Supporting Information

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1. General information

- Chemicals were purchased from Acros or Aldrich and used without further purification unless otherwise noted. Solvents were predistilled according to standard laboratory methods.
- Chromatographic purification of the products was performed on Merck silica gel 60, particle size 0.040-0.063 mm (230-240 mesh, flash).
- Analytical TLC: SIL G-25 UV254 from MACHEREY&NAGEL. Visualization of the developed TLC plates was performed with ultraviolet irradiation (254 nm) or by staining with basic potassium permanganate solution.
- Melting points were determined using a Büchi 510 apparatus and are uncorrected.
- Mass spectra were acquired on a Finnigan SSQ7000 (EI/CI) spectrometer and high resolution mass spectra on a Finnigan MAT 95 (EI/CI) or on a ThermoFisher Scientific LTQOrbitrap XL or Thermo Scientific Q Exactive Plus.
- IR spectra were taken on a Perkin-Elmer FT-IR Spectrum 100 using a Diamant/KRS5 ATR. Evaluation was done using the supplementary software. The absorption bands are given in wave numbers (cm\(^{-1}\)).
- \(^1\)H- and \(^13\)C- NMR spectra were recorded at ambient temperature on Bruker AV-500, VNMRS 600 and Inova 400 instruments. The chemical shifts are reported in ppm downfield of tetramethylsilane (TMS) and referenced to residual solvent peaks resonance as internal standard. The order of citation in parentheses is a) multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd= doublet of doublet, ddd= doublet of doublet of doublet, td = triplet of doublet, m = multiplet), b) coupling constants, c) number of protons. Coupling constants (J) are reported in Hertz (Hz).
- The precursors 1a-1i are known compounds that prepared according to the reported literature procedures.[1]

2. General procedure for the synthesis of products 3a-3y and control experiments:

a) synthesis of 3a-3y:

A 10 mL glass tube equipped with a stirring bar was charged with precursors 1 (0.12 mmol, 1.2 equiv.), sulfonium salts 2 (0.10 mmol, 1.0 equiv.), Cs$_2$CO$_3$ (0.12 mmol, 1.2 equiv.), MnO$_2$ (0.5 mmol, 5.0 equiv.) and CH$_2$Cl$_2$ (1.0 mL). The resulting solution was stirred at room temperature for 24 h. Then the solvent was evaporated under reduced pressure to give a residue, which was directly purified by flash column chromatography (PE/EtOAc from 10/1 to 2/1) to provide the desired product 3a-3y.

The large scale reaction for the synthesis of 3a was carried out in a similar manner.

A 50 mL round-bottom flask equipped with a stirring bar was charged with 1a (1.2 mmol, 0.559 g), sulfonium salts 2a (1.0 mmol, 0.261 g), Cs$_2$CO$_3$ (0.12 mmol, 1.2 equiv.), MnO$_2$ (0.5 mmol, 5.0 equiv.) and CH$_2$Cl$_2$ (10.0 mL). The resulting solution was stirred at room temperature for 24 h. Then the solvent was evaporated under reduced pressure to give a residue, which was directly purified by flash column chromatography (PE/EtOAc from 10/1 to 2/1) to provide the desired product 3a (0.465 g, 80%). The analytical data of the large scale reaction of 3a are consistent with those of the 0.1 mmol scale experiment.

b) control experiments:

A 10 mL glass tube equipped with a stirring bar was charged with precursors 1 (0.10 mmol, 46.5 mg, 1.0 equiv), MnO$_2$ (0.5 mmol, 5.0 equiv), Cs$_2$CO$_3$ (0.12 mmol, 1.2 equiv.), and CH$_2$Cl$_2$ (1.0 mL). The resulting solution was stirred at room temperature for 24 h. Then the solvent was evaporated under reduced pressure to give a residue, which was directly purified by flash column chromatography (PE/EtOAc from 20/1 to 10/1) to provide 1a' as a yellow solid (39.9 mg, 86% yield).

A 10 mL glass tube equipped with a stirring bar was charged with 1a' (39.9 mg, 1.0 equiv), MnO$_2$ (37.3 mg, 5.0 equiv), sulfonium salts 2a (22.4 mg, 1.0 equiv), Cs$_2$CO$_3$ (33.6 mg, 1.2 equiv),
and CH₂Cl₂ (1.0 mL). The resulting solution was stirred at room temperature for 24 h. Then the solvent was evaporated under reduced pressure to give a residue, which was directly purified by flash column chromatography (PE/EtOAc from 15/1 to 10/1) to provide 3a as a colorless solid (47.0 mg, 86% yield).

3. Proposed mechanism:
4. Characterization Data for 3a-3y:

((2S,3S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-tosylindolin-2-yl)(phenyl)methanone (3a)

According to general procedure, 3a was obtained as a colorless solid (48 mg, 82% yield).

**Melting Point:** 199-200 °C

**1H NMR** (500 MHz, CDCl₃) δ 7.85 (d, J = 7.9 Hz, 4H), 7.62-7.59 (m, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.29-7.27 (m, 1H), 7.00 (t, J = 7.5 Hz, 1H), 6.92 (d, J = 7.4 Hz, 1H), 6.55 (s, 2H), 5.44 (d, J = 6.4 Hz, 1H), 5.16 (s, 1H), 4.35 (d, J = 6.3 Hz, 1H), 2.43 (s, 3H), 1.27 (s, 18H) ppm.

**13C NMR** (126 MHz, CDCl₃) δ 195.6, 153.2, 144.3, 141.9, 136.2, 135.0, 134.6, 133.6, 132.4, 132.2, 129.8 (2C), 129.2 (2C), 128.6 (2C), 127.7 (2C), 126.0, 124.6 (2C), 123.8, 113.9, 74.1, 52.1, 34.2 (2C), 30.1 (6C), 21.6 ppm.

**HRMS (ESI):** m/z [M-H]⁻ calcd for C₃₆H₃₈NO₄S 580.2522; found 580.2494

((2S,3S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-tosylindolin-2-yl)(4-methoxyphenyl)methanone (3b)

According to general procedure, 3b was obtained as a colorless solid (41 mg, 67% yield).

**Melting Point:** 167-169 °C

**1H NMR** (500 MHz, CDCl₃) δ 7.84 (t, J = 8.6 Hz, 4H), 7.61 (d, J = 8.1 Hz, 1H), 7.30-7.26 (m, 3H), 6.99 (t, J = 7.4 Hz, 1H), 6.94-6.88 (m, 3H), 6.56 (s, 2H), 5.38 (d, J = 6.5 Hz, 1H), 5.16 (s, 1H), 4.34 (d, J = 6.4 Hz, 1H), 3.89 (s, 3H), 2.42 (s, 3H), 1.27 (s, 18H) ppm.

**13C NMR** (126 MHz, CDCl₃) δ 194.1, 163.9, 153.2, 144.3, 142.0, 136.1, 134.9, 132.5, 132.3, 131.5 (2C), 129.8 (2C), 128.6, 127.7 (2C), 127.5, 126.0, 124.7 (2C), 123.8, 113.8 (2C), 73.8, 55.5, 523, 34.2 (2C), 30.1 (6C), 21.6 ppm.

**HRMS (ESI):** m/z [M-H]⁻ calcd for C₃₇H₄₀NO₅S 610.2627; found 610.2597
((2S,3S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-tosylindolin-2-yl)(p-tolyl)methanone (3c)

According to general procedure, 3c was obtained as a colorless solid (41 mg, 69% yield).

**Melting Point:** 189-191 °C

**$^1$H NMR (500 MHz, CDCl$_3$)** $\delta$ 7.85 (d, $J = 8.2$ Hz, 2H), 7.74 (d, $J = 8.1$ Hz, 2H), 7.61 (d, $J = 8.2$ Hz, 1H), 7.32-7.26 (m, 3H), 7.23 (d, $J = 8.0$ Hz, 2H), 6.99 (t, $J = 7.5$ Hz, 1H), 6.91 (d, $J = 7.5$ Hz, 1H), 6.54 (s, 2H), 5.40 (d, $J = 6.5$ Hz, 1H), 5.16 (s, 1H), 4.33 (d, $J = 6.4$ Hz, 1H), 2.43 (s, 3H), 2.42 (s, 3H), 1.26 (s, 18H) ppm.

**$^{13}$C NMR (126 MHz, CDCl$_3$)** $\delta$ 195.3, 153.2, 146.3, 144.3, 142.0, 139.8, 136.2, 134.9, 133.4, 132.4, 132.2, 129.8 (2C), 129.7, 129.0 (2C), 128.6, 128.3, 127.8 (2C), 127.3 (4C), 126.0, 124.7 (2C), 123.9, 113.9, 74.2, 52.2, 34.2 (2C), 30.1 (6C), 21.7, 21.6 ppm.

**HRMS (ESI):** m/z [M-H] $^-$ calcd for C$_{37}$H$_{40}$NO$_4$S 594.2678; found 594.2653

[1,1'-biphenyl]-4-yl((2S,3S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-tosylindolin-2-yl)methanone (3d)

According to general procedure, 3d was obtained as a colorless solid (46 mg, 70% yield).

**Melting Point:** 167-168 °C

**$^1$H NMR (500 MHz, CDCl$_3$)** $\delta$ 7.93 (d, $J = 8.3$ Hz, 2H), 7.87 (d, $J = 8.2$ Hz, 2H), 7.67-7.62 (m, 5H), 7.50 (t, $J = 7.5$ Hz, 2H), 7.44 (t, $J = 7.3$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 3H), 7.02 (t, $J = 7.4$ Hz, 1H), 6.94 (d, $J = 7.5$ Hz, 1H), 6.59 (s, 2H), 5.44 (d, $J = 6.6$ Hz, 1H), 5.17 (s, 1H), 4.41 (d, $J = 6.6$ Hz, 1H), 2.43 (s, 3H), 1.27 (s, 18H) ppm.

**$^{13}$C NMR (126 MHz, CDCl$_3$)** $\delta$ 195.3, 153.2, 146.3, 144.3, 142.0, 139.8, 136.2, 134.9, 133.4, 132.4, 132.2, 129.8 (2C), 129.7, 129.0 (2C), 128.6, 128.3, 127.8 (2C), 127.3 (4C), 126.0, 124.7 (2C), 123.9, 113.9, 74.2, 52.2, 34.2 (2C), 30.1 (6C), 21.6 ppm.

**HRMS (ESI):** m/z [M-H] $^-$ calcd for C$_{42}$H$_{40}$NO$_4$S 656.2815; found 656.2835
((2S,3S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-tosylindolin-2-yl)(4-(trifluoromethyl)phenyl) methanone (3e)

According to general procedure, 3e was obtained as a colorless solid (46 mg, 71% yield).

Melting Point: 173-175 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.95 (d, $J = 8.2$ Hz, 2H), 7.82 (d, $J = 8.3$ Hz, 2H), 7.70 (d, $J = 8.3$ Hz, 2H), 7.67 (d, $J = 8.2$ Hz, 1H), 7.34-7.30 (m, 3H), 7.04 (t, $J = 7.5$ Hz, 1H), 6.93 (d, $J = 7.5$ Hz, 1H), 6.51 (s, 2H), 5.30 (d, $J = 7.2$ Hz, 1H), 5.19 (s, 1H), 4.38 (d, $J = 7.2$ Hz, 1H), 2.43 (s, 3H), 1.26 ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 195.1, 153.4, 144.6, 141.7, 137.6, 136.4, 134.8, 134.5, 134.2, 132.1, 131.7, 129.9 (2C), 129.5 (2C), 128.8, 127.8 (2C), 126.1, 125.7, 124.6 (2C), 124.2, 122.4, 114.1, 74.6, 52.2, 34.2 (2C), 30.0 (6C), 21.6 ppm.

HRMS (ESI): m/z [M-H]$^-$ calcd for C$_{37}$H$_{37}$F$_3$NO$_4$S 648.2395; found 648.2367

(4-bromophenyl)((2S,3S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-tosylindolin-2-yl) methanone (3f)

According to general procedure, 3f was obtained as a colorless solid (44 mg, 67% yield).

Melting Point: 187-189 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J = 8.2$ Hz, 2H), 7.69 (d, $J = 8.5$ Hz, 2H), 7.64 (d, $J = 8.2$ Hz, 1H), 7.57 (d, $J = 8.4$ Hz, 2H), 7.33-7.29 (m, 3H), 7.02 (t, $J = 7.4$ Hz, 1H), 6.92 (d, $J = 7.5$ Hz, 1H), 6.53 (s, 2H), 5.29 (d, $J = 7.0$ Hz, 1H), 5.18 (s, 1H), 4.34 (d, $J = 7.0$ Hz, 1H), 2.43 (s, 3H), 1.27 ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 194.9, 153.3, 144.5, 141.8, 136.3, 134.5, 133.5, 132.2, 131.9 (2C), 131.8, 130.6 (2C), 129.9 (2C), 128.9, 128.7, 127.8 (2C), 127.2, 126.0, 124.6 (2C), 124.0, 114.0, 74.3, 52.2, 34.2 (2C), 30.0 (6C), 21.6 ppm.

HRMS (ESI): m/z [M-H]$^-$ calcd for C$_{36}$H$_{37}$BrNO$_4$S 658.1627; found 658.1603
(4-chlorophenyl)((2S,3S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-tosylindolin-2-yl) methanone (3g)

According to general procedure, 3g was obtained as a colorless solid (45 mg, 73% yield).

Melting Point: 188-190 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J = 8.2$ Hz, 2H), 7.78 (d, $J = 8.5$ Hz, 2H), 7.63 (d, $J = 8.2$ Hz, 1H), 7.41 (d, $J = 8.5$ Hz, 2H), 7.30 (d, $J = 8.1$ Hz, 3H), 7.01 (t, $J = 7.5$ Hz, 1H), 6.92 (d, $J = 7.5$ Hz, 1H), 6.53 (s, 2H), 5.31 (d, $J = 7.0$ Hz, 1H), 5.18 (s, 1H), 4.34 (d, $J = 6.9$ Hz, 1H), 2.43 (s, 3H), 1.27 (s, 18H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 194.7, 153.3, 144.5, 141.8, 140.1, 136.3, 134.5, 133.0, 132.2, 131.9, 130.5 (2C), 130.1, 129.9 (2C), 128.9 (2C), 128.7, 127.8 (2C), 126.0, 124.6 (2C), 124.0, 114.0, 74.3, 52.2, 34.2 (2C), 30.1 (6C), 21.6 ppm.

HRMS (ESI): m/z [M-H$^-$] calcd for C$_{36}$H$_{37}$ClNO$_4$S 614.2132; found 614.2104

((2S,3S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-tosylindolin-2-yl)(4-fluorophenyl) methanone (3h)

According to general procedure, 3h was obtained as a colorless solid (53 mg, 88% yield).

Melting Point: 172-173 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.90-7.86 (m, 2H), 7.84 (d, $J = 8.3$ Hz, 2H), 7.63 (d, $J = 8.2$ Hz, 1H), 7.30 (d, $J = 8.0$ Hz, 3H), 7.11 (t, $J = 8.6$ Hz, 2H), 7.01 (td, $J = 7.5$, 0.8 Hz, 1H), 6.92 (d, $J = 7.5$ Hz, 1H), 6.55 (s, 2H), 5.34 (d, $J = 6.8$ Hz, 1H), 5.18 (s, 1H), 4.35 (d, $J = 6.8$ Hz, 1H), 2.43 (s, 3H), 1.27 (s, 18H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 194.2, 167.0, 165.0, 153.3, 144.4, 141.8, 136.3, 134.7, 132.3, 132.0, 131.9, 131.8, 131.1, 129.8 (2C), 128.7, 127.7 (2C), 126.0, 124.6 (2C), 124.0, 115.9, 115.7, 113.9, 74.2, 52.2, 34.2 (2C), 30.1 (6C), 21.6 ppm.

HRMS (ESI): m/z [M-H$^-$] calcd for C$_{36}$H$_{37}$FNO$_4$S 598.2427; found 598.2402
(2S,3S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-tosylindolin-2-yl(3-fluorophenyl)
methanone (3i)
According to general procedure, 3i was obtained as a colorless solid (51 mg, 85% yield).

Melting Point: 183-185 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.84 (d, $J = 8.2$ Hz, 2H), 7.63 (dd, $J = 7.9$, 3.0 Hz, 2H), 7.52 (d, $J = 9.4$ Hz, 1H), 7.42 (td, $J = 8.0$, 5.6 Hz, 1H), 7.32 (m, 4H), 7.01 (t, $J = 7.5$ Hz, 1H), 6.92 (d, $J = 7.5$ Hz, 1H), 6.55 (s, 2H), 5.34 (d, $J = 6.7$ Hz, 1H), 5.19 (s, 1H), 4.35 (d, $J = 6.6$ Hz, 1H), 2.43 (s, 3H), 1.27 (s, 18H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 194.5, 163.7, 161.7, 153.3, 144.5, 141.8, 136.7, 136.3, 134.6, 132.2, 131.9, 130.3, 129.9 (2C), 128.7, 127.7 (2C), 126.0, 124.9, 124.6 (2C), 124.0, 120.6, 116.0, 113.9, 74.3, 52.1, 34.2 (2C), 30.0 (6C), 21.6 ppm.

HRMS (ESI): m/z [M-H]$^-$ calcld for C$_{36}$H$_{37}$FNO$_4$S 598.2427; found 598.2405

(2S,3S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-tosylindolin-2-yl(2-fluorophenyl)
methanone (3j)
According to general procedure, 3j was obtained as a colorless solid (47 mg, 79% yield).

Melting Point: 169-171 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.86 (td, $J = 7.6$, 1.6 Hz, 1H), 7.80 (d, $J = 8.2$ Hz, 2H), 7.68 (d, $J = 8.2$ Hz, 1H), 7.58-7.53 (m, 1H), 7.31-7.25 (m, 4H), 7.08 (dd, $J = 10.8$, 8.4 Hz, 1H), 7.00 (t, $J = 7.5$ Hz, 1H), 6.90 (d, $J = 7.5$ Hz, 1H), 6.45 (s, 2H), 5.41 (d, $J = 6.6$ Hz, 1H), 5.11 (s, 1H), 4.36 (d, $J = 6.5$ Hz, 1H), 2.40 (s, 3H), 1.23 (s, 18H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 195.1, 162.20, 153.0, 144.3, 142.0, 135.9, 134.8, 134.43, 132.3, 132.2, 131.6, 129.8 (2C), 128.6, 127.8 (2C), 125.9, 124.6, 124.4 (2C), 123.9, 116.6, 116.4, 114.0, 76.5, 51.6, 34.1 (2C), 30.0 (6C), 21.6 ppm.

HRMS (ESI): m/z [M-H]$^-$ calcld for C$_{30}$H$_{37}$FNO$_4$S 598.2427; found 598.2402
(2S,3S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-tosylindolin-2-yl)(2,4-difluorophenyl) methanone (3k)

According to general procedure, 3k was obtained as a colorless solid (54 mg, 87% yield).

Melting Point: 156-157 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.92 (td, $J = 8.4, 6.6$ Hz, 1H), 7.79 (d, $J = 8.3$ Hz, 2H), 7.68 (d, $J = 8.2$ Hz, 1H), 7.31-7.26 (m, 1H), 7.03-6.99 (m, 2H), 6.90 (d, $J = 7.5$ Hz, 1H), 6.80 (ddd, $J = 10.9, 8.7, 2.4$ Hz, 1H), 6.46 (s, 2H), 5.32 (d, $J = 6.9$ Hz, 1H), 5.13 (s, 1H), 4.36 (d, $J = 6.8$ Hz, 1H), 2.41 (s, 3H), 1.24 (s, 18H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 193.9, 164.9, 163.1, 153.1, 144.4, 142.0, 136.0, 134.1, 133.6, 132.3, 131.9, 129.8 (2C), 128.6, 127.8 (2C), 125.9, 124.4 (2C), 124.0, 120.9, 114.1, 112.5, 104.7, 76.4, 51.7, 34.1 (2C), 30.0 (6C), 21.6 ppm.

HRMS (ESI): m/z [M-H]$^-$ calcd for C$_{36}$H$_{36}$F$_2$NO$_4$S 616.2333; found 616.2307

(2S,3S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-tosylindolin-2-yl)(3,4-dichlorophenyl) methanone (3l)

According to general procedure, 3l was obtained as a colorless solid (47 mg, 72% yield).

Melting Point: 186-188 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J = 8.2$ Hz, 2H), 7.78 (d, $J = 1.9$ Hz, 1H), 7.69 (dd, $J = 8.4, 1.9$ Hz, 1H), 7.63 (d, $J = 8.2$ Hz, 1H), 7.51 (d, $J = 8.4$ Hz, 1H), 7.32-7.29 (m, 3H), 7.02 (t, $J = 7.5$ Hz, 1H), 6.92 (d, $J = 7.5$ Hz, 1H), 6.56 (s, 2H), 5.27 (d, $J = 7.3$ Hz, 1H), 5.21 (s, 1H), 4.34 (d, $J = 7.3$ Hz, 1H), 2.44 (s, 3H), 1.28 (s, 18H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 193.9, 153.5, 144.6, 141.7, 138.2, 136.5, 134.3, 133.3, 132.1, 131.5, 131.0, 130.7, 129.9 (2C), 128.8, 128.0, 127.8, 126.0, 124.6, 124.2, 114.0, 74.3, 52.3, 34.2 (2C), 30.0 (6C), 21.6 ppm.

HRMS (ESI): m/z [M-H]$^-$ calcd for C$_{36}$H$_{36}$Cl$_2$NO$_4$S 648.1742; found 648.1711
According to general procedure, 3m was obtained as a colorless solid (43 mg, 67% yield).

**Melting Point:** 216-217 °C

**1H NMR** (500 MHz, CDCl₃) δ 7.83 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 8.2 Hz, 1H), 7.36 (d, J = 3.2 Hz, 1H), 7.29-7.22 (m, 3H), 7.06 (dd, J = 9.0, 3.2 Hz, 1H), 6.96 (t, J = 7.3 Hz, 1H), 6.87 (d, J = 7.5 Hz, 1H), 6.77 (d, J = 9.0 Hz, 1H), 6.51 (s, 2H), 5.78 (d, J = 6.4 Hz, 1H), 5.09 (s, 1H), 4.32 (d, J = 6.4 Hz, 1H), 3.82 (s, 3H), 3.20 (s, 3H), 2.41 (s, 3H), 1.25 (s, 18H) ppm.

**13C NMR** (126 MHz, CDCl₃) δ 197.5, 153.6, 153.0, 148.9, 144.3, 142.0, 136.2, 134.7, 132.5, 132.3, 129.8 (2C), 128.6, 127.8 (2C), 125.9, 124.8 (2C), 123.9, 123.7, 114.0, 111.3, 110.1, 73.8, 56.1, 55.6, 52.5, 34.2 (2C), 30.1 (6C), 21.6 ppm.

**HRMS (ESI):** m/z [M-H]⁻ calcd for C₃₈H₄₂NO₆S 640.2733; found 640.2710

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According to general procedure, 3n was obtained as a colorless solid (34 mg, 53% yield).

**Melting Point:** 221-223 °C

**1H NMR** (500 MHz, CDCl₃) δ 7.85 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 8.2 Hz, 1H), 7.42-7.37 (m, 1H), 7.31-7.26 (m, 3H), 7.00 (t, J = 7.4 Hz, 1H), 6.91 (d, J = 7.5 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 6.58 (s, 2H), 5.38 (d, J = 7.0 Hz, 1H), 5.17 (s, 1H), 4.36 (d, J = 7.0 Hz, 1H), 3.95 (s, 3H), 3.75 (s, 3H), 2.43 (s, 3H), 1.26 (s, 18H) ppm.

**13C NMR** (126 MHz, CDCl₃) δ 194.2, 153.6, 153.2, 148.9, 144.3, 142.0, 136.2, 134.7, 132.5, 132.3, 129.8 (2C), 128.6, 127.8 (2C), 125.9, 124.8 (2C), 123.9, 123.7, 114.0, 111.3, 110.1, 73.8, 56.1, 55.6, 52.5, 34.2 (2C), 30.1 (6C), 21.6 ppm.

**HRMS (ESI):** m/z [M-H]⁻ calcd for C₃₈H₄₂NO₆S 640.2733; found 640.2709
((2S,3S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-tosylindolin-2-yl)(naphthalen-2-yl) methanone (3o)

According to general procedure, 3o was obtained as a colorless solid (51 mg, 81% yield).

**Melting Point:** 196-198 °C

**1H NMR (500 MHz, CDCl₃)** δ 8.06 (s, 1H), 8.04 (dd, J = 8.6, 1.5 Hz, 1H), 7.91-7.88 (m, 4H), 7.69 (d, J = 8.1 Hz, 1H), 7.64-7.61 (m, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.32-7.30 (m, 3H), 7.01 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 7.5 Hz, 1H), 6.60 (d, J = 6.9 Hz, 1H), 5.17 (s, 1H), 4.40 (d, J = 6.9 Hz, 1H), 2.44 (s, 3H), 1.21 (s, 18H) ppm.

**13C NMR (126 MHz, CDCl₃)** δ 195.5, 153.3, 144.4, 142.0, 136.3, 135.8, 134.9, 132.5, 132.0, 131.1, 129.8 (2C), 129.7, 128.8, 128.6, 128.5, 127.8 (2C), 127.7, 126.7, 125.9, 124.8 (2C), 124.6, 123.9, 113.9, 74.2, 52.5, 34.2 (2C), 30.0 (6C), 21.6 ppm.

**HRMS (ESI):** m/z [M-H]⁻ calcd for C₄₀H₄₀NO₄S 630.2678; found 630.2650

---

(2S,3S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-N-phenyl-1-tosylindoline-2-carboxamide (3p)

According to general procedure, 3p was obtained as a colorless solid (46 mg, 77% yield).

**Melting Point:** 197-198°C

**1H NMR (500 MHz, CDCl₃)** δ 8.65 (s, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.64 (d, J = 7.9 Hz, 2H), 7.56 (d, J = 8.2 Hz, 2H), 7.37 (t, J = 7.8 Hz, 3H), 7.16 (t, J = 8.4 Hz, 2H), 7.10 (d, J = 7.9 Hz, 3H), 6.64 (s, 2H), 5.09 (s, 1H), 4.82 (d, J = 4.5 Hz, 1H), 4.63 (d, J = 4.7 Hz, 1H), 2.32 (s, 3H), 1.29 (s, 18H) ppm.

**13C NMR (126 MHz, CDCl₃)** δ 168.7, 152.7, 144.7, 141.0, 137.3, 135.7, 133.0, 132.8, 129.7 (2C), 128.9 (2C), 128.6, 128.0 (2C), 126.9, 125.2, 124.7, 124.2 (2C), 120.4 (2C), 116.3, 73.2, 50.6, 34.2 (2C), 30.1 (6C), 21.7 ppm.

**HRMS (ESI):** m/z [M-H]⁻ calcd for C₃₆H₃₉N₂O₄S 595.2631; found 595.2598
(2S,3S)-ethyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-tosylindoline-2-carboxylate (3q)

According to general procedure, 3q was obtained as a colorless solid (44 mg, 80% yield).

Melting Point: 144-146°C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J = 8.2$ Hz, 2H), 7.66 (d, $J = 8.2$ Hz, 1H), 7.27 (t, $J = 7.9$ Hz, 1H), 7.22 (d, $J = 8.1$ Hz, 2H), 7.01 (t, $J = 7.4$ Hz, 1H), 6.93 (d, $J = 7.5$ Hz, 1H), 6.61 (s, 2H), 5.14 (s, 1H), 4.50 (d, $J = 6.4$ Hz, 1H), 4.45 (d, $J = 6.4$ Hz, 1H), 4.43-4.29 (m, 2H), 2.38 (s, 3H), 1.37 (t, $J = 7.1$ Hz, 3H), 1.30 (s, 18H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 171.01, 153.1, 144.3, 141.6, 136.0, 134.3, 132.6, 129.7 (2C), 128.5, 127.7 (2C), 125.9, 124.3 (2C), 123.9, 114.2, 71.4, 61.7, 51.9, 34.2 (2C), 30.1 (6C), 21.6, 14.3 ppm.

HRMS (ESI): m/z [M-H]$^-$ calcd for C$_{32}$H$_{38}$NO$_5$S 548.2471; found 548.2440

(2S,3S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-methyl-1-tosylindolin-2-yl)(phenyl) methanone (3r)

According to general procedure, 3r was obtained as a colorless solid (41 mg, 69% yield).

Melting Point: 195-197 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.84 (dd, $J = 7.9$, 2.9 Hz, 4H), 7.60 (t, $J = 7.2$ Hz, 1H), 7.51 (d, $J = 8.3$ Hz, 1H), 7.43 (t, $J = 7.7$ Hz, 2H), 7.30 (d, $J = 8.7$ Hz, 2H), 7.09 (d, $J = 8.3$ Hz, 1H), 6.73 (s, 1H), 6.55 (s, 2H), 5.36 (d, $J = 6.5$ Hz, 1H), 5.17 (s, 1H), 4.31 (d, $J = 6.5$ Hz, 1H), 2.42 (s, 3H), 2.24 (s, 3H), 1.27 (s, 18H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 195.7, 153.2, 144.2, 139.6, 136.2, 134.8, 134.7, 133.6, 133.5, 132.4, 129.8 (2C), 129.3, 129.2 (2C), 128.6 (2C), 127.8 (2C), 126.4, 124.7 (2C), 113.7, 74.4, 52.2, 34.2 (2C), 30.1 (6C), 21.6, 20.8 ppm.

HRMS (ESI): m/z [M-H]$^-$ calcd for C$_{37}$H$_{40}$NO$_5$S 594.2678; found 594.2654
((2S,3S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-fluoro-1-tosylindolin-2-yl)(phenyl) methanone (3s)
According to general procedure, 3s was obtained as a colorless solid (43 mg, 71% yield).
**Melting Point:** 187-189 °C

\[ ^1H \text{ NMR (500 MHz, CDCl}_3 \delta 7.83 \text{ (dd, } J = 7.7, 3.8 \text{ Hz, 4H), 7.62 \text{ (t, } J = 7.4 \text{ Hz, 1H), 7.57 \text{ (dd, } J = 8.9, 4.4 \text{ Hz, 1H), 7.45 \text{ (t, } J = 7.8 \text{ Hz, 2H), 7.32 \text{ (d, } J = 8.1 \text{ Hz, 2H), 6.99 \text{ (td, } J = 8.8, 2.6 \text{ Hz, 1H), 6.63 \text{ (dd, } J = 7.9, 2.4 \text{ Hz, 1H), 6.53 \text{ (s, 2H), 5.45 \text{ (d, } J = 6.5 \text{ Hz, 1H), 5.20 \text{ (s, 1H), 4.31 \text{ (d, } J = 6.5 \text{ Hz, 1H), 2.44 \text{ (s, 3H), 1.27 (s, 18H) ppm.}}}
\]

**HRMS (ESI):** m/z [M-H] calcd for C_{36}H_{37}FNO_4S 598.2427; found 598.2399

![3s](image)

((2S,3S)-5-chloro-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-tosylindolin-2-yl)(phenyl) methanone (3t)
According to general procedure, 3t was obtained as a colorless solid (42 mg, 68% yield).
**Melting Point:** 169-170 °C

\[ ^1H \text{ NMR (500 MHz, CDCl}_3 \delta 7.83 \text{ (dd, } J = 8.1, 1.7 \text{ Hz, 4H), 7.62 \text{ (t, } J = 7.4 \text{ Hz, 1H), 7.55 \text{ (d, } J = 8.7 \text{ Hz, 1H), 7.44 \text{ (t, } J = 7.8 \text{ Hz, 2H), 7.32 \text{ (d, } J = 8.1 \text{ Hz, 2H), 7.25 \text{ (dd, } J = 8.7, 1.9 \text{ Hz, 1H), 6.89 \text{ (s, 1H), 6.54 \text{ (s, 2H), 5.47 \text{ (d, } J = 6.4 \text{ Hz, 1H), 5.21 \text{ (s, 1H), 4.29 \text{ (d, } J = 6.3 \text{ Hz, 1H), 2.44 \text{ (s, 3H), 1.28 (s, 18H) ppm.}}}
\]

**HRMS (ESI):** m/z [M-H] calcd for C_{36}H_{37}ClNO_4S 614.2132; found 614.2107

![3t](image)

((2S,3S)-5-bromo-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-tosylindolin-2-yl)(phenyl) methanone (3u)
According to general procedure, 3u was obtained as a colorless solid (48 mg, 72% yield).
**Melting Point:** 168-169 °C

![3u](image)
\textbf{H NMR (500 MHz, CDCl}\textsubscript{3}) \(\delta\) 7.82 (dd, \(J = 7.7, 3.9\) Hz, 4H), 7.62 (t, \(J = 7.4\) Hz, 1H), 7.49 (d, \(J = 8.7\) Hz, 1H), 7.44 (t, \(J = 7.8\) Hz, 2H), 7.40 (dd, \(J = 8.7, 1.8\) Hz, 2H), 7.03 (s, 1H), 6.54 (s, 2H), 5.46 (d, \(J = 6.3\) Hz, 1H), 5.21 (s, 1H), 4.30 (d, \(J = 6.3\) Hz, 1H), 2.44 (s, 3H), 1.28 (s, 18H) ppm.

\textbf{\({\text{13C}}\)NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 195.0, 153.5, 144.6, 136.4, 134.7, 133.4, 133.8, 131.6, 131.5, 130.0 (2C), 129.2 (2C), 128.9, 128.7 (2C), 127.7 (2C), 124.6 (2C), 116.4, 115.3, 74.2, 51.8, 34.2 (2C), 30.0 (6C), 21.7 ppm.

\textbf{HRMS (ESI)}: m/z [M+H]+ calcld for C\textsubscript{36}H\textsubscript{39}BrNO\textsubscript{4}S 660.1783; found 660.1755

\textbf{According to general procedure, 3v was obtained as a colorless solid (39 mg, 77% yield).}

\textbf{Melting Point:} 176-179 °C

\textbf{\textit{H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.86 (d, \(J = 7.2\) Hz, 2H), 7.82 (d, \(J = 8.3\) Hz, 2H), 7.77 (d, \(J = 8.2\) Hz, 1H), 7.61 (t, \(J = 7.4\) Hz, 1H), 7.45 (t, \(J = 7.8\) Hz, 2H), 7.33-7.29 (m, 3H), 6.99 (td, \(J = 7.5, 0.7\) Hz, 1H), 6.82 (d, \(J = 7.5\) Hz, 1H), 6.15 (s, 2H), 5.42 (d, \(J = 5.5\) Hz, 1H), 4.68 (s, 1H), 4.20 (d, \(J = 5.4\) Hz, 1H), 2.45 (s, 3H), 2.04 (s, 6H) ppm.

\textbf{\textit{13C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 194.9, 151.6, 144.3, 141.5, 134.8, 134.2, 133.9, 133.6, 133.0, 129.9 (2C), 129.2 (2C), 128.7 (2C), 127.9 (2C), 127.6 (2C), 125.8, 124.2, 123.4, 114.4, 74.0, 51.0, 21.7, 15.8 (2C) ppm.

\textbf{HRMS (ESI)}: m/z [M-H]- calcld for C\textsubscript{30}H\textsubscript{26}NO\textsubscript{4}S 496.1583; found 496.1560

\textbf{(2S,3S)-3-(4-hydroxy-3,5-dimethylphenyl)-1-toslylindolin-2-yl)(phenyl)methanone (3v)}

According to general procedure, 3v was obtained as a colorless solid (39 mg, 77% yield).

\textbf{Melting Point:} 202-204 °C

\textbf{\textit{H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 8.00 (d, \(J = 7.9\) Hz, 2H), 7.88 (d, \(J = 7.4\) Hz, 2H), 7.62 (td, \(J = 7.4, 1.1\) Hz, 2H), 7.57 (d, \(J = 8.2\) Hz, 1H), 7.52 (t, \(J = 7.8\) Hz, 2H), 7.46 (t, \(J = 7.8\) Hz, 2H), 7.29 (d, \(J = 8.5\) Hz, 1H), 7.01 (t, \(J = 7.4\) Hz, 1H), 6.94 (d, \(J = 7.5\) Hz, 1H), 6.60 (s, 2H), 5.54 (d, \(J = 6.1\) Hz, 1H), 5.18 (s, 1H), 4.37 (d, \(J = 6.1\) Hz, 1H), 1.28 (s, 18H) ppm.

\textbf{(2S,3S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-(phenylsulfonyl)indolin-2-yl)(phenyl)methanone (3w)}

According to general procedure, 3w was obtained as a colorless solid (40 mg, 71% yield).

\textbf{Melting Point:} 202-204 °C

\textbf{\textit{H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 8.00 (d, \(J = 7.9\) Hz, 2H), 7.88 (d, \(J = 7.4\) Hz, 2H), 7.62 (td, \(J = 7.4, 1.1\) Hz, 2H), 7.57 (d, \(J = 8.2\) Hz, 1H), 7.52 (t, \(J = 7.8\) Hz, 2H), 7.46 (t, \(J = 7.8\) Hz, 2H), 7.29 (d, \(J = 8.5\) Hz, 1H), 7.01 (t, \(J = 7.4\) Hz, 1H), 6.94 (d, \(J = 7.5\) Hz, 1H), 6.60 (s, 2H), 5.54 (d, \(J = 6.1\) Hz, 1H), 5.18 (s, 1H), 4.37 (d, \(J = 6.1\) Hz, 1H), 1.28 (s, 18H) ppm.
$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 195.5, 153.2, 141.8, 138.2, 136.3, 134.6, 133.6, 133.4, 132.4, 132.2, 129.2 (4C), 128.7 (2C), 127.7 (2C), 126.0, 124.5 (2C), 123.9, 113.8, 74.0, 52.0, 34.2 (2C), 30.1 (6C) ppm.

HRMS (ESI): m/z [M-H$^-]$ calcd for C$_{35}$H$_{36}$NO$_5$S 596.2365; found 566.2338

According to general procedure, 3x was obtained as a colorless solid (42 mg, 70% yield).

Melting Point: 220-222 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.91 (d, $J = 8.9$ Hz, 2H), 7.86 (d, $J = 7.5$ Hz, 2H), 7.59 (t, $J = 7.8$ Hz, 2H), 7.44 (t, $J = 7.7$ Hz, 2H), 7.29 (t, $J = 8.0$ Hz, 1H), 7.00 (t, $J = 7.5$ Hz, 1H), 6.97 (d, $J = 8.9$ Hz, 2H), 6.93 (d, $J = 7.5$ Hz, 1H), 6.58 (s, 2H), 5.45 (d, $J = 6.5$ Hz, 1H), 5.18 (s, 1H), 4.36 (d, $J = 6.4$ Hz, 1H), 3.87 (s, 3H), 1.28 (s, 18H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 195.8, 163.5, 153.2, 142.0, 136.2, 134.7, 133.6, 132.5, 132.3 129.9 (2C), 129.5, 129.2 (2C), 128.6 (2C), 126.0, 124.6 (2C), 123.8, 114.3 (2C), 113.9, 74.1, 55.5, 52.1, 34.2 (2C), 30.1 (6C) ppm.

HRMS (ESI): m/z [M-H$^-]$ calcd for C$_{36}$H$_{38}$NO$_5$S 596.2471; found 596.2445

According to general procedure, 3y was obtained as a colorless solid (45 mg, 77% yield).

Melting Point: 219-221 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.07-8.01 (m, 2H), 7.87 (d, $J = 7.3$ Hz, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.51 (d, $J = 8.2$ Hz, 1H), 7.46 (t, $J = 7.8$ Hz, 2H), 7.29 (t, $J = 7.7$ Hz, 1H), 7.20 (t, $J = 8.5$ Hz, 2H), 7.02 (t, $J = 7.4$ Hz, 1H), 6.96 (d, $J = 7.5$ Hz, 1H), 6.62 (s, 2H), 5.55 (d, $J = 6.0$ Hz, 1H), 5.20 (s, 1H), 4.36 (d, $J = 5.9$ Hz, 1H), 1.30 (s, 18H) ppm.
13C NMR (126 MHz, CDCl3) δ 195.4, 166.6, 164.5, 153.3, 141.6, 136.3, 134.4, 133.7, 132.4, 132.1, 130.5, 130.4, 129.2 (2C), 128.7 (2C), 126.1, 124.5 (2C), 124.0, 116.5, 116.3, 113.6, 74.1, 51.9, 34.2 (2C), 30.1 (6C) ppm.

HRMS (ESI): m/z [M-H]− calcld for C35H35FNO4S 584.2271; found 584.2245

N-(2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phenyl)-4-methylbenzenesulfonamide (1a’)

Melting Point: 183-185°C

1H NMR (500 MHz, CDCl3) δ 7.67 (d, J = 8.3 Hz, 2H), 7.50 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.26 (d, J = 7.5 Hz, 1H), 7.25-7.21 (m, 3H), 7.09 (d, J = 2.1 Hz, 1H), 6.83 (d, J = 2.2 Hz, 1H), 6.73 (s, 1H), 6.67 (d, J = 5.1 Hz, 1H), 2.36 (s, 3H), 1.34 (s, 9H), 1.26 (s, 9H) ppm.

13C NMR (126 MHz, CDCl3) δ 186.4, 149.7, 148.2, 144.2, 136.4, 136.1, 135.0, 134.3, 133.9, 131.5, 130.1, 129.8 (2C), 127.2 (2C), 126.0, 124.9, 35.4, 35.0, 29.5 (6C), 21.6 ppm.

IR (ATR): 3301, 2945, 2920, 1640, 1610, 1575, 1577, 1500, 1388, 1360, 1160, 1089, 1023, 954, 919, 901, 820, 757, 744, 665 cm⁻¹.

HRMS (ESI): m/z [M-H]− calcld for C28H32NO3S: 462.2103; found 462.2050.
5. Crystal structure of 3g:

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S = 1.017  Npar= 798
6. NMR Spectra:

$^1$H NMR of 3a:

$^{13}$C NMR of 3a:
$^{1}$H NMR of $3b$:

$^{13}$C NMR of $3b$: 
$^1\text{H NMR of } 3\text{c}:

![H NMR spectrum of 3c]

$^{13}\text{C NMR of } 3\text{c}:

![C NMR spectrum of 3c]
**$^1$H NMR of 3d:**

![H NMR Spectrum](image)

**$^{13}$C NMR of 3d:**

![C NMR Spectrum](image)
$^1$H NMR of 3e:

$^{13}$C NMR of 3e:
$^1$H NMR of 3g:

$^{13}$C NMR of 3g:
$^1$H NMR of 3h:

$^{13}$C NMR of 3h:
$^1$H NMR of 3i:

$^{13}$C NMR of 3i:
$^1$H NMR of 3j:

$^{13}$C NMR of 3j:
$^1$H NMR of 3k:

$^{13}$C NMR of 3k:
$^1$H NMR of 31:

$t$-Bu

OH

$\text{N}$

$\text{Ts}$

$\text{Cl}$

$\text{Cl}$

31

$^1$C NMR of 31:
$^1$H NMR of 3m:

$^{13}$C NMR of 3m:
$^1$H NMR of $3n$:

$^{13}$C NMR of $3n$: 
$^1$H NMR of 3o:

\[
\begin{array}{c}
\text{H} \quad \text{N} \quad \text{M} \quad \text{R} \\
\end{array}
\]

$^{13}$C NMR of 3o:
$^1$H NMR of 3p:

$^{13}$C NMR of 3p:
$^1$H NMR of 3q:

$^{13}$C NMR of 3q:
$^1$H NMR of 3r:

$^{13}$C NMR of 3r:
$^{1}$H NMR of 3s:

$^{13}$C NMR of 3s:
$^1$H NMR of 3t:

![H NMR Spectrum](image1)

$^{13}$C NMR of 3t:

![C NMR Spectrum](image2)
$^1$H NMR of 3u:

$^{13}$C NMR of 3u:
$^1$H NMR of 3w:

![$^1$H NMR spectrum of 3w](image)

$^{13}$C NMR of 3w:

![$^{13}$C NMR spectrum of 3w](image)
$^1$H NMR of 3x:

$^{13}$C NMR of 3x:
$^1$H NMR of 3y:

$^{13}$C NMR of 3y:
$^{13}$CNMR of \( \text{p-QMs} \ 1^\prime \):