

SUPPORTING INFORMATION

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**An Enamide-Benzyne [2 + 2] Cycloaddition:
Stereoselective Tandem [2 + 2]–
Pericyclic Ring-Opening–Intramolecular *N*-Tethered [4 + 2] Cycloadditions.**

authored by

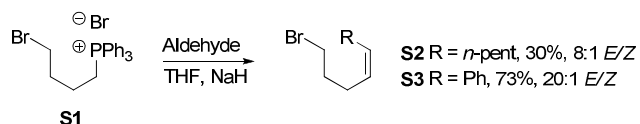
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GENERAL EXPERIMENTAL INFORMATION

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, anisaldehyde and I₂ stains. Low-resolution mass spectra were obtained using an Agilent 1100 series LS/MSD and are APCI. All spectral data obtained for new compounds are reported here.

SYNTHESIS OF *N*-ALKENYL TETHERED AMIDES



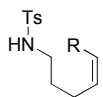
Wittig olefination of **S1** was demonstrated by the literature method.ⁱ



GENERAL PROCEDURE.

To an oven-dried round bottom flask with magnetic stir bar was added bromide (1.1 equiv), TsNH₂ (1.0 equiv), K₂CO₃ (2.0 equiv) and acetone (1.0 *M*). The round bottom flask was heated at 60 °C. Upon completion of the reaction (16 h), the solution was cooled to RT, filtered through a plug of CeliteTM and rinsed with EtOAc, and solvent was removed *in vacuo* to afford a crude product. Purification of the resulting crude residue via silica gel flash column chromatography (gradient eluent: EtOAc in hexane) afforded the desired alkylated product.

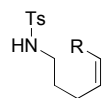
CHARACTERIZATIONS.



S7: R = *n*-pent

S7: R_f = 0.48 [25% EtOAc/hexanes]; colorless oil;

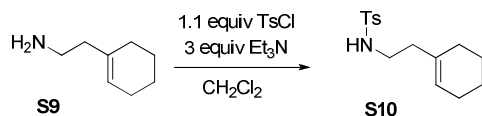
^1H NMR (500 MHz, CDCl_3) δ 0.83 (t, 3H, J = 7.0 Hz), 1.21-1.34 (m, 6H), 1.52 (p, 2H, J = 7.0 Hz), 1.91 (q, 2H, J = 7.0 Hz), 2.02 (q, 2H, J = 7.0 Hz), 2.43 (s, 3H), 2.96 (q, 2H, J = 7.0 Hz), 4.28 (t, 1H, J = 6.0 Hz), 5.24 (dddd, 1H, J = 7.5, 9.5, 11.0, 13.0 Hz), 5.37 (dddd, 1H, J = 7.5, 9.5, 11.0, 13.0 Hz), 7.30 (d, 2H, J = 7.5 Hz), 7.73 (d, 2H, J = 7.5 Hz).



S8: R = Ph

S8: R_f = 0.22 [25% EtOAc/hexanes]; colorless oil;

^1H NMR (500 MHz, CDCl_3) δ 1.60 (p, 2H, J = 7.0 Hz), 2.31 (dq, 2H, J = 1.5, 7.0 Hz), 2.42 (s, 3H), 2.96 (q, 2H, J = 7.0 Hz), 4.22 (bs, 1H), 5.54 (dq, 1H, J = 7.5, 11.5 Hz), 6.45 (d, 1H, J = 11.5 Hz), 7.21 (d, 2H, J = 7.5 Hz), 7.24-7.29 (m, 3H), 7.33 (t, 2H, J = 7.5 Hz), 7.69 (d, 2H, J = 8.0 Hz).



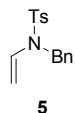
Tosyl protection of commercially available amine **S9** was accomplished, with characterizations in accord with literature precedent.ⁱⁱ

GENERAL PROCEDURE FOR ENAMIDE SYNTHESIS VIA CROSS COUPLING

Procedure A: To an oven-dried screw-cap vial fitted with magnetic stir bar was added amide (1.0 equiv), vinyl bromide (1.0 *M* soln in THF, 2.0 equiv), CuI (0.05 equiv), *N,N'*-dimethylethylenediamine (0.10 equiv), and K_2CO_3 (2.0 equiv). The vial was tightly sealed using Teflon tape and heated to 80 °C to stir overnight. Upon completion of the reaction, the mixture was filtered through a pad of CeliteTM, rinsing with EtOAc, and solvent was removed *in vacuo* to afford a crude product. Purification of the resulting crude residue via silica gel flash chromatography (gradient elution: EtOAc in *n*-hexanes) afforded the desired enamide.

Procedure B: Same as procedure A, except performed in a sealed tube at 115 °C overnight.

CHARACTERIZATIONS.



Enamide **5** (638.0 mg, 2.22 mmol) was isolated in 58% yield from N-Benzyl-p-toluenesulfonamide (1.00 g, 3.83 mmol) according to the general procedure A.

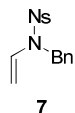
5: R_f = 0.56 [1:4 EtOAc/hexanes]; yellow solid; mp 99-100 °C;

^1H NMR (400 MHz, CDCl_3) δ 2.43 (s, 3H), 4.14 (dd, 1H, J = 1.2, 15.6 Hz), 4.26 (dd, 1H, J = 1.2, 9.2 Hz), 4.53 (s, 2H), 6.96 (dd, 1H, J = 9.2, 15.6 Hz), 7.21-7.33 (m, 7H), 7.69 (d, 2H, J = 8.4 Hz);

^{13}C NMR (125 MHz, CDCl_3) δ 21.8, 49.1, 94.9, 127.1, 127.2, 127.7, 128.8, 130.1, 132.4, 135.7, 136.4, 144.2;

IR (thin film) cm^{-1} 3066w, 2981m, 2886w, 2362w, 1920w, 1625m, 1495m, 1455m, 1347s, 1318m, 1238m, 1163s;

mass spectrum (APCI): m/e (% relative intensity) 288.2 (100) $(\text{M}+\text{H})^+$.



Enamide **7** (384.0 mg, 1.20 mmol) was isolated in 69% yield from N-Benzyl-4-nitrobenzenesulfonamide (511.0 mg, 1.75 mmol) according to the general procedure A.

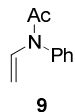
7: R_f = 0.48 [1:4 EtOAc/hexanes]; yellow solid; mp 122-123 °C;

^1H NMR (400 MHz, CDCl_3) δ 4.32 (dd, 1H, J = 1.6, 16.0 Hz), 4.42 (dd, 1H, J = 1.6, 9.2 Hz), 4.61 (s, 2H), 6.94 (dd, 1H, 9.2, 16.0 Hz), 7.22-7.32 (m, 5H), 7.94 (d, 2H, J = 9.2 Hz), 8.32 (d, 2H, J = 9.2 Hz);

^{13}C NMR (100 MHz, CDCl_3) δ 49.2, 96.9, 124.7, 127.2, 128.0, 128.4, 128.9, 131.6, 134.8, 144.9, 150.4;

IR (thin film) cm^{-1} 3106w, 2981m, 2886w, 2361w, 1943w, 1749w, 1627m, 1528s, 1455m, 1401m, 1348s, 1314s, 1237m, 1166s;

mass spectrum (APCI): m/e (% relative intensity) 319.1 (100) $(\text{M}+\text{H})^+$.



Enamide **9** (152.0 mg, 0.94 mmol) was isolated in 47% yield from acetanilide (270.0 mg, 2.00 mmol) according to the general procedure A.

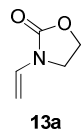
9: R_f = 0.36 [1:4 EtOAc/hexanes]; white solid; mp 47-50 °C;

^1H NMR (400 MHz, CDCl_3) δ 1.87 (s, 3H), 3.85 (d, 1H, J = 16.0Hz), 4.38 (d, 1H, J = 8.8 Hz), 7.16-7.21 (m, 2H), 7.40-7.46 (m, 1H), 7.46-7.52 (m, 2H), 7.64-7.76 (m, 1H);

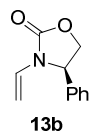
^{13}C NMR (100 MHz, CDCl_3) δ 23.5, 96.4, 128.9, 129.1, 130.2, 133.9, 139.4, 168.9;

IR (thin film) cm^{-1} 3118w, 3061w, 3006w, 2632w, 1959w, 1681s, 1629s, 1597m, 1494m, 1451w, 1427w, 1410w, 1369s, 1303s;

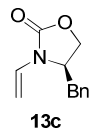
mass spectrum (APCI): m/e (% relative intensity) 120.1 (100), 162.1 (10) ($\text{M}+\text{H}$) $^+$.



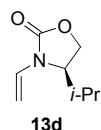
Enamide **13a** (268.0 mg, 2.37 mmol) was isolated in 95% yield from 2-oxazolidinone (218.0 mg, 2.50 mmol) according to the general procedure A. Characterization has been previously reported in the literature.ⁱⁱⁱ



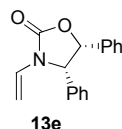
Enamide **13b** (472.0 mg, 2.49 mmol) was isolated in 95% yield from (*R*)-4-Phenyl-2-oxazolidinone (408.0 mg, 2.50 mmol) according to the general procedure A. Characterization has been previously reported in the literature.^{iv}



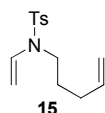
Enamide **13c** (246.0 mg, 1.21 mmol) was isolated in 43% yield from (*R*)-4-Benzyl-2-oxazolidinone (500.0 mg, 2.82 mmol) according to the general procedure A. Characterization has been previously reported in the literature.^{iv}



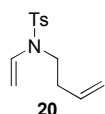
Enamide **13d** (150.0 mg, 0.97 mmol) was isolated in 62% yield from (*R*)-4-Isopropyl-2-oxazolidinone (200.0 mg, 1.55 mmol) according to the general procedure A. Characterization for the enantiomer has been previously reported in the literature.^v



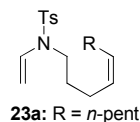
Enamide **13e** (208.0 mg, 0.78 mmol) was isolated in 78% yield from (4*S*,5*R*)-(-)-cis-4,5-Diphenyl-2-oxazolidinone (239.0 mg, 1.00 mmol) according to the general procedure A. Characterization has been previously reported in the literature.^{vi}



Enamide **15** (444.0 mg, 1.67 mmol) was isolated in 84% yield from **S5** (478.0 mg, 2.00 mmol) according to the general procedure B. Characterization has been previously reported in the literature.^{vii}



Enamide **20** (223.0 mg, 0.89 mmol) was isolated in 40% yield from **S6** (500.0 mg, 2.22 mmol) according to the general procedure A. Characterization has been previously reported in the literature.^{vii}



Enamide **23a** (58.4 mg, 0.17 mmol) was isolated in 32% yield from **S7** (169.0 mg, 0.55 mmol) according to the general procedure B.

23a: R_f = 0.67 [25% EtOAc/hexanes]; purple oil;

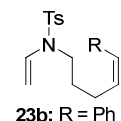
¹H NMR (500 MHz, CDCl₃) δ 0.88 (t, 3H, J = 7.0 Hz), 1.22-1.35 (m, 6H), 1.64 (p, 2H, J = 7.5 Hz), 1.99 (q, 2H, J = 7.5 Hz), 2.05 (q, 2H, J = 7.0 Hz), 2.41 (s, 3H), 3.30 (t, 2H, J = 7.5 Hz),

4.25 (dd, 1H, $J = 1.0, 7.5$ Hz), 4.33 (dd, 1H, $J = 1.5, 9.5$ Hz), 5.33 (dddd, 1H, $J = 0.5, 7.0, 8.5, 10.5$ Hz), 5.40 (dddd, 1H, $J = 0.5, 7.0, 8.5, 10.5$ Hz), 6.89 (dd, 1H, $J = 9.5, 16.0$ Hz), 7.29 (d, 2H, $J = 8.0$ Hz), 7.66 (d, 2H, $J = 8.0$ Hz);

^{13}C NMR (125 MHz, CDCl_3) δ 14.3, 21.8, 22.8, 24.7, 27.0, 27.5, 29.6, 31.8, 44.7, 93.0, 127.1, 128.2, 130.0, 131.6, 132.4, 136.7, 143.9;

IR (neat) cm^{-1} 3293w, 2926m, 2858m, 2360m, 1726m, 1623m, 1461m, 1355m;

mass spectrum (APCI): m/e (% relative intensity) 336 (100) ($\text{M}+\text{H}$) $^+$.



Enamide **23b** (123.0 mg, 0.17 mmol) was isolated in 24% yield from **S8** (475.0 mg, 1.51 mmol) according to the general procedure B.

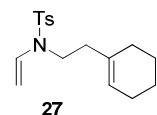
23b: $R_f = 0.59$ [25% EtOAc/hexanes]; colorless oil;

^1H NMR (500 MHz, CDCl_3) δ 1.74 (q, 2H, $J = 7.5$ Hz), 2.34 (dq, 2H, $J = 2.0, 6.0$ Hz), 2.41 (s, 3H), 3.30 (t, 2H, $J = 7.5$ Hz), 4.25 (dd, 1H, $J = 1.5, 15.5$ Hz), 4.33 (dd, 1H, $J = 1.5, 9.5$ Hz), 5.62 (ddd, 1H, $J = 7.5, 12.0, 14.5$ Hz), 6.46 (d, 1H, $J = 11.5$ Hz), 6.88 (dd, 1H, $J = 9.0, 15.5$ Hz), 7.20-7.34 (m, 7H), 7.65 (d, 2H, $J = 8.0$ Hz);

^{13}C NMR (125 MHz, CDCl_3) δ 21.8, 26.1, 27.3, 44.7, 93.0, 127.0, 127.1, 128.5, 129.0, 130.1, 130.2, 131.4, 132.4, 136.6, 137.6, 144.0;

IR (neat) cm^{-1} 2928w, 2361w, 1737w, 1624m, 1494w, 1447w, 1352m;

mass spectrum (APCI): m/e (% relative intensity) 342 (100) ($\text{M}+\text{H}$) $^+$.



Enamide **27** (610.0 mg, 2.00 mmol) was isolated in 100% yield from **S10** (558.0 mg, 2.00 mmol) according to the general procedure A.

27: $R_f = 0.61$ [1:4% EtOAc/hexanes]; white solid, mp 46-49 $^{\circ}\text{C}$;

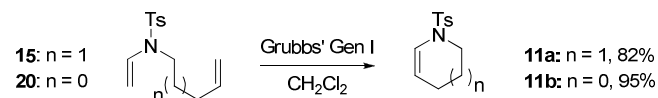
^1H NMR (500 MHz, CDCl_3) δ 1.50-1.64 (m, 4H), 1.90-2.00 (m, 4H), 2.18 (dd, 2H, $J = 8.0, 8.0$ Hz), 2.42 (s, 3H), 3.37 (m, 2H), 4.27 (dd, 1H, $J = 1.6, 16.0$ Hz), 4.32 (dd, 1H, $J = 1.6, 9.6$ Hz), 5.42 (m, 1H), 6.88 (dd, 1H, $J = 9.6, 16.0$ Hz), 7.29 (d, 2H, $J = 8.0$ Hz), 7.66 (d, 2H, $J = 8.0$ Hz);

^{13}C NMR (100 MHz, CDCl_3) δ 21.8, 22.4, 23.0, 25.4, 28.6, 35.2, 44.2, 92.7, 123.7, 127.1, 130.0,

132.3, 134.6, 136.8, 143.9;

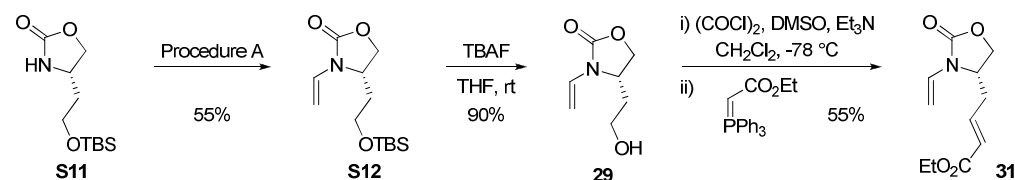
IR (neat) cm^{-1} 2926w, 2835w, 2360w, 1918w, 1622m, 1598w, 1494w, 1459w, 1410w, 1353m, 1316m, 1231w, 1162s;

mass spectrum (APCI): m/e (% relative intensity) 306.2 (100) $(\text{M}+\text{H})^+$.

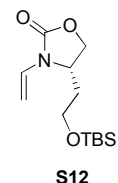


Cyclic enamides **11a** and **11b** were prepared according to literature precedent.^{vii}

PREPARATION OF CHIRAL ENAMIDE **31**.



Characterization for **S11** has been previously reported in the literature.^{viii}



Enamide **S12** (1.21 g, 4.47 mmol) was isolated in 55% yield from **S11** (2.00 g, 8.16 mmol) according to the general procedure A.

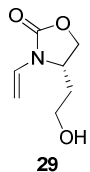
S12: $R_f = 0.35$ [1:4 EtOAc/hexanes]; $[\alpha]_D^{23} = +38.6^\circ$ [c 0.1076 CH_2Cl_2]; clear oil;

^1H NMR (400 MHz, CDCl_3) δ 0.06 (s, 6H), 0.90 (s, 9H), 1.73 (dddd, 1H, $J = 4.0, 6.4, 9.2, 13.2$ Hz), 2.19 (dddd, 1H, $J = 2.4, 4.0, 6.4, 13.2$ Hz), 3.73(m, 2H), 4.21 (tt, 1H, $J = 2.8, 8.8$ Hz), 4.31 (dd, 1H, $J = 3.2, 8.4$ Hz), 4.40 (dd, 1H, $J = 1.2, 16.0$ Hz), 4.43 (td, 1H, $J = 0.8, 8.0$ Hz), 4.45 (dd, 1H, $J = 1.2, 9.6$ Hz), 6.77 (dd, 1H, $J = 9.6, 16.0$ Hz);

^{13}C NMR (100 MHz, CDCl_3) δ 0.00, 23.7, 31.4, 38.6, 57.6, 65.0, 74.0, 99.3, 134.4, 160.9;

IR (thin film) cm^{-1} 2954w, 2930w, 2857w, 2360w, 1760s, 1637m, 1472w, 1427m, 1399m, 1361w, 1327w, 1243m, ;

mass spectrum (APCI): m/e (% relative intensity) 246.2 (100), 272.2 (10) $(\text{M}+\text{H})^+$.



Enamide **29** (519.0 mg, 3.28 mmol) was isolated in 90% yield from **S12** (989.0 mg, 3.65 mmol).

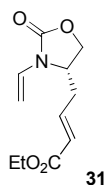
29: R_f = 0.06 [2:3 EtOAc/hexanes]; $[\alpha]_D^{23}$ = +69.2° [c 0.0215 CH₂Cl₂] clear oil;

¹H NMR (400 MHz, CDCl₃) δ 1.60 (brs, 1H), 1.82 (dddd, 1H, J = 4.4, 6.4, 8.8, 10.8 Hz), 2.20 (dddd, 1H, J = 2.4, 5.2, 7.2, 12.4 Hz), 3.80 (m, 2H), 4.27 (dddd, 1H, J = 3.2, 3.2, 8.4, 8.8 Hz), 4.32 (dd, 1H, J = 2.8, 8.8 Hz), 4.42-4.49 (m, 3H), 6.77 (dd, 1H, J = 9.2, 16.0 Hz);

¹³C NMR (100 MHz, CDCl₃) δ 33.0, 52.2, 58.7, 69.7, 94.7, 128.7, 155.9;

IR (thin film) cm⁻¹ 3432m, 2958w, 2360w, 1729s, 1637s, 1481w, 1429m, 1402m, 1354w, 1322m, 1275m, 1238s;

mass spectrum (APCI): m/e (% relative intensity) 158.1 (100) (M+H)⁺.



Enamide **31** (78.8 mg, 0.35 mmol) was isolated in 55% yield from **29** (100.0 mg, 0.63 mmol) according to known procedure.^{ix}

31: R_f = 0.38 [2:3 EtOAc/hexanes]; $[\alpha]_D^{23}$ = +51.5° [c 0.0229 CH₂Cl₂] clear oil;

¹H NMR (500 MHz, CDCl₃) δ 1.30 (t, 3H, J = 7.5 Hz), 2.53 (dtd, 1H, J = 1.5, 8.5, 15.0 Hz), 2.79 (dtd, 1H, J = 2.5, 6.5, 15.0 Hz), 4.15 (dd, 1H, J = 3.0, 9.0 Hz), 4.21 (q, 2H, J = 7.5 Hz), 4.22 (m, 1H), 4.41 (dd, 1H, J = 1.5, 16.0 Hz), 4.42 (t, 1H, J = 8.5 Hz), 4.53 (dd, 1H, J = 1.5, 9.5 Hz), 5.95 (dt, 1H, J = 1.5, 16.0 Hz), 6.78 (dd, 1H, J = 9.5, 16.0 Hz), 6.80 (ddd, 1H, J = 6.5, 8.5, 16.0 Hz);

¹³C NMR (125 MHz, CDCl₃) δ 14.4, 33.2, 52.4, 60.6, 60.9, 67.0, 94.6, 126.3, 128.8, 140.7, 155.1, 165.7;

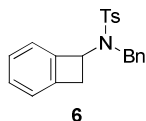
IR (thin film) cm⁻¹ 2982w, 2360w, 1751s, 1715s, 1639m, 1479w, 1428m, 1403m, 1369m, 1325m, 1270m, 1242s, 1173m;

mass spectrum (APCI): m/e (% relative intensity) 226.1 (100) (M+H)⁺.

GENERAL PROCEDURE FOR ENAMIDE-BENZYNE [2 + 2] CYCLOADDITION.

To an oven-dried screw-cap vial fitted with magnetic stir bar was added enamide (1.0 equiv), CsF (4.0 equiv) and anhydrous 1,4-dioxane (0.05 *M*). *Ortho*-(trimethylsilyl)phenyl triflate (3.0 equiv) was added dropwise via gastight syringe and the vial was heated at 110 °C overnight. Upon completion of the reaction, the solution was cooled to RT, filtered through a plug of celite and rinsed with EtOAc, and solvent was removed *in vacuo* to afford a crude product. Purification of the resulting crude residue via silica gel flash column chromatography (gradient elution: EtOAc in *n*-hexanes) afforded the desired amidobenzocyclobutane.

CHARACTERIZATIONS.



Amidobenzocyclobutane **6** (24.7 mg, 0.068 mmol) was isolated in 87% yield from enamide **5** (22.4 mg, 0.078 mmol) according to the general procedure.

6: R_f = 0.27 [1:9 EtOAc/hexanes]; white solid; mp 119-121 °C;

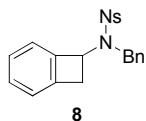
^1H NMR (400 MHz, CDCl_3) δ 2.49 (s, 3H), 2.73 (dd, 1H, J = 2.4, 15.2 Hz), 3.29 (dd, 1H, J = 5.6, 15.2 Hz), 4.08 (d, 1H, J = 16.0 Hz), 4.36 (d, 1H, J = 16.0 Hz), 5.60 (dd, 1H, J = 2.4, 5.6 Hz), 6.21 (d, 1H, J = 7.2 Hz), 6.94 (d, 1H, J = 7.2 Hz), 6.99 (t, 1H, J = 7.2 Hz), 7.14-7.29 (m, 6H), 7.37 (d, 2H, J = 8.4 Hz), 7.82 (d, 2H, J = 8.4 Hz);

^{13}C NMR (100 MHz, CDCl_3) δ 21.8, 37.6, 48.3, 58.0, 123.1, 123.9, 127.3, 127.5, 127.6, 127.8, 128.5, 129.5, 130.1, 137.4, 138.8, 142.6, 143.7, 143.8;

IR (thin film) cm^{-1} 3066w, 3032w, 2929w, 2361m, 1598m, 1495m, 1456m, 1340s, 1210w, 1161s;

mass spectrum (APCI): m/e (% relative intensity) 364.2 (100) ($\text{M}+\text{H}$) $^+$;

HRMS (ESI, m/e) calcd for $\text{C}_{22}\text{H}_{21}\text{NNaO}_2\text{S}$ 386.1186, found 386.1197.



Amidobenzocyclobutane **8** (13.7 mg, 0.035 mmol) was isolated in 63% yield from enamide **7** (17.4 mg, 0.055 mmol) according to the general procedure.

8: R_f = 0.45 [1:4 EtOAc/hexanes]; white solid; mp 163-164 °C;

^1H NMR (400 MHz, CDCl_3) δ 2.81 (dd, 1H, J = 1.6, 14.8 Hz), 3.37 (dd, 1H, J = 5.2, 14.8 Hz),

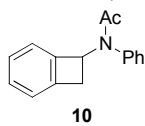
4.22 (d, 1H, $J = 15.6$ Hz), 4.41 (d, 1H, $J = 15.6$ Hz), 5.60 (dd, 1H, $J = 1.6, 5.2$ Hz), 6.38 (d, 1H, $J = 7.6$ Hz), 6.99 (d, 1H, $J = 7.6$ Hz), 7.07 (t, 1H, $J = 7.6$ Hz), 7.13 (m, 2H), 7.20-7.27 (m, 4H), 8.05 (d, 2H, $J = 8.0$ Hz), 8.38 (d, 2H, $J = 8.0$ Hz);

^{13}C NMR (100 MHz, CDCl_3) δ 37.9, 48.7, 57.9, 123.4, 123.8, 124.6, 127.7, 127.9, 127.9, 128.6, 128.7, 130.0, 137.5, 142.3, 142.9, 146.4, 150.3;

IR (thin film) cm^{-1} 3070w, 2928w, 2360m, 1606w, 1530s, 1496w, 1455w, 1401w, 1350s, 1313m, 1210w, 1167s;

mass spectrum (APCI): m/e (% relative intensity) 395.1 (100) ($\text{M}+\text{H}$) $^+$;

HRMS (ESI, m/e) calcd for $\text{C}_{21}\text{H}_{18}\text{N}_2\text{NaO}_4\text{S}$ 417.0880, found 417.0876.



Amidobenzocyclobutane **10** (15.6 mg, 0.066 mmol) was isolated in 63% yield from enamide **9** (17.0 mg, 0.105 mmol) according to the general procedure.

10: $R_f = 0.17$ [1:4 EtOAc/hexanes]; white solid; mp 69-72 $^{\circ}\text{C}$;

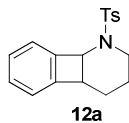
^1H NMR (400 MHz, CDCl_3) δ 1.87 (br. s, 3H), 3.03 (dd, 1H, $J = 2.8, 14.4$ Hz), 3.60 (dd, 1H, $J = 5.2, 14.4$ Hz), 6.16 (br. s, 1H), 6.89 (d, 1H, $J = 7.2$ Hz), 6.95 (d, 1H, $J = 7.2$ Hz), 7.06-7.11 (m, 3H), 7.15 (t, 1H, $J = 7.2$ Hz), 7.24-7.32 (m, 3H);

^{13}C NMR (100 MHz, CDCl_3) δ 23.5, 38.0, 55.7, 123.1, 123.6, 127.2, 128.9, 129.4, 129.5, 140.2, 142.6, 145.0, 170.9;

IR (thin film) cm^{-1} 3066m, 2930m, 2361s, 1772w, 1654s, 1594m, 1494m, 1382s, 1307s, 1263m;

mass spectrum (APCI): m/e (% relative intensity) 238.1 (100) ($\text{M}+\text{H}$) $^+$;

HRMS (ESI, m/e) calcd for $\text{C}_{16}\text{H}_{15}\text{NNaO}$ 260.1046, found 260.1053.



Amidobenzocyclobutane **12a** (21.0 mg, 0.067 mmol) was isolated in 100% yield from enamide **11a** (16.0 mg, 0.067 mmol) according to the general procedure.

12a: $R_f = 0.55$ [25% EtOAc/hexanes]; colorless oil;

^1H NMR (500 MHz, CDCl_3) δ 0.19 (m, 1H), 1.60 (dddd, 1H, $J = 4.0, 8.0, 13.0, 17.0$ Hz), 1.91 (dd, 2H, $J = 4.0, 8.0$ Hz), 2.48 (s, 3H), 3.03 (ddd, 1H, $J = 3.5, 8.5, 12.0$ Hz), 3.48 (ddd, 1H, $J = 0.5, 9.0, 17.0$ Hz), 3.98 (dd, 1H, $J = 4.5, 9.0$ Hz), 5.31 (d, 1H, $J = 6.0$ Hz), 6.40 (d, 1H, $J = 7.5$

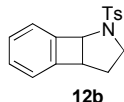
Hz), 7.02 (d, 1H, $J = 7.5$ Hz), 7.09 (t, 1H, $J = 7.5$ Hz), 7.24 (t, 1H, $J = 7.5$ Hz), 7.38 (d, 2H, $J = 8.5$ Hz), 7.80 (d, 2H, $J = 8.5$ Hz);

^{13}C NMR (125 MHz, CDCl_3) δ 17.9, 21.9, 24.1, 41.5, 44.8, 55.7, 122.7, 123.9, 127.7, 127.9, 129.5, 130.1, 136.7, 143.6, 145.3, 146.0;

IR (neat) cm^{-1} 2926w, 2258w, 1741w, 1600w, 1456m;

mass spectrum (APCI): m/e (% relative intensity) 314 (100) ($\text{M}+\text{H}$) $^+$;

HRMS (ESI, m/e) calcd for $\text{C}_{18}\text{H}_{20}\text{NO}_2\text{S}$ 314.1210, found 314.1206.



Amidobenzocyclobutane **12b** (22.4 mg, 0.075 mmol) was isolated in 100% yield from enamide **11b** (16.7 mg, 0.075 mmol) according to the general procedure.

12b: $R_f = 0.45$ [25% EtOAc/hexanes]; colorless oil;

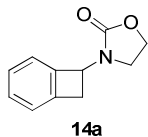
^1H NMR (500 MHz, CDCl_3) δ 1.62-1.69 (m, 1H), 1.83 (dd, 1H, $J = 6.0, 13.0$ Hz), 2.44 (s, 3H), 2.99 (ddd, 1H, $J = 6.0, 11.5, 17.0$ Hz), 3.77 (dd, 1H, $J = 8.0, 11.0$ Hz), 4.11 (dd, 1H, $J = 4.0, 8.0$ Hz), 5.40 (d, 1H, $J = 3.5$ Hz), 6.78 (d, 1H, $J = 7.5$ Hz), 7.02 (d, 1H, $J = 7.5$ Hz), 7.13 (t, 1H, $J = 7.5$ Hz), 7.25 (t, 1H, $J = 7.5$ Hz), 7.32 (d, 2H, $J = 8.0$ Hz), 7.79 (d, 2H, $J = 8.0$ Hz);

^{13}C NMR (125 MHz, CDCl_3) δ 21.8, 28.4, 47.0, 50.0, 63.5, 122.3, 124.0, 127.6, 128.5, 129.8, 130.0, 137.5, 142.4, 143.7, 145.2;

IR (neat) cm^{-1} 2938w, 2361w, 1598w, 1457w;

mass spectrum (APCI): m/e (% relative intensity) 300 (100) ($\text{M}+\text{H}$) $^+$;

HRMS (ESI, m/e) calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_2\text{S}$ 300.1053, found 300.1067.



Amidobenzocyclobutane **14a** (17.1 mg, 0.090 mmol) was isolated in 62% yield from enamide **13a** (14.5 mg, 0.128 mmol) according to the general procedure.

14a: $R_f = 0.29$ [2:3 EtOAc/hexanes]; yellow solid; mp 81-83 $^{\circ}\text{C}$;

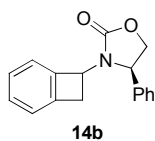
^1H NMR (400 MHz, CDCl_3) δ 3.24 (dd, 1H, $J = 2.4, 14.4$ Hz), 3.44 (ddd, 1H, $J = 7.6, 8.4, 8.4$ Hz), 3.49 (ddd, 1H, $J = 7.6, 8.4, 8.4$ Hz), 3.62 (dd, 1H, $J = 4.8, 14.4$ Hz), 4.35 (dd, 2H, $J = 8.4, 8.4$ Hz), 5.57 (dd, 1H, $J = 2.4, 4.8$ Hz), 7.15 (d, 2H, $J = 7.6$ Hz), 7.26 (t, 1H, $J = 7.6$ Hz), 7.32 (t, 1H, $J = 7.6$ Hz);

^{13}C NMR (100 MHz, CDCl_3) δ 36.7, 41.4, 53.8, 62.3, 123.4, 123.5, 127.8, 129.8, 142.8, 143.5, 158.0;

IR (thin film) cm^{-1} 2929w, 2361w, 1735s, 1637m, 1482m, 1457m, 1418s, 1268s, 1240s;

mass spectrum (APCI): m/e (% relative intensity) 190.1 (100) $(\text{M}+\text{H})^+$;

HRMS (ESI, m/e) calcd for $\text{C}_{11}\text{H}_{12}\text{NO}_2$ 190.0863, found 190.0869.



Amidobenzocyclobutane **14b** (14.5 mg, 0.055 mmol) was isolated in 55% yield, 2:1 *dr* from enamide **13b** (18.9 mg, 0.10 mmol) according to the general procedure.

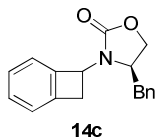
14b: R_f = 0.23 [25% EtOAc/hexanes]; colorless oil;

^1H NMR (500 MHz, CDCl_3) δ 2.50 (dd, 1H, J = 2.5, 14.0 Hz, major), 3.23 (dd, 1H, J = 5.0, 14.5 Hz, major), 3.39 (dd, 1H, J = 2.5, 14.0 Hz, minor), 3.59 (dd, 1H, J = 4.5, 14.0 Hz, minor), 4.17 (dd, 1H, J = 5.0, 8.5 Hz, minor), 4.23 (dd, 1H, J = 6.0, 9.0 Hz, major), 4.65 (t, 1H, J = 8.5 Hz, major and minor), 4.75 (dd, 1H, J = 5.5, 9.0 Hz, major and minor), 5.42 (dd, 1H, J = 2.5, 5.0 Hz, minor), 5.49 (dd, 1H, J = 2.5, 5.0 Hz, major), 6.15 (d, 1H, J = 7.5 Hz, minor), 6.81-6.87 (m, 1H, minor and major), 7.00-7.31 (m, 8H, major and minor);

IR (neat) cm^{-1} 3483w, 2919w, 2360w, 2250w, 1741s, 1458m, 1407m;

mass spectrum (APCI): m/e (% relative intensity) 266 (100) $(\text{M}+\text{H})^+$;

HRMS (ESI, m/e) calcd for $\text{C}_{17}\text{H}_{16}\text{NO}_2$ 266.1176, found 266.1177.



Amidobenzocyclobutane **14c** (25.5 mg, 0.091 mmol) was isolated in 55% yield, 1:1 *dr* from enamide **13c** (20.3 mg, 0.10 mmol) according to the general procedure.

14c: R_f = 0.20 [25% EtOAc/hexanes]; colorless oil;

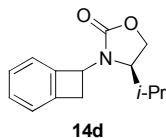
^1H NMR (500 MHz, CDCl_3) δ 2.56-2.62 (m, 1H), 2.72 (dd, 0.5H, J = 3.5, 13.5 Hz), 2.97 (dd, 0.5H, J = 3.0, 13.5 Hz), 3.28 (dd, 0.5H, J = 2.0, 14.5 Hz), 3.48 (dd, 0.5H, J = 2.5, 15.0 Hz), 3.66 (dd, 0.5H, J = 5.0, 14.5 Hz), 3.77 (dd, 0.5H, J = 5.0, 14.5 Hz), 4.01-4.15 (m, 3H), 5.52 (dd, 0.5H, J = 2.5, 5.0 Hz), 5.57 (dd, 1H, J = 2.5, 5.0 Hz), 6.82 (d, 1H, J = 6.5 Hz), 7.01 (d, 1H, J =

7.0 Hz), 7.18-7.41 (m, 7H);

IR (neat) cm^{-1} 2933w, 2361w, 1744s, 1455w, 1411m;

mass spectrum (APCI): m/e (% relative intensity) 280 (100) ($M+H$)⁺;

HRMS (ESI, m/e) calcd for $C_{18}H_{18}NO_2$ 280.1333, found 280.1320.



Amidobenzocyclobutane **14d** (14.7 mg, 0.064 mmol) was isolated in 64% yield, 1:1 *dr* from enamide **13d** (15.6 mg, 0.10 mmol) according to the general procedure.

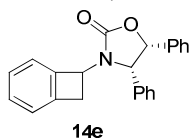
14d: R_f = 0.18 [1:4 EtOAc/hexanes]; yellow oil;

^1H NMR (400 MHz, CDCl_3) δ 0.71 (d, 3H, J = 7.2 Hz), 0.78 (d, 3H, J = 7.2 Hz), 0.89 (d, 3H, J = 7.2 Hz), 0.94 (d, 3H, J = 7.2 Hz), 1.63 (dq, 1H, J = 3.2, 7.2, 7.2 Hz), 1.80 (dq, 1H, J = 3.2, 7.2, 7.2 Hz), 3.24 (dd, 1H, J = 2.8, 14.4 Hz), 3.45 (dd, 1H, J = 2.8, 14.4 Hz), 3.59 (dd, 1H, J = 5.2, 14.4 Hz), 3.65 (dd, 1H, J = 5.2, 14.4 Hz), 3.82 (ddd, 1H, J = 3.6, 4.4, 9.2 Hz), 3.89 (ddd, 1H, J = 3.6, 4.4, 8.8 Hz), 4.09-4.15 (m, 2H), 4.20 (t, 1H, J = 8.8 Hz), 4.24 (t, 1H, J = 9.2 Hz), 5.42 (dd, 1H, J = 2.4, 5.2 Hz), 5.47 (dd, 1H, J = 2.4, 5.2 Hz), 7.12-7.35 (m, 8H);

IR (thin film) cm^{-1} 2963m, 2361w, 1727s, 1469m, 1458m, 1414s, 1306w, 1254m;

mass spectrum (APCI): m/e (% relative intensity) 232.1 (100) ($M+H$)⁺;

HRMS (ESI, m/e) calcd for $C_{14}H_{18}NO_2$ 232.1333, found 232.1338.



Amidobenzocyclobutane **14e** (19.8 mg, 0.058 mmol) was isolated in 77% yield, 1:1 *dr* from enamide **13e** (19.9 mg, 0.075 mmol) according to the general procedure.

14e: R_f = 0.32 [25% EtOAc/hexanes]; white solid; mp

^1H NMR (500 MHz, CDCl_3) δ 2.78 (dd, 0.5H, J = 2.5, 14.5 Hz), 3.29 (dd, 0.5H, J = 5.5, 14.5 Hz), 3.43 (dd, 0.5H, J = 1.5, 14.5 Hz), 3.72 (dd, 0.5H, J = 5.0, 14.5 Hz), 4.93 (d, 0.5H, J = 8.0 Hz), 5.00 (d, 0.5H, J = 7.5 Hz), 5.39 (dd, 0.5H, J = 2.0, 4.5 Hz), 5.54 (dd, 0.5H, J = 2.0, 5.0 Hz), 5.85 (d, 0.5H, J = 7.0 Hz), 5.91 (d, 0.5H, J = 8.5 Hz), 6.15 (d, 0.5H, J = 7.0 Hz), 6.87-6.93 (m, 2H), 6.98-7.10 (m, 9H), 7.18 (t, 1H, J = 7.5 Hz), 7.24-7.29 (m, 2H);

IR (neat) cm^{-1} 2919w, 2361m, 1746s, 1456m, 1404m, 1351w;

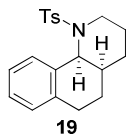
mass spectrum (APCI): m/e (% relative intensity) 342 (100) ($M+H$)⁺;

HRMS (ESI, m/e) calcd for $C_{23}H_{19}NNaO_2$ 364.1308, found 364.1292.

GENERAL PROCEDURE FOR TANDEM [2 + 2]–[4 + 2] CYCLOADDITIONS.

To an oven-dried screw-cap vial fitted with magnetic stir bar was added enamide (1.0 equiv), CsF (4.0 equiv) and anhyd 1,4-dioxane (conc = 0.05 *M*). *Ortho*-(trimethylsilyl)phenyl triflate (3.0 equiv) was added dropwise via gastight syringe and the vial was heated at 110 °C overnight. Upon completion of the reaction, the solution was cooled to RT, filtered through a plug of CeliteTM and rinsed with EtOAc, and solvent was removed *in vacuo* to afford a crude product. Purification of the resulting crude residue via silica gel flash column chromatography (gradient eluent: EtOAc in hexane) afforded the desired cycloadduct.

CHARACTERIZATIONS.



Aza-tricycle **19** (22.2 mg, 0.065 mmol) was isolated in 98% yield from enamide **15** (17.5 mg, 0.066 mmol) according to the general procedure.

19: R_f = 0.50 [1:4 EtOAc/hexanes]; white solid; mp 180 °C (decomp);

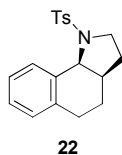
¹H NMR (400 MHz, $CDCl_3$) δ 1.22-1.30 (m, 1H), 1.34-1.44 (m, 3H), 1.72-1.76 (m, 1H), 1.83-1.87 (m, 1H), 1.90-1.98 (m, 1H), 2.45 (s, 3H), 2.65-2.84 (m, 2H), 3.80 (dd, 1H, J = 2.0, 14.5 Hz), 5.18 (d, 1H, J = 4.5 Hz), 7.06 (d, 1H, J = 7.0 Hz), 7.16 (t, 1H, J = 7.0 Hz), 7.18 (t, 1H, J = 7.0 Hz), 7.32 (d, 2H, J = 8.0 Hz), 7.45 (d, 1H, J = 7.0 Hz), 7.81 (d, 2H, J = 8.0 Hz);

¹³C NMR (100 MHz, $CDCl_3$) δ 21.8, 23.8, 24.4, 24.6, 27.6, 32.7, 41.1, 56.5, 126.8, 127.1, 127.2, 127.5, 129.1, 130.0, 134.1, 137.2, 139.4, 143.2;

IR (thin film) cm^{-1} 3061w, 2927w, 2859w, 2361m, 2342m, 1598w, 1491w, 1453w, 1374m, 1335w;

mass spectrum (APCI): m/e (% relative intensity) 342.2 (100) ($M+H$)⁺;

HRMS (ESI, m/e) calcd for $C_{20}H_{24}NO_2S$ 342.1523, found 342.1518.



Aza-tricycle **22** (12.0 mg, 0.037 mmol) was isolated in 66% yield from enamide **20** (14.0 mg, 0.056 mmol) according to the general procedure.

22: R_f = 0.20 [1:9 EtOAc/hexanes]; white solid; mp 127-129 °C;

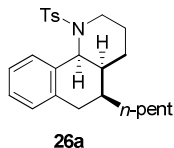
^1H NMR (400 MHz, CDCl_3) δ 1.50-1.60 (m, 1H), 1.60-1.68 (m, 1H), 1.68-1.78 (m, 1H), 1.90-2.05 (m, 2H), 2.45 (s, 3H), 2.57 (ddd, 1H, J = 5.2, 5.2, 16.0 Hz), 2.73 (ddd, 1H, 5.2, 9.6, 16.0 Hz), 3.29-3.42 (m, 2H), 4.82 (d, 1H, J = 7.6 Hz), 7.04 (d, 1H, J = 7.6 Hz), 7.17 (t, 1H, J = 7.6 Hz), 7.27 (t, 1H, J = 7.6 Hz), 7.32 (d, 2H, J = 8.0 Hz), 7.78 (d, 2H, J = 8.0 Hz), 7.93 (d, 1H, J = 7.6 Hz);

^{13}C NMR (100 MHz, CDCl_3) δ 21.8, 24.4, 25.9, 29.1, 37.3, 48.1, 60.8, 126.9, 127.2, 127.9, 128.0, 130.0, 130.0, 135.5, 135.9, 136.8, 143.7;

IR (thin film) cm^{-1} 3059w, 2931m, 2361w, 1922w, 1597w, 1492m, 1455m, 1339s, 1204m, 1156s;

mass spectrum (APCI): m/e (% relative intensity) 328.1 (100) ($\text{M}+\text{H}$) $^+$;

HRMS (ESI, m/e) calcd for $\text{C}_{19}\text{H}_{21}\text{NNaO}_2\text{S}$ 350.1186, found 350.1189.



Aza-tricycle **26a** (13.3 mg, 0.032 mmol) was isolated in 64% yield from enamide **23a** (17.0 mg, 0.050 mmol) according to the general procedure.

26a: R_f = 0.55 [25% EtOAc/hexanes]; colorless oil;

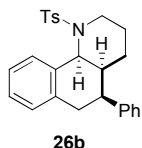
^1H NMR (500 MHz, CDCl_3) δ 0.91 (t, 3H, J = 7.0 Hz), 1.18-1.38 (m, 12H), 1.45 (bd, 1H, J = 10.0 Hz), 1.69-1.73 (m, 1H), 1.87-1.88 (m, 1H), 2.45 (s, 3H), 2.71-2.78 (m, 2H), 3.82 (dd, 1H, J = 2.0, 12.5 Hz), 5.16 (d, 1H, J = 4.5 Hz), 7.05-7.19 (m, 3H), 7.33 (d, 2H, J = 8.0 Hz), 7.44 (dd, 1H, J = 2.0, 8.5 Hz), 7.83 (d, 2H, J = 8.5 Hz);

^{13}C NMR (125 MHz, CDCl_3) δ 14.4, 18.8, 21.8, 223.0, 24.2, 26.8, 32.2, 33.2, 36.6, 37.3, 41.7, 58.1, 126.9, 127.2, 127.3, 129.1, 130.0, 134.1, 137.3, 139.4, 143.2;

IR (neat) cm^{-1} 2930m, 2361m, 1453w;

mass spectrum (APCI): m/e (% relative intensity) 412 (100) ($\text{M}+\text{H}$) $^+$;

HRMS (ESI, m/e) calcd for $\text{C}_{25}\text{H}_{34}\text{NO}_2\text{S}$ 412.2227, found 412.2233.



Aza-tricycle **26b** (13.3 mg, 0.032 mmol) was isolated in 64% yield from enamide **23b** (17.0 mg, 0.050 mmol) according to the general procedure.

26b: R_f = 0.48 [25% EtOAc/hexanes]; colorless oil;

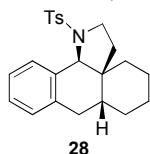
^1H NMR (500 MHz, CDCl_3) δ 1.07-1.32 (m, 5H), 1.91 (ddd, 1H, J = 6.0, 9.0, 12.5 Hz), 2.44 (s, 3H), 2.76 (dt, 1H, J = 2.5, 15.5 Hz), 2.93 (d, 1H, J = 12.5 Hz), 3.22-3.27 (m, 2H), 3.81 (d, 1H, J = 15.0 Hz), 5.44 (d, 1H, J = 5.0 Hz), 7.16-7.34 (m, 10H), 7.53 (d, 1H, J = 7.0 Hz), 7.85 (d, 2H, J = 8.5 Hz);

^{13}C NMR (125 MHz, CDCl_3) δ 19.0, 21.8, 24.1, 29.3, 39.8, 41.5, 43.2, 58.3, 126.8, 127.3, 127.3, 127.5, 127.6, 127.8, 127.8, 128.7, 129.4, 130.1, 130.1, 133.6, 136.6, 139.3, 142.8, 143.4;

IR (neat) cm^{-1} 3028w, 2929m, 2361w, 1599m, 1495m, 1452m;

mass spectrum (APCI): m/e (% relative intensity) 418 (100) ($\text{M}+\text{H}$) $^+$;

HRMS (ESI, m/e) calcd for $\text{C}_{26}\text{H}_{27}\text{NNaO}_2\text{S}$ 440.1655, found 440.1669.



Aza-tetracycle **28** (8.30 mg, 0.022 mmol) was isolated in 31% yield from enamide **27** (21.7 mg, 0.071 mmol) according to the general procedure.

28: R_f = 0.47 [1:4 EtOAc/hexanes]; white residue;

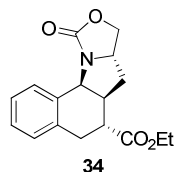
^1H NMR (500 MHz, CDCl_3) δ 0.73 (ddd, 1H, J = 8.0, 8.0, 13.5 Hz), 0.81 (d, 1H, J = 13.5 Hz), 1.16-1.27 (m, 4H), 1.37 (ddd, 1H, J = 4.5, 4.5, 13.0 Hz), 1.48 (m, 1H), 1.63 (m, 1H), 1.75 (m, 1H), 2.15 (ddd, 1H, J = 9.5, 9.5, 12.5 Hz), 2.45 (s, 3H), 2.46 (m, 1H), 3.12 (dd, 1H, J = 6.0, 17.5 Hz), 3.25 (d, 1H, J = 9.5 Hz), 3.26 (d, 1H, J = 9.5 Hz), 4.87 (s, 1H), 7.02 (d, 1H, J = 7.5 Hz), 7.17 (t, 1H, J = 7.5 Hz), 7.27 (t, 1H, J = 7.5 Hz), 7.31 (d, 2H, J = 7.5 Hz), 7.81 (d, 2H, J = 7.5 Hz), 8.17 (d, 1H, J = 7.5 Hz);

^{13}C NMR (125 MHz, CDCl_3) δ 21.8, 23.3, 25.9, 30.3, 33.1, 34.0, 34.9, 38.1, 45.4, 45.5, 61.3, 126.9, 127.3, 128.1, 128.9, 129.8, 131.4, 134.5, 135.9, 136.0, 143.6;

IR (neat) cm^{-1} 2981m, 2932m, 2887m, 1917w, 1654w, 1598w, 1493m, 1473m, 1381m, 1341s, 1159s;

mass spectrum (APCI): m/e (% relative intensity) 382.2 (100) (M+H)⁺;

HRMS (ESI, m/e) calcd for C₂₃H₂₇NNaO₂S 404.1655, found 404.1670.



34 (21.2 mg, 0.070 mmol) was isolated in 81% yield from enamide **31** (19.6 mg, 0.087 mmol) according to the general procedure.

34: R_f = 0.44 [2:3 EtOAc/hexanes]; $[\alpha]_D^{23}$ = -68.9° [c 0.0133 CH₂Cl₂] yellow oil;

¹H NMR (500 MHz, CDCl₃) δ 1.30 (t, 3H, J = 7.5 Hz), 1.90 (ddd, 1H, J = 8.5, 10.5, 11.5 Hz), 2.04 (dd, 1H, J = 5.5, 13.0 Hz), 2.43 (td, 1H, J = 3.5, 12.0 Hz), 2.82 (dd, 1H, J = 12.5, 15.0 Hz), 2.95 (dd, 1H, J = 3.5, 15.0 Hz), 3.11 (ddd, 1H, J = 8.5, 8.5, 11.5 Hz), 3.99 (m, 1H), 4.22 (q, 2H, 7.5 Hz), 4.22 (m, 1H), 4.51 (td, 1H, J = 1.5, 8.0 Hz), 5.01 (d, 1H, J = 8.5 Hz), 7.11 (d, 1H, J = 7.5 Hz), 7.21 (t, 1H, J = 7.5 Hz), 7.28 (t, 1H, J = 7.5 Hz), 7.71 (d, 1H, J = 7.5 Hz);

¹³C NMR (125 MHz, CDCl₃) δ 14.6, 32.6, 36.7, 42.2, 43.5, 57.2, 58.5, 61.3, 67.4, 127.6, 127.7, 128.0, 129.8, 134.9, 135.0, 162.7, 174.6;

IR (thin film) cm⁻¹ 3065w, 2981m, 2908m, 2361w, 1749s, 1726s, 1507m, 1456m, 1392s, 1321m, 1235s, 1176s;

mass spectrum (APCI): m/e (% relative intensity) 302.1 (100) (M+H)⁺;

HRMS (ESI, m/e) calcd for C₁₇H₁₉NNaO₄ 324.1207, found 324.1208.

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