

SUPPORTING INFORMATION

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**An Approach to Cyclohepta[b]indoles through an Allenamide
(4 + 3) Cycloaddition–Grignard Cyclization–Chugaev Elimination Sequence.**

authored by

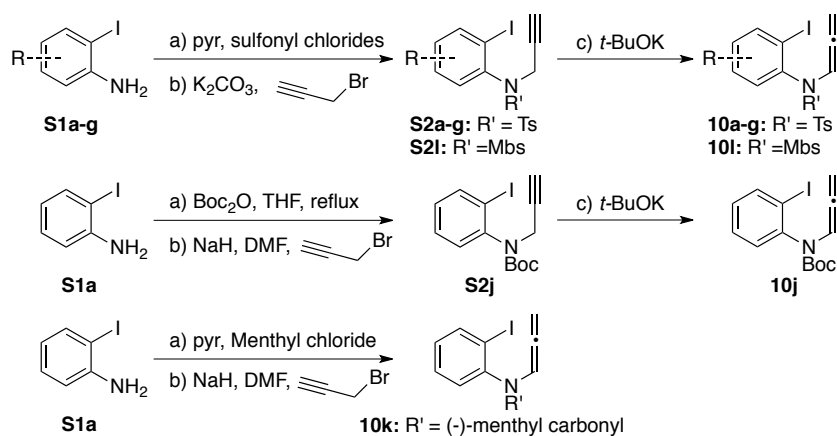
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GENERAL EXPERIMENTAL INFORMATION.

All reactions were performed in flame-dried glassware under nitrogen atmosphere. Solvents were distilled prior to use. Reagents were used as purchased from Aldrich, Acros, Alfa Aesar, or TCI unless otherwise noted. Chromatographic separations were performed using Silicycle 43-60 Å SiO₂. ¹H and ¹³C NMR spectra were obtained on Varian VI-400 and VI-500 spectrometers using CDCl₃ with TMS or residual solvent as standard unless otherwise noted. Melting points were determined using a Laboratory Devices MEL-TEMP and are uncorrected/calibrated. Infrared spectra were obtained on Bruker EQUINOX 55 FTIR. TLC analysis was performed using Aldrich 254 nm polyester-backed plates (60 Å, 250 μm) and visualized using UV, *p*-anisaldehyde and phosphomolybdic acid stains. Low-resolution mass spectra were obtained using Waters LCT® (ESI) and Agilent 1100 series LS/MSD (APCI). All spectral data obtained for new compounds are reported here.

PREPARATIONS OF ALLENAMIDES 10a–l.



General Procedure for Synthesis of Propargyl Amides S2a-g and S2l Using S2a as the Example.

To a solution of *o*-iodoaniline **S1a** (1.00 g, 4.56 mmol) in pyridine (4.60 mL) was added *p*-TsCl (0.95 g, 4.83 mmol, 1.05 equiv) at 0°C. The reaction was stirred at rt overnight (for **S1g**, the reaction was heated to 80°C for 24h) before being quenched with H₂O. The quenched mixture was extracted three times with Et₂O. The combined organic layers were first washed with 1 M HCl to remove excess pyridine, and then with sat aq NaHCO₃, H₂O, and sat aq NaCl, and dried over anhyd MgSO₄. The solution was filtered and

concentrated under reduced pressure to give the crude sulfonamide that was used in the next step without further purification.

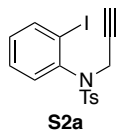
To a solution of the above crude sulfonamide (1.55 g, 4.20 mmol) in acetone (42 mL) were added K_2CO_3 (2.90 g, 21.0 mmol, 5.0 equiv) and propargyl bromide (0.92 mL, 10.4 mmol, 2.5 equiv). The reaction was heated to reflux for 2–4 h and the reaction progress was monitored using TLC analysis. After the reaction was complete, the mixture was filtered through CeliteTM. The filtrate was concentrated under reduced pressure and purified using silica gel flash column chromatography [eluent: 15% EtOAc/Hexane] to give the desired propargyl amide **S2a** (1.58 g, 85% yield over two steps).

Synthesis of Propargyl Amide S2j.

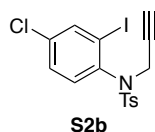
To a solution of *o*-iodoaniline **S1a** (2.00 g, 9.14 mmol) in THF (20 mL) was added Boc_2O (2.19 g, 10.05 mmol, 1.10 equiv). The reaction was refluxed for 24 h before being quenched with H_2O . The mixture was extracted three times with Et_2O . The combined organic layers were washed with sat aq NaCl and dried over anhyd $MgSO_4$. The solution was filtered and concentrated under reduced pressure to give the crude Boc-protected anilide that was used in the next step without further purification.

To a solution of the above crude Boc-protected anilide in DMF (45 mL) were added NaH (546 mg, 13.65 mmol, 1.50 equiv) and propargyl bromide (0.97 mL, 10.92 mmol, 1.20 equiv) at 0°C. The reaction was stirred at rt for 2 h and the reaction progress was monitored using TLC analysis. After the reaction was complete, the reaction was quenched with sat aq NH_4Cl . The quenched mixture was poured into H_2O and extracted three times with Et_2O . The combined organic layers were washed with equal volume of sat aq NaCl and dried over anhyd $MgSO_4$. After filtration and concentration under reduced pressure, the crude product was purified using silica gel flash column chromatography [eluent: 15% EtOAc/Hexane] to give the desired propargyl amide **S2j** (2.86 g, 88% yield over two steps).

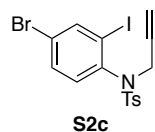
CHARACTERIZATIONS OF PROPARGYL AMIDES **S2a-g**, **S2j** and **S2l**.



S2a: white solid, mp 118-119°C; ^1H NMR (400 MHz, CDCl_3) δ 2.16 (t, $J = 2.4$ Hz, 1H), 2.44 (s, 3H), 4.12 (dd, $J = 18.4, 2.4$ Hz, 1H), 4.76 (dd, $J = 18.0, 2.4$ Hz, 1H), 7.06 (td, $J = 8.0, 1.6$ Hz, 1H), 7.14 (dd, $J = 8.0, 2.0$ Hz, 1H), 7.26-7.30 (m, 3H), 7.71 (d, $J = 8.4$ Hz, 2H), 7.91 (dd, $J = 8.0, 1.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.9, 40.9, 74.3, 77.9, 102.8, 128.6, 129.0, 129.7, 130.7, 131.4, 136.8, 140.5, 140.9, 144.2; IR (neat) cm^{-1} 3251m, 2924w, 2339m, 1596w, 1463m, 1340s, 1159s, 1095s, 1021m, 871s, 812m, 769m, 738m, 713s, 691s, 656s; mass spectrum (ESI): m/e (% relative intensity) 429.1 (100) ($\text{M}+\text{NH}_4$) $^+$.

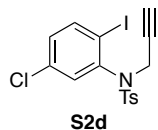


S2b: 2.44 g (69% yield over 2 steps from **S1b**), brown solid, mp 125-126°C; ^1H NMR (400 MHz, CDCl_3) δ 2.18 (t, $J = 2.4$ Hz, 1H), 2.44 (s, 3H), 4.09 (dd, $J = 18.0, 2.4$ Hz, 1H), 4.73 (dd, $J = 18.0, 2.4$ Hz, 1H), 7.05 (d, $J = 8.4$ Hz, 1H), 7.27 (dd, $J = 8.4, 2.4$ Hz, 1H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.89 (d, $J = 2.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.9, 40.8, 74.7, 77.6, 103.3, 128.5, 129.2, 129.8, 131.8, 135.7, 136.5, 139.6, 139.8, 144.5; IR (neat) cm^{-1} 3280w, 2923w, 1737w, 1598m, 1570w, 1463s, 1343s, 1158s, 1091s, 1041s, 883s, 812m, 774s, 723s, 667s, 656s; mass spectrum (ESI): m/e (% relative intensity) 463.0 (100) ($\text{M}+\text{NH}_4$) $^+$.

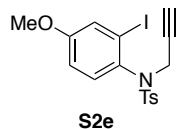


S2c: 2.75 g (88% yield over 2 steps from **S1c**), white solid, mp 136-137°C; ^1H NMR (400 MHz, CDCl_3) δ 2.18 (t, $J = 2.4$ Hz, 1H), 2.44 (s, 3H), 4.09 (dd, $J = 18.0, 2.4$ Hz, 1H), 4.73 (dd, $J = 18.4, 2.4$ Hz, 1H), 6.99 (d, $J = 8.4$ Hz, 1H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.41 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.70 (d, $J = 8.4$ Hz, 2H), 8.05 (d, $J = 2.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.9, 40.8, 74.6, 103.7, 123.8, 128.5, 129.8, 132.2, 136.5, 140.1, 142.6, 144.4; IR (neat) cm^{-1} 3280m, 2921w, 1738m, 1597m, 1461s, 1344s,

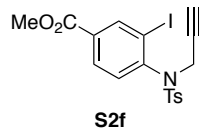
1158s, 1091s, 1041s, 1018m, 880m, 812m, 762s, 720s, 665s; mass spectrum (ESI): *m/e* (% relative intensity) 507.0 (100), 509.0 (98) (M+NH₄)⁺.



S2d: 3.84 g (86% yield over 2 steps from **S1d**), white solid, mp 85-86°C; ¹H NMR (400 MHz, CDCl₃) δ 2.20 (t, *J* = 2.4 Hz, 1H), 2.46 (s, 3H), 4.11 (m, 1H), 4.72 (dd, *J* = 18.0, 2.4 Hz, 1H), 7.08 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.10 (d, *J* = 2.4 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.9, 40.8, 74.8, 77.4, 100.3, 128.5, 129.8, 130.9, 131.6, 134.7, 136.4, 141.0, 142.1, 144.6; IR (neat) cm⁻¹ 3249m, 2970w, 2115w, 1740s, 1597m, 1459m, 1384m, 1342s, 1237m, 1157s, 1092s, 1038m, 1011m, 887s, 818s, 774s, 718s, 683s, 656s; mass spectrum (ESI): *m/e* (% relative intensity) 463.0 (100) (M+NH₄)⁺.

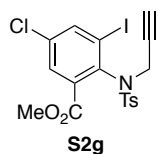


S2e: 1.85 g (65% yield over 2 steps from **S1e**), orange solid, mp 99-100°C; ¹H NMR (400 MHz, CDCl₃) δ 2.16 (t, *J* = 2.4 Hz, 1H), 2.44 (s, 3H), 3.78 (s, 3H), 4.08 (dd, *J* = 18.4, 2.8 Hz, 1H), 4.75 (dd, *J* = 18.0, 2.4 Hz, 1H), 6.79 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 2.8 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 21.9, 41.1, 55.9, 74.2, 78.1, 103.3, 114.6, 125.3, 128.5, 129.7, 131.4, 133.5, 136.9, 144.1, 160.1; IR (neat) cm⁻¹ 3261m, 2968m, 1738m, 1590m, 1482m, 1345s, 1287m, 1214s, 1160s, 1091s, 1026s, 869s, 830m, 814s, 739m, 705m, 688s, 654s; mass spectrum (ESI): *m/e* (% relative intensity) 459.1 (100) (M+NH₄)⁺.

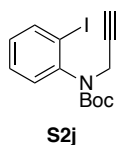


S2f: 2.84 g (84% yield over 2 steps from **S1f**), yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 2.18 (t, *J* = 2.4 Hz, 1H), 2.45 (s, 3H), 3.92 (s, 3H), 4.15 (d, *J* = 18.4 Hz, 1H), 4.75 (d, *J* = 18.4 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.95 (dd, *J* = 8.0, 2.8 Hz, 1H), 8.56 (d, *J* = 2.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 21.9, 40.7, 52.8, 74.7, 77.5, 102.5, 128.5, 129.8, 130.1, 131.2, 132.0, 136.4, 141.5, 144.5, 144.9, 165.1; IR (neat) cm⁻¹ 3277w, 2952w, 1723s, 1593m, 1435m,

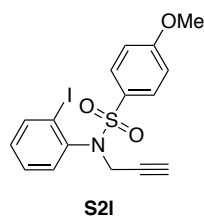
1354s, 1282s, 1248s, 1160s, 1114s, 1091s, 1045m, 866m, 814m, 745s, 716s, 659s; mass spectrum (ESI): m/e (% relative intensity) 487.1 (100) (M+NH₄)⁺.



S2g: 1.62 g (32% yield over 2 steps from **S1g**, inseparable with the bis-Ts protected **S1g**), yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 2.22 (t, *J* = 2.4 Hz, 1H), 2.41 (s, 3H), 3.72 (s, 3H), 4.54 (dd, *J* = 16.8, 2.4 Hz, 1H), 4.74 (dd, *J* = 16.8, 2.4 Hz, 1H), 7.26 (d, *J* = 7.2 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 2.4 Hz, 1H), 7.99 (d, *J* = 2.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.8, 42.2, 53.0, 75.2, 77.6, 106.0, 128.0, 129.9, 130.6, 131.4, 135.5, 138.2, 139.5, 142.9, 145.5, 165.0; IR (neat) cm⁻¹ 3301w, 2952w, 1730s, 1514m, 1434s, 1354s, 1274s, 1161s, 1092s, 1065s, 973m, 891m, 751s, 721s, 707s, 657s; mass spectrum (ESI): m/e (% relative intensity) 521.1 (100) (M+NH₄)⁺.



S2j: 2.92 g (90% yield over 2 steps from **S1a**), yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 1.36 (s, 3H), 2.17 (s, 1H), 3.90 (dd, *J* = 17.6, 2.4 Hz, 1H), 4.79 (dd, *J* = 17.6, 2.4 Hz, 1H), 7.02 (m, 1H), 7.37 (m, 2H), 7.87 (d, *J* = 7.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 28.4, 38.4, 72.7, 79.5, 81.2, 100.3, 129.1, 129.4, 130.3, 139.5, 143.6, 153.7; IR (neat) cm⁻¹ 3297w, 2978m, 1701s, 1580w, 1471s, 1421m, 1378s, 1366s, 1301s, 1251s, 1228s, 1151s, 1063m, 1013s, 945m, 857m, 757s, 724s, 623s; mass spectrum (ESI): m/e (% relative intensity) 375.1 (100) (M+NH₄)⁺.



S2i: 3.52 g (82% yield over 2 steps from **S1a**), yellow solid, mp 100-101°C; ¹H NMR (400 MHz, CDCl₃) δ 2.17 (t, *J* = 2.4 Hz, 1H), 3.89 (s, 3H), 4.10 (dd, *J* = 18.4, 2.8 Hz, 1H), 4.76 (dd, *J* = 18.4, 2.8 Hz, 1H), 6.96 (d, *J* = 9.2 Hz, 2H), 7.06 (td, *J* = 7.6, 1.6 Hz, 1H), 7.18 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.29 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.77 (d, *J* = 9.2 Hz, 2H), 7.91 (dd, *J* = 8.0, 1.6 Hz, 1H); ¹³C NMR (100 MHz,

CDCl₃) δ 40.8, 55.9, 74.2, 78.0, 102.8, 114.2, 129.0, 130.7, 131.4, 140.5, 141.0, 163.5; IR (neat) cm⁻¹ 3252m, 2970m, 1738s, 1593m, 1470m, 1441m, 1366s, 1346s, 1261s, 1230s, 1156s, 1095s, 1021s, 861s, 837s, 804s, 703s, 665s, 610s; mass spectrum (ESI): m/e (% relative intensity) 445.1 (100) (M+NH₄)⁺.

General Procedure for Synthesis of Allenamides 10a-j and 10l Using 10a as an Example.

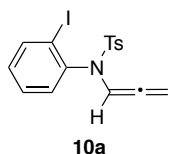
To a solution of **S2a** (1.00 g, 2.43 mmol) in THF (13 mL) was added *t*-BuOK (1.0 M solution in THF, 0.72 mL, 0.72 mmol, 0.30 equiv) at 0°C. The reaction was stirred at rt for 1 h before being concentrated under reduced pressure. Subsequently, the residue was first suspended in Et₂O and then filtered through Celite™. The filtrate was concentrated under reduced pressure and the crude residue was purified using silica gel flash column chromatography [eluent: 15% EtOAc/Hexane] to give the desired allenamide **10a** (0.80 mg, 80% yield).

Synthesis of Allenamide 10k.

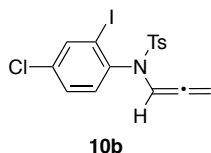
To a solution of *o*-iodoaniline **S1a** (1.00 g, 4.56 mmol) in CH₂Cl₂ (22 mL) was added pyridine (1.10 mL, 13.70 mmol, 3.00 equiv) and (-)-menthyl carbonyl chloride (1.40 mL, 6.84 mmol, 1.50 equiv). The reaction was stirred at rt overnight before being quenched by H₂O. The quenched mixture was extracted three times with Et₂O. The combined organic layers were washed with 1 M HCl, sat aq NaHCO₃, H₂O, and sat aq NaCl, and dried over anhyd MgSO₄. The solution was filtered and concentrated under reduced pressure to give the crude carbamate that was used in the next step without further purification.

To a solution of the above crude carbamate in DMF (25 mL) were added NaH (273 mg, 6.84 mmol, 1.50 equiv) at 0°C and propargyl bromide (0.49 mL, 5.47 mmol, 1.20 equiv). The reaction was stirred at rt for 2 h and the reaction progress was monitored using TLC analysis. After the reaction was complete, the reaction was quenched with sat aq NH₄Cl. The quenched mixture was poured into H₂O and extracted three times with Et₂O. The combined organic layers were washed with sat aq NaCl and dried over anhyd MgSO₄. After filtration and concentration under reduced pressure, the crude product was purified using silica gel column chromatography [gradient eluent: 10% to 15% EtOAc/Hexane] to give the allenamide **10k** directly (0.64 g, 32% yield over two steps).

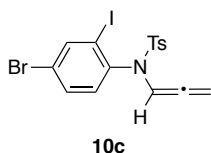
CHARACTERIZATIONS OF ALLENAMIDES 10a-l.



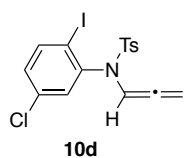
10a: 1.26g (80% yield); yellow solid, mp 78-79°C; ^1H NMR (400 MHz, CDCl_3) δ 2.45 (s, 3H), 5.00 (dd, $J = 18.0, 6.0$ Hz, 2H), 6.76 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.02 (td, $J = 8.0, 1.6$ Hz, 1H), 7.09 (t, $J = 6.4$ Hz, 1H), 7.22 (td, $J = 8.0, 1.6$ Hz, 1H), 7.32 (d, $J = 8.0$ Hz, 1H), 7.68 (dd, $J = 6.4, 1.6$ Hz, 2H), 7.89 (dd, $J = 8.0, 1.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.9, 87.9, 102.2, 128.2, 128.8, 130.0, 130.4, 130.5, 136.3, 140.2, 140.5, 144.4, 201.5; IR (neat) cm^{-1} 3043m, 2360m, 1434s, 1353s, 1159s, 1018s, 714s, 661s; mass spectrum (ESI): m/e (% relative intensity) 412.1 (100) ($\text{M}+\text{NH}_4$) $^+$.



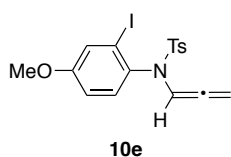
10b: 0.39 g (66% yield); white solid; mp 150-151°C; ^1H NMR (400 MHz, CDCl_3) δ 2.46 (s, 3H), 5.04 (dd, $J = 19.6, 6.4$ Hz, 2H), 6.80 (d, $J = 8.4$ Hz, 1H), 7.07 (t, $J = 6.0$ Hz, 1H), 7.20 (dd, $J = 8.4, 2.4$ Hz, 1H), 7.33 (d, $J = 8.4$ Hz, 2H), 7.67 (dd, $J = 6.4, 2.0$ Hz, 2H), 7.88 (d, $J = 2.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.9, 88.3, 102.0, 102.5, 128.2, 129.1, 130.1, 130.9, 135.5, 136.0, 138.9, 140.0, 144.7, 201.3; IR (neat) cm^{-1} 2970m, 2361m, 1717m, 1354s, 1161s, 720s, 665s; mass spectrum (ESI): m/e (% relative intensity) 446.1 (100) ($\text{M}+\text{H}$) $^+$.



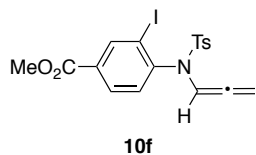
10c: 0.74 g (71% yield); brown solid; mp 154-155°C; ^1H NMR (400 MHz, CDCl_3) δ 2.46 (s, 3H), 5.04 (dd, $J = 19.2, 6.0$ Hz, 2H), 6.62 (d, $J = 8.4$ Hz, 1H), 7.06 (t, $J = 6.4$ Hz, 1H), 7.34 (m, 3H), 7.66 (dd, $J = 6.8, 1.6$ Hz, 2H), 8.03 (d, $J = 2.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.9, 88.4, 102.0, 103.0, 123.6, 128.2, 130.1, 131.4, 132.1, 136.0, 139.4, 142.7, 144.7, 201.3; IR (neat) cm^{-1} 2970m, 2360m, 1737s, 1355s, 1161s, 716, 665s; mass spectrum (ESI): m/e (% relative intensity) 492.0 (100), 490.0 (97%) ($\text{M}+\text{H}$) $^+$.



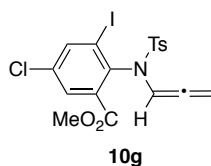
10d: 1.03 g (54% yield); white solid; mp 122-123°C; ¹H NMR (400 MHz, CDCl₃) δ 2.47 (s, 3H), 5.05 (dd, *J* = 9.6, 6.0 Hz, 2H), 6.74 (d, *J* = 2.4 Hz, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.4, 2.0 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.9, 88.3, 99.6, 101.8, 128.2, 130.1, 130.7, 130.7, 134.4, 135.9, 141.1, 141.4, 144.8, 201.4; IR (neat) cm⁻¹ 2359m, 1738m, 1357s, 1164s, 970s, 819s, 712s, 661s; mass spectrum (ESI): m/e (% relative intensity) 446.0 (100) (M+H)⁺.



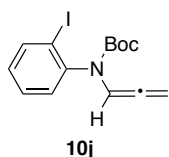
10e: 0.40 g (40% yield); white solid; mp 150-151°C; ¹H NMR (400 MHz, CDCl₃) δ 2.45 (s, 3H), 3.77 (s, 3H), 4.98 (dd, *J* = 10.0, 6.0 Hz, 1H), 5.06 (dd, *J* = 10.0, 6.0 Hz, 1H), 6.62 (d, *J* = 8.8 Hz, 1H), 6.73 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.09 (t, *J* = 6.0 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 2.4 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 21.9, 55.9, 88.0, 102.5, 102.6, 114.6, 125.2, 128.1, 129.9, 130.5, 132.8, 136.3, 144.3, 159.9, 201.5; IR (neat) cm⁻¹ 2925m, 2360m, 1737m, 1485s, 1355s, 1227s, 1162s, 837s, 667s; mass spectrum (ESI): m/e (% relative intensity) 442.1 (100) (M+H)⁺.



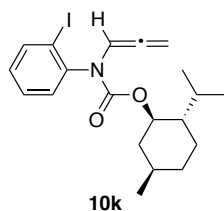
10f: 0.67 g (48% yield); yellow solid; mp 104-105°C; ¹H NMR (400 MHz, CDCl₃) δ 2.46 (s, 3H), 3.91 (s, 3H), 5.01 (s, 2H), 6.85 (d, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 6.4 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.89 (dd, *J* = 8.0, 2.0 Hz, 1H), 8.54 (d, *J* = 2.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.9, 52.8, 88.3, 101.8, 128.2, 130.0, 130.1, 130.3, 131.9, 136.0, 141.6, 144.3, 144.8, 165.1, 201.4; IR (neat) cm⁻¹ 3464w, 3360w, 3944m, 2361m, 1718s, 1280s, 1163s, 663s; mass spectrum (ESI): m/e (% relative intensity) 470.1 (100) (M+NH₄)⁺.



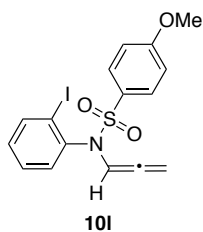
10g: 0.76 g (47% yield); orange oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.42 (s, 3H), 3.76 (s, 3H), 5.09 (dd, $J = 9.6, 6.0$ Hz, 1H), 5.18 (dd, $J = 9.6, 6.0$ Hz, 1H), 7.11 (t, $J = 6.0$ Hz, 1H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.61 (dd, $J = 6.4, 1.6$ Hz, 2H), 7.86 (d, $J = 2.8$ Hz, 1H), 7.93 (d, $J = 2.8$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 21.8, 53.0, 88.4, 101.8, 103.2, 127.9, 129.5, 130.1, 130.6, 131.6, 135.5, 135.6, 137.5, 138.0, 143.1, 144.4, 164.6, 201.4; IR (neat) cm^{-1} 3462w, 3002w, 2360m, 1709s, 1433s, 1360s, 1275s, 1221s, 1186s, 1164s, 968s, 719s, 659s; mass spectrum (ESI): m/e (% relative intensity) 504.0 (100) ($\text{M}+\text{H}$) $^+$.



10j: 2.3 g (79% yield); yellow solid; mp 68-69°C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.38-1.59 (m, 10H), 5.00 (m, 2H), 7.00 (td, $J = 8.0, 1.6$ Hz, 1H), 7.09 (t, $J = 7.6$ Hz, 1H), 7.18-7.36 (m, 3H), 7.85 (d, $J = 7.2$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 28.3, 81.7, 87.1, 99.8, 101.3, 124.9, 129.0, 129.3, 129.8, 139.1, 139.5, 142.1, 151.6, 201.9; IR (neat) cm^{-1} 3394w, 2977m, 2359w, 1734s, 1515s, 1365s, 1319s, 1154s, 1016s, 857s, 758s; mass spectrum (ESI): m/e (% relative intensity) 375.1 (100) ($\text{M}+\text{NH}_4$) $^+$.

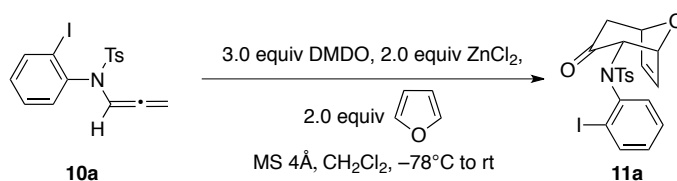


10k: 0.64 g (32% yield over two steps from **S1a**); colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 0.73-1.11 (m, 12H), 1.43-1.69 (m, 4H), 1.92-2.18 (m, 2H), 4.59 (m, 1H), 4.95-5.08 (m, 2H), 7.02 (t, $J = 7.6$ Hz, 1H), 7.18 (d, $J = 7.6$ Hz, 1H), 7.33-7.38 (m, 2H), 7.86 (d, $J = 7.2$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.9, 21.0, 22.2, 23.9, 26.6, 31.6, 34.4, 41.3, 47.0, 87.2, 100.0, 101.6, 129.0, 129.2, 129.6, 129.8, 139.6, 141.8, 152.5, 201.8; IR (neat) cm^{-1} 2955m, 1702s, 1310m, 1017s, 755s, 732s; mass spectrum (ESI): m/e (% relative intensity) 440.2 (100) ($\text{M}+\text{H}$) $^+$.

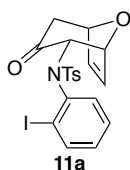


10i: 1.17 g (78% yield); yellow solid, mp 86-87 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.89 (s, 3H), 4.97 (dd, *J* = 9.6, 6.0 Hz, 1H), 5.04 (dd, *J* = 9.6, 6.0 Hz, 1H), 6.81 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 7.02 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.07 (t, *J* = 6.0 Hz, 1H), 7.23 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.89 (dd, *J* = 8.0, 1.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 55.7, 87.6, 101.9, 114.2, 128.5, 130.1, 130.2, 130.3, 130.7, 140.0, 140.3, 163.4, 201.3; IR (thin film) cm⁻¹ 3055w, 2841w, 1594m, 1577w, 1496m, 1464m, 1439w, 1358s; mass spectrum (ESI): *m/e* (% relative intensity) 428.1 (100) (M+H)⁺.

GENERAL PROCEDURE FOR (4 + 3) CYCLOADDITION USING ALLENAMIDE 10A.

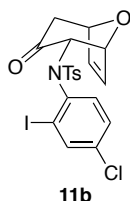


To a solution of allenamide **10a** (123 mg, 0.30 mmol) in CH₂Cl₂ (5 mL) containing anhyd 4Å MS were added ZnCl₂ (1.0 *M* solution in CH₂Cl₂, 0.60 mL, 0.60 mmol, 2.0 equiv) and furan (0.07 mL, 0.90 mmol, 3.0 equiv) at -78 °C. After which, a dry ice chilled solution of DMDO (0.08 *M* solution in acetone, 12 mL, 3.0 equiv) was added via syringe pump over 1.5 h. The reaction mixture was allowed to warm to rt slowly over 3–4 h before being filtered through CeliteTM. The filtrate was concentrated under reduced pressure and purified by silica gel flash column chromatography [eluent: 15% EtOAc/Hexane] to afford the desired cycloadduct **11a** (108 mg, 70% yield).

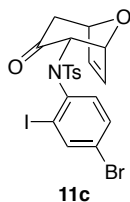


11a: white oil; ¹H NMR (400 MHz, CDCl₃) δ 2.27 (d, *J*_{ab} = 15.6 Hz, 1H), 2.43 (s, 3H), 2.80 (dd, *J*_{ab} = 15.6 Hz, *J* = 4.8 Hz, 1H), 4.77 (dd, *J* = 6.4, 1.6 Hz, 1H), 4.90 (d, *J* = 5.2 Hz, 1H), 5.44 (d, *J* = 4.4 Hz,

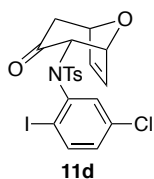
1H), 5.76 (dd, $J = 4.4, 2.0$ Hz, 1H), 5.94 (dd, $J = 6.0, 1.6$ Hz, 1H), 7.04-7.11 (m, 2H), 7.20-7.30 (m, 3H), 7.99 (dd, $J = 7.6, 1.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.9, 46.0, 74.2, 78.1, 80.7, 106.5, 128.7, 129.3, 129.8, 130.9, 131.8, 134.3, 134.9, 137.5, 140.7, 141.0, 143.8, 201.3; IR (neat) cm^{-1} 2926w, 2359w, 1710s, 1491m, 1357s, 1221s, 1162s, 1099s, 701s, 664s; mass spectrum (ESI): m/e (% relative intensity) 513.1 (100) ($\text{M}+\text{NH}_4$) $^+$.



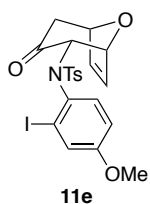
11b: 165 mg (73% yield); white solid; mp 190-191°C; ^1H NMR (400 MHz, CDCl_3) δ 2.28 (d, $J_{\text{ab}} = 16.0$ Hz, 1H), 2.43 (s, 3H), 2.80 (d, $J_{\text{ab}} = 16.0$ Hz, $J = 4.8$ Hz, 1H), 4.92 (m, 2H), 5.43 (d, $J = 4.4$, 1H), 5.73 (dd, $J = 4.4, 2.0$ Hz, 1H), 5.99 (dd, $J = 6.0, 1.6$ Hz, 1H), 7.21 (d, $J = 2.4$ Hz, 1H), 7.22 (s, 1H), 7.25 (d, $J = 8.0$ Hz, 2H), 7.50 (d, $J = 8.4$ Hz, 2H), 7.98 (d, $J = 2.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.9, 46.0, 74.2, 78.1, 80.6, 107.0, 128.7, 129.4, 131.7, 134.7, 135.2, 136.1, 137.1, 139.5, 140.3, 144.1, 202.2; IR (neat) cm^{-1} 2360s, 2341s, 1746s, 1601m, 1419w, 1360w, 1217m; mass spectrum (ESI): m/e (% relative intensity) 547.1 (100) ($\text{M}+\text{NH}_4$) $^+$.



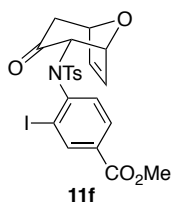
11c: 141 mg (50% yield); yellow solid; mp 201-202°C; ^1H NMR (400 MHz, CDCl_3) δ 2.27 (d, $J_{\text{ab}} = 15.6$ Hz, 1H), 2.44 (s, 3H), 2.80 (d, $J_{\text{ab}} = 16.0$ Hz, $J = 5.2$ Hz, 1H), 4.92 (m, 2H), 5.43 (d, $J = 4.8$, 1H), 5.73 (dd, $J = 4.8, 2.0$ Hz, 1H), 5.99 (dd, $J = 6.0, 2.0$ Hz, 1H), 7.17 (d, $J = 8.4$ Hz, 1H), 7.26 (d, $J = 7.6$ Hz, 2H), 7.35 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.49 (dd, $J = 6.8, 1.6$ Hz, 2H), 8.13 (d, $J = 2.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.9, 46.0, 74.2, 78.1, 80.6, 107.5, 124.3, 128.7, 129.4, 131.7, 132.5, 134.7, 135.6, 137.1, 140.0, 143.0, 144.1, 202.2; IR (neat) cm^{-1} 2970m, 2360m, 1739s, 1436m, 1365s, 1229s, 1217s; mass spectrum (ESI): m/e (% relative intensity) 593.1 (100), 591.1 (97%) ($\text{M}+\text{NH}_4$) $^+$.



11d: 94 mg (35% yield); white solid; mp 191-192°C ^1H NMR (400 MHz, CDCl_3) δ 2.30 (d, $J_{\text{ab}} = 16.0$ Hz, 1H), 2.45 (s, 3H), 2.79 (d, $J_{\text{ab}} = 15.6$ Hz, $J = 5.2$ Hz, 1H), 4.92 (m, 2H), 5.41 (d, $J = 4.4$, 1H), 5.74 (dd, $J = 4.4$, 1.6 Hz, 1H), 6.02 (dd, $J = 6.0$, 1.6 Hz, 1H), 7.09 (dd, $J = 8.4$, 2.4 Hz, 1H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 2.4$ Hz, 1H), 7.51 (dd, $J = 6.4$, 1.6 Hz, 2H), 7.90 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 21.9, 46.0, 74.2, 78.2, 80.6, 104.1, 128.5, 128.7, 129.5, 131.3, 131.5, 134.9, 135.0, 137.1, 141.4, 142.0, 144.3, 201.9; IR (neat) cm^{-1} 2922m, 2360m, 1738s, 1436m, 1365s, 1228s, 1217s; mass spectrum (ESI): m/e (% relative intensity) 547.1 (100) ($\text{M}+\text{NH}_4$) $^+$.

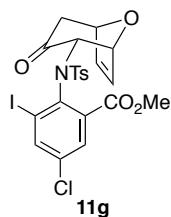


11e: 120 mg (46% yield); yellow solid; mp 186-187°C; ^1H NMR (400 MHz, CDCl_3) δ 2.27 (d, $J_{\text{ab}} = 15.6$ Hz, 1H), 2.42 (s, 3H), 2.79 (d, $J_{\text{ab}} = 15.6$ Hz, $J = 4.8$ Hz, 1H), 3.80 (s, 3H), 4.88 (dd, $J = 6.0$, 2.0 Hz, 1H), 4.91 (d, $J = 5.6$ Hz, 1H), 5.42 (d, $J = 4.4$, 1H), 5.75 (dd, $J = 4.4$, 1.6 Hz, 1H), 5.95 (dd, $J = 6.0$, 1.6 Hz, 1H), 6.72 (dd, $J = 8.8$, 3.2 Hz, 1H), 7.15 (d, $J = 8.8$ Hz, 1H), 7.24 (d, $J = 8.4$ Hz, 2H), 7.47 (d, $J = 2.8$ Hz, 1H), 7.49 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.9, 46.0, 55.9, 74.2, 78.1, 80.7, 106.7, 114.7, 125.8, 127.8, 128.7, 129.3, 129.8, 132.0, 133.0, 134.2, 134.9, 137.4, 143.8, 160.1, 202.4; IR (neat) cm^{-1} 3016w, 2970w, 2360s, 2341s, 1739s, 1723s, 1589s, 1445s, 1355s, 1445m, 1355s, 1288m, 1217s, 1092m, 660s; mass spectrum (ESI): m/e (% relative intensity) 543.1 (100) ($\text{M}+\text{NH}_4$) $^+$.

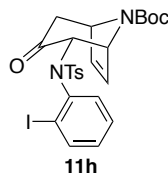


11f: 100 mg (42% yield); yellow solid; mp 175-176°C; ^1H NMR (400 MHz, CDCl_3) δ 2.28 (d, $J_{\text{ab}} = 15.6$ Hz, 1H), 2.44 (s, 3H), 2.80 (d, $J_{\text{ab}} = 15.6$ Hz, $J = 5.2$ Hz, 1H), 3.94 (s, 3H), 4.83 (dd, $J = 6.0$, 1.6 Hz, 1H), 4.91 (d, $J = 5.2$ Hz, 1H), 5.44 (d, $J = 4.8$, 1H), 5.75 (dd, $J = 4.4$, 1.6 Hz, 1H), 5.96 (dd, $J = 6.0$, 2.0

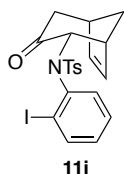
Hz, 1H), 7.25 (d, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 8.4$ Hz, 1H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.87 (dd, $J = 8.4$, 2.0 Hz, 1H), 8.63 (d, $J = 2.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.9, 46.0, 52.9, 74.2, 78.1, 80.5, 106.4, 128.6, 129.4, 130.2, 131.5, 132.1, 134.6, 134.8, 137.2, 141.8, 144.2, 144.9, 165.0, 202.1; IR (neat) cm^{-1} 2917w, 2360s, 2341s, 1740s, 1594m, 1435m, 1361m, 1217m, 1091m, 667s; mass spectrum (ESI): m/e (% relative intensity) 571.2 (100) ($\text{M}+\text{NH}_4$) $^+$.



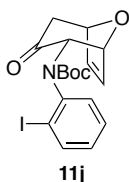
11g: 160 mg (58% yield); yellow solid; mp 135-136°C; ^1H NMR (400 MHz, CDCl_3) δ 2.40 (s, 3H), 2.44 (d, $J_{\text{ab}} = 15.2$ Hz, 1H) 2.99 (dd, $J_{\text{ab}} = 15.2$ Hz, $J = 4.8$ Hz, 1H), 4.02 (s, 3H), 4.99 (m, 2H), 5.52 (dd, $J = 6.0$, 1.2 Hz, 1H), 5.56 (d, $J = 4.0$ Hz, 1H), 6.23 (dd, $J = 6.0$, 1.6 Hz, 1H), 7.24 (d, $J = 8.0$, 2H), 7.63 (d, $J = 8.0$, 2H), 7.96 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.8, 45.4, 53.0, 74.4, 78.5, 80.7, 107.1, 103.2, 129.0, 129.2, 129.9, 131.8, 132.1, 136.1, 136.3, 137.5, 137.9, 138.5, 143.3, 144.1, 165.6, 200.1; IR (neat) cm^{-1} 2956m, 1732s, 1432m, 1337m, 1272s, 1157s, 1089s, 1036s, 966s, 905s, 719s, 666s; mass spectrum (ESI): m/e (% relative intensity) 605.1 (100) ($\text{M}+\text{NH}_4$) $^+$.



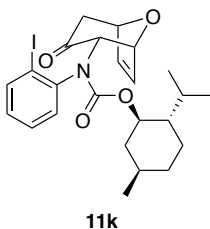
11h: 29 mg (50% yield); colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 1.62 (s, 9H), 2.28 (d, $J_{\text{ab}} = 15.6$ Hz, 1H), 2.43 (s, 3H), 2.82 (d, $J_{\text{ab}} = 15.6$ Hz, 1H), 4.63 (s, 2H), 5.30 (s, 1H), 5.89 (dd, $J = 6.0$, 2.0 Hz, 1H), 7.07 (m, 2H), 7.23 (d, $J = 8.4$ Hz, 2H), 7.47 (d, $J_{\text{ab}} = 7.6$ Hz, 2H), 7.66 (m, 1H), 8.01 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.9, 28.6, 44.6, 56.4, 61.0 73.8, 81.9, 106.4, 122.4, 127.7, 128.7, 129.3, 130.0, 131.0, 134.9, 137.3, 137.6, 141.1, 143.8, 150.5, 202.5; IR (neat) cm^{-1} 3453w, 2970w, 2359w, 1707s, 1363s, 1221s, 1163s, 1090s, 715s, 663s; mass spectrum (ESI): m/e (% relative intensity) 612.2 (100) ($\text{M}+\text{NH}_4$) $^+$.



11i: 100 mg (40% yield); white solid; mp didn't obtained (sample decomposed at 200°C before melting) ¹H NMR (400 MHz, CDCl₃) δ 2.00 (d, *J* = 11.2 Hz, 1H), 2.16-2.21 (m, 1H), 2.24 (dt, *J*_{ab} = 16.0 Hz, *J* = 2.8 Hz, 1H), 2.41 (s, 3H), 2.48 (d, *J*_{ab} = 16.0 Hz, *J* = 3.2 Hz, 1H), 2.78 (m, 1H), 3.75 (m, 1H), 4.41 (dd, *J* = 5.6, 2.8 Hz, 1H), 5.30 (d, *J* = 4.4, 1H), 5.68 (dd, *J* = 5.6, 2.8 Hz, 1H), 7.04 (td, *J* = 7.6, 1.6 Hz, 1H), 7.17-7.25 (m, 3H), 7.99 (dd, *J* = 7.6, 1.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 21.9, 39.3, 44.9, 45.1, 45.4, 75.4, 106.0, 128.8, 129.0, 129.1, 130.7, 133.4, 135.0, 136.6, 137.8, 141.0, 141.1, 143.4, 205.6; IR (neat) cm⁻¹ 2970m, 2360m, 1738s, 1435m, 1365s, 1229s, 1217s; mass spectrum (ESI): *m/e* (% relative intensity) 511.1 (100) (M+NH₄)⁺.

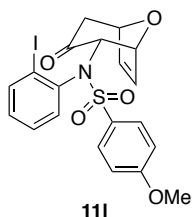


11j: 154 mg (62% yield); colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 1.36 (s, 9H), 2.40 (d, *J*_{ab} = 15.6 Hz, 1H), 2.90 (d, *J*_{ab} = 15.6 Hz, *J* = 5.2 Hz, 1H), 4.61 (dd, *J* = 6.0, 1.6 Hz, 1H), 4.94 (d, *J* = 5.6 Hz, 1H), 5.35 (dd, *J* = 4.4, 1.6 Hz, 1H), 5.46 (d, *J* = 4.4 Hz, 1H), 5.99 (dd, *J* = 6.0, 1.6 Hz, 1H), 7.01 (td, *J* = 7.6, 1.6 Hz, 1H), 7.26-7.35 (m, 2H), 7.89 (dd, *J* = 8.0, 1.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 15.6, 28.3, 28.5, 45.6, 64.0, 71.4, 78.3, 79.9, 81.3, 103.4, 104.4, 129.2, 129.7, 132.2, 132.3, 133.8, 139.5, 142.7, 154.3, 202.5; IR (neat) cm⁻¹ 3416m, 2970w, 2359w, 1703s, 1366s, 1228s, 1165m; mass spectrum (ESI): *m/e* (% relative intensity) 442.2 (100) (M+H)⁺.



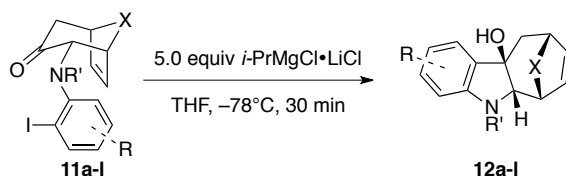
11k: 140 mg (55% yield, 4:1 diastereomeric mixture); colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.74-1.05 (m, 12H), 1.40-1.72 (m, 4H), 1.98-2.32 (m, 2H), 2.40 (d, *J*_{ab} = 15.6 Hz, 1H), 2.93 (d, *J*_{ab} = 15.6 Hz, *J* = 5.2 Hz, 1H), 4.54 (td, *J* = 10.8, 4.0 Hz, 1H), 4.57-4.61 (m, 1H), 4.95 (d, *J* = 5.2 Hz, 1H), 5.38 (dd, *J*

= 4.4, 1.6 Hz, 1H), 5.46 (m, 1H), 5.99 (dd, $J = 6.4, 1.6$ Hz, 1H), 7.04 (m, 1H), 7.26-7.35 (m, 2H), 7.90 (dd, $J = 8.0, 1.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 16.9, 20.7, 21.1, 24.0, 26.7, 31.6, 34.4, 41.3, 45.5, 47.3, 71.7, 76.7, 78.3, 79.8, 103.6, 129.1, 130.0, 132.3, 132.6, 133.9, 139.6, 142.3, 155.1, 202.2; IR (neat) cm^{-1} 3405m, 2955m, 2360w, 1704s, 1470m, 1364s, 1304s, 1219s, 1018m, 962m, 725s; mass spectrum (ESI): m/e (% relative intensity) 524.2 (100) ($\text{M}+\text{H}$) $^+$.



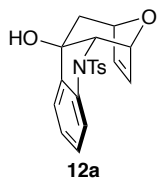
11I: 96 mg (38% yield); white solid, mp 176-177 °C; ^1H NMR (500 MHz, CDCl_3) δ 2.28 (d, $J_{\text{ab}} = 15.5$ Hz, 1H), 2.80 (dd, $J_{\text{ab}} = 15.5$ Hz, $J = 5.0$ Hz, 1H), 3.87 (s, 3H), 4.78 (dd, $J = 6.0, 1.5$ Hz, 1H), 4.91 (d, $J = 5.0$ Hz, 1H), 5.43 (d, $J = 4.0$ Hz, 1H), 5.76 (dd, $J = 4.5, 2.0$ Hz, 1H), 5.94 (dd, $J = 6.5, 2.0$ Hz, 1H), 6.91 (d, $J = 9.0$ Hz, 2H), 7.06 (dt, $J = 8.0, 1.5$ Hz, 1H), 7.22 (dt, $J = 8.0, 1.5$ Hz, 1H), 7.30 (dd, $J = 8.0, 2.0$ Hz, 1H), 7.55 (d, $J = 9.0$ Hz, 2H), 7.99 (dd, $J = 8.0, 1.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 45.8, 55.5, 74.0, 77.9, 80.4, 106.2, 113.5, 129.0, 130.6, 130.7, 131.5, 131.9, 134.1, 134.8, 140.5, 140.8, 163.1, 202.1; IR (neat) cm^{-1} 3367brs, 2922w, 1728m, 1595m, 1578w, 1497m, 1462m, 1440w, 1428w, 1412w; mass spectrum (ESI): m/e (% relative intensity) 529.1 (100) ($\text{M}+\text{NH}_4$) $^+$.

GENERAL PROCEDURE FOR INTRAMOLECULAR NUCLEOPHILIC CYCLIZATION.

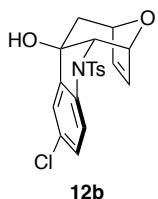


To a solution of **11a** (160 mg, 0.32 mmol) in THF (10 mL) was added $i\text{-PrMgCl}\cdot\text{LiCl}$ complex (1.3 M solution in THF, 1.9 mL, 2.5 mmol, 7.5 equiv) in one shot at -78 °C. The reaction was stirred at -78 °C for 30 min before being quenched by sat aq NH_4Cl . The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with equal volume of sat aq NaCl and dried over anhyd MgSO_4 . After filtration and concentration under reduced pressure, the crude product was purified

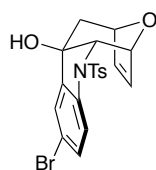
using silica gel flash column chromatography [eluent: 20% EtOAc/Hexane] to give the desired tetracycle **12a** (75 mg, 63% yield).



12a: white solid; mp 142-143°C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.23 (dd, $J_{ab} = 14.4$ Hz, $J = 4.8$ Hz, 1H), 2.31 (d, $J_{ab} = 14.0$ Hz, 1H), 2.32 (s, 3H), 4.13 (d, $J = 5.6$ Hz, 1H), 4.82 (d, $J = 4.8$ Hz, 1H), 5.05 (dd, $J = 5.6$, 2.0 Hz, 1H), 5.65 (dd, $J = 6.0$, 1.6 Hz, 1H), 5.79 (dd, $J = 6.0$, 2.0 Hz, 1H), 7.01 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.07 (td, $J = 7.6$, 0.8 Hz, 1H), 7.19 (d, $J = 8.0$ Hz, 2H), 7.31 (td, $J = 8.0$, 1.2 Hz, 1H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.68 (d, $J = 8.4$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 21.7, 34.4, 69.0, 75.5, 77.8, 79.4, 110.0, 117.1, 122.0, 125.4, 127.3, 130.0, 130.6, 133.5, 134.5, 138.7, 141.2, 144.7; IR (neat) cm^{-1} 2970m, 2360m, 1738s, 1436m, 1365s, 1229s, 1217s; mass spectrum (ESI): m/e (% relative intensity) 387.2 (100) ($\text{M}+\text{NH}_4$) $^+$.

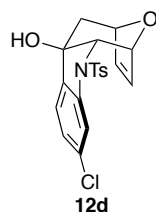


12b: 55 mg (60% yield); white solid; mp 178-179°C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.25 (m, 2H), 2.36 (s, 3H), 4.13 (d, $J = 5.6$ Hz, 1H), 4.85 (t, $J = 2.0$ Hz, 1H), 5.07 (dd, $J = 5.6$, 2.0 Hz, 1H), 5.73 (dd, $J = 6.0$, 1.6 Hz, 1H), 5.84 (dd, $J = 6.0$, 2.0 Hz, 1H), 6.90 (d, $J = 2.4$ Hz, 1H), 7.24 (d, $J = 8.4$ Hz, 2H), 7.29 (dd, $J = 8.4$, 2.0 Hz, 1H), 7.62-7.65 (m, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 21.8, 34.4, 69.2, 75.4, 77.7, 79.3, 118.3, 122.4, 127.3, 130.0, 130.1, 130.6, 130.6, 133.8, 134.2, 139.9, 140.5, 145.1; IR (neat) cm^{-1} 3513w, 2969m, 2360m, 2342m, 1739s, 1363s, 1229s, 1217s, 1110s, 1089m, 1056m, 1042m, 1012m, 665s; mass spectrum (ESI): m/e (% relative intensity) 421.2 (100) ($\text{M}+\text{NH}_4$) $^+$.



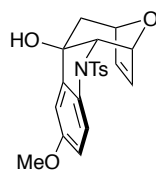
12c

12c: 66 mg (62% yield); yellow solid; mp 187-188°C; ^1H NMR (400 MHz, CDCl_3) δ 2.24 (m, 2H), 2.36 (s, 3H), 4.12 (d, $J = 5.6$ Hz, 1H), 4.85 (t, $J = 2.0$ Hz, 1H), 5.06 (dd, $J = 5.6, 1.6$ Hz, 1H), 5.74 (dd, $J = 6.0, 1.6$ Hz, 1H), 5.84 (dd, $J = 6.0, 2.0$ Hz, 1H), 7.13 (d, $J = 2.0$ Hz, 1H), 7.24 (d, $J = 8.0$ Hz, 2H), 7.43 (dd, $J = 8.4, 2.0$ Hz, 1H), 7.58 (d, $J = 8.4$ Hz, 1H), 7.63 (dd, $J = 6.4, 1.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.8, 34.5, 69.1, 75.3, 77.7, 79.3, 118.0, 118.6, 125.4, 127.3, 130.0, 130.2, 133.5, 133.9, 134.2, 140.4, 140.8, 145.1; IR (neat) cm^{-1} 3432m, 2969m, 2361m, 1739s, 1429m, 1347s, 1166s, 1109s, 1090s, 1043m, 1018s, 822s, 811s, 772m, 704m, 662s; mass spectrum (ESI): m/e (% relative intensity) 467.1 (100), 465.1 (97%) ($\text{M}+\text{NH}_4$) $^+$.



12d

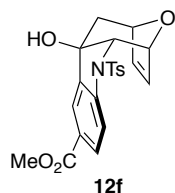
12d: 47 mg (60% yield); white solid; mp 189-190°C; ^1H NMR (400 MHz, CDCl_3) δ 2.25 (d, $J = 4.4$ Hz, 1H), 2.27 (d, $J = 1.6$ Hz, 1H), 2.36 (s, 3H), 4.13 (d, $J = 5.6$ Hz, 1H), 4.85 (d, $J = 4.4$ Hz, 1H), 5.07 (dd, $J = 5.6, 1.6$ Hz, 1H), 5.70 (dd, $J = 6.0, 2.0$ Hz, 1H), 5.85 (dd, $J = 6.0, 2.0$ Hz, 1H), 6.95 (d, $J = 8.4$ Hz, 1H), 7.05 (dd, $J = 8.4, 2.0$ Hz, 1H), 7.25 (d, $J = 8.8$ Hz, 2H), 7.66 (d, $J = 8.4$ Hz, 2H), 7.70 (d, $J = 1.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.8, 34.5, 69.3, 75.0, 77.7, 77.7, 79.3, 117.2, 122.9, 125.5, 127.3, 130.0, 130.2, 133.8, 134.3, 136.3, 137.2, 142.4, 145.1; IR (neat) cm^{-1} 2970m, 2360s, 2340s, 1739s, 1365s, 1228s, 1217s; mass spectrum (ESI): m/e (% relative intensity) 421.2 (100) ($\text{M}+\text{NH}_4$) $^+$.



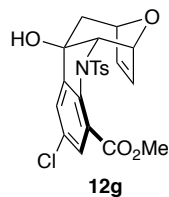
12e

12e: 35 mg (33% yield); yellow solid; mp 132-133°C; ^1H NMR (400 MHz, CDCl_3) δ 2.21 (m, 2H), 2.34 (s, 3H), 3.77 (s, 3H), 4.11 (d, $J = 5.6$ Hz, 1H), 4.84 (t, $J = 2.0$ Hz, 1H), 5.04 (dd, $J = 6.0, 2.0$ Hz, 1H), 5.69 (dd, $J = 6.0, 1.6$ Hz, 1H), 5.81 (dd, $J = 6.0, 2.0$ Hz, 1H), 6.54 (d, $J = 2.4$ Hz, 1H), 6.87 (dd, $J = 8.8,$

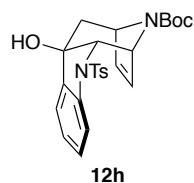
2.8 Hz, 1H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.60 (d, $J = 8.4$ Hz, 1H), 7.63 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.8, 34.1, 55.8, 69.3, 75.8, 77.7, 79.4, 107.4, 115.8, 118.7, 127.4, 130.0, 130.1, 133.3, 134.2, 134.4, 140.3, 144.7, 158.0; IR (neat) cm^{-1} 2970m, 2360s, 2341s, 1739s, 1540m, 1354s, 1229s, 1217s; mass spectrum (ESI): m/e (% relative intensity) 417.2 (100) ($\text{M}+\text{NH}_4$) $^+$.



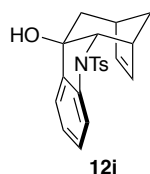
12f: 100 mg (86% yield); yellow solid; mp 173-174°C; ^1H NMR (400 MHz, CDCl_3) δ 2.30 (dd, $J_{\text{ab}} = 14.0$ Hz, $J = 4.8$ Hz, 1H), 2.34 (s, 3H), 2.43 (d, $J_{\text{ab}} = 14.0$ Hz, 1H), 3.88 (s, 3H), 4.20 (d, $J = 6.0$ Hz, 1H), 4.87 (d, $J = 4.8$ Hz, 1H), 5.11 (dd, $J = 5.6, 1.6$ Hz, 1H), 5.71 (dd, $J = 6.0, 2.0$ Hz, 1H), 5.83 (dd, $J = 6.0, 1.6$ Hz, 1H), 7.22 (d, $J = 8.0$ Hz, 1H), 7.66 (d, $J = 8.4$ Hz, 2H), 7.71 (m, 2H), 8.02 (dd, $J = 8.4, 1.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.8, 29.5, 34.7, 52.4, 69.4, 75.0, 77.8, 79.3, 116.0, 123.7, 127.0, 127.3, 129.8, 130.1, 132.6, 134.1, 134.5, 138.9, 145.1, 145.3, 166.4; IR (neat) cm^{-1} 2970m, 2360s, 2341s, 1739s, 1456m, 1364s, 1229s, 1217s; mass spectrum (ESI): m/e (% relative intensity) 445.2 (100) ($\text{M}+\text{NH}_4$) $^+$.



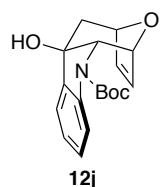
12g: 76 mg (70% yield); yellow solid; mp 180-181°C; ^1H NMR (400 MHz, CDCl_3) δ 2.20 (m, 2H), 2.40 (s, 3H), 3.97 (s, 3H), 4.10 (d, $J = 6.0$ Hz, 1H), 4.79 (m, 2H), 5.62 (dd, $J = 6.0, 1.6$ Hz, 1H), 5.80 (dd, $J = 6.0, 1.6$ Hz, 1H), 7.17 (d, $J = 2.0$ Hz, 1H), 7.30 (d, $J = 8.4$ Hz, 2H), 7.64 (d, $J = 8.0$ Hz, 2H), 7.66 (d, $J = 2.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.9, 34.0, 53.0, 69.0, 75.2, 77.6, 78.7, 125.3, 126.7, 128.3, 130.3, 131.0, 132.2, 133.3, 133.8, 137.9, 144.6, 145.6, 166.6; IR (neat) cm^{-1} 2925m, 2360s, 2341s, 1739s, 1364s, 1229s, 1217s, 668s; mass spectrum (ESI): m/e (% relative intensity) 479.2 (100) ($\text{M}+\text{NH}_4$) $^+$.



12h: 20 mg (32% yield); colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 1.26 (s, 9H), 2.34 (s, 3H), 2.32-2.41 (m, 2H), 4.12 (s, 1H), 4.64 (s, 1H), 4.90 (s, 1H), 5.60 (s, 1H), 5.74 (s, 1H), 7.02-7.10 (m, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.33 (td, $J = 7.6, 1.6$ Hz, 1H), 7.63 (d, $J = 7.6$ Hz, 2H), 7.71 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.8, 28.7, 29.9, 56.4, 67.5, 76.6, 77.4, 84.7, 101.5, 112.1, 117.1, 122.0, 125.4, 127.3, 130.0, 130.6, 133.8, 138.7, 157.7; IR (neat) cm^{-1} 3454m, 2922m, 2359s, 1707s, 1419s, 1362s, 1223s, 1166s, 1093m; mass spectrum (ESI): m/e (% relative intensity) 486.3 (100) ($\text{M}+\text{NH}_4$) $^+$.

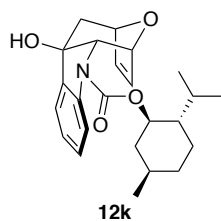


12i: 12 mg (32% yield); colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 1.69 (d, $J = 11.2$ Hz, 1H), 1.92 (dd, $J = 13.6, 3.2$ Hz, 1H), 1.96 (ddd, $J = 11.2, 5.6, 2.4$ Hz, 1H), 2.32 (s, 3H), 2.38 (dt, $J = 14.0, 2.4$ Hz, 1H), 2.70 (dt, $J = 8.0, 2.8$ Hz, 1H), 3.16 (td, $J = 4.8$ Hz, 1H), 4.05 (d, $J = 4.4$ Hz, 1H), 5.42 (dd, $J = 6.0, 2.8$ Hz, 1H), 5.52 (dd, $J = 6.0, 2.8$ Hz, 1H), 7.00 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.06 (td, $J = 7.6, 1.2$ Hz, 1H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.30 (td, $J = 8.0, 1.6$ Hz, 1H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.69 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.7, 34.7, 38.3, 40.0, 35.2, 73.0, 77.4, 116.9, 122.0, 125.0, 127.2, 129.9, 130.2, 131.5, 134.9, 135.6, 139.4, 141.4, 144.4; IR (neat) cm^{-1} 3419w, 2936m, 1707s, 1461m, 1351s, 1223m, 1162s, 1092m, 1035m, 966m, 764m, 715m, 663s; mass spectrum (ESI): m/e (% relative intensity) 385.2 (100) ($\text{M}+\text{NH}_4$) $^+$.

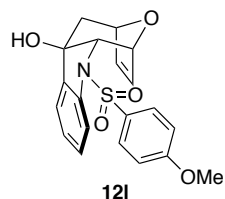


12j: 50 mg (78% yield); colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 1.38 (s, 9H), 2.38 (dd, $J_{\text{ab}} = 14.0$ Hz, $J = 4.8$ Hz, 1H), 2.47 (dd, $J_{\text{ab}} = 14.0$ Hz, $J = 1.2$ Hz, 1H), 4.32 (s, 1H), 4.88 (d, $J = 4.8$ Hz, 1H), 5.09 (s, 1H), 5.69 (ddd, $J = 14.0, 6.0, 1.6$ Hz, 2H), 6.98 (td, $J = 7.6, 0.8$ Hz, 1H), 7.11 (dd, $J = 7.6, 0.8$ Hz, 1H), 7.26 (t, $J = 7.6$ Hz, 1H), 7.82 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 28.7, 34.8, 67.1, 74.8, 77.0,

81.7, 115.7, 121.4, 123.3, 129.3, 130.2, 133.7, 137.2, 142.0, 152.0; IR (neat) cm^{-1} 3448m, 2970w, 2359w, 1704s, 1481m, 1391s, 1364s, 1223s, 1150s, 1110m; mass spectrum (ESI): m/e (% relative intensity) 333.3 (100) ($\text{M}+\text{NH}_4$)⁺.

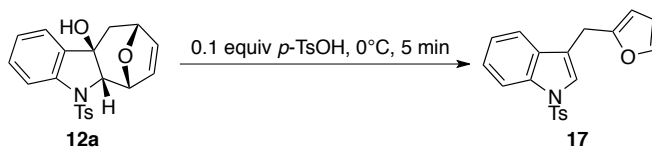


12k: 70 mg (77% yield, obtained as diastereomeric mixture); colorless oil; ¹H NMR (400 MHz, CDCl_3) δ 0.82-0.95 (m, 9H), 1.06-1.15 (m, 2H), 1.52 (m, 2H), 1.74 (m, 2H), 1.94-2.10 (m, 3H), 2.39(dd, $J_{\text{ab}} = 14.0$ Hz, $J = 4.8$ Hz, 1H), 2.48 (d, $J_{\text{ab}} = 13.6$ Hz, $J = 1.2$ Hz, 1H), 4.38 (s, 1H), 4.80 (td, $J = 11.2, 4.4$ Hz, 1H), 4.91 (d, $J = 4.4$ Hz, 1H), 5.09 (s, 1H), 5.67 (dd, $J = 6.0, 1.6$ Hz, 1H), 5.72 (dd, $J = 6.0, 1.6$ Hz, 1H), 7.01 (t, $J = 7.6$ Hz, 1H), 7.13 (d, $J = 7.6$ Hz, 1H), 7.29 (d, $J = 8.0$ Hz, 1H), 7.86 (s, 1H); ¹³C NMR (100 MHz, CDCl_3) δ 16.7, 21.2, 22.2, 23.7, 26.6, 31.7, 34.4, 34.8, 41.7, 47.6, 66.9, 76.1, 77.5, 78.0, 115.7, 115.9, 121.4, 123.5, 129.3, 130.3, 133.8, 137.3, 152.8; IR (neat) cm^{-1} 3415m, 2956m, 2360w, 1705s, 1481s, 1399s, 1363s, 1302s, 1285s, 1229s, 1055s, 1017s, 983s, 760s, 716s; mass spectrum (ESI): m/e (% relative intensity) 398.3 (100) ($\text{M}+\text{H}$)⁺.



12l: 59 mg (56% yield), white solid, mp 72-73 °C; ¹H NMR (400 MHz, CDCl_3) δ 2.26 (dd, $J_{\text{ab}} = 14.0$ Hz, $J = 0.8$ Hz, 1H), 2.33 (d, $J_{\text{ab}} = 12.8$ Hz, 1H), 3.79 (s, 3H), 4.15 (d, $J = 5.6$ Hz, 1H), 4.86 (d, $J = 4.8$ Hz, 1H), 5.08 (dd, $J = 5.6, 1.6$ Hz, 1H), 5.67 (dd, $J = 6.0, 6.2$ Hz, 1H), 5.82 (dd, $J = 6.0, 2.0$ Hz, 1H), 6.87 (d, $J = 8.8$ Hz, 2H), 7.04 (dt, $J = 8.0, 0.8$ Hz, 1H), 7.08 (t, $J = 7.2$ Hz, 1H), 7.67-7.70 (m, 3H); ¹³C NMR (100 MHz, CDCl_3) δ 34.2, 55.5, 68.8, 75.3, 77.6, 79.2, 114.2, 117.0, 121.7, 125.1, 128.9, 129.2, 129.8, 130.4, 133.2, 138.5, 141.1, 163.4; IR (neat) cm^{-1} 3365brs, 2921w, 1738w, 1595m, 1578w, 1497m, 1475w, 1461m, 1414w; IR (neat) cm^{-1} ; mass spectrum (ESI): m/e (% relative intensity) 403.2 (100) ($\text{M}+\text{NH}_4$)⁺.

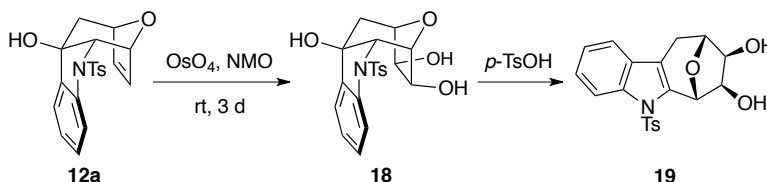
PROCEDURE FOR ACID INDUCED FRAGMENTATION



To a solution of **12a** (40.0 mg, 0.11 mmol) in CH₂Cl₂ (1 mL) was added TsOH (2.00 mg, 0.011 mmol) at 0 °C. The reaction was stirred at 0 °C for 5 min before being quenched by sat aq NaHCO₃. The aqueous layer was extracted three times with Et₂O. The combined organic layers were washed with sat aq NaCl and dried over anhyd MgSO₄. After filtration and concentration under reduced pressure, the crude product was purified using silica gel flash column chromatography [gradient eluent: 5% to 10% EtOAc/Hexane] to give indole **17** as a colorless oil (33.0 mg, 85% yield).

17: ¹H NMR (400 MHz, CDCl₃) δ 2.32 (s, 3H), 4.01 (s, 2H), 5.98 (dd, *J* = 3.2, 1.2 Hz, 1H), 6.28 (dd, *J* = 3.2, 1.6 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.20 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.30 (td, *J* = 6.8 Hz, 1H), 7.11 (td, *J* = 7.6, 0.8 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.30 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.32 (dd, *J* = 2.0, 0.8 Hz, 1H), 7.40 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.8, 24.5, 106.6, 110.6, 113.9, 119.5, 119.9, 123.4, 124.2, 125.0, 127.0, 130.1, 130.8, 135.5, 141.7, 145.0, 153.0; IR (neat) cm⁻¹ 3415m, 2359w, 1709s, 1362s, 1172s, 1119s, 1094s, 745s, 670s; mass spectrum (APCI): *m/e* (% relative intensity) 352.1 (100) (M+H)⁺.

PROCEDURE FOR DIHYDROXYLATION AND ACID INDUCED ELIMINATION



To a solution of **12a** (40.0 mg, 0.11 mmol) in acetone/ H₂O (2 mL, 3/1) was added OsO₄ (0.137 mL, 0.08 M in *t*-BuOH, 0.011 mmol) and NMO (23.0 mg, 0.22 mmol). The reaction was stirred for 3 d and then stirred with sat aq NaHSO₃ for an additional 1 h. The aqueous layer was extracted three times with

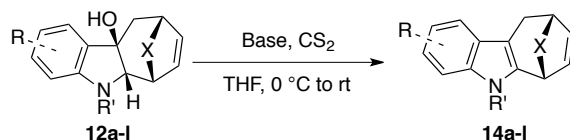
EtOAc. The combined organic layers were dried over anhyd MgSO_4 . After filtration and concentration under reduced pressure, the crude product was purified using silica gel flash column chromatography [eluent: 75% EtOAc/Hexane] to give diol **18** as a colorless oil (23.0 mg, 52% yield).

18: mp 167-168°C; ^1H NMR (400 MHz, CD_3OD) δ 2.17 (dd, $J_{\text{ab}} = 14.4$ Hz, $J = 5.6$ Hz, 1H), 2.31 (s, 3H), 2.59 (d, $J_{\text{ab}} = 14.0$ Hz, 1H), 3.45 (d, $J = 6.4$ Hz, 1H), 3.54 (d, $J = 6.4$ Hz, 1H), 4.17 (d, $J = 5.2$ Hz, 1H), 4.20 (d, $J = 6.4$ Hz, 1H), 4.42 (d, $J = 6.8$ Hz, 1H), 7.11 (td, $J = 7.6, 0.8$ Hz, 1H), 7.22 (d, $J = 8.4$ Hz, 2H), 7.30 (dd, $J = 7.6, 0.8$ Hz, 1H), 7.37 (td, $J = 8.0, 1.6$ Hz, 1H), 7.62 (d, $J = 8.4$ Hz, 1H), 7.80 (dd, $J = 6.0, 2.0$ Hz, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 20.3, 37.5, 69.2, 69.6, 73.2, 73.3, 82.6, 84.8, 115.4, 123.6, 124.5, 127.4, 129.4, 130.7, 134.8, 135.3, 142.1, 144.5; IR (neat) cm^{-1} 2960m, 2361m, 1738s, 1365s, 1216s; mass spectrum (ESI): m/e (% relative intensity) 421.2 (100) ($\text{M}+\text{NH}_4$) $^+$.

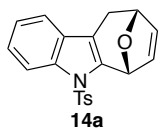
To a solution of **18** (20.0 mg, 0.050 mmol) in CH_2Cl_2 (1 mL) was added *p*-TsOH (1.00 mg, 0.0050 mmol) at 0°C. The reaction was stirred at 0°C for 1 h before being quenched with sat aq NaHCO_3 . The aqueous layer was extracted three times with Et_2O . The combined organic layers were washed with sat aq NaCl and dried over anhyd MgSO_4 . After filtration and concentration under reduced pressure, the crude product was purified using silica gel flash column chromatography [eluent: 15% EtOAc/Hexane] to give **19** as a colorless oil (5.80 mg, 30% yield).

19: mp 204-205°C; ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$) δ 2.36 (s, 3H), 2.60 (d, $J_{\text{ab}} = 16.4$ Hz, 1H), 2.82 (d, $J = 13.2$ Hz, 1H), 3.03 (dd, $J_{\text{ab}} = 16.4$ Hz, $J = 5.6$ Hz, 1H), 4.21 (d, $J = 6.0$ Hz, 1H), 4.35 (d, $J = 6.0$ Hz, 1H), 4.47 (d, $J = 5.2$ Hz, 1H), 5.60 (s, 1H), 7.25 (t, $J = 8.0$, 1H), 7.35 (t, $J = 8.0$ Hz, 1H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.83 (dd, $J = 6.8, 1.6$ Hz, 1H), 8.11 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$) δ 20.7, 26.7, 76.7, 77.7, 80.0, 82.6, 114.3, 114.9, 119.0, 123.8, 124.8, 126.7, 129.7, 130.4, 134.9, 135.7, 136.1, 145.9; IR (neat) cm^{-1} 2969m, 2360m, 1738s, 1365s, 1217s; mass spectrum (ESI): m/e (% relative intensity) 403.2 (100) ($\text{M}+\text{NH}_4$) $^+$.

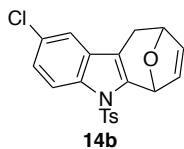
GENERAL PROCEDURE FOR CHUGEAU ELIMINATION USING **12a**.



To a solution of **12a** (45 mg, 0.12 mmol) in THF (1.5 mL) was added *t*-BuOK (1.0M solution in THF, 0. mL, 0.24 mmol, 2.00 equiv) solution at 0°C. After stirred at rt for 30 min, CS₂ (0.013 mL, 0.24 mmol, 2.00 equiv) was added. The reaction was stirred at rt for an additional 10–30min, and the reaction progress was monitored using TLC analysis. After the reaction was complete, the reaction was quenched using sat aq NH₄Cl. The aqueous phase was extracted three times with Et₂O, and the combined organic layers were washed with H₂O and sat aq NaCl, and dried over anhyd MgSO₄. After filtration and concentration under reduced pressure, the crude product was purified using silica gel flash column chromatography [eluent: 10% EtOAc/Hexane] to give the desired cyclohepta[*b*]indole **14a** (35 mg, 82% yield)

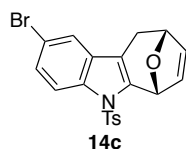


14a: white solid; mp 198-199°C; ¹H NMR (400 MHz, CDCl₃) δ 2.34 (s, 3H), 2.38 (d, *J*_{ab} = 16.8 Hz, 1H), 3.20 (ddd, *J*_{ab} = 16.8 Hz, *J* = 6.0, 0.8 Hz, 1H), 5.20 (dd, *J* = 6.0, 2.0 Hz, 1H), 6.00 (dd, *J* = 6.0, 2.0 Hz, 1H), 6.07 (s, 1H), 6.67 (dd, *J* = 6.0, 2.0 Hz, 1H), 7.18-7.32 (m, 5H), 7.72 (dd, *J* = 6.4, 1.6 Hz, 2H), 8.05 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.8, 24.8, 76.7, 78.2, 112.3, 114.4, 118.2, 123.7, 124.3, 126.7, 128.1, 130.2, 130.8, 135.4, 135.8, 137.5, 138.2, 145.2; IR (neat) cm⁻¹ 2961m, 2923m, 2852m, 2361m, 1592w, 1359s, 1305s, 1166s, 1083s, 1026s, 954s, 817s, 799s, 754s, 701s, 661s; mass spectrum (ESI): *m/e* (% relative intensity) 352.1 (100) (M+H)⁺.

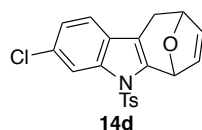


14b: 35 mg (91% yield); white solid; mp 181-182°C; ¹H NMR (400 MHz, CDCl₃) δ 2.33 (d, *J*_{ab} = 16.8 Hz, 1H), 2.35 (s, 3H), 3.15 (ddd, *J*_{ab} = 16.8 Hz, *J* = 6.0, 0.8 Hz, 1H), 5.19 (dd, *J* = 6.0, 2.0 Hz, 1H), 6.01

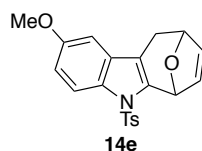
(dd, $J = 6.0, 2.0$ Hz, 1H), 6.04 (s, 1H), 6.65 (dd, $J = 6.0, 2.0$ Hz, 1H), 7.19 (d, $J = 2.0$ Hz, 1H), 7.21 (d, $J = 2.4$ Hz, 1H), 7.24 (d, $J = 8.0$ Hz, 2H), 7.27 (d, $J = 2.0$ Hz, 1H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.96 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.8, 24.6, 76.6, 78.2, 111.7, 115.4, 118.1, 124.4, 126.7, 128.3, 129.6, 130.3, 132.2, 133.7, 135.5, 138.0, 139.1, 145.5; IR (neat) cm^{-1} 2969m, 2360w, 1738s, 1436m, 1366s, 1216s; mass spectrum (ESI): m/e (% relative intensity) 403.2 (100) ($\text{M}+\text{NH}_4$) $^+$.



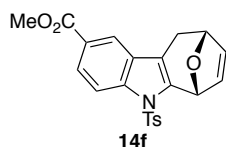
14c: 33 mg (86% yield); white solid; mp 145-146°C; ^1H NMR (400 MHz, CDCl_3) δ 2.33 (d, $J_{\text{ab}} = 16.0$ Hz, 1H), 2.35 (s, 3H), 3.15 (dd, $J_{\text{ab}} = 16.8$ Hz, $J = 6.0$ Hz, 1H), 5.19 (dd, $J = 6.0, 2.0$ Hz, 1H), 6.01 (dd, $J = 6.0, 2.0$ Hz, 1H), 6.04 (s, 1H), 6.65 (dd, $J = 6.0, 2.0$ Hz, 1H), 7.23 (d, $J = 8.4$ Hz, 2H), 7.34 (dd, $J = 9.2, 2.0$ Hz, 1H), 7.43 (d, $J = 2.0$ Hz, 1H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.91 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.8, 24.6, 76.6, 78.2, 111.6, 115.8, 117.3, 121.1, 126.7, 127.1, 128.3, 130.3, 132.6, 134.1, 135.4, 138.0, 139.0, 145.5; IR (neat) cm^{-1} 2969m, 2360m, 1738s, 1436m, 1365s, 1217s; mass spectrum (ESI): m/e (% relative intensity) 449.1 (100), 447.1 (97%) ($\text{M}+\text{NH}_4$) $^+$.



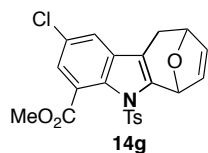
14d: 35 mg (98% yield); yellow solid; mp 185-186°C; ^1H NMR (400 MHz, CDCl_3) δ 2.35 (d, $J_{\text{ab}} = 16.8$ Hz, 1H), 2.36 (s, 3H), 3.17 (dd, $J_{\text{ab}} = 16.8$ Hz, $J = 6.0$ Hz, 1H), 5.19 (d, $J = 6.0$ Hz, 1H), 6.01 (d, $J = 6.0$ Hz, 1H), 6.02 (s, 1H), 6.65 (d, $J = 5.6$ Hz, 1H), 7.19 (dd, $J = 16.0, 8.4$ Hz, 1H), 7.25 (d, $J = 6.0$ Hz, 2H), 7.72 (d, $J = 8.4$ Hz, 2H), 8.07 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.8, 24.6, 76.6, 78.2, 111.7, 115.4, 118.1, 124.4, 126.7, 128.3, 129.6, 130.3, 132.2, 133.7, 135.5, 138.0, 139.1, 145.5; IR (neat) cm^{-1} 2922m, 2360w, 1738s, 1371s, 1170s; mass spectrum (ESI): m/e (% relative intensity) 403.2 (100) ($\text{M}+\text{NH}_4$) $^+$.



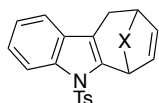
14e: 13 mg (91% yield); white solid; mp 184-185°C; ¹H NMR (400 MHz, CDCl₃) δ 2.33 (d, *J*_{ab} = 16.8 Hz, 1H), 2.33 (s, 3H), 3.16 (dd, *J*_{ab} = 16.8 Hz, *J* = 6.0 Hz, 1H), 3.80 (s, 3H), 5.19 (dd, *J* = 6.0, 1.6 Hz, 1H), 6.00 (dd, *J* = 5.6, 2.0 Hz, 1H), 6.04 (s, 1H), 6.66 (dd, *J* = 6.0, 1.6 Hz, 1H), 6.73 (d, *J* = 2.4 Hz, 1H), 6.85 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 9.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.8, 24.8, 55.9, 76.7, 78.2, 101.0, 112.5, 112.9, 115.3, 126.6, 128.1, 130.1, 131.9, 135.6, 138.1, 138.3, 145.1, 156.8; IR (neat) cm⁻¹ 2969m, 2361w, 1738s, 1435m, 1365s, 1217s; mass spectrum (ESI): *m/e* (% relative intensity) 399.2 (100) (M+NH₄)⁺.



14f: 25 mg (58% yield); white solid; mp 165-166°C; ¹H NMR (400 MHz, CDCl₃) δ 2.35 (s, 3H), 2.43 (d, *J*_{ab} = 16.8 Hz, 1H), 3.23 (dd, *J*_{ab} = 16.8 Hz, *J* = 6.0 Hz, 1H), 3.91 (s, 3H), 5.22 (dd, *J* = 6.0, 1.6 Hz, 1H), 6.03 (dd, *J* = 5.6, 2.0 Hz, 1H), 6.05 (s, 1H), 6.66 (dd, *J* = 6.0, 1.6 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.73 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.95 (dd, *J* = 8.8, 1.6 Hz, 1H), 8.04 (d, *J* = 1.6 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.8, 24.7, 52.3, 76.6, 78.2, 112.5, 114.0, 120.5, 125.5, 125.7, 126.7, 128.3, 130.4, 130.7, 135.5, 138.0, 145.6, 167.4; IR (neat) cm⁻¹ 2970m, 2360m, 1738s, 1365s, 1216s; mass spectrum (ESI): *m/e* (% relative intensity) 427.2 (100) (M+NH₄)⁺.

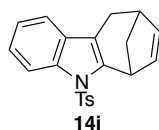


14g: 12 mg (42% yield); colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 2.28 (d, *J*_{ab} = 16.8 Hz, 1H), 2.36 (s, 3H), 3.05 (dd, *J*_{ab} = 16.8 Hz, *J* = 5.6 Hz, 1H), 3.86 (s, 3H), 5.15 (dd, *J* = 5.6, 1.6 Hz, 1H), 5.84 (s, 1H), 6.02 (dd, *J* = 6.0, 2.0 Hz, 1H), 6.64 (dd, *J* = 5.6, 1.6 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 2.0 Hz, 1H), 7.24 (d, *J* = 2.0 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 21.9, 24.5, 52.9, 77.9, 114.9, 120.6, 124.3, 125.4, 126.8, 128.4, 128.5, 129.9, 130.3, 131.7, 134.7, 135.1, 138.2, 142.5, 145.3, 167.9; IR (neat) cm⁻¹ 3455m, 2921w, 2360w, 1708s, 1433s, 1223s, 1176s; mass spectrum (ESI): *m/e* (% relative intensity) 461.2 (100) (M+NH₄)⁺.



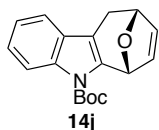
14h: X = NBoc

14h: 4 mg (28% yield from 14 mg **12h**); colorless oil; ^1H NMR (mixture of two rotamers, 400 MHz, CDCl_3) δ 1.42 (s, 4.5H), 1.44 (s, 4.5H), 2.32 (s, 1.5H), 2.35 (s, 1.5H), 2.39 (d, $J = 5.6$ Hz, 0.5H), 2.43 (d, $J = 7.6$ Hz, 0.5H), 3.25 (dd, $J = 16.8, 5.2$ Hz, 0.5H), 3.35 (dd, $J = 17.2, 5.2$ Hz, 0.5H), 4.86 (s, 0.5H), 4.99 (s, 0.5H), 5.94 (s, 1H), 6.04 (s, 0.5H), 6.15 (s, 0.5H), 6.47 (s, 0.5H), 6.64 (s, 0.5H), 7.14-7.31 (m, 5H), 7.76 (d, $J = 7.6$ Hz, 2H), 7.96 (d, $J = 8.0$ Hz, 1H), 8.05 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.8, 24.8, 28.6, 57.3, 80.7, 113.3, 114.5, 118.1, 118.3, 123.4, 123.6, 124.2, 124.4, 126.8, 127.8, 128.5, 129.1, 129.9, 130.1, 138.2, 138.5, 144.2, 152.0; IR (neat) cm^{-1} 3510m, 2004w, 2360m, 1707s, 1420m, 1361s, 1222s, 1092m, 1022m, 668m; mass spectrum (ESI): m/e (% relative intensity) 468.3 (100) ($\text{M}+\text{NH}_4$) $^+$.



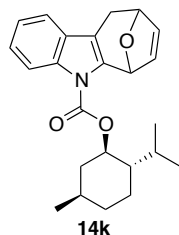
14i

14i: 16 mg (84% yield); yellow solid; mp 114-115°C; ^1H NMR (400 MHz, CDCl_3) δ 1.85 (d, $J = 10.0$ Hz, 1H), 2.25 (dt, $J = 4.8, 4.8$ Hz, 1H), 2.34 (s, 3H), 2.41 (d, $J_{\text{ab}} = 16.8$ Hz, 1H), 2.85 (dd, $J_{\text{ab}} = 16.8$ Hz, $J = 5.2$ Hz, 1H), 3.02 (m, 1H), 4.26 (dd, $J = 4.8, 2.8$ Hz, 1H), 5.76 (dd, $J = 5.2, 2.8$ Hz, 1H), 6.16 (dd, $J = 5.2, 2.8$ Hz, 1H), 7.16-7.28 (m, 5H), 7.66 (d, $J = 8.4$ Hz, 2H), 8.13 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.8, 24.9, 38.4, 38.7, 42.2, 113.5, 114.8, 117.7, 123.5, 123.7, 126.6, 130.0, 131.3, 131.8, 136.0, 136.5, 139.3, 140.6, 144.8; IR (neat) cm^{-1} 3015m, 2359m, 1738s, 1436m, 1365s, 1216s; mass spectrum (ESI): m/e (% relative intensity) 350.2 (100) ($\text{M}+\text{H}$) $^+$.

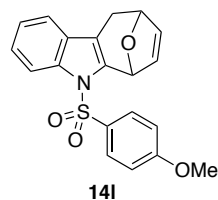


14j

14j: 21 mg (45% yield); white solid; mp 94-95°C; ^1H NMR (400 MHz, CDCl_3) δ 1.69 (s, 9H), 2.40 (d, $J_{\text{ab}} = 16.8$ Hz, 1H), 3.25 (ddd, $J_{\text{ab}} = 16.8$ Hz, $J = 6.0, 0.8$ Hz, 1H), 5.21 (dd, $J = 6.0, 1.6$ Hz, 1H), 6.01 (d, $J = 1.6$ Hz, 1H), 6.03 (d, $J = 2.0$ Hz, 1H), 6.60 (dd, $J = 6.0, 1.6$ Hz, 1H), 7.17-7.26 (m, 2H), 7.35 (d, $J = 7.6$ Hz, 1H), 8.10 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 24.7, 28.5, 77.4, 78.3, 84.3, 110.3, 115.7, 117.7, 123.0, 123.9, 128.1, 130.3, 135.1, 137.8, 150.2; IR (neat) cm^{-1} 2969m, 2360w, 1738s, 1449m, 1363s, 1216s, 1040m; mass spectrum (ESI): m/e (% relative intensity) 298.2 (100) ($\text{M}+\text{H}$) $^+$.



14k: 30 mg (52% yield, obtained as diastereomeric mixture); white solid; mp 90-91°C; ¹H NMR (400 MHz, CDCl₃) δ 0.84 (d, *J* = 7.2 Hz, 3H), 0.96 (m, 6H), 1.14-1.27 (m, 2H), 1.54-1.65 (m, 2H), 1.74-1.80 (m, 2H), 2.00-2.09 (m, 2H), 2.26 (m, 1H), 2.42 (d, *J*_{ab} = 16.8 Hz, 1H), 3.26 (dddd, *J*_{ab} = 16.4 Hz, *J* = 6.0, 3.2, 0.8 Hz, 1H), 5.00 (m, 1H), 5.22, (d, *J* = 6.4 Hz, 1H), 6.03 (m, 2H), 6.64 (dd, *J* = 16.0, 6.0 Hz, 1H), 7.19-7.25 (m, 2H), 7.36 (d, *J* = 6.4 Hz, 1H), 8.12 (d, *J* = 7.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 16.4, 21.2, 22.2, 23.5, 24.7, 26.5, 31.7, 34.3, 41.5, 47.7, 77.9, 78.2, 110.7, 115.8, 117.8, 123.2, 124.1, 128.1, 128.3, 130.4, 135.1, 137.7, 137.8, 151.3; IR (neat) cm⁻¹ 2952m, 2362w, 1732s, 1452s, 1370s, 1229s, 1210s, 979s, 687s; mass spectrum (ESI): *m/e* (% relative intensity) 380.3 (100) (M+H)⁺.



14l: 35 mg (80% yield), white solid, mp 60-61 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.38 (d, *J* = 9.2 Hz, 1H), 3.20 (ddd, *J* = 20.4, 6.0, 0.8 Hz, 1H), 3.79 (s, 3H), 5.20 (dd, *J* = 6.0, 2.0 Hz, 1H), 6.00 (dd, *J* = 6.0, 2.0 Hz, 1H), 6.07 (s, 1H), 6.67 (dd, *J* = 6.0, 2.0 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 7.18-7.28 (m, 2H), 7.31 (ddd, *J* = 8.0, 1.6, 0.8 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 2H), 8.05 (td, *J* = 8.4, 0.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 24.5, 55.8, 76.5, 78.0, 112.0, 114.1, 114.5, 118.0, 123.4, 124.0, 127.8, 128.7, 129.9, 130.6, 135.1, 137.2, 137.9, 163.7; IR (neat) cm⁻¹ 3398brs, 2292w, 1738w, 1594m, 1578w, 1497m, 1446m, 141w, 1367s; mass spectrum (ESI): *m/e* (% relative intensity) 385.2 (100) (M+NH₄)⁺.