

Supporting Information

Palladium-Catalyzed Migratory Allylic Sulfonylation of Allylic Alcohols Using Sulfonyl Hydrazides

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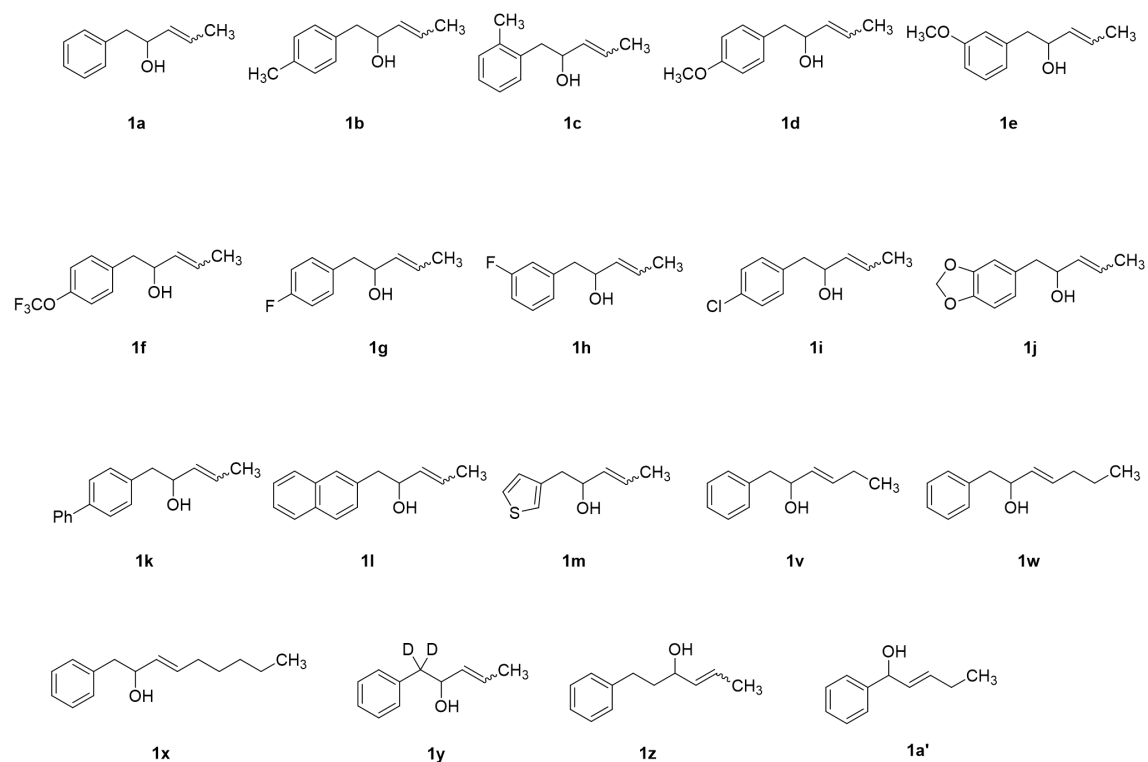
General information

Unless otherwise noted, all reactions were carried out in standard Schlenk techniques with magnetic stirring bar. Materials obtained from commercial suppliers were used directly without further purification. ^1H NMR spectra were recorded on a BRUKER 400 (400 MHz) spectrometer in CDCl_3 . Chemical shifts are reported in ppm, using the residual solvent peak in CDCl_3 ($\text{H} = 7.26$) as internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on a BRUKER 400 (100 MHz) spectrometer in CDCl_3 with complete proton decoupling. Chemical shifts are reported in ppm with the deuterium solvent as the internal standard (CDCl_3 : 77.0 ppm). HRMS were recorded using EI and ESI techniques.

Anhydrous tetrahydrofuran (THF), toluene, acetonitrile and dichloromethane (DCM) were obtained from solvent purification system. Unless otherwise noted, analytical grade solvents and commercially available reagents were used directly.

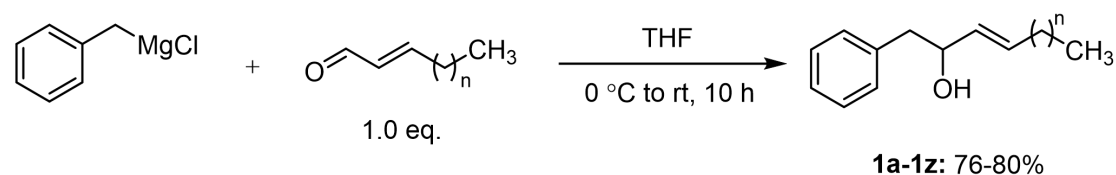
Reactions were monitored by thin layer chromatography (TLC) using pre-coated silica gel plates. Flash column chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Yantai, China).

Preparation of starting materials



1a, 1a', 1b, 1c, 1d, 1e, 1f, 1g, 1h, 1i, 1j, 1k, 1l, 1m, 1n, 1o, 1p, 1q, 1r, 1s, 1t, 1u, 1v, 1w, 1x, 1y and 1z are known compounds and prepared according to our previous work.^[1]

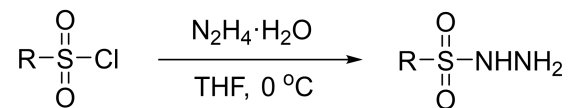
Synthesis of 3-en-2-ol (**1a-1z**)



To a solution of aldehyde (5 mmol) in dry THF (20 mL) under N₂ at 0 °C was added the benzyl magnesium chloride (5 mL, 5 mmol, 1.0 M in THF). Then reaction mixture was allowed to gradually warm to room temperature, and stirred for additional 10 h. After completion, the reaction was quenched by with saturated NH₄Cl (aq.) and diluted with EtOAc (10 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (10 mL×3). The combined organic layers were washed with brine (10 mL), dried over Na₂SO₄, and concentrated in

vacuo. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 40/1) gave the desired products.

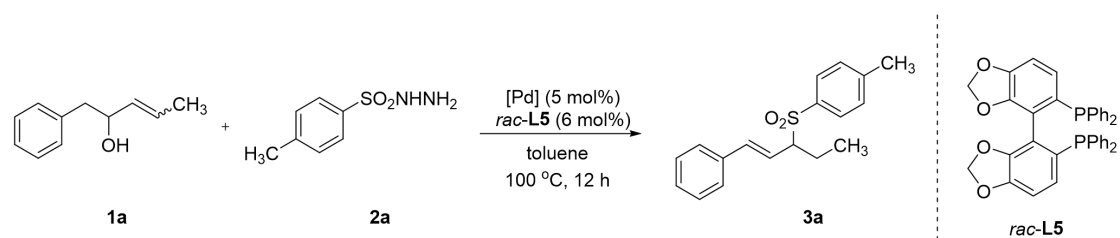
Synthesis of Sulfonyl Hydrazides



Sulfonyl hydrazides were prepared according to reported literature procedure.^[2] To a solution of sulfonyl chloride (3.0 mmol) in THF (15 mL) was added dropwise hydrazine monohydrate (375 mg, 7.5 mmol) under nitrogen at 0 °C. After being vigorously stirring for 30 min at 0 °C, the reaction mixture was added ethyl acetate (3 × 20 mL), and washed with saturated brine (3 × 10 mL). The organic layers were separated, combined, and dried over sodium sulfate. After filtration, the mixture was concentrated and added to hexane (12 mL) over 5 min. The mixture was filtered, and the collected solid was dried in vacuum.

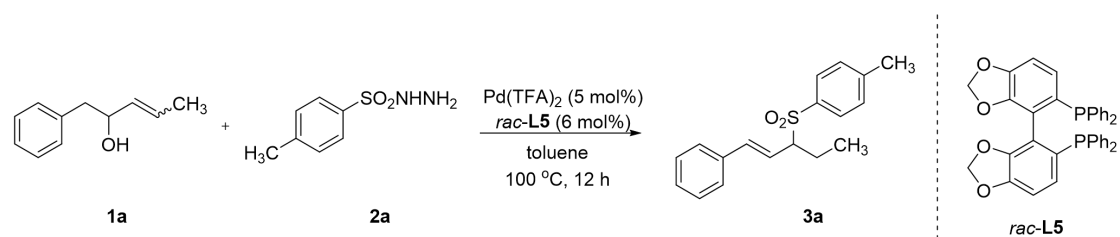
Optimization of the reaction conditions

Table S1. Screening of palladium sources



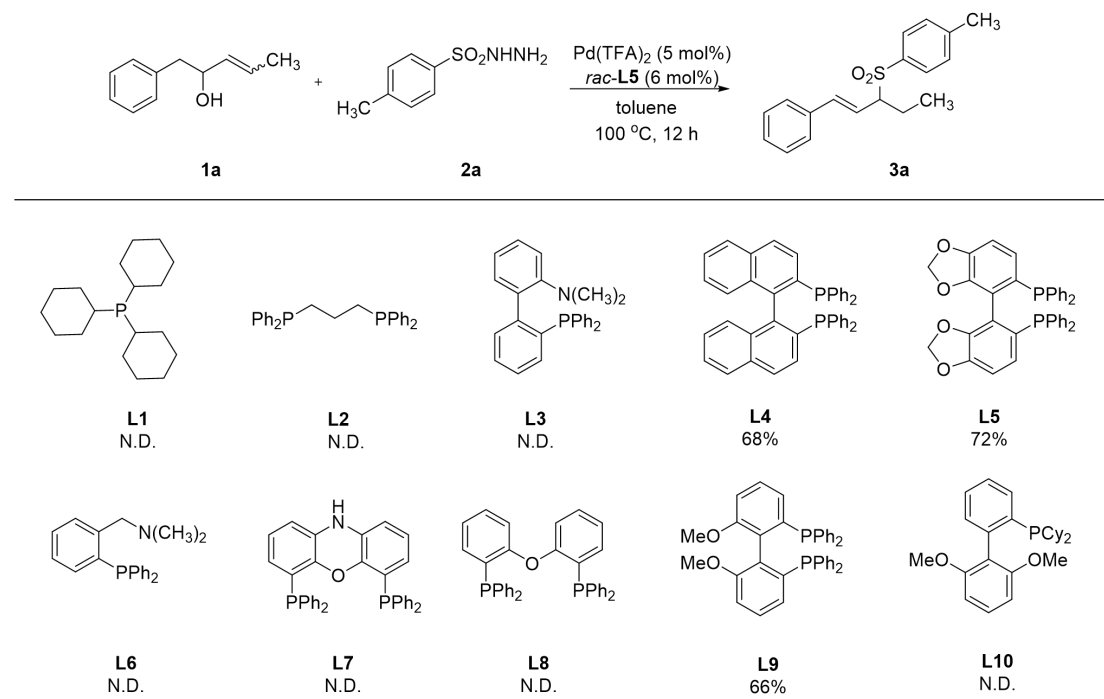
Entry	[Pd]	Yield of 3a (%) ^a
1	Pd ₂ (dba) ₃	20
2	Pd(dba) ₂	20
3	Pd ₂ (allyl) ₂ Cl ₂	17
4	Pd(TFA) ₂	36
5	PdCl ₂	20
6	Pd(CN) ₂ Cl ₂	N.D.
7	Pd(dppf)Cl ₂	N.D.
8	Pd(OAc) ₂	30
9	Pd(PPh ₃) ₂ Cl ₂	14
10	Pd(PPh ₃) ₄	trace

Reaction conditions: the reaction was carried out with **1a** (0.20 mmol), **2a** (0.40 mmol), [Pd] (5 mol%), and *rac*-L5 (6 mol%) in toluene (1.0 mL) at 100 °C for 12 h. ^aYields were determined by ¹H NMR analysis using CH₂Br₂ as the internal standard.

Table S2. Screening of the ratio of **1a** to **2a**

Entry	1a (mmol)	2a (mmol)	Yield of 3a (%) ^a
1	2.0	4.0	36
2	3.0	2.0	63
3	4.0	2.0	72
4	5.0	2.0	70

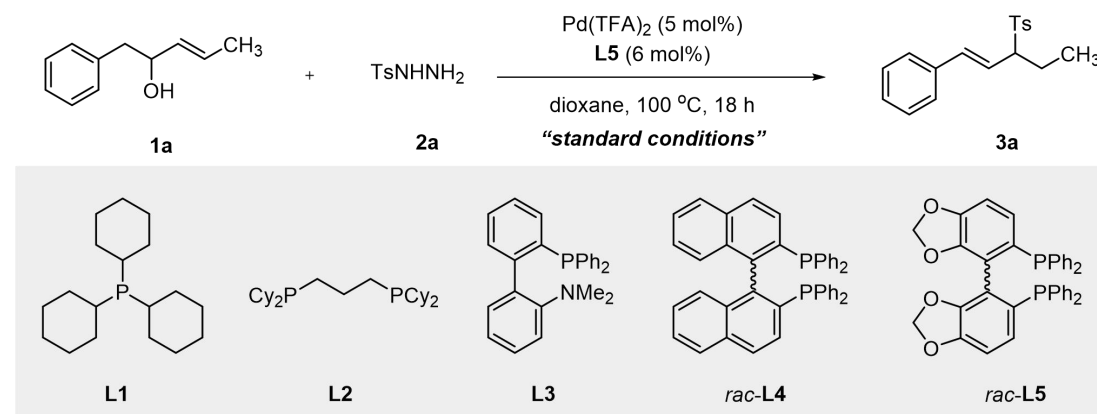
Reaction conditions: the reaction was carried out with [Pd] (5 mol%), and *rac*-L5 (6 mol%) in toluene (1.0 mL) at 100 °C for 12 h. ^aYields were determined by ¹H NMR analysis using CH₂Br₂ as the internal standard.

Table S3. Screening of ligands

Reaction conditions: the reaction was carried out with Pd(TFA)₂ (5 mol%), and ligand (6 mol%) in toluene (1.0 mL) at 100 °C for 12 h. Yields were determined by ¹H NMR analysis using CH₂Br₂ as

the internal standard.

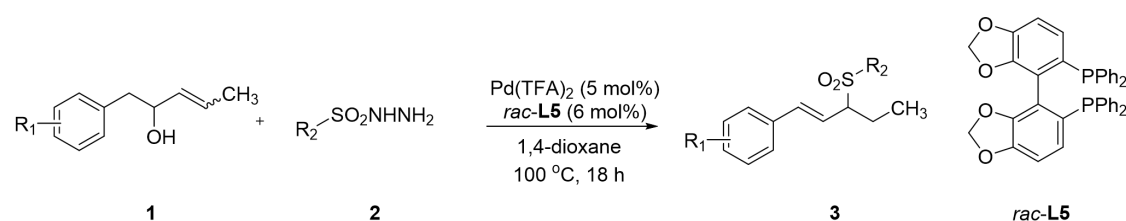
Table S4. Optimization of reaction conditions^a



Entry	deviation from “ <i>standard conditions</i> ”	yield of 3a (%) ^b
1	none	84 (81)
2	L1 instead of L5	N.D.
3	L2 instead of L5	N.D.
4	L3 instead of L5	N.D.
5	L4 instead of L5	70
6	70 °C instead of 100 °C	22
7	80 °C instead of 100 °C	70
8	DCE instead of dioxane	36
9	ⁿ hexane instead of dioxane	38
10	DME instead of dioxane	66
11	toluene instead of dioxane	80

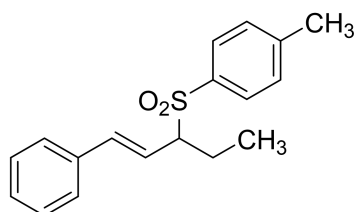
^aUnless otherwise noted, the reaction was carried out with **1a** (0.40 mmol), **2a** (0.20 mmol), Pd(TFA)₂ (5 mol%), and ligand (6 mol%) in indicated solvent (1.0 mL) at 100 °C for 18 h. ^bYields were determined by ¹H NMR analysis using CH₂Br₂ as the internal standard, and value in parentheses is the isolated yield.

General procedure for the palladium-catalyzed migratory allylic sulfonylation of allylic alcohols



Under a nitrogen atmosphere, to a mixture of Pd(TFA)₂ (3.3 mg, 0.01 mmol), *rac*-L5 (6.7 mg, 0.012 mmol), and sulfonyl hydrazide (0.2 mmol) was added a solution of allylic alcohol **1** (0.4 mmol) in 1,4-dioxane (1.0 mL). The reaction was sealed and stirred at 100 °C for 18 h. Subsequently, the reaction was cooled down to room temperature, and the mixture was evaporated and purified via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford desired product.

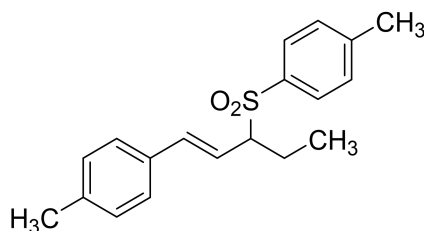
(E)-1-Methyl-4-((1-phenylpent-1-en-3-yl)sulfonyl)benzene (**3a**, yxz-4-70)^[3]



3a

83% isolated yield from **1a** (eluent: petroleum ether/ethyl acetate = 30/1), colorless oil; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.36-7.20 (m, 7H), 6.31 (d, *J* = 15.8 Hz, 1H), 5.90 (dd, *J* = 15.9, 9.4 Hz, 1H), 3.57-3.51 (m, 1H), 2.41 (s, 3H), 2.33-2.18 (m, 1H), 1.84-1.68 (m, 1H), 0.98 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 144.5, 138.0, 135.9, 134.6, 129.4, 129.1, 128.6, 128.3, 126.5, 121.1, 71.1, 21.6, 21.0, 11.3; HRMS (ESI) *m/z* calculated for C₁₈H₂₀O₂SN⁺ [M+Na]⁺: 323.1076, found: 323.1076.

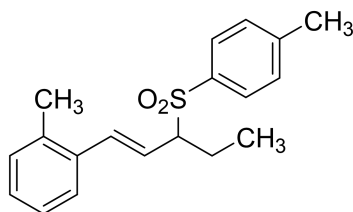
(E)-1-Methyl-4-((1-(*p*-tolyl)pent-1-en-3-yl)sulfonyl)benzene (**3b**, yxz-4-75)



3b

85% isolated yield from **1b** (eluent: petroleum ether/ethyl acetate = 30/1), colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, $J = 8.3$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.22-7.05 (m, 4H), 6.27 (d, $J = 15.8$ Hz, 1H), 5.84 (dd, $J = 15.8, 9.4$ Hz, 1H), 3.55-3.49 (m, 1H), 2.41 (s, 3H), 2.33 (s, 3H), 2.30-2.19 (m, 1H), 1.81-1.68 (m, 1H), 0.98 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.4, 138.3, 137.9, 134.7, 133.2, 129.4, 129.3, 129.2, 126.4, 120.0, 71.1, 21.6, 21.2, 21.0, 11.3; HRMS (ESI) m/z calculated for $\text{C}_{19}\text{H}_{26}\text{NO}_2\text{S}^+$ $[\text{M}+\text{NH}_4]^+$: 332.1679, found: 332.1684.

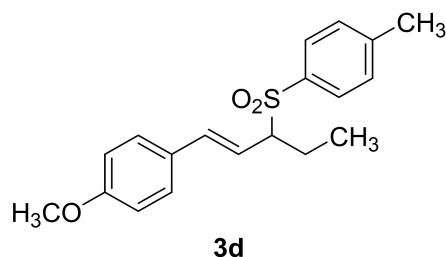
(E)-1-Methyl-2-(3-tosylpent-1-en-1-yl)benzene (**3c**, yxz-4-74)



3c

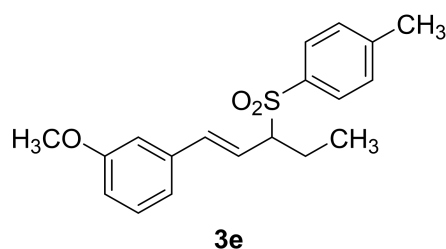
80% isolated yield from **1c** (eluent: petroleum ether/ethyl acetate = 30/1), colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, $J = 8.3$ Hz, 2H), 7.42-7.26 (m, 3H), 7.22-7.12 (m, 2H), 7.12-7.07 (m, 1H), 6.48 (d, $J = 15.7$ Hz, 1H), 5.77 (dd, $J = 15.7, 9.5$ Hz, 1H), 3.60-3.54 (m, 1H), 2.42 (s, 3H), 2.36-2.22 (m, 1H), 2.12 (s, 3H), 1.85-1.74 (m, 1H), 1.01 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.5, 136.2, 135.5, 135.2, 134.8, 130.2, 129.4, 129.2, 128.2, 126.2, 125.8, 122.7, 71.3, 21.6, 20.8, 19.4, 11.4; HRMS (ESI) m/z calculated for $\text{C}_{19}\text{H}_{26}\text{NO}_2\text{S}^+$ $[\text{M}+\text{NH}_4]^+$: 332.1679, found: 332.1682

(E)-1-Methoxy-4-(3-tosylpent-1-en-1-yl)benzene (**3d**, yxz-4-76)



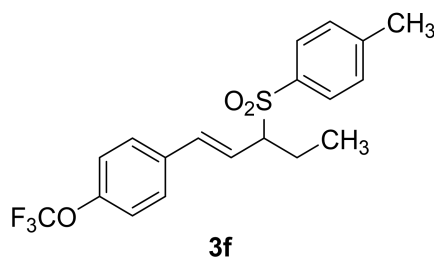
79% isolated yield from **1d** (eluent: petroleum ether/ethyl acetate = 20/1), colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, $J = 8.3$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.22 (d, $J = 8.7$ Hz, 2H), 6.84 (d, $J = 8.7$ Hz, 2H), 6.25 (d, $J = 15.8$ Hz, 1H), 5.74 (dd, $J = 15.8, 9.4$ Hz, 1H), 3.80 (s, 3H), 3.54-3.48 (m, 1H), 2.41 (s, 3H), 2.29-2.17 (m, 1H), 1.82-1.69 (m, 1H), 0.97 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.7, 144.4, 137.5, 134.7, 129.4, 129.2, 128.7, 127.8, 118.6, 114.0, 71.2, 55.3, 21.6, 21.0, 11.3; HRMS (ESI) m/z calculated for $\text{C}_{19}\text{H}_{26}\text{NO}_3\text{S}^+$ $[\text{M}+\text{NH}_4]^+$: 348.1628, found: 348.1626.

(E)-1-Methoxy-3-(3-tosylpent-1-en-1-yl)benzene (**3e**, yxz-4-80)



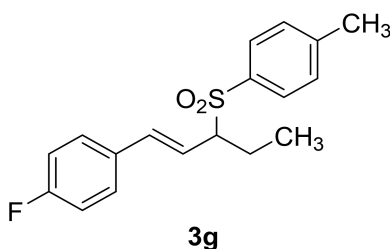
71% isolated yield from **1e** (eluent: petroleum ether/ethyl acetate = 20/1), colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, $J = 8.3$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.22 (t, $J = 7.7$ Hz, 1H), 6.88-6.81 (m, 3H), 6.28 (d, $J = 15.8$ Hz, 1H), 5.90 (dd, $J = 15.8, 9.4$ Hz, 1H), 3.81 (s, 3H), 3.56-3.50 (m, 1H), 2.42 (s, 3H), 2.30-2.20 (m, 1H), 1.81-1.72 (m, 1H), 0.98 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.8, 144.5, 138.0, 137.3, 134.6, 129.6, 129.4, 129.2, 121.4, 119.2, 113.9, 111.8, 71.1, 55.2, 21.6, 21.0, 11.3; HRMS (ESI) m/z calculated for $\text{C}_{19}\text{H}_{26}\text{NO}_3\text{S}^+$ $[\text{M}+\text{NH}_4]^+$: 348.1628, found: 348.1635.

(E)-1-Methyl-4-((1-(4-(trifluoromethoxy)phenyl)pent-1-en-3-yl)sulfonyl)benzene (**3f**, yxz-4-77)



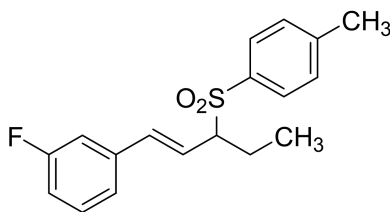
60% isolated yield from **1f** (eluent: petroleum ether/ethyl acetate = 20/1), colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.3 Hz, 4H), 7.16 (d, J = 8.4 Hz, 2H), 6.32 (d, J = 15.8 Hz, 1H), 5.89 (dd, J = 15.8, 9.4 Hz, 1H), 3.57-3.51 (m, 1H), 2.43 (s, 3H), 2.28-2.18 (m, 1H), 1.81-1.70 (m, 1H), 0.98 (t, J = 7.4 Hz, 3H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -57.8; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.0, 144.6, 136.5, 134.6, 129.5, 129.3, 129.1, 127.8, 122.2, 121.1, 120.4 (q, J = 255.7 Hz), 71.0, 21.6, 21.1, 11.3; HRMS (ESI) m/z calculated for $\text{C}_{19}\text{H}_{23}\text{F}_3\text{NO}_3\text{S}^+$ $[\text{M}+\text{NH}_4]^+$: 402.1345, found: 402.1351.

(E)-1-Fluoro-4-(3-tosylpent-1-en-1-yl)benzene (**3g**, yxz-4-86)



60% isolated yield from **1g** (eluent: petroleum ether/ethyl acetate = 20/1), colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, J = 8.3 Hz, 2H), 7.31-7.24 (m, 4H), 7.02-6.98 (m, 2H), 6.29 (d, J = 15.9 Hz, 1H), 5.82 (dd, J = 15.9, 9.4 Hz, 1H), 3.56-3.50 (m, 1H), 2.42 (s, 3H), 2.26-2.19 (m, 1H), 1.79-1.69 (m, 1H), 0.97 (t, J = 7.5 Hz, 3H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.1; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.68 (d, J = 246.8 Hz), 144.5, 136.9, 134.6, 132.1, 129.3 (d, J = 3.1 Hz), 128.2, 128.1 (d, J = 7.8 Hz), 115.59 (d, J = 22.4 Hz), 71.0, 21.6, 21.1, 11.3; HRMS (ESI) m/z calculated for $\text{C}_{18}\text{H}_{23}\text{FNO}_2\text{S}^+$ $[\text{M}+\text{NH}_4]^+$: 336.1428, found: 336.1434.

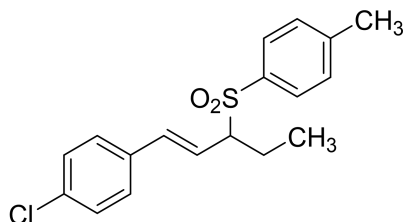
(E)-1-Fluoro-3-(3-tosylpent-1-en-1-yl)benzene (**3h**, yxz-4-94)



3h

57% isolated yield from **1h** (eluent: petroleum ether/ethyl acetate = 20/1), colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, $J = 8.3$ Hz, 2H), 7.31-7.24 (m, 3H), 7.05 (d, $J = 7.7$ Hz, 1H), 6.98-6.93 (m, 2H), 6.29 (d, $J = 15.8$ Hz, 1H), 5.91 (dd, $J = 15.8, 9.4$ Hz, 1H), 3.57-3.51 (m, 1H), 2.43 (s, 3H), 2.26-2.21 (m, 1H), 1.79-1.72 (m, 1H), 0.98 (t, $J = 7.5$ Hz, 3H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.1; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.0 (d, $J = 243.8$ Hz), 144.6, 138.2 (d, $J = 7.4$ Hz), 136.9 (d, $J = 1.8$ Hz), 134.6, 130.2 (d, $J = 7.1$ Hz), 129.5, 129.2, 122.7, 122.4 (d, $J = 2.4$ Hz), 115.2 (d, $J = 21.6$ Hz), 113.0 (d, $J = 21.4$ Hz), 70.9, 21.6, 21.1, 11.3; HRMS (ESI) m/z calculated for $\text{C}_{18}\text{H}_{23}\text{FNO}_2\text{S}^+ [\text{M}+\text{NH}_4]^+$: 336.1428, found: 336.1434.

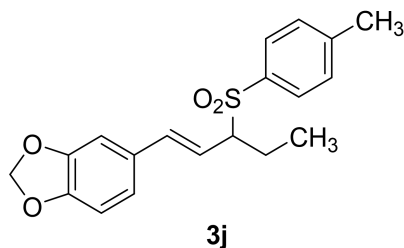
(E)-1-Chloro-4-(3-tosylpent-1-en-1-yl)benzene (**3i**, yxz-4-84)



3i

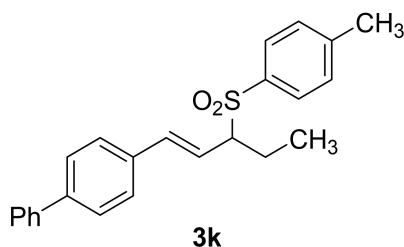
65% isolated yield from **1i** (eluent: petroleum ether/ethyl acetate = 20/1), colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, $J = 8.3$ Hz, 2H), 7.30-7.26 (m, 4H), 7.21 (d, $J = 8.5$ Hz, 2H), 6.27 (d, $J = 15.9$ Hz, 1H), 5.88 (dd, $J = 15.9, 9.4$ Hz, 1H), 3.56-3.50 (m, 1H), 2.42 (s, 3H), 2.28-2.18 (m, 1H), 1.79-1.71 (m, 1H), 0.97 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.6, 136.8, 134.6, 134.4, 134.1, 129.5, 129.1, 128.8, 127.7, 121.8, 71.0, 21.6, 21.0, 11.3; HRMS (ESI) m/z calculated for $\text{C}_{18}\text{H}_{23}^{35}\text{ClNO}_2\text{S}^+ [\text{M}+\text{NH}_4]^+$: 352.1133, found: 352.1138.

(E)-5-(3-Tosylpent-1-en-1-yl)benzo[*d*][1,3]dioxole (**3j**, yxz-4-81)



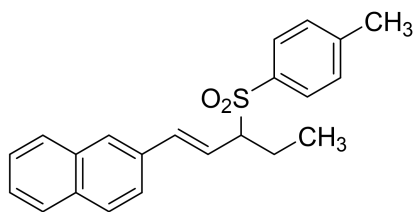
65% isolated yield from **1j** (eluent: petroleum ether/ethyl acetate = 10/1), colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, $J = 8.3$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 6.83 (s, 1H), 6.75-6.68 (m, 2H), 6.22 (d, $J = 15.8$ Hz, 1H), 5.96 (s, 2H), 5.70 (dd, $J = 15.8, 9.4$ Hz, 1H), 3.53-3.47 (m, 1H), 2.42 (s, 3H), 2.28-2.18 (m, 1H), 1.78-1.66 (m, 1H), 0.97 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.1, 147.8, 144.5, 137.7, 134.6, 130.4, 129.4, 129.2, 121.5, 119.1, 108.3, 105.7, 101.2, 71.1, 21.6, 21.1, 11.3; HRMS (ESI) m/z calculated for $\text{C}_{19}\text{H}_{24}\text{NO}_4\text{S}^+$ $[\text{M}+\text{NH}_4]^+$: 362.1421, found: 362.1424.

(E)-4-(3-Tosylpent-1-en-1-yl)-1,1'-biphenyl (**3k**, yxz-4-87)



69% isolated yield from **1k** (eluent: petroleum ether/ethyl acetate = 20/1), white solid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, $J = 8.3$ Hz, 2H), 7.60-7.53 (m, 4H), 7.46-7.25 (m, 7H), 6.35 (d, $J = 15.8$ Hz, 1H), 5.95 (dd, $J = 15.8, 9.4$ Hz, 1H), 3.59-3.53 (m, 1H), 2.42 (s, 3H), 2.28-2.24 (m, 1H), 1.80-1.76 (m, 1H), 1.00 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.5, 141.1, 140.4, 137.6, 135.0, 134.7, 129.5, 129.2, 128.9, 127.5, 127.3, 127.1, 127.0, 121.2, 71.2, 21.7, 21.1, 11.4; HRMS (ESI) m/z calculated for $\text{C}_{24}\text{H}_{28}\text{NO}_2\text{S}^+$ $[\text{M}+\text{NH}_4]^+$: 394.1835, found: 394.1838.

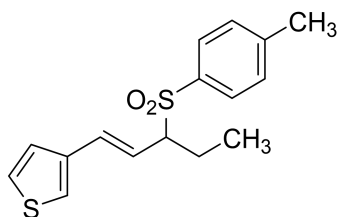
(E)-2-(3-Tosylpent-1-en-1-yl)naphthalene (**3l**, yxz-4-83)



3l

71% isolated yield from **1l** (eluent: petroleum ether/ethyl acetate = 20/1), colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.80-7.44 (m, 9H), 7.27 (d, $J = 8.1$ Hz, 2H), 6.46 (d, $J = 15.8$ Hz, 1H), 6.03 (dd, $J = 15.8, 9.4$ Hz, 1H), 3.63-3.57 (m, 1H), 2.40 (s, 3H), 2.34-2.24 (m, 1H), 1.87-1.75 (m, 1H), 1.01 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.5, 138.1, 134.6, 133.3, 133.3, 133.2, 129.4, 129.2, 128.3, 128.0, 127.7, 126.8, 126.4, 126.3, 123.3, 121.4, 71.2, 21.6, 21.0, 11.4; HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{26}\text{NO}_2\text{S}^+$ [$\text{M}+\text{NH}_4$] $^+$: 368.1679, found: 368.1684.

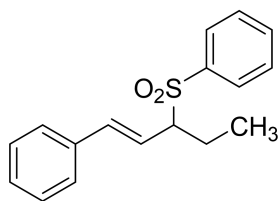
(E)-3-(3-Tosylpent-1-en-1-yl)thiophene (**3m**, yxz-4-89)



3m

67% isolated yield from **1m** (eluent: petroleum ether/ethyl acetate = 20/1), colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, $J = 8.3$ Hz, 2H), 7.33-7.28 (m, 3H), 7.17 (d, $J = 5.1$ Hz, 1H), 7.12 (d, $J = 2.9$ Hz, 1H), 6.37 (d, $J = 15.8$ Hz, 1H), 5.76 (dd, $J = 15.8, 9.4$ Hz, 1H), 3.54-3.48 (m, 1H), 2.44 (s, 3H), 2.29-2.19 (m, 1H), 1.80-1.68 (m, 1H), 0.99 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.5, 138.6, 134.7, 132.1, 129.4, 129.2, 126.3, 124.8, 123.4, 120.7, 71.1, 21.6, 21.1, 11.3; HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{22}\text{NO}_2\text{S}_2^+$ [$\text{M}+\text{NH}_4$] $^+$: 324.1086, found: 324.1090.

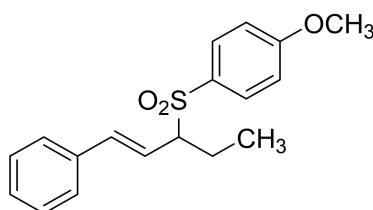
(E)-((1-Phenylpent-1-en-3-yl)sulfonyl)benzene (**3n**, yxz-5-9)^[3]



3n

81% isolated yield from **1a** (eluent: petroleum ether/ethyl acetate = 20/1), white solid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.87-7.85 (m, 2H), 7.65-7.61 (m, 1H), 7.54-7.50 (m, 2H), 7.33-7.27 (m, 5H), 6.30 (d, $J = 15.9$ Hz, 1H), 5.93 (dd, $J = 15.9, 9.5$ Hz, 1H), 3.62-3.56 (m, 1H), 2.35-2.25 (m, 1H), 1.85-1.77 (m, 1H), 1.02 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.3, 137.6, 135.8, 133.5, 129.1, 128.8, 128.6, 128.4, 126.5, 121.0, 71.1, 20.9, 11.3; HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{22}\text{NO}_2\text{S}^+$ [$\text{M}+\text{NH}_4$] $^+$: 304.1366, found: 304.1371.

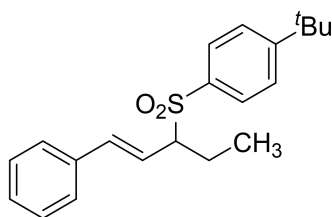
(E)-1-Methoxy-4-((1-phenylpent-1-en-3-yl)sulfonyl)benzene (**3o**, yxz-5-6)



3o

80% isolated yield from **1a**(eluent: petroleum ether/ethyl acetate = 15/1), colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, $J = 8.9$ Hz, 2H), 7.36-7.29 (m, 5H), 6.97 (d, $J = 8.9$ Hz, 2H), 6.34 (d, $J = 15.9$ Hz, 1H), 5.93 (dd, $J = 15.9, 9.4$ Hz, 1H), 3.88 (s, 3H), 3.58-3.52 (m, 1H), 2.31-2.23 (m, 1H), 1.82-1.74 (m, 1H), 1.01 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.6, 138.0, 135.9, 131.3, 129.1, 128.6, 128.3, 126.5, 121.3, 114.0, 71.3, 55.6, 21.1, 11.4; HRMS (ESI) m/z calculated for $\text{C}_{18}\text{H}_{20}\text{O}_3\text{SNa}^+$ [$\text{M}+\text{Na}$] $^+$: 339.1025, found: 339.1031.

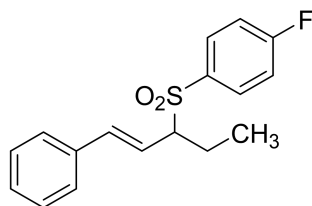
(E)-1-(*tert*-Butyl)-4-((1-phenylpent-1-en-3-yl)sulfonyl)benzene (**3p**, yxz-5-21)



3p

71% isolated yield from **1a** (eluent: petroleum ether/ethyl acetate = 20/1), colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H), 7.30-7.24 (m, 5H), 6.28 (d, J = 15.9 Hz, 1H), 5.91 (dd, J = 15.9, 9.4 Hz, 1H), 3.58-3.52 (m, 1H), 2.30-2.2 (m, 1H), 1.82-1.74 (m, 1H), 1.32 (s, 9H), 0.98 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.4, 138.2, 135.9, 134.5, 129.0, 128.6, 128.3, 126.5, 125.8, 121.1, 71.2, 35.2, 31.0, 21.0, 11.4; HRMS (ESI) m/z calculated for $\text{C}_{21}\text{H}_{30}\text{NO}_2\text{S}^+$ [$\text{M}+\text{NH}_4$] $^+$: 360.1992, found: 360.2000.

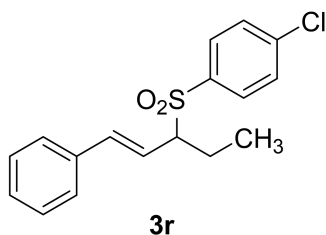
(E)-1-Fluoro-4-((1-phenylpent-1-en-3-yl)sulfonyl)benzene (**3q**, yxz-5-7) ^[3]



3q

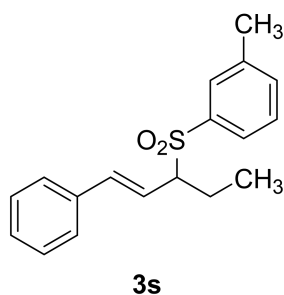
71% isolated yield from **1a** (eluent: petroleum ether/ethyl acetate = 20/1), colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.86-7.82 (m, 2H), 7.34-7.18 (m, 5H), 7.18-7.15 (m, 2H), 6.28 (d, J = 15.9 Hz, 1H), 5.90 (dd, J = 15.9, 9.4 Hz, 1H), 3.57-3.52 (m, 1H), 2.31-2.25 (m, 1H), 1.83-1.75 (m, 1H), 1.01 (t, J = 7.5 Hz, 3H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.7; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.7 (d, J = 253.7 Hz), 138.4, 135.6, 133.6 (d, J = 2.6 Hz), 132.0 (d, J = 9.3 Hz), 128.7, 128.5, 126.5, 120.8, 116.1 (d, J = 22.3 Hz), 71.3, 20.8, 11.3; HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{21}\text{FNO}_2\text{S}^+$ [$\text{M}+\text{NH}_4$] $^+$: 322.1272, found: 322.1275.

(E)-1-Chloro-4-((1-phenylpent-1-en-3-yl)sulfonyl)benzene (**3r**, yxz-5-58) ^[3]



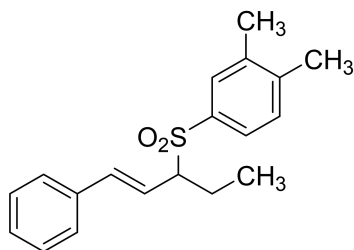
66% isolated yield from **1a** (eluent: petroleum ether/ethyl acetate = 20/1), white solid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.34-7.29 (m, 5H), 6.31 (d, J = 15.9 Hz, 1H), 5.90 (dd, J = 15.9, 9.4 Hz, 1H), 3.59-3.53 (m, 1H), 2.30-2.23 (m, 1H), 1.84-1.72 (m, 1H), 1.00 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 140.31, 138.50, 136.06, 135.59, 130.60, 129.10, 128.67, 128.50, 126.52, 120.61, 71.15, 20.83, 11.27; HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{21}^{35}\text{ClNO}_2\text{S}^+$ [$\text{M}+\text{NH}_4$] $^+$: 338.0976, found: 338.0984.

(E)-1-Methyl-3-((1-phenylpent-1-en-3-yl)sulfonyl)benzene (**3s**, yxz-5-23)



75% isolated yield from **1a** (eluent: petroleum ether/ethyl acetate = 20/1), colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.64-7.61 (m, 2H), 7.42-7.35 (m, 2H), 7.33-7.24 (m, 5H), 6.28 (d, J = 15.9 Hz, 1H), 5.90 (dd, J = 15.9, 9.4 Hz, 1H), 3.58-3.52 (m, 1H), 2.35 (s, 3H), 2.29-2.22 (m, 1H), 1.82-1.76 (m, 1H), 0.99 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.0, 138.2, 137.4, 135.9, 134.3, 129.6, 128.6, 128.6, 128.3, 126.5, 126.3, 121.1, 71.1, 21.1, 20.9, 11.3; HRMS (ESI) m/z calculated for $\text{C}_{18}\text{H}_{24}\text{NO}_2\text{S}^+$ [$\text{M}+\text{NH}_4$] $^+$: 318.1522, found: 318.1529.

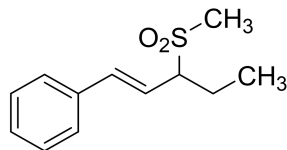
(E)-1,2-Dimethyl-4-((1-phenylpent-1-en-3-yl)sulfonyl)benzene (**3t**, yxz-5-20)



3t

68% isolated yield from **1a** (eluent: petroleum ether/ethyl acetate = 20/1), colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.61-7.53 (m, 2H), 7.29-7.23 (m, 6H), 6.32 (d, J = 15.9 Hz, 1H), 5.90 (dd, J = 15.9, 9.4 Hz, 1H), 3.56-3.50 (m, 1H), 2.34-2.21 (m, 7H), 1.81-1.69 (m, 1H), 0.98 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.2, 138.0, 137.5, 136.0, 134.8, 130.0, 129.9, 128.6, 128.3, 126.7, 126.5, 121.2, 71.1, 21.0, 20.0, 19.6, 11.4; HRMS (ESI) m/z calculated for $\text{C}_{19}\text{H}_{26}\text{NO}_2\text{S}^+$ $[\text{M}+\text{NH}_4]^+$: 332.1679, found: 332.1686.

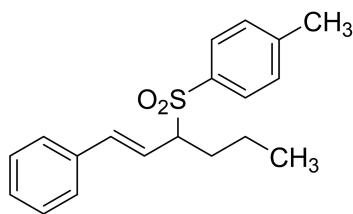
(E)-(3-(Methylsulfonyl)pent-1-en-1-yl)benzene (**3u**, yxz-5-1) ^[3]



3u

78% isolated yield from **1a** (eluent: petroleum ether/ethyl acetate = 20/1), colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.44-7.41 (m, 2H), 7.38-7.29 (m, 3H), 6.70 (d, J = 15.9 Hz, 1H), 6.13 (dd, J = 15.9, 9.7 Hz, 1H), 3.55-3.49 (m, 1H), 2.86 (s, 3H), 2.34-2.24 (m, 1H), 1.87-1.79 (m, 1H), 1.05 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.0, 135.5, 128.8, 128.7, 126.7, 121.8, 70.0, 38.4, 19.7, 11.2; HRMS (ESI) m/z calculated for $\text{C}_{12}\text{H}_{16}\text{NaO}_2\text{S}^+$ $[\text{M}+\text{Na}]^+$: 247.0763, found: 247.0766.

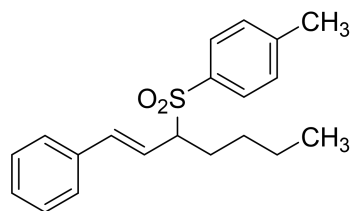
(E)-1-Methyl-4-((1-phenylhex-1-en-3-yl)sulfonyl)benzene (**3v**, yxz-4-90)



3v

55% isolated yield from **1v** (eluent: petroleum ether/ethyl acetate = 30/1), colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, $J = 8.3$ Hz, 2H), 7.33-7.24 (m, 7H), 6.29 (d, $J = 15.9$ Hz, 1H), 5.89 (dd, $J = 15.9, 9.5$ Hz, 1H), 3.66-3.60 (m, 1H), 2.41 (s, 3H), 2.18-2.11 (m, 1H), 1.78-1.72 (m, 1H), 1.50-1.44 (m, 1H), 1.34-1.27 (m, 1H), 0.92 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.5, 137.8, 135.9, 134.7, 129.4, 129.2, 128.6, 128.3, 126.5, 121.5, 69.4, 29.4, 21.6, 20.0, 13.6; HRMS (ESI) m/z calculated for $\text{C}_{19}\text{H}_{26}\text{NO}_2\text{S}^+ [\text{M}+\text{NH}_4]^+$: 332.1679, found: 332.1686.

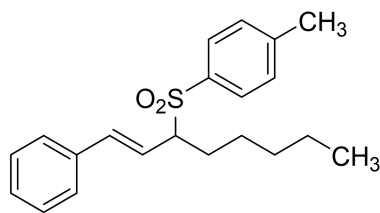
(E)-1-Methyl-4-((1-phenylhept-1-en-3-yl)sulfonyl)benzene (**3w**, yxz-4-91)



3w

49% isolated yield from **1w** (eluent: petroleum ether/ethyl acetate = 30/1), colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, $J = 8.3$ Hz, 2H), 7.33-7.25 (m, 7H), 6.28 (d, $J = 15.9$ Hz, 1H), 5.90 (dd, $J = 15.9, 9.4$ Hz, 1H), 3.64-3.58 (m, 1H), 2.41 (s, 3H), 2.22-2.18 (m, 1H), 1.76-1.73 (m, 1H), 1.41-1.25 (m, 4H), 0.87 (t, $J = 6.7$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.4, 137.8, 135.9, 134.7, 129.4, 129.2, 128.6, 128.3, 126.5, 121.5, 69.7, 28.8, 27.1, 22.3, 21.6, 13.8.; HRMS (ESI) m/z calculated for $\text{C}_{20}\text{H}_{24}\text{O}_2\text{SNa}^+ [\text{M}+\text{Na}]^+$: 351.1389, found: 351.1389.

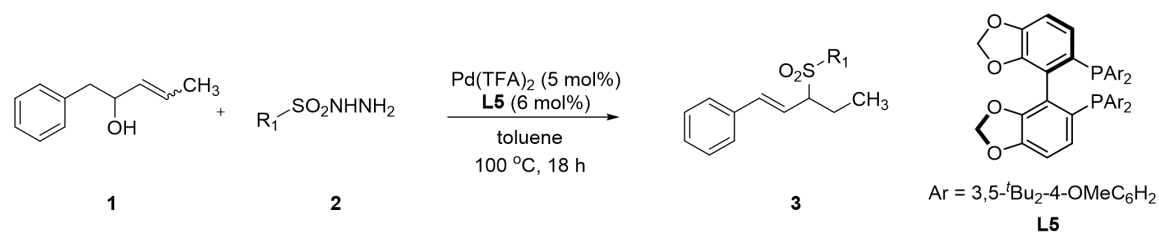
(E)-1-Methyl-4-((1-phenyloct-1-en-3-yl)sulfonyl)benzene (**3x**, yxz-4-92)



3x

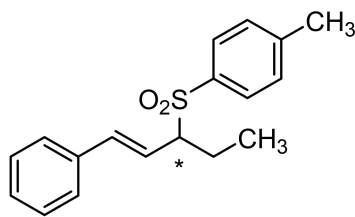
53% isolated yield from **1x** (eluent: petroleum ether/ethyl acetate = 30/1), colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, J = 8.2 Hz, 2H), 7.31-7.26 (m, 7H), 6.28 (d, J = 15.9 Hz, 1H), 5.89 (dd, J = 15.9, 9.4 Hz, 1H), 3.64-3.58 (m, 1H), 2.41 (s, 3H), 2.22-2.14 (m, 1H), 1.78-1.69 (m, 1H), 1.42-1.39 (m, 1H), 1.31-1.25 (m, 5H), 0.85 (t, J = 4.8 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.4, 137.8, 136.0, 134.7, 129.4, 129.2, 128.6, 128.3, 126.5, 121.5, 69.7, 31.3, 27.3, 26.4, 22.3, 21.6, 13.9; HRMS (ESI) m/z calculated for $\text{C}_{21}\text{H}_{30}\text{NO}_2\text{S}^+$ $[\text{M}+\text{NH}_4]^+$: 360.1992, found: 360.1997.

General procedure for asymmetric palladium-catalyzed migratory allylic sulfonylation of allylic alcohols



Under a nitrogen atmosphere, to a mixture of $\text{Pd}(\text{TFA})_2$ (3.3 mg, 0.01 mmol), **L5** (14.1 mg, 0.012 mmol), and sulfonyl hydrazide (0.4 mmol) was added a solution of allylic alcohol **1** (0.2 mmol) in toluene (1.0 mL). The reaction was sealed and stirred at 100 °C for 18 h. Subsequently, the reaction was cooled down to room temperature, and the mixture was evaporated and purified via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford desired product.

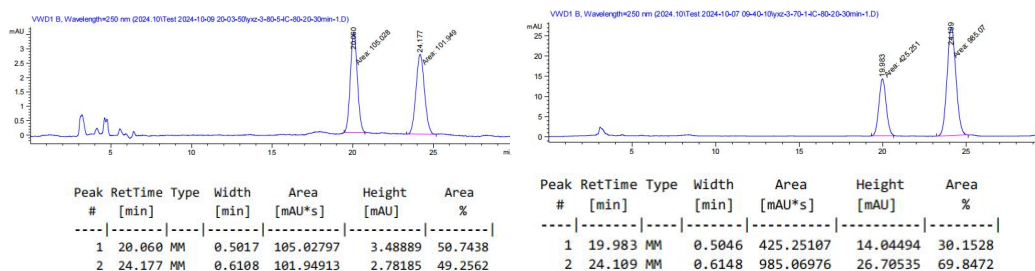
(E)-1-Methyl-4-((1-phenylpent-1-en-3-yl)sulfonyl)benzene (**3a**, yxz-3-70)^[3]



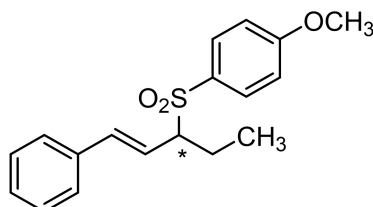
3a

60% isolated yield from **1a** (eluent: petroleum ether/ethyl acetate = 30/1), colorless oil;

70:30 *er*; HPLC analysis: Chiralcel IC column; detected at 250 nm, 25 °C; 20% *i*-PrOH in *n*-hexane; flow = 1.0 mL/min; Retention time: 19.9 min (minor), 24.1 min (major).

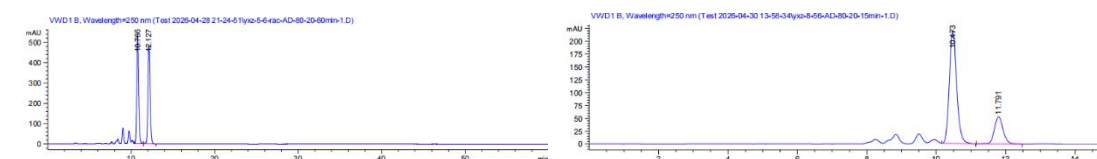


(E)-1-Methoxy-4-((1-phenylpent-1-en-3-yl)sulfonyl)benzene (**3o**, yxz-8-56) [3]



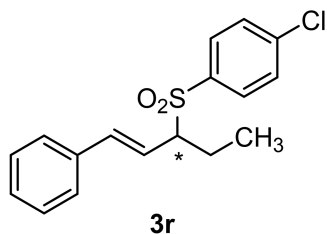
3o

34% isolated yield from **1a** (eluent: petroleum ether/ethyl acetate = 15/1), colorless oil; 78:22 *er*; HPLC analysis: Chiralcel AD column; detected at 250 nm, 25 °C; 20% *i*-PrOH in *n*-hexane; flow = 1.0 mL/min; Retention time: 10.5 min (major), 11.8 min (minor).

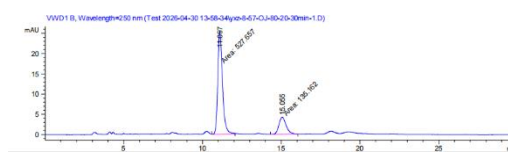
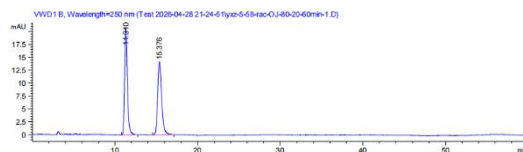


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.766	BB	0.2487	8688.19043	537.19696	49.8986	1	10.473	BB	0.2245	3208.88843	219.52364	77.8115
2	12.127	BB	0.2790	8723.51367	482.29193	50.1014	2	11.791	VB R	0.2683	915.03723	52.77918	22.1885

(*E*)-1-Chloro-4-((1-phenylpent-1-en-3-yl)sulfonyl)benzene (**3r**, yxz-8-57) [3]

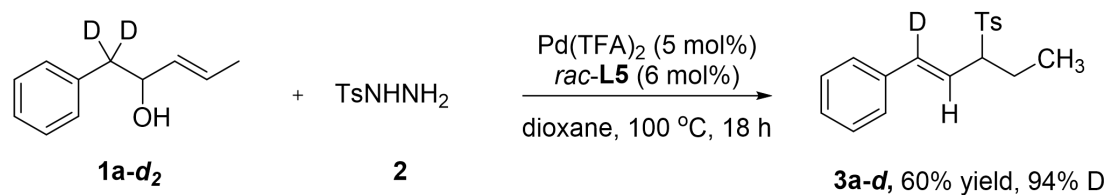


30% isolated yield from **1a** (eluent: petroleum ether/ethyl acetate = 20/1), white solid; 80:20 *er*; HPLC analysis: Chiralcel OJ column; detected at 250 nm, 25 °C; 20% *i*-PrOH in *n*-hexane; flow = 1.0 mL/min; Retention time: 11.0 min (major), 15.0 min (minor).

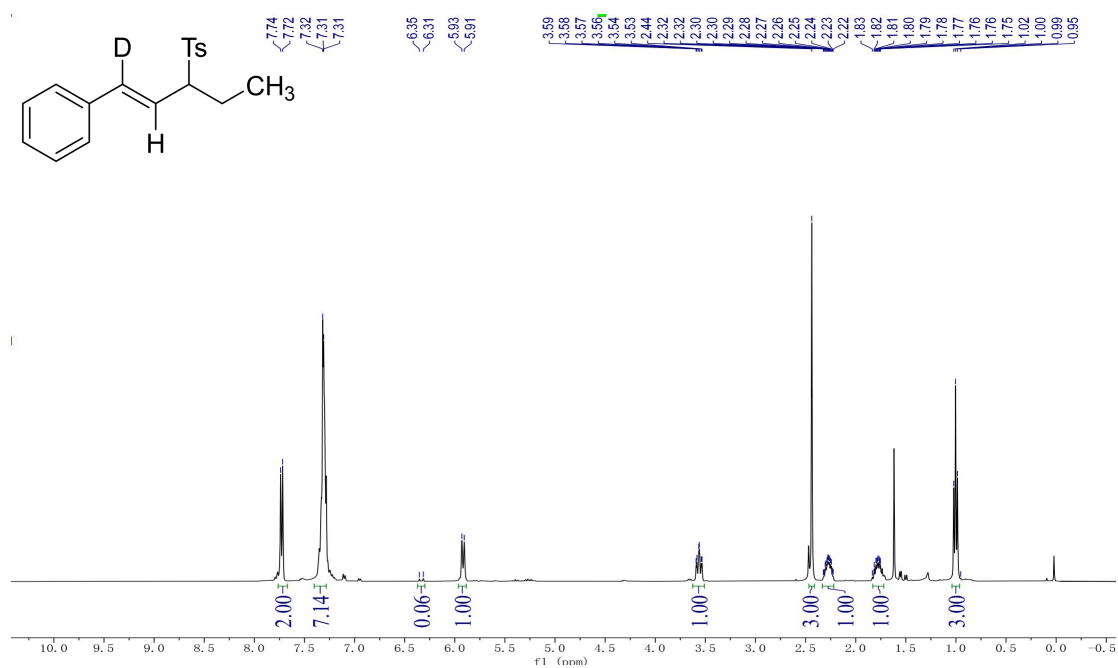


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.310	BB	0.3531	478.81076	20.75767	50.0632	1	11.097	MM	0.3463	527.65662	25.39371	79.6080
2	15.376	BB	0.5148	477.60208	14.18531	49.9368	2	15.055	MM	0.5320	135.16187	4.23439	20.3920

Deuterium labeling experiments



Under a nitrogen atmosphere, to a mixture of Pd(TFA)₂ (3.3 mg, 0.01 mmol), *rac-L5* (6.7 mg, 0.012 mmol), and sulfonyl hydrazide (0.2 mmol) was added a solution of **1a-d₂** (0.4 mmol) in 1,4-dioxane (1.0 mL). The reaction was sealed and stirred at 100 °C for 18 h. Subsequently, the reaction was cooled down to room temperature, and the mixture was evaporated and purified via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired product **3a-d**: colorless oil.



References

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^1H NMR and ^{13}C NMR spectra for compounds

