Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Enantioselective Diels-Alder-Lactamization Organocascades Employing Furan-Based Dienes

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General Procedures

All non-aqueous reactions were performed under a nitrogen atmosphere in oven-dried glassware. Dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), diethyl ether (Et_2O), acetonitrile (CH_3CN) and toluene (PhMe) were dried by passing through activated alumina (solvent purification system). (*E*)-4,4,4-trifluoro-2-butenoic acid was purchased from Oakwood Chemical and used as received. Other solvents and reagents were used as received from commercially available sources. Deuterated solvents were purchased from Cambridge Isotopes and used as received. ^{1}H NMR spectra were measured at 500 MHz and referenced relative to residual chloroform (7.26 ppm) and were reported in parts per million. Coupling constants (*J*) were reported in Hertz (Hz), with multiplicity reported following usual convention: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; dt, doublet of triplets; td, triplet of doublets; ddd, doublet of doublet of doublets; m, multiplet. ^{13}C NMR spectra were measured at 125 MHz and referenced relative to residual chloroform (77.23 ppm) and were reported in parts per million (ppm). Flash column chromatography was performed with 60Å Silica Gel (230-400 mesh) as stationary phase on an automated flash chromatography system (EtOAc/hexanes as eluent unless indicated otherwise). High-resolution mass spectra (ESI) were obtained through the Laboratory for Biological Mass Spectrometry (Texas A&M University). Thin Layer Chromatography (TLC) was performed using glass-backed silica gel F254 (Silicycle, 250 μm thickness). Visualization of developed plates was performed by fluorescence quenching or by treating with Seebach's[1] staining solution. *Fourier* Transform Infrared (FTIR) spectra were recorded as thin films on NaCl plates. Optical rotations were recorded on a polarimeter at 589 nm employing a 25 mm cell. High Performance Liquid Chromatography (HPLC) was performed on a chromatographic system using various chiral columns (25 cm) as noted. X-ray diffraction was obtained by the X-ray Diffraction Laboratory at Texas A&M University. (*S*)-(–)-BTM and (*S*)-(–)-TM·HCl were purchased from TCI chemicals and used as

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[1] D. Seebach, R. Imwinkelried and G. Stucky, *Helv. Chim. Acta.*, 1987, **70**, 448.

received. All unsaturated acid chlorides were purchased from Sigma-Aldrich and used as received without further purification. Protected furanyl amines **8a**,**h**,**i**,[2] **8b**,[3] **8c**,[4] **8d**,[5] **8e**,[6] **8f**,[7] **8g**,[8] were prepared according to the literature procedures.

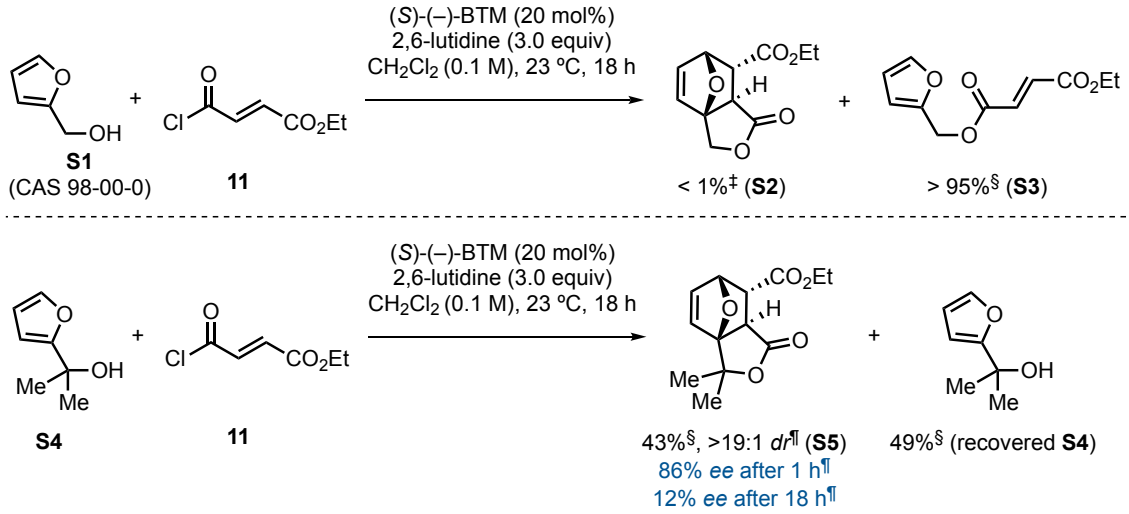
Abbreviation List

(*S*)-(–)-BTM	=	(*S*)-(–)-benzotetramisole
(*S*)-(–)-TM·HCl	=	(*S*)-(–)-tetramisole (levamisole) hydrochloride
*m*CPBA	=	*meta*-chloroperoxybenzoic acid

[2] A. Kamal, J. S. Reddy, E. V. Bharathi and D. Dastagiri, *Tetrahedron Lett.*, 2008, **49**, 348. Compounds **8h** and **8i** were prepared in a similar fashion.
[3] N. Choony, N. Kuhnert, P. G. Sammes, G. Smith and R. W. Ward, *J. Chem. Soc. Perk. Trans. 1*, 2002, **17**, 1999.
[4] S. V. Chankeshwara, A. K. Chakraborti, *Synthesis*, 2006, **16**, 2784.
[5] K. Yeung; Knaus, *Eur. J. Med. Chem.*, 1986, **21**, 181.
[6] M. E. Jung, J. Gervay, *J. Am. Chem. Soc.*, 1991, **113**, 224.
[7] J. Roger, H. Doucet, *Eur. J. Org. Chem.*, 2010, **23**, 4412.
[8] S. Yrjölä, T. Parkkari, D. Navia-Paldanius, T. Laitinen, A. A. Kaczor, T. Kokkola, F. Adusei-Mensah, J. R. Savinainen, J. T. Laitinen, A. Poso, A. Alexander, J. Penman, L. Stott, M. Anskat, A. J. Irving, T. J. Nevalainen, *Eur. J. Med. Chem.*, 2016, **107**, 119.

Representative examples of the DAL process with furanyl alcohols (Table S1): Ester **S3,**[9] alcohol **S4**,[10] cycloadduct **S5**[11] are known compounds.

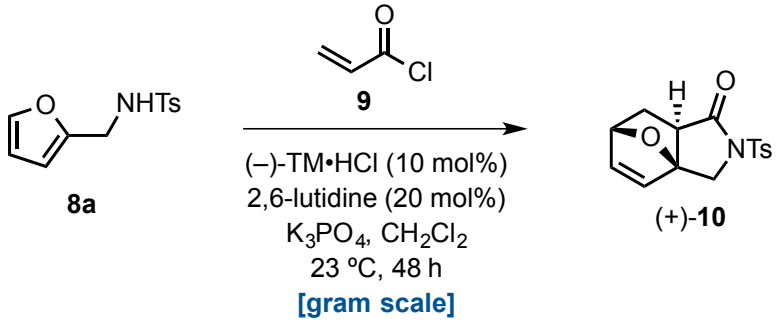
Table S1. Representative examples of the DAL process with furanyl alcohols.†



†Reactions were performed with dienes **S1**, **S4** (1.0 equiv), ethyl fumaroyl chloride (**11)** (1.2 equiv), (*S*)-(–)-BTM (20 mol%) and 2,6-lutidine (3.0 equiv) in CH_2Cl_2 (0.1 *M*) at ambient temperature (23 ºC) for 18 h. ‡The desired cycloadduct **S2** was not detected (< 1%) by LC/MS and ^{1}H NMR (500 MHz) analysis of the crude reaction mixture. §A known amount of CH_2Cl_2 was added to the reaction contents at the end of the reaction to serve as an internal standard. Percent conversions were determined by ^{1}H NMR (500 MHz) integration of product (**S3**, **S5** or recovered **S4**) resonances versus the 5.2 ppm resonance of CH_2Cl_2. ¶Diastereomeric (*endo/exo*) ratio of **S5** was determined by ^{1}H NMR (500 MHz) analysis of the crude reaction mixture. Enantiomeric excess (*ee*) of **S5** was determined by chiral-phase HPLC analysis of the crude reaction mixture.

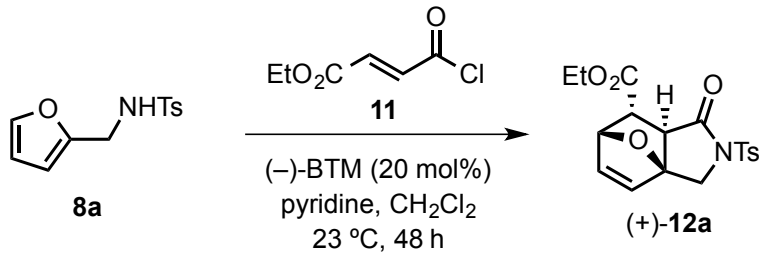
[9] T. Jumina, Z. Iqmal and A. Karim, *Indonesian J. Pharm.*, 2002, **13**, 207.
[10] G. W. Gribble, D. J. Keavy, S. E. Branz, W. J. Kelly and M. A. Pals, *Tetrahedron Lett.*, 1988, **29**, 6227.
[11] M. E. Jung and J. Gervay, *J. Am. Chem. Soc.*, 1989, **111**, 5469.

Representative procedure for the DAL process as described for γ-lactam (+)-10:

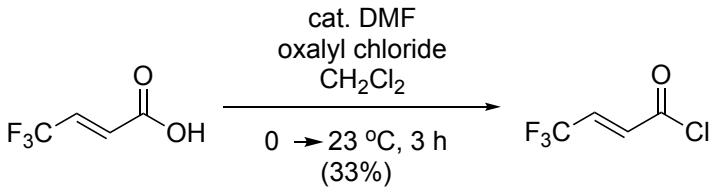


(3aS,6S,7aR)-2-tosyl-2,3,7,7a-tetrahydro-3a,6-epoxyisoindol-1(6H)-one ((+)-10): To an oven-dried, 25-mL round-bottomed flask equipped with a magnetic stir bar was added furanyldiene sulfonamide **8a** (4.60 g, 18.3 mmol, 1.0 equiv), (–)-Levamisole·HCl (442 mg, 1.83 mmol, 10 mol%), 2,6-lutidine (0.43 mL, 3.66 mmol, 20 mol%), K_3PO_4 (9.7 g, 45.8 mmol, 2.5 equiv) and anhydrous CH_2Cl_2 (185 mL, to make final concentration of furanyldiene sulfonamide **8a**, 0.1 M) at ambient temperature (23 ºC). With vigorous stirring, acryloyl chloride **9** (1.8 mL, 21.9 mmol, 1.2 equiv) in CH_2Cl_2 (1.2 mL) was added over a period of 5 min. After stirring for an additional 48 h, the reaction mixture was filtered through a pad of Celite and concentrated by rotary evaporation. Purification by automated flash chromatography (10→80% EtOAc/hexanes) afforded a single diastereomer (as judged by ^{1}H NMR) of tricyclic γ-lactam (+)-**10** (4.24 g, 76% yield, 91% *ee*) as a white solid: TLC (EtOAc:hexanes, 1:1 *v/v*): R_f = 0.44; $[\alpha]_D^{20.0}$ = +5.88 (*c* = 3.40, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis in comparison with authentic racemic material using a Chiralcel AS-H column: hexanes:^{i}PrOH = 40:60, flow rate 1.0 mL/min, λ = 230 nm: t_{minor} = 12.1 min, t_{major} = 14.8 min; 91% *ee*. Absolute stereochemistry was assigned by analogy to epoxide (+)-**14**. ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.90 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 6.41 (dd, J = 5.8, 1.6 Hz, 1H), 6.38 (d, J = 5.8 Hz, 1H), 4.98 (dd, J = 4.5, 1.5 Hz, 1H), 4.45 (d, J = 12.0 Hz, 1H), 4.32 (d, J = 12.0 Hz, 1H), 2.55 (dd, J = 8.7, 3.2 Hz, 1H), 2.42 (s, 3H), 2.09 (dt, J = 11.9, 3.9 Hz, 1H), 1.55 (dd, J = 12.0, 8.7 Hz, 1H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 172.6, 145.1, 138.0, 135.2, 132.3, 129.7 (2), 128.0 (2), 87.8, 78.9, 49.9, 48.3,

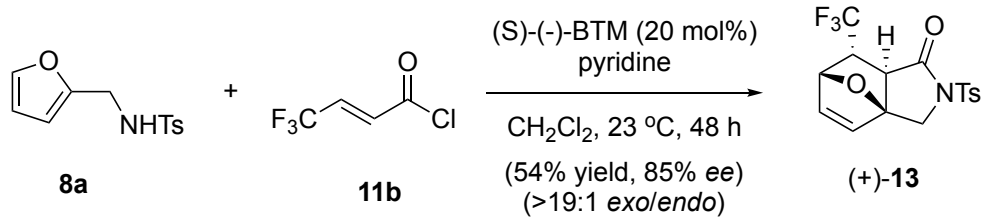
28.9, 21.7; IR (thin film): 2956, 1741 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{15}H_{16}NO_4S$ $[M+H]^+$: 306.0800, found: 306.0811.



Ethyl (3a*S*,6*R*,7*R*,7a*R*)-1-oxo-2-tosyl-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carboxylate ((+)-12a): Prepared according to the representative procedure using furanyldiene sulfonamide **8a** (360 mg, 1.43 mmol, 1.0 equiv), (*S*)-(–)-BTM (72 mg, 0.143 mmol, 20 mol%), pyridine (0.13 mL, 1.57 mmol, 1.1 equiv) in anhydrous CH_2Cl_2 (14.5 mL, to make initial concentration of furanyldiene sulfonamide 0.1 M) and ethyl fumaroyl chloride **11** (0.23 mL, 1.72 mmol, dissolved in 0.7 mL CH_2Cl_2, 1.2 equiv, added by syringe pump over 5 h) at ambient temperature (23 ºC). Upon completion (as judged by TLC), the reaction mixture was purified by automated flash chromatography (10→80% EtOAc/hexanes) to afford a single *endo* diastereomer (as judged by ^{1}H NMR) of tricyclic γ-lactam (+)-**12a** (460 mg, 85% yield, 94% *ee*) as an off-white solid: TLC (EtOAc:hexanes, 1:1 *v/v*): R_f = 0.62; $[\alpha]_D^{19.9}$ +72.63 (*c* = 3.80, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis in comparison with authentic racemic material using a Chiralcel AD-H column: hexanes:^{i}PrOH = 60:40, flow rate 0.5 mL/min, λ = 230 nm: t_{minor} = 27.2 min, t_{major} = 30.9 min; 94% *ee*. Absolute stereochemistry was assigned by analogy to epoxide (+)-**14**. ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.91 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 6.53 (d, J = 5.8 Hz, 1H), 6.34 (dd, J = 5.8, 1.6 Hz, 1H), 5.18 (dd, J = 4.9, 1.5 Hz, 1H), 4.45 (d, J = 12.2 Hz, 1H), 4.31 (d, J = 12.2 Hz, 1H), 4.09 (q, J = 7.1 Hz, 2H), 3.36 (dd, J = 4.8, 3.4 Hz, 1H), 3.03 (d, J = 3.3 Hz, 1H), 2.44 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 171.1, 169.6, 145.3, 135.8, 134.9, 134.31, 134.30, 129.7 (2), 128.1 (2), 89.1, 80.2, 61.4, 52.1, 49.8, 47.6, 21.7, 14.1; IR (thin film): 2983, 1734 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{18}H_{20}NO_6S$ $[M+H]^+$: 378.1011, found: 378.1018.



Synthesis of (E)-4,4,4-trifluoro-2-butenoic acid chloride 11b.[12] To a solution of of (*E*)-4,4,4-trifluoro-2-butenoic acid (520 mg, 3.70 mmol, 1.0 equiv) in 6 mL CH_2Cl_2 was added dry DMF (14 mL, 0.18 mmol, 0.05 equiv), followed by dropwise addition of oxalyl chloride (0.38 mL, 4.4 mmol, 1.2 equiv) at 0 °C. The reaction mixture was warmed to 23 °C and stirring was continued for 3 h. The reaction was then concentrated carefully (23 °C, 300-350 mbar) to afford 193 mg (33%) of the volatile acid chloride **11b** as a yellow solid. The product is readily hydrolyzed and volatile so was directly used in the subsequent DAL without purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (dq, J = 15.5, $J_{H\text{-}F}$ = 6.2 Hz, 1H), 6.70 (dq, J = 15.5, $J_{H\text{-}F}$ = 1.8 Hz, 1H).



8a **11b** (+)-**13**

(3aS,6R,7R,7aR)-2-tosyl-7-(trifluoromethyl)-2,3,7,7a-tetrahydro-3a,6-epoxyisoindol-1(6H)-one (13). The procedure employed was nearly identical to that used for fumaroyl chloride described above. Furanyl sulfonamide **8a** (134 mg, 0.5 mmol, 1.0 equiv), (S)-(–)-BTM (25 mg, 0.1 mmol, 20 mol%), and pyridine (47 μL, 0.55 mmol, 1.1 equiv) was dissolved in anhydrous CH_2Cl_2 (5.0 mL, to make the initial concentration of furanyl sulfonamide 0.1 M). Trifluorocrotonyl chloride **11b** (98 mg,

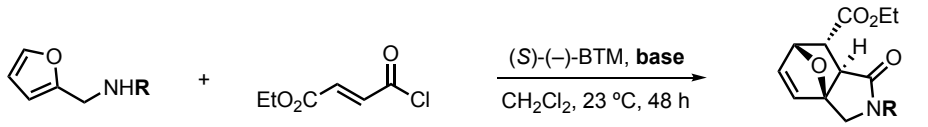
[12] K. Hobel, P. Margaretha *Res. Chem. Int.* 1989, **12**, 263. This acid chloride is commercially available from Sigma-Aldrich but expensive.

0.6 mmol, 1.2 equiv, dissolved in 0.5 mL CH_2Cl_2) was added by syringe pump over 5 h at ambient temperature (23 ºC). Upon completion (as judged by TLC), the reaction mixture was purified by automated flash chromatography (0→100% EtOAc/hexanes) to afford a single *endo* diastereomer (as judged by ^{1}H NMR) of tricyclic γ-lactam (+)-**13** (101 mg, 54% yield, 85% ee) as an off-white solid: TLC (EtOAc:hexanes, 1:1 v/v): R_f = 0.65; $[\alpha]_D^{25}$ +27.20 (*c* 1.0, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis in comparison with authentic racemic material using a Chiralcel AD-H column: hexanes:^{i}PrOH = 60:40, flow rate 1.0 mL/min, λ = 230 nm: t_{minor} = 8.6 min, t_{major} = 7.8 min; 85% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.57 (d, *J* = 5.8 Hz, 1H), 6.42 (app dt, *J* = 6.0, 1.7 Hz, J_{H-F} = 1.7 Hz, 1H), 5.09 (dd, *J* = 4.4, 1.6 Hz, 1H), 4.47 (d, *J* = 12.3 Hz, 1H), 4.33 (d, *J* = 12.3 Hz, 1H), 3.12 (m,1H), 2.68 (d, *J* = 4.0 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 145.6, 135.3, 134.7, 134.4, 129.8, 128.1, 124.4(q, *J* = 278.8 Hz), 89.3, 78.7(q, *J* = 2.6 Hz), 58.8(q, *J* = 2.0 Hz), 49.7, 46.5(q, *J* = 28.7 Hz), 21.7. IR (thin film): 2925, 1737 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{16}H_{14}F_3NO_4SNa$ $[M+Na]^+$: 396.0493, found: 396.0490.

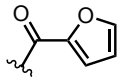
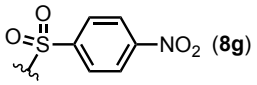
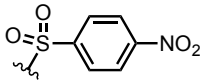
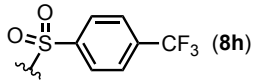
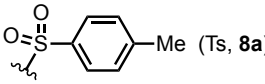
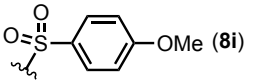
Representative procedure for varying the *N*-substituent on amino furans 8a-i in the DAL process with acid chloride 11 providing lactams 12a-i as described for bicyclic γ-lactam (+)-12a (Table 1, entry 13):

Into a dried, 2-mL clear-glass vial (12 × 32 mm) equipped with a magnetic stir bar was added amino furan **8a** (25 mg, 0.10 mmol, 1.0 equiv), (*S*)-(–)-BTM (5 mg, 0.020 mmol, 20 mol%), pyridine (24 μL, 0.30 mmol, 3.0 equiv) and anhydrous CH_2Cl_2 (1.0 mL, to make final concentration of the furanyl alcohol 0.1 M) at ambient temperature (23 ºC). With vigorous stirring, ethyl fumaroyl chloride **11** (16 μL, 0.12 mmol, 1.2 equiv) was added dropwise by syringe pump over 5 h. After stirring for an additional 43 h, the reaction mixture was purified by automated flash chromatography (10→80% EtOAc/hexanes) to afford a single *endo* diastereomer (as judged by ^{1}H NMR) of tricyclic

γ-lactam (+)-**12a** (30 mg, 82% yield, 94% *ee*) as an off-white solid: All spectral data matched that reported on pages S6, S87.

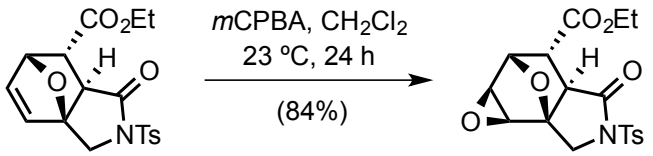


8a–i **11** **12a–i** (>19:1 *exo*/*endo*)

entry	R (21a-i)	catalyst loading (mol%)	base	*ee* (yield[†]) %
1	CPh_3 (**8b**)	100	2,6-lutidine	*n.r.*
2	Boc (**8c**)	100	2,6-lutidine	*n.r.*
3	Bz (**8d**)	100	2,6-lutidine	*n.r.*
4	 (**8e**)	100	2,6-lutidine	*n.r.*
5	Bn (**8f**)	100	2,6-lutidine	3 (92)
6	 (**8g**)	0	2,6-lutidine	– (28)
7		100	2,6-lutidine	40 (46)
8	 (**8h**)	100	2,6-lutidine	51 (40)
9	 (Ts, **8a**)	100	2,6-lutidine	70 (75)
10	 (**8i**)	100	2,6-lutidine	75 (82)
11	Ts	20	2,6-lutidine	42 (86)
12	Ts	20	pyridine	83 (88)
13[‡]	Ts	20	pyridine	94 (85)

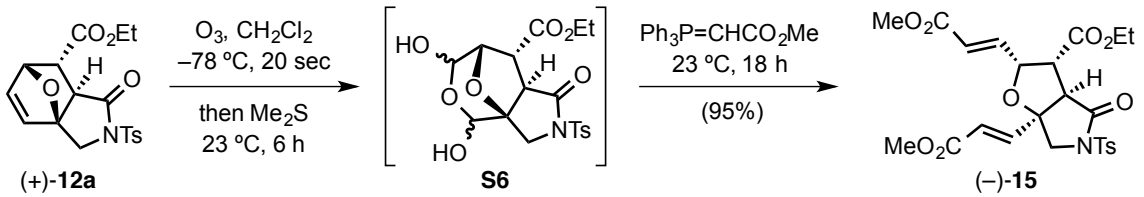
[a]Screening studies were performed with dienes **8a–i** (1.0 equiv), ethyl fumaroyl chloride **11** (1.2 equiv), (*S*)-(–)-BTM (20-100 mol%) and Brønsted base (1.0 equiv) in CH_2Cl_2 (0.1 M). [†]All yields refer to isolated, purified yields of cycloadducts. Diastereomeric (*endo*/*exo*) ratios were determined by ^1H NMR (500 MHz) analysis of the crude reaction mixture. Enantiomeric excess (*ee*) was determined by chiral phase HPLC. [‡]Acid chloride **11** was added as a solution in CH_2Cl_2 by syringe pump over 5 h.

Synthetic applications of γ-lactam (+)-12a:



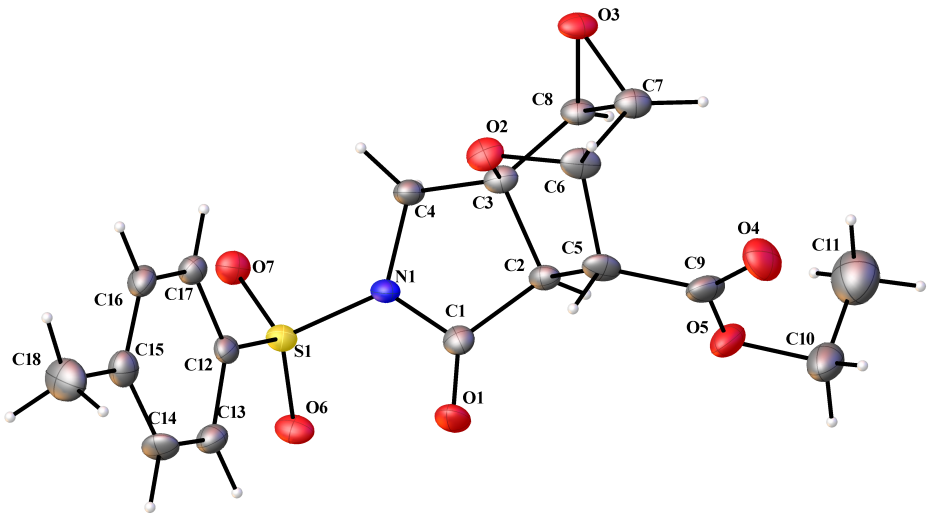
(+)-**12a** (+)-**14**

Ethyl (1aS,2S,3R,3aR,6aS,6bS)-4-oxo-5-tosyloctahydro-2,6a-epoxyoxireno[2,3-e]isoindole-3-carboxylate ((+)-14): Under ice cooling (0 ºC), (+)-**12a** (70 mg, 0.19 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (2.0 mL, to make initial concentration of (+)-**12a** 0.1 M). After stirring for 10 min, a solution of *m*CPBA (70–75%, 182 mg, 0.74 mmol, 4.0 equiv) in CH_2Cl_2 (2.0 mL) was slowly added. The solution was stirred for 24 h at 23 ºC. The reaction mixture was purified by automated flash chromatography system (20→80% EtOAc/hexanes) providing 61 mg (76% yield) of epoxide (+)-**14** as a clear colorless oil. Recrystallization from CH_2Cl_2 using a slow evaporation method provided crystals suitable for X-ray analysis: m.p. 184-187 ^{o}C; TLC (EtOAc:hexanes, 1:1 *v/v*): R_f = 0.44; $[\alpha]_D^{19.7}$ +43.81 (*c* = 0.21, $CHCl_3$). Absolute stereochemistry was assigned based on X-ray analysis using anomalous dispersion (**Figure S1**). ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.89 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 4.70 (d, J = 5.2 Hz, 1H), 4.35 (d, J = 12.4 Hz, 1H), 4.28 (d, J = 12.3 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.56 (dd, J = 3.2, 0.8 Hz, 1H), 3.43 (dd, J = 3.3, 0.7 Hz, 1H), 3.33 (t, J = 4.4 Hz, 1H), 3.26 (d, J = 3.8 Hz, 1H), 2.44 (s, 3H), 1.28 (td, J = 7.1, 0.9 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 170.4, 168.7, 145.5, 134.7, 129.8 (2), 128.1 (2), 84.9, 76.3, 62.0, 52.5, 51.0, 48.6, 48.31, 48.19, 21.7, 14.2; IR (thin film): 2984, 1734, 1171 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{18}H_{20}NO_7S$ $[M+H]^+$: 394.0960, found: 394.0972.



Dimethyl 3,3'-((2R,3R,3aR,6aS)-3-(ethoxycarbonyl)-4-oxo-5-tosylhexahydro-6aH-furo[2,3-c]pyrrole-2,6a-diyl)(2E,2'E)-diacrylate ((–)-15): A solution of tricyclic γ-lactam (+)-**12a** (200 mg, 0.53 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (10.0 mL, to make initial concentration of (+)-**12a** 0.05 M) and cooled to –78 °C. Ozone was bubbled through the reaction solution until a blue color persisted. Excess ozone was removed by blowing N_2 gas into the solution with stirring for 10 min. Dimethylsulfide (0.70 mL, 10.6 mmol, 20.0 equiv) was added by syringe and the reaction was slowly warmed to ambient temperature (23 °C) over 6 h at which time TLC indicated the reaction was complete. ^{1}H NMR analysis from an aliquot of the crude reaction mixture indicated the formation of **S6** intermediate. To a resultant crude mixture of **S6** was added at once methyl (triphenylphosphoranylidene)acetate (445 mg, 1.33 mmol, 2.5 equiv). The solution was stirred for 18 h at 23 ºC. The reaction mixture was purified by automated flash chromatography system (5→50% EtOAc/hexanes) providing 262 mg (95% yield) of lactam (–)-**15** as a clear colorless oil: TLC (EtOAc:hexanes, 1:1 *v/v*): R_f = 0.66; $[\alpha]_D^{20.1}$ –36.87 (*c* = 1.15, $CHCl_3$). ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.91 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 15.5 Hz, 1H), 6.86 (dd, J = 15.6, 4.9 Hz, 1H), 6.16 (d, J = 15.5 Hz, 1H), 6.06 (dd, J = 15.6, 1.7 Hz, 1H), 4.57 (ddd, J = 6.5, 4.9, 1.7 Hz, 1H), 4.16-3.97 (m, 5H), 3.75 (s, 3H), 3.75 (s, 3H), 3.52-3.45 (m, 1H), 2.46 (s, 3H), 1.14 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz; $CDCl_3$): δ 170.7, 168.4, 166.08, 165.89, 146.0, 145.7, 145.4, 141.5, 134.3, 130.0 (2), 128.1 (2), 122.0, 121.7, 83.8, 80.2, 61.7, 56.8, 56.1, 52.1, 51.8, 21.8, 13.9; IR (thin film): 2985, 2954, 1728, 1665, 1597 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{24}H_{28}NO_{10}S$ $[M+H]^+$: 522.1434, found: 522.1433.

Figure S1. Single crystal X-ray structure (ORTEP) of epoxide (+)**-14.** The crystals were grown from a concentrated solution of epoxide (+)-**14** in CH_2Cl_2 (4.0 mL), using a slow evaporation method (probability ellipsoids are shown at the 50% level). X-ray crystallographic data have been deposited in the Cambridge Crystallographic Data Centre database (http://www.ccdc.cam.ac.uk/) under accession code CCDC 1426167.



Alert level B:

THETM01_ALERT_3_B The value of sine(theta_max)/wavelength is less than 0.575. Calculated sin(theta_max)/wavelength = 0.5679.

Author Response: Data was collected on a Bruker GADDS instrument with Cu-source and MWPC (multiwire proportional counter) detector. Under these experimental conditions the maximum angle that can be collected is 120 degrees two-theta.

PLAT019_ALERT_1_B _diffrn_measured_fraction_theta_full/_max < 1.0 0.857 Report

Author Response: Data was collected on a Bruker GADDS instrument with Cu-source and MWPC (multiwire proportional counter) detector which has geometrical restrictions.

Table 1. Crystal data and structure refinement for DRB_MA_150407_G_EpoN.

Crystal Parameters	Crystal Data
Identification code	epon
Empirical formula	C_{18} H_{19} N O_7 S
Formula weight	393.40
Temperature	110.15 K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P 1 21 1
Unit cell dimensions	a = 12.8722(5) Å α = 90º
	b = 6.6204(2) Å β = 92.069(2)º
	c = 20.7083(8) Å γ = 90º
Volume	1763.59(11) $Å^3$
Z	4
Density (calculated)	1.482 Mg/m^3
Absorption coefficient	2.019 mm^{-1}
F(000)	824
Crystal size	0.54 x 0.02 x 0.02 mm^3
Theta range for data collection	2.135 to 61.119º
Index ranges	$-14 \leq h \leq 14$, $-7 \leq k \leq 6$, $-23 \leq l \leq 23$
Reflections collected	31880
Independent reflections	5106 [R(int) = 0.0431]
Completeness to theta = 67.679º	83.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7519 and 0.5733
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5106 / 166 / 515

Goodness-of-fit on F^2	1.116
Final R indices [I>2sigma(I)]	$R_1 = 0.0370$, $wR_2 = 0.0966$
R indices (all data)	$R_1 = 0.0428$, $wR_2 = 0.1092$
Absolute structure parameter	0.02(2)
Extinction coefficient	0.0099(8)
Largest diff. peak and hole	0.742 and -0.456 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for DRB_MA_150407_G_EpoN. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

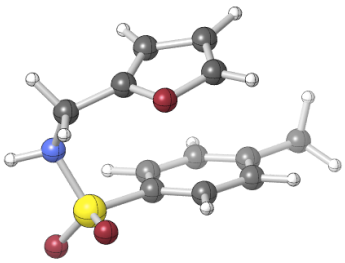
Atom	x	y	z	U(eq)
S(1)	9919(1)	-663(2)	6245(1)	17(1)
O(1)	8844(3)	2066(5)	5252(2)	27(1)
O(2)	6770(2)	-2054(5)	5451(2)	23(1)
O(3)	6245(2)	-5170(5)	4845(2)	24(1)
O(4)	5750(3)	680(6)	3656(2)	37(1)
O(6)	10712(2)	522(5)	5974(2)	23(1)
O(7)	10157(2)	-2589(5)	6528(2)	24(1)
N(1)	9024(3)	-1169(6)	5674(2)	18(1)
C(1)	8648(3)	266(8)	5232(2)	19(1)
C(2)	7955(3)	-843(7)	4741(2)	17(1)
C(3)	7664(3)	-2765(7)	5114(2)	18(1)
C(4)	8564(3)	-3222(7)	5582(2)	19(1)
C(5)	6885(3)	125(7)	4581(2)	22(1)
C(6)	6159(3)	-1452(7)	4890(2)	22(1)
C(7)	6177(3)	-3332(8)	4472(2)	23(1)
C(8)	7187(3)	-4270(7)	4633(2)	19(1)

C(9)	6624(4)	503(8)	3871(3)	28(1)
O(5A)	7471(9)	1390(30)	3636(7)	34(1)
C(10A)	7267(18)	1920(40)	2962(9)	40(2)
C(11A)	7270(30)	-110(60)	2637(13)	60(2)
O(5)	7476(3)	508(11)	3503(2)	34(1)
C(10)	7346(7)	737(16)	2806(4)	40(2)
C(11)	7232(8)	-1480(20)	2582(4)	60(2)
C(12)	9299(3)	823(7)	6820(2)	17(1)
C(13)	9574(3)	2847(7)	6887(2)	22(1)
C(14)	9155(4)	3937(7)	7384(2)	22(1)
C(15)	8471(4)	3071(8)	7812(2)	24(1)
C(16)	8189(3)	1077(8)	7717(2)	22(1)
C(17)	8604(3)	-81(7)	7226(2)	19(1)
C(18)	8050(4)	4274(10)	8356(2)	37(1)
S(1M)	4581(1)	9471(2)	8775(1)	22(1)
O(1M)	5708(3)	12675(5)	9647(2)	26(1)
O(2M)	7897(2)	9359(5)	9212(1)	22(1)
O(3M)	8924(2)	6465(5)	9692(2)	28(1)
O(4M)	8133(3)	10524(6)	11252(2)	39(1)
O(6M)	3872(2)	10870(6)	9034(2)	30(1)
O(7M)	4286(3)	7413(5)	8670(2)	31(1)
N(1M)	5611(3)	9356(6)	9278(2)	19(1)
C(1M)	6011(3)	10941(8)	9658(2)	19(1)
C(2M)	6895(3)	10075(7)	10078(2)	19(1)
C(3M)	7243(3)	8302(7)	9652(2)	16(1)
C(4M)	6275(3)	7525(7)	9310(2)	21(1)
C(5M)	7885(4)	11407(7)	10125(2)	21(1)
C(6M)	8619(3)	10173(7)	9690(2)	22(1)
C(7M)	8957(3)	8301(8)	10070(2)	25(1)

C(8M)	8019(3)	7005(7)	10045(2)	19(1)
C(9M)	8319(3)	11647(8)	10813(2)	24(1)
O(5M)	8960(30)	13180(40)	10853(11)	36(1)
C(10M)	9379(15)	13580(20)	11503(10)	42(2)
C(11M)	8725(10)	15020(20)	11827(5)	55(2)
O(5N)	8940(50)	13210(70)	10864(19)	36(1)
C(10N)	9470(30)	13780(40)	11471(19)	42(2)
C(11N)	9097(19)	15730(40)	11677(10)	55(2)
C(12M)	5077(3)	10437(7)	8060(2)	20(1)
C(13M)	5293(4)	12493(8)	8005(2)	24(1)
C(14M)	5719(4)	13197(8)	7449(2)	25(1)
C(15M)	5926(3)	11908(8)	6931(2)	24(1)
C(16M)	5681(3)	9894(8)	6989(2)	25(1)
C(17M)	5258(3)	9117(8)	7550(2)	24(1)
C(18M)	6436(4)	12727(9)	6343(2)	30(1)

Details of computational study of the Diels-Alder step in the DAL process:[13]

Furanyl diene:



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Imaginary Frequencies: none found

Zero-point correction = 0.238202 (Hartree/Particle)

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Sum of electronic and thermal Free Energies =

-1143.114432 hartrees (-717315.73722432 kcal/mol)

Coordinates (from last standard orientation):

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[13] Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian, Inc.*, Wallingford CT, 2009.

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.080265	1.839306	-0.460650
2	6	-0.039966	2.117052	-1.292418
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6	6	0.431102	2.843784	0.760743
7	1	1.915309	3.140308	-0.811573
8	1	0.792151	3.248117	1.694894
9	6	-2.386291	1.138640	-0.649274
10	1	-2.993400	1.269023	0.253099
11	1	-2.926268	1.568957	-1.496076
12	7	-2.196223	-0.284415	-0.984912
13	1	-3.037243	-0.711451	-1.377227
14	16	-1.644508	-1.278350	0.239738
15	8	-2.003469	-2.628774	-0.186149
16	8	-2.084078	-0.794195	1.546196
17	6	0.114591	-1.085704	0.155768
18	6	0.789589	-1.550310	-0.971624
19	6	0.787399	-0.490334	1.216211
20	6	2.168255	-1.400344	-1.032233
21	1	0.244082	-2.018569	-1.785911
22	6	2.170380	-0.351209	1.136849
23	1	0.233683	-0.141693	2.081911
24	6	2.875941	-0.796652	0.016256
25	1	2.708912	-1.756819	-1.904927

26	1	2.708252	0.115222	1.958078
27	6	4.365285	-0.601277	-0.076119
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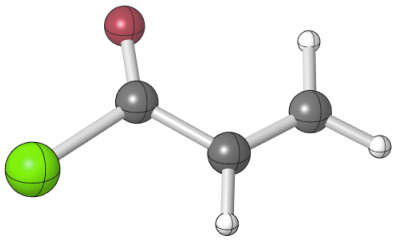

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-651.387753 hartrees (-408752.32888503 kcal/mol)

Coordinates (from last standard orientation):

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5	1	2.613696	0.723459	0.003162
6	8	0.157793	1.519571	-0.000556
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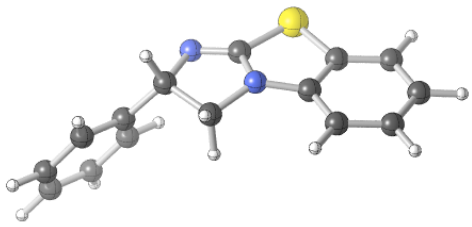
(S)-(–)-BTM catalyst:



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Imaginary Frequencies: none found

Zero-point correction = 0.238948 (Hartree/Particle)

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Sum of electronic and thermal Free Energies =

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Coordinates (from last standard orientation):

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4	6	-4.207606	0.432725	0.561787
5	6	-4.746737	-0.845244	0.732328
6	6	-3.978352	-1.979555	0.473061
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8	1	-4.800047	1.317910	0.772337
9	1	-5.771715	-0.949580	1.072628
10	1	-4.410212	-2.965542	0.613459
11	6	-0.539268	1.070167	-0.533267
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13	7	-0.860156	-0.271737	-0.595974
14	6	0.395774	-1.012047	-0.630557
15	6	1.379397	0.139158	-1.027978
16	7	0.675758	1.406318	-0.721608
17	6	2.713946	0.013122	-0.330895
18	6	3.702254	-0.807909	-0.878940
19	6	2.957188	0.651293	0.886801
20	6	4.914045	-0.995064	-0.218440
21	1	3.520707	-1.300931	-1.831631
22	6	4.171891	0.470832	1.545054
23	1	2.193991	1.298559	1.309570
24	6	5.151970	-0.354415	0.996466
25	1	5.674328	-1.635977	-0.655503
26	1	4.353595	0.977589	2.488602
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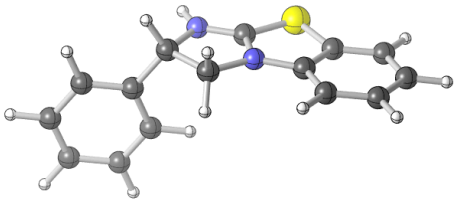
28	1	0.621577	-1.422838	0.361589

29	1	0.374413	-1.817883	-1.366373
30	1	1.544570	0.099252	-2.112384

(S)-(–)-BTMH^{+} catalyst:



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Imaginary Frequencies: none found

Zero-point correction = 0.252177 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-1086.464936 hartrees (-681767.61198936 kcal/mol)

Coordinates (from last standard orientation):

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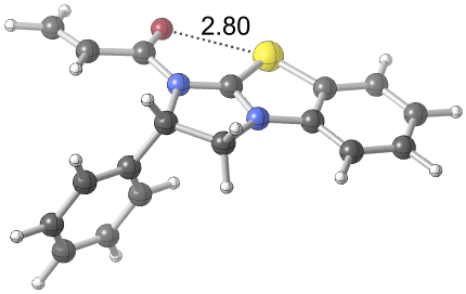
5	6	-4.703673	-0.888323	0.565448
6	6	-3.981804	-1.954046	0.019502
7	1	-2.095513	-2.616651	-0.824150
8	1	-4.687680	1.198952	1.133952
9	1	-5.730768	-1.039168	0.880075
10	1	-4.456073	-2.924127	-0.085294
11	6	-0.516153	1.131255	-0.341776
12	16	-1.829364	2.009836	0.361225
13	7	-0.800848	-0.145068	-0.590833
14	6	0.349696	-0.845956	-1.171867
15	1	0.631074	-1.688015	-0.536040
16	1	0.099113	-1.200776	-2.172759
17	6	1.448700	0.268075	-1.200094
18	7	0.715701	1.448732	-0.674863
19	6	2.670304	-0.036010	-0.364351
20	6	3.931711	-0.055251	-0.955602
21	6	2.541015	-0.297076	1.003213
22	6	5.060598	-0.339353	-0.187717
23	1	4.031461	0.148751	-2.018696
24	6	3.666879	-0.576404	1.769515
25	1	1.555907	-0.281245	1.466950
26	6	4.928873	-0.598196	1.173484
27	1	6.040740	-0.356114	-0.654352
28	1	3.562114	-0.777816	2.831264

29	1	5.807348	-0.819166	1.772115
30	1	1.746049	0.477425	-2.229628
31	1	1.143848	2.357782	-0.535728

Chiral acylammonium dienophile derived from (S)-(–)-BTM and acryloyl chloride:



Charge = 1 Multiplicity = 1

Imaginary Frequencies: none found

Zero-point correction = 0.296520 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-1277.087048 hartrees (-801384.89349048 kcal/mol)

Coordinates (from last standard orientation):

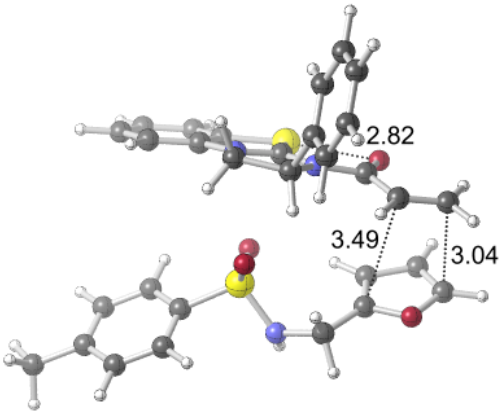
Center	Atomic	Coordinates (Angstroms)

Number	Number	X	Y	Z
1	6	-3.277877	-1.839434	-0.605224
2	6	-2.532234	-0.703183	-0.307264
3	6	-3.093937	0.403640	0.340799
4	6	-4.434871	0.403077	0.711405
5	6	-5.186047	-0.728948	0.414705
6	6	-4.615429	-1.833282	-0.232622
7	6	-0.737039	0.704946	-0.197898
8	6	-0.160667	-1.257724	-1.279016
9	6	1.109220	-0.360029	-1.133432
10	6	2.191799	-0.989674	-0.287568
11	6	3.372181	-1.421614	-0.890785
12	6	1.998945	-1.182860	1.082453
13	6	4.355580	-2.050198	-0.129149
14	6	2.983701	-1.805575	1.842236
15	6	4.162264	-2.241787	1.236443
16	6	1.228558	2.078511	-0.180499
17	6	2.627862	2.199734	-0.632610
18	6	3.354551	3.231925	-0.204089
19	1	-2.822526	-2.685864	-1.108947
20	1	-4.879483	1.257010	1.211455
21	1	-6.234788	-0.754253	0.690958
22	1	-5.228836	-2.700932	-0.451349
23	1	-0.037882	-2.223815	-0.786963
24	1	-0.453776	-1.397819	-2.320916
25	1	3.520770	-1.263879	-1.956438
26	1	1.080369	-0.844510	1.558479
27	1	5.273098	-2.385316	-0.602947

28	1	2.831718	-1.951200	2.907267
29	1	4.929869	-2.728295	1.830496
30	1	1.498397	-0.105116	-2.120958
31	1	3.034977	1.455336	-1.308063
32	1	2.935556	3.965861	0.478745
33	8	0.611030	2.928705	0.431287
34	7	-1.188017	-0.473569	-0.585503
35	7	0.561011	0.883147	-0.505225
36	16	-1.900649	1.691214	0.587327
37	1	4.384376	3.361532	-0.520547

DAL process leading to endo cycloadduct:

Reactant:



Charge = 1 Multiplicity = 1

Imaginary Frequencies: none found

Zero-point correction = 0.535897 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-2420.199164 hartrees (-1518699.17740164 kcal/mol)

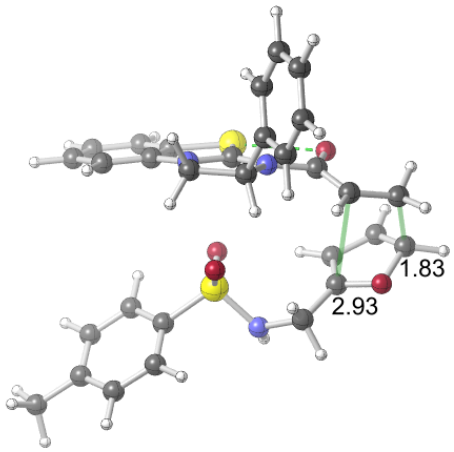
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.876841	-3.353288	0.357633
2	6	-0.893576	-2.533028	0.901822
3	6	-0.876747	-2.200780	2.263162
4	6	-1.857926	-2.685398	3.121777
5	6	-2.846170	-3.502992	2.582747
6	6	-2.854320	-3.832296	1.220999
7	6	0.921337	-1.156866	1.004052
8	6	0.648281	-1.967164	-1.145343
9	6	1.811977	-0.927030	-1.134361
10	6	3.125353	-1.480534	-1.634981
11	6	3.636588	-1.026090	-2.850252
12	6	3.814356	-2.461988	-0.917316
13	6	4.826993	-1.550080	-3.350626
14	6	5.006087	-2.980407	-1.414699
15	6	5.512919	-2.525841	-2.632539
16	6	2.730101	0.412464	0.921719
17	6	3.504378	1.282044	0.020494
18	6	4.418097	2.100546	0.545645
19	6	0.825969	3.482910	0.399144
20	6	0.790700	2.995101	1.669653
21	6	1.926891	3.556683	2.340970
22	6	2.557766	4.335311	1.426933

23	6	-0.089155	3.376188	-0.782556
24	6	-3.251574	0.921885	-0.812855
25	6	-3.692798	1.409399	-2.044230
26	6	-4.079100	0.173938	0.016722
27	6	-4.994344	1.141160	-2.437778
28	6	-5.383539	-0.084228	-0.398522
29	6	-5.856576	0.390712	-1.623454
30	6	-7.263881	0.112473	-2.076198
31	1	-1.873431	-3.598340	-0.699534
32	1	-1.854628	-2.431846	4.176771
33	1	-3.623122	-3.891341	3.232775
34	1	-3.637578	-4.473491	0.830556
35	1	1.001496	-2.977463	-1.365597
36	1	-0.148010	-1.677062	-1.829341
37	1	3.102233	-0.257840	-3.403961
38	1	3.422129	-2.821061	0.031937
39	1	5.218487	-1.190345	-4.297131
40	1	5.539836	-3.740857	-0.852983
41	1	6.443210	-2.931285	-3.018442
42	1	1.517959	-0.051921	-1.715030
43	1	3.296023	1.262005	-1.043991
44	1	4.622724	2.095115	1.612053
45	1	0.048722	2.321363	2.076257
46	1	2.231481	3.387187	3.363748
47	1	3.440799	4.956629	1.457211
48	1	4.992523	2.777462	-0.079040
49	1	-0.259907	4.373603	-1.199713
50	1	0.344274	2.764042	-1.578562
51	1	-1.880287	3.296354	0.310234

52	1	-3.029374	1.994445	-2.674401
53	1	-3.711157	-0.194822	0.968990
54	1	-5.354743	1.517256	-3.391442
55	1	-6.041712	-0.664995	0.241506
56	1	-7.811843	-0.472755	-1.334066
57	1	-7.807574	1.047440	-2.247557
58	1	-7.264717	-0.441069	-3.021049
59	8	2.742892	0.460211	2.136909
60	8	1.894844	4.304571	0.240737
61	8	-1.418412	0.676940	1.031729
62	8	-0.669973	0.618931	-1.356708
63	7	0.162542	-1.919324	0.238090
64	7	1.877359	-0.523688	0.304693
65	7	-1.401792	2.817298	-0.454646
66	16	0.489639	-1.148331	2.662245
67	16	-1.566692	1.172178	-0.338185

Transition state 1 (TS1):



Charge = 1 Multiplicity = 1

Imaginary Frequencies: 1 (-345.8703 1/cm)

Zero-point correction = 0.536311 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-2420.171089 hartrees (-1518681.56005839 kcal/mol)

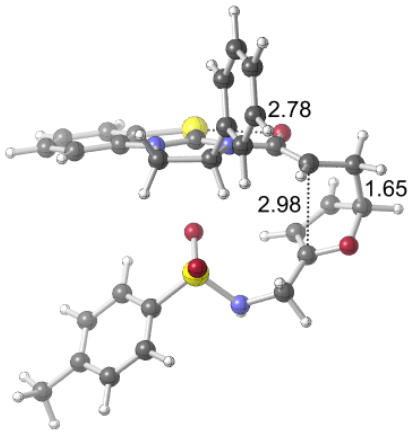
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.794895	-3.483645	-0.057538
2	6	0.839441	-2.679478	-0.669545
3	6	0.840523	-2.455041	-2.053353
4	6	1.807577	-3.039014	-2.862458
5	6	2.768830	-3.843972	-2.255862
6	6	2.761303	-4.061855	-0.873699
7	6	-0.926212	-1.242501	-0.889991
8	6	-0.680711	-1.882208	1.317614
9	6	-1.814446	-0.813510	1.201099
10	6	-3.158928	-1.294376	1.698618
11	6	-3.751199	-0.688218	2.805332
12	6	-3.803907	-2.362263	1.068442
13	6	-4.977456	-1.147842	3.284464
14	6	-5.029462	-2.817477	1.542733
15	6	-5.617271	-2.211354	2.653600
16	6	-2.607526	0.483699	-0.945253
17	6	-3.177374	1.508515	-0.165088
18	6	-3.922558	2.503365	-0.848401

19	6	-0.918025	3.329013	-0.552523
20	6	-0.824393	2.792339	-1.833863
21	6	-1.994487	3.150164	-2.481011
22	6	-2.819359	3.801051	-1.520498
23	6	0.058278	3.367553	0.584350
24	6	3.275132	1.004117	0.724795
25	6	3.748542	1.646883	1.869730
26	6	4.087926	0.172703	-0.037723
27	6	5.070245	1.454759	2.240848
28	6	5.412279	-0.006316	0.354083
29	6	5.919427	0.627076	1.490598
30	6	7.348072	0.429754	1.918300
31	1	1.780722	-3.644012	1.015522
32	1	1.816189	-2.869703	-3.934463
33	1	3.534806	-4.308336	-2.868088
34	1	3.522418	-4.693273	-0.426988
35	1	-1.064621	-2.853155	1.639047
36	1	0.124047	-1.552652	1.973553
37	1	-3.251367	0.144644	3.294329
38	1	-3.346742	-2.838078	0.202904
39	1	-5.432808	-0.671630	4.147451
40	1	-5.526806	-3.645275	1.046638
41	1	-6.573498	-2.568286	3.023868
42	1	-1.515239	0.095564	1.725572
43	1	-3.012800	1.562097	0.903830
44	1	-4.418637	2.188479	-1.764534
45	1	-0.015333	2.175565	-2.201085
46	1	-2.298773	2.887395	-3.484317
47	1	-3.510364	4.605516	-1.747171

48	1	-4.548005	3.139211	-0.224892
49	1	0.202205	4.412197	0.880024
50	1	-0.339264	2.836877	1.453349
51	1	1.840139	3.257089	-0.528843
52	1	3.095516	2.292756	2.449429
53	1	3.694094	-0.317213	-0.922776
54	1	5.457132	1.953352	3.125609
55	1	6.060558	-0.647460	-0.236273
56	1	7.908742	-0.144208	1.176795
57	1	7.847899	1.392782	2.062476
58	1	7.394201	-0.106448	2.872468
59	8	-2.640830	0.392161	-2.178219
60	8	-2.009189	4.073600	-0.415980
61	8	1.399223	0.568283	-1.043363
62	8	0.710737	0.688871	1.361216
63	7	-0.197557	-1.982134	-0.062314
64	7	-1.842994	-0.520203	-0.258277
65	7	1.367670	2.815755	0.261587
66	16	-0.488658	-1.387855	-2.546685
67	16	1.573114	1.168319	0.279408

Intermediate (INT):



Charge = 1 Multiplicity = 1

Imaginary Frequencies: none found

Zero-point correction = 0.537064 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-2420.171447 hartrees (-1518681.78470697 kcal/mol)

Coordinates (from last standard orientation):

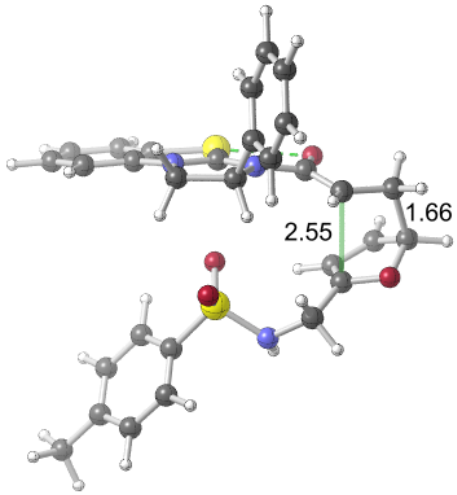
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.669753	3.752528	0.275274
2	6	-0.748258	2.992142	-0.436645
3	6	-0.728959	2.982060	-1.837812
4	6	-1.631143	3.750634	-2.563229
5	6	-2.555034	4.516612	-1.856244
6	6	-2.574831	4.513588	-0.457486
7	6	0.960045	1.521263	-0.843346
8	6	0.560666	1.693397	1.421898

9	6	1.674941	0.631338	1.155656
10	6	2.972095	0.924385	1.873334
11	6	3.342357	0.142502	2.967092
12	6	3.778728	1.996021	1.483775
13	6	4.508751	0.431907	3.673387
14	6	4.945842	2.281202	2.185546
15	6	5.311207	1.500918	3.283087
16	6	2.541099	-0.275012	-1.141561
17	6	3.139881	-1.363943	-0.522744
18	6	3.840067	-2.295907	-1.397826
19	6	0.908479	-3.257676	-1.069518
20	6	0.687788	-2.492241	-2.225740
21	6	1.839011	-2.589315	-2.964220
22	6	2.810121	-3.331430	-2.171677
23	6	0.003371	-3.603374	0.073130
24	6	-3.161368	-1.228400	0.776297
25	6	-3.814917	-2.043408	1.702299
26	6	-3.836997	-0.259111	0.044031
27	6	-5.178989	-1.878261	1.882990
28	6	-5.207436	-0.110378	0.242976
29	6	-5.893202	-0.911636	1.158160
30	1	-1.674457	3.745393	1.360512
31	1	-1.619146	3.750969	-3.648705
32	1	-3.270380	5.122240	-2.402681
33	1	-3.307625	5.115966	0.069373
34	1	0.919567	2.522201	2.035708
35	1	-0.325725	1.243950	1.875725
36	1	2.715007	-0.695391	3.262650
37	1	3.497074	2.604302	0.626791

38	1	4.790725	-0.180020	4.524789
39	1	5.571369	3.113390	1.877081
40	1	6.221657	1.726009	3.830283
41	1	1.306734	-0.358978	1.436514
42	1	4.365688	-1.808933	-2.222186
43	1	-0.198610	-1.911241	-2.438417
44	1	2.049509	-2.134425	-3.921591
45	1	4.515895	-2.964674	-0.863002
46	1	-0.146047	-4.689151	0.064544
47	1	0.486960	-3.358051	1.023884
48	1	-1.820024	-3.111995	-0.843389
49	1	-3.263328	-2.792905	2.262483
50	1	-3.303071	0.363785	-0.666510
51	1	-5.704874	-2.506183	2.597271
52	1	-5.749613	0.642339	-0.322166
53	8	2.510140	-0.047947	-2.369490
54	8	2.049657	-3.906974	-1.113889
55	8	-0.972230	-0.424214	-0.428510
56	8	-0.734109	-1.390491	1.864893
57	7	0.244320	2.164752	0.073345
58	7	1.821676	0.663811	-0.320500
59	7	-1.305810	-2.969689	0.027687
60	16	0.532022	1.900523	-2.468854
61	16	-1.416897	-1.399280	0.571129
62	6	-7.372254	-0.749862	1.378808
63	1	-7.575627	-0.426418	2.405313
64	1	-7.798440	-0.011955	0.695357
65	1	-7.892625	-1.701546	1.230171
66	1	3.095205	-1.522954	0.546427

67	1	3.415379	-4.093981	-2.658516

Transition state 2 (TS2):



Charge = 1 Multiplicity = 1

Imaginary Frequencies: 1 (-140.0196 1/cm)

Zero-point correction = 0.536243 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-2420.172570 hartrees (-1518682.4894007 kcal/mol)

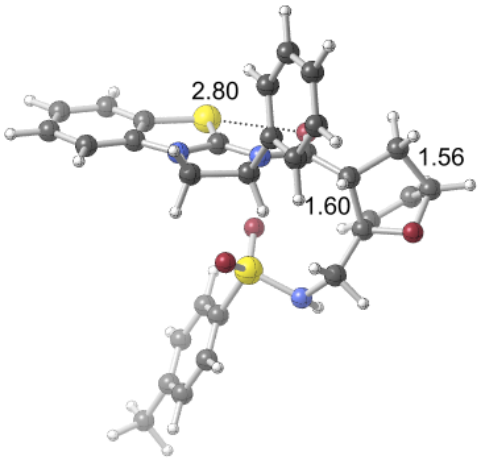
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.426448	3.952549	0.468582
2	6	-0.603051	3.133591	-0.297365
3	6	-0.639107	3.155876	-1.697749
4	6	-1.501431	4.013116	-2.370464
5	6	-2.328931	4.835146	-1.609893
6	6	-2.292044	4.802170	-0.211212
7	6	0.954709	1.537082	-0.805749
8	6	0.662775	1.682904	1.478179
9	6	1.701510	0.563290	1.148105
10	6	3.055255	0.784133	1.782299
11	6	3.449390	-0.020248	2.850686
12	6	3.893022	1.811884	1.343263
13	6	4.672157	0.201542	3.481990
14	6	5.115865	2.029795	1.970315
15	6	5.506382	1.225726	3.041651
16	6	2.379346	-0.358125	-1.206503
17	6	2.897889	-1.540547	-0.637500
18	6	3.664855	-2.398686	-1.531543
19	6	0.951219	-3.161300	-0.937493
20	6	0.618665	-2.552097	-2.176290
21	6	1.653081	-2.833817	-3.016681
22	6	2.665124	-3.531069	-2.226095
23	6	0.125233	-3.372386	0.299846

24	6	-3.239739	-1.202075	0.737733
25	6	-3.898294	-2.057508	1.623023
26	6	-3.924133	-0.255826	-0.016481
27	6	-5.276109	-1.958854	1.737268
28	6	-5.307762	-0.173329	0.116746
29	6	-5.998780	-1.016887	0.989242
30	1	-1.386365	3.921512	1.552554
31	1	-1.531637	4.038367	-3.455030
32	1	-3.012596	5.511120	-2.112718
33	1	-2.948683	5.452477	0.357386
34	1	1.089402	2.470440	2.102313
35	1	-0.236300	1.271559	1.941716
36	1	2.794522	-0.820348	3.188455
37	1	3.591084	2.439389	0.507147
38	1	4.972540	-0.427970	4.314007
39	1	5.765987	2.827216	1.623233
40	1	6.461045	1.397175	3.529726
41	1	1.298751	-0.405439	1.454621
42	1	4.121878	-1.866455	-2.366297
43	1	-0.236063	-1.911611	-2.349030
44	1	1.798715	-2.479620	-4.028075
45	1	4.406640	-3.005398	-1.011054
46	1	0.065185	-4.453023	0.469902
47	1	0.608232	-2.939740	1.180448
48	1	-1.733686	-3.113582	-0.644731
49	1	-3.340001	-2.787247	2.202194
50	1	-3.384995	0.401056	-0.691848
51	1	-5.805925	-2.619909	2.418029
52	1	-5.857174	0.560436	-0.466047

53	8	2.351165	-0.085441	-2.412744
54	8	1.968054	-4.001254	-1.085805
55	8	-1.044688	-0.331816	-0.413392
56	8	-0.865705	-1.119393	1.949077
57	7	0.335309	2.212518	0.152958
58	7	1.763224	0.594814	-0.334939
59	7	-1.236359	-2.857574	0.210249
60	16	0.505081	1.995938	-2.401698
61	16	-1.480187	-1.267304	0.628975
62	6	-7.492110	-0.922488	1.141972
63	1	-7.755255	-0.608275	2.157775
64	1	-7.919133	-0.203208	0.439373
65	1	-7.963111	-1.895931	0.972155
66	1	2.934128	-1.679421	0.435610
67	1	3.267452	-4.318155	-2.672503

Product:



Charge = 1 Multiplicity = 1

Imaginary Frequencies: none found

Zero-point correction = 0.540950 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-2420.200296 hartrees (-1518699.88774296 kcal/mol)

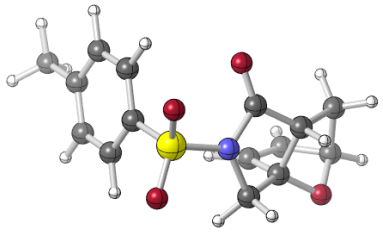
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.451652	4.581019	-0.784546
2	6	0.085359	3.514159	0.030243
3	6	0.365836	3.501961	1.402801
4	6	1.026917	4.569584	2.001696
5	6	1.393568	5.639487	1.192830
6	6	1.109695	5.644173	-0.179526
7	6	-0.792299	1.500063	0.649133
8	6	-1.101849	1.850757	-1.616431
9	6	-1.807442	0.522349	-1.198672
10	6	-3.307716	0.546036	-1.383708
11	6	-3.878279	-0.188102	-2.423518
12	6	-4.122912	1.316264	-0.549935
13	6	-5.255101	-0.147182	-2.635809
14	6	-5.497916	1.352080	-0.759843
15	6	-6.065337	0.621711	-1.803989
16	6	-1.657286	-0.679194	1.127716
17	6	-2.116463	-1.974516	0.526325
18	6	-3.125402	-2.733690	1.420108
19	6	-0.960834	-3.073662	0.370822
20	6	-0.326608	-3.259933	1.742839

21	6	-1.232270	-3.922530	2.462526
22	6	-2.421471	-4.119547	1.545569
23	6	-0.070388	-3.001744	-0.874851
24	6	3.415307	-0.985529	-0.548971
25	6	3.974567	-1.283046	-1.792854
26	6	4.200097	-0.633695	0.542873
27	6	5.353180	-1.229698	-1.929606
28	6	5.582541	-0.586467	0.382778
29	6	6.175164	-0.884059	-0.846040
30	1	0.228664	4.572974	-1.846333
31	1	1.248435	4.565213	3.064045
32	1	1.907984	6.485367	1.636404
33	1	1.408493	6.494300	-0.783628
34	1	-1.805172	2.574802	-2.031109
35	1	-0.274103	1.676087	-2.304169
36	1	-3.242840	-0.794097	-3.065208
37	1	-3.685015	1.885940	0.267249
38	1	-5.694153	-0.721080	-3.446161
39	1	-6.127284	1.950161	-0.108075
40	1	-7.138522	0.650107	-1.965919
41	1	-1.362957	-0.306026	-1.750144
42	1	-3.277503	-2.254630	2.388460
43	1	0.602052	-2.806055	2.067680
44	1	-1.212345	-4.157273	3.520057
45	1	-4.085247	-2.833479	0.909641
46	1	-0.039566	-4.009913	-1.296050
47	1	-0.494356	-2.342402	-1.636895
48	1	1.829206	-3.220753	-0.017992
49	1	3.341389	-1.552075	-2.633082

50	1	3.736381	-0.402753	1.496346
51	1	5.806492	-1.457961	-2.890555
52	1	6.207961	-0.313209	1.227675
53	8	-1.429561	-0.504254	2.305595
54	8	-1.794115	-4.224624	0.265626
55	8	1.333873	-0.628337	1.011478
56	8	1.008660	-0.259557	-1.436672
57	7	-0.578527	2.348387	-0.339973
58	7	-1.432014	0.389752	0.241550
59	7	1.328257	-2.613956	-0.670563
60	16	-0.221541	2.021967	2.177353
61	16	1.659346	-1.016481	-0.363678
62	1	-2.531258	-1.816822	-0.470199
63	1	-3.080371	-4.966606	1.729043
64	6	7.669482	-0.852138	-1.015094
65	1	8.060712	-1.865111	-1.160126
66	1	7.951035	-0.266152	-1.895467
67	1	8.159391	-0.420891	-0.138798

Lactam:



Charge = 0 Multiplicity = 1

Imaginary Frequencies: none found

Zero-point correction = 0.285169 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-1333.723404 hartrees (-836924.77324404 kcal/mol)

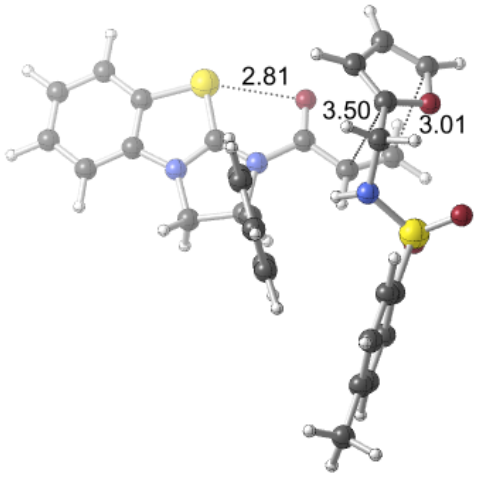
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.217397	0.627771	1.155317
2	6	-2.590653	0.121585	0.807775
3	6	-3.384162	-1.081645	1.316300
4	6	-2.366851	-0.240358	-0.685431
5	6	-1.544986	-1.521227	-0.762466
6	6	-2.386650	-2.493466	-0.416892
7	6	-3.679404	-1.777297	-0.076266
8	6	-1.683656	1.006211	-1.217195
9	6	1.847187	0.621933	-0.110256
10	6	2.185674	-0.049128	-1.286049
11	6	2.349917	0.231998	1.127306
12	6	3.042684	-1.138650	-1.207410
13	6	3.210073	-0.860743	1.180903
14	6	3.560802	-1.562438	0.023850
15	1	-2.830447	-1.747171	1.980896
16	1	-0.482941	-1.565500	-0.981092
17	1	-2.193477	-3.548512	-0.264252
18	1	-4.303306	-0.765471	1.811842
19	1	-1.083539	0.849196	-2.114568
20	1	-2.378274	1.837341	-1.367753
21	1	1.798983	0.289436	-2.242416

22	1	2.070983	0.773895	2.024287
23	1	3.321047	-1.668288	-2.114783
24	1	3.614385	-1.174663	2.139102
25	8	-0.554171	0.551875	2.160134
26	8	-3.669809	-0.679036	-1.022033
27	8	0.925330	2.854328	0.935580
28	8	0.725405	2.511226	-1.558813
29	7	-0.801746	1.268284	-0.041138
30	16	0.715866	1.979431	-0.203287
31	1	-3.238046	1.007958	0.800997
32	1	-4.615089	-2.328231	-0.144900
33	6	4.478379	-2.753769	0.085596
34	1	3.931399	-3.673838	-0.148599
35	1	5.286848	-2.661604	-0.646307
36	1	4.920075	-2.865251	1.078674

DAL process leading to endo cycloadduct (opposite enantiomer):

Reactant:



Charge = 1 Multiplicity = 1

Imaginary Frequencies: none found

Zero-point correction = 0.536310 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-2420.192652 hartrees (-1518695.09105652 kcal/mol)

Coordinates (from last standard orientation):

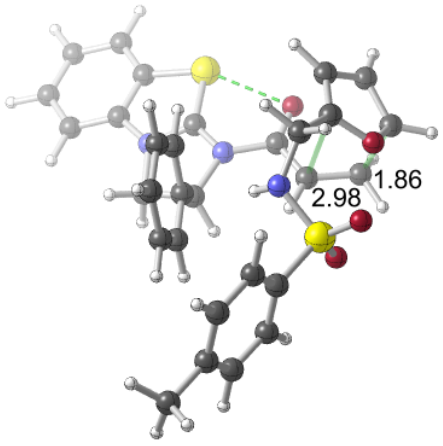
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-5.552436	-2.889935	-0.002115
2	6	-4.975051	-1.631138	-0.133811
3	6	-5.702710	-0.455522	0.088946
4	6	-7.044321	-0.509357	0.452777
5	6	-7.626307	-1.765006	0.588167
6	6	-6.891713	-2.936791	0.362052

7	6	-3.384893	-0.041358	-0.535822
8	6	-2.515827	-2.151619	-0.894389
9	6	-1.365826	-1.096661	-0.979374
10	6	-0.334878	-1.282595	0.113561
11	6	0.817149	-2.020734	-0.173234
12	6	-0.557275	-0.824530	1.415475
13	6	1.725537	-2.323911	0.839403
14	6	0.357136	-1.124524	2.424385
15	6	1.494034	-1.880478	2.139770
16	6	-1.639497	1.504398	-1.119066
17	6	-0.241316	1.623704	-1.555886
18	6	0.168402	2.770827	-2.103155
19	6	1.213655	3.052005	1.291387
20	6	-0.069086	3.320299	1.662389
21	6	-0.483620	4.452151	0.887939
22	6	0.578487	4.775433	0.106209
23	6	2.204232	2.033215	1.738789
24	6	4.296169	-0.553541	-0.370770
25	6	4.242234	-1.398362	-1.470846
26	6	4.966228	-0.918628	0.797224
27	6	4.874666	-2.639059	-1.397477
28	6	5.590726	-2.155401	0.852031
29	6	5.557648	-3.031259	-0.244397
30	6	6.259537	-4.360326	-0.168311
31	1	-4.972695	-3.789335	-0.182106
32	1	-7.615070	0.396815	0.627647
33	1	-8.670598	-1.834986	0.873495
34	1	-7.376233	-3.900851	0.474538
35	1	-2.315722	-2.919451	-0.146149

36	1	-2.734210	-2.611063	-1.860456
37	1	0.998403	-2.362200	-1.189817
38	1	-1.442829	-0.238478	1.649017
39	1	2.623010	-2.890122	0.605128
40	1	0.178955	-0.766535	3.433996
41	1	2.207436	-2.107454	2.926243
42	1	-0.892444	-1.140971	-1.961944
43	1	0.428102	0.774947	-1.459425
44	1	-0.519665	3.600296	-2.235757
45	1	-0.638501	2.785607	2.410717
46	1	-1.442625	4.949452	0.906851
47	1	0.754541	5.547923	-0.628072
48	1	1.194177	2.884460	-2.438127
49	1	1.855315	1.595587	2.678003
50	1	3.176863	2.496844	1.919886
51	1	1.569321	0.417528	0.538998
52	1	3.709283	-1.091016	-2.364855
53	1	4.986887	-0.247445	1.651627
54	1	4.840471	-3.308629	-2.252450
55	1	6.117684	-2.451795	1.755346
56	1	5.978102	-4.901717	0.740382
57	1	6.021322	-4.985541	-1.032272
58	1	7.345611	-4.219241	-0.139930
59	8	-2.430154	2.418493	-0.985321
60	8	1.618065	3.936176	0.345286
61	8	4.452614	2.069644	-0.065425
62	8	2.815099	1.109269	-1.728610
63	7	-3.660922	-1.331612	-0.482649
64	7	-2.101105	0.194891	-0.862114

65	7	2.415749	0.920700	0.807114
66	16	-4.706961	0.988749	-0.172648
67	16	3.497434	1.030819	-0.435821

Transition state 1(TS1):



Charge = 1 Multiplicity = 1

Imaginary Frequencies: 1 (-381.5746 1/cm)

Zero-point correction = 0.536963 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-2420.166207 hartrees (-1518678.49655457 kcal/mol)

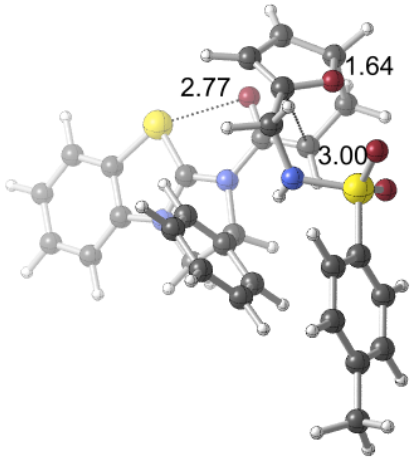
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-5.469924	-2.924467	-0.246197
2	6	-4.902738	-1.655080	-0.218744
3	6	-5.650506	-0.518953	0.116138
4	6	-6.999105	-0.628069	0.435736
5	6	-7.572290	-1.895942	0.413705
6	6	-6.818158	-3.026393	0.076812
7	6	-3.317839	-0.009989	-0.402928
8	6	-2.435547	-2.049511	-1.023796
9	6	-1.302845	-0.972587	-0.974698
10	6	-0.266684	-1.299940	0.078286
11	6	0.878743	-2.006520	-0.301123
12	6	-0.486119	-1.009391	1.427922
13	6	1.787816	-2.437828	0.663485
14	6	0.426002	-1.441729	2.389579
15	6	1.558948	-2.161455	2.010110
16	6	-1.618357	1.638638	-0.876645
17	6	-0.295903	1.862050	-1.312722
18	6	0.000546	3.170046	-1.765552

19	6	0.985460	2.875279	1.178512
20	6	-0.294480	3.328712	1.481434
21	6	-0.589355	4.301366	0.538168
22	6	0.487911	4.313063	-0.385863
23	6	1.879781	1.869603	1.829459
24	6	4.325097	-0.425571	-0.300250
25	6	4.350794	-1.122553	-1.501175
26	6	4.930314	-0.930703	0.850663
27	6	4.993320	-2.358984	-1.545054
28	6	5.564729	-2.162019	0.788069
29	6	5.605663	-2.893677	-0.409226
30	6	6.314530	-4.219911	-0.459753
31	1	-4.875499	-3.792863	-0.510627
32	1	-7.586464	0.247010	0.694597
33	1	-8.622600	-2.006555	0.661890
34	1	-7.292560	-4.002089	0.066008
35	1	-2.211547	-2.907489	-0.388417
36	1	-2.655739	-2.379968	-2.041232
37	1	1.056617	-2.219993	-1.352739
38	1	-1.368041	-0.448345	1.729118
39	1	2.682078	-2.975317	0.359116
40	1	0.249756	-1.215745	3.437084
41	1	2.269866	-2.493794	2.760611
42	1	-0.830958	-0.876012	-1.954915
43	1	0.436089	1.066087	-1.373251
44	1	-0.834882	3.749089	-2.154980
45	1	-0.921485	2.954599	2.278878
46	1	-1.507931	4.859883	0.429521
47	1	0.836262	5.180541	-0.934748

48	1	0.915037	3.268071	-2.346908
49	1	1.349403	1.393723	2.657086
50	1	2.760039	2.379754	2.233233
51	1	1.570150	0.269715	0.529204
52	1	3.872667	-0.707340	-2.382589
53	1	4.890866	-0.371950	1.781581
54	1	5.018368	-2.915731	-2.477764
55	1	6.035520	-2.569888	1.678706
56	1	6.057109	-4.835957	0.407135
57	1	6.061948	-4.772788	-1.367945
58	1	7.400426	-4.073703	-0.444616
59	8	-2.474895	2.503620	-0.661079
60	8	1.515690	3.567046	0.179931
61	8	4.377122	2.140706	0.386493
62	8	2.906938	1.398732	-1.523749
63	7	-3.584506	-1.306507	-0.498765
64	7	-2.046926	0.278885	-0.681876
65	7	2.336481	0.809676	0.936571
66	16	-4.667188	0.958562	0.046155
67	16	3.497968	1.141246	-0.211369

Intermediate (INT):



Charge = 1 Multiplicity = 1

Imaginary Frequencies: none found

Zero-point correction = 0.538023 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-2420.167204 hartrees (-1518679.12218204 kcal/mol)

Coordinates (from last standard orientation):

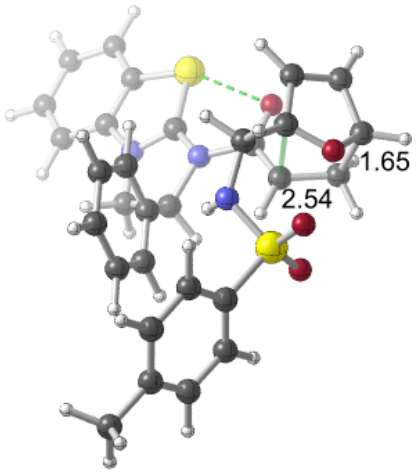
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-5.469824	-2.920873	-0.219987
2	6	-4.894150	-1.655490	-0.210650
3	6	-5.628848	-0.513446	0.134082
4	6	-6.970497	-0.614325	0.482431
5	6	-7.552758	-1.879031	0.478076
6	6	-6.812277	-3.014544	0.131229
7	6	-3.302198	-0.018504	-0.436540

8	6	-2.448806	-2.062891	-1.076702
9	6	-1.309246	-0.992833	-1.040399
10	6	-0.266560	-1.322706	0.006055
11	6	0.893110	-1.999731	-0.382639
12	6	-0.496519	-1.066617	1.361344
13	6	1.805208	-2.437239	0.576821
14	6	0.417391	-1.506088	2.317717
15	6	1.564605	-2.197355	1.928096
16	6	-1.593122	1.624463	-0.931179
17	6	-0.294615	1.842203	-1.361039
18	6	0.032095	3.222930	-1.721659
19	6	0.916024	2.829982	1.204526
20	6	-0.385016	3.259935	1.514924
21	6	-0.725041	4.160458	0.539424
22	6	0.362824	4.184037	-0.434621
23	6	1.809712	1.822377	1.855993
24	6	4.350774	-0.372788	-0.255357
25	6	4.418930	-1.034271	-1.474286
26	6	4.930374	-0.902980	0.897879
27	6	5.079921	-2.260334	-1.535443
28	6	5.582512	-2.123776	0.817873
29	6	5.667104	-2.819737	-0.398582
30	1	-4.886032	-3.794363	-0.491298
31	1	-7.547579	0.265293	0.749356
32	1	-8.598344	-1.981873	0.748699
33	1	-7.291496	-3.988012	0.135067
34	1	-2.214835	-2.930577	-0.458357
35	1	-2.693538	-2.379022	-2.093296
36	1	1.078806	-2.187416	-1.437800

37	1	-1.390135	-0.528613	1.671072
38	1	2.709418	-2.953641	0.265468
39	1	0.231403	-1.308424	3.369322
40	1	2.276690	-2.536241	2.674621
41	1	-0.843481	-0.899312	-2.023955
42	1	-0.793753	3.743896	-2.212972
43	1	-0.981522	2.898952	2.341280
44	1	-1.651726	4.705253	0.432270
45	1	0.703592	5.145318	-0.814814
46	1	0.938729	3.291215	-2.324339
47	1	1.270471	1.318725	2.660677
48	1	2.672591	2.341154	2.286757
49	1	1.540516	0.287912	0.471356
50	1	3.960512	-0.599885	-2.356847
51	1	4.859083	-0.371362	1.842772
52	1	5.140978	-2.787708	-2.483414
53	1	6.035563	-2.550218	1.709119
54	8	-2.450581	2.499069	-0.680937
55	8	1.433266	3.499707	0.206327
56	8	4.343534	2.168081	0.521185
57	8	2.969864	1.475653	-1.479471
58	7	-3.579421	-1.317591	-0.516790
59	7	-2.042559	0.261466	-0.743277
60	7	2.292688	0.805562	0.932239
61	16	-4.637956	0.960272	0.038977
62	16	3.504189	1.181714	-0.151642
63	6	6.385044	-4.140535	-0.464036
64	1	5.994753	-4.835535	0.286329
65	1	6.279459	-4.601623	-1.449065

66	1	7.453427	-4.009000	-0.261324
67	1	0.426183	1.045409	-1.496175

Transition state 2 (TS2):



Charge = 1 Multiplicity = 1

Imaginary Frequencies: 1 (-151.6403 1/cm)

Zero-point correction = 0.537385 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-2420.165694 hartrees (-1518678.17464194 kcal/mol)

Coordinates (from last standard orientation):

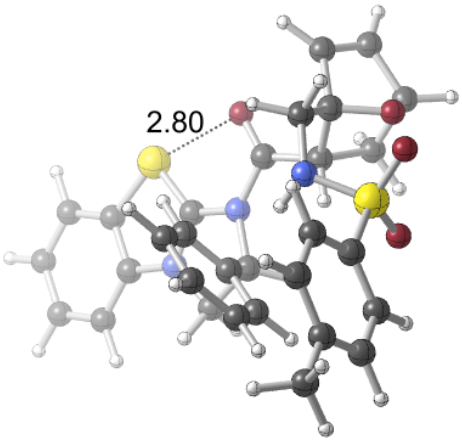
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-5.524239	-2.923595	-0.341118
2	6	-4.946145	-1.663241	-0.232692

3	6	-5.686941	-0.541482	0.159353
4	6	-7.041260	-0.654825	0.452276
5	6	-7.626225	-1.913356	0.347907
6	6	-6.877778	-3.030127	-0.043295
7	6	-3.341026	-0.027716	-0.298924
8	6	-2.475700	-2.042930	-1.021145
9	6	-1.341698	-0.965974	-0.966022
10	6	-0.238278	-1.378092	-0.019464
11	6	0.900595	-1.998196	-0.541544
12	6	-0.388536	-1.257435	1.364983
13	6	1.875409	-2.508446	0.315720
14	6	0.590505	-1.763585	2.218152
15	6	1.719011	-2.394244	1.695263
16	6	-1.643961	1.637214	-0.701635
17	6	-0.309079	1.898270	-1.079303
18	6	-0.062448	3.220373	-1.665479
19	6	0.809887	2.794321	1.011815
20	6	-0.391244	3.444124	1.410697
21	6	-0.599950	4.426443	0.495248
22	6	0.448256	4.287726	-0.520810
23	6	1.613888	1.752466	1.727262
24	6	4.384812	-0.338025	-0.226469
25	6	4.557599	-0.970480	-1.450697
26	6	4.903791	-0.874619	0.952308
27	6	5.261649	-2.173134	-1.491322
28	6	5.598852	-2.073014	0.892949
29	6	5.788511	-2.739068	-0.328199
30	1	-4.933874	-3.781120	-0.646655
31	1	-7.624119	0.210311	0.751496

32	1	-8.681225	-2.027468	0.573520
33	1	-7.361120	-3.998526	-0.118626
34	1	-2.247450	-2.906897	-0.394986
35	1	-2.698746	-2.365127	-2.040264
36	1	1.022143	-2.082036	-1.619112
37	1	-1.268747	-0.768373	1.776252
38	1	2.764338	-2.978330	-0.096303
39	1	0.471264	-1.663286	3.292904
40	1	2.482519	-2.783035	2.362208
41	1	-0.935273	-0.793094	-1.965526
42	1	-0.948724	3.671237	-2.114951
43	1	-1.029352	3.127118	2.224298
44	1	-1.452919	5.086381	0.410743
45	1	0.867435	5.170047	-0.998038
46	1	0.762691	3.200214	-2.378482
47	1	0.973597	1.222649	2.436153
48	1	2.394609	2.269891	2.296628
49	1	1.574513	0.145210	0.411071
50	1	4.141655	-0.532627	-2.352428
51	1	4.749364	-0.367545	1.900688
52	1	5.402408	-2.677972	-2.443004
53	1	6.003948	-2.504681	1.804592
54	8	-2.519952	2.483615	-0.494882
55	8	1.455051	3.519036	0.112483
56	8	4.249748	2.201345	0.551734
57	8	2.983190	1.456343	-1.500975
58	7	-3.622577	-1.311293	-0.479908
59	7	-2.061183	0.264742	-0.538883
60	7	2.246291	0.750449	0.884232

61	16	-4.690325	0.927356	0.180461
62	16	3.476053	1.183272	-0.151723
63	6	6.552673	-4.034949	-0.371112
64	1	6.177236	-4.736197	0.380688
65	1	6.476812	-4.507611	-1.353471
66	1	7.613329	-3.864448	-0.156615
67	1	0.384453	1.088837	-1.275789

Product:



Charge = 1 Multiplicity = 1

Imaginary Frequencies: none found

Zero-point correction = 0.541134 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-2420.195648 hartrees (-1518696.97107648 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-5.493805	-2.754021	-0.903094
2	6	-4.901236	-1.588070	-0.428795
3	6	-5.581794	-0.699985	0.413174
4	6	-6.890638	-0.957273	0.808502
5	6	-7.488651	-2.120359	0.336729
6	6	-6.800284	-3.004363	-0.505445
7	6	-3.324159	0.036086	-0.125140
8	6	-2.529606	-1.590974	-1.556768

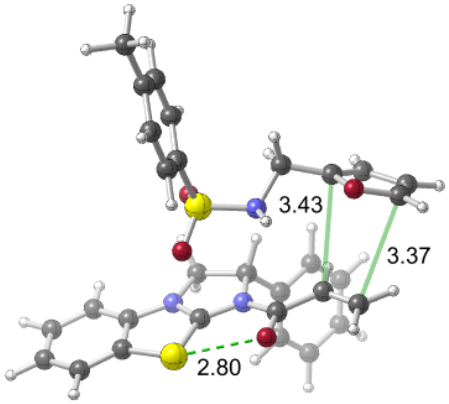
9	6	-1.365443	-0.633032	-1.160183
10	6	-0.331566	-1.293900	-0.269666
11	6	0.772279	-1.912066	-0.865866
12	6	-0.478431	-1.333875	1.120666
13	6	1.707268	-2.581511	-0.078793
14	6	0.466195	-1.995455	1.904695
15	6	1.555819	-2.623921	1.306904
16	6	-1.572063	1.671961	0.066385
17	6	-0.251514	2.122756	-0.485061
18	6	-0.430144	3.231113	-1.569238
19	6	0.716008	2.849559	0.530374
20	6	-0.048927	4.003904	1.169357
21	6	-0.154252	4.927693	0.214920
22	6	0.523298	4.329610	-1.002641
23	6	1.535989	1.968020	1.453703
24	6	4.295999	-0.475335	-0.132487
25	6	4.641635	-1.175666	-1.281711
26	6	4.702933	-0.904546	1.130782
27	6	5.399082	-2.338936	-1.159732
28	6	5.451503	-2.068219	1.233703
29	6	5.809188	-2.802346	0.092459
30	1	-4.950627	-3.428864	-1.556444
31	1	-7.425423	-0.272698	1.458835
32	1	-8.509506	-2.345500	0.626405
33	1	-7.297270	-3.902494	-0.856556
34	1	-2.295441	-2.633673	-1.339572
35	1	-2.829619	-1.475238	-2.600315
36	1	0.902050	-1.862009	-1.944249
37	1	-1.318934	-0.845778	1.607100

38	1	2.565745	-3.054099	-0.546359
39	1	0.348038	-2.014092	2.983524
40	1	2.294423	-3.133940	1.917462
41	1	-0.900318	-0.226974	-2.060281
42	1	-1.459131	3.583498	-1.666999
43	1	-0.482266	3.991094	2.161380
44	1	-0.702483	5.861871	0.233327
45	1	0.940041	5.007895	-1.745280
46	1	-0.076847	2.871422	-2.537463
47	1	0.892889	1.582588	2.251504
48	1	2.315281	2.581630	1.913115
49	1	1.514473	0.084193	0.529470
50	1	4.309512	-0.822716	-2.252651
51	1	4.418744	-0.344915	2.017021
52	1	5.671661	-2.896524	-2.051591
53	1	5.767598	-2.418551	2.213026
54	8	-2.270908	2.290660	0.841559
55	8	1.543985	3.530400	-0.405573
56	8	4.166594	2.154244	0.175593
57	8	2.827319	1.043973	-1.656664
58	7	-3.616916	-1.120103	-0.691529
59	7	-2.080459	0.455776	-0.436390
60	7	2.173897	0.798357	0.842676
61	16	-4.574587	0.691899	0.845914
62	16	3.367162	1.029289	-0.296635
63	6	6.623357	-4.060693	0.228838
64	1	6.130181	-4.774545	0.896870
65	1	6.774457	-4.542910	-0.739996
66	1	7.606406	-3.840862	0.658785

67	1	0.295330	1.283832	-0.920589

DAL process leading to exo cycloadduct:

Reactant:



Charge = 1 Multiplicity = 1

Imaginary Frequencies: none found

Zero-point correction = 0.535602 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-2420.201981 hartrees (-1518700.94509731 kcal/mol)

Coordinates (from last standard orientation):

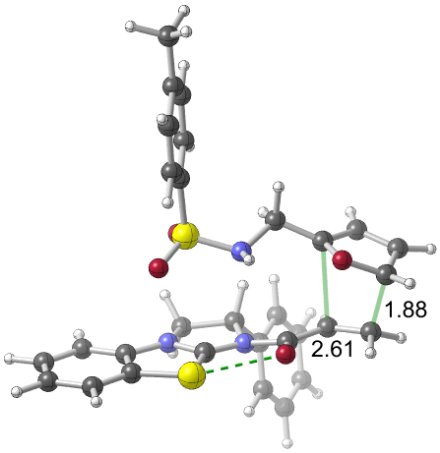
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.635449	4.329608	-1.480646
2	6	-1.562353	3.427415	-0.423821
3	6	-1.409738	3.852710	0.901974

4	6	-1.318826	5.207115	1.206242
5	6	-1.389611	6.113255	0.154167
6	6	-1.546030	5.680113	-1.169215
7	6	-1.536079	1.433607	0.686243
8	6	-1.829954	1.091463	-1.585308
9	6	-1.866325	-0.285461	-0.848388
10	6	-3.175974	-1.019185	-1.027656
11	6	-3.214444	-2.182797	-1.794839
12	6	-4.352509	-0.523350	-0.459733
13	6	-4.421649	-2.849382	-1.997049
14	6	-5.556257	-1.191826	-0.658507
15	6	-5.592371	-2.354939	-1.428260
16	6	-1.433644	-0.736135	1.693938
17	6	-1.515169	-3.009495	2.518437
18	6	-1.521190	-2.192916	1.464347
19	6	1.145153	-3.600813	-0.167226
20	6	0.330030	-4.493342	-0.789142
21	6	0.074798	-5.533550	0.166119
22	6	0.752108	-5.184327	1.289125
23	6	1.784988	-2.326595	-0.587076
24	6	3.477810	0.417531	-0.346686
25	6	4.086304	0.144315	-1.568735
26	6	4.224676	0.731846	0.789014
27	6	5.474487	0.193756	-1.650305
28	6	5.608013	0.777022	0.684598
29	6	6.250954	0.510412	-0.531680
30	6	7.750230	0.589787	-0.627334
31	1	-1.754487	3.981539	-2.501390
32	1	-1.199953	5.544097	2.230818

33	1	-1.322997	7.175337	0.365326
34	1	-1.598824	6.412464	-1.968082
35	1	-2.774195	1.311821	-2.087255
36	1	-0.994378	1.159588	-2.281434
37	1	-2.296229	-2.567762	-2.232141
38	1	-4.330723	0.384589	0.139752
39	1	-4.443888	-3.755526	-2.594371
40	1	-6.467794	-0.804897	-0.213536
41	1	-6.533299	-2.874576	-1.581244
42	1	-1.024898	-0.903792	-1.174003
43	1	-1.432268	-2.614673	3.527581
44	1	-1.609835	-2.566703	0.450515
45	1	-0.033032	-4.425886	-1.805365
46	1	-0.528104	-6.419711	0.027921
47	1	0.869057	-5.640225	2.261336
48	1	-1.606557	-4.083168	2.395476
49	1	1.551142	-1.354451	1.256106
50	1	3.484860	-0.089155	-2.441927
51	1	3.728465	0.950472	1.729798
52	1	5.962556	-0.011263	-2.599005
53	1	6.202424	1.027960	1.558970
54	1	2.878900	-2.414981	-0.543460
55	1	1.492513	-2.108340	-1.616955
56	1	8.225423	0.062087	0.205030
57	1	8.112164	0.159649	-1.564155
58	1	8.081685	1.633163	-0.583573
59	8	-1.239683	-0.209257	2.772957
60	8	1.413060	-4.014908	1.098612
61	8	1.148065	0.476834	-1.548091

62	8	1.279781	1.187113	0.875567
63	7	-1.630567	2.038747	-0.483527
64	7	-1.624585	0.095340	0.576996
65	7	1.306836	-1.223072	0.270966
66	16	-1.359269	2.485926	2.025474
67	16	1.715446	0.316694	-0.211708

Transition state (TS):



Charge = 1 Multiplicity = 1

Imaginary Frequencies: 1 (-391.4247 1/cm)

Zero-point correction = 0.536995 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-2420.170366 hartrees (-1518681.10636866 kcal/mol)

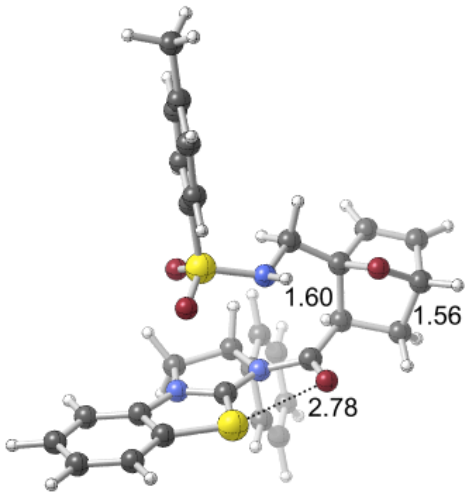
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.149449	4.424639	1.093271
2	6	0.443370	3.449186	0.146994
3	6	0.174959	3.635764	-1.214934
4	6	-0.409373	4.814092	-1.665389
5	6	-0.702519	5.796354	-0.724467
6	6	-0.426373	5.603466	0.634546
7	6	1.194713	1.475412	-0.730666
8	6	1.580684	1.543727	1.543238
9	6	1.979124	0.143354	0.983630
10	6	3.378640	-0.257066	1.386773
11	6	3.555377	-1.208162	2.391191
12	6	4.492739	0.342170	0.794898
13	6	4.839092	-1.558311	2.806438
14	6	5.773843	-0.013433	1.205181
15	6	5.948985	-0.962898	2.212442
16	6	1.814905	-0.710523	-1.489382
17	6	2.538901	-2.916480	-2.176415
18	6	2.356665	-1.985103	-1.130100
19	6	0.040035	-3.050189	-0.581286
20	6	0.691742	-4.163602	-0.026276
21	6	1.250902	-4.842329	-1.084692
22	6	1.028031	-4.038024	-2.238473
23	6	-0.973535	-2.173096	0.075472
24	6	-3.516348	-0.326609	0.611821
25	6	-3.821886	-1.056160	1.757898

26	6	-4.458452	-0.118498	-0.395548
27	6	-5.102122	-1.584403	1.892473
28	6	-5.730064	-0.653624	-0.240374
29	6	-6.069378	-1.392243	0.901165
30	6	-7.460784	-1.940508	1.063723
31	1	0.362580	4.261993	2.144724
32	1	-0.627047	4.965362	-2.717807
33	1	-1.153133	6.727021	-1.053145
34	1	-0.666276	6.387094	1.345622
35	1	2.451645	2.111487	1.880901
36	1	0.834313	1.470302	2.333619
37	1	2.685535	-1.678315	2.844508
38	1	4.356195	1.080338	0.007938
39	1	4.969819	-2.300625	3.587814
40	1	6.637351	0.449825	0.737663
41	1	6.949885	-1.239472	2.529526
42	1	1.257741	-0.609877	1.318301
43	1	2.440526	-2.508982	-3.180512
44	1	2.804553	-2.130737	-0.157442
45	1	0.757325	-4.384640	1.030411
46	1	1.892305	-5.712995	-1.054886
47	1	0.986914	-4.382146	-3.264359
48	1	3.343279	-3.639159	-2.079788
49	1	-1.301526	-0.805415	-1.480364
50	1	-3.075517	-1.195835	2.533719
51	1	-4.201830	0.462558	-1.276309
52	1	-5.355380	-2.152297	2.783235
53	1	-6.475543	-0.496289	-1.014968
54	1	-1.948749	-2.678675	0.002549

55	1	-0.715804	-2.092268	1.134654
56	1	-7.846904	-2.322483	0.114449
57	1	-7.486828	-2.745859	1.802119
58	1	-8.143711	-1.153091	1.402672
59	8	1.375088	-0.389261	-2.591372
60	8	0.037153	-3.128999	-1.914208
61	8	-1.222910	0.349418	1.692541
62	8	-1.936728	1.486445	-0.454183
63	7	1.008696	2.197105	0.364221
64	7	1.804091	0.308385	-0.486138
65	7	-1.020178	-0.827431	-0.497904
66	16	0.645475	2.223809	-2.173866
67	16	-1.874771	0.298972	0.386538

Product:



Charge = 1 Multiplicity = 1

Imaginary Frequencies: none found

Zero-point correction = 0.540638 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-2420.207727 hartrees (-1518704.55076977 kcal/mol)

Coordinates (from last standard orientation):

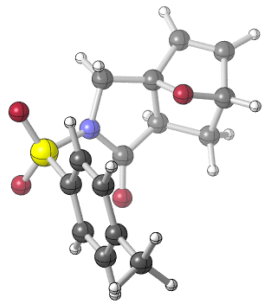
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.616576	4.506113	-1.113659
2	6	-0.796031	3.490553	-0.179548
3	6	-0.551790	3.686351	1.185532
4	6	-0.111681	4.919541	1.655959
5	6	0.071194	5.938366	0.727585
6	6	-0.177539	5.734085	-0.636624
7	6	-1.294779	1.430767	0.663844
8	6	-1.635675	1.470499	-1.623009

9	6	-1.900108	0.027535	-1.088606
10	6	-3.283779	-0.481463	-1.419216
11	6	-3.436996	-1.488970	-2.371384
12	6	-4.410908	0.074639	-0.809342
13	6	-4.710974	-1.935566	-2.718721
14	6	-5.681509	-0.375244	-1.153138
15	6	-5.833050	-1.379384	-2.110139
16	6	-1.537204	-0.836222	1.356850
17	6	-2.124253	-3.177489	2.035960
18	6	-1.606478	-2.268052	0.891052
19	6	-0.146608	-2.884866	0.685182
20	6	-0.382134	-4.261940	0.074277
21	6	-0.819427	-5.023854	1.074578
22	6	-0.894010	-4.098921	2.277309
23	6	0.944482	-2.082765	0.011213
24	6	3.544283	-0.116633	-0.550845
25	6	3.816575	-0.834270	-1.713512
26	6	4.534062	0.148895	0.393577
27	6	5.112400	-1.290027	-1.928250
28	6	5.821799	-0.316401	0.159198
29	6	6.128510	-1.040836	-0.998937
30	1	-0.811976	4.332267	-2.166830
31	1	0.081070	5.079516	2.711810
32	1	0.413865	6.909275	1.069208
33	1	-0.024898	6.549122	-1.336079
34	1	-2.542888	1.932882	-2.017771
35	1	-0.835121	1.493194	-2.361757
36	1	-2.556972	-1.924007	-2.839578
37	1	-4.292858	0.857517	-0.062930

38	1	-4.824363	-2.718711	-3.461894
39	1	-6.554796	0.057961	-0.675272
40	1	-6.825760	-1.728025	-2.377993
41	1	-1.139719	-0.651824	-1.480613
42	1	-2.333608	-2.586787	2.928492
43	1	-2.190286	-2.348120	-0.026326
44	1	-0.284325	-4.491392	-0.980662
45	1	-1.178352	-6.045538	1.045158
46	1	-0.815887	-4.536360	3.270648
47	1	-3.016987	-3.736196	1.752165
48	1	1.517658	-0.840715	1.604858
49	1	3.032150	-1.017387	-2.441292
50	1	4.300635	0.718272	1.288290
51	1	5.340116	-1.847324	-2.832798
52	1	6.603746	-0.115501	0.886224
53	1	1.861451	-2.685477	0.023728
54	1	0.663364	-1.908349	-1.031407
55	8	-1.348563	-0.491347	2.503971
56	8	0.190445	-3.196616	2.028301
57	8	1.164763	0.474505	-1.490895
58	8	1.928976	1.576132	0.652017
59	7	-1.215142	2.185898	-0.415590
60	7	-1.682654	0.170718	0.383665
61	7	1.136216	-0.783097	0.658637
62	16	-0.872311	2.221084	2.122417
63	16	1.886519	0.410330	-0.220923
64	6	7.533548	-1.514393	-1.255001
65	1	8.089994	-0.764648	-1.829341
66	1	8.071533	-1.679174	-0.317788

67	1	7.539894	-2.443398	-1.831380

Lactam:



Charge = 0 Multiplicity = 1

Imaginary Frequencies: none found

Zero-point correction = 0.285295 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-1333.747866 hartrees (-836940.12339366 kcal/mol)

Coordinates (from last standard orientation):

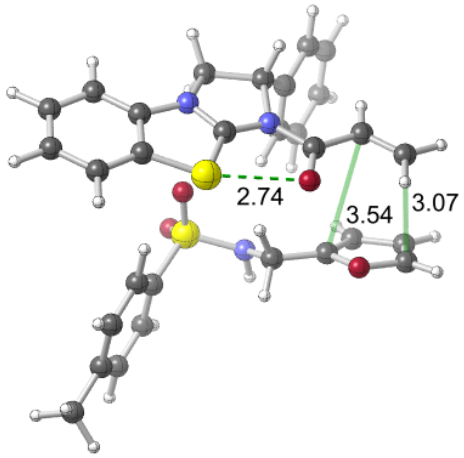
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.112092	0.544741	-1.209613
2	6	2.729669	-1.470075	-1.396716
3	6	2.509537	-0.003034	-0.989170
4	6	2.553269	-0.087389	0.568462
5	6	3.973213	-0.388643	0.994317
6	6	4.166269	-1.659439	0.634053

7	6	2.852468	-2.123348	0.017364
8	6	1.690535	1.044318	1.082583
9	6	-1.890890	0.592434	0.144866
10	6	-2.167647	-0.053994	1.347002
11	6	-2.460835	0.181914	-1.058865
12	6	-3.036285	-1.139553	1.335636
13	6	-3.325995	-0.904638	-1.045445
14	6	-3.621641	-1.580857	0.144816
15	1	1.859784	-1.867669	-1.925837
16	1	3.234425	0.701958	-1.406072
17	1	4.683383	0.332640	1.379951
18	1	5.082644	-2.236729	0.660043
19	1	2.615007	-3.184731	0.069859
20	1	3.618327	-1.616522	-2.012313
21	1	-1.723225	0.294386	2.274201
22	1	-2.222388	0.703045	-1.979327
23	1	-3.262460	-1.653270	2.265824
24	1	-3.778651	-1.239029	-1.975264
25	1	1.152958	0.761955	1.989840
26	1	2.267224	1.954871	1.262591
27	8	0.402163	0.425106	-2.181451
28	8	1.899668	-1.346493	0.752450
29	8	-0.706953	2.515651	1.496227
30	8	-1.010328	2.796633	-0.994181
31	7	0.757877	1.234701	-0.046081
32	16	-0.755730	1.948431	0.155780
33	6	-4.573404	-2.746383	0.138269
34	1	-5.606552	-2.397157	0.029516
35	1	-4.365074	-3.417565	-0.700201

36	1	-4.507382	-3.317491	1.067559

DAL process leading to exo cycloadduct (opposite enantiomer):

Reactant:



Charge = 1 Multiplicity = 1

Imaginary Frequencies: none found

Zero-point correction = 0.535793 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-2420.197322 hartrees (-1518698.02152822 kcal/mol)

Coordinates (from last standard orientation):

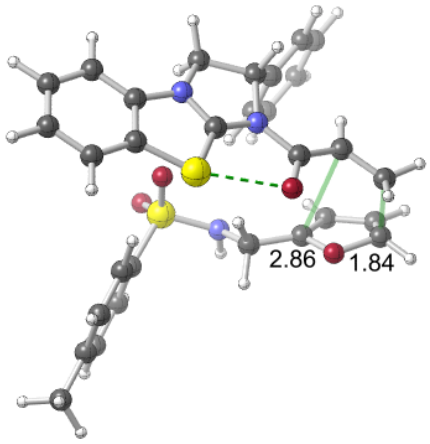
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.860144	4.103024	0.742641

2	6	1.252917	3.215903	-0.140085
3	6	1.956569	2.624838	-1.196484
4	6	3.303140	2.911957	-1.400994
5	6	3.916913	3.794584	-0.518944
6	6	3.205406	4.380289	0.536726
7	6	-0.359101	1.886660	-1.055566
8	6	-1.149691	2.909392	0.845103
9	6	-2.325828	2.176148	0.138026
10	6	-3.124434	1.342642	1.109151
11	6	-4.361781	1.810824	1.550828
12	6	-2.608396	0.149728	1.616461
13	6	-5.075275	1.093175	2.509424
14	6	-3.323180	-0.565050	2.572071
15	6	-4.556045	-0.093127	3.022873
16	6	-2.116066	0.512696	-1.906000
17	6	-4.033962	-0.661451	-2.770356
18	6	-3.529370	0.116932	-1.809599
19	6	-1.530844	-2.644030	-0.865486
20	6	-2.605471	-2.997157	-0.108627
21	6	-3.561677	-3.559469	-1.017190
22	6	-2.991876	-3.497124	-2.247246
23	6	-0.186001	-2.076442	-0.542572
24	6	2.684947	-1.510879	1.021567
25	6	3.269403	-2.616376	1.641596
26	6	3.317123	-0.843806	-0.021022
27	6	4.508765	-3.052568	1.196682
28	6	4.562338	-1.295097	-0.450882
29	6	5.171527	-2.401122	0.145957
30	6	6.521681	-2.885102	-0.308883

31	1	1.299481	4.548447	1.557881
32	1	3.856558	2.456718	-2.216341
33	1	4.967471	4.030343	-0.651747
34	1	3.713743	5.063091	1.209399
35	1	-0.842806	2.399587	1.762824
36	1	-1.378582	3.956046	1.044320
37	1	-4.765470	2.736500	1.148236
38	1	-1.652869	-0.222186	1.257420
39	1	-6.036657	1.461828	2.853432
40	1	-2.911049	-1.488995	2.968239
41	1	-5.111022	-0.650087	3.771638
42	1	-2.973712	2.900895	-0.363902
43	1	-3.418895	-0.982642	-3.605939
44	1	-4.126394	0.459169	-0.972865
45	1	-5.071505	-0.978362	-2.749278
46	1	-2.701560	-2.874084	0.960443
47	1	-4.541102	-3.950401	-0.780876
48	1	-3.310967	-3.797794	-3.234394
49	1	0.599865	-2.673635	-1.024481
50	1	-0.099593	-1.052266	-0.922579
51	1	0.025178	-2.951015	1.352891
52	1	2.767530	-3.115981	2.465380
53	1	2.850044	0.025324	-0.473074
54	1	4.977310	-3.909401	1.673559
55	1	5.068642	-0.775694	-1.259808
56	1	7.269115	-2.739660	0.478607
57	1	6.495501	-3.955158	-0.537772
58	1	6.856042	-2.348705	-1.200143
59	8	-1.344404	0.128926	-2.768060

60	8	-1.751756	-2.946920	-2.166902
61	8	0.988339	-1.161408	2.996847
62	8	0.805170	0.315787	0.945994
63	7	-0.069742	2.784889	-0.134612
64	7	-1.612269	1.400068	-0.932219
65	7	-0.036710	-2.031495	0.912002
66	16	0.927228	1.528754	-2.131514
67	16	1.078816	-0.986075	1.554931

Transition state (TS):



Charge = 1 Multiplicity = 1

Imaginary Frequencies: 1 (-346.2447 1/cm)

Zero-point correction = 0.535935 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-2420.171535 hartrees (-1518681.83992785 kcal/mol)

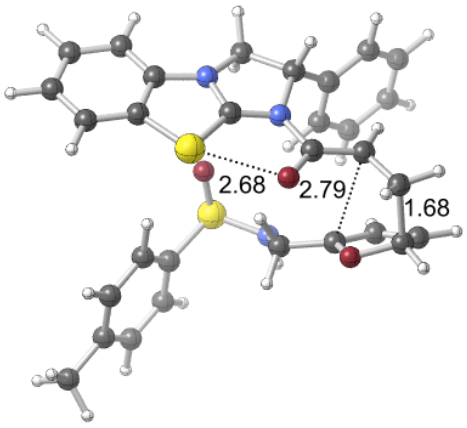
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.675773	4.296565	0.802051
2	6	1.164723	3.353832	-0.082562
3	6	1.945983	2.797485	-1.102316
4	6	3.270891	3.184823	-1.269657
5	6	3.790472	4.127472	-0.386276
6	6	3.004021	4.672053	0.635294
7	6	-0.318157	1.880881	-1.017309
8	6	-1.252733	2.909074	0.811283
9	6	-2.336330	2.071345	0.073529
10	6	-3.142832	1.242378	1.042362
11	6	-4.474141	1.566850	1.299925
12	6	-2.541096	0.186754	1.727104
13	6	-5.196642	0.841894	2.247357
14	6	-3.261916	-0.537221	2.670315
15	6	-4.592287	-0.209095	2.933443
16	6	-1.918691	0.327955	-1.909051
17	6	-3.658948	-1.174546	-2.743011
18	6	-3.190354	-0.261364	-1.764725
19	6	-1.570258	-2.454564	-0.889059
20	6	-2.702127	-2.824601	-0.146501
21	6	-3.654331	-3.193052	-1.073169
22	6	-3.119611	-2.891550	-2.359351
23	6	-0.187239	-2.050744	-0.498793
24	6	2.678488	-1.599465	1.029723
25	6	3.237730	-2.722522	1.641263

26	6	3.300678	-0.967299	-0.040916
27	6	4.440664	-3.214902	1.156424
28	6	4.508440	-1.476359	-0.510826
29	6	5.090316	-2.603200	0.074247
30	6	6.397360	-3.153098	-0.428534
31	1	1.057593	4.712361	1.590869
32	1	3.882915	2.760686	-2.059715
33	1	4.823987	4.440195	-0.491667
34	1	3.435883	5.400953	1.312999
35	1	-0.961561	2.451145	1.761587
36	1	-1.565566	3.941920	0.966260
37	1	-4.946563	2.384642	0.761305
38	1	-1.509208	-0.068598	1.508199
39	1	-6.232135	1.099479	2.448048
40	1	-2.780369	-1.355069	3.199343
41	1	-5.155661	-0.770632	3.672628
42	1	-2.997772	2.726894	-0.501568
43	1	-3.176922	-1.104207	-3.717200
44	1	-3.802526	-0.019627	-0.907451
45	1	-4.735892	-1.310069	-2.811104
46	1	-2.783307	-2.792884	0.930410
47	1	-4.676601	-3.494534	-0.886048
48	1	-3.346604	-3.431691	-3.271721
49	1	0.525351	-2.742774	-0.967476
50	1	0.014750	-1.053723	-0.911517
51	1	-0.019029	-2.932356	1.390680
52	1	2.744640	-3.193085	2.487103
53	1	2.855442	-0.082828	-0.485664
54	1	4.889922	-4.086426	1.625226

55	1	5.005985	-0.986770	-1.343187
56	1	7.178556	-3.046657	0.331936
57	1	6.309252	-4.220225	-0.656082
58	1	6.726165	-2.632426	-1.331064
59	8	-1.065400	0.087679	-2.773073
60	8	-1.756136	-2.673200	-2.177953
61	8	1.021264	-1.205748	3.035706
62	8	0.877879	0.305938	1.005301
63	7	-0.124431	2.832289	-0.114709
64	7	-1.515507	1.297953	-0.915766
65	7	-0.059796	-2.009989	0.953207
66	16	1.028587	1.615856	-2.056411
67	16	1.108256	-1.010074	1.596556

Intermediate (INT):



Charge = 1 Multiplicity = 1

Imaginary Frequencies: none found

Zero-point correction = 0.537320 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-2420.168195 hartrees (-1518679.74404445 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.025899	4.167822	0.509876
2	6	1.492340	3.146759	-0.268770
3	6	2.287821	2.386877	-1.135310
4	6	3.650387	2.641110	-1.249994
5	6	4.192625	3.658890	-0.469756
6	6	3.390856	4.409238	0.398107
7	6	-0.051848	1.680439	-1.114560

8	6	-1.010864	3.021963	0.482652
9	6	-2.111203	2.191068	-0.235287
10	6	-3.078947	1.585507	0.751038
11	6	-4.366561	2.110003	0.855636
12	6	-2.681276	0.547603	1.594715
13	6	-5.252985	1.602790	1.805017
14	6	-3.568109	0.038888	2.538269
15	6	-4.855475	0.566126	2.645955
16	6	-1.732065	0.170644	-1.942159
17	6	-3.563640	-1.282787	-2.733910
18	6	-3.049083	-0.274757	-1.825080
19	6	-1.782508	-2.451342	-0.635200
20	6	-2.994863	-2.613998	0.086377
21	6	-3.932496	-2.958539	-0.842499
22	6	-3.308980	-2.837774	-2.150960
23	6	-0.383408	-2.169914	-0.206331
24	6	2.437198	-1.620659	1.140964
25	6	2.696817	-2.986088	1.229332
26	6	3.358792	-0.737880	0.581876
27	6	3.902191	-3.471740	0.734963
28	6	4.559634	-1.242848	0.098818
29	6	4.846831	-2.611393	0.164706
30	1	1.395211	4.744752	1.178185
31	1	4.272807	2.059362	-1.923075
32	1	5.254435	3.871502	-0.536988
33	1	3.840380	5.195337	0.995942
34	1	-0.831143	2.664626	1.501321
35	1	-1.237792	4.088217	0.487459
36	1	-4.674921	2.915698	0.193909

37	1	-1.680424	0.136376	1.500186
38	1	-6.253416	2.016976	1.884759
39	1	-3.251211	-0.769918	3.191203
40	1	-5.546461	0.169474	3.383649
41	1	-2.656079	2.818654	-0.948217
42	1	-3.027727	-1.314488	-3.684219
43	1	-4.639596	-1.229436	-2.902443
44	1	-3.111057	-2.462771	1.150419
45	1	-4.991109	-3.121071	-0.685103
46	1	-3.543635	-3.536409	-2.949688
47	1	0.252455	-2.997315	-0.550245
48	1	-0.043221	-1.273367	-0.743334
49	1	-0.359918	-2.814236	1.785806
50	1	1.971222	-3.666972	1.668119
51	1	3.135356	0.323583	0.529798
52	1	4.113909	-4.535529	0.792295
53	1	5.288683	-0.564194	-0.336527
54	8	-0.836260	-0.256731	-2.693136
55	8	-1.918937	-2.815835	-1.885666
56	8	0.888539	-1.142451	3.244629
57	8	0.720245	0.342409	1.209069
58	7	0.165873	2.733188	-0.334770
59	7	-1.300119	1.221489	-1.038078
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61	16	1.337910	1.152234	-1.984456
62	16	0.921809	-0.978860	1.798257
63	1	-3.698012	0.144161	-1.069279
64	6	6.149410	-3.137016	-0.374302
65	1	6.237605	-4.214985	-0.219923

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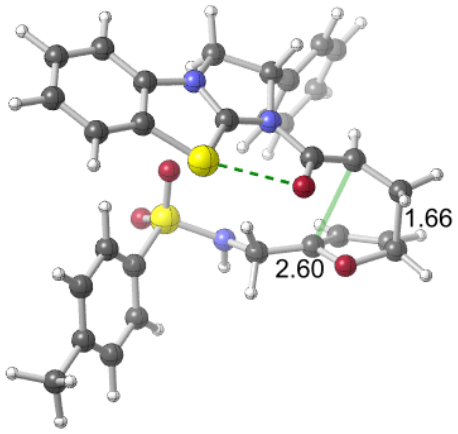
67	1	6.997092	-2.647877	0.116348

Transition state 2 (TS2):



Charge = 1 Multiplicity = 1

Imaginary Frequencies: 1 (-118.7920 1/cm)

Zero-point correction = 0.537206 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-2420.169404 hartrees (-1518680.50270404 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
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4	6	3.676245	2.637242	-1.261701
5	6	4.221441	3.653560	-0.482079
6	6	3.422290	4.407430	0.385523
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8	6	-0.979510	3.024415	0.483720
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10	6	-3.062553	1.610563	0.751869
11	6	-4.347304	2.144339	0.844648
12	6	-2.677819	0.573623	1.602538
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14	6	-3.575079	0.072236	2.539833
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19	6	-1.804078	-2.389684	-0.672218
20	6	-3.011024	-2.626846	0.054662
21	6	-3.927321	-3.015470	-0.871716
22	6	-3.300104	-2.856305	-2.182845
23	6	-0.404520	-2.124434	-0.222244
24	6	2.409355	-1.632080	1.163329
25	6	2.656560	-2.996448	1.294180
26	6	3.334222	-0.777208	0.567971
27	6	3.852284	-3.510063	0.804690
28	6	4.524904	-1.309753	0.089656
29	6	4.799081	-2.678297	0.196516
30	1	1.428288	4.749557	1.166925
31	1	4.296709	2.052961	-1.934319
32	1	5.283966	3.862491	-0.549281

33	1	3.874828	5.192443	0.982459
34	1	-0.793822	2.661397	1.499234
35	1	-1.205802	4.090699	0.494633
36	1	-4.646204	2.949417	0.177912
37	1	-1.680731	0.153608	1.513487
38	1	-6.241947	2.066697	1.860896
39	1	-3.268550	-0.737505	3.196402
40	1	-5.559034	0.218009	3.368905
41	1	-2.617148	2.828808	-0.952660
42	1	-3.044467	-1.271375	-3.662213
43	1	-4.632745	-1.204383	-2.834953
44	1	-3.136480	-2.471932	1.117545
45	1	-4.978326	-3.223880	-0.718573
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51	1	3.122216	0.284656	0.485616
52	1	4.054550	-4.573494	0.894782
53	1	5.255535	-0.652457	-0.375049
54	8	-0.840546	-0.219744	-2.726600
55	8	-1.911560	-2.824967	-1.910291
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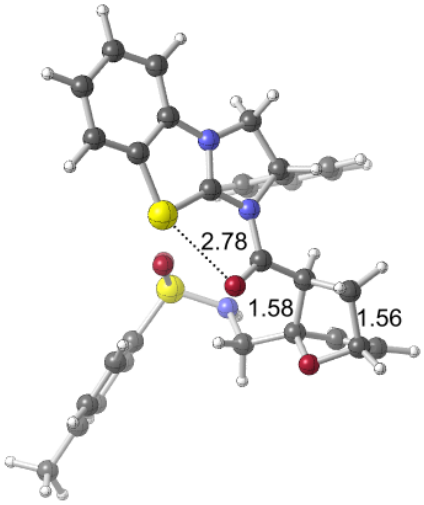
Product:



Charge = 1 Multiplicity = 1

Imaginary Frequencies: none found

Zero-point correction = 0.540302 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-2420.201742 hartrees (-1518700.79512242 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	5.353866	-1.967153	0.597749
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6	6	5.863847	-3.246363	0.420423
7	6	2.327798	-0.465957	-0.702272
8	6	3.718953	0.828516	0.617718
9	6	2.475366	1.677099	0.196883
10	6	1.725943	2.221661	1.389338
11	6	1.796553	3.586289	1.671947
12	6	1.007107	1.371115	2.230297
13	6	1.155533	4.099344	2.797402
14	6	0.359167	1.886794	3.348978
15	6	0.437195	3.249461	3.635757
16	6	0.560317	0.957060	-1.454162
17	6	0.193484	3.177440	-2.594251
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21	6	-1.889309	4.387238	-2.014606
22	6	-1.255599	3.497132	-3.070140
23	6	-2.340242	0.979862	-0.824674
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25	6	-4.186247	-1.628039	1.649196

26	6	-3.080653	-2.436915	-0.360223
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59	7	1.680048	0.713376	-0.632837
60	7	-1.971794	0.861234	0.590690
61	16	1.989942	-1.937770	-1.513085
62	16	-1.671117	-0.662033	1.183048
63	1	0.196174	2.792674	-0.413382
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65	1	-6.595795	-4.880870	0.409302
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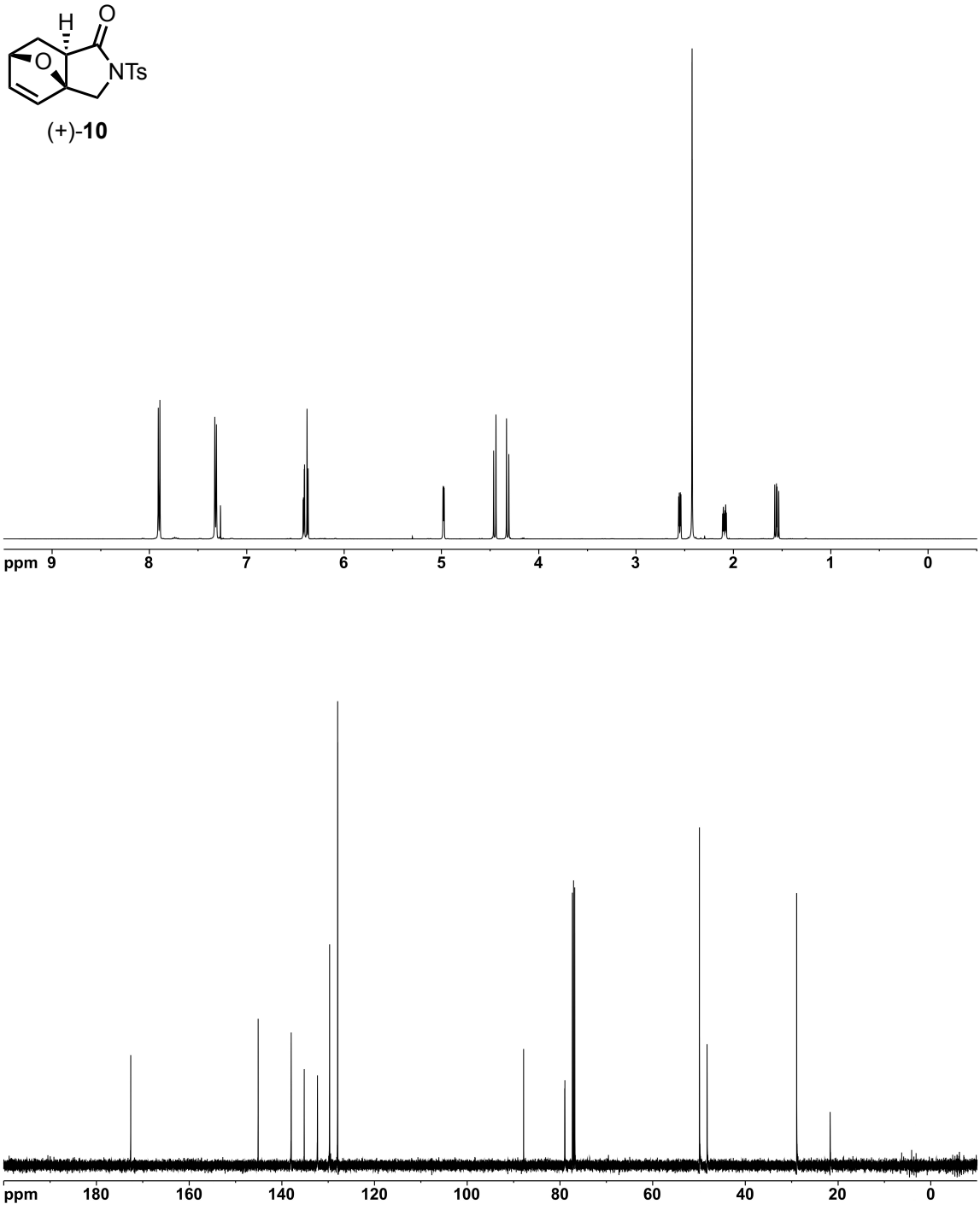
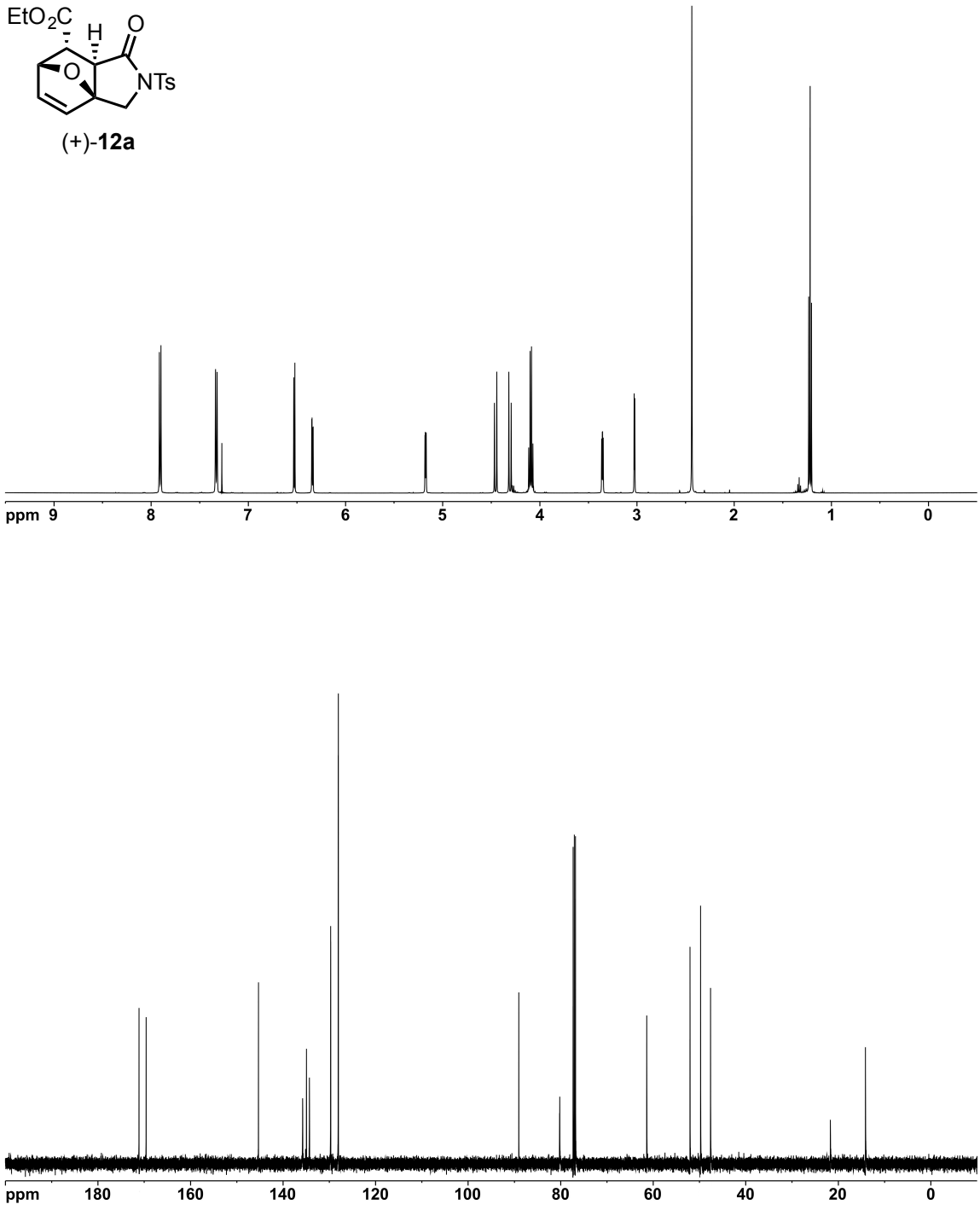
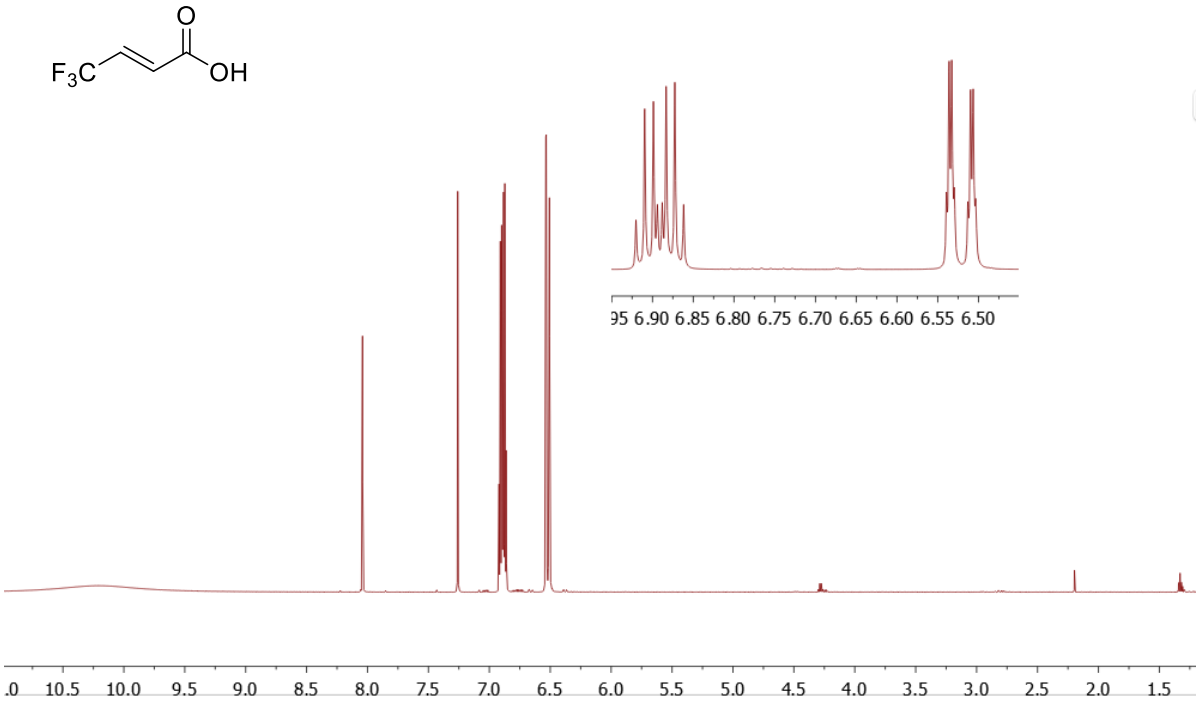


^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of lactam (+)-**10** in $CDCl_3$



^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of lactam (+)-**12a** in $CDCl_3$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F3C
OH
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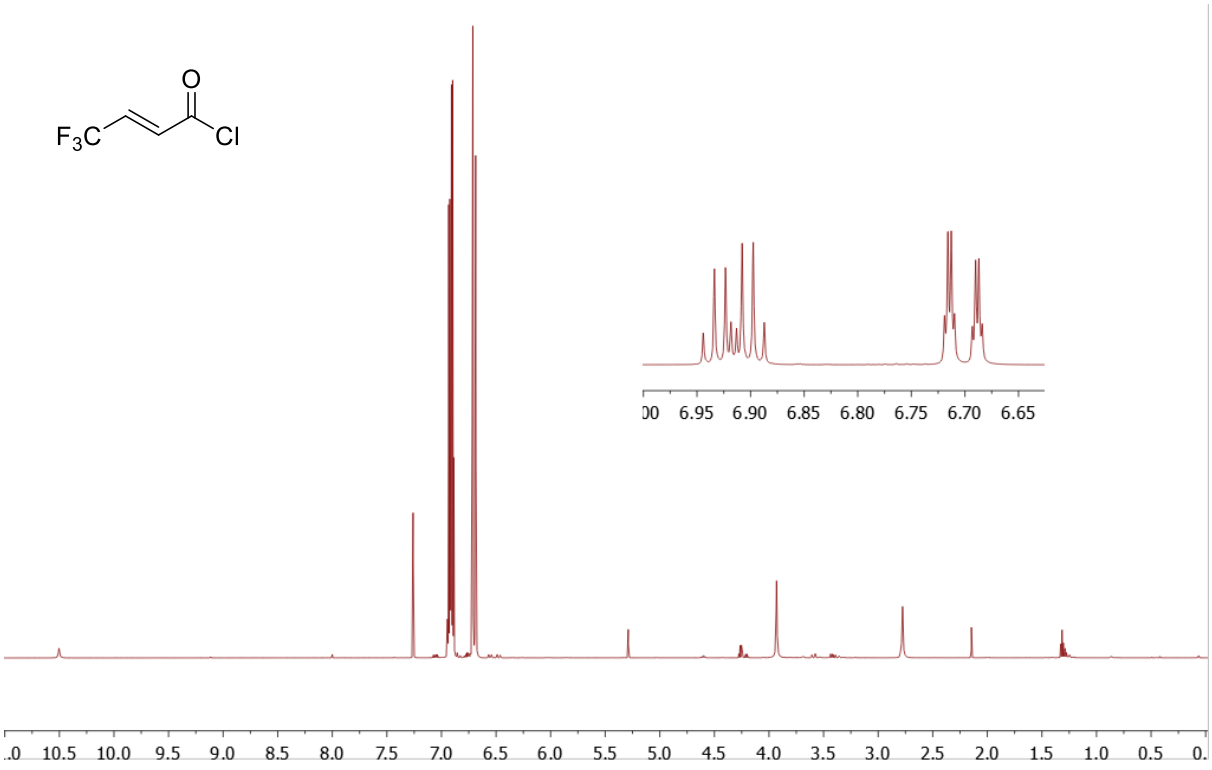
O
F3C
Cl
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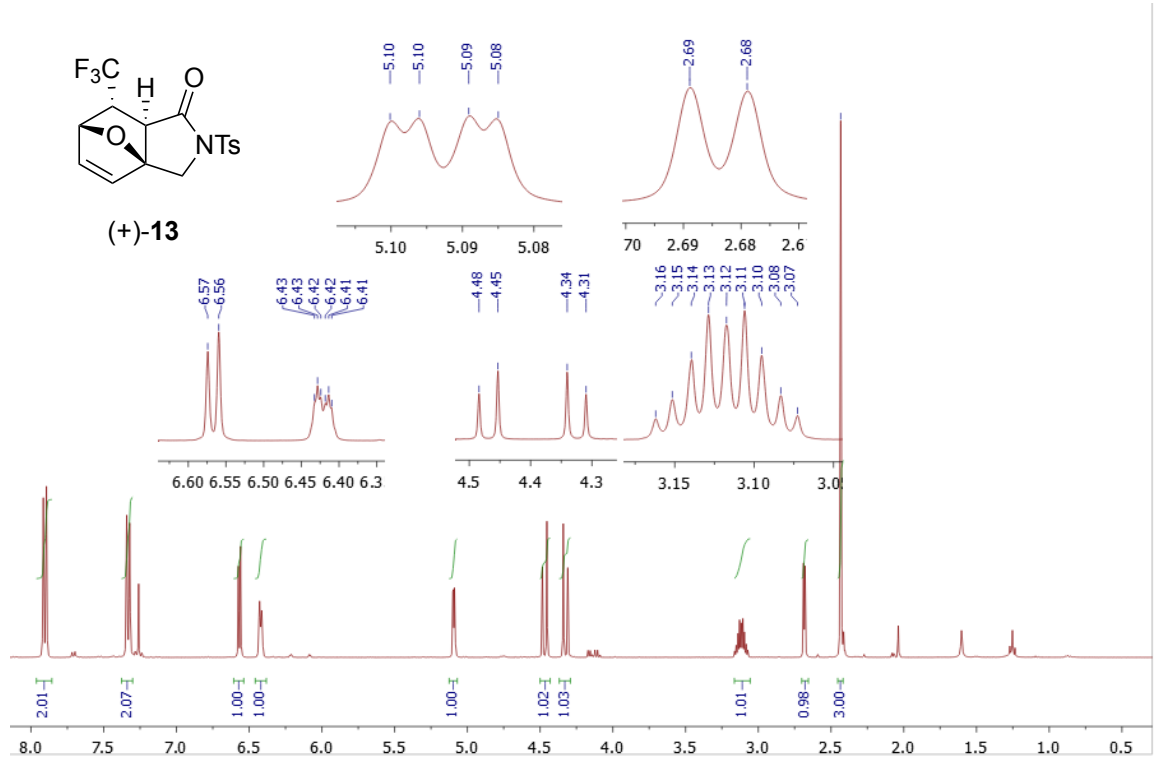
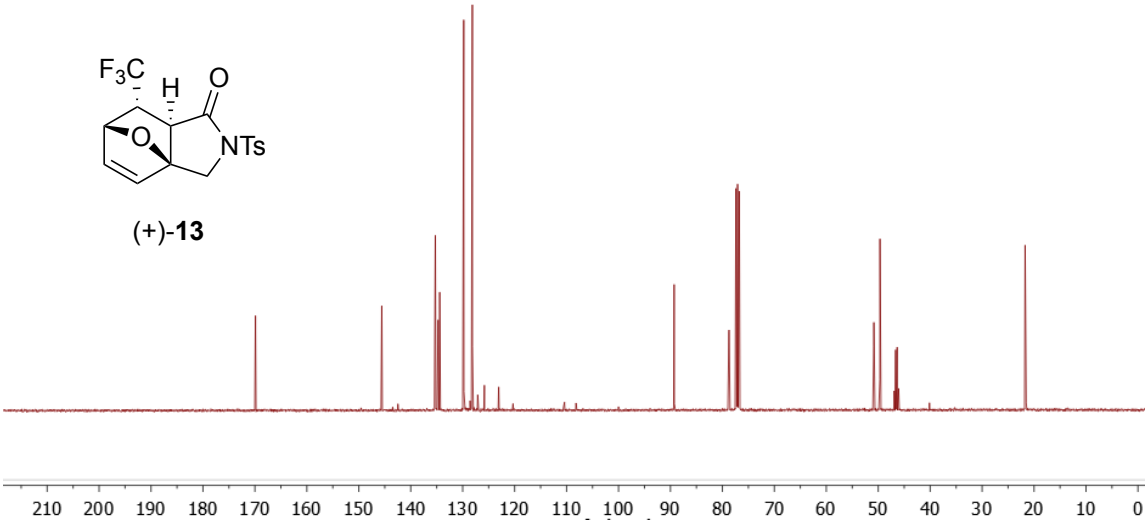
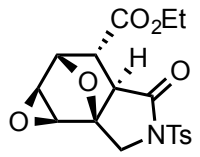
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.

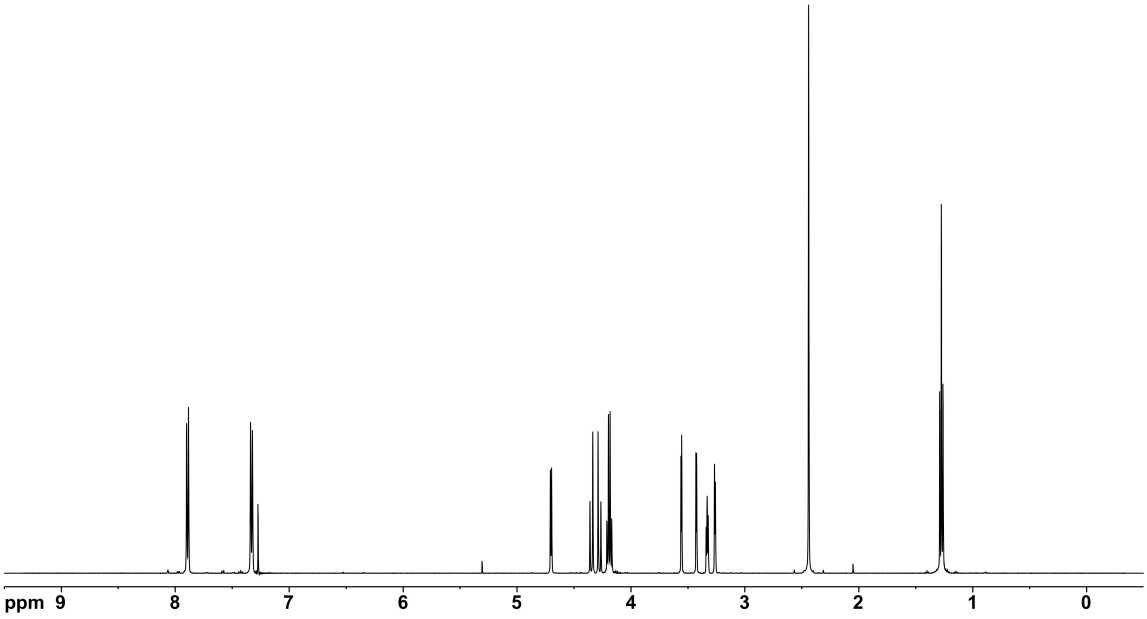


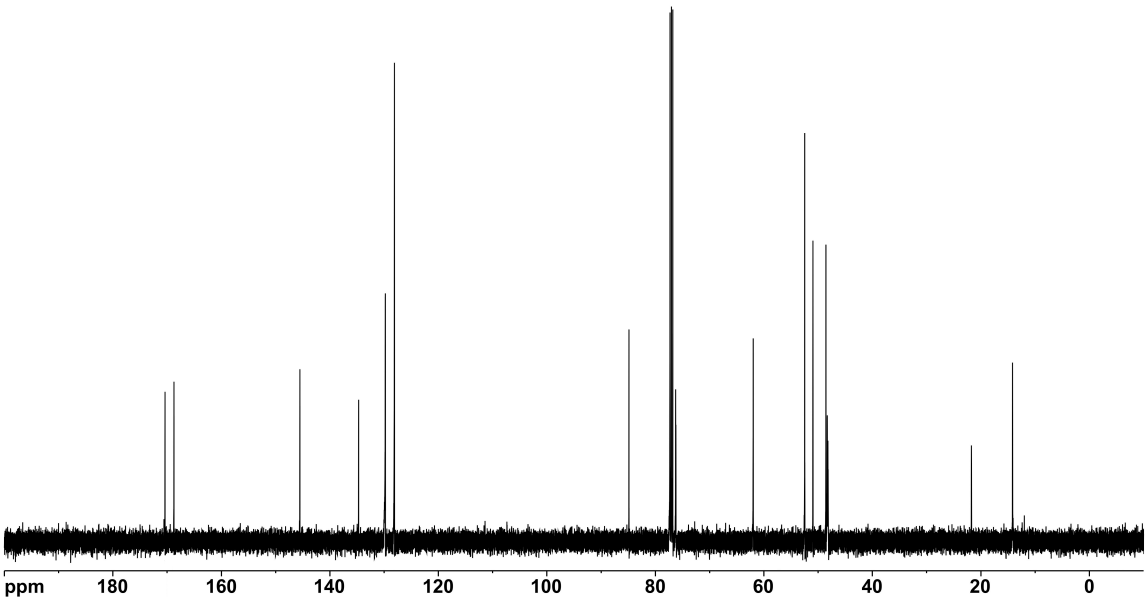


^{1}H (400 MHz) and ^{13}C NMR (101 MHz) spectra of lactam (+)-**13** in $CDCl_3$

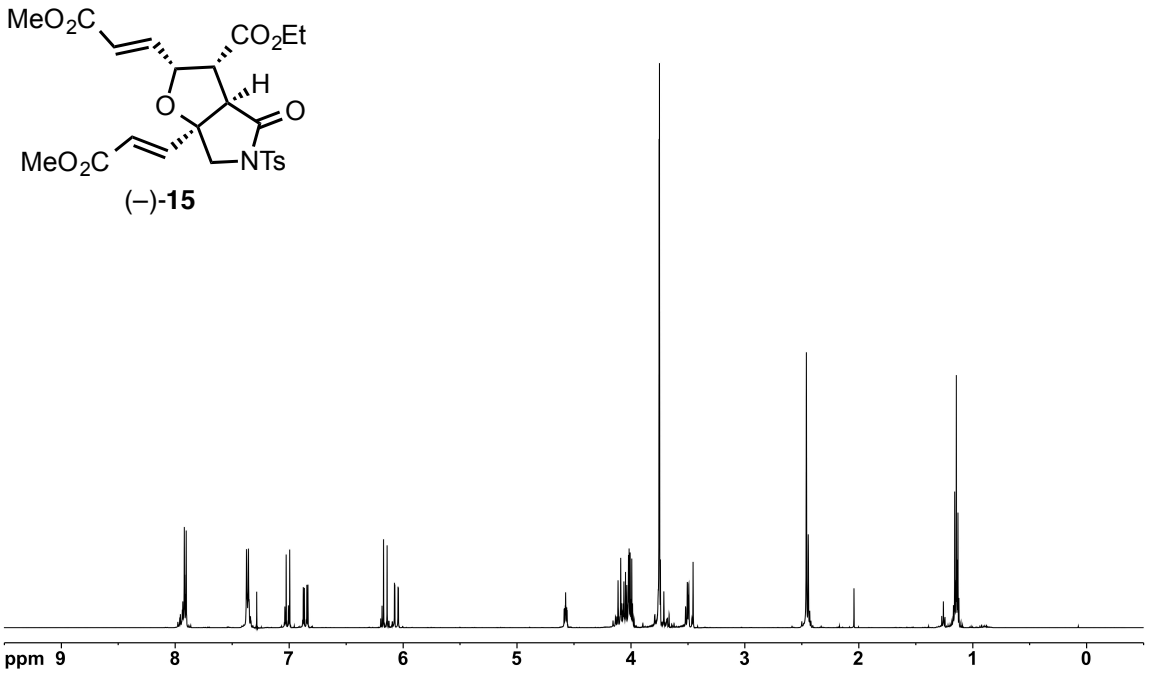


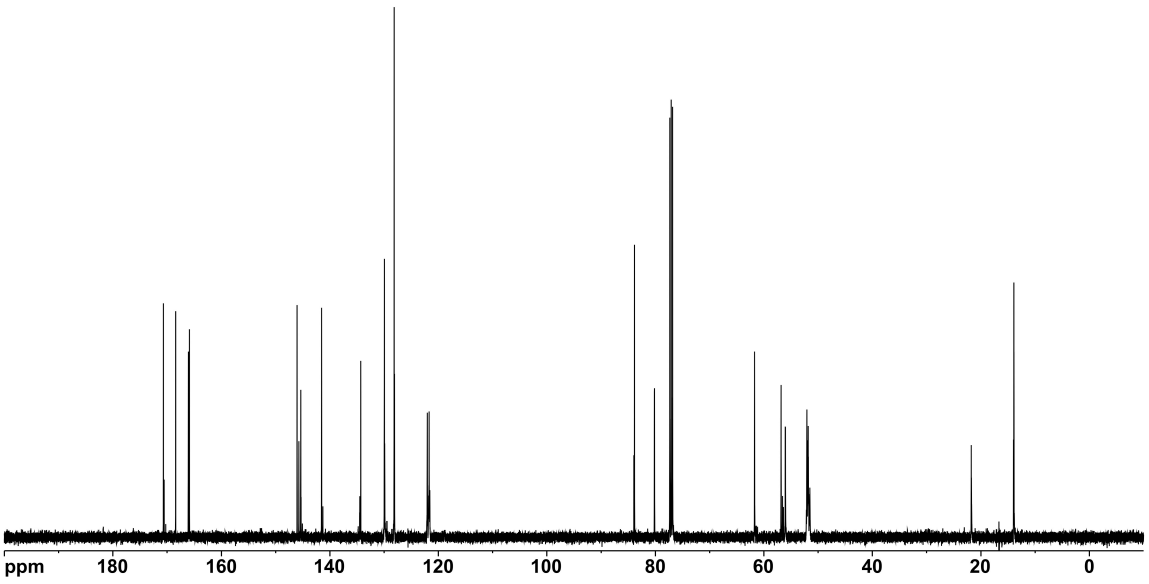
(+)-**14**





^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of epoxide (+)-**14** in $CDCl_3$

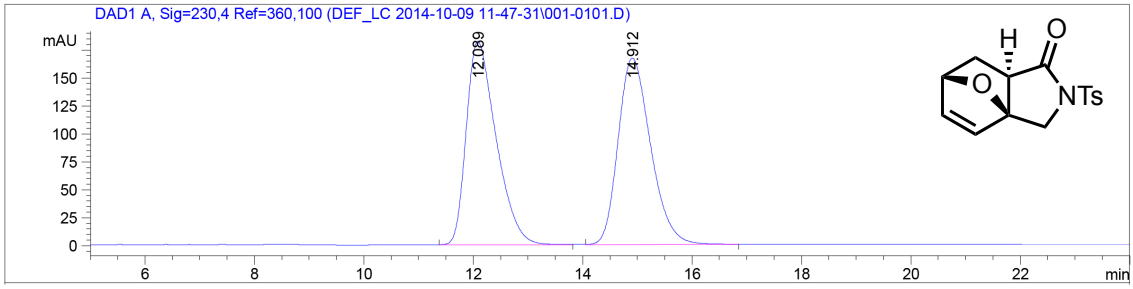




^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of lactam (–)-**15** in $CDCl_3$

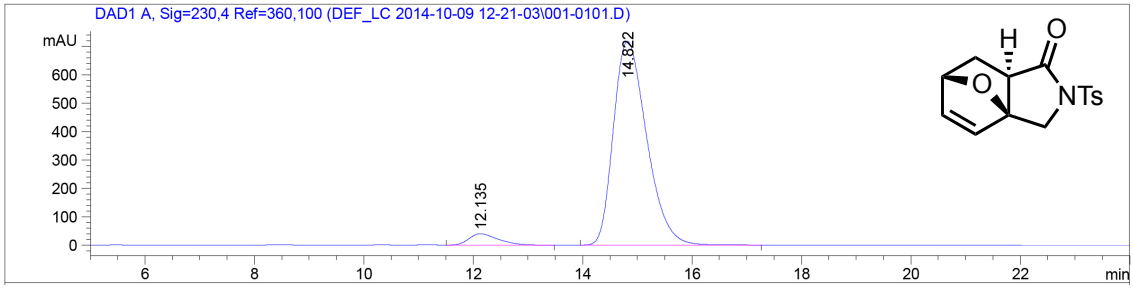
Figure S2: Chiral HPLC determinations of enantiomeric excess of tricyclic γ-lactams (+)-10 and (+)-12a:

Chiral HPLC analysis of tricyclic γ-lactam (+)-10: Chiralcel AS-H column: hexanes:^{i}PrOH = 40:60, flow rate 1.0 mL/min, λ = 230 nm: t_{minor} = 12.1 min, t_{major} = 14.8 min; 91% *ee*.



Signal 1: DAD1 A, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.089	VB	0.5743	6905.38037	182.16231	50.0142
2	14.912	BB	0.6347	6901.46826	166.79213	49.9858

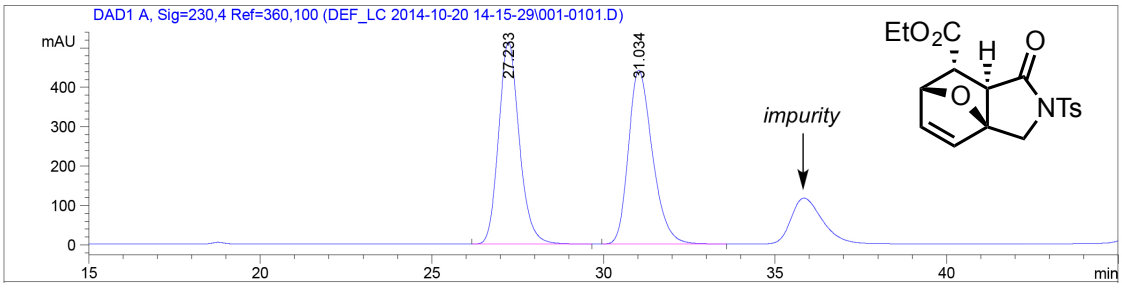


Signal 1: DAD1 A, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.135	VB	0.5555	1479.92871	40.01673	4.6714
2	14.822	BB	0.6515	3.02009e4	716.84735	95.3286

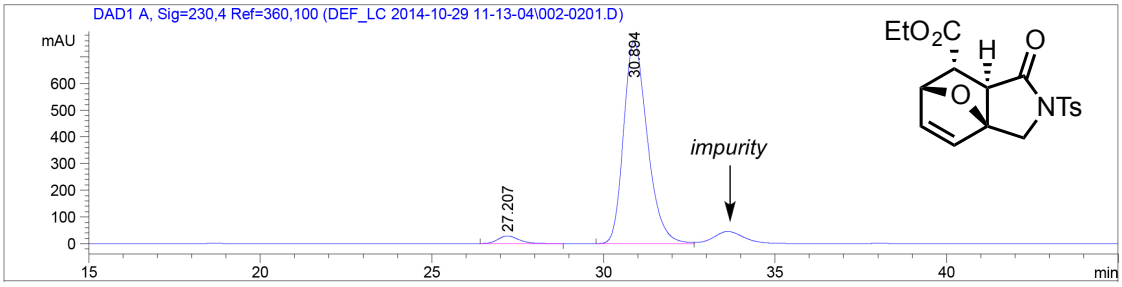
Determination of enantiomeric excess of tricyclic γ-lactam (+)-12a:

Chiral HPLC analysis of tricyclic γ-lactam (+)-12a: Chiralcel AD-H column: hexanes:^{i}PrOH = 60:40, flow rate 0.5 mL/min, λ = 230 nm: t_{minor} = 27.2 min, t_{major} = 30.9 min; 94% *ee*.



Signal 1: DAD1 A, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.233	BB	0.6407	2.14784e4	512.79865	49.9649
2	31.034	BB	0.7523	2.15086e4	441.53778	50.0351

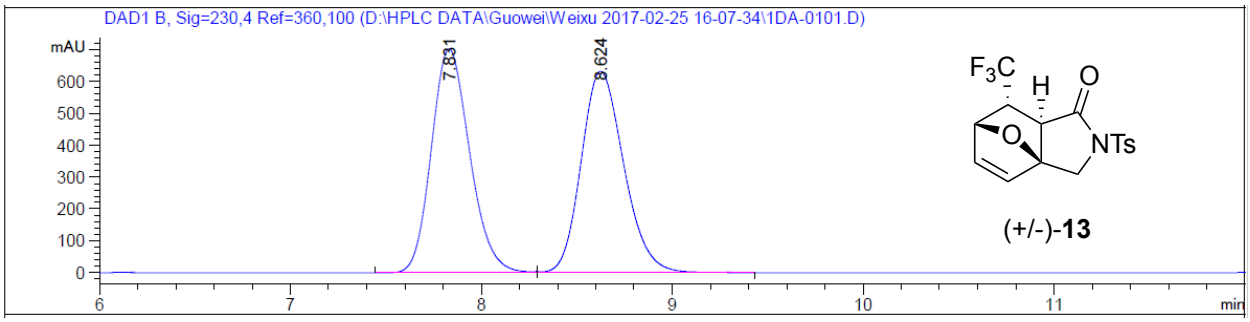


Signal 1: DAD1 A, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.207	BB	0.6536	1205.83008	28.50200	3.2022
2	30.894	BV	0.7379	3.64501e4	756.85626	96.7978

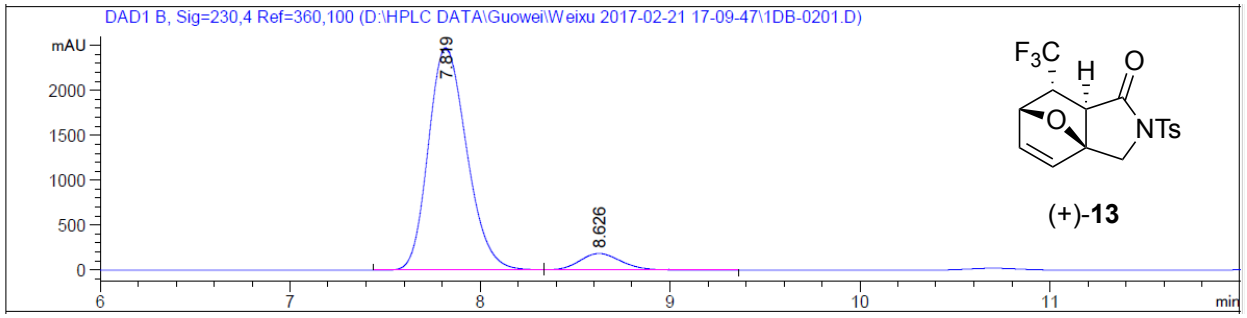
Determination of enantiomeric excess of tricyclic γ-lactam (+)-13:

Chiral HPLC analysis of tricyclic γ-lactam (+)-13: Chiralcel AD-H column: hexanes:^{i}PrOH = 60:40, flow rate 1.0 mL/min, λ = 230 nm: t_{minor} = 8.62 min, t_{major} = 7.83 min; 85% ee.



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.831	BV	0.2116	9769.82617	701.05981	49.9963
2	8.624	VB	0.2362	9771.26660	630.81213	50.0037
Totals :				1.95411e4	1331.87195	



Signal 2: DAD1 B, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.819	BV	0.1680	3.46395e4	2463.77759	92.3583
2	8.626	VB	0.2208	2866.07642	185.48206	7.6417
Totals :				3.75056e4	2649.25964	