Supporting Information

Synthesis of Tetrahydroazepines through Silyl Aza-Prins Cyclization Mediated by Iron(III) Salts

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1. Supporting schemes and tables

1.1. Synthesis of 1-amino-3-triphenylsilyl-4-pentenes 6a-b.

![Scheme S1. Synthetic route for 1-amino-3-triphenylsilyl-4-pentenes 6a-b.]

1.2. Catalyst optimization for SAPC of 1-amino-3-triphenylsilyl-4-pentene 6a.

Table S1. Catalyst optimization reaction conditions.

| Entry | Catalyst (equiv.) | Time (min) | Yield 7a:8 (%)<sup>a</sup> | Conversion (%) |
|-------|-------------------|------------|-----------------------------|----------------|
| 1     | FeCl<sub>3</sub> (0.3) | 1         | 67:30                       | 100            |
| 2     | FeCl<sub>3</sub> (0.1) | 50        | 55:19                       | 100            |
| 3     | Fe(acac)<sub>3</sub> (0.1)/ TMSCl (1.0) | 30        | 58:21                       | 100            |
| 4     | Fe(OTf)<sub>3</sub> (0.1) | 55        | 48:32                       | 100            |
| 5     | FeBr<sub>2</sub> (0.1) | 240       | 20:0                        | 53             |
| 6     | FeBr<sub>2</sub> (1.0) | 270       | 33:14                       | 78             |
| 7     | CuCl (0.1) | 200       | N.R.                        | N.R.           |
| 8     | InBr<sub>3</sub> (0.1) | 240       | 48:30                       | 86             |
| 9     | InCl<sub>3</sub> (0.1) | 240       | 13:0                        | 23             |

<sup>a</sup> Reaction conditions: 6a (0.10 mmol), isovaleraldehyde (0.12 mmol), DCM (0.1 M). Isolated yield.

1.3. Synthesis of 1-amino-3-triphenylsilyl-4-pentenes 9a-b substituted at β position

![Scheme S2. Synthetic route for 1-amino-3-triphenylsilyl-4-pentenes 9a-b.]

S2
1.4. Catalyst optimization for SAPC of 1-amino-3-triphenylsilyl-4-pentene 9a.

**Table S2. Catalyst optimization reaction conditions.**

| Entry | Catalyst (equiv.) | Temperature(ºC) | Yield 10a:11 (%) \( a \) | Conversion (%) |
|-------|-------------------|-----------------|--------------------------|---------------|
| 1     | FeBr₃ (0.3)\( b \) | -20             | N. R.                    | N.R.          |
| 2     | FeBr₃ (0.3)\( b \) | 0               | 22:21                    | 69            |
| 3     | FeBr₃ (0.3)       | 10              | 43:11                    | 93            |
| 4     | FeCl₃ (0.3)       | 10              | 45:18                    | 100           |
| 5     | InCl₃ (0.3)       | 10              | 7:0                      | 27            |
| 6     | InBr₃ (0.3)       | 10              | 11:6                     | 38            |
| 7     | Fe(acac)₃ (0.3)/  | 10              | 33:17                    | 100           |
|       | TMSCl (1.0)       |                 |                          |               |
| 8     | Fe(OTf)₃ (0.3)    | 10              | 0:50                     | 100           |

\( a \) Reaction conditions: 9a (0.098 mmol), isovaleraldehyde (0.15 mmol), DCM (0.1 M). Isolated yield. \( b \) After 3 hours of reaction, another 0.3 equivalents of FeBr₃ were added.

1.5. NMR study for the diastereoselectivity determination

![NMR spectra](image URI)

\(^1H\)-GOESY NMR (CDCl₃, 500 MHz)
2. Experimental Procedures and Compound Data

2.1. General procedure for tosylation of alcohols

To a solution of corresponding alcohol (1.0 equiv.) in dry DCM (0.1 M) at room temperature under inert atmosphere were added Et₃N (2.0 equiv.), TsCl (1.5 equiv.) and a small amount of DMAP. Once the reaction was complete, the solvent was removed under reduced pressure and the residue was purified by flash silica gel column chromatography (n-hexane/EtOAc solvent system).

2.2. General procedure for substitution of tosylate by sulfonylamide

To a solution of corresponding tosylate (1.0 equiv.) in dry DMF (0.25 M) at room temperature under inert atmosphere were added TsNH₂ or MsNH₂ (2.0 equiv.) and Cs₂CO₃ (1.5 equiv.). The reaction mixture was warmed to 80 ºC until the starting material was completely consumed. Then, it was allowed to reach room temperature and the reaction mixture was filtered through a pad of silica gel. The solvent was removed under reduced pressure and the residue was purified by flash silica gel column chromatography (n-hexane/EtOAc solvent system).

2.3. General procedure for α-alkylation of esters

Following the procedure described by Panek and coworkers,¹ to a solution of i-Pr₂NH (2.0 equiv.) in dry THF (0.94 M vs i-Pr₂NH) at -78 ºC under inert atmosphere was added n-BuLi (2.0 equiv.). The mixture was stirred at 0 ºC for 10 min. and then cooled to -78 ºC. Next, a solution of the ester (1.0 equiv.) in dry THF (2.35 M) was added dropwise. This mixture was stirred at -78 ºC for 30 min. and alkyl iodide (2.7 equiv.) in dry THF (4.7 M) was added. The reaction mixture was allowed to reach room temperature and stirred overnight. It was quenched with saturated aqueous NH₄Cl. The phases were separated and the aqueous layer was extracted with 3 x EtOAc. The combined organic phases were dried over anhydrous MgSO₄, filtrated, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (n-hexane/EtOAc solvent system).

2.4. General procedure for reduction of esters to alcohols

To a solution of ester (1.0 equiv.) in dry Et₂O (0.06 M) at 0 ºC under inert atmosphere was added LiAlH₄ (2.0 equiv.). Then, the ice-bath was removed and the mixture was stirred at room temperature. Once the reaction was completed, saturated aqueous K₂CO₃ solution and water were added. The solid was filtrated and the organic phase was concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (n-hexane/EtOAc solvent system).

2.5. Compound data

(E)-(3-bromoprop-1-en-1-yl)triphenylsilane (16)

Following the procedure described by Corriu,²³ to a solution of commercially available allyltriphénylsilane (6.00 g, 20.0 mmol, 1.0 equiv.) in tetrachloromethane (CCl₄, 40.0 mL, 0.5 M) at
room temperature, were added N-bromosuccinimide (NBS, 3.56 g, 20.0 mmol, 1.0 equiv.) and benzoyl peroxide (0.485 g, 2.00 mmol, 0.1 equiv.). The reaction mixture was heated to reflux and monitored by TLC (Heat-On™ Block System). Then, it was allowed to cool to room temperature, and filtered through a short plug of Celite. The solvent was removed under reduced pressure and the reaction mixture was purified by flash silica gel column chromatography (n-hexane/EtOAc 95:5 solvent system) to afford 7.36 g of allyl bromide 16 as a white amorphous solid (9.0 mmol, 75% yield).

Rf = 0.55 (n-hexane/EtOAc 95:5); 'H-NMR (CDCl₃, 400 MHz) δ = 7.51 (m, 6H), 7.46-7.35 (m, 9H), 6.50 (d, J = 18.1 Hz, 1H), 6.27 (dt, J = 18.2 & 6.7 Hz, 1H), 4.06 (dd, J = 6.7 & 0.6 Hz, 2H); 13C['H]-NMR (CDCl₃, 125 MHz) δ = 146.0 (CH), 135.9 (6 x CH), 133.7 (3 x C), 129.7 (3 x CH), 129.6 (CH), 128.0 (6 x CH), 34.7 (CH₂); HRMS (ESI+): m/z [M+Na]+ calcd. for C₉H₉BrNaSi: 401.0337; found: 401.0341.

3-(triphenylsilyl)pent-4-en-1-ol (17)

To a solution of Mg (0.380 g, 15.6 mmol, 1.3 equiv.) in 40 mL of dry Et₂O (0.3 M) at room temperature was added allyl-TPS bromide 16 (5.00 g, 13.2 mmol, 1.1 equiv.) dissolved in 13 mL of dry Et₂O (1.0 M). The reaction mixture was heated to reflux for 2 h (Heat-On™ Block System). Then, ethylene oxide 2.5-3.3 M in THF (4.8 mL, 12.0 mmol, 1.0 equiv.) was added dropwise at the refluxing temperature. At the same time, 8 mL of dry DCM was added dropwise, to dissolve the alcohol and avoid the formation of an insoluble gel to afford 3.10 g of bis-homoallylic alcohol 17 as pale yellow oil (9.0 mmol, 75% yield).

Rf = 0.40 (n-hexane/EtOAc 80:20); 'H-NMR (CDCl₃, 500 MHz) δ = 7.57 (m, 6H), 7.44-7.39 (m, 3H), 7.39-7.33 (m, 6H), 5.77 (dt, J = 10.0 & 17.0 Hz, 1H), 4.99 (m, 2H), 3.72 (m, 1H), 2.67 (m, 1H), 2.01 (m, 1H), 1.74 (m, 1H), 1.29 (brt, J = 5.5 Hz, 1H); 13C['H]-NMR (CDCl₃, 125 MHz) δ = 138.4 (CH), 136.1 (6 x CH), 133.6 (3 x C), 129.5 (3 x CH), 127.8 (6 x CH), 115.2 (CH₂), 62.1 (CH₃), 32.0 (CH₃), 28.5 (CH); HRMS (ESI+): m/z [M+Na]+ calcd. for C₉H₉ONaSi: 367.1494; found: 367.1501.

3-(triphenylsilyl)pent-4-en-1-yl 4-methylbenzenesulfonate (18)

Following the general procedure 2.1, alcohol 17 (2.00 g, 5.81 mmol, 1.0 equiv.) was dissolved in 58 mL of dry DCM (0.1 M) and Et₃N (1.6 mL, 11.6 mmol, 2.0 equiv.), TsCl (1.66 g, 8.72 mmol, 1.5 equiv.) and DMAP (0.355 g, 2.90 mmol, 0.5 equiv.) were added to give 2.17 g of tosylate 18 as a white amorphous solid (4.36 mmol, 75% yield).

Rf = 0.51 (n-hexane/EtOAc 80:20); 'H-NMR (CDCl₃, 400 MHz) δ = 7.75 (m, 2H), 7.52 (m, 6H), 7.44-7.39 (m, 3H), 7.39-7.32 (m, 6H), 7.32-7.28 (m, 2H), 5.56 (m, 1H), 4.92 (d, J = 10.3 Hz, 1H), 4.80 (d, J = 16.9 Hz, 1H), 4.05 (m, 2H), 2.60 (brt, J = 10.9 Hz, 1H), 2.44 (s, 3H), 2.14 (m, 1H), 1.67 (m, 1H); 13C['H]-NMR (CDCl₃, 100 MHz) δ = 144.5 (C), 136.6 (CH), 136.0 (6 x CH), 133.2 (C), 133.1 (3 x C), 129.7 (3 x CH), 129.6 (4 x CH), 127.8 (6 x CH), 116.1 (CH₂), 69.2 (CH₃), 28.4 (CH₂), 27.5 (CH), 21.6 (CH₃). HRMS (ESI+): m/z [M+Na]+ calcd. for C₁₀H₇O₂NaSi: 521.1583; found: 521.1585.

4-methyl-N-(3-(triphenylsilyl)pent-4-en-1-yl)benzenesulfonylamide (6a)
Following the general procedure 2.2, to a solution of tosylate 18 (1.00 g, 2.00 mmol, 1.0 equiv.) in 8.0 mL of dry DMF (0.25 M) were added TsNH₂ (0.685 g, 4.00 mmol, 2.0 equiv.) and Cs₂CO₃ (0.977 g, 3.00 mmol, 1.5 equiv.) to obtain 0.627 g of tosylamide 6a as a white amorphous solid (1.26 mmol, 73% yield).

Rf = 0.34 (n-hexane/EtOAc 80:20); ¹H-NMR (CDCl₃, 400 MHz) δ = 7.67 (brd, J = 8.3 Hz, 2H), 7.49 (m, 6H), 7.41 (m, 3H), 7.35 (m, 6H), 7.24 (brd, J = 7.9 Hz, 2H), 5.61 (dt, J = 10.0 & 17.1 Hz, 1H), 4.95 (t, J = 6.3 Hz, 1H), 4.25 (t, J = 17.1 Hz, 1H), 4.86 (dd, J = 1.2 & 10.2 Hz, 1H), 3.04 (m, 1H), 2.95 (m, 1H), 2.50 (m, 1H), 2.41 (s, 3H), 1.87 (m, 1H), 1.56 (m, 1H); ¹³C {¹H}-NMR (CDCl₃, 100 MHz) δ = 143.3 (C), 137.5 (CH), 137.1 (C), 136.1 (6 x CH), 133.3 (3 x C), 129.7 (5 x CH), 127.9 (6 x CH), 127.1 (2 x CH), 115.8 (CH₂), 42.6 (CH₃), 29.4 (CH), 29.2 (CH₃), 21.5 (CH₃); HRMS (ESI⁺): m/z [M+Na⁺] calcd. for C₃₀H₃₁NO₂NaSiS: 520.1742; found: 520.1744.

N-(3-(triphenylsilyl)pent-4-en-1-yl) methanesulfonamide (6b)

Following the general procedure 2.2, to a solution of tosylate 18 (0.500 g, 1.00 mmol, 1.0 equiv.) in 4.0 mL of dry DMF (0.25 M) were added MsNH₂ (0.190 g, 2.00 mmol, 2.0 equiv.) and Cs₂CO₃ (0.488 g, 1.50 mmol, 1.5 equiv.) to obtain 0.371 g of mesylamide 6a as a white amorphous solid (0.88 mmol, 88% yield).

Rf = 0.51 (n-hexane/EtOAc 60:40); ¹H-NMR (CDCl₃, 400 MHz) δ = 7.57 (m, 6H), 7.46-7.34 (m, 9H), 5.73 (dt, J = 9.9 & 17.1 Hz, 1H), 5.03 (m, 2H), 4.36 (brt, J = 6.2 Hz, 1H), 3.24 (m, 1H), 3.10 (m, 1H), 2.86 (s, 3H), 2.63 (m, 1H), 2.00 (m, 1H), 1.74 (m, 1H); ¹³C {¹H}-NMR (CDCl₃, 125 MHz) δ = 137.6 (CH), 136.1 (6 x CH), 133.2 (3 x C), 129.7 (3 x CH), 127.9 (6 x CH), 116.0 (CH₃), 42.6 (CH₃), 40.3 (CH₃), 29.6 (CH₃), 29.5 (CH); HRMS (ESI⁺): m/z [M+Na⁺] calcd. for C₂₄H₂₇NO₂NaSiS: 444.1429; found: 444.1429.

3-(triphenylsilyl)pent-4-enoic acid (precursor of 19)

To a solution of bis-homoallylic alcohol 17 (0.250 g, 0.73 mmol, 1.0 equiv.) in 2.4 mL of dry DMF (0.3 M) at room temperature under inert atmosphere was added PDC (1.37 g, 3.65 mmol, 5.0 equiv.) and a small amount of MgSO₄. The reaction mixture was stirred overnight. Then, it was filtered through a pad of Celite. Water was added and aqueous phase was extracted with 3 x EtOAc. The combined organic layers were dried over anhydrous MgSO₄, filtered through a pad of silica, and concentrated under reduced pressure. This crude reaction was used in the next step without further purification.

Ethyl 3-(triphenylsilyl)pent-4-enoate (19)
To a solution of the previous carboxylic acid crude (0.56 mmol, 1.0 equiv.) in 2.8 mL of dry EtOH (0.2 M) at room temperature was added TMSCI (0.16 mL, 1.23 mmol, 2.2 equiv.) to afford 155 mg of bis-homoallylic ester 19 as a pale yellow oil (0.40 mmol, 71% yield in two steps).

\[ R_f = 0.64 \ (n\text{-hexane/EtOAc 90:10}) \]

\( ^1H\text{-NMR (CDCl}_3, 400 \text{ MHz}) \) \( \delta = 7.58 \) (dd, \( J = 7.7 \) & 13 Hz, 6H), 7.39 (m, 9H), 5.86 (ddd, \( J = 17.3, 10.5 \) & 8.1 Hz, 1H), 4.95 (m, 2H), 4.08 (q, \( J = 7.1 \) Hz, 2H), 3.14 (m, 1H), 2.68 (dd, \( J = 15.7 \) & 2.8 Hz, 1H), 2.49 (dd, \( J = 15.7 \) & 12.2 Hz, 1H), 1.20 (t, \( J = 7.1 \) Hz, 3H); \( ^1C[^1H]\text{-NMR (CDCl}_3, 100 \text{ MHz}) \) \( \delta = 173.0 \) (C), 137.2 (CH), 136.1 (6 x CH), 133.1 (3 x C), 129.7 (3 x CH), 127.9 (6 x CH), 114.7 (CH), 60.4 (CH), 34.5 (CH), 28.0 (CH), 14.2 (CH); \( \text{HRMS (ESI)}^+ \): m/z [M+Na]^+ calcd. for C_{26}H_{30}O_3NaSi: 498.1913; found: 498.1912.

\[ \text{Ethyl 2-methyl-3-(triphenylsilyl)pent-4-enoate (20a)} \]

Following the general procedure 2.3, to a solution of i-Pr_NH (0.77 mmol, 2.0 equiv.) in 6.1 mL of dry THF (0.94 M), were added n-BuLi 2.5 M in hexane (2.2 mL, 5.46 mmol, 2.5 equiv.), ester 19 (1.06 g, 2.73 mmol, 1.0 equiv.) in 1.2 mL of dry THF and iodomethane (0.45 mL, 7.37 mmol, 2.7 equiv.) in 1.6 mL of dry THF to obtain 0.941 g of \( \alpha \)-methyl ester 20a as a white amorphous solid (2.32 mmol, 85% yield).

\[ R_f = 0.71 \ (n\text{-hexane/EtOAc 90:10}) \]

\( ^1H\text{-NMR (CDCl}_3, 500 \text{ MHz}) \) \( \delta = 7.61 \) (m, 6H), 7.44-7.39 (m, 3H), 7.39-7.33 (m, 6H), 5.82 (dt, \( J = 16.9 \) & 10.4 Hz, 1H), 5.00 (m, 2H), 3.89 (m, 1H), 3.78 (m, 1H), 3.11 (dd, \( J = 10.8 \) & 5.4 Hz, 1H), 2.93 (m, 1H), 1.15 (t, \( J = 7.1 \) Hz, 3H), 1.06 (d, \( J = 7.1 \) Hz, 3H); \( ^1C[^1H]\text{-NMR (CDCl}_3, 125 \text{ MHz}) \) \( \delta = 175.8 \) (C), 136.4 (6 x CH), 134.9 (CH), 133.7 (3 x C), 129.5 (3 x CH), 127.8 (6 x CH), 117.4 (CH), 60.2 (CH), 39.5 (CH), 35.4 (CH), 15.1 (CH), 14.2 (CH); \( \text{HRMS (ESI)}^+ \): m/z [M+Na]^+ calcd. for C_{26}H_{30}O_3NaSi: 423.1756; found: 423.1729.

\[ \text{Ethyl 2-allyl-3-(triphenylsilyl)pent-4-enoate (20b)} \]

Following the general procedure 2.3, to a solution of i-Pr_NH (0.46 mL, 3.23 mmol, 2.5 equiv.) in 3.4 mL of dry THF (0.94 M), were added n-BuLi 2.5 M in hexane (1.3 mL, 3.23 mmol, 2.5 equiv.), ester 19 (0.50 g, 1.29 mmol, 1.0 equiv.) in 0.6 mL of dry THF and allyl iodide (0.36 mL, 3.87 mmol, 3.0 equiv.) in 0.8 mL of dry THF to afford 0.443 g of \( \alpha \)-allyl ester 20b as a pale yellow oil (1.04 mmol, 85% yield).

\[ R_f = 0.55 \ (n\text{-hexane/EtOAc 90:10}) \]

\( ^1H\text{-NMR (CDCl}_3, 400 \text{ MHz}) \) \( \delta = 7.62 \) (dd, \( J = 7.8 \) & 1.3 Hz, 6H), 7.38 (m, 9H), 5.75 (dt, \( J = 16.9 \) & 10.5 Hz, 1H), 5.60 (ddt, \( J = 17.0, 10.2 \) & 6.9 Hz, 1H), 5.03 (dd, \( J = 10.1 \) & 1.5 Hz, 1H), 4.97 (dd, \( J = 17.0 \) & 1.0 Hz, 1H), 4.90-4.80 (m, 2H), 3.75 (dq, \( J = 10.8 \) & 7.1 Hz, 1H), 3.56 (dq, \( J = 14.3 \) & 7.1 Hz, 1H), 3.00 (dd, \( J = 10.8 \) & 6.7 Hz, 1H), 2.84 (dd, \( J = 10.9, 6.9 \) & 3.2 Hz, 1H), 2.33 (m, 1H), 2.16 (m, 1H), 1.09 (t, \( J = 7.1 \) Hz, 3H); \( ^1C[^1H]\text{-NMR (CDCl}_3, 100 \text{ MHz}) \) \( \delta = 174.3 \) (C), 136.4 (6 x CH), 135.8 (CH), 135.3 (CH), 135.3 (3 x C), 129.5 (3 x CH), 127.7 (6 x CH), 117.5 (CH), 116.3 (CH), 60.0 (CH), 45.4 (CH), 35.2 (CH), 34.8 (CH), 14.1 (CH); \( \text{HRMS (ESI)}^+ \): m/z [M+Na]^+ calcd. for C_{26}H_{30}O_2NaSi: 449.1913; found: 449.1913.

2-methyl-3-(triphenylsilyl)pent-4-en-1-ol (21a)
Following the general procedure 2.4, to the solution of α-methyl ester 20a (1.01 g, 2.53 mmol, 1.0 equiv.) in 42 mL of dry Et₂O (0.06M) was added LiAlH₄ (0.192 g, 5.06 mmol, 2.0 equiv.) to give 0.878 g of alcohol 21a as a white amorphous solid (2.45 mmol, 97% yield).

Rf = 0.37 (n-hexane/EtOAc 80:20); 1H-NMR (CDCl₃, 500 MHz)  δ = 7.60 (m, 6H), 7.44–7.33 (m, 9H), 5.91 (dt, J = 10.7 & 16.5 Hz, 1H), 5.04 (m, 1H), 5.01 (m, 1H), 3.48 (m, 2H), 2.93 (dd, J = 2.8 & 11.0 Hz, 1H), 2.22 (m, 1H), 1.32 (brs, 1H), 0.75 (d, J = 7.2 Hz, 3H); 13C[1H]-NMR (CDCl₃, 125 MHz) δ = 136.3 (6 x CH), 134.3 (3 x CH), 129.4 (3 x CH), 127.8 (6 x CH), 117.2 (CH₃), 67.7 (CH₂), 35.2 (CH), 33.9 (CH), 14.0 (CH₃); HRMS (ESI⁺): m/z [M+Na⁺] calcd. for C₁₆H₁₄ONaSi: 381.1651; found: 381.1658.

2-allyl-3-(triphenylsilyl)pent-4-en-1-ol (21b)

Following the general procedure 2.4, to the solution of α-allyl ester 20b (0.890 g, 2.09 mmol, 1.0 equiv.) in 35 mL of dry Et₂O (0.06M) was added LiAlH₄ (0.158 g, 4.17 mmol, 2.0 equiv.) to obtain 0.657 g of alcohol 21b as a colorless oil (1.71 mmol, 82% yield).

Rf = 0.38 (n-hexane/EtOAc 80:20); 1H-NMR (CDCl₃, 500 MHz)  δ = 7.61 (dd, J = 7.6 & 1.5 Hz, 6H), 7.38 (m, 9H), 5.89 (m, 1H), 5.59 (m, 1H), 5.05 (m, 2H), 4.88 (dd, J = 10.1 Hz, 1H), 4.81 (dd, J = 17.0 & 1.0 Hz, 1H), 3.63 (dt, J = 10.9 & 4.5 Hz, 1H), 3.48 (dt, J = 10.8 & 7.4 Hz, 1H), 3.04 (dd, J = 11.1 & 3.1 Hz, 1H), 2.13 (m, 1H), 2.04 (m, 1H), 1.83 (m, 1H), 1.33 (dd, J = 7.0 & 4.8 Hz, 1H); 13C[1H]-NMR (CDCl₃, 100 MHz) δ = 137.2 (CH), 136.3 (6 x CH), 135.8 (CH), 134.2 (3 x C), 129.5 (3 x CH), 127.8 (6 x CH), 117.4 (CH₃), 65.0 (CH₂), 40.5 (CH), 33.8 (CH), 33.5 (CH₃); HRMS (ESI⁺): m/z [M+Na⁺] calcd. for C₁₆H₁₄ONaSi: 407.1807; found: 407.1815.

2-methyl-3-(triphenylsilyl)pent-4-en-1-yl 4-methylbenzenesulfonate (22a)

Following the general procedure 2.1, to the solution of alcohol 21a (0.880 g, 2.45 mmol, 1.0 equiv.) in 25 mL of dry DCM (0.1 M) were added Et₃N (0.68 mL, 4.90 mmol, 2.0 equiv.), TsCl (0.701 g, 3.68 mmol, 1.5 equiv.) and a small amount of DMAP to give 1.09 g of tosylate 22a as a white amorphous solid (2.13 mmol, 87% yield).

Rf = 0.67 (n-hexane/EtOAc 90:10); 1H-NMR (CDCl₃, 500 MHz)  δ = 7.34 (d, J = 8.3 Hz, 2H), 7.54 (m, 6H), 7.41 (m, 3H), 7.34–7.28 (m, 8H), 5.72 (dt, J = 17.2 & 10.6 Hz, 1H), 4.97 (dd, J = 10.1 & 1.7 Hz, 1H), 4.86 (dd, J = 16.8 & 1.7 Hz, 1H), 3.86 (m, 1H), 3.74 (dd, J = 9.2 & 6.2 Hz, 1H), 2.75 97 (dd, J = 11.1 & 2.4 Hz, 1H), 2.44 (s, 3H), 2.40 (m, 1H), 0.66 (d, J = 7.0 Hz, 3H); 13C[1H]-NMR (CDCl₃, 125 MHz) δ = 144.6 (C), 136.2 (6 x CH), 133.8 (3 x C), 133.3 (CH), 133.1 (C), 129.8 (2 x CH), 129.6 (3 x CH), 127.9 (2 x CH), 127.8 (6 x CH), 118.5 (CH₃), 74.1 (CH₂), 32.3 (CH), 32.7 (CH), 21.7 (CH₃), 13.7 (CH₃); HRMS (ESI⁺): m/z [M+Na⁺] calcd. for C₂₀H₁₄OSNaSi: 535.1739; found: 535.1745.

2-allyl-3-(triphenylsilyl)pent-4-en-1-yl 4-methylbenzenesulfonate (22b)
Following the general procedure 2.1, to the solution of alcohol 21b (0.625 g, 1.63 mmol, 1.0 equiv.) in 16 mL of dry DCM (0.1 M) were added Et₃N (0.57 mL, 4.08 mmol, 2.5 equiv.), TsCl (0.465 g, 2.44 mmol, 1.5 equiv.) and a small amount of DMAP to afford 0.754 g of tosylate 22b as a white amorphous solid (1.40 mmol, 86% yield).

Rₚ = 0.50 (n-hexane/EtOAc 80:20); ¹H-NMR (CDCl₃, 400 MHz)  δ = 7.74 (d, J = 8.2 Hz, 2H), 7.56 (m, 6H), 7.44-7.29 (m, 1H), 5.67 (dt, J = 17.0 & 10.6 Hz, 1H), 5.38 (m, 1H), 4.99 (dd, J = 10.0 & 1.6 Hz, 1H), 4.84 (m, 2H), 4.70 (dd, J = 17.0 & 0.8 Hz, 1H), 3.93 (dd, J = 9.4 & 4.2 Hz, 1H), 3.85 (t, J = 9.2 Hz, 1H), 2.88 (dd, J = 11.2 & 6.2 Hz, 1H), 2.45 (s, 3H), 2.29 (m, 1H), 1.95 (m, 1H), 1.60 (m, 1H); ¹³C¹H]-NMR (CDCl₃, 100 MHz)  δ = 144.5 (C), 136.2 (6 x CH), 135.4 (CH), 133.7 (CH), 133.6 (3 x C), 129.7 (2 x CH), 129.6 (3 x CH), 127.9 (2 x CH), 127.8 (6 x CH), 118.8 (CH₃), 116.9 (CH₃), 71.1 (CH₂), 37.5 (CH), 32.4 (CH₃), 32.3 (CH), 21.6 (CH₃); HRMS (ESI⁺): m/z [M+Na]⁺ calcd. for C₃₅H₃₈O₇N: 561.1906; found: 561.1900.

4-methyl-N-(2-methyl-3-(triphenylsilyl)pent-4-en-1-yl)benzenesulfonylamine (9a)

Following the general procedure 2.2, to a solution of tosylate 22a (1.09 g, 2.13 mmol, 1.0 equiv.) in 11 mL of dry DMF (0.2 M) were added TsNH₂ (0.729 g, 4.26 mmol, 2.0 equiv.) and Cs₂CO₃ (1.04 g, 3.20 mmol, 1.5 equiv.) to obtain 0.732 g of tosylamine 9a as a white amorphous solid (1.43 mmol, 67% yield).

Rₚ = 0.55 (n-hexane/EtOAc 90:10); ¹H-NMR (CDCl₃, 400 MHz)  δ = 7.65 (d, J = 8.1 Hz, 2H), 7.52 (m, 6H), 7.43-7.38 (m, 3H), 7.37-7.31 (m, 6H), 7.23 (d, J = 8.0 Hz, 2H), 5.80 (dt, J = 17.1 & 10.6 Hz, 1H), 5.00 (dd, J = 10.0 & 1.7 Hz, 1H), 4.92 (dd, J = 16.9 & 1.4 Hz, 1H), 4.27 (brt, J = 6.5 Hz, 1H), 2.85 (m, 1H), 2.7-2.72 (dd, J = 12.5 & 6.3 Hz, 1H), 2.72-2.68 (dd, J = 11.1 & 2.7 Hz, 1H), 2.40 (s, 3H), 2.13 (m, 1H), 0.72 (d, J = 6.9 Hz, 3H); ¹³C¹H]-NMR (CDCl₃, 100 MHz)  δ = 143.2 (C), 137.1 (C), 136.2 (6 x CH), 134.2 (CH), 133.9 (3 x C), 129.6 (2 x CH), 129.5 (3 x CH), 127.8 (6 x CH), 127.0 (2 x CH), 117.9 (CH₃), 49.0 (CH₂), 34.8 (CH), 32.9 (CH), 21.5 (CH₃), 15.4 (CH₃); HRMS (ESI⁺): m/z [M-H]⁻ calcd. for C₃₅H₃₈O₇N: 510.1923; found: 510.1925.

N-(2-allyl-3-(triphenylsilyl)pent-4-en-1-yl)-4-methylbenzenesulfonylamine (9b)

Following the general procedure 2.2, to a solution of tosylate 22b (0.400 g, 0.74 mmol, 1.0 equiv.) in 3.7 mL of dry DMF (0.2 M) were added TsNH₂ (0.254 g, 1.48 mmol, 2.0 equiv.) and Cs₂CO₃ (0.362 g, 1.11 mmol, 1.5 equiv.) to give 0.231 g of tosylamine 9b as a white amorphous solid (0.43 mmol, 58% yield).

Rₚ = 0.45 (n-hexane/EtOAc 80:20); ¹H-NMR (CDCl₃, 500 MHz)  δ = 7.63 (d, J = 8.2 Hz, 2H), 7.54 (m, 5H), 7.41 (m, 3H), 7.35 (m, 7H), 7.23 (d, J = 8.0 Hz, 2H), 5.77 (dt, J = 16.9 & 10.5 Hz, 1H), 5.45 (m, 1H), 5.02 (dd, J = 9.0 & 1.4 Hz, 1H), 4.95 (d, J = 16.9 Hz, 1H), 4.87 (d, J = 10.1 Hz, 1H), 4.75 (d, J = 17.1 Hz, 1H), 4.35 (dd, J = 7.1 & 6.0 Hz, 1H), 2.86 (m, 3H), 2.40 (s, 3H), 2.03 (m, 2H), 1.73 (m, 1H); ¹³C¹H]-NMR (CDCl₃, 100 MHz)  δ = 143.2 (C), 136.9 (CH), 136.4 (5 x CH), 136.2 (C), 134.9 (CH), 133.7 (3 x C), 132.5 (C), 130.8 (3 x CH), 129.9 (2 x CH), 127.3 (6 x CH), 126.9 (2 x CH), 116.1 (CH₂), 114.4 (CH₃), 40.0 (CH₂), 37.5 (CH₂), 32.5 (CH), 21.6 (CH₃); HRMS (ESI⁺): m/z [M+Na]⁺ calcd. for C₃₅H₃₈O₇N: 510.1923; found: 510.1925.
129.6 (5 x CH), 127.9 (7 x CH), 127.0 (2 x CH), 118.1 (CH$_2$), 116.8 (CH$_2$), 45.8 (CH$_2$), 38.0 (CH), 34.3 (CH), 34.2 (CH$_2$), 21.5 (CH$_3$); **HRMS (ESI$^+$):** $m/z$ [M+Na]$^+$ calcd. for C$_{33}$H$_{35}$NO$_2$NaSi: 560.2055; found: 560.2056.
3. NMR spectra

\(^1\text{H}-\text{NMR (CDCl}_3, 400 \text{ MHz)}\)

\(^{13}\text{C-}{\text{H}}-\text{NMR (CDCl}_3, 125 \text{ MHz)}\)
$^1$H-NMR (CDCl$_3$, 500 MHz)

$^{13}$C-$^1$H-NMR (CDCl$_3$, 125 MHz)
$^{1}$H-NMR (CDCl$_3$, 400 MHz)

$^{1}$C{[H]}-NMR (CDCl$_3$, 100 MHz)
$^1$H-NMR (CDCl$_3$, 400 MHz)

$^{13}$C-NMR (CDCl$_3$, 100 MHz)
$^1$H-NMR (CDCl$_3$, 400 MHz)

$^{13}$C-$^1$H-NMR (CDCl$_3$, 125 MHz)
$^1$H-NMR (CDCl$_3$, 400 MHz)

$^{13}$C-NMR (CDCl$_3$, 125 MHz)
$^{1}H$-NMR (CDCl$_3$, 400 MHz)

$^{13}C$-$^{1}H$-NMR (CDCl$_3$, 100 MHz)
$^1$H-GOESY NMR (CDCl$_3$, 500 MHz)
$^1$H-NMR (CDCl$_3$, 400 MHz)

$^{13}$C{H}-NMR (CDCl$_3$, 100 MHz)
$^1$H-NMR (CDCl$_3$, 400 MHz)

$^{13}$C-$^1$H-NMR (CDCl$_3$, 100 MHz)
$^1$H-NMR (CDCl$_3$, 400 MHz)

$^{13}$C$\{^1$H$\}$-NMR (CDCl$_3$, 100 MHz)
$^1$H-NMR (CDCl$_3$, 400 MHz)

$^{13}$C-$^1$H-NMR (CDCl$_3$, 125 MHz)
$^1$H-NMR (CDCl$_3$, 400 MHz)

$^{13}$C{H}-NMR (CDCl$_3$, 125 MHz)
$^1$H-NMR (CDCl$_3$, 500 MHz)

$^{13}$C-$^1$H-NMR (CDCl$_3$, 125 MHz)
$^1$H-NMR (CDCl$_3$, 400 MHz)

$^{13}$C-NMR (CDCl$_3$, 100 MHz)

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$^1$H-NMR (CDCl$_3$, 400 MHz)

$^{13}$C{H}-NMR (CDCl$_3$, 100 MHz)
$^1$H-NMR (CDCl$_3$, 500 MHz)

$^{13}$C-$^1$H-NMR (CDCl$_3$, 125 MHz)
$^1$H-NMR (CDCl$_3$, 400 MHz)

$^{13}$C-$^1$H-NMR (CDCl$_3$, 100 MHz)
$^1$H-NMR (CDCl$_3$, 500 MHz)

$^{13}$C$^1$H-NMR (CDCl$_3$, 125 MHz)
$^1$H-NMR (CDCl$_3$, 400 MHz)

$^{13}$C$\{^1$H$\}$-NMR (CDCl$_3$, 100 MHz)
$^1$H-NMR (CDCl$_3$, 500 MHz)

$^{13}$C{$_^1$H}-NMR (CDCl$_3$, 125 MHz)

$^{13}$C[$_^1$H]-NMR (CDCl$_3$, 125 MHz)
$^1$H-NMR (CDCl$_3$, 400 MHz)

$^{13}$C-$^1$H-NMR (CDCl$_3$, 100 MHz)
$^1$H-NMR (CDCl$_3$, 500 MHz)

$^{13}$C{$_^1$H}-NMR (CDCl$_3$, 100 MHz)

$^{13}$C-NMR (CDCl$_3$, 100 MHz)
$^1$H-NMR (CDCl$_3$, 400 MHz)

$^{13}$C$[^1]$H-NMR (CDCl$_3$, 100 MHz)
$^1$H-NMR (CDCl$_3$, 500 MHz)

$^{13}$C{H}-NMR (CDCl$_3$, 100 MHz)
$^1$H-NMR (CDCl$_3$, 500 MHz)

$^{13}$C-{^1}H-NMR (CDCl$_3$, 100 MHz)
$^1$H-NMR (CDCl$_3$, 500 MHz)

$^{13}$C{$_^1$H} - NMR (CDCl$_3$, 125 MHz)

$^{13}$C{$_^1$H}-NMR (CDCl$_3$, 125 MHz)
4. Computational details

All the calculations reported in this paper were obtained with the Gaussian 09 suite of programs. All species were optimized using the B3LYP functional in conjunction with the D3 dispersion correction suggested by Grimme et al. using the standard double-ζ quality def2-SVP basis sets for all atoms. Solvents effects were taken into account during the geometry optimizations using the polarizable continuum model (PCM). All stationary points were characterized by frequency calculations. Reactants and products have positive definite Hessian matrices, whereas transition structures show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the intrinsic reaction coordinate (IRC) method. Compounds involving iron(III) were computed using a high-spin (S = 5/2) configuration. Single-point energy refinements were carried out at the same DFT level the much larger triple-ζ quality def2-TZVPP basis sets. This level is denoted PCM(CH2Cl2)-B3LYP-D3/def2-TZVPP//PCM(CH2Cl2)-B3LYP-D3/def2-SVP.

4.1. Cartesian coordinates (in Å) and electronic energies (in a.u.) of all the stationary points discussed in the text. All calculations have been performed at the PCM(CH2Cl2)-B3LYP-D3/def2-TZVPP//PCM(CH2Cl2)-B3LYP-D3/def2-SVP.

13: E = -10964.6881364

|  |  |  |  |
|---|---|---|---|
| C | -0.933151000 | -2.328487000 | -1.661519000 |
| C | -1.249596000 | -1.684856000 | -0.528912000 |
| C | -1.808061000 | -0.296116000 | -0.395181000 |
| C | 1.384590000 | 0.683429000 | 0.135553000 |
| C | -1.583098000 | 0.637057000 | -1.597413000 |
| C | -0.115376000 | 1.003567000 | -1.840939000 |
| H | -1.045065000 | -1.871848000 | -2.649098000 |
| H | -1.114947000 | -2.222516000 | 0.417015000 |
| H | -1.344042000 | 0.166917000 | 0.494017000 |
| H | -1.987932000 | 0.187565000 | -2.518826000 |
| H | 1.091383000 | -0.347949000 | -0.104579000 |
| H | -0.551199000 | -3.352426000 | -1.635938000 |
| H | -2.136858000 | 1.575861000 | -1.450163000 |
| H | 0.467672000 | 0.122117000 | -2.144210000 |
| H | -0.041771000 | 1.736057000 | -2.655691000 |
| N | 0.543953000 | 1.546175000 | -0.628877000 |
| S | 0.328432000 | 3.193337000 | -0.260232000 |
| C | 1.941610000 | 3.193337000 | -0.260232000 |
| H | 2.181007000 | 3.850346000 | -1.595150000 |
| H | 1.852070000 | 4.981818000 | -0.224850000 |
| H | 2.680625000 | 3.402983000 | 0.088746000 |
| Element | X      | Y      | Z     |
|---------|--------|--------|-------|
| O       | 0.003588000 | 3.330446000 | 1.164766000 |
| O       | -0.602867000 | 3.707250000 | -1.267802000 |
| C       | 1.438293000 | 0.862703000 | 1.640309000 |
| H       | 2.027453000 | 0.049403000 | 2.084372000 |
| H       | 1.884562000 | 1.821387000 | 1.928211000 |
| H       | 0.419888000 | 0.821391000 | 2.045587000 |
| Si      | -3.669856000 | -0.346909000 | 0.076025000 |
| C       | -3.918124000 | -1.496776000 | 1.555794000 |
| C       | -5.098634000 | -2.248703000 | 1.712232000 |
| C       | -2.955545000 | -1.563156000 | 2.583419000 |
| C       | -5.309101000 | -3.039979000 | 2.847060000 |
| H       | -5.868105000 | -2.220443000 | 0.935660000 |
| C       | -3.158909000 | -2.353897000 | 3.718457000 |
| H       | -2.028022000 | -0.987539000 | 2.507814000 |
| C       | -4.338330000 | -3.095373000 | 3.852353000 |
| H       | -6.233271000 | -3.615744000 | 2.945842000 |
| H       | -2.396276000 | -2.390869000 | 4.500877000 |
| H       | -4.499730000 | -3.714507000 | 4.738731000 |
| C       | -4.198738000 | 1.404624000 | 0.558421000 |
| C       | -5.559803000 | 1.770986000 | 0.573179000 |
| C       | -3.256044000 | 2.371655000 | 0.957371000 |
| C       | -5.960381000 | 3.054013000 | 0.960288000 |
| H       | -6.323240000 | 1.046614000 | 0.273678000 |
| C       | -3.648757000 | 3.658499000 | 1.337654000 |
| H       | -2.189584000 | 2.144721000 | 0.973859000 |
| C       | -5.003872000 | 4.003553000 | 1.339564000 |
| H       | -7.021986000 | 3.315655000 | 0.962126000 |
| H       | -2.885251000 | 4.386674000 | 1.622919000 |
| H       | -5.315707000 | 5.009080000 | 1.634477000 |
| C       | -4.644879000 | -0.957277000 | -1.417237000 |
| C       | -4.710248000 | -2.335229000 | -1.709905000 |
| C       | -5.234543000 | -0.060874000 | -2.330600000 |
| C       | -5.349380000 | -2.800646000 | -2.863418000 |
| H       | -4.256469000 | -3.058344000 | -1.027031000 |
| C       | -5.874607000 | -0.521546000 | -3.486225000 |
| H       | -5.196390000 | 1.014887000 | -2.138953000 |
| C       | -5.934888000 | -1.893341000 | -3.753700000 |
| H       | -5.390531000 | -3.873545000 | -3.068577000 |
| H       | -6.328153000 | 0.192312000 | -4.179055000 |
| H       | -6.437098000 | -2.253999000 | -4.654765000 |
| O       | 2.792574000 | 0.821565000 | -0.368849000 |
| H       | 2.760051000 | 1.042147000 | -1.316773000 |
| Fe      | 4.292960000 | -0.541196000 | -0.017732000 |
| Br      | 5.641016000 | -0.189623000 | -1.900541000 |
| Br      | 3.124373000 | -2.586280000 | 0.001995000 |
| Br      | 5.201937000 | 0.117443000 | 2.041109000 |

14: E= -1902.1060825
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H  2.661076000  -0.870376000  -2.977952000
H  2.494098000  0.737261000  -2.255636000
N  3.269427000  -0.715328000  -0.978560000
S  3.779328000  0.662568000  0.173164000
C  5.521043000  0.788410000  -0.185969000
H  5.623196000  1.023320000  -0.235950000
H  5.877334000  1.619591000  0.439755000
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N  3.269427000  -0.715328000  -0.978560000
S  3.779328000  0.662568000  0.173164000
C  5.521043000  0.788410000  -0.185969000
H  5.623196000  1.023320000  -0.235950000
H  5.877334000  1.619591000  0.439755000
H  6.019536000  0.870376000  -0.870376000
Si -1.287367000  0.101041000  0.047078000
C -1.580684000  0.290337000  1.901017000
C -2.848330000  0.054610000  2.467850000
C -0.552004000  0.742778000  2.752450000
C -3.081032000  0.256023000  3.831706000
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H -4.073083000  0.064732000  4.249214000
H -0.034621000  1.293101000  4.758787000
S -1.265635000 -3.418989000  0.729538000
C  1.487796000 -2.579779000  0.125817000
C  1.035929000 -1.346273000  0.571090000
C  0.584867000 -0.274538000  -0.703535000
C  3.308640000 -1.912829000  -0.557436000
C  0.858507000 -0.435319000  -1.796355000
C  2.361515000 -0.330183000  -2.154914000
H  1.733693000 -3.344723000  0.865061000
H  1.132750000 -1.114025000  1.635764000
H  0.966705000  0.680203000  0.111221000
H  0.437786000 -1.391201000 -2.140709000

TS(14-15):  \[ E = -1902.0943715 \]
|  | x         | y          | z            |
|---|-----------|------------|--------------|
| H | 3.226243000 | -2.605303000 | -1.390436000 |
| H | 1.140623000 | -2.952559000 | -0.839931000 |
| H | 0.321145000 | 0.342720000  | -2.355714000 |
| H | 2.636005000 | -1.037371000 | -2.951308000 |
| H | 2.603997000 | 0.674617000  | -2.514880000 |
| N | 3.255970000 | -0.613974000 | -1.004264000 |
| S | 3.640775000 | 0.748921000  | 0.034363000  |
| C | 5.408520000 | 0.909088000  | -0.148012000 |
| H | 5.627309000 | 1.054698000  | -1.213236000 |
| H | 5.680623000 | 1.797910000  | 0.438264000  |
| H | 2.636005000 | -1.037371000 | -2.951308000 |
| H | 0.321145000 | 0.342720000  | -2.355714000 |
| N | 3.255970000 | -0.613974000 | -1.004264000 |
| S | 3.640775000 | 0.748921000  | 0.034363000  |
| C | 5.408520000 | 0.909088000  | -0.148012000 |
| H | 5.627309000 | 1.054698000  | -1.213236000 |
| H | 5.680623000 | 1.797910000  | 0.438264000  |
| H | 2.636005000 | -1.037371000 | -2.951308000 |
| H | 0.321145000 | 0.342720000  | -2.355714000 |

7: E= -917.5074536
Br₃Fe···OHSiPh₃: E = -10047.2199483

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15': E= -10964.6721859
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