

Supporting Information for:

Alkenyl Exchange of Allyamines via Nickel(0)-Catalyzed C–C Bond Cleavage

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CONTENTS:

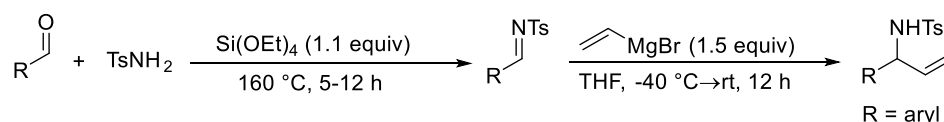
1. General Information.....	S2
2. Preparation and Analysis of Allylamine Substrates.....	S2
3. General Procedure and Optimization	S6
4. Charateration of Products.....	S8
5. Mechanism Experiments.....	S20
6. Synthesis of BW B70C.....	S23
7. NMR Spectra of New Compounds.....	S27

1. General Information

Unless mentioned otherwise, all manipulations were performed in an argon-filled glove box MBRAUN LABstar or using standard Schlenk techniques. NMR spectra were recorded on a Bruker AV 400 spectrometer at 400 MHz (^1H NMR), 101 MHz (^{13}C NMR). Chemical shifts were reported in ppm related to internal TMS for ^1H NMR data, deuterated solvent for ^{13}C NMR data, respectively. Data are presented in the following space: chemical shift, multiplicity, coupling constant in hertz (Hz), and signal area integration in natural numbers. High-resolution mass spectra were recorded on an IonSpec FT-ICR mass spectrometer with ESI or MALDI resource. GC analysis was performed using Agilent Technologies 7890A GC System. All the solvents used for reactions were distilled under argon after drying over an appropriate drying agent. $\text{Ni}(\text{COD})_2$ and PCy_3 was purchased from Strem Chemicals. Other commercially available reagents were purchased from Acros, Sigma-Adrich and Alfa Aesar Chemical Company. All of the liquid alkenes were distilled before use. All of the solid allylamine substrates were recrystallized before use.

2. Preparation and Analysis of Allylamine Substrates

Procedure A¹

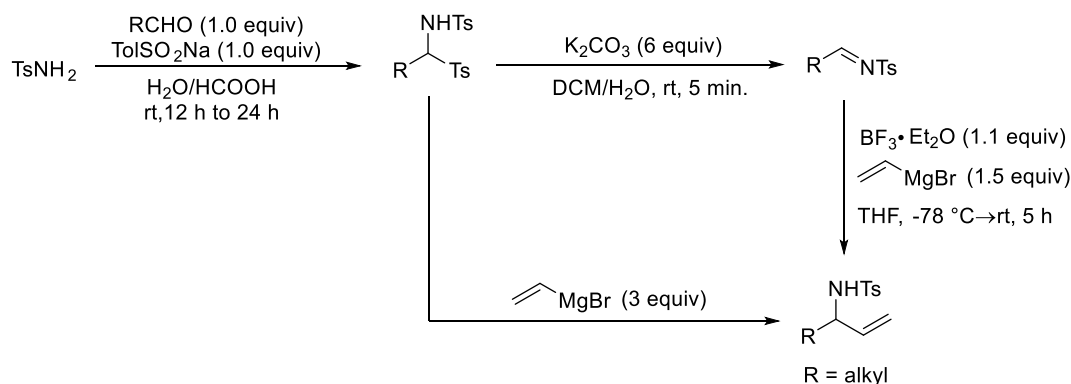


A 50 mL round bottom flask was charged with aldehyde (10 mmol), TsNH_2 (10 mmol), $\text{Si}(\text{OEt})_4$ (4.7 mL), and a magnet stirring bar. The flask was equipped with a short condenser and a receiving bottle to collect EtOH. The reaction mixture was heated at 160 °C for 5 to 12 hours and then cooled to rt. 10 mL Et_2O was added and imine products were precipitated in a short period of time. Precipitates was then washed with hexane and collected.

A 25 mL Schlenk tube was charged with crude imine (1 mmol) and a magnet stirring bar. 4 mL THF was added and the solution was cooled to -40 °C under an argon balloon. Vinylmagnesium bromide (1.5 mL, 1M in THF) was added dropwise and the reaction mixture was allowed to warm to rt. After quenching with diluted HCl (1N) the reaction mixture was extracted with Et_2O three times. Organic layer was collected and dried with Na_2SO_4 . The ether was removed under vacuum and the residue was purified by

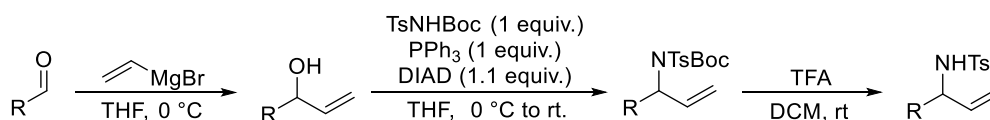
recrystallization or flash column chromatography (PE/EA = 10:1).

Procedure B²



Alkyl substituted *N*-tosyl allylamines were prepared in an alternative way. To a 100 mL round bottom flask charged with TsNH₂ (10 mmol), *p*-TolSO₂Na (10 mmol) and a magnet stirring bar, HCOOH and H₂O (15 mL each) were added, and then alkyl aldehyde (10 mmol) was added. The mixture was stirred at rt for 12 hours to 24 hours. White precipitate was collected and washed with water and petroleum ether (100 mL each), and dissolved in 50 mL DCM. The solution was shaken with 50 mL saturated K₂CO₃ solution for 5 min. The water phase was separated and extracted with DCM (3 x 10 mL). The organic phase was collected and dried with Na₂SO₄. After removing solvent under vacuum the crude imine was obtained, which are pure enough to be used in reactions. From these imines, the alkyl substituted *N*-tosyl allylamines were prepared by using the same procedure as that described in **Procedure A**. In particular cases (R = Me, cyclopropyl), imine intermediates would be hydrolyzed during the shaking process. Alternatively, the corresponding *N*-tosyl allylamines were prepared by treating the adduct with 3 equivalent vinylmagnesium bromide in THF at 0 °C.

Procedure C³

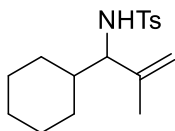


The *N*-tosyl allylamines containing 5-hexeneyl and CH₂OCH₂Ph were prepared by Mitsunobu reaction. A solution of the aldehyde (10 mmol, 0.3 M) in THF was treated with 2 equivalent vinylmagnesium bromide at 0 °C. After addition of vinylmagnesium bromide, the reaction mixture was allowed to warm to room temperature and quenched with diluted HCl (1N), and extracted with Et₂O three times. Organic layer was collected

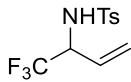
and dried with Na₂SO₄. After removing the solvent under vacuum the crude allyl alcohol was obtained, which was dissolved in 50 mL THF. TsNHBoc (10 mmol) and PPh₃ (10 mmol) were added, and the mixture was cooled to 0 °C and DIAD (11 mmol) was added over 20 min. The reaction mixture was allowed to warm to room temperature and stirred for 6 h. Solvents was removed and the residue was purified by flash column chromatography (PE/EA = 20:1). The Boc group was removed by treatment with 10 equivalent TFA in 10 mL DCM for 3 h. The pure *N*-tosyl allylamines was obtained by purification with flash column chromatography (PE/EA = 10:1).

The analytical data for new *N*-tosyl allylamines are listed below.

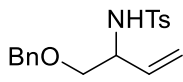
***N*-(1-cyclohexyl-2-methylallyl)-4-methylbenzenesulfonamide (2d)**

 White solid. Mp: 134-135 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 4.67 (p, *J* = 1.5 Hz, 1H), 4.63 (s, 1H), 4.56 (d, *J* = 8.3 Hz, 1H), 3.47 (t, *J* = 8.5 Hz, 1H), 2.41 (s, 3H), 1.91 – 1.81 (m, 1H), 1.77 – 1.59 (m, 3H), 1.48 – 1.41 (m, 4H), 1.35 – 1.25 (m, 1H), 1.21 – 1.08 (m, 3H), 0.93 – 0.78 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 142.9, 142.1, 138.1, 129.2, 127.2, 114.1, 64.8, 39.6, 30.0, 29.1, 26.1, 26.0, 25.9, 21.5, 17.7. HRMS (ESI) Calcd for [C₁₇H₂₅NNaO₂S, M+Na]⁺: 330.1504, Found: 330.1501.

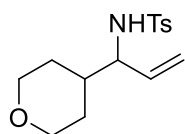
4-methyl-*N*-(1,1,1-trifluorobut-3-en-2-yl)benzenesulfonamide (2j)

 White solid. Mp: 85-86 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.74 (ddd, *J* = 16.7, 10.4, 5.8 Hz, 1H), 5.37 (d, *J* = 5.3 Hz, 1H), 5.34 (s, 1H), 5.24 (d, *J* = 9.5 Hz, 1H), 4.46 (dq, *J* = 14.7, 7.3 Hz, 1H), 2.43 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 144.0, 137.3, 129.7, 127.9, 127.0, 123.7 (q, *J* = 282.8), 121.8, 57.3 (q, *J* = 31.9), 21.6. HRMS (ESI) Calcd for [C₁₁H₁₂F₃NNaO₂S, M+Na]⁺: 302.0439, Found: 302.0438.

***N*-(1-(benzyloxy)but-3-en-2-yl)-4-methylbenzenesulfonamide (2l)**

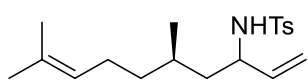
 White semi-solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.12 (m, 7H), 5.69 (ddd, *J* = 17.0, 10.4, 6.3 Hz, 1H), 5.25 – 5.04 (m, 2H), 5.01 – 4.92 (m, 1H), 4.41 (s, 2H), 3.92 (ddd, *J* = 6.5, 5.0, 1.5 Hz, 1H), 3.40 (m, 2H), 2.41 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 143.3, 137.6, 137.4, 135.1, 129.5, 128.4, 127.9, 127.7, 127.2, 117.5, 73.2, 71.8, 55.7, 21.5. HRMS (ESI) Calcd for [C₁₈H₂₀NO₃S, M-H]⁻: 330.1164, Found: 330.1166.

4-methyl-*N*-(1-(tetrahydro-2H-pyran-4-yl)allyl)benzenesulfonamide (2m)



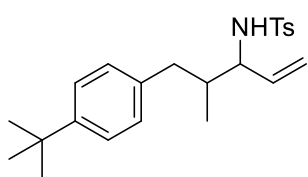
White solid. Mp: 107-108 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 5.50 (ddd, J = 17.4, 10.4, 7.2 Hz, 1H), 4.98 (d, J = 10.4 Hz, 1H), 4.89 (d, J = 17.1 Hz, 1H), 4.62 (d, J = 6.9 Hz, 1H), 3.95 (dt, J = 11.2, 5.5 Hz, 2H), 3.60 (q, J = 7.2 Hz, 1H), 3.29 (tdd, J = 11.7, 5.6, 2.1 Hz, 2H), 2.42 (s, 3H), 1.66 – 1.57 (m, 1H), 1.53 – 1.43 (m, 1H), 1.37 – 1.21 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.3, 137.2, 135.2, 129.5, 127.2, 117.4, 67.7, 67.6, 60.8, 39.9, 28.9, 28.8, 21.5. HRMS (ESI) Calcd for $[\text{C}_{15}\text{H}_{21}\text{NNaO}_3\text{S}, \text{M}+\text{Na}]^+$: 318.1140, Found: 318.1142.

***N*-(5-(5,9-dimethyldeca-1,8-dien-3-yl)-4-methylbenzenesulfonyl)-4-methylbenzenesulfonamide (2p)**



Colorless oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 9.8 Hz, 2H), 5.60 – 5.43 (m, 1H), 5.08 – 4.89 (m, 3H), 4.31 (dd, J = 18.4, 7.8 Hz, 1H), 3.81 (dt, J = 14.3, 6.9 Hz, 1H), 2.42 (s, 3H), 2.00 – 1.75 (m, 2H), 1.68 (d, J = 7.6 Hz, 3H), 1.58 (d, J = 4.1 Hz, 3H), 1.49 – 1.36 (m, 2H), 1.32 – 1.17 (m, 2H), 1.16 – 1.01 (m, 1H), 0.79 (dd, J = 18.5, 6.4 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.2, 138.5, 138.1, 137.8, 131.5, 131.4, 129.7, 129.5, 129.5, 127.2, 124.5, 116.1, 115.4, 54.7, 54.3, 43.2, 36.9, 36.8, 28.8, 28.6, 25.7, 25.7, 25.2, 21.5, 19.3, 19.1, 17.7, 17.7. HRMS (ESI) Calcd for $[\text{C}_{19}\text{H}_{29}\text{NNaO}_2\text{S}, \text{M}+\text{Na}]^+$: 358.1817, Found: 358.1816.

***N*-(5-(4-(tert-butyl)phenyl)-4-methylpent-1-en-3-yl)-4-methylbenzenesulfonamide (2q)**



White solid. Mp: 150-150 °C. dr = 1.2:1. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.70 (m, 1H), 7.67 (d, J = 8.2 Hz, 1H), 7.31 – 7.24 (m, 4H), 6.98 (m, 2H), 5.71 – 5.47 (m, 1H), 5.14 – 4.87 (m, 2H), 4.75 (dd, J = 23.9, 8.5 Hz, 1H), 3.92 – 3.80 (m, 0.45H), 3.74 – 3.66 (m, 0.55H), 2.66 (ddd, J = 23.5, 13.6, 5.5 Hz, 1H), 2.41 (s, 3H), 2.25 (s, 1H), 1.92 (dd, J = 6.2, 2.0 Hz, 1H), 1.31 (d, J = 3.8 Hz, 9H), 0.79 (dd, J = 11.3, 6.8 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.8, 143.2, 143.1, 138.1, 137.7, 137.2, 136.8, 136.02, 134.7, 129.5, 129.5, 128.7, 128.6, 127.2, 125.2, 117.4, 116.6, 60.3, 59.8, 39.8, 39.6, 38.5, 38.5, 34.4, 31.4, 21.6, 14.8, 14.7. HRMS (ESI) Calcd for $[\text{C}_{23}\text{H}_{31}\text{NNaO}_2\text{S}, \text{M}+\text{Na}]^+$: 408.1973, Found: 408.1972.

3. General Procedure and Optimization

In an argon-filled glove-box, an oven-dried sealed tube was charged with a stir bar,

catalyst precursor Ni(COD)₂, ligand PCy₃, and *N*-tosyl allylamine. The styrene and solvent were injected into the tube. For liquid allylamine, they were added in the end otherwise it would cause the formation of nickel black. The mixture was stirred at room temperature for 5 min and heated at 100 °C for 12 h. After cooling to room temperature, the reaction mixture was quenched with 100 μL HCl (1 N) and passed through a short silica gel column eluted with ethyl acetate. The pure product was obtained by column chromatography on silica gel (PE/EA = 10:1, v/v) or recrystallization. NMR yields were listed in parentheses.

Table S1. Optimization of reaction condition A

$\text{1a} + \text{2a} \xrightarrow[\text{solvents, additive}]{\text{Ni(COD)}_2 (10 \text{ mol } \%), \text{PCy}_3 (20 \text{ mol } \%), 100^\circ\text{C}, 12 \text{ h}}$
 $\text{3a} + \text{allyl}$

entry	solvents	additive (10 mol%)	temperature (°C)	yield (%) ^b
1	toluene	--	100	68
2	toluene	TsNH ₂	100	77
3	toluene	Ts _F NH ₂	100	74
4	toluene	PhCO ₂ H	100	<5
5	toluene	saccharin	100	--
6	THF	TsNH ₂	100	80
7	hexane	TsNH ₂	100	95
8	hexane	--	100	>99
9 ^c	hexane	--	100	40
10	hexane	--	80	65
11	hexane	--	120	85

^a Reaction condition: **1a** (0.25 mmol), **2a** (0.30 mmol), solvent (1 mL). ^b Yields were determined by ¹H NMR analysis using diphenylmethane as internal standard. ^c 5 mol % catalyst was used.

Table S2. Optimization of reaction condition B

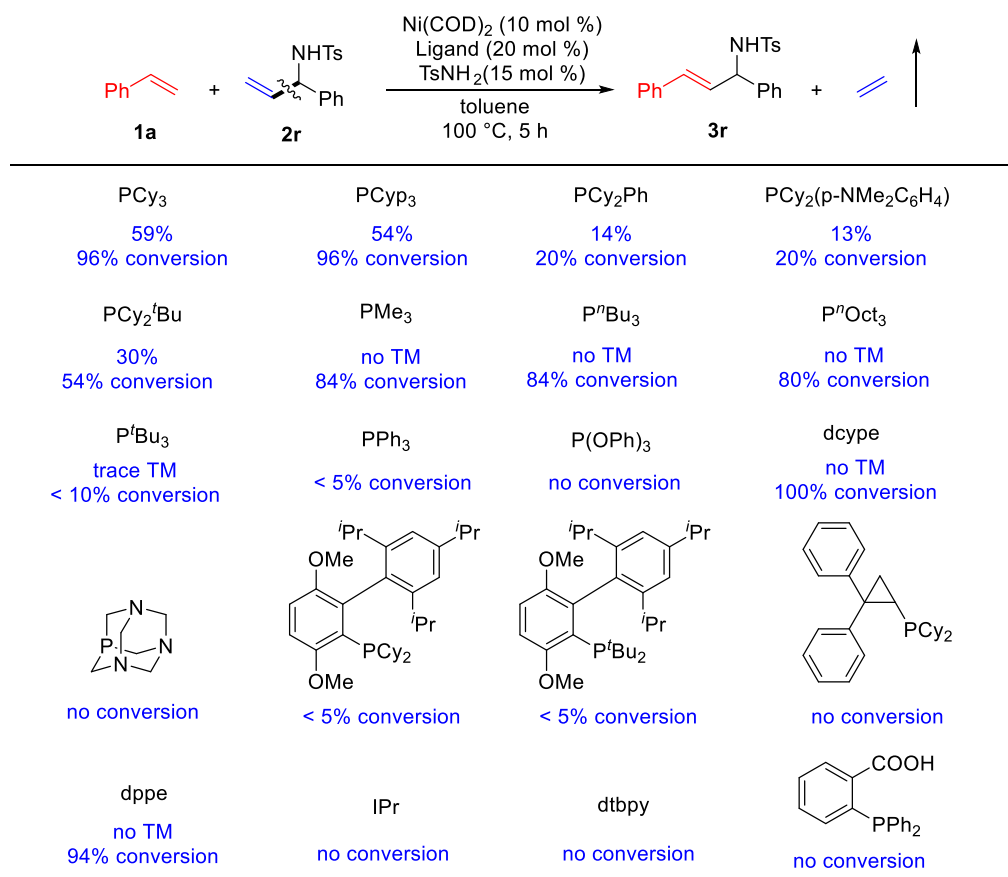
$\text{1a} + \text{2r} \xrightarrow[\text{solvents}]{\text{Ni(COD)}_2 (10 \text{ mol } \%), \text{PCy}_3 (20 \text{ mol } \%), 100^\circ\text{C}, 5 \text{ h}}$
 $\text{3r} + \text{allyl}$

entry	2m (x equiv.)	solvents	TsNH ₂	temperature (°C)	yield (%) ^b
1	0.5	toluene	15 mol %	100	59
2	0.5	hexane	15 mol %	100	37
3	0.5	THF	15 mol %	100	21

4	0.5	toluene	15 mol %	90	51
5	0.5	toluene	15 mol %	110	49
6	1.5	toluene	15 mol %	100	45
7 ^c	1.5	toluene	30 mol %	100	54
8 ^c	2.0	toluene	30 mol %	100	76
9 ^c	2.2	toluene	30 mol %	100	68
10 ^c	2.5	toluene	30 mol %	100	61

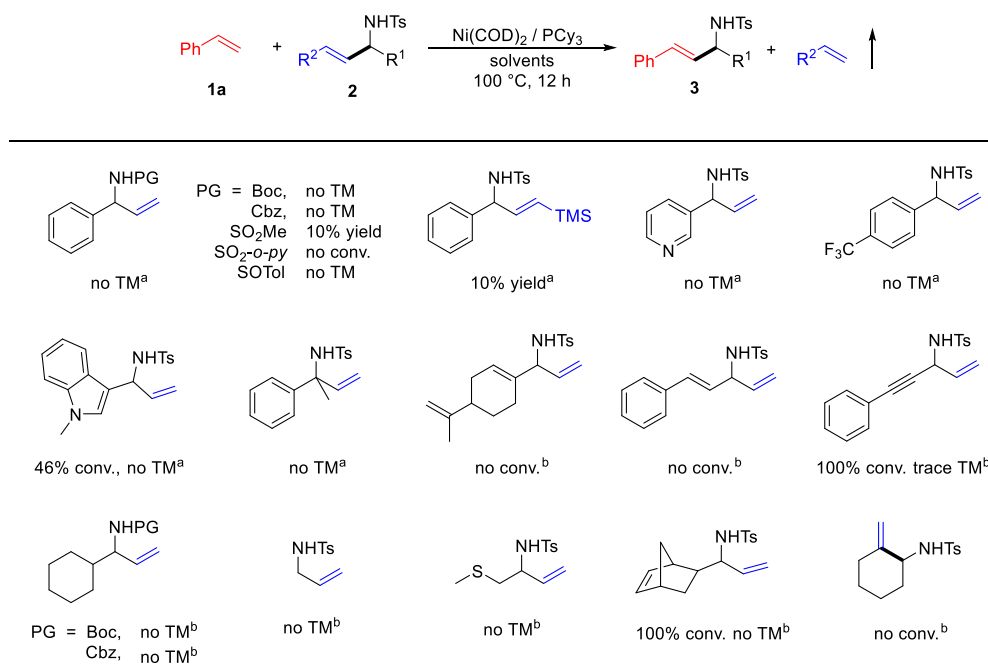
^a Reaction condition: **1a** (0.5 mmol), **2r** (0.25 mmol), Ni(COD)₂ (10 mol %), PCy₃ (20 mol %), solvent (1.0 mL) at 100 °C for 5 h. ^b NMR yield, diphenylmethane as internal standard. For entries 1-5, yields were based on **2r**. For entries 6-10, yields were based on **1a**. ^c Ni(COD)₂ (20 mol %) and PCy₃ (40 mol %) were used.

Scheme S1. Ligands screening ^{a,b}



^a Reaction condition: **1a** (0.5 mmol), **2r** (1.0 mmol), Ni(COD)₂ (0.05 mmol), ligand (Ni/P = 1:2), TsNH₂ (0.075 mmol), toluene (1 mL). 100 °C, 5 h. ^b Yields were determined by ¹H NMR analysis using diphenylmethane as internal standard.

Scheme S2. Unsuccessful substrates ^{a,b,c}



^a Condition A: **1a** (0.25 mmol), **2** (0.3 mmol), Ni(COD)₂ (10 mol %), PCy₃ (20 mol %) in hexane (1 mL) at 100 °C for 12 h. ^b Condition B: **1** (0.5 mmol), **2** (1.0 mmol), Ni(COD)₂ (20 mol %), PCy₃ (40 mol %), TsNH₂ (30 mol %) in toluene (1 mL) at 100 °C for 5 h. ^c NMR yields. Diphenylmethane was used as internal standards.

4. Characteration of products

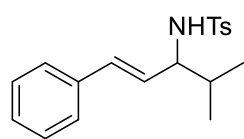
(*E*)-*N*-(1-cyclohexyl-3-phenylallyl)-4-methylbenzenesulfonamide (**3a**)⁴

White solid, 88% yield (99% NMR yield). Mp: 158–160 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.28–7.16 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 7.1 Hz, 2H), 6.04 (d, *J* = 15.9 Hz, 1H), 5.69 (dd, *J* = 15.8, 8.1 Hz, 1H), 4.93 (d, *J* = 8.4 Hz, 1H), 3.71 (dd, *J* = 14.7, 7.9 Hz, 1H), 1.81 (d, *J* = 12.6 Hz, 2H), 1.74–1.61 (m, 4H), 1.47–1.41 (m, 1H), 1.23–1.08 (m, 3H), 1.05–0.94 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 143.2, 138.3, 136.5, 132.2, 129.5, 128.4, 127.7, 127.4, 126.4, 61.6, 43.1, 29.2, 29.2, 26.4, 26.1, 21.4.

(*E*)-4-methyl-*N*-(1-phenylnon-1-en-3-yl)benzenesulfonamide (**3e**)

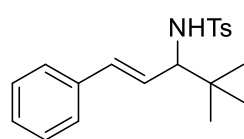
White solid, 98% yield. Mp: 123–124 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.9 Hz, 2H), 7.28–7.13 (m, 5H), 7.10 (d, *J* = 7.3 Hz, 2H), 6.19 (d, *J* = 15.8 Hz, 1H), 5.71 (dd, *J* = 15.9, 7.6 Hz, 1H), 4.87 (d, *J* = 7.8 Hz, 1H), 3.90 (p, *J* = 7.3 Hz, 1H), 2.28 (s, 3H), 1.53 (hept, *J* = 7.1, 6.4 Hz, 2H), 1.35–1.10 (m, 8H), 0.85 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 143.2, 138.1, 136.3, 131.3, 129.5, 129.0, 128.4, 127.6, 127.3, 126.3, 56.4, 35.9, 31.6, 28.9, 25.4, 22.5, 21.4, 14.1. HRMS (ESI) Calcd for [C₂₂H₂₉NNaO₂S, M+Na]⁺: 394.1817, Found: 394.1815.

(E)-4-methyl-N-(4-methyl-1-phenylpent-1-en-3-yl)benzenesulfonamide (3f)⁴



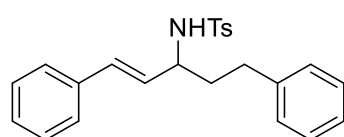
White crystal, 95% yield. Mp: 137-138 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.26–7.16 (m, 3H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.06 (d, *J* = 15.9 Hz, 1H), 5.71 (dd, *J* = 15.9, 8.0 Hz, 1H), 5.31 (d, *J* = 8.5 Hz, 1H), 3.70 (q, *J* = 7.8 Hz, 1H), 2.23 (s, 3H), 1.80 (dt, *J* = 13.1, 6.5 Hz, 1H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 143.2, 138.2, 136.5, 132.2, 129.5, 128.4, 127.6, 127.4, 127.0, 126.4, 62.1, 33.3, 21.4, 18.6, 18.5.

(E)-N-(4,4-dimethyl-1-phenylpent-1-en-3-yl)-4-methylbenzenesulfonamide (3g)⁴



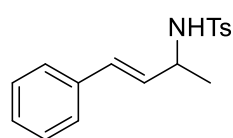
White crystal, 97% yield. Mp: 126-128 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.26–7.11 (m, 3H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 6.9 Hz, 2H), 5.89 (d, *J* = 15.8 Hz, 1H), 5.69 (dd, *J* = 15.8, 8.8 Hz, 1H), 5.54 (d, *J* = 9.5 Hz, 1H), 3.54 (t, *J* = 9.1 Hz, 1H), 2.14 (s, 3H), 0.93 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 143.1, 138.1, 136.4, 132.9, 129.4, 128.3, 127.5, 127.4, 126.3, 125.5, 65.7, 35.0, 26.5, 21.3.

(E)-N-(1,5-diphenylpent-1-en-3-yl)-4-methylbenzenesulfonamide (3h)⁴



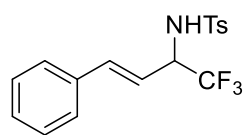
White solid, 92% yield. Mp: 97-99 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.29–7.15 (m, 6H), 7.12–7.02 (m, 6H), 6.15 (d, *J* = 15.9 Hz, 1H), 5.79–5.65 (m, 1H), 5.52 (d, *J* = 8.2 Hz, 1H), 3.93 (p, *J* = 7.3 Hz, 1H), 2.71–2.53 (m, 2H), 2.21 (s, 3H), 1.93–1.76 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 143.2, 141.1, 138.1, 136.3, 131.7, 129.6, 128.5, 128.5, 128.4, 128.4, 127.7, 127.3, 126.4, 126.0, 56.1, 37.4, 31.7, 21.4.

(E)-4-methyl-N-(4-phenylbut-3-en-2-yl)benzenesulfonamide (3i)



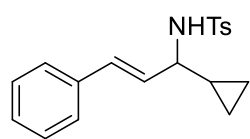
White crystal, 95% yield. Mp: 80–82 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.29–7.17 (m, 5H), 7.14 (d, *J* = 7.0 Hz, 2H), 6.28 (d, *J* = 15.9 Hz, 1H), 5.83 (dd, *J* = 15.9, 6.7 Hz, 1H), 4.87 (d, *J* = 7.6 Hz, 1H), 4.08 (h, *J* = 6.9 Hz, 1H), 2.33 (s, 3H), 1.27 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 143.3, 138.0, 136.2, 130.5, 130.1, 129.6, 128.4, 127.7, 127.3, 126.4, 51.7, 21.9, 21.4. HRMS (ESI) Calcd for [C₁₇H₁₉NNaO₂S, M+Na]⁺: 324.1034, Found: 324.1032.

(E)-4-methyl-N-(1,1,1-trifluoro-4-phenylbut-3-en-2-yl)benzenesulfonamide (3j)



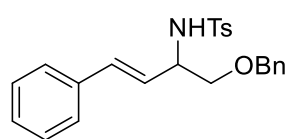
White solid. Mp: 112-113 °C. 63% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.16 (m, 7H), 6.49 (d, *J* = 15.9 Hz, 1H), 5.90 (dd, *J* = 15.9, 7.0 Hz, 1H), 5.26 (d, *J* = 9.3 Hz, 1H), 4.58 (h, *J* = 7.1 Hz, 1H), 2.34 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 144.1, 137.3, 136.9, 134.9, 129.8, 128.8, 128.6, 127.2, 126.8, 123.9 (q, *J* = 282.2 Hz), 118.2, 57.49 (q, *J* = 32.2 Hz), 21.5. HRMS (ESI) Calcd for [C₁₇H₁₆F₃NNaO₂S, M+Na]⁺: 378.0752, Found: 378.0750.

(E)-N-(1-(cyclopropyl-3-phenylallyl)-4-methylbenzenesulfonamide (3k)



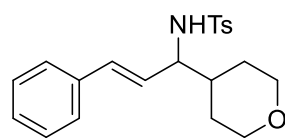
White crystal, 36% yield. Mp: 80–82 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.29–7.11 (m, 7H), 6.29 (d, *J* = 15.9 Hz, 1H), 5.84 (dd, *J* = 15.8, 7.1 Hz, 1H), 5.27 (d, *J* = 6.7 Hz, 1H), 3.36 (q, *J* = 7.3 Hz, 1H), 2.31 (s, 3H), 1.01–0.89 (m, 1H), 0.53–0.39 (m, 2H), 0.30–0.15 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 143.2, 136.4, 131.3, 129.5, 128.4, 127.9, 127.6, 127.4, 126.4, 60.4, 21.5, 16.4, 3.7, 3.3. HRMS (ESI) Calcd for [C₁₉H₂₀NO₂S, M-H]⁻: 326.1215, Found: 326.1218.

(E)-N-(1-(benzyloxy)-4-phenylbut-3-en-2-yl)-4-methylbenzenesulfonamide (3l)



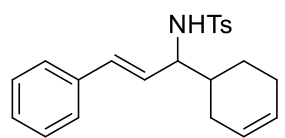
Colorless oil, 58% yield (64% NMR yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.35–7.20 (m, 9H), 7.18–7.13 (m, 3H), 6.36 (dd, *J* = 16.0, 1.0 Hz, 1H), 5.88 (dd, *J* = 16.0, 7.3 Hz, 1H), 5.22 (d, *J* = 6.6 Hz, 1H), 4.43 (s, 2H), 4.14–4.07 (m, 1H), 3.53–3.41 (m, 2H), 2.30 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 143.3, 137.8, 137.4, 136.2, 132.6, 129.5, 128.5, 128.4, 127.9, 127.8, 127.8, 127.4, 126.5, 126.1, 73.3, 72.1, 55.8, 21.5. HRMS (ESI) Calcd for [C₂₄H₂₅NNaO₃S, M+Na]⁺: 430.1453, Found: 430.1450.

(E)-4-methyl-N-(3-phenyl-1-(tetrahydro-2H-pyran-4-yl)allyl)benzenesulfonamide (3m)



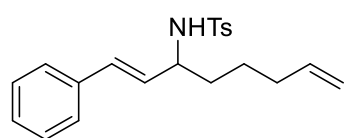
White foam, 61% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.27–7.17 (m, 3H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.04 (d, *J* = 7.0 Hz, 2H), 6.03 (d, *J* = 15.8 Hz, 1H), 5.66 (dd, *J* = 15.8, 8.4 Hz, 1H), 5.33 (d, *J* = 8.7 Hz, 1H), 3.93 (td, *J* = 11.5, 3.2 Hz, 2H), 3.67 (q, *J* = 8.2 Hz, 1H), 3.28 (q, *J* = 10.6 Hz, 2H), 2.23 (s, 3H), 1.78–1.60 (m, 2H), 1.56–1.46 (m, 1H), 1.41–1.22 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 143.3, 138.0, 136.0, 132.8, 129.5, 128.4, 127.7, 127.3, 126.3, 126.2, 67.7, 67.5, 61.2, 40.2, 29.4, 29.2, 27.9, 21.3. HRMS (ESI) Calcd for [C₂₁H₂₄NO₃S, M-H]⁻: 370.1477, Found: 370.1480.

(E)-N-(1-(cyclohex-3-en-1-yl)-3-phenylallyl)-4-methylbenzenesulfonamide (3n)



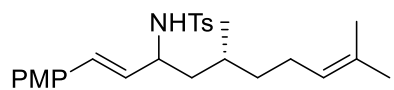
White solid, 79% yield (82% NMR yield). Mp: 142–143 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.28–7.11 (m, 5H), 7.09–7.01 (m, 2H), 6.05 (dd, *J* = 15.8, 10.3 Hz, 1H), 5.74–5.57 (m, 3H), 4.97 (dd, *J* = 12.7, 8.6 Hz, 1H), 3.78 (qd, *J* = 8.0, 4.9 Hz, 1H), 2.24 (d, *J* = 4.1 Hz, 3H), 2.20–1.67 (m, 6H), 1.37–1.22 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 143.2, 143.2, 138.1, 136.2, 132.6, 132.2, 129.5, 128.3, 127.6, 127.6, 127.3, 127.3, 127.1, 126.9, 126.8, 126.3, 126.3, 125.7, 125.6, 60.9, 60.6, 38.8, 28.0, 27.9, 24.9, 24.9, 24.9, 24.7, 21.3, 21.3. HRMS (ESI) Calcd for [C₂₂H₂₅NNaO₂S, M+Na]⁺: 390.1504, Found: 390.1507.

(E)-4-methyl-N-(1-phenylocta-1,7-dien-3-yl)benzenesulfonamide (3o)



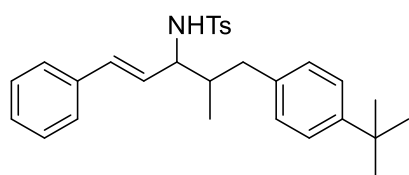
Colorless oil, 42% yield. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, J = 8.2 Hz, 2H), 7.28–7.14 (m, 5H), 7.09 (d, J = 6.8 Hz, 2H), 6.19 (d, J = 15.8 Hz, 1H), 5.78–5.62 (m, 2H), 5.01–4.85 (m, 2H), 4.73 (d, J = 7.9 Hz, 1H), 3.92 (p, J = 7.2 Hz, 1H), 2.29 (s, 3H), 2.00 (qt, J = 7.1, 1.4 Hz, 2H), 1.63–1.50 (m, 2H), 1.46–1.32 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.2, 138.1, 136.2, 131.4, 129.5, 128.7, 128.4, 127.7, 127.3, 126.3, 114.9, 56.3, 35.3, 33.2, 24.7, 21.4. HRMS (ESI) Calcd for $[\text{C}_{21}\text{H}_{25}\text{NNaO}_2\text{S}, \text{M}+\text{Na}]^+$: 378.1504, Found: 378.1501.

N-((5R,E)-1-(4-methoxyphenyl)-5,9-dimethyldeca-1,8-dien-3-yl)-4-methylbenzenesulfonamide (3p)



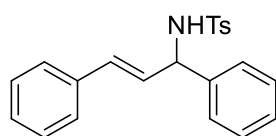
Colorless oil, 48% yield. dr = 1:1. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.03 (t, J = 7.8 Hz, 2H), 6.78 (dd, J = 8.7, 2.3 Hz, 2H), 6.14 (dd, J = 15.8, 7.1 Hz, 1H), 5.51 (dt, J = 15.6, 7.1 Hz, 1H), 5.04 (q, J = 7.0 Hz, 1H), 4.46 (dd, J = 20.1, 7.6 Hz, 1H), 3.97 (h, J = 7.1 Hz, 1H), 3.80 (s, 3H), 2.30 (s, 3H), 2.03 – 1.88 (m, 2H), 1.88 – 1.73 (m, 2H), 1.66 (d, J = 9.7 Hz, 3H), 1.58 (d, J = 9.1 Hz, 3H), 1.51 – 1.35 (m, 2H), 1.17 – 1.06 (m, 1H), 0.89 – 0.78 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.2, 159.2, 143.1, 138.3, 131.4, 131.3, 131.1, 130.5, 129.4, 129.1, 129.0, 127.5, 127.5, 127.3, 127.2, 126.6, 124.5, 113.8, 55.3, 54.9, 54.5, 43.5, 43.4, 36.9, 36.8, 35.6, 35.0, 31.2, 31.1, 29.7, 28.9, 28.7, 27.7, 27.6, 27.0, 26.9, 26.6, 26.4, 26.3, 26.2, 25.7, 25.2, 21.4, 19.3, 19.3, 17.7. HRMS (ESI) Calcd for $[\text{C}_{26}\text{H}_{35}\text{NNaO}_3\text{S}, \text{M}+\text{Na}]^+$: 464.2235, Found: 464.2230.

(E)-N-(5-(4-(tert-butyl)phenyl)-4-methyl-1-phenylpent-1-en-3-yl)-4-methylbenzenesulfonamide (3q)



White solid, 95% yield. dr = 1:1. Mp: 150–152 $^{\circ}\text{C}$. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.71 (dd, J = 19.8, 8.0 Hz, 2H), 7.33–6.95 (m, 11H), 6.11 (d, J = 15.8 Hz, 1H), 5.76 (dd, J = 15.8, 8.0 Hz, 1H), 5.05 (d, J = 8.2 Hz, 0.8H), 4.97 (d, J = 8.6 Hz, 0.2H), 3.95 (td, J = 8.1, 4.4 Hz, 0.2H), 3.85 (td, J = 8.0, 5.0 Hz, 0.8H), 2.83–2.71 (m, 1H), 2.39–2.20 (m, 4H), 2.01 (h, J = 6.2 Hz, 1H), 1.31 (s, 9H), 0.86 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.8, 143.2, 137.9, 137.1, 136.8, 136.3, 132.8, 132.2, 129.5, 128.8, 128.7, 128.4, 127.7, 127.3, 126.3, 126.3, 125.9, 125.2, 60.5, 60.3, 40.4, 40.1, 38.8, 38.6, 34.4, 31.4, 21.4, 15.2. HRMS (ESI) Calcd for $[\text{C}_{29}\text{H}_{34}\text{NO}_2\text{S}, \text{M}-\text{H}]^-$: 460.2311, Found: 460.2313.

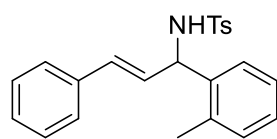
(E)-N-(1,3-diphenylallyl)-4-methylbenzenesulfonamide (3r)⁵



White solid, 76% yield. Mp: 129–131 $^{\circ}\text{C}$. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, J = 7.9 Hz, 2H), 7.34–6.98 (m, 12H), 6.35 (d, J = 15.9 Hz, 1H), 6.07 (dd, J = 15.8, 6.7 Hz, 1H), 5.11 (t, J = 6.8 Hz, 1H), 5.00 (d, J = 7.0 Hz, 1H), 2.32 (s, 3H). ^{13}C

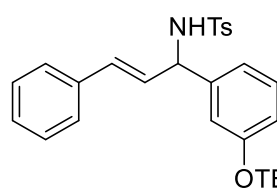
NMR (101 MHz, CDCl₃) δ 143.4, 139.8, 137.9, 136.2, 132.3, 129.6, 128.9, 128.6, 128.3, 128.0, 128.0, 127.5, 127.2, 126.7, 59.9, 21.6.

(E)-4-methyl-N-(3-phenyl-1-(o-tolyl)allyl)benzenesulfonamide (3s)⁵



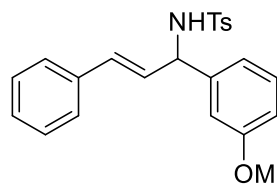
White solid, 62% yield. Mp: 137–139 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.24–7.00 (m, 12H), 6.24 (d, *J* = 15.9 Hz, 1H), 6.07 (dd, *J* = 15.9, 6.3 Hz, 1H), 5.45 (d, *J* = 7.1 Hz, 1H), 5.35 (d, *J* = 6.7 Hz, 1H), 2.28 (s, 3H), 2.27 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 143.2, 137.9, 137.7, 136.2, 135.5, 131.8, 130.7, 129.4, 128.5, 128.1, 127.9, 127.7, 127.3, 126.9, 126.6, 126.4, 56.4, 21.5, 19.3.

(E)-N-(1-(3-((tert-butyldimethylsilyl)oxy)phenyl)-3-phenylallyl)-4-methylbenzenesulfonamide (3t)



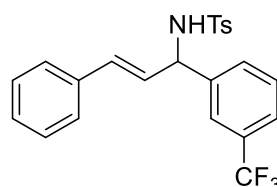
Colorless viscous oil, 69% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.28–7.03 (m, 8H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.71–6.62 (m, 3H), 6.33 (d, *J* = 15.8 Hz, 1H), 6.06 (dd, *J* = 15.8, 6.7 Hz, 1H), 5.26 (d, *J* = 7.4 Hz, 1H), 5.04 (t, *J* = 7.0 Hz, 1H), 2.30 (s, 3H), 0.95 (s, 9H), 0.14 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 155.9, 143.2, 141.2, 136.1, 132.0, 129.7, 129.4, 128.4, 128.3, 127.8, 127.3, 126.5, 119.9, 119.4, 118.8, 59.6, 25.7, 21.5, 18.2, -4.4. HRMS (ESI) Calcd for [C₂₈H₃₄NO₃SSi, M-H]⁺: 492.2029, Found: 492.2030

(E)-N-(1-(3-methoxyphenyl)-3-phenylallyl)-4-methylbenzenesulfonamide (3u)



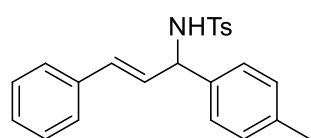
Off-white solid, 62% yield. Mp: 102–103 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 7.6 Hz, 2H), 7.28–7.08 (m, 8H), 6.82–6.67 (m, 3H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.06 (dd, *J* = 15.8, 6.5 Hz, 1H), 5.33 (d, *J* = 7.4 Hz, 1H), 5.07 (t, *J* = 7.0 Hz, 1H), 3.70 (s, 3H), 2.30 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 159.8, 143.3, 141.2, 137.7, 136.1, 132.1, 129.8, 129.4, 128.5, 128.0, 127.9, 127.3, 126.5, 119.3, 113.5, 112.5, 59.7, 55.2, 21.4. HRMS (ESI) Calcd for [C₂₃H₂₂NO₃S, M-H]⁺: 392.1321, Found: 392.1323.

(E)-4-methyl-N-(3-phenyl-1-(3-(trifluoromethyl)phenyl)allyl)benzenesulfonamide (3v)



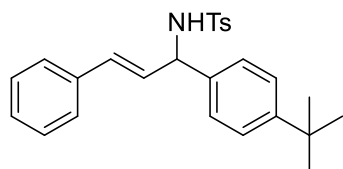
Yellow solid, 65% yield. Mp: 120–121 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.31–7.10 (m, 8H), 6.82–6.72 (m, 2H), 6.70 (s, 1H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.06 (dd, *J* = 15.8, 6.2 Hz, 1H), 5.15–5.04 (m, 2H), 3.71 (s, 3H), 2.32 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 143.6, 140.6, 137.3, 135.6, 133.0, 130.6, 129.5, 129.2, 128.5, 128.2, 127.2, 127.1, 126.6, 123.8, 59.4, 21.4. HRMS (ESI) Calcd for [C₂₃H₁₉F₃NO₂S, M-H]⁺: 430.1089, Found: 430.1092.

(E)-4-methyl-N-(3-phenyl-1-(p-tolyl)allyl)benzenesulfonamide (3w)⁵



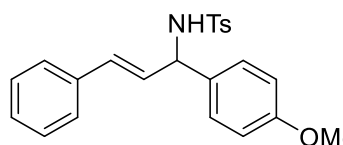
White solid, 66% yield. Mp: 135-136 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, J = 8.0 Hz, 2H), 7.28–7.20 (m, 3H), 7.14 (dd, J = 11.7, 8.1 Hz, 4H), 7.06 (q, J = 8.1 Hz, 4H), 6.33 (d, J = 15.8 Hz, 1H), 6.06 (dd, J = 15.8, 6.6 Hz, 1H), 5.13 (d, J = 7.1 Hz, 1H), 5.06 (t, J = 6.9 Hz, 1H), 2.31 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.3, 137.9, 137.7, 136.8, 136.3, 132.0, 129.5, 129.5, 128.5, 128.5, 127.9, 127.5, 127.1, 126.6, 59.7, 21.5, 21.2.

(*E*)-*N*-(1-(4-(*tert*-butyl)phenyl)-3-phenylallyl)-4-methylbenzenesulfonamide (3x)⁴



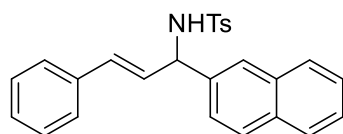
White solid, 72% yield. Mp: 143-145 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, J = 7.1 Hz, 2H), 7.26–7.00 (m, 11H), 6.35 (d, J = 15.7 Hz, 1H), 6.08 (dd, J = 15.4, 6.0 Hz, 1H), 5.35 (d, J = 6.4 Hz, 1H), 5.17–5.00 (m, 1H), 2.28 (s, 3H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.9, 143.1, 138.0, 136.7, 136.3, 131.9, 129.4, 128.5, 128.5, 127.9, 127.4, 126.9, 126.6, 125.6, 59.7, 34.6, 31.4, 21.5.

(*E*)-*N*-(1-(4-methoxyphenyl)-3-phenylallyl)-4-methylbenzenesulfonamide (3y)⁴



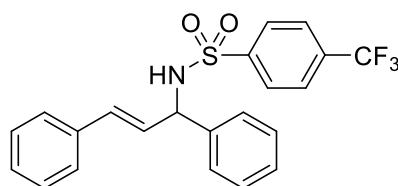
White solid, 44% yield. Mp: 134-136 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, J = 8.3 Hz, 2H), 7.27–7.18 (m, 3H), 7.17–7.07 (m, 6H), 6.74 (d, J = 8.7 Hz, 2H), 6.31 (d, J = 15.8 Hz, 1H), 6.05 (dd, J = 15.8, 6.7 Hz, 1H), 5.34 (d, J = 7.4 Hz, 1H), 5.05 (t, J = 7.0 Hz, 1H), 3.73 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.2, 143.2, 137.9, 136.2, 131.9, 131.8, 129.5, 128.5, 128.5, 128.4, 127.9, 127.4, 126.6, 114.1, 59.3, 55.3, 21.5.

(*E*)-4-methyl-*N*-(1-(naphthalen-2-yl)-3-phenylallyl)benzenesulfonamide (3z)⁵



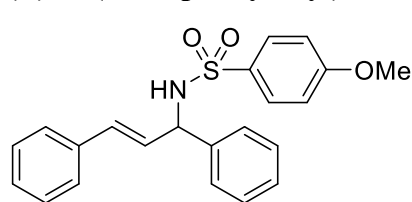
White solid, 36% yield. Mp: 164-166 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.73–7.49 (m, 6H), 7.55 (d, J = 8.3 Hz, 2H), 7.25–7.11 (m, 6H), 6.95 (d, J = 8.3 Hz, 2H), 6.33 (d, J = 16.0 Hz, 1H), 6.14 (dd, J = 16.0, 6.7 Hz, 1H), 5.22 (d, J = 7.3 Hz, 1H), 5.05 (t, J = 7.0 Hz, 1H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.4, 137.7, 136.7, 136.1, 133.0, 132.9, 132.5, 129.4, 128.6, 128.5, 128.1, 128.1, 128.0, 127.6, 127.3, 126.6, 126.3, 126.2, 126.1, 124.9, 59.9, 21.3.

(*E*)-*N*-(1,3-diphenylallyl)-4-trifluoromethylbenzenesulfonamide (3aa)⁴



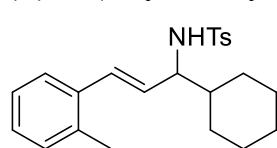
White solid, 46% yield. Mp: 128-129 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 7.23–7.05 (m, 10H), 6.33 (d, J = 15.8 Hz, 1H), 6.05 (dd, J = 15.8, 6.9 Hz, 1H), 5.98 (d, J = 7.8 Hz, 1H), 5.18 (t, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.3, 138.9, 135.7, 133.9 (q, J = 33.0 Hz), 132.6, 128.8, 128.6, 128.2, 128.1, 127.7, 127.7, 127.1, 126.5, 125.9 (q, J = 3.5 Hz), 123.2 (q, J = 272.9 Hz), 60.2.

(E)-N-(1,3-diphenylallyl)-4-methoxybenzenesulfonamide (3ab)⁵



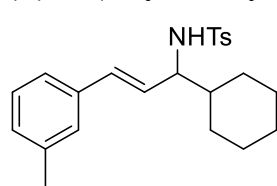
Semi-solid, 69% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.9 Hz, 2H), 7.30–7.13 (m, 10H), 6.77 (d, *J* = 8.9 Hz, 2H), 6.33 (d, *J* = 15.9 Hz, 1H), 6.07 (dd, *J* = 15.9, 6.9 Hz, 1H), 5.46 (d, *J* = 7.6 Hz, 1H), 5.08 (t, *J* = 7.1 Hz, 1H), 3.74 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.0, 139.8, 136.4, 133.0, 132.9, 129.5, 128.9, 128.8, 128.5, 128.0, 127.9, 127.3, 126.5, 113.5, 60.0, 55.6.

(E)-N-(1-cyclohexyl-3-(*o*-tolyl)allyl)-4-methylbenzenesulfonamide (4a)



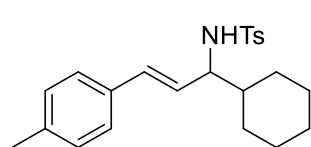
White solid, 74% yield (80% NMR yield). Mp: 169–172 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.15–6.95 (m, 4H), 6.30 (d, *J* = 15.7 Hz, 1H), 5.60 (dd, *J* = 15.7, 8.1 Hz, 1H), 5.25–5.13 (m, 1H), 3.74 (q, *J* = 7.7 Hz, 1H), 2.26 (s, 3H), 2.15 (s, 3H), 1.83 (d, *J* = 12.9 Hz, 1H), 1.75–1.55 (m, 4H), 1.52–1.41 (m, 1H), 1.25–0.93 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 143.1, 138.3, 135.5, 135.2, 130.1, 129.8, 129.4, 128.8, 127.4, 127.2, 125.8, 125.6, 61.6, 43.0, 29.1, 29.0, 26.3, 26.0, 26.0, 21.4, 19.6. HRMS (ESI) Calcd for [C₂₃H₂₉NNaO₂S, M+Na]⁺: 406.1817, Found: 406.1818.

(E)-N-(1-cyclohexyl-3-(*m*-tolyl)allyl)-4-methylbenzenesulfonamide (4b)



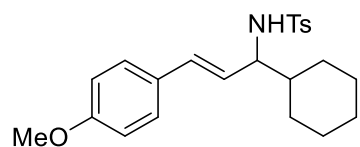
White solid, 82% yield (94% NMR yield). Mp: 145–147 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 7.9 Hz, 2H), 7.13 (dd, *J* = 12.7, 7.7 Hz, 3H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.4 Hz, 2H), 6.00 (d, *J* = 15.9 Hz, 1H), 5.69 (dd, *J* = 15.8, 8.2 Hz, 1H), 5.29 (d, *J* = 8.6 Hz, 1H), 3.70 (q, *J* = 7.8 Hz, 1H), 2.30 (s, 3H), 2.26 (s, 3H), 1.84 (d, *J* = 12.8 Hz, 1H), 1.78–1.57 (m, 4H), 1.52–1.39 (m, 1H), 1.24–0.91 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 143.0, 138.2, 137.8, 136.4, 132.1, 129.4, 128.3, 128.2, 127.3, 127.1, 126.9, 123.5, 61.6, 42.9, 29.1, 29.1, 26.3, 26.0, 26.0, 21.4. HRMS (ESI) Calcd for [C₂₃H₂₉NNaO₂S, M+Na]⁺: 406.1817, Found: 406.1816.

(E)-N-(1-cyclohexyl-3-(*p*-tolyl)allyl)-4-methylbenzenesulfonamide (4c)



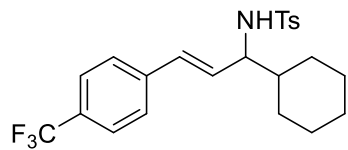
White solid, 76% yield (92% NMR yield). Mp: 130–131 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 7.9 Hz, 2H), 5.99 (d, *J* = 15.8 Hz, 1H), 5.65 (dd, *J* = 15.8, 8.2 Hz, 1H), 5.22 (d, *J* = 8.6 Hz, 1H), 3.69 (q, *J* = 7.8 Hz, 1H), 2.31 (s, 3H), 2.25 (s, 3H), 1.83 (d, *J* = 12.7 Hz, 1H), 1.76–1.56 (m, 4H), 1.51–1.38 (m, 1H), 1.27–0.91 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 143.0, 138.2, 137.3, 133.6, 131.9, 129.4, 129.0, 127.3, 126.2, 126.2, 61.6, 42.9, 29.1, 29.0, 26.2, 26.0, 26.0, 21.4, 21.2. HRMS (ESI) Calcd for [C₂₃H₂₉NNaO₂S, M+Na]⁺: 406.1817, Found: 406.1815.

(E)-N-(1-cyclohexyl-3-(4-methoxyphenyl)allyl)-4-methylbenzenesulfonamide (4d)



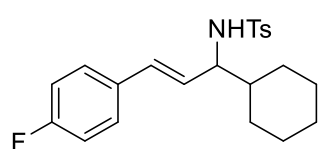
Colorless solid, 90% yield. Mp: 50–51 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, J = 8.2 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.04–6.93 (m, 2H), 6.83–6.73 (m, 2H), 5.96 (d, J = 15.8 Hz, 1H), 5.55 (dd, J = 15.8, 8.2 Hz, 1H), 5.12 (d, J = 8.5 Hz, 1H), 3.78 (s, 3H), 3.67 (td, J = 8.2, 6.1 Hz, 1H), 2.26 (s, 3H), 1.81 (d, J = 12.9 Hz, 1H), 1.73–1.58 (m, 4H), 1.50 – 1.37 (m, 1H), 1.20–0.92 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.1, 142.9, 138.3, 131.4, 129.3, 129.2, 127.4, 127.3, 125.1, 113.7, 61.6, 55.3, 42.9, 29.1, 29.0, 26.3, 26.0, 21.4. HRMS (ESI) Calcd for $[\text{C}_{23}\text{H}_{29}\text{NNaO}_3\text{S}, \text{M}+\text{Na}]^+$: 422.1766, Found: 422.1765.

(*E*)-*N*-(1-cyclohexyl-3-(4-(trifluoromethyl)phenyl)allyl)-4-methylbenzenesulfonamide (4e)



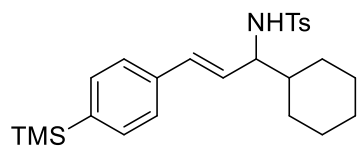
Colorless solid, 90% yield. Mp: 120–121 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.78–7.69 (m, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.14 (t, J = 7.9 Hz, 4H), 6.10 (d, J = 15.9 Hz, 1H), 5.81 (dd, J = 15.9, 8.0 Hz, 1H), 5.20 (d, J = 8.5 Hz, 1H), 3.73 (td, J = 8.2, 6.2 Hz, 1H), 2.23 (s, 3H), 1.81 (d, J = 13.0 Hz, 1H), 1.74–1.58 (m, 4H), 1.52–1.40 (m, 1H), 1.21 – 0.92 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.2, 138.1, 130.6, 130.2, 129.4, 127.3, 126.4, 125.3, 125.2, 61.3, 42.7, 29.1, 29.0, 26.2, 25.9, 21.3. HRMS (ESI) Calcd for $[\text{C}_{23}\text{H}_{26}\text{F}_3\text{NNaO}_2\text{S}, \text{M}+\text{Na}]^+$: 460.1534, Found: 460.1530.

(*E*)-*N*-(1-cyclohexyl-3-(4-fluorophenyl)allyl)-4-methylbenzenesulfonamide (4f)



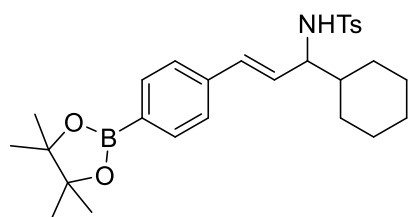
White powder, 80% yield (93% NMR yield). Mp: 161–162 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.75–7.70 (m, 2H), 7.13 (d, J = 8.1 Hz, 2H), 7.04–6.98 (m, 2H), 6.90 (t, J = 8.7 Hz, 2H), 5.99 (d, J = 15.8 Hz, 1H), 5.61 (dd, J = 15.8, 8.2 Hz, 1H), 5.27 (d, J = 8.6 Hz, 1H), 3.67 (td, J = 8.3, 6.2 Hz, 1H), 2.24 (s, 3H), 1.81 (d, J = 12.6 Hz, 1H), 1.74–1.56 (m, 4H), 1.49–1.37 (m, 1H), 1.21–0.90 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.4, 160.9, 143.0, 138.2, 132.6, 132.5, 130.7, 129.4, 127.8, 127.7, 127.3, 127.1, 127.1, 61.5, 42.8, 29.1, 29.0, 26.2, 25.9, 21.3. HRMS (ESI) Calcd for $[\text{C}_{22}\text{H}_{26}\text{FNNaO}_2\text{S}, \text{M}+\text{Na}]^+$: 410.1566, Found: 410.1570.

(*E*)-*N*-(1-cyclohexyl-3-(4-(trimethylsilyl)phenyl)allyl)-4-methylbenzenesulfonamide (4g)



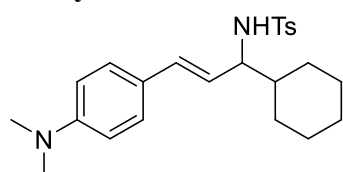
Colorless solid, 88% yield. Mp: 101–102 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.80–7.69 (m, 2H), 7.45–7.34 (m, 2H), 7.14 (d, J = 8.1 Hz, 2H), 7.09–7.01 (m, 2H), 6.03 (d, J = 15.8 Hz, 1H), 5.73 (dd, J = 15.8, 8.2 Hz, 1H), 5.19 (d, J = 8.5 Hz, 1H), 3.71 (td, J = 8.3, 6.2 Hz, 1H), 2.23 (s, 3H), 1.83 (d, J = 13.0 Hz, 1H), 1.74–1.59 (m, 4H), 1.52–1.40 (m, 1H), 1.19–0.92 (m, 5H), 0.26 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.2, 140.9, 139.3, 137.9, 134.5, 133.1, 130.6, 128.7, 128.4, 126.7, 62.6, 44.0, 30.2, 30.1, 27.4, 27.1, 27.1, 22.4, 0.0. HRMS (ESI) Calcd for $[\text{C}_{25}\text{H}_{35}\text{NNaO}_2\text{SSi}, \text{M}+\text{Na}]^+$: 464.2055, Found: 464.2053.

(E)-N-(1-cyclohexyl-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)allyl)-4-methylbenzenesulfonamide (4h)



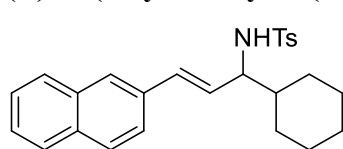
Colorless solid, 94% yield. Mp: 176–177 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.68 (dd, J = 16.5, 8.0 Hz, 4H), 7.12 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 7.8 Hz, 2H), 6.01 (d, J = 15.8 Hz, 1H), 5.75 (dd, J = 15.9, 8.1 Hz, 1H), 5.07 (dd, J = 11.5, 8.4 Hz, 1H), 3.71 (td, J = 8.2, 6.1 Hz, 1H), 2.24 (s, 3H), 1.82 (d, J = 12.8 Hz, 1H), 1.77–1.57 (m, 4H), 1.52–1.37 (m, 1H), 1.34 (s, 12H), 1.21–0.93 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.1, 139.0, 138.1, 134.8, 132.0, 129.4, 128.4, 127.3, 125.5, 83.8, 61.4, 42.9, 29.1, 29.0, 26.2, 26.0, 24.8, 21.4. HRMS (ESI) Calcd for $[\text{C}_{28}\text{H}_{38}\text{BNNaO}_4\text{S}, \text{M}+\text{Na}]^+$: 518.2512, Found: 518.2513.

(E)-N-(1-cyclohexyl-3-(4-(dimethylamino)phenyl)allyl)-4-methylbenzenesulfonamide (4i)



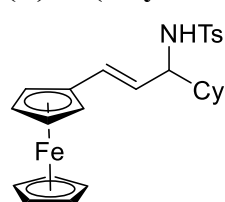
Orange solid, 93% yield. Mp: 146–147 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 7.9 Hz, 2H), 7.00–6.88 (m, 2H), 6.64–6.54 (m, 2H), 5.91 (d, J = 15.8 Hz, 1H), 5.47 (dd, J = 15.8, 8.2 Hz, 1H), 4.76 (dd, J = 8.3, 5.9 Hz, 1H), 3.66 (td, J = 8.2, 6.0 Hz, 1H), 2.93 (s, 6H), 2.28 (s, 3H), 1.80 (d, J = 12.9 Hz, 1H), 1.74–1.58 (m, 4H), 1.48–1.37 (m, 1H), 1.21–0.91 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.0, 142.9, 138.2, 132.0, 129.4, 127.3, 127.2, 124.9, 122.7, 112.2, 61.7, 43.1, 40.5, 29.2, 28.9, 26.3, 26.0, 26.0, 21.4. HRMS (ESI) Calcd for $[\text{C}_{24}\text{H}_{32}\text{N}_2\text{NaO}_2\text{S}, \text{M}+\text{Na}]^+$: 435.2082, Found: 435.2080.

(E)-N-(1-cyclohexyl-3-(naphthalen-2-yl)allyl)-4-methylbenzenesulfonamide (4j)



White crystal, 98% yield. Mp: 98–99 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.81–7.62 (m, 5H), 7.42 (ddd, J = 11.9, 4.7, 1.8 Hz, 3H), 7.23 (dd, J = 8.5, 1.8 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 6.17 (d, J = 15.8 Hz, 1H), 5.80 (dd, J = 15.8, 8.2 Hz, 1H), 5.22 (d, J = 8.5 Hz, 1H), 3.76 (q, J = 7.8 Hz, 1H), 2.12 (s, 3H), 1.86 (d, J = 12.7 Hz, 1H), 1.78–1.56 (m, 4H), 1.53–1.43 (m, 1H), 1.24–0.94 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.0, 138.3, 133.9, 133.4, 132.9, 132.1, 129.4, 127.8, 127.8, 127.6, 127.3, 126.2, 126.2, 125.8, 123.5, 61.6, 42.9, 29.1, 26.3, 26.0, 21.3. HRMS (ESI) Calcd for $[\text{C}_{26}\text{H}_{29}\text{NNaO}_2\text{S}, \text{M}+\text{Na}]^+$: 442.1817, Found: 442.1815.

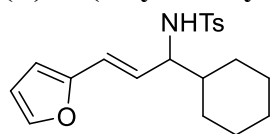
(E)-N-(1-cyclohexyl-3-(ferrocenyl)allyl)-4-methylbenzenesulfonamide (4k)



Orange solid, 95% yield. Mp: 116–117 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 5.87 (d, J = 15.7 Hz, 1H), 5.40 (dd, J = 15.7, 7.8 Hz, 1H), 4.87 (d, J = 8.2 Hz, 1H), 4.14 (s, 3H), 4.10 (s, 1H), 4.00 (s, 5H), 3.59 (q, J = 7.5 Hz, 1H), 2.35 (s, 3H), 1.81–1.57 (m, 5H), 1.46–1.35 (m, 1H), 1.24–0.90 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.0, 138.3, 129.5, 129.5, 127.2, 124.5, 82.2, 69.0, 68.6, 68.6, 67.1, 66.1, 61.3, 42.9, 29.1, 28.9, 26.3, 26.0, 26.0, 21.5.

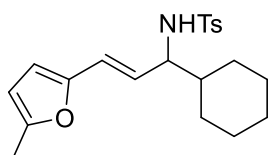
HRMS (ESI) Calcd for $[C_{26}H_{31}FeNNaO_2S, M+Na]^+$: 500.1323, Found: 500.1320.

(E)-N-(1-cyclohexyl-3-(furan-2-yl)allyl)-4-methylbenzenesulfonamide (4l)



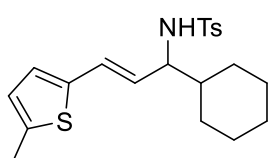
Viscous liquid, 60% yield. 1H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 5.2 Hz, 1H), 7.18 (d, J = 8.1 Hz, 2H), 6.31 (dd, J = 3.2, 1.8 Hz, 1H), 6.03 (d, J = 3.2 Hz, 1H), 5.91 (d, J = 15.8 Hz, 1H), 5.69 (dd, J = 15.8, 7.8 Hz, 1H), 4.70 (d, J = 8.4 Hz, 1H), 3.67 (q, J = 7.9 Hz, 1H), 2.32 (s, 3H), 1.79–1.56 (m, 5H), 1.49–1.37 (m, 1H), 1.23–0.84 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 143.1, 141.8, 138.0, 129.4, 127.3, 125.9, 120.3, 111.2, 107.9, 61.0, 42.9, 28.9, 28.9, 26.2, 25.9, 25.9, 21.4. HRMS (ESI) Calcd for $[C_{20}H_{25}NNaO_3S, M+Na]^+$: 382.1453, Found: 382.1450.

(E)-N-(1-cyclohexyl-3-(5-methylfuran-2-yl)allyl)-4-methylbenzenesulfonamide (4m)



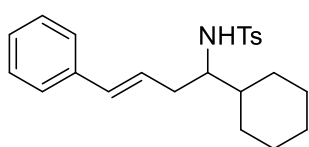
White solid, 90% yield. Mp: 141–142 °C. 1H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 5.88 (q, J = 3.5 Hz, 2H), 5.80 (d, J = 15.7 Hz, 1H), 5.59 (dd, J = 15.8, 8.0 Hz, 1H), 5.13 (d, J = 8.5 Hz, 1H), 3.63 (q, J = 7.7 Hz, 1H), 2.31 (s, 3H), 2.22 (s, 3H), 1.81–1.73 (m, 1H), 1.72–1.54 (m, 4H), 1.42 (tdt, J = 12.0, 6.5, 3.2 Hz, 1H), 1.19–0.90 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 145.1, 137.6, 132.9, 124.0, 122.0, 118.9, 115.1, 103.8, 101.9, 56.0, 37.6, 23.7, 23.6, 20.9, 20.7, 20.7, 16.0, 8.3. HRMS (ESI) Calcd for $[C_{21}H_{27}NNaO_3S, M+Na]^+$: 396.1609, Found: 396.1610.

(E)-N-(1-cyclohexyl-3-(5-methylthiophen-2-yl)allyl)-4-methylbenzenesulfonamide (4n)



Yellow powder, 45% yield. Mp: 107–108 °C. 1H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 6.60–6.49 (m, 2H), 6.10 (d, J = 15.6 Hz, 1H), 5.41 (dd, J = 15.6, 8.0 Hz, 1H), 4.65 (d, J = 8.4 Hz, 1H), 3.67 (td, J = 8.1, 6.1 Hz, 1H), 2.44 (s, 3H), 2.34 (s, 3H), 1.84–1.59 (m, 5H), 1.43 (s, 1H), 1.26–0.90 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 139.3, 139.0, 138.1, 129.4, 127.3, 125.9, 125.6, 125.5, 125.3, 61.2, 42.9, 29.0, 29.0, 26.2, 25.9, 21.4, 15.5. HRMS (ESI) Calcd for $[C_{21}H_{27}NNaO_2S_2, M+Na]^+$: 412.1381, Found: 412.1380.

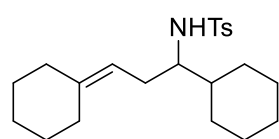
(E)-N-(1-cyclohexyl-4-phenylbut-3-en-1-yl)-4-methylbenzenesulfonamide (4o)



White solid, 83% yield. Mp: 152–153 °C. 1H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, J = 8.2 Hz, 2H), 7.30–7.24 (m, 2H), 7.21 (d, J = 7.1 Hz, 1H), 7.19–7.13 (m, 4H), 6.22 (d, J = 15.8 Hz, 1H), 5.76 (dt, J = 15.3, 7.4 Hz, 1H), 4.62 (d, J = 8.4 Hz, 1H), 3.17 (p, J = 6.2, 5.6 Hz, 1H), 2.35 (s, 3H), 2.22 (qt, J = 14.4, 6.6 Hz, 2H), 1.78–1.67 (m, 3H), 1.67–1.60 (m, 2H), 1.54–1.43 (m, 1H), 1.24–0.85 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 138.2, 137.0, 133.3, 129.5, 128.4, 127.3, 127.0, 126.1,

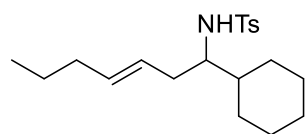
125.5, 58.6, 41.4, 35.2, 28.9, 28.7, 26.3, 26.1, 21.5. HRMS (ESI) Calcd for $[C_{23}H_{28}NO_2S, M-H]^-$: 382.1841, Found: 382.1843.

***N*-(1-cyclohexyl-3-cyclohexylidenepropyl)-4-methylbenzenesulfonamide (4p)**



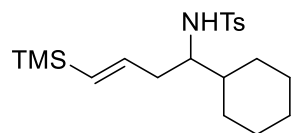
White solid, 38% yield. Mp: 108–109 °C. 1H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 4.72 (t, J = 7.3 Hz, 1H), 4.44 (d, J = 8.4 Hz, 1H), 3.01 (dt, J = 12.0, 6.0 Hz, 1H), 2.42 (s, 3H), 2.10–1.85 (m, 6H), 1.78–1.33 (m, 12H), 1.23–0.80 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 142.9, 138.3, 129.5, 127.1, 115.8, 58.9, 40.6, 37.2, 29.2, 29.0, 28.7, 28.5, 28.4, 27.8, 26.7, 26.4, 26.2, 21.5. HRMS (ESI) Calcd for $[C_{22}H_{34}NO_2S, M+H]^+$: 376.2310, Found: 376.2306.

***(E)*-N-(1-cyclohexylhept-3-en-1-yl)-4-methylbenzenesulfonamide (4q)**



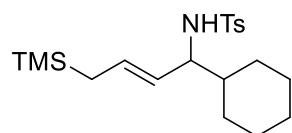
Colorless oil, 36% yield. 1H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 5.28 (dt, J = 14.0, 6.7 Hz, 1H), 5.00 (dt, J = 14.8, 7.2 Hz, 1H), 4.39 (d, J = 8.3 Hz, 1H), 3.12–2.99 (m, 1H), 2.42 (s, 3H), 1.98 (q, J = 6.4 Hz, 2H), 1.84 (q, J = 7.2 Hz, 2H), 1.75–1.65 (m, 3H), 1.65–1.55 (m, 2H), 1.45–1.35 (m, 1H), 1.29 (q, J = 7.0 Hz, 2H), 1.17–1.05 (m, 3H), 1.02–0.90 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 138.4, 134.7, 129.4, 127.1, 124.9, 58.4, 40.8, 34.6, 34.5, 29.0, 28.7, 26.3, 26.2, 22.5, 21.5, 13.6. HRMS (ESI) Calcd for $[C_{20}H_{32}NO_2S, M+H]^+$: 350.2154, Found: 350.2151.

***(E)*-N-(1-cyclohexyl-4-(trimethylsilyl)but-3-en-1-yl)-4-methylbenzenesulfonamide (4r-H)**



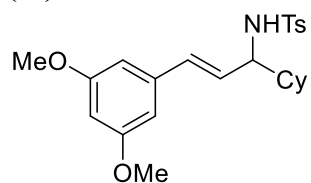
Colorless liquid, 15% yield. 1H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 5.77 (dt, J = 18.4, 6.5 Hz, 1H), 5.65 (d, J = 18.5 Hz, 1H), 4.43 (d, J = 8.2 Hz, 1H), 3.21 (dt, J = 12.1, 6.0 Hz, 1H), 2.52 (s, 3H), 2.22 (t, J = 6.3 Hz, 2H), 1.84–1.64 (m, 5H), 1.58–1.46 (m, 1H), 1.22 (dq, J = 21.6, 12.5 Hz, 3H), 1.11–0.90 (m, 2H), 0.09 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 142.8, 139.6, 136.5, 130.9, 128.4, 59.3, 42.3, 40.2, 30.1, 30.0, 27.7, 27.5, 22.8, 0.0. HRMS (ESI) Calcd for $[C_{20}H_{33}NNaO_2SSi, M+Na]^+$: 402.1899, Found: 402.1898.

***(E)*-N-(1-cyclohexyl-4-(trimethylsilyl)but-3-en-1-yl)-4-methylbenzenesulfonamide (4r-A)**



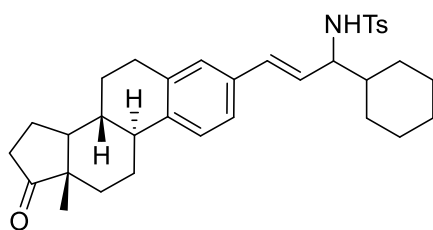
Colorless liquid, 42% yield. 1H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 5.19 (dt, J = 15.6, 8.1 Hz, 1H), 4.90 (dd, J = 15.2, 8.0 Hz, 1H), 4.64 (d, J = 8.1 Hz, 1H), 3.49 (q, J = 7.9 Hz, 1H), 2.40 (s, 3H), 1.76–1.57 (m, 5H), 1.39–1.29 (m, 1H), 1.26–0.82 (m, 7H), –0.10 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 140.5, 131.8, 131.3, 129.2, 127.9, 63.4, 45.1, 31.1, 30.6, 28.3, 28.0, 28.0, 24.7, 23.5, 0.0. HRMS (ESI) Calcd for $[C_{20}H_{33}NNaO_2SSi, M+Na]^+$: 402.1899, Found: 402.1897.

(E)-N-(1-cyclohexyl-3-(3,5-dimethoxyphenyl)allyl)-4-methylbenzenesulfonamide (4s)



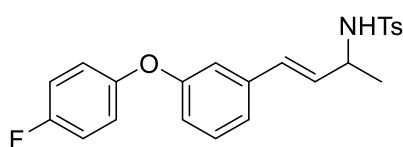
White solid. Mp: 137-138 °C. 78% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 6.31 (s, 1H), 6.21 (s, 2H), 5.98 (d, *J* = 15.8 Hz, 1H), 5.68 (dd, *J* = 15.8, 8.1 Hz, 1H), 5.23 (d, *J* = 8.5 Hz, 1H), 3.75 (s, 7H), 2.27 (s, 3H), 1.80 (d, *J* = 7.3 Hz, 1H), 1.75 – 1.56 (m, 4H), 1.50 – 1.38 (m, 1H), 1.22 – 0.89 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 160.7, 143.1, 138.5, 138.3, 132.0, 129.4, 127.9, 127.3, 104.5, 99.7, 61.4, 55.3, 42.9, 29.1, 29.1, 26.2, 26.0, 21.3. HRMS (ESI) Calcd for [C₂₄H₃₁NNaO₄S, M+Na]⁺: 452.1871, Found: 452.1870.

N-((E)-1-cyclohexyl-3-((8*R*,9*S*,13*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)allyl)-4-methylbenzenesulfonamide (4t)



White foam. Mp: 134-135 °C. 97% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.20 – 7.09 (m, 3H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.79 (s, 1H), 5.98 (d, *J* = 15.8 Hz, 1H), 5.66 (dd, *J* = 16.5, 8.6 Hz, 1H), 4.88 – 4.80 (m, 1H), 3.67 (q, *J* = 7.4 Hz, 1H), 2.91 – 2.76 (m, 2H), 2.49 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.42 – 2.35 (m, 1H), 2.30 – 2.20 (m, 4H), 2.18 – 1.89 (m, 4H), 1.77 (d, *J* = 12.6 Hz, 1H), 1.72 – 1.35 (m, 12H), 1.22 – 0.90 (m, 5H), 0.88 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 220.8, 142.9, 139.3, 138.3, 136.4, 134.0, 131.7, 129.4, 127.3, 127.0, 126.8, 125.4, 123.9, 123.7, 100.0, 61.4, 50.5, 48.0, 44.4, 43.0, 38.2, 35.9, 31.6, 29.4, 29.1, 29.0, 26.5, 26.3, 26.0, 25.7, 21.6, 21.4, 13.8. HRMS (ESI) Calcd for [C₃₄H₄₃NNaO₃S, M+Na]⁺: 568.2861, Found: 568.2860.

(E)-N-(4-(3-(4-fluorophenoxy)phenyl)but-3-en-2-yl)-4-methylbenzenesulfonamide (4u)



Colorless oil. 62% yield (72% yield for gram scale). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.27 – 7.16 (m, 3H), 7.02 (t, *J* = 8.6 Hz, 2H), 6.98 – 6.92 (m, 2H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.82 – 6.74 (m, 2H), 6.25 (d, *J* = 15.9 Hz, 1H), 5.82 (dd, *J* = 15.9, 6.7 Hz, 1H), 5.03 (d, *J* = 7.6 Hz, 1H), 4.05 (q, *J* = 6.8 Hz, 1H), 2.34 (s, 3H), 1.23 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 160.0, 157.7, 157.6, 152.8, 143.3, 138.3, 138.0, 131.2, 129.8, 129.8, 129.6, 127.3, 121.5, 120.4, 120.3, 117.5, 116.5, 116.2, 116.2, 51.6, 21.8, 21.4. HRMS (ESI) Calcd for [C₂₃H₂₂FNNaO₃S, M+Na]⁺: 434.1202, Found: 434.1200.

5. Mechanism study

5.1 Exclusion of alkene metathesis mechanism

Table S3 Alkenyl exchange of styrene with allylamines containing different vinyl groups

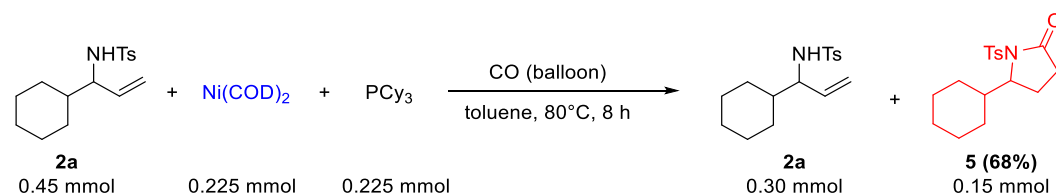
 1a + 2a-d $\xrightarrow[\text{hexane, 100 } ^\circ\text{C, 12 h}]{\text{Ni(COD)}_2 \text{ (10 mol \%), PCy}_3 \text{ (20 mol \%)}}$ 3a + 2a-d				
Allylamines 2	 2a	 2b	 2c	 2d*
Conversion and yield of 3a	100% conv. 99% yield	89% conv. 86% yield	67% conv. 64% yield	20% conv. 18% yield

* 15 mol% of TsNH₂ was added

Reaction was conducted under condition A. Products were analyzed by NMR using diphenylmethane as internal standard. The allylamine substrates containing different vinyl group (**2a-d**) afforded the same product **3a**, which shows that the reaction proceeds via alkenyl exchange mechanism, instead of alkene metathesis mechanism.

5.2 Quenching experiment

Scheme S3 Capture intermediate by CO



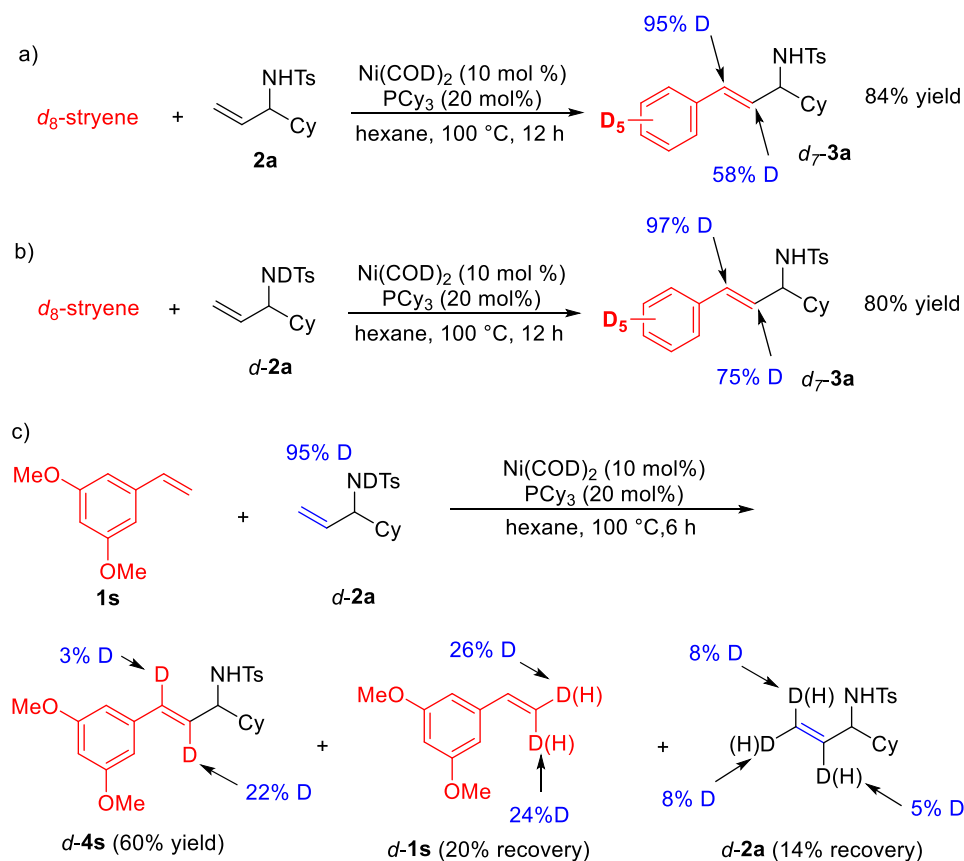
In an argon-filled glove-box, an oven-dried Schlenk tube was charged with a stir bar, catalyst precursor Ni(COD)₂ (61.8 mg, 0.225 mmol), ligand PCy₃ (69 mg, 0.225 mmol), and 2 mL toluene was added subsequently. The catalytic system was stirred 15 minutes until nickel precursor was completely dissolved. Then **2a** (0.45 mmol, 131.9 mg) was added to the solution and kept stirring at 80 °C for 0.5 h. The solution's color turned to bright red and no precipitate appeared. Then Argon balloon was replaced fast with a CO balloon. CO was allowed to diffuse slowly into the tube. The reaction mixture was hold still in the 80 °C oil bath for additional 7.5 hours. The color of the reaction mixture turned gradually from red to pale yellow and it was then quenched with diluted HCl and extracted with Et₂O (15 mL, 3 times). Combined organic phase was dried with Na₂SO₄. Then it was filtered and the solvent were removed under vacuum. The pure product **5** was obtained by column chromatography on silica gel (PE/EA = 10:1, v/v). The yield for **5** is 68% based on the amount of nickel catalyst.

5-cyclohexyl-1-tosylpyrrolidin-2-one⁶ (5)

White solid, 68% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 4.34 (dd, *J* = 9.1, 2.6 Hz, 1H), 2.49 – 2.29 (m, 5H), 2.17 – 2.02 (m, 2H), 1.96 – 1.88 (m, 1H), 1.85 – 1.76 (m, 1H), 1.75 – 1.62 (m, 3H), 1.38 – 1.24 (m, 2H), 1.15 – 0.98 (m, 3H), 0.88 – 0.82 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 173.99, 144.88, 135.97, 129.38, 128.38, 64.78, 41.62, 31.79, 29.52, 26.34, 26.15, 25.80, 25.74, 21.67, 19.77.

5.3 Deuterium-labeling experiment

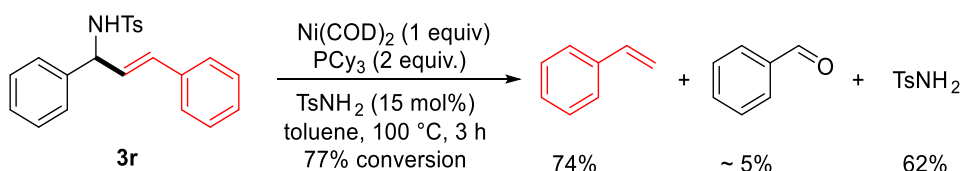
Scheme S4 The alkenyl exchange reactions with deuterium-labeled styrene, deuterium-labeled **2a**



The reactions in Scheme S4 were carried out under the standard conditions while substrates ratios are 1:1. Deuterium ratios were determined by NMR. Reaction was stopped ahead of standard time in order to track all separable deuterated substances.

5.4 Decomposition experiment

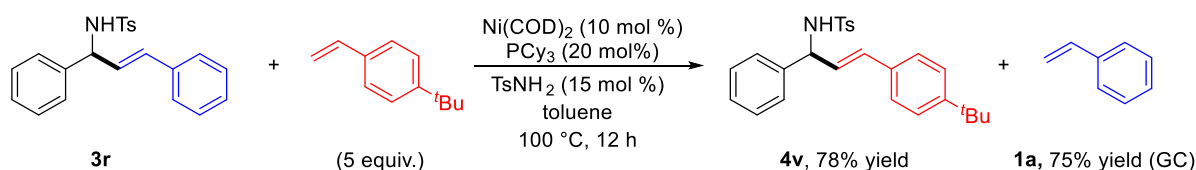
Scheme S5. Decomposition of **3r**



The decomposition of **3r** was carried out under the standard condition. After quenching reaction, styrene and benzaldehyde were detected by GC, TsNH₂ and remained **3r** were detected by NMR.

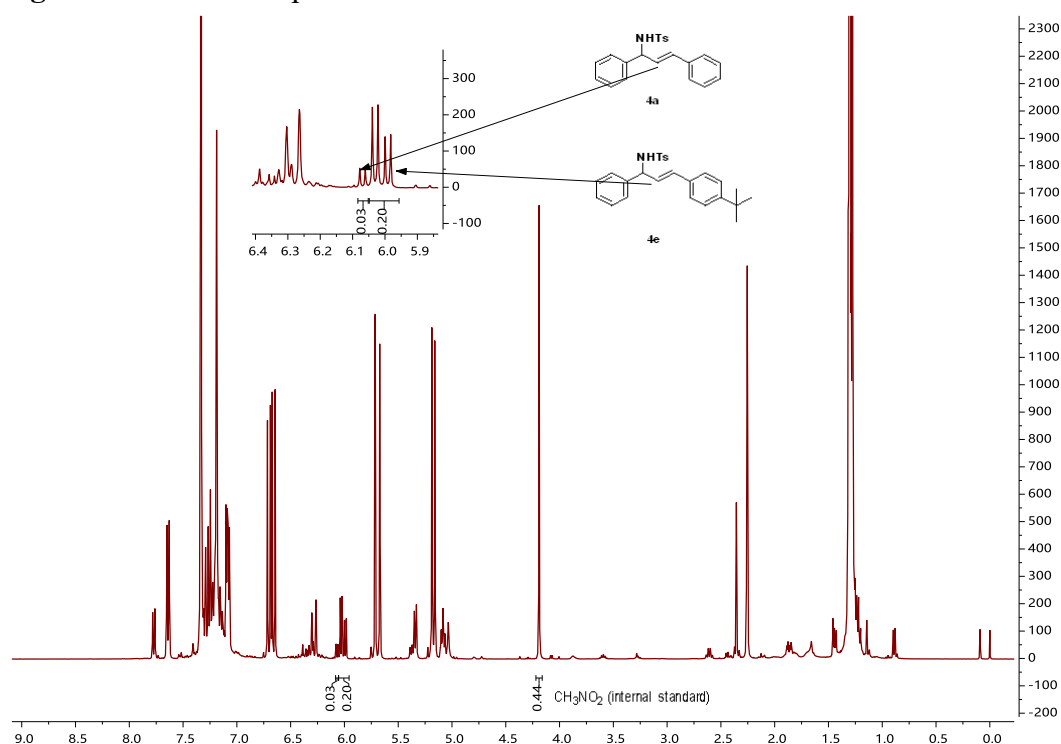
5.5 Reversible evidence

Scheme S6 Reaction **3r** and 4-*t*Bu-styrene



Under our previous standard conditions, **3r** was used as starting material and reacted with 5 equiv. of 4-*t*Bu-styrene (Scheme S6). After 12 hours, the reaction mixture was quenched and analyzed by GC and NMR using CH₃NO₂ as internal standard (Fig. S1). **4v** was obtained in 78% yield. There is no 1-phenyl-2-(4-*t*Bu-phenyl)ethene was observed. This experiment shows a fully reversible mechanism of alkenyl exchange reaction, instead of a metathesis reaction.

Fig. S1. Crude NMR spectrum of scheme S6

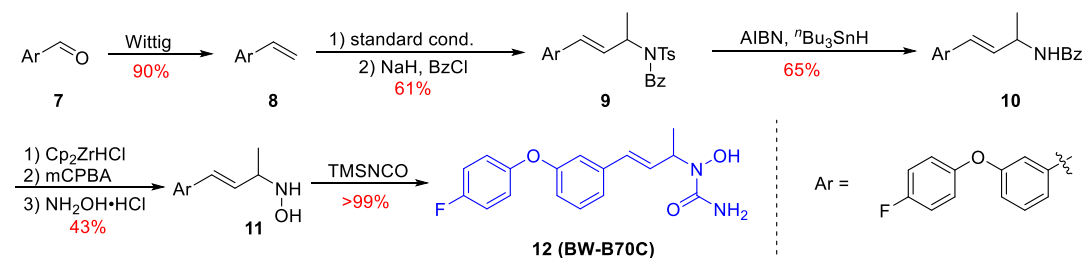


6. Synthesis of BW B70C

Gram scale experiment to acquire 4u

In an argon-filled glove-box, an oven-dried 120 mL sealed tube was charged with a stir bar, catalyst precursor $\text{Ni}(\text{COD})_2$, ligand PCy_3 . 20 mL hexane was injected into the tube and the mixture was stirred for 5 min at room temperature. 6 mmol of the corresponding alkene was added and the yellow solution turned red instantly. 8 mmol of liquid **2i** was added in one portion when all the catalyst precursors were dissolved. (Attention: liquid allylamine would deactivate solid $\text{Ni}(\text{COD})_2$ instantly by direct contact.) The tube was sealed and heated at 100 °C for 16 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and quenched with 0.5 mL HCl (1 N). It was passed through a shot pad of silica gel and dried with Na_2SO_4 . Crude product was obtained when solvent was removed under vacuum. Yield was determined by NMR using CH_2Br_2 as internal standard. It was used without further purification.

Scheme S7 Synthesis route of BW B70C



Aldehyde **7** was purchased from Alfa Aesar or prepared by the literature procedure.⁷ Corresponding alkene **8** was synthesized by Wittig reaction following our previous protocol.⁴

(E)-N-(4-(3-(4-fluorophenoxy)phenyl)but-3-en-2-yl)benzamide (**9**)

The titled compound was synthesized from crude **4u** which was prepared in the gram scale experiment. An oven-dried 100 mL Schlenk bottle equipped with magnetic stir bar was charged with NaH (10 mmol, 2.4 g) and 30 mL THF. Crude **4u** was dissolved in 10 mL THF and transferred to the NaH suspension via a syringe. Benzoyl chloride was added. The mixture was stirred for additional 2 h and monitored by TLC (PE:EA=5:1, R_F = 0.65). It was then quenched with saturated NH_4Cl and extract with EA. Crude product was purified by flash column chromatography to afford sticky colorless liquid (2.3 g, 61% for two steps). Attention, remaining **2i** from the last step would form amide as well and hard to exclude them all. However, it would be easier to separate when obtaining the hydroxylamine. ^1H NMR (400 MHz, CHCl_3 - d) δ 7.68 (d, J = 8.2 Hz, 2H), 7.48 (t, J = 6.7 Hz, 3H), 7.35 (t, J = 7.7 Hz, 2H), 7.25 (t, J = 7.9 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.08 – 7.00 (m, 3H), 7.02 – 6.93 (m, 2H), 6.90 (s, 1H), 6.84 (d, J = 8.1 Hz, 1H), 6.50 (dd, J = 16.0, 7.4 Hz, 1H), 6.25 (d, J = 16.0 Hz, 1H), 4.89 (p, J = 6.7 Hz, 1H), 2.35 (s, 3H), 1.66 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz,

CDCl₃) δ 172.0, 161.3, 160.0, 157.8, 157.6, 152.9, 144.7, 138.4, 136.7, 136.3, 131.7, 131.6, 130.1, 129.9, 129.5, 128.5, 128.3, 128.1, 121.5, 120.4, 120.4, 117.7, 116.6, 116.5, 116.2, 58.8, 21.6, 20.1. HRMS (ESI) Calcd for [C₃₀H₂₆FNNaO₄S, M+Na]⁺: 538.1464, Found: 538.1465.

(*E*)-*N*-(4-(3-(4-fluorophenoxy)phenyl)but-3-en-2-yl)hydroxylamine (11)

Desulfonylation was conducted according to literature.⁸ A solution of crude **9** (1.8 g, 3 mmol) in degassed toluene (100 mL) was heated to reflux and freshly distilled Bu₃SnH (2.18 g, 7.5 mmol) and AIBN (98 mg, 0.6 mmol) were added in one portion as a solution in toluene (20 mL) under an nitrogen atmosphere. 0.1 Equivalents of AIBN was added portionwise in toluene (2 mL) every 0.5h until the reaction had gone to completion (2.5 h) as indicated by TLC analysis (PE:EA=5:1, RF = 0.18). The toluene was then removed in vacuo and diethyl ether (100 mL) and aqueous potassium fluoride (8%, 50mL) were added to the residue and the mixture stirred for 2 h. The organic layer was separated, washed with water and brine, dried (MgSO₄) and evaporated under reduced pressure to afford crude benzamide **10**. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.1 Hz, 2H), 7.53 – 7.48 (m, 1H), 7.44 (t, *J* = 7.3 Hz, 2H), 7.26 (d, *J* = 15.7 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.07 – 6.92 (m, 5H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.23 (dd, *J* = 16.0, 5.7 Hz, 1H), 6.13 (d, *J* = 7.8 Hz, 1H), 4.95 (h, *J* = 7.2 Hz, 2H), 1.44 (d, *J* = 6.8 Hz, 3H).

Hydroxylamine was synthesized according to literature⁹ with slight modification. A solution of crude benzamide **10** (1 mmol, 1equiv.) in anhydrous DCM (3.0 mL) was added dropwise to a suspension of Cp₂ZrHCl (2.5 mmol) in anhydrous DCM (20 mL) at -20 °C under argon atmosphere. After 10 minutes, the mixture is gradually warmed to RT, and stirred 50 min. at rt. The solution¹⁰ was concentrated to around 3 mL and 50 mL anhydrous hexane was added. The mixture was then passed through a pad of basic alumina and washed with hexane. The filtrate (crude imine, PE:EA = 20:1, RF = 0.8) was concentrated and dissolved in 5 mL DCM. A solution of meta-chloroperbenzoic acid (85%, 1 mmol) in DCM (6 mL) was added dropwise at 0 °C over 1.5 h. The mixture was stirred for 30 min and the white precipitate was then filtered off. The filtrate was washed with a 10% solution of K₂CO₃ (70 mL), dried with MgSO₄, and concentrated under reduced pressure to give a pale yellow oil (crude oxaziridine, PE:EA = 20:1, RF = 0.85, unstable on silica gel). The oxaziridine was dissolved in methanol (2 mL) and hydroxylamine hydrochloride (5 mmol) was added. The mixture was stirred overnight. 4N hydrochloric acid (2 mL) was added and the mixture was concentrated under reduced pressure. The residue was dissolved in water and ether and the aqueous phase was washed with diethyl ether until no nonpolar compounds were observed by TLC analysis (crude hydroxylamine, DCM:MeOH = 20:1, RF = 0.3). The aqueous phase was neutralized with sodium carbonate, saturated with sodium chloride, and then extracted with chloroform (8 x 5 mL). The organic phases were combined, dried with MgSO₄, and concentrated under reduced pressure to afford crude product which was purified by flash column chromatography (colorless oil, 77 mg, from **9** to **11**, 28% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.19 (m, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.04 – 6.90 (m, 5H), 6.82 (d, *J* = 7.9 Hz, 1H), 6.47 (d, *J* = 15.9 Hz, 1H), 6.12 (dd,

$J = 15.9, 7.5$ Hz, 1H), 3.68 (p, $J = 6.5$ Hz, 1H), 1.22 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 160.0, 157.9, 157.6, 152.9, 152.9, 138.8, 131.5, 131.2, 129.9, 121.4, 120.5, 120.5, 117.6, 116.5, 116.2, 116.2, 59.7, 18.0. The free hydroxylamine obtained decomposes in a few hours and HRMS was not successful.

(*E*)-1-(4-(3-(4-fluorophenoxy)phenyl)but-3-en-2-yl)-1-hydroxyurea (12)

Hydroxylamine was synthesized according to literature¹¹ with slight modification. To a solution of hydroxylamine **11** (77 mg, 0.28 mmol) in degassed THF (2 mL) was added TMSNCO (1.5 mmol) at room temperature, and the resulting solution was heated to 60°C and stirred for 2 h. Several drops of water were then introduced, and the resulting mixture was stirred for an additional 30 min (TLC, DCM:MeOH=20:1, RF = 0.4). The mixture was concentrated in *vacuo*, and the residue was loaded to silica gel and purified by flash column chromatography (white solid, 89 mg, 99% yield, Mp: 130-131 °C). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.05 (s, 1H), 7.33 (t, $J = 7.9$ Hz, 1H), 7.28 – 7.15 (m, 3H), 7.11 – 7.04 (m, 2H), 7.01 (s, 1H), 6.85 (dd, $J = 7.9, 2.2$ Hz, 1H), 6.47 (d, $J = 16.2$ Hz, 1H), 6.38 (s, 2H), 6.29 (dd, $J = 16.2, 6.2$ Hz, 1H), 4.81 (p, $J = 6.3$ Hz, 1H), 1.21 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 161.5, 161.5, 159.3, 157.3, 156.9, 152.6, 139.0, 131.5, 130.2, 128.9, 121.2, 120.6, 120.5, 117.1, 116.7, 116.4, 115.7, 54.1, 16.5. HRMS (ESI) Calcd for $[\text{C}_{17}\text{H}_{17}\text{FN}_2\text{NaO}_3, \text{M}+\text{Na}]^+$: 339.1121, Found: 339.1120.

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7. NMR Spectra of New Compounds

