Supporting Information

Phosphine-Catalyzed Intramolecular Rauhut-Currier Reaction:
Enantioselective Synthesis of Hydro-2H-Indole Derivatives

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I. General Information

All the starting materials were obtained from commercial sources and used without further purification unless otherwise stated. Yields referred to isolated compounds through flash column chromatography performed using 300-400 mesh silica gel. NMR spectra were recorded on Varian Brucker ARX 400 spectrometer in CDCl$_3$ solution and the chemical shifts were reported in parts per million (ppm) relative to internal standard TMS (0 ppm) for $^1$H NMR and chloroform-d (77.0 ppm) for $^{13}$C NMR. Coupling constants were given in Hertz (Hz). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), brs (broad singlet) and m (multiplet). Enantiomeric excesses of the RC products were determined by Agilent 6890 chiral-phase high performance liquid chromatography (HPLC) or LabAlliance PC2001, using chiralcel AD-H, OD-H, and IC. Optical rotations were performed on Perkin-Elmer-341 MC digital polarimeter. Infrared spectra (IR) spectra were recorded on a Perkin-Elmer 983G instrument. High resolution mass spectrometry (HRMS) were obtained on an IonSpec FT-ICR mass spectrometer with ESI or MALDI resource. Melting points were measured on a RY-I apparatus and are reported uncorrected.

II. Preparation of the N-tosylacrylamide *

![Diagram](image)

* Unless otherwise specified, all starting materials N-tosylacrylamide (1a to 1v) were prepared as above process.
The Synthesis of B: A round bottom flask was charged with a methylene chloride solution of \( p \)-anisidine \( A \) (100 mmol, 12.3 g), followed by the addition of pyridine (200 mmol, 16.1 mL). Tosyl chloride (105 mmol, 20 g) was added in many ports. The reaction mixture was allowed to stir at room temperature until completion of the reaction monitored by TLC. The reaction was then quenched with dilute hydrochloric acid solution, extracted with methylene chloride, washed with sodium bicarbonate solution, and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the crude product \( B \) was obtained without further purification and used for the next synthesis step.

The Synthesis of C: To a stirred solution of sulfonamide \( B \) (50 mmol, 13.9 g) in anhydrous methanol (80 mL) at 0 °C (ice bath) was added (Diacetoxyiodo)benzene\(^{[1]}\) (50 mmol, 16.1 g) slowly. The reaction mixture was stirred at the same temperature for another 1 h after the addition of (Diacetoxyiodo)benzene. Then the precipitates were filtered from the reaction mixture, collected and dried and used directly in the next step.

The Synthesis of D: To a flame dried round bottle flask with a magnetic stirring bar under Argon atmosphere were added bromobenzene (12 mmol, 1.26 mL) and anhydrous tetrahydrofuran (15 mL). The resulting mixture was cooled to –78 °C for 20 min, and \( n \)-butyllithium solution (3.52 mL) (2.5 mol/L in hexane) was added in one port under Argon atmosphere. The reaction mixture was kept at –78 °C for another 2 h. And then a solution of sulfonyl imides \( C \) (8 mmol, 2.46 g) in anhydrous tetrahydrofuran was added, and the reaction mixture was still kept at –78 °C for 10 h. The reaction was then quenched at –78 °C with hydrochloric acid solution, and another 3 h were needed for the reaction at room temperature. After that the mixture was extracted with ethyl acetate (2 \( \times \) 100 mL). The combined organic extracts were washed by water (2 \( \times \) 100 mL) and dried over anhydrous magnesium sulfate and concentrated in vacuo. The residue was recrystallization with ethyl acetate and \( n \)-hexane.

The Synthesis of 1a: A round bottom flask was charged with a methylene chloride solution of amine \( D \) (3 mmol, 1.017 g), which were easily accessible from the corresponding \( p \)-anisidine, followed by the addition of ethyldiisopropylamine (6
mmol, 990 μL). And the reaction mixture was cooled to 0 °C (ice bath) for 10 min. Acrolyl chloride (4.5 mmol, 365 μL) in methylene chloride (5 mL) was added drop wise slowly. The reaction mixture was allowed to stir for another 10 minutes at same temperature after the addition of acrolyl chloride. The solvent was removed in vacuo and the crude product was directly purified by silica gel flash column chromatography using petroleum ether/ethyl acetate as an elutant to give the desired product 1a as a white or pale solid and recovered D.

### III. Preparation of the Catalysts

To a stirred solution of salicylic acid (0.6 mmol, 83 mg), triethylamine (3 mmol, 416 μL), BOP (0.625 mmol, 277 mg) in anhydrous tetrahydrofuran (3 mL) at 0 °C under Ar, a solution of aminophosphine E[2,3](0.5 mmol, 143 mg) in anhydrous tetrahydrofuran (3 mL) was added. After 1 h at 0 °C, the solution was then stirred at room temperature for 10 h until completion of the reaction monitored by TLC. Then saturated sodium bicarbonate solution (10 mL) was added to quench the reaction. The reaction mixture was extracted with ethyl acetate, the combined organic layers were dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate as the eluent to afford the catalyst 3c.

**N-((2S,3S)-1-(diphenylphosphino)-3-methylpentan-2-yl)-2-hydroxybenzamide**

\[ [\alpha]_{D}^{29} = +8.8 \ (c = 1.0, \text{CH}_2\text{Cl}_2) \]

\[ ^{1}H \text{NMR (400 MHz, CDCl}_3) \delta 12.32 \ (s, 1H), \ 7.37 \ (dt, \]
J = 36.5, 12.5 Hz, 1H), 6.94 (d, J = 8.2 Hz, 1H), 6.78 (d, J = 7.4 Hz, 1H), 6.69 (t, J = 7.4 Hz, 1H), 6.00 (d, J = 7.7 Hz, 1H), 4.28 (s, 1H), 2.41 (d, J = 12.0 Hz, 1H), 2.37 – 2.29 (m, 1H), 1.84 (m, 1H), 1.48 (d, J = 6.2 Hz, 1H), 1.15 (dt, J = 21.6, 7.6 Hz, 1H), 0.94 (d, J = 6.5 Hz, 3H), 0.88 (t, J = 7.1 Hz, 3H); 13C NMR (101 MHz, CDCl3) δ 169.14 (s), 161.52 (s), 138.12 (dd, J = 31.7, 12.7 Hz), 138.12 (dd, J = 31.7, 12.7 Hz), 133.98 (s), 132.82 (t, J = 18.8 Hz), 129.25 – 128.49 (m), 125.13 (s), 118.40 (d, J = 6.4 Hz), 114.25 (s), 51.80 (d, J = 13.5 Hz), 39.12 (d, J = 7.7 Hz), 30.33 (d, J = 14.7 Hz), 25.48 (s), 14.90 (s), 11.63 (s); 31P NMR (162 MHz, CDCl3) δ -23.40 (s); HRMS (ESI) m/z calcd for C25H28N2O2P [M+H]+ =406.1930, found = 406.1937.

Catalyst 3e was prepared from 2-methoxybenzoic acid following the procedure described for the preparation of 3c.

IV. References

V. General Procedure and Spectroscopic Data and HPLC Chromatogram
To a stirred solution of 1 (0.1 mmol) in toluene (1.0 mL) at 0 °C, chiral aminophosphine catalyst 3e (0.02 mmol) was added in one portion. Then the reaction mixture was stirred at this temperature. After completion of the reaction (monitored by TLC), the reaction mixture was directly applied to a silica gel dropper column plug (petroleum ether/ethyl acetate as eluent) to give desired product 2.
N-(4-oxo-[1,1'-biphenyl]-1(4H)-yl)-N-tosylacrylamide

(1a) 70% yield; white solid; mp 121-124°C; ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, J = 8.3 Hz, 2H), 7.32 (s, 1H), 7.27 (ddd, J = 12.8, 6.3, 3.9 Hz, 8H), 6.94 (dd, J = 16.8, 10.2 Hz, 1H), 6.22 (d, J = 16.8 Hz, 1H), 6.04 (d, J = 10.2 Hz, 2H), 5.78 (d, J = 10.2 Hz, 1H), 2.44 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 184.76 (C=O, C20), 169.49 (C=O, C10), 148.01 (CH, C18, C22), 145.73 (C, Ar), 138.68 (C, Ar), 136.46 (C, Ar), 133.32 (CH, C9), 130.93 (CH₂, C8), 129.86 (CH, C19, C21), 129.42 (CH, Ar), 128.62 (CH, Ar), 128.56 (CH, Ar), 127.73 (CH, Ar), 125.09 (CH, Ar), 65.66 (C11), 21.77 (CH₃, C1); IR (neat): ν 2989, 2377, 2350, 2314, 1671, 1504, 1275, 1261, 763 cm⁻¹; HRMS (ESI) m/z calcd for C₂₂H₁₉NO₄S [M+H]⁺ = 394.1113, found = 394.1113.

N-(4'-fluoro-4-oxo-[1,1'-biphenyl]-1(4H)-yl)-N-tosylacrylamide

(1b) 78% yield; white solid; mp 108-110°C; ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, J = 8.3 Hz, 2H), 7.28 (dd, J = 12.1, 5.1 Hz, 6H), 6.94 (dt, J = 16.9, 9.5 Hz, 3H), 6.23 (d, J = 16.8 Hz, 1H), 6.04 (d, J = 10.2 Hz, 2H), 5.80 (d, J = 10.6 Hz, 1H), 2.44 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 184.48, 169.45, 163.63, 161.16, 147.69, 145.82, 136.29, 134.51 (d, J = 3.4 Hz), 133.19, 131.16, 129.86, 128.50, 127.72, 126.91 (d, J = 8.3 Hz), 116.39 (d, J = 21.9 Hz), 65.02, 21.74; IR (neat): ν 2989, 2377, 2350, 2314, 1671, 1504, 1275, 1261, 763, 750 cm⁻¹; HRMS (ESI) m/z calcd for C₂₂H₁₈FNO₄S
[M+H]^+ = 412.1019, found = 412.1044.

N-(4'-chloro-4-oxo-[1,1'-biphenyl]-1(4H)-yl)-N-tosylacrylamide

(1c) 88% yield; white solid; mp 122-124°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.62 (d, \(J = 8.4\) Hz, 2H), 7.31 – 7.22 (m, 8H), 6.95 (dd, \(J = 16.8, 10.2\) Hz, 1H), 6.24 (dd, \(J = 16.8, 1.0\) Hz, 1H), 6.05 (d, \(J = 10.3\) Hz, 2H), 5.81 (dd, \(J = 10.2, 1.0\) Hz, 1H), 2.44 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 184.43, 169.35, 147.44, 145.88, 137.36, 136.26, 134.52, 133.07, 131.28, 129.88, 129.58, 128.49, 127.91, 126.37, 65.11, 21.74; IR (neat): ν 2989, 2377, 2350, 2320, 1699, 1671, 1398, 1359, 1275, 1261, 1192, 1087, 987, 763, 750 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{22}\)H\(_{18}\)ClNO\(_4\)S [M+H]^+ = 428.0723, found = 428.0728.

N-(3'-chloro-4-oxo-[1,1'-biphenyl]-1(4H)-yl)-N-tosylacrylamide

(1d) 52% yield; white solid; mp 158-160°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.54 (d, \(J = 7.9\) Hz, 2H), 7.19 (dd, \(J = 20.6, 9.7\) Hz, 8H), 6.89 (dd, \(J = 16.7, 10.2\) Hz, 1H), 6.17 (d, \(J = 16.8\) Hz, 1H), 6.00 (d, \(J = 9.9\) Hz, 2H), 5.76 (d, \(J = 10.2\) Hz, 1H), 2.38 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 184.45, 169.33, 147.26, 145.91, 140.76, 136.24, 135.32, 133.03, 131.32, 130.57, 129.90, 128.80, 128.48, 128.10, 125.32, 123.15, 65.14, 21.76; IR (neat): ν 2989, 2377, 2350, 2319, 1699, 1671, 1398, 1359, 1275, 1261, 1086, 991, 763, 750 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{22}\)H\(_{18}\)ClNO\(_4\)S [M+H]^+ = 428.0723, found = 428.0728.

N-(4'-bromo-4-oxo-[1,1'-biphenyl]-1(4H)-yl)-N-tosylacrylamide
(1e) 75% yield; white solid; mp 123-126°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (d, $J$ = 8.3 Hz, 2H), 7.43 (d, $J$ = 8.7 Hz, 2H), 7.29 (t, $J$ = 10.0 Hz, 4H), 7.19 (d, $J$ = 8.7 Hz, 2H), 6.98 (dd, $J$ = 16.8, 10.2 Hz, 1H), 6.27 (d, $J$ = 16.8 Hz, 1H), 6.08 (d, $J$ = 10.2 Hz, 2H), 5.84 (d, $J$ = 10.3 Hz, 1H), 2.47 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 184.42, 169.33, 147.38, 145.89, 137.93, 136.25, 133.04, 132.52, 131.32, 129.89, 128.48, 127.94, 126.64, 122.66, 65.18, 21.75; IR (neat): ν 2989, 2377, 2350, 2319, 1699, 1670, 1397, 1360, 1275, 1261, 1085, 986, 763, 750 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{22}$H$_{18}$BrNO$_4$S [M+H]$^+$ = 472.0218, found = 472.0218.

N-(4-oxo-4′-(trifluoromethyl)-[1,1′-biphenyl]-1(4H)-yl)-N-tosylacrylamide

(1f) 79% yield; white solid; mp 140-142°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56 (d, $J$ = 8.3 Hz, 2H), 7.47 (d, $J$ = 8.4 Hz, 2H), 7.34 (d, $J$ = 8.4 Hz, 2H), 7.20 (dd, $J$ = 13.6, 6.9 Hz, 4H), 6.93 (dd, $J$ = 16.8, 10.2 Hz, 1H), 6.17 (d, $J$ = 16.8 Hz, 1H), 6.02 (d, $J$ = 10.2 Hz, 2H), 5.76 (d, $J$ = 10.3 Hz, 1H), 2.38 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 184.29, 169.20, 147.06, 145.99, 142.97, 136.24, 132.79, 131.49, 130.44, 129.94, 128.45, 128.27, 126.40 (d, $J$ = 3.7 Hz), 126.35, 125.27, 65.34, 21.73; IR (neat): ν 2989, 2377, 2350, 2319, 1699, 1672, 1398, 1325, 1275, 1261, 1086, 988, 763, 750 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{23}$H$_{18}$F$_3$NO$_4$S [M+H]$^+$ = 462.0987, found = 462.0977.

N-(4-oxo-3′,5′-bis(trifluoromethyl)-[1,1′-biphenyl]-1(4H)-yl)-N-tosylacrylamide
N-tosyl-N-(3',4',5'-trifluoro-4-oxo-[1,1'-biphenyl]-1(4H)-yl)acrylamide

(1g) 85% yield; white solid; mp 169-172°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.77 (s, 1H), 7.71 (s, 2H), 7.62 (d, \(J = 8.3\) Hz, 2H), 7.31 (d, \(J = 8.1\) Hz, 2H), 7.29 – 7.22 (m, 2H), 7.01 (dd, \(J = 16.8, 10.3\) Hz, 1H), 6.24 (d, \(J = 16.8\) Hz, 1H), 6.15 (d, \(J = 10.2\) Hz, 2H), 5.86 (d, \(J = 10.3\) Hz, 1H), 2.46 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 183.87, 169.34, 146.21 (d, \(J = 17.0\) Hz), 142.18, 136.00, 132.91, 132.55 (d, \(J = 3.8\) Hz), 132.05, 130.05, 128.93, 128.41, 125.02 (d, \(J = 3.2\) Hz), 124.11, 122.46, 121.40, 64.86, 21.76; IR (neat): \(\tilde{\nu}\) 2989, 2377, 2349, 2314, 1697, 1673, 1364, 1277, 1261, 1178, 1136, 918, 763, 750 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{24}\)H\(_{17}\)F\(_6\)NO\(_4\)S [M+H]\(^+\) = 530.0861, found = 530.0873.

N-(3'-methyl-4-oxo-[1,1'-biphenyl]-1(4H)-yl)-N-tosylacrylamide

(1h) 37% yield; white solid; mp 139-141°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.67 (d, \(J = 8.3\) Hz, 2H), 7.33 (t, \(J = 8.6\) Hz, 4H), 7.03 – 6.85 (m, 3H), 6.28 (d, \(J = 16.8\) Hz, 1H), 6.21 (d, \(J = 10.2\) Hz, 2H), 5.82 (d, \(J = 10.3\) Hz, 1H), 2.47 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 184.06, 168.30, 145.80, 145.23, 136.53, 131.91, 131.12, 129.89, 129.09, 128.28, 123.42, 120.98, 112.79 (d, \(J = 3.4\) Hz), 112.62 (d, \(J = 3.0\) Hz), 63.45, 21.73; IR (neat): \(\tilde{\nu}\) 2989, 2377, 2349, 2314, 1693, 1673, 1510, 1473, 1275, 1261, 1089, 926, 763, 750 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{24}\)H\(_{17}\)F\(_6\)NO\(_4\)S [M+H]\(^+\) = 530.0861, found = 530.0873.
(1i) 88% yield; white solid; mp 139-140°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62 (d, $J = 8.3$ Hz, 2H), 7.31 (s, 1H), 7.29 (d, $J = 2.1$ Hz, 2H), 7.26 (s, 1H), 7.16 (t, $J = 7.7$ Hz, 1H), 7.09 (d, $J = 8.2$ Hz, 1H), 7.05 (d, $J = 7.1$ Hz, 2H), 6.93 (dd, $J = 16.8, 10.2$ Hz, 1H), 6.22 (d, $J = 16.8$ Hz, 1H), 6.03 (d, $J = 10.2$ Hz, 2H), 5.79 (d, $J = 10.4$ Hz, 1H), 2.44 (s, 3H), 2.26 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 184.82, 169.53, 148.11, 145.65, 139.24, 138.41, 136.45, 133.38, 130.80, 129.78, 129.44, 129.23, 128.54, 127.59, 125.72, 122.22, 65.62, 21.73, 21.58; IR (neat): $\tilde{\nu}$ 2989, 2377, 2349, 2320, 1699, 1669, 1397, 1359, 1275, 1261, 1086, 984, 763, 750 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{23}$H$_{21}$NO$_4$S [M+H]$^+$ = 408.1270, found = 408.1292.

$\text{N-(3'-methoxy-4-oxo-[1,1'-biphenyl]-1(4H)-yl)-N-tosylacrylamide}$

(1j) 28% yield; white solid; mp 149-152°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 – 7.42 (m, 3H), 7.30 – 7.15 (m, 4H), 6.95 (dd, $J = 16.2, 10.7$ Hz, 1H), 6.88 (d, $J = 7.0$ Hz, 1H), 6.78 (d, $J = 12.9$ Hz, 2H), 6.24 (d, $J = 16.4$ Hz, 1H), 6.04 (d, $J = 9.4$ Hz, 2H), 5.80 (d, $J = 9.7$ Hz, 1H), 3.73 (s, 3H), 2.44 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 184.74, 169.45, 160.15, 147.81, 145.68, 140.09, 136.43, 133.30, 130.88, 130.40, 129.80, 128.51, 127.71, 117.36, 113.51, 111.38, 65.55, 55.24, 21.72; IR (neat): $\tilde{\nu}$ 2989, 2377, 2350, 2319, 1699, 1670, 1275, 1261, 1133, 763, 750 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{23}$H$_{21}$NO$_5$S [M+H]$^+$ = 424.1219, found = 424.1231.

$\text{N-(4-oxo-[1,1':4',1''-terphenyl]-1(4H)-yl)-N-tosylacrylamide}$
(1k) 59% yield; white solid; mp 113-115°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.64 (d, \(J = 8.1 \) Hz, 2H), 7.51 (t, \(J = 7.3 \) Hz, 4H), 7.41 (t, \(J = 7.5 \) Hz, 2H), 7.35 (d, \(J = 9.3 \) Hz, 5H), 7.29 (d, \(J = 8.2 \) Hz, 2H), 6.98 (dd, \(J = 16.8, 10.2 \) Hz, 1H), 6.25 (d, \(J = 16.8 \) Hz, 1H), 6.07 (d, \(J = 10.1 \) Hz, 2H), 5.81 (d, \(J = 10.3 \) Hz, 1H), 2.45 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta \) 184.73, 169.51, 147.92, 145.74, 141.44, 139.84, 137.38, 136.41, 133.28, 131.03, 129.85, 129.61, 128.84, 128.53, 128.03, 127.73, 127.03, 125.51, 65.49, 21.76; IR (neat): \(\nu \) 2989, 2377, 2349, 2319, 1699, 1669, 1485, 1397, 1359, 1275, 1261, 1086, 985, 763, 750 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{28}\)H\(_{23}\)NO\(_4\)S [M+H]\(^+\) = 470.1426, found = 470.1437.

N-(1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-N-tosylacrylamide

(II) 30% yield; white solid; mp 76-78°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.63 (d, \(J = 8.3 \) Hz, 2H), 7.31 – 7.25 (m, 2H), 7.10 (d, \(J = 10.2 \) Hz, 2H), 6.77 (dd, \(J = 16.9, 10.2 \) Hz, 1H), 6.47 (d, \(J = 16.9 \) Hz, 1H), 6.00 (d, \(J = 10.2 \) Hz, 2H), 5.95 (d, \(J = 10.3 \) Hz, 1H), 2.43 (s, 3H), 1.56 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta \) 184.39, 170.42, 150.29, 145.39, 136.59, 134.02, 131.70, 129.78, 128.36, 127.64, 126.35, 124.35, 121.76; IR (neat): \(\nu \) 2989, 2377, 2350, 2319, 1700, 1668, 1397, 1350, 1275, 1261, 1176, 1159, 1086, 1042, 971, 860, 763, 750 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{17}\)H\(_{17}\)NO\(_4\)S [M+H]\(^+\) = 332.0956, found = 332.0960.

N-(1-ethyl-4-oxocyclohexa-2,5-dien-1-yl)-N-tosylacrylamide
(1m) 61% yield; white solid; mp 89-91°C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.58 (d, $J$ = 6.8 Hz, 2H), 7.24 (d, $J$ = 6.8 Hz, 2H), 7.07 (d, $J$ = 9.3 Hz, 2H), 6.82 (dd, $J$ = 16.2, 10.4 Hz, 1H), 6.50 (d, $J$ = 16.9 Hz, 1H), 5.99 (dd, $J$ = 20.5, 9.8 Hz, 3H), 2.42 (s, 3H), 1.94 (d, $J$ = 6.7 Hz, 2H), 0.74 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 184.67, 170.84, 148.67, 145.41, 136.54, 134.56, 131.53, 129.68, 128.87, 128.57, 64.10, 31.02, 21.68, 8.19; IR (neat): ν 2988, 2377, 2350, 2319, 1699, 1669, 1455, 1398, 1354, 1275, 1261, 1175, 1085, 975, 763, 750 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{18}$H$_{19}$NO$_4$S [M+H]$^+$ = 346.1113, found = 346.1112.

N-(4-oxo-1-vinylcyclohexa-2,5-dien-1-yl)-N-tosylacrylamide

(1n) 68% yield; white solid; mp 111-114°C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.63 (d, $J$ = 8.3 Hz, 2H), 7.29 (s, 2H), 7.07 (d, $J$ = 10.1 Hz, 2H), 6.85 (dd, $J$ = 16.9, 10.2 Hz, 1H), 6.43 (d, $J$ = 16.8 Hz, 1H), 6.06 (d, $J$ = 10.1 Hz, 2H), 5.91 (d, $J$ = 10.3 Hz, 1H), 5.69 (dd, $J$ = 17.2, 10.4 Hz, 1H), 5.22 (d, $J$ = 17.2 Hz, 1H), 5.13 (d, $J$ = 10.4 Hz, 1H), 2.44 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 184.72, 169.31, 147.07, 145.57, 136.58, 134.99, 133.31, 131.37, 129.82, 128.39, 128.03, 117.09, 64.22, 21.70; IR (neat): ν 2989, 2377, 2349, 2319, 1699, 1669, 1398, 1355, 1275, 1261, 1176, 1086, 983, 924, 764, 750 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{18}$H$_{17}$NO$_4$S [M+H]$^+$ = 344.0956, found = 344.0966.

N-(4-oxo-1-((trimethylsilyl)ethynyl)cyclohexa-2,5-dien-1-yl)-N-tosylacrylamide
(1o) 87% yield; white solid; mp 136-138°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.74 (d, \(J = 8.3\) Hz, 2H), 7.31 (d, \(J = 8.2\) Hz, 2H), 7.02 (d, \(J = 10.0\) Hz, 2H), 6.70 (dd, \(J = 16.8, 10.2\) Hz, 1H), 6.44 (d, \(J = 16.8\) Hz, 1H), 6.13 (d, \(J = 10.0\) Hz, 2H), 5.89 (d, \(J = 10.2\) Hz, 1H), 2.45 (s, 3H), 0.06 (s, 9H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 184.89, 168.86, 145.93, 145.70, 133.28, 132.08, 130.48, 128.65, 128.45, 96.38, 95.08, 78.03, 77.71, 77.39, 57.14, 22.34, -0.00 (TMS); IR (neat): \(\nu\) 2989, 2377, 2350, 2319, 1702, 1671, 1456, 1398, 1357, 1275, 1261, 1176, 1149, 853, 763, 750 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{21}\)H\(_{23}\)N\(_2\)O\(_4\)SSi [M+H]\(^+\) = 414.1195, found = 414.1207.

N-(1-cyclopentyl-4-oxocyclohexa-2,5-dien-1-yl)-N-tosylacrylamide

(1p) 20% yield; oil solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.54 (d, \(J = 8.1\) Hz, 2H), 7.22 (d, \(J = 7.9\) Hz, 2H), 7.06 (d, \(J = 10.2\) Hz, 2H), 6.82 (dd, \(J = 16.9, 10.1\) Hz, 1H), 6.50 (d, \(J = 16.9\) Hz, 1H), 6.01 (d, \(J = 10.2\) Hz, 2H), 5.94 (d, \(J = 10.1\) Hz, 1H), 2.93 – 2.72 (m, 1H), 2.40 (s, 3H), 1.46 (s, 6H), 1.28 – 1.18 (m, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 184.82, 171.16, 147.31, 145.37, 136.52, 134.76, 130.89, 129.72, 129.61, 128.70, 66.26, 43.10, 27.62, 26.11, 21.68; IR (neat): \(\nu\) 2988, 2377, 2350, 2319, 2308, 2239, 1702, 1671, 1456, 1398, 1357, 1275, 1261, 1176, 1149, 853, 763, 750 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{21}\)H\(_{23}\)N\(_2\)O\(_4\)S [M+H]\(^+\) = 386.1426, found = 386.1473.

N-(4-oxo-[1,1’-bi(cyclohexane)]-2,5-dien-1-yl)-N-tosylacrylamide
(1q) 44% yield; oil solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 (d, $J = 8.1$ Hz, 2H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.06 (d, $J = 10.2$ Hz, 2H), 6.90 (dd, $J = 16.9$, 10.1 Hz, 1H), 6.48 (d, $J = 16.9$ Hz, 1H), 6.01 (d, $J = 10.2$ Hz, 2H), 5.89 (d, $J = 10.1$ Hz, 1H), 2.40 (s, 3H), 2.17 (t, $J = 11.9$ Hz, 1H), 1.69 (d, $J = 12.5$ Hz, 2H), 1.58 (d, $J = 11.2$ Hz, 3H), 1.17 – 0.98 (m, 3H), 0.89 (dd, $J = 23.6$, 11.6 Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 184.94, 170.62, 147.30, 145.31, 136.84, 134.60, 130.34, 129.75, 129.60, 128.53, 67.56, 42.04, 27.55, 26.27, 26.05, 21.66; IR (neat): $\nu$ 2988, 2933, 2857, 2377, 2350, 2319, 1698, 1670, 1398, 1355, 1275, 1261, 1175, 1085, 980, 763, 750 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{22}$H$_{25}$NO$_4$S [M+H]$^+$ =400.1583, found =400.1592.

N-(4'-bromo-4-oxo-[1,1'-biphenyl]-1(4H)-yl)-N-(phenylsulfonyl)acrylamide

(1r) 72% yield; white solid; mp 125-127°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J = 7.7$ Hz, 2H), 7.64 (t, $J = 7.4$ Hz, 1H), 7.50 (t, $J = 7.8$ Hz, 2H), 7.40 (d, $J = 8.6$ Hz, 2H), 7.26 (d, $J = 10.0$ Hz, 2H), 7.17 (d, $J = 8.6$ Hz, 2H), 6.95 (dd, $J = 16.8$, 10.2 Hz, 1H), 6.26 (d, $J = 16.8$ Hz, 1H), 6.04 (d, $J = 10.2$ Hz, 2H), 5.83 (d, $J = 10.3$ Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 184.33, 169.34, 147.23, 139.20, 137.79, 134.52, 133.06, 132.55, 131.52, 129.33, 128.44, 127.97, 126.69, 122.74, 65.14; IR (neat): $\nu$ 2989, 2924, 2377, 2349, 2319, 1699, 1670, 1397, 1360, 1275, 1261, 1183, 1134, 1086, 985, 763, 750 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{22}$H$_{16}$BrNO$_4$S [M+H]$^+$ =458.0062, found =458.0049.

N-((4-bromophenyl)sulfonyl)-N-(4-oxo-[1,1'-biphenyl]-1(4H)-yl)acrylamide

N-((4-bromophenyl)sulfonyl)-N-(4-oxo-[1,1'-biphenyl]-1(4H)-yl)acrylamide
(1s) 71% yield; white solid; mp 121-123°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.64 (d, \(J = 8.6\) Hz, 2H), 7.59 (d, \(J = 8.7\) Hz, 2H), 7.35 – 7.27 (m, 7H), 6.87 (dd, \(J = 16.9, 10.2\) Hz, 1H), 6.25 (d, \(J = 16.8\) Hz, 1H), 6.11 (d, \(J = 10.2\) Hz, 2H), 5.82 (d, \(J = 10.2\) Hz, 1H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 184.45, 169.36, 147.80, 138.32, 138.19, 133.08, 132.55, 131.68, 129.84, 129.67, 129.45, 128.81, 127.94, 125.23, 65.68; IR (neat): ν 3007, 2989, 2377, 2349, 2319, 1701, 1670, 1548, 1394, 1361, 1275, 1261, 1185, 1132, 1085, 1068, 984, 763, 750 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{21}\)H\(_{16}\)BrNO\(_4\)S [M+H]\(^+\) =458.0062, found =458.0056.

N-(4-oxo-[1,1'-biphenyl]-1(4H)-yl)-N-((4-(trifluoromethyl)phenyl)sulfonyl)acrylamide

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\text{O} \\
\text{SO}_2 \\
\text{CF}_3 \\
\text{O} \\
\end{array}
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(1t) 37% yield; white solid; mp 111-113°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.87 (d, \(J = 8.3\) Hz, 2H), 7.76 (d, \(J = 8.4\) Hz, 2H), 7.33 (s, 1H), 7.31 (s, 1H), 7.27 (d, \(J = 4.8\) Hz, 5H), 6.85 (dd, \(J = 16.8, 10.2\) Hz, 1H), 6.28 (d, \(J = 16.7\) Hz, 1H), 6.10 (d, \(J = 10.2\) Hz, 2H), 5.84 (d, \(J = 10.3\) Hz, 1H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 184.25, 169.25, 147.60, 142.85, 137.93, 135.93, 135.59, 132.94, 132.12, 129.46, 128.96 (d, \(J = 5.5\) Hz), 128.05, 126.35 (d, \(J = 3.7\) Hz), 125.38, 124.23, 121.52, 65.72; IR (neat): ν 3007, 2989, 2377, 2350, 2319, 1701, 1671, 1401, 1364, 1275, 1261, 1177, 1133, 1062, 984, 763, 750 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{21}\)H\(_{16}\)BrNO\(_4\)S [M+H]\(^+\) =448.0830, found =448.0823.

N-(3-chloro-4-oxo-[1,1'-biphenyl]-1(4H)-yl)-N-tosylacrylamide

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\text{Cl} \\
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\text{Ph} \\
\text{Ns} \\
\text{N} \\
\text{O} \\
\end{array}
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(1u) 70% yield; white solid; mp 132-134°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.70 –
7.52 (m, 2H), 7.43 (d, J = 2.9 Hz, 1H), 7.37 (dt, J = 10.1, 2.9 Hz, 1H), 7.34 – 7.23 (m, 7H), 6.96 (dd, J = 16.8, 10.2, 2.9 Hz, 1H), 6.24 (dd, J = 16.9, 1.9 Hz, 1H), 6.14 (dd, J = 10.1, 3.0 Hz, 1H), 5.82 (dd, J = 10.2, 1.9 Hz, 1H), 2.45 (d, J = 2.3 Hz, 3H); 13C NMR (101 MHz, CDCl3) δ 177.74, 169.50, 148.81, 146.26, 143.21, 137.92, 135.76, 133.33, 132.74, 131.11, 130.10, 129.58, 128.95, 128.33, 125.53, 124.96, 66.93, 21.76; IR (neat): ν 3007, 2989, 2377, 2350, 2319, 1699, 1677, 1275, 1261, 763, 750 cm⁻¹; HRMS (ESI) m/z calcd for C22H18ClNO4S [M+H]^+ =428.0723, found =428.0778.

N-(2-methoxy-4-oxo-[1,1'-biphenyl]-1(4H)-yl)-N-tosylacrylamide

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\text{N} \ \text{Ts} \\
\text{OMe}
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(1v) 30% yield; white solid; mp 63-65°C; 1H NMR (400 MHz, CDCl3) δ 7.70 (d, J = 8.1 Hz, 2H), 7.44 – 7.36 (m, 2H), 7.35 – 7.22 (m, 6H), 6.78 (dd, J = 16.8, 10.3 Hz, 1H), 6.42 (d, J = 10.0 Hz, 1H), 6.08 (d, J = 16.8 Hz, 1H), 5.61 (d, J = 10.3 Hz, 1H), 5.52 (s, 1H), 3.73 (s, 3H), 2.43 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 186.20, 173.38, 168.70, 145.15, 143.98, 137.87, 137.30, 131.54, 131.26, 129.63, 129.28, 128.62, 128.60, 128.28, 126.23, 102.32, 67.94, 56.20, 21.69; IR (neat): ν 3007, 2989, 2377, 2349, 2314, 1699, 1661, 1594, 1356, 1275, 1261, 1226, 1151, 1058, 985, 763, 750 cm⁻¹; HRMS (ESI) m/z calcd for C23H13ClNO4S [M+H]^+ =424.1219, found =424.1225.

N-(4-oxocyclopent-2-en-1-yl)-N-tosylacrylamide

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\begin{array}{c}
\text{TsN} \\
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\text{O}
\end{array}
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(1w) 30% yield; white solid; mp 88-90°C; 1H NMR (400 MHz, CDCl3) δ 7.76 (d, J = 8.4 Hz, 2H), 7.46 – 7.39 (m, 2H), 7.39 (s, 1H), 7.06 (dd, J = 16.7, 10.4 Hz, 1H), 6.34 (dd, J = 16.7, 1.5 Hz, 1H), 6.26 (dd, J = 5.7, 2.4 Hz, 1H), 5.81 (dd, J = 10.4, 1.5 Hz, 5.81 (dd, J = 10.4, 1.5 Hz,
1H), 5.49 (ddd, J = 7.3, 4.9, 2.4 Hz, 1H), 2.59 (s, 1H), 2.58 (s, 1H), 2.48 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 204.65, 166.12, 161.08, 145.75, 136.43, 134.42, 131.73, 130.39, 129.40, 127.25, 58.33, 39.87, 21.72; IR (neat): ν 3007, 2989, 2377, 2349, 2319, 1717, 1687, 1548, 1275, 1261, 1159, 763, 750 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{15}$H$_{15}$NO$_3$S [M+H]$^+$ = 306.0800, found = 306.0834.

(3aR,7aR)-3-methylene-7a-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione

(2a) 94% yield; white solid; mp 150-152°C; $[\alpha]^{28}_D = -70.1$ (c = 0.5, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.85 (d, J = 8.1 Hz, 2H), 7.52 (d, J = 10.5 Hz, 1H), 7.45 (d, J = 6.5 Hz, 3H), 7.41 (d, J = 7.5 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 6.33 (d, J = 10.5 Hz, 1H), 6.24 (d, J = 3.0 Hz, 1H), 5.45 (d, J = 2.6 Hz, 1H), 3.42 (s, 1H), 2.69 (dd, J = 16.8, 3.0 Hz, 1H), 2.60 (dd, J = 16.8, 5.3 Hz, 1H), 2.45 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 194.59 (C=O, C17), 165.83 (C=O, C22), 145.70 (C20), 144.65 (C, Ar), 139.54 (CH, C15), 138.41 (C, Ar), 135.56 (C, Ar), 130.33 (CH, C16), 129.40 (CH, Ar), 129.22 (CH, Ar), 128.99 (CH, Ar), 128.90 (CH, Ar), 125.84 (CH, Ar), 120.69 (CH$_2$, C21), 69.98 (C8), 48.81 (CH, C19), 35.09 (CH$_2$, C18), 21.78 (CH$_3$, C1); IR (neat): ν 3006, 2989, 2321, 1730, 1694, 1359, 1275, 1261, 1173, 1153, 1068, 763, 750 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{22}$H$_{19}$NO$_4$S [M+H]$^+$ =394.1113, found =394.1131; Enantiomeric excess: 96%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t$_R$ = 18.3 min, second peak: t$_R$ = 23.3 min.

(3aR,7aR)-7a-(4-fluorophenyl)-3-methylene-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione

S17
(2b) 75% yield; white solid; mp 181-183°C; $[\alpha]^{28}_D = -64.9$ ($c = 0.5$, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (d, $J = 8.0$ Hz, 2H), 7.49 (d, $J = 10.2$ Hz, 1H), 7.43 – 7.37 (m, 2H), 7.34 (d, $J = 7.9$ Hz, 2H), 7.15 (t, $J = 8.2$ Hz, 2H), 6.33 (d, $J = 10.4$ Hz, 1H), 6.24 (s, 1H), 5.46 (s, 1H), 3.38 (s, 1H), 2.70 (d, $J = 15.8$ Hz, 1H), 2.59 (dd, $J = 16.8$, 5.1 Hz, 1H), 2.46 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 194.25, 165.64, 164.00, 161.53, 145.85, 144.23, 138.14, 135.48, 130.43, 129.48, 129.14, 127.76 (d, $J = 8.3$ Hz), 120.91, 116.04 (d, $J = 21.9$ Hz), 69.40, 48.86, 34.99, 21.78; IR (neat): $\nu$ 3007, 2989, 2377, 2349, 2320, 1734, 1697, 1511, 1275, 1261, 1173, 763, 750 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{22}$H$_{18}$FNO$_4$S [M+H]$^+$ = 412.1019, found = 412.1031; Enantiomeric excess: 96%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; $\lambda = 220$ nm) first peak: $t_R = 16.0$ min, second peak: $t_R = 21.2$ min.

(3aR,7aR)-7a-(4-chlorophenyl)-3-methylene-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione
763, 750 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{22}\)H\(_{18}\)ClNO\(_4\)S [M+H]\(^+\) =428.0723, found =428.0721; Enantiomeric excess: 87%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; \(\lambda = 220\) nm) first peak: \(t_R = 17.5\) min, second peak: \(t_R = 22.5\) min.

(3aR,7aR)-7a-(3-chlorophenyl)-3-methylene-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione

(2d) 82% yield; white solid; mp 214-217°C; \([\alpha]^{28}_{D} = -58.5\) (c = 0.5, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 (d, \(J = 8.0\) Hz, 2H), 7.46 (d, \(J = 10.5\) Hz, 1H), 7.41 (d, \(J = 5.1\) Hz, 2H), 7.36 (d, \(J = 8.1\) Hz, 2H), 7.32 (d, \(J = 6.5\) Hz, 2H), 6.35 (d, \(J = 10.4\) Hz, 1H), 6.27 (d, \(J = 2.6\) Hz, 1H), 5.47 (s, 1H), 3.37 (s, 1H), 2.72 (d, \(J = 15.0\) Hz, 1H), 2.60 (dd, \(J = 16.9, 5.2\) Hz, 1H), 2.47 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 194.13, 165.61, 145.93, 143.86, 141.66, 138.03, 135.35, 135.14, 130.67, 130.32, 129.60, 129.17, 129.15, 126.13, 124.18, 121.05, 69.45, 48.62, 34.90, 21.79; IR (neat): v 3007, 2989, 2377, 2349, 2320, 1733, 1696, 1572, 1275, 1261, 1173, 1120, 1087, 763, 750 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{23}\)H\(_{18}\)ClNO\(_4\)S [M+H]\(^+\) =428.0723, found =428.0717; Enantiomeric excess: 96%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 25°C; \(\lambda = 220\) nm) first peak: \(t_R = 20.8\) min, second peak: \(t_R = 23.1\) min.

(3aR,7aR)-7a-(4-bromophenyl)-3-methylene-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione
(2e) 68% yield; white solid; mp 108-110°C; \([\alpha]_D^{28} = -82.9\) \((c = 0.5, \text{CH}_2\text{Cl}_2)\); \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta 7.86\) (d, \(J = 6.8\) Hz, 2H), 7.59 (d, \(J = 7.0\) Hz, 2H), 7.46 (d, \(J = 9.9\) Hz, 1H), 7.33 (dd, \(J = 18.9, 7.2\) Hz, 4H), 6.33 (d, \(J = 10.1\) Hz, 1H), 6.24 (s, 1H), 5.46 (s, 1H), 3.35 (s, 1H), 2.70 (d, \(J = 16.0\) Hz, 1H), 2.58 (d, \(J = 16.0\) Hz, 1H), 2.46 (s, 3H); \(^{13}\text{C}\) NMR (101 MHz, CDCl\(_3\)) \(\delta 194.13, 165.60, 145.90, 143.87, 138.84, 138.03, 135.38, 132.18, 130.62, 129.50, 129.19, 127.52, 123.06, 121.03, 69.42, 48.69, 34.97, 17.81; IR (neat): \(\nu\) 3007, 2989, 2377, 2350, 2320, 1734, 1698, 1572, 1548, 1327, 1275, 1261, 763, 750 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{22}\)H\(_{18}\)BrNO\(_4\)S \([\text{M+H}]^+ = 472.0218\), found = 472.0223; Enantiomeric excess: 88%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; \(\lambda = 220\) nm) first peak: \(t_R = 20.1\) min, second peak: \(t_R = 24.9\) min.

(3aR,7aR)-3-methylene-1-tosyl-7a-(4-(trifluoromethyl)phenyl)-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione

(3aR,7aR)-3-methylene-1-tosyl-7a-(4-(trifluoromethyl)phenyl)-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione

(2f) 66% yield; white solid; mp 206-208°C; \([\alpha]_D^{28} = -80.1\) \((c = 0.5, \text{CH}_2\text{Cl}_2)\); \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta 7.86\) (d, \(J = 8.1\) Hz, 2H), 7.73 (d, \(J = 8.1\) Hz, 2H), 7.57 (d, \(J = 8.0\) Hz, 2H), 7.49 (d, \(J = 10.4\) Hz, 1H), 7.36 (d, \(J = 8.0\) Hz, 2H), 6.38 (d, \(J = 10.5\) Hz, 1H), 6.27 (d, \(J = 2.8\) Hz, 1H), 5.48 (d, \(J = 2.3\) Hz, 1H), 3.38 (s, 1H), 2.77 – 2.66 (m, 1H), 2.58 (dd, \(J = 16.9, 5.3\) Hz, 1H), 2.47 (s, 3H); \(^{13}\text{C}\) NMR (101 MHz, CDCl\(_3\)) \(\delta 193.97, 165.54, 143.85, 143.49, 134.97, 134.97, 133.63, 130.90, 129.57, 129.20, 128.24, 126.15, 126.10 (d, \(J = 3.6\) Hz), 126.04, 121.32, 69.33, 48.62, 34.97, 17.81; IR (neat): \(\nu\) 3007, 2989, 2377, 2350, 2320, 1734, 1698, 1548, 1327, 1275, 1261, 1172, 763, 750 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{23}\)H\(_{18}\)F\(_3\)NO\(_4\)S \([\text{M+H}]^+ = 462.0987\), found = 462.0981; Enantiomeric excess: 90%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 85/15; flow rate 1.0 mL/min; 25°C; \(\lambda = 220\) nm) first peak: \(t_R = 17.3\) min, second peak: \(t_R = 24.2\) min.

(3aR,7aR)-7a-(3,5-bis(trifluoromethyl)phenyl)-3-methylene-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione
(2g) 93% yield; white solid; mp 112-114°C; \([\alpha]^{28}_D = -71.3\) (c = 0.5, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.99 (s, 1H), 7.90 – 7.78 (m, 4H), 7.49 (d, $J = 10.4$ Hz, 1H), 7.36 (d, $J = 8.1$ Hz, 2H), 6.44 (d, $J = 10.4$ Hz, 1H), 6.34 (d, $J = 2.6$ Hz, 1H), 5.53 (s, 1H), 3.35 (s, 1H), 2.78 (d, $J = 16.8$ Hz, 1H), 2.56 (dd, $J = 17.0$, 5.2 Hz, 1H), 2.47 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 193.28, 165.41, 146.40, 142.93, 142.41, 137.32, 134.88, 132.78, 132.44, 131.64, 129.72, 129.11, 125.98 (d, $J = 2.3$ Hz), 123.09 (d, $J = 3.4$ Hz), 121.95, 68.93, 48.54, 34.62, 21.78; IR (neat): $\nu$ 3006, 2989, 2377, 2350, 2320, 1732, 1696, 1366, 1277, 1261, 1175, 1136, 1018, 901, 763, 750 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{24}$H$_{17}$F$_6$NO$_4$S [M+H]$^+$ =530.0861, found =530.0867; Enantiomeric excess: 95%, determined by HPLC (Chiralpak AD-H, hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25°C; $\lambda = 220$ nm) first peak: $t_R = 6.9$ min, second peak: $t_R = 12.1$ min.

(3aR,7aR)-3-methylene-1-tosyl-7a-(3,4,5-trifluorophenyl)-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione

(2h) 83% yield; white solid; mp 197-199°C; $[\alpha]^{28}_D = -118.1$ (c = 0.5, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J = 8.2$ Hz, 2H), 7.44 (d, $J = 10.4$ Hz, 1H), 7.34 (d, $J = 8.1$ Hz, 2H), 7.18 (dd, $J = 14.0$, 6.4 Hz, 1H), 7.10 (dd, $J = 16.2$, 7.7 Hz, 1H), 6.30 (t, $J = 7.3$ Hz, 2H), 5.50 (d, $J = 2.7$ Hz, 1H), 3.67 (s, 1H), 2.76 (dd, $J = 17.0$, 2.6 Hz, 1H), 2.58 (dd, $J = 16.9$, 5.4 Hz, 1H), 2.46 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 192.70, 163.86, 145.01, 142.15, 136.61, 133.89, 129.14, 128.48, 127.73, 122.88, 121.70, 120.38, 111.43 (d, $J = 3.9$ Hz), 111.26 (d, $J = 3.8$ Hz), 65.79, 44.06, 34.36,
20.75; IR (neat): ν 3006, 2989, 2377, 2350, 2320, 1732, 1697, 1513, 1476, 1275, 1261, 1188, 1173, 1153, 1170, 1011, 763, 750 cm⁻¹; HRMS (ESI) m/z calcd for C₂₂H₁₆F₃NO₄S [M+H]⁺ = 448.0830, found = 448.0834; Enantiomeric excess: 97%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: tᵣ = 16.1 min, second peak: tᵣ = 18.6 min.

(3aR,7aR)-3-methylene-7a-(m-tolyl)-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione

(2i) 91% yield; white solid; mp 152-154°C; [α]²⁸D = -64.1 (c = 0.5, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 8.3 Hz, 2H), 7.51 (dd, J = 10.5, 1.4 Hz, 1H), 7.34 (t, J = 7.5 Hz, 3H), 7.24 (d, J = 7.5 Hz, 1H), 7.19 (d, J = 7.8 Hz, 1H), 7.14 (s, 1H), 6.32 (d, J = 10.5 Hz, 1H), 6.24 (d, J = 3.2 Hz, 1H), 5.44 (d, J = 2.9 Hz, 1H), 3.40 (s, 1H), 2.68 (dd, J = 16.8, 2.9 Hz, 1H), 2.60 (dd, J = 16.8, 5.3 Hz, 1H), 2.46 (s, 3H), 2.37 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 194.69, 165.87, 145.64, 144.88, 139.36, 138.67, 138.53, 135.68, 130.20, 129.69, 129.36, 129.18, 128.84, 126.47, 123.06, 120.55, 70.07, 48.78, 35.08, 21.76, 21.60; IR (neat): ν 3006, 2989, 2377, 2350, 2320, 1732, 1694, 1275, 1260, 1231, 1173, 1151, 763, 750 cm⁻¹; HRMS (ESI) m/z calcd for C₂₃H₂₁NO₄S [M+Na]⁺ = 430.1089, found = 430.1153; Enantiomeric excess: 98%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: tᵣ = 13.3 min, second peak: tᵣ = 15.8 min.

(3aR,7aR)-7a-(3-methoxyphenyl)-3-methylene-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione

(3aR,7aR)-3-methylene-7a-(m-tolyl)-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione

(2i) 91% yield; white solid; mp 152-154°C; [α]²⁸D = -64.1 (c = 0.5, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 8.3 Hz, 2H), 7.51 (dd, J = 10.5, 1.4 Hz, 1H), 7.34 (t, J = 7.5 Hz, 3H), 7.24 (d, J = 7.5 Hz, 1H), 7.19 (d, J = 7.8 Hz, 1H), 7.14 (s, 1H), 6.32 (d, J = 10.5 Hz, 1H), 6.24 (d, J = 3.2 Hz, 1H), 5.44 (d, J = 2.9 Hz, 1H), 3.40 (s, 1H), 2.68 (dd, J = 16.8, 2.9 Hz, 1H), 2.60 (dd, J = 16.8, 5.3 Hz, 1H), 2.46 (s, 3H), 2.37 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 194.69, 165.87, 145.64, 144.88, 139.36, 138.67, 138.53, 135.68, 130.20, 129.69, 129.36, 129.18, 128.84, 126.47, 123.06, 120.55, 70.07, 48.78, 35.08, 21.76, 21.60; IR (neat): ν 3006, 2989, 2377, 2350, 2320, 1732, 1694, 1275, 1260, 1231, 1173, 1151, 763, 750 cm⁻¹; HRMS (ESI) m/z calcd for C₂₃H₂₁NO₄S [M+Na]⁺ = 430.1089, found = 430.1153; Enantiomeric excess: 98%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: tᵣ = 13.3 min, second peak: tᵣ = 15.8 min.
(2j) 73% yield; white solid; mp 162-164°C; $[\alpha]^{28}_{D} = -70.8$ ($c = 0.45$, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 (d, $J = 7.9$ Hz, 2H), 7.49 (d, $J = 10.3$ Hz, 1H), 7.35 (dd, $J = 17.8$, 8.0 Hz, 3H), 7.02 – 6.93 (m, 2H), 6.91 (s, 1H), 6.32 (d, $J = 10.4$ Hz, 1H), 6.23 (d, $J = 1.8$ Hz, 1H), 5.44 (s, 1H), 3.80 (s, 3H), 3.42 (s, 1H), 2.69 (dd, $J = 16.9$, 2.1 Hz, 1H), 2.62 (dd, $J = 16.9$, 5.0 Hz, 1H), 2.45 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 194.64, 165.82, 160.00, 145.69, 144.54, 141.13, 138.42, 135.56, 130.28, 130.09, 129.40, 129.24, 120.67, 118.10, 113.94, 111.97, 69.91, 55.34, 48.66, 35.18, 21.77; IR (neat): v 3006, 2989, 2377, 2349, 2320, 1733, 1696, 1275, 1261, 1151, 763, 750 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{23}$H$_{21}$NO$_5$S [M+Na]$^+$ = 446.1038, found = 446.1026; Enantiomeric excess: >99%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; $\lambda = 220$ nm) first peak: $t_R = 27.4$ min, second peak: $t_R = 34.1$ min.

(3aR,7aR)-7a-[(1,1'-biphenyl]-4-y]-3-methylene-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione

(2k) 77% yield; white solid; mp 103-105°C; $[\alpha]^{28}_{D} = -78.9$ ($c = 0.5$, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89 (d, $J = 8.2$ Hz, 2H), 7.65 (dd, $J = 15.4$, 7.8 Hz, 4H), 7.55 (d, $J = 10.3$ Hz, 1H), 7.48 (t, $J = 7.5$ Hz, 4H), 7.40 (t, $J = 7.3$ Hz, 1H), 7.34 (d, $J = 8.1$ Hz, 2H), 6.36 (d, $J = 10.4$ Hz, 1H), 6.26 (d, $J = 2.9$ Hz, 1H), 5.46 (d, $J = 2.5$ Hz, 1H), 3.45 (s, 1H), 2.71 (dd, $J = 16.8$, 2.9 Hz, 1H), 2.65 (dd, $J = 16.9$, 5.2 Hz, 1H), 2.46 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 194.58, 165.83, 145.75, 144.58, 141.77, 140.04, 138.46, 138.38, 135.54, 130.39, 129.44, 129.24, 128.96, 127.85, 127.64, 127.17, 126.30, 120.78, 69.84, 48.81, 35.15, 21.79; IR (neat): v 3006, 2989, 2377, 2351, 2321, 1731, 1694, 1359, 1275, 1261, 1152, 763, 750 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{28}$H$_{23}$NO$_4$S [M+H]$^+$ =470.1426, found =470.1414; Enantiomeric excess: 92%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; $\lambda = 220$ nm) first peak: $t_R = 32.4$ min, second peak: $t_R = 36.7$ min.
(3aR,7aR)-7a-methyl-3-methylene-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione

![Chemical structure](image)

(2l) 77% yield; white solid; mp 161-163°C; [α]$_{28}^D$ = -65.1 (c = 0.4, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.98 (d, $J$ = 8.3 Hz, 2H), 7.35 (d, $J$ = 8.2 Hz, 2H), 7.24 (d, $J$ = 10.4 Hz, 1H), 6.17 (d, $J$ = 3.0 Hz, 1H), 6.02 (d, $J$ = 10.4 Hz, 1H), 5.46 (d, $J$ = 2.7 Hz, 1H), 3.17 (s, 1H), 2.80 (dd, $J$ = 16.9, 5.6 Hz, 1H), 2.73 (dd, $J$ = 16.9, 4.4 Hz, 1H), 2.45 (s, 3H), 1.99 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 194.38, 165.40, 146.87, 145.52, 139.84, 135.94, 129.64, 128.63, 128.17, 120.83, 64.82, 45.26, 36.28, 25.19, 21.75; IR (neat): ν 3006, 2989, 2377, 2351, 2320, 1688, 1572, 1275, 1261, 763, 750 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{17}$H$_{17}$NO$_4$S [M+H]$^+$ =332.0956, found =332.0990; Enantiomeric excess: 72%, determined by HPLC (Chiralpak AD-H, hexane/2-propanol = 95/5; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: $t_R$ = 61.0 min, second peak: $t_R$ = 66.2 min.

(3aR,7aR)-7a-ethyl-3-methylene-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione

![Chemical structure](image)

(2m) 66% yield; white solid; mp 72-74°C; [α]$_{28}^D$ = -60.1 (c = 0.2, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.97 (d, $J$ = 7.9 Hz, 2H), 7.34 (d, $J$ = 7.8 Hz, 2H), 7.28 (d, $J$ = 9.8 Hz, 1H), 6.17 (s, 1H), 6.12 (d, $J$ = 10.4 Hz, 1H), 5.47 (s, 1H), 3.36 (s, 1H), 2.69 (dd, $J$ = 16.7, 5.8 Hz, 1H), 2.61 (dd, $J$ = 16.7, 5.7 Hz, 1H), 2.44 (s, 3H), 2.39 (d, $J$ = 6.8 Hz, 1H), 2.17 (td, $J$ = 14.2, 6.9 Hz, 1H), 1.09 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 194.91, 165.68, 146.51, 145.51, 139.08, 135.65, 129.51, 128.96, 128.17, 120.94, 68.22, 40.53, 37.97, 30.40, 21.74, 8.80; IR (neat): ν 2985, 2925, 2377, 2350, 2320, 1728, 1691, 1595, 1357, 1275, 1261, 1187, 1158, 1085, 1039, 909, 764, 750 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{18}$H$_{19}$NO$_4$S [M+H]$^+$ =346.1113, found =346.1118; Enantiomeric excess: 84%, determined by HPLC (Chiralpak AD-H, hexane/2-propanol = 98/2; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: $t_R$ =
115.6 min, second peak: \( t_R = 127.0 \) min.

(3aR,7aR)-3-methylene-1-tosyl-7a-vinyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione

\( \begin{align*} &\text{O} \\
&\text{N} \\
&\text{O} \\
&\text{Ts} \\
\end{align*} \)

(2n) 87\% yield; white solid; mp 157-159°C; \([\alpha]^{28}_D = -101.0 \) (c = 0.45, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.01 (d, \( J = 8.3 \) Hz, 2H), 7.37 (d, \( J = 8.1 \) Hz, 2H), 7.13 (dd, \( J = 10.4, 1.3 \) Hz, 1H), 6.27 - 6.15 (m, 3H), 5.50 (d, \( J = 10.6 \) Hz, 1H), 5.45 (d, \( J = 2.8 \) Hz, 1H), 5.35 (d, \( J = 17.4 \) Hz, 1H), 3.19 (s, 1H), 2.75 (d, \( J = 4.5 \) Hz, 2H), 2.45 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 194.45, 165.17, 145.65, 143.67, 138.04, 136.83, 135.84, 130.43, 129.69, 128.80, 120.94, 117.32, 68.31, 44.09, 34.55, 21.77; IR (neat): \( \nu \) 3007, 2989, 2965, 2377, 2350, 2320, 1732, 1695, 1578, 1275, 1261, 1172, 1086, 763, 750 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{18}\)H\(_{17}\)NO\(_4\)S \([M+H]^+\) =344.0956, found =344.0994; Enantiomeric excess: 85\%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; \( \lambda = 220 \) nm) first peak: \( t_R = 14.8 \) min, second peak: \( t_R = 18.8 \) min.

(3aR,7aR)-3-methylene-1-tosyl-7a-(trimethylsilyl)ethynyl)-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione

\( \begin{align*} &\text{O} \\
&\text{N} \\
&\text{O} \\
&\text{Ts} \\
&\text{TMS} \\
\end{align*} \)

(2o) 42\% yield; white solid; mp 102-105°C; \([\alpha]^{28}_D = +19.6 \) (c = 0.5, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.10 (d, \( J = 7.3 \) Hz, 2H), 7.36 (d, \( J = 7.2 \) Hz, 2H), 7.21 (d, \( J = 10.0 \) Hz, 1H), 6.18 (s, 1H), 6.05 (d, \( J = 10.0 \) Hz, 1H), 5.45 (s, 1H), 3.59 (s, 1H), 3.07 - 2.93 (m, 1H), 2.82 (d, \( J = 16.7 \) Hz, 1H), 2.46 (s, 3H), 0.27 (s, 9H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 194.12, 164.52, 145.96, 143.70, 137.83, 136.01, 129.89, 129.14, 128.34, 121.34, 100.04, 94.17, 59.54, 46.85, 36.21, 22.13, 0.00; IR (neat): \( \nu \) 3007, 2988, 2965, 2377, 2350, 2320, 1737, 1697, 1596, 1365, 1275, 1260, 1175, 1087, 1017,
920, 844, 763, 750 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{18}\)H\(_{17}\)NO\(_4\)S [M+Na]\(^+\) = 436.1015, found = 436.1012; Enantiomeric excess: 88%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25°C; \(\lambda = 220\) nm) first peak: \(t_R = 9.4\) min, second peak: \(t_R = 10.7\) min.

**(3aR,7aR)-7a-cyclopentyl-3-methylene-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione**

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\begin{array}{c}
\text{O} \\
\text{N} \\
\text{O} \\
\end{array}
\]

\((2p)\) 88% yield; white solid; mp 127-130°C; \([\alpha]^{28}D = +24.0\) (c = 0.25, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.91 (d, \(J = 8.0\) Hz, 2H), 7.45 (d, \(J = 10.6\) Hz, 1H), 7.32 (d, \(J = 8.0\) Hz, 2H), 6.23 (d, \(J = 10.6\) Hz, 1H), 6.13 (s, 1H), 5.47 (s, 1H), 3.35 (t, \(J = 7.6\) Hz, 1H), 3.07 – 2.92 (m, 1H), 2.57 (dd, \(J = 16.3, 6.3\) Hz, 1H), 2.43 (s, 3H), 2.41 – 2.33 (m, 1H), 1.85 – 1.74 (m, 2H), 1.68 (d, \(J = 15.8\) Hz, 4H), 1.31 (dd, \(J = 23.4, 13.4\) Hz, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 195.57, 165.36, 146.48, 145.04, 140.70, 135.56, 129.63, 129.47, 128.81, 120.45, 68.62, 49.16, 41.19, 38.87, 28.42, 27.52, 25.43, 25.03, 21.72; IR (neat): v 3006, 2988, 2377, 2350, 2321, 1725, 1694, 1275, 1261, 1159, 763, 750 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{21}\)H\(_{23}\)NO\(_4\)S [M+H]\(^+\) =386.1426, found =386.1424; Enantiomeric excess: 95%, determined by HPLC (Chiralpak IC, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; \(\lambda = 220\) nm) first peak: \(t_R = 72.5\) min, second peak: \(t_R = 95.0\) min.

**(3aR,7aR)-7a-cyclohexyl-3-methylene-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione**

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\begin{array}{c}
\text{O} \\
\text{N} \\
\text{O} \\
\end{array}
\]

\((2q)\) 87% yield; white solid; mp 169-171°C; \([\alpha]^{28}D = -9.2\) (c = 0.5, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.94 (d, \(J = 8.2\) Hz, 2H), 7.38 (d, \(J = 10.6\) Hz, 1H), 7.33 (d, \(J = 7.6\) Hz, 1H), 7.23 (d, \(J = 8.0\) Hz, 2H), 6.23 (d, \(J = 10.6\) Hz, 1H), 6.15 (s, 1H), 5.45 (s, 1H), 3.08 – 2.93 (m, 1H), 2.58 (dd, \(J = 16.3, 6.3\) Hz, 1H), 2.43 (s, 3H), 2.42 – 2.34 (m, 1H), 1.88 – 1.78 (m, 2H), 1.69 (d, \(J = 15.8\) Hz, 4H), 1.31 (dd, \(J = 23.4, 13.4\) Hz, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 195.54, 165.36, 146.48, 145.04, 140.70, 135.56, 129.63, 129.47, 128.81, 120.45, 68.62, 49.16, 41.19, 38.87, 28.42, 27.52, 25.43, 25.03, 21.72; IR (neat): v 3006, 2988, 2377, 2350, 2321, 1725, 1694, 1275, 1261, 1159, 763, 750 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{21}\)H\(_{23}\)NO\(_4\)S [M+H]\(^+\) =386.1426, found =386.1424; Enantiomeric excess: 95%, determined by HPLC (Chiralpak IC, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; \(\lambda = 220\) nm) first peak: \(t_R = 72.5\) min, second peak: \(t_R = 95.0\) min.
8.0 Hz, 2H), 6.23 (d, \( J = 10.6 \) Hz, 1H), 6.13 (d, \( J = 1.7 \) Hz, 1H), 5.45 (s, 1H), 3.44 (t, \( J = 6.8 \) Hz, 1H), 2.62 (dd, \( J = 16.5, 6.4 \) Hz, 1H), 2.52 (dd, \( J = 21.8, 9.8 \) Hz, 2H), 2.43 (s, 3H), 1.79 (dt, \( J = 26.5, 13.1 \) Hz, 5H), 1.31 (dt, \( J = 20.7, 10.5 \) Hz, 2H), 1.18 – 0.93 (m, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 195.49, 165.67, 147.07, 145.45, 140.36, 135.50, 130.28, 129.41, 128.97, 120.49, 70.69, 45.80, 40.86, 37.82, 28.85, 27.17, 26.41, 26.13, 26.04, 21.71; IR (neat): \( \nu \) 3006, 2989, 2378, 2350, 2320, 1722, 1690, 1573, 1275, 1157, 763, 750 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{22}\)H\(_{25}\)NO\(_4\)S [M+H]\(^+\) =400.1583, found =400.1579; Enantiomeric excess: 97%, determined by HPLC (Chiralpak AD-H, hexane/2-propanol = 95/5; flow rate 1.0 mL/min; 25°C; \( \lambda = 220 \) nm) first peak: \( t_R = 38.0 \) min, second peak: \( t_R = 42.1 \) min, third peak: \( t_R = 46.4 \) min, fourth peak: \( t_R = 56.6 \) min.

(3aR,7aR)-7a-(4-bromophenyl)-3-methylene-1-(phenylsulfonyl)-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{N} & \quad \text{S} \\
\text{Br} & \quad \text{O}
\end{align*}
\]

(2r) 79% yield; white solid; mp 93-96°C; \([\alpha]^{28}_D = -64.1 \) (c = 0.5, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.98 (d, \( J = 6.7 \) Hz, 2H), 7.68 (d, \( J = 6.0 \) Hz, 1H), 7.58 (s, 4H), 7.47 (d, \( J = 9.9 \) Hz, 1H), 7.34 – 7.26 (m, 2H), 6.35 (d, \( J = 10.2 \) Hz, 1H), 6.26 (s, 1H), 5.47 (s, 1H), 3.37 (s, 1H), 2.71 (d, \( J = 16.2 \) Hz, 1H), 2.59 (d, \( J = 16.5 \) Hz, 1H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 194.10, 165.61, 143.81, 138.89, 138.33, 137.93, 134.60, 132.21, 130.70, 129.09, 128.91, 127.56, 123.13, 121.24, 69.49, 48.69, 34.96; IR (neat): \( \nu \) 3007, 2989, 2378, 2350, 2320, 1732, 1695, 1275, 1261, 763, 750 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{21}\)H\(_{16}\)BrNO\(_4\)S [M+H]\(^+\) =458.0062, found =458.0058; Enantiomeric excess: 91%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; \( \lambda = 220 \) nm) first peak: \( t_R = 22.9 \) min, second peak: \( t_R = 45.7 \) min.

(3aR,7aR)-1-((4-bromophenyl)sulfonyl)-3-methylene-7a-phenyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione
(2s) 51% yield; white solid; mp 147-149°C; $[\alpha]^{28}_D = -100.1$ ($c = 0.25$, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, $J = 8.2$ Hz, 2H), 7.68 (d, $J = 8.2$ Hz, 2H), 7.53 – 7.43 (m, 4H), 7.39 (s, 2H), 6.34 (d, $J = 10.4$ Hz, 1H), 6.27 (s, 1H), 5.49 (s, 1H), 3.44 (s, 1H), 2.71 (d, $J = 16.3$ Hz, 1H), 2.60 (dd, $J = 16.7$, 4.9 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 194.36, 165.82, 144.30, 139.22, 138.10, 137.39, 132.12, 130.63, 130.50, 129.99, 129.06, 128.15, 121.18, 70.15, 48.80, 35.01; IR (neat): ν 3006, 2989, 2378, 2350, 2320, 1731, 1694, 1572, 1275, 1261, 1150, 1067, 763, 750 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{21}$H$_{16}$BrNO$_4$S [M+H]$^+$ =458.0062, found =458.0066; Enantiomeric excess: 95%, determined by HPLC (Chiralpak AD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: $t_R = 17.3$ min, second peak: $t_R = 33.5$ min.

(3aR,7aR)-3-methylene-7a-phenyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione

(2t) 76% yield; white solid; mp 83-85°C; $[\alpha]^{28}_D = -54.1$ ($c = 0.4$, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.09 (d, $J = 7.6$ Hz, 2H), 7.81 (d, $J = 7.6$ Hz, 2H), 7.49 (d, $J = 17.8$ Hz, 4H), 7.40 (s, 2H), 6.36 (d, $J = 10.3$ Hz, 1H), 6.28 (s, 1H), 5.51 (s, 1H), 3.47 (s, 1H), 2.72 (d, $J = 16.7$ Hz, 1H), 2.66 – 2.56 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 194.22, 165.83, 144.14, 141.80, 139.08, 137.94, 136.06, 135.73, 130.63, 129.73, 129.15 (d, $J = 7.9$ Hz), 125.94 (d, $J = 3.7$ Hz), 125.89, 124.40, 121.47, 70.27, 48.81, 35.01; IR (neat): ν 3006, 2989, 2378, 2350, 2320, 1731, 1694, 1572, 1275, 1261, 1150, 1067, 763, 750 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{22}$H$_{16}$F$_3$NO$_4$S [M+H]$^+$ =448.0830, found =448.0838; Enantiomeric excess: 86%, determined by HPLC
(Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; \( \lambda = 220 \) nm) first peak: \( t_R = 12.0 \) min, second peak: \( t_R = 17.3 \) min.

\((3aR,7aS)-6\text{-chloro-3-methylene-7a-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione}\)

\(\text{(2u)}\) 33\% yield; white solid; mp 223-225°C; \([\alpha]^{28}_D = -27.4\) (c = 0.3, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.83\) (d, \(J = 7.9\) Hz, 2H), 7.74 (s, 1H), 7.46 (s, 3H), 7.40 (s, 2H), 7.34 (d, \(J = 7.7\) Hz, 2H), 6.27 (s, 1H), 5.47 (s, 1H), 3.44 (s, 1H), 2.88 (d, \(J = 15.0\) Hz, 1H), 2.71 (dd, \(J = 16.7, 5.0\) Hz, 1H), 2.46 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 187.07, 165.46, 145.93, 140.96, 139.13, 137.67, 135.31, 134.22, 129.48, 129.17, 125.71, 121.30, 71.09, 48.56, 35.29, 21.79; IR (neat): v 3006, 2989, 2370, 2350, 2320, 1732, 1710, 1364, 1275, 1261, 1188, 1158, 1085, 763, 750 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{22}\)H\(_{18}\)ClNO\(_4\)S \[M+H\]^+ =428.0723, found =428.0769; Enantiomeric excess: 96\%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; \( \lambda = 220 \) nm) first peak: \( t_R = 20.9 \) min, second peak: \( t_R = 23.4 \) min.

\((3aR,7aR)-7\text{-methoxy-3-methylene-7a-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione}\)

\(\text{(2u)}\) 47\% yield; white solid; mp 215-217°C; \([\alpha]^{28}_D = -82.5\) (c = 0.5, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.01\) (d, \(J = 8.3\) Hz, 2H), 7.47 (s, 4H), 7.34 (d, \(J = 8.2\) Hz, 3H), 6.20 (d, \(J = 3.2\) Hz, 1H), 5.64 (s, 1H), 5.43 (d, \(J = 2.9\) Hz, 1H), 3.87 (s, 3H), 3.47 (dd, \(J = 5.1, 2.5\) Hz, 1H), 2.65 (dd, \(J = 17.2, 1.9\) Hz, 1H), 2.45 (s, 3H), 2.41 (dd, \(J = 13.3, 4.0\) Hz, 1H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 194.24, 170.50, 165.95, 145.22, 137.93, 137.03, 136.34, 129.89, 129.08, 128.72, 128.07, 126.54, 119.61, 104.87, 104.87,
73.29, 56.46, 50.33, 33.51, 21.71; IR (neat): ν 3007, 2989, 2370, 2350, 2320, 1732, 1671, 1608, 1454, 1364, 1275, 1261, 1226, 1169, 763, 750 cm⁻¹; HRMS (ESI) m/z calcd for C_{23}H_{21}NO_{5}S [M+H]^+ = 424.1219, found = 424.1211; Enantiomeric excess: 73%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 21.8 min, second peak: t_R = 27.3 min.

(3aR,6aR)-3-methylene-1-tosyltetrahydrocyclopenta[b]pyrrole-2,5(1H,3H)-dione

(2w) 49% yield; white solid; mp 94-96°C; [α]_{28}^D = -10.3 (c = 0.35, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 7.4 Hz, 2H), 7.36 (d, J = 7.4 Hz, 2H), 6.27 (s, 1H), 5.56 (s, 1H), 4.96 (dd, J = 14.2, 6.5 Hz, 1H), 3.71 (s, 1H), 2.97 (dd, J = 19.3, 8.1 Hz, 1H), 2.79 (dd, J = 19.3, 10.0 Hz, 1H), 2.45 (s, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 212.99, 165.10, 145.78, 141.24, 135.12, 129.83, 128.53, 122.94, 57.06, 44.46, 42.98, 37.41, 21.74; IR (neat): ν 3006, 2958, 2923, 2851, 2370, 2350, 2320, 1728, 1657, 1595, 1358, 1275, 1261, 1226, 1169, 1088, 1038, 763, 750 cm⁻¹; HRMS (ESI) m/z calcd for C_{13}H_{15}NO₄S [M+H]^+ = 306.0800, found = 306.0896; Enantiomeric excess: 91%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t_R = 75.4 min, second peak: t_R = 83.3 min.

Dimethyl-2-(((3R,3aR,7aR)-2,5-dioxo-7a-phenyl-1-tosyl-2,3,3a,4,5,7a-hexahydro-1H-indol-3-yl)methyl)malonate

(4a) 82% yield; white solid; mp 115-117°C; [α]_{25}^D = -52.0 (c = 0.5, CH₂Cl₂); ¹H NMR...
NMR (400 MHz, CDCl$_3$) $\delta$ 7.73 (d, $J = 8.0$ Hz, 2H), 7.56 (d, $J = 10.4$ Hz, 1H), 7.42 (s, 3H), 7.37 – 7.28 (m, 4H), 6.43 (d, $J = 10.4$ Hz, 1H), 3.95 (t, $J = 7.3$ Hz, 1H), 3.70 (d, $J = 2.6$ Hz, 6H), 2.62 – 2.48 (m, 3H), 2.46 (s, 3H), 2.42 (d, $J = 5.9$ Hz, 1H), 2.17 – 2.07 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 194.49 (C=O, C17), 173.95 (C=O, C22), 169.17 (C=O, C24, C25), 168.88 (C, Ar), 145.65 (C, Ar), 144.43 (CH, C15), 139.22 (C, Ar), 135.48 (C, C16), 130.79 (CH, Ar), 129.34 (CH, Ar), 129.25 (CH, Ar), 128.91 (CH, Ar), 126.05 (CH, Ar), 69.67 (C8), 52.90 (C19), 52.81 (CH3, C26), 49.61 (CH, C23), 48.53 (CH, C19), 42.21 (CH, C20), 34.65 (CH2, C18), 27.08 (CH2, C21), 21.77 (CH3, C1); IR (neat): $\nu$ 2961, 2924, 2853, 2360, 2340, 2271, 1749, 1717, 1684, 1558, 1261, 1155, 1074, 871, 805, 764 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{27}$H$_{27}$NO$_8$S [M+H]$^+$ = 526.1536, found = 526.1544; Enantiomeric excess: 93%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; $\lambda$ = 220 nm) first peak: $t_R = 20.4$ min, second peak: $t_R = 48.5$ min.

Benzyl-(1R,3a'R,7a'R)-2',5'-dioxo-7a'-phenyl-1'-tosyl-1',2',3a',4',5',7a'-hexahydrospiro[cyclopentane-1,3'-indol]-3-ene-3-carboxylate

(4b) 95% yield; white solid; mp > 230°C; $[^{[\alpha]}]^{25}_D = -77.7$ (c = 0.5, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.77 (d, $J = 7.8$ Hz, 2H), 7.66 (d, $J = 10.3$ Hz, 1H), 7.41 (d, $J = 2.7$ Hz, 5H), 7.37 – 7.27 (m, 7H), 6.66 (s, 1H), 6.51 (d, $J = 10.4$ Hz, 1H), 5.12 (q, $J = 12.4$ Hz, 2H), 3.01 (d, $J = 18.6$ Hz, 1H), 2.85 (s, 1H), 2.58 (s, 2H), 2.50 (d, $J = 6.3$ Hz, 1H), 2.44 (s, 3H), 2.41 (s, 1H), 2.33 (d, $J = 19.3$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 194.82 (C=O, C17), 176.76 (C=O, C22), 163.28 (C=O, C26), 145.70 (C25), 145.54 (CH, C24), 140.66 (CH, C15), 140.55 (C, Ar), 135.77 (C, Ar), 135.13 (C, Ar), 133.91 (C, Ar), 131.08 (CH,C16), 129.43 (CH, Ar), 129.15 (CH, Ar), 129.01 (CH, Ar), 128.78 (CH, Ar), 128.55 (CH, Ar), 128.24 (CH, Ar), 128.21 (CH, Ar), 125.83 (CH, Ar), 68.86 (C8), 66.34 (CH2, C27), 53.05 (C20), 52.86 (CH, C19), 42.92 (CH2, C21),
37.70 (CH$_2$, C23), 33.40 (CH$_2$, C18), 21.76 (CH$_3$, C1); IR (neat): ν 2961, 2924, 2853, 2360, 2340, 2271, 1761, 1699, 1647, 1576, 1075, 860, 804 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{33}$H$_{29}$NO$_6$S [M+H]$^+$ = 568.1794, found = 568.1792; Enantiomeric excess: 94%, determined by HPLC (Chiralpak AD-H, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 220 nm) first peak: t$_R$ = 49.1 min, second peak: t$_R$ = 93.2 min.
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$^{1}H$ NMR spectra of 1b

$^{13}C$ NMR spectra of 1b
$^1$H NMR spectra of $1c$

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$^1$H NMR spectra of 1d

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H NMR spectra of 1e

\[ \text{13C NMR spectra of 1e} \]

S37
$^1$H NMR spectra of 1g

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

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

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

\[ \text{\^{1}H NMR spectra of 1j} \]

\[ \text{\^{13}C NMR spectra of 1j} \]
$^1$H NMR spectra of 1k

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$^{13}$C NMR spectra of 1o
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$^{13}$C NMR spectra of 1s
**$^1$H NMR spectra of 1t**

**$^{13}$C NMR spectra of 1t**
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$^{13}$C NMR spectra of 1u
$^1$H NMR spectra of 1v

$^{13}$C NMR spectra of 1v
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\[ \text{H NMR spectra of 2a} \]

\[ \text{\(^{13}\)C NMR spectra of 2a} \]
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$^1$H NMR spectra of 2c

$^{13}$C NMR spectra of 2c
$^1$H NMR spectra of 2d

$^{13}$C NMR spectra of 2d
$^1$H NMR spectra of 2e

$^{13}$C NMR spectra of 2e
H NMR spectra of 2f

$^{13}$C NMR spectra of 2f
$^{1}H$ NMR spectra of 2g

$^{13}C$ NMR spectra of 2g
$\text{H NMR spectra of 2h}$

$\text{C NMR spectra of 2h}$
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$^{1}H$ NMR spectra of 2j

$^{13}C$ NMR spectra of 2j
$\text{H NMR spectra of } 2k$

$\text{C NMR spectra of } 2k$

$\text{H NMR spectra of } 2k$

$\text{C NMR spectra of } 2k$
$\text{H NMR spectra of 2l}$

$\text{\textsuperscript{13}C NMR spectra of 2l}$
$^1$H NMR spectra of 2m

$^{13}$C NMR spectra of 2m
H NMR spectra of \(2n\)

\[\begin{align*}
\text{\(1^H\) NMR spectra of \(2n\)}\end{align*}\]

\[\begin{align*}
\text{\(13C\) NMR spectra of \(2n\)}\end{align*}\]

S69
$\text{H NMR spectra of 2o}$

$\text{C NMR spectra of 2o}$
$^1$H NMR spectra of 2p

$^{13}$C NMR spectra of 2p
$^1$H NMR spectra of 2q

$^{13}$C NMR spectra of 2q
$^1$H NMR spectra of 2r

$^{13}$C NMR spectra of 2r
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$^{13}$C NMR spectra of 2t
$^1$H NMR spectra of 2u

$^{13}$C NMR spectra of 2u
S77

$^1$H NMR spectra of 2v

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$^1$H NMR spectra of 2w

$^{13}$C NMR spectra of 2w
H NMR spectra of 4a

^13^C NMR spectra of 4a
$^{1}H$ NMR spectra of 4b

$^{13}C$ NMR spectra of 4b
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S81
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*Figure: Chromatograms of 2b with peak areas and times.*
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![Graph of 2g](image1)

![Graph of 2g](image2)
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**Chart 1**

[Image of a chart with peaks labeled as 2n and Ts, and time ranging from 3 to 30 minutes.]

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**Chart 2**

[Image of a chart with peaks labeled as 2n and Ts, and time ranging from 3 to 30 minutes.]

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*Figure 1: Chromatogram of compound 2r showing the elution profiles and areas under the peaks.*
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4b
VI. X-ray crystal structure

Crystallographic data for compound 1e (CCDC-1524099) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).

* A tool (PLATON SQUEEZE) for the calculation of the disordered solvent contribution to the calculated structure factors was used, see: L. S. Anthony, Acta Cryst. 2015, C71, 9-18.

Crystallographic data for compound 2b (CCDC-1524100) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).

Figure S1: X-ray structure of 1e (The H-atoms are omitted for clarity)  CCDC NO.1524099
Figure S2: X-ray structure of 2b (The H-atoms are omitted for clarity) CCDC NO. 1524100