Electronic Supplementary Information for

Merging alkenyl C-H activation with ring-opening of

1,2-oxazetidines: ruthenium-catalyzed aminomethylation of enamides

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1. General information

Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification.

Thin layer chromatography was used to monitor the reaction on Merck 60 F254 precoated silica gel plate (0.2 mm thickness). TLC spots were visualized by UV-light irradiation on Spectroline Model ENF-24061/F 254 nm. Other visualization method was staining with a basic solution of potassium permanganate, followed by heating.

Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system.

¹H NMR and ¹³C NMR spectra were recorded at 25 °C on Bruker Advance 400 MHz NMR and JEOL 400 MHz spectrometers (CDCl₃, DMSO-*d*₆, or CD₃OD as solvent). Chemical shifts for ¹H NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe₄ (δ 0.0) and relative to the signal of SiMe₄ (δ 0.00 singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplet) and etc. Coupling constants are reported as a *J* value in Hz. ¹³C NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe₄ (δ 0.0) and relative to the signal of chloroform-*d* (δ 77 triplet). High resolution mass spectral analysis (HRMS) was performed on Waters-XEVOG2Q-TOF (Waters Corporation).

2. Experimental section

2.1 General procedure for the synthesis of enamides 1a-1p



Compounds 1a-1p were prepared according to the reported literatures.¹



(1) To a solution of ketone S^1 (10 mmol, 1.0 equiv) in EtOH-H₂O (7.5/22.5 mL) was added hydroxylamine hydrochloride (1.04 g, 15 mmol, 1.5 equiv) and NaOAc (2.05 g, 25 mmol, 2.5 equiv). After stirring at 95 °C in oil bath for 2 h, the mixture was concentrated in vacuo and the residue was extracted with EtOAc. The organic layer was separated, washed with brine, dried over Na_2SO_4 , and concentrated to give the crude product S^2 .

(2) A mixture of ketoxime S^2 (10 mmol, 1.0 equiv), the anhydride (20 mmol, 2.0 equiv), NaHSO₃ (3.12 g, 30 mmol, 3.0 equiv), and CuI (190 mg, 1 mmol, 0.1 equiv) was stirred in 1,2-DCE (100 mL) at 120 °C in oil bath under N2 for 12 h. After completion of the reaction, the reaction mixture was cooled to room temperature, diluted with EtOAc (25 mL), and washed with 2 M NaOH (20 mL) and brine (20 mL). The organic layers were dried over Na₂SO₄ and evaporated in vacuo. The desired enamide was obtained after purification by flash chromatography on silica gel with PE/ EtOAc as the eluent.

¹H NMR data for the enamides 1a–1p:

N-(1-Phenylvinyl)acetamide (1a)



Following the general procedure, **1a** was obtained as a white solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.34 (m, 5H), 6.79 (s, 1H), 5.89 (s, 1H), 5.10 (s, 1H), 2.15 (s, 3H).

N-(1-(2-Fluorophenyl)vinyl)acetamide (1b)



Following the general procedure, **1b** was obtained as a yellow solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.37 (m, 1H), 7.35 – 7.30 (m, 1H), 7.17 – 7.13 (m, 1H), 7.12 – 7.04 (m, 1H), 6.99 (s, 1H), 6.01 (s, 1H), 5.01 (s, 1H), 2.09 (s, 3H).

N-(1-(2-Chlorophenyl)vinyl)acetamide (1c)



Following the general procedure, **1c** was obtained as a white solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.35 (m, 2H), 7.33 – 7.28 (m, 2H), 6.74 (s, 1H), 6.03 (s, 1H), 4.84 (s, 1H), 2.09 (s, 3H).

N-(1-(2-Bromophenyl)vinyl)acetamide (1d)



Following the general procedure, **1d** was obtained as a white solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.58 (dd, J = 8.0, 1.1 Hz, 1H), 7.38 – 7.35 (m, 1H), 7.34 – 7.30 (m, 1H), 7.24 – 7.20 (m, 1H), 6.77 (s, 1H), 6.00 (s, 1H), 4.80 (s, 1H), 2.07 (s, 3H).

N-(1-(2-Iodophenyl)vinyl)acetamide (1e)



Following the general procedure, **1e** was obtained as a white solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.87 (dd, J = 7.8, 1.1 Hz, 1H), 7.40 – 7.31 (m, 2H), 7.07 – 7.03 (m, 1H), 6.59 (s, 1H), 6.01 (s, 1H), 4.77 (s, 1H), 2.09 (s, 3H).

N-(1-(2-(Trifluoromethyl)phenyl)vinyl)acetamide (1f)



Following the general procedure, **1f** was obtained as a white solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 9.0 Hz, 1H), 7.61 – 7.53 (m, 1H), 7.52 – 7.42 (m, 2H), 6.73 (s, 1H), 5.98 (s, 1H), 4.78 (s, 1H), 2.05 (s, 3H).

N-(1-(*o*-Tolyl)vinyl)acetamide (1g)



Following the general procedure, **1g** was obtained as a white solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.26 (m, 1H), 7.24 – 7.23 (m, 1H), 7.21 – 7.16 (m, 2H), 6.51 (s, 1H), 6.07 (s, 1H), 4.69 (s, 1H), 2.34 (s, 3H), 2.06 (s, 3H).

N-(1-(2-Methoxyphenyl)vinyl)acetamide (1h)



Following the general procedure, **1h** was obtained as a white solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.34 (m, 2H), 7.34 – 7.30 (m, 1H), 6.98 (td, J = 7.5, 1.1 Hz, 1H), 6.93 (dd, J = 8.3, 1.0 Hz), 6.06 (s, 1H), 4.78 (s, 1H), 3.89 (s, 3H), 2.08 (s, 3H).

N-(1-(3-Methoxyphenyl)vinyl)acetamide (1i)



Following the general procedure, **1i** was obtained as a white solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 7.8 Hz, 1H), 7.04 – 6.87 (m, 3H), 6.84 (s, 1H), 5.88 (s, 1H), 5.09 (s, 1H), 3.83 (s, 3H), 2.13 (s, 3H).

N-(1-(4-Chlorophenyl)vinyl)acetamide (1j)



Following the general procedure, **1j** was obtained as a white solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.35 (s, 4H), 6.79 (s, 1H), 5.81 (s, 1H), 5.09 (s, 1H), 2.14 (s, 3H).

Methyl 4-(1-acetamidovinyl)benzoate (1k)



Following the general procedure, **1k** was obtained as a white solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* =

8.1 Hz, 2H), 6.87 (s, 1H), 5.90 (s, 1H), 5.21 (s, 1H), 3.93 (s, 3H), 2.16 (s, 3H).

N-(1-(Naphthalen-2-yl)vinyl)acetamide (11)



Following the general procedure, **11** was obtained as a white solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.85 (dd, J = 7.6, 1.2 Hz, 4H), 7.55 (d, J = 9.8 Hz, 1H), 7.53 – 7.48 (m, 2H), 6.92 (s, 1H), 5.97 (s, 1H), 5.25 (s, 1H), 2.20 (s, 3H).

N-(1H-Inden-3-yl)acetamide (1m)



Following the general procedure, **1m** was obtained as a brown solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 6.9 Hz, 2H), 7.31 (dd, *J* = 14.7, 7.9 Hz, 2H), 6.88 (s, 1H), 3.44 (d, *J* = 2.3 Hz, 2H), 2.25 (s, 3H).

N-(3,3-Dimethylbut-1-en-2-yl)acetamide (1n)



Following the general procedure, **1n** was obtained as a white solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 6.44 (s, 1H), 5.62 (s, 1H), 4.79 (s, 1H), 2.09 (s, 3H), 1.12 (s, 9H).

N-(1-((1s,3s)-Adamantan-1-yl)vinyl)acetamide (10)



Following the general procedure, **1r** was obtained as a white solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 6.47 (s, 1H), 5.62 (s, 1H), 4.73 (s, 1H), 2.08 (s, 3H), 2.07 – 2.00 (m, 5H), 1.77 – 1.71 (m, 6H), 1.66 (d, *J* = 12.4 Hz, 4H).

N-(1-Phenylvinyl)propionamide (1p)



Following the general procedure, **1p** was obtained as a white solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.32 (m, 5H), 6.79 (s, 1H), 5.92 (s, 1H), 5.08 (s, 1H), 2.36 (q, *J* = 7.5 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H).

2.2 General procedures for the synthesis of 1,2-oxazetidines 2b-2j



Compounds 2b-2i were prepared according to the following procedure A.^{2,3}



1) To a solution of *N*-hydroxyphthalimide (9.8 g, 60 mmol) in *N*,*N*-dimethyl formamide (80 mL) was added 1,2-dibromoethane (120 mmol) and triethylamine (120 mmol). The solution was allowed to stand at room temperature with stirring, until the red color of the mixture turned colorless (18 h). The precipitate of triethylammonium bromide was filtered at suction. The filtrate was diluted with ice cold water (500 mL) and the solid precipitate was filtered off. The precipitate was recrystallized by ethanol to afford the desired product S^1 (8.75 g, 32.4 mmol, 54% yield).

2) A suspension of phthalimidoxyethyl bromide S^1 (3.2 g, 0.012 mol) in glacial acetic acid (10 mL) and aqueous 48% hydrobromic acid solution (15 mL) was stirred at 130 °C for 5 min. After cooling down, 1,2-phthalic acid was filtered off. Removal of the solvent afforded the crude product S^2 as a yellow solid.

3) A suspension of S^2 (8.70 mmol, 1.0 equiv) in pyridine (15 mL) was stirred for 5 min at

room temperature. Then arylsulfonyl chloride (20.87 mmol, 2.4 equiv) was added in portions. The resulting brown suspension was stirred for 5 h. The reaction mixture was poured into 1.0 M HCl solution and extracted with EtOAc. Purification by flash column chromatography (EtOAc/PE 1:3) afforded the product S^3 .

4) To a solution of S^3 (0.166 mmol, 1.0 equiv) in anhydrous THF (4 mL) under argon was added NaH (60% in mineral oil, 0.374 mmol, 15.0 mg, 2.25 equiv). After stirring for 1.5 h, the reaction mixture was carefully poured into 1.0 M HCl solution and extracted with EtOAc. Purification by flash column chromatography (EtOAc/PE 1:2) afforded the final product **2** as a white solid.

Compound 2j was prepared according to the following procedure B.



1) To a solution of S^2 (7.15 mmol, 1.0 equiv) in DCM (15 ml) benzyl chloroformate (1.46 g, 8.58 mmol, 1.2 equiv) was added in one portion followed by dropwise addition of triethylamine (1.4 mL, 10.0 mmol, 1.4 equiv). The resulting white suspension was stirred overnight. The reaction mixture was poured into 1.0 M HCl solution and extracted with DCM. Purification by column chromatography (EtOAc/PE 1:4) afforded S^4 as a white solid.

2) To a solution of S^4 (0.166 mmol, 1.0 equiv) in anhydrous THF (4 mL) under N₂ was added NaH (60% in mineral oil, 0.374 mmol, 15.0 mg, 2.25 equiv). After stirring for 1.5 h, the reaction mixture was carefully poured into 1.0 M HCl solution and extracted with EtOAc. Purification by flash column chromatography (EtOAc/PE 1:2) afforded the final product **2j** as a white solid.

2-(Naphthalen-1-ylsulfonyl)-1,2-oxazetidine (2b)



Following the procedure A, **2b** was obtained as a white solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.65 (s, 1H), 8.07 – 8.01 (m, 3H), 7.98 (dd, J = 8.1, 1.2 Hz, 1H), 7.75 – 7.65 (m, 2H), 4.69 – 4.65 (m, 2H), 4.56 – 4.51 (m, 2H).

2-(Phenylsulfonyl)-1,2-oxazetidine (2c)



Following the procedure A, **2c** was obtained as a yellow solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.05 (dd, J = 8.4, 1.4 Hz, 2H), 7.80 – 7.69 (m, 1H), 7.63 (dd, J = 8.5, 7.1 Hz, 2H), 4.63 (t, J = 8.1 Hz, 2H), 4.46 (t, J = 8.0 Hz,

2H).

2-(Mesitylsulfonyl)-1,2-oxazetidine (2d)



2-((4-Methoxyphenyl)sulfonyl)-1,2-oxazetidine (2e)



Following the procedure A, **2e** was obtained as a white solid. ¹H NMR (401 MHz, Chloroform-*d*) δ 7.98 (dd, J = 9.1, 0.9 Hz, 2H), 7.10 – 7.07 (m, 2H), 4.68 (t, J = 8.2 Hz, 2H), 4.45 (t, J = 8.2 Hz, 2H), 3.92 (s, 3H).

2-((4-(tert-Butyl)phenyl)sulfonyl)-1,2-oxazetidine (2f)



Following the procedure A, **2f** was obtained as a yellow solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.96 (m, 2H), 7.64 – 7.62 (m, 2H), 4.70 (t, *J* = 8.2 Hz, 2H), 4.49 (t, *J* = 8.2 Hz, 2H), 1.37 (s, 9H).

2-((4-Chlorophenyl)sulfonyl)-1,2-oxazetidine (2g)



Following the procedure A, **2g** was obtained as a yellow solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.97 (m, 2H), 7.62 – 7.59 (m, 2H), 4.74 (t, *J* = 8.3 Hz, 2H), 4.50 (t, *J* = 8.1 Hz, 2H).

2-((3-Bromophenyl)sulfonyl)-1,2-oxazetidine (2h)



Following the procedure A, **2h** was obtained as a white solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.16 (s, 1H), 7.98 (dd, J = 7.8, 1.3 Hz, 1H),

7.86 (dt, *J* = 8.1, 1.3 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 1H), 4.69 (t, *J* = 8.3 Hz, 2H), 4.48 (t, *J* = 8.2 Hz, 2H).

2-((4-Fluorophenyl)sulfonyl)-1,2-oxazetidine (2i)



Benzyl 1,2-oxazetidine-2-carboxylate (2j)



Following the procedure B, **2j** was obtained as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.35 (m, 5H), 5.25 (s, 2H), 4.92 (t, *J* = 8.1 Hz, 2H), 4.65 (t, *J* = 8.1 Hz, 2H).

2.3 Optimization of the reaction conditions

Table S1 Effect of additives on aminomethylation of 1a with $2a^a$

la la	H + NHAc	Ts [Ru(p-	cymene)Cl ₂] ₂ (2.5 AgNTf ₂ (10 mol%) additive (5 mol%) NaHSO ₃ , DCE 60 °C, 12 h	5 mol%)	NHTs NHAc 3aa
Entry	Additive	Yield $(\%)^b$	Entry	Additive	Yield $(\%)^b$
1	CsOPiv	40	7	NaOAc	19
2	NaOPiv	30	8	PhCO ₂ Na	27
3	KOPiv	17	9	Cs_2CO_3	14
4	AgOPiv	7	10 ^c	CsOPiv	30
5	LiOAc	29	11	AdCO ₂ Na	<5
6	KOAc	25	12	PivOH	<5

^{*a*} Reaction conditions: **1a** (0.15 mmol), **2a** (0.18 mmol), [Ru(*p*-cymene)Cl₂]₂ (2.5 mol%), AgNTf₂ (10 mol%), additive (5 mol%) and NaHSO₃ (0.15 mmol) in DCE (1.0 mL) at 60 °C for 12 h under N₂. ^{*b*} Yield of isolated product. ^{*c*} 10 mol%. Ad = adamantyl.

	H NHAc + LO 2a	Ts	[Ru(<i>p</i> -cymene)Cl ₂] ₂ AgNTf ₂ (4x m CsOPiv (5 mol NaHSO ₃ , 4 Å l CHCl ₃ (y mL), T,	2 (x mol%) ol%) 1%) MS 12 h	NHTs NHAc 3aa
Entry	Ratio (1a : 2a)	Х	у	T (°C)	Yield $(\%)^b$
1	1:1.2	2.5	1.0	60	57
2	1:1.2	4	1.0	60	47
3	1.2 : 1	2.5	1.0	60	60
4	1.2 : 1	2.5	1.0	70	55
5	1.2:1	2.5	1.0	80	56
6	1.5 : 1	2.5	1.0	60	59
7	2.0:1	2.5	1.0	60	58
8	1.2:1	2.5	1.5	60	50
9	1.2:1	2.5	0.8	60	50
10^{c}	1.2 : 1	2.5	1.0	60	52
11^d	1.2:1	2.5	1.0	60	<5

Table S2 Variation of other parameters for the aminomethylation reaction^a

^{*a*} Reaction conditions (0.15 mmol scale): **1a**, **2a**, [Ru(*p*-cymene)Cl₂]₂ (x mol%), AgNTf₂ (4x mol%), CsOPiv (5 mol%) NaHSO₃ (1.0 equiv) and 4 Å MS in CHCl₃ (y mL) for 12 h under N₂. ^{*b*} Yield of isolated product. ^{*c*} 2.0 equiv of NaHSO₃. ^{*d*} Anhydrous MgSO₄ was used instead of 4 Å MS.

2.4 General procedure for the synthesis of 3aa-3pa and 3ab-3aj



A 10 mL screw-capped Schlenk tube was charged with enamide **1** (0.18 mmol, 1.2 equiv), 1,2-oxazetidine **2** (0.15 mmol, 1.0 equiv), $[Ru(p-cymene)_2Cl_2]_2$ (2.3 mg, 0.0038 mmol, 2.5 mol%), AgNTf₂ (5.8 mg, 0.015 mmol, 10 mol%), NaHSO₃ (15.6 mg, 0.15 mmol, 1.0 equiv), CsOPiv (1.8 mg, 0.0075 mmol, 5 mol%) and 4 Å MS (150 mg) in CHCl₃ (1.0 mL). The mixture was stirred at 60 °C for 12 h under N₂ atmosphere. After the full conversion, the mixture was purified by flash chromatography (PE/ EtOAc) on silica gel to afford the desired product **3**.

3. Derivatization of the product

3.1 Large scale synthesis of 3aa



A 25 mL screw-capped Schlenk tube was charged with **1a** (0.1934 g, 1.2 mmol, 1.2 equiv), **2a** (0.2133 g, 1.0 mmol, 1.0 equiv), $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (15.3 mg, 0.025 mmol, 2.5 mol%), NaHSO₃ (0.1040 g, 1.0 mmol, 1.0 equiv), AgNTf₂ (38.8 mg, 0.1 mmol, 10 mol%), CsOPiv (11.7 mg, 0.05 mmol, 5 mol%), 4 Å MS (1.00 g) in CHCl₃(5 mL). The mixture was stirred at 60 °C for 12 h under N₂ atmosphere. After full conversion, the resulting residue was directly purified by column chromatography to give **3aa** as a white solid (0.1949 g, 0.566 mmol, 57%) by flash column chromatography (EtOAc/PE 1:3).

3.2 Synthesis of β-amino ketone 4



Aqueous HCl solution (1 mL, 1.0 M) was added to a solution of compound **3aa** (34.4 mg, 0.1 mmol) in MeOH (1.0 mL). The reaction mixture was stirred at 80 °C for 4 h. Upon the completion, the mixture was then concentrated and the residue was purified by chromatography on silica gel (PE/EtOAc) to afford the product **4** as a white solid (25.1 mg, 0.083 mmol, 83%). mp: 58.9 – 60.0 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.7 Hz, 2H), 5.39 (q, *J* = 6.1 Hz, 1H), 3.33 (q, *J* = 6.0 Hz, 2H), 3.20 (t, *J* = 5.7 Hz, 2H), 2.39 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 198.83, 143.31, 136.90, 135.96, 133.58, 129.68 × 2, 128.59 × 2, 127.88 × 2, 126.90 × 2, 38.22, 38.09, 21.41. HRMS (ESI): m/z calculated for C₁₆H₁₈NO₃S [M + H]⁺: 304.1007, found: 304.1008.

3.3 Synthesis of 1, 3-diamine 5



Compound **3aa** (34.4 mg, 0.1 mmol, 1.0 equiv), Pd/C (4.0 mg, 10 wt %), EtOH (1.0 mL) were added to a two-necked round-bottom-flask, sealed with a septum. After two vacuum/H₂ cycles to replace the air from inside the flask with hydrogen, the mixture was vigorously stirred at 75 °C for 12 h under hydrogen atmosphere provided by a hydrogen balloon. The reaction mixture was filtered through a small pad of celite. The crude product was purified by flash column chromatography (PE/EtOAc) to afford the product **5** as a white solid (26.9 mg, 0.078 mmol, 78%). mp: 94.8 – 96.5 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.27 (m, 5H), 7.20 – 7.15 (m, 2H), 6.04 – 5.94 (m, 1H), 5.87 (dd, *J* = 8.3, 4.8 Hz, 1H), 5.02 – 4.93 (m, 1H), 3.26 – 2.97 (m, 1H), 2.89 – 2.70 (m, 1H), 2.40 (s, 3H), 2.03 – 1.97 (m, 1H), 1.93 (s, 3H), 1.89 – 1.85 (m, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 170.35, 143.17, 140.83, 137.20, 129.62 × 2, 128.89 × 2, 127.86, 127.01 × 2, 126.50 × 2, 50.66, 40.01, 36.00, 23.21, 21.47. HRMS (ESI): m/z calculated for C₁₈H₂₃N₂O₃S [M + H]⁺: 347.1429, found: 347.1428.

4. Mechanistic studies

4.1 Reactivity of other formaldimine precursors

4.1.1 Reactivity of the formaldimine precursor 6a⁴



(1) A 4 mL sample bottle was charged with 4-methyl-*N*-(phenylsulfonylmethyl) benzenesulfonamide **6a** (34.8 mg, 0.15 mmol, 1.0 equiv), CHCl₃ (1.2 mL), sat. aq. NaHCO₃ (1.0 mL). After stirring at rt for 15 min, the aqueous layer was removed and the organic layer was dried over Na₂SO₄ to afford the solution of formaldimine in chloroform.

(2) A 10 mL screw-capped Schlenk tube was charged with the enamide **1a** (29.0 mg, 0.18 mmol, 1.2 equiv), $[Ru(p-cymene)_2Cl_2]_2$ (2.3 mg, 0.0038 mmol, 2.5 mol%), AgNTf₂ (5.8 mg, 0.015 mmol, 10 mol%), NaHSO₃ (15.6 mg, 0.15 mmol, 1.0 equiv), CsOPiv (1.8 mg, 0.075 mmol, 5 mol%), 4 Å MS (150 mg) and the freshly prepared chloroform solution of formaldimine. The mixture was stirred at 60 °C for 8 h under N₂ atmosphere. After the full conversion, the mixture was purified by flash chromatography (PE/EtOAc) on silica gel to afford the product **3aa** (6.8 mg, 0.0197 mmol, 13%).

4.1.2 Reactivity of the formaldimine precursors 6b and 6c



A 10 mL screw-capped Schlenk tube was charged with the enamide **1a** (29.0 mg, 0.18 mmol, 1.2 equiv), bis(tosylamido)methane **6b** (53.2 mg, 0.15 mmol, 1.0 equiv) or 1,3,5-tritosyl-1,3,5-triazinane **6c** (82.5 mg, 0.15 mmol, 1.0 equiv), $[Ru(p-cymene)_2Cl_2]_2$ (2.3 mg, 0.0038 mmol, 2.5 mol%), AgNTf₂ (5.8 mg, 0.015 mmol, 10 mol%), NaHSO₃ (15.6 mg, 0.15 mmol, 1.0 equiv), CsOPiv (1.8 mg, 0.075 mmol, 5 mol%), 4 Å MS (150 mg) in CHCl₃ (1.0 mL). The mixture was stirred at 60 °C for 12 h under N₂ atmosphere. The reaction mixture was quenched with sat. aq. NaCl and extracted with EtOAc. The resultant solution was concentrated and the residue was checked by the crude ¹H NMR analysis. No desired product **3aa** was detected.

4.2 Radical-trapping experiment



A 10 mL screw-capped Schlenk tube was charged with **1a** (29.0 mg, 0.18 mmol, 1.2 equiv), **2a** (32.0 mg, 0.15 mmol, 1.0 equiv), TEMPO (23.4 mg, 0.15 mmol, 1.0 equiv), $[Ru(p-cymene)_2Cl_2]_2$ (2.3 mg, 0.0038 mmol, 2.5 mol%), AgNTf₂ (5.8 mg, 0.015 mmol, 10 mol%), NaHSO₃ (15.6 mg, 0.15 mmol, 1.0 equiv), CsOPiv (1.8 mg, 0.0075 mmol, 5 mol%), 4 Å MS (150 mg) in CHCl₃ (1.0 mL). The mixture was stirred at 60 °C for 12 h under N₂ atmosphere. After that, the mixture was purified by flash chromatography (PE/EtOAc) on silica gel to afford the product **3aa** (14.5 mg, 0.042 mmol, 28%).





A 10 mL screw-capped Schlenk tube was charged with $1a-d_2$ (80% deuterium, 18.4 mg, 0.113 mmol), 1a (10.9 mg, 0.068 mmol), 1,2-oxazetidine (32.0 mg, 0.15 mmol, 1.0 equiv), $[Ru(p-cymene)_2Cl_2]_2$ (2.3 mg, 0.0038 mmol, 2.5 mol%), AgNTf₂ (5.8 mg, 0.015 mmol, 10 mol%), NaHSO₃ (15.6 mg, 0.15 mmol, 1.0 equiv), CsOPiv (1.8 mg, 0.075 mmol, 5 mol%), 4 Å MS (150 mg) in CHCl₃ (1.0 mL). The mixture was stirred at 60 °C for 1 h under N₂ atmosphere. Then, the mixture was cooled down and concentrated under vacuum directly. The resultant residue was purified by flash chromatography (PE/EtOAc) on silica gel to afford the mixture products **3aa** and **3aa**- d_1 (11.8 mg, 0.034 mmol, 23%).

7 7 7 3 7 7 3 1 1 7 3 1 1 2 3 7 7 3 1 1 2 3 1<



5. NMR data of the products

(Z)-N-(3-((4-Methylphenyl)sulfonamido)-1-phenylprop-1-en-1-yl)acetamide

NHAcFollowing the typical procedure, **3aa** was obtained as a white solid(30.9 mg, 0.090 mmol, 60%) by flash column chromatography
(EtOAc/PE 1:1). mp: 158.8 – 160.0 °C. ¹H NMR (401 MHz,Chloroform-d) δ 7.75 (d, J = 8.1 Hz, 2H), 7.31 – 7.25 (m, 7H), 7.15 (s, 1H), 5.69 (t, J = 7.7Hz, 1H), 5.60 (t, J = 6.3 Hz, 1H), 3.55 (t, J = 7.0 Hz, 2H), 2.42 (s, 3H), 2.06 (s, 3H). ¹³CNMR (101 MHz, Chloroform-d) δ 169.26, 143.29, 136.88, 136.83, 136.19, 129.59 × 2,128.88, 128.53 × 2, 127.22 × 2, 126.00 × 2, 118.97, 41.42, 23.35, 21.48. HRMS (ESI): m/zcalculated for C₁₈H₂₁N₂O₃S [M + H]⁺: 345.1273, found: 345.1277.

(Z)-N-(1-(2-Fluorophenyl)-3-((4-methylphenyl)sulfonamido)prop-1-en-1-yl)acetamide

NHAc Following the typical procedure, **3ba** was obtained as a yellow solid (29.9 mg, 0.083 mmol, 55%) by flash column chromatography

(EtOAc/PE 1:1). mp: 165.1 – 167.2 °C. ¹H NMR (401 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 3H), 7.21 – 7.16 (m, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.04 – 6.98 (m, 2H), 5.63 (t, *J* = 7.8 Hz, 1H), 5.48 (t, *J* = 6.3 Hz, 1H), 3.58 (t, *J* = 7.0 Hz, 2H), 2.41 (s, 3H), 2.02 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 169.06, 159.81 (d, *J* = 248.9 Hz), 143.34, 136.89, 132.17, 130.28 (d, *J*_{C-F} = 8.6 Hz), 129.72 (d, *J*_{C-F} = 3.0 Hz), 129.61 × 2, 127.22 × 2, 125.20 (d, *J*_{C-F} = 11.4 Hz), 124.30 (d, *J*_{C-F} = 3.6 Hz), 122.27 (d, *J*_{C-F} = 3.0 Hz), 115.93 (d, *J*_{C-F} = 22.2 Hz), 40.94, 23.37, 21.48. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -116.31. HRMS (ESI): m/z calculated for C₁₈H₂₀FN₂O₃S [M + H]⁺: 363.1179, found: 363.1175.

(Z)-N-(1-(2-Chlorophenyl)-3-((4-methylphenyl)sulfonamido)prop-1-en-1-yl)acetamide

NHACFollowing the typical procedure, **3ca** was obtained as a yellow solid
(39.7 mg, 0.105 mmol, 70%) by flash column chromatography
(EtOAc/PE 1:1). mp: 120.9 – 121.6 °C. ¹H NMR (400 MHz,
Chloroform-d) δ 7.67 (d, J = 8.1 Hz, 2H), 7.22 (t, J = 8.0 Hz, 3H), 7.16 (dd, J = 6.7, 2.4 Hz,
1H), 7.14 – 7.09 (m, 3H), 5.58 (t, J = 6.3 Hz, 1H), 5.32 (t, J = 7.6 Hz, 1H), 3.51 (t, J = 7.0 Hz,
2H), 2.33 (s, 3H), 1.89 (s, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ 168.95, 143.33, 136.70,
136.41, 135.00, 132.16, 131.26, 129.76, 129.72, 129.59 × 2, 127.16 × 2, 126.85, 121.77,
40.85, 23.26, 21.45. HRMS (ESI): m/z calculated for C₁₈H₂₀³⁵ClN₂O₃S [M + H]⁺: 379.0883,
found: 379.0879.

(Z)-N-(1-(2-Bromophenyl)-3-((4-methylphenyl)sulfonamido)prop-1-en-1-yl)acetamide

NHAc Following the typical procedure, **3da** was obtained as a yellow solid (38.9 mg, 0.092 mmol, 61%) by flash column chromatography (EtOAc/PE 1:1). mp: 150.0 – 151.6 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, J = 8.0 Hz, 2H), 7.51 – 7.49 (m, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.17 (d, J = 7.5 Hz, 2H), 7.10 (s, 1H), 5.58 (t, J = 6.4 Hz, 1H), 5.38 (t, J = 7.7Hz, 1H), 3.56 (t, J = 7.0 Hz, 2H), 2.41 (s, 3H), 1.97 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 168.71, 143.30, 138.41, 136.78, 136.20, 132.99, 131.59, 129.94, 129.59 × 2, 127.43, 127.20 × 2, 121.68, 121.38, 40.95, 23.41, 21.48. HRMS (ESI): m/z calculated for C₁₈H₂₀⁷⁹BrN₂O₃S [M + H]⁺: 423.0378, found: 423.0373.

(Z)-N-(1-(2-Iodophenyl)-3-(4-methylphenylsulfonamido)prop-1-en-1-yl)acetamide



2H), 7.29 (d, J = 8.3 Hz, 3H), 7.15 (dd, J = 7.7, 1.8 Hz, 1H), 7.10 (s, 1H), 6.98 (td, J = 7.7, 1.8 Hz, 1H), 5.56 (t, J = 6.4 Hz, 1H), 5.30 (t, J = 7.7 Hz, 1H), 3.56 (t, J = 7.1 Hz, 2H), 2.41 (s, 3H), 1.98 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 168.64, 143.32, 142.18, 139.54, 138.40, 136.75, 131.04, 129.92, 129.61 × 2, 128.13, 127.20 × 2, 120.58, 96.38, 40.99, 23.53, 21.47. HRMS (ESI): m/z calculated for C₁₈H₂₀IN₂O₃S [M + H]⁺: 471.0239, found: 471.0236.

(Z) - N - (3 - ((4 - Methylphenyl) sulfon a mido) - 1 - (2 - (trifluoromethyl) phenyl) prop - 1 - en - 1 - yl) ac etamide

NHAcFollowing the typical procedure, **3fa** was obtained as a yellow solid
(39.9 mg, 0.097 mmol, 65%) by flash column chromatography
(EtOAc/PE 1:1). mp: 168.3 – 169.4 °C. ¹H NMR (400 MHz,
Chloroform-d) δ 7.74 (d, J = 7.8 Hz, 2H), 7.60 (d, J = 7.7 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H),
7.40 (t, J = 7.6 Hz, 1H), 7.31 – 7.25 (m, 4H), 5.56 (t, J = 6.3 Hz, 1H), 5.28 (t, J = 7.5 Hz, 1H),
3.54 (t, J = 7.0 Hz, 2H), 2.40 (s, 3H), 1.92 (s, 3H). ¹⁹F NMR (376 MHz, Chloroform-d) δ
-58.36. ¹³C NMR (101 MHz, Chloroform-d) δ 168.58, 143.40, 136.82 (d, J_{C-F} = 2.1 Hz),
136.63, 134.94, 131.57, 129.64, 128.62, 127.76 (d, J_{C-F} = 30.2 Hz), 127.20, 126.15 (q, J_{C-F} =
5.5 Hz), 123.88 (d, J_{C-F} = 273.6 Hz), 120.49, 40.74, 23.46, 21.49. HRMS (ESI): m/z
calculated for C₁₉H₂₀F₃N₂O₃S [M + H]⁺: 413.1147, found: 143.1142.

(Z)-N-(3-((4-Methylphenyl)sulfonamido)-1-(o-tolyl)prop-1-en-1-yl)acetamide

NHAc NHAc NHTs Following the typical procedure, **3ga** was obtained as a yellow solid (34.5 mg, 0.096 mmol, 64%) by flash column chromatography (EtOAc/PE 1:1). mp: 120.1 – 120.5 °C. ¹H NMR (400 MHz, Chloroform-d) δ 7.76 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.15 – 7.10 (m, 2H), 7.05 (d, J = 7.4 Hz, 1H), 6.75 (s, 1H), 5.58 (t, J = 6.2 Hz, 1H), 5.32 (t, J = 7.8 Hz, 1H), 3.52 (t, J = 7.1 Hz, 2H), 2.41 (s, 3H), 2.20 (s, 3H), 1.96 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 168.26, 143.20, 137.51, 136.80, 136.49, 136.17, 130.47, 129.53 × 2, 129.47, 128.69, 127.23 × 2, 125.80, 119.95, 41.27, 23.34, 21.47, 19.62. HRMS (ESI): m/z calculated for C₁₉H₂₃N₂O₃S [M + H]⁺: 359.1429, found: 359.1428.

(Z)-N-(1-(2-Methoxyphenyl)-3-((4-methylphenyl)sulfonamido)prop-1-en-1-yl)acetamide

Following the typical procedure, **3ha** was obtained as a yellow solid (35.0 mg, 0.093 mmol, 62%) by flash column chromatography (EtOAc/PE 1:1). mp: 182.1 – 183.5 °C. ¹H NMR (401 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 3H), 7.22 (s, 1H), 7.11 – 7.05 (m, 1H), 6.93 – 6.89 (m, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 5.72 (t, *J* = 6.3 Hz, 1H), 5.59 (t, *J* = 8.0 Hz, 1H), 3.84 (s, 3H), 3.57 – 3.49 (m, 2H), 2.43 (s, 3H), 1.96 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 168.69, 156.11, 143.02, 137.20, 135.10, 129.89, 129.86, 129.49 × 2, 127.36 × 2, 126.85, 121.85, 121.16, 110.80, 55.66, 41.30, 23.67, 21.49. HRMS (ESI): m/z calculated for C₁₉H₂₃N₂O₄S [M + H]⁺: 375.1379, found: 375.1378.

(Z)-N-(1-(3-Methoxyphenyl)-3-((4-methylphenyl)sulfonamido)prop-1-en-1-yl)acetamide

NHAcFollowing the typical procedure, **3ia** was obtained as a yellow solid(28.2 mg, 0.075 mmol, 50%) by flash column chromatography(EtOAc/PE 1:1). mp: 179.1 – 180.5 °C. ¹H NMR (400 MHz,
Chloroform-d) δ 7.73 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 7.2 Hz, 2H),7.21 (t, J = 8.0 Hz, 1H), 6.97 (s, 1H), 6.83 (dd, J = 8.0, 2.1 Hz, 2H), 6.77 (t, J = 2.1 Hz, 1H),5.69 (t, J = 7.7 Hz, 1H), 5.51 (t, J = 6.3 Hz, 1H), 3.78 (s, 3H), 3.53 (t, J = 7.0 Hz, 2H), 2.40 (s,3H), 2.05 (s, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ 169.30, 159.61, 143.32, 138.32,136.81, 135.89, 129.59 × 2, 129.54, 127.19 × 2, 119.18, 118.41, 113.99, 111.93, 55.26, 41.39,23.31, 21.46. HRMS (ESI): m/z calculated for C₁₉H₂₃N₂O₄S [M + H]⁺: 375.1379, found:375.1376.

(Z)-N-(1-(4-Chlorophenyl)-3-(4-methylphenylsulfonamido)prop-1-en-1-yl)acetamide

NHAc Following the typical procedure, **3ja** was obtained as a yellow solid (26.1 mg, 0.069 mmol, 46%). mp: 143.1 – 144.8 °C. ¹H

NMR (401 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 4H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.99 (s, 1H), 5.66 (t, *J* = 7.5 Hz, 1H), 5.36 (t, *J* = 5.6 Hz, 1H), 3.57 (t, *J* = 6.8 Hz, 2H), 2.42 (s, 3H), 2.09 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 169.25, 143.45, 136.84, 135.63, 135.37, 134.71, 129.65 × 2, 128.70 × 2, 127.27 × 2, 127.16 × 2, 119.22, 41.19, 23.36, 21.50. HRMS (ESI): m/z calculated for C₁₈H₂₀ClN₂O₃S [M + H]⁺: 379.0883, found: 379.0886.

(Z)-Methyl 4-(1-acetamido-3-(4-methylphenylsulfonamido)prop-1-en-1-yl)benzoate

 $\begin{array}{l} \mbox{NHAc} & \mbox{Following the typical procedure, 3ka was obtained as a white} \\ \mbox{solid (24.0 mg, 0.060 mmol, 40\%). mp: 161.1 - 162.7 °C. ¹H} \\ \mbox{NMR (400 MHz, DMSO-d_6) δ 9.35 (s, 1H), 7.89 (d, J = 8.5 Hz, 2H), 7.78 (s, 1H), 7.70 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 5.59 (t, J = 6.1 Hz, 1H), 3.85 (s, 3H), 3.46 (d, J = 6.1 Hz, 2H), 2.38 (s, 3H), 1.98 (s, 3H). ¹³C \\ \mbox{NMR (101 MHz, DMSO-d_6) δ 168.61, 166.42, 143.29, 142.40, 138.17, 134.13, 130.22 \times 2, 129.69 \times 2, 129.33, 127.21 \times 2, 126.33 \times 2, 122.28, 52.68, 41.60, 23.24, 21.49. HRMS (ESI): \\ \mbox{m/z calculated for $C_{20}H_{23}N_2O_5S [M + H]^+: 403.1328, found: 403.1330.} \end{array}$

(Z)-N-(3-((4-Methylphenyl)sulfonamido)-1-(naphthalen-2-yl)prop-1-en-1-yl)acetamide

NHAc NHTs

Following the typical procedure, **3la** was obtained as a yellow rs solid (46.6 mg, 0.118 mmol, 79%) by flash column chromatography (EtOAc/PE 1:1). mp: 158.6 – 159.3 °C. ¹H NMR

(400 MHz, DMSO- d_6) δ 9.38 (s, 1H), 7.91 – 7.87 (m, 2H), 7.84 (d, J = 8.7 Hz, 1H), 7.80 (t, J = 5.7 Hz, 1H), 7.72 (d, J = 8.2 Hz, 2H), 7.69 (s, 1H), 7.52 – 7.49 (m, 2H), 7.42 (d, J = 8.1 Hz, 2H), 7.32 (dd, J = 8.6, 1.9 Hz, 1H), 5.59 (t, J = 6.1 Hz, 1H), 3.47 (t, J = 5.9 Hz, 2H), 2.38 (s, 3H), 2.03 (s, 3H). ¹³C NMR (101 MHz, Methanol- d_4) δ 170.87, 143.43, 137.85, 134.66, 134.19, 133.37, 133.25, 129.51 × 2, 127.95, 127.71, 127.25, 126.98 × 2, 126.15, 126.09, 124.63, 123.40, 120.61, 41.25, 21.43, 20.17. HRMS (ESI): m/z calculated for C₂₂H₂₃N₂O₃S [M + H]⁺: 395.1429 , found: 395.1427.

N-(2-(((4-Methylphenyl)sulfonamido)methyl)-1*H*-inden-3-yl)acetamide



Following the typical procedure, **3ma** was obtained as a yellow solid (28.6 mg, 0.080 mmol, 53%) by flash column chromatography (EtOAc/PE 1:1). mp: 186.9 – 188.5 °C. ¹H NMR (400 MHz,

Chloroform-*d*) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.25 – 7.17 (m, 6H), 5.65 (t, *J* = 6.4 Hz, 1H), 3.78 (d, *J* = 6.3 Hz, 2H), 3.34 (s, 2H), 2.40 (s, 3H), 2.15 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 169.35, 143.20, 141.59, 140.94, 136.78, 133.88, 132.23, 129.50 × 2, 127.10 × 2, 126.27, 125.77, 123.97, 118.15, 40.74, 38.29, 23.45, 21.48. HRMS (ESI): m/z calculated for C₁₉H₂₁N₂O₃S [M + H]⁺: 357.1273, found: 357.1270.

(Z)-N-(4,4-Dimethyl-1-((4-methylphenyl)sulfonamido)pent-2-en-3-yl)acetamide

Following the typical procedure, **3na** was obtained as a yellow solid *t*-Bu NHTs (31.3 mg, 0.096 mmol, 64%) by flash column chromatography (EtOAc/PE 1:1). mp: 121.1 – 122.8 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, J = 8.4Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 6.25 (s, 1H), 5.55 (t, J = 5.7 Hz, 1H), 5.34 (t, J = 7.8 Hz, 1H), 3.35 (t, J = 7.4 Hz, 2H), 2.41 (s, 3H), 1.95 (s, 3H), 0.96 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 169.38, 143.94, 143.05, 137.11, 129.46 × 2, 127.28 × 2, 116.69, 41.26, 36.12, 27.66, 23.19, 21.44 × 2. HRMS (ESI): m/z calculated for C₁₆H₂₅N₂O₃S [M + H]⁺: 325.1586, found: 325.1589.

$\label{eq:linear} N-((Z)-1-((3s)-Adamantan-1-yl)-3-((4-methylphenyl)sulfonamido) prop-1-en-1-yl) acetamide$



Following the typical procedure, **30a** was obtained as a white solid (29.5 mg, 0.073 mmol, 49%) by flash column chromatography (EtOAc/PE 1:1). mp: 204.8 – 205.9 °C. ¹H NMR (400 MHz,

Chloroform-*d*) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 6.34 (s, 1H), 5.60 (t, *J* = 6.2 Hz, 1H), 5.21 (t, *J* = 7.8 Hz, 1H), 3.36 (dd, *J* = 7.8, 6.2 Hz, 2H), 2.41 (s, 3H), 1.96 (s, 6H), 1.72 – 1.65 (m, 3H), 1.59 – 1.55 (m, 3H), 1.48 (d, *J* = 2.8 Hz, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 169.54, 144.28, 142.99, 137.31, 129.47, 127.30, 117.07, 41.15, 39.58 × 3, 37.68, 36.46 × 3, 28.01 × 3, 23.19, 21.44. HRMS (ESI): m/z calculated for C₁₇H₃₁N₂O₃S [M + H]⁺: 403.2055, found: 403.2059.

(Z)-N-(3-((4-Methylphenyl)sulfonamido)-1-phenylprop-1-en-1-yl)propionamide

Following the typical procedure, **3pa** was obtained as a yellow oil (26.1 mg, 0.073 mmol, 49%). ¹H NMR (401 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.26 (m, 6H), 7.25 – 7.24 (m, 1H), 6.72 (s, 1H), 5.70 (t, *J* = 7.9 Hz, 1H), 5.47 (t, *J* = 6.3 Hz, 1H), 3.56 – 3.53

(m, 2H), 2.41 (s, 3H), 2.32 (q, J = 7.6 Hz, 2H), 1.16 (t, J = 7.6 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 172.81, 143.22, 137.01 (d, J = 14.1 Hz), 136.06, 129.56 × 2, 128.92, 128.57 × 2, 127.23 × 2, 126.04 × 2, 118.69, 41.58, 29.89, 21.47, 9.76. HRMS (ESI): m/z calculated for C₁₉H₂₃N₂O₃S [M + H]⁺: 359.1429, found: 359.1427.

(Z)-N-(1-(Naphthalen-2-yl)-3-(naphthalene-2-sulfonamido)prop-1-en-1-yl)acetamide



Following the typical procedure, **3ab** was obtained as a yellow solid (34.0 mg, 0.079 mmol, 53%) by flash column chromatography (EtOAc/PE 1:1). mp: 167.3 –

168.8 °C. ¹H NMR (401 MHz, DMSO-*d*₆) δ 9.36 (s, 1H), 8.48 (s, 1H), 8.18 (t, *J* = 9.0 Hz, 2H), 8.08 (d, *J* = 8.1 Hz, 1H), 8.01 (s, 1H), 7.88 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.86 – 7.82 (m, 1H), 7.73 – 7.70 (m, 3H), 7.67 – 7.64 (m, 1H), 7.54 (s, 1H), 7.48 – 7.46 (m, 2H), 7.21 (dd, *J* = 8.7, 1.8 Hz, 1H), 5.57 (t, *J* = 6.1 Hz, 1H), 3.55 (d, *J* = 6.0 Hz, 2H), 1.98 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 168.55, 138.26, 135.07, 134.76, 134.68, 133.09, 132.99, 132.27, 129.93, 129.68, 129.21, 128.48, 128.33, 128.11, 128.07, 127.98, 127.84, 126.82, 126.66, 124.80, 124.15, 122.87, 120.33, 41.82, 23.26. HRMS (ESI): m/z calculated for C₂₅H₂₃N₂O₃S [M + H]⁺: 431.1429, found: 431.1427.

(Z)-N-(1-(Naphthalen-2-yl)-3-(phenylsulfonamido)prop-1-en-1-yl)acetamide



Following the typical procedure, **3ac** was obtained as a yellow solid (36.4 mg, 0.096 mmol, 64%) by flash column chromatography (EtOAc/PE 1:1). mp: $156.3 - 156.9 \ ^{\circ}C$. ¹H

NMR (400 MHz, DMSO- d_6) δ 9.38 (s, 1H), 8.05 – 7.96 (m, 1H), 7.92 – 7.83 (m, 6H), 7.80 – 7.73 (m, 1H), 7.73 – 7.69 (m, 1H), 7.67 (s, 1H), 7.57 – 7.46 (m, 2H), 7.33 – 7.30 (m, 1H), 5.59 – 5.56 (m, 1H), 3.53 (t, J = 5.9 Hz, 2H), 2.05 (s, 3H). ¹³C NMR (100 MHz, DMSO- d_6) δ 168.57, 141.18, 135.11, 134.77, 133.18, 133.08, 132.93, 129.76 × 2, 128.53, 128.24, 127.91,

 $127.09 \times 2, \ 126.92, \ 126.70, \ 124.87, \ 124.24, \ 120.30, \ 41.79, \ 23.29. \ HRMS \ (ESI): \ m/z \ calculated for C_{21}H_{21}N_2O_3S \ [M+H]^+: \ 381.1273, \ found: \ 381.1275.$

(Z) - N - (1 - (Naphthalen - 2 - yl) - 3 - ((2, 4, 6 - trimethylphenyl) sulfonamido) prop - 1 - en - 1 - yl) aceta mide

(Z)-N-(1-(2-Chlorophenyl)-3-((4-methoxyphenyl)sulfonamido)prop-1-en-1-yl)acetamide



Following the typical procedure, **3ae** was obtained as a colorless solid (38.1 mg, 0.096 mmol, 64%) by flash column chromatography (EtOAc/PE 1:1). mp: 152.2 – 151.1 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J*

= 8.9 Hz, 2H), 7.36 – 7.29 (m, 1H), 7.26 – 7.23 (m, 1H), 7.23 – 7.17 (m, 2H), 6.99 – 6.94 (m, 3H), 5.49 – 5.42 (m, 2H), 3.86 (s, 3H), 3.57 (dd, J = 7.7, 6.4 Hz, 2H), 2.00 (s, 3H) . ¹³C NMR (100 MHz, Chloroform-*d*) δ 168.80, 162.79, 136.47, 135.04, 132.18, 131.34, 131.30, 129.81, 129.79, 129.33 × 2, 126.91, 121.82, 114.14 × 2, 55.58, 40.90, 23.37. HRMS (ESI): m/z calculated for C₁₈H₂₀³⁵ClN₂O₄S [M + H]⁺: 395.0832, found: 395.0836.

(Z) - N - (3 - ((4 - (Tert-butyl)phenyl)sulfonamido) - 1 - (2 - chlorophenyl)prop - 1 - en - 1 - yl)acetamide



Following the typical procedure, **3af** was obtained as a yellow solid (35.7 mg, 0.085 mmol, 57%) by flash column

chromatography (EtOAc/PE 1:1). mp: 163.2 – 163.5 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, J = 8.6 Hz, 2H), 7.50 (d, J = 8.6 Hz, 2H), 7.37 – 7.28 (m, 1H), 7.26 – 7.21 (m, 1H), 7.21 – 7.15 (m, 2H), 7.04 (s, 1H), 5.55 (t, J = 4.9 Hz, 1H), 5.39 (t, J = 7.7 Hz, 1H), 3.83 – 3.46 (m, 2H), 1.97 (s, 3H), 1.31 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 168.71, 156.29, 136.78, 136.51, 135.05, 132.19, 131.23, 129.80, 129.76, 127.05 × 2, 126.91, 125.96 × 2, 121.85, 40.95, 35.07, 31.04 × 3, 23.35. HRMS (ESI): m/z calculated for C₂₁H₂₆³⁵ClN₂OS [M + H]⁺: 421.1353, found: 421.1354.

(Z)-N-(1-(2-Chlorophenyl)-3-((4-chlorophenyl)sulfonamido)prop-1-en-1-yl)acetamide



Following the typical procedure, **3ag** was obtained as a yellow solid (32.9 mg, 0.082 mmol, 55%) by flash column chromatography (EtOAc/PE 1:1). mp: 144.2 – 144.6 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.6 Hz, 2H),

7.47 (d, J = 8.5 Hz, 2H), 7.33 (dd, J = 7.7, 1.5 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.25 – 7.20 (m, 1H), 7.17 – 7.15 (m, 1H), 6.97 (s, 1H), 5.77 (t, J = 6.2 Hz, 1H), 5.45 (t, J = 7.8 Hz, 1H), 3.58 – 3.55 (m, 2H), 1.99 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 168.89, 138.94, 138.42, 136.34, 135.04, 132.22, 131.28, 130.00, 129.91, 129.23 × 2, 128.69 × 2, 127.02, 121.79, 41.09, 23.43. HRMS (ESI): m/z calculated for C₁₇H₁₇³⁵Cl₂N₂O₃S [M + H]⁺: 399.0337, found: 399.0335.

(Z)-N-(3-((3-Bromophenyl)sulfonamido)-1-(2-chlorophenyl)prop-1-en-1-yl)acetamide



Following the typical procedure, **3ah** was obtained as a yellow solid (38.4 mg, 0.087 mmol, 58%) by flash column chromatography (EtOAc/PE 1:1). mp: 135.6 – 136.8 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.85 – 7.79

(m, 1H), 7.71 - 7.65 (m, 1H), 7.43 - 7.30 (m, 3H), 7.25 - 7.18 (m, 2H), 6.90 (d, J = 16.6 Hz, 1H), 5.84 - 5.79 (m, 1H), 5.51 - 5.46 (m, 1H), 3.57 (t, J = 7.1 Hz, 2H), 2.01 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 168.96, 141.73, 136.35, 135.51, 135.07, 132.27, 131.32, 130.52, 130.07, 130.02, 129.93, 127.04, 125.80, 122.89, 121.78, 41.19, 23.47. HRMS (ESI): m/z calculated for C₁₇H₁₇⁷⁹Br³⁵ClN₂O₃S [M + H]⁺: 442.9832, found: 442.9830.

(Z)-N-(3-((4-Fluorophenyl)sulfonamido)-1-phenylprop-1-en-1-yl)acetamide



Following the typical procedure, **3ai** was obtained as a white solid (20.8 mg, 0.060 mmol, 40%) by flash column chromatography (EtOAc/PE 1:1). mp: 145.3 – 146.6 $^{\circ}$ C. ¹H

NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.88 (m, 2H), 7.34 – 7.33 (m, 3H), 7.30 – 7.28 (m, 2H), 7.17 (t, *J* = 8.6 Hz, 2H), 6.72 (s, 1H), 5.75 (t, *J* = 7.9 Hz, 1H), 5.60 (t, *J* = 6.2 Hz, 1H), 3.56 (dd, *J* = 7.9, 6.3 Hz, 2H), 2.10 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 169.26, 164.95 (d, *J* = 254.3 Hz), 136.77, 136.20, 129.99 × 2, 129.90, 129.09, 128.65 × 2, 126.05 × 2, 118.73, 116.13 × 2 (d, *J* = 22.5 Hz), 41.59, 23.44. ¹⁹F NMR (377 MHz, Chloroform-*d*) δ -105.54. HRMS (ESI): m/z calculated for C₁₇H₁₈FN₂O₃S [M+H]⁺: 349.1022, found: 349.1024.

Benzyl (Z)-(3-acetamido-3-phenylallyl)carbamate

NHAc Following the typical procedure, **3aj** was obtained as a white solid (21.9 mg, 0.068 mmol, 45%). mp: 149.3 – 150.2 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.34 (s, 1H), 7.40 – 7.30 (m, 10H), 5.65 (t, *J* =

8.0 Hz, 1H), 5.42 (t, J = 6.5 Hz, 1H), 5.11 (s, 2H), 3.85 – 3.82 (m, 2H), 2.17 (s, 3H). ¹³ C NMR (101 MHz, Chloroform-*d*) δ 169.34, 157.40, 137.75, 137.18, 136.23, 128.49 × 2, 128.43, 128.35 × 2, 128.14 × 2, 127.99 × 2, 125.94, 118.60, 66.93, 38.46, 23.43. HRMS (ESI): m/z calculated for C₁₉H₂₁N₂O₃ [M + H]⁺: 325.1522, found: 325.1524.

6. References

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- (4) H. Zhou, H. H. C. Lakmal, J. M. Baine, H. U. Valle, X. Xu and X. Cui, Chem. Sci., 2017, 8, 6520.

7. NMR spectra of the compounds



¹H NMR spectrum for compound 1a (CDCl₃)



¹H NMR spectrum for compound 1b (CDCl₃)



¹H NMR spectrum for compound 1c (CDCl₃)



¹H NMR spectrum for compound 1d (CDCl₃)



¹H NMR spectrum for compound 1e (CDCl₃)









¹H NMR spectrum for compound 1g (CDCl₃)



¹H NMR spectrum for compound 1h (CDCl₃)

-2.13



¹H NMR spectrum for compound 1i (CDCl₃)







¹H NMR spectrum for compound 1k (CDCl₃)



¹H NMR spectrum for compound 11 (CDCl₃)



¹H NMR spectrum for compound 1m (CDCl₃)



¹H NMR spectrum for compound 1n (CDCl₃)























¹H NMR spectrum for compound 2d (CDCl₃)



¹H NMR spectrum for compound 2e (CDCl₃)





















¹H NMR spectrum for compound 2j (CDCl₃)









¹H NMR and ¹³C NMR spectra for product 3aa (CDCl₃)



7.7



10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)

 ^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra for product 3ba (CDCl_3)



¹H NMR and ¹³C NMR spectra for product 3ca (CDCl₃)



¹H NMR and ¹³C NMR spectra for product 3da (CDCl₃)





¹H NMR and ¹³C NMR spectra for product 3ea (CDCl₃)





¹H NMR, ¹³C NMR, and ¹⁹F NMR spectra for product 3fa (CDCl₃)



¹H NMR and ¹³C NMR spectra for product 3ga (CDCl₃)

 $\begin{array}{c} 7.32\\ 7.79\\ 7.79\\ 7.79\\ 7.32\\ 7.32\\ 7.09\\ 7.09\\ 7.09\\ 7.09\\ 7.09\\ 7.00$



¹H NMR and ¹³C NMR spectra for product 3ha (CDCl₃)





¹H NMR and ¹³C NMR spectra for product 3ia (CDCl₃)







¹H NMR and ¹³C NMR spectra for product 3ja (CDCl₃)



¹H NMR and ¹³C NMR spectra for product 3ka (DMSO-*d*₆)



¹H NMR (DMSO-*d*₆) and ¹³C NMR (Methanol-*d*₄) spectra for product 3la





¹H NMR and ¹³C NMR spectra for product 3ma (CDCl₃)



¹H NMR and ¹³C NMR spectra for product 3na (CDCl₃)



¹H NMR and ¹³C NMR spectra for product 3oa (CDCl₃)



NOESY analysis of product 3oa



¹H NMR and ¹³C NMR spectra for product 3pa (CDCl₃)



¹H NMR and ¹³C NMR spectra for product 3ab (DMSO-*d*₆)

9.38 8.801 8



¹H NMR and ¹³C NMR spectra for product 3ac (DMSO-*d*₆)



¹H NMR and ¹³C NMR spectra for product 3ad (CDCl₃)



¹H NMR and ¹³C NMR spectra for product 3ae (CDCl₃)





¹H NMR and ¹³C NMR spectra for product 3af (CDCl₃)



¹H NMR and ¹³C NMR spectra for product 3ag (CDCl₃)



¹H NMR and ¹³C NMR spectra for product 3ah (CDCl₃)



S65



¹H NMR, ¹³C NMR, and ¹⁹F NMR spectra for product 3ai (CDCl₃)





¹H NMR and ¹³C NMR spectra for product 3aj (CDCl₃)



¹H NMR and ¹³C NMR spectra for product 4 (CDCl₃)



¹H NMR and ¹³C NMR spectra for product 5 (CDCl₃)