Supporting Information

Oxidant-Directed Chemoselective Sulfonylation and Sulfonyloximation of Alkenes via Cleaving C-S Bond in TosMIC

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1. General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Unless otherwise noted, all reactions were carried out under air using undistilled solvent, without the need of precautions to exclude air and moisture. Melting points were recorded on an Electrothermal digital melting point apparatus. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. $^1$H, $^{19}$F, and $^{13}$C NMR spectra were recorded in CDCl$_3$ or DMSO-$d_6$ on Bruker Avance or Joel 400 MHz spectrometers. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. High resolution mass spectra (HRMS) were obtained using a commercial apparatus (ESI or EI Source). Column chromatography was generally performed on silica gel (300-400 mesh) or alkali alumina (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions.

2. General procedures for the synthesis of vinyl sulfones 3 or allyl sulfones 4

A solution of alkene 1 (0.6 mmol, 2 equiv), 1-((isocyanomethyl)sulfonyl)-4-methylbenzene (2a; 59 mg, 0.3 mmol, 1 equiv), $N,N'$-bis(salicylidene)ethylenediamine cobalt(II) (10 mg, 0.03 mmol, 0.1 equiv), perfluorobutyl iodide (166 mg, 0.48 mmol, 1.6 equiv), Na$_2$CO$_3$ (127 mg, 1.2 mmol, 4 equiv), and tert-butyl hydroperoxide (142 mg, 1.1 mmol, 3.67 equiv, TBHP, 70% solution in H$_2$O) in THF (1.5 mL) was stirred under air atmosphere at 70 °C (oil bath) for 24 h. The reaction was then quenched by saturated NaHSO$_3$ solution (20 mL) and diluted with EtOAc (20 mL). The organic layer was separated and washed with saturated brine twice, dried over MgSO$_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (20/1~6/1) as eluent to afford the pure product vinyl sulfone 3 or allyl sulfone 4.

3. General procedures for the synthesis of α-sulfonylethanone oximes 5

A solution of alkene 1 (0.6 mmol, 2 equiv), 1-((isocyanomethyl)sulfonyl)-4-methylbenzene (2a; 59 mg, 0.3 mmol, 1 equiv), $N,N'$-bis(salicylidene)ethylenediamine cobalt(II) (10 mg, 0.03 mmol, 0.1 equiv), perfluorobutyl iodide (166 mg, 0.48 mmol, 1.6 equiv), Na$_2$CO$_3$ (127 mg, 1.2 mmol, 4 equiv), and tert-butyl nitrite (114 mg, 1.1 mmol, 3.67 equiv, TBN) in THF (1.5 mL) was stirred under air atmosphere at 70 °C (oil bath) for 24 h. The reaction was then quenched by saturated NaHSO$_3$ solution (20 mL) and diluted with EtOAc (20 mL). The organic layer was separated and washed with saturated brine twice, dried over MgSO$_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (20/1~6/1) as eluent to afford the pure product vinyl sulfone 3 or allyl sulfone 4.
ether/ethyl acetate (20/1–3/1) as eluent to afford the pure product α-sulfonylethanone oxime 5.

4. 10 mmol scale synthesis of (E)-1-methyl-4-(styrylsulfonyl)benzene (3a)

A solution of styrene (1a; 2.08 g, 20 mmol, 2 equiv), 1-((isocyanomethyl)sulfonyl)-4-methylbenzene (2a; 1.95 g, 10 mmol, 1 equiv), N,N'-bis(salicylidene)ethylenediamine cobalt(II) (0.33 g, 1 mmol, 0.1 equiv), perfluorobutyl iodide (5.53 g, 16 mmol, 1.6 equiv), Na₂CO₃ (4.23 g, 40 mmol, 4 equiv), and tert-butyl hydroperoxide (4.73 g, 36.7 mmol, 3.67 equiv, TBHP, 70% solution in H₂O) in THF (50 mL) was stirred under air atmosphere at 70 °C (oil bath) for 36 h. The reaction was then quenched by saturated NaHSO₃ solution (200 mL) and diluted with EtOAc (200 mL). The organic layer was separated and washed with saturated brine twice, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (20/1~3/1) as eluent to afford the pure product (E)-1-methyl-4-(styrylsulfonyl)benzene (3a) in 46% yield (1.19 g).

5. 10 mmol scale synthesis of 1-phenyl-2-tosylethan-1-one oxime (5a)

A solution of styrene (1a; 2.08 g, 20 mmol, 2 equiv), 1-((isocyanomethyl)sulfonyl)-4-methylbenzene (2a; 1.95 g, 10 mmol, 1 equiv), N,N'-bis(salicylidene)ethylenediamine cobalt(II) (0.33 g, 1 mmol, 0.1 equiv), perfluorobutyl iodide (5.53 g, 16 mmol, 1.6 equiv), Na₂CO₃ (4.23 g, 40 mmol, 4 equiv), and tert-butyl nitrite (3.79 g, 36.7 mmol, 3.67 equiv, TBN) in THF (50 mL) was stirred under air atmosphere at 70 °C (oil bath) for 36 h. The reaction was then quenched by saturated NaHSO₃ solution (200 mL) and diluted with EtOAc (200 mL). The organic layer was separated and washed with saturated brine twice, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (20/1~3/1) as eluent to afford the pure product 1-phenyl-2-tosylethan-1-one oxime (5a) in 51% yield (1.47 g).

6. Table S1. Optimization of the reaction conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Base</th>
<th>Oxidant</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Yield of 3a (%)</th>
<th>Yield of 5a (%)</th>
</tr>
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1) Trapping experiment with 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO)

7. Mechanistic studies

1) Trapping experiment with 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO)
A solution of styrene (1a; 63 mg, 0.6 mmol, 2 equiv), 1-((isocyanomethyl)sulfonyl)-4-methylbenzene (2a; 59 mg, 0.3 mmol, 1 equiv), N,N'-bis(salicylidene)ethylenediamine cobalt(II) (10 mg, 0.03 mmol, 0.1 equiv), perfluorobutyl iodide (166 mg, 0.48 mmol, 1.6 equiv), Na₂CO₃ (127 mg, 1.2 mmol, 4 equiv), 2,2,6,6-tetramethylpiperidin-1-oxyl (141 mg, 0.9 mmol, 3 equiv, TEMPO), and tert-butyl hydroperoxide (142 mg, 1.1 mmol, 3.67 equiv, TBHP, 70% solution in H₂O) in THF (1.5 mL) was stirred under air atmosphere at 70 °C (oil bath) for 24 h. No (E)-1-methyl-4-(styrylsulfonyl)benzene (3a) was detected.

A solution of styrene (1a; 63 mg, 0.6 mmol, 2 equiv), 1-((isocyanomethyl)sulfonyl)-4-methylbenzene (2a; 59 mg, 0.3 mmol, 1 equiv), N,N'-bis(salicylidene)ethylenediamine cobalt(II) (10 mg, 0.03 mmol, 0.1 equiv), perfluorobutyl iodide (166 mg, 0.48 mmol, 1.6 equiv), Na₂CO₃ (127 mg, 1.2 mmol, 4 equiv), 2,2,6,6-tetramethylpiperidin-1-oxyl (141 mg, 0.9 mmol, 3 equiv, TEMPO), and tert-butyl nitrite (114 mg, 1.1 mmol, 3.67 equiv, TBN) in THF (1.5 mL) was stirred under air atmosphere at 70 °C (oil bath) for 24 h. No 1-phenyl-2-tosylethan-1-one oxime (5a) was detected.
2) Control experiment without 1-((isocyanomethyl)sulfonyl)-4-methylbenzene (2a)

A solution of styrene (1a; 63 mg, 0.6 mmol, 2 equiv), N,N’-bis(salicylidene)ethylenediamine cobalt(II) (10 mg, 0.03 mmol, 0.1 equiv), perfluorobutyl iodide (166 mg, 0.48 mmol, 1.6 equiv), Na₂CO₃ (127 mg, 1.2 mmol, 4 equiv), and tert-butyl hydroperoxide (142 mg, 1.1 mmol, 3.67 equiv, TBHP, 70% solution in H₂O) in THF (1.5 mL) was stirred under air atmosphere at 70 °C (oil bath) for 24 h. No products I-IV were obtained under the optimized conditions.

3) Control experiment without styrene (1a)

A solution of 1-((isocyanomethyl)sulfonyl)-4-methylbenzene (2a; 59 mg, 0.3 mmol, 1 equiv), N,N’-bis(salicylidene)ethylenediamine cobalt(II) (10 mg, 0.03 mmol, 0.1 equiv), perfluorobutyl iodide (166 mg, 0.48 mmol, 1.6 equiv), Na₂CO₃ (127 mg, 1.2 mmol, 4 equiv), and tert-butyl hydroperoxide (142 mg, 1.1 mmol, 3.67 equiv, TBHP, 70% solution in H₂O) in THF (1.5 mL) was stirred under air atmosphere at 70 °C (oil bath) for 24 h. No 1-((isocyanomethyl)sulfonyl)-4-methylbenzene 2a was recovered under the optimized conditions. The reaction is efficient for the cleavage of C-S bond in TosMIC.

4) Control experiment without perfluorobutyl iodide
A solution of styrene (1a; 63 mg, 0.6 mmol, 2 equiv), 1-((isocyanomethyl)sulfonyl)-4-methylbenzene (2a; 59 mg, 0.3 mmol, 1 equiv), \(N,N'-\)bis(salicylidene)ethylenediamine cobalt(II) (10 mg, 0.03 mmol, 0.1 equiv), \(\text{Na}_2\text{CO}_3\) (127 mg, 1.2 mmol, 4 equiv), and tert-butyl hydroperoxide (142 mg, 1.1 mmol, 3.67 equiv, TBHP, 70% solution in \(\text{H}_2\text{O}\)) in THF (1.5 mL) was stirred under air atmosphere at 70 °C (oil bath) for 24 h. Yields were determined by NMR analysis with 1,4-dimethoxybenzene as an internal standard.

5) Control experiment using iodine instead of perfluorobutyl iodide

A solution of styrene (1a; 63 mg, 0.6 mmol, 2 equiv), 1-((isocyanomethyl)sulfonyl)-4-methylbenzene (2a; 59 mg, 0.3 mmol, 1 equiv), \(N,N'-\)bis(salicylidene)ethylenediamine cobalt(II) (10 mg, 0.03 mmol, 0.1 equiv), iodine (122 mg, 0.48 mmol, 1.6 equiv), \(\text{Na}_2\text{CO}_3\) (127 mg, 1.2 mmol, 4 equiv), and tert-butyl hydroperoxide (142 mg, 1.1 mmol, 3.67 equiv, TBHP, 70% solution in \(\text{H}_2\text{O}\)) in THF (1.5 mL) was stirred under air atmosphere at 70 °C (oil bath) for 24 h. The reaction was then quenched by saturated \(\text{NaHSO}_3\) solution (20 mL) and diluted with EtOAc (20 mL). The organic layer was separated and washed with saturated brine twice, dried over MgSO\(_4\), filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (20/1~6/1) as eluent to afford the pure product (E)-1-methyl-4-(styrylsulfonyl)benzene (3a) in 51% yield (40 mg).

6) Control experiments using other perfluoroalkyl halides instead of perfluorobutyl iodide

A solution of styrene (1a; 63 mg, 0.6 mmol, 2 equiv), 1-((isocyanomethyl)sulfonyl)-4-methylbenzene (2a; 59 mg, 0.3 mmol, 1 equiv), \(N,N'-\)bis(salicylidene)ethylenediamine cobalt(II) (10 mg, 0.03 mmol, 0.1 equiv), \(n-C\text{F}_{2n-1}\)I (0.48 mmol, 1.6 equiv), \(\text{Na}_2\text{CO}_3\) (127 mg, 1.2 mmol, 4 equiv), and tert-butyl hydroperoxide (TBHP; 142 mg, 1.1 mmol, 3.67 equiv, 70% solution in \(\text{H}_2\text{O}\)) in THF (1.5 mL) was stirred under air atmosphere at 70 °C (oil bath) for 24 h. The reaction was then quenched by saturated \(\text{NaHSO}_3\) solution (20 mL) and diluted with EtOAc (20 mL). The organic
layer was separated and washed with saturated brine twice, dried over MgSO₄, filtered, and concentrated under reduced pressure. Yields were determined by NMR analysis with 1,4-dimethoxybenzene as an internal standard.

7) Control experiment by using (E)-1-methyl-4-(styrylsulfonyl)benzene (3a)

A solution of (E)-1-methyl-4-(styrylsulfonyl)benzene (3a; 78 mg, 0.3 mmol, 1 equiv), N,N'-bis(salicylidene)ethylenediamine cobalt(II) (10 mg, 0.03 mmol, 0.1 equiv), perfluorobutyl iodide (166 mg, 0.48 mmol, 1.6 equiv), Na₂CO₃ (127 mg, 1.2 mmol, 4 equiv), and tert-butyl nitrite (114 mg, 1.1 mmol, 3.67 equiv, TBN) in THF (1.5 mL) was stirred under air atmosphere at 70 °C (oil bath) for 24 h. No 1-phenyl-2-tosylethan-1-one oxime (5a) was detected.

8) Control experiment by using cinnamic acid (6)

A solution of cinnamic acid (6; 89 mg, 0.3 mmol, 1 equiv), 1-((isocyanomethyl)sulfonyl)-4-methylbenzene (2a; 59 mg, 0.3 mmol, 1 equiv), N,N'-bis(salicylidene)ethylenediamine cobalt(II) (10 mg, 0.03 mmol, 0.1 equiv), perfluorobutyl iodide (166 mg, 0.48 mmol, 1.6 equiv), Na₂CO₃ (127 mg, 1.2 mmol, 4 equiv), and tert-butyl hydroperoxide (TBHP; 142 mg, 1.1 mmol, 3.67 equiv, 70% solution in H₂O) in THF (1.5 mL) was stirred under air atmosphere at 70 °C (oil bath) for 24 h. However, no desired product of (E)-1-methyl-4-(styrylsulfonyl)benzene (3a) was detected.

8. Characterization data for products

(E)-1-Methyl-4-(styrylsulfonyl)benzene (3a):
Yield = 75% (58 mg). White solid. M.p. = 173.4–173.8 °C.

IR (KBr): ν = 3045, 2923, 1595, 1449, 1304, 1143, 973, 810 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.86 – 7.81 (m, 2H), 7.66 (d, J = 15.4 Hz, 1H), 7.49 (s, 2H), 7.42 – 7.36 (m, 3H), 7.34 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 15.4 Hz, 1H), 2.43 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 144.4, 141.9, 137.6, 132.4, 131.1, 129.9, 129.0, 128.5, 127.7, 127.5, 21.6 ppm.

(E)-1-Fluoro-4-(2-tosylvinyl)benzene (3b):

Yield = 49% (41 mg). White solid. M.p. = 177.1–178.5 °C.

**IR (KBr):** ν = 3269, 2927, 1582, 1151, 945, 816 cm⁻¹.

**¹H NMR** (400 MHz, CDCl₃): δ = 7.82 (dd, J = 8.4, 1.9 Hz, 2H), 7.62 (d, J = 15.4 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.12 – 7.04 (m, 2H), 6.79 (d, J = 15.4 Hz, 1H), 2.43 (s, 3H) ppm.

**¹⁹F NMR** (376 MHz, CDCl₃): δ = -107.8 (s) ppm.

**¹³C NMR** (100 MHz, CDCl₃): δ = 164.2 (d, J_C-F = 251.0 Hz), 144.4, 140.6, 137.6, 130.5 (d, J_C-F = 8.7 Hz), 130.0, 128.7 (d, J_C-F = 3.4 Hz), 127.6, 127.4 (d, J_C-F = 2.6 Hz), 116.2 (d, J_C-F = 21.9 Hz), 21.6 ppm.

**HRMS (m/z):** calcd for C₁₅H₁₄FO₂S [M+H]⁺ 277.0693, found: 277.0699.

(E)-1-Chloro-4-(2-tosylvinyl)benzene (3c):

Yield = 57% (50 mg). Light yellow solid. M.p. = 127.1–129.2 °C.

**IR (KBr):** ν = 3053, 2922, 1613, 1489, 1304, 1011, 787 cm⁻¹.

**¹H NMR** (400 MHz, CDCl₃): δ = 7.82 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 15.4 Hz, 2H), 7.43 – 7.32 (m, 6H), 6.84 (d, J = 15.4 Hz, 1H), 2.43 (s, 3H) ppm.

**¹³C NMR** (100 MHz, CDCl₃): δ = 144.5, 140.3, 137.4, 137.0, 130.8, 130.0, 129.6, 129.3, 128.1, 127.7, 21.6 ppm.

**HRMS (m/z):** calcd for C₁₅H₁₄ClO₂S [M+H]⁺ 293.0398, found: 293.0403.
(E)-1-Chloro-3-(2-tosylvinyl)benzene (3d):
Yield = 47% (41 mg). Brown oil.

IR (KBr): \( \nu = 3051, 2926, 1594, 1301, 1085, 810, 778 \ \text{cm}^{-1} \).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.85 - 7.80 \ (m, 2H), 7.59 \ (d, J = 15.4 \ \text{Hz}, 1H), 7.45 \ (t, J = 1.7 \ \text{Hz}, 1H), 7.39 - 7.30 \ (m, 5H), 6.87 \ (d, J = 15.4 \ \text{Hz}, 1H), 2.44 \ (s, 3H) \ \text{ppm.} \)

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 144.6, 140.1, 137.2, 135.0, 134.2, 130.9, 130.3, 130.0, 129.1, 128.1, 127.8, 126.7, 21.6 \ \text{ppm.} \)

HRMS (m/z): calcd for C\(_{15}\)H\(_{14}\)ClO\(_2\)S \([\text{M+H}]^+\) 293.0398, found: 293.0406.

\[ \text{Cl} - \begin{array}{c} \text{O} \\ \text{O} \\ \text{O} \\ \text{O} \end{array} - \begin{array}{c} \text{H} \\ \text{H} \\ \text{H} \\ \text{H} \end{array} \]

(\(E\))-1-Chloro-2-(2-tosylvinyl)benzene (3e):
Yield = 42% (37 mg). Yellow solid. M.p. = 159.8–160.4 °C.

IR (KBr): \( \nu = 3055, 2922, 1706, 1439, 1320, 1145, 964, 808 \ \text{cm}^{-1} \).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 8.05 \ (d, J = 15.5 \ \text{Hz}, 1H), 7.87 - 7.81 \ (m, 2H), 7.50 \ (dd, J = 7.8, 1.7 \ \text{Hz}, 1H), 7.41 \ (dd, J = 8.0, 1.3 \ \text{Hz}, 1H), 7.38 - 7.33 \ (m, 2H), 7.32 \ (dd, J = 8.0, 1.7 \ \text{Hz}, 1H), 7.28 - 7.25 \ (m, 1H), 6.90 \ (d, J = 15.4 \ \text{Hz}, 1H), 2.44 \ (s, 3H) \ \text{ppm.} \)

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 144.6, 137.7, 137.2, 135.1, 131.8, 130.6, 130.3, 130.2, 130.0, 128.1, 127.8, 127.1, 21.6 \ \text{ppm.} \)

HRMS (m/z): calcd for C\(_{15}\)H\(_{14}\)ClO\(_2\)S \([\text{M+H}]^+\) 293.0398, found: 293.0403.

\[ \text{Br} - \begin{array}{c} \text{O} \\ \text{O} \\ \text{O} \\ \text{O} \end{array} - \begin{array}{c} \text{H} \\ \text{H} \\ \text{H} \\ \text{H} \end{array} \]

(\(E\))-1-Bromo-4-(2-tosylvinyl)benzene (3f):
Yield = 53% (54 mg). Yellow solid. M.p. = 145.5–146.9 °C.

IR (KBr): \( \nu = 3043, 2925, 1619, 1487, 1303, 1142, 813 \ \text{cm}^{-1} \).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.86 - 7.79 \ (m, 2H), 7.58 \ (d, J = 15.4 \ \text{Hz}, 1H), 7.54 - 7.48 \ (m, 2H), 7.34 \ (td, J = 6.7, 1.2 \ \text{Hz}, 4H), 6.86 \ (d, J = 15.4 \ \text{Hz}, 1H), 2.43 \ (s, 3H) \ \text{ppm.} \)

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 144.5, 140.4, 137.3, 132.3, 131.3, 130.0, 129.8, 128.2, 127.7, 125.4, 21.6 \ \text{ppm.} \)
HRMS (m/z): calcd for C$_{15}$H$_{14}$IO$_2$S [M+H]$^+$ 336.9892, found: 336.9898.

(E)-1-Iodo-4-(2-tosylvinyl)benzene (3g):
Yield = 55% (64 mg). White solid. M.p. = 165.2–167.2 °C.
IR (KBr): $\nu$ = 3041, 1617, 1580, 1303, 1142, 972, 857 cm$^{-1}$.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.82 (d, $J$ = 8.2 Hz, 2H), 7.75 – 7.70 (m, 2H), 7.56 (d, $J$ = 15.4 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.21 – 7.17 (m, 2H), 6.86 (d, $J$ = 15.4 Hz, 1H), 2.43 (s, 3H) ppm.
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 144.5, 140.6, 138.2, 137.3, 131.8, 130.0, 129.8, 128.3, 127.7, 97.6, 21.6 ppm.
HRMS (m/z): calcd for C$_{15}$H$_{14}$IO$_2$S [M+H]$^+$ 384.9754, found: 384.9759.

(E)-1-Methyl-4-(4-methylstyrlylsulfonyl)benzene (3h):
Yield = 56% (46 mg). White solid. M.p. = 133.4–135.0 °C.
IR (KBr): $\nu$ = 3045, 2921, 1607, 1314, 1141, 795, 659 cm$^{-1}$.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.82 (d, $J$ = 8.2 Hz, 2H), 7.63 (d, $J$ = 15.4 Hz, 1H), 7.35 (dd, $J$ = 12.4, 8.1 Hz, 4H), 7.18 (d, $J$ = 7.9 Hz, 2H), 6.80 (d, $J$ = 15.4 Hz, 1H), 2.43 (s, 3H), 2.36 (s, 3H) ppm.
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 144.2, 141.9, 141.7, 137.8, 129.9, 129.7, 129.6, 128.5, 127.6, 126.3, 21.6, 21.5 ppm. 144.2, 141.9, 141.7, 137.8, 129.8, 129.7, 129.6, 128.5, 127.6, 126.3,
HRMS (m/z): calcd for C$_{16}$H$_{17}$O$_2$S [M+H]$^+$ 273.0944, found: 273.0939.

(E)-1-Methyl-3-(2-tosylvinyl)benzene (3i):
Yield = 50% (41 mg). Light yellow oil.
IR (KBr): $\nu$ = 3047, 2922, 1614, 1452, 1301, 1144, 1085, 844, 663 cm$^{-1}$.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.84 – 7.80 (m, 2H), 7.62 (d, $J$ = 15.4 Hz, 1H), 7.36 – 7.31 (m,
2H), 7.30 – 7.25 (m, 3H), 7.23 – 7.19 (m, 1H), 6.83 (d, J = 15.4 Hz, 1H), 2.43 (s, 3H), 2.34 (s, 3H) ppm.

\(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta = 144.3, 142.1, 138.7, 137.7, 132.3, 131.9, 129.9, 129.0, 128.9, 127.6, 127.2, 125.7, 21.6, 21.2\) ppm.

\(\text{HRMS (m/z):}\) calcd for C\(_{16}\)H\(_{17}\)O\(_2\)S [M+H]\(^+\) 273.0944, found: 273.0949.

\((E)-1\text{-Methyl-2-(2-tosylviny)benzene (3j)}:\)

Yield = 50\% (41 mg). Brown solid. M.p. = 174.4–176.0 °C.

\(\text{IR (KBr):}\) \(\nu = 3058, 2966, 1614, 1596, 1302, 1143, 1086, 961, 760\) cm\(^{-1}\).

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta = 7.94 (d, J = 15.3\) Hz, 1H), 7.83 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 7.7 Hz, 1H), 7.34 (d, J = 8.1 Hz, 2H), 7.31 – 7.25 (m, 1H), 7.21 – 7.15 (m, 2H), 6.78 (d, J = 15.3 Hz, 1H), 2.44 (s, 3H), 2.43 (s, 3H) ppm.

\(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta = 144.3, 139.5, 138.0, 137.6, 131.2, 130.9, 130.7, 129.9, 128.4, 127.6, 126.7, 126.4, 21.5, 19.7\) ppm.

\(\text{HRMS (m/z):}\) calcd for C\(_{19}\)H\(_{23}\)O\(_2\)S [M+H]\(^+\) 315.1413, found: 315.1415.

\((E)-1\text{-}(\text{Tert-butyl)-4-(2-tosylviny)benzene (3k)}:\)

Yield = 53\% (50 mg). White solid. M.p. = 149.4–150.3 °C.

\(\text{IR (KBr):}\) \(\nu = 3051, 2964, 1615, 1316, 1084, 975, 800\) cm\(^{-1}\).

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta = 7.82 (d, J = 8.3\) Hz, 2H), 7.64 (d, J = 15.4 Hz, 1H), 7.44 – 7.38 (m, 4H), 7.33 (d, J = 8.1 Hz, 2H), 6.81 (d, J = 15.4 Hz, 1H), 2.42 (s, 3H), 1.30 (s, 9H) ppm.

\(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta = 154.8, 144.2, 141.9, 137.9, 129.9, 129.6, 128.3, 127.6, 126.5, 126.0, 34.9, 31.0, 21.5\) ppm.

\(\text{HRMS (m/z):}\) calcd for C\(_{19}\)H\(_{23}\)O\(_2\)S [M+H]\(^+\) 315.1413, found: 315.1415.
(\(\text{E}\)-1-Methoxy-4-(2-tosylvinyl)benzene (3l):

Yield = 34\% (29 mg). Yellow solid. M.p. = 79.8–80.3 °C.

\(\text{IR (KBr): } \nu = 2923, 1603, 1513, 1316, 1141, 1024, 974, 757 \text{ cm}^{-1}.\)

\(\text{H NMR (400 MHz, CDCl}_3\)): \(\delta = 7.82 \text{ (d, } J = 8.3 \text{ Hz, 2H}), 7.61 \text{ (d, } J = 15.3 \text{ Hz, 1H}), 7.42 \text{ (d, } J = 8.7 \text{ Hz, 2H}), 7.33 \text{ (d, } J = 8.0 \text{ Hz, 2H}), 6.89 \text{ (d, } J = 8.8 \text{ Hz, 2H}), 6.70 \text{ (d, } J = 15.3 \text{ Hz, 1H}), 3.83 \text{ (s, 3H), } 2.43 \text{ (s, 3H) ppm.}\)

\(\text{C NMR (100 MHz, CDCl}_3\)): \(\delta = 161.9, 144.1, 141.7, 138.1, 130.3, 129.8, 127.5, 125.0, 124.7, 114.4, 55.4, 21.6 \text{ ppm.}\)

\(\text{HRMS (m/z): calcd for } C_{16}H_{17}O_3 [M+H]^+ 289.0893, \text{ found: } 289.0898.\)

\((\text{E})-1-(2\text{-Tosylvinyl})\text{naphthalene (3m):}\)

Yield = 58\% (54 mg). Yellow oil.

\(\text{IR (KBr): } \nu = 3045, 2929, 1595, 1301, 1144, 1084, 792 \text{ cm}^{-1}.\)

\(\text{H NMR (400 MHz, CDCl}_3\)): \(\delta = 8.49 \text{ (d, } J = 15.2 \text{ Hz, 1H}), 8.15 \text{ (d, } J = 8.3 \text{ Hz, 1H}), 7.92 – 7.84 \text{ (m, 4H)}, 7.65 – 7.52 \text{ (m, 3H)}, 7.43 \text{ (t, } J = 7.7 \text{ Hz, 1H}), 7.35 \text{ (d, } J = 8.0 \text{ Hz, 2H}), 6.95 \text{ (d, } J = 15.2 \text{ Hz, 1H}), 2.43 \text{ (s, 3H) ppm.}\)

\(\text{C NMR (100 MHz, CDCl}_3\)): \(\delta = 144.4, 138.9, 137.5, 133.6, 131.3, 131.2, 130.3, 129.8, 129.5, 128.8, 127.7, 127.2, 126.4, 125.6, 125.2, 123.0, 21.6 \text{ ppm.}\)

\(\text{HRMS (m/z): calcd for } C_{19}H_{17}O_2S [M+H]^+ 309.0944, \text{ found: } 309.0949.\)

\((\text{E})-1\text{-Methyl-4-(styrylsulfonyl)ferrocene (3n):}\)

Yield = 50\% (55 mg). Brown solid. M.p. = 131.0–132.3 °C.
IR (KBr): $\nu = 3047, 2918, 1609, 1311, 1084, 963, 722$ cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.86 – 7.72$ (m, 2H), $7.57$ (d, $J = 15.2$ Hz, 1H), $7.32$ (d, $J = 8.7$ Hz, 2H), $6.40$ (d, $J = 15.1$ Hz, 1H), $4.47 – 4.44$ (m, 2H), $4.44 – 4.42$ (m, 2H), $4.14$ (s, 5H), $2.42$ (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 143.9, 143.6, 138.4, 129.8, 127.3, 123.0, 76.3, 71.4, 69.7, 68.9, 21.6$ ppm.

HRMS (m/z): calcd for C$_{19}$H$_{19}$FeO$_2$S [M+H]$^+$ 367.0450, found: 367.0457.

1-Methyl-4-((2-phenylallylsulfonyl)benzene (4a):

Yield = 25% (20 mg). White solid. M.p. = 93.1–94.7 °C.

IR (KBr): $\nu = 3058, 2976, 1624, 1446, 1313, 709$ cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.66$ (d, $J = 8.3$ Hz, 2H), $7.29 – 7.18$ (m, 7H), $5.59$ (s, 1H), $5.21$ (s, 1H), $4.25$ (s, 2H), $2.39$ (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 144.6, 138.8, 136.5, 135.3, 129.5, 128.6, 128.3, 127.9, 126.2, 121.7, 62.1, 21.6$ ppm.

HRMS (m/z): calcd for C$_{16}$H$_{17}$O$_2$S [M+H]$^+$ 273.0944, found: 273.0949.

1-(Cinnamylsulfonyl)-4-methylbenzene (4b):

Yield = 22% (18 mg). White solid. M.p. = 113.4–114.8 °C.

IR (KBr): $\nu = 3022, 2920, 1592, 1489, 1318, 1151, 964, 816$ cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.78 – 7.74$ (m, 2H), $7.35 – 7.27$ (m, 7H), $6.39$ (d, $J = 15.9$ Hz, 1H), $6.16 – 6.05$ (m, 1H), $3.94$ (d, $J = 8.6$ Hz, 2H), $2.44$ (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 144.7, 139.0, 135.8, 135.4, 129.7, 128.6, 128.3, 128.4, 126.6, 115.3, 60.5, 21.6$ ppm.

HRMS (m/z): calcd for C$_{16}$H$_{17}$O$_2$S [M+H]$^+$ 273.0944, found: 273.0949.
1-Phenyl-2-tosylethan-1-one oxime (5a):
Yield = 73% (63 mg). Light yellow solid. M.p. = 170.8–171.9 °C.

IR (KBr): υ = 3061, 2920, 1593, 1464, 1318, 1151, 739 cm⁻¹.

¹H NMR (400 MHz, DMSO-D₆): δ = 11.75 (s, 1H), 7.62 – 7.57 (m, 4H), 7.34 – 7.30 (m, 5H), 4.87 (s, 2H), 2.34 (s, 3H) ppm.

¹³C NMR (100 MHz, DMSO-D₆): δ = 145.7, 144.4, 136.9, 134.6, 129.5, 129.0, 128.2, 127.9, 126.4, 51.4, 21.1 ppm.

HRMS (m/z): calcd for C₁₅H₁₆NO₃S [M+H]⁺ 290.0845, found: 290.0851.

1-(4-Fluorophenyl)-2-tosylethan-1-one oxime (5b):
Yield = 61% (56 mg). White solid. M.p. = 194.0–195.6 °C.

IR (KBr): υ = 3241, 3082, 2960, 2383, 1594, 1317, 1150, 843, 671 cm⁻¹.

¹H NMR (400 MHz, MeOH-D₄): δ = 7.68 – 7.61 (m, 4H), 7.31 (d, J = 8.5 Hz, 2H), 7.07 – 7.01 (m, 2H), 4.84 (s, 2H), 2.41 (s, 3H) ppm.

¹⁹F NMR (376 MHz, MeOH-D₄): δ = -114.5 (s) ppm.

¹³C NMR (100 MHz, MeOH-D₄): δ = 164.7 (d, J_C-F = 245.8 Hz), 146.4 (d, J_C-F = 10.7 Hz), 138.0, 132.4 (d, J_C-F = 3.3 Hz), 130.5, 129.8, 129.8, 129.5, 116.1 (d, J_C-F = 21.9 Hz), 52.9, 21.6 ppm.

HRMS (m/z): calcd for C₁₅H₁₅FNO₃S [M+H]⁺ 308.0751, found: 308.0757.

1-(4-Chlorophenyl)-2-tosylethan-1-one oxime (5c):
Yield = 49% (48 mg). White solid. M.p. = 167.4–169.0 °C.

IR (KBr): υ = 3289, 2928, 2405, 1593, 1317, 953, 767 cm⁻¹.

¹H NMR (400 MHz, MeOH-D₄): δ = 7.64 (d, J = 8.3 Hz, 2H), 7.61 – 7.57 (m, 2H), 7.32 – 7.27 (m, 4H), 4.83 (s, 2H), 2.40 (s, 3H) ppm.
$^{13}$C NMR (100 MHz, MeOH-$D_4$): $\delta = 157.0, 146.4, 137.9, 136.0, 134.7, 130.6, 129.5, 129.4, 129.2, 52.7, 21.6$ ppm.

HRMS (m/z): calcd for C$_{15}$H$_{15}$ClNO$_3$S [M+H]$^+$ 324.0456, found: 324.0461.

![Chemical Structure](attachment:image.png)

1-(3-Chlorophenyl)-2-tosylethan-1-one oxime (5d):

Yield = 38% (37 mg). Light yellow solid. M.p. = 161.1–162.6 °C.

IR (KBr): $\nu =$ 3045, 2923, 2409, 1595, 1449, 1304, 1143, 973, 810, 747 cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 8.56 (s, 1H, NOH), 7.74 – 7.68 (m, 2H), 7.55 – 7.50 (m, 2H), 7.35 – 7.33 (m, 1H), 7.30 – 7.28 (m, 1H), 7.26 – 7.23 (m, 2H), 4.70 (s, 2H), 2.40 (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 146.7, 145.1, 136.2, 135.4, 134.6, 129.8, 129.7, 129.6, 128.4, 126.5, 124.9, 52.5, 21.6 ppm.

HRMS (m/z): calcd for C$_{15}$H$_{15}$ClNO$_3$S [M+H]$^+$ 324.0456, found: 324.0461.

![Chemical Structure](attachment:image.png)

1-(4-Bromophenyl)-2-tosylethan-1-one oxime (5f):

Yield = 61% (67 mg). Light yellow solid. M.p. = 172.3–174.1 °C.

IR (KBr): $\nu =$ 3292, 2929, 2413, 1587, 1409, 1317, 954, 831 cm$^{-1}$.

$^1$H NMR (400 MHz, MeOH–$D_4$): $\delta =$ 7.67 – 7.62 (m, 2H), 7.55 – 7.50 (m, 2H), 7.48 – 7.43 (m, 2H), 7.31 (d, $J =$ 8.4 Hz, 2H), 4.84 (s, 2H), 2.42 (s, 3H) ppm.

$^{13}$C NMR (100 MHz, MeOH–$D_4$): $\delta =$ 146.5, 146.5, 137.9, 135.1, 132.4, 130.6, 129.5, 129.4, 124.2, 52.6, 21.6 ppm.

HRMS (m/z): calcd for C$_{15}$H$_{15}$I$_2$BrNO$_3$S [M+H]$^+$ 367.9951, found: 367.9956.

![Chemical Structure](attachment:image.png)

1-(4-Iodophenyl)-2-tosylethan-1-one oxime (5g):

Yield = 59% (74 mg). Light yellow solid. M.p. = 186.4–187.1 °C.
**1**-(p-Tolyl)-2-tosylethan-1-one oxime (5h):

Yield = 64% (58 mg). Light yellow solid. M.p. = 151.3–152.0 °C.

**IR** (KBr): \( \nu = 3265, 3005, 2919, 2404, 1595, 1405, 1320, 1163, 947, 772 \) cm\(^{-1}\).

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)):

\[ \delta = 8.85 (s, 1H, NOH), 7.69 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.0 Hz, 1H), 7.33 (s, 1H), 7.24 – 7.18 (m, 4H), 4.72 (s, 2H), 2.36 (s, 3H), 2.32 (s, 3H) \] ppm.

**\(^{13}\)C NMR** (100 MHz, CDCl\(_3\)):

\[ \delta = 144.8, 138.1, 136.4, 133.5, 130.5, 130.0, 129.4, 128.4, 128.4, 127.1, 123.7, 52.8, 21.5, 21.3 \] ppm.

**HRMS** (m/z): calcd for C\(_{16}\)H\(_{18}\)NO\(_3\)S [M+H]\(^+\) 304.1002, found: 304.1007.

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**1**-(m-Tolyl)-2-tosylethan-1-one oxime (5i):

Yield = 66% (60 mg). Light yellow solid. M.p. = 131.8–132.6 °C.

**IR** (KBr): \( \nu = 3045, 2389, 1599, 1407, 1068, 955 \) cm\(^{-1}\).

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)):

\[ \delta = 8.85 (s, 1H, NOH), 7.39 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.0 Hz, 1H), 7.33 (s, 1H), 7.24 – 7.18 (m, 4H), 4.72 (s, 2H), 2.36 (s, 3H), 2.32 (s, 3H) \] ppm.

**\(^{13}\)C NMR** (100 MHz, CDCl\(_3\)):

\[ \delta = 144.8, 138.1, 136.4, 133.5, 130.5, 130.0, 129.4, 128.4, 128.4, 127.1, 123.7, 52.8, 21.5, 21.3 \] ppm.

**HRMS** (m/z): calcd for C\(_{16}\)H\(_{18}\)NO\(_3\)S [M+H]\(^+\) 304.1002, found: 304.1007.
1-(4-(Tert-butyl)phenyl)-2-tosylethan-1-one oxime (5j):

Yield = 48% (50 mg). Light yellow solid. M.p. = 181.7–183.6 °C.

IR (KBr): \( \nu = 3056, 2962, 2389, 1681, 1568, 1506, 1093, 798 \text{ cm}^{-1} \).

\( ^1H \text{ NMR} \ (400 \text{ MHz, CDCl}_3): \delta = 8.67 \text{ (s, 1H, NOH)}, 7.72 - 7.67 \text{ (m, 2H)}, 7.55 - 7.49 \text{ (m, 2H)}, 7.37 - 7.33 \text{ (m, 2H)}, 7.23 - 7.18 \text{ (m, 2H)}, 4.72 \text{ (s, 2H)}, 2.36 \text{ (s, 3H)}, 1.32 \text{ (s, 9H) ppm.} \)

\( ^13C \text{ NMR} \ (100 \text{ MHz, CDCl}_3): \delta = 153.1, 147.6, 144.7, 136.5, 130.7, 129.4, 128.4, 126.3, 125.5, 52.6, 34.7, 31.1, 21.6 \text{ ppm.} \)

HRMS (m/z): calcd for C\(_{19}\)H\(_{24}\)NO\(_3\)S [M+H]\(^+\) 346.1471, found: 346.1477.

1-(4-Methoxyphenyl)-2-tosylethan-1-one oxime (5k):

Yield = 32% (31 mg). Yellow solid. M.p. = 155.9–157.9 °C.

IR (KBr): \( \nu = 3319, 2989, 2845, 1605, 1514, 1316, 1250, 945, 813 \text{ cm}^{-1} \).

\( ^1H \text{ NMR} \ (400 \text{ MHz, CDCl}_3): \delta = 8.62 \text{ (s, 1H, NOH)}, 7.70 \text{ (d, } J = 8.3 \text{ Hz, 2H)}, 7.56 \text{ (d, } J = 8.7 \text{ Hz, 2H)}, 7.23 \text{ (d, } J = 8.0 \text{ Hz, 2H)}, 6.87 \text{ (d, } J = 8.9 \text{ Hz, 2H)}, 4.70 \text{ (s, 2H)}, 3.83 \text{ (s, 3H)}, 2.38 \text{ (s, 3H) ppm.} \)

\( ^13C \text{ NMR} \ (100 \text{ MHz, CDCl}_3): \delta = 160.9, 147.3, 144.8, 136.4, 129.4, 128.4, 128.0, 126.1, 113.9, 55.3, 52.6, 21.6 \text{ ppm.} \)

HRMS (m/z): calcd for C\(_{16}\)H\(_{18}\)NO\(_4\)S [M+H]\(^+\) 320.0951, found: 320.0955.
9. The $^1$H, $^{19}$F, $^{13}$C spectra of products
S28