(1,2-diphenyl-2-(trimethylsilyl) vinyl)-3-methylphenyl) trimethylsilane (5b)

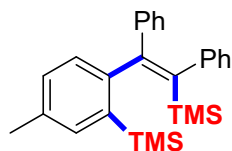
Colorless oil (169.8 mg, 82% yield, eluent: petroleum ether: ethyl acetate= 200:1). 1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.42-7.46(m, 3 H), 7.31-7.37(m, 3 H), 7.16-7.25(m, 2 H), 7.03-7.06(m, 3 H), 6.97-6.99(m, 2 H), 2.52(s, 3 H), 0.10(s, 9 H), -0.15(s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 152.8, 146.9, 144.0, 143.9, 141.7, 138.4, 135.8, 132.8, 131.8, 131.6, 130.8, 128.8, 127.1, 126.9, 126.3, 125.2, 21.4, 0.1, 0.1. HRMS calcd for $C_{27}H_{35}Si_2$ $[M+H]^+$ 415.2272; found: 415.2270.



(Z)-(2-(1,2-diphenyl-2-(trimethylsilyl) vinyl)-4-methylphenyl) trimethylsilane (5c)

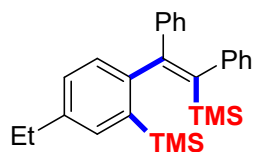
Colorless oil (173.9 mg, 84% yield, eluent: petroleum ether: ethyl acetate= 200:1). 1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.56(d, J = 7.2 Hz, 1 H), 7.43-7.46(m, 1 H), 7.23-

7.37(m, 6 H), 7.03-7.05(m, 3 H), 6.99-7.01(m, 2 H), 2.57(s, 3 H), 0.10(s, 9 H), -0.15(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 153.0, 149.7, 144.0, 143.8, 141.4, 137.8, 135.1, 135.1, 132.9, 131.6, 130.8, 128.3, 127.3, 126.9, 126.3, 125.2, 21.3, 0.1. HRMS calcd for $\text{C}_{27}\text{H}_{35}\text{Si}_2$ $[\text{M}+\text{H}]^+$ 415.2272; found: 415.2277.



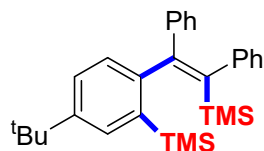
(Z)-2-(1,2-diphenyl-2-(trimethylsilyl) vinyl)-5-methylphenyl trimethylsilane (5d)

Colorless oil (192.5 mg, 93% yield, eluent: petroleum ether: ethyl acetate= 200:1). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.44-7.46(m, 2 H), 7.42(d, J = 7.6 Hz, 1 H), 7.32-7.37(m, 2 H), 7.15-7.30(m, 3 H), 7.02-7.04(m, 3 H), 6.98-7.00(m, 2 H), 2.52(s, 3 H), 0.10(s, 9 H), -0.15(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 152.8, 146.9, 144.0, 143.9, 141.7, 138.4, 135.8, 131.8, 131.6, 130.8, 128.8, 128.3, 128.2, 126.9, 126.3, 125.2, 21.4, 0.1, 0.1. HRMS calcd for $\text{C}_{27}\text{H}_{35}\text{Si}_2$ $[\text{M}+\text{H}]^+$ 415.2272; found: 415.2269.



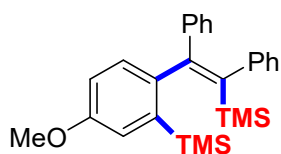
(Z)-2-(1,2-diphenyl-2-(trimethylsilyl) vinyl)-5-ethylphenyl trimethylsilane (5e)

Colorless oil (194.4 mg, 79% yield, eluent: petroleum ether: ethyl acetate= 200:1). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.48-7.51(m, 2 H), 7.35-7.43(m, 3H), 7.21-7.29(m, 3 H), 7.07-7.09(m, 3 H), 7.02-7.05(m, 2 H), 2.86(dd, J = 7.2 Hz, 2 H), 1.45(t, J = 7.6 Hz, 3 H), 0.15(s, 9 H), -0.12(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 152.8, 147.1, 144.0, 143.9, 142.2, 141.7, 138.3, 134.7, 131.8, 131.6, 130.8, 128.3, 127.5, 126.9, 126.2, 125.1, 28.7, 15.7, 0.1, 0.0. HRMS calcd for $\text{C}_{28}\text{H}_{37}\text{Si}_2$ $[\text{M}+\text{H}]^+$ 429.2429; found: 429.2415.



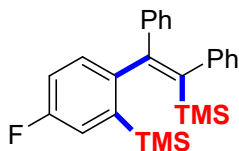
(Z)-5-(tert-butyl)-2-(1,2-diphenyl-2-(trimethylsilyl)vinyl) phenyl trimethylsilane (5f)

Colorless solid (180.2 mg, 79% yield, eluent: petroleum ether: ethyl acetate= 100:1). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.71(d, *J* = 2.0 Hz, 1 H), 7.57-7.59(m, 1 H), 7.48(d, *J* = 7.6 Hz, 1 H), 7.34-7.40(m, 2 H), 7.20-7.28(m, 3 H), 7.07-7.09(m, 3 H), 7.02-7.04(m, 3 H), 1.52(s, 9 H), 0.15(s, 9 H), -0.15(s, 9 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 152.8, 149.0, 146.7, 144.1, 141.7 137.7, 131.8, 131.5, 130.8, 129.6, 127.7, 126.9, 126.2, 125.1, 125.0, 34.6, 31.5, 0.2, -0.1. HRMS calcd for C₃₀H₄₁Si₂ [M+H]⁺ 457.2742; found: 457.2750.



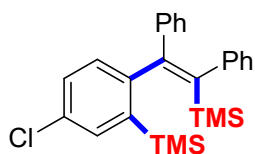
(Z)-2-(1,2-diphenyl-2-(trimethylsilyl)vinyl)-5-methoxyphenyl trimethylsilane(5g)

Colorless solid (189.2 mg, 88% yield, eluent: petroleum ether: ethyl acetate= 40:1). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.44(d, *J* = 8.4 Hz, 1 H), 7.28-7.34(m, 2 H), 7.13-7.23(m, 4 H), 7.00-7.06(m, 4 H), 6.94-6.97(m, 2 H), 3.96(s, 3 H), 0.08(s, 9 H), -0.15(s, 9 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 158.1, 152.5, 144.2, 144.0, 142.3, 141.8, 140.4, 133.0, 130.9, 129.5, 127.7, 126.9, 126.3, 125.2, 121.5, 112.1, 55.1, 0.1, -0.1. HRMS calcd for C₂₇H₃₅OSi₂ [M+H]⁺ 431.2221; found: 431.2221.



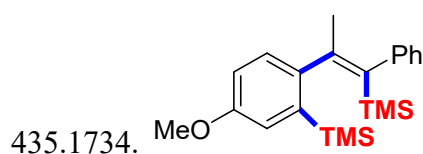
(Z)-2-(1,2-diphenyl-2-(trimethylsilyl) vinyl)-5-fluorophenyl trimethylsilane (5h)

Colorless solid (146.3 mg, 70% yield, eluent: petroleum ether: ethyl acetate= 200:1). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.48(dd, *J* = 8.0 Hz, 1 H), 7.29-7.35(m, 3 H), 7.13-7.24(m, 4 H), 7.01-7.04(m, 3 H), 6.92-6.95(m, 2 H), 0.09(s, 9 H), -0.15(s, 9 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 161.8, 151.7, 145.7, 144.7, 143.7, 142.1, 141.3, 133.4, 131.6, 130.8, 128.3, 127.0, 126.5, 125.3, 121.6, 114.7, 0.1, -0.2. ¹⁹F NMR (400 MHz, CDCl₃) δ= -116.0. HRMS calcd for C₂₆H₃₂FSi₂ [M+H]⁺ 419.2021; found: 419.2019.



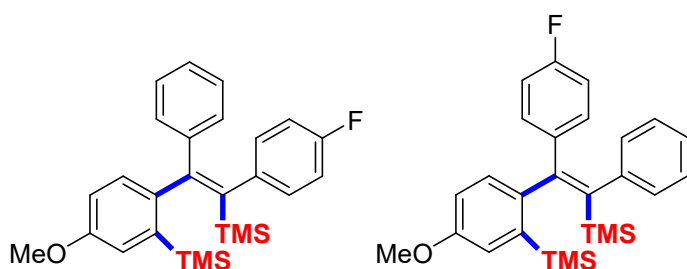
(Z)-(5-chloro-2-(1,2-diphenyl-2-(trimethylsilyl) vinyl)phenyl)trimethylsilane (5i)

White solid (160.6 mg, 74% yield, eluent: petroleum ether: ethyl acetate= 200:1). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.59(d, J = 2.4 Hz, 1 H), 7.51-7.53(m, 1 H), 7.43-7.46(m, 2 H), 7.29-7.35(m, 2 H), 7.20-7.24(m, 1 H), 7.01-7.05(m, 4 H), 6.91-6.93(m, 2 H), 0.09(s, 9 H), -0.15(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 151.5, 148.0, 144.7, 143.6, 141.7, 141.0, 134.9, 133.2, 133.1, 131.6, 130.8, 128.3, 128.1, 127.0, 126.6, 125.4, 0.1, -0.2. HRMS calcd for $\text{C}_{26}\text{H}_{32}\text{ClSi}_2$ $[\text{M}+\text{H}]^+$ 435.1726; found:



(Z)-(5-methoxy-2-(1-phenyl-1-(trimethylsilyl)prop-1-en-2-yl)phenyl)trimethylsilane (5j)⁶

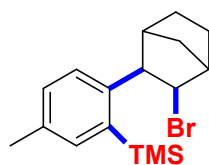
Colorless oil (138.4mg, 75% yield, eluent: petroleum ether: ethyl acetate= 200:1). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.46-7.50(m, 1 H), 7.31-7.35(m, 2 H), 7.17-7.21(m, 1 H), 7.09 (t, J = 2.8 Hz, 1 H), 7.03-7.06(m, 2 H), 6.83-6.86(m, 1 H), 3.83(s, 3 H), 1.73(s, 3 H) 0.35(s, 9 H), -0.34(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 157.6, 150.6, 144.9, 144.1, 141.3, 131.8, 130.2, 128.1, 127.9, 125.1, 121.0, 112.8, 55.1, 26.1, 0.1, -0.1. HRMS calcd for $\text{C}_{22}\text{H}_{32}\text{OSi}_2$ $[\text{M}+\text{H}]^+$ 369.2065; found: 369.2048.



(Z)-(2-(2-(4-fluorophenyl)-1-phenyl-2-(trimethylsilyl)vinyl)-5-methoxyphenyl)trimethylsilane (5k)

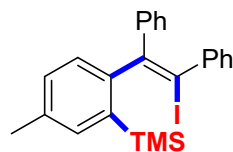
(Z)-(2-(2-(4-fluorophenyl)-2-(4-methoxy-2-(trimethylsilyl)phenyl)-1-phenylvinyl)trimethylsilane (5k')

White solid (157.9 mg, 70% yield, regioisomer ratio $\approx$ 1:1, eluent: petroleum ether: ethyl acetate= 200:1). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.31(d, J = 8.0 Hz, 1 H), 7.20-7.23(m, 1 H), 7.09-7.14(m, 2 H), 6.94-6.96(m, 5 H), 6.81-6.84(m, 2 H), 6.62(t, J = 8.8 Hz, 1 H), 3.87(s, 3 H), -0.03--0.01(m, 9 H), -0.25(s, 9H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 162.3, 159.9, 158.2, 158.2, 153.3, 151.3, 144.3, 143.9, 143.1, 142.1, 142.1, 141.7, 140.4, 140.4, 139.8, 139.8, 138.0, 132.9, 132.5, 132.4, 130.9, 127.0, 126.4, 125.3, 121.6, 121.5, 113.9, 113.7, 112.2, 112.1, 55.1, 0.1, -0.1, -0.1. ^{19}F NMR (400 MHz, CDCl_3) δ = -115.6, -118.1. HRMS calcd for $\text{C}_{27}\text{H}_{33}\text{FOSi}_2$ $[\text{M}+\text{H}]^+$ 449.2127; found: 449.2104.



(2-((2R)-3-bromobicyclo[2.2.1]heptan-2-yl)-5-methylphenyl)trimethylsilane (6)

Colorless solid (147.8 mg, 88% yield, eluent: petroleum ether). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.59(s, 1H), 7.53(d, J = 7.6 Hz, 1 H), 7.31(d, J = 8.8 Hz, 1 H), 3.65(d, J = 10.4 Hz, 1 H), 2.64(d, J = 5.2 Hz, 2 H), 7.31(s, 3 H), 2.10(d, J = 9.6 Hz, 1 H), 1.98-2.04(m, 1 H), 1.86-1.92(m, 1 H), 1.62-1.73(m, 4 H), 0.00(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 142.2, 137.0, 132.8, 127.9, 127.8, 126.6, 49.2, 43.6, 40.3, 39.0, 38.3, 32.4, 32.1, 20.5, -0.5. HRMS calcd for $\text{C}_{17}\text{H}_{26}\text{BrSi}$ $[\text{M}+\text{H}]^+$ 337.0982; found: 337.0988.



(Z)-(2-(2-iodo-1,2-diphenylvinyl)-5-methylphenyl)trimethylsilane (7)

colorless oil (170.8 mg, 73% yield, eluent: petroleum ether: ethyl acetate= 200:1). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.87(s, 1H), 7.65-7.67(m, 1 H), 7.53(d, J = 7.6 Hz, 1 H), 7.40-7.42(m, 2 H), 7.36-7.38(m, 1 H), 7.32-7.34(m, 1 H), 7.21-7.24(m, 4 H), 7.13-7.15(m, 2 H), 2.51(s, 3 H), 0.00(s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 153.5, 145.4, 144.9, 143.6, 140.9, 139.8, 138.8, 135.6, 130.5, 128.8, 127.7, 127.6, 127.0,

126.1, 125.2, 101.3, 20.6, 0.0. HRMS calcd for C₂₄H₂₆ISi [M+H]⁺ 469.0843; found: 469.0839.

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V.NMR spectra

