Supporting Information

for

Intermolecular Iodofunctionalization of Allenamides with indoles, pyrrole, and furan: Synthesis of iodine-substituted Z-enamides

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1. General considerations

All reactions were performed using Schlenk tubes, septa, and syringes without protection of nitrogen. THF, toluene and DCM, DCE were freshly distilled over sodium/benzophenone and calcium hydride, respectively. Commercial reagents were used as supplied or were purified by standard techniques where necessary. Column chromatography was performed using Qingdao Haiyang Chemical Co., Ltd silica gel (200–300 mesh) with the appropriate solvent system, as determined by TLC analysis (Qingdao Haiyang Chemical Co., Ltd, silica gel F254) using UV light and KMnO₄ stain to visualize the reaction components. Melting points were determined using a WRS-1B digital melting point instrument. IR spectra were recorded on a Nicoletisso FTIR spectrometer using KBr disks. Unless otherwise noted, nuclear magnetic resonance spectra were recorded at room temperature on an Agilent 400 MHz spectrometer using CDCl₃ as the solvent and TMS as the internal reference. Chemical shifts for ¹³C NMR spectra were recorded in parts per million relative to tetramethylsilane using the central peak of deuterochloroform (77.0 ppm) as the internal standard. HRMS was performed using a Bruker Daltonics Bio TOF mass spectrometer.

Allenamides 1a-1p were prepared according to the published methods.¹, ², ³ Indoles, pyrroles, 2-methylfuran, imidazole were obtained commercially and used without further purification.

**General procedure for N-iodosuccinimide-mediated intermolecular nucleophilic addition of allenamide 1a with indole 2a.**

To a Schlenk tube were added allenamide 1a (0.1 mmol), N-Methylindole 2a (2.0 equiv.), N-iodosuccinimide (1.05 equiv.) and CH₂CN (anhydrous, 3 mL). Then the reaction mixture was stirred at r t for 1 min until complete consumption of starting material as monitored by TLC. Concentration of the reaction mixture in vacuo followed by purification through flash chromatography on silica gel column (hexane/EtOAc = 5/1 as the eluent) afforded 4a (46.5 mg, 86% yield) as a white solid.
2. Analytical Data

(Z)-N-(2-ido-3-(1-methyl-1H-indol-3-yl)prop-1-en-1-yl)-4-methyl-N-phenylbenzenesulfonamide (4a)
White solid; yield, 86%; m p 141.5-142.2°C; IR (neat) 3041, 2934, 2858, 1499, 1457, 758, 700 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 7.53 (d, J = 7.8 Hz, 1H), 7.41- 7.37 (m, 3H), 7.33 – 7.27 (m, 4H), 7.24 – 7.20 (m, 1H), 7.16 – 7.07 (m, 5H), 7.01 – 6.98 (m, 1H), 3.99 (s, 2H), 3.73 (s, 3H), 2.38 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 144.14, 139.64, 136.69, 133.77, 131.74, 129.64, 128.72, 128.22, 127.52, 127.46, 127.12, 127.05, 121.13, 118.87, 118.45, 110.17, 109.98, 109.61, 37.80, 32.31, 21.03. HRMS (ESI) calcd for C₂₅H₂₃IN₂NaO₂S [M+Na]^+ 565.0423; found, 565.0422.

(Z)-N-(2-ido-3-(1-methyl-1H-indol-3-yl)prop-1-en-1-yl)-4-methyl-N-(p-tolyl)benzenesulfonamide (4b)
White solid; yield, 84%; m p 150-150.5°C; IR (neat) 3038, 2934, 2858, 1499, 1459, 756, 702 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 7.52 (d, J = 7.9 Hz, 1H), 7.39 (t, J = 8.4 Hz, 3H), 7.33 (d, J = 8.1 Hz, 2H), 7.15 (t, J = 7.5 Hz, 1H), 7.12 – 7.05 (m, 4H), 6.99 (t, J = 7.4 Hz, 1H), 6.94 (d, J = 8.2 Hz, 2H), 3.98 (s, 2H), 3.73 (s, 3H), 2.38 (s, 3H), 2.24 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 144.06, 137.01, 136.69, 136.51, 133.77, 131.84, 129.62, 129.20, 128.20, 127.55, 127.50, 127.11, 121.12, 118.87, 118.43, 110.19, 109.60, 109.32, 37.84, 32.30, 21.02, 20.52. HRMS (ESI) calcd for C₂₆H₂₅IN₂NaO₂S [M+Na]^+ 579.0579; found, 579.0573.

(Z)-N-(2-ido-3-(1-methyl-1H-indol-3-yl)prop-1-en-1-yl)-4-methyl-N-(o-tolyl)benzenesulfonamide (4c)
White solid; yield, 89%; m p 99.8-100.5°C; IR (neat) 3041, 2934, 2861, 1499, 1451, 758, 700 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 7.45 – 7.42 (m, 3H), 7.39 (d, J = 8.3 Hz, 1H), 7.36 (d, J = 8.1 Hz, 2H), 7.24 – 7.22 (m, 2H), 7.20 (t, J = 7.6 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.09 (s, 1H), 7.07 (t, J = 7.0 Hz, 1H), 6.96 (t, J = 7.4 Hz, 1H), 6.69 (d, J = 7.9 Hz, 1H), 3.95 (s, 2H), 3.73 (s, 3H), 2.42 (s, 3H), 2.20 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 144.35, 138.49, 137.00, 136.72, 133.99, 131.98, 131.04, 129.83, 129.73, 128.24, 127.76, 127.09, 126.10, 121.12, 118.83, 118.42, 110.50, 109.65, 99.68, 38.87, 32.31, 21.10, 19.35. HRMS (ESI) calcd for C₂₆H₂₇IN₂NaO₂S [M+Na]^+ 579.0579; found, 579.0584.
(Z)-N-(2-iodo-3-(1-methyl-1H-indol-3-yl)prop-1-en-1-yl)-N-(4-methoxyphenyl)-4-methylbenzenesulfonyl amide (4d)

White solid; yield, 79%; m.p 137.3-138.3 °C; IR (neat) 3038, 2931, 2861, 1499, 1454, 761, 700 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 7.50 (d, J = 7.8 Hz, 1H), 7.10 – 7.37 (m, 3H), 7.34 (d, J = 8.2 Hz, 2H), 7.14 (t, J = 7.6 Hz, 1H), 7.10 (d, J = 4.0 Hz, 2H), 7.02 – 6.93 (m, 3H), 6.86 – 6.83 (m, 2H), 3.97 (s, 2H), 3.73 (s, 3H), 3.71 (s, 2H), 2.39 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 158.11, 144.05, 136.70, 133.65, 131.99, 129.62, 129.43, 128.19, 127.61, 127.11, 121.12, 118.88, 118.44, 113.86, 110.26, 109.60, 109.50, 108.08, 55.23, 37.92, 32.30, 21.04. HRMS (ESI) calcd for C₂₁H₂₁N₂NaO₂S [M+Na]⁺ 595.0528; found, 595.0523.

(Z)-N-(3-fluorophenyl)-N-(2-iodo-3-(1-methyl-1H-indol-3-yl)prop-1-en-1-yl)-4-methylbenzenesulfonyl amide (4e)

White solid; yield, 79%; m.p 134.8-135.6 °C; IR (neat) 3041, 2934, 2861, 1499, 1454, 758, 700 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 7.54 (d, J = 7.9 Hz, 1H), 7.47 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.5 Hz, 1H), 7.36 (d, J = 8.2 Hz, 2H), 7.32 (t, J = 8.3 Hz, 1H), 7.16 – 7.13 (m, 3H), 7.09 (t, J = 8.3 Hz, 1H), 7.00 (d, J = 7.4 Hz, 1H), 6.95 (t, J = 8.3 Hz, 2H), 4.01 (s, 2H), 3.73 (s, 3H), 2.38 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 161.63 (d, J = 242.8 Hz), 144.44, 141.22 (d, J = 9.9 Hz)136.71, 133.62, 131.31, 130.30 (d, J = 9.5 Hz), 129.79, 128.30, 127.53, 127.11, 122.89 (d, J = 3.1 Hz), 121.16, 118.85, 118.45, 114.07 (d, J = 23.7 Hz), 113.81 (d, J = 20.9 Hz), 111.54, 110.04, 109.65, 37.68, 32.32, 21.05. HRMS (ESI) calcd for C₂₅H₂₅F₂N₂NaO₂S [M+Na]⁺ 583.0328; found, 583.0326.

(Z)-N-(4-fluorophenyl)-N-(2-iodo-3-(1-methyl-1H-indol-3-yl)prop-1-en-1-yl)-4-methylbenzenesulfonyl amide (4f)

White solid; yield, 80%; m.p 154.1-154.6 °C; IR (neat) 3035, 2934, 2861, 1496, 1457, 756, 702 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 7.50 (d, J = 7.9 Hz, 1H), 7.44 – 7.32 (m, 5H), 7.20 – 7.07 (m, 7H), 6.99 (t, J = 7.4 Hz, 1H), 3.98 (s, 2H), 3.73 (s, 3H), 2.39 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 160.64 (d, J = 243.6 Hz), 159.42, 144.30, 136.70, 135.81, 133.43, 131.68, 129.95, 129.90 (d, J = 8.9 Hz), 128.23, 127.59, 127.11, 121.14, 118.85, 118.47, 115.62 (d, J = 22.7 Hz), 110.15, 109.62, 109.42, 37.81, 32.31, 21.05. HRMS (ESI) calcd for C₂₅H₂₅F₂N₂NaO₂S [M+Na]⁺ 583.0328; found, 583.0322.
(Z)-N-(4-bromophenyl)-N-(2-iodo-3-(1-methyl-1H-indol-3-yl)prop-1-en-1-yl)-4-methylbenzenesulfonamide (4g)

White solid; yield, 78%; mp 149.5-150.2 °C; IR (neat) 3038, 2934, 2858, 1501, 1457, 756, 702 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 7.51 (dd, J = 8.6, 2.7 Hz, 3H), 7.44 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 7.3 Hz, 1H), 7.12 (d, J = 5.9 Hz, 2H), 7.04 (d, J = 8.7 Hz, 2H), 6.99 (t, J = 7.1 Hz, 1H), 3.99 (s, 2H), 3.73 (s, 3H), 2.38 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 144.39, 139.00, 136.69, 133.50, 131.74, 131.37, 129.80, 129.34, 128.25, 127.53, 127.10, 121.15, 119.86, 118.83, 118.48, 110.41, 110.09, 109.63, 37.72, 32.31, 21.05. HRMS (ESI) calcd for C₂₅H₂₅BrIN₃NaO₂S [M+Na]⁺ 642.9528; found, 642.9517.

(Z)-N-(2,4-dimethylphenyl)-N-(2-iodo-3-(1-methyl-1H-indol-3-yl)prop-1-en-1-yl)-4-methylbenzenesulfonamide (4h)

White solid; yield, 83%; mp 54.1-54.9 °C; IR (neat) 3041, 2931, 2861, 1501, 1451, 758, 700 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 7.45 – 7.34 (m, 6H), 7.22 (s, 1H), 7.14 (t, J = 7.5 Hz, 1H), 7.09 (s, 1H), 7.03 (s, 1H), 6.95 (t, J = 7.3 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 6.52 (d, J = 8.1 Hz, 1H), 3.94 (s, 2H), 3.73 (s, 3H), 2.42 (s, 3H), 2.22 (s, 3H), 2.14 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 144.31, 138.21, 137.63, 136.73, 134.39, 134.00, 132.06, 131.59, 129.74, 129.58, 128.26, 127.80, 127.10, 126.72, 121.13, 118.87, 118.42, 110.53, 109.68, 99.06, 38.98, 32.34, 21.12, 20.58, 19.27. HRMS (ESI) calcd for C₂₇H₂₇N₃NaO₂S [M+Na]⁺ 593.0736; found, 593.0728.

(Z)-N-(3,5-dimethoxyphenyl)-N-(2-iodo-3-(1-methyl-1H-indol-3-yl)prop-1-en-1-yl)-4-methylbenzenesulfonamide (4i)

White solid; yield, 84%; mp 141.9-142.0 °C; IR (neat) 3038, 2937, 2861, 1501, 1499, 761, 705 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 7.54 (d, J = 7.9 Hz, 1H), 7.51 (d, J = 8.2 Hz, 2H), 7.39 – 7.35 (m, 3H), 7.14 – 7.11 (m, 3H), 6.95 (t, J = 7.4 Hz, 1H), 6.34 (t, J = 2.0 Hz, 1H), 6.18 (d, J = 2.1 Hz, 2H), 4.02 (s, 2H), 3.73 (s, 3H), 3.52 (s, 6H), 2.39 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 159.99, 144.22, 141.08, 136.72, 133.93, 131.57, 129.63, 128.27, 127.60, 127.08, 121.10, 118.81, 118.43, 110.09, 110.02, 109.63, 105.47, 98.72, 55.10, 37.89, 32.30, 21.03. HRMS (ESI) calcd for C₂₇H₂₇N₃NaO₂S [M+Na]⁺ 625.0634; found, 625.0629.
(Z)-N-benzyl-N-(2-iodo-3-(1-methyl-1H-indol-3-yl)prop-1-en-1-yl)-4-methylbenzenesulfonamide (4j)

White solid; yield, 84%; m p 119.2-119.8 °C; IR (neat) 3041, 2931, 2856, 1499, 1457, 758, 700 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 7.68 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 7.38 – 7.25 (m, 7H), 7.14 (t, J = 7.4 Hz, 1H), 6.98 (t, J = 7.4 Hz, 1H), 6.81 (s, 1H), 6.13 (s, 1H), 4.36 (s, 2H), 3.85 (s, 2H), 3.69 (s, 3H), 2.40 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 143.73, 136.57, 135.42, 135.05, 130.73, 129.78, 128.92, 128.13, 127.91, 127.65, 127.40, 127.03, 121.11, 118.68, 118.47, 114.67, 110.18, 109.54, 53.32, 38.03, 32.29, 21.04. HRMS (ESI) calcd for C₂₆H₂₃N₂NaO₂S [M+Na]⁺ 579.0579; found, 579.0577.

(Z)-N-(2-iodo-3-(1-methyl-1H-indol-3-yl)prop-1-en-1-yl)-N-(4-methoxybenzyl)-4-methylbenzenesulfonamide (4k)

White solid; yield, 77%; m p 137.3-138.3 °C; IR (neat) 3038, 2931, 2861, 1499, 1454, 761, 700 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 7.67 (d, J = 7.9 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 7.38 – 7.29 (m, 2H), 7.18 - 7.14 (m, 3H), 6.98 (t, J = 7.4 Hz, 1H), 6.84 (s, 1H), 6.81 (d, J = 4.3 Hz, 2H), 6.05 (s, 1H), 4.27 (s, 2H), 3.85 (s, 2H), 3.73 (s, 3H), 3.69 (s, 3H), 2.40 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 158.74, 143.67, 136.57, 135.06, 130.66, 130.36, 129.77, 127.93, 127.39, 127.13, 127.06, 121.11, 118.71, 118.44, 114.90, 113.48, 110.21, 109.53, 55.00, 52.76, 37.97, 32.24, 21.03. HRMS (ESI) calcd for C₂₇H₂₆FN₂NaO₂S [M+Na]⁺ 609.0685; found, 609.0683.

(Z)-N-(4-fluorobenzyl)-N-(2-iodo-3-(1-methyl-1H-indol-3-yl)prop-1-en-1-yl)-4-methylbenzenesulfonamide (4l)

White solid; yield, 81%; m p 134.7-135.7 °C; IR (neat) 3035, 2934, 2864, 1501, 1459, 758, 700 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 7.67 (d, J = 8.2 Hz, 2H), 7.43 – 7.35 (m, 3H), 7.34 – 7.26 (m, 3H), 7.17 – 7.06 (m, 3H), 6.98 (t, J = 7.4 Hz, 1H), 6.88 (s, 1H), 6.08 (s, 1H), 4.31 (s, 2H), 3.86 (s, 2H), 3.71 (s, 3H), 2.41 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 161.60 (d, J = 242.0 Hz), 143.80, 136.59, 134.89, 131.58, 131.12 (d, J = 8.3 Hz), 130.56, 129.82, 127.98, 127.41, 127.03, 121.13, 118.68, 118.44, 115.49, 114.89 (d, J = 21.3 Hz), 110.14, 109.57, 52.57, 38.00, 32.27, 21.04. HRMS (ESI) calcd for C₂₆H₁₄FN₂NaO₂S [M+Na]⁺ 597.0485; found, 597.0489.
(Z)-N-(2-iodo-3-(1-methyl-1H-indol-3-yl)prop-1-en-1-yl)-4-methyl-N-phenethylbenzenesulfonamide (4m)

White solid; yield, 81%; m p 118.8-119.6 °C; IR (neat) 3038, 2931, 2859, 1501, 1457, 756, 700 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 7.62 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 7.8 Hz, 1H), 7.41 (d, J = 8.2 Hz, 1H), 7.36 (d, J = 8.1 Hz, 2H), 7.26 (t, J = 7.2 Hz, 2H), 7.20 (d, J = 7.5 Hz, 1H), 7.18 (s, 1H), 7.15 (d, J = 7.8 Hz, 1H), 7.11 (d, J = 8.0 Hz, 2H), 7.04 (t, J = 7.4 Hz, 1H), 6.19 (s, 1H), 4.00 (s, 2H), 3.76 (s, 3H), 3.33 – 3.31 (m, 2H), 2.74 – 2.64 (m, 2H), 2.38 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 143.69, 138.06, 136.73, 134.80, 130.54, 129.80, 128.58, 128.41, 128.36, 127.30, 127.09, 126.40, 121.18, 118.76, 118.51, 115.53, 110.08, 109.71, 38.87, 38.08, 34.01, 32.35, 21.00. HRMS (ESI) calcd for C₂₇H₂₁N₂NaO₃S [M+Na]^+ 593.0736; found, 593.0729.

(Z)-N-butyl-N-(2-iodo-3-(1-methyl-1H-indol-3-yl)prop-1-en-1-yl)-4-methylbenzenesulfonamide (4n)

White solid; yield, 86%; m p 91.8-92.3 °C; IR (neat) 3038, 2937, 2859, 1496, 1457, 764, 700 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 7.60 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 7.8 Hz, 1H), 7.40 (d, J = 8.2 Hz, 1H), 7.36 (d, J = 8.1 Hz, 2H), 7.19 – 7.13 (m, 2H), 7.04 (t, J = 7.4 Hz, 1H), 6.00 (s, 1H), 3.99 (s, 2H), 3.74 (s, 3H), 3.06 (t, J = 6.9 Hz, 2H), 2.38 (s, 3H), 1.36 – 1.24 (m, 7.3 Hz, 4H), 0.79 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, DMSO) δ 143.55, 136.71, 134.76, 130.78, 129.71, 128.26, 127.29, 127.09, 121.18, 118.74, 118.45, 115.54, 110.17, 109.67, 49.42, 38.14, 32.33, 29.53, 20.99, 19.57, 13.49. HRMS (ESI) calcd for C₃₂H₂₇N₂NaO₃S [M+Na]^+ 545.0736; found, 545.0728.

(Z)-N-(3,5-dimethoxyphenyl)-N-(2-iodo-3-(1-methyl-1H-indol-3-yl)prop-1-en-1-yl)acetamide (4o)

Colorless oil liquid; yield, 82%; IR (neat) 3038, 2934, 2858, 1499, 1457, 758, 700 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 7.59 (d, J = 7.8 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.20 (d, J = 6.9 Hz, 2H), 7.14 (t, J = 7.6 Hz, 1H), 6.99 (t, J = 7.4 Hz, 1H), 6.51 (d, J = 1.7 Hz, 2H), 6.39 (s, 1H), 4.02 (s, 2H), 3.74 (s, 3H), 3.65 (s, 6H), 2.03 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 160.19, 145.52, 136.75, 133.87, 133.60, 133.58, 128.40, 127.17, 121.14, 118.79, 118.51, 117.06, 109.70, 109.55, 106.59, 55.21, 41.33, 32.34, 26.45, 24.31. HRMS (ESI) calcd for C₂₉H₂₇N₂NaO₃S [M+Na]^+ 513.0651; found, 513.0648.
(Z)-3-(2-iodo-3-(1-methyl-1H-indol-3-yl)prop-1-en-1-yl)oxazolidin-2-one (4p)

White solid; yield, 71%; m p 117.1-117.7°C; IR (neat) 3038, 2934, 2858, 1501, 1454, 761, 702 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 7.54 (d, J = 7.9 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.20 (s, 1H), 7.17 – 7.11 (m, 1H), 7.07 (s, 1H), 7.04 – 6.98 (m, 1H), 4.38 – 4.34 (m, 2H), 4.11 – 4.07 (m, 2H), 3.96 (s, 2H), 3.75 (s, 3H).

¹³C NMR (100 MHz, DMSO) δ 156.57, 136.74, 129.24, 128.29, 127.25, 121.08, 118.74, 118.53, 110.77, 109.65, 90.39, 63.11, 44.55, 39.39, 32.31. HRMS (ESI) calcd for C₁₅H₁₅IN₂NaO₂S [M+Na]⁺ 405.0076; found, 405.0070.

(Z)-N-(3-(1H-indol-3-yl)-2-iodoprop-1-en-1-yl)-4-methyl-N-phenylbenzenesulfonamide (7b)

White solid; yield, 57%; m p 41.9-42.8°C; IR (neat) 3040, 2934, 2863, 1498, 1456, 758, 699 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 10.92 (s, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.40 – 7.26 (m, 7H), 7.26 – 7.20 (m, 1H), 7.14 (s, 1H), 7.10 – 7.06 (m, 4H), 6.96 (t, J = 7.4 Hz, 1H), 4.00 (s, 2H), 2.37 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 144.16, 139.69, 136.28, 133.74, 131.71, 129.67, 128.76, 127.52, 127.43, 127.09, 126.80, 124.00, 121.04, 118.64, 118.37, 111.44, 110.93, 110.39, 38.00, 21.06. HRMS (ESI) calcd for C₂₄H₂₁IN₂NaO₂S [M+Na]⁺ 551.0266; found, 551.0261.

(Z)-N-(2-iodo-3-(6-methoxy-1H-indol-3-yl)prop-1-en-1-yl)-4-methyl-N-phenylbenzenesulfonamide (7c)

White solid; yield, 77%; m p 94.5-95.4°C; IR (neat) 3041, 2937, 2864, 1499, 1454, 758, 700 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 10.78 (s, 1H), 7.34 (d, J = 7.9 Hz, 2H), 7.31 – 7.20 (m, 6H), 7.11 (s, 1H), 7.10 – 7.03 (m, 3H), 7.01 (s, 1H), 6.73 (d, J = 8.8 Hz, 1H), 3.97 (s, 2H), 3.70 (s, 3H), 2.36 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 153.04, 144.16, 139.74, 133.63, 131.65, 131.41, 129.64, 128.77, 127.48, 127.38, 127.11, 124.70, 112.16, 111.39, 110.63, 110.31, 109.56, 100.22, 55.17, 38.14, 21.04. HRMS (ESI) calcd for C₂₅H₂₃IN₂NaO₃S [M+Na]⁺ 581.0372; found, 581.0372.
(Z)-N-(3-(5-fluoro-1H-indol-3-yl)-2-iodoprop-1-en-1-yl)-4-methyl-N-phenylbenzenesulfonamide (7d)
White solid; yield, 43%; m p 147.5-148.4°C; IR (neat) 3041, 2934, 2861, 1499, 1454, 756, 700 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 11.02 (s, 1H), 7.40 (d, J = 8.1 Hz, 2H), 7.34-7.27 (m, 6H), 7.24 (d, J = 7.1 Hz, 1H), 7.22 (s, 1H), 7.15 (s, 1H), 7.08 (d, J = 7.5 Hz, 2H), 6.91 (t, J = 9.2 Hz, 1H), 3.97 (s, 2H), 2.38 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 156.65 (d, J = 8.6 Hz), 127.11, 127.00, 126.14, 112.35 (d, J = 7.6 Hz, 2H), 6.77 (d, J = 7.1 Hz, 1H), 3.97 (s, 2H), 2.38 (s, 3H). HRMS (ESI) calcd for C₂₄H₂₅BrF₂N₂NaO₂S [M+Na]+ 569.0172; found, 569.0173.

(Z)-N-(3-(5-bromo-1H-indol-3-yl)-2-iodoprop-1-en-1-yl)-4-methyl-N-phenylbenzenesulfonamide (7e)
White solid; yield, 50%; m p 147.2-147.8°C; IR (neat) 3041, 2931, 2864, 1496, 1454, 758, 700 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 11.14 (s, 1H), 7.72 (s, 1H), 7.41 (d, J = 8.0 Hz, 2H), 7.36 – 7.26 (m, 5H), 7.24 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 11.3 Hz, 2H), 7.09 (d, J = 7.7 Hz, 2H), 3.99 (s, 2H), 2.38 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 144.15, 139.74, 135.00, 133.76, 131.95, 129.67, 128.75, 128.63, 127.49, 127.39, 127.09, 125.79, 123.49, 121.06, 113.44, 111.18, 110.79, 109.54, 37.62, 21.06. HRMS (ESI) calcd for C₂₄H₂₅Br₂N₂NaO₂S [M+Na]+ 628.9371; found, 628.9368.

(Z)-N-(2-iodo-3-(4-methyl-1H-indol-3-yl)prop-1-en-1-yl)-4-methyl-N-phenylbenzenesulfonamide (7f)
White solid; yield, 80%; m p 135-135.9°C; IR (neat) 3038, 2937, 2861, 1496, 1454, 756, 702 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 10.94 (s, 1H), 7.35 – 7.22 (m, 5H), 7.14 (d, J = 8.0 Hz, 2H), 7.09 (s, 1H), 7.03-6.99 (m, 3H), 6.94 (d, J = 7.6 Hz, 2H), 6.77 (d, J = 7.1 Hz, 1H), 6.37 (s, 1H), 4.07 (s, 2H), 2.54 (s, 3H), 2.32 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 144.08, 139.70, 136.77, 133.15, 131.97, 129.61, 129.55, 128.83, 127.36, 127.27, 125.23, 124.39, 121.33, 120.17, 111.96, 110.97, 109.56, 109.53, 40.16, 21.02, 19.39. HRMS (ESI) calcd for C₂₅H₂₂I₂N₂NaO₂S [M+Na]+ 565.0423; found, 565.0419.
(Z)-N-(2-iodo-3-(7-methyl-1H-indol-3-yl)prop-1-en-1-yl)-4-methyl-N-phenylbenzenesulfonamide (7g)

White solid; yield, 66%; mp 145.3-146°C; IR (neat) 3040, 2934, 2863, 1495, 1453, 755, 696 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 10.89 (s, 1H), 7.38 (d, J = 8.0 Hz, 2H), 7.32 – 7.21 (m, 5H), 7.12 (s, 1H), 7.07-7.05 (m, 3H), 6.87 (d, J = 4.2 Hz, 2H), 5.76 (s, 1H), 3.98 (s, 2H), 2.44 (s, 3H), 2.37 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 144.14, 139.72, 135.83, 133.78, 131.69, 129.64, 128.74, 127.53, 127.42, 127.08, 126.51, 123.71, 121.58, 120.49, 118.63, 116.27, 111.38, 110.52, 40.13, 21.05, 16.76. HRMS (ESI) calcd for C₂₃H₂₁N₂NaO₂S [M+Na]⁺ 656.0423; found, 656.0417.

(Z)-N-(2-iodo-3-(2-methyl-1H-indol-3-yl)prop-1-en-1-yl)-4-methyl-N-phenylbenzenesulfonamide (7h)

White solid; yield, 66%; mp 68-68.9°C; IR (neat) 3042, 2937, 2860, 1496, 1454, 756, 698 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 10.83 (s, 1H), 7.42 (d, J = 6.5 Hz, 2H), 7.39 (s, 1H), 7.32 (d, J = 8.2 Hz, 2H), 7.29 – 7.19 (m, 4H), 7.08 (s, 1H), 7.07 (d, J = 7.7 Hz, 2H), 7.00 (t, J = 7.5 Hz, 1H), 6.91 (t, J = 7.4 Hz, 1H), 3.97 (s, 2H), 2.37 (s, 3H), 2.32 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 144.13, 139.72, 135.11, 133.84, 133.16, 131.09, 129.65, 128.71, 128.02, 127.51, 127.42, 127.02, 120.07, 118.19, 117.79, 110.92, 110.37, 106.67, 36.58, 21.06, 11.52. HRMS (ESI) calcd for C₂₃H₂₃N₂NaO₂S [M+Na]⁺ 565.0423; found, 565.0422.

(Z)-N-(3-(1-benzyl-1H-indol-3-yl)-2-iodoprop-1-en-1-yl)-4-methyl-N-phenylbenzenesulfonamide (7i)

White solid; yield, 70%; mp 133.3-133.8°C; IR (neat) 3041, 2934, 2861, 1499, 1454, 758, 700 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 7.54 (d, J = 7.8 Hz, 1H), 7.41 (d, J = 8.2 Hz, 1H), 7.35 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 9.5 Hz, 2H), 7.28 – 7.20 (m, 7H), 7.13 (d, J = 6.2 Hz, 2H), 7.09 (d, J = 7.9 Hz, 1H), 7.07 (s, 1H), 7.05 (d, J = 8.6 Hz, 2H), 6.99 (t, J = 7.5 Hz, 1H), 5.38 (s, 2H), 4.02 (s, 2H), 2.35 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 144.12, 139.66, 138.29, 136.15, 135.66, 131.81, 129.62, 128.73, 128.43, 127.89, 127.47, 127.44, 127.22, 127.09, 126.77, 121.34, 119.05, 118.73, 111.02, 110.13, 109.81, 109.53, 48.86, 37.82, 21.03. HRMS (ESI) calcd for C₂₅H₂₃N₂NaO₂S [M+Na]⁺ 641.0736; found, 641.0733.
\[\text{(Z)-N-(2-iodo-3-(1H-pyrrol-2-yl)prop-1-en-1-yl)-4-methyl-N-phenylbenzenesulfonamide (7j)}\]

White solid; yield, 62%; m p 118.7-119.2 °C; IR (neat) 3038, 2934, 2858, 1496, 1454, 758, 702 cm\(^{-1}\); \(^1\)H NMR (400 MHz, DMSO) \(\delta \) 10.58 (s, 1H), 7.41 – 7.35 (m, 4H), 7.30 (d, \(J = 7.5\) Hz, 2H), 7.25 (d, \(J = 6.5\) Hz, 1H), 7.09 (d, \(J = 8.0\) Hz, 2H), 6.85 (s, 1H), 6.63 (s, 1H), 5.90 (s, 1H), 5.74 (s, 1H), 3.81 (s, 2H), 2.38 (s, 3H).

\(^{13}\)C NMR (100 MHz, DMSO) \(\delta \) 144.28, 139.66, 133.61, 132.10, 129.75, 128.79, 127.55, 127.49, 127.10, 117.06, 109.57, 107.50, 106.76, 106.46, 40.20, 21.07. HRMS (ESI) calcd for \(\text{C}_{20}\text{H}_{19}\text{IN}_{2}\text{NaO}_{2}\text{S} [\text{M+Na}]^{+} 501.0110\); found, 501.0109.

\[\text{(Z)-N-(2-iodo-3-(5-methylfuran-2-yl)prop-1-en-1-yl)-4-methyl-N-phenylbenzenesulfonamide (7k)}\]

White solid; yield, 67%; m p 80.6-81.5 °C; IR (neat) 3041, 2931, 2864, 1499, 1451, 756, 697 cm\(^{-1}\); \(^1\)H NMR (400 MHz, DMSO) \(\delta \) 7.45 (d, \(J = 8.2\) Hz, 2H), 7.37 (d, \(J = 8.1\) Hz, 2H), 7.33 (t, \(J = 7.8\) Hz, 1H), 7.25 (t, \(J = 6.9\) Hz, 1H), 7.09 (d, \(J = 7.1\) Hz, 2H), 7.08 (s, 1H), 5.97 (d, \(J = 4.2\) Hz, 2H), 3.89 (s, 2H), 2.38 (s, 3H), 2.19 (s, 3H). \(^{13}\)C NMR (100 MHz, DMSO) \(\delta \) 150.68, 149.74, 144.34, 139.48, 133.68, 133.33, 129.75, 128.81, 127.52, 127.39, 127.11, 108.27, 106.51, 102.88, 40.14, 21.04, 13.28. HRMS (ESI) calcd for \(\text{C}_{21}\text{H}_{20}\text{IN}_{3}\text{NaO}_{3} [\text{M+Na}]^{+} 516.0106\); found, 516.0102.

\[\text{N-(1-(1H-imidazol-1-yl)-2-iodoallyl)-4-methyl-N-phenylbenzenesulfonamide (7l)}\]

White solid; yield, 96%; m p 100.6-101.4 °C; IR (neat) 3041, 2934, 2804, 1499, 1454, 758, 700 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.48 (d, \(J = 8.0\) Hz, 2H), 7.38 (s, 1H), 7.34 (t, \(J = 7.5\) Hz, 1H), 7.25 - 7.20 (m, 4H), 6.97 (d, \(J = 8.7\) Hz, 2H), 6.78 (d, \(J = 7.6\) Hz, 2H), 6.75 (s, 1H), 6.68 (s, 1H), 6.25 (s, 1H), 2.42 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta \) 144.52, 137.25, 135.61, 134.17, 132.00, 131.93, 129.71, 129.60, 129.28, 129.11, 127.82, 119.01, 102.83, 76.33, 21.61. HRMS (ESI) calcd for \(\text{C}_{19}\text{H}_{18}\text{IN}_{4}\text{NaO}_{2} [\text{M+Na}]^{+} 502.0062\); found, 502.0047.
3. General procedure and spectral data of 5a and 6a

To a Schlenk tube were added allenamide 1a (0.3 mmol) N-iodosuccinimide (1.05 equiv.) and CH$_3$CN (anhydrous, 5 mL). Then the reaction mixture was stirred at r t for 2 minutes until complete consumption of starting material as monitored by TLC. Concentration of the reaction mixture in vacuo followed by purification through flash chromatography on silica gel column (hexane/EtOAc = 15/1 as the eluent) afforded 6a (6 mg, 6% yield) as a white solid, (hexane/EtOAc = 7/1 as the eluent) afforded 4-methyl-N-phenylbenzenesulfonamide (27 mg, 36% yield) as a white solid, (hexane/EtOAc = 5/1 as the eluent) afforded 5a (30 mg, 31% yield) as a white solid.

\[
\begin{align*}
\text{Ts} & \quad N \quad Ts \quad (Z)\text{-}N,N'\text{-}(2\text{-iodoprop-1-ene-1,3-diy})\text{bis}(4\text{-methyl-}N\text{-phenylbenzenesulfonamide}) \ (5a) \\
\text{Ts} & \quad N \quad Ts \quad (N,N'\text{-}(2\text{-iodoprop-2-ene-1,1-diy})\text{bis}(4\text{-methyl-}N\text{-phenylbenzenesulfonamide}) \ (6a)
\end{align*}
\]

White solid; yield, 31%; m p 140.4-141.3 °C: IR (neat) 3041, 2934, 2861, 1499, 1457, 761, 702 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 (d, $J$ = 8.1 Hz, 2H), 7.28 – 7.25 (m, 7H), 7.20 (t, $J$ = 8.3 Hz, 3H), 7.14 (t, $J$ = 7.6 Hz, 2H), 7.01 – 6.97 (m, 3H), 6.59 (d, $J$ = 7.9 Hz, 2H), 4.50 (s, 2H), 2.44 (s, 3H), 2.42 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.25, 143.75, 137.98, 137.96, 135.66, 135.09, 134.23, 129.49, 129.46, 129.25, 128.90, 128.60, 128.01, 127.71, 127.57, 127.46, 109.96, 90.22, 60.64, 21.60, 21.57. HRMS (ESI) calcd for C$_{29}$H$_{27}$IN$_2$NaO$_4$S$_2$ [M+Na]$^+$ 681.0355; found, 681.0337.

White solid; yield, 6%; m p 167.1-167.9 °C: IR (neat) 3040, 2934, 2863, 1498, 1450, 758, 699, 545 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 (d, $J$ = 7.9 Hz, 4H), 7.29 (d, $J$ = 7.3 Hz, 2H), 7.24 (d, $J$ = 8.1 Hz, 4H), 7.13 (t, $J$ = 7.6 Hz, 4H), 7.07 (s, 1H), 6.68 (d, $J$ = 8.1 Hz, 4H), 6.52 (s, 1H), 5.93 (s, 1H), 2.42 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.01, 134.70, 134.89, 133.90, 131.49, 129.15, 128.64, 128.46, 110.01, 107.98, 81.40, 21.63. HRMS (ESI) calcd for C$_{29}$H$_{27}$IN$_2$NaO$_4$S$_2$ [M+Na]$^+$ 681.0355; found, 681.0332.
4. General procedure and spectral data of $9^4$

A mixture of $4a$ (110 mg, 0.2 mmol), $\text{Pd(PPh}_3\text{)}_4$ (24 mg, 10 mmol%), $\text{Cs}_2\text{CO}_3$ (131 mg, 2 equiv.), and phenylboronic acid (30 mg, 1.2 equiv.) in acetonitrile–toluene (3 : 3 mL) in a flask under an argon atmosphere was stirred for 5 h at 110 °C. The reaction was monitored by TLC analysis. After the reaction was complete, the mixture was poured into ethyl acetate, filtered, evaporated under vacuum and purified through flash chromatography on silica gel column (hexane/EtOAc = 10/1 as the eluent) afforded $9$ (81.8 mg, 83% yield) as a white solid.

![Chemical structure](image)

(Z)-4-methyl-N-(3-(1-methyl-1H-indol-3-yl)-2-phenylprop-1-en-1-yl)-N-phenylbenzenesulfonamide ($9$)

Yellow solid; yield, 83%; m p 122.5-124.0 °C; IR (neat) 3038, 2934, 2861, 1499, 1459, 758, 705, 542 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO) δ 7.58 (d, $J$ = 7.8 Hz, 1H), 7.37 – 7.27 (m, 5H), 7.15 (t, $J$ = 7.5 Hz, 1H), 7.12 – 6.97 (m, 9H), 6.96 (s, 1H), 6.74 – 6.67 (m, 2H), 6.70 (d, $J$ = 6.2 Hz, 1H), 3.78 (s, 2H), 3.67 (s, 3H), 2.37 (s, 3H). $^{13}$C NMR (100 MHz, DMSO) δ 143.83, 140.59, 138.13, 137.63, 136.74, 133.79, 129.58, 128.26, 127.90, 127.46, 127.40, 127.36, 126.92, 126.88, 126.55, 124.62, 121.05, 118.99, 118.37, 110.27, 109.54, 32.22, 31.56, 21.02. HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{28}\text{N}_2\text{NaO}_2\text{S}$ [M+Na]$^+$ 515.1769; found, 515.1780.

5. References

6. NMR Spectra for 4a – 4p
S19
4n
7. NMR Spectra for 5a and 6a
8. NMR Spectra for 7b – 7l
9. NMR Spectra for 9