Supporting Information

Regioselective Annulation of Alkylidenecyclopropanes by Rh(III)-Catalyzed C–H/C–C Activation to Access Spirocyclic Benzosultams

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1. General Information

All the reactions were carried out under argon atmosphere using standard sealed Schlenk technique. The substrates imine 1\textsuperscript{[1]}, ACP 2\textsuperscript{[2]} were prepared following literature procedures. \textsuperscript{1}H NMR (400 MHz), \textsuperscript{13}C NMR (101 MHz), and \textsuperscript{19}F (376 MHz) were recorded on a NMR spectrometer with DMSO-\textit{d}_6 and CDCl\textsubscript{3} as solvent. Chemical shifts of \textsuperscript{1}H, \textsuperscript{13}C and \textsuperscript{19}F NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl\textsubscript{3}: \textit{δ}_H = 7.26 ppm, \textit{δ}_C = 77.16 ppm; DMSO-\textit{d}_6: \textit{δ}_H = 2.50 ppm, \textit{δ}_C = 39.43 ppm). All coupling constants (\textit{J} values) were reported in Hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), triplet (t), triplet of doublets (td), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200–300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm and 365 nm). High-resolution mass spectrometry (HRMS) was done on a FTICR-mass spectrometer (0.3 mm thickness). Column chromatography was performed on silica gel (200-300 mesh) using EtOAc/petroleum ether (PE).

2. General Procedure for the Synthesis of 3

A mixture of 1 (0.1 mmol, 1.0 equiv), 2 (0.12 mmol, 1.2 equiv), [Cp*Rh(CH\textsubscript{3}CN\textsubscript{3}](SbF\textsubscript{6})\textsubscript{2} (10.0 mol%), Cu(OAc)\textsubscript{2} (0.05 mmol, 0.5 equiv) was weighed in a sealed Schlenk tube equipped with a stir bar. Dry \textit{t}-AmOH (1 mL) was added and the suspended mixture was stirred at 100 °C for 18 h under an Ar atmosphere. After the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was purified by a silica gel column using PE/EtOAc (20/1-10/1) as eluent to give pure product 3.
3. Large scale reaction

A mixture of 1a (3 mmol, 1.0 equiv), 2d (3.6 mmol, 1.2 equiv), [Cp*Rh(CH$_3$CN)$_3$](SbF$_6$)$_2$ (10.0 mol%), Cu(OAc)$_2$ (1.5 mmol, 0.5 equiv) was weighed in a sealed Schlenk tube equipped with a stir bar. Dry t-AmOH (5 mL) was added and the mixture was stirred at 100 °C for 18 h under an Ar atmosphere. After the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was purified by a silica gel column using PE/EtOAc (20/1-10/1) as eluent to give pure product 3d.

4. Mechanistic Studies

4.1. Deuterium-labeling experiments.

Procedures for the reaction without 2d: A mixture of 1a (0.1 mmol, 1.0 equiv), [Cp*Rh(CH$_3$CN)$_3$](SbF$_6$)$_2$ (10.0 mol%), Cu(OAc)$_2$ (0.05 mmol, 0.5 equiv), CD$_3$OD (10 equiv) was weighed in a sealed Schlenk tube equipped with a stir bar. Dry t-AmOH (1 mL) was added and the mixture was stirred at 100 °C for 18 h under Ar atmosphere. After the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure. The recovered 1a were obtained by flash column chromatography on silica gel (eluent: EtOAc/PE = 1/10).
Procedures for the reaction in the presence of 2d: A mixture of 1a (0.1 mmol, 1.0 equiv), 2d (0.12 mmol, 1.2 equiv), [Cp*Rh(CH$_3$CN)$_3$](SbF$_6$)$_2$ (10.0 mol%), Cu(OAc)$_2$ (0.05 mmol, 0.5 equiv), CD$_3$OD (10 equiv) was weighed in a sealed Schlenk tube equipped with a stir bar. Dry t-AmOH (1 mL) was added and the mixture was stirred at 100 °C for 18 h under Ar atmosphere. After the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure. 3ad' were obtained by flash column chromatography on silica gel (eluent: EtOAc/PE = 1/10).
Figure S2 $^1$H NMR spectra (400 MHz, DMSO) of D-3ad’

4.2 KIE Experiments

Procedure for independent reaction: A mixture of 1a (0.1 mmol, 0.5 equiv), or 1a-ds (0.1 mmol, 0.5 equiv), 2d (0.24 mmol, 1.2 equiv), [Cp*Rh(CH$_3$CN)$_3$](SbF$_6$)$_2$ (10.0 mol%), Cu(OAc)$_2$ (0.1 mmol, 0.5 equiv) were separately weighted in two Schlenk tube equipped with a stir bar. Dry $t$-AmOH (1 mL) was added and the mixture was stirred at 60 °C for 45 minutes under Ar atmosphere. Afterwards, the two tubes were rapidly combined and the solvent was rapidly evaporated under reduced pressure. The residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: EtOAc/PE= 1:10).
Figure S4 $^1$H NMR of product obtained from the KIE experiment for independent reactions

5. Experimental Data

$^{(E)}$-3'-Ethylidene-2'-phenyl-2',3'-dihydro-2H-spiro[benzo[d]isothiazole-3,1'-indene] 1,1-dioxide (3aa): White solid. M.p. 157 – 158 °C. $^1$H NMR (400 MHz, DMSO) $\delta$ 8.60 (s, 1H), 7.81 (d, $J$ = 7.8 Hz, 1H), 7.74 (d, $J$ = 7.7 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.40 – 7.34 (m, 1H), 7.28 (t, $J$ = 7.3 Hz, 1H), 7.16 – 6.93 (m, 4H), 6.83 (dd, $J$ = 17.0, 6.7 Hz, 3H), 6.49 (qd, $J$ = 7.0, 1.8 Hz, 1H), 6.14 (d, $J$ = 7.9 Hz, 1H), 4.71 (s, 1H), 1.52 (d, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 142.8, 142.6, 141.2, 140.8, 139.5, 136.9, 131.4, 129.8, 128.9, 128.8, 127.9, 126.6, 125.9, 125.7, 119.9, 119.7, 118.9, 74.8, 59.8, 14.9. HRMS (ESI) calcd for C$_{23}$H$_{20}$NO$_2$S$^+$ [M+H]$^+$ 374.1215, found 374.1212.
(E)-3'-Ethylidene-2'-(4-fluorophenyl)-2',3'-dihydro-2H-spiro[benzo[d]isothiazole-3,1'-indene] 1,1-dioxide (3ab): White solid. M.p. 110 – 112 °C. $^1$H NMR (400 MHz, DMSO) $\delta$ 8.63 (s, 1H), 7.78 (dd, $J = 20.9, 7.8$ Hz, 2H), 7.43 (dt, $J = 24.2, 7.5$ Hz, 2H), 7.29 (t, $J = 7.5$ Hz, 1H), 7.19 (t, $J = 7.6$ Hz, 1H), 7.00 – 6.72 (m, 5H), 6.50 (q, $J = 6.7$ Hz, 1H), 6.18 (d, $J = 7.8$ Hz, 1H), 4.71 (s, 1H), 1.51 (d, $J = 7.0$ Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 161.2 (d, $J = 243.4$ Hz), 143.1, 142.9, 141.5, 141.3, 136.2 (d, $J = 2.4$ Hz), 132.0, 130.4, 129.5 (d, $J = 24.2$ Hz), 126.4, 126.2, 120.4, 120.3, 119.7, 115.2 (d, $J = 21.3$ Hz), 75.2, 59.4, 15.4. $^{19}$F NMR (376 MHz, DMSO) $\delta$ -115.7. HRMS (ESI) calcd for C$_{23}$H$_{19}$FNO$_2$S$^+$ [M+H]$^+$ 392.1121, found 392.1114.

(E)-2'-(4-Chlorophenyl)-3'-ethylidene-2',3'-dihydro-2H-spiro[benzo[d]isothiazole-3,1'-indene] 1,1-dioxide (3ac): White solid. M.p. 162 – 163 °C. $^1$H NMR (400 MHz, DMSO) $\delta$ 8.71 (s, 1H), 7.78 (dd, $J = 12.2, 7.8$ Hz, 2H), 7.43 (ddd, $J = 21.7, 11.4, 4.1$ Hz, 2H), 7.28 (t, $J = 7.4$ Hz, 1H), 7.21 – 6.98 (m, 3H), 6.88 (dd, $J = 16.9, 8.1$ Hz, 3H), 6.50 (tt, $J = 7.2, 3.5$ Hz, 1H), 6.23 (d, $J = 7.9$ Hz, 1H), 4.75 (s, 1H), 1.49 (d, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 143.1, 142.8, 141.3, 141.2, 138.9, 137.4, 132.0, 131.7, 130.4, 129.7, 129.4, 128.4, 126.5, 126.2, 120.4, 120.3, 119.9, 75.2, 59.6, 15.4. HRMS (ESI) calcd for C$_{23}$H$_{19}$ClNO$_2$S$^+$ [M+H]$^+$ 408.0825, found 408.0813.

(E)-2'-(4-Bromophenyl)-3'-ethylidene-2',3'-dihydro-2H-spiro[benzo[d]isothiazole-3,1'-indene] 1,1-dioxide (3ad): White solid. M.p. 197 – 199 °C. $^1$H NMR (400 MHz, DMSO) $\delta$ 8.66 (s, 1H), 7.78 (dd, $J = 18.5, 7.8$ Hz, 2H), 7.44 (dt, $J = 19.5, 7.6$ Hz, 2H), 7.25 (dt, $J = 32.5,$
7.5 Hz, 4H), 6.82 (dd, \( J = 43.2 \), 7.7 Hz, 3H), 6.57 – 6.45 (m, 1H), 6.22 (d, \( J = 7.8 \) Hz, 1H), 4.68 (s, 1H), 1.50 (d, \( J = 7.1 \) Hz, 3H). \(^{13}\text{C NMR (101 MHz, DMSO)}\) \( \delta \) 143.1, 142.8, 141.2, 141.1, 139.4, 137.3, 132.1, 131.4, 130.4, 129.7, 129.4, 126.5, 126.2, 120.5, 120.3, 120.1, 119.8, 75.1, 59.6, 15.4. \( \text{HRMS (ESI)} \) calcd for C\textsubscript{23}H\textsubscript{19}BrNO\textsubscript{2}S\textsuperscript{+} [M+H]\textsuperscript{+} 452.0320, found 452.0306.

(E)-4-(3'-Ethylidene-1,1-dioxido-2',3'-dihydro-2\( \text{H} \)-spiro[benzo[d]isothiazole-3,1'-inden]-2'-yl)benzonitrile (3ae): White solid. M.p. 114 – 115 °C. \(^{1}\text{H NMR (400 MHz, DMSO)}\) \( \delta \) 8.77 (s, 1H), 7.79 (dd, \( J = 23.8 \), 7.8 Hz, 2H), 7.45 (dt, \( J = 27.1 \), 7.6 Hz, 4H), 7.30 (t, \( J = 7.5 \) Hz, 1H), 7.19 (t, \( J = 7.6 \) Hz, 1H), 7.01 (d, \( J = 7.9 \) Hz, 2H), 6.89 (d, \( J = 7.7 \) Hz, 1H), 6.55 (tt, \( J = 7.1 \), 3.5 Hz, 1H), 6.21 (d, \( J = 7.9 \) Hz, 1H), 4.79 (s, 1H), 1.48 (d, \( J = 7.1 \) Hz, 3H). \(^{13}\text{C NMR (101 MHz, DMSO)}\) \( \delta \) 145.8, 142.8, 142.6, 140.8, 140.7, 137.2, 132.5, 132.2, 130.6, 129.9, 129.6, 126.3, 126.2, 120.5, 120.4, 120.3, 119.1, 109.8, 75.1, 60.1, 15.5. \( \text{HRMS (ESI)} \) calcd for C\textsubscript{24}H\textsubscript{19}N\textsubscript{2}O\textsubscript{2}S\textsuperscript{+} [M+H]\textsuperscript{+} 399.1167, found 399.1157.

(E)-3'-Ethylidene-2'-(\( p \)-tolyl)-2',3'-dihydro-2\( \text{H} \)-spiro[benzo[d]isothiazole-3,1'-indene] 1,1-dioxide (3af): White solid. M.p. 174 – 175 °C. \(^{1}\text{H NMR (400 MHz, DMSO)}\) \( \delta \) 8.56 (s, 1H), 7.79 (d, \( J = 7.8 \) Hz, 1H), 7.73 (d, \( J = 7.7 \) Hz, 1H), 7.45 (t, \( J = 7.5 \) Hz, 1H), 7.38 (t, \( J = 7.5 \) Hz, 1H), 7.27 (t, \( J = 7.5 \) Hz, 1H), 7.14 (t, \( J = 7.6 \) Hz, 1H), 6.68 – 6.85 (m, 5H), 6.52 – 6.41 (m, 1H), 6.16 (d, \( J = 7.9 \) Hz, 1H), 4.65 (s, 1H), 2.11 (s, 3H), 1.50 (d, \( J = 7.0 \) Hz, 3H). \(^{13}\text{C NMR (101 MHz, DMSO)}\) \( \delta \) 143.5, 143.0, 141.8, 141.4, 137.3, 136.8, 135.9, 131.8, 130.2, 129.4, 129.2, 129.0, 126.5, 126.1, 120.3, 120.1, 119.3, 75.3, 59.9, 21.0, 15.4. \( \text{HRMS (ESI)} \) calcd for C\textsubscript{24}H\textsubscript{22}NO\textsubscript{2}S\textsuperscript{+} [M+H]\textsuperscript{+} 388.1371, found 388.1365.
\[(E)-3'-\text{Ethylidene}-2'-(4\text{-methoxyphenyl})-2',3'-\text{dihydro-}2\text{H-spiro[benzo}\[d]\text{isothiazole-3,1'-indene}]\, 1,1\text{-dioxide (3ag):} \text{White solid. M.p. 224 – 225 °C.}\]

\[\delta \text{ H NMR (400 MHz, DMSO)} \delta 8.55 \text{ (s, 1H), 7.76 (dd,} J = 19.5, 7.8 \text{ Hz, 2H), 7.43 (dt,} J = 22.6, 7.6 \text{ Hz, 2H), 7.27 (t,} J = 7.4 \text{ Hz, 1H), 7.18 (t,} J = 7.6 \text{ Hz, 1H), 6.85 (d,} J = 7.6 \text{ Hz, 1H), 6.76 – 6.42 \text{ (m, 5H), 6.17 (d,} J = 7.9 \text{ Hz, 1H), 4.64 (s, 1H), 3.59 (s, 3H), 1.52 (d,} J = 7.0 \text{ Hz, 3H).}\]

\[\delta \text{ 13C NMR (101 MHz, DMSO)} \delta 158.2, 143.4, 143.0, 141.9, 141.5, 137.4, 131.9, 131.8, 130.3, 129.4, 129.2, 126.5, 126.1, 120.3, 120.2, 119.3, 113.8, 75.4, 59.5, 55.3, 15.3.\]

\[\text{HRMS (ESI) calegd for C}_{24}\text{H}_{22}\text{NO}_{3}\text{S}^+ [M+H]^+ 404.1320, \text{ found 404.1312.}\]

\[(E)-3'-\text{Ethylidene}-2'-(m\text{-tolyl})-2',3'-\text{dihydro-}2\text{H-spiro[benzo}\[d]\text{isothiazole-3,1'-indene}]\, 1,1\text{-dioxide (3ah):} \text{White solid. M.p. 164 – 165 °C.}\]

\[\delta \text{ H NMR (400 MHz, DMSO)} \delta 8.58 \text{ (s, 1H), 7.77 (dd,} J = 24.4, 7.7 \text{ Hz, 2H), 7.46 (t,} J = 7.5 \text{ Hz, 1H), 7.38 (t,} J = 7.5 \text{ Hz, 1H), 7.28 (t,} J = 7.5 \text{ Hz, 1H), 7.13 (t,} J = 7.6 \text{ Hz, 1H), 6.83 (dd,} J = 18.1, 7.3 \text{ Hz, 3H), 6.61 (d,} J = 3.9 \text{ Hz, 2H), 6.52 – 6.44 \text{ (m, 1H), 6.14 (d,} J = 6.5 \text{ Hz, 1H), 4.66 (s, 1H), 2.02 (s, 3H), 1.53 (d,} J = 7.0 \text{ Hz, 3H).}\]

\[\delta \text{ 13C NMR (101 MHz, DMSO)} \delta 143.4, 143.0, 141.6, 141.3, 139.8, 137.3, 131.8, 130.3, 129.4, 129.2, 128.3, 127.7, 126.4, 126.1, 120.4, 120.1, 119.5, 75.4, 60.2, 15.4.\]

\[\text{HRMS (ESI) calegd for C}_{24}\text{H}_{22}\text{NO}_{2}\text{S}^+ [M+H]^+ 388.1371, \text{ found 388.1362.}\]

\[(E)-2'-(3\text{-Chlorophenyl})-3'-\text{ethylidene}-2',3'-\text{dihydro-}2\text{H-spiro[benzo}\[d]\text{isothiazole-3,1'-indene}]\, 1,1\text{-dioxide (3ai):} \text{White solid. M.p. 199 – 200 °C.}\]

\[\delta \text{ H NMR (400 MHz, DMSO)} \delta 8.68 \text{ (s, 1H), 7.79 (dd,} J = 16.4, 7.8 \text{ Hz, 2H), 7.44 (dt,} J = 23.9, 7.5 \text{ Hz, 2H), 7.29 (t,} J = 7.4 \text{ Hz, 3H).}\]

\[\delta \text{ 13C NMR (101 MHz, DMSO)} \delta 143.4, 143.0, 141.6, 141.3, 139.8, 137.3, 131.8, 130.3, 129.4, 129.2, 128.3, 127.7, 126.4, 126.1, 120.4, 120.1, 119.5, 75.4, 60.2, 15.4.\]

\[\text{HRMS (ESI) calegd for C}_{24}\text{H}_{22}\text{NO}_{2}\text{S}^+ [M+H]^+ 388.1371, \text{ found 388.1362.}\]
Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 7.07 (d, J = 5.7 Hz, 2H), 6.88 (d, J = 7.6 Hz, 1H), 6.81 (s, 2H), 6.58 – 6.47 (m, 1H), 6.20 (d, J = 7.8 Hz, 1H), 4.71 (s, 1H), 1.52 (d, J = 7.0 Hz, 3H). 13C NMR (101 MHz, DMSO) δ 142.9, 142.7, 142.3, 141.1, 140.8, 137.3, 133.1, 132.1, 130.5, 130.3, 129.7, 129.4, 127.1, 126.3, 126.2, 120.5, 120.0, 75.2, 59.7, 15.5. HRMS (ESI) calcd for C23H19ClNO2S+ [M+H]+ 408.0825, found 408.0818.

(E)-3’-Ethylidene-2’-(o-tolyl)-2’,3’-dihydro-2H-spiro[benzo[d]isothiazole-3,1’-indene] 1,1-dioxide (3aj): White solid. M.p. 177 – 179 °C. 1H NMR (400 MHz, DMSO) δ 8.71 (s, 1H), 7.80 (d, J = 7.7 Hz, 2H), 7.47 (dd, J = 16.4, 8.1 Hz, 2H), 7.25 (t, J = 7.4 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 7.01 (dd, J = 4.8, 2.9 Hz, 2H), 6.91 – 6.86 (m, 1H), 6.84 – 6.77 (m, 1H), 6.69 (d, J = 7.7 Hz, 1H), 6.43 (q, J = 6.9 Hz, 1H), 5.97 (d, J = 7.9 Hz, 1H), 4.79 (s, 1H), 1.87 (s, 3H), 1.52 (d, J = 6.8 Hz, 3H). 13C NMR (101 MHz, DMSO) δ 145.0, 143.4, 142.9, 139.4, 138.3, 137.9, 137.7, 131.8, 130.5, 130.2, 123.0, 129.3, 127.6, 126.4, 126.1, 125.5, 120.4, 120.3, 119.1, 75.0, 56.7, 19.8, 15.3. HRMS (ESI) calcd for C24H22NO2S+ [M+H]+ 388.1371, found 388.1369.

(E)-2’-(2-Chlorophenyl)-3’-ethylidene-2’,3’-dihydro-2H-spiro[benzo[d]isothiazole-3,1’-indene] 1,1-dioxide (3ak): White solid. M.p. 196 – 198 °C. 1H NMR (400 MHz, DMSO) δ 8.72 (s, 1H), 7.80 (d, J = 7.8 Hz, 2H), 7.56 – 7.41 (m, 2H), 7.29 – 7.10 (m, 5H), 6.99 – 6.90 (m, 1H), 6.67 (d, J = 7.6 Hz, 1H), 6.49 (q, J = 6.6 Hz, 1H), 5.91 (d, J = 7.9 Hz, 1H), 5.03 (s, 1H), 1.53 (d, J = 7.0 Hz, 3H). 13C NMR (101 MHz, DMSO) δ 145.0, 142.3, 142.1, 138.9, 138.2, 137.5, 135.4, 131.8, 130.3, 130.1, 129.6, 129.5, 129.3, 127.5, 125.8, 125.4, 120.7, 120.5, 119.9, 74.7, 57.1, 15.3. HRMS (ESI) calcd for C23H19ClNO2S+ [M+H]+ 408.0825, found 408.0813.
(E)-2’-(3,4-Dimethylphenyl)-3’-ethylidene-2’,3’-dihydro-2H-spiro[benzo[d]isothiazole-3,1’-indene] 1,1-dioxide (3al): White solid. M.p. 190 – 191 °C. $^1$H NMR (400 MHz, DMSO) $\delta$ 8.53 (d, $J = 2.1$ Hz, 1H), 7.75 (dd, $J = 22.6$, 6.8 Hz, 2H), 7.51 – 7.33 (m, 2H), 7.26 (t, $J = 6.5$ Hz, 1H), 7.14 (t, $J = 6.7$ Hz, 1H), 6.81 (t, $J = 15.6$ Hz, 2H), 6.50 (dd, $J = 33.4$, 8.8 Hz, 3H), 6.16 (d, $J = 7.1$ Hz, 1H), 4.61 (s, 1H), 1.98 (d, $J = 35.2$ Hz, 6H), 1.51 (d, $J = 5.5$ Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 143.0, 142.5, 141.2, 140.9, 136.8, 136.6, 135.4, 134.1, 131.2, 129.7, 128.9, 128.7, 126.0, 125.5, 119.8, 119.6, 118.8, 74.9, 59.4, 18.9, 14.9. HRMS (ESI) calcd for C$_{25}$H$_{24}$NO$_2$S$^+$ [M+H]$^+$ 402.1528, found 402.1518.

(E)-2’-(3,4-Dichlorophenyl)-3’-ethylidene-2’,3’-dihydro-2H-spiro[benzo[d]isothiazole-3,1’-indene] 1,1-dioxide (3am): White solid. M.p. 210 – 211 °C. $^1$H NMR (400 MHz, DMSO) $\delta$ 8.74 (s, 1H), 7.81 (dd, $J = 12.9$, 7.8 Hz, 2H), 7.53 – 7.41 (m, 2H), 7.26 (m, 2H), 6.82 (d, $J = 12.9$ Hz, 1H), 6.91 (d, $J = 12.9$ Hz, 1H), 6.61 – 6.49 (m, 1H), 6.28 (d, $J = 12.9$ Hz, 1H), 4.71 (s, 1H), 1.52 (d, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 171.6, 150.9, 148.7, 142.7, 139.0, 138.3, 137.9, 137.1, 132.2, 131.3, 129.5, 129.1, 129.0, 127.9, 127.8, 126.5, 122.7, 122.5, 122.4, 122.0, 121.9, 121.8, 120.8, 110.5, 61.6, 60.7, 40.5, 39.4, 14.0. HRMS (ESI) calcd for C$_{23}$H$_{16}$Cl$_2$NO$_2$S$^+$ [M+H]$^+$ 440.0279, found 440.0287.

(E)-3’-Ethylidene-2’-(thiophen-2-yl)-2’,3’-dihydro-2H-spiro[benzo[d]isothiazole-3,1’-indene] 1,1-dioxide (3an): White solid. M.p. 79 – 80 °C. $^1$H NMR (400 MHz, DMSO) $\delta$
8.59 (s, 1H), 7.78 (d, J = 7.7 Hz, 2H), 7.46 (t, J = 7.5 Hz, 2H), 7.26 (ddd, J = 15.0, 10.7, 4.3 Hz, 2H), 7.14 (dd, J = 5.1, 1.1 Hz, 1H), 6.87 (d, J = 7.6 Hz, 1H), 6.69 (dd, J = 5.1, 3.5 Hz, 1H), 6.47 (ddd, J = 14.0, 9.5, 2.7 Hz, 2H), 6.33 (d, J = 7.8 Hz, 1H), 4.90 (s, 1H), 1.61 (d, J = 6.9 Hz, 3H) 

$^{13}$C NMR (101 MHz, DMSO) δ 142.4, 142.2, 141.7, 141.4, 140.7, 136.9, 131.7, 129.9, 129.3, 128.8, 126.5, 125.9, 125.6, 125.3, 124.7, 120.0, 119.8, 119.7, 74.7, 54.9, 14.8.

HRMS (ESI) calcd for C$_{21}$H$_{18}$NO$_2$S$_2$ $\text{[M+H]}^+$ 380.0779, found 380.0773.

(E)-2'-(4-Bromophenyl)-3'-ethylidene-5'-fluoro-2',3'-dihydro-2$\text{H}$-spiro[benzo[d]isothiazole-3,1'-indene] 1,1-dioxide (3bd): white solid. M.p. 221 – 222 °C.

$^1$H NMR (400 MHz, DMSO) δ 8.67 (s, 1H), 7.76 (d, J = 7.7 Hz, 1H), 7.67 (d, J = 9.4 Hz, 1H), 7.42 (t, J = 7.2 Hz, 1H), 7.16 (dt, J = 17.4, 8.2 Hz, 4H), 6.93 – 6.85 (m, 1H), 6.76 (s, 2H), 6.58 (q, J = 6.8 Hz, 1H), 6.25 (d, J = 7.8 Hz, 1H), 4.70 (s, 1H), 1.50 (d, J = 6.9 Hz, 3H).

$^{13}$C NMR (101 MHz, DMSO) δ 164.2 (d, J = 245.0 Hz), 145.3, 140.5 (d, J = 3.1 Hz), 139.2, 138.9, 137.3, 132.2, 131.4, 129.8, 128.2 (d, J =9.5 Hz), 126.4, 121.9, 120.4, 120.2, 116.7 (d, J = 23.9 Hz), 107.2, 107.0, 74.5, 60.0, 15.4.

$^{19}$F NMR (376 MHz, DMSO) δ -111.98. HRMS (ESI) calcd for C$_{23}$H$_{18}$BrFNO$_2$S$^+$ $\text{[M+H]}^+$ 470.0226, found 470.0213.

(E)-2'-(4-Bromophenyl)-5'-chloro-3'-ethylidene-2',3'-dihydro-2$\text{H}$-spiro[benzo[d]isothiazole-3,1'-indene] 1,1-dioxide (3cd): white solid. M.p. 222 – 223 °C.

$^1$H NMR (400 MHz, DMSO) δ 8.72 (s, 1H), 7.93 (d, J = 1.9 Hz, 1H), 7.77 (d, J = 7.7 Hz, 1H), 7.47 – 7.39 (m, 1H), 7.37 – 7.05 (m, 4H), 6.88 (d, J = 8.2 Hz, 1H), 6.77 (d, J = 5.7 Hz, 2H), 6.62 (qd, J = 6.9, 1.8 Hz, 1H), 6.27 (d, J = 7.8 Hz, 1H), 4.70 (s, 1H), 1.50 (d, J = 7.1 Hz, 3H).

$^{13}$C NMR (101 MHz, DMSO) δ 144.3, 141.2, 140.2, 139.6, 138.5, 136.8, 135.0, 131.7, 130.9, 129.4, 128.8, 127.5, 125.9, 121.6, 120.0, 119.9, 119.8, 74.0, 59.2, 15.0. HRMS (ESI) calcd for C$_{23}$H$_{18}$BrNO$_2$S$^+$ $\text{[M+H]}^+$ 485.9930, found 485.9905.
(E)-2'-((4-Bromophenyl)-3'-ethylidene-5'-methyl-2',3'-dihydro-2\textsubscript{H}-
\textsuperscript{1}H NMR (400 MHz, DMSO) \(\delta\) 8.57 (s, 1H), 7.74 (d, \(J = 7.7\) Hz, 1H), 7.60 (s, 1H), 7.41 (t, \(J = 7.3\) Hz, 1H), 7.34 – 7.07 (m, 4H), 6.82 – 6.68 (m, 3H), 6.45 (tt, \(J = 7.1, 3.4\) Hz, 1H), 6.20 (d, \(J = 7.8\) Hz, 1H), 4.67 (s, 1H), 2.38 (s, 3H), 1.49 (d, \(J = 7.1\) Hz, 3H). \textsuperscript{13}C NMR (101 MHz, DMSO) \(\delta\) 143.0, 141.4, 141.3, 140.3, 140.0, 139.6, 137.4, 132.0, 131.4, 130.4, 129.6, 126.4, 125.9, 120.6, 120.3, 120.1, 119.4, 74.9, 59.9, 21.6, 15.4. HRMS (ESI) calcd for 
C\textsubscript{24}H\textsubscript{21}BrNO\textsubscript{2}S\textsuperscript{+} [M+H]\textsuperscript{+} 466.0476, found 466.0474.

(\textit{E})-2'-((4-Bromophenyl)-3'-ethylidene-5'-methoxy-2',3'-dihydro-2\textsubscript{H}-
\textsuperscript{1}H NMR (400 MHz, DMSO) \(\delta\) 8.57 (s, 1H), 7.74 (d, \(J = 7.7\) Hz, 1H), 7.60 (s, 1H), 7.41 (t, \(J = 7.3\) Hz, 1H), 7.34 – 7.07 (m, 4H), 6.82 – 6.68 (m, 3H), 6.45 (tt, \(J = 7.1, 3.4\) Hz, 1H), 6.20 (d, \(J = 7.8\) Hz, 1H), 4.67 (s, 1H), 2.38 (s, 3H), 1.49 (d, \(J = 7.1\) Hz, 3H). \textsuperscript{13}C NMR (101 MHz, DMSO) \(\delta\) 143.0, 141.4, 141.3, 140.3, 140.0, 139.6, 137.4, 132.0, 131.4, 130.4, 129.6, 126.4, 126.0, 120.6, 120.3, 120.1, 119.4, 74.9, 59.9, 21.6, 15.4. HRMS (ESI) calcd for 
C\textsubscript{24}H\textsubscript{21}BrNO\textsubscript{3}S\textsuperscript{+} [M+H]\textsuperscript{+} 482.0426, found 482.0423.

(\textit{E})-2'-((4-Bromophenyl)-5'-(tert-butyl)-3'-ethylidene-2',3'-dihydro-2\textsubscript{H}-
\textsuperscript{1}H NMR (400 MHz, DMSO) \(\delta\) 8.58 (s, 1H), 7.80 (d, \(J = 1.3\) Hz, 1H), 7.75 (d, \(J = 7.8\) Hz, 1H), 7.44 – 7.14 (m, 5H), 6.79 (dd, \(J = 16.8, 8.0\) Hz, 3H), 6.60 – 6.49 (m, 1H), 6.23 (d, \(J = 7.8\) Hz, 1H), 4.69 (s, 1H), 1.50 (d, \(J = 7.1\) Hz, 3H), 1.35 (s, 9H). \textsuperscript{13}C NMR (101 MHz, DMSO) \(\delta\)
(E)-2′-(4-Bromophenyl)-3′-ethylidene-6′-methyl-2′,3′-dihydro-2H-spiro[benzo[d]isothiazole-3,1′-indene] 1,1-dioxide (3gd): White solid. M.p. 120 – 121 °C. 

**1H NMR (400 MHz, DMSO)** \( \delta \) 8.61 (s, 1H), 7.74 (d, \( J = 7.7 \) Hz, 1H), 7.69 (d, \( J = 8.0 \) Hz, 1H), 7.41 (t, \( J = 7.5 \) Hz, 1H), 7.34 – 7.14 (m, 4H), 6.75 (d, \( J = 6.1 \) Hz, 2H), 6.67 (s, 1H), 6.46 – 6.36 (m, 1H), 6.23 (d, \( J = 7.8 \) Hz, 1H), 4.65 (s, 1H), 2.24 (s, 3H), 1.48 (d, \( J = 7.0 \) Hz, 3H).

**13C NMR (101 MHz, DMSO)** \( \delta \) 142.8, 140.6, 139.8, 139.0, 138.5, 136.8, 131.6, 131.0, 130.8, 129.2, 126.0, 125.7, 119.8, 119.6, 118.1, 74.6, 59.3, 20.9, 14.9. **HRMS (ESI)** calcd for C\(_{24}\)H\(_{21}\)BrNO\(_2\)S\(^+\) [M+H]\(^+\) 466.0476, found 466.0440.


**1H NMR (400 MHz, DMSO)** \( \delta \) 8.70 (s, 1H), 7.75 (d, \( J = 7.7 \) Hz, 1H), 7.65 (d, \( J = 7.8 \) Hz, 1H), 7.45 – 7.29 (m, 3H), 7.21 – 7.02 (m, 3H), 6.82 (d, \( J = 8.3 \) Hz, 1H), 6.72 (d, \( J = 7.9 \) Hz, 1H), 6.46 (qd, \( J = 6.9, 1.9 \) Hz, 1H), 6.21 (d, \( J = 7.9 \) Hz, 1H), 4.63 (s, 1H), 1.56 (s, 3H), 1.46 (d, \( J = 7.1 \) Hz, 3H). **13C NMR (101 MHz, DMSO)** \( \delta \) 143.2, 141.6, 140.5, 139.8, 139.7, 136.7, 136.2, 132.3, 132.0, 131.6, 131.3, 130.5, 129.6, 129.3, 126.2, 120.6, 120.0, 119.3, 118.1, 75.0, 60.2, 17.9, 15.4. **HRMS (ESI)** calcd for C\(_{24}\)H\(_{21}\)BrNO\(_2\)S\(^+\) [M+H]\(^+\) 466.0476, found 466.0460.

$^1$H NMR (400 MHz, DMSO) $\delta$ 8.57 (s, 1H), 7.80 (d, $J = 7.6$ Hz, 1H), 7.61 (d, $J = 7.8$ Hz, 1H), 7.46 (t, $J = 7.0$ Hz, 1H), 7.36 – 7.05 (m, 4H), 6.89 (d, $J = 7.6$ Hz, 1H), 6.73 (s, 2H), 6.51 (q, $J = 6.5$ Hz, 1H), 5.91 (s, 1H), 4.64 (s, 1H), 1.98 (s, 3H), 1.52 (d, $J = 6.5$ Hz, 3H).

$^{13}$C NMR (101 MHz, DMSO) $\delta$ 143.0, 142.8, 142.4, 141.4, 141.1, 139.5, 134.7, 131.2, 130.4, 130.3, 129.4, 126.6, 1263, 120.4, 120.1, 120.1, 119.8, 75.0, 59.7, 21.1, 15.5. HRMS (ESI) calcd for C$_{24}$H$_{21}$BrNO$_2$S $^{[M+H]}$ 466.0476, found 466.0460.


$^1$H NMR (400 MHz, DMSO) $\delta$ 8.51 (s, 1H), 7.80 (d, $J = 7.8$ Hz, 1H), 7.68 (d, $J = 8.6$ Hz, 1H), 7.51 – 7.44 (m, 1H), 7.28 (dd, $J = 27.3$, 19.9 Hz, 3H), 7.00 – 6.89 (m, 2H), 6.76 (s, 2H), 6.51 (qd, $J = 6.9$, 1.6 Hz, 1H), 5.52 (d, $J = 2.2$ Hz, 1H), 4.67 (s, 1H), 1.98 (s, 3H), 1.53 (d, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (101 MHz, DMSO) $\delta$ 161.6, 143.2, 142.4, 142.3, 140.8, 139.1, 131.0, 130.0, 129.5, 128.9, 125.9, 121.3, 119.9, 119.7, 119.4, 116.7, 109.3, 74.3, 59.2, 55.30 14.9. HRMS (ESI) calcd for C$_{24}$H$_{21}$BrNO$_3$S $^{[M+H]}$ 482.0426, found 482.0419.


$^1$H NMR (400 MHz, DMSO) $\delta$ 8.85 (s, 1H), 7.83 (t, $J = 8.9$ Hz, 2H), 7.54 – 7.45 (m, 2H), 7.43 – 7.09 (m, 3H), 6.94 (d, $J = 7.7$ Hz, 1H), 6.76 (s, 2H), 6.52 (qd, $J = 6.9$, 1.6 Hz, 1H), 6.09 (d, $J = 1.7$ Hz, 1H), 4.69 (s, 1H), 1.53 (d, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (101 MHz, DMSO) $\delta$ 143.0, 142.4, 141.6, 140.4, 138.8, 136.7, 135.8, 131.0, 130.2, 129.5, 129.1, 125.8, 125.6, 121.8, 120.0, 119.7, 74.3, 59.2, 14.9. HRMS (ESI) calcd for C$_{23}$H$_{18}$BrClNO$_2$S $^{[M+H]}$ 485.9930, found 485.9915.
(E)-2'-{(4-Bromophenyl)-3'-ethylidene-2',3'-dihydro-2H-spiro[benzo[d]isothiazole-3,1'-
cyclopenta[a]naphthalene] 1,1-dioxide (3ld): White solid. M.p. 224 – 225 °C. $^1$H NMR (400 MHz, DMSO) $\delta$ 8.97 (s, 1H), 8.06 (d, $J = 8.6$ Hz, 1H), 8.01 – 7.93 (m, 2H), 7.83 (d, $J = 7.7$ Hz, 1H), 7.40 (dt, $J = 14.6$, 7.4 Hz, 2H), 7.32 – 7.24 (m, 1H), 7.23 – 7.07 (m, 3H), 6.98 (d, $J = 8.5$ Hz, 1H), 6.86 (d, $J = 8.3$ Hz, 2H), 6.68 – 6.52 (m, 1H), 6.18 (d, $J = 7.8$ Hz, 1H), 4.79 (s, 1H), 1.50 (d, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 141.9, 141.7, 140.8, 139.4, 135.9, 135.5, 134.7, 132.2, 132.0, 131.3, 129.8, 129.6, 127.2, 126.5, 126.1, 123.6, 120.8, 120.2, 118.7, 75.5, 60.5, 15.5. HRMS (ESI) calcd for C$_{27}$H$_{21}$BrNO$_2$S$^+$ [M+H]$^+$ 502.0476, found 502.0463.

(E)-2'-(4-bromophenyl)-3'-ethylidene-2',3'-dihydro-3H-spiro[benzo[e][1,2,3]oxathiazine-
4,1'-indene] 2,2-dioxide (3md): White solid. M.p. 206 – 207 °C. $^1$H NMR (400 MHz, DMSO) $\delta$ 9.00 (s, 1H), 7.81 (d, $J = 7.8$ Hz, 1H), 7.49 (t, $J = 7.4$ Hz, 1H), 7.24 (ddd, $J = 15.3$, 14.1, 8.8 Hz, 4H), 7.08 (d, $J = 8.3$ Hz, 1H), 6.93 (d, $J = 7.7$ Hz, 1H), 6.79 (d, $J = 8.0$ Hz, 2H), 6.65 (t, $J = 7.5$ Hz, 1H), 6.50 (q, $J = 6.8$ Hz, 1H), 5.88 (d, $J = 7.9$ Hz, 1H), 5.27 (s, 1H), 1.53 (d, $J = 6.9$ Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 151.7, 144.1, 142.7, 141.3, 139.2, 131.3, 130.7, 130.4, 130.1, 129.0, 127.5, 123.8, 122.5, 120.4, 120.27, 120.2, 118.3, 75.3, 57.2, 15.2. HRMS (ESI) calcd for C$_{23}$H$_{17}$BrNO$_3$S$^+$ [M-H]$^+$ 466.0113, found 466.0104.
6. Molecular Structures of 3ac and 3al

Figure S5. The molecular structures of 3ac and 3al.

CCDC: 1942883 (3ac), 1951366 (3al)
7. Copies of $^1$H, $^{13}$C and $^{19}$F NMR Spectra for Compounds

$^1$H NMR spectrum of 3aa

$^{13}$C NMR spectrum of 3aa
$^1$H NMR spectrum of 3ab

$^{13}$C NMR spectrum of 3ab
$^{19}$F NMR spectrum of 3ab

$^1$H NMR spectrum of 3ac
$^{13}$C NMR spectrum of 3ac

$^1$H NMR spectrum of 3ad
$^{13}$C NMR spectrum of 3ad

$^1$H NMR spectrum of 3ae
$^{13}$C NMR spectrum of 3ae

$^1$H NMR spectrum of 3af
$^{13}$C NMR spectrum of 3af

$^1$H NMR spectrum of 3ag
$^{13}$C NMR spectrum of 3ag

$^1$H NMR spectrum of 3ah
$^{13}$C NMR spectrum of 3ah

$^{1}$H NMR spectrum of 3ai
$^1$H NMR spectrum of 3aj

$^{13}$C NMR spectrum of 3ai
$\text{\textsuperscript{13}C NMR spectrum of 3aj}$

$\text{\textsuperscript{1}H NMR spectrum of 3ak}$
$^{13}\text{C NMR spectrum of 3ak}$

$^{1}\text{H NMR spectrum of 3al}$
$^{13}$C NMR spectrum of 3a1

$^1$H NMR spectrum of 3am
$^{13}\text{C}$ NMR spectrum of 3am

$^1\text{H}$ NMR spectrum of 3an
$^{13}$C NMR spectrum of 3an

$^1$H NMR spectrum of 3bd
$^{13}$C NMR spectrum of 3bd

$^{19}$F NMR spectrum of 3bd
\(^1\)H NMR spectrum of 3cd

\(^{13}\)C NMR spectrum of 3cd
$^1$H NMR spectrum of 3dd

13C NMR spectrum of 3dd
$^1$H NMR spectrum of 3ed

$^{13}$C NMR spectrum of 3ed
$^1$H NMR spectrum of 3fd

$^{13}$C NMR spectrum of 3fd
$^{1}H$ NMR spectrum of 3gd

$^{13}C$ NMR spectrum of 3gd
$^1$H NMR spectrum of 3hd

$^{13}$C NMR spectrum of 3hd
$^1$H NMR spectrum of 3id

$^{13}$C NMR spectrum of 3id
$^1$H NMR spectrum of 3jd

$^{13}$C NMR spectrum of 3jd
$^1$H NMR spectrum of 3kd

[Image of 1H NMR spectrum]

$^{13}$C NMR spectrum of 3kd

[Image of 13C NMR spectrum]
$^1$H NMR spectrum of 3ld

$^{13}$C NMR spectrum of 3ld
$^1$H NMR spectrum of 3md

$^{13}$C NMR spectrum of 3md
8. References
