Supporting Information

C-H Alkenylation/Cyclization and Sulfamidation of 2-Phenylisatogens Using N-Oxide as a Directing Group

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1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. Except for the specially mentioned, all the reactions were monitored by thin-layer chromatography (TLC) and were visualized using UV light. The product purification was done using silica gel column chromatography. Thin layer chromatography (TLC) characterization was performed with precoated silica gel GF254 (0.2 mm), while column chromatography characterization was performed with silica gel (100-200 mesh). $^1$H-NMR, $^{13}$C-NMR and $^{19}$F NMR spectra were recorded with tetramethylsilane (TMS, $\delta = 0.00$ ppm) as the internal standard. $^1$H-NMR spectra were recorded at 400 or 600 MHz (Varian), $^{13}$C NMR spectra were recorded at 100 or 150 MHz (Varian) and $^{19}$F NMR spectra were recorded at 376 MHz (Varian). Chemical shifts are reported in ppm downfield from CDCl$_3$ ($\delta = 7.26$ ppm) or DMSO-$d_6$ ($\delta = 2.50$ ppm) for $^1$H NMR and chemical shifts for $^{13}$C NMR spectra are reported in ppm relative to the central CDCl$_3$ ($\delta = 77.0$ ppm) or DMSO-$d_6$ ($\delta = 39.6$ ppm). Chemical shifts ($\delta$) were reported as parts per million (ppm) downfield from tetramethylsilane and the proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (br). HRMS spectra were recorded on a Waters Q-TOF Premier. Melting points were measured with YRT-3 melting point apparatus (Shantou Keyi Instrument & Equipment Co., Ltd., Shantou, China). Commercial reagents were from Best-reagent (Homepage: http://www.best-reagent.com) or Astatech Chemical Technology Co, Ltd. (Homepage: http://www.astabio-chem.com).

2. Preparation of substrates

2-Phenylisatogens$^1$-$^3$, internal alkynes ($2a$-$2j$ and $2l$)$^4$ and sulfonyl azides$^5$ were prepared according to the procedure described in the literatures. Compounds $2m$-$2o$ and $2k$ are commercially available.

1) Preparation of 2-phenylisatogens
Following a literature procedure\textsuperscript{1-3}, 1-Iodo-2-nitrobenzene (2.0 mmol) was dissolved in freshly distilled triethylamine (8.0 mL) to which alkyne (2.0 eq) was added. The reaction was stirred at ambient temperature under Ar for 30 min at which point Pd(Ph\textsubscript{3}P\textsubscript{2})\textsubscript{2}Cl\textsubscript{2} (3 mol\%) and CuI (10 mol\%) were added. The mixture was stirred at room temperature for 12 h and monitored by TLC. The reaction mixture was filtered and washed with ethyl acetate. Then the combined solutions were evaporated to dryness, leaving an oil. The crude product was dissolved in CH\textsubscript{3}CN (8.0 mL) and HOAc (2.0 mL), stirred at 45 ºC for 24 h. The reaction mixture was concentrated, and the residue obtained was purified by column chromatography (ethyl acetate in petroleum ether) to afford the desired product.

\textbf{2) Preparation of internal aryl alkynes via the Sonogashira reaction}

According to the classical Sonogashira procedure\textsuperscript{4}, a dry round bottle was charged with aryl iodide (2.0 mmol), Pd(Ph\textsubscript{3}P\textsubscript{2})\textsubscript{2}Cl\textsubscript{2} (5 mol\%) and CuI (10 mol\%). The mixture was vacuumed and flushed with Ar for three times. Et\textsubscript{3}N (4.0 mL) and the alkyne substrate (1.2 eq) was then added. The mixture was stirred at room temperature until all the aryl iodide was consumed. The reaction mixture was diluted with ethyl acetate, washed with water and brine, dried with anhydrous Na\textsubscript{2}SO\textsubscript{4}, and filtered. The filtrate was concentrated under vacuum. The residue was purified through silica gel flash chromatography.

\textbf{3) Preparation of sulfonyl azides}\textsuperscript{5}

Organic chloride (1.0 mmol) was taken in a 25 mL round bottom flask charged with a magnetic stirring bar and dissolved in 5 mL acetone. Aqueous solution of NaN\textsubscript{3} (1.5 mmol in 5 mL water) was added dropwise to the reaction mixture. Then the reaction mixture was allowed to stir at room temperature for overnight. After completion of the reaction, acetone was removed under reduced pressure and the aqueous layer was extracted with ethyl acetate for several times. The combined organic layers were dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and concentrated in vacuum. The residue was purified using silica gel column chromatography (petroleum ether / ethyl acetate).
3. Optimization of the C–H sulfamidation reaction

Table S1. Optimization of the C–H sulfamidation reaction

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Sliver salt</th>
<th>Additive</th>
<th>Solvent</th>
<th>T/°C</th>
<th>t/h</th>
<th>Yield b (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>[IrCp*Cl₂₂]</td>
<td>AgNTf₂</td>
<td>—</td>
<td>DCE</td>
<td>rt</td>
<td>24</td>
<td>N.R.</td>
</tr>
<tr>
<td>2</td>
<td>[IrCp*Cl₂₂]</td>
<td>AgNTf₂</td>
<td>HOAc</td>
<td>DCE</td>
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<td>24</td>
<td>10</td>
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<tr>
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<td>[IrCp*Cl₂₂]</td>
<td>AgNTf₂</td>
<td>HOAc</td>
<td>DCE</td>
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<td>24</td>
<td>80</td>
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<tr>
<td>4</td>
<td>[RhCp*Cl₂₂]</td>
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<td>HOAc</td>
<td>DCE</td>
<td>90</td>
<td>24</td>
<td>N.R.</td>
</tr>
<tr>
<td>5</td>
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<tr>
<td>6</td>
<td>[Ru(ρ-cymene)Cl₂₂]</td>
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<td>HOAc</td>
<td>TFE</td>
<td>rt</td>
<td>5</td>
<td>90</td>
</tr>
</tbody>
</table>

* Reaction conditions: 1a (0.1 mmol), 4a (0.2 mmol), catalyst (5 mol%), sliver salt (20 mol%), additive (0.2 mmol) and solvent (1.0 mL), under Ar. b Isolated yields by chromatography on silica gel.
We started our investigation with 2-phenylisatogen 1a and TsN$_3$ 4a as the model substrates. Initially, in presence of [IrCp*Cl$_2$]$_2$, AgNTf$_2$ in DCE under argon at room temperature for 24 h (Table S1, entry 1). However, there was no reaction. When we turned our attention to HOAc, we were glad to find that the desired product 5aa was formed albeit in low yield (Table S1, entry 2). Gratifyingly, the desired product 5aa was isolated with improved 80% yield when we increased the temperature (Table S1, entry 3). [IrCp*Cl$_2$]$_2$ is crucial for this transformation, for all other catalysts, such as [Cp*RhCl$_2$]$_2$, [Ru($p$-cymene)Cl$_2$]$_2$ and [Cp*CoI$_2$]$_2$, failed to promote this reaction (Table S1, entries 4-6). Interestingly, when AgNTf$_2$ was replaced with either AgSbF$_6$, AgBF$_4$ or AgOTf, poor yields were obtained (Table S1, entries 7-9). Changing the additive from HOAc to pivalic acid or 1-adamantanecarboxylic acid gave similar results (Table S1, entries 10 and 11). Further optimization of solvents showed that TFE was a better solvent than DCE, with the isolation of 5aa in 86% yield (Table S1, entry 16). Finally, the reaction temperature and time were evaluated. The yield was not decreased by bringing the temperature down to room temperature and shortening the reaction time to 5 h (Table S1, entries 17 and 18). Thus, the optimal conditions for the reaction as follows: 5 mol% [Cp*IrCl$_2$]$_2$, 20 mol% AgNTf$_2$, 2.0 equiv. of HOAc and 2.0 equiv. of TsN$_3$ in TFE under argon at room temperature for 5 h.

4. Experimental procedures

1) General procedure for the synthesis of 3 (taking 3aa as an example):

A 15 mL sealed tube was charged with 2-phenylisatogen 1a (22.3 mg, 0.1 mmol), 1-phenyl-1-hexyne 2a (31.6 mg, 0.2 mmol), [Ru($p$-cymene)Cl$_2$]$_2$ (3.1 mg, 0.005 mmol), AgSbF$_6$ (7.9 mg, 0.02 mmol), Cu(OAc)$_2$ (18.2 mg, 0.1 mmol) and DCE (1.0 mL). The mixture was stirred at 80 °C for 28 h under Ar atmosphere and monitored by TLC. Then the solvent was evaporated in vacuo. The residue was further purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as the eluent to get yellow solid 3aa.

2) General procedure for the synthesis of 5 (taking 5aa as an example):
A 15 mL test tube with a magnetic stir bar was charged with 2-phenylisatogen 1a (22.3 mg, 0.1 mmol), TsN₃ 4a (39.5 mg, 0.20 mmol), [IrCp*Cl₂]₂ (2.0 mg, 0.005 mmol), AgNTf₂ (7.8 mg, 0.020 mmol), HOAc (12.0 mg, 0.2 mmol) and TFE (1.0 mL). The mixture was stirred at rt for 5 h under Ar atmosphere and monitored by TLC. Then the solvent was evaporated in vacuo and the residue was further purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as the eluent to get orange solid 5aa.

5. Characterization data of products

3-butyl-2-phenylspiro[indene-1,2'-indolin]-3'-one (3aa)

Yellow solid, yield 81%, m.p: 51 - 52 °C; ¹H NMR (400 MHz, DMSO-d₆) δ 7.71 (s, 1H), 7.49 - 7.37 (m, 3H), 7.39 - 7.30 (m, 1H), 7.28 (t, J = 7.2 Hz, 2H), 7.26 - 7.17 (m, 1H), 7.18 - 7.08 (m, 3H), 6.91 (t, J = 8.0 Hz, 2H), 6.68 (t, J = 7.2 Hz, 1H), 2.63 - 2.52 (m, 2H), 1.66 - 1.51 (m, 2H), 1.40 - 1.29 (m, 2H), 0.82 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, DMSO-d₆) δ 198.3, 162.5, 145.1, 143.2, 143.1, 140.8, 137.7, 134.3, 128.3, 128.2, 128.2, 127.4, 125.9, 124.6, 120.5, 120.4, 120.2, 117.1, 112.4, 81.3, 30.4, 25.3, 22.0, 13.7; HRMS (ESI): calcd for C₂₆H₂₃NO [M + Na]⁺ 388.1672, found 388.1675.

3-butyl-5-methyl-2-phenylspiro[indene-1,2'-indolin]-3'-one (3ba)

Yellow solid, yield 78%, m.p: 74 - 75 °C; ¹H NMR (600 MHz, DMSO-d₆) δ 7.67 (s, 1H), 7.43 (t, J = 7.8 Hz, 1H), 7.40 (d, J = 7.8 Hz, 1H), 7.29-7.25 (m, 3H), 7.21 (t, J = 7.2 Hz, 1H), 7.13 (d, J = 7.8 Hz, 2H), 6.93 (d, J = 7.8 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 6.80 (d, J = 7.8 Hz, 1H), 6.67 (t, J = 7.2 Hz, 1H), 2.57 - 2.35 (m, 2H), 2.35 (s, 3H), 1.62 - 1.55 (m, 2H), 1.36 - 1.31 (m, 2H), 0.82 (t, J = 7.2 Hz, 3H); ¹³C NMR (150 MHz, DMSO-d₆) δ 197.4, 162.9, 148.8, 145.0, 143.3, 143.0, 141.0, 134.4, 128.3, 128.2, 128.2, 127.4, 125.9, 124.4, 120.4, 120.2, 118.9,
3-butyl-5-methoxy-2-phenylspiro[indene-1,2'-indolin]-3'-one (3ca)

Yellow syrup, yield 72%; \( ^1H \text{NMR} \) (400 MHz, DMSO-\( d_6 \)) \( \delta \)
7.67 (s, 1H), 7.45 – 7.37 (m, 2H), 7.27 (t, \( J = 7.2 \) Hz, 2H),
7.23 – 7.19 (m, 1H), 7.13 (d, \( J = 1.6 \) Hz, 1H), 7.11 (s, 1H),
6.98 (d, \( J = 2.4 \) Hz, 1H), 6.88 (d, \( J = 8.0 \) Hz, 1H), 6.82 (d, \( J =
8.0 \) Hz, 1H), 6.69 – 6.62 (m, 2H), 3.78 (s, 3H); \( ^13C \text{NMR} \) (100 MHz, DMSO-\( d_6 \)) \( \delta \)
198.6, 162.4, 160.0, 146.7, 143.0, 142.0, 137.5, 134.7, 134.3, 135.1, 128.1, 124.5, 121.1, 120.3, 117.0, 112.3, 110.6, 106.7, 80.7, 55.4, 30.4,

3,5-dibutyl-2-phenylspiro[indene-1,2'-indolin]-3'-one (3da)

Yellow solid, yield 68%, m.p: 160 – 161 °C; \( ^1H \text{NMR} \) (400 MHz, DMSO-\( d_6 \)) \( \delta \)
7.68 (s, 1H), 7.47 – 7.37 (m, 2H), 7.31 – 7.18 (m, 4H), 7.13 (d, \( J = 7.2 \) Hz, 2H), 6.94 (d, \( J = 7.6 \) Hz, 1H), 6.89 (d, \( J = 8.4 \) Hz, 1H), 6.81 (d, \( J = 7.6 \) Hz, 1H), 6.67 (t, \( J = 7.2 \) Hz, 1H), 2.64 – 2.60 (m, 2H), 2.59 – 2.52 (m, 2H),
1.61 – 1.53 (m, 4H), 1.37 – 1.30 (m, 4H), 0.91 (t, \( J = 7.2 \) Hz, 3H), 0.82 (t, \( J = 7.2 \) Hz, 3H); \( ^13C \text{NMR} \) (100 MHz, DMSO-\( d_6 \)) \( \delta \)
198.6, 162.5, 145.3, 143.3, 142.7, 140.9, 140.4, 137.6, 134.4, 128.2, 127.3, 125.9, 124.6, 120.4, 120.2, 117.0, 112.3, 81.0, 35.0, 30.4, 26.4, 25.2, 21.9, 21.8, 13.8, 13.7; HRMS (ESI): calcd for C\(_{30}\)H\(_{31}\)NO \([M + Na]^+ \) 444.2298, found 444.2301.

3-butyl-5-fluoro-2-phenylspiro[indene-1,2'-indolin]-3'-one (3ea)

Yellow solid, yield 56%, m.p: 46 – 47 °C, \( ^1H \text{NMR} \) (400 MHz,
DMSO-\( d_6 \)) \( \delta \)
7.74 (s, 1H), 7.48 – 7.38 (m, 2H), 7.34 – 7.25 (m, 3H), 7.25 – 7.20 (m, 1H), 7.16 – 7.08 (m, 2H), 6.92 (dd, \( J =
10.4, 7.6 Hz, 3H), 6.68 (t, J = 7.2 Hz, 1H), 2.63 – 2.51 (m, 2H), 1.58 – 1.50 (m, 2H),
1.37 – 1.28 (m, 2H), 0.81 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, DMSO-d6) δ
198.0, 162.8 (d, J=241 Hz), 162.5,147.6 (d, J=9 Hz), 143.0, 142.5 (d, J=3 Hz),
138.6(d, J=2 Hz), 137.8, 133.9, 128.3, 128.1, 127.6, 124.7, 121.8 (d, J=9 Hz), 120.2,
117.3, 112.40, 112.2 (d, J=23 Hz), 107.8 (d, J=24 Hz), 80.7, 30.3, 25.1, 21.9, 13.6;
19F NMR (376 MHz, DMSO-d6) δ -113.92; HRMS (ESI): calcd for C26H22FNO [M +
Na]+ 406.1578, found 406.1580.

3-butyl-5-chloro-2-phenylspiro[indene-1,2'-indolin]-3'-one (3fa)

Yellow solid, yield 60%, m.p: 173 – 175 °C; 1H NMR (400 MHz, DMSO-d6) δ 7.79 (s, 1H), 7.50 – 7.44 (m, 2H), 7.44 –
7.38 (m, 2H), 7.29 (t, J = 7.2 Hz, 2H), 7.25 – 7.20 (m, 1H),
7.17 – 7.06 (m, 2H), 6.97 – 6.86 (m, 2H), 6.71 (t, J = 7.6 Hz,
1H), 2.63 – 2.51 (m, 2H), 1.62 – 1.48 (m, 2H), 1.37 – 1.27 (m,
2H), 0.81 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, DMSO-d6) δ 197.4, 162.5, 145.0,
143.9, 142.4, 141.6, 137.9, 133.8, 130.4, 128.2 (2s), 128.1, 127.6, 124.7, 121.6, 120.5,
120.1, 117.4, 112.5, 80.9, 30.2, 25.1, 21.8, 13.6; HRMS (ESI): calcd for C26H22ClNO [M +
Na]+ 422.1282, found 422.1288.

5-bromo-3-butyl-2-phenylspiro[indene-1,2'-indolin]-3'-one (3ga)

Yellow solid, yield 55%, m.p: 116 – 118 °C; 1H NMR (400 MHz, DMSO-d6) δ 7.77 (s, 1H), 7.63 (d, J = 2.0 Hz, 1H), 7.50
– 7.38 (m, 2H), 7.35 – 7.19 (m, 4H), 7.12 (d, J = 7.2 Hz, 2H),
6.90 (dd, J = 12.0, 8.0 Hz, 2H), 6.69 (t, J = 7.6 Hz, 1H), 2.60 –
2.51 (m, 2H), 1.59 – 1.49 (m, 2H), 1.39 – 1.25 (m, 2H), 0.81 (t,
J = 7.2 Hz, 3H); 13C NMR (100 MHz, DMSO-d6) δ 197.5, 162.4, 147.5, 142.6, 142.4,
142.1, 137.8, 133.7, 128.4, 128.2, 128.1, 127.6, 124.7, 123.0, 122.3, 121.5, 120.2,
117.3, 112.4, 80.9, 30.3, 24.9, 21.8, 13.6; HRMS (ESI): calcd for C26H22BrNO [M +
Na]+ 466.0777, found 466.0781.

3-butyl-2-phenyl-5-(trifluoromethyl)spiro[indene-1,2'-indolin]-3'-one (3ha)

s8
Yellow solid, yield 46%, m.p: 154 – 157 °C; \(^1\)H NMR (600 MHz, DMSO-\(d_6\)) \(\delta\) 7.83 (s, 1H), 7.74 (s, 1H), 7.49 (dd, \(J = 18.0, 7.8\) Hz, 2H), 7.44 (d, \(J = 7.8\) Hz, 1H), 7.34 – 7.28 (m, 2H), 7.28 – 7.23 (m, 1H), 7.16 (d, \(J = 7.8\) Hz, 3H), 6.95 (d, \(J = 8.4\) Hz, 1H), 6.71 (t, \(J = 7.2\) Hz, 1H), 2.65 – 2.62 (m, 2H), 1.58 – 1.36 (m, 2H), 1.36 – 1.31 (m, 2H), 0.80 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 197.1, 162.5, 147.3, 146.0, 143.0, 142.4, 137.9, 133.6, 129.2 (q, \(J \approx 31\) Hz), 128.2, 128.1, 127.7, 125.7, 124.7, 123.0 (d, \(J = 5\) Hz), 121.1, 120.2, 117.4, 116.4 (d, \(J = 4\) Hz), 112.5, 81.2, 30.2, 24.8, 21.7, 13.5; \(^{19}\)F NMR (376 MHz, DMSO-\(d_6\)) \(\delta\) -60.54; HRMS (ESI): calcd for C\(_{27}\)H\(_{22}\)F\(_3\)NO \([\text{M + Na}^+]\) 456.1546, found 456.1551.

\(n\)-Butyl-6-methyl-2-phenylspiro[indene-1,2'-indolin]-3'-one (3ia)

Yellow solid, yield 79%, m.p: 57 – 59 °C, \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.71 (s, 1H), 7.48 – 7.38 (m, 2H), 7.33 – 7.24 (m, 3H), 7.20 (t, \(J = 7.2\) Hz, 1H), 7.17 – 7.10 (m, 3H), 6.90 (d, \(J = 8.4\) Hz, 1H), 6.73 (s, 1H), 6.68 (t, \(J = 7.2\) Hz, 1H), 2.58 – 2.54 (m, 2H), 2.24 (s, 3H), 1.62 – 1.54 (m, 2H), 1.37 – 1.30 (m, 2H), 0.82 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 198.4, 162.4, 143.3, 143.1, 142.5, 139.8, 137.6, 135.3, 134.4, 128.7, 128.1, 128.1, 127.2, 124.6, 121.1, 120.3, 119.9, 117.0, 112.3, 81.1, 30.4, 25.3, 21.9, 20.8, 13.6; HRMS (ESI): calcd for C\(_{27}\)H\(_{25}\)NO \([\text{M + Na}^+]\) 402.1828, found 402.1830.

\(n\)-Butyl-6-chloro-2-phenylspiro[indene-1,2'-indolin]-3'-one (3ja)

Yellow solid, yield 58%, m.p: 199 – 201 °C, \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.77 (s, 1H), 7.49-7.46 (m, 2H), 7.44 – 7.38 (m, 2H), 7.29 (t, \(J = 7.2\) Hz, 2H), 7.25 – 7.20 (m, 1H), 7.13 (d, \(J = 7.6\) Hz, 2H), 6.96 – 6.88 (m, 2H), 6.71 (t, \(J = 7.2\) Hz, 1H), 2.64 – 2.52 (m, 2H), 1.64 – 1.48 (m, 2H), 1.42 – 1.25 (m, 2H), 0.81 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz,
DMSO-\(d_6\) \(\delta\) 197.7, 162.6, 145.1, 144.1, 142.6, 141.7, 138.1, 133.9, 130.5, 128.4, 128.2, 127.7, 124.9, 121.8, 120.7, 120.2, 117.6, 112.6, 81.1, 30.4, 25.2, 22.0, 13.7; HRMS (ESI): calcd for C\(_{28}\)H\(_{22}\)ClNO [M + Na]\(^{+}\) 422.1282, found 422.1280.

3-butyl-6'-methyl-2-phenylspiro[indene-1,2'-indolin]-3'-one (3ka)

Yellow solid, yield 66%, m.p: 54 – 56 °C, \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.66 (s, 1H), 7.43 (d, \(J = 7.6\) Hz, 1H), 7.35 (d, \(J = 7.6\) Hz, 1H), 7.29 (t, \(J = 8.0\) Hz, 3H), 7.23 (d, \(J = 7.2\) Hz, 1H), 7.16 – 7.08 (m, 3H), 6.91 (d, \(J = 7.6\) Hz, 1H), 6.70 (s, 1H), 6.51 (d, \(J = 8.0\) Hz, 1H), 2.61 – 2.52 (m, 2H), 2.29 (s, 3H), 1.63 – 1.53 (m, 2H), 1.37 – 1.30 (m, 2H), 0.82 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (150 MHz, DMSO-\(d_6\)) \(\delta\) 198.6, 162.5, 145.3, 143.2, 141.0, 140.2, 137.7, 137.6, 134.4, 128.2, 128.2, 127.3, 126.4, 124.6, 120.9, 120.3, 120.2, 117.0, 112.3, 81.0, 30.4, 25.3, 22.0, 21.2, 13.7; HRMS (ESI): calcd for C\(_{27}\)H\(_{25}\)NO [M + Na]\(^{+}\) 402.1829, found 402.1829.

3-butyl-6'-methoxy-2-phenylspiro[indene-1,2'-indolin]-3'-one (3la)

Light yellow oil, yield 40%; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.74 (s, 1H), 7.43 (d, \(J = 7.6\) Hz, 1H), 7.35 – 7.28 (m, 4H), 7.23 (t, \(J = 7.2\) Hz, 1H), 7.16 – 7.10 (m, 3H), 6.94 (d, \(J = 7.2\) Hz, 1H), 6.32 (d, \(J = 2.0\) Hz, 1H), 6.26 (dd, \(J = 8.8, 2.0\) Hz, 1H), 3.80 (s, 3H), 2.59 – 2.54 (m, 2H), 1.63 – 1.53 (m, 2H), 1.38 – 1.30 (m, 2H), 0.82 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 195.4, 167.4, 164.6, 145.0, 143.5, 142.9, 141.1, 134.4, 128.2, 128.2, 128.2, 127.3, 126.1, 125.9, 120.5, 120.1, 113.9, 107.4, 94.0, 81.7, 55.6, 30.4, 25.3, 22.0, 13.7; HRMS (ESI): calcd for C\(_{27}\)H\(_{25}\)NO\(_2\) [M + Na]\(^{+}\) 418.1778, found 418.1772.

methyl 3-butyl-3'-oxo-2-phenylspiro[indene-1,2'-indoline]-6'-carboxylate (3ma)

Yellow oil, yield 50%; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 8.02 (s, 1H), 7.53 (d, \(J = 8.0\) Hz, 1H), 7.48 – 7.42 (m, 2H), 7.37 (t, \(J = 7.6\) Hz, 1H), 7.29 (t, \(J = 7.2\) Hz, 2H), 7.24 – 7.19 (m, 2H), 7.14 (t, \(J = 7.2\) Hz, 3H), 6.97 (d, \(J = 8.0\) Hz, 1H), 2.18 (s, 3H), 1.61 – 1.53 (m, 2H), 1.38 – 1.30 (m, 2H), 0.82 (t, \(J = 7.3\) Hz, 3H); HRMS (ESI): calcd for C\(_{27}\)H\(_{25}\)NO\(_2\) [M + Na]\(^{+}\) 418.1778, found 418.1772.
= 7.2 Hz, 1H), 3.86 (s, 3H), 2.62 – 2.53 (m, 2H), 1.63 – 1.54 (m, 2H), 1.38 – 1.29 (m, 2H), 0.82 (t, J = 7.2 Hz, 3H); \(^1\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 198.6, 165.8, 162.0, 145.0, 143.7, 142.4, 140.4, 137.5, 134.0, 128.6, 128.3, 128.2, 127.5, 126.2, 125.0, 123.2, 120.7, 120.4, 117.2, 112.9, 81.8, 52.6, 30.4, 25.2, 22.0, 13.7; HRMS (ESI): calcd for C\(_{28}\)H\(_{25}\)NO\(_3\) [M + Na]\(^+\) 446.1727, found 446.1732.

3-butyl-2-(p-tolyl)spiro[indene-1,2'-indolin]-3'-one (3ab)

Yellow solid, yield 74%, m.p: 52 – 54°C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.69 (s, 1H), 7.46 – 7.40 (m, 3H), 7.34 (t, J = 7.6 Hz, 1H), 7.14 – 7.02 (m, 5H), 6.92 – 6.89 (m, 2H), 6.68 (t, J = 7.2 Hz, 1H), 2.62 – 2.52 (m, 2H), 2.23 (s, 3H), 1.63 – 1.54 (m, 2H), 1.38 – 1.32 (m, 2H), 0.84 (t, J = 7.3 Hz, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 198.9, 163.0, 145.7, 143.5, 143.3, 141.3, 138.1, 137.1, 131.8, 129.3, 128.8, 128.5, 126.3, 125.1, 120.9, 120.8, 120.5, 117.5, 112.8, 81.7, 30.9, 25.8, 22.5, 21.2, 14.2; HRMS (ESI): calcd for C\(_{27}\)H\(_{23}\)NO [M + Na]\(^+\) 402.1828, found 402.1834.

3-butyl-2-(4-methoxyphenyl)spiro[indene-1,2'-indolin]-3'-one

Yellow solid, yield 71%, m.p: 44 – 45°C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.69 (s, 1H), 7.45 (t, J = 7.2 Hz, 1H), 7.41 (d, J = 7.6 Hz, 2H), 7.33 (t, J = 7.6 Hz, 1H), 7.12 – 7.05 (m, 3H), 6.92 – 6.89 (m, 2H), 6.68 (t, J = 7.2 Hz, 1H), 2.62 – 2.52 (m, 2H), 2.23 (s, 3H), 1.63 – 1.54 (m, 2H), 1.38 – 1.32 (m, 2H), 0.84 (t, J = 7.3 Hz, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 198.5, 162.5, 158.5, 145.3, 143.0, 142.4, 140.6, 137.7, 129.4, 128.3, 126.4, 125.7, 124.6, 120.4, 120.4, 120.0, 117.1, 113.7, 112.4, 81.3, 54.9, 30.4, 25.3, 22.1, 13.7; HRMS (ESI): calcd for C\(_{27}\)H\(_{28}\)NO\(_2\) [M + Na]\(^+\) 418.1778, found 418.1781.

3-butyl-2-(4-fluorophenyl)spiro[indene-1,2'-indolin]-3'-one (3ad)

Yellow oil, yield 60%; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.73 (s, 1H), 7.48 – 7.42 (m, 2H), 7.40 (d, J = 7.6 Hz, 1H), 7.35 (t, 1H), 7.18 – 7.13 (m, 2H), 7.00 – 6.94 (m, 2H), 6.89 (t, J = 7.6 Hz, 1H), 2.62 – 2.52 (m, 2H), 2.23 (s, 3H), 1.63 – 1.54 (m, 2H), 1.38 – 1.32 (m, 2H), 0.84 (t, J = 7.3 Hz, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 198.5, 162.5, 158.5, 145.3, 143.0, 142.4, 140.6, 137.7, 129.4, 128.3, 126.4, 125.7, 124.6, 120.4, 120.4, 120.0, 117.1, 113.7, 112.4, 81.3, 54.9, 30.4, 25.3, 22.1, 13.7; HRMS (ESI): calcd for C\(_{27}\)H\(_{25}\)NO\(_2\) [M + Na]\(^+\) 418.1778, found 418.1781.

3-butyl-2-(4-fluorophenyl)spiro[indene-1,2'-indolin]-3'-one (3ad)
\[ J = 7.6 \text{ Hz, 1H}), 7.22 - 7.08 \text{ (m, 5H), 6.93 (t, } J = 7.6 \text{ Hz, 2H), 6.68 (t, } J = 7.2 \text{ Hz, 1H), 2.61 - 2.51 \text{ (m, 2H), 1.61 - 1.53 \text{ (m, 2H), 1.38 - 1.29 \text{ (m, 2H), 0.82 (t, } J = 7.2 \text{ Hz, 3H);} \]

\(^{13}\text{C NMR}\) (100 MHz, DMSO-\(d_6\)) \(\delta\) 198.2, 162.4, 161.4 (d, \(J = 243 \text{ Hz}\)), 144.9, 143.5, 142.9, 139.7, 137.7, 130.50 (d, \(J = 3 \text{ Hz}\)), 130.4 (d, \(J = 8 \text{ Hz}\)), 128.3, 126.0, 124.5, 120.5, 120.3, 120.2, 117.1, 115.1 (d, \(J = 21 \text{ Hz}\)), 112.3, 81.3, 30.3, 25.1, 21.85, 13.6;

\(^{19}\text{F NMR}\) (376 MHz, DMSO-\(d_6\)) \(\delta\) -114.39; HRMS (ESI): calecd for C\(_{26}\)H\(_{22}\)FNO [M + Na\(^+\)] 406.1578, found 406.1576.

3-buty1-2-(4-chlorophenyl)spiro[indene-1,2'-indolin]-3'-one (3ae)

Yellow solid, yield 77%, m.p: 42 – 43 °C; \(^1\text{H NMR}\) (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.72 (s, 1H), 7.49 – 7.43 (m, 2H), 7.41 (d, \(J = 8.0 \text{ Hz, 1H}), 7.37 (d, \(J = 8.8 \text{ Hz, 3H}), 7.14 (dd, \(J = 8.0, 6.0 \text{ Hz, 3H}), 6.96 – 6.89 (m, 2H), 6.70 (t, \(J = 7.6 \text{ Hz, 1H}), 2.61 – 2.52 (m, 2H), 1.62 – 1.53 (m, 2H), 1.38 – 1.29 (m, 2H), 0.83 (t, \(J = 7.2 \text{ Hz, 3H);} \]

\(^{13}\text{C NMR}\) (100 MHz, DMSO-\(d_6\)) \(\delta\) 198.2, 162.5, 144.8, 143.9, 142.9, 139.4, 137.8, 133.1, 132.2, 130.0, 128.4, 128.4, 126.2, 124.7, 120.6, 120.4, 120.3, 117.3, 112.4, 81.3, 30.4, 25.2, 21.9, 13.7; HRMS (ESI): calecd for C\(_{26}\)H\(_{22}\)ClNO [M + Na\(^+\)] 422.1282, found 422.1283.

2-(4-bromophenyl)-3-buty1spiro[indene-1,2'-indolin]-3'-one (3af)

Yellow solid, yield 61%, m.p: 52 – 53 °C; \(^1\text{H NMR}\) (600 MHz, DMSO-\(d_6\)) \(\delta\) 7.73 (s, 1H), 7.57 – 7.43 (m, 4H), 7.41 (d, \(J = 7.8 \text{ Hz, 1H}), 7.36 (t, \(J = 7.8 \text{ Hz, 1H}), 7.14 (t, \(J = 7.8 \text{ Hz, 1H}), 7.12 – 7.03 (m, 2H), 6.93 (t, \(J = 8.4 \text{ Hz, 2H}), 6.70 (t, \(J = 7.8 \text{ Hz, 1H}), 2.57 – 2.54 (m, 2H), 1.60 – 1.54 (m, 2H), 1.35 – 1.33 (m, 2H), 0.83 (t, \(J = 7.2 \text{ Hz, 3H);} \]

\(^{13}\text{C NMR}\) (100 MHz, DMSO-\(d_6\)) \(\delta\) 198.1, 162.5, 144.8, 143.9, 143.0, 139.5, 137.8, 133.5, 131.3, 130.3, 128.4, 126.2, 124.7, 120.8, 120.6, 120.4, 120.3, 117.3, 112.4, 81.2, 30.4, 25.2, 21.9, 13.7; HRMS (ESI): calecd for C\(_{26}\)H\(_{22}\)BrNO [M + Na\(^+\)] 466.0777, found 466.0779.
methyl 4-(3-butyl-3'-oxospiro[indene-1,2'-indolin]-2-yl)benzoate (3ag)

Yellow solid, yield 64%, m.p: 166 – 168 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.91 – 7.83 (m, 2H), 7.75 (s, 1H), 7.51 – 7.40 (m, 3H), 7.37 (t, \(J = 7.6\) Hz, 1H), 7.28 (d, \(J = 8.4\) Hz, 2H), 7.16 (t, \(J = 7.6\) Hz, 1H), 6.96 – 6.91 (m, 2H), 6.70 (t, \(J = 7.2\) Hz, 1H), 3.81 (s, 3H), 2.67 – 2.54 (m, 2H), 1.63 – 1.54 (m, 2H), 1.37 – 1.30 (m, 2H), 0.82 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 198.0, 165.9, 162.5, 144.7, 144.7, 143.0, 139.7, 139.4, 137.9, 129.1, 128.5, 128.5, 128.4, 126.4, 124.7, 120.6, 120.5, 120.3, 117.3, 112.4, 81.3, 52.1, 30.4, 25.2, 21.9, 13.6; HRMS (ESI): calcd for C\(_{28}\)H\(_{25}\)NO\(_3\) [M + Na]\(^+\) 446.1727, found 446.1733.

3-butyl-2-(3-chlorophenyl)spiro[indene-1,2'-indolin]-3'-one (3ah)

Yellow oil, yield 82%; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.76 (s, 1H), 7.49 – 7.44 (m, 2H), 7.42 (d, \(J = 7.6\) Hz, 1H), 7.38 – 7.28 (m, 3H), 7.19 – 7.13 (m, 2H), 7.10 (dt, \(J = 7.2, 1.6\) Hz, 1H), 6.95 (dd, \(J = 7.6, 4.0\) Hz, 2H), 6.70 (t, \(J = 7.2\) Hz, 1H), 2.62 – 2.52 (m, 2H), 1.63 – 1.54 (m, 2H), 1.37 – 1.30 (m, 2H), 0.83 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (150 MHz, DMSO-\(d_6\)) \(\delta\) 198.1, 162.5, 144.7, 144.4, 142.9, 139.1, 137.9, 136.4, 132.8, 130.2, 128.4, 127.9, 127.4, 127.0, 126.3, 124.7, 120.6, 120.5, 120.3, 117.3, 112.4, 81.2, 30.3, 25.1, 21.9, 13.6; HRMS (ESI): calcd for C\(_{26}\)H\(_{22}\)ClNO [M + Na]\(^+\) 422.1282, found 422.1285.

methyl 3-(3-butyl-3'-oxospiro[indene-1,2'-indolin]-2-yl)benzoate (3ai)

Yellow solid, yield 68%, m.p: 160 – 161 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.83 – 7.80 (m, 1H), 7.79 (s, 1H), 7.53 – 7.31 (m, 7H), 7.15 (t, \(J = 7.2\) Hz, 1H), 6.95 (d, \(J = 7.2\) Hz, 1H), 6.92 (d, \(J = 8.4\) Hz, 1H), 6.70 (t, \(J = 7.6\) Hz, 1H), 2.63 – 2.54 (m, 2H), 1.68 – 1.53 (m, 2H), 1.43 – 1.28 (m, 2H), 0.82 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 198.2, 165.9, 162.6, 144.8, 144.3,
3-butyl-2-(thiophen-2-yl)spiro[indene-1,2'-indolin]-3'-one (3aj)

Yellow oil, yield 43%; \(^1H\) NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.85 (s, 1H), 7.57 (t, \(J = 7.6\) Hz, 1H), 7.51 – 7.43 (m, 3H), 7.35 (t, \(J = 7.6\) Hz, 1H), 7.13 (t, \(J = 7.2\) Hz, 1H), 7.04 (d, \(J = 8.2\) Hz, 1H), 7.00 (dd, \(J = 5.2, 3.6\) Hz, 1H), 6.90 (d, \(J = 7.2\) Hz, 1H), 6.83 – 6.76 (m, 2H), 2.90 – 2.85 (m, 2H), 1.69 – 1.61 (m, 2H), 1.56 – 1.47 (m, 2H), 0.96 (t, \(J = 7.2\) Hz, 3H); \(^{13}C\) NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 198.1, 162.6, 145.0, 142.7, 142.7, 138.0, 135.5, 133.2, 128.7, 127.4, 126.4, 126.3, 125.4, 124.9, 120.3, 120.2, 120.2, 117.7, 112.8, 80.6, 30.2, 25.9, 22.5, 13.9; HRMS (ESI): calcd for C\(_{23}\)H\(_{25}\)NO\(_3\) [M + Na]\(^+\) 446.1727, found 446.1730.

3-methyl-2-phenylspiro[indene-1,2'-indolin]-3'-one (3ak)

Yellow solid, yield 79%, m.p: 216 – 217 °C; \(^1H\) NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.70 (s, 1H), 7.54 – 7.39 (m, 3H), 7.36 (t, \(J = 7.2\) Hz, 1H), 7.31-7.27 (m, 2H), 7.23 (d, \(J = 7.2\) Hz, 1H), 7.20 – 7.10 (m, 3H), 6.94 (d, \(J = 8.4\) Hz, 1H), 6.91 (d, \(J = 7.6\) Hz, 1H), 6.72 (t, \(J = 7.6\) Hz, 1H), 2.22 (s, 3H); \(^{13}C\) NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 198.7, 162.6, 146.0, 142.9, 140.3, 139.1, 137.9, 134.2, 128.6, 128.4, 128.2, 127.4, 126.3, 124.8, 120.4, 120.2, 120.1, 117.4, 112.6, 81.2, 12.0; HRMS (ESI): calcd for C\(_{23}\)H\(_{17}\)NO [M + Na]\(^+\) 346.1202, found 346.1205.

3-cyclopropyl-2-phenylspiro[indene-1,2'-indolin]-3'-one (3al)

Yellow solid, yield 77%, m.p: 57 – 59 °C; \(^1H\) NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.72 (s, 1H), 7.49 – 7.41 (m, 3H), 7.34 (t, \(J = 7.2\) Hz, 1H), 7.27 – 7.21 (m, 5H), 7.12 (t, \(J = 7.2\) Hz, 1H), 6.96 – 6.84 (m, 2H), 6.70 (t, \(J = 7.2\) Hz, 1H), 1.96–1.91 (m, 1H), 0.92 – 0.84 (m, 2H), 0.55 – 0.46 (m, 2H); \(^{13}C\) NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 198.3, 162.5,
145.2, 143.4, 142.9, 137.8, 134.0, 128.4, 127.9, 127.4, 126.0, 124.7, 120.5, 120.3, 120.3, 117.2, 112.4, 80.9, 8.9, 6.8, 6.4; HRMS (ESI): calcd for \( \text{C}_{25}\text{H}_{19}\text{NO} \ [\text{M + Na}^+] 372.1359, \) found 372.1358.

**2,3-diphenylspiro[indene-1,2'-indolin]-3'-one (3am)**

Yellow solid, yield 56%, m.p: 223 – 224 °C; \(^{1}\text{H NMR} \) (400 MHz, DMSO-\( \text{d}_6 \)) \( \delta \) 7.88 (s, 1H), 7.55 – 7.47 (m, 2H), 7.44 (dd, \( J = 8.0, \) 6.4 Hz, 2H), 7.40 – 7.36 (m, 1H), 7.35 – 7.28 (m, 3H), 7.23 (d, \( J = 7.6 \) Hz, 1H), 7.19 (t, \( J = 7.6 \) Hz, 1H), 7.14 – 7.07 (m, 3H), 7.04 – 6.93 (m, 4H), 6.76 (t, \( J = 7.2 \) Hz, 1H);

\(^{13}\text{C NMR} \) (100 MHz, DMSO-\( \text{d}_6 \)) \( \delta \) 197.8, 162.5, 144.6, 143.0, 142.9, 141.9, 138.0, 133.9, 133.7, 128.9, 128.9, 128.5, 128.4, 128.0 (2s), 127.4, 126.5, 124.9, 120.8, 120.7, 120.3, 117.5, 112.6, 81.2; HRMS (ESI): calcd for \( \text{C}_{28}\text{H}_{19}\text{NO} \ [\text{M + Na}^+] \) 408.1359, found 408.1356.

**methyl 3'-oxo-2-phenylspiro[indene-1,2'-indoline]-3-carboxylate (3an)**

Yellow solid, yield 56%, m.p: 172 – 174°C; \(^{1}\text{H NMR} \) (400 MHz, DMSO-\( \text{d}_6 \)) \( \delta \) 7.92 (s, 1H), 7.70 (d, \( J = 7.6 \) Hz, 1H), 7.54 – 7.44 (m, 2H), 7.40 (t, \( J = 7.6 \) Hz, 1H), 7.32 – 7.24 (m, 3H), 7.22 (t, \( J = 7.6 \) Hz, 1H), 7.14 – 7.12 (m, 2H), 6.98 (dd, \( J = 15.2, \) 8.0 Hz, 2H), 6.74 (t, \( J = 7.6 \) Hz, 1H), 3.71 (s, 3H); \(^{13}\text{C NMR} \) (100 MHz, DMSO-\( \text{d}_6 \)) \( \delta \) 196.3, 164.4, 162.6, 152.7, 142.1, 141.0, 138.2, 133.0, 132.8, 128.7, 128.6, 128.0, 127.6, 126.9, 125.1, 122.2, 121.0, 120.0, 117.8, 112.6, 81.6, 51.8; HRMS (ESI): calcd for \( \text{C}_{24}\text{H}_{17}\text{NO}_3 \ [\text{M + Na}^+] \) 390.1101, found 390.1009.

**dimethyl 3'-oxospiro[indene-1,2'-indoline]-2,3-dicarboxylate (3ao)**

Yellow solid, yield 48% m.p: 153 – 155°C; \(^{1}\text{H NMR} \) (400 MHz, DMSO-\( \text{d}_6 \)) \( \delta \) 7.74 (s, 1H), 7.58 – 7.53 (m, 3H), 7.45 (t, \( J = 7.6 \) Hz, 1H), 7.36 (t, \( J = 7.6 \) Hz, 1H), 7.07 (d, \( J = 7.6 \) Hz, 1H), 7.02 (d, \( J = 8.0 \) Hz, 1H), 6.82 (t, \( J = 7.2 \) Hz, 1H), 3.94 (s, 3H), 3.60 (s, 3H); \(^{13}\text{C NMR} \) (100 MHz, DMSO-\( \text{d}_6 \)) \( \delta \) 195.2, 163.9, 162.7, 162.0,
144.2, 143.4, 138.9, 137.8, 137.1, 129.7, 129.3, 125.2, 123.1, 121.8, 120.8, 117.8, 112.9, 78.7, 52.8, 52.2; HRMS (ESI): calcd for C_{20}H_{15}NO_5 [M + Na]^+ 372.0842, found 372.0840.

2-(2-((4-methylphenyl)sulfonamido)phenyl)-3-oxo-3H-indole 1-oxide (5aa)

Orange solid, yield 91%, m.p: 203 – 205 °C; \(^1\)H NMR (400 MHz, DMSO-d_6) \(\delta \) 9.07 (s, 1H), 7.89–7.85 (m, 1H), 7.78 (d, \(J = 7.6 \) Hz, 1H), 7.75 – 7.70 (m, 2H), 7.60 – 7.55 (m, 1H), 7.47 (dd, \(J = 8.4, 1.6 \) Hz, 1H), 7.37 (m, 2H), 7.31 (d, \(J = 8.4 \) Hz, 2H), 6.98 (d, \(J = 8.0 \) Hz, 2H), 2.19 (s, 3H); \(^{13}\)C NMR (100 MHz, DMSO-d_6) \(\delta \) 183.8, 146.9, 143.4, 136.6, 136.1, 135.3, 135.1, 132.2, 132.0, 131.8, 129.6, 126.0, 125.7, 125.6, 123.0, 121.9, 118.7, 114.4, 20.9; HRMS (ESI): calcd for C_{21}H_{16}N_2O_4S [M + Na]^+ 415.0723, found 415.0720.

2-(4-methyl-2-((4-methylphenyl)sulfonamido)phenyl)-3-oxo-3H-indole 1-oxide (5ba)

Orange solid, yield 89%, m.p: 190 – 192 °C; \(^1\)H NMR (400 MHz, DMSO-d_6) \(\delta \) 8.92 (s, 1H), 7.90 – 7.83 (m, 1H), 7.76 (d, \(J = 7.6 \) Hz, 1H), 7.73 – 7.66 (m, 2H), 7.37 (d, \(J = 8.0 \) Hz, 1H), 7.28 – 7.20 (m, 4H), 6.89 (d, \(J = 8.0 \) Hz, 2H), 2.37 (s, 3H), 2.15 (s, 3H); \(^{13}\)C NMR (100 MHz, DMSO-d_6) \(\delta \) 184.1, 147.3, 143.8, 143.1, 137.0, 136.5, 135.9, 135.7, 132.4, 132.2, 130.0, 127.6, 127.5, 126.2, 123.3, 122.4, 116.7, 114.8, 21.6, 21.4; HRMS (ESI): calcd for C_{22}H_{18}N_2O_4S [M + Na]^+ 429.0879, found 429.0882.

2-(4-methoxy-2-((4-methylphenyl)sulfonamido)phenyl)-3-oxo-3H-indole 1-oxide (5ca)

Red solid, yield 90%, m.p: 173 – 175 °C; \(^1\)H NMR (400 MHz, DMSO-d_6) \(\delta \) 9.18 (s, 1H), 7.88 – 7.84 (m, 1H), 7.75 (d, \(J = 7.6 \) Hz, 1H), 7.72 – 7.65 (m, 2H), 7.43 (d, \(J = 8.8 \) Hz, 1H), 7.30 (d, \(J = 8.0 \) Hz, 2H), 7.01 (dd, \(J = 8.8, 2.0 \) Hz, 1H),
6.93 (d, \( J = 8.0 \) Hz, 3H), 3.82 (s, 3H), 2.16 (s, 3H); \(^{13}\text{C} \text{NMR} \) (100 MHz, DMSO-\( d_6 \)) \( \delta \) 183.9, 162.1, 146.9, 143.4, 138.4, 135.9, 135.5, 135.1, 133.6, 131.5, 129.6, 125.9, 122.8, 122.0, 114.3, 112.0, 111.4, 110.9, 55.7, 20.9; HRMS (ESI): calcld for C\(_{22}\)H\(_{18}\)N\(_2\)O\(_5\)S \([M + Na]^+\) 445.0829, found 445.0831.

2-(4-butyl-2-((4-methylphenyl)sulfonamido)phenyl)-3-oxo-3\textit{H}-indole 1-oxide (5da)

Orange solid, yield 90\%, m.p: 155 – 157 °C; \(^1\text{H} \text{NMR} \) (400 MHz, DMSO-\( d_6 \)) \( \delta \) 9.03 (s, 1H), 7.89 – 7.85 (m, 1H), 7.76 (d, \( J = 7.6 \) Hz, 1H), 7.72 – 7.69 (m, 2H), 7.38 (d, \( J = 8.0 \) Hz, 1H), 7.27 (d, \( J = 8.4 \) Hz, 2H), 7.22 (dd, \( J = 8.0 \), 1.6 Hz, 1H), 7.18 (d, \( J = 1.6 \) Hz, 1H), 6.95 (d, \( J = 8.0 \) Hz, 2H), 2.61 (t, \( J = 7.6 \) Hz, 2H), 2.17 (s, 3H), 1.55 – 1.47 (m, 2H), 1.28 – 1.19 (m, 2H), 0.88 (t, \( J = 7.6 \) Hz, 3H); \(^{13}\text{C} \text{NMR} \) (100 MHz, DMSO-\( d_6 \)) \( \delta \) 183.9, 147.0, 146.9, 143.3, 136.5, 136.0, 135.4, 135.2, 132.0, 131.7, 129.5, 126.2, 126.0, 126.0, 122.9, 121.9, 116.4, 114.3, 34.6, 32.6, 21.5, 20.9, 13.8; HRMS (ESI): calcld for C\(_{25}\)H\(_{24}\)N\(_2\)O\(_4\)S \([M + Na]^+\) 471.1349, found 471.1348.

2-(4-fluoro-2-((4-methylphenyl)sulfonamido)phenyl)-3-oxo-3\textit{H}-indole 1-oxide (5ea)

Orange solid, yield 85\%, m.p: 168 – 170 °C; \(^1\text{H} \text{NMR} \) (400 MHz, DMSO-\( d_6 \)) \( \delta \) 9.54 (s, 1H), 7.89 – 7.85 (m, 1H), 7.81 – 7.76 (m, 1H), 7.75 – 7.69 (m, 2H), 7.50 (m, 3H), 7.25 – 7.16 (m, 2H), 7.11 (d, \( J = 8.0 \) Hz, 2H), 2.24 (s, 3H); \(^{19}\text{F} \text{NMR} \) (376 MHz, DMSO-\( d_6 \)) \( \delta \) -107.09; HRMS (ESI): calcld for C\(_{21}\)H\(_{15}\)FN\(_2\)O\(_4\)S \([M + Na]^+\) 433.0629, found 433.0628.

2-(4-chloro-2-((4-methylphenyl)sulfonamido)phenyl)-3-oxo-3\textit{H}-indole 1-oxide
Orange solid, yield 75%, m.p: 150 – 152 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 9.30 (s, 1H), 7.91 – 7.84 (m, 1H), 7.78 (d, \(J = 7.6\) Hz, 1H), 7.74 (d, \(J = 4.4\) Hz, 2H), 7.61 (dd, \(J = 8.8, 2.4\) Hz, 1H), 7.51 (d, \(J = 2.4\) Hz, 1H), 7.41 (d, \(J = 8.0\) Hz, 2H), 7.36 (d, \(J = 8.8\) Hz, 1H), 7.08 (d, \(J = 8.0\) Hz, 2H), 2.23 (s, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 183.8, 146.9, 143.7, 136.0, 135.7, 135.3, 133.9, 132.0, 131.6, 131.4, 129.8, 129.4, 126.3 (2s), 123.1, 122.0, 120.1, 114.5, 21.0; HRMS (ESI): calcd for C\(_{21}\)H\(_{15}\)ClN\(_2\)O\(_4\)S \([\text{M + Na}]^+\) 449.0333, found 449.0336.

2-(4-bromo-2-((4-methylphenyl)sulfonamido)phenyl)-3-oxo-3\(^{1}\)H-indole 1-oxide (5ga)

Orange solid, yield 90%, m.p: 169 – 171 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 9.46 (s, 1H), 7.88–7.84 (m, 1H), 7.78 (d, \(J = 7.6\) Hz, 1H), 7.73 (d, \(J = 4.8\) Hz, 2H), 7.57 (dd, \(J = 8.6, 2.0\) Hz, 1H), 7.52 (d, \(J = 2.0\) Hz, 1H), 7.46 – 7.38 (m, 3H), 7.10 (d, \(J = 8.0\) Hz, 2H), 2.23 (s, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 183.8, 147.0, 143.8, 138.0, 135.9, 135.3, 134.3, 133.8, 131.9, 129.8, 128.3, 126.6, 126.3, 124.9, 123.1, 122.0, 117.3, 114.4, 21.0; HRMS (ESI): calcd for C\(_{21}\)H\(_{15}\)BrN\(_2\)O\(_4\)S \([\text{M + Na}]^+\) 492.9828, found 492.9826.

2-(2-((4-methylphenyl)sulfonamido)-4-(trifluoromethyl)phenyl)-3-oxo-3\(^{1}\)H-indole 1-oxide (5ha)

Orange solid, yield 32%, m.p: 168 – 170 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 9.71 (s, 1H), 7.92 – 7.85 (m, 1H), 7.79 (s, 1H), 7.75 (d, \(J = 6.0\) Hz, 2H), 7.69 (s, 2H), 7.58 (s, 1H), 7.50 (d, \(J = 8.0\) Hz, 2H), 7.17 (d, \(J = 8.0\) Hz, 2H), 2.26 (s, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 184.0, 147.1, 144.0, 137.5, 135.8, 135.2, 133.7, 133.5, 132.1, 131.3 (q, \(J = 32\) Hz) 129.8, 126.5, 123.4 (q, \(J = 272\) Hz), 123.3, 122.0, 121.6, 121.3 (d, \(J = 4\) Hz), 119.2 (d, \(J = 5\) Hz), 114.5, 21.0; \(^{19}\)F NMR
(376 MHz, DMSO-\(d_6\)) \(\delta\) -61.90; HRMS (ESI): calcd for \(C_{22}H_{18}F_3N_2O_4S\) [M + Na]\(^+\) 483.0597, found 483.0593.

2-(5-methyl-2-((4-methylphenyl)sulfonamido)phenyl)-3-oxo-3\(H\)-indole 1-oxide (5ia)

Orange solid, yield 88%, m.p: 130 – 132 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 8.86 (s, 1H), 7.87 (td, \(J = 7.2, 2.0\) Hz, 1H), 7.76 (d, \(J = 7.8\) Hz, 1H), 7.74 – 7.67 (m, 2H), 7.41 (dd, \(J = 8.4, 2.0\) Hz, 1H), 7.29 – 7.24 (m, 4H), 6.93 (d, \(J = 8.0\) Hz, 2H), 2.32 (s, 3H), 2.16 (s, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 183.7, 146.8, 143.2, 136.1, 135.5, 135.4, 135.2, 134.1, 132.8, 132.1, 131.8, 129.5, 126.7, 125.9, 122.8, 121.9, 119.2, 114.4, 20.9, 20.4; HRMS (ESI): calcd for \(C_{22}H_{18}N_2O_4S\) [M + Na]\(^+\) 429.0879, found 429.0878.

2-(5-chloro-2-((4-methylphenyl)sulfonamido)phenyl)-3-oxo-3\(H\)-indole 1-oxide (5ja)

Orange solid, yield 89%, m.p: 144 – 145 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 9.34 (s, 1H), 7.90 – 7.86 (m, 1H), 7.79 (d, \(J = 7.6\) Hz, 1H), 7.76 – 7.70 (m, 2H), 7.61 (dd, \(J = 8.8, 2.4\) Hz, 1H), 7.55 – 7.47 (m, 1H), 7.46 – 7.39 (m, 2H), 7.38 – 7.34 (m, 1H), 7.09 (d, \(J = 8.0\) Hz, 2H), 2.23 (s, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 183.6, 146.9, 143.5, 136.0, 135.7, 135.2, 133.8, 131.9, 131.5, 129.7, 129.4, 126.2, 126.2, 123.0, 121.9, 120.1, 114.4, 20.9; HRMS (ESI): calcd for \(C_{21}H_{15}ClN_2O_4S\) [M + Na]\(^+\) 449.0333, found 449.0332.

6-methyl-2-(2-((4-methylphenyl)sulfonamido)phenyl)-3-oxo-3\(H\)-indole 1-oxide (5ka)

Orange solid, yield 90%, m.p: 210 – 212 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 9.01 (s, 1H), 7.64 (s, 1H), 7.58 (t, \(J = 6.8\) Hz, 2H), 7.51 (d, \(J = 7.2\) Hz, 1H), 7.46 (d, \(J = 7.2\) Hz, 1H), 7.38 (t, \(J = 7.2\) Hz, 2H), 7.28 (d, \(J = 8.0\) Hz, 2H), 6.96 (d, \(J = 8.0\) Hz, 2H), 2.18 (s, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 183.6, 146.9, 143.5, 136.0, 135.7, 135.2, 133.8, 131.9, 131.5, 129.7, 129.4, 126.2, 126.2, 123.0, 121.9, 120.1, 114.4, 20.9; HRMS (ESI): calcd for \(C_{21}H_{15}ClN_2O_4S\) [M + Na]\(^+\) 449.0333, found 449.0332.
8.0 Hz, 2H), 2.55 (s, 3H), 2.18 (s, 3H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$ 183.4, 147.3, 147.1, 143.4, 136.7, 136.0, 135.4, 132.2, 132.1, 131.8, 129.6, 126.3, 126.0, 125.9, 122.0, 120.5, 119.2, 115.2, 21.8, 21.0; HRMS (ESI): calcd for C$_{22}$H$_{18}$N$_2$O$_5$S $[M + Na]^+$ 429.0879, found 429.0883.

6-methoxy-2-(2-((4-methylphenyl)sulfonamido)phenyl)-3-oxo-3H-indole 1-oxide (5la)

Red solid, yield 60%, m.p: 168 – 170 °C; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.95 (s, 1H), 7.65 – 7.59 (m, 2H), 7.47 (d, $J$ = 7.6 Hz, 1H), 7.44 – 7.35 (m, 2H), 7.34 (d, $J$ = 2.4 Hz, 1H), 7.26 (d, $J$ = 7.6 Hz, 2H), 7.16 (dd, $J$ = 8.0, 2.4 Hz, 1H), 6.95 (d, $J$ = 8.0 Hz, 2H), 4.01 (s, 3H), 2.17 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 182.2, 165.5, 149.6, 143.4, 136.7, 136.0, 132.3, 132.2, 129.7, 126.8, 126.2, 125.8, 124.1 (2s), 119.3, 115.8, 115.0, 101.8, 56.8, 21.0; HRMS (ESI): calcd for C$_{22}$H$_{18}$N$_2$O$_5$S $[M + Na]^+$ 445.0829, found 445.0828.

6-(methoxycarbonyl)-2-(2-((4-methylphenyl)sulfonamido)phenyl)-3-oxo-3H-indole 1-oxide (5ma)

Orange solid, yield 82%, m.p: 136 – 138 °C; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 9.16 (s, 1H), 8.30 (d, $J$ = 7.6 Hz, 1H), 8.10 (s, 1H), 7.88 (d, $J$ = 7.6 Hz, 1H), 7.60 – 7.53 (m, 1H), 7.48 (d, $J$ = 7.2 Hz, 1H), 7.43 – 7.33 (m, 4H), 7.06 (d, $J$ = 8.0 Hz, 2H), 3.98 (s, 3H), 2.22 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 183.2, 164.6, 147.0, 143.5, 136.7, 136.2, 136.2, 135.5, 133.2, 132.2, 129.7, 126.6, 126.2, 125.6, 125.1, 122.2, 118.3, 114.0, 53.1, 21.0; HRMS (ESI): calcd for C$_{23}$H$_{18}$N$_2$O$_6$S $[M + Na]^+$ 473.0778, found 473.0779.

3-oxo-2-(2-(phenylsulfonamido)phenyl)-3H-indole 1-oxide (5ab)

Orange solid, yield 96%, m.p: 185 – 187 °C; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 9.33 (s, 1H), 7.90 – 7.84 (m, 1H), 7.79 (d, $J$ = 7.6 Hz, 1H), 7.72 (q, $J$ = 6.8 Hz, 2H), 7.53 (t, $J$ = 7.6 Hz,
3H), 7.50 – 7.41 (m, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 184.1, 147.1, 139.1, 136.6, 135.3, 135.1, 133.0, 132.2, 131.9, 131.9, 129.2, 126.2, 125.6, 124.7, 123.1, 122.1, 118.6, 114.4; HRMS (ESI): calcd for C$_{20}$H$_{14}$N$_2$O$_4$S $[M + Na]^+$ 401.0566, found 401.0565.

2-(2-((4-methoxyphenyl)sulfonamido)phenyl)-3-oxo-3H-indole 1-oxide (5ac)

Orange solid, yield 93%, m.p:166 – 168 °C; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.03 (s, 1H), 7.87 (td, J = 7.6, 1.6 Hz, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.75 – 7.67 (m, 2H), 7.59 – 7.54 (m, 1H), 7.48 (dd, J = 8.0, 1.6 Hz, 1H), 7.41 – 7.33 (m, 4H), 6.72 (d, J = 8.8 Hz, 2H), 3.69 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 184.0, 162.4, 147.0, 136.8, 135.4, 135.2, 132.2, 132.0, 131.8, 130.5, 128.3, 125.7, 125.5, 123.0, 122.0, 118.7, 114.4, 114.3, 55.6; HRMS (ESI): calcd for C$_{21}$H$_{16}$N$_2$O$_5$S $[M + Na]^+$ 431.0672, found 431.0671.

2-(2-((4-chlorophenyl)sulfonamido)phenyl)-3-oxo-3H-indole 1-oxide (5ad)

Orange solid, yield 88%, m.p:175 – 177 °C; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.38 (s, 1H), 7.91 – 7.84 (m, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.60 – 7.53 (m, 1H), 7.53 – 7.46 (m, 3H), 7.43 – 7.30 (m, 4H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 184.1, 147.0, 138.0, 137.9, 136.3, 135.4, 135.0, 132.3, 132.1, 131.9, 129.4, 128.1, 126.0, 125.4, 122.9, 122.0, 119.0, 114.4; HRMS (ESI): calcd for C$_{20}$H$_{13}$ClN$_2$O$_4$S $[M + Na]^+$ 435.0177, found 435.0178.

2-(2-((4-nitrophenyl)sulfonamido)phenyl)-3-oxo-3H-indole 1-oxide (5ae)

Orange solid, yield 90%, m.p: 220 – 223 °C; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.73 (s, 1H), 8.14 (d, J = 8.4 Hz, 2H), 7.86-7.64 (m, 6H), 7.60 – 7.45 (m, 2H), 7.44 – 7.25 (m, 2H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 184.7, 150.0, 147.3, 145.2, 136.3, 135.7, 135.2, 132.7, 132.4, 132.4, 128.4,
126.6, 125.6, 125.0, 123.3, 122.2, 119.7, 114.8; HRMS (ESI): calcd for C_{20}H_{13}N_{3}O_{6}S [M + Na]^+ 446.0417, found 446.0415.

**2-(2-(methylsulfonamido)phenyl)-3-oxo-3H-indole 1-oxide (5af)**

Orange solid, yield 81%, m.p: 185 – 187 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 9.27 (s, 1H), 7.84 (t, \(J = 7.6\) Hz, 1H), 7.76-7.67 (m, 4H), 7.56 (t, \(J = 7.6\) Hz, 1H), 7.50 (d, \(J = 7.6\) Hz, 1H), 7.30 (t, \(J = 7.6\) Hz, 1H), 3.08 (s, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 185.4, 147.5, 137.7, 134.9, 134.8, 132.3, 131.8, 131.7, 124.1, 123.7, 121.8, 120.9, 116.7, 114.2, 39.7; HRMS (ESI): calcd for C_{15}H_{12}N_{2}O_{4}S [M + Na]^{+} 339.0410, found 339.0418.

### 6. Mechanistic Studies

1) Mechanistic studies of Ru-catalyzed C-H alkenylation/cyclization

![Scheme S1](image)

**Scheme S1** Mechanistic studies of Ru-catalyzed C-H alkenylation/cyclization

**a) Control experiment**

A 15 mL sealed tube was charged with phenyl-3H-indol-3-one 6 (20.7 mg, 0.1 mmol), 1-phenyl-1-hexyne 2a (31.6 mg, 0.2 mmol), [Ru(p-cymene)Cl\(_2\)]\(_2\) (3.1 mg, 0.005 mmol), AgSbF\(_6\) (7.9 mg, 0.02 mmol), Cu(OAc)\(_2\) (18.2 mg, 0.1 mmol) and DCE (1.0 mL). The mixture was stirred at 80 °C for 28 h under Ar atmosphere and monitored by TLC. There was no reaction, which suggests that \(N\)-oxide might be the
growing group of this reaction.

b) Reversible D/H exchange

To a 15 mL sealed tube was added 2-phenylisatogen 1a (22.3 mg, 0.1 mmol), [Ru(p-cymene)Cl$_2$]$_2$ (3.1 mg, 0.005 mmol), AgSbF$_6$ (7.9 mg, 0.020 mmol), Cu(OAc)$_2$ (18.2 mg, 0.1 mmol) in DCE (0.9 mL):CH$_3$COOD (0.1 mL). The mixture was stirred at 80 °C for 1 h under Ar atmosphere and monitored by TLC. Then the solvent was evaporated in vacuo. The residue was further purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as the eluent to get the mixture of [Dn]-1a (orange solid), which was analyzed by $^1$H NMR in DMSO-$d_6$. H/D exchange of 1a at the ortho-position of benzene ring was observed by $^1$H NMR (with 16% D), suggesting reversible C-H activation.

![Figure S1. The $^1$H NMR of the mixture of [Dn]-1a](image)

c) Kinetic isotope effect test

Two 15 mL sealed tubes were each added 1a (22.3 mg, 0.1 mmol) or [D$_5$]-1a (22.8 mg, 0.1 mmol) 2a (31.6 mg, 0.2 mmol), [Ru(p-cymene)Cl$_2$]$_2$ (3.1 mg, 0.005 mmol), AgSbF$_6$ (7.9 mg, 0.02 mmol), Cu(OAc)$_2$ (18.2 mg, 0.1 mmol), and DCE (1.0 mL). The two mixtures were stirred side-by-side at 80 °C for 1 h under Ar atmosphere
and monitored by TLC. Then the solvent was evaporated in vacuo. The residue was further purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as the eluent to afford 3aa and [D₄]-3aa. The KIE value was determined to be kH/kD = 2.3 on the yield ratio of 3aa and [D₄]-3aa, indicates that cleavage of the C–H bond is likely involved in the turnover limiting step.

2) Mechanistic studies of the Ir-catalyzed C–H sulfamidation

![Scheme S2](image)

a) Control experiment

A 15 mL test tube with a magnetic stir bar was charged with phenyl-3H-indol-3-one 6 (20.7 mg, 0.1 mmol), TsN₃ 4a (39.5 mg, 0.20 mmol), [IrCp*Cl₂]₂ (2.0 mg, 0.005 mmol), AgNTf₂ (7.8 mg, 0.020 mmol), HOAc (12.0 mg, 0.2 mmol) and TFE (1.0 mL). The mixture was stirred at rt for 5 h under Ar atmosphere and monitored by TLC. There was no reaction, which confirms that N-oxide might be the guiding group of this reaction.

b) Reversible D/H exchange

A 15 mL test tube with a magnetic stir bar was charged with 2-phenylisatogen 1a (22.3 mg, 0.1 mmol), [IrCp*Cl₂]₂ (2.0 mg, 0.005 mmol), AgNTf₂ (7.8 mg, 0.020 mmol), and TFE (0.9 mL):CH₃COOD(0.1 mL). The mixture was stirred at rt under Ar atmosphere. The reaction was stopped after 15 minutes, and the mixture of 1a and
[Dn]-1a were analyzed by $^1$HNMR spectroscopy. H/D exchange of 1a at the ortho-position of benzene ring was observed (with 10% D). It suggests the C-H activation is a reversible process.

Figure S2. The $^1$H NMR of the mixture of [Dn]-1a

c) Kinetic isotope effect test

Two 15 mL test tubes were each added 1a (22.3 mg, 0.1 mmol) or [D$_5$]-1a (22.8 mg, 0.1 mmol), 2a (31.6 mg, 0.2 mmol), TsN$_3$ 4a (39.5 mg, 0.20 mmol), [IrCp*Cl$_2$]$_2$ (2.0 mg, 0.005 mmol), AgNTf$_2$ (7.8 mg, 0.020 mmol), HOAc (12.0 mg, 0.2 mmol) and TFE. The two mixtures were stirred side-by-side at rt for 15 minutes under Ar atmosphere and monitored by TLC. Then the solvent was evaporated in vacuo and the residue was further purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as the eluent to get 5aa and [D$_4$]-5aa. The KIE value was determined to be kH/kD= 2.1, indicates that the C–H bond cleavage is likely to be involved in the turnover limiting step.
7. References


8. NMR spectra of compounds

Figure S3. $^1$H NMR spectra of compound 3aa

Figure S4. $^{13}$C NMR spectra of compound 3aa
Figure S5. $^1$H NMR spectra of compound 3ba

Figure S6. $^{13}$C NMR spectra of compound 3ba
Figure S7. NOE spectra of compound 3ba

Figure S8. $^1$H NMR spectra of compound 3ca
Figure S9. $^{13}$C NMR spectra of compound 3ca

Figure S10. $^1$H NMR spectra of compound 3da
Figure S11. $^{13}$C NMR spectra of compound 3da

Figure S12. $^1$H NMR spectra of compound 3ea
Figure S13. $^{13}$C NMR spectra of compound 3ea

Figure S14. $^{19}$F NMR spectra of compound 3ea
Figure S15. $^1$H NMR spectra of compound 3fa

Figure S16. $^{13}$C NMR spectra of compound 3fa
Figure S17. $^1$H NMR spectra of compound 3ga

Figure S18. $^{13}$C NMR spectra of compound 3ga
Figure S19. $^1$H NMR spectra of compound 3ha

Figure S20. $^{13}$C NMR spectra of compound 3ha
Figure S21. $^{19}$F NMR spectra of compound 3ha

Figure S22. $^1$H NMR spectra of compound 3ia
Figure S23. $^{13}$C NMR spectra of compound 3ia

Figure S24. $^1$H NMR spectra of compound 3ja
Figure S25. $^{13}$C NMR spectra of compound 3ja

Figure S26. $^1$H NMR spectra of compound 3ka
Figure S27. $^{13}$C NMR spectra of compound 3ka

Figure S28. $^1$H NMR spectra of compound 3la
Figure S29. $^{13}$C NMR spectra of compound 3la

Figure S30. $^1$H NMR spectra of compound 3ma
Figure S31. $^{13}$C NMR spectra of compound 3ma

Figure S32. $^1$H NMR spectra of compound 3ab
Figure S33. $^{13}$C NMR spectra of compound 3ab

Figure S34. $^1$H NMR spectra of compound 3ac
Figure S35. $^{13}$C NMR spectra of compound 3ac

Figure S36. $^1$H NMR spectra of compound 3ad
Figure S37. $^{13}$C NMR spectra of compound 3ad

Figure S38. $^{19}$F NMR spectra of compound 3ad
Figure S39. $^1$H NMR spectra of compound 3ae

Figure S40. $^{13}$C NMR spectra of compound 3ae
Figure S41. $^1$H NMR spectra of compound 3af

Figure S42. $^{13}$C NMR spectra of compound 3af
Figure S43. $^1$H NMR spectra of compound 3ag

Figure S44. $^{13}$C NMR spectra of compound 3ag
Figure S45. $^1$H NMR spectra of compound 3ah

Figure S46. $^{13}$C NMR spectra of compound 3ah
Figure S47. $^1$H NMR spectra of compound 3ai

Figure S48. $^{13}$C NMR spectra of compound 3ai
Figure S49. $^1$H NMR spectra of compound 3aj

Figure S50. $^{13}$C NMR spectra of compound 3aj
Figure S51. $^1$H NMR spectra of compound 3ak

Figure S52. $^{13}$C NMR spectra of compound 3ak
Figure S53. $^1$H NMR spectra of compound 3al

Figure S54. $^{13}$C NMR spectra of compound 3al
Figure S55. $^1$H NMR spectra of compound 3am

Figure S56. $^{13}$C NMR spectra of compound 3am
Figure S57. $^1$H NMR spectra of compound 3an

Figure S58. $^{13}$C NMR spectra of compound 3an
Figure S59. NOE spectra of compound 3an

Figure S60. $^1$H NMR spectra of compound 3ao
Figure S61. $^{13}$C NMR spectra of compound 3ao

Figure S62. $^1$H NMR spectra of compound 5aa
Figure S63. $^{13}$C NMR spectra of compound 5aa

Figure S64. $^1$H NMR spectra of compound 5ba
Figure S65. $^{13}$C NMR spectra of compound 5ba

Figure S66. $^1$H NMR spectra of compound 5ca
Figure S67. $^{13}$C NMR spectra of compound 5ca

Figure S68. $^1$H NMR spectra of compound 5da
Figure S69. $^{13}$C NMR spectra of compound 5da

Figure S70. $^1$H NMR spectra of compound 5ea
Figure S71. $^{13}$C NMR spectra of compound 5ea

Figure S72. $^{19}$F NMR spectra of compound 5ea
Figure S73. $^1$H NMR spectra of compound 5fa

Figure S74. $^{13}$C NMR spectra of compound 5fa
Figure S75. $^1$H NMR spectra of compound 5ga

Figure S76. $^{13}$C NMR spectra of compound 5ga
Figure S77. $^1$H NMR spectra of compound 5ha

Figure S78. $^{13}$C NMR spectra of compound 5ha
Figure S79. $^{19}$F NMR spectra of compound 5ha

Figure S80. $^1$H NMR spectra of compound 5ia
Figure S81. $^{13}$C NMR spectra of compound 5ia

Figure S82. $^1$H NMR spectra of compound 5ja
Figure S83. $^{13}$C NMR spectra of compound 5ja

Figure S84. $^1$H NMR spectra of compound 5ka
Figure S85. $^{13}$C NMR spectra of compound 5ka

Figure S86. $^1$H NMR spectra of compound 5la
Figure S87. $^{13}$C NMR spectra of compound 5la

Figure S88. $^1$H NMR spectra of compound 5ma
Figure S89. $^{13}$C NMR spectra of compound 5ma

Figure S90. $^1$H NMR spectra of compound 5ab
Figure S91. $^{13}$C NMR spectra of compound 5ab

Figure S92. $^1$H NMR spectra of compound 5ac
Figure S93. $^{13}$C NMR spectra of compound 5ac

Figure S94. $^1$H NMR spectra of compound 5ad
Figure S95. $^{13}$C NMR spectra of compound 5ad

Figure S96. $^1$H NMR spectra of compound 5ae
Figure S97. $^{13}$C NMR spectra of compound 5ae

Figure S98. $^1$H NMR spectra of compound 5af
Figure S99. $^{13}$C NMR spectra of compound 5af