Supporting Information

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Methods and Materials

General. Unless otherwise stated, reactions were performed under a nitrogen atmosphere using freshly distilled solvents. Diethyl ether (Et₂O) and tetrahydrofuran (THF) were distilled from sodium/benzophenone. Methylene chloride and benzene were distilled from calcium hydride. All other commercially obtained reagents were used as received. All reactions were monitored by thin-layer chromatography using E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Flash chromatography was performed with indicated solvents using silica gel (partical size 0.032-0.063) purchased from Bodman. ¹H and ¹³C NMR spectra were recorded on Bruker Avance DPX-500 or Bruker Avance DPX-400 spectrometers. Chemical shifts are reported relative to internal chloroform (¹H, δ = 7.26, ¹³C, δ = 77.1), dimethyl sulfoxide (¹H, δ = 2.50, ¹³C, δ = 40.3), methanol (¹H, δ = 3.31, ¹³C, δ = 49.2) or methylene chloride (¹H, δ = 5.32, ¹³C, δ = 54.0) as indicated. Melting points were obtained on a Gallenkamp variable temperature melting point apparatus and are uncorrected. Infrared spectra were recorded on a Midac M-1200 FTIR. High resolution mass spectra were acquired at the University of Illinois
Mass Spectrometry Center. Low resolution mass spectra were acquired on a Waters Micromass ZQ mass spectrometer.

Preparative Procedures.

3-(2-aminophenyl)-cyclohex-2-en-1-one (6).

To a mixture of 2-iodoaniline (5.5 g, 25 mmol), tri-o-tolyl phosphine (0.75 g, 2.5 mmol) and Pd(OAc)$_2$ (0.28 g, 1.25 mmol) under an N$_2$ atmosphere was added CH$_3$CN (150 mL), cyclohex-2-en-1-one (2.65 mL, 27.5 mmol) and Et$_3$N (7.0 mL, 50 mmol). After stirring 24 h at reflux, the solution was cooled to rt, diluted with EtOAc (300 mL) and extracted with water (2 x 100 mL) and brine (100 mL). The organic layer was dried over Na$_2$SO$_4$ and purified by chromatography on silica gel (gradient elution, 1% Et$_3$N/2.5% Et$_2$O/CH$_2$Cl$_2$ to 1% Et$_3$N/10% Et$_2$O/CH$_2$Cl$_2$). The enone was recovered as a green oil that solidified on standing at -20 °C (0.99 g, 21% yield). $^1$H NMR (CDCl$_3$) δ = 2.11-2.18 (m, 2H), 2.50 (t, $J = 6.7$, 2H), 2.66 (dt, $J = 1.5, 6.0$, 2H), 3.87 (bs, 2H), 6.25 (t, $J = 1.5$, 1H), 6.72 (dd, $J = 0.7, 8.1$, 1H), 6.77 (dt, $J = 1.2, 7.5$, 1H), 7.06 (dd, $J = 1.5, 8.0$, 1H), 7.11-7.16 (m, 1H). $^{13}$C NMR (CDCl$_3$) δ = 23.2, 30.3, 37.4, 116.3, 118.4, 125.6, 127.8, 128.0, 129.8, 142.9, 161.3, 199.6. FTIR (KBr) 3425, 3340, 2935, 1649, 1629, 1606, 1451 cm$^{-1}$. LRMS (ES+) $m/z$ 210.2 [calc for C$_{12}$H$_{13}$NNaO (M+Na) 210.1].

Oxindole 7 (Table 1).

Phosgene (0.159 mL 20% soln. in toluene, 0.36 mmol) was added to a solution of enone 6 (50 mg, 0.27 mmol) and Et$_3$N (0.083 mL, 0.59 mmol) in THF (1.35 mL) at 0 °C. The
heterogeneous mixture was stirred at 0 °C for 30 min at which time volatile liquids were removed under reduced pressure. Dry Et₂O (10 mL) was added, the resultant suspension was filtered through a pad of Celite, and the pad was washed with Et₂O (10 mL). The filtrate was concentrated on a rotary evaporator and the residue was dissolved in THF (10 mL). To this solution was added t-BuOH (0.026 mL, 0.27 mmol). The solution was cooled to -78 °C and degassed by bubbling N₂ for 10 min. A mixture of SmI₂ (5.7 mL 0.1 M soln in THF, 0.57 mmol) and LiCl (96 mg, 2.3 mmol) was stirred for 10 min at rt, then added via canula over 5 min to the isocyanate solution. After complete addition of SmI₂, the reaction solution was stirred for 2 min at -78 °C, and then quenched by the addition of saturated aqueous NH₄Cl. The mixture was allowed to warm to room temperature, diluted with water (20 mL) and EtOAc (20 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (2 x 20 mL). The organic layer was dried over Na₂SO₄ and purified by chromatography on silica gel (gradient elution, 20 to 40% EtOAc/Hexanes). Oxindole 7 was recovered as a tan viscous oil (51 mg, 88%). ¹H NMR (CDCl₃) δ = 1.85-1.93 (m, 1H), 2.10-2.21 (m, 2H), 2.33-2.40 (m, 1H), 2.40 (d, J = 14.4, 1H), 2.53-2.67 (m, 2H) 2.67 (d, J = 14.4, 1H), 6.95 (d, J = 7.8, 1H), 7.04 (dt, J = 1.1, 7.7, 1H), 7.14 (d, J = 6.7, 1H), 7.24 (dt, J = 1.3, 7.7, 1H), 8.52 (bs, 1H). ¹³C NMR (CDCl₃) δ = 21.7, 32.7, 40.7, 46.2, 51.4, 110.4, 122.7, 123.7, 128.5, 132.8, 139.8, 180.8, 209.1. FTIR (thin film, NaCl) 3261, 1717 (s) 1618, 1471. LRMS (ES+) m/z 238.1 [calc for C₁₃H₁₃NNaO₂ (M+Na) 238.1]. Experiments corresponding to the data presented in Table 1, entries 1-4 were performed analogously.

**Reduction of enone 6 (eq 2)**

![Reduction of enone 6](attachment:image)

A solution of enone 6 (36 mg, 0.19 mmol) and t-BuOH (0.018 mL, 0.19 mmol) in THF (10 mL) was cooled to -78 °C, and N₂ was bubbled through the solution for 10 min. A mixture of SmI₂ (0.1 M in THF, 4 mL, 0.4 mL) and LiCl (67 mg, 1.6 mmol) was stirred
for 10 min, and then added to the enone via canula over 5 min. After complete addition of SmI₂, the reaction solution was stirred for 2 min at -78 °C then quenched by the addition of saturated aqueous NH₄Cl. The mixture was allowed to warm to room temperature, diluted with water (20 mL) and EtOAc (20 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (2 x 20 mL). The organic layer was dried over Na₂SO₄ and purified by chromatography on silica gel (gradient elution, 1 to 4% MeOH/CH₂Cl₂) to provide aminal 11 as a white solid (7 mg, 19%) and diamino diol 12 (25 mg, 70%) as a 4:1 mixture of diastereomers.

11: ⁴H NMR (CDCl₃) δ = 1.42-1.40 (m, 1H), 1.55-1.60 (m, 1H), 1.64 (t, J = 3.5, 1H), 1.66 (t, J = 3.5), 1.84 (d, J = 3.4, 1H), 1.87 (d, J = 3.4, 1H), 1.90-1.95 (m, 1H), 1.98 (d, J = 3.1, 1H), 2.06 (bs, 1H), 3.09-3.14 (m, 1H), 4.16 (bs, 1H), 6.50 (dd, J = 0.7, 7.7, 1H), 6.65 (dt, J = 0.7, 7.7, 1H), 6.65 (dt, J = 1.6, 7.6, 1H), 7.01 (dt, J = 1.5, 7.7, 1H). ¹³C NMR (CDCl₃) δ = 19.5, 33.4, 36.7, 38.7, 40.7, 80.5, 113.1, 117.7, 125.6, 127.2, 128.0, 144.0. FTIR (KBr) 3507, 3325, 2942, 2847, 1606, 1490, 1075, 1062. LRMS (ES+) m/z 172.2 [calc for C₁₂H₁₄N (M-OH)+] 172.1], 190.2 [calc for C₁₂H₁₄NO (M+H)+ 190.1], 212.2 [calc for C₁₂H₁₄NNaO (M+Na)+ 212.1]. The diastereomers 12a and 12b decomposed to unidentified material over the course of a few hours in solution or in a few minutes if adsorbed onto dry silica gel. They could be separated by preparative HPLC (Microsorb Si 80-120-C5, 7.5%IPA/CH₂Cl₂, retention time (major) = 25 min, retention time (minor) = 29 min). Higher Rf isomer (major): ¹H NMR (CD₂Cl₂) δ = 1.67 (dt, J = 4.0, 13.3, 1H), 1.79 (d, J = 13.3, 1H), 1.83-1.92 (m, 2H), 2.17-2.25 (m, 1H), 2.30 (d, J = 16.6, 1H), 2.67 (bs, 1H), 3.84 (bs, 1H), 5.99 (s, 1H), 6.69 (d, J = 8.6, 1H), 6.72 (d, J = 7.2, 1H), 6.97 (d, J = 7.0, 1H), 7.05 (dt, J = 1.6, 7.2, 1H). ¹³C NMR (CD₂Cl₂) δ =20.0, 30.2, 31.0, 74.5, 115.9, 118.5, 128.3, 128.5, 128.9, 129.7, 141.9, 143.9. FTIR (KBr) 3344, 2936, 1613, 1494, 1449 cm⁻¹. LRMS (ES+) m/z 399.2 [calc for C₂₄H₂₈N₂NaO₂ (M-Na)+ 399.2]. Lower Rf isomer (minor), isolated in ca. 85% purity contaminated with ca. 15% of the major diastereomer. ¹H NMR (CD₂Cl₂) δ = 1.71 (dr, J = 4.8, 12.5, 1H), 1.82-1.91 (m, 2H), 1.95 (d, J = 14.1, 1H), 2.14-2.23 (m, 1H), 2.29 (d, J = 18.9, 1H), 2.38 (bs, 1H), 3.79 (bs, 2H), 5.91 (s, 1H), 6.66 (d, J = 7.9, 1H), 6.69 (d, J = 7.7, 1H), 6.95 (dt, J = 1.0, 8.1, 1H), 7.02 (dt, J = 1.3, 7.7, 1H). ¹³C NMR (CD₂Cl₂) δ = 19.9, 30.2, 31.1, 75.0, 116.0, 118.6, 128.4, 128.6, 128.9, 129.5, 142.8, 143.8. FTIR
(thin film, NaCl) 3362, 2932, 1611, 1493, 1450 cm$^{-1}$. LRMS (ES+) $m/z$ 399.2 [calc for C$_{24}$H$_{28}$N$_2$NaO$_2$ (M-Na)$^+$ 399.2].

**Reduction of Phenyl Isocyanate.**

Freshly distilled phenyl isocyanate (0.021 mL, 0.19 mmol) was subjected to identical reaction conditions as described for enone 6 above. The reaction was quenched at -78°C with NaOMe (1 mL, 1M in MeOH) and NH$_4$Cl (5 mL). Following extractive workup, N-phenyl urea was isolated (26 mg, quant.) and found to be identical ($^1$H NMR, $^{13}$C NMR) to a commercially available sample.

**Cyclobutaneone 9.**

A solution of diene 13 (8.22 g, 54.1 mmol)$^1$ and Et$_3$N (54.0 mL, 387 mmol) in THF (210 mL) was brought to reflux and maintained at this temperature while isobutyryl chloride (40.0 mL, 382 mmol) was introduced over a period of 15 hours. The mixture was allowed to stir at reflux for an additional 12 hours before the reaction was cooled to room temperature and filtered to remove the triethylamine hydrochloride salt. The solution was then concentrated under reduced pressure (rotary evaporator) keeping the temperature under 10 °C to provide an orange oil containing a large amount of a white precipitate. To this mixture was added 750 mL of a 20% EtOAc/hexanes solution. Following removal of approximately half of this volume under reduced pressure, an additional 300 mL of hexanes was introduced and the mixture was filtered to remove the white precipitate, which consisted entirely of 2,2,4,4-tetramethyl-cyclobutane-1,3-dione, resulting from the dimerization of dimethyl diketene. This precipitate was washed well with hexanes, and the resulting filtrate was concentrated. The resulting residue was subjected to silica gel chromatography (gradient elution, 2 to 10% EtOAc/hexanes) to
provide cyclobutanone 9 (10.21 g, 85% yield) as a white solid. m.p. 93.5-95.5 °C. $^1$H NMR (CDCl$_3$) δ = 0.99 (s, 3H), 1.35 (s, 3H), 1.38 (s, 6H), 2.73-2.70 (m, 1H), 4.14 (dd, $J = 2.2$, 9.3 Hz, 1H), 4.42 (dd, $J = 1.1$, 5.7 Hz, 1H), 4.60 (dd, $J = 1.9$, 5.1 Hz, 1H), 5.80-5.72 (m, 2H). $^{13}$C NMR (CDCl$_3$) δ = 17.0, 24.8, 26.4, 28.0, 33.8, 53.3, 63.3, 69.5, 69.6, 108.9, 125.6, 128.3, 212.3. FTIR (thin film/NaCl) 3056, 2993, 1773, 1262, 1053, 736 cm$^{-1}$. HRMS (EI) $m/z$ 222.1255 [calc for C$_{13}$H$_{18}$O$_3$ (M$^+$) 222.1256].

**Triazene 11.**

![Image of triazene 11]

To a solution of triazene 10 (1.0 g, 3.94 mmol)$^2$ in THF (75 mL) at -78 °C was added $t$-BuLi (4.63 mL of 1.7M solution in pentane, 7.87 mmol). Stirring was continued at -78 °C for 30 min at which time a solution of MgBr$_2$ [26 mL of 0.25M solution in THF (freshly prepared from 1 equiv dibromoethane and 1.2 equiv Mg turnings at rt), 6.57 mmol] was added. The reaction solution was stirred at -78 °C for 15 min, and then a solution of ketone 9 (0.728 g, 3.28 mmol) in THF (15 mL) was added dropwise. The reaction flask was immediately placed in a preheated oil bath (100 °C) and the reaction solution was brought to reflux. After stirring 2 min at reflux, the reaction mixture was allowed to cool to rt, carefully quenched with water, diluted with EtOAc (200 mL) and water (100 mL). The layers were separated, and the organic layer was extracted with water, dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure. Analysis of the crude reaction mixture indicated that the product had been formed as a single diastereomer. Chromatography on silica gel (gradient elution, 2 to 10% EtOAc/hex) provided triazene 11 as an orange foam (1.14 g, 88% yield). $^1$H NMR (CDCl$_3$) δ = 0.67 (s, 3H), 0.93 (s, 3H), 1.30 (s, 3H), 1.36 (s, 3H), 1.96 (bs, 4H), 2.24-2.28 (m, 1H), 3.55 (bs, 2H), 3.79 (d, $J = 8.5$, 1H), 3.88 (bs, 2H), 4.48 (d, $J = 5.6$, 1H), 4.65-4.69 (m, 1H), 5.68 (d, $J = 10.9$, 1H), 5.76 (ddd, $J = 1.1$, 4.2, 10.7, 1H), 5.88 (bs, 1H), 7.08 (dt, $J = 1.3$, 7.6, 1H), 7.14 (dt, $J = 1.3$, 7.6, 1H), 7.34 (dd, $J = 1.1$, 7.9, 1H), 7.38 (J = 1.1, 7.8, 1H). $^{13}$C NMR (CDCl$_3$) δ = 19.2, 23.7, 23.9, 26.7, 27.5, 28.3, 24.6, 37.1, 46.1, 46.8, 51.5, 71.2,
72.0, 82.6, 107.3, 117.3, 125.2, 126.6, 127.0, 127.8, 127.9, 135.0, 148.8. FTIR (KBr) 3316, 2979, 2954, 2884, 1418, 1049, 761 cm\(^{-1}\). HRMS (ES+) \(m/z\) 420.2 [calc for \(\text{C}_{23}\text{H}_{31}\text{N}_{3}\text{NaO}_{3} (\text{M+Na})^{+}\) 420.2]. The relative configuration was determined by X-ray crystallographic analysis of a more advanced intermediate (see III below).

\(\alpha,\beta\)-unsaturated ketone 12.

To a solution of triazene 11 (4.0 g, 10 mmol) in MeOH (1.2 L) was added Raney Ni [400 g of 50% solution in water, washed with water (5x400 mL) and MeOH (3x400 mL), PYROPHORIC] in MeOH (300 mL). The reaction mixture was stirred for 30 min with a mechanical stirrer. After 30 min, the mixture was filtered through Celite under N\(_2\), and the Celite was washed with EtOAc (4L). The combined filtrates were concentrated under reduced pressure to provide the amino alcohol II as a white powder. The crude amino alcohol was routinely used without purification, but chromatography on silica gel (gradient elution, 5 to 20% EtOAc/Hexanes) provided an analytically pure sample. \(^1\)H NMR (CDCl\(_3\)) \(\delta = 0.98\) (s, 3H), 1.28 (s, 3H), 1.39 (s, 3H), 1.43 (s, 3H), 2.35 (m, 1H), 2.38 (bs, 1H), 3.87 (dd, \(J = 1.2, 8.4, 1\)H), 4.12 (bs, 2H), 4.50 (d, \(J = 6.0, 1\)H), 4.66 (dd, \(J = 1.5, 5.6, 1\)H), 5.81 (ddd, \(J = 2.3, 2.3, 10.6, 1\)H), 5.95 (ddd, \(J = 0.6, 4.0, 10.6, 1\)H), 6.64 (dd, \(J = 1.0, 7.8, 1\)H), 6.76 (ddd, \(J = 1.2, 7.4, 7.4, 1\)H), 7.10 (ddd, \(J = 1.6, 7.6, 7.6, 1\)H), 7.29 (d, \(J = 7.6, 1\)H). \(^{13}\)C NMR (CDCl\(_3\)) \(\delta = 19.8, 26.7, 27.0, 28.3, 36.4, 37.0, 46.0, 71.0, 71.4, 83.6, 1079, 117.2, 118.1, 126.4, 127.28, 127.31, 129.11, 129.11, 145.9. FTIR (thin film, NaCl) 3252, 2983, 2930, 1721, 1597, 1370, 1053 cm\(^{-1}\). LRMS (APCI+) \(m/z\) 316.8 [calc for \(\text{C}_{19}\text{H}_{26}\text{NO}_{3} (\text{M+H})^{+}\) 316.2].
To a mixture of amino alcohol II, NaHCO$_3$ (1.09 g, 13 mmol), t-butyl methyl ether (14 mL) and water (28 mL) was added 4-nitrophenyl chloroformate (2.23 g, 11.1 mmol). The pale yellow mixture was stirred 1h at rt at which time NaOH (23 mL of 1M solution) was added. Stirring was continued for 3 h, and the mixture was diluted with EtOAc (100 mL) and extracted with 1M NaOH (3x100 mL). The organic layer was dried with Na$_2$SO$_4$, filtered and concentrated under reduced pressure to provide the carbamate III. Crude carbamate III was routinely used without purification, but chromatography on silica gel (gradient elution, 10 to 70% EtOAc/hexanes) provided an analytically pure sample. $^1$H NMR (CDCl$_3$) $\delta$ = 0.88 (s, 3H), 1.16, (s, 3H), 1.35 (s, 3H), 1.43 (s, 3H), 2.47 (m, 1H), 3.71 (d, $J$ = 8.5, 1H), 4.36 (d, $J$ = 6.0, 1H), 4.78 (d, $J$ = 4.0, 1H), 5.76 (dd, $J$ = 3.8, 10.8, 1H), 5.83 (d, $J$ = 10.5, 1H), 6.87 (d, $J$ = 7.5, 1H), 7.12 (dd, $J$ = 7.5, 7.5, 1H), 7.29 (dd, $J$ = 7.5, 7.5, 1H), 7.32 (d, $J$ =7.5, 1H), 9.04 (bs, 1H). $^{13}$C NMR (CDCl$_3$) $\delta$ = 18.9, 26.8, 26.9, 28.3, 35.6, 37.2, 48.5, 70.1, 71.5, 90.5, 108.1, 114.8, 119.6, 123.2, 125.6, 126.2, 128.2, 129.6, 135.6, 153.7. FTIR (thin film, NaCl) 3453, 3368, 2963, 1613, 1453, 1048 cm$^{-1}$. LRMS (APCI+) $m/z$ 342.4 [calc for C$_{20}$H$_{23}$NO$_4$ (M+H)$^+$ 342.2]. A crystal of the N-benzyl derivative suitable for X-ray diffraction was grown by slow evaporation from EtOAc/Hexanes (Figure S1, for crystallographic details, see Appendix 1).

Figure S1. X-ray structure of N-benzyl-III. ORTEP plot generated with the program ORTEP-3 for windows.$^3$
Carbamate III was dissolved in AcOH (100 mL) and water (60 mL), and the solution was stirred at 70 °C for 12 h. The solution was cooled, and the AcOH was quenched by adding small portions of NaOH. The reaction mixture was partitioned between EtOAc (100 mL) and 1M NaOH (100 mL). The aqueous layer was extracted with EtOAc (2x100 mL). The combined organic layers were dried with Na₂SO₄, filtered and concentrated under reduced pressure to provide diol IV as a white solid. Diol IV was routinely used without purification, but chromatography on silica gel (gradient elution, EtOAc to 10% MeOH/EtOAc) provided an analytically pure sample. 

\(^1\)H NMR (MeOD-d₃) δ = 0.66 (s, 3H), 1.17 (s, 3H), 2.65 (ddd, J = 2.2, 3.4, 9.4, 1H), 3.36 (dd, J = 9.0, 9.0, 1H), 4.25 (dd, J = 3.4, 5.8, 1H), 4.43 (dd, J = 3.2, 9.2, 1H), 5.82 (dd, J = 3.6, 10, 1H), 6.08, (ddd, J = 2.3, 5.9, 9.7, 1H) 7.95 (dd, J = 1.2, 7.6, 1H), 7.17 (ddd, J = 1.2, 7.6, 7.6, 1H), 7.30 (ddd, J = 1.2, 7.6, 7.6, 1H), 7.45 (d, 7.6, 1H). 

\(^1\)H NMR (MeOD-d₃) δ = 49., 21.3, 27.0, 41.1, 42.1, 67.1, 68.1, 86.2, 115.2, 124.2, 124.5,125.7, 129.8, 130.2, 130.6, 137.1, 154.8. FTIR (Nujol Mull) 3244, 1709, 1596, 1068 cm\(^{-1}\). LRMS (APCI+) \(m/z\) 302.4 [calc for C\(_{17}\)H\(_{19}\)NO\(_4\) (M+H)\(^+\) 302.1].

A solution of diol IV and dibutyltin oxide (2.6g, 10.5 mmol) in MeOH (300 mL) was stirred at reflux for 3h, cooled and concentrated under reduced pressure. To the resulting solid was added N-bromosuccinimide (2.05 g, 11.5 mmol) and CHCl₃ (100 ml). The reaction solution was stirred for 30 min, poured into a separatory funnel, extracted with water (100 mL) and brine (50 mL). The organic layer was dried with Na₂SO₄, filtered and concentrated under reduced pressure. Chromatography on silica gel (2:1 EtOAc:hex) provided α,β-unsaturated ketone 12 as a white solid (2.2g, 74% yield over 4 steps). 

\(^1\)H NMR (MeOD-d₃) δ = 0.80 (s, 3H), 1.26 (s, 3H), 2.90 (ddd, 1.8, 4.2, 9.0, 1H), 3.51 (dd, J = 7.6, 9.2, 1H), 4.74 (d, J = 1.2, 1H), 6.17 (dd, J = 1.6, 10, 1H), 6.89 (dd, J = 4.2, 10.2, 1H), 6.91 (dd, J = 1.0, 7.8, 1H), 7.17 (ddd, J = 1.5, 7.5, 7.5, 1H), 7.32 (ddd, J = 1.2, 7.8, 7.8, 1H), 7.45 (dd, J = 1.4, 7.8, 1H). FTIR (thin film, NaCl) 3408, 2962, 1720, 1260, 1092, 1010 cm\(^{-1}\). LRMS (APCI+) \(m/z\) 300.2 [calc for C\(_{17}\)H\(_{17}\)NO\(_4\) (M+H)\(^+\) 300.1].
Dithiolane V.

To a solution of α,β-unsaturated ketone 12 (245 mg, 0.81 mmol) and 1,2-ethanedithiol (0.103 mL, 1.20 mmol) in CH₂Cl₂ (16 mL) at 0 °C was added BF₃•Et₂O (0.123 mL, 0.97 mmol). The reaction mixture was stirred at 0 °C for 5h, at which time saturated aqueous NaHCO₃ (1 mL) was added. The mixture was partitioned between CH₂Cl₂ (50 mL) and saturated aqueous NaHCO₃ (50 mL). The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (50 mL). The combined organic layers were dried with Na₂SO₄, filtered and concentrated under reduced pressure. Chromatography on silica gel (gradient elution, 10 to 20% CH₃CN/CH₂Cl₂) provided alcohol V as a white solid in approximately 95% purity; this material converted directly into ketone 13. ¹H NMR (CDCl₃) δ = 0.66 (s, 3H), 1.25 (s, 3H), 2.61 (ddd, J = 2.6, 3.3, 9.8), 2.66 (d, J = 4.9, 1H), 3.30-3.45 (m, 4H), 3.51-3.54 (m, 1H), 4.80 (dd, J = 4.8, 9.8, 1H), 5.58 (dd, J = 3.6, 9.4, 1H), 6.18 (dd, J = 2.0, 9.6, 1H), 6.85 (dd, J = 0.8, 7.9, 1H), 7.17 (dt, 1.0, 7.7, 1H), 7.28 (dt, 1.3, 7.8, 1H), 7.39 (d, 7.6, 1H), 8.37 (bs, 1H). ¹³C NMR (CDCl₃) δ = 21.1, 26.5, 40.0, 41.1, 41.7, 44.6, 49.0, 69.2, 72.4, 84.4, 114.3, 122.5, 123.6, 124.2, 124.9, 129.2, 134.7, 135.0, 152.9. FTIR (thin film, NaCl) 3446, 3250, 2925, 1717 (s), 1597 cm⁻¹. LRMS (ES+) m/z 376.1 [calc for C₁₉H₂₂N₂O₃S₂ (M+H)⁺ 376.1].

Ketone 13.
To a solution of (COCl)$_2$ (0.089 mL, 1.01 mmol) in CH$_2$Cl$_2$ (7 mL) at -78 °C was added DMSO (0.142 mL, 2.02 mmol). The reaction mixture was stirred for 15 min at -78 °C, and then alcohol V (190 mg, 0.5 mmol) was added dropwise as a solution in CH$_2$Cl$_2$ (25 mL). The temperature of the dry ice/acetone bath was allowed to warm to -65 °C over 20 min at which time Et$_3$N (0.57 mL, 4.04 mmol) was added. The reaction mixture was stirred at -65 °C for 5 min and -20 °C for 20 min and then quenched with saturated aqueous NaHCO$_3$. The reaction mixture was partitioned between CH$_2$Cl$_2$ (100 mL) and 1M HCl (100 mL). The organic layer was extracted with 1M HCl (2x100 mL) and brine (50 mL), dried with Na$_2$SO$_4$, filtered and concentrated under reduced pressure. Chromatography on silica gel (10% Et$_2$O/CH$_2$Cl$_2$) provided ketone 13 as a tan solid (140 mg, 75% yield, 46% yield from 12). $^1$H NMR (CDCl$_3$) $\delta$ = 0.92 (s, 3H), 1.24 (s, 3H), 2.95 (ddd, $J = 2.7$, 2.7, 8.6, 1H), 3.29 (ddd, $J = 6.6$, 8.1, 11.6, 1H), 3.39 (ddd, $J = 4.2$, 5.6, 11.6, 1H), 3.51-3.62 (m, 2H), 4.34 (d, $J = 8.6$, 1H), 6.06 (dd, $J = 2.5$, 9.9, 1H), 6.21 (dd, $J = 2.3$, 10.2, 1H), 6.71 (dd, $J = 0.9$, 7.8, 1H), 7.11 (dt, $J = 1.1$, 7.6, 1H), 7.15 (bs, 1H), 7.25-7.29 (m, 1H), 7.33 (d, $J = 7.7$, 1H). $^{13}$C NMR (CDCl$_3$) $\delta$ = 19.1, 25.9, 41.0, 42.3, 43.2, 47.9, 66.4, 90.3, 91.4, 113.9, 119.2, 122.1, 126.6, 127.3, 129.4, 131.5, 135.8, 150.8, 197.9. IR (KBr) 3426, 2929, 1719, 1598, 1346, 1061, 758 cm$^{-1}$. LRMS (ES+) m/z 396.1 [calc for C$_{19}$H$_{19}$NNaO$_3$S$_2$ (M+Na)$^+$ 396.1]. Crystals suitable for X-ray diffraction were grown by slow evaporation from CH$_2$Cl$_2$/Hexanes (Figure S2). For crystallographic details, see Appendix 2.

**Figure S2.** X-ray structure of ketone 13. ORTEP plot generated with the program ORTEP-3 for windows.$^3$
Oxindole 15.

To a solution of ketone 13 (25 mg, 0.067 mmol) in THF (0.7 mL) was added 1,8-diazabicyclo[4.3.0]undec-7-ene (DBU, 0.004 mL, 0.026 mmol), and after 3h, TLC analysis indicated complete conversion of the starting material. The reaction mixture was cooled to 0 °C, and Et$_3$N (0.019 mL, 0.13 mmol) and phosgene (0.041 mL of a 20% solution in toluene, ca. 0.084 mmol) were added. After 30 min, the reaction mixture was concentrated under reduced pressure, suspended in Et$_2$O (10 mL) and filtered through a pad of Celite. The Celite was washed with Et$_2$O (10 mL) and the combined filtrate was concentrated under reduced pressure. The resulting residue was dissolved in THF (0.6 mL) and cooled to -78 °C. Following addition of $t$-BuOH (0.0064 mL, 0.067 mmol), the reaction solution was degassed by bubbling N$_2$ for ca. 10 min. A mixture of SmI$_2$ (1.4 mL of 0.1M solution in THF, 0.14 mmol) and LiCl (11 mg, 0.27 mmol) that had been premixed for ca. 10 min was added dropwise over 5 min. Stirring was maintained for 30 min at which time the reaction was quenched at -78 °C with saturated aqueous NH$_4$Cl. The mixture was allowed to warm to rt, diluted with EtOAc (30 mL) and extracted with saturated aqueous NH$_4$Cl. The organic layer was dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure. Analysis of the crude reaction mixture by $^1$H NMR indicated the product had been formed as a 7:1 mixture of diastereomers [integration of the peaks corresponding to the proton adjacent to the carbonyl, 3.8 ppm (major), 3.6 ppm (minor)]. The desired oxindole 15 was isolated as a sparingly soluble white solid as a 7:1 mixture of diastereomers (17 mg, 71% yield) following chromatography on silica gel (gradient elution, 0.5 to 2% MeOH/CH$_2$Cl$_2$). $^1$H NMR (CDCl$_3$/DMSO-$d_6$, 2:1) $\delta = 0.65$ (S, 3H), 1.01 (s, 3H), 2.91 (ddd, $J = 5.8, 5.8, 11.7, 1$H), 3.14 (ddd, $J = 4.9, 4.9, 11.6, 1$H),
3.28-3.32 (m, 2H), 3.38 (ddd, $J = 1.6, 3.8, 9.4, 1H$), 3.79 (d, $J = 9.4, 1H$), 5.73 (dd, $J = 4.0, 9.8, 1H$), 5.96, (dd, $J = 1.9, 9.9, 1H$), 6.58 (d, $J = 7.6, 1H$), 6.66 (dt, 1.0, 7.6, 1H), 6.77 (dd, $J = 0.5, 7.3, 1H$), 6.89 (dt, $J = 1.3, 7.6, 1H$), 9.56 (bs, 1H).

$^{13}$C NMR (CDCl$_3$/DMSO-$d_6$, 2:1) $\delta = 22.7, 24.7, 28.9, 40.9, 42.3, 44.4, 45.1, 57.8, 66.1, 109.1, 120.2, 125.3, 127.3, 127.5, 128.0, 130.1, 142.0, 179.0, 199.1$. FTIR (KBr) 3172, 2926, 1696 (s), 1608, 1467 cm$^{-1}$. LRMS (ES+) m/z 380.1 [calc for C$_{19}$H$_{19}$NNaO$_2$S$_2$ (M+Na)$^+$ 380.1].

**Figure S3.** Selected COSY cross peaks and NOE enhancements observed for oxindole 15

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**References**