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Supporting Information

Single-Atom-Nickel Photocatalytic Site-Selective Sulfonation of Enamides Access to Amidosulfones

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1. General information

The glassware was oven dried at 100 °C for 3 hours and cooled down under vacuum. Sulfinic acids were prepared according to reported procedures.¹ All of the reaction solvents of CH₃CN (99.9%, Extra Dry with molecular sieves, Water 50 ppm) and others were purchased from Innochem. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. X-ray diffraction (XRD) patterns were recorded on a Rigaku smartlab system at 45 kV and 200 mA with Cu-Ka radiation. Fourier transform infrared (FT-IR) were measured using Bruker VERTEX 70 spectrophotometers. The spherical aberration corrected Transmission Electron Microscope (ACTEM) was carried out on a FEI Themis G2 microscope at 100 kV. The scanning electron microscope (SEM) was carried out on a ZEISS Merlin. The elemental composition was characterized with an energy dispersive X-ray spectroscope (EDX, EMAX-5770, HORIBA). UV-vis absorbance spectra were obtained on a Scan UV-vis spectrophotometer (PerkinElmer, Lambda 750S) at the range of 200 - 800 nm. Inductively coupled plasma mass spectrometry (ICP-MS) result was obtained on a GSE200plus. Xray photoelectron spectroscopy (XPS) data were collected using the AXIS Nova spectrometer (Kratos Analytical) equipped with a monochromatic Al K α X-ray source. The Al anode was powered at 10 mA and 15 kV. Gas chromatography (Shimazu: Nexis GC-2030). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60 - 90 °C). ¹H, ¹³C and ¹⁹F NMR data were recorded with Bruker Advance III (500 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.00 ppm, chloroform), respectively.

2. Preparation of photocatalysts

Synthesis of Ni/TiO₂: Typically, NiCl₂•6H₂O (35.7 mg) and TiO₂ (P25: 500 mg) were added into formamide (15.0 mL) under sonication for 10 min. Then the mixture was transferred into a 20 mL Teflon-lined autoclave and heated at 180 °C for 12 h. The resulted black product was washed with deionized water and ethanol 3 times and dried at 60 °C overnight.

3. Characterization of the photocatalysts



Figure S1. XPS results of Ni/TiO₂. (a) Ni2p; (b) N 1s; (c) Ti2p; (d) O1s; (e) C1s.

Sample	Sampling Quality/g	Constant Volume/mL	Constant Volume	Element	Swot mg/mL	Content mg/kg
Ni/TiO ₂	0.0464	25	1	Ni	0.4017	10821.8
Recycle-1	0.7814	10	1	Ni	0.1471	0. 0115
Recycle-2	0. 7798	10	1	Ni	0. 1521	0.0118
Recycle-3	0. 7835	10	1	Ni	0. 7325	0.0574
Recycle-4	0.7784	10	1	Ni	0. 4016	0. 0313
Recycle-5	0. 7801	10	1	Ni	0. 3067	0. 0239

Table S1. ICP-MS results of Ni/TiO₂.

Recycle 1-5: This is the content of Ni in the reaction solution.

4. General procedure for single-atom-nickel photocatalytic site-selective sulfonation of enamides access to amidosulfones.



A schlenk tube equipped with a stir bar was loaded with 1.25 mg (0.625 mg/mL) of Ni/TiO₂, enamides **1** or **1'** (0.5 mmol), Sulfonic acid **2** (1.0 mmol) and 4 ÅMS (40.0 mg) in 2.0 mL CH₃CN under air atmosphere. The solution was then stirred at room temperature under the irradiation of blue LED lamp (460 nm) for 3.5 h. After the completion of reaction, the reaction mixture was washed with saturated potassium carbonate solution and extracted with CH_2Cl_2 (10 mL × 3). The organic layers were combined, dried over Na_2SO_4 , and concentrated. Then, the pure product was obtained by flash column chromatography on silica gel (petroleum: ethyl ether = 5:1 - 1:1) to afford corresponding products **3** or **3'**.

- Blue LED (460 nm), air, 3.5 h Me 3ab 1a 2b Yield of 3ab (%) [b] Entry Solvent (mL) 33 1 CH₃OH 2 EtOH 37 3 Toluene 62 4 DCE 57 5 DMF 48 82 6 DMSO 7 THF 49 8 1,4-dioxane 39 9 CH₃CN 97 10 CH₃CN 61° 85^d 11 CH₃CN 12 82^{f} CH₃CN
- **5.** Table S2. Optimization of the reaction conditions [^{*a*}]

^[a] Standard Conditions: **1a** (0.5 mmol), **2b** (1.0 mmol), Ni/TiO₂ (2.5 mg), 4 ÅMS (40.0 mg), anhydrous solvent (2.0 mL), air, blue LED (460 nm), r. t., 3.5 h. ^[b] GC yield, 2-phenylphenol as internal standard. ^[c] 1 h. ^[d] 2 h. ^[f] **1a** : **2b** = 1 : 1.

6. Gram-scale experiments



A round-bottom flask (50.0 mL) equipped with a stir bar was loaded with 1.25 mg of Ni/TiO₂, **1a**, **1f** (5.0 mmol), *p*-methylbenzenesulfinic acid **2b** (20.0 mmol) and 4 ÅMS (400.0 mg) in 20.0 mL CH₃CN under air atmosphere. The solution was then stirred at room temperature under the irradiation of blue LED lamp (460 nm) for 48 h. After the completion of reaction, the reaction mixture was washed with saturated potassium carbonate solution and extracted with CH_2Cl_2 (10 mL × 3). The organic layers were combined, dried over Na₂SO₄, and concentrated. The pure product was obtained in 90% (**3ab**, 1.2 g, TON: 18963) and 64% (**3fa**, 0.814 g, TON: 13469) yields by flash column chromatography on silica gel.

7. Preliminary mechanistic studies

(1) Active species trapping experiments



A schlenk tube equipped with a stir bar was loaded with 1.25 mg of Ni/TiO₂, **1a** (0.50 mmol), 4methylbenzenesulfinic acid **2b** (1.0 mmol), 4 ÅMS (40.0 mg) and three equivalent of ammonium oxalate (AO: hole scavenger), or benzoquinone (BQ: superoxide scavenger) or sodium azide (NaN₃: singlet oxygen scavenger) in 2.0 mL CH₃CN under air atmosphere. The mixture was then stirred at room temperature under the irradiation of blue LED lamp (460 nm) for 3.5 h. After the completion of reaction, it was washed with saturated potassium carbonate solution and then extracted with CH₂Cl₂ (10 mL × 3). The organic layers were combined, dried over Na₂SO₄, and concentrated. Subsequently, the pure product was obtained by flash column chromatography on silica gel (petroleum: ethyl ether = 1 : 1) to afford products **3ab** in yield of 45%, trace and n.d., respectively. (2) The reaction of 1a and 2b with TEMPO or BHT under the standard conditions.



In an oven-dried schlenk tube equipped with a stir bar, Ni/TiO₂ (1.25 mg), **1a** (0.5 mmol), 4methylbenzenesulfinic acid **2b** (1.0 mmol), 4 ÅMS (40.0 mg), TEMPO or BHT (1.5 mmol) and CH₃CN (2.0 mL) were separately added. The mixture was then stirred at room temperature under the irradiation of blue LED lamp (460 nm) for 3.5 h. When the reaction was completed, the product **3ab** can be obtained with a yield of 30% when BHT was added in the reaction system.

(3) The ¹H NMR results of 3fa before and after irradiation





Figure S2. ¹H NMR results of 3ea. (a) before; (b) irradiation 2 min in CDCl₃.

8. References

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- 9. Detail descriptions for products.



1-(1-(phenylsulfonyl)ethyl)pyrrolidin-2-one (3aa):² white solid was obtained with 99% isolated yield (125.3 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 5.36 (q, *J* = 7.1 Hz, 1H), 3.75 (dd, *J* = 14.7, 8.3 Hz, 1H), 3.41 (dd, *J* = 16.2, 7.8 Hz, 1H), 2.17 (dt, *J* = 16.4, 8.4 Hz, 1H), 2.08 – 1.85 (m, 3H), 1.61 (d, *J* = 7.1 Hz, 3H¹³C NMR (126 MHz, CDCl₃) δ 174.7, 136.6, 134.3, 129.1, 128.8, 66.9, 42.8, 30.2, 18.3, 10.1. HRMS (EI) calcd for C₁₂H₁₅NO₃SNa

[M+Na]+: 276.0665; found: 276.0664.



1-(1-tosylethyl)pyrrolidin-2-one (3ab): white solid was obtained with 97% isolated yield (129.5 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.33 (q, *J* = 7.1 Hz, 1H), 3.76 – 3.71 (m, 1H), 3.43 – 3.34 (m, 1H), 2.38 (s, 3H), 2.22 – 2.12 (m, 1H), 2.07 – 1.98 (m, 1H), 1.96 – 1.87 (m, 2H), 1.58 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 173.8, 144.3, 132.5, 128.7, 127.8, 65.9, 41.8, 29.2, 20.7, 17.3, 9.1. HRMS (EI) calcd for C₁₃H₁₇NO₃SNa [M+Na]⁺: 290.0821; found: 290.0816.



1-(1-((4-methoxyphenyl)sulfonyl)ethyl)pyrrolidin-2-one (3ac): white oil was obtained with 99% isolated yield (140.1 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.79 (d, *J* = 8.9 Hz, 2H), 7.00 (d, *J* = 8.9 Hz, 2H), 5.36 (q, *J* = 7.1 Hz, 1H), 3.87 (s, 3H), 3.82 – 3.77 (m, 1H), 3.49 – 3.41 (m, 1H), 2.23 (dt, *J* = 16.8, 8.1 Hz, 1H), 2.15 – 2.06 (m, 1H), 2.03 – 1.94 (m, 2H), 1.64 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 174.8, 164.2, 130.9, 127.7, 114.4, 67.0, 55.6, 42.8, 30.3, 18.3, 10.2. HRMS (EI) calcd for C₁₃H₁₇NO₄SNa [M+Na]⁺: 306.0770; found: 306.0766.



1-(1-((4-(tert-butyl)phenyl)sulfonyl)ethyl)pyrrolidin-2-one (3ad): white oil was obtained with 92% isolated yield (142.1 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 5.39 (q, *J* = 6.9 Hz, 1H), 3.76 (dd, *J* = 14.9, 7.5 Hz, 1H), 3.43 (dd, *J* = 15.9, 7.9 Hz, 1H), 2.21 (dt, *J* = 16.2, 8.0 Hz, 1H), 2.00 (m, 3H), 1.60 (d, *J* = 7.1 Hz, 3H), 1.32 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 174.7, 158.2, 133.5, 128.6, 126.0, 67.0, 42.8, 35.2, 31.0, 30.2, 18.2, 10.3. HRMS (EI) calcd for C₁₆H₂₃NO₃SNa [M+Na]⁺: 332.1291; found: 332.1286.



1-(1-([1,1'-biphenyl]-4-ylsulfonyl)ethyl)pyrrolidin-2-one (3ae): white solid was obtained with 79% isolated yield (130.0 mg). ¹H NMR (500 MHz, DMSO) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 5.30 (q, *J* = 7.1 Hz, 1H), 3.59 (dt, *J* = 9.1, 6.6 Hz, 1H), 3.48 – 3.42 (m, 1H), 2.14 (dt, *J* = 15.3, 7.5 Hz, 1H), 2.02 – 1.88 (m, 3H), 1.56 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, DMSO) δ 174.6, 146.0, 138.6, 135.5, 129.8, 129.7, 129.3, 127.8, 127.6, 67.4, 42.8, 30.2, 18.3, 10.3. HRMS (EI) calcd for C₁₈H₁₉NO₃SNa [M+Na]⁺:352.0978; found: 352.0974.



1-(1-((4-chlorophenyl)sulfonyl)ethyl)pyrrolidin-2-one (3af): white oil was obtained with 92% isolated yield (132.0 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 5.37 (q, *J* = 7.1 Hz, 1H), 3.74 (td, *J* = 8.8, 5.3 Hz, 1H), 3.41 (dd, *J* = 16.4, 7.8 Hz, 1H), 2.26 – 2.15 (m, 1H), 2.09 – 1.87 (m, 3H), 1.62 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 174.8, 141.0, 135.2, 130.3, 129.4, 67.1, 42.8, 30.2, 18.3, 10.0. HRMS (EI) calcd for C₁₂H₁₄NO₃ClSNa [M+Na]⁺: 310.0275; found:310.0271.



1-(1-((4-bromophenyl)sulfonyl)ethyl)pyrrolidin-2-one (3ag): white oil was obtained with 82% isolated yield (135.7 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.72 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.6 Hz, 2H), 5.40 (q, J = 7.1 Hz, 1H), 3.81 – 3.69 (m, 1H), 3.48 – 3.38 (m, 1H), 2.28 – 2.16 (m, 1H), 2.14 – 1.88 (m, 3H), 1.64 (d, J = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 174.8, 135.8, 132.4, 130.3, 129.7, 67.1, 42.8, 30.2, 18.4, 10.0. HRMS (EI) calcd for C₁₂H₁₄NO₃BrSNa [M+Na]⁺: 353.9770; found: 353.9765.



1-(1-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)pyrrolidin-2-one (3ah): white oil was obtained with 83% isolated yield (133.2 mg). ¹H NMR (500 MHz, CDCl₃) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 8.3 Hz, 2H), 5.44 (q, *J* = 7.1 Hz, 1H), 3.86 – 3.70 (m, 1H), 3.45 (dd, *J* = 16.5, 7.6 Hz, 1H), 2.27 – 2.15 (m, 1H), 2.08 – 1.90 (m, 3H), 1.66 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 174.8, 140.6, 135.8 (q, *J* = 33.2 Hz), 129.5, 126.2 (q, *J* = 3.6 Hz), 124.6 (q, *J* = 273.7 Hz), 67.1, 42.8, 30.1, 18.3, 9.9. HRMS (EI) calcd for C₁₃H₁₄NO₃F₃SNa [M+Na]⁺: 344.0539; found: 344.0535.



1-(1-((4-(trichloromethyl)phenyl)sulfonyl)ethyl)pyrrolidin-2-one (3ai): white oil was obtained with 86% isolated yield (158.7 mg). ¹H NMR (500 MHz, CDCl₃) δ 8.00 (d, *J* = 8.1 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 5.43 (q, *J* = 7.1 Hz, 1H), 3.76 (td, *J* = 8.9, 5.1 Hz, 1H), 3.44 (dd, *J* = 16.5, 7.5 Hz, 1H), 2.26 – 2.14 (m, 1H), 2.08 – 1.89 (m, 3H), 1.65 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 174.8, 146.9, 135.2, 130.2, 129.4, 97.5, 67.0, 42.8, 30.2, 18.3, 10.0. HRMS (EI) calcd for C₁₃H₁₅NO₃Cl₃ [M+H]⁺: 369.9833; found: 369.9830.



N-(4-((1-(2-oxopyrrolidin-1-yl)ethyl)sulfonyl)phenyl)acetamide (3aj): white oil was obtained with 90% isolated yield (139.5 mg). ¹H NMR (500 MHz, CDCl₃) δ 8.31 (s, 1H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 2H), 5.36 (q, *J* = 7.1 Hz, 1H), 3.84 (dt, *J* = 9.7, 6.8 Hz, 1H), 3.48 (dt, *J* = 9.7, 7.3 Hz, 1H), 2.29 – 2.22 (m, 1H), 2.17 (s, 3H), 2.15 – 2.09 (m, 1H), 2.06 – 1.99 (m, 2H), 1.67 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, DMSO) δ 170.4, 164.3, 139.1, 125.7, 125.3, 114.3, 62.4, 38.3, 25.7, 19.9, 13.5, 5.4. HRMS (EI) calcd for C₁₄H₁₈N₂O₄SNa [M+Na]⁺: 333.0879; found: 333.0878.



1-(1-((3-chlorophenyl)sulfonyl)ethyl)pyrrolidin-2-one (3ak): white oil was obtained with 71% isolated yield (101.9 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.84 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.63 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 1H), 5.39 (q, *J* = 7.1 Hz, 1H), 3.88 – 3.76 (m, 1H), 3.54 – 3.40 (m, 1H), 2.29 – 2.20 (m, 1H), 2.17 – 2.07 (m, 1H), 2.06 – 1.99 (m, 2H), 1.67 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 174.8, 138.4, 135.2, 134.4, 130.5, 128.9, 127.1, 67.3, 4, 30.2, 18.1, 9.9. HRMS (EI) calcd for C₁₂H₁₄NO₃CISNa [M+Na]⁺: 310.0275; found:310.0271.



1-(1-((3-bromophenyl)sulfonyl)ethyl)pyrrolidin-2-one (3al): white oil was obtained with 64% isolated yield (105.9 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.94 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 5.33 (q, *J* = 7.1 Hz, 1H), 3.76 (dd, *J* = 14.4, 8.4 Hz, 1H), 3.42 (dd, *J* = 16.8, 7.5 Hz, 1H), 2.21 (dt, *J* = 16.8, 8.4 Hz, 1H), 2.12 – 1.88 (m, 3H), 1.62 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 174.7, 138.4, 137.3, 131.7, 130.8, 127.5, 122.9, 67.3, 42.8, 30.2, 18.3, 9.9. HRMS (EI) calcd for C₁₂H₁₄NO₃BrSNa [M+Na]⁺: 353.9770; found: 353.9765.



1-(1-(o-tolyIsulfonyI)ethyl)pyrrolidin-2-one (3am): white oil was obtained with 76% isolated yield (101.5 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.91 (d, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.39 – 7.28 (m, 2H), 5.52 (q, *J* = 7.1 Hz, 1H), 3.83 – 3.70 (m, 1H), 3.43 (dd, *J* = 15.7, 7.8 Hz, 1H), 2.78 (s, 3H), 2.23 – 2.14 (m, 1H), 2.02 – 1.86 (m, 3H), 1.65 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 175.0, 140.1, 134.5, 134.2, 133.1, 130.5, 125.8, 65.9, 42.9, 30.2, 20.4, 18.3, 9.9. HRMS (EI) calcd for C₁₃H₁₇NO₃SNa [M+Na]⁺: 290.0821; found: 290.0816.



1-(1-((2-bromophenyl)sulfonyl)ethyl)pyrrolidin-2-one (3an): white oil was obtained with 77% isolated yield (127.4 mg). ¹H NMR (500 MHz, CDCl₃) δ 8.06 – 7.96 (m, 1H), 7.80 – 7.71 (m, 1H), 7.49 – 7.41 (m, 2H), 5.92 (q, *J* = 7.2 Hz, 1H), 3.86 – 3.77 (m, 1H), 3.41 (dt, *J* = 9.3, 7.7 Hz, 1H), 2.23 – 2.14 (m, 1H), 2.04 – 1.86 (m, 3H), 1.67 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 175.4, 136.2, 135.9, 135.2, 132.4, 127.4, 122.6, 65.4, 43.1, 30.3, 18.4, 9.7. HRMS (EI) calcd for C₁₂H₁₄NO₃BrSNa [M+Na]⁺: 353.9770; found: 353.9765.



1-(1-(naphthalen-2-ylsulfonyl)ethyl)pyrrolidin-2-one (3ao): white solid was obtained with 88% isolated yield (133.3 mg) ¹H NMR (500 MHz, DMSO) δ 7.94 (d, *J* = 8.6 Hz, 2H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.80 – 7.75 (m, 2H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.49 – 7.44 (m, 1H), 5.30 (q, *J* = 7.1 Hz, 1H), 3.59 (dt, *J* = 9.1, 6.6 Hz, 1H), 3.45 (dt, *J* = 9.2, 7.2 Hz, 1H), 2.16 – 2.07 (m, 1H), 2.03 – 1.85 (m, 3H), 1.56 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, DMSO) δ 174.6, 146.0, 138.6, 135.5, 129.8, 129.7, 129.3, 127.8, 127.6, 67.4, 42.8, 30.2, 18.3, 10.3. HRMS (EI) calcd for C₁₆H₁₇NO₃SNa [M + Na]⁺: 326.0821; found: 326.0820



1-(1-(thiophen-2-ylsulfonyl)ethyl)pyrrolidin-2-one (3ap): white oil was obtained with 60% isolated yield (77.7 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.75 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.71 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.18 (dd, *J* = 4.9, 3.8 Hz, 1H), 5.47 (q, *J* = 7.1 Hz, 1H), 3.91 – 3.83 (m, 1H), 3.50 – 3.42 (m, 1H), 2.34 – 2.17 (m, 2H), 2.13 – 1.95 (m, 3H), 1.69 (d, *J* = 7.1 Hz, 3H ¹³C NMR (126 MHz, CDCl₃) δ 174.9, 137.0, 135.5, 135.2, 128.3, 68.3, 42.8, 30.3, 18.4, 10.2. HRMS (EI) calcd for C₁₀H₁₃NO₃SNa [M + Na]⁺: 282.0229; found: 282.0226.



1-(1-tosylethyl)azepan-2-one (3ba): white solid was obtained with 99% isolated yield (146.0 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 5.94 (q, *J* = 7.1 Hz, 1H), 3.61 (dd, *J* = 15.5, 7.2 Hz, 1H), 3.32 (dd, *J* = 15.6, 9.7 Hz, 1H), 2.35 (s, 3H), 2.23 (dd, *J* = 7.3, 4.1 Hz, 2H), 1.89 – 1.77 (m, 1H), 1.73 – 1.65 (m, 1H), 1.56 – 1.47 (m, 5H), 1.43 – 1.33 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 175.8, 144.9, 134.1, 129.5, 128.8, 67.6, 43.8, 36.6, 29.6, 29.1, 23.1, 21.6, 10.7. HRMS (EI) calcd for C₁₅H₂₁NO₃SNa [M+Na] ⁺: 318.1134; found: 318.1131.



9-(1-tosylethyl)-9H-carbazole (3ca): white solid was obtained with 67% isolated yield (116.9 mg). ¹H NMR (500 MHz, CDCl₃) δ 8.17 (s, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.82 (s, 1H), 7.46 – 7.42 (m, 2H), 7.41 (d, *J* = 3.6 Hz, 2H), 7.25 – 7.19 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 1H), 2.35 (s, 3H), 1.85 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 144.3, 139.8, 139.6, 134.1, 129.3, 129.3, 127.2, 126.1, 124.5, 123.3, 123.0, 121.3, 120.4, 119.6, 110.7, 110.4, 66.4, 21.6, 14.7. HRMS (EI) calcd for C₂₁H₁₉NO₂SNa [M+Na]⁺: 372.1029; found: 372.1028.



N-methyl-N-(1-tosylethyl)acetamide (3da): white oil was obtained with 95% isolated yield (121.1 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.00 (q, *J* = 7.1 Hz, 1H), 3.07 (s, 3H), 2.42 (s, 3H), 1.87 (s, 3H), 1.59 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, DMSO) δ 166.3, 140.3, 129.3, 124.9, 124.1, 62.5, 26.1, 16.9, 16.8, 5.4. HRMS (EI) calcd for C₁₂H₇NO₃SNa [M+Na] ⁺: 278.0821; found: 278.2820.



N-(1-tosylethyl)acetamide (3ea): white oil was obtained with 92% isolated yield (110.8 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 6.72 (d, *J* = 10.2 Hz, 1H), 5.42 – 5.33 (m, 1H), 2.44 (s, 3H), 1.85 (s, 3H), 1.60 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (126 MHz, DMSO) δ 164.4, 140.6, 128.6, 125.1, 124.3, 60.3, 17.9, 16.9, 8.4. HRMS (EI) calcd for C₁₁H₁₅O₃SNa [M+Na]⁺: 264.0665; found: 264.0663.



N,N-dimethyl-3-tosylpropanamide (3fa): white oil was obtained with 76% isolated yield (96.9 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 3.43 (t, *J* = 7.8 Hz, 2H), 2.98 (s, 3H), 2.88 (s, 3H), 2.78 (t, *J* = 8.1 Hz, 2H), 2.43 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 168.7, 144.8, 136.2, 129.9, 127.9, 52.2, 37.1, 35.6, 26.3, 21.6. HRMS (EI) calcd for C₁₂H₁₈NO₃S [M+H]⁺: 256.1002 ; found: 256.1000.



3-((4-methoxyphenyl)sulfonyl)-N,N-dimethylpropanamide (3fb): white oil was obtained with 64% isolated yield (86.7 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.84 (d, *J* = 8.9 Hz, 2H), 7.02 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H), 3.44 (t, *J* = 7.9 Hz, 2H), 3.01 (s, 3H), 2.91 (s, 3H), 2.81 (t, *J* = 8.1 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 168.8, 163.8, 130.7, 130.2, 114.5, 55.7, 52.4, 37.1, 35.6, 26.3. HRMS (EI) calcd for C₁₂H₁₈NO₄S [M+H]⁺: 272.0951 ; found: 272.0952.



3-([1,1'-biphenyl]-4-ylsulfonyl)-N,N-dimethylpropanamide (3fd): white oil was obtained with 58%

isolated yield (91.9 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.98 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 7.2 Hz, 2H), 7.50 (d, J = 7.1 Hz, 2H), 7.44 (t, J = 7.3 Hz, 1H), 3.52 (t, J = 7.8 Hz, 2H), 3.02 (s, 3H), 2.92 (s, 3H), 2.85 (t, J = 8.0 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 168.7, 146.8, 139.1, 137.6, 132.1, 129.1, 128.5, 127.9, 127.4, 52.2, 37.1, 35.6, 26.2, 21.1. HRMS (EI) calcd for C₁₇H₂₀NO₃S [M+H]⁺: 318.1158 ; found: 318.1158.



3-((4-bromophenyl)sulfonyl)-N,N-dimethylpropanamide (3ff): white oil was obtained with 76% isolated yield (121.2 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.6 Hz, 2H), 3.46 (t, *J* = 7.7 Hz, 2H), 3.00 (s, 3H), 2.90 (s, 3H), 2.80 (t, *J* = 7.9 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 168.5, 138.2, 132.7, 129.5, 129.3, 52.1, 37.1, 35.7, 26.1. HRMS (EI) calcd for C₁₁H₁₅BrNO₃S [M+H]⁺: 319.9951 ; found: 319.9949.



N,N-dimethyl-3-((4-(trifluoromethyl)phenyl)sulfonyl)propanamide (3fh): white oil was obtained with 79% isolated yield (122.0 mg). ¹H NMR (500 MHz, CDCl₃) δ 8.06 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 8.1 Hz, 2H), 3.51 (t, *J* = 7.6 Hz, 2H), 3.01 (s, 3H), 2.89 (s, 3H), 2.83 (t, *J* = 7.8 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 168.3, 142.7, 135.6 (q, *J* = 33.2 Hz), 128.6 (d, *J* = 15.8 Hz), 126.5 (q, *J* = 3.6 Hz), 125.9 (q, *J* = 273.4 Hz), 52.0, 37.1, 35.6, 25.9. HRMS (EI) calcd for C₁₂H₁₅NO₃F₃S [M+H]⁺: 310.0719 ; found: 310.0716.



3-((4-acetamidophenyl)sulfonyl)-N,N-dimethylpropanamide (3fi): white oil was obtained with 71% isolated yield (105.8 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.98 (s, 1H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 3.44 (t, *J* = 7.7 Hz, 2H), 3.01 (s, 3H), 2.91 (s, 3H), 2.80 (t, *J* = 8.0 Hz, 2H), 2.21 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 169.1, 168.8, 143.4, 133.2, 129.2, 119.4, 52.2, 37.2, 35.7, 26.3. HRMS

(EI) calcd for C₁₃H₁₉N₂O₄S [M+H] ⁺: 299.1060; found: 299.1058.



3-((3,5-dichlorophenyl)sulfonyl)-N,N-dimethylpropanamide (3fj): white oil was obtained with 68% isolated yield (105.1 mg). ¹H NMR (500 MHz, DMSO) δ 8.06 (t, J = 1.8 Hz, 1H), 7.94 (s, 1H), 7.93 (s, 1H), 3.66 (t, J = 7.3 Hz, 2H), 2.93 (s, 3H), 2.75 (s, 3H), 2.69 (t, J = 7.3 Hz, 2H). ¹³C NMR (126 MHz, DMSO) δ 168.6, 142.4, 135.6, 133.9, 127.0, 51.3, 37.0, 35.5, 26.3. HRMS (EI) calcd for C₁₁H₁₃Cl₂NNaO₃S [M+Na]⁺: 331.9985 ; found: 331.9882.



N,N-dimethyl-3-(naphthalen-2-ylsulfonyl)propanamide (3fn): white oil was obtained with 66% isolated yield (96.0 mg). ¹H NMR (500 MHz, DMSO) δ 8.60 (s, 1H), 8.22 (d, *J* = 8.1 Hz, 1H), 8.18 (d, *J* = 8.7 Hz, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 7.92 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.75 (t, *J* = 7.3 Hz, 1H), 7.70 (t, *J* = 7.4 Hz, 1H), 3.60 (t, *J* = 7.4 Hz, 2H), 2.89 (s, 3H), 2.69 (t, *J* = 7.8 Hz, 2H), 2.66 (s, 3H). ¹³C NMR (126 MHz, DMSO) δ 168.7, 136.3, 135.3, 132.2, 130.0, 129.9, 129.8, 129.8, 128.4, 128.2, 123.2, 51.6, 36.9, 35.4, 26.4. HRMS (EI) calcd for C₁₅H₁₈NO₃S [M+H]⁺:292.1002; found: 292.1000.



N,N-diethyl-3-tosylpropanamide (3ga): white oil was obtained with 80% isolated yield (113.2 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.80 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 3.47 (t, J = 7.7 Hz, 2H), 3.31 (dq, J = 11.8, 7.1 Hz, 4H), 2.81 (t, J = 7.9 Hz, 2H), 2.45 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H), 1.06 (t, J= 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 167.8, 144.8, 136.2, 129.9, 127.9, 52.2, 41.9, 40.5, 25.9, 21.6, 14.2, 12.9. HRMS (EI) calcd for C₁₂H₂₄NO₃S [M+H]⁺: 284.1315 ; found: 284.1311.



3-tosylpropanamide (3ha): white oil was obtained with 71% isolated yield (80.5 mg). ¹H NMR (500 MHz, DMSO) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 3.44 (t, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 2.37 (t, *J* = 7.8 Hz, 2H). ¹³C NMR (126 MHz, DMSO) δ 170.7, 144.9, 136.3, 130.4, 128.2, 51.4, 28.6, 21.5. HRMS (EI) calcd for C₁₀H₁₃NO₃SNa [M+Na]⁺: 250.0508 ; found: 250.0506.



1,3-diphenyl-3-tosylpropan-1-one (3ia): white solid was obtained with 71% isolated yield (80.5 mg). ¹H NMR (500 MHz, DMSO) δ 7.96 (d, J = 7.6 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.52 (m, 4H), 7.33 (d, J = 8.1 Hz, 2H), 7.26 (m, 5H), 5.04 (dd, J = 9.1, 4.3 Hz, 1H), 4.03 (dd, J = 18.0, 9.2 Hz, 1H), 3.89 (dd, J = 18.0, 4.3 Hz, 1H), 2.36 (s, 3H). ¹³C NMR (126 MHz, DMSO) δ 195.7, 145.0, 136.3, 134.3, 134.1, 132.9, 130.4, 130.0, 129.2, 129.0, 128.5, 65.9, 37.2, 21.5. HRMS (EI) calcd for C₂₂H₂₀NO₃SNa [M+Na]⁺: 387.1025 ; found: 387.1024.



3-tosylcyclohexan-1-one (3ja): white solid was obtained with 86% isolated yield (108.3 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 3.21 (m, 1H), 2.49 (td, *J* = 14.0, 8.4 Hz, 2H), 2.37 (s, 3H), 2.31 (dd, *J* = 13.5, 1.4 Hz, 1H), 2.17 (m, 3H), 1.80 (m, 1H), 1.56 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 206.5, 145.3, 133.5, 130.0, 128.9, 62.2, 40.4, 40.3, 23.7, 23.3, 21.6. HRMS (EI) calcd for C₁₃H₁₆O₃SNa [M+Na]⁺: 275.0712 ; found: 275.0708.



diethyl 2-(1-tosylethyl)malonate (3ka): white solid was obtained with 98% isolated yield (167.5 mg).

¹H NMR (500 MHz, DMSO) δ 7.76 (d, J = 8.3 Hz, 2H), 7.50 (d, J = 8.1 Hz, 2H), 4.14 (t, J = 7.1 Hz, 2H), 4.08 (t, J = 7.1 Hz, 2H), 3.90 (dd, J = 14.1, 7.0 Hz, 1H), 3.74 (d, J = 6.9 Hz, 1H), 2.43 (s, 3H), 1.27 (d, J = 7.1 Hz, 3H), 1.17 (t, J = 7.5 Hz, 6H). ¹³C NMR (126 MHz, DMSO) δ 166.5, 166.2, 145.7, 133.8, 130.5, 129.3, 62.3, 62.1, 58.5, 51.0, 21.5, 14.2, 14.1, 11.4. HRMS (EI) calcd for C₁₆H₂₂NO₆SNa [M+Na]⁺: 365.1029 ; found: 365.1027.



diphenyl(2-tosylethyl)phosphane (3la):): white solid was obtained with 51% isolated yield (93.8 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.34 (m, 12H), 3.08 (m, 2H), 2.45 (s, 3H), 2.40 (m, 2H). ¹³C NMR (126 MHz, DMSO) δ 140.1, 131.6, 130.9, 127.9, 125.2, 124.5, 124.0, 123.4, 48.4, 16.9, 15.8. HRMS (EI) calcd for C₂₁H₂₂PO₂S [M+H]⁺: 369.1073 ; found: 369.1071.







0 190 110 100 90 f1 (ppm) 0 -1 140 130



20 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1 f1 (ppm)





-1 100 90 f1 (ppm)



¹³C NMR













¹³C NMR









3ah









3ai

¹³C NMR

















3ak















D0 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1 f1 (ppm)



3am











¹³C NMR





































3ff



00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)



















3fn















S51



