Rhodium(III)-catalyzed sulfonamide directed ortho C–H carbenoid functionalization via metal carbene migratory insertion

Yi Dong, a,b Jiajing Chen a,b and Heng Xu* a,b

a State Key Laboratory of Bioactive Substance and Function of Natural Medicines, Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing 100050, China.

b Beijing Key Laboratory of Active Substances Discovery and Druggability Evaluation, Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing 100050, China.
Table of content

General methods.......................................................................................................................................................S1
Synthetic procedure, ^1^H NMR, ^13^C NMR and MS data of substrates.................................................................S1
Synthetic procedure ^1^H NMR, ^13^C NMR and HRMS data of products...............................................................S12
Copies of NMR spectra of products......................................................................................................................S27
Copies of ^1^H NMR of 1g and [D]-1g...................................................................................................................S80
Analysis for ratio of 47/47' and 48/48'..................................................................................................................S81
General methods

Dried solvent, such as DCE, MeOH and toluene were purchased from domestic corporations and used without purification. Analytical thin layer chromatography (TLC) plates, preparative TLC and the silica gel for column chromatography were phased from Qingdao Haiyang Chemical and Special Silica Gel Co, Ltd.

High-resolution LC-MS was carried out by Agilent LC/MSD TOF using a column of Agilent ZORBAX SB-C18 (rapid resolution, 3.5 μm, 2.1 × 30 mm) at a flow of 0.40 mL/min. The solvent was MeOH/water (75:25 (v/v)), containing 5 mmol/L ammonium formate. The ion source is electrospray ionization (ESI).

Proton nuclear magnetic resonance (\(^1\)H NMR) and carbon nuclear magnetic resonance (\(^{13}\)C NMR) spectroscopy were performed on Bruker Advance 400M NMR and 600M NMR spectrometers. Chemical shifts of \(^1\)H NMR spectra are reported as in units of parts per million (ppm) downfield from SiMe4 (δ 0.0) and relative to the signal of chloroform-d (δ = 7.260, singlet) and DMSO-d6 (δ = 2.500, quintet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); m (multiplets), etc. The number of protons (n) for a given resonance is indicated by nH. Carbon nuclear magnetic resonance spectra (\(^{13}\)C NMR) are reported as in units of parts per million (ppm) downfield from SiMe4 (δ 0.0) and relative to the signal of chloroform-d (δ = 77.230, triplet) and DMSO-d6 (δ = 39.510, septet).

Acetylation of sulfonamide derivatives:

General procedure for synthesis of sulfonamide derivatives:

Method A:

\[
\begin{align*}
\text{Sulfonamide (5 mmol)} & \quad \text{Acid anhydride} \\
& \quad \text{ZnCl}_2 \\
\text{pyrimidine} & \quad \text{Method A} \\
\end{align*}
\]

Method B:

\[
\begin{align*}
\text{Sulfonamide (5 mmol)} & \quad \text{Acid anhydride} \\
& \quad \text{pyrimidine} \\
\end{align*}
\]

Method C:

\[
\begin{align*}
\text{Sulfonamide (5 mmol)} & \quad \text{Acid anhydride} \\
& \quad \text{pyrimidine} \\
\end{align*}
\]

Method D:

\[
\begin{align*}
\text{Sulfonamide (5 mmol)} & \quad \text{Acid anhydride} \\
& \quad \text{pyrimidine} \\
\end{align*}
\]

S1. General procedure for synthesis of sulfonamide derivatives and diazo compounds

Method A:

Sulfonamide (5 mmol) was dissolved in 5 mL acid anhydride, 0.1eq~1eq anhydrous ZnCl₂ was added, the reaction mixture was stirred at room temperature and monitored by TLC until the free sulfonamide was consumed completely, then poured into a mixture of EtOAc and water (100mL, v/v =
1:1). The organic layer was separated and the aqueous phase was extracted by EtOAc (50 mL). The organic layers were combined and washed with saturated NaCl solution, dried over anhydrous Na₂SO₄, concentrated in vacuo to afford solid powder and washed with cold toluene to give the acetyl or propionyl sulfonamide without further purification, the purity was detected by ¹H NMR.

Method B:
Sulfonamide (5 mmol) and DMAP (61 mg, 0.5 mmol) were dissolved in 5 mL pyridine, then Ac₂O (4.7 mL, 50 mmol, 10 equiv) was added. The reaction mixture was stirred at room temperature overnight, and concentrated. The residue was dissolved in EtOAc (50 mL) and washed with saturated NH₄Cl (50 mL). The organic layer was dried over Na₂SO₄, concentrated again in vacuo, the residue was purified by silica gel chromatography.

Method C:
Amine (5 mmol) was dissolved in 20 mL DCM, the mixture was cooled to 0°C, then sulfonyl chloride (5 mmol) was added. The reaction mixture was warmed to room temperature and stirred overnight, and concentrated. The residue was dissolved in EtOAc (50 mL) and washed with saturated NH₄Cl (50 mL). The organic layer was dried over Na₂SO₄, concentrated again in vacuo, the residue was purified by silica gel chromatography.

Method D:
1,3-dicarbonyl compound (50 mmol) and tosyl azide (55 mmol) were dissolved in acetonitrile (100 mL), the mixture was cooled to 0°C. DBU (55 mmol) was added dropwise, and the reaction mixture was stirred for 3h. Solvent was removed and the residue was dissolved in DCM, washed with water, the aqueous layer was extracted by DCM, and the organic layers were combined and washed with brine, and dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by silica gel chromatography.

N-methoxy-3-methylbenzenesulfonamide (1c)

Method C, (94%, white powder), Rf = 0.4 (EtOAc/Petroleum ether = 1:1). m.p.: 79 – 80°C. ¹H NMR (400 MHz, DMSO-d6) δ 10.48 (s, 1H), 7.68 – 7.63 (m, 2H), 7.54 – 7.50 (m, 2H), 3.65 (s, 3H), 2.40 (s, 3H). ¹³C NMR (101 MHz, DMSO-d6) δ 138.8, 137.2, 134.1, 129.0, 128.1, 125.2, 64.3, 20.8. MS (ESI): m/z (M + H⁺) 202.2.

N-(tert-butyl)-3-methylbenzenesulfonamide (1d)

Method C, (92%, white powder), Rf = 0.4 (EtOAc/Petroleum ether = 1:1). m.p.: 82 – 83°C. ¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.60 (m, 2H), 7.47 – 7.36 (m, 2H), 2.37 (s, 3H), 1.08 (s, 9H). ¹³C NMR (101 MHz, DMSO-d6) δ 144.2, 138.5, 132.4, 128.8, 126.4, 123.4, 53.2, 29.7, 20.9. MS (ESI): m/z (M + H⁺) 228.2.
**N-(m-tolylsulfonyl)acetamide (1e)**

Method A, (95%, white powder), \( R_t = 0.4 \) (EtOAc/Petroleum ether = 1:1). m.p.: 95 – 96°C. 

\(^1\)H NMR (400 MHz, DMSO-d6) \( \delta \) 12.04 (s, 1H), 7.73 – 7.67 (m, 2H), 7.53 – 7.49 (m, 2H), 2.40 (s, 3H), 1.92 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-d6) \( \delta \) 168.7, 139.4, 138.8, 134.2, 129.0, 127.5, 124.6, 23.2, 20.8. MS (ESI): m/z (M + H\(^+\)) 214.2.

**tert-butyl (m-tolylsulfonyl)carbamate (1f)**

Method B, (70%, white powder), \( R_t = 0.4 \) (EtOAc/Petroleum ether = 1:1). m.p.: 105 – 107°C. 

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 11.56 (s, 1H), 7.71 – 7.65 (m, 2H), 7.54 – 7.50 (m, 2H), 2.40 (s, 3H), 1.28 (s, 9H). \(^{13}\)C NMR (101 MHz, DMSO-d6) \( \delta \) 149.8, 139.6, 138.7, 134.0, 129.0, 127.3, 124.4, 82.1, 27.5, 20.8. MS (ESI): m/z (M + H\(^+\)) 272.2.

**N-((3-phenethylphenyl)sulfonyl)acetamide (1g)**

\( \text{NiCl}_2 \cdot 6\text{H}_2\text{O} \) (7.75 mmol, 1.84 g) and \( \text{NaBH}_4 \) (19.36 mmol, 732 mg) were dissolved in a mixture of 15 mL dry THF and 10 mL MeOH, and the reaction mixture was stirred at room temperature overnight. 50 mL H\(_2\)O was added and the mixture was extracted by ethyl acetate. Organic layer was washed by sat. NaCl solution and dried over anhydrous Na\(_2\)SO\(_4\). Solvent was removed, and the residue was purified by silica gel chromatography (50% yield, white powder, \( R_t = 0.4 \) (EtOAc/Petroleum ether = 1:2). m.p.: 77–78°C. 

\(^1\)H NMR (400 MHz, DMSO-d6) \( \delta \) 12.01 (s, 1H), 7.76 – 7.71 (m, 2H), 7.58 – 7.49 (m, 2H), 7.30 – 7.15 (m, 5H), 3.02 – 2.95 (m, 2H), 2.93 – 2.87 (m, 2H), 1.92 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-d6) \( \delta \) 168.69, 142.69, 140.92, 139.33, 133.73, 128.99, 128.41, 128.23, 127.00, 125.94, 125.08, 36.61, 36.55, 23.24. MS (ESI): m/z (M + H\(^+\)) 304.2.

**N-((3-(furan-2-yl)phenyl)sulfonyl)acetamide (1i)**

Method B, (90%, white powder), \( R_t = 0.4 \) (EtOAc/Petroleum ether = 1:1). m.p.: 118 – 119°C. 

\(^1\)H NMR (400 MHz, DMSO-d6) \( \delta \) 12.17 (s, 1H), 8.18 (s, 1H), 8.02 (d, \( J = 7.6 \) Hz, 1H), 7.83 (s, 2H), 7.67 (t, \( J = 7.8 \) Hz, 1H), 7.11 (s, 1H), 6.64 (s, 1H), 1.95 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-d6) \( \delta \) 168.9, 141.0, 140.2, 138.5, 131.9, 129.9, 129.2, 128.4, 126.9, 126.3, 125.6, 23.3. MS (ESI): m/z (M + H\(^+\)) 266.2.
Method B, (85%, white powder), Rf = 0.4 (EtOAc/Petroleum ether = 1:1). m.p.: 126 – 127°C. 1H NMR (400 MHz, DMSO-d6) δ 12.13 (s, 1H), 8.15 (t, J = 1.7 Hz, 1H), 8.07 – 8.02 (m, 1H), 8.00 (dd, J = 2.9, 1.4 Hz, 1H), 7.85 – 7.82 (m, 1H), 7.72 – 7.65 (m, 2H), 7.57 (dd, J = 5.0, 1.4 Hz, 1H), 1.95 (s, 3H). 13C NMR (101 MHz, DMSO-d6) δ 169.0, 140.2, 139.6, 129.9, 127.9, 126.0, 125.9, 124.7, 122.8, 23.3. MS (ESI): m/z (M + H+) 282.1.

**[(E)-N-((3-styrylphenyl)sulfonyl)acetamide (1k)]**

Method A, (82%, white powder), Rf = 0.4 (EtOAc/Petroleum ether = 1:1). m.p.: 158 – 160°C. 1H NMR (400 MHz, DMSO-d6) δ 12.13 (s, 1H), 8.08 (d, J = 1.8 Hz, 1H), 7.97 (d, J = 9.1 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.74 – 7.59 (m, 3H), 7.46 – 7.25 (m, 5H), 1.95 (s, 3H). 13C NMR (101 MHz, DMSO-d6) δ 168.8, 140.0, 138.1, 136.5, 130.8, 130.7, 129.6, 128.7, 128.2, 126.8, 126.7, 125.3, 23.3. MS (ESI): m/z (M + H+) 302.2.

**Methyl 3-[N-acetylsulfamoyl]benzoate (1l)**

Method A, (85%, white powder), Rf = 0.3 (EtOAc/Petroleum ether = 1:1). m.p.: 122 – 123°C. 1H NMR (400 MHz, DMSO-d6) δ 7.76 (s, 1H), 7.41 (dd, J = 17.0, 7.9 Hz, 2H), 6.88 (t, J = 7.8 Hz, 1H), 3.12 (s, 3H), 1.16 (s, 3H). 13C NMR (101 MHz, DMSO-d6) δ 161.4, 157.2, 131.9, 125.8, 123.8, 122.7, 121.0, 120.5, 43.6, 13.8. MS (ESI): m/z (M + H+) 258.1.

**N-((3-acetylphenyl)sulfonyl)acetamide (1m)**

Method A, (88%, white powder), Rf = 0.3 (EtOAc/Petroleum ether = 2:1). m.p.: 146 – 147°C. 1H NMR (400 MHz, DMSO-d6) δ 12.23 (s, 1H), 8.37 (s, 1H), 8.29 (d, J = 7.8 Hz, 1H), 8.15 (d, J = 9.1 Hz, 1H), 8.00 (dd, J = 2.9, 1.4 Hz, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.63 (t, J = 8.1 Hz, 1H), 1.94 (s, 3H), 2.04 (s, 3H). 13C NMR (101 MHz, DMSO-d6) δ 196.7, 169.0, 140.1, 137.2, 133.4, 131.6, 129.9, 126.5, 26.8, 126.7, 125.3, 23.3. MS (ESI): m/z (M + H+) 242.2.

**N-((3-((trimethylsilyl)ethynyl)phenyl)sulfonyl)acetamide (1n)**

Method A, (92%, white powder), Rf = 0.5 (EtOAc/Petroleum ether = 1:1). m.p.: 136 – 137°C. 1H NMR (400 MHz, DMSO-d6) δ 12.18 (s, 1H), 7.94 – 7.90 (m, 2H), 7.76 (d, J = 7.8 Hz, 1H), 7.63 (t, J = 8.1 Hz, 1H), 1.94 (s, 3H), 2.04 (s, 3H). 13C NMR (101 MHz, DMSO-d6) δ 168.9, 139.8, 136.2, 130.4, 129.8, 127.7, 123.0, 103.0, 96.6, 23.2, -0.3. MS (ESI): m/z (M + H+) 296.2.

**N-(o-tolylsulfonyl)acetamide (1o)**

Method A, (94%, white powder), Rf = 0.5 (EtOAc/Petroleum ether = 1:1). m.p.: 124 – 125°C. 1H NMR (400 MHz, DMSO-d6) δ 12.18 (s, 1H), 7.94 (dd, J = 7.5, 1.4 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.42 (t, J = 7.6 Hz, 2H), 2.62 – 2.54 (m, 3H), 1.97 – 1.92 (m, 3H).
\(^{13}\text{C} \text{NMR}\) (101 MHz, DMSO-\(d_6\)) \(\delta\) 168.6, 137.4, 136.9, 133.5, 132.4, 130.2, 126.2, 23.1, 19.5. \text{MS} (ESI): m/z (M + H\(^+\)) 214.2.

\(N\)-(2-(benzyloxy)phenyl)sulfonyl)acetamide (1p)

\begin{align*}
\text{Method A, (92\%, white powder), } R_f &= 0.4 \text{ (EtOAc/Petroleum ether = 1:1). m.p.: 140 – 141\°C.} \\
\text{\(1^H \text{NMR}\) (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.15 (d, \(J = 7.9 \text{ Hz}, 1H\)), 6.74 – 6.64 (m, 3H), 6.58 – 6.46 (m, 3H), 6.34 (d, \(J = 8.4 \text{ Hz}, 1H\)), 6.24 (t, \(J = 7.6 \text{ Hz}, 1H\)), 4.52 (s, 2H), 1.12 (s, 3H).
\end{align*}

\(13\text{C} \text{NMR}\) (101 MHz, DMSO-\(d_6\)) \(\delta\) 161.6, 147.8, 128.8, 127.1, 123.2, 120.2, 119.6, 119.0, 118.6, 111.8, 105.6, 61.9, 13.8.

\text{MS} (ESI): m/z (M + H\(^+\)) 306.2.

\(N\)-(1,1'-biphenyl)-2-ysulfonyl)acetamide (1q)

\begin{align*}
\text{Method A, (91\%, white powder), } R_f &= 0.5 \text{ (EtOAc/Petroleum ether = 1:1). m.p.: 180 – 182\°C.} \\
\text{\(1^H \text{NMR}\) (400 MHz, DMSO-\(d_6\)) \(\delta\) 11.50 (s, 1H), 8.08 (d, \(J = 8.0 \text{ Hz}, 1H\)), 7.71 (t, \(J = 7.4 \text{ Hz}, 1H\)), 7.62 (t, \(J = 7.7 \text{ Hz}, 1H\)), 7.46 – 7.41 (m, 3H), 7.38 – 7.32 (m, 3H), 1.72 (s, 3H).
\end{align*}

\(13\text{C} \text{NMR}\) (101 MHz, DMSO-\(d_6\)) \(\delta\) 168.5, 140.5, 138.7, 137.4, 133.0, 132.5, 129.6, 128.9, 127.9, 127.8, 23.0. \text{MS} (ESI): m/z (M + H\(^+\)) 276.2.

\(N\)-(2-(2-methoxyethoxy)phenyl)sulfonyl)acetamide(1r)

\begin{align*}
\text{Method A, (95\%, white powder), } R_f &= 0.3 \text{ (EtOAc/Petroleum ether = 2:1). m.p.: 95 – 96\°C.} \\
\text{\(1^H \text{NMR}\) (400 MHz, DMSO-\(d_6\)) \(\delta\) 11.77 (s, 1H), 7.82 (dd, \(J = 7.9, 1.7 \text{ Hz}, 1H\)), 7.65 – 7.59 (m, 1H), 7.26 (d, \(J = 8.5 \text{ Hz}, 1H\)), 7.13 – 7.07 (m, 1H), 4.32 – 4.25 (m, 2H), 3.78 – 3.70 (m, 2H), 3.31 (s, 3H), 1.93 (s, 3H).
\end{align*}

\(13\text{C} \text{NMR}\) (101 MHz, DMSO-\(d_6\)) \(\delta\) 168.8, 155.8, 135.5, 130.8, 126.9, 120.2, 114.0, 70.1, 68.3, 58.2, 23.1. \text{MS} (ESI): m/z (M + H\(^+\)) 274.2.

\(N\)-(2-(trifluoromethoxy)phenyl)sulfonyl)acetamide (1s)

\begin{align*}
\text{Method A, (91\%, white powder), } R_f &= 0.5 \text{ (EtOAc/Petroleum ether = 1:1). m.p.: 166 – 168\°C.} \\
\text{\(1^H \text{NMR}\) (400 MHz, DMSO-\(d_6\)) \(\delta\) 12.49 (s, 1H), 8.06 (dd, \(J = 8.1, 1.7 \text{ Hz}, 1H\)), 7.88 – 7.81 (m, 1H), 7.65 – 7.58 (m, 2H), 1.95 (s, 3H).
\end{align*}

\(13\text{C} \text{NMR}\) (101 MHz, DMSO-\(d_6\)) \(\delta\) 169.0, 145.2, 136.1, 132.3, 131.2, 127.4, 120.9, 120.0 (q, \(J = 260.6 \text{ Hz}\)), 23.0. \text{MS} (ESI): m/z (M + H\(^+\)) 284.1.

Methyl 2-((N-acetysulfamoyl)benzoate (1t)

\begin{align*}
\text{Method A, (75\%, white powder), } R_f &= 0.4 \text{ (EtOAc/Petroleum ether = 1:1). m.p.: 146 – 147\°C.} \\
\text{\(1^H \text{NMR}\) (400 MHz, DMSO-\(d_6\)) \(\delta\) 12.10 (s, 1H), 8.11 – 8.06 (m, 1H), 7.77 (pd, \(J = 7.5, 1.6 \text{ Hz}, 2H\)), 7.70 – 7.66 (m, 1H), 3.87 (s, 3H), 1.96 (s, 3H).
\end{align*}

\(13\text{C} \text{NMR}\) (101 MHz, DMSO-\(d_6\)) \(\delta\) 168.8, 167.0, 136.4, 133.7, 132.1, 130.75, 130.74, 129.0, 53.2, 23.2. \text{MS} (ESI): m/z (M + H\(^+\)) 258.2.

\(N\)-(2-nitrophenyl)sulfonyl)acetamide (1u)
Method A, (75%, white powder), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:1). m.p.: 166 – 167°C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 12.62 (d, $J = 38.3$ Hz, 1H), 8.15 (dd, $J = 7.5$, 1.7 Hz, 1H), 8.00 (dd, $J = 7.7$, 1.5 Hz, 1H), 7.94 – 7.84 (m, 2H), 1.97 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 169.1, 147.6, 135.5, 132.4, 132.2, 130.7, 124.6, 23.1. MS (ESI): m/z (M + H$^+$) 215.2.

$N$-((2,4-dimethylphenyl)sulfonyl)acetamide (1v)

Method A, (95%, white powder), $R_f = 0.3$ (EtOAc/Petroleum ether = 1:1). m.p.: 137 – 138°C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 12.07 (s, 1H), 7.88 – 7.79 (m, 1H), 7.25 – 7.18 (m, 2H), 2.53 (s, 3H), 2.34 (s, 3H), 1.92 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 168.5, 143.9, 136.7, 134.5, 132.8, 130.4, 126.6, 23.1, 20.8, 19.4. MS (ESI): m/z (M + H$^+$) 228.2.

Methyl 5-($N$-acetylsulfamoyl)-2-methoxybenzoate (1w)

Method A, (77%, white powder), $R_f = 0.3$ (EtOAc/Petroleum ether = 2:1). m.p.: 169 – 171°C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 12.06 (s, 1H), 8.16 (d, $J = 2.5$ Hz, 1H), 8.05 (dd, $J = 8.9$, 2.5 Hz, 1H), 7.38 (d, $J = 9.0$ Hz, 1H), 3.93 (s, 3H), 3.83 (s, 3H), 1.91 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 168.9, 164.7, 161.8, 133.4, 130.8, 130.4, 119.8, 113.2, 56.6, 52.4, 23.2. MS (ESI): m/z (M + H$^+$) 288.2.

$N$-((2-methoxy-4-methylphenyl)sulfonyl)acetamide (1x)

Method A, (95%, white powder), $R_f = 0.4$ (EtOAc/Petroleum ether = 2:1). m.p.: 202 – 204°C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 11.87 (s, 1H), 7.68 (d, $J = 8.0$ Hz, 1H), 7.07 (s, 1H), 6.91 (d, $J = 8.0$ Hz, 1H), 3.89 (s, 3H), 2.37 (s, 3H), 1.90 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 168.7, 156.5, 146.4, 130.8, 123.8, 120.7, 113.6, 56.2, 23.1, 21.4. MS (ESI): m/z (M + H$^+$) 244.1.

$N$-((3,4-dimethoxyphenyl)sulfonyl)acetamide (1y)

Method A, (95%, white powder), $R_f = 0.3$ (EtOAc/Petroleum ether = 2:1). m.p.: 125 – 126°C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 11.89 (s, 1H), 7.51 (dd, $J = 8.5$, 2.1 Hz, 1H), 7.36 (d, $J = 2.0$ Hz, 1H), 7.16 (d, $J = 8.6$ Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 1.91 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 168.7, 152.9, 148.3, 130.8, 121.6, 111.1, 110.1, 55.9, 55.8, 23.2. MS (ESI): m/z (M + H$^+$) 260.2.

$N$-((4-bromo-3-methylphenyl)sulfonyl)acetamide (1z)

Method A, (87%, brown powder), $R_f = 0.5$ (EtOAc/Petroleum ether = 1:1). m.p.: 166 – 167°C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 12.14 (s, 1H), 7.86 – 7.83 (m, 2H), 7.63 (ddd, $J = 8.5$, 2.4, 0.6 Hz, 1H), 2.43 (s, 3H), 1.93 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$
168.9, 138.7, 132.9, 130.0, 129.4, 126.7, 23.3, 22.4. **MS (ESI): m/z (M + H\(^+\)) 292.1.**

**N-(2,5-dimethoxyphenyl)sulfonyl)acetamide (1aa)**

![Structure of 1aa]

Method A, (92%, white powder), \(R_f = 0.2\) (EtOAc/Petroleum ether = 1:1). m.p.: 164 – 165°C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 12.00 (s, 1H), 7.31 (s, 1H), 7.24 (d, \(J = 9.1\) Hz, 1H), 7.18 (d, \(J = 9.0\) Hz, 1H), 3.85 (s, 3H), 3.76 (s, 3H), 1.93 (s, 3H). 13C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 168.8, 152.2, 150.6, 127.2, 120.7, 115.5, 114.7, 56.7, 55.8, 23.1. **MS (ESI): m/z (M + H\(^+\)) 260.1.**

**N-(thiophen-2-ylsulfonyl)acetamide (1ab)**

![Structure of 1ab]

Method A, (85%, white powder), \(R_f = 0.3\) (EtOAc/Petroleum ether = 1:1). m.p.: 90 – 91°C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 12.24 (s, 1H), 8.02 (d, \(J = 4.9\) Hz, 1H), 7.78 (d, \(J = 3.2\) Hz, 1H), 7.19 (t, \(J = 4.2\) Hz, 1H), 1.95 (s, 3H). 13C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 168.8, 139.7, 134.6, 134.1, 127.5, 23.3.

**N-tosylacetamide (1ac)**

![Structure of 1ac]

Method A, (95%, white powder), \(R_f = 0.5\) (EtOAc/Petroleum ether = 1:1). m.p.: 133 – 135°C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 12.03 (s, 1H), 7.80 – 7.77 (m, 2H), 7.44 – 7.41 (m, 2H), 2.39 (s, 3H), 1.90 (s, 3H). 13C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 168.7, 144.2, 136.5, 129.5, 127.6, 23.2, 21.1. **MS (ESI): m/z (M + H\(^+\)) 214.2.**

**N-((4-methoxyphenyl)sulfonyl)acetamide (1ad)**

![Structure of 1ad]

Method A, (97%, white powder), \(R_f = 0.4\) (EtOAc/Petroleum ether = 2:1). m.p.: 142 – 143°C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 11.94 (s, 1H), 7.86 (d, \(J = 8.7\) Hz, 2H), 7.11 (d, \(J = 8.7\) Hz, 2H), 3.82 (s, 3H), 1.90 (s, 3H). 13C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 168.8, 163.2, 130.9, 130.0, 114.3, 55.8, 23.2. **MS (ESI): m/z (M + H\(^+\)) 230.2.**

**N-((4-chlorophenyl)sulfonyl)acetamide (1ae)**

![Structure of 1ae]

Method A, (88%, white powder), \(R_f = 0.5\) (EtOAc/Petroleum ether = 1:1). m.p.: 192 – 193°C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 12.21 (s, 1H), 7.94 – 7.89 (m, 2H), 7.74 – 7.69 (m, 2H), 1.93 (s, 3H). 13C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 169.0, 138.7, 138.1, 129.5, 129.3, 23.2. **MS (ESI): m/z (M + H\(^+\)) 234.1.**

**Methyl 4-(N-acetylsulfamoyl)benzoate (1af)**

![Structure of 1af]

Method A, (77%, white powder), \(R_f = 0.3\) (EtOAc/Petroleum ether = 1:1). m.p.: 193 – 195°C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 12.27 (s, 1H), 8.15 – 8.10 (m, 2H), 8.03 – 7.98 (m, 2H), 3.86 (s, 3H), 1.90 (s, 3H). 13C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 169.0, 165.0, 143.2, 133.9, 129.9, 128.0, 52.7, 23.2. **MS (ESI): m/z (M + H\(^+\)) 258.2.**

**N-((4-nitrophenyl)sulfonyl)acetamide (1ag)**

![Structure of 1ag]

Method A, (75%, white powder), \(R_f = 0.2\) (EtOAc/Petroleum ether = 1:1). m.p.: 196 – 198°C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 12.43 (s, 1H), 8.42 – 8.37 (m, 2H), 8.15 – 8.11
(m, 2H), 1.92 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) $\delta$ 169.1, 150.3, 144.5, 129.2, 124.5, 23.3. **MS** (ESI): m/z (M + H$^+$) 215.2.

**N-(quinolin-8-ylsulfonyl)acetamide (1ah)**

**Method B**, (77%, white powder), $R_f$ = 0.4 (EtOAc/Petroleum ether = 1:1). **m.p.**: 200 – 201°C. **$^1$H NMR** (400 MHz, DMSO-$d_6$) $\delta$ 12.30 (s, 1H), 9.09 (dd, $J$ = 4.2, 1.7 Hz, 1H), 8.56 (dd, $J$ = 8.4, 1.7 Hz, 1H), 8.46 (dd, $J$ = 7.4, 1.4 Hz, 1H), 8.35 (dd, $J$ = 8.2, 1.3 Hz, 1H), 7.83 – 7.78 (m, 1H), 7.72 (dd, $J$ = 8.3, 4.2 Hz, 1H), 1.88 (s, 3H).

**$^{13}$C NMR** (101 MHz, DMSO-$d_6$) $\delta$ 169.0, 151.5, 142.8, 137.1, 135.2, 134.7, 133.1, 128.4, 125.6, 122.6, 23.1. **MS** (ESI): m/z (M + H$^+$) 250.2.

**N-((2-(tert-butyl)benzo[d]oxazol-7-yl)sulfonyl)acetamide (1ai)**

**Method A**, (89%, gray powder), $R_f$ = 0.5 (EtOAc/Petroleum ether = 1:1). **m.p.**: 178 – 179°C. **$^1$H NMR** (400 MHz, DMSO-$d_6$) $\delta$ 12.64 (s, 1H), 8.06 (dd, $J$ = 8.0, 1.1 Hz, 1H), 7.82 (dd, $J$ = 7.9, 1.1 Hz, 1H), 7.54 (t, $J$ = 7.9 Hz, 1H), 1.95 (s, 3H), 1.47 (s, 9H).

**$^{13}$C NMR** (101 MHz, DMSO-$d_6$) $\delta$ 174.2, 169.0, 145.2, 142.3, 125.2, 124.9, 124.4, 122.9, 34.0, 27.9, 23.1. **MS** (ESI): m/z (M + H$^+$) 297.2.

**N-(benzo[c][1,2,5]thiadiazol-4-ylsulfonyl)acetamide (1aj)**

**Method B**, (85%, red powder), $R_f$ = 0.3 (EtOAc/Petroleum ether = 1:2). **m.p.**: 209–211°C. **$^1$H NMR** (400 MHz, DMSO-$d_6$) $\delta$ 12.38 (s, 1H), 8.39 (d, $J$ = 8.8 Hz, 1H), 8.33 (d, $J$ = 7.0 Hz, 1H), 7.88 (dd, $J$ = 8.5, 7.3 Hz, 1H), 1.88 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) $\delta$ 170.0, 154.9, 148.4, 132.5, 131.3, 128.7, 126.5, 123.6. **HRMS** (ESI): m/z (M + H$^+$) calcd for C$_8$H$_8$O$_3$N$_3$S$_2$, 258.0001, found: 258.0003.

**N-((5-(dimethylamino)naphthalen-1-yl)sulfonyl)acetamide (1ak)**

**Method B**, (87%, yellow powder), $R_f$ = 0.4 (EtOAc/Petroleum ether = 1:1). **m.p.**: 216 – 218°C. **$^1$H NMR** (400 MHz, DMSO-$d_6$) $\delta$ 12.38 (s, 1H), 8.52 (d, $J$ = 8.5 Hz, 1H), 8.29 (d, $J$ = 7.3 Hz, 1H), 8.21 (d, $J$ = 8.6 Hz, 1H), 7.65 (dt, $J$ = 16.1, 8.0 Hz, 2H), 7.25 (d, $J$ = 7.5 Hz, 1H), 2.82 (s, 6H), 1.89 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) $\delta$ 168.5, 151.6, 134.2, 130.9, 130.7, 128.8, 128.8, 128.4, 123.5, 117.9, 115.2, 45.0, 23.2. **MS** (ESI): m/z (M + H$^+$) 293.2.

**N-((2-(4-methoxypiperidin-1-yl)phenyl)sulfonyl)acetamide (1ah)**

**Method A**, (85%, yellow powder), $R_f$ = 0.4 (EtOAc/Petroleum ether = 1:1). **m.p.**: 125 – 127°C. **$^1$H NMR** (400 MHz, DMSO-$d_6$) $\delta$ 11.67 (s, 1H), 7.93 (d, $J$ = 7.9 Hz, 1H), 7.64 (t, $J$ = 7.6 Hz, 1H), 7.50 (d, $J$ = 7.9 Hz, 1H), 7.34 (t, $J$ = 7.6 Hz, 1H), 3.38 – 3.30 (m, 1H), 3.28 (s, 3H), 2.98 – 2.91 (m, 2H), 2.74 – 2.68 (m, 2H), 2.02 – 1.94 (m, 2H), 1.92 (s, 3H), 1.85 – 1.74 (m, 2H). **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) $\delta$ 168.3, 152.7, 135.4, 134.7, 131.1, 125.1, 124.6, 75.3, 54.9, 51.1, 30.3, 22.9. **MS** (ESI): m/z (M + H$^+$) 313.2.
**N-((3-[dimethylamino]phenyl)sulfonyl)acetamide (1ai)**

*Method B*, (83%, white powder), $R_f = 0.3$ (EtOAc/Petroleum ether = 1:1). m.p.: 112 – 113°C. $^1$H NMR (400 MHz, DMSO-d$_6$) δ 11.92 (s, 1H), 7.42 – 7.35 (m, 1H), 7.16 – 7.11 (m, 2H), 7.01 – 6.96 (m, 1H), 2.95 (s, 6H), 1.92 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-d$_6$) δ 168.64, 150.1, 140.2, 129.6, 116.6, 114.0, 109.7, 39.8, 23.3. MS (ESI): m/z (M + H$^+$) 243.2.

**N-((3-(2,5-dimethyl-1H-pyrrol-1-yl)phenyl)sulfonyl)acetamide (1aj)**

*Method B*, (88%, brown powder), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:1). m.p.: 193 – 194°C. $^1$H NMR (400 MHz, DMSO-d$_6$) δ 12.22 (s, 1H), 7.96 (d, $J_1 = 7.7$ Hz, 1H), 7.78 (t, $J_2 = 7.9$ Hz, 1H), 7.71 (s, 1H), 7.66 (d, $J_3 = 7.8$ Hz, 1H), 5.85 (s, 2H), 1.98 (s, 6H), 1.95 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-d$_6$) δ 167.0, 140.2, 138.6, 133.1, 130.4, 127.7, 127.0, 126.3, 106.7, 23.2, 12.7. MS (ESI): m/z (M + H$^+$) 293.2.

**N-((3-(quinolin-8-yl)phenyl)sulfonyl)acetamide (1ak)**

*Method B*, (82%, white powder), $R_f = 0.3$ (EtOAc/Petroleum ether = 1:1). m.p.: 173°C. $^1$H NMR (400 MHz, DMSO-d$_6$) δ 12.13 (s, 1H), 8.92 (d, $J_1 = 4.1$, 1.8 Hz, 1H), 8.48 (dd, $J_2 = 8.3$, 1.7 Hz, 1H), 8.21 (t, $J_3 = 1.7$ Hz, 1H), 8.08 (dd, $J_4 = 8.2$, 1.4 Hz, 1H), 8.03 – 8.00 (m, 1H), 7.97 (ddd, $J_5 = 7.9$, 1.7, 1.1 Hz, 1H), 7.84 (dd, $J_6 = 7.1$, 1.4 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.61 (dd, $J_7 = 8.3$, 4.1 Hz, 1H), 1.96 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-d$_6$) δ 168.9, 150.6, 144.8, 139.8, 139.0, 137.8, 136.6, 135.7, 130.3, 129.3, 128.8, 128.6, 128.4, 126.5, 126.1, 121.7, 23.3. HRMS (ESI): m/z (M + H$^+$) calcd for C$_{17}$H$_{15}$O$_3$N$_2$S, 327.0798, found: 327.0786.

**N-((3-methyl-4-(quinolin-8-yl)phenyl)sulfonyl)acetamide (1al)**

*Method B*, (80%, white powder), $R_f = 0.3$ (EtOAc/Petroleum ether = 1:1). m.p.: 215°C. $^1$H NMR (400 MHz, DMSO-d$_6$) δ 12.14 (s, 1H), 8.83 (d, $J_1 = 4.2$, 1.8 Hz, 1H), 8.46 (dd, $J_2 = 8.3$, 1.7 Hz, 1H), 8.07 (dt, $J_3 = 7.5$, 3.7 Hz, 1H), 7.84 (d, $J_4 = 1.4$ Hz, 1H), 7.61 (dd, $J_5 = 8.3$, 4.2 Hz, 1H), 7.45 (d, $J_6 = 8.0$ Hz, 1H), 2.73 (s, 3H), 1.96 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-d$_6$) δ 168.9, 150.6, 144.8, 139.8, 139.0, 137.8, 136.6, 135.7, 130.3, 129.3, 128.8, 128.6, 128.4, 126.5, 126.1, 121.7, 23.3. HRMS (ESI): m/z (M + H$^+$) calcd for C$_{18}$H$_{17}$O$_3$N$_2$S, 341.0954, found: 341.0945.

**E)-N-((3-methyl-4-(phenyldiazenyl)phenyl)sulfonyl)acetamide (1am)**

*Method B*, (85%, red powder), $R_f = 0.3$ (EtOAc/Petroleum ether = 1:2). m.p.: 137-138°C. $^1$H NMR (400 MHz, DMSO-d$_6$) δ 12.17 (s, 1H), 7.97 – 7.93 (m, 3H), 7.86 (dd, $J_1 = 8.5$, 1.8 Hz, 1H), 7.68 (d, $J_2 = 8.5$ Hz, 1H), 7.65 – 7.61 (m, 3H), 2.73 (s, 3H), 1.96 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-d$_6$) δ 168.9, 152.6, 152.2, 140.7, 137.9, 132.4, 130.4,
129.6, 126.2, 123.0, 116.2, 23.3, 17.1. HRMS (ESI): m/z (M + H\(^+\)) calcd for C\(_{15}\)H\(_{16}\)O\(_3\)N\(_3\)S, 318.0907, found: 318.0897

\(N\)-((4-acetamido-3-methylphenyl)sulfonyl)acetamide (1an)

**Method B.** (82%, light yellow powder), \(R_t = 0.5\) (EtOAc/Petroleum ether = 1:1). m.p.: 238-240°C. \(^1\)H NMR (400 MHz, DMSO-d6) \(\delta\) 11.98 (s, 1H), 9.46 (s, 1H), 7.82 (d, \(J = 8.5\) Hz, 1H), 7.73 – 7.67 (m, 2H), 2.30 (s, 3H), 2.12 (s, 3H), 1.91 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-d6) \(\delta\) 168.8, 168.7, 141.4, 134.4, 130.7, 129.4, 125.7, 123.6, 23.6, 23.2, 17.9. HRMS (ESI): m/z (M + H\(^+\)) calcd for C\(_{15}\)H\(_{16}\)O\(_3\)N\(_3\)S, 318.0747, found: 318.0737.

\(N\)-((4-(2,5-dimethyl-1H-pyrrol-1-yl)phenyl)sulfonyl)acetamide (1ao)

**Method B.** (81%, gray powder), \(R_t = 0.5\) (EtOAc/Petroleum ether = 1:1). m.p.: 204 – 206°C. \(^1\)H NMR (400 MHz, DMSO-d6) \(\delta\) 12.22 (s, 1H), 8.04 (d, \(J = 8.5\) Hz, 2H), 7.51 (t, \(J = 10.8\) Hz, 2H), 5.85 (s, 2H), 1.99 (s, 6H), 1.97 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-d6) \(\delta\) 169.0, 142.7, 138.1, 128.7, 128.5, 127.7, 107.0, 23.3, 12.9.

\(N\)-((2,3-dihydro-1H-inden-5-yl)sulfonyl)acetamide (1ap)

**Method A.** (95%, white powder), \(R_t = 0.4\) (EtOAc/Petroleum ether = 1:1). m.p.: 136 – 137°C. \(^1\)H NMR (400 MHz, DMSO-d6) \(\delta\) 11.97 (s, 1H), 7.73 (s, 1H), 7.68 (d, \(J = 7.9\) Hz, 1H), 7.44 (d, \(J = 7.9\) Hz, 1H), 2.93 (td, \(J = 7.3, 2.6\) Hz, 4H), 2.06 (p, \(J = 7.5\) Hz, 2H), 1.91 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-d6) \(\delta\) 168.6, 150.4, 144.9, 137.3, 125.9, 124.6, 123.2, 32.4, 32.1, 25.0, 23.2. MS (ESI): m/z (M + H\(^+\)) 293.2.

\(N\)-((4-(5-methyl-3-phenylisoxazol-4-yl)phenyl)sulfonyl)propionamide (1aq)

**Method A.** (89%, white powder), \(R_t = 0.4\) (EtOAc/Petroleum ether = 1:1). m.p.: 142 – 143°C. \(^1\)H NMR (400 MHz, DMSO-d6) \(\delta\) 12.09 (s, 1H), 7.95 – 7.89 (m, 2H), 7.50 – 7.39 (m, 5H), 7.36 – 7.31 (m, 2H), 2.49 (s, 3H), 2.24 (q, \(J = 7.4\) Hz, 2H), 0.90 (t, \(J = 7.5\) Hz, 3H). \(^{13}\)C NMR (101 MHz, DMSO-d6) \(\delta\) 172.4, 167.8, 160.7, 137.8, 130.1, 129.8, 128.8, 128.3, 128.2, 127.9, 114.0, 28.8, 11.5, 8.3. MS (ESI): m/z (M + H\(^+\)) 371.2.

\(N\)-((3-methyl-4-(1H-pyrazol-1-yl)phenyl)sulfonyl)acetamide (1ar)

**Method B.** (77%, light yellow powder), \(R_t = 0.3\) (EtOAc/Petroleum ether = 1:1). m.p.: 148-149°C. \(^1\)H NMR (400 MHz, DMSO-d6) \(\delta\) 12.21 (s, 1H), 8.19 (d, \(J = 2.4\) Hz, 1H), 7.91 (d, \(J = 1.8\) Hz, 1H), 7.85 (d, \(J = 8.4, 2.1\) Hz, 1H), 7.80 (d, \(J = 1.6\) Hz, 1H), 7.64 (d, \(J = 8.4\) Hz, 1H), 6.57 – 6.52 (m, 1H), 2.35 (s, 3H), 1.93 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-d6) \(\delta\) 174.2, 167.8, 160.7, 137.8, 130.1, 129.8, 128.8, 128.3, 128.2, 127.9, 114.0, 28.8, 11.5, 8.3. MS (ESI): m/z (M + H\(^+\)) 280.1.
N-((3-methyl-4-(pyridin-2-yl)phenyl)sulfonyl)acetamide (1as)

**Method B**, (86%, white powder), $R_f = 0.3$ (EtOAc/Petroleum ether = 1:1). **m.p.**: 187 – 189°C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 12.17 (s, 1H), 8.68 (ddd, $J$ = 4.7, 1.6, 0.9 Hz, 1H), 7.95 (td, $J$ = 7.6, 1.7 Hz, 1H), 7.87 – 7.81 (m, 2H), 7.62 (ddd, $J$ = 7.7, 2.5, 1.3 Hz, 2H), 7.45 (ddd, $J$ = 7.7, 4.8, 1.1 Hz, 1H), 2.40 (s, 3H), 1.95 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 169.3, 157.5, 149.4, 144.8, 139.2, 137.0, 136.7, 130.5, 129.2, 125.1, 124.3, 122.9, 23.5, 20.2. **MS (ESI)**: m/z (M + H$^+$) 291.1.

**Dimethyl 2-diazo malonate (2a)**

**Method C**, (78%, yellow oil), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:4). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.79 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.6, 52.6. **MS (ESI)**: m/z (M + H$^+$) 159.2.

**Methyl 2-diazo-3-oxobutanoate (2b)**

**Method C**, (76%, yellow oil), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:4). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.80 (s, 3H), 2.43 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 189.9, 161.7, 52.1, 28.0. **MS (ESI)**: m/z (M + H$^+$) 143.2.

**Methyl 2-diazo-2-(diethoxyphosphoryl)acetate (2c)**

**Method C**, (76%, yellow oil), $R_f = 0.3$ (EtOAc/Petroleum ether = 1:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.28 – 4.05 (m, 4H), 3.77 (s, 3H), 1.35 – 1.30 (m, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 163.4, 63.5, 63.4, 52.3, 15.9, 15.8. **MS (ESI)**: m/z (M + H$^+$) 237.2.

**Methyl 2-diazo-2-(methylsulfonyl)acetate (2d)**

**Method C**, (75%, white thick solid), $R_f = 0.3$ (EtOAc/Petroleum ether = 1:2). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.86 (s, 3H), 3.28 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.1, 53.3, 45.0. **MS (ESI)**: m/z (M + H$^+$) 179.1.

**Methyl 2-diazo-2-tosylacetate (2e)**

**Method C**, (75%, yellow powder), $R_f = 0.3$ (EtOAc/Petroleum ether = 1:2). **m.p.**: 68 – 69°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.03 – 7.99 (m, 2H), 7.67 – 7.61 (m, 1H), 7.57 – 7.52 (m, 2H), 3.74 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.2, 141.8, 134.3, 129.4, 128.0, 53.0. **MS (ESI)**: m/z (M + H$^+$) 254.1.

**General procedure for the Rh-catalyzed C-H bond carbenoid functionalization:** A 10 mL tube equipped with a magnetic stir bar was charged with [RhCp*Cl$_2$]$_2$ (2.5 ~ 5.0 mol%), AgOAc (10 ~ 20 mol%), N-Ac substituted sulfonamide (0.25 mmol) and 2.5 mL DCE, then diazo compound (1.1 ~ 2.0 equivalent) was added. The tube was sealed, and the reaction mixture was stirred at 60°C for 5h. DCE was removed under vacuo, and 10 mL DCM was added. The mixture was then filtered, the filtrate was concentrated,
and the residue was purified by preparative TLC on silica gel to afford desired compound.

**Dimethyl 2-[(N-acetyl)sulfamoyl]-4-methylphenyl]malonate (3)**

A 10 mL tube equipped with a magnetic stir bar was charged with [RhCp*Cl]2 (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), 1a (53.3 mg, 0.25 mmol) and 2.5 mL DCE, then 2a (79 mg, 0.5 mmol) was added. The tube was sealed, and the reaction mixture was stirred at 60°C for 5h. DCE was removed under vacuo, and 10 mL DCM was added. The mixture was then filtered, the filtrate was concentrated, and the residue was purified by preparative TLC on silica gel (EAOAc/Petroleum ether = 1:1, Rf = 0.4) to afford 3 (80 mg) which was dissolved in 2 mL toluene and followed by adding a small amount of petroleum ether under ultrasonic condition to 71.5 mg white powder (83% yield). m.p.: 157 – 159°C. **1H NMR** (400 MHz, DMSO-d6) δ 12.40 (s, 1H), 7.83 (d, J = 1.3 Hz, 1H), 7.54 (dd, J = 8.0, 1.4 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 5.73 (s, 1H), 3.69 (s, 6H), 2.40 (s, 3H), 1.89 (s, 3H). **13C NMR** (101 MHz, DMSO-d6) δ 168.8, 168.0, 138.4, 137.4, 134.5, 130.8, 130.8, 128.4, 53.0, 52.2, 23.1, 20.5. **HRMS** (ESI): m/z (M + H+) calcd for C14H18O7NS, 344.0798, found: 344.0792.

**Dimethyl 2-[(N-acetyl)sulfamoyl]-4-phenethylphenyl]malonate (4)**

[RhCp*Cl]2 (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), N-((3-phenethylphenyl)sulfonyl)acetamide (75.7 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C for 5h. 85.2 mg 4 was obtained (79% yield, white powder, EAOAc/Petroleum ether = 1:1, Rf = 0.3). m.p.: 101 – 102°C. **1H NMR** (400 MHz, DMSO-d6) δ 7.81 (d, J = 1.8 Hz, 1H), 7.41 (dd, J = 7.9, 1.5 Hz, 1H), 7.31 – 7.28 (m, 4H), 7.26 – 7.15 (m, 2H), 6.03 (s, 1H), 3.65 (s, 6H), 3.01 – 2.80 (m, 4H), 1.69 (s, 3H). **13C NMR** (101 MHz, DMSO-d6) δ 173.4, 168.6, 142.5, 141.3, 141.0, 131.2, 129.9, 128.7, 128.3, 128.3, 126.0, 125.3, 52.6 (X2), 36.7, 36.6, 25.4. **HRMS** (ESI): m/z (M + H+) calcd for C21H24O7NS, 434.1268, found: 434.1269.

**Dimethyl 2-[(N-acetyl)sulfamoyl]-[1,1'-biphenyl]-4-yl]malonate (5)**

[RhCp*Cl]2 (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), N-([1,1'-biphenyl]-3-ylsulfonyl)acetamide (68.7 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C for 5h. 89 mg 5 was obtained (88% yield, white powder, EAOAc/Petroleum ether = 1:1, Rf = 0.3). m.p.: 97–98°C. **1H NMR** (400 MHz, CDCl3) δ 9.63 (s, 1H), 8.46 (d, J = 2.0 Hz, 1H), 7.87 (d, J = 8.2, 2.0 Hz, 1H), 7.06 – 7.48 (m, 2H), 7.49 – 7.44 (m, 2H), 7.24 – 7.15 (m, 1H), 5.96 (s, 1H), 3.79 (s, 6H), 2.02 (s, 3H). **13C NMR** (101 MHz, CDCl3) δ 168.7, 168.6, 142.1, 138.5, 137.8, 132.6, 132.2, 130.3, 130.2, 129.3, 128.7, 127.4, 23.5. **HRMS** (ESI): m/z (M + H+) calcd for C19H16O7NS, 406.0955, found: 406.0949.

**Dimethyl 2-[(N-acetyl)sulfamoyl]-4-(furan-2-yl)phenyl]malonate (6)**

[RhCp*Cl]2 (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), N-((3-(furan-2-yl)CO2Me)2S), NHAc (8.3 mg, 20 mol%), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C for 5h. 89 mg 6 was obtained (88% yield, white powder, EAOAc/Petroleum ether = 1:1, Rf = 0.3). m.p.: 97–98°C. **1H NMR** (400 MHz, CDCl3) δ 9.63 (s, 1H), 8.46 (d, J = 2.0 Hz, 1H), 7.87 (d, J = 8.2, 2.0 Hz, 1H), 7.06 – 7.48 (m, 2H), 7.49 – 7.44 (m, 2H), 7.24 – 7.15 (m, 1H), 5.96 (s, 1H), 3.79 (s, 6H), 2.02 (s, 3H). **13C NMR** (101 MHz, CDCl3) δ 168.7, 168.6, 142.1, 138.5, 137.8, 132.6, 132.2, 130.3, 130.2, 129.3, 128.7, 127.4, 23.5. **HRMS** (ESI): m/z (M + H+) calcd for C19H16O7NS, 406.0955, found: 406.0949.
2-yl)phenyl)sulfonyl]acetamide (66.2 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C for 5h. 86 mg 6 was obtained (87% yield, white powder, EAOAc/ Petroleum ether = 2:1, Rf = 0.4). m.p.: 155 – 156°C. 1H NMR (400 MHz, DMSO-d6) δ 8.13 (d, J = 2.0 Hz, 1H), 7.79 (dd, J = 1.8, 0.7 Hz, 1H), 7.73 (dd, J = 8.1, 2.0 Hz, 1H), 7.29 (d, J = 8.1 Hz, 1H), 6.97 (dd, J = 3.4, 0.7 Hz, 1H), 6.63 (dd, J = 3.4, 1.8 Hz, 1H), 6.19 (s, 1H), 3.64 (s, 6H), 1.59 (s, 3H). 13C NMR (101 MHz, DMSO-d6) δ 175.7, 168.8, 152.2, 145.7, 143.5, 130.2, 129.3, 129.1, 124.8, 123.3, 112.3, 106.7, 52.9, 52.5, 26.5. HRMS (ESI): m/z (M + H+) calcd for C17H18O8NS, 396.0748, found: 396.0744.

Dimethyl 2-(2-([N-acetylsulfamoyl]-4-(thiophen-3-yl)phenyl)malonate (7)  
[RhCp*Cl2]2 (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), N-(3-thiophen-3-yl)phenyl)sulfonyl]acetamide (70.2 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C for 5h. 87.7 mg 7 was obtained (85% yield, white powder, EAOAc/ Petroleum ether = 2:1, RF = 0.4). m.p.: 144 – 145°C. 1H NMR (400 MHz, DMSO-d6) δ 8.09 (d, J = 2.0 Hz, 1H), 7.87 (dd, J = 2.9, 1.3 Hz, 1H), 7.75 (dd, J = 8.1, 2.0 Hz, 1H), 7.68 (dd, J = 5.0, 2.9 Hz, 1H), 7.51 (dd, J = 5.0, 1.3 Hz, 1H), 7.29 (d, J = 8.1 Hz, 1H), 6.18 (s, 1H), 3.65 (s, 6H), 1.61 (s, 3H). 13C NMR (101 MHz, DMSO-d6) δ 175.2, 168.8, 145.3, 136.8, 135.8, 129.8, 129.5, 129.3, 128.7, 127.9, 127.5, 126.1, 125.9, 121.8, 52.8, 52.5, 26.3. HRMS (ESI): m/z (M + H+) calcd for C17H18O7NS2, 412.0519, found: 412.0514.

Dimethyl (E)-2-(2-([N-acetylsulfamoyl]-4-styrylphenyl)malonate (8)  
[RhCp*Cl2]2 (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), (E)-N-(3-styrylphenyl)sulfonyl]acetamide (75.2 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C for 5h. 94 mg 8 was obtained (87% yield, white powder, EAOAc/ Petroleum ether = 2:1, RF = 0.5). m.p.: 211 – 212°C. 1H NMR (400 MHz, DMSO-d6) δ 8.02 (d, J = 1.7 Hz, 1H), 7.66 (d, J = 7.5 Hz, 3H), 7.39 (t, J = 7.6 Hz, 2H), 7.36 – 7.22 (m, 4H), 6.19 (s, 1H), 3.64 (s, 6H), 1.59 (s, 3H). 13C NMR (101 MHz, DMSO-d6) δ 175.3, 168.8, 145.3, 134.0, 130.1, 129.1, 127.6, 127.5, 126.1, 125.9, 121.8, 52.8, 52.5, 26.3. HRMS (ESI): m/z (M + H+) calcd for C21H22O7NS, 432.1111, found: 432.1109.

Dimethyl 2-(2-([N-acetylsulfamoyl]-4-(methoxycarbonyl)phenyl)malonate (9)  
[RhCp*Cl2]2 (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), methyl 3-(N-acetylsulfamoyl)benzoate (64.2 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 67.3 mg 9 was obtained (69% yield, white powder, EAOAc/ Petroleum ether = 2:1, RF = 0.5). m.p.: 171 – 172°C. 1H NMR (400 MHz, DMSO-d6) δ 12.66 (s, 1H), 8.54 (d, J = 1.5 Hz, 1H), 8.25 (dd, J = 8.1, 1.3 Hz, 1H), 7.66 (d, J = 8.2 Hz, 1H), 5.89 (s, 1H), 3.92 (s, 3H), 3.71 (s, 6H).
\[ \delta 169.8, 167.4, 164.7, 135.9, 133.6, 131.7, 131.1, 129.6, 53.2, 52.7, 52.6, 23.4. \]

**Dimethyl 2-\{(4-acetyl-2-(N-acetyl)sulfamoyl)phenyl\}malonate (10)**

\[ \text{[RhCp}^\text{*} \text{Cl}_2, (7.8 \text{ mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), N-\{(3-acetylphenyl)sulfonyl\}acetamide (60.2 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 70 mg 10 was obtained (71% yield, white powder, EAOAc/Petroleum ether = 2:1, \( R_f \) = 0.5). m.p.: 125 – 126°C.} \]

\[ \delta 8.48 (s, 1H), 8.27 (d, \( J = 6.0 \text{ Hz}, 1H \)), 7.63 (d, \( J = 6.7 \text{ Hz}, 1H \)), 5.92 (s, 1H), 3.70 (s, 6H), 2.64 (s, 3H), 1.87 (s, 3H). \]

**Dimethyl 2-\{(2-(N-acetyl)sulfamoyl)-4-((trimethylsilyl)ethynyl)phenyl\}malonate (11)**

\[ \text{[RhCp}^\text{*} \text{Cl}_2, (7.8 \text{ mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), N-\{(3-(trimethylsilyl)ethynyl)phenyl)sulfonyl\}acetamide (73.7 mg, 0.25 mmol), 2a (59.2 mg, 0.375 mmol), 2.5 mL DCE, 60°C for 5h. 44.5 mg 11 was obtained (42% yield, white powder, EAOAc/Petroleum ether = 2:1, \( R_f \) = 0.5). m.p.: 88 – 89°C.} \]

\[ \delta 8.27 (s, 1H), 7.66 (d, \( J = 8.0 \text{ Hz}, 1H \)), 7.56 (d, \( J = 8.1 \text{ Hz}, 1H \)), 5.83 (s, 1H), 3.75 (s, 6H), 2.02 (s, 3H), 0.22 (s, 9H). \]

**Dimethyl 2-\{(2-(N-acetyl)sulfamoyl)-3-methylphenyl\}malonate (12)**

\[ \text{[RhCp}^\text{*} \text{Cl}_2, (3.9 \text{ mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), N-\{(o-tolyl)sulfonyl\}acetamide (53.2 mg, 0.25 mmol), 2a (40 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 78 mg 12 was obtained (91% yield, white powder, EAOAc/Petroleum ether = 1:1, \( R_f \) = 0.4). m.p.: 160 – 161°C.} \]

\[ \delta 12.46 (s, 1H), 7.56 (t, \( J = 7.7 \text{ Hz}, 1H \)), 7.41 (d, \( J = 7.3 \text{ Hz}, 1H \)), 7.18 (d, \( J = 7.1 \text{ Hz}, 1H \)), 6.10 (s, 1H), 3.67 (s, 6H), 2.66 (s, 3H), 1.93 (s, 3H). \]

\[ \delta 12.46 (s, 1H), 7.56 (t, \( J = 7.7 \text{ Hz}, 1H \)), 7.41 (d, \( J = 7.3 \text{ Hz}, 1H \)), 7.18 (d, \( J = 7.1 \text{ Hz}, 1H \)), 6.10 (s, 1H), 3.67 (s, 6H), 2.66 (s, 3H), 1.93 (s, 3H). \]

**Dimethyl 2-\{(2-(N-acetyl)sulfamoyl)-3-(benzyloxy)phenyl\}malonate (13)**

\[ \text{[RhCp}^\text{*} \text{Cl}_2, (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), N-\{(2-benzyloxy)sulfonyl\}acetamide (76.2 mg, 0.25 mmol), 2a (40 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 100 mg 13 was obtained (92% yield, white powder, EAOAc/Petroleum ether = 2:1, \( R_f \) = 0.4). m.p.: 178°C.} \]

\[ \delta 12.46 (s, 1H), 7.56 (t, \( J = 7.7 \text{ Hz}, 1H \)), 7.41 (d, \( J = 7.3 \text{ Hz}, 1H \)), 7.18 (d, \( J = 7.1 \text{ Hz}, 1H \)), 6.10 (s, 1H), 3.67 (s, 6H), 2.66 (s, 3H), 1.93 (s, 3H). \]
– 179°C. \(^{1}H\) NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 12.24 (s, 1H), 7.55 – 7.48 (m, 3H), 7.41 – 7.35 (m, 2H), 7.30 (ddd, \(J = 7.2, 3.8, 1.3\) Hz, 1H), 7.25 – 7.21 (m, 1H), 6.77 (dd, \(J = 7.9, 0.8\) Hz, 1H), 6.08 (s, 1H), 5.42 (s, 2H), 3.67 (s, 6H), 1.95 (s, 3H). \(^{13}C\) NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 169.7, 168.7, 157.0, 136.4, 135.4, 134.2, 128.5, 127.9, 127.2, 125.8, 114.5, 69.8, 54.2, 52.6, 23.1. HRMS (ESI): \(m/z\) (M + H\(^{+}\)) calcd for C\(_{20}\)H\(_{22}\)O\(_8\)N\(_2\), 436.1061, found: 436.1054.

Dimethyl 2-\((N\text{-acetylsulfamoyl})\)-1,1'-biphenyl)-3-yl)malonate (14)

\[
\text{[RhCp*Cl}_2\text{]_2 (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), } N-\{(1,1'-biphenyl)-2-ylsulfonyl\}acetamide (68.7 mg, 0.25 mmol), 2a (40 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 89.4 mg 14 was obtained (88% yield, white powder, EAOAc/Petroleum ether = 1:1, \(R_f = 0.3\), m.p.: 147 – 148°C. \(^{1}H\) NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 11.92 (s, 1H), 7.63 (t, \(J = 7.7\) Hz, 1H), 7.40 (d, \(J = 7.7\) Hz, 1H), 7.36 – 7.28 (m, 5H), 7.20 (d, \(J = 7.5\) Hz, 1H), 6.15 (s, 1H), 3.70 (s, 6H), 1.76 (s, 3H). \(^{13}C\) NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 170.2, 168.6, 143.3, 141.1, 137.5, 133.2, 133.1, 131.7, 130.3, 128.9, 127.2, 126.9, 54.1, 52.8, 23.5. HRMS (ESI): \(m/z\) (M + H\(^{+}\)) calcd for C\(_{19}\)H\(_{20}\)O\(_7\)N\(_2\), 406.0955, found: 406.0947.

Dimethyl 2-\((N\text{-acetylsulfamoyl})\)-2-(3-(2-methoxyethoxy)phenyl)malonate (15)

\[
\text{[RhCp*Cl}_2\text{]_2 (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), } N-\{(2-(2-methoxyethoxy)phenyl)sulfonyl\}acetamide (68.2 mg, 0.25 mmol), 2a (40 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 93.7 mg 15 was obtained (93% yield, white powder, EAOAc/Petroleum ether = 3:1, \(R_f = 0.4\), m.p.: 159 – 160°C. \(^{1}H\) NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 11.80 (s, 1H), 7.60 (t, \(J = 8.2\) Hz, 1H), 7.33 (d, \(J = 8.0\) Hz, 1H), 6.82 (d, \(J = 7.8\) Hz, 1H), 6.03 (s, 1H), 4.37 – 4.26 (m, 2H), 3.77 – 3.74 (m, 2H), 3.68 (s, 6H), 3.32 (s, 3H), 1.93 (s, 3H). \(^{13}C\) NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 169.6, 168.3, 157.8, 135.1, 134.4, 126.1, 121.8, 115.0, 70.1, 69.0, 58.3, 54.3, 52.7, 23.0. HRMS (ESI): \(m/z\) (M + H\(^{+}\)) calcd for C\(_{16}\)H\(_{22}\)O\(_9\)N\(_2\), 404.1010, found: 404.1002.

Dimethyl 2-\((N\text{-acetylsulfamoyl})\)-2-(3-(trifluoromethoxy)phenyl)malonate (16)

\[
\text{[RhCp*Cl}_2\text{]_2 (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), } N-\{(2-(trifluoromethoxy)phenyl)sulfonyl\}acetamide (70.7 mg, 0.25 mmol), 2a (40 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 93 mg 16 was obtained (90% yield, white powder, EAOAc/Petroleum ether = 1:1, \(R_f = 0.3\), m.p.: 153 – 154°C. \(^{1}H\) NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 12.70 (s, 1H), 7.83 (t, \(J = 8.1\) Hz, 1H), 7.63 (d, \(J = 8.4\) Hz, 1H), 7.36 (d, \(J = 7.2\) Hz, 1H), 6.12 (s, 1H), 3.71 (s, 6H), 1.94 (s, 3H). \(^{13}C\) NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 170.2, 168.3, 146.9, 146.9, 136.3, 135.1, 130.6, 129.2, 121.5, 119.9 (q, \(J = 260.5\), 53.8, 52.9, 23.0. HRMS (ESI)): \(m/z\) (M + H\(^{+}\)) calcd for C\(_{14}\)H\(_{14}\)O\(_4\)N\(_2\)F\(_3\), 414.0465, found: 414.0456.

Dimethyl 2-\((N\text{-acetylsulfamoyl})\)-2-(methoxycarbonyl)phenyl)malonate (17)
[RhCp*Cl₂]₂ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), methyl 2-(N-acetyl)sulfamoyl)benzoate (64.2 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C for 5 h. 74 mg was obtained (76% yield, yellow powder, DCM/MeOH = 25:1, Rf = 0.3), m.p.: 177 – 178°C. ¹H NMR (400 MHz, DMSO-d₆) δ 7.46 (t, J = 7.7 Hz, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.23 (d, J = 7.5 Hz, 1H), 6.35 (s, 1H), 3.70 (s, 3H), 3.63 (s, 6H), 1.59 (s, 3H).

¹³C NMR (101 MHz, DMSO-d₆) δ 175.7, 169.8, 168.7, 142.0, 133.7, 131.8, 131.2, 129.6, 126.5, 53.2, 52.5, 52.3, 26.3.

HRMS (ESI): m/z (M + H⁺) calcd for C₁₅H₁₈O₉NS, 388.0697, found: 388.0689.

Dimethyl 2-(2-(N-acetyl)sulfamoyl)-3-nitrophenyl)malonate (18)

[RhCp*Cl₂]₂ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), N-((2-nitrophenyl)sulfonyl)acetamide (61 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 31 mg was obtained (33% yield, white powder, DCM/MeOH = 20:1, Rf = 0.3), m.p.: 168 – 169°C. ¹H NMR (400 MHz, DMSO-d₆) δ 7.67 – 7.50 (m, 2H), 7.45 (d, J = 6.8 Hz, 1H), 6.47 (d, J = 45.7 Hz, 1H), 3.65 (s, 6H), 1.61 (s, 3H).

¹³C NMR (101 MHz, DMSO-d₆) δ 175.5, 168.5, 149.7, 136.6, 133.4, 132.3, 130.7, 122.7, 53.2, 52.7, 26.1.

HRMS (ESI): m/z (M + H⁺) calcd for C₁₃H₁₅O₉N₂S, 375.0493, found: 375.0476.

Dimethyl 2-(2-(N-acetyl)sulfamoyl)-3,5-dimethylphenyl)malonate (19)

[RhCp*Cl₂]₂ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), N-((2,4-dimethylphenyl)sulfonyl)acetamide (56.7 mg, 0.25 mmol), 2a (40 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5 h. 81.2 mg was obtained (91% yield, white powder, EAOAc/Petroleum ether = 2:1, Rf = 0.5), m.p.: 175 – 176°C. ¹H NMR (400 MHz, DMSO-d₆) δ 12.38 (s, 1H), 7.24 (s, 1H), 6.95 (s, 1H), 6.05 (s, 1H), 3.68 (s, 6H), 2.62 (s, 3H), 2.32 (s, 3H), 1.92 (s, 3H). ¹³C NMR (101 MHz, DMSO-d₆) δ 169.6, 168.7, 143.1, 140.1, 134.2, 133.4, 129.0, 54.1, 52.7, 22.9, 22.1, 20.7. HRMS (ESI): m/z (M + H⁺) calcd for C₁₅H₂₀O₇NS, 358.0955, found: 358.0942.

HRMS (ESI): m/z (M + H⁺) calcd for C₁₅H₂₀O₇NS, 358.0955, found: 358.0942.

Dimethyl 2-(2-(N-acetyl)sulfamoyl)-5-methoxy-4-(methoxycarbonyl)phenyl)malonate (20)

[RhCp*Cl₂]₂ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), methyl 5-(N-acetyl)sulfamoyl)-2-methoxybenzoate (71.7 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C for 5 h. 74 mg was obtained (71% yield, white powder, EAOAc/Petroleum ether = 3:1, Rf = 0.4), m.p.: 178 – 179°C. ¹H NMR (400 MHz, DMSO-d₆) δ 8.24 (s, 1H), 7.05 (s, 1H), 5.96 (s, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 3.71 (s, 6H), 1.77 (s, 3H). ¹³C NMR (101 MHz, DMSO-d₆) δ 171.3, 167.7, 164.6, 160.3, 136.6, 133.3, 132.1, 118.8, 114.0, 56.4, 53.1, 52.7, 52.4, 24.3. HRMS (ESI): m/z (M + H⁺) calcd for C₁₈H₂₀O₁₀NS, 418.0802, found: 418.0792.

Dimethyl 2-(2-(N-acetyl)sulfamoyl)-3-methoxy-5-methylphenyl)malonate (21)
[RhCp*Cl₂] (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), N-[(2-methoxy-4-methylphenyl)sulfonyl]acetamide (60.7 mg, 0.25 mmol), 2a (40 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 88.6 mg 21 was obtained (95% yield, white powder, EAOAc/ Petroleum ether = 2:1, Rₜ = 0.4), m.p.: 167 – 168°C. ¹H NMR (400 MHz, DMSO-d₆) δ 12.03 (s, 1H), 7.13 (s, 1H), 6.59 (s, 1H), 6.02 (s, 1H), 3.90 (s, 3H), 3.68 (s, 6H), 2.35 (s, 3H), 1.90 (s, 3H). ¹³C NMR (101 MHz, DMSO-d₆) δ 169.6, 168.7, 158.4, 145.2, 134.8, 123.0, 122.2, 114.3, 56.9, 54.0, 52.6, 23.0, 21.4. HRMS (ESI): m/z (M + H⁺) calcd for C₁₅H₂₀O₈NS, 374.0904, found: 374.0895.

Dimethyl 2-[(N-acetylsulfamoyl)-4,5-dimethoxyphenyl]malonate (22)

[RhCp*Cl₂] (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), N-[(3,4-dimethoxyphenyl)sulfonyl]acetamide (64.7 mg, 0.25 mmol), 2a (40 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 1h. 78.8 mg 22 was obtained (81% yield, white powder, EAOAc/ Petroleum ether = 2:1, Rₜ = 0.3), m.p.: 171 – 172°C. ¹H NMR (400 MHz, DMSO-d₆) δ 12.31 (s, 1H), 7.47 (s, 1H), 6.92 (s, 1H), 5.76 (s, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.70 (s, 6H), 1.87 (s, 3H). ¹³C NMR (101 MHz, DMSO-d₆) δ 168.9, 168.0, 152.2, 147.5, 129.8, 124.8, 113.5, 112.8, 55.9, 53.0, 52.0, 23.1. HRMS (ESI): m/z (M + H⁺) calcd for C₁₅H₂₀O₉NS, 390.0853, found: 390.0843.

Dimethyl 2-[(N-acetylsulfamoyl)-5-bromo-4-methylphenyl]malonate (23)

[RhCp*Cl₂] (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), N-[(4-bromo-3-methylphenyl)sulfonyl]acetamide (73 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C for 5h. 74 mg 23 was obtained (70% yield, white powder, EAOAc/ Petroleum ether = 2:1, Rₜ = 0.4), m.p.: 141 – 142°C. ¹H NMR (400 MHz, DMSO-d₆) δ 7.79 (s, 1H), 7.41 (s, 1H), 6.11 (s, 1H), 3.65 (s, 6H), 2.37 (s, 3H), 1.60 (s, 3H). ¹³C NMR (101 MHz, DMSO-d₆) δ 175.31, 168.47, 143.98, 136.58, 132.75, 130.88, 129.71, 125.71, 52.75, 52.24, 26.18, 22.09. HRMS (ESI): m/z (M + H⁺) calcd for C₁₄H₁₇O₇NBrS, 421.9904, found: 421.9894.

Dimethyl 2-[(N-acetylsulfamoyl)-3,6-dimethoxyphenyl]malonate (24)

[RhCp*Cl₂] (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), N-[(2,5-dimethoxyphenyl)sulfonyl]acetamide (64.7 mg, 0.25 mmol), 2a (40 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 92.4 mg 24 was obtained (95% yield, white powder, EAOAc/ Petroleum ether = 2:1, Rₜ = 0.4), m.p.: 195 – 196°C. ¹H NMR (400 MHz, DMSO-d₆) δ 12.10 (s, 1H), 7.40 (d, J = 9.2 Hz, 1H), 7.27 (d, J = 9.2 Hz, 1H), 6.13 (s, 1H), 3.87 (s, 3H), 3.68 (s, 3H), 3.61 (s, 6H), 1.93 (s, 3H). ¹³C NMR (101 MHz, DMSO-d₆) δ 169.5, 167.9, 152.3, 152.1, 126.5, 125.1, 119.1, 114.7, 57.4, 57.2, 52.1, 49.5, 23.1. HRMS (ESI): m/z (M + H⁺) calcd for C₁₅H₂₀O₉NS, 390.0853, found: 390.0843.

Dimethyl 2-[(N-acetylsulfamoyl)thiophen-3-yl]malonate (25)
[RhCp*Cl₂]₂ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), N-(thiophen-2-ylsulfonyl)acetamide (51.2 mg, 0.25 mmol), 2a (40 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 68 mg 25 was obtained (81% yield, white powder, EAOAc/Petroleum ether = 2:1, Rf = 0.4), m.p.: 121 – 122°C. 

1H NMR (400 MHz, DMSO-d6) δ 12.44 (s, 1H), 8.02 (d, J = 5.2 Hz, 1H), 7.16 (d, J = 5.2 Hz, 1H), 5.65 (s, 1H), 3.70 (s, 6H), 1.92 (s, 3H).

13C NMR (101 MHz, DMSO-d6) δ 169.1, 167.2, 137.0, 136.7, 133.0, 129.5, 53.2, 50.1, 23.2.

HRMS (ESI): m/z (M + H⁺) calcd for C₁₁H₁₄O₇NS₂, 336.0206, found: 336.0198.

Methyl (E)-2-(2-(N-acetylsulfamoyl)-3-methylphenyl)-3-hydroxybut-2-enoate and methyl 2-(2-(N-acetylsulfamoyl)-3-methylphenyl)-3-oxobutanoate (26 + 26')

[RhCp*Cl₂]₂ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), N-(o-tolylsulfonyl)acetamide (53.2 mg, 0.25 mmol), 2b (35.5 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 71 mg 26 and 26' were obtained (87% yield, white powder, EAOAc/Petroleum ether = 1:1, Rf = 0.5), m.p.: 195 – 197°C. 

26: 
1H NMR (400 MHz, DMSO-d6) δ 12.75 (s, 1H), 12.03 (s, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.37 (d, J = 7.6 Hz, 1H), 7.18 – 7.12 (m, 1H), 3.54 (s, 3H), 2.66 (s, 3H), 1.90 (s, 3H), 1.73 (s, 3H).

26': 
1H NMR (400 MHz, DMSO-d6) δ 12.48 (s, 1H), 7.55 (t, J = 7.8 Hz, 1H), 7.42 (d, J = 7.3 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 6.28 (s, 1H), 3.65 (s, 3H), 2.67 (s, 3H), 2.16 (s, 3H), 1.96 (s, 3H).

26+26': 13C NMR (101 MHz, DMSO-d6) δ 202.1, 172.0, 171.1, 170.1, 169.2, 168.9, 140.3, 139.2, 137.2, 136.3, 135.9, 134.3, 133.1, 132.9, 132.8, 132.6, 132.3, 129.2, 103.1, 61.2, 52.4, 51.5, 29.5, 23.1, 22.9, 22.2, 21.8, 19.8. 
HRMS (ESI): m/z (M + H⁺) calcd for C₁₄H₁₈O₆NS, 328.0849, found: 328.0841.

Methyl 2-(2-(N-acetylsulfamoyl)-3-methylphenyl)-2-(diethoxyphosphoryl)acetate (27)

[RhCp*Cl₂]₂ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), N-(o-tolylsulfonyl)acetamide (53.2 mg, 0.25 mmol), 2c (59 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 95 mg 27 was obtained (90% yield, white powder, DCM/MeOH = 30:1, Rf = 0.3), m.p.: 163 – 164°C. 

1H NMR (400 MHz, DMSO-d6) δ 12.44 (s, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.31 (d, J = 7.4 Hz, 1H), 6.07 (d, J = 28.2 Hz, 1H), 4.16 – 4.02 (m, 2H), 3.92 – 3.77 (m, 1H), 3.76 – 3.66 (m, 1H), 3.65 (s, 3H), 2.65 (s, 3H), 1.83 (s, 3H), 1.24 (t, J = 7.0 Hz, 3H), 0.94 (t, J = 7.0 Hz, 3H).

13C NMR (101 MHz, DMSO-d6) δ 170.7, 167.5 (d, J = 4.4 Hz), 139.5, 137.8, 132.6 (d, J = 4.7 Hz), 132.4, 131.1, 130.9 (d, J = 5.8 Hz), 62.6 (t, J = 6.1 Hz), 52.5, 47.2, 46.0, 23.7, 22.7, 16.2 (d, J = 5.9 Hz), 15.8 (d, J = 5.8 Hz). 
HRMS (ESI): m/z (M + H⁺) calcd for C₁₆H₂₅O₈NPS, 422.1033, found: 422.1023.

Methyl 2-(2-(N-acetylsulfamoyl)-3-methylphenyl)-2-(methylsulfonyl)acetate (28)

[RhCp*Cl₂]₂ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), N-(o-tolylsulfonyl)acetamide (53.2 mg, 0.25 mmol), 2d (44.5 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 71 mg 28 was obtained (87% yield, white powder, EAOAc/Petroleum ether = 1:1, Rf = 0.4), m.p.: 121 – 122°C. 

1H NMR (400 MHz, DMSO-d6) δ 12.44 (s, 1H), 8.02 (d, J = 5.2 Hz, 1H), 7.16 (d, J = 5.2 Hz, 1H), 5.65 (s, 1H), 3.70 (s, 6H), 1.92 (s, 3H).

13C NMR (101 MHz, DMSO-d6) δ 169.1, 167.2, 137.0, 136.7, 133.0, 129.5, 53.2, 50.1, 23.2. 
HRMS (ESI): m/z (M + H⁺) calcd for C₁₁H₁₄O₇NS₂, 336.0206, found: 336.0198.
DCE, 60°C for 5h. 82.5 mg 28 was obtained (91% yield, white powder, EAOAc/ Petroleum ether = 3:1, \( R_f = 0.4 \)). \( \text{m.p.}: 204 - 205°C. \) \(^1\)H NMR (400 MHz, DMSO-d6) \( \delta \) 12.63 (s, 1H), 7.66 (d, \( J = 7.6 \) Hz, 1H), 7.49 (t, \( J = 7.7 \) Hz, 1H), 7.37 (d, \( J = 7.3 \) Hz, 1H), 7.27 (s, 1H), 3.74 (s, 3H), 3.18 (s, 3H), 2.65 (s, 3H), 1.79 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-d6) \( \delta \) 172.8, 165.1, 140.5, 139.4, 133.4, 130.4, 129.7, 128.7, 68.1, 53.2, 42.2, 24.6, 22.6. HRMS (ESI): m/z (M + H\(^+\)) calcd for C\(_{13}\)H\(_{18}\)O\(_7\)NS\(_2\), 364.0519, found: 364.0511.

**Methyl 2-(2-(N-acetylsulfamoyl)-3-methylphenyl)-2-(phenylsulfonyl)acetate (29)**

[RhCp*Cl\(_2\)] (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), \( N\)-(o-tolylsulfonyl)acetamide (53.2 mg, 0.25 mmol), 2e (60 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 94.7 mg 29 was obtained (89% yield, white powder, EAOAc/ Petroleum ether = 2:1, \( R_f = 0.4 \)), \( \text{m.p.}: 171 - 172°C. \) \(^1\)H NMR (400 MHz, DMSO-d6) \( \delta \) 12.54 (s, 1H), 7.94 – 7.90 (m, 2H), 7.87 (d, \( J = 7.2 \) Hz, 1H), 7.79 (ddd, \( J = 8.5, 2.2, 1.1 \) Hz, 1H), 7.71 – 7.60 (m, 3H), 7.48 (d, \( J = 7.4 \) Hz, 1H), 7.38 (s, 1H), 3.56 (s, 3H), 2.66 (s, 3H), 1.86 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-d6) \( \delta \) 170.8, 164.7, 139.8, 139.3, 138.2, 134.3, 134.1, 131.6, 130.5, 129.2, 129.1, 128.7, 68.7, 52.8, 23.5, 22.5. HRMS (ESI): m/z (M + H\(^+\)) calcd for C\(_{18}\)H\(_{20}\)O\(_7\)NS\(_2\), 426.0676, found: 426.0663.

**Tetramethyl 2,2’-(2-(N-acetylsulfamoyl)-5-methyl-1,3-phenylene)dimalonate (30)**

[RhCp*Cl\(_2\)] (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), \( N\) -tosylacetamide (53.2 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 98 mg 30 was obtained (83% yield, white powder, EAOAc/ Petroleum ether = 3:1, \( R_f = 0.4 \)), \( \text{m.p.}: 173 – 174°C. \) \(^1\)H NMR (400 MHz, DMSO-d6) \( \delta \) 12.77 (s, 1H), 7.15 (s, 2H), 6.03 (s, 2H), 3.69 (s, 12H), 2.37 (s, 3H), 1.91 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-d6) \( \delta \) 171.12, 169.01, 143.85, 134.83, 132.01, 120.00, 54.53, 53.36, 23.61, 21.38. HRMS (ESI): m/z (M + H\(^+\)) calcd for C\(_{19}\)H\(_{24}\)O\(_{11}\)NS, 474.1065, found: 474.1059.

**Tetramethyl 2,2’-(2-(N-acetylsulfamoyl)-5-methoxy-1,3-phenylene)dimalonate (31)**

[RhCp*Cl\(_2\)] (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), \( N\) -((4-methoxyphenyl)sulfonyl)acetamide (57.2 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 104.2 mg 31 was obtained (85% yield, white powder, EAOAc/ Petroleum ether = 3:1, \( R_f = 0.3 \)), \( \text{m.p.}: 183 – 184°C. \) \(^1\)H NMR (400 MHz, DMSO-d6) \( \delta \) 12.69 (s, 1H), 6.85 (s, 2H), 6.05 (s, 2H), 6.03 (s, 2H), 6.03 (s, 2H), 3.82 (s, 3H), 3.70 (s, 3H), 1.92 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-d6) \( \delta \) 170.3, 168.3, 161.2, 136.7, 130.0, 116.1, 55.8, 54.1, 53.0, 23.0. HRMS (ESI): m/z (M + H\(^+\)) calcd for C\(_{18}\)H\(_{20}\)O\(_7\)NS, 490.1014, found: 490.0997.

**Tetramethyl 2,2’-(2-(N-acetylsulfamoyl)-5-chloro-1,3-phenylene)dimalonate**

[RhCp*Cl\(_2\)] (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), \( N\) -tosylacetamide (53.2 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 98 mg 30 was obtained (83% yield, white powder, EAOAc/ Petroleum ether = 3:1, \( R_f = 0.4 \)), \( \text{m.p.}: 173 – 174°C. \) \(^1\)H NMR (400 MHz, DMSO-d6) \( \delta \) 12.77 (s, 1H), 7.15 (s, 2H), 6.03 (s, 2H), 3.69 (s, 12H), 2.37 (s, 3H), 1.91 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-d6) \( \delta \) 171.12, 169.01, 143.85, 134.83, 132.01, 120.00, 54.53, 53.36, 23.61, 21.38. HRMS (ESI): m/z (M + H\(^+\)) calcd for C\(_{19}\)H\(_{24}\)O\(_{11}\)NS, 474.1065, found: 474.1059.
phenylene)dimalonate (32)

[RhCp*Cl2]2 (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), N-((4-chlorophenyl)sulfonyl)acetamide (58 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 96.5 mg 32 was obtained (78% yield, white powder, DCM/ MeOH = 25:1, Rf = 0.3, m.p.: 193 – 194°C. 1H NMR (400 MHz, DMSO-d6) δ 7.16 (s, 2H), 6.61 (s, 2H), 3.65 (s, 12H), 1.61 (s, 3H). 13C NMR (101 MHz, DMSO) δ 171.8, 168.5, 137.4, 136.7, 131.1, 125.8, 54.1, 53.66, 23.8. HRMS (ESI): m/z (M + H+) calcd for C18H21O11NClS, 494.0518, found: 494.0516.

Tetramethyl 2,2’-(2-((N-acetylsulfamoyl)-5-nitro-1,3-phenylene)dimalonate (33)

[RhCp*Cl2]2 (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), N-((4-nitrophenyl)sulfonyl)acetamide (61 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 44 mg 33 was obtained (35% yield, white powder, DCM/ MeOH = 20:1, Rf = 0.3, m.p.: 217 – 218°C. 1H NMR (400 MHz, DMSO-d6) δ 8.01 (s, 2H), 6.69 (s, 2H), 3.67 (s, 12H), 1.64 (s, 3H). 13C NMR (101 MHz, DMSO-d6) δ 177.1, 168.8, 150.9, 146.4, 134.9, 124.0, 53.8, 52.76, 26.0. HRMS (ESI): m/z (M + H+) calcd for C18H21O13N2S, 505.0759, found: 505.0756.

Tetramethyl 2,2’-(2-((N-acetylsulfamoyl)-5-(methoxycarbonyl)-1,3-phenylene)dimalonate (34)

[RhCp*Cl2]2 (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), methyl 4-((N-acetylsulfamoyl)benzoate (64.2 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 92 mg 34 was obtained (71% yield, white powder, DCM/ MeOH = 20:1, Rf = 0.3, m.p.: 161 – 162°C. 1H NMR (400 MHz, DMSO-d6) δ 7.75 (s, 1H), 6.64 (s, 1H), 3.87 (s, 2H), 3.64 (s, 7H), 1.62 (s, 3H). 13C NMR (101 MHz, DMSO-d6) δ 176.9, 169.3, 165.1, 149.2, 133.6, 130.0, 129.4, 54.0, 52.7, 52.5, 26.1. HRMS (ESI): m/z (M + H+) calcd for C20H24O13NS, 518.0963, found: 518.0961.

Dimethyl 2-8-((N-acetylsulfamoyl)quinolin-7-yl)malonate (35)

[RhCp*Cl2]2 (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), N-(quinolin-8-ylsulfonyl)acetamide (62.5 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 73 mg 35 was obtained (77% yield, white powder, EAOAc/ Petroleum ether = 2:1, Rf = 0.4, m.p.: 235 – 237°C. 1H NMR (400 MHz, DMSO-d6) δ 12.47 (s, 1H), 9.09 (dd, J = 4.1, 1.7 Hz, 1H), 8.53 (dd, J = 8.2, 1.4 Hz, 1H), 8.32 (d, J = 8.6 Hz, 1H), 7.72 (dd, J = 8.3, 4.2 Hz, 1H), 7.50 (d, J = 8.6 Hz, 1H), 6.56 (s, 1H), 3.71 (s, 6H), 1.86 (s, 3H). 13C NMR (101 MHz, DMSO-d6) δ 170.2, 168.4, 151.1, 143.9, 137.1, 136.7, 134.2, 133.7, 127.8, 127.7, 122.6, 54.2, 52.8, 23.2. HRMS (ESI): m/z (M + H+) calcd for C16H17O2N2S, 381.0750, found: 381.0747.
Dimethyl 2-(7-(N-acetylsulfamoyl)-2-(tert-butyl)benzo[d]oxazol-6-yl)malonate (36)

[RhCp*Cl₂]₂ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), N-(2-(7-(N-acetylsulfamoyl)-2-(tert-butyl)benzo[d]oxazol-7-yl)sulfonyl)acetamide (74 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 89.1 mg 36 was obtained (84% yield, white powder, EAOAc/ Petroleum ether = 2:1, Rf = 0.4), m.p.: 171 – 172°C. ¹H NMR (400 MHz, DMSO-d₆) δ 12.79 (s, 1H), 8.04 (d, J = 8.3 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 6.02 (s, 1H), 3.70 (s, 6H), 1.47 (s, 9H). ¹³C NMR (101 MHz, DMSO-d₆) δ 175.0, 169.6, 168.1, 147.4, 142.1, 128.9, 126.2, 124.4, 122.3, 53.0, 52.4, 34.0, 27.8, 23.1. HRMS (ESI): m/z (M + H⁺) calcd for C₁₈H₂₃O₈N₂S, 427.1170, found: 427.1163.

Dimethyl 2-(4-(N-acetylsulfamoyl)benzo[c][1,2,5]thiadiazol-5-yl)malonate (37)

[RhCp*Cl₂]₂ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), N-(benzo[c][1,2,5]thiadiazol-4-ylsulfonyl)acetamide (64.2 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 63 mg 37 was obtained (65% yield, white powder, EAOAc/ Petroleum ether = 2:1, Rf = 0.3), m.p.: 202 – 203°C. ¹H NMR (400 MHz, DMSO-d₆) δ 12.86 (s, 1H), 8.44 (d, J = 9.2 Hz, 1H), 7.70 (d, J = 9.2 Hz, 1H), 6.57 (s, 1H), 3.73 (s, 6H), 1.89 (s, 3H). ¹³C NMR (151 MHz, DMSO-d₆) δ 170.2, 167.7, 153.9, 149.6, 137.0, 131.5, 125.9, 53.1, 52.6, 23.1. HRMS (ESI): m/z (M + H⁺) calcd for C₁₃H₁₄O₇N₃S₂, 388.068, found: 388.0265.

Dimethyl 2-(1-(N-acetylsulfamoyl)-5-(dimethylamino)naphthalen-2-yl)malonate (38)

[RhCp*Cl₂]₂ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), N-((5-(dimethylamino)naphthalen-1-yl)sulfonyl)acetamide (73 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 93 mg 38 was obtained (88% yield, yellow powder, EAOAc/ Petroleum ether = 2:1, Rf = 0.4), m.p.: 108 – 109°C. ¹H NMR (400 MHz, DMSO-d₆) δ 12.71 (s, 1H), 8.52 (d, J = 9.0 Hz, 1H), 8.39 (d, J = 8.9 Hz, 1H), 7.64 – 7.57 (m, 1H), 7.38 (d, J = 9.0 Hz, 1H), 7.27 (d, J = 7.5 Hz, 1H), 6.50 (s, 1H), 2.82 (s, 6H), 1.91 (s, 3H). ¹³C NMR (101 MHz, DMSO-d₆) δ 170.0, 168.8, 151.3, 135.0, 133.2, 130.6, 130.2, 128.6, 128.3, 126.0, 119.6, 115.3, 54.8, 52.7, 45.1, 23.1. HRMS (ESI): m/z (M + H⁺) calcd for C₁₉H₂₃O₇N₂S, 423.1220, found: 423.1216.

Dimethyl 2-(2-(N-acetylsulfamoyl)-3-(4-methoxypiperidin-1-yl)phenyl)malonate (39)

[RhCp*Cl₂]₂ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), N-((2-(4-methoxypiperidin-1-yl)phenyl)sulfonyl)acetamide (40 mg, 0.25 mmol), 2a (40 mg, 0.25 mmol), 2.5 mL DCE, 60°C overnight. 98.3 mg 39 was obtained (89% yield, brown powder, DCE/MeOH = 20:1, Rf = 0.5), m.p.: 172 – 174°C. ¹H NMR (400 MHz, DMSO-d₆) δ 11.75 (s, 1H), 7.69 – 7.63 (m, 2H), 7.13 (dd, J = 6.0, 2.5 Hz, 1H), 6.05 (s, 1H), 3.68 (s, 6H), 3.32 (s, 1H), 3.29 (s, 3H), 3.14 – 2.63 (m, 4H), 2.08 – 1.94
(m, 2H), 1.90 (s, 3H), 1.88 – 1.74 (m, 2H). 13C NMR (101 MHz, DMSO-d6) δ 170.7, 169.1, 153.9, 135.8, 135.4, 134.3, 128.5, 126.0, 77.1, 55.4, 55.0, 53.1, 49.6, 31.1, 23.5. HRMS (ESI): m/z (M + H+) calcd for C19H27O3N5S, 443.1483, found: 443.1480.

**Dimethyl 2-(2-(N-acetylsulfamoyl)-4-(dimethylamino)phenyl)malonate (40)**

[RhCp*Cl2]2 (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), N-((3-(dimethylamino)sulfonyl)acetamide (60.5 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 78.1 mg 40 was obtained (84% yield, white powder, EAOAc/ Petroleum ether = 2:1, Rf = 0.4). m.p.: 148 – 149°C. 1H NMR (400 MHz, DMSO-d6) δ 7.21 (d, J = 2.9 Hz, 1H), 7.15 (d, J = 8.7 Hz, 1H), 6.87 (dd, J = 8.7, 2.8 Hz, 1H), 5.81 (s, 1H), 3.63 (s, 6H), 2.94 (s, 6H), 1.74 (s, 3H). 13C NMR (101 MHz, DMSO-d6) δ 171.9, 169.0, 149.1, 141.6, 130.8, 117.2, 114.9, 112.4, 52.5, 51.9, 39.9, 24.7. HRMS (ESI): m/z (M + H+) calcd for C15H21O7N2S, 373.1064, found: 373.1061.

**Dimethyl 2-(2-(N-acetylsulfamoyl)-4-(2,5-dimethyl-1H-pyrrol-1-yl)phenyl)malonate (41)**

[RhCp*Cl2]2 (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), N-((3-(2,5-dimethyl-1H-pyrrol-1-yl)phenyl)sulfonyl)acetamide (73 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 85.8 mg 41 was obtained (81% yield, white powder, EAOAc/ Petroleum ether = 3:1, Rf = 0.5). m.p.: 243 – 244°C. 1H NMR (400 MHz, DMSO-d6) δ 7.64 (s, 1H), 7.48 – 7.32 (m, 2H), 6.15 (s, 1H), 5.82 (s, 2H), 3.68 (s, 6H), 2.00 (s, 6H), 1.63 (s, 3H). 13C NMR (101 MHz, DMSO-d6) δ 175.5, 168.6, 145.5, 136.8, 130.4, 129.4, 129.2, 128.1, 127.7, 106.3, 52.7, 52.5, 26.3, 13.0. HRMS (ESI): m/z (M + H+) calcd for C19H23O7N2S, 423.1220, found: 423.1216.

**Dimethyl 2-(2-(N-acetylsulfamoyl)-4-(quinolin-8-yl)phenyl)malonate (42)**

[RhCp*Cl2]2 (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), N-((3-(quinolin-8-yl)phenyl)sulfonyl)acetamide (81.4 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 82 mg 42 was obtained (72% yield, white powder, EAOAc/ Petroleum ether = 2:1, Rf = 0.3). m.p.: 233 – 235°C. 1H NMR (400 MHz, DMSO-d6) δ 12.48 (s, 1H), 8.94 (dd, J = 4.1, 1.8 Hz, 1H), 8.49 (dd, J = 8.3, 1.7 Hz, 1H), 8.31 (d, J = 1.9 Hz, 1H), 8.13 – 8.04 (m, 2H), 7.86 (dd, J = 7.1, 1.3 Hz, 1H), 7.80 – 7.73 (m, 1H), 7.66 – 7.58 (m, 2H), 5.88 (s, 1H), 3.75 (s, 6H), 1.92 (s, 3H). 13C NMR (101 MHz, DMSO-d6) δ 169.0, 167.9, 150.7, 144.7, 139.1, 137.2, 137.2, 136.7, 135.8, 132.5, 130.3, 129.9, 129.0, 128.4, 126.6, 125.3, 121.8, 53.1, 52.4, 23.1. HRMS (ESI): m/z (M + H+) calcd for C22H22O3N5S, 457.1064, found: 457.1051.

**Dimethyl 2-(2-(N-acetylsulfamoyl)-4-methyl-5-(quinolin-8-yl)phenyl)malonate (43)**

[RhCp*Cl2]2 (3.9 mg, 5.0 mol%), AgOAc (4.2 mg, 20 mol%), N-((3-methyl-4-(quinolin-8-yl)phenyl)sulfonyl)acetamide (42.5 mg, 0.125 mmol), 2a
(22 mg, 1.1 equiv), 12.5 mL toluene, 60°C overnight. 53 mg 43 was obtained (91% yield, white powder, EAOAc/ Petroleum ether = 2:1, \( R_f = 0.3 \), m.p.: 143 – 145°C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 9.05 (s, 1H), 8.43 (d, \( J = 7.8 \text{ Hz}, 1\text{H} \)), 8.17 (s, 1H), 8.02 – 7.99 (m, 1H), 7.73 (d, \( J = 4.7 \text{ Hz}, 2\text{H} \)), 7.63 – 7.56 (m, 2\text{H})), 6.26 (s, 1\text{H})), 3.77 (s, 3\text{H})), 3.70 (s, 3\text{H})), 2.24 (s, 3\text{H})), 1.86 (s, 3\text{H})). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 169.7, 169.0, 149.8, 144.8, 143.9, 139.2, 139.0, 137.7, 133.7, 132.4, 132.0, 130.5, 129.1, 128.9, 127.4, 121.9, 53.3, 53.0, 23.5, 20.6. HRMS (ESI): m/z (M + H\(^+\)) calcd for C\(_{23}\)H\(_{23}\)O\(_7\)N\(_2\)S, 471.1220, found: 471.1225.

**Dimethyl (E)-2-(N-acetamido-2-(N-acetylsulfamoyl)-4-methyl-5-(phenyldiazenyl)phenyl)malonate (44)**

[RhCp*Cl\(_2\)] (7.8 mg, 5 mol%), AgOAc (8.3 mg, 20 mol%), \((E)-N-((3-methyl-4-(phenyldiazenyl)phenyl)sulfonyl)acetamide \( (79.2 \text{ mg, } 0.25 \text{ mmol}, \ 2a \ (79 \text{ mg, } 0.5 \text{ mmol), 2.5 mL DCE, 60°C overnight. 95 mg 44 was obtained (85% yield, red powder, EAOAc/ Petroleum ether = 2:1, \( R_f = 0.4 \), m.p.: 211 – 212°C. \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \( \delta \) 12.55 (s, 1H), 8.10 (s, 1H), 7.99 – 7.93 (m, 2H), 7.66 – 7.62 (m, 3H), 7.60 (s, 1H), 5.79 (s, 1H), 3.71 (s, 6H), 2.73 (s, 3H), 1.92 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-d\(_6\)) \( \delta \) 169.1, 167.8, 152.2, 152.0, 137.3, 133.8, 132.5, 132.0, 124.5, 129.6, 122.9, 119.9, 117.5, 51.2, 52.2, 23.2, 16.8. HRMS (ESI): m/z (M + H\(^+\)) calcd for C\(_{20}\)H\(_{22}\)O\(_8\)N\(_3\)S, 448.1773, found: 448.1158.

**Dimethyl 2-(5-acetamido-2-(N-acetylsulfamoyl)-4-methylphenyl)malonate (45)**

[RhCp*Cl\(_2\)] (7.8 mg, 5 mol%), AgOAc (8.3 mg, 20 mol%), \( N-((4-acetamido-3-methylphenyl)sulfonyl)acetamide \( (67.4 \text{ mg, } 0.25 \text{ mmol), 2a \ (79 \text{ mg, } 0.5 \text{ mmol), 2.5 mL DCE, 60°C overnight. 92 mg 45 was obtained (92% yield, white powder, EAOAc/ Petroleum ether = 1:1, \( R_f = 0.3 \), m.p.: 219 – 221°C. \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \( \delta \) 9.48 (s, 1H), 7.86 (s, 1H), 7.81 (d, \( J = 8.6 \text{ Hz}, 1\text{H} \)), 5.68 (s, 1H), 3.68 (s, 6H), 2.31 (s, 3H), 1.88 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-d\(_6\)) \( \delta \) 168.9, 168.7, 167.9, 141.5, 132.7, 132.1, 129.6, 129.4, 124.5, 52.9, 52.5, 23.7, 17.7. HRMS (ESI): m/z (M + H\(^+\)) calcd for C\(_{16}\)H\(_{21}\)O\(_8\)N\(_2\)S, 401.0997.

**Tetramethyl 2,2′-(2-(N-acetylsulfamoyl)-5-(2,5-dimethyl-1H-pyrrol-1-yl)-1,3-phenylene)dimalonate (46)**

[RhCp*Cl\(_2\)] (7.8 mg, 5 mol%), AgOAc (8.3 mg, 20 mol%), \( N-((4-(2,5-dimethyl-1H-pyrrol-1-yl)phenyl)sulfonyl)acetamide \( (73 \text{ mg, } 0.25 \text{ mmol), 2a \ (79 \text{ mg, } 0.5 \text{ mmol), 2.5 mL DCE, 60°C overnight. 100.8 mg 46 was obtained (73% yield, white powder, DCM/MeOH = 20:1, \( R_f = 0.3 \), m.p.: 267 – 268°C. \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \( \delta \) 7.01 (s, 2H), 6.66 (s, 2H), 5.84 (s, 2H), 3.63 (s, 12H), 1.99 (s, 6H), 1.67 (s, 3H), 1.67 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-d\(_6\)) \( \delta \) 176.8, 169.2, 143.7, 137.6, 133.8, 128.4, 127.5, 107.0, 53.7, 52.4, 26.3, 12.9. HRMS (ESI): m/z (M + H\(^+\)) calcd for C\(_{24}\)H\(_{29}\)O\(_{11}\)N\(_2\)S, 553.1487, found: 553.1492.
Dimethyl 2-[(N-acetylsulfamoyl)-4-methyl-5-(1H-pyrazol-1-yl)phenyl]malonate (47) and Dimethyl 2-[(N-acetylsulfamoyl)-3-methyl-2-(1H-pyrazol-1-yl)phenyl]malonate (47')

![Chemical structure](image)

[RhCp*Cl₂]₂ (7.8 mg, 5.0 mol%), AgOAc (8.4 mg, 20 mol%), N-((3-methyl-4-(1H-pyrazol-1-yl)phenyl)sulfonyl)acetamide (69.4 mg, 0.25 mmol), 2a (44 mg, 1.1 equiv), 2.5 mL DCE, 60°C overnight. 15.6 mg 47 was obtained (15% yield, white powder, DCM/MeOH = 20:1, Rᵣ = 0.3, m.p.: 83 – 85°C. ¹H NMR (400 MHz, DMSO-d₆) δ 12.60 (s, 1H), 8.18 (s, 1H), 8.00 (s, 1H), 7.80 (s, 1H), 7.46 (s, 1H), 6.57 (s, 1H), 5.89 (s, 1H), 3.69 (s, 6H), 2.37 (s, 3H), 1.85 (s, 3H). ¹³C NMR (101 MHz, DMSO-d₆) δ 170.3, 167.8, 142.4, 141.1, 136.9, 133.4, 132.2, 131.8, 129.6, 126.9, 107.3, 53.0, 52.0, 23.8, 18.2. HRMS (ESI): m/z (M + H⁺) calcd for C₁₇H₂₀O₇N₃S, 410.1016, found: 410.1007; 67 mg 47' was obtained (66% yield, white powder, DCM/MeOH = 20:1, Rᵣ = 0.4, m.p.: 157 – 159°C. ¹H NMR (400 MHz, DMSO-d₆) δ 12.31 (br s, 1H), 8.01 (d, J = 1.8 Hz, 1H), 7.96 (s, 1H), 7.90 (s, 1H), 7.82 (s, 1H), 6.59 (s, 1H), 4.24 (s, 1H), 3.66 (s, 6H), 2.07 (s, 3H), 1.96 (s, 3H). ¹³C NMR (101 MHz, DMSO-d₆) δ 169.1, 167.0, 142.6, 141.3, 140.0, 137.5, 132.7, 131.8, 129.2, 126.2, 107.1, 53.1, 51.9, 23.4, 17.3. HRMS (ESI): m/z (M + H⁺) calcd for C₁₇H₂₀O₇N₃S, 410.1011.

Dimethyl 2-[(N-acetylsulfamoyl)-3-methyl-2-(pyridin-2-yl)phenyl]malonate (48')

![Chemical structure](image)

[RhCp*Cl₂]₂ (7.8 mg, 5.0 mol%), AgOAc (8.4 mg, 20 mol%), N-((3-methyl-4-(pyridin-2-yl)phenyl)sulfonyl)acetamide (72.4 mg, 0.25 mmol), 2a (44 mg, 1.1 equiv), 2.5 mL DCE, 60°C overnight. 80 mg 48' was obtained (76% yield, white powder, DCM/MeOH = 20:1, Rᵣ = 0.4, m.p.: 187 – 188°C. ¹H NMR (400 MHz, DMSO-d₆) δ 12.18 (s, 1H), 8.71 (d, J = 4.7 Hz, 1H), 7.96 (t, J = 7.7 Hz, 1H), 7.86 (s, 1H), 7.81 (s, 1H), 7.50 – 7.45 (m, 1H), 7.39 (d, J = 7.7 Hz, 1H), 4.41 (s, 1H), 3.63 (s, 6H), 2.10 (s, 3H), 1.95 (s, 3H). ¹³C NMR (101 MHz, DMSO-d₆) δ 169.2, 167.5, 155.5, 149.9, 145.0, 139.4, 137.4, 137.1, 132.1, 128.2, 125.3, 124.7, 123.2, 54.1, 52.9, 23.5, 20.2. HRMS (ESI): m/z (M + H⁺) calcd for C₁₉H₂₁O₇N₂S, 421.1064, found: 421.1055.

Methyl 2-[(N-acetylsulfamoyl)-3-methylphenyl]acetate (49)

The mixture of 12 (2.803 g, 8.17 mmol), LiCl (520 mg, 12.26 mmol), H₂O (1.634 mL) in 65 mL DMSO was refluxed at 150°C for 3.5 h, then poured into 100 mL sat. NaCl solution and extracted by ethyl acetate. The organic layers were dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by silica gel chromatography to afford 49 as yellow solid (1.304 g, 56% yield, EAOAc/ Petroleum ether = 1:2, Rᵣ = 0.5, m.p.: 152 – 153°C. ¹H NMR (400 MHz, DMSO-d₆) δ 12.23 (s, 1H), 8.71 (d, J = 4.7 Hz, 1H), 7.96 (t, J = 7.7 Hz, 1H), 7.86 (s, 1H), 7.81 (s, 1H), 7.50 – 7.45 (m, 1H), 4.41 (s, 1H), 3.63 (s, 6H), 2.10 (s, 3H), 1.95 (s, 3H). ¹³C NMR (101 MHz, DMSO-d₆) δ 171.5, 169.4, 139.1, 136.5, 136.2, 132.7, 132.3, 132.0, 51.4, 40.1, 23.0, 21.7. HRMS (ESI): m/z (M + H⁺) calcd for C₁₃H₁₄O₃N₂S, 286.0744, found: 286.0732.
8-Methyl-2H-benzo[e][1,2]thiazin-3(4H)-one 1,1-dioxide (50)

The mixture of 49 (163 mg, 0.57 mmol) and p-TsOH (11 mg, 0.057 mmol) in 20 mL toluene was refluxed at 150°C overnight, then poured into 30 mL sat. NaCl solution and extracted by ethyl acetate. The organic layers were dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by silica gel chromatography to afford 50 as light yellow solid (115.5 mg, 96% yield, EAOAc/ Petroleum ether = 1:2, Rf = 0.2). m.p.: 213 – 215°C. ¹H NMR (400 MHz, DMSO-d6) δ 7.51 (t, J = 7.6 Hz, 1H), 7.35 (d, J = 7.3 Hz, 2H), 4.01 (s, 2H), 2.60 (s, 3H). ¹³C NMR (101 MHz, DMSO-d6) δ 169.6, 134.3, 134.1, 132.2, 132.1, 131.0, 127.1, 37.3, 19.4. HRMS (ESI): m/z (M + H⁺) calcd for C₉H₁₀O₃NS, 212.0375, found: 212.0371.

8-Methyl-3,4-dihydro-2H-benzo[e][1,2]thiazine 1,1-dioxide (51)

The mixture of 50 (32 mg, 0.15 mmol) and LiAlH₄ (12 mg, 0.3 mmol) in 5 mL dry THF was stirred at room temperature for 1h. Solvent was removed in vacuo, and the residue was purified by silica gel chromatography to afford 51 as light yellow solid (26.5 mg, 90% yield, EAOAc/ Petroleum ether = 1:2, Rf = 0.3). m.p.: 163 – 164°C. ¹H NMR (400 MHz, CDCl₃) δ 7.26 (t, J = 7.6 Hz, 1H), 7.12 (dd, J = 7.6, 0.4 Hz, 1H), 7.01 (d, J = 7.7 Hz, 1H), 3.71 (s, 2H), 2.94 (t, J = 5.9 Hz, 2H), 2.66 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 137.2, 137.1, 136.08, 131.5, 131.0, 127.5, 41.9, 30.2, 20.4. HRMS (ESI): m/z (M + H⁺) calcd for C₉H₁₂O₂NS, 198.0583, found: 198.0580.

Dimethyl 2-(6-(N-acetylsulfamoyl)-2,3-dihydro-1H-inden-5-yl)malonate (52)

[RhCp*Cl₂]₂ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), N-((2,3-dihydro-1H-inden-5-yl)sulfonyl)acetamide (59.7 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C for 1h. 56.1 mg 52 was obtained (61% yield, white powder, EAOAc/ Petroleum ether = 1:2, Rf = 0.3). m.p.: 165 – 166°C. ¹H NMR (400 MHz, DMSO-d6) δ 7.78 (s, 1H), 7.18 (s, 1H), 5.96 (s, 1H), 3.65 (s, 6H), 2.94 – 2.86 (s, 4H), 2.14 – 2.00 (m, 2H), 1.73 (s, 3H). ¹³C NMR (101 MHz, DMSO-d6) δ 172.0, 168.6, 148.2, 143.5, 139.3, 129.0, 125.6, 125.4, 52.7, 52.6, 32.3, 32.0, 25.0, 24.7. HRMS (ESI): m/z (M + H⁺) calcd for C₁₆H₂₀O₇NS, 370.0955, found: 370.0950.

Dimethyl 2-(6-sulfamoyl-2,3-dihydro-1H-inden-5-yl)malonate (53)

52 (55mg, 0.15 mmol) was dissolved in 3.0 mL MeOH, and 2 drops con. H₂SO₄ was added, the reaction mixture was stirred at room temperature for 4h. 47.5 mg 53 was obtained (97% yield, white solid, EAOAc/ Petroleum ether = 1:1, Rf = 0.3). m.p.: 174 – 176°C. ¹H NMR (400 MHz, DMSO-d6) δ 7.77 (s, 1H), 7.56 (s, 2H), 7.21 (s, 1H), 5.72 (s, 1H), 3.67 (s, 6H), 2.92 (t, J = 7.4 Hz, 4H), 2.06 (p, J = 7.5 Hz, 2H). ¹³C NMR (151 MHz, DMSO-d6) δ 168.4, 148.3, 144.2, 140.5, 128.5, 126.1, 123.2, 53.2, 52.7, 32.3, 32.0, 25.0. HRMS (ESI): m/z (M + H⁺) calcd for C₁₆H₂₀O₇NS, 328.0849, found: 328.0843.

Tetramethyl 2,2′-(5-(5-methyl-3-phenylisoxazol-4-yl)-2-(N-propionylsulfamoyl)-1,3-phenylene)dimalonate (54)
[RhCp*Cl]₂ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), \(N\)-(4-(5-methyl-3-phenylisoxazol-4-yl)phenyl)sulfonyl)propionamide (92.5 mg, 0.25 mmol), 2a (79 mg, 0.5 mmol), 2.5 mL toluene, 60°C overnight. 127.6 mg 54 was obtained (81% yield, white powder, EAOAc/ Petroleum ether = 3:1, Rf = 0.3, m.p.: 215 – 216°C. \(^1\)H NMR (400 MHz, DMSO-d6) δ 12.86 (s, 1H), 7.53 – 7.49 (m, 1H), 7.48 – 7.43 (m, 2H), 7.38 – 7.35 (m, 2H), 7.24 (s, 2H), 6.05 (s, 2H), 6.0 (s, 12H), 2.28 – 2.20 (m, 2H), 0.95 (t, J = 7.5 Hz, 3H). \(^{13}\)C NMR (151 MHz, DMSO-d6) δ 174.7, 170.8, 169.1, 168.6, 160.8, 135.0, 134.0, 131.8, 130.3, 129.5, 128.6, 128.4, 113.5, 54.3, 53.3, 29.5, 12.0, 9.0. HRMS (ESI): m/z (M + H\(^+\)) calcd for C\(_{29}\)H\(_{31}\)O\(_3\)N\(_2\)S, 631.1592, found: 631.1578.

\(^1\)H NMR of compound 3

\(^{13}\)C NMR of compound 3
$^1$H NMR of compound 4

$^{13}$C NMR of compound 4
$^1$H NMR of compound 5
$^{13}$C NMR of compound 5

$^1$H NMR of compound 6
\(^{13}\)C NMR of compound 6

\(^{1}H\) NMR of compound 7
$^{13}$C NMR of compound 7

$^1$H NMR of compound 8
$^{13}$C NMR of compound 8

$^1$H NMR of compound 9

$^{13}$C NMR of compound 9
$^1$H NMR of compound 10

$^{13}$C NMR of compound 10
$^1$H NMR of compound 11

$^{13}$C NMR of compound 11
$^1$H NMR of compound 12

$^{13}$C NMR of compound 12
$^1$H NMR of compound 13

$^{13}$C NMR of compound 13
$^{1}H$ NMR of compound 14

$^{13}C$ NMR of compound 14
$^1$H NMR of compound 15
$^{13}$C NMR of compound 15

$^{1}$H NMR of compound 16
$^{13}$C NMR of compound 16

$^1$H NMR of compound 17
$^{13}$C NMR of compound 17

$^1$H NMR of compound 18

$^{13}$C NMR of compound 18
**1H NMR of compound 19**

**13C NMR of compound 19**
$^1$H NMR of compound 20
$^{13}$C NMR of compound 20

$^1$H NMR of compound 21
$^{13}$C NMR of compound 21

$^1$H NMR of compound 22
$^{13}$C NMR of compound 22

$^1$H NMR of compound 23
$^{13}$C NMR of compound 23

$^1$H NMR of compound 24

$^{13}$C NMR of compound 24
$^1$H NMR of compound 25
$^{13}$C NMR of compound 25

$^1$H NMR of compound 26
$^{13}$C NMR of compound 26

$^1$H NMR of compound 27
$^{13}$C NMR of compound 28

$^1$H NMR of compound 29
$^{13}$C NMR of compound 29

$^1$H NMR of compound 30
$^{13}$C NMR of compound 30

$^1$H NMR of compound 31
$^{13}$C NMR of compound 31

$^1$H NMR of compound 32

$^{13}$C NMR of compound 32
$^1$H NMR of compound 33

$^{13}$C NMR of compound 33
$^1$H NMR of compound 34

$^{13}$C NMR of compound 34
$^1$H NMR of compound 35
$^{13}$C NMR of compound 35

$^1$H NMR of compound 36

$^{13}$C NMR of compound 36
$^1$H NMR of compound 37
$^{13}$C NMR of compound 37

$^1$H NMR of compound 38
$^{13}$C NMR of compound 38

$^1$H NMR of compound 39

$^{13}$C NMR of compound 39
$^1$H NMR of compound 40

$^{13}$C NMR of compound 40
$^1$H NMR of compound 41
$^{13}$C NMR of compound 41

$^{1}$H NMR of compound 42

$^{13}$C NMR of compound 42
$^1$H NMR of compound 43

$^{13}$C NMR of compound 43
$^1$H NMR of compound 44
$^{13}$C NMR of compound 44

$^1$H NMR of compound 45
$^{13}$C NMR of compound 45

$^1$H NMR of compound 46
$^{13}$C NMR of compound 46

$^1$H NMR of compound 47

$^{13}$C NMR of compound 47
$^1$H NMR of compound 47"
$^{13}$C NMR of compound 47'

$^1$H NMR of compound 48'
$^{13}$C NMR of compound 48'

$^1$H NMR of compound 49
$^{13}$C NMR of compound 49

$^1$H NMR of compound 50
$^{13}$C NMR of compound 50

$^1$H NMR of compound 51
$^{13}$C NMR of compound 51

$^1$H NMR of compound 52
\(^{13}\)C NMR of compound 52

\(^1\)H NMR of compound 53
$^{13}$C NMR of compound 54

$^1$H NMR of 1g

579
Analysis for the ratio of 47:47'
Analysis for the ratio of 48:48'