Supporting information

^{1}H NMR (300, 200 MHz) and ^{13}C NMR (75, 50 MHz) spectra were recorded in deuterated chloroform on Brucker AM 200 and Brucker Avance 300 spectrometers relative to $(CH_3)_4Si$ and $CDCl_3$ respectively. Chemical shifts are expressed in parts per million (ppm). Low resolution and high resolution mass spectra were recorded on Unicam ATI Automass and Jeol 500 spectrometers, respectively. IR spectra were recorded on Perkin-Elmer 16PC FT-IR spectrometers.

Representative procedure for the catalyzed reactions: To a solution of 1-*p*-toluenesulfonylindole-3-carboxaldehyde **4** (0.06 g, 0.2 mmol) in dry dichloromethane (0.5 mL) at room temperature was added a 1M solution of zinc chloride in dry tetrahydrofuran (20 μL). The mixture was stirred for 15 minutes. A 0.01M solution of hydroquinone in dry Ether (100 μL) and distilled cyclohexadiene **5b** (230 μL, 2.4 mmol) were then added to this stirring solution. The resultant mixture was transfered into a high-pressure vessel and compressed to 16 kbar at 25°C. After 48 hours and decompression, the mixture was evaporated under reduced pressure. Chromatography of the residue on silica and elution with a 9 :1 mixture of heptane/ethyl acetate led to the isolation of the cycloadduct (47 mg, 62%).
The ketones resulting from the hydrolysis of cycloadducts **6c** and **7c** were obtained in the following manner. The above procedure was used without zinc chloride; removal of the excess diene was achieved by Kugelrohr distillation under reduced pressure (150ºC/0.1bar). The residue (0.3 mmol scale) was then stirred overnight in methanol (2 mL) in the presence of silica (100 mg). Filtration and purification as above delivered the desired products.
The same hydrolysis procedure was followed for the isolation of compound **8**.

Analytical data for compounds **6a**, **6b**, **7b**, the ketones resulting from hydrolysis of **6c** and **7c**, **8**, **11** *and* **12**.
6a. ^{1}H-NMR δ 1.51 (s, 3H), 1.66 (s, 3H), 2.15 (d, 1H, ^{2}J=14.7 Hz), 2.26 (s, 3H), 2.37-2.50 (m, 1H), 2.45 (d, 1H, ^{2}J=14.7 Hz), 2.53 (dd, 1H, J=5.6 Hz, ^{2}J=14.7 Hz), 4.49 (dd, 1H, ^{3}J=5.6 Hz, ^{3}J=7.2 Hz), 6.93 (dd, 1H, ^{4}J=1.5 Hz, ^{3}J=7.5 Hz), 6.99 (dd, 1H, ^{3}J=7.2 Hz, ^{3}J=7.5 Hz), 7.10 (d, 2H, ^{3}J=8.3 Hz), 7.21 (ddd, 1H, ^{4}J=1.5 Hz, ^{3}J=7.2 Hz, ^{3}J=8.3 Hz), 7.51 (d, 2H, ^{3}J=8.3 Hz), 7.62 (d, 1H, ^{3}J=8.3 Hz), 9.02 (s, 1H). ^{13}C-NMR δ 19.0, 19.0, 21.3, 35.0, 37.1, 61.3, 62.4, 116.1, 124.1, 124.7, 126.0, 127.1, 127.4, 129.4, 129.4, 131.0, 133.7, 142.5, 144.1, 196.3. MS (EI) m/z (%): 381 (53), 352 (93), 299 (100), 196 (54), 155 (71), 91 (75). Exact mass (EI) *m/z* calcd for $C_{22}H_{23}NO_3S$: 381.1399. Found 381.1395.

6b. ^{1}H-NMR δ 0.90-1.30 (m, 3H), 1.70-1.90 (ddd, 1H, ^{3}J=2.4 Hz, ^{3}J=6.4 Hz, ^{2}J=16.6 Hz), 2.26 (s, 3H), 2.85-3.00 (m, 1H), 3.18 (m, 1H), 4.31 (dd, 1H, ^{4}J=1.1 Hz, ^{3}J=3.8 Hz), 6.24 (d, 1H, ^{3}J=3.7 Hz), 6.25 (d, 1H, ^{3}J=3.7 Hz), 6.90-7.05 (m, 2H), 7.10 (d, 2H, ^{3}J=8.3 Hz), 7.15-7.30 (m, 1H), 7.52 (d, 2H, ^{3}J=8.3 Hz), 7.69 (d, 1H, ^{3}J=8.3 Hz), 8.73 (s, 1H). ^{13}C-NMR δ 17.7, 21.6, 22.0, 34.4, 36.2, 64.3, 65.9, 116.8, 125.1, 125.4, 127.7, 129.5, 130.0, 130.3, 133.6, 134.2, 134.5, 143.9, 144.7, 197.0. MS (EI) m/z (%): 379 (11), 300 (100), 299 (73), 155 (66), 91 (57). Exact mass (EI) *m/z* calcd for $C_{22}H_{21}NO_3S$: 379.1242. Found 379.1264.

Ketone from the hydrolysis of **6c**. ^{1}H-NMR δ 2.31 (s, 3H), 2.68-3.15 (m, 2H), 3.19 (s, 3H), 3.40-3.60 (m, 2H), 5.50 (d, 1H, ^{3}J=6.2 Hz), 5.65 (dd, 1H, ^{3}J=3.8 Hz, ^{3}J=12.4 Hz), 6.80-7.50 (m, 9H). ^{13}C-NMR δ 21.6, 41.4, 45.4, 57.1, 60.6, 64.8, 74.6, 113.9, 120.0, 123.6, 125.4, 126.9, 128.2, 130.0, 134.9, 135.3, 145.3, 162.9, 191.6. MS (EI) m/z (%): 399 (37), 367 (35), 297 (13), 212 (36), 184 (100). Exact mass (EI) *m/z* calcd for $C_{21}H_{21}NO_5S$: 399.1141. Found 399.1130.

7b. ^{1}H-NMR δ 0.60-2.00 (m, 4H), 2.26 (s, 3H), 3.02-3.10 (m, 1H), 3.20-3.30 (m, 1H), 4.58 (d, 1H, ^{3}J=3.0 Hz), 5.84 (dd, 1H, ^{3}J=7.2 Hz, ^{3}J=7.2 Hz), 6.25 (d, 1H, ^{3}J=7.5 Hz, ^{3}J=7.5 Hz), 6.90-7.70 (m, 8H), 9.19 (s, 1H). ^{13}C-NMR δ 17.7, 21.3, 22.0, 35.8, 36.4, 64.3, 65.9, 116.1, 124.3, 124.7, 127.7, 129.5, 129.7, 129.9, 132.5, 133.3, 134.2, 143.8, 144.5, 197.5. Exact mass (EI) *m/z* calcd for $C_{22}H_{21}NO_3S$: 379.1242. Found 379.1234.

Ketone from the hydrolysis of **7c**. ^{1}H-NMR δ 2.10-2.88 (m, 4H), 2.31 (s, 3H), 3.19 (s, 3H), 4.77 (dd, 1H, ^{3}J=2.2 Hz, ^{3}J=8.4 Hz), 4.88 (dd, 1H, ^{3}J=4.7 Hz, ^{3}J=9.5 Hz), 6.80-7.50 (m, 9H). ^{13}C-NMR δ 21.6, 46.3, 47.8, 56.8, 60.6, 64.8, 74.6, 113.8, 120.0, 123.3, 125.1, 126.9, 128.2, 130.0, 135.0, 135.3, 145.2, 162.9, 191.6. MS (EI) m/z (%): 399 (1), 367 (72), 297 (100), 212 (23), 184 (24), 142 (86), 115 (45), 91 (35). Exact mass (ketone-MeOH) (EI) *m/z* calcd for $C_{21}H_{21}NO_5S$: 367.0879. Found 367.0894.

8. ^{1}H-NMR δ 2.28 (s, 3H), 2.75 (dd, 1H, ^{3}J=3.8 Hz, ^{2}J=16.6 Hz), 2.99 (dd, 1H, ^{3}J=13.0 Hz, ^{2}J=16.6 Hz), 5.47 (d, 1H, ^{3}J=6.0 Hz), 5.64 (dd, 1H, ^{3}J=3.8 Hz, ^{3}J=13.0 Hz), 7.10-7.34 (m, 4H), 7.37 (d, 1H, ^{3}J=6.0 Hz), 7.53 (d, 1H, ^{3}J=7.9 Hz), 7.54 (s, 1H), 7.72 (d, 2H, ^{3}J=8.3 Hz), 7.93 (d, 1H, ^{3}J=8.7 Hz). ^{13}C-NMR δ 21.6, 41.4, 74.6, 107.6, 113.8, 119.3, 120.0, 123.5, 124.0, 125.3, 126.9, 128.2, 130.0, 134.9, 135.3, 145.3, 162.8, 191.5. MS (EI) m/z (%): 367 (73), 297 (100), 212 (22), 184 (32), 142 (96), 115 (54), 91 (37). Exact mass (EI) *m/z* calcd for $C_{20}H_{17}NO_4S$: 367.0879. Found 367.0862.

11. ^{1}H-NMR δ 0.69 (t, 3H, ^{3}J=7.2 Hz), 1.04 (t, 3H, ^{3}J=7.2 Hz), 2.14-2.60 (m, 4H), 2.28 (s, 3H), 2.57-3.48 (m, 4H), 3.19 (s, 3H), 4.81 (dd, 1H, ^{3}J=3.4 Hz, ^{3}J=8.3 Hz), 5.20 (dd, 1H, ^{3}J=6.0 Hz, ^{3}J=6.4 Hz), 6.97 (m, 1H), 7.12 (d, 2H, ^{3}J=7.9 Hz), 7.16-7.30 (m, 2H), 7.53-7.64 (m, 3H). ^{13}C-NMR δ 11.4, 12.3, 20.5, 38.0, 38.6, 40.5), 43.6, 56.3, 60.4, 63.7, 76.0, 114.7, 123.6, 125.9, 126.5, 126.9, 128.6, 129.1, 133.1, 141.5, 143.3, 164.3, 196.5, 204.7. MS (EI) m/z (%): 399 (3), 344 (7), 284 (16), 242 (29), 184 (37), 156 (28), 138 (19), 100 (100). Anal. Calcd for $C_{26}H_{30}N_2O_6S$ C, 62.63; H, 6.06; N, 5.62; S, 6.43. Found C, 62.58; H, 6.21; N, 5.41; S, 6.44.

12. ^{1}H-NMR δ 0.61 (t, 3H, ^{3}J=7.2 Hz), 1.05 (t, 3H, ^{3}J=7.2 Hz), 1.88 (dd, 1H, ^{2}J=18.5Hz, ^{3}J = 2.3 Hz), 2.05-2.42 (m, 2H), 2.28 (s, 3H), 2.57 (dd, 1H, ^{2}J =18.5 Hz, ^{3}J = 3.0 Hz), 3.01 (dd, 1H, ^{2}J=17.0 Hz, ^{3}J=3.0 Hz), 3.08-3.43 (m. 3H), 3.25 (s, 3H), 4.67 (dd, 1H, ^{3}J=3.0 Hz, ^{3}J=2.3 Hz), 5.42 (dd, 1H, ^{3}J=5.6 Hz, ^{3}J=2.3 Hz), 6.95 (m, 1H), 7.11 (d, 2H, ^{3}J=7.9 Hz), 7.43 (m, 1H), 7.59 (m, 1H), 7.66 (d, 2H, ^{3}J=7.9 Hz). 7.68 (m, 1H). ^{13}C-NMR δ 11.3, 12.3, 20.6, 36.4, 38.1, 40.4, 43.2, 55.7, 60.4, 62.9, 79.4, 115.1, 123.6, 125.2, 126.5, 126.9, 128.6, 129.6, 132.8, 141.1, 143.3, 164.1, 193.9, 205.6. Exact mass (DCI, *iso*butane) *m/z* calcd for $C_{26}H_{31}N_2O_6S$: 499.1903. Found 499.1907.