Supporting information

for

Transition-metal-free, visible-light-induced oxidative cross-coupling

for constructing β -acetylamino acrylosulfones from sodium sulfinates

and enamides

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General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. Anhydrous solvents (including MeCN, DCM, DMSO, Me₂CO, THF and DMF) and CDCl₃ were purchased from Energy Chemical. Materials (used as received commercially available chemicals) were obtained from Bidepharmatech Ltd., Energy Chemical, Aladdin®, Meryer (Shanghai) Chemical Technology Co., Ltd, and used as received unless otherwise stated. ¹H, ¹⁹F and ¹³C NMR spectra were recorded on a 400 MHz Bruker spectrometer (¹H 400 MHz, ¹⁹F 376, ¹³C 101 MHz). Chemical shifts (δ) for ¹H, ¹⁹F and ¹³C spectra are given in ppm relative to TMS. The residual solvent signals were used as references for ¹H and ¹³C NMR spectra and the chemical shifts were converted to the TMS scale (CDCl₃: $\delta H =$ 7.26 ppm, $\delta C = 77.16$ ppm; DMSO- d_6 , $\delta H = 2.50$ ppm, $\delta C = 39.52$ ppm). The following abbreviations were used to indicate multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet, coupling constant in Herts (Hz) and integration. HRMS (ESI) spectra was recorded on ThermoFisher MicroTOF II. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm. Silica gel (200-300 mesh) and silica gel GF254 (10-40 µm) were used for column chromatography and preparative thin layer chromatography (PTLC), respectively. For irradiation with green light was performed using High Power 530 nm 5W® TaoYuan LED (5W, $\lambda = 530 \pm 10$ nm, 700mA).

Experimental section

Substrate synthesis

1a-1n were synthesized using reported methods.^[1]

The sodium salts of alkyl and aryl sulfonates **2** were synthesized following the reported methods.^[2]

Optimization of reaction conditions



^{*a*} Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), photocatalyst (2.5 mol %), oxidant, solvent (2 mL), 5 W green LEDs, rt, air, 17 h. ^{*b*} Isolated yield of the product **3a**. ^{*c*} Without light irradiation. ^{*d*} Under N₂. ^{*e*} Under air. ^{*f*} Without oxidant under N₂. ^{*s*} 5 W blue LEDs, rt, air.

General Procedure for the Synthesis of 3:

A mixture of 1 (0.2 mmol), 2 (0.6 mmol), nitrobenzene (49 mg, 0.4 mmol) and RB (2.5 mol%) in DMF/H₂O (2.0 mL, v/v=3:1) was illuminated with a commercially available green LEDs (5 W LED light bulbs 8 cm away from the vial) and stirred under an air atmosphere at room temperature for 17 h. After the reaction was completed (monitored by TLC), water was added and the mixture was extracted with ethyl acetate (20 mL x 4). The combined organic layer was washed with water (10 mL x 4), brine (10 mL x 3), dried over Na₂SO₄ and concentrated under reduced pressure. The resulting residue was purified by PTLC to afford **3a -3x**.

Gram-scale experiments

To a clear-colored glass round bottom flask equipped with a stir bar was added **2a** (2.95g, 18 mmol), RB (2.5 mol%) and DMF/H₂O (60 mL), followed by **1a** (1.123 g, 6 mmol) and nitrobenzene (1.476 g, 12 mmol). The reaction mixture was then illuminated with green LEDs (2 x 5 W LED light bulbs 8 cm away from the flask) and stirred at room temperature under air atmosphere. The reaction was observed by TLC. After the reaction was completed, water (30 mL) was added and the mixture was extracted with ethyl acetate (60 mL x 4). The combined organic layer was washed with water (40 mL x 4), brine (40 mL x 4), dried over Na₂SO₄ and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (PE/EA= 5:1 to 1:1) to afford the desired product **3a** (1.691 g, 86%).

Hydrolyzation

To a clear glass equipped with a stir bar was added **3a** (65 mg, 0.2 mmol), dioxane (1 mL) and HCl solution (1 mL, 5 M in H₂O). The mixture was stirred at 80 °C. After the reaction was completed (monitored by TLC), water (10 mL) was added and the mixture was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with water (10 mL x 3), brine (10 mL x 2), dried over Na₂SO₄ and concentrated under reduced pressure. The resulting residue was purified by PTLC to afford the desired product **4a** (43 mg, 75%).

Oxidation

To a clear glass equipped with a stir bar was added **3a** (65 mg, 0.2 mmol), toluene (3 mL) and DDQ (227 mg, 1 mmol). The mixture was stirred at reflux. After the reaction was completed (monitored by TLC), water (10 mL) was added and the mixture was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with water (10 mL x 3), brine (10 mL x 2), dried over Na₂SO₄ and concentrated under reduced pressure. The resulting residue was purified by PTLC to afford the desired product **5a** (46 mg, 71%).

Control Experiment

Reaction condition 1:

A mixture of 1a (0.2 mmol), 2a (38 mg, 0.6 mmol), nitrobenzene (50 mg, 0.4 mmol)

and RB (2.5 mol%) and DMF/H₂O (2.0 mL) was added in Schlenk tube. The Schlenk tube was deaerated by vacuum until the bubble was disappear, then cooled by liquid nitrogen and exchanged adequately by N₂ (about 10 times), irradiation with a commercially available green LEDs (5 W LED light bulbs 8 cm away from the tube) and stirred at room temperature for 18 h. After the reaction was completed (monitored by TLC), water was added and the mixture was extracted with ethyl acetate (20 mL x 4). The combined organic layer was washed with water (10 mL x 4), brine (10 mL x 3), dried over Na₂SO₄ and concentrated under reduced pressure. The resulting residue was purified by PTLC to afford the desired product **3a** in 87% yield. Nitrobenzene (19 mg, 38%) and azoxybenzen^[3] (11 mg, 28%) were obtained.

Reaction condition 2:

A mixture of **1a** (0.2 mmol), **2a** (38 mg, 0.6 mmol), nitrobenzene (50 mg, 0.4mmol) and RB (2.5 mol%) in DMF/H₂O (2.0 mL) was illuminated with a commercially available green LEDs (5 W LED light bulbs 8 cm away from the vial) and stirred under an air atmosphere at room temperature for 17 h. After the reaction was completed (monitored by TLC), water was added and the mixture was extracted with ethyl acetate (20 mL x 4). The combined organic layer was washed with water (10 mL x 4), brine (10 mL x 3), dried over Na₂SO₄ and concentrated under reduced pressure. The resulting residue was purified by PTLC to afford the desired product **3a** in 89% yield and nitrobenzene 91% recovered.

TEMPO as radical scavenger

To a clear-colored glass vial equipped with a stir bar was added the **2a** (98 mg, 0.6 mmol), RB (2.5 mol%). DMF/H₂O (2 mL) was then added, followed by **1a** (38 mg, 0.2 mmol), nitrobenzene (49 mg, 0.4 mmol) and TEMPO (63 mg, 0.4 mmol). The reaction was then illuminated with green LEDs (5 W LED light bulbs 8 cm away from the vial) and stirred at room temperature for 17 h. Then, water was added and the mixture was extracted with ethyl acetate (20 mL x 4). The combined organic layer was washed with water (10 mL x 4), brine (10 mL x 3), dried over Na₂SO₄ and concentrated under reduced pressure. The resulting residue was purified by PTLC to recover the substrate **1a** (33 mg, 87%).

Light/Dark Experiments^[4]

A mixture of **1a** (76 mg, 0.4 mmol), **2a** (196 mg, 1.2 mmol), nitrobenzene (99 mg, 0.8 mol) and RB (2.5 mol%) in DMF/H₂O (4.0 mL) was illuminated with a commercially available green LEDs (5 W LED light bulbs 8 cm away from the vial) and stirred under an air atmosphere at room temperature for 17 h. The lights were removed and the reaction vial was completely covered in aluminum foil during the following time increments: 2-14 h. Aliquots of 0.2 mL were taken at each of the times listed in the table below, water was added and the mixture was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with water (10 mL x 4), brine (10 mL x 2), dried over Na₂SO₄ and concentrated under reduced pressure. The residues were diluted with DMSO- d_6 and analyzed by ¹H-NMR spectroscopy based on 1-bromo-4-methylbenzene as an internal standard.





Characterization of Products



N-(2-(phenylsulfonyl)-3,4-dihydronaphthalen-1-yl)acetamide

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.51 (s, 1H), 7.98 – 7.91 (m, 2H), 7.71 (t, J = 7.3 Hz, 1H), 7.63 (t, J = 7.6 Hz, 2H), 7.31 (td, J = 7.1, 1.9 Hz, 1H), 7.30 – 7.16 (m, 3H), 2.73 (t, J = 7.7 Hz, 2H), 2.59 (t, J = 7.8 Hz, 2H), 2.01 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 169.02, 140.81, 140.22, 136.66, 133.62, 130.91, 130.59, 130.23, 129.30, 127.59, 127.17, 126.64, 125.38, 26.85, 23.37, 22.77. HRMS (ESI) *m*/*z* [M+Na]⁺ calculated for C₁₈H₁₇NNaO₃S 350.0824, found 350.0821.



N-(7-bromo-2-(phenylsulfonyl)-3,4-dihydronaphthalen-1-yl)acetamide ¹H NMR (400 MHz, DMSO- d_6) δ 9.54 (s, 1H), 7.94 (d, J = 7.7 Hz, 2H), 7.72 (t, J = 7.4 Hz, 1H), 7.64 (t, J = 7.6 Hz, 2H), 7.50 (dd, J = 8.0, 2.1 Hz, 1H), 7.33 (d, J = 2.1 Hz, 1H), 7.19 (d, J = 8.0 Hz, 1H), 2.70 (t, J = 7.6 Hz, 2H), 2.59 (t, J = 7.8 Hz, 2H), 2.02 (s, 3H). ¹³C NMR (101 MHz, DMSO- d_6) δ 169.24, 140.44, 138.75, 135.94, 133.81, 133.25, 132.69, 132.37, 129.81, 129.38, 127.46, 127.24, 119.51, 26.25, 23.22, 22.77. HRMS (ESI) *m*/*z* [M+Na]⁺ calculated for C₁₈H₁₆BrNNaO₃S 427.9919, found 427.9926.



N,N'-(2-(phenylsulfonyl)-3,4-dihydronaphthalene-1,7-diyl)diacetamide ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.96 (s, 1H), 9.55 (s, 1H), 7.93 (d, *J* = 7.6 Hz, 2H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.63 (t, *J* = 7.2 Hz, 3H), 7.46 (d, *J* = 2.3 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 2.66 (t, *J* = 7.5 Hz, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 2.00 (d, *J* = 2.8 Hz, 6H). ¹³C NMR (101 MHz, DMSO- d_6) δ 168.91, 168.23, 140.79, 140.29, 138.06, 133.63, 131.21, 131.06, 130.91, 129.30, 127.72, 127.16, 120.61, 116.06, 26.25, 23.95, 23.59, 22.74. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₀H₂₀N₂NaO₄S 407.1033, found 407.1036.



N-(7-methoxy-2-(phenylsulfonyl)-3,4-dihydronaphthalen-1-yl)acetamide ¹H NMR (400 MHz, DMSO- d_6) δ 9.49 (s, 1H), 7.97 – 7.90 (m, 2H), 7.74 – 7.67 (m, 1H), 7.63 (dd, J = 8.3, 6.8 Hz, 2H), 7.12 (d, J = 8.2 Hz, 1H), 6.90 (dd, J = 8.2, 2.6 Hz, 1H), 6.78 (d, J = 2.6 Hz, 1H), 3.70 (s, 3H), 2.65 (t, J = 7.6 Hz, 2H), 2.55 (t, J = 7.7 Hz, 2H), 2.02 (s, 3H). ¹³C NMR (101 MHz, DMSO- d_6) δ 169.27, 158.10, 140.82, 140.12, 133.77, 132.16, 131.44, 129.42, 128.73, 128.64, 127.28, 115.08, 111.52, 55.28, 26.06, 23.96, 22.82. HRMS (ESI) m/z [M+Na]⁺ calculated for C₁₉H₁₉NNaO₄S 380.0929, found 380.0927.



N-(6-methoxy-2-(phenylsulfonyl)-3,4-dihydronaphthalen-1-yl)acetamide ¹H NMR (400 MHz, DMSO- d_6) δ 9.46 (s, 1H), 7.94 (d, J = 7.6 Hz, 2H), 7.67 (dt, J = 31.5, 7.6 Hz, 3H), 7.21 (d, J = 8.4 Hz, 1H), 6.80 (d, J = 8.6 Hz, 2H), 3.77 (s, 3H), 2.71 (t, J = 7.6 Hz, 2H), 2.02 (s, 3H). ¹³C NMR (101 MHz, DMSO- d_6) δ 168.95, 160.89, 141.16, 140.39, 138.91, 133.44, 129.25, 127.39, 127.23, 127.05, 123.64, 113.17, 111.98, 55.33, 27.28, 23.39, 22.83. HRMS (ESI) m/z [M+Na]⁺ calculated for C₁₉H₁₉NNaO₄S 380.0930, found 380.0927.



N-(5-methoxy-2-(phenylsulfonyl)-3,4-dihydronaphthalen-1-yl)acetamide ¹H NMR (400 MHz, DMSO- d_6) δ 9.48 (s, 1H), 7.94 (d, J = 7.7 Hz, 2H), 7.70 (t, J = 7.3 Hz, 1H), 7.62 (t, J = 7.5 Hz, 2H), 7.20 (t, J = 8.1 Hz, 1H), 7.03 (d, J = 8.2 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 3.77 (s, 3H), 2.68 (t, J = 7.8 Hz, 2H), 2.56 (d, J = 7.9 Hz, 1H), 1.99 (s, 3H). ¹³C NMR (101 MHz, DMSO- d_6) δ 169.04, 155.50, 140.79, 140.11, 133.62, 132.03, 130.85, 129.29, 127.18, 126.99, 124.22, 117.77, 113.11, 55.68, 22.91, 22.73, 19.54. HRMS (ESI) m/z [M+Na]⁺ calculated for C₁₉H₁₉NNaO₄S 380.0928, found 380.0927.



N-(6-(benzyloxy)-2-(phenylsulfonyl)-3,4-dihydronaphthalen-1-yl)acetamide ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.44 (s, 1H), 7.99 – 7.88 (m, 2H), 7.74 – 7.66 (m, 1H), 7.66 – 7.56 (m, 2H), 7.47 – 7.28 (m, 5H), 7.20 (d, *J* = 8.5 Hz, 1H), 6.92 – 6.83 (m, 2H), 5.12 (s, 2H), 2.69 (t, *J* = 7.7 Hz, 2H), 2.55 (t, *J* = 7.8 Hz, 2H), 2.01 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 169.04, 159.99, 141.16, 140.36, 138.94, 136.72,

133.49, 129.29, 128.49, 127.95, 127.69, 127.43, 127.08, 125.60, 123.85, 114.12, 112.73, 69.33, 27.29, 23.42, 22.87. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₅H₂₃NNaO₄S 456.1261, found 456.1240.



N-(7-phenyl-2-(phenylsulfonyl)-3,4-dihydronaphthalen-1-yl)acetamide ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.55 (s, 1H), 8.00 – 7.93 (m, 2H), 7.76 – 7.69 (m, 1H), 7.69 – 7.58 (m, 3H), 7.55 (d, J = 7.2 Hz, 2H), 7.50 – 7.43 (m, 3H), 7.37 (t, J = 7.3 Hz, 1H), 7.32 (d, J = 7.8 Hz, 1H), 2.78 (t, J = 7.7 Hz, 2H), 2.63 (t, J = 7.9 Hz, 2H), 2.04 (s, 3H). ¹³C NMR (101 MHz, DMSO- d_6) δ 169.17, 140.75, 140.00, 139.64, 138.69, 135.95, 133.69, 131.45, 131.07, 129.34, 129.05, 128.56, 128.33, 127.55, 127.20, 126.48, 123.35, 26.53, 23.46, 22.8. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₄H₂₁NNaO₃S 426.1145, found 426.1134.



N-(4-phenyl-2-(phenylsulfonyl)-3,4-dihydronaphthalen-1-yl)acetamide

¹H NMR (400 MHz, DMSO- d_6) δ 9.55 (s, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.45 – 7.25 (m, 7H), 7.19 – 7.05 (m, 5H), 7.04 – 6.97 (m, 1H), 4.23 (t, J = 5.7 Hz, 1H), 2.98 (qd, J = 16.9, 5.7 Hz, 2H), 2.02 (s, 3H). ¹³C NMR (101 MHz, DMSO- d_6) δ 169.08, 142.03, 140.87, 139.75, 138.67, 133.36, 131.17, 130.67, 129.01, 128.22, 128.13, 127.81, 127.12, 126.89, 126.52, 125.74, 41.49, 31.54, 22.82. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₄H₂₁NNaO₃S 426.1149, found 426.1134.



N-(4-(3,4-dichlorophenyl)-2-(phenylsulfonyl)-3,4-dihydronaphthalen-1-yl)acetamide ¹H NMR (400 MHz, DMSO- d_6) δ 9.74 (s, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.38 (dp, J = 23.9, 7.7, 7.2 Hz, 7H), 7.24 (d, J = 8.3 Hz, 1H), 7.16 (d, J = 10.1 Hz, 2H), 7.01 (d, J = 8.3 Hz, 1H), 4.29 (d, J = 6.3 Hz, 1H), 3.08 (dd, J = 17.1, 6.6 Hz, 1H), 2.81 (d, J = 17.0 Hz, 1H), 2.12 (s, 3H). ¹³C NMR (101 MHz, DMSO- d_6) δ 169.11, 142.75, 140.97, 138.89, 137.24, 133.15, 131.19, 130.83, 129.99, 129.92, 129.19, 128.74, 128.35, 128.22, 127.56, 126.69, 125.95, 39.94, 31.51, 22.79. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₄H₁₉Cl₂NNaO₃S 494.0348, found 494.0355.



4-acetamido-3-(phenylsulfonyl)-1,2-dihydronaphthalen-1-yl acetate

¹H NMR (400 MHz, DMSO- d_6) δ 9.63 (s, 1H), 7.96 – 7.86 (m, 2H), 7.80 – 7.71 (m, 1H), 7.65 (dd, J = 8.4, 6.8 Hz, 2H), 7.42 (td, J = 8.7, 7.1, 3.7 Hz, 4H), 5.76 (t, J = 3.5 Hz, 1H), 2.92 (s, 2H), 2.06 (s, 3H), 1.70 (s, 3H). ¹³C NMR (101 MHz, DMSO- d_6) δ 169.34, 169.26, 140.02, 139.37, 133.77, 132.83, 130.98, 130.66, 129.34, 128.91, 127.30, 125.97, 66.73, 29.24, 22.87, 20.70. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₀H₁₉NNaO₅S 408.0872, found 408.0876.



N-(3-(phenylsulfonyl)-2H-chromen-4-yl)acetamide

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.71 (s, 1H), 8.08 – 7.92 (m, 2H), 7.75 (t, *J* = 7.3 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 2H), 7.36 (td, *J* = 7.8, 1.7 Hz, 1H), 7.28 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 8.1 Hz, 1H), 4.97 (s, 2H), 2.07 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 169.11, 155.48, 140.40, 138.90, 134.05, 132.86, 129.49, 127.29, 126.41, 122.10, 122.02, 120.18, 116.42, 63.64, 22.80. HRMS (ESI) *m/z* [M+Na]⁺ calculated for C₁₇H₁₅NNaO₄S 352.0615, found 352.0614.



(Z)-N-(1-phenyl-2-(phenylsulfonyl)prop-1-en-1-yl)acetamide

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.61 (s, 1H), 7.99 – 7.91 (m, 2H), 7.72 (t, *J* = 7.3 Hz, 1H), 7.65 (dd, *J* = 8.4, 6.7 Hz, 2H), 7.36 (p, *J* = 4.4, 3.5 Hz, 3H), 7.32 – 7.22 (m, 2H), 1.92 (s, 3H), 1.80 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 168.02, 143.53, 140.52, 136.12, 133.53, 129.23, 128.96, 128.55, 128.07, 127.12, 125.68, 23.00, 15.29. HRMS (ESI) *m/z* [M+Na]⁺ calculated for C₁₇H₁₇NNaO₃S 338.0819, found 338.0821.



(E)-N-(1-phenyl-2-(phenylsulfonyl)prop-1-en-1-yl)acetamide

3m

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.71 (s, 1H), 7.64 – 7.56 (m, 1H), 7.55 – 7.44 (m, 4H), 7.40 – 7.32 (m, 1H), 7.32 – 7.25 (m, 2H), 7.22 – 7.13 (m, 2H), 1.94 (s, 3H), 1.87 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 166.91, 143.68, 141.00, 135.87, 132.91, 129.95, 129.15, 128.93, 128.32, 127.38, 126.90, 23.16, 17.05. HRMS (ESI) *m/z* [M+Na]⁺ calculated for C₁₇H₁₇NNaO₃S 338.0818, found 338.0821.



(Z)-N-(1-phenyl-2-(phenylsulfonyl)vinyl)acetamide

¹H NMR (400 MHz, Chloroform-*d*) δ 9.73 (s, 1H), 8.02 – 7.87 (m, 2H), 7.70 – 7.59 (m, 1H), 7.57 (dd, J = 8.4, 6.8 Hz, 2H), 7.47 – 7.33 (m, 1H), 7.39 – 7.27 (m, 4H), 5.66 (s, 1H), 2.19 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 168.20, 150.45, 141.69, 134.85, 133.83, 130.54, 129.60, 128.51, 127.16, 126.90, 110.53, 24.78. HRMS (ESI) m/z [M+Na]⁺ calculated for C₁₆H₁₅NNaO₃S 324.0670, found 324.0665.



(E)-N-(1-phenyl-2-(phenylsulfonyl)vinyl)acetamide

¹H NMR (400 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.53 – 7.39 (m, 4H), 7.34 (td, J = 7.7, 2.6 Hz, 4H), 7.21 (s, 2H), 6.97 (s, 1H), 2.05 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 169.28, 147.13, 142.81, 133.45, 132.66, 130.21, 128.88, 128.79, 128.50, 127.31, 115.66, 25.01. HRMS (ESI) *m/z* [M+Na]⁺ calculated for C₁₆H₁₅NNaO₃S 324.0667, found 324.0665.



N-(2-(phenylsulfonyl)-3,4-dihydronaphthalen-1-yl)propionamide

1H NMR (400 MHz, DMSO- d_6) δ 9.40 (s, 1H), 7.97 – 7.90 (m, 2H), 7.76 – 7.58 (m, 3H), 7.35 – 7.17 (m, 4H), 2.73 (t, J = 7.8 Hz, 2H), 2.57 (t, J = 7.9 Hz, 2H), 2.33 (q, J = 8.1, 7.5 Hz, 2H), 1.03 (t, J = 7.6 Hz, 3H). 13C NMR (101 MHz, DMSO- d_6) δ 172.52, 140.82, 140.23, 136.64, 133.56, 130.94, 130.18, 129.28, 127.55, 127.07, 126.61, 125.29, 28.49, 26.85, 23.39, 9.30. HRMS (ESI) *m*/*z* [M+Na]⁺ calculated for C₁₉H₁₉NNaO₃S 364.0984, found 364.0978.



benzyl (2-(phenylsulfonyl)-3,4-dihydronaphthalen-1-yl)carbamate

1H NMR (400 MHz, Chloroform-*d*) δ 8.77 (s, 1H), 7.87 – 7.80 (m, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.44 – 7.32 (m, 8H), 7.29 (td, J = 7.5, 1.5 Hz, 1H), 7.22 (td, J = 7.6, 1.4 Hz, 1H), 7.12 (d, J = 7.3 Hz, 1H), 5.13 (s, 2H), 2.75 – 2.66 (m, 2H), 2.66 – 2.57 (m, 2H). 13C NMR (101 MHz, Chloroform-d) δ 153.24, 141.56, 141.04, 137.18,135.87, 133.55, 130.53, 129.58, 129.35, 128.63, 128.38, 127.60, 127.04, 126.48, 126.44, 123.77, 67.53, 27.77, 23.62. HRMS (ESI) *m/z* [M+Na]⁺ calculated for C₂₄H₂₁NNaO₄S 442.1076, found 442.1083.



N-(2-tosyl-3,4-dihydronaphthalen-1-yl)acetamide

¹H NMR (400 MHz, DMSO- d_6) δ 9.48 (s, 1H), 7.83 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.34 – 7.15 (m, 4H), 2.71 (t, J = 7.7 Hz, 2H), 2.55 (t, J = 7.9 Hz, 2H), 2.39 (s, 3H), 2.04 (s, 3H). ¹³C NMR (101 MHz, DMSO- d_6) δ 169.23, 144.29, 139.91, 138.01, 136.68, 131.03, 130.68, 130.25, 129.86, 127.64, 127.34, 126.71, 125.46, 26.97, 23.55, 22.91, 21.19. HRMS (ESI) m/z [M+Na]⁺ calculated for C₁₉H₁₉NNaO₃S 364.0982, found 364.0978.



N-(2-((4-methoxyphenyl)sulfonyl)-3,4-dihydronaphthalen-1-yl)acetamide ¹H NMR (400 MHz, DMSO- d_6) δ 9.49 (s, 1H), 7.90 (d, J = 8.5 Hz, 2H), 7.35 – 7.13 (m, 6H), 3.86 (s, 3H), 2.73 (t, J = 7.7 Hz, 2H), 2.57 (t, J = 7.8 Hz, 2H), 2.07 (s, 3H). ¹³C NMR (101 MHz, DMSO- d_6) δ 169.08, 163.15, 139.33, 136.55, 132.30, 131.05, 130.07, 129.63, 127.55, 126.62, 125.34, 114.53, 55.78, 26.93, 23.48, 22.87. HRMS (ESI) m/z [M+Na]⁺ calculated for C₁₉H₁₉NNaO₄S 380.0934, found 380.0927.



N-(2-((4-(tert-butyl)phenyl)sulfonyl)-3,4-dihydronaphthalen-1-yl)acetamide ¹H NMR (400 MHz, DMSO- d_6) δ 9.48 (s, 1H), 7.86 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H), 7.34 – 7.16 (m, 4H), 2.73 (t, J = 7.7 Hz, 2H), 2.57 (t, J = 7.8 Hz, 2H), 2.02 (s, 3H), 1.29 (s, 9H). ¹³C NMR (101 MHz, DMSO- d_6) δ 168.99, 156.71, 139.79, 137.90, 136.58, 130.96, 130.56, 130.14, 127.55, 127.15, 126.60, 126.15, 125.37, 34.96, 30.72, 26.86, 23.38, 22.80. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₂H₂₅NNaO₃S 406.1453 , found 406.1447.



N-(2-((4-fluorophenyl)sulfonyl)-3,4-dihydronaphthalen-1-yl)acetamide ¹H NMR (400 MHz, DMSO- d_6) δ 9.51 (s, 1H), 8.02 (dd, J = 8.7, 5.2 Hz, 2H), 7.48 (t, J = 8.8 Hz, 2H), 7.36 – 7.16 (m, 4H), 2.76 (t, J = 7.7 Hz, 2H), 2.61 (t, J = 7.8 Hz, 2H), 2.02 (s, 3H). 19F NMR (376 MHz, DMSO- d_6): δ -104.95. ¹³C NMR (101 MHz, DMSO- d_6) δ 169.09, 164.87 (d, J = 252.5 Hz) 140.28, 137.18 (d, J = 3 Hz), 136.72, 130.92, 130.48 (d, J = 10 Hz), 130.32, 127.62, 126.68, 125.34, 116.53(d, J = 23 Hz), 26.86, 23.31, 22.75. HRMS (ESI) m/z [M+Na]⁺ calculated for C₁₈H₁₆FNNaO₃S 368.0729, found 368.0727.



N-(2-((4-chlorophenyl)sulfonyl)-3,4-dihydronaphthalen-1-yl)acetamide ¹H NMR (400 MHz, DMSO- d_6) δ 9.53 (s, 1H), 7.96 (d, J = 8.3 Hz, 2H), 7.71 (d, J = 8.3 Hz, 2H), 7.35 – 7.16 (m, 4H), 2.76 (t, J = 7.7 Hz, 2H), 2.61 (t, J = 7.8 Hz, 2H), 2.02 (s, 3H). ¹³C NMR (101 MHz, DMSO- d_6) δ 169.10, 140.60, 139.70, 138.62, 136.77, 130.87, 130.70, 130.39, 129.46, 129.20, 127.64, 126.69, 125.37, 26.86, 23.30, 22.75. HRMS (ESI) m/z [M+Na]⁺ calculated for C₁₈H₁₆ClNNaO₃S 384.0429, found 384.0432.



N-(2-((4-(trifluoromethyl)phenyl)sulfonyl)-3,4-dihydronaphthalen-1-yl)acetamide ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.57 (s, 1H), 8.16 (d, *J* = 8.1 Hz, 2H), 8.02 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.16 (m, 4H), 2.79 (t, *J* = 7.5 Hz, 2H), 2.66 (t, *J* = 7.9 Hz, 2H), 1.98 (s, 3H). 19F NMR (376 MHz, DMSO-*d*₆): δ -104.95. ¹³C NMR (101 MHz, DMSO-*d*₆) δ 169.08, 144.75, 141.26, 136.89, 133.09 (q, *J* = 32.4 Hz), 130.63 (d, *J* = 30.9 Hz), 130.55, 128.23, 127.69, 126.72, 126.50 (d, J = 4.2 Hz), 125.40, 123.41 (d, J = 273.2 Hz), 26.82, 23.21, 22.68. HRMS (ESI) m/z[M+Na]⁺ calculated for C₁₉H₁₆F₃NNaO₃S 418.0700, found 418.0695.



N-(2-(naphthalen-2-ylsulfonyl)-3,4-dihydronaphthalen-1-yl)acetamide ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.55 (s, 1H), 8.64 (s, 1H), 8.18 (dd, *J* = 23.4, 8.3 Hz, 2H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.93 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.77 – 7.64 (m, 2H), 7.34 – 7.13 (m, 4H), 2.85 – 2.59 (m, 4H), 2.01 (s, 3H). ¹³C NMR (101 MHz, DMSO *d*₆) δ 169.00, 140.43, 137.81, 136.71, 134.69, 131.62, 130.93, 130.74, 130.24, 129.50, 129.43, 129.25, 128.57, 127.91, 127.73, 127.59, 126.63, 125.37, 122.36, 26.90, 23.43, 22.78. HRMS (ESI) *m*/*z* [M+Na]⁺ calculated for C₂₂H₁₉NNaO₃S 400.0979, found 400.0978.



N-(2-(thiophen-2-ylsulfonyl)-3,4-dihydronaphthalen-1-yl)acetamide ¹H NMR (400 MHz, DMSO- d_6) δ 9.53 (s, 1H), 8.08 (dd, J = 4.9, 1.4 Hz, 1H), 7.83 (dd, J = 3.9, 1.4 Hz, 1H), 7.36 – 7.17 (m, 5H), 2.74 (t, J = 7.6 Hz, 2H), 2.65 (dd, J =9.6, 6.4 Hz, 2H), 2.09 (s, 3H). ¹³C NMR (101 MHz, DMSO- d_6) δ 169.09, 141.63, 139.91, 136.74, 135.32, 134.03, 130.93, 130.60, 130.37, 128.33, 127.65, 126.71, 125.61, 27.05, 23.56, 23.00. HRMS (ESI) m/z [M+Na]⁺calculated for C₁₆H₁₅NNaO₃S₂

356.0393, found 356.0386



N-(2-(ethylsulfonyl)-3,4-dihydronaphthalen-1-yl)acetamide ¹H NMR (400 MHz, DMSO- d_6) δ 9.50 (s, 1H), 7.30 (ddd, J = 20.1, 7.8, 5.1 Hz, 4H), 3.22 (q, J = 7.4 Hz, 2H), 2.84 (t, J = 7.8 Hz, 2H), 2.65 (t, J = 7.8 Hz, 2H), 2.06 (s, 3H), 1.19 (t, J = 7.4 Hz, 3H). ¹³C NMR (101 MHz, DMSO- d_6) δ 169.29, 140.49, 137.01, 131.03, 130.13, 129.15, 127.61, 126.62, 125.37, 47.50, 26.86, 23.64, 22.92, 6.47. HRMS (ESI) m/z [M+Na]⁺ calculated for C₁₄H₁₇NNaO₃S 302.0823, found 302.0821.



N-(2-(methylsulfonyl)-3,4-dihydronaphthalen-1-yl)acetamide

¹H NMR (400 MHz, DMSO- d_6) δ 9.50 (s, 1H), 7.40 – 7.32 (m, 2H), 7.31 – 7.23 (m, 2H), 3.10 (s, 3H), 2.86 (t, *J* = 7.8 Hz, 2H), 2.70 (t, *J* = 7.7 Hz, 2H), 2.06 (s, 3H). ¹³C NMR (101 MHz, DMSO- d_6) δ 169.30, 138.62, 136.96, 131.24, 131.14, 130.14, 127.61, 126.68, 125.28, 40.96, 26.92, 23.28, 22.99. HRMS (ESI) *m*/*z* [M+Na]⁺ calculated for C₁₃H₁₅NNaO₃S 288.0671, found 288.0665.



N-(2-(phenethylsulfonyl)-3,4-dihydronaphthalen-1-yl)acetamide

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.57 (s, 1H), 7.32 (d, *J* = 25.5 Hz, 9H), 3.54 (t, *J* = 8.1 Hz, 2H), 3.09 – 2.59 (m, 6H), 2.08 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 169.41, 140.59, 138.08, 137.07, 131.07, 130.20, 129.81, 128.50, 128.47, 127.62, 126.63, 126.52, 125.37, 53.93, 27.58, 26.86, 23.53, 22.93. HRMS (ESI) *m/z* [M+Na]⁺ calculated for C₂₀H₂₁NNaO₃S 378.1133, found 378.1134.



2-(phenylsulfonyl)-3,4-dihydronaphthalen-1(2H)-one

¹H NMR (400 MHz, Chloroform-*d*) δ 7.98 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.95 – 7.88 (m, 2H), 7.71 – 7.62 (m, 1H), 7.57 (t, *J* = 7.7 Hz, 2H), 7.51 (td, *J* = 7.5, 1.5 Hz, 1H), 7.35 – 7.23 (m, 2H), 4.12 (t, *J* = 5.8 Hz, 1H), 3.50 (ddd, *J* = 16.9, 9.6, 4.7 Hz, 1H), 2.99 (dt,

J = 17.0, 5.5 Hz, 1H), 2.85 (dq, J = 17.3, 5.9 Hz, 1H), 2.66 (ddt, J = 14.6, 10.0, 5.1 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 188.65, 143.58, 138.99, 134.55, 134.03, 131.76, 129.13, 129.04, 128.98, 127.97, 127.09, 69.67, 26.62, 23.67. HRMS (ESI) *m/z* [M+Na]⁺ calculated for C₁₆H₁₄NaO₃S 309.055, found 309.0556.



N-(2-(phenylsulfonyl)naphthalen-1-yl)acetamide

¹H NMR (400 MHz, Chloroform-*d*) δ 8.51 (s, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 7.98 – 7.84 (m, 5H), 7.68 – 7.47 (m, 5H), 2.20 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 168.56, 140.70, 136.66, 134.75, 133.70, 131.54, 129.72, 129.35, 129.26, 128.32, 128.07, 127.53, 127.00, 125.88, 123.50, 23.80. HRMS (ESI) *m/z* [M+Na]⁺ calculated for C₁₈H₁₅NaO₃S 348.0659, found 348.0665.



Azoxybenzene^{[3] 1}H NMR (400 MHz, Chloroform-d) δ 8.36 – 8.21 (m, 2H), 8.17 (dd, J = 8.0, 1.6 Hz, 2H), 7.61 – 7.45 (m, 5H), 7.45 – 7.35 (m, 1H). ¹³C NMR (101 MHz, Chloroform-d) δ 148.49, 144.14, 131.72, 129.74, 128.93, 128.83, 125.65, 122.48. HRMS (ESI) *m*/*z* [M+Na]⁺ calculated for C₁₂H₁₀N₂NaO 221.0695, found 221.0685.

References

- [1] (a) Z. H. Guan, Z. Y. Zhang, Z. H. Ren, Y. Y. Wang, and X. M. Zhang, J. Org. Chem., 2011, 76, 339; (b) C. X. Sun, S. M. Weinreb, Synthesis, 2006, 21, 3585.
- [2] (a) J. Liu, X. Zhou, H. Rao, F. Xiao, C. J. Li, and G. J. Deng, *Chem. Eur. J.*, 2011, **17**, 7996;
 (b) A. U. Meyer, K. Straková, T. Slanina, B. König, *Chem. Eur. J.*, 2016, **22**, 8694; (c) A. U. Meyer, S. Jäger, D. P. Hari and B. König, *Adv. Synth. Catal.*, 2015, **357**, 2050.
- [3] (a) E. Voutyritsa, A. Theodorou, M. G. Kokotou, C. G. Kokotos, *Green Chem.*, 2017, 19, 1291; Z. Long, Z. G. Wang, D. N. Zhou, D. Y. Wan, and J. S. You, *Org. Lett.*, 2017, 19, 2777.
- [4] C.-J. Wallentin, J. D. Nguyen, P. Finkbeiner and C. R. J. Stephenson, J. Am. Chem. Soc., 2012, 134, 8875.

Copies of NMR spectra



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









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



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- 169.10 140.60 138.77 138.77 138.77 138.77 130.87 130.87 130.39 122.69 122.69













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