Acylammonium Salts as Dienophiles in Diels-Alder-Lactonization Organocascades

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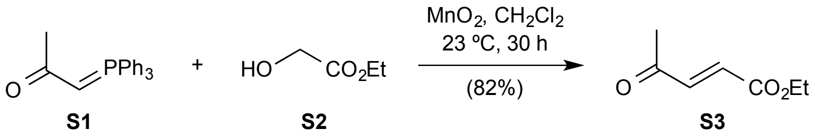
General procedures

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). Diisopropylethylamine ($EtN(^iPr)_2$) and triethylamine (Et_3N) were distilled from calcium hydride prior to use. 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) or benzene (7.16 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; dq, doublet of quartets; qd, quartet of doublets; td, triplet of doublets; tt, triplet of triplets; ddd, doublet of doublet of doublets; ddt, doublet of doublet of triplets; ddq, doublet of doublet of quartets; dddd, doublet of doublet of doublet of doublets; ddddt, doublet of doublet of doublet of doublet of triplets; ddquint, doublet of doublet of quintets; m, multiplet, br s, broad singlet. ^{13}C NMR spectra were measured at 125 MHz and referenced relative to residual chloroform (77.23 ppm) or benzene (128.06 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. (*R*)-(–)-HBTM,[2] TMSQD[3] and BzQN[4] were synthesized according to literature procedures. (*S*)-(–)-BTM and (*R*)-(+)-BTM were purchased from TCI chemicals and used as received. $(DHQ)_2$PHAL, (*S*)-(–)-Tetramisole and (–)-Tröger's base were purchased from Sigma-Aldrich and used as received. (*R*)-(+)-PPY* was purchased from Strem chemicals and used as received. All unsaturated acid chlorides were purchased from Sigma-Aldrich and used as received without further purification.

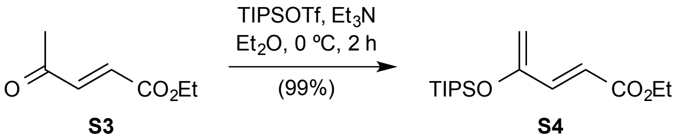
Abbreviation list

DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene
$EtN(^iPr)_2$ = *N*,*N*-diisopropylethylamine
Et_3N = triethylamine
DTBP = 2,6-di-*tert*-butylpyridine
DIBAl-H = diisobutylaluminum hydride
TIPSOTf = triisopropylsilyl trifluoromethanesulfonate
TBHP = *tert*-butyl hydroperoxide
$Rh_2(cap)_4$ = dirhodium tetracaprolactamate
TsCl = 4-toluenesulfonyl chloride
TASF = tris(dimethylamino)sulfonium difluorotrimethylsilicate
(*R*)-(–)-HBTM = (*R*)-(–)-homobenzotetramisole
(*S*)-(–)-BTM = (*S*)-(–)-benzotetramisole
TMSQD = *O*-trimethylsilyl quinidine
BzQN = *O*-benzoyl quinine
$(DHQ)_2$PHAL = Hydroquinine 1,4-phthalazinediyl diether
(*R*)-(+)-PPY* = (*R*)-(+)-4-pyrrolidinopyrindinyl(pentamethylcyclopentadienyl)iron

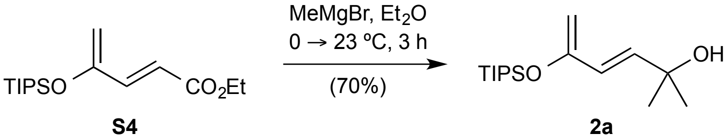
Preparation of compounds S3, S4, S7, S8, S11, S12, S14, S15, S17, S18, 2a-f, and (±)-2g:



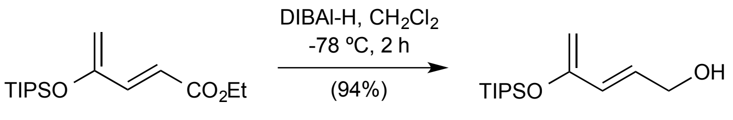
(*E*)-ethyl 4-oxopent-2-enoate (S3): (*E*)-ethyl 4-oxopent-2-enoate **S3** was prepared by a modified reported procedure.[5] To a solution of 1-(triphenylphosphoranylidene)-2-propanone **S1** (21.0 g, 65.9 mmol, 1.0 equiv.) and ethyl glycolate **S2** (7.5 mL, 79.2 mmol, 1.2 equiv.) in anhydrous CH_2Cl_2 (220 mL) was added MnO_2 (57.5 g, 661.3 mmol, 10.0 equiv.) and vigorously stirred at ambient temperature (23 ºC) for 30 h. The mixture was filtered through a short pad of celite and the filtrate was concentrated using rotary evaporation. The residue was then diluted with cold Et_2O (100 mL), filtered through a plug of celite and washed with additional Et_2O (50 mL). The filtrate was concentrated by rotary evaporation and purified by an automated flash chromatography system (5 → 20% EtOAc/hexanes) providing 7.68 g (82% yield) of ketoester **S3** as a pale yellow liquid: TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.38; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.99 (d, *J* = 16.1 Hz, 1H), 6.62 (dd, *J* = 16.1, 0.4 Hz, 1H), 4.24 (qd, *J* = 7.1, 0.4 Hz, 2H), 2.34 (s, 3H), 1.30 (td, *J* = 7.1, 0.5 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 197.7, 165.5, 140.0, 131.7, 61.5, 28.2, 14.2; IR (thin film): 2985, 1726, 1703, 1687 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_7H_{10}LiO_3$ $[M+Li]^+$: 149.0790, found: 149.0784.



(*E*)-ethyl 4-((triisopropylsilyl)oxy)penta-2,4-dienoate (S4): To a solution of ketoester **S3** (2.25 g, 15.8 mmol, 1.0 equiv.) in anhydrous Et_2O (32 mL) at 0 ºC was added Et_3N (4.4 mL, 31.6 mmol, 2.0 equiv.) dropwise. After stirring for 10 min, TIPSOTf (5.1 mL, 18.9 mmol, 1.2 equiv.) was added over a period of 30 min. The reaction was stirred for 2 h at 0 ºC then quenched with a saturated aqueous solution of $NaHCO_3$ (30 mL). The aqueous layer was extracted with Et_2O (2 × 50 mL) and the combined organic extracts were then washed with brine (50 mL). The organic layer was then dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation. The residue was purified by an automated flash chromatography system (0.5 → 10% EtOAc/hexanes) providing 4.70 g (99% yield) of diene **S4** as a clear colorless liquid: TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.73; ^1H NMR (500 MHz, $CDCl_3$): δ 7.07 (d, J = 15.2 Hz, 1H), 6.18 (d, J = 15.2 Hz, 1H), 4.62 (dd, J = 1.3, 0.5 Hz, 1H), 4.61 (dd, J = 1.2, 0.6 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H), 1.28–1.20 (m, 3H), 1.10 (d, J = 7.3 Hz, 18H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 167.3, 154.0, 142.6, 119.2, 101.8, 60.6, 18.1 (6), 14.4, 12.9 (3); IR (thin film): 2946, 2869, 1719, 1638, 1593 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{16}H_{31}O_3Si$ $[M+H]^+$: 299.2037, found: 299.2054.

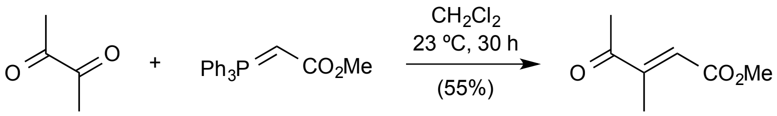


(*E*)-2-methyl-5-((triisopropylsilyl)oxy)hexa-3,5-dien-2-ol (2a): To a solution of diene **S4** (5.20 g, 17.4 mmol, 1.0 equiv.) in anhydrous Et_2O (60 mL) at 0 ºC was added MeMgBr (3.0 M solution in Et_2O, 13.4 mL, 40.2 mmol, 2.3 equiv.) was added over a period of 1 h. The reaction was stirred for 2 h at 23 ºC then quenched with a saturated aqueous solution of NH_4Cl (30 mL). The aqueous layer was extracted with Et_2O (2 × 50 mL) and the combined organic extracts were then washed with brine (30 mL). The organic layer was then dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation. The residue was purified by an automated flash chromatography system (0.5 → 15% EtOAc/hexanes) providing 3.47 g (70% yield) of silyloxydiene alcohol **2a** as a clear colorless oil: TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.35; ^1H NMR (500 MHz; $CDCl_3$): δ 6.18 (d, J = 15.4 Hz, 1H), 6.05 (d, J = 15.4 Hz, 1H), 4.31 (s, 1H), 4.28 (s, 1H), 1.34 (s, 6H), 1.26–1.21 (m, 3H), 1.10 (d, J = 7.3 Hz, 18H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 155.1, 138.2, 124.8, 95.2, 70.8, 29.9 (2), 18.2 (6), 12.9 (3); IR (thin film): 3374, 2945, 2868, 1591 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{16}H_{33}O_2Si$ $[M+H]^+$: 285.2250, found: 285.2242.



S4 **2b**

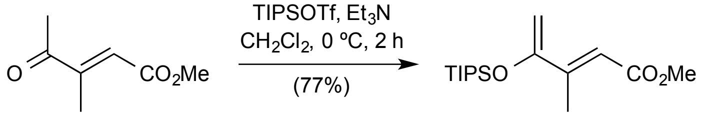
(*E*)-4-((triisopropylsilyl)oxy)penta-2,4-dien-1-ol (2b): To a solution of diene **S4** (4.70 g, 15.7 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (120 mL) at -78 ºC was added DIBAl-H (1.0 M solution in CH_2Cl_2, 47.0 mL, 3.0 equiv.) dropwise. The reaction was stirred for 2 h then carefully quenched in sequence with H_2O (1.9 mL), 15% aqueous NaOH (1.9 mL), and H_2O (4.7 mL). The dry ice/acetone bath was removed and the mixture was allowed to warm up to ambient temperature (23 ºC) on its own accord. Subsequently, anhydrous $MgSO_4$ was added and the reaction mixture was vigorously stirred for 30 min, filtered through a pad of celite and concentrated by rotary evaporation. The residue was purified by an automated flash chromatography (5 → 20% EtOAc/hexanes) providing 3.78 g (94% yield) of silyloxydiene alcohol **2b** as a pale yellow oil: TLC (EtOAc:hexanes, 1:9 *v/v*): $R_f = 0.32$; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.19 (dt, *J* = 15.2, 5.4 Hz, 1H), 6.09 (dt, *J* = 15.2, 1.4 Hz, 1H), 4.31 (d, *J* = 0.5 Hz, 1H), 4.27 (d, *J* = 0.4 Hz, 1H), 4.24 (d, *J* = 5.2 Hz, 2H), 1.27–1.20 (m, 3H), 1.10 (d, *J* = 7.3 Hz, 18H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 154.8, 129.2, 129.0, 95.1, 63.1, 18.2 (6), 12.9 (3); IR (thin film): 3318, 2945, 2868, 1662, 1591 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{14}H_{29}O_2Si$ $[M+H]^+$: 257.1937, found: 257.1926.



S5 **S6** **S7**

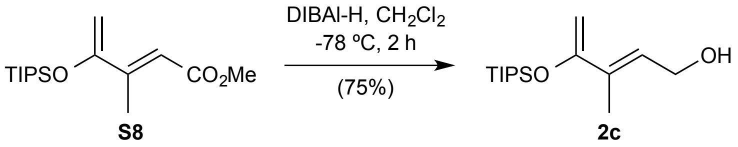
Methyl (*E*)-3-methyl-4-oxopent-2-enoate (S7): To a solution of 2,3-butanedione **S5** (2.6 mL, 30.0 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (150 mL) was added methyl (triphenylphosphoranylidene)acetate **S6** (10.0 g, 30.0 mmol, 1.0 equiv.) and stirred at ambient temperature (23 ºC) for 30 h. The mixture was filtered through a short pad of celite and the filtrate was concentrated using rotary evaporation. The residue was then diluted with cold Et_2O (80 mL), filtered through a plug of celite and washed with additional Et_2O (40 mL). The filtrate was concentrated by rotary evaporation and purified by an automated flash chromatography system (5 → 20% EtOAc/hexanes) providing

2.34 g (55% yield) of ketoester **S7** as a clear colorless oil: TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.45; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.56 (q, *J* = 1.5 Hz, 1H), 3.77 (s, 3H), 2.36 (s, 3H), 2.19 (d, *J* = 1.5 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 199.9, 166.7, 150.9, 126.1, 51.9, 26.3, 13.2; IR (thin film): 2955,1728, 1687, 1642 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_7H_{10}LiO_3$ $[M+Li]^+$: 149.0790, found: 149.0797.

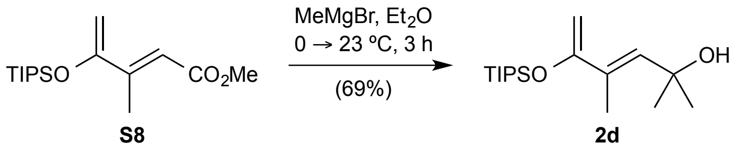


S7 **S8**

Methyl (*E*)-3-methyl-4-((triisopropylsilyl)oxy)penta-2,4-dienoate (S8): To a solution of ketoester **S7** (2.34 g, 16.5 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (60 mL) at 0 ºC was added Et_3N (5.7 mL, 41.2 mmol, 2.5 equiv.) dropwise. After stirring for 10 min, TIPSOTf (5.3 mL, 19.8 mmol, 1.2 equiv.) was added over a period of 30 min. The reaction was stirred for 2 h at 0 ºC then quenched with a saturated aqueous solution of $NaHCO_3$ (30 mL). The aqueous layer was extracted with Et_2O (2 × 50 mL) and the combined organic extracts were then washed with brine (50 mL). The organic layer was then dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation. The residue was purified by an automated flash chromatography system (0.5 → 10% EtOAc/hexanes) providing 3.79 g (77% yield) of diene **S8** as a yellow oil: TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.76; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.39 (d, *J* = 0.6 Hz, 1H), 4.80 (d, *J* = 1.9 Hz, 1H), 4.56 (d, *J* = 1.9 Hz, 1H), 3.71 (s, 3H), 2.28 (d, *J* = 1.2 Hz, 3H), 1.28-1.20 (m, 3H), 1.10 (d, *J* = 7.3 Hz, 18H).^{13}C NMR (125 MHz; $CDCl_3$): δ 168.1, 156.6, 149.8, 115.8, 96.2, 51.2, 18.2 (6), 14.6, 12.9 (3); IR (thin film): 2947, 2869, 1722, 1629, 1597 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{16}H_{31}O_3Si$ $[M+H]^+$: 299.2042, found: 299.2029.

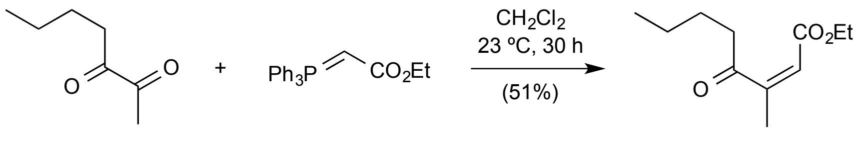


(*E*)-3-methyl-4-((triisopropylsilyl)oxy)penta-2,4-dien-1-ol (2c): To a solution of diene **S8** (7.5 g, 25.1 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (180 mL) at -78 ºC was added DIBAl-H (1.0 M solution in CH_2Cl_2, 72.0 mL, 3.0 equiv.) dropwise. The reaction was stirred for 2 h at -78 ºC then carefully quenched in sequence with H_2O (2.9 mL), 15% aqueous NaOH (2.9 mL), and H_2O (7.2 mL). The dry ice/acetone bath was removed and the mixture was allowed to warm up to ambient temperature (23 ºC) on its own accord. Subsequently, anhydrous $MgSO_4$ was added and the reaction mixture was vigorously stirred for 30 min, filtered through a pad of celite and concentrated by rotary evaporation. The residue was purified by an automated flash chromatography (5 → 20% EtOAc/hexanes) providing 4.88 g (75% yield) of silyloxydiene alcohol **2c** as a clear colorless oil: TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.30; ^1H NMR (500 MHz, C_6D_6): δ 6.44 (tt, *J* = 6.48, 0.55 Hz, 1H), 4.45 (d, *J* = 1.2 Hz, 1H), 4.36 (d, *J* = 0.9 Hz, 1H), 4.06 (d, *J* = 6.3 Hz, 2H), 1.62 (d, *J* = 0.9 Hz, 3H), 1.23-1.18 (m, 3H), 1.14 (d, *J* = 6.2 Hz, 18H); ^{13}C NMR (125 MHz; C_6D_6): δ 157.7, 132.6, 128.1, 91.1, 59.8, 18.4 (6), 13.5, 13.2 (3); IR (thin film): 3320, 2945, 2868, 1593 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{15}H_{31}O_2Si$ $[M+H]^+$: 271.2093, found: 271.2092.



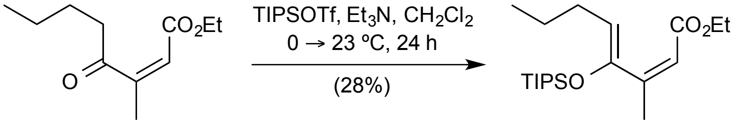
(*E*)-2,4-dimethyl-5-((triisopropylsilyl)oxy)hexa-3,5-dien-2-ol (2d): To a solution of diene **S8** (1.0 g, 3.2 mmol, 1.0 equiv.) in anhydrous Et_2O (10 mL) at 0 ºC was added MeMgBr (3.0 M solution in Et_2O, 2.5 mL, 7.4 mmol, 2.3 equiv.) over a period of 1 h. The reaction was stirred for 2 h at 23 ºC then quenched with a saturated aqueous solution of NH_4Cl (5 mL). The aqueous layer was extracted with Et_2O (2 × 10 mL) and the combined organic extracts were then washed with brine (5 mL). The organic layer was then dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation. The residue was purified by an automated flash chromatography system (0.5 → 15%

EtOAc/hexanes) providing 0.65 g (69% yield) of silyloxydiene alcohol **2d** as a clear colorless oil: TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.48; ^{1}H-NMR (500 MHz; $CDCl_3$): δ 6.25 (s, 1H), 4.47 (s, 1H), 4.29 (s, 1H), 2.02 (s, 3H), 1.40 (s, 6H), 1.27-1.20 (m, 3H), 1.09 (d, *J* = 7.5 Hz, 18H).; ^{13}C NMR (125 MHz; $CDCl_3$): δ 158.0, 134.6, 132.8, 91.2, 71.2, 31.4 (2), 18.2 (6), 14.0, 12.9 (3); IR (thin film): 3406, 2945, 2868, 1664, 1593 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{17}H_{35}O_2Si$ $[M+H]^+$: 299.2406, found: 299.2420.



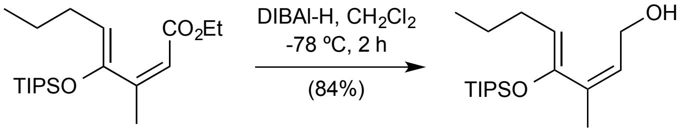
S9 **S10** **S11**

Ethyl (*Z*)-3-methyl-4-oxooct-2-enoate (S11): To a solution of 2,3-heptanedione **S9** (16.8 mL, 120.0 mmol, 1.2 equiv.) in anhydrous CH_2Cl_2 (250 mL) was added ethyl (triphenylphosphoranylidene)acetate **S10** (35.0 g, 100.0 mmol, 1.0 equiv.) and stirred at ambient temperature (23 °C) for 30 h. The mixture was filtered through a short pad of celite and the filtrate was concentrated using rotary evaporation. The residue was then diluted with cold Et_2O (200 mL), filtered through a plug of celite and washed with additional Et_2O (50 mL). The filtrate was concentrated by rotary evaporation and purified by an automated flash chromatography system (5 → 15% EtOAc/hexanes) providing 10.15 g (51% yield) of ketoester **S11** as a pale yellow oil: TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.59; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.52 (q, *J* = 1.5 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.68 (t, *J* = 7.4 Hz, 2H), 2.20 (d, *J* = 1.5 Hz, 3H), 1.62-1.56 (m, 2H), 1.36-1.28 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 202.6, 166.4, 150.8, 125.3, 60.8, 38.1, 26.4, 22.4, 14.3, 14.0, 13.5; IR (thin film): 2961, 2936, 1725, 1687 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{11}H_{18}LiO_3$ $[M+Li]^+$: 205.1416, found: 205.1424.



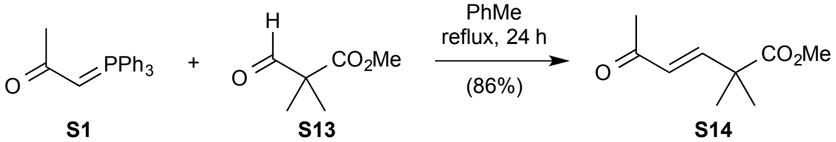
S11 **S12**

Ethyl (2*Z*,4*Z*)-3-methyl-4-((triisopropylsilyl)oxy)octa-2,4-dienoate (S12): To a solution of ketoester **S11** (3.51 g, 17.7 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (60 mL) at 0 °C was added Et_3N (3.7 mL, 26.6 mmol, 1.5 equiv.) dropwise. After stirring for 10 min, TIPSOTf (5.7 mL, 21.2 mmol, 1.2 equiv.) was added over a period of 30 min. The reaction was stirred for 2 h at 0 °C. The mixture was then allowed to warm up to ambient temperature (23 °C) on its own accord and stirred for 22 h. The reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (30 mL). The aqueous layer was extracted with Et_2O (2 × 50 mL) and the combined organic extracts were then washed with brine (50 mL). The organic layer was then dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation. The residue was purified by an automated flash chromatography system (5 → 25% CH_2Cl_2/hexanes) providing 1.75 g (28% yield) of diene **S12** as a pale yellow oil: TLC (CH_2Cl_2:hexanes, 1:4 *v/v*): R_f = 0.41; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.11 (d, *J* = 0.5 Hz, 1H), 5.18 (t, *J* = 7.2 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.27 (d, *J* = 0.8 Hz, 3H), 2.15 (q, *J* = 7.4 Hz, 2H), 1.40 (q, *J* = 7.5 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.21-1.14 (m, 3H), 1.09 (d, *J* = 1.9 Hz, 18H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz; $CDCl_3$): δ 167.7, 152.1, 151.3, 115.8, 114.8, 59.7, 28.7, 22.7, 18.1 (6), 15.4, 14.5, 14.1, 13.9 (3); IR (thin film): 2960, 2869, 1716, 1623 cm^{-1}; HRMS (MALDI+) *m/z* calcd for $C_{20}H_{39}O_3Si$ $[M+H]^+$: 355.2668, found: 355.2644.

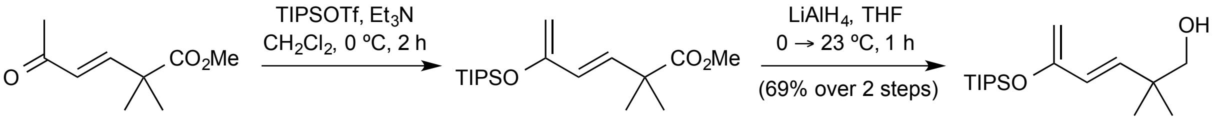


S12 **2e**

(2*Z*,4*Z*)-3-methyl-4-((triisopropylsilyl)oxy)octa-2,4-dien-1-ol (2e): To a solution of diene **S12** (1.1 g, 3.1 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (25 mL) at -78 °C was added DIBAl-H (1.0 M solution in CH_2Cl_2, 9.3 mL, 3.0 equiv.) dropwise. The reaction was stirred for 2 h at -78 °C then carefully quenched in sequence with H_2O (0.37 mL), 15% aqueous NaOH (0.37 mL), and H_2O (0.93 mL). The dry ice/acetone bath was removed and the mixture was allowed to warm up to ambient temperature (23 ºC) on its own accord. Subsequently, anhydrous $MgSO_4$ was added and the reaction mixture was vigorously stirred for 30 min, filtered through a pad of celite and concentrated by rotary evaporation. The residue was purified by an automated flash chromatography (5 → 20% EtOAc/hexanes) providing 0.80 g (84% yield) of silyloxydiene alcohol **2e** as a clear colorless oil: TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.36; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.95 (td, *J* = 6.8, 0.8 Hz, 1H), 4.84 (t, *J* = 7.1 Hz, 1H), 4.26 (d, *J* = 6.8 Hz, 2H), 2.11 (q, *J* = 7.4 Hz, 2H), 1.79 (d, *J* = 1.1 Hz, 3H), 1.38 (dq, *J* = 14.9, 7.4 Hz, 2H), 1.21-1.16 (m, 3H), 1.10 (d, *J* = 6.8 Hz, 18H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 151.3, 135.8, 124.5, 110.9, 59.9, 28.4, 23.0, 18.2 (6), 14.3, 14.2, 14.0 (3); IR (thin film): 3332, 2959, 2868, 1626 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{18}H_{37}O_2Si$ $[M+H]^+$: 313.2563, found: 313.2571.



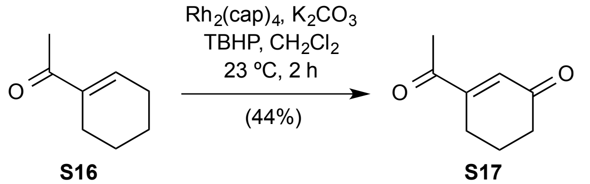
Methyl (*E*)-2,2-dimethyl-5-oxohex-3-enoate (S14): To a solution of 1-(triphenylphosphoranylidene)-2-propanone **S1** (4.32 g, 13.6 mmol, 1.3 equiv.) in anhydrous PhMe (35 mL) was added methyl 2,2-dimethyl-3-oxopropanoate **S13** (1.36 g, 10.5 mmol, 1.0 equiv.), which was freshly prepared from methyl 2,2-dimethyl-3-hydroxypropionate[6] and used immediately without purification, and the mixture was refluxed (115-120 ºC) for 24 h. The mixture was filtered through a short pad of celite and the filtrate was concentrated using rotary evaporation. The residue was then diluted with cold Et_2O (25 mL), filtered through a plug of celite and washed with additional Et_2O (10 mL). The filtrate was concentrated by rotary evaporation and purified by an automated flash chromatography system (5 → 20% EtOAc/hexanes) providing 1.52 g (86% yield) of ketoester **S14** as a clear colorless oil: TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.26; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.92 (d, *J* = 16.3 Hz, 1H), 6.05 (d, *J* = 16.3 Hz, 1H), 3.68 (s, 3H), 2.25 (s, 3H), 1.34 (s, 6H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 198.7, 175.4, 150.4, 128.8, 52.6, 44.8, 27.3, 24.6 (2); IR (thin film): 2983, 2954, 1734, 1702, 1681, 1626 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_9H_{14}LiO_3$ $[M+Li]^+$: 177.1103, found: 177.1108.



S14 **S15** **2f**

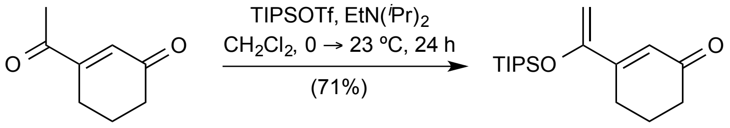
(*E*)-2,2-dimethyl-5-((triisopropylsilyl)oxy)hexa-3,5-dien-1-ol (2f): To a solution of ketoester **S14** (1.52 g, 8.9 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (45 mL) at 0 ºC was added Et_3N (1.5 mL, 10.7 mmol, 1.2 equiv.) dropwise. After stirring for 10 min, TIPSOTf (2.6 mL, 9.6 mmol, 1.1 equiv.) was added over a period of 30 min. The reaction was stirred for 2 h at 0 ºC then quenched with a saturated aqueous solution of $NaHCO_3$ (20 mL). The aqueous layer was extracted with Et_2O (2 × 50 mL) and the combined organic extracts were then washed with brine (50 mL). The organic layer was then dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation to afford crude diene **S15** as a pale yellow oil. The crude material was of sufficient purity to be carried on directly to the next step (Note: purification of this compound led to extensive loss of material on SiO_2).

To a solution of crude diene **S15** in anhydrous THF (64 mL) at 0 ºC was added $LiAlH_4$ (2.0 M solution in THF, 4.5 mL, 1.1 equiv.) dropwise. The reaction was stirred for 30 min at 0 ºC then allowed to warm up to ambient temperature (23 ºC) and stirred for 30 min. The reaction was then cooled to 0 ºC and carefully quenched in sequence with 0.36 mL H_2O, 0.36 mL 15% aqueous NaOH, and 0.90 mL H_2O. The ice bath was removed and the mixture was allowed to warm up to ambient temperature (23 ºC) on its own accord. Subsequently, anhydrous $MgSO_4$ was added and the reaction mixture was vigorously stirred for 30 min, filtered through a pad of celite and concentrated by rotary evaporation. The residue was purified by an automated flash chromatography (5 → 20% EtOAc/hexanes) providing 1.83 g (69% yield over 2 steps) of silyloxydiene alcohol **2f** as a clear colorless oil: TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.29; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.00 (d, *J* = 15.6 Hz, 1H), 5.89 (dd, *J* = 15.6, 0.8 Hz, 1H), 4.29 (s, 1H), 4.25 (s, 1H), 3.35 (s, 2H), 1.27-1.19 (m, 3H), 1.10 (d, *J* = 7.3 Hz, 18H), 1.05 (s, 6H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 155.2, 137.5, 127.0, 94.5, 71.7, 38.4, 23.9 (2), 18.2 (6), 12.9 (3); IR (thin film): 3377, 2948, 2870, 1593 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{17}H_{35}O_2Si$ [M+H]$^+$: 299.2406, found: 299.2413.



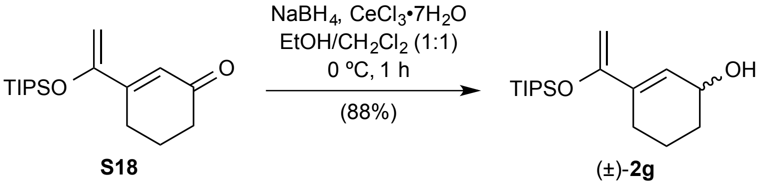
S16 **S17**

3-acetylcyclohex-2-en-1-one (S17): 3-acetylcyclohex-2-en-1-one **S17** was prepared by a modified reported procedure.[7] To a solution of 1-acetyl-1-cyclohexene **S16** (5.2 mL, 40.3 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (150 mL) was added in sequence K_2CO_3 (2.78 g, 20.2 mmol, 0.5 equiv.), $Rh_2(cap)_4$ (42 mg, 0.064 mmol, 0.0016 equiv.) and TBHP (5.0-6.0 M solution in decane, 40.0 mL, 201.5 mmol, 5.0 equiv.). The reaction mixture was exposed to air and vigorously stirred at ambient temperature (23 ºC) for 2 h. The mixture was filtered through a short pad of SiO_2 and the filtrate was concentrated using rotary evaporation. Purification by an automated flash chromatography system (5 → 20% EtOAc/hexanes) afforded 2.42 g (44% yield) of diketone **S17** as a yellow oil: TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.20; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.55 (t, *J* = 1.7 Hz, 1H), 2.49 (td, *J* = 6.0, 1.7 Hz, 2H), 2.44 (t, *J* = 6.8 Hz, 2H), 2.38 (s, 3H), 2.01 (dt, *J* = 13.1, 6.4 Hz, 2H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 201.5, 200.2, 154.7, 132.5, 38.0, 26.2, 23.4, 22.0; IR (thin film): 2955, 1681 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_8H_{10}LiO_2$ [M+Li]$^+$: 145.0841, found: 145.0838.



S17 **S18**

3-(1-((triisopropylsilyl)oxy)vinyl)cyclohex-2-en-1-one (S18): To a solution of diketone **S17** (3.28 g, 23.7 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (100 mL) at 0 ºC was added EtN(^{i}Pr)$_2$ (9.1 mL, 52.2 mmol, 2.2 equiv.) dropwise. After stirring for 10 min, TIPSOTf (7.7 mL, 28.5 mmol, 1.2 equiv.) was added over a period of 30 min. The reaction was stirred for 2 h at 0 ºC. The mixture was then allowed to warm up to ambient temperature (23 ºC) on its own accord and stirred for 22 h. The reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (50 mL). The aqueous layer was extracted with Et_2O (2 × 50 mL) and the combined organic extracts were then washed with brine (50 mL). The organic layer was then dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation. The residue was purified by an automated flash chromatography system (5 → 15% EtOAc/hexanes) providing 4.94 g (71% yield) of diene **S18** as a yellow oil: TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.49; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.44 (s, 1H), 4.83 (dd, *J* = 2.1, 0.5 Hz, 1H), 4.61 (dd, *J* = 2.1, 0.5 Hz, 1H), 2.48 (td, *J* = 6.1, 1.3 Hz, 2H), 2.40 (t, *J* = 6.7 Hz, 2H), 2.06-2.01 (m, 2H), 1.28-1.23 (m, 3H), 1.09 (d, *J* = 7.3 Hz, 18H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 200.9, 155.2, 155.1, 124.6, 96.9, 37.7, 25.6, 22.7, 18.2 (6), 12.9 (3); IR (thin film): 2945, 2867, 1669 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{17}H_{31}O_2Si$ $[M+H]^+$: 295.2093, found: 295.2116.



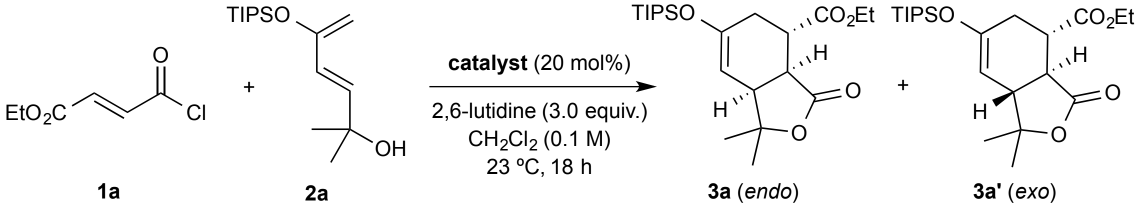
3-(1-((triisopropylsilyl)oxy)vinyl)cyclohex-2-en-1-ol ((±)-2g): To a solution of diene **S18** (3.11 g, 10.6 mmol, 1.0 equiv.) in absolute EtOH (105 mL) and anhydrous CH_2Cl_2 (105 mL) at 0 ºC was added $CeCl_3•7H_2O$ (4.33 g, 11.6 mmol, 1.1 equiv.) in one portion. After stirring for 20 min, $NaBH_4$ (1.0 g, 26.4 mmol, 2.5 equiv.) was added portionwise over a period of 30 min. The reaction was stirred for 30 min at 0 ºC then quenched with a saturated aqueous solution of $NaHCO_3$ (20 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 80 mL) and the combined organic extracts were then washed with brine (20 mL). The organic layer was then dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation. The residue was purified by an automated flash chromatography system (5 → 15% EtOAc/hexanes) providing 2.75 g (88% yield) of silyloxydiene alcohol (±)-**2g** as a clear colorless oil: TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.46; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.30-6.30 (m, 1H), 4.41 (dt, *J* = 1.6, 0.5 Hz, 1H), 4.33-4.30 (m, 1H), 4.28 (d, *J* = 1.6 Hz, 1H), 2.22-2.15 (m, 1H), 2.13-2.07 (m, 1H), 1.91-1.86 (m, 1H), 1.83-1.76 (m, 1H), 1.65-1.51 (m, 2H), 1.28-1.20 (m, 3H), 1.10 (d, *J* = 6.7 Hz, 18H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 156.2, 136.3, 126.8, 91.1, 66.5, 31.9, 25.1, 19.5, 18.3 (6), 13.0 (3); IR (thin film): 3333, 2943, 2867, 1662, 1593 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{17}H_{33}O_2Si$ $[M+H]^+$: 297.2250, found: 297.2264.

DAL optimization studies (Tables S1-S3):

NOTE: The relative and absolute configuration of *trans*-fused bicyclic γ-lactone (+)-**3c'** was unambiguously assigned by X-ray analysis using anomalous dispersion (see **Figure S3**, page 46). Based on this structure, detailed 2D NMR analysis, and computational studies (see **Figure S6**, page 125) which predict the *endo* transition state as the lowest energy pathway, we propose the relative and absolute configurations of bicyclic γ-lactones **3a** and **3a'** as shown in **Table 1a**.

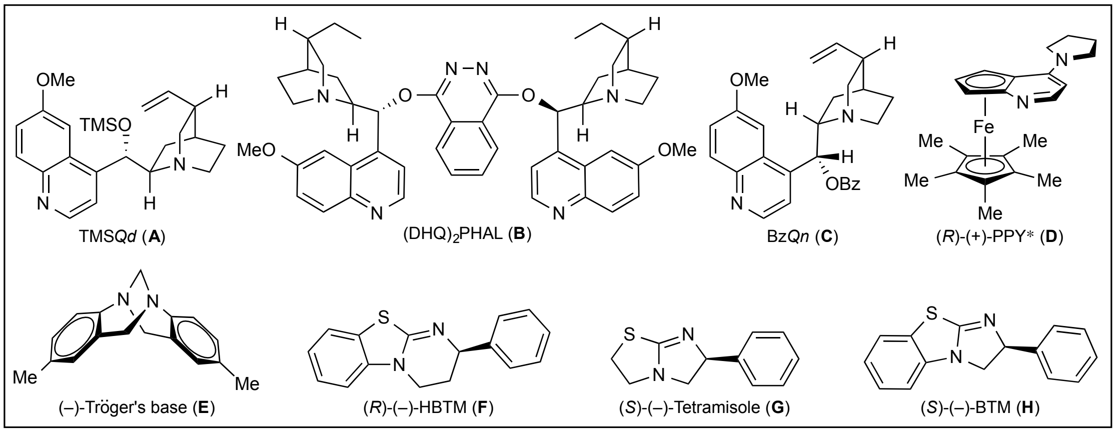
Catalyst screening studies for the enantioselective DAL process (Table S1): Into a dried, 2-mL clear-glass vial (12 × 32 mm) equipped with a magnetic stir bar was added silyloxydiene alcohol **2a** (28 mg, 0.10 mmol, 1.0 equiv.), *catalyst* (0.020 mmol, 20 mol%), 2,6-lutidine (35 μL, 0.30 mmol, 3.0 equiv.) and anhydrous CH_2Cl_2 (1.0 mL, to make final concentration of silyloxydiene alcohol 0.1 M) at ambient temperature (23 ºC). With vigorous stirring, ethyl fumaroyl chloride **1a** (16 μL, 0.12 mmol, 1.2 equiv.) was added dropwise. After stirring for 18 h at ambient temperature (23 ºC), the reaction mixture was concentrated by rotary evaporation and purified by an automated flash chromatography (5 → 20% EtOAc/hexanes) to afford an inseparable 1.5:1 mixture of endo/exo diastereomers (as judged by ^{1}H NMR) of bicyclic γ-lactones **3a** and **3a'** as a clear colorless oil: TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.47. (HPLC data is provided for the 1.5:1 mixture of endo/exo diastereomers) Enantiomeric excess was determined by chiral HPLC analysis in comparison with authentic racemic material using a Chiralcel OD-H column: hexanes:^{i}PrOH = 95:05, flow rate 0.5 mL/min, λ = 210 nm: t_{major} = 10.3 min, t_{minor} = 10.9 min; t_{minor} = 12.7 min, t_{major} = 19.4 min. Absolute stereochemistry was assigned by analogy to bicyclic γ-lactone (+)-**3c'**. (NMR data is provided for the 1.5:1 mixture of *endo*/*exo* diastereomers) ^{1}H NMR (500 MHz; $CDCl_3$): δ 4.78 (s, 1.0H), 4.67 (dd, *J* = 3.3, 2.3 Hz, 1.5H), 4.22-4.06 (m, 5.1H), 3.45 (dd, J = 7.6, 2.3 Hz, 1.5H), 3.25-3.22 (m, 2.4H), 2.96-2.93 (m, 1.6H), 2.90-2.85 (m, 0.9H), 2.43 (d, *J* = 16.8 Hz, 1.5H), 2.34 (ddt, *J* = 17.4, 6.5, 2.5 Hz, 1.5H), 2.17-2.08 (m, 2.9H), 1.43 (s, 3.1H), 1.42 (s, 3.3H), 1.32 (s, 4.6H), 1.29 (s, 4.4H), 1.24-1.19 (m, 7.4H), 1.13-1.07 (m, 7.7H), 1.03-1.00 (m, 45.3H). ^{13}C NMR (125 MHz; $CDCl_3$): δ 176.4, 174.2, 172.9, 172.1, 152.8, 150.9, 101.2, 99.3, 86.2, 84.7, 61.17, 61.16, 46.9, 42.7, 41.5, 40.3, 38.3, 30.5, 30.1, 28.0, 27.6, 27.5, 24.3, 21.0, 17.9 (12), 14.16, 14.08, 12.57 (3), 12.48 (3); IR (thin film): 2945, 2868, 1778, 1769, 1739, 1732, 1666, 1645 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{22}H_{39}O_5Si$ $[M+H]^+$: 411.2567, found: 411.2576.

Table S1. Catalyst screening studies for the enantioselective DAL process.



entry	**catalyst** (20 mol%)	**temperature** (ºC)	***dr*** (*endo*/*exo*)¶	**% ee** (*endo*)§,‡	**yield** (%)Ø
1	–	23	1.2 : 1	0	21
2	**A**	23	1.5 : 1	2	40
3	**B**	23	1.5 : 1	4	31
4	**C**	23	1.5 : 1	7	34
5	**D**	23	1.5 : 1	10	52
6	**E**	23	1.5 : 1	11	35
7	**F**	23	1.5 : 1	82	56
8	**G**	23	1.5 : 1	90	64
9†	**G**	23	1.5 : 1	95	60
10	**H**	23	1.5 : 1	92	63
11†	**H**	23	1.5 : 1	99	58

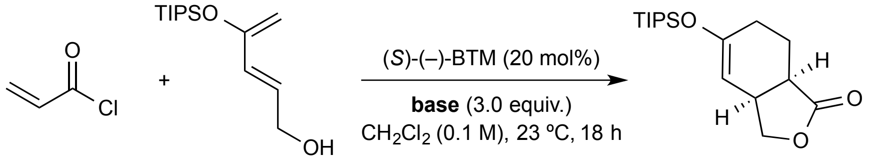
¶Determined by ^1H NMR analysis of the crude reaction mixture. §Determined by chiral HPLC analysis. ‡Enantiomeric excess of the major **3a** (*endo*) diastereomer. ØIsolated yield of the 1.5:1 diastereomeric mixture. †Ethyl fumaroyl chloride **1a** in CH_2Cl_2 (0.3 mL) was added over a period of 5 h by syringe pump addition.



Base screening studies for the enantioselective DAL process (Table S2): Into a dried, 2-mL clear-glass vial (12 × 32 mm) equipped with a magnetic stir bar was added silyloxydiene alcohol **2b** (26 mg, 0.10 mmol, 1.0 equiv.), (*S*)-(–)-BTM (5.0 mg, 0.020

mmol, 20 mol%), *base* (0.30 mmol, 3.0 equiv.) and anhydrous CH_2Cl_2 (1.0 mL, to make final concentration of silyloxydiene alcohol 0.1 M) at ambient temperature (23 ºC). With vigorous stirring, acryloyl chloride **1b** (10 μL, 0.12 mmol, 1.2 equiv.) was added dropwise. After stirring for 18 h at ambient temperature (23 ºC), the reaction mixture was filtered through a short pad of celite and the filtrate was concentrated using rotary evaporation. The crude mixture was analyzed by ^{1}H NMR (500 MHz) and purified by an automated flash chromatography (5 → 20% EtOAc/hexanes) to afford bicyclic γ-lactone (–)-**3b**. All spectral data matched that reported on pages S19-S20.

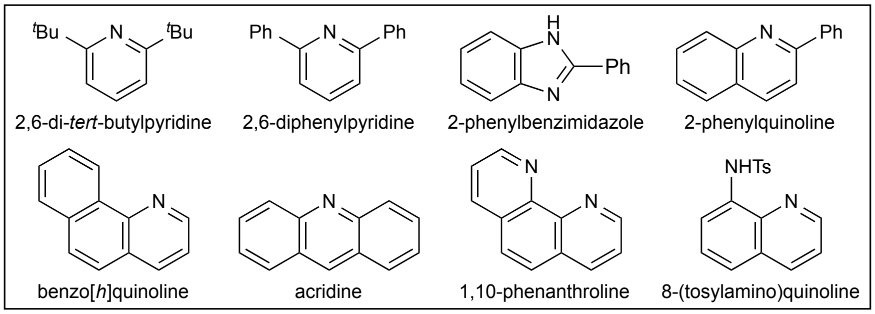
Table S2. Base screening studies for the enantioselective DAL process.



1b **2b** (–)-**3b**

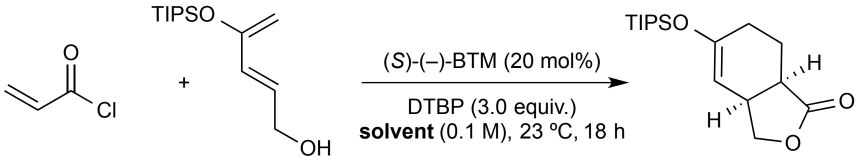
entry	base	*dr* (*endo*/*exo*)¶	*ee* (%)§,‡	conversion (%)†,¶
1	–	*n.d.*	*n.d.*	<5
2	K_2CO_3	*n.d.*	*n.d.*	<5
3	Et_3N	2.4 : 1	60	>95 (60)
4	$EtN(^iPr)_2$	2.4 : 1	65	>95 (55)
5	DBU	2.1 : 1	11	>95 (30)
6	pyridine	3.2 : 1	85	>95 (46)
7	2,6-lutidine	1 : 1	99	>95 (68)
8	2,6-di-*tert*-butylpyridine	>19 : 1	99	>95 (43)
9	K_3PO_4/2,6-lutidine (20 mol%)	>19 : 1	99	>95 (64)
10	2-phenylbenzimidazole	1.7 : 1	84	>95
11	2-phenylquinoline	12 : 1	96	>95
12	benzo[*h*]quinoline	2.8 : 1	96	>95
13	acridine	2.8 : 1	99	>95
14	1,10-phenanthroline	4.4 : 1	97	>95
15	8-(tosylamino)quinoline	6.5 : 1	96	>95
16	2,6-diphenylpyridine	*n.d.*	*n.d.*	<5

¶Determined by ^{1}H NMR analysis of the crude reaction mixture. §Determined by chiral HPLC analysis. ‡Enantiomeric excess of the major (–)-**3b** (*endo*) diastereomer. † Yields in parentheses refer to isolated yields. *n.d.* = not determined.



Solvent screening studies for the enantioselective DAL process (Table S3): Into a dried, 2-mL clear-glass vial (12 × 32 mm) equipped with a magnetic stir bar was added silyloxydiene alcohol **2b** (26 mg, 0.10 mmol, 1.0 equiv.), (*S*)-(–)-BTM (5.0 mg, 0.020 mmol, 20 mol%), 2,6-di-*tert*-butylpyridine (0.30 mmol, 3.0 equiv.) and anhydrous *solvent* (1.0 mL, to make final concentration of silyloxydiene alcohol 0.1 M) at ambient temperature (23 ºC). With vigorous stirring, acryloyl chloride **1b** (10 μL, 0.12 mmol, 1.2 equiv.) was added dropwise. After stirring for 18 h at ambient temperature (23 ºC), the reaction mixture was filtered through a short pad of celite and the filtrate was concentrated using rotary evaporation. The crude mixture of bicyclic γ-lactone (–)-**3b** was analyzed by ^{1}H NMR (500 MHz) and chiral HPLC. All spectral data matched that reported on pages S19-S20.

Table S3. Solvent screening studies for the enantioselective DAL process.



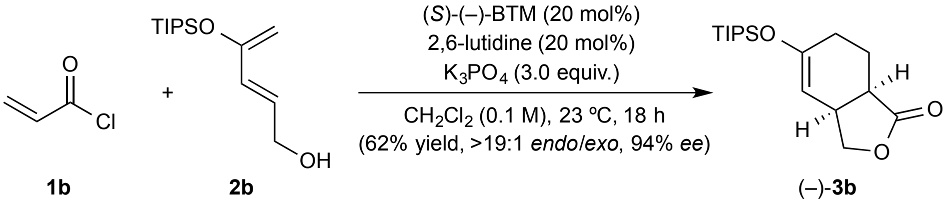
1b **2b** (–)-**3b**

entry	solvent	relative polarity[¶]	*dr* (*endo*/*exo*)[Ø]	*ee* (%)[‡,§]
1	PhMe[†,€]	0.099	8.3 : 1	92
2	PhH[†,€]	0.111	11.7 : 1	92
3	Et_2O[†,€]	0.117	2.8 : 1	48
4	1,4-dioxane[†]	0.164	*n.d.*	*n.d.*
5	THF[†]	0.207	*n.d.*	*n.d.*
6	EtOAc[†]	0.228	*n.d.*	*n.d.*
7	DME[†,€]	0.231	>19 : 1	78
8	$CHCl_3$	0.259	>19 : 1	97
9	CH_2Cl_2	0.309	>19 : 1	99
10	DCE	0.327	>19 : 1	93
11	acetone[†]	0.355	*n.d.*	*n.d.*
12	DMF	0.386	3.7 : 1	36
13	DMSO[Δ]	0.444	*n.d.*	*n.d.*
14	MeCN	0.460	2.1 : 1	67

[¶] The values for relative polarity are normalized from measurements of solvent shifts of absorption spectra and were extracted from Christian Reichardt, Solvents and Solvent Effects in Organic Chemistry, Wiley-VCH Publishers, 3rd ed., 2003. [Ø] Determined by ^{1}H NMR analysis of the crude reaction mixture. [‡] Determined by chiral HPLC analysis. [§] Enantiomeric excess of the major (–)-**3b** (*endo*) diastereomer. [†] Instantaneous formation of precipirate (insoluble acylammonium salt) upon addition of acid chloride. [€] Reaction mixture became homogeneous over a period of 18 h. [Δ] Instantaneous exothermic reaction upon addition of acid chloride. *n.d.* = not determined.

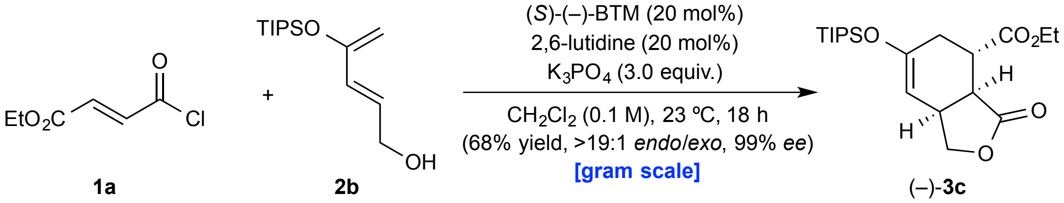
Representative procedure for the enantioselective DAL process as described for bicyclic γ-lactone (–)-3b:

NOTE: The relative and absolute configuration of *trans*-fused bicyclic γ-lactone (+)-**3c'** was unambiguously assigned by X-ray analysis using anomalous dispersion (see **Figure S3**, page 46). Based on this structure, detailed 2D NMR analysis, and computational studies (see **Figure S6**, page 125) which predict the *endo* transition state as the lowest energy pathway, we propose the relative and absolute configurations of bicyclic lactones **3b–j** as shown in **Scheme 1**.



(3a*S*,7a*R*)-5-((triisopropylsilyl)oxy)-3a,6,7,7a-tetrahydroisobenzofuran-1(3*H*)-on ((–)-3b): To an oven-dried, 25-mL round-bottomed flask equipped with a magnetic stir bar was added silyloxydiene alcohol **2b** (144 mg, 0.56 mmol, 1.0 equiv.), (*S*)-(–)-BTM (28 mg, 0.11 mmol, 20 mol%), 2,6-lutidine (13 μL, 0.11 mmol, 20 mol%), K_3PO_4 (0.36 g, 1.68 mmol, 3.0 equiv.) and anhydrous CH_2Cl_2 (4.0 mL, to make final concentration of silyloxydiene alcohol 0.1 M) at ambient temperature (23 ºC). With vigorous stirring, acryloyl chloride **1b** (68 μL, 0.84 mmol, 1.5 equiv.) in CH_2Cl_2 (1.6 mL) was added over a period of 5 h by syringe pump addition. After stirring for an additional 13 h, the reaction mixture was filtered through a pad of celite and concentrated by rotary evaporation. Purification by an automated flash chromatography (5 → 20% EtOAc/hexanes) afforded a single diastereomer (as judged by ^{1}H NMR) of bicyclic γ-lactone (–)-**3b** (107 mg, 62% yield, 94% *ee*) as a clear colorless oil: TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.34; $[\alpha]_D^{17.7}$ = –52.31 (*c* = 1.30, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis in comparison with authentic racemic material using a Chiralcel OD-H column: hexanes:^{i}PrOH = 98:02, flow rate 0.5 mL/min, λ = 210 nm: t_{major} = 15.9 min, t_{minor} = 17.9 min; 94% *ee*. Absolute stereochemistry was assigned by analogy to bicyclic γ-lactone

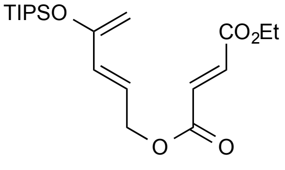
(+)-**3c’**. ^{1}H NMR (500 MHz; CDCl$_3$): δ 4.77-4.77 (m, 1H), 4.33 (dd, *J* = 8.8, 5.9 Hz, 1H), 3.99 (dd, *J* = 8.8, 2.0 Hz, 1H), 3.17-3.13 (m, 1H), 2.75 (dt, *J* = 7.6, 4.0 Hz, 1H), 2.22-2.14 (m, 2H), 2.03-1.97 (m, 1H), 1.87-1.80 (m, 1H), 1.15-1.11 (m, 3H), 1.06 (dd, *J* = 7.1, 2.9 Hz, 18H); ^{13}C NMR (125 MHz; CDCl$_3$): δ 178.6, 153.8, 102.2, 73.2, 37.7, 35.6, 26.2, 20.7, 18.0 (6), 12.7 (3); IR (thin film): 2944, 2867, 1775, 1665 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{17}H_{30}LiO_3Si$ [M+Li]$^+$: 317.2124, found: 317. 2119.



Ethyl (3a*S*,4*S*,7a*S*)-3-oxo-6-((triisopropylsilyl)oxy)-1,3,3a,4,5,7a-hexahydroisobenzofuran-4-carboxylate ((–)-3c): Prepared according to the representative procedure using silyloxydiene alcohol **2b** (1.44 g, 5.6 mmol, 1.0 equiv.), (*S*)-(–)-BTM (283 mg, 1.1 mmol, 20 mol%), 2,6-lutidine (0.13 mL, 1.1 mmol, 20 mol%), K$_3$PO$_4$ (3.6 g, 16.8 mmol, 3.0 equiv.) in anhydrous CH$_2$Cl$_2$ (40 mL, to make final concentration of silyloxydiene alcohol 0.1 M) and ethyl fumaroyl chloride **1a** (0.97 mL, 7.3 mmol, dissolved in 16 mL CH$_2$Cl$_2$, 1.3 equiv.) at ambient temperature (23 ºC). Upon completion (as judged by TLC), the reaction mixture was purified by an automated flash chromatography (5 → 20% EtOAc/hexanes) to afford a single diastereomer (as judged by ^{1}H NMR) of bicyclic γ-lactone (–)-**3c** (1.46 g, 68% yield, 99% *ee*) and ester **S19** (0.41 g, 19% yield) shown below.

(–)-**3c**: clear colorless oil; TLC (EtOAc:hexanes, 1:9 *v/v*): R$_f$ = 0.49; $[\alpha]_D^{22.1}$ = –81.33 (*c* = 3.00, CHCl$_3$). Enantiomeric excess was determined by chiral HPLC analysis in comparison with authentic racemic material using a Chiralcel OD-H column: hexanes:^{i}PrOH = 95:05, flow rate 0.5 mL/min, λ = 210 nm: t$_{minor}$ = 15.4 min, t$_{major}$ = 18.1 min; 99% *ee*. Absolute stereochemistry was assigned by analogy to bicyclic γ-lactone (+)-**3c’**. ^{1}H NMR (500 MHz; CDCl$_3$): δ 4.73 (t, *J* = 2.5 Hz, 1H), 4.37 (dd, *J* = 8.8, 5.6 Hz, 1H), 4.22-4.09 (m, 2H), 4.03 (d, *J* = 8.8 Hz, 1H), 3.30-3.26 (m, 2H), 3.20 (dd, *J* = 7.3, 2.3 Hz, 1H), 2.49 (dd, *J* = 17.7, 1.4 Hz, 1H), 2.39 (ddt, *J* = 17.7, 6.9, 2.4 Hz, 1H), 1.25 (t,

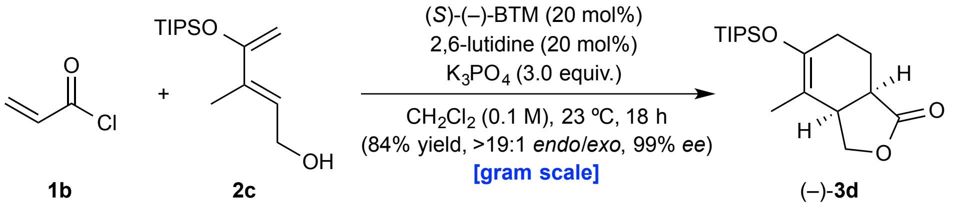
J = 7.1 Hz, 3H), 1.16-1.09 (m, 3H), 1.04 (d, J = 6.4 Hz, 18H); ^{13}C NMR (125 MHz; CDCl$_3$): δ 177.2, 172.9, 151.3, 101.7, 73.3, 61.3, 39.4, 37.8, 34.1, 27.9, 17.9 (6), 14.1, 12.6 (3); IR (thin film): 2945, 2867, 1773, 1732, 1668 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{20}H_{34}NaO_5Si$ [M+Na]$^+$: 405.2068, found: 405.2088.



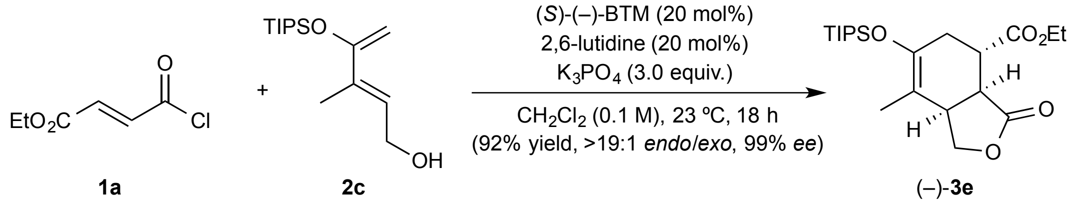
S19

Ethyl ((*E*)-4-((triisopropylsilyl)oxy)penta-2,4-dien-1-yl) fumarate (S19): pale yellow oil; TLC (EtOAc:hexanes, 1:9 *v/v*): R$_f$ = 0.78. ^{1}H NMR (500 MHz; CDCl$_3$): δ 6.92-6.80 (m, 2H), 6.16-6.08 (m, 2H), 4.77 (d, J = 4.8 Hz, 2H), 4.37 (s, 1H), 4.32 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H), 1.27-1.20 (m, 3H), 1.10 (d, J = 7.3 Hz, 18H); ^{13}C NMR (125 MHz; CDCl$_3$): δ 165.1, 164.8, 154.3, 134.1, 133.5, 132.3, 123.1, 96.3, 65.1, 61.5, 18.2 (6), 14.3, 12.9 (3); IR (thin film): 2946, 2869, 1727, 1594 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{20}H_{34}LiO_5Si$ [M+Li]$^+$: 389.2336, found: 389.2332.

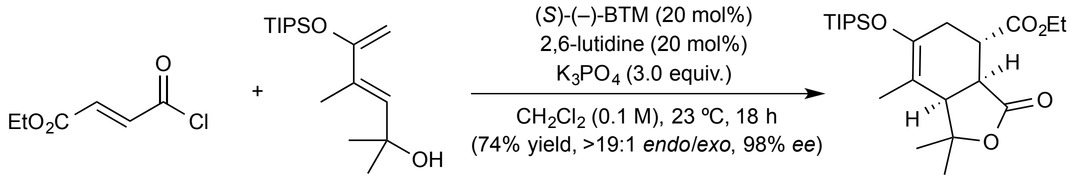
Use of a lower catalyst loading for the DAL (10 mol%) as described for bicyclic γ-lactone (–)-3c: This reaction was performed according to the procedure described above for (–)-**3c** with the exception that a lower catalyst loading (10 vs. 20 mol%), a lower "shuttle" base loading (10 vs. 20 mol%) and a longer addition time (10 vs. 5 h) were employed. Silyloxydiene alcohol **2b** (100 mg, 0.39 mmol, 1.0 equiv.), (*S*)-(–)-BTM (10 mg, 0.039 mmol, 10 mol%), 2,6-lutidine (4.5 μL, 0.039 mmol, 10 mol%), K_3PO_4 (248 mg, 1.2 mmol, 3.0 equiv.) in anhydrous CH_2Cl_2 (3.0 mL, to make final concentration of silyloxydiene alcohol 0.1 M) and ethyl fumaroyl chloride **1a** (68 μL, 0.51 mmol, dissolved in 0.9 mL CH_2Cl_2, 1.3 equiv.). The solution of ethyl fumaroyl chloride **1a** was added by syringe pump over 10 h and the reaction was allowed to stir for 8 h at ambient temperature (23 ºC). Upon completion (as judged by TLC), the reaction mixture was purified by an automated flash chromatography (5 → 20% EtOAc/hexanes) to afford a single diastereomer (as judged by ^{1}H NMR) of bicyclic γ-lactone (–)-**3c** (59 mg, 40% yield, 98% *ee*) and ester **S19** (34 mg, 23% yield). Enantiomeric excess was determined by chiral HPLC analysis in comparison with authentic racemic material using a Chiralcel OD-H column: hexanes:^{i}PrOH = 95:05, flow rate 0.5 mL/min, λ = 210 nm: t_{minor} = 15.3 min, t_{major} = 18.2 min; 98% *ee*. All spectral data matched that reported above.



(3a*R*,7a*R*)-4-methyl-5-((triisopropylsilyl)oxy)-3a,6,7,7a-tetrahydroisobenzofuran-1(3*H*)-one ((–)-3d): Prepared according to the representative procedure using silyloxydiene alcohol **2c** (4.0 g, 14.8 mmol, 1.0 equiv.), (*S*)-(–)-BTM (747 mg, 2.9 mmol, 20 mol%), 2,6-lutidine (0.34 mL, 2.9 mmol, 20 mol%), K_3PO_4 (9.4 g, 44.4 mmol, 3.0 equiv.) in anhydrous CH_2Cl_2 (130 mL, to make final concentration of silyloxydiene alcohol 0.1 M) and acryloyl chloride **1b** (1.8 mL, 22.2 mmol, dissolved in 18 mL CH_2Cl_2, 1.5 equiv.) at ambient temperature (23 ºC). Upon completion (as judged by TLC), the reaction mixture was purified by an automated flash chromatography (5 → 20% EtOAc/hexanes) to afford a single diastereomer (as judged by ^{1}H NMR) of bicyclic γ-lactone (–)-**3d** (4.03 g, 84% yield, 99% *ee*) as a clear colorless oil: TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.37; $[\alpha]_D^{20.3}$ = –87.50 (*c* = 1.60, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis in comparison with authentic racemic material using a Chiralcel AS-H column: hexanes:^{i}PrOH = 99:01, flow rate 1.0 mL/min, λ = 210 nm: t_{major} = 10.3 min, t_{minor} = 11.5 min; 99% *ee*. Absolute stereochemistry was assigned by analogy to bicyclic γ-lactone (+)-**3c'**. ^{1}H NMR (500 MHz; $CDCl_3$): δ 4.32 (dd, *J* = 9.0, 6.5 Hz, 1H), 4.14 (dd, *J* = 9.0, 3.1 Hz, 1H), 3.04-3.01 (m, 1H), 2.77 (dt, *J* = 7.7, 5.0 Hz, 1H), 2.24-2.17 (m, 1H), 2.13-2.08 (m, 1H), 2.07-2.01 (m, 1H), 1.86-1.79 (m, 1H), 1.66 (s, 3H), 1.14-1.09 (m, 3H), 1.06 (dd, *J* = 6.6, 2.1 Hz, 18H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 178.9, 146.8, 107.7, 71.2, 40.6, 38.5, 27.0, 21.2, 18.1 (6), 14.2, 13.3 (3); IR (thin film): 2944, 2867, 1775, 1677 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{18}H_{32}NaO_3Si$ $[M+Na]^+$: 347.2018, found: 347.2024.

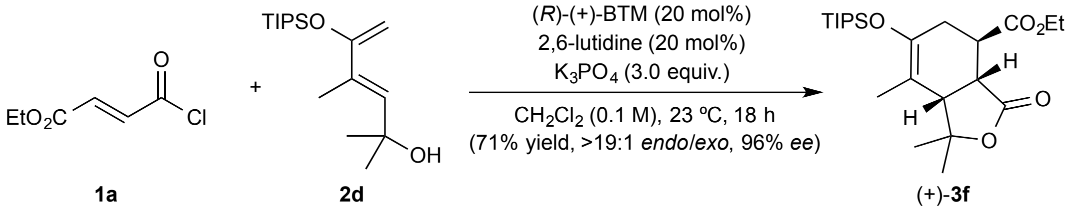


Ethyl (3a*S*,4*S*,7a*R*)-7-methyl-3-oxo-6-((triisopropylsilyl)oxy)-1,3,3a,4,5,7a-hexahydroisobenzofuran-4-carboxylate ((–)-3e): Prepared according to the representative procedure using silyloxydiene alcohol **2c** (50 mg, 0.19 mmol, 1.0 equiv.), (*S*)-(–)-BTM (9.3 mg, 0.037 mmol, 20 mol%), 2,6-lutidine (4.3 μL, 0.037 mmol, 20 mol%), K_3PO_4 (98 mg, 0.46 mmol, 3.0 equiv.) in anhydrous CH_2Cl_2 (1.0 mL, to make final concentration of silyloxydiene alcohol 0.1 M) and ethyl fumaroyl chloride **1a** (37 μL, 0.28 mmol, dissolved in 0.9 mL CH_2Cl_2, 1.5 equiv.) at ambient temperature (23 ºC). Upon completion (as judged by TLC), the reaction mixture was purified by an automated flash chromatography (5 → 20% EtOAc/hexanes) to afford a single diastereomer (as judged by ^{1}H NMR) of bicyclic γ-lactone (–)-**3e** (67 mg, 92% yield, 99% *ee*) as a clear colorless oil: TLC (EtOAc:hexanes, 1:4 *v/v*): R_f = 0.62; $[\alpha]_D^{20.2}$ = –78.86 (*c* = 3.50, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis in comparison with authentic racemic material using a Chiralcel OD-H column: hexanes:^{i}PrOH = 98:02, flow rate 0.4 mL/min, λ = 210 nm: t_{major} = 20.0 min, t_{minor} = 21.3 min; 99% *ee*. Absolute stereochemistry was assigned by analogy to bicyclic γ-lactone (+)-**3c'**. ^{1}H NMR (500 MHz; $CDCl_3$): δ 4.33 (dd, *J* = 9.1, 6.0 Hz, 1H), 4.23-4.20 (m, 1H), 4.20-4.08 (m, 2H), 3.24 (ddd, *J* = 7.5, 3.2, 1.2 Hz, 1H), 3.22-3.20 (m, 1H), 3.19-3.16 (m, 1H), 2.51 (ddq, *J* = 17.1, 2.4, 1.2 Hz, 1H), 2.43 (ddquint, *J* = 17.1, 6.5, 2.3 Hz, 1H), 1.63 (t, *J* = 0.9 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.16-1.10 (m, 3H), 1.05 (dd, *J* = 6.9, 3.3 Hz, 18H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 177.5, 172.8, 144.2, 107.4, 71.0, 61.3, 40.0, 39.2, 38.0, 28.5, 18.0 (6), 14.1, 13.9, 13.2 (3); IR (thin film): 2945, 2868, 1777, 1732, 1679 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{21}H_{37}O_5Si$ $[M+H]^+$: 397.2410, found: 397.2432.

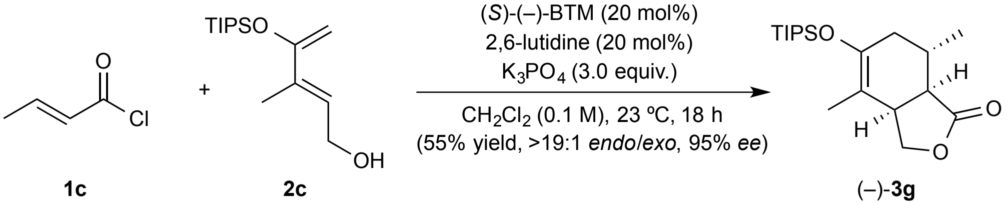


1a **2d** (–)-**3f**

Ethyl (3a*S*,4*S*,7a*R*)-1,1,7-trimethyl-3-oxo-6-((triisopropylsilyl)oxy)-1,3,3a,4,5,7a-hexahydroisobenzofuran-4-carboxylate ((–)-3f): Prepared according to the representative procedure using silyloxydiene alcohol **2d** (30 mg, 0.10 mmol, 1.0 equiv.), (*S*)-(–)-BTM (5.0 mg, 0.020 mmol, 20 mol%), 2,6-lutidine (2.3 μL, 0.020 mmol, 20 mol%), K_3PO_4 (64 mg, 0.30 mmol, 3.0 equiv.) in anhydrous CH_2Cl_2 (0.7 mL, to make final concentration of silyloxydiene alcohol 0.1 M) and ethyl fumaroyl chloride **1a** (20 μL, 0.15 mmol, dissolved in 0.3 mL CH_2Cl_2, 1.5 equiv.) at ambient temperature (23 ºC). Upon completion (as judged by TLC), the reaction mixture was purified by an automated flash chromatography (5 → 20% EtOAc/hexanes) to afford a single diastereomer (as judged by ^{1}H NMR) of bicyclic γ-lactone (–)-**3f** (25 mg, 74% yield, 98% *ee*) as a clear colorless oil: TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.35; $[\alpha]_D^{18.4}$ = –25.60 (*c* = 2.50, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis in comparison with authentic racemic material using a Chiralcel OD-H column: hexanes:^{i}PrOH = 95:05, flow rate 0.5 mL/min, λ = 210 nm: t_{major} = 11.6 min, t_{minor} = 13.6 min; 98% *ee*. Absolute stereochemistry was assigned by analogy to bicyclic γ-lactone (+)-**3c'**. ^{1}H NMR (500 MHz; $CDCl_3$): δ 4.17 (q, *J* = 7.1 Hz, 2H), 3.37 (ddd, *J* = 9.1, 6.3, 0.9 Hz, 1H), 3.10 (q, *J* = 5.9 Hz, 1H), 2.92 (d, *J* = 9.5 Hz, 1H), 2.50 (ddd, *J* = 16.4, 5.6, 1.2 Hz, 1H), 2.30 (ddt, *J* = 16.4, 5.4, 1.8 Hz, 1H), 1.65 (s, 3H), 1.52 (s, 3H), 1.34 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.15-1.10 (m, 3H), 1.08 (d, *J* = 6.8 Hz, 18H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 176.5, 172.9, 145.5, 107.1, 87.5, 61.3, 49.3, 42.0, 40.5, 30.4, 30.3, 25.3, 18.1 (6), 17.0, 14.3, 13.3 (3); IR (thin film): 2945, 2868, 1768, 1735, 1671 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{23}H_{41}O_5Si$ $[M+H]^+$: 425.2723, found: 425.2705.

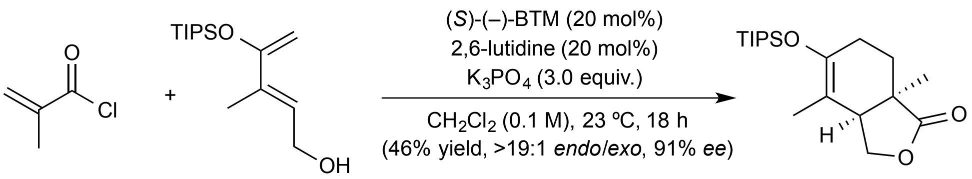


Ethyl (3a*R*,4*R*,7a*S*)-1,1,7-trimethyl-3-oxo-6-((triisopropylsilyl)oxy)-1,3,3a,4,5,7a-hexahydroisobenzofuran-4-carboxylate ((+)-3f): Prepared according to the representative procedure using silyloxydiene alcohol **2d** (554 mg, 1.86 mmol, 1.0 equiv.), (*R*)-(+)-BTM (94 mg, 0.37 mmol, 20 mol%), 2,6-lutidine (43 μL, 0.37 mmol, 20 mol%), K_3PO_4 (1.20 g, 5.57 mmol, 3.0 equiv.) in anhydrous CH_2Cl_2 (13 mL, to make final concentration of silyloxydiene alcohol 0.1 M) and ethyl fumaroyl chloride **1a** (0.37 mL, 2.78 mmol, dissolved in 5.5 mL CH_2Cl_2, 1.5 equiv.) at ambient temperature (23 ºC). Upon completion (as judged by TLC), the reaction mixture was purified by an automated flash chromatography (5 → 20% EtOAc/hexanes) to afford a single diastereomer (as judged by ^{1}H NMR) of bicyclic γ-lactone (+)-**3f** (558 mg, 71% yield, 96% *ee*) as a clear colorless oil: $[\alpha]_D^{19.0}$ = +27.83 (*c* = 2.30, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis in comparison with authentic racemic material using a Chiralcel OD-H column: hexanes:^{i}PrOH = 95:05, flow rate 0.5 mL/min, λ = 210 nm: t_{minor} = 11.4 min, t_{major} = 13.5 min; 96% *ee*. Absolute stereochemistry was assigned by analogy to bicyclic γ-lactone (+)-**3c'**. All spectral data matched that reported above.



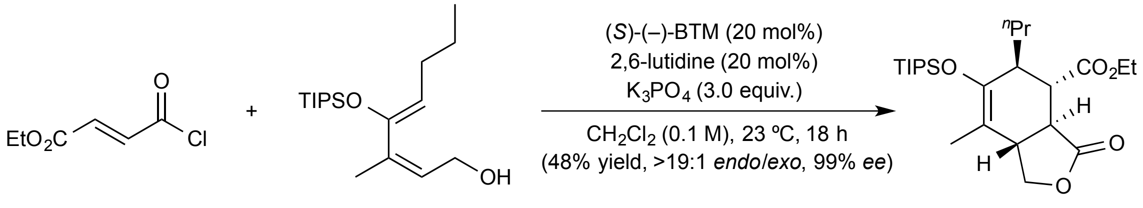
(3a*R*,7*S*,7a*R*)-4,7-dimethyl-5-((triisopropylsilyl)oxy)-3a,6,7,7a-tetrahydroisobenzofuran-1(3*H*)-one ((–)-3g): Prepared according to the representative procedure using silyloxydiene alcohol **2c** (287 mg, 1.06 mmol, 1.0 equiv.), (*S*)-(–)-BTM (53 mg, 0.21 mmol, 20 mol%), 2,6-lutidine (25 μL, 0.21 mmol, 20 mol%), K_3PO_4 (675 mg, 3.18 mmol, 3.0 equiv.) in anhydrous CH_2Cl_2 (7.5 mL, to make final concentration of silyloxydiene alcohol 0.1 M) and crotonoyl chloride **1c** (0.15 mL, 1.6 mmol, dissolved in 2.5 mL

CH_2Cl_2, 1.5 equiv.) at ambient temperature (23 ºC). Upon completion (as judged by TLC), the reaction mixture was purified by an automated flash chromatography (5 → 20% EtOAc/hexanes) to afford a single diastereomer (as judged by ^{1}H NMR) of bicyclic γ-lactone (–)-**3g** (197 mg, 55% yield, 95% *ee*) as a clear colorless oil: TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.43; $[\alpha]_D^{20.5}$ = –64.57 (*c* = 7.00, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis in comparison with authentic racemic material using a Chiralcel OD-H column: hexanes:^{i}PrOH = 98:02, flow rate 0.5 mL/min, λ = 210 nm: t_{minor} = 16.0 min, t_{major} = 17.0 min; 95% *ee*. Absolute stereochemistry was assigned by analogy to bicyclic γ-lactone (+)-**3c'**. ^{1}H NMR (500 MHz; $CDCl_3$): δ 4.33 (dd, *J* = 8.8, 6.7 Hz, 1H), 4.09 (dd, *J* = 8.8, 4.7 Hz, 1H), 2.99 (q, *J* = 5.8 Hz, 1H), 2.39 (t, *J* = 6.8 Hz, 1H), 2.33-2.30 (m, 1H), 2.29-2.27 (m, 1H), 1.85-1.80 (m, 1H), 1.63 (s, 3H), 1.13-1.09 (m, 6H), 1.05 (dd, *J* = 6.7, 2.3 Hz, 18H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 178.3, 144.9, 106.4, 71.5, 44.6, 39.8, 35.2, 26.9, 19.2, 18.1 (6), 13.9, 13.2 (3); IR (thin film): 2945, 2868, 1772, 1678 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{19}H_{35}O_3Si$ $[M+H]^+$: 339.2355, found: 339.2382.



1d **2c** (–)-**3h**

(3a*S*,7a*R*)-4,7a-dimethyl-5-((triisopropylsilyl)oxy)-3a,6,7,7a-tetrahydroisobenzofuran-1(3*H*)-one ((–)-3h): Prepared by a modified representative procedure. To an oven-dried, 50-mL round-bottomed flask equipped with a magnetic stir bar was added (*S*)-(–)-BTM (87 mg, 0.34 mmol, 20 mol%), 2,6-lutidine (40 μL, 0.34 mmol, 20 mol%), K_3PO_4 (1.10 g, 5.16 mmol, 3.0 equiv.) and anhydrous CH_2Cl_2 (10 mL, to make final concentration of silyloxydiene alcohol 0.07 M) at ambient temperature (23 ºC). With vigorous stirring, silyloxydiene alcohol **2c** (464 mg, 1.72 mmol, 1.0 equiv.) in CH_2Cl_2 (3.5 mL) and methacryloyl chloride **1d** (0.25 mL, 2.58 mmol, 1.5 equiv.) in CH_2Cl_2 (3.5 mL) were simultaneously added over a period of 8 h using two separate syringe pumps. After stirring for an additional 10 h, the reaction mixture was filtered through a pad of celite and concentrated by rotary evaporation. Purification by an automated flash chromatography (5 → 20% EtOAc/hexanes) afforded a single diastereomer (as judged by ^{1}H NMR) of bicyclic γ-lactone (–)-**3h** (266 mg, 46% yield, 91% *ee*) as a clear colorless oil: TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.45; $[\alpha]_D^{20.4}$ = –60.00 (*c* = 0.40, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis in comparison with authentic racemic material using a Chiralcel AS-H column: hexanes:^{i}PrOH = 98:02, flow rate 0.5 mL/min, λ = 210 nm: t_{major} = 11.8 min, t_{minor} = 14.0 min; 91% *ee*. Absolute stereochemistry was assigned by analogy to bicyclic γ-lactone (+)-**3c'**. ^{1}H NMR (500 MHz; $CDCl_3$): δ 4.45 (dd, *J* = 8.9, 7.3 Hz, 1H), 3.97 (dd, *J* = 8.9, 6.2 Hz, 1H), 2.63 (t, *J* = 6.7 Hz, 1H), 2.17-2.13 (m, 2H), 1.94 (ddd, *J* = 13.2, 7.3, 5.9 Hz, 1H), 1.64 (s, 3H), 1.63-1.59 (m, 1H), 1.25 (s, 3H), 1.15-1.11 (m, 3H), 1.08 (d, *J* = 6.3 Hz, 18H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 181.7, 145.6, 107.7, 70.6, 47.8, 41.1, 28.6, 26.7, 21.5, 18.1 (6), 17.8, 13.3 (3); IR (thin film): 2944, 2867, 1776, 1680 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{19}H_{34}NaO_3Si$ [M+Na]$^+$: 361.2175, found: 361.2181.

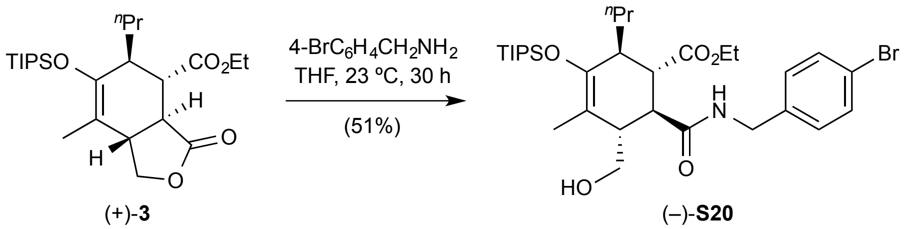


1a **2e** (+)-**3i**

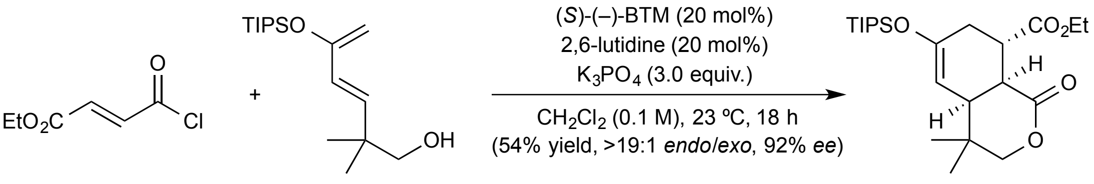
Ethyl (3a*S*,4*S*,5*S*,7a*S*)-7-methyl-3-oxo-5-propyl-6-((triisopropylsilyl)oxy)-1,3,3a,4,5,7a-hexahydroisobenzofuran-4-carboxylate ((+)-3i): Prepared according to the representative procedure using silyloxydiene alcohol **2e** (740 mg, 2.37 mmol, 1.0 equiv.), (*S*)-(–)-BTM (120 mg, 0.47 mmol, 20 mol%), 2,6-lutidine (55 μL, 0.47 mmol, 20 mol%), K_3PO_4 (1.50 g, 7.11 mmol, 3.0 equiv.) in anhydrous CH_2Cl_2 (17 mL, to make final concentration of silyloxydiene alcohol 0.1 M) and ethyl fumaroyl chloride **1a** (0.47 mL, 3.56 mmol, dissolved in 6.0 mL CH_2Cl_2, 1.5 equiv.) at ambient temperature (23 ºC). Upon completion (as judged by TLC), the reaction mixture was purified by an automated flash chromatography (5 → 20% EtOAc/hexanes) to afford a single diastereomer (as judged by ^{1}H NMR) of bicyclic γ-lactone (+)-**3i** (496 mg, 48% yield, 99% *ee*) as a clear colorless oil: TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.44; $[\alpha]_D^{19.0}$ = +61.33 (*c* = 1.50, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis in comparison with authentic racemic material using a Chiralcel AD-H column: hexanes:^{i}PrOH = 95:05, flow rate 0.5 mL/min, λ = 210 nm: t_{major} = 11.4 min, t_{minor} = 12.7 min; 99% *ee*. The relative stereochemistry of bicyclic γ-lactone (+)-**3i** was assigned based on detailed 2D NMR analysis following γ-lactone ring opening with 4-bromobenzylamine as described for amide (–)-**S20** (page S29). Absolute stereochemistry was assigned by analogy to bicyclic γ-lactone (+)-**3c'**. ^{1}H NMR (500 MHz; $CDCl_3$): δ 4.39 (dd, *J* = 7.9, 6.1 Hz, 1H), 4.29-4.17 (m, 2H), 3.90 (dd, *J* = 10.9, 8.0 Hz, 1H), 2.85 (dd, *J* = 11.5, 6.3 Hz, 1H), 2.80-2.74 (m, 1H), 2.69 (dd, *J* = 13.6, 11.5 Hz, 1H), 2.53 (t, *J* = 6.2 Hz, 1H), 1.65-1.57 (m, 5H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.28-1.25 (m, 1H), 1.19-1.13 (m, 4H), 1.10 (d, *J* = 5.7 Hz, 18H), 0.84 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.6, 170.9, 148.2, 109.0, 70.6, 61.1, 44.0, 43.9, 43.6, 41.2, 32.9, 22.0, 18.2 (6), 14.8, 14.2, 13.8, 13.1 (3); IR (thin film): 2946, 2869, 1794, 1736, 1658 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{24}H_{43}O_5Si$ $[M+H]^+$: 439.2880, found: 439.2882.

Use of a lower catalyst loading for the DAL (5 mol%) as described for bicyclic γ-lactone (+)-3i: This reaction was performed according to the procedure described above for (+)-**3i** with the exception that a lower catalyst loading (5 vs. 20 mol%), a lower "shuttle" base loading (5 vs. 20 mol%) and a longer addition time (15 vs. 5 h) were employed. Silyloxydiene alcohol **2e** (31 mg, 0.10 mmol, 1.0 equiv.), (*S*)-(–)-BTM (1.3 mg, 0.0050 mmol, 5 mol%), 2,6-lutidine (0.6 μL, 0.0050 mmol, 5 mol%), K_3PO_4 (64 mg, 0.30 mmol, 3.0 equiv.) in anhydrous CH_2Cl_2 (0.7 mL, to make final concentration of silyloxydiene alcohol 0.1 M) and ethyl fumaroyl chloride **1a** (20 μL, 0.15 mmol, dissolved in 0.3 mL CH_2Cl_2, 1.5 equiv.). The solution of ethyl fumaroyl chloride **1a** was added by syringe pump over 15 h and the reaction was allowed to stir for 3 h at ambient temperature (23 ºC). Upon completion (as judged by TLC), the reaction mixture was purified by an automated flash chromatography (5 → 20% EtOAc/hexanes) to afford a single diastereomer (as judged by ^{1}H NMR) of bicyclic γ-lactone (+)-**3i** (16 mg, 37% yield, 97% *ee*) as a clear colorless oil. Enantiomeric excess was determined by chiral

HPLC analysis in comparison with authentic racemic material using a Chiralcel AD-H column: hexanes:^{i}PrOH = 95:05, flow rate 0.5 mL/min, λ = 210 nm: t_{major} = 11.4 min, t_{minor} = 12.8 min; 97% *ee*. All spectral data matched that reported above.

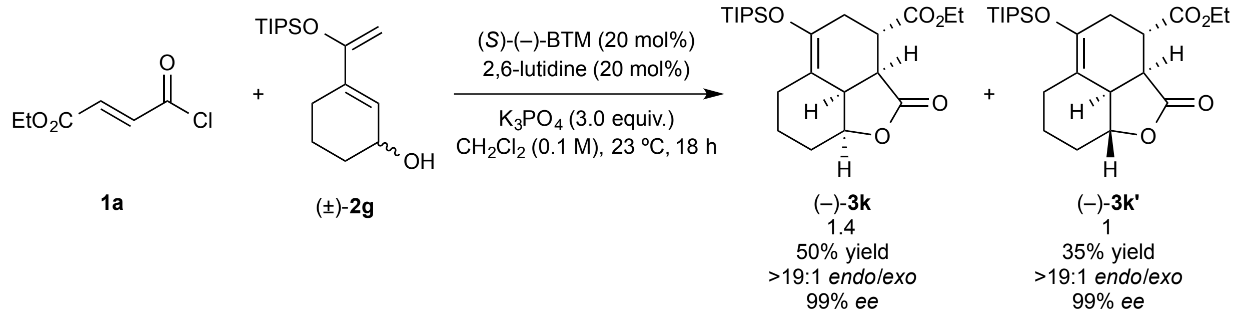


Ethyl (1*S*,2*S*,5*S*,6*S*)-6-((4-bromobenzyl)carbamoyl)-5-(hydroxymethyl)-4-methyl-2-propyl-3-((triisopropylsilyl)oxy)cyclohex-3-ene-1-carboxylate ((–)-S20): Into an oven-dried, 10-mL round-bottomed flask containing a solution of bicyclic γ-lactone (+)-**3i** (120 mg, 0.27 mmol, 1.0 equiv.) in THF (2.7 mL, to make final concentration of bicyclic γ-lactone 0.1 M), was added dropwise 4-bromobenzylamine (0.14 mL, 1.1 mmol, 4.0 equiv.). The reaction was allowed to stir at ambient temperature (23 ºC) for 30 h. Upon completion (as judged by TLC), the reaction was concentrated by rotary evaporation and purified by an automated flash chromatography system (20 → 50% EtOAc/hexanes) to afford amide (–)-**S20** (86 mg, 51% yield) as a pale yellow solid: m.p. 126-130 ºC; TLC (EtOAc:hexanes, 1:2 *v/v*): R_f = 0.55; $[\alpha]_D^{18.1}$ = –14.10 (*c* = 8.60, CHCl$_3$). ^{1}H NMR (500 MHz; CDCl$_3$): δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.70 (t, *J* = 5.8 Hz, 1H), 4.43 (dd, *J* = 15.0, 6.1 Hz, 1H), 4.31 (dd, *J* = 15.0, 5.6 Hz, 1H), 4.10-4.00 (m, 2H), 3.70 (dd, *J* = 11.1, 4.6 Hz, 1H), 3.63 (dd, *J* = 11.2, 2.5 Hz, 1H), 3.15 (dd, *J* = 12.4, 4.5 Hz, 1H), 2.98 (dd, *J* = 12.3, 8.6 Hz, 1H), 2.49-2.45 (m, 2H), 1.60 (s, 3H), 1.44-1.37 (m, 2H), 1.27-1.13 (m, 8H), 1.11 (t, *J* = 6.3 Hz, 18H), 0.81 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz; CDCl$_3$): δ 175.4, 173.7, 150.8, 137.7, 131.7 (2), 129.6 (2), 121.2, 107.3, 62.6, 60.6, 45.7, 44.9, 43.1, 42.0, 40.9, 34.2, 21.6, 18.2 (6), 14.9, 14.1, 14.0, 13.6 (3); IR (thin film): 3424, 3288, 2945, 2868, 1731, 1676, 1632, 1556 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{31}H_{51}BrNO_5Si$ [M+H]$^+$: 624.2720, found: 624.2693.



Ethyl (4a*S*,8*S*,8a*S*)-4,4-dimethyl-1-oxo-6-((triisopropylsilyl)oxy)-3,4,4a,7,8,8a-hexahydro-1*H*-isochromene-8-carboxylate ((+)-3j): Prepared according to the representative procedure using silyloxydiene alcohol **2f** (30 mg, 0.10 mmol, 1.0 equiv.), (*S*)-(–)-BTM (5.0 mg, 0.020 mmol, 20 mol%), 2,6-lutidine (2.3 μL, 0.020 mmol, 20 mol%), K_3PO_4 (64 mg, 0.30 mmol, 3.0 equiv.) in anhydrous CH_2Cl_2 (0.7 mL, to make final concentration of silyloxydiene alcohol 0.1 M) and ethyl fumaroyl chloride **1a** (20 μL, 0.15 mmol, dissolved in 0.3 mL CH_2Cl_2, 1.5 equiv.) at ambient temperature (23 ºC). Upon completion (as judged by TLC), the reaction mixture was purified by an automated flash chromatography (5 → 20% EtOAc/hexanes) to afford a single diastereomer (as judged by ^{1}H NMR) of bicyclic δ-lactone (+)-**3j** (23 mg, 54% yield, 92% *ee*) as a clear colorless oil: TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.35; $[\alpha]_D^{18.6}$ = +21.05 (*c* = 0.57, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis in comparison with authentic racemic material using a Chiralcel OD-H column: hexanes:^{i}PrOH = 95:05, flow rate 0.5 mL/min, λ = 210 nm: t_{minor} = 10.7 min, t_{major} = 12.5 min; 92% *ee*. Absolute stereochemistry was assigned by analogy to bicyclic γ-lactone (+)-**3c'**. ^{1}H NMR (500 MHz; $CDCl_3$): δ 4.79-4.78 (m, 1H), 4.17-4.04 (m, 2H), 3.94 (d, *J* = 10.9 Hz, 1H), 3.80 (dd, *J* = 10.9, 1.5 Hz, 1H), 3.49 (dt, *J* = 4.8, 2.4 Hz, 1H), 3.32 (dd, *J* = 7.1, 3.1 Hz, 1H), 2.49-2.44 (m, 2H), 2.31 (ddt, *J* = 17.5, 6.2, 3.0 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.14 (s, 3H), 1.12-1.07 (m, 3H), 1.02 (d, *J* = 6.7 Hz, 18H), 0.90 (s, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 172.9, 172.2, 152.2, 100.4, 75.8, 61.0, 40.1, 39.4, 38.4, 33.2, 27.7, 24.3, 22.6, 18.0 (6), 14.2, 12.6 (3); IR (thin film): 2945, 2868, 1730, 1661 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{23}H_{41}O_5Si$ $[M+H]^+$: 425.2723, found: 425.2725.

Representative procedure for the stereodivergent DAL process as described for bicyclic γ-lactones (–)-3k and (+)-3k':

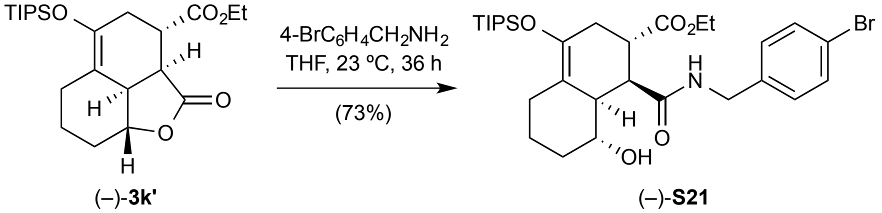


Ethyl (2a*S*,2a^1*R*,3*S*,8a*S*)-2-oxo-5-((triisopropylsilyl)oxy)-2a,2a^1,3,4,6,7,8,8a-octahydro-2*H*-naphtho[1,8-*bc*]furan-3-carboxylate ((–)-3k) and ethyl (2a*S*,2a^1*R*,3*S*,8a*R*)-2-oxo-5-((triisopropylsilyl)oxy)-2a,2a^1,3,4,6,7,8,8a-octahydro-2*H*-naphtho[1,8-*bc*]furan-3-carboxylate ((–)-3k'): Prepared according to the representative procedure using silyloxydiene alcohol (±)-**2g** (250 mg, 0.84 mmol, 1.0 equiv.), (*S*)-(–)-BTM (43 mg, 0.17 mmol, 20 mol%), 2,6-lutidine (20 μL, 0.17 mmol, 20 mol%), K_3PO_4 (535 mg, 2.52 mmol, 3.0 equiv.) in anhydrous CH_2Cl_2 (6.5 mL, to make final concentration of silyloxydiene alcohol 0.1 M) and ethyl fumaroyl chloride **1a** (0.17 mL, 1.26 mmol, dissolved in 1.9 mL CH_2Cl_2, 1.5 equiv.) at ambient temperature (23 ºC). Upon completion (as judged by TLC), the reaction mixture was purified by an automated flash chromatography (5 → 20% EtOAc/hexanes) to afford a single *endo* diastereomer (as judged by ^{1}H NMR) of bicyclic γ-lactone (–)-**3k** (179 mg, 50% yield, 99% *ee*) and a single *endo* diastereomer (as judged by ^{1}H NMR) of bicyclic γ-lactone (–)-**3k'** (124 mg, 35% yield, 99% *ee*).

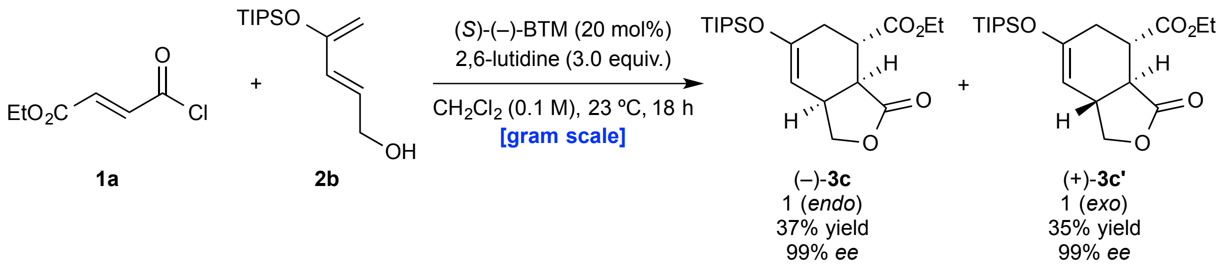
(–)-**3k**: colorless solid; m.p. 58-61 ºC (recrystallized from hexanes); TLC (EtOAc:hexanes, 1:9 *v/v*): R_f = 0.30; $[\alpha]_D^{19.2}$ = –31.30 (*c* = 2.30, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis in comparison with authentic racemic material using a Chiralcel AS-H column: hexanes:^{i}PrOH = 97:03, flow rate 0.5 mL/min, λ = 210 nm: t_{major} = 21.1 min, t_{minor} = 28.6 min; 99% *ee*. Absolute stereochemistry was assigned based on X-ray analysis using anomalous dispersion (see **Figure S1**, page S38). ^{1}H NMR (500 MHz; $CDCl_3$): δ 4.56 (q, *J* = 3.3 Hz, 1H), 4.18-4.05 (m, 2H), 3.23-

3.19 (m, 2H), 3.03-3.01 (m, 1H), 2.92-2.89 (m, 1H), 2.52-2.50 (m, 2H), 2.15-2.12 (m, 1H), 1.71-1.64 (m, 1H), 1.58-1.54 (m, 1H), 1.48-1.35 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.14-1.08 (m, 3H), 1.03 (d, *J* = 6.6 Hz, 18H); ^{13}C NMR (125 MHz; CDCl$_3$): δ 177.6, 173.2, 142.9, 109.6, 79.5, 61.3, 43.0, 38.4, 36.6, 27.9, 27.6, 24.4, 20.7, 18.0 (6), 14.2, 13.3 (3); IR (thin film): 2944, 2867, 1778, 1733, 1677 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{23}H_{39}O_5Si$ [M+H]$^+$: 423.2567, found: 423.2558.

(–)-**3k'**: clear colorless oil; TLC (EtOAc:hexanes, 1:9 *v/v*): R$_f$ = 0.42; $[\alpha]_D^{19.0}$ = –13.33 (*c* = 0.60, CHCl$_3$). Enantiomeric excess was determined by chiral HPLC analysis in comparison with authentic racemic material using a Chiralcel OD-H column: hexanes:^{i}PrOH = 95:05, flow rate 0.5 mL/min, λ = 210 nm: t$_{minor}$ = 17.4 min, t$_{major}$ = 25.7 min; 99% *ee*. Absolute stereochemistry was assigned by derivatization as described below. ^{1}H NMR (500 MHz; CDCl$_3$): δ 4.27-4.15 (m, 2H), 3.86 (td, *J* = 11.2, 3.4 Hz, 1H), 2.93-2.86 (m, 2H), 2.75 (ddd, *J* = 14.0, 5.1, 1.5 Hz, 1H), 2.56-2.50 (m, 1H), 2.47 (dd, *J* = 11.0, 6.8 Hz, 1H), 2.26 (dq, *J* = 11.4, 3.5 Hz, 1H), 2.18 (dd, *J* = 15.6, 3.2 Hz, 1H), 1.98-1.93 (m, 1H), 1.74-1.69 (m, 1H), 1.65 (td, *J* = 12.0, 4.0 Hz, 1H), 1.49-1.39 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.12-1.08 (m, 3H), 1.06 (d, *J* = 4.5 Hz, 18H); ^{13}C NMR (125 MHz; CDCl$_3$): δ 175.7, 172.6, 140.0, 110.9, 83.9, 61.4, 47.7, 40.9, 38.8, 33.2, 30.4, 24.8, 24.5, 18.0 (6), 14.2, 13.1 (3); IR (thin film): 2945, 2868, 1787, 1737, 1697 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{23}H_{39}O_5Si$ [M+H]$^+$: 423.2567, found: 423.2571.



Ethyl (1*S*,2*S*,8*R*,8a*R*)-1-((4-bromobenzyl)carbamoyl)-8-hydroxy-4-((triisopropylsilyl)oxy)-1,2,3,5,6,7,8,8a-octahydronaphthalene-2-carboxylate ((–)-S21): Into an oven-dried, 5-mL round-bottomed flask containing a solution of tricyclic γ-lactone (–)-**3k'** (57 mg, 0.14 mmol, 1.0 equiv.) in THF (1.4 mL, to make final concentration of tricyclic γ-lactone 0.1 M), was added dropwise 4-bromobenzylamine (68 μL, 0.54 mmol, 4.0 equiv.). The reaction was allowed to stir at ambient temperature (23 °C) for 36 h. Upon completion (as judged by TLC), the reaction was concentrated by rotary evaporation and purified by an automated flash chromatography system (20 → 50% EtOAc/hexanes) to afford bicyclic amide (–)-**S21** (60.1 mg, 73% yield) as a white solid: m.p. 143-147 ºC (recrystallized from Et_2O); TLC (EtOAc:hexanes, 1:2 *v/v*): R_f = 0.40; $[\alpha]_D^{18.5}$ = –42.00 (*c* = 6.00, $CHCl_3$). Absolute stereochemistry was assigned based on X-ray analysis using anomalous dispersion (see **Figure S2**, page S42). ^1H NMR (500 MHz; $CDCl_3$): δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.44 (t, *J* = 5.7 Hz, 1H), 4.51 (dd, *J* = 15.0, 6.3 Hz, 1H), 4.23 (dd, *J* = 15.0, 5.2 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.67 (td, *J* = 9.9, 4.4 Hz, 1H), 3.53 (br s, 1H), 3.13 (td, *J* = 11.0, 5.7 Hz, 1H), 2.85 (d, *J* = 12.8 Hz, 1H), 2.71 (dd, *J* = 11.1, 5.4 Hz, 1H), 2.41 (dd, *J* = 16.3, 5.7 Hz, 1H), 2.34 (dd, *J* = 9.6, 5.3 Hz, 1H), 2.26-2.21 (m, 1H), 2.02-1.98 (m, 1H), 1.73-1.69 (m, 1H), 1.42-1.31 (m, 2H), 1.29-1.25 (m, 1H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.12-1.08 (m, 3H), 1.05 (d, *J* = 4.3 Hz, 18H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 177.0, 174.9, 140.6, 137.2, 131.7 (2), 129.7 (2), 121.4, 115.3, 71.3, 61.0, 48.5, 45.6, 43.3, 39.4, 35.6, 33.5, 27.2, 24.9, 18.1 (6), 14.2, 13.2 (3); IR (thin film): 3286, 2942, 2867, 1732, 1714, 1680, 1644, 1557 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{30}H_{47}BrNO_5Si$ $[M+H]^+$: 608.2407, found: 608.2386.



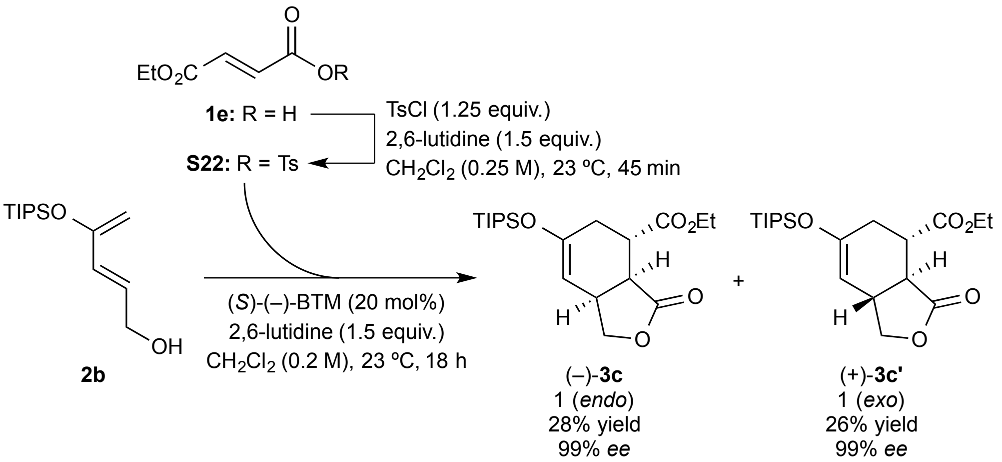
Ethyl (3a*S*,4*S*,7a*S*)-3-oxo-6-((triisopropylsilyl)oxy)-1,3,3a,4,5,7a-hexahydroisobenzofuran-4-carboxylate ((–)-3c) and ethyl (3a*S*,4*S*,7a*R*)-3-oxo-6-((triisopropylsilyl)oxy)-1,3,3a,4,5,7a-hexahydroisobenzofuran-4-carboxylate ((+)-3c'): To an oven-dried, 250-mL round-bottomed flask equipped with a magnetic stir bar was added silyloxydiene alcohol **2b** (2.12 g, 8.22 mmol, 1.0 equiv.), (*S*)-(–)-BTM (416 mg, 1.64 mmol, 20 mol%), 2,6-lutidine (2.9 mL, 24.6 mmol, 3.0 equiv.) and anhydrous CH_2Cl_2 (70 mL, to make final concentration of silyloxydiene alcohol 0.1 M) at ambient temperature (23 ºC). With vigorous stirring, ethyl fumaroyl chloride **1a** (1.31 mL, 9.86 mmol, 1.5

equiv.) in CH_2Cl_2 (12 mL) was added over a period of 5 h by syringe pump addition. After stirring for an additional 13 h, the reaction mixture was filtered through a short pad of SiO_2 and the filtrate was concentrated by rotary evaporation. Purification by an automated flash chromatography (5 → 20% EtOAc/hexanes) afforded bicyclic γ-lactones (–)-**3c** (1.16 g, 37% yield, 99% *ee*) and (+)-**3c'** (1.10 g, 35% yield, 99% *ee*).

(–)-**3c**: All spectral data matched that reported on pages S20-S21.

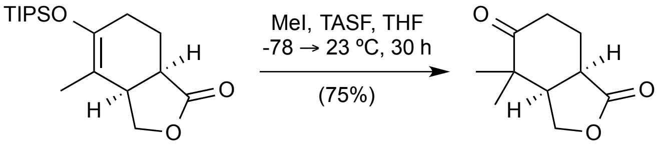
(+)-**3c'**: colorless solid; m.p. 62.1-64.7 °C (recrystallized from CH_2Cl_2); TLC (EtOAc:hexanes, 1:4 *v/v*): R_f = 0.58; $[\alpha]_D^{21.8}$ = +66.67 (*c* = 3.00, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis in comparison with authentic racemic material using a Chiralcel OD-H column: hexanes:^{i}PrOH = 95:05, flow rate 0.5 mL/min, λ = 210 nm: t_{minor} = 22.1 min, t_{major} = 26.1 min; 99% *ee*. Absolute stereochemistry was assigned based on X-ray analysis using anomalous dispersion (see **Figure S3**, page S46). ^{1}H NMR (500 MHz; $CDCl_3$): δ 4.92 (d, *J* = 1.3 Hz, 1H), 4.40 (dd, *J* = 8.0, 6.6 Hz, 1H), 4.28-4.20 (m, 2H), 3.84 (dd, *J* = 11.3, 8.0 Hz, 1H), 2.93 (ddddt, *J* = 13.2, 11.5, 6.6, 3.3, 1.7 Hz, 1H), 2.81 (ddd, *J* = 11.6, 10.6, 7.1 Hz, 1H), 2.58 (dd, *J* = 13.3, 11.7 Hz, 1H), 2.52 (dddd, *J* = 17.6, 7.1, 2.0, 1.2 Hz, 1H), 2.44 (dddd, *J* = 17.7, 10.5, 3.3, 1.9 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.19-1.12 (m, 3H), 1.06 (d, *J* = 6.9 Hz, 18H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 173.9, 172.9, 152.8, 99.5, 71.5, 61.4, 45.1, 40.1, 39.5, 34.4, 18.0 (6), 14.2, 12.6 (3); IR (thin film): 2945, 2868, 1792, 1737, 1650 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{20}H_{34}LiO_5Si$ $[M+Li]^+$: 389.2336, found: 389.2334.

Use of TsCl for *in situ* activation of carboxylic acid (1e) for the stereodivergent DAL process as described for bicyclic γ-lactones (–)-3c and (+)-3c':



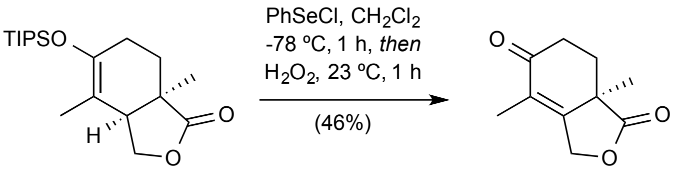
To a solution of *mono*-ethyl fumarate **1e** (18.7 mg, 0.13 mmol, 1.3 equiv.) and TsCl (23.8 mg, 0.125 mmol, 1.25 equiv.) in anhydrous CH_2Cl_2 (0.5 mL, to make final concentration of mixed tosyl anhydride **S22** 0.25 M) was added 2,6-lutidine (18 μL, 0.15 mmol, 1.5 equiv.). The mixture was stirred for 45 min at ambient temperature (23 ºC) and then drawn into the syringe. The solution of **S22** was then transferred *via* syringe pump into a second flask containing silyloxydiene alcohol **2b** (25.6 mg, 0.10 mmol, 1.0 equiv.), (*S*)-(–)-BTM (5.0 mg, 0.020 mmol, 20 mol%), 2,6-lutidine (18 μL, 0.15 mmol, 1.5 equiv) and anhydrous CH_2Cl_2 (0.5 mL) over 5 h. The reaction was stirred for an additional 13 h at ambient temperature (23 ºC), concentrated by rotary evaporation, and then directly purified by an automated flash chromatography (5 → 20% EtOAc/hexanes) to afford bicyclic γ-lactones (–)-**3c** (10.8 mg, 28% yield, 99% *ee*) and (+)-**3c'** (10.2 mg, 26% yield, 99% *ee*). All spectral data matched that reported above.

Synthetic applications of bicyclic γ-lactones (–)-3d and (–)-3h:



(–)-**3d** (–)-**4**

(3a*R*,7a*R*)-4,4-dimethyltetrahydroisobenzofuran-1,5(3*H*,4*H*)-dione ((–)-4): Into an oven-dried, 5-mL round-bottomed flask containing a solution of bicyclic γ-lactone (–)-**3d** (50 mg, 0.17 mmol, 1.0 equiv.) and MeI (0.11 mL, 1.77 mmol, 10.0 equiv.) in THF (0.20 mL, to make final concentration of bicyclic γ-lactone 0.9 M), was added TASF (73 mg, 0.26 mmol, 1.5 equiv.) in one portion at -78 ºC. The dry ice/acetone bath was removed and the mixture was allowed to warm up to ambient temperature (23 ºC) on its own accord and the reaction was allowed to stir for 30 h. Upon completion (as judged by TLC), the mixture was filtered through a short pad of celite, concentrated by rotary evaporation and purified by an automated flash chromatography system (20 → 50% EtOAc/hexanes) to afford α,α-dimethyl ketone (–)-**4** (24 mg, 75% yield) as a clear colorless oil: TLC (EtOAc:hexanes, 1:1 *v/v*): R_f = 0.31; $[\alpha]_D^{19.0}$ = –10.67 (*c* = 0.75, $CHCl_3$). ^1H NMR (500 MHz; $CDCl_3$): δ 4.37 (dd, *J* = 9.7, 7.7 Hz, 1H), 4.04 (dd, *J* = 9.7, 7.9 Hz, 1H), 2.99 (q, *J* = 7.9 Hz, 1H), 2.81 (q, *J* = 7.9 Hz, 1H), 2.61-2.54 (m, 1H), 2.42-2.32 (m, 2H), 2.18-2.10 (m, 1H), 1.24 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 213.1, 178.5, 68.8, 47.2, 44.9, 37.0, 35.8, 26.5, 23.4, 21.2; IR (thin film): 2971, 1771, 1710 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{10}H_{15}O_3$ $[M+H]^+$: 183.1021, found: 183.1027.

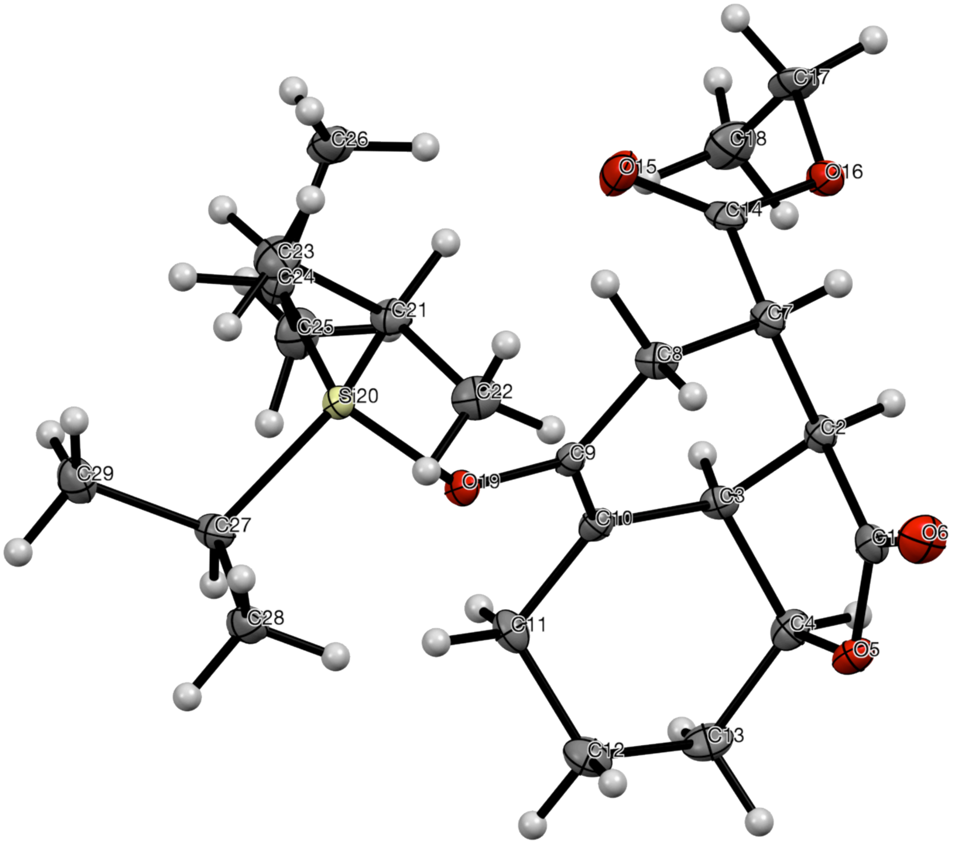


(–)-**3h** (–)-**5**

(*R*)-4,7*a*-dimethyl-7,7a-dihydroisobenzofuran-1,5(3*H*,6*H*)-dione ((–)-5): Into an oven-dried, 25-mL round-bottomed flask containing a solution of bicyclic γ-lactone (–)-**3h** (130 mg, 0.38 mmol, 1.0 equiv.) in CH_2Cl_2 (4.7 mL, to make initial concentration of bicyclic γ-lactone 0.08 M), was added PhSeCl (88 mg, 0.46 mmol, 1.2 equiv.) in CH_2Cl_2 (3.0 mL, to make final concentration of bicyclic γ-lactone 0.05 M) dropwise at -78 ºC. After stirring for 15 min, H_2O_2 (35% wt. % in H_2O, 52 μL, 3.8 mmol, 10.0 equiv.) was added dropwise. The dry ice/acetone bath was removed and the mixture was allowed to warm up to ambient temperature (23 ºC) on its own accord over 45 min. Upon completion (as judged by TLC), the mixture was filtered through a short pad of celite, concentrated by rotary evaporation and purified by an automated flash chromatography system (10 → 40% EtOAc/hexanes) to afford enone γ-lactone **(–)-5** (31 mg, 46% yield) as a white crystalline semisolid: TLC (EtOAc:hexanes, 1:2 *v/v*): R_f = 0.29; $[\alpha]_D^{18.9}$ = –11.11 (*c* = 0.36, $CHCl_3$). ^{1}H NMR (500 MHz; $CDCl_3$): δ 4.99 (q, *J* = 1.1 Hz, 2H), 2.66-2.53 (m, 2H), 2.22 (ddd, *J* = 13.3, 5.2, 2.2 Hz, 1H), 2.09 (td, *J* = 13.4, 6.0 Hz, 1H), 1.74 (t, *J* = 1.1 Hz, 3H), 1.51 (s, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 196.7, 178.4, 154.7, 129.0, 67.4, 41.5, 32.6, 29.7, 21.4, 10.9; IR (thin film): 2924, 1778, 1668 cm^{-1}; HRMS (ESI+) *m/z* calcd for $C_{10}H_{11}O_3$ $[M–H]^+$: 179.0708, found: 179.0711.

Single crystal X-ray structures and selected crystallographic data for compounds (–)-3k, (–)-S21 and (+)-3c’ (Figures S1-S3):

Figure S1. Single crystal X-ray structure (ORTEP) of tricyclic γ-lactone (–)-3k. The crystals were grown from a concentrated solution of tricyclic γ-lactone (–)-**3k** in hexanes (2.0 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 972245.



Alert level B:

THETM01_ALERT_3_B The value of sine(theta_max)/wavelength is less than 0.575. Calculated sin(theta_max)/wavelength = 0.5614. 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.

Table 1. Crystal data and structure refinement for DRB_MA_130730_G_B2.

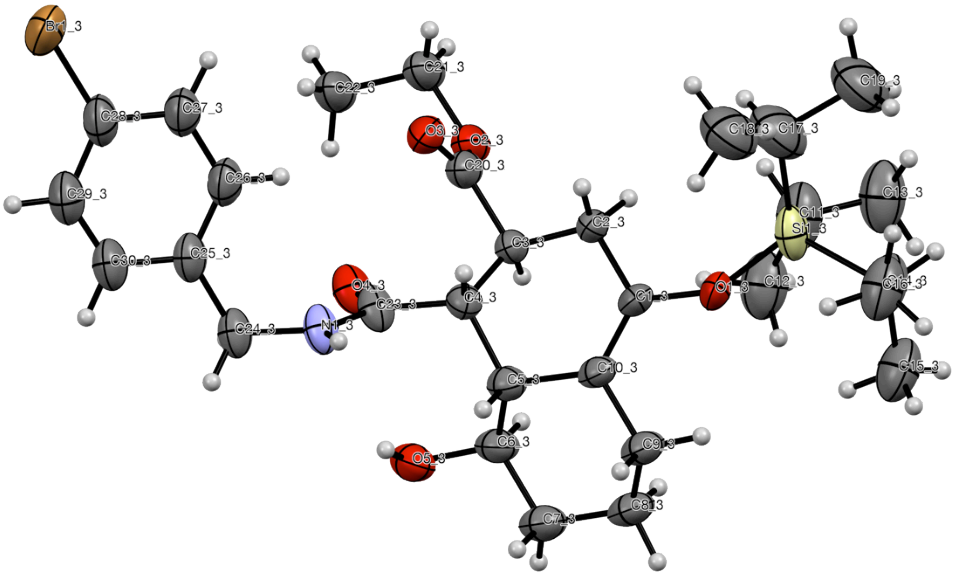
Identification code	b2	
Empirical formula	$C_{23}H_{38}O_5Si$	
Formula weight	422.62	
Temperature	110(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.6924(6) Å	α = 90º
	b = 8.9976(6) Å	β = 90º
	c = 29.0972(18) Å	γ = 90º
Volume	2275.7(3) $Å^3$	
Z	4	
Density (calculated)	1.234 Mg/m^3	
Absorption coefficient	1.157 mm^{-1}	
F(000)	920	
Crystal size	0.13 × 0.07 × 0.03 mm^3	
Theta range for data collection	3.04 to 59.95º	
Index ranges	$-9 \le h \le 9$, $-9 \le k \le 10$, $-32 \le l \le 31$	
Reflections collected	18633	
Independent reflections	3357 [R(int) = 0.0615]	
Completeness to theta = 59.95º	99.8%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9661 and 0.8641	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3357 / 0 / 269	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R_1 = 0.0299, wR_2 = 0.0708	
R indices (all data)	R_1 = 0.0322, wR_2 = 0.0715	
Absolute structure parameter	0.00(2)	
Largest diff. peak and hole	0.167 and -0.240 e.$Å^{-3}$	

Table 2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for DRB_MA_130730_G_B2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
Si(20)	4673(1)	4355(1)	5769(1)	12(1)
O(16)	9567(2)	-615(2)	6467(1)	17(1)
O(19)	5729(1)	4434(2)	6248(1)	14(1)
O(5)	9365(2)	4100(1)	7441(1)	18(1)
O(15)	7446(2)	105(2)	6084(1)	24(1)
O(6)	10899(2)	4472(2)	6835(1)	25(1)
C(14)	8607(2)	404(2)	6285(1)	15(1)
C(1)	9985(2)	3702(2)	7033(1)	17(1)
C(10)	6605(2)	3117(2)	6893(1)	13(1)
C(7)	9199(2)	1964(2)	6372(1)	14(1)
C(9)	6780(2)	3508(2)	6454(1)	12(1)
C(27)	3109(2)	5732(2)	5901(1)	16(1)
C(2)	9344(2)	2199(2)	6891(1)	14(1)
C(22)	7020(3)	6156(2)	5350(1)	21(1)
C(3)	7806(2)	2194(2)	7141(1)	13(1)
C(4)	8292(2)	2929(2)	7595(1)	17(1)
C(29)	1694(2)	5606(2)	5586(1)	22(1)
C(8)	8143(2)	3128(2)	6158(1)	15(1)
C(11)	5281(2)	3646(2)	7186(1)	17(1)
C(25)	3485(3)	1700(2)	6151(1)	23(1)
C(18)	7855(3)	-2535(2)	6774(1)	27(1)
C(17)	9061(3)	-2154(2)	6424(1)	21(1)
C(21)	5919(2)	4863(2)	5261(1)	16(1)
C(12)	5896(2)	4514(2)	7598(1)	22(1)
C(26)	4707(3)	1402(2)	5368(1)	23(1)
C(24)	3803(2)	2455(2)	5686(1)	18(1)

C(28)	3667(3)	7343(2)	5916(1)	21(1)
C(13)	7021(3)	3593(2)	7878(1)	22(1)
C(23)	4979(3)	5129(3)	4820(1)	24(1)

Figure S2. Single crystal X-ray structure (ORTEP) of bicyclic amide (–)-S21. The crystals were grown from a concentrated solution of bicyclic amide (–)-**S21** in Et_2O (2.0 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 972248.



Alert level B:

Crystal system given = triclinic. PLAT019_ALERT_1_B Check _diffrn_measured_ fraction_theta_full/_max = 0.927. Author Response: Physical limitations of the GADDS X-ray diffractometer and triclinic system.

PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) … 4.4 Ratio. Author Response: Possible disorder in the terminal groups. The disorder was not modeled.

PLAT242_ALERT_2_B Low Ueq as Compared to Neighbors for … Si1_4 Check. Author Response: Possible disorder in the Si terminal groups. The disorder was not modeled.

PLAT341_ALERT_3_B Low Bond Precision on C-C Bonds … 0.0194 Ang. Author Response: Diffuse scattering due to disorder lowers the precision of the C-C bond length determination.

Table 1. Crystal data and structure refinement for DR89.

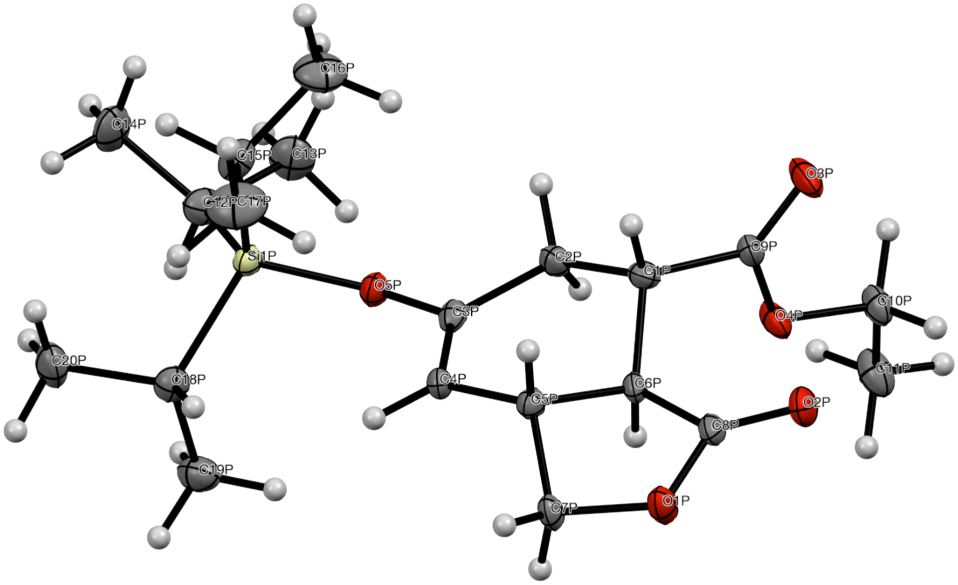
Identification code	dr89	
Empirical formula	$C_{30} H_{46} Br N O_5 Si$	
Formula weight	608.68	
Temperature	110(2) K	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 13.4034(9) Å	α = 89.539(5)°
	b = 13.4037(9) Å	β = 89.620(5)°
	c = 17.8225(13) Å	γ = 87.393(5)°
Volume	3198.4(4) $Å^3$	
Z	4	
Density (calculated)	1.264 Mg/m^3	
Absorption coefficient	2.400 mm^{-1}	
F(000)	1288.0	
Crystal size	0.11 × 0.1 × 0.01 mm^3	
Radiation	CuK α (λ = 1.54178)	
Theta range for data collection	4.958 to 128.74°	
Index ranges	$-15 \leq h \leq 15$, $-15 \leq k \leq 15$, $-20 \leq l \leq 20$	
Reflections collected	55755	
Independent reflections	18937 [R(int) = 0.0831]	
Data / restraints / parameters	18937 / 2631 / 1372	
Goodness-of-fit on F^2	1.089	
Final R indices [I>2sigma(I)]	R_1 = 0.0896, wR_2 = 0.2171	
R indices (all data)	R_1 = 0.1063, wR_2 = 0.2373	
Largest diff. peak and hole	0.84 and -0.73 $e.Å^{-3}$	

Table 2. Fractional atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for DR89. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
Br1_3	10682(3)	15286(3)	10137.5(16)	81.8(9)
Si1_3	9768(4)	14978(4)	2986(3)	56.5(14)
O1_3	9221(7)	14314(6)	3624(4)	43(2)
O2_3	8532(9)	17264(7)	5792(6)	56(2)
O3_3	9470(9)	16079(9)	6369(7)	56(3)
O4_3	7289(8)	15692(8)	6721(6)	52(3)
O5_3	6011(8)	14206(10)	5963(6)	54(3)
N1_3	7793(10)	14158(8)	7106(5)	47(2)
C1_3	8766(10)	14473(9)	4301(6)	38(2)
C2_3	9095(10)	15341(10)	4752(6)	40(2)
C3_3	8383(9)	15607(8)	5397(6)	40(2)
C4_3	8190(8)	14644(8)	5820(5)	39(2)
C5_3	7630(7)	13926(8)	5334(6)	42(2)
C6_3	6489(7)	14178(10)	5245(7)	49(2)
C7_3	6045(9)	13404(12)	4750(8)	55(3)
C8_3	6539(9)	13318(12)	4003(8)	53(3)
C9_3	7673(9)	13055(10)	4074(7)	48(3)
C10_3	8092(8)	13839(8)	4559(6)	40(2)
C11_3	9086(12)	16206(10)	2802(8)	86(5)
C12_3	7970(13)	16218(17)	2957(14)	88(5)
C13_3	9268(18)	16626(16)	2046(11)	90(5)
C14_3	9813(13)	14210(11)	2111(7)	75(4)
C15_3	8822(14)	13897(16)	1847(12)	82(5)
C16_3	10498(16)	13237(14)	2269(11)	76(5)
C17_3	11044(10)	15212(12)	3317(9)	101(5)
C18_3	11520(14)	14410(20)	3861(14)	99(6)

C19_3	11774(13)	15440(20)	2663(13)	106(6)
C20_3	8853(10)	16338(9)	5910(7)	52(2)
C21_3	8929(13)	18013(11)	6287(9)	62(3)
C22_3	8415(16)	17993(17)	7043(9)	66(4)
C23_3	7695(10)	14872(8)	6569(6)	45(2)
C24_3	7414(9)	14304(12)	7852(6)	49(3)
C25_3	8225(10)	14564(13)	8400(6)	51(3)
C26_3	9024(11)	15094(13)	8193(7)	55(3)
C27_3	9749(12)	15362(14)	8706(6)	57(3)
C28_3	9645(11)	15075(15)	9459(7)	60(3)
C29_3	8875(12)	14467(16)	9660(7)	64(3)
C30_3	8190(11)	14213(14)	9146(7)	59(3)

Figure S3. Single crystal X-ray structure (ORTEP) of bicyclic γ-lactone (+)-3c'. The crystals were grown from a concentrated solution of bicyclic γ-lactone (+)-**3c'** in CH_2Cl_2 (2.0 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 972247.



Alert level B:

THETM01_ALERT_3_B The value of sine(theta_max)/wavelength is less than 0.575. Calculated sin(theta_max)/wavelength = 0.5617. 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.

Table 1. Crystal data and structure refinement for DRB_MA_130306_G_904F2.

Identification code	drb
Empirical formula	$C_{20}H_{34}O_5Si$
Formula weight	382.56
Temperature	110(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic

Space group	P2(1)	
Unit cell dimensions	a = 16.6474(7) Å	α = 90°
	b = 34.4793(14) Å	β = 95.850(2)°
	c = 19.1312(8) Å	γ = 90°
Volume	10923.9(8) Å^3	
Z	20	
Density (calculated)	1.163 Mg/m^3	
Absorption coefficient	1.155 mm^{-1}	
F(000)	4160	
Crystal size	0.28 × 0.06 × 0.05 mm^3	
Theta range for data collection	2.32 to 60.00°	
Index ranges	$-18 \leq h \leq 18$, $-37 \leq k \leq 35$, $-21 \leq l \leq 21$	
Reflections collected	225412	
Independent reflections	31523 [R(int) = 0.0593]	
Completeness to theta = 60.00°	99.3%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9445 and 0.7380	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	31523 / 1 / 2412	
Goodness-of-fit on F^2	1.069	
Final R indices [I>2sigma(I)]	R_1 = 0.0551, wR_2 = 0.1469	
R indices (all data)	R_1 = 0.0610, wR_2 = 0.1564	
Absolute structure (Hooft / Flack) parameter	-0.006(7) / 0.013(14)	
Extinction coefficient	0.00031(2)	
Largest diff. peak and hole	0.720 and -0.591 e.Å^{-3}	

Table 2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for DRB_MA_130306_G_904F2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
Si(1P)	6042(1)	7578(1)	6596(1)	16(1)
O(1P)	7243(1)	7429(1)	10228(1)	22(1)
O(2P)	8590(1)	7377(1)	10271(1)	25(1)
O(3P)	9775(1)	7420(1)	8850(1)	31(1)
O(4P)	9083(1)	6861(1)	8811(1)	23(1)
O(5P)	6727(1)	7326(1)	7110(1)	18(1)
C(1P)	8323(2)	7436(1)	8634(2)	17(1)
C(2P)	7926(2)	7322(1)	7896(2)	19(1)
C(3P)	7020(2)	7388(1)	7795(2)	16(1)
C(4P)	6558(2)	7482(1)	8303(2)	15(1)
C(5P)	6959(2)	7552(1)	9028(2)	16(1)
C(6P)	7734(2)	7319(1)	9152(2)	16(1)
C(7P)	6557(2)	7434(1)	9677(2)	19(1)
C(8P)	7942(2)	7376(1)	9925(2)	17(1)
C(9P)	9146(2)	7246(1)	8778(2)	17(1)
C(10P)	9836(2)	6646(1)	8958(2)	22(1)
C(11P)	9644(2)	6225(1)	8786(2)	29(1)
C(12P)	6146(2)	7366(1)	5698(2)	24(1)
C(13P)	6983(2)	7195(1)	5615(2)	33(1)
C(14P)	5908(2)	7651(1)	5103(2)	33(1)
C(15P)	6291(2)	8109(1)	6643(2)	25(1)
C(16P)	7199(2)	8182(1)	6627(2)	36(1)
C(17P)	5966(2)	8328(1)	7261(2)	43(1)
C(18P)	4999(2)	7481(1)	6854(2)	20(1)
C(19P)	4865(2)	7044(1)	6963(2)	28(1)
C(20P)	4340(2)	7644(1)	6315(2)	30(1)

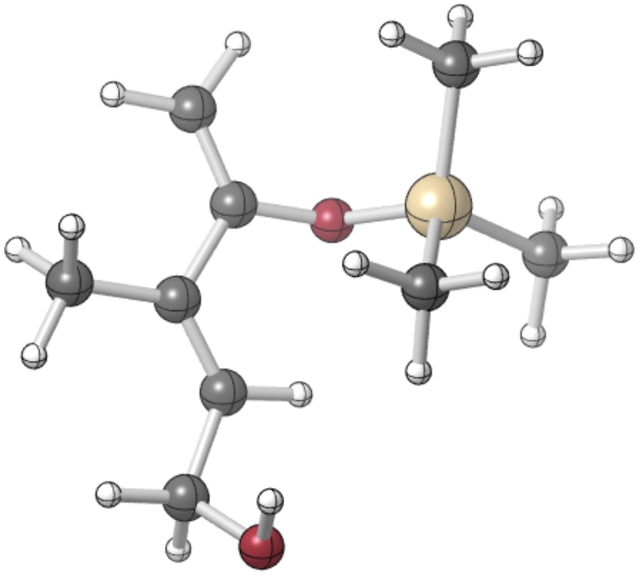
Computational data

General methods: All calculations were performed using Gaussian09.[8,9] Conformational analyses on reactants and transition state structures were performed using the Spartan10 software suite.[10] Geometries were optimized at the uM06-2X/6-31G(d)[11,12] level using “guess=(mix,always)” keywords to assure that diradical processes were not missed. The identities of all minima and transition state structures were verified by frequency analysis. Implicit solvent effects of dichloromethane were modeled using the SMD continuum model.[13] Products of the reaction were located by decreasing and constraining the length of the shorter forming bond to ~1.55 Å in the transition state structure and optimizing the complex to a minimum, which resulted in the formation of the second bond, and therefore, the cyclohexene ring. NBO6.0[14] was used with the keywords “E2PERT=0.1” and “STERIC=0.1” for the natural bond orbital analysis of sulfur•••lone pair interactions. Structural drawings were produced using CYLView.[15]

Conformational search: The conformational searches of reactants and transition state structures for the Diels-Alder reactions were done using Spartan10. Conformer distribution at the ground state using Molecular Mechanics (MMFF) and keywords “searchmethod=systematic” and “maxenergy=50” were used.

Calculated coordinates and energies

Silyloxydiene alcohol (2c):



Charge = 0 Multiplicity = 1

mem = 20GB, nproc = 16

Link 0: opt m062x/6-31g(d) freq=noraman scrf=(smd,solvent=dichloromethane)

Job cpu time: 0 days 5 hours 6 minutes 28.9 seconds.

File lengths (MBytes): RWF= 180 Int= 0 D2E= 0 Chk= 8 Scr= 1

Normal termination of Gaussian 09 at Tue Oct 15 02:33:37 2013.

```
Item                    Value       Threshold   Converged?
Maximum Force           0.000023    0.000450    YES
RMS Force               0.000005    0.000300    YES
Maximum Displacement    0.001517    0.001800    YES
RMS Displacement        0.000412    0.001200    YES
Predicted change in Energy = -1.292192D-08
Optimization completed.
        -- Stationary point found.
```

```
Link 1: N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
Job cpu time: 0 days 0 hours 45 minutes 35.1 seconds.
File lengths (MBytes): RWF= 264 Int= 0 D2E= 0 Chk= 13 Scr= 1
Normal termination of Gaussian 09 at Tue Oct 15 02:36:32 2013.
Item                    Value       Threshold   Converged?
Maximum Force           0.000023    0.000450    YES
RMS Force               0.000005    0.000300    YES
Maximum Displacement    0.002559    0.001800    NO
RMS Displacement        0.000680    0.001200    YES
Predicted change in Energy = -2.142063D-08

Values come from Link 1:
HF = -793.4977666 hartrees (-497927.783519166 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.255956 (Hartree/Particle)

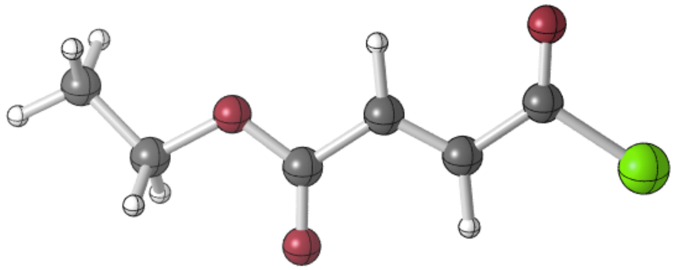
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
Sum of electronic and thermal Free Energies =
     -793.286374 hartrees (-497795.13254874 kcal/mol)

Comments:

Coordinates (from last standard orientation):
---------------------------------------------------------------------
 Center        Atomic         Coordinates (Angstroms)
 Number        Number         X          Y          Z
---------------------------------------------------------------------
    1       6          -1.789481   -0.288014   -0.572437
    2       6           0.380319    2.656051   -0.177700
    3       6          -3.090830   -0.997507   -0.350989
    4       6          -0.048458    1.411338   -0.423352
```

5	6	0.791570	-1.302206	1.391004
6	6	3.117543	0.624855	0.841751
7	6	2.564231	-1.710651	-1.107445
8	6	-1.445877	0.955064	-0.200382
9	6	-2.378693	1.946485	0.443736
10	1	-1.034051	-0.907485	-1.051103
11	1	1.413073	2.925175	-0.374643
12	1	-0.283560	3.425212	0.196776
13	1	-3.831018	-0.372046	0.161086
14	1	-3.524191	-1.299905	-1.310550
15	1	0.046637	-1.982972	0.964440
16	1	1.448027	-1.888470	2.045693
17	1	0.266990	-0.572411	2.018642
18	1	3.697007	1.161466	0.082416
19	1	2.678684	1.363738	1.521178
20	1	3.816673	0.014203	1.425967
21	1	3.238273	-2.390030	-0.573475
22	1	1.786506	-2.316488	-1.585546
23	1	3.140843	-1.217469	-1.897471
24	1	-2.480754	-1.965170	1.218249
25	1	-1.969850	2.302424	1.395567
26	1	-2.512158	2.823853	-0.199200
27	1	-3.365079	1.520991	0.631188
28	8	0.810376	0.473233	-0.934987
29	8	-2.871154	-2.210857	0.364149
30	14	1.810874	-0.464008	0.059455

Ethyl fumaroyl chloride (1a):



Charge = 0 Multiplicity = 1

mem = 20GB

```
Link 0: opt freq=noraman m062x/6-31g(d) scrf=(smd,solvent=dichloromethane)
Job cpu time: 0 days 0 hours 41 minutes 50.0 seconds.
File lengths (MBytes): RWF= 61 Int= 0 D2E= 0 Chk= 5 Scr= 1
Normal termination of Gaussian 09 at Tue Oct 15 10:51:54 2013.
Item                    Value       Threshold   Converged?
Maximum Force           0.000017    0.000450    YES
RMS     Force           0.000004    0.000300    YES
Maximum Displacement    0.000879    0.001800    YES
RMS Displacement        0.000217    0.001200    YES
Predicted change in Energy = -4.982950D-09
Optimization completed.
     -- Stationary point found.
```

```
Link 1: N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
Job cpu time: 0 days 0 hours 13 minutes 39.0 seconds.
File lengths (MBytes): RWF= 112 Int= 0 D2E= 0 Chk= 8 Scr= 1
Normal termination of Gaussian 09 at Tue Oct 15 10:52:46 2013.
Item                    Value       Threshold   Converged?
Maximum Force           0.000017    0.000450    YES
RMS Force               0.000004    0.000300    YES
```

```
Maximum Displacement     0.001760      0.001800      YES
RMS Displacement         0.000477      0.001200      YES
Predicted change in Energy = -9.981294D-09
Optimization completed.
        -- Stationary point found.

Values come from Link 1:
HF = -918.5039922 hartrees (-576370.440145422 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.126267 (Hartree/Particle)

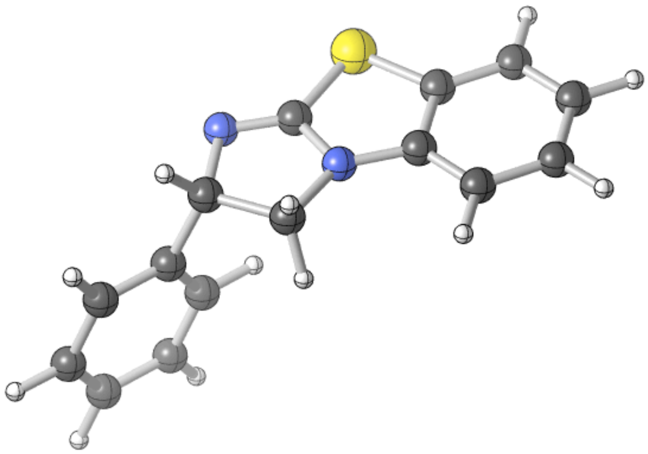
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
Sum of electronic and thermal Free Energies =
    -918.416338 hartrees (-576315.43625838 kcal/mol)

Comments:

Coordinates (from last standard orientation):
---------------------------------------------------------------------
 Center       Atomic        Coordinates (Angstroms)
 Number       Number        X          Y          Z
---------------------------------------------------------------------
     1       6          -2.404785    0.535097   -0.020979
     2       6           0.008958    0.346013   -0.031898
     3       6          -1.169862   -0.277188   -0.025157
     4       6           1.268965   -0.453229   -0.032192
     5       6           3.616705   -0.317867   -0.008249
     6       6           4.675205    0.755901    0.080148
     7       1           0.088461    1.428999   -0.034584
     8       1          -1.250380   -1.358672   -0.017684
     9       1           3.699592   -0.904604   -0.927911
```

```
   10          1             3.655164   -1.005150    0.841606
   11          1             4.570953    1.326879    1.006880
   12          1             5.665622    0.292605    0.068215
   13          1             4.604344    1.443500   -0.767095
   14          8            -2.491100    1.719758   -0.059931
   15          8             2.334266    0.343047   -0.005009
   16          8             1.311464   -1.661878   -0.054280
   17         17            -3.896583   -0.468432    0.059665
---------------------------------------------------------------------
```

(*S*)-(–)-BTM catalyst:



Charge = 0 Multiplicity = 1

mem = 57GB

```
Link 0: opt freq=noraman M062X/6-31g(d) scrf=(smd,solvent=dichloromethane)
Job cpu time: 0 days 3 hours 11 minutes 45.7 seconds.
File lengths (MBytes): RWF= 237 Int= 0 D2E= 0 Chk= 11 Scr= 1
Normal termination of Gaussian 09 at Tue Oct 15 04:29:26 2013.
Item                    Value       Threshold   Converged?
Maximum Force           0.000187    0.000450    YES
RMS Force               0.000033    0.000300    YES
Maximum Displacement    0.000258    0.001800    YES
RMS Displacement        0.000054    0.001200    YES
Predicted change in Energy = -1.391136D-08
Optimization completed.
     -- Stationary point found.
```

```
Link 1: N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
Job cpu time: 0 days 1 hours 22 minutes 44.0 seconds.
File lengths (MBytes): RWF= 424 Int= 0 D2E= 0 Chk= 16 Scr= 1
```

```
Normal termination of Gaussian 09 at Tue Oct 15 04:38:05 2013.
Item                    Value       Threshold   Converged?
Maximum Force           0.000187    0.000450    YES
RMS Force               0.000033    0.000300    YES
Maximum Displacement    0.153336    0.001800    NO
RMS Displacement        0.032624    0.001200    NO
Predicted change in Energy = -1.867818D-05

Values come from Link 1:
HF = -1086.2208184 hartrees (-681614.425754184 kcal/mol)
Imaginary Frequencies: 1 (-14.6567 1/cm)
Zero-point correction = 0.238538 (Hartree/Particle)

Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
Sum of electronic and thermal Free Energies =
   -1086.022849 hartrees (-681490.19797599 kcal/mol)

Comments:

Coordinates (from last standard orientation):
---------------------------------------------------------------------
 Center       Atomic        Coordinates (Angstroms)
 Number       Number        X          Y          Z
---------------------------------------------------------------------
     1        6          -2.622757   -1.835345   -0.226202
     2        6          -2.051143   -0.567243   -0.191749
     3        6          -2.800831    0.543358    0.240477
     4        6          -4.119368    0.401802    0.639518
     5        6          -4.694017   -0.871669    0.604275
     6        6          -3.951076   -1.971754    0.177476
     7        1          -2.040013   -2.689223   -0.557279
```

8	1	-4.695008	1.261072	0.970043
9	1	-5.726304	-0.999322	0.913007
10	1	-4.410423	-2.955214	0.155941
11	6	-0.453291	1.125987	-0.427716
12	16	-1.834591	2.037413	0.195902
13	7	-0.767979	-0.208171	-0.537803
14	6	0.374198	-0.911640	-1.099338
15	1	0.711082	-1.709620	-0.431290
16	1	0.126795	-1.338116	-2.075938
17	6	1.417213	0.264382	-1.204627
18	7	0.716092	1.500830	-0.770152
19	6	2.655307	0.014957	-0.368832
20	6	3.880315	-0.258566	-0.975907
21	6	2.574811	0.025786	1.027006
22	6	5.011046	-0.524068	-0.203338
23	1	3.949754	-0.262956	-2.061207
24	6	3.700723	-0.238619	1.800282
25	1	1.624399	0.245994	1.508614
26	6	4.922813	-0.515315	1.185873
27	1	5.959686	-0.733435	-0.689213
28	1	3.627323	-0.226295	2.883940
29	1	5.802044	-0.721590	1.789173
30	1	1.723671	0.389164	-2.247721

Chloride anion (Cl⁻):

Charge = -1 Multiplicity = 1

mem = 57GB, nproc = 16

```
Link 0: opt freq=noraman M062X/6-31g(d) scrf=(smd,solvent=dichloromethane)
Job cpu time: 0 days 0 hours 0 minutes 48.6 seconds.
File lengths (MBytes): RWF= 9 Int= 0 D2E= 0 Chk= 1 Scr= 1
Normal termination of Gaussian 09 at Tue Oct 15 04:19:55 2013.
Item                    Value       Threshold   Converged?
Maximum Force           0.000000    0.000450    YES
RMS Force               0.000000    0.000300    YES
Maximum Displacement    0.000000    0.001800    YES
RMS Displacement        0.000000    0.001200    YES
Predicted change in Energy = 0.000000D+00
Optimization completed.
     -- Stationary point found.
```

```
Link 1: N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
Job cpu time: 0 days 0 hours 1 minutes 17.4 seconds.
File lengths (MBytes): RWF= 9 Int= 0 D2E= 0 Chk= 2 Scr= 1
Normal termination of Gaussian 09 at Tue Oct 15 04:20:00 2013.
Item                    Value       Threshold   Converged?
Maximum Force           0.000000    0.000450    YES
RMS   Force             0.000000    0.000300    YES
Maximum Displacement    0.000000    0.001800    YES
RMS   Displacement      0.000000    0.001200    YES
Predicted change in Energy = 0.000000D+00
Optimization completed.
     -- Stationary point found.
```

Values come from Link 1:

HF = -460.31703 hartrees (-288853.5394953 kcal/mol)

Imaginary Frequencies: none found

Zero-point correction = 0.000000 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-460.332053 hartrees (-288862.96657803 kcal/mol)

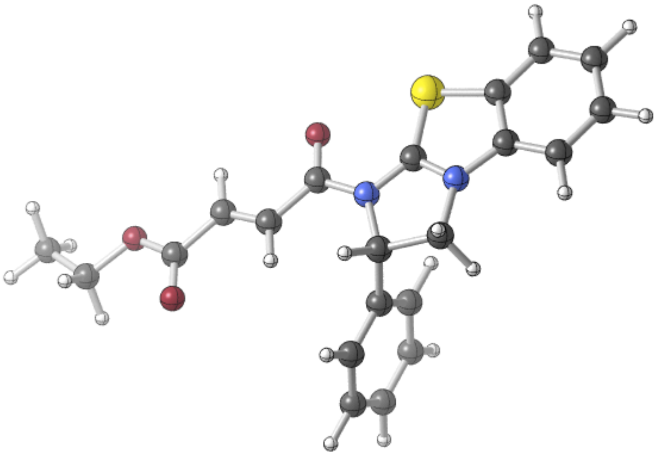
Comments:

Coordinates (from last standard orientation):

atom 1 is isolated, type=Cl

```
---------------------------------------------------------------------
 Center       Atomic        Coordinates (Angstroms)
 Number       Number         X          Y          Z
---------------------------------------------------------------------
     1        17          0.000000   0.000000   0.000000
---------------------------------------------------------------------
```

Acylammonium cation (lowest energy conformer; 0º dihedral angle):



Charge = 1 Multiplicity = 1

mem = 20GB, nproc = 16

```
Link 0: opt m062x/6-31g(d) freq=noraman scrf=(smd,solvent=dichloromethane)
Job cpu time: 0 days 8 hours 45 minutes 18.1 seconds.
File lengths (MBytes): RWF= 520 Int= 0 D2E= 0 Chk= 20 Scr= 1
Normal termination of Gaussian 09 at Tue Oct 15 03:57:42 2013.
Item                    Value       Threshold   Converged?
Maximum Force           0.000021    0.000450    YES
RMS Force               0.000003    0.000300    YES
Maximum Displacement    0.001572    0.001800    YES
RMS Displacement        0.000344    0.001200    YES
Predicted change in Energy = -8.895401D-09
Optimization completed.
        -- Stationary point found.
```

```
Link 1: N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
Job cpu time: 0 days 3 hours 54 minutes 45.1 seconds.
File lengths (MBytes): RWF= 1305 Int= 0 D2E= 0 Chk= 27 Scr= 1
```

```
Normal termination of Gaussian 09 at Tue Oct 15 04:12:33 2013.
Item                    Value        Threshold    Converged?
Maximum Force           0.000021     0.000450     YES
RMS Force               0.000003     0.000300     YES
Maximum Displacement    0.002485     0.001800     NO
RMS Displacement        0.000557     0.001200     YES
Predicted change in Energy = -1.499555D-08

Values come from Link 1:
HF = -1544.4297238 hartrees (-969145.095981738 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.369165 (Hartree/Particle)

Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
Sum of electronic and thermal Free Energies =
   -1544.116364 hartrees (-968948.45957364 kcal/mol)

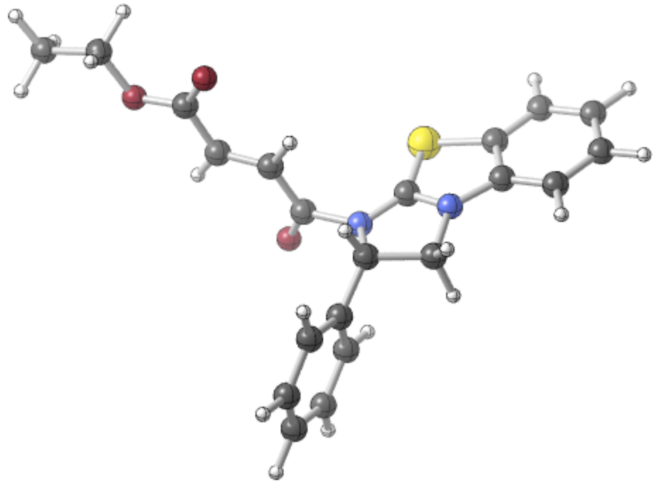
Comments:

Coordinates (from last standard orientation):
---------------------------------------------------------------------
 Center        Atomic        Coordinates (Angstroms)
 Number        Number        X          Y          Z
---------------------------------------------------------------------
     1       6           5.118716    0.557519   -0.672996
     2       6           3.974890   -0.164938   -0.347371
     3       6           4.040338   -1.399776    0.309957
     4       6           5.267544   -1.951514    0.663092
     5       6           6.413808   -1.233568    0.341594
     6       6           6.339917    0.001845   -0.316444
     7       6           1.761554   -0.694356   -0.172008
```

8	6	2.022552	1.329876	-1.262766
9	6	0.498065	1.049299	-1.064955
10	6	-0.190536	2.083743	-0.205172
11	6	-1.070458	2.989354	-0.797295
12	6	0.079524	2.167238	1.162976
13	6	-1.678312	3.977323	-0.025250
14	6	-0.532674	3.151049	1.932707
15	6	-1.411009	4.057704	1.338928
16	6	-0.592561	-1.111837	-0.066609
17	6	-1.932593	-0.601409	-0.422289
18	6	-3.012540	-1.280471	-0.035926
19	6	-4.367303	-0.762183	-0.384195
20	6	-6.676979	-1.141952	-0.167468
21	6	-7.590487	-2.172525	0.452224
22	1	5.045797	1.512466	-1.182892
23	1	5.328840	-2.907601	1.172213
24	1	7.383695	-1.640446	0.607450
25	1	7.253691	0.536706	-0.552594
26	1	2.332151	2.255339	-0.774399
27	1	2.311331	1.339976	-2.314685
28	1	-1.281692	2.918143	-1.861515
29	1	0.766426	1.464302	1.630031
30	1	-2.365469	4.678106	-0.489042
31	1	-0.324464	3.210434	2.996500
32	1	-1.889008	4.824148	1.941246
33	1	0.002605	0.968826	-2.034460
34	1	-2.032994	0.319274	-0.987940
35	1	-6.823075	-0.148272	0.265787
36	1	-6.812969	-1.067522	-1.250148
37	1	-7.427071	-2.237296	1.531413
38	1	-8.631574	-1.888294	0.275606

```
    39        1          -7.421666   -3.158099    0.009803
    40        1          -2.941252   -2.200389    0.536454
    41        8          -0.376005   -2.165968    0.498049
    42        8          -4.567629    0.250598   -1.015778
    43        8          -5.319754   -1.557245    0.094370
    44        7           2.650206    0.183925   -0.595405
    45        7           0.496113   -0.306196   -0.426096
    46       16           2.427552   -2.077844    0.590884
---------------------------------------------------------------------
```

Acylammonium cation (100º dihedral angle):



Charge = 1 Multiplicity = 1

mem = 7200MB

```
Link 0: hf/3-21g----
1/38=1/1;2/12=2,17=6,18=5,40=1/2;3/5=5,11=9,16=1,25=1,30=1/1,2,3;4//1;5/5=2,38=5/
2;6/7=2,8=2,9=2,10=2,28=1/1;99/5=1,9=1/99; ----Title---- Symbolic Z-matrix: Charge = 1
Multiplicity = 1C 4.68387 -1.02853 -1.14043 C 3.48635 -1.10242 -0.44016 C
3.20572 -2.17348 0.41637 C 4.1149 -3.20842 0.5902 C 5.31573 -3.13727 -
0.10966 C 5.59525 -2.06295 -0.96014 C 1.40876 -0.51036 0.34146 C 2.23597
1.14936 -1.01566 C 0.72875 1.40484 -0.73246 C 0.39431 2.82034 -0.34686 C -
0.19471 3.66347 -1.28804 C 0.7094 3.3015 0.92609 C -0.45418 4.99255 -0.96364
C 0.43921 4.62615 1.24953 C -0.13714 5.4727 0.30347 C -0.8748 0.25319
0.95912 C -1.82593 -0.46144 0.09061 C -3.0958 -0.62703 0.4694 C -4.02944 -
1.36631 -0.44119 C -6.22214 -2.15958 -0.70462 C -7.51836 -2.14883 0.07185 H
4.89632 -0.19448 -1.80105 H 3.90056 -4.04062 1.25198 H 6.0462 -3.92923
0.01137 H 6.54013 -2.03316 -1.49139 H 2.87009 1.85234 -0.46538 H 2.46964
1.18447 -2.08032 H -0.45135 3.28444 -2.27446 H 1.13928 2.63517 1.66973 H -
0.90991 5.64837 -1.69797 H 0.67332 4.99716 2.24182 H -0.34689 6.5064
0.55834 H 0.13404 1.09906 -1.60376 H -1.48811 -0.85776 -0.86391 H -6.30526
```

```
-1.65167 -1.6695 H      -5.84909 -3.1714 -0.88664 H      -7.85689 -1.12473 0.24603 H
-8.28972 -2.6767 -0.49409 H      -7.39536 -2.64606 1.03684 H      -3.47016 -0.24388
1.41451 O     -1.08408 0.71018 2.04303 O     -3.69182 -1.81102 -1.5113 O     -5.23998
-1.45614 0.09073 N      2.41718 -0.20357 -0.47446 N      0.46614 0.42363 0.36678 S
1.61517 -1.99421 1.18878     Input orientation:

Job cpu time: 0 days 0 hours 3 minutes 35.1 seconds.
File lengths (MBytes): RWF= 34 Int= 0 D2E= 0 Chk= 4 Scr= 1
Normal termination of Gaussian 09 at Sat Oct 19 15:40:13 2013.
No convergence data found for this link.
HF = -1528.7887896 hartrees (-959330.253361896 kcal/mol)

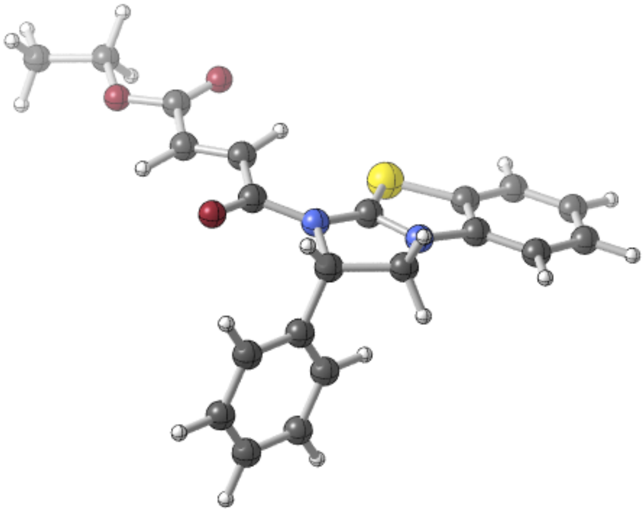
Comments:

Coordinates (from last standard orientation):
---------------------------------------------------------------------
 Center       Atomic        Coordinates (Angstroms)
 Number       Number        X          Y          Z
---------------------------------------------------------------------
     1        6          4.683870   -1.028527   -1.140428
     2        6          3.486347   -1.102417   -0.440158
     3        6          3.205715   -2.173478    0.416368
     4        6          4.114901   -3.208424    0.590200
     5        6          5.315733   -3.137265   -0.109656
     6        6          5.595253   -2.062954   -0.960140
     7        6          1.408756   -0.510359    0.341463
     8        6          2.235973    1.149365   -1.015656
     9        6          0.728747    1.404843   -0.732458
    10        6          0.394306    2.820342   -0.346864
    11        6         -0.194714    3.663466   -1.288038
    12        6          0.709395    3.301504    0.926090
```

13	6	-0.454183	4.992547	-0.963642
14	6	0.439210	4.626151	1.249534
15	6	-0.137144	5.472698	0.303471
16	6	-0.874796	0.253194	0.959116
17	6	-1.825932	-0.461444	0.090605
18	6	-3.095799	-0.627027	0.469395
19	6	-4.029444	-1.366307	-0.441192
20	6	-6.222142	-2.159582	-0.704620
21	6	-7.518363	-2.148826	0.071854
22	1	4.896322	-0.194480	-1.801048
23	1	3.900556	-4.040620	1.251979
24	1	6.046202	-3.929230	0.011373
25	1	6.540132	-2.033157	-1.491387
26	1	2.870090	1.852336	-0.465383
27	1	2.469642	1.184474	-2.080320
28	1	-0.451354	3.284443	-2.274461
29	1	1.139276	2.635165	1.669727
30	1	-0.909907	5.648372	-1.697966
31	1	0.673323	4.997155	2.241825
32	1	-0.346887	6.506401	0.558343
33	1	0.134043	1.099058	-1.603764
34	1	-1.488110	-0.857755	-0.863906
35	1	-6.305257	-1.651667	-1.669500
36	1	-5.849090	-3.171403	-0.886637
37	1	-7.856890	-1.124734	0.246033
38	1	-8.289716	-2.676704	-0.494090
39	1	-7.395361	-2.646063	1.036843
40	1	-3.470162	-0.243875	1.414510
41	8	-1.084077	0.710177	2.043027
42	8	-3.691822	-1.811020	-1.511300
43	8	-5.239975	-1.456138	0.090729

```
    44         7            2.417182   -0.203570   -0.474464
    45         7            0.466143    0.423629    0.366781
    46        16            1.615171   -1.994206    1.188782
---------------------------------------------------------------------
```

Acylammonium cation (180º dihedral angle):



Charge = 1 Multiplicity = 1

mem = 7200MB

```
Link 0: hf/3-21g----
1/38=1/1;2/12=2,17=6,18=5,40=1/2;3/5=5,11=9,16=1,25=1,30=1/1,2,3;4//1;5/5=2,38=5/
2;6/7=2,8=2,9=2,10=2,28=1/1;99/5=1,9=1/99; ----Title---- Symbolic Z-matrix: Charge =
1 Multiplicity = 1C 4.40731 -1.86212 -0.32001 C 3.03795 -1.63608 -0.22928 C
2.17441 -2.57984 0.33649 C 2.65595 -3.78718 0.82947 C 4.02447 -4.0165
0.74182 C 4.88574 -3.06844 0.1754 C 1.01243 -0.56811 -0.46456 C 2.73258
0.72169 -1.33116 C 1.44182 1.57948 -1.24317 C 1.49475 2.67397 -0.20418 C
1.05071 3.95479 -0.52526 C 1.97616 2.40605 1.08041 C 1.10163 4.96827
0.42804 C 2.01916 3.41648 2.03363 C 1.58509 4.70004 1.70508 C -0.97372
0.89064 -1.02705 C -1.9642 -0.14033 -0.66123 C -3.22578 0.20727 -0.40839 C
-4.2 -0.87272 -0.04893 C -6.44061 -1.3395 0.47173 C -7.73239 -0.57521 0.64641
H 5.07125 -1.12661 -0.76203 H 1.98945 -4.52313 1.26592 H 4.4292 -4.94875
1.11959 H 5.94812 -3.27864 0.12023 H 3.5625 1.18938 -0.79806 H 3.02802
0.49178 -2.35833 H 0.65209 4.15297 -1.51619 H 2.31922 1.40654 1.34694 H
0.75971 5.96562 0.17238 H 2.39375 3.206 3.02999 H 1.6244 5.49029 2.44781 H
```

```
1.16572 1.99055 -2.21524 H      -1.70431 -1.19412 -0.62277 H      -6.4969 -2.08058 -
0.33059 H     -6.12965 -1.8537 1.38547 H     -8.00652 -0.06207 -0.27832 H     -8.53566
-1.26779 0.90941 H     -7.63865 0.16584 1.44369 H     -3.56516 1.23789 -0.4538 O     -
1.23585 1.98654 -1.45165 O      -3.88654 -2.03401 0.06282 O      -5.41727 -0.37901
0.12562 N     2.32694 -0.51608 -0.65636 N     0.40346 0.55325 -0.88418 S     0.49732 -
2.01536 0.31698     Input orientation:

Job cpu time: 0 days 0 hours 3 minutes 34.7 seconds.
File lengths (MBytes): RWF= 34 Int= 0 D2E= 0 Chk= 4 Scr= 1
Normal termination of Gaussian 09 at Sat Oct 19 15:41:39 2013.
No convergence data found for this link.
HF = -1528.8026458 hartrees (-959338.948265958 kcal/mol)

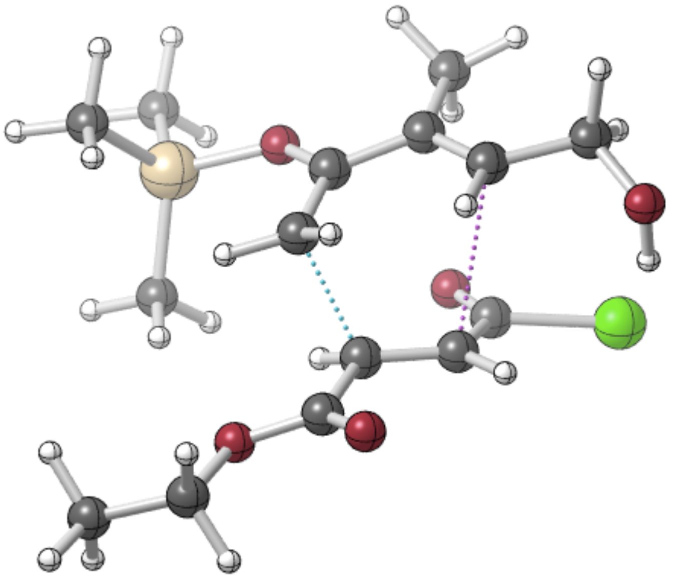
Comments:

Coordinates (from last standard orientation):
---------------------------------------------------------------------
 Center      Atomic        Coordinates (Angstroms)
 Number      Number      X          Y          Z
---------------------------------------------------------------------
     1       6          4.407314   -1.862115   -0.320008
     2       6          3.037947   -1.636082   -0.229284
     3       6          2.174414   -2.579839    0.336494
     4       6          2.655947   -3.787180    0.829474
     5       6          4.024465   -4.016496    0.741823
     6       6          4.885737   -3.068440    0.175398
     7       6          1.012431   -0.568109   -0.464564
     8       6          2.732576    0.721685   -1.331155
     9       6          1.441819    1.579483   -1.243168
    10       6          1.494753    2.673973   -0.204180
    11       6          1.050713    3.954788   -0.525257
```

12	6	1.976159	2.406049	1.080414
13	6	1.101634	4.968269	0.428037
14	6	2.019163	3.416483	2.033629
15	6	1.585092	4.700042	1.705075
16	6	-0.973717	0.890644	-1.027046
17	6	-1.964201	-0.140327	-0.661228
18	6	-3.225775	0.207273	-0.408391
19	6	-4.199995	-0.872717	-0.048931
20	6	-6.440613	-1.339497	0.471730
21	6	-7.732394	-0.575213	0.646406
22	1	5.071248	-1.126605	-0.762031
23	1	1.989449	-4.523132	1.265923
24	1	4.429197	-4.948754	1.119594
25	1	5.948115	-3.278640	0.120230
26	1	3.562502	1.189380	-0.798055
27	1	3.028023	0.491778	-2.358334
28	1	0.652091	4.152972	-1.516186
29	1	2.319223	1.406543	1.346944
30	1	0.759709	5.965616	0.172376
31	1	2.393746	3.205996	3.029990
32	1	1.624402	5.490285	2.447809
33	1	1.165717	1.990545	-2.215238
34	1	-1.704308	-1.194121	-0.622771
35	1	-6.496904	-2.080580	-0.330593
36	1	-6.129647	-1.853699	1.385467
37	1	-8.006522	-0.062068	-0.278318
38	1	-8.535655	-1.267789	0.909411
39	1	-7.638654	0.165836	1.443692
40	1	-3.565157	1.237891	-0.453799
41	8	-1.235846	1.986537	-1.451646
42	8	-3.886536	-2.034008	0.062824

```
    43          8           -5.417274   -0.379010    0.125617
    44          7            2.326941   -0.516083   -0.656362
    45          7            0.403463    0.553248   -0.884179
    46         16            0.497315   -2.015363    0.316982
---------------------------------------------------------------------
```

EndoBottom TSS (background reaction; leads to *endo* cycloadduct):



Charge = 0 Multiplicity = 1

mem = 50GB

Dipole moment (field-independent basis, Debye):

X = 8.9322 Y = –2.1207 Z = 2.4065 Tot = 9.4907

Link 0: opt=(calcfc,ts,noeigen) freq=noraman M062X/6-31g(d) scrf=(smd,solvent= dichloromethane)

Job cpu time: 3 days 3 hours 32 minutes 31.3 seconds.

File lengths (MBytes): RWF= 1059 Int= 0 D2E= 0 Chk= 23 Scr= 1

Normal termination of Gaussian 09 at Mon Oct 7 00:33:02 2013.

Item	Value	Threshold	Converged?
Maximum Force	0.000006	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.000534	0.001800	YES
RMS Displacement	0.000113	0.001200	YES

Predicted change in Energy = -2.287133D-09

```
Optimization completed.
        -- Stationary point found.

Link 1: N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
Job cpu time: 0 days 3 hours 12 minutes 22.4 seconds.
File lengths (MBytes): RWF= 1059 Int= 0 D2E= 0 Chk= 32 Scr= 1
Normal termination of Gaussian 09 at Mon Oct 7 00:45:20 2013.
Item                    Value       Threshold   Converged?
Maximum Force           0.000006    0.000450    YES
RMS Force               0.000001    0.000300    YES
Maximum Displacement    0.001144    0.001800    YES
RMS Displacement        0.000221    0.001200    YES
Predicted change in Energy = -5.719982D-09
Optimization completed.
        -- Stationary point found.

Values come from Link 1:
HF = -1712.0012625 hartrees (-1074297.91223137 kcal/mol)
Imaginary Frequencies: 1 (-372.8605 1/cm)
Zero-point correction = 0.384682 (Hartree/Particle)

Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
Sum of electronic and thermal Free Energies =
    -1711.674450 hartrees (-1074092.8341195 kcal/mol)
```

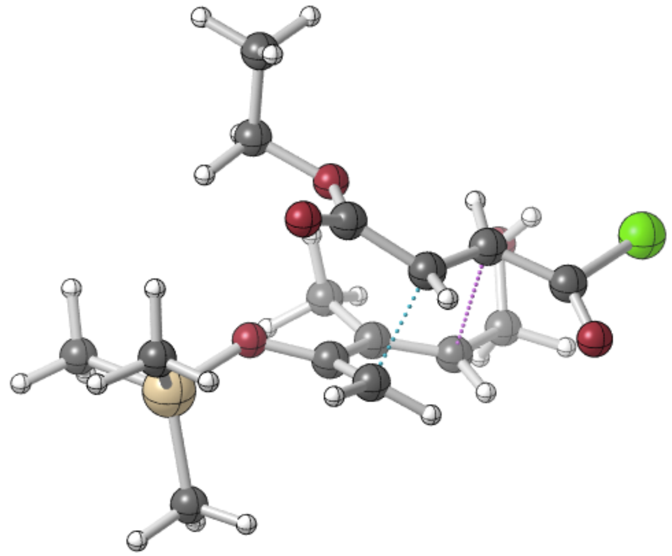
Comments:

Coordinates (from last standard orientation):

```
---------------------------------------------------------------------
 Center      Atomic        Coordinates (Angstroms)
 Number      Number        X          Y          Z
---------------------------------------------------------------------
     1        6        -1.914100    0.344829   -1.433254
     2        6         0.046593    1.302003   -0.460606
     3        6        -1.331866    1.361819   -0.628438
     4        6        -2.189280   -0.344562    1.450524
     5        6         0.634395    0.099066    1.154345
     6        6        -1.386174   -1.357780    1.035562
     7        6         0.031202   -1.120049    0.865302
     8        6        -3.687251   -0.402118    1.565667
     9        6         3.360566   -2.242173    1.413405
    10        6         2.831588   -0.956549   -1.371656
    11        6         2.377968   -3.968023   -0.947818
    12        6        -1.919889   -2.687187    0.571733
    13        6         0.720289    2.512040    0.103794
    14        6         2.777643    3.638632    0.323082
    15        6         4.212645    3.443299   -0.106903
    16       17        -3.743829    0.622910   -1.718302
    17        1         0.629688    0.725079   -1.171581
    18        1        -1.932426    2.149006   -0.192521
    19        1        -1.766065    0.580838    1.829170
    20        1         1.713063    0.186708    1.064870
    21        1         0.188806    0.732276    1.911995
    22        1        -4.126670   -1.015832    0.768883
    23        1        -3.957468   -0.872346    2.520586
    24        1         3.004105   -2.992704    2.127586
```

```
    25          1           4.405161   -2.477523    1.177381
    26          1           3.343806   -1.267574    1.911074
    27          1           2.876467    0.048179   -0.937297
    28          1           3.828785   -1.188156   -1.766572
    29          1           2.140898   -0.934438   -2.222385
    30          1           3.400867   -4.239108   -1.232538
    31          1           2.004853   -4.736710   -0.262566
    32          1           1.760714   -3.991169   -1.852267
    33          1          -4.203119    1.237721    0.680188
    34          1          -2.950055   -2.844694    0.894870
    35          1          -1.879694   -2.747454   -0.522066
    36          1          -1.310348   -3.505124    0.965576
    37          1           2.670827    3.643315    1.411747
    38          1           2.355238    4.569287   -0.066327
    39          1           4.292920    3.433703   -1.197476
    40          1           4.825220    4.263172    0.278323
    41          1           4.610025    2.501611    0.282997
    42          8          -1.420823   -0.618465   -1.945900
    43          8           0.686102   -2.113036    0.261101
    44          8          -4.255428    0.892370    1.586119
    45          8           2.019337    2.533044   -0.206800
    46          8           0.168457    3.356069    0.772133
    47         14           2.339455   -2.284776   -0.152298
---------------------------------------------------------------------
```

ExoTop TSS (background reaction; leads to *exo* cycloadduct):



Charge = 0 Multiplicity = 1

mem = 50GB

Dipole moment (field-independent basis, Debye):

X = 8.1597 Y = –2.2281 Z = 1.5963 Tot = 8.6077

Link 0: opt=(calcfc,ts,noeigen) freq=noraman m062x/6-31g(d) scrf=(smd,solvent= dichloromethane)

Job cpu time: 1 days 18 hours 10 minutes 1.7 seconds.

File lengths (MBytes): RWF= 1056 Int= 0 D2E= 0 Chk= 22 Scr= 1

Normal termination of Gaussian 09 at Sun Oct 6 22:23:23 2013.

Item	Value	Threshold	Converged?
Maximum Force	0.000025	0.000450	YES
RMS Force	0.000004	0.000300	YES
Maximum Displacement	0.000803	0.001800	YES
RMS Displacement	0.000192	0.001200	YES

Predicted change in Energy = -5.773393D-09

Optimization completed.

```
          -- Stationary point found.

Link 1: N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
Job cpu time: 0 days 3 hours 24 minutes 42.4 seconds.
File lengths (MBytes): RWF= 1056 Int= 0 D2E= 0 Chk= 31 Scr= 1
Normal termination of Gaussian 09 at Sun Oct 6 22:36:26 2013.
Item                      Value        Threshold    Converged?
Maximum Force             0.000025     0.000450     YES
RMS Force                 0.000004     0.000300     YES
Maximum Displacement      0.001013     0.001800     YES
RMS Displacement          0.000231     0.001200     YES
Predicted change in Energy = -6.934533D-09
Optimization completed.
          -- Stationary point found.

Values come from Link 1:
HF = -1711.9989726 hartrees (-1074296.47529623 kcal/mol)
Imaginary Frequencies: 1 (-383.8352 1/cm)
Zero-point correction = 0.384864 (Hartree/Particle)

Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
Sum of electronic and thermal Free Energies =
    -1711.671561 hartrees (-1074091.02124311 kcal/mol)

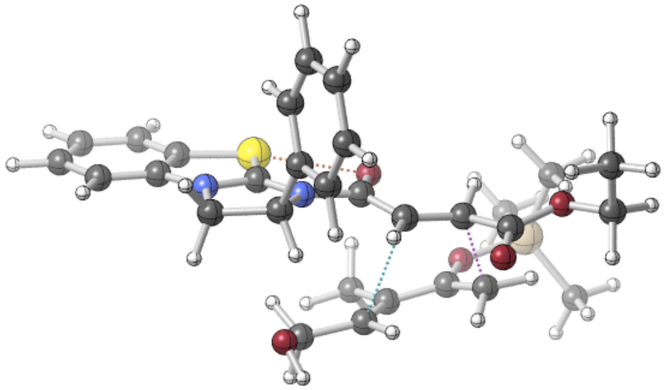
Comments:

Coordinates (from last standard orientation):
---------------------------------------------------------------------
 Center        Atomic        Coordinates (Angstroms)
 Number        Number        X          Y          Z
---------------------------------------------------------------------
```

1	6	-3.080620	0.352505	-1.359739
2	6	-0.781102	1.052854	-1.220941
3	6	-1.991994	0.816312	-0.571769
4	6	-1.619592	-1.802151	0.310900
5	6	0.305695	-0.671984	-1.511669
6	6	-0.363073	-1.503903	0.738263
7	6	0.621344	-1.026766	-0.204360
8	6	-2.751963	-2.159950	1.243732
9	6	3.770284	0.615103	-1.464383
10	6	3.387969	-2.454943	-1.339117
11	6	4.485989	-0.888917	1.110981
12	6	0.026703	-1.514038	2.192648
13	6	0.293149	1.817723	-0.517611
14	6	1.238163	2.313287	1.590083
15	6	0.994364	3.797337	1.772958
16	17	-4.668713	0.275045	-0.364539
17	1	-0.792086	1.210637	-2.296002
18	1	-2.123792	1.003386	0.483604
19	1	-1.824113	-1.906520	-0.750204
20	1	1.102184	-0.310861	-2.157078
21	1	-0.512751	-1.161310	-2.027303
22	1	-3.651691	-2.384089	0.659602
23	1	-2.494627	-3.068993	1.800961
24	1	4.830531	0.562727	-1.742929
25	1	3.186178	0.642409	-2.389711
26	1	3.605249	1.560924	-0.939063
27	1	2.665488	-2.447683	-2.162454
28	1	4.381626	-2.621762	-1.770826
29	1	3.154566	-3.307253	-0.691505
30	1	5.534683	-0.979941	0.806424
31	1	4.387959	0.032473	1.695998

```
     32          1           4.248261   -1.733505    1.766470
     33          1          -3.454177   -0.429971    1.754062
     34          1           1.009444   -1.976101    2.320858
     35          1           0.095613   -0.489197    2.575090
     36          1          -0.702448   -2.051872    2.799448
     37          1           2.195098    2.115572    1.100057
     38          1           1.208126    1.781698    2.543084
     39          1           0.016080    3.969990    2.230668
     40          1           1.761632    4.217711    2.430112
     41          1           1.035735    4.318785    0.813344
     42          8          -3.138251    0.008296   -2.503832
     43          8           1.808776   -0.699301    0.324665
     44          8          -3.011123   -1.160730    2.215236
     45          8           0.187905    1.711511    0.809566
     46          8           1.173548    2.420288   -1.090280
     47         14           3.366186   -0.851310   -0.379874
 ---------------------------------------------------------------------
```

EndoTop TSS (asymmetric reaction; leads to *endo* cycloadduct):



Charge = 1 Multiplicity = 1

mem = 57GB

Dipole moment (field-independent basis, Debye):

X = 6.4375 Y = 1.2759 Z = 3.3855 Tot = 7.3845

Link 0: opt=(calcfc,ts,noeigen) freq=noraman uM062X/6-31g(d) scrf=(smd,solvent=dichloromethane) guess=(mix,always)

Job cpu time: 27 days 6 hours 0 minutes 44.0 seconds.

File lengths (MBytes): RWF= 7631 Int= 0 D2E= 0 Chk= 62 Scr= 1

Normal termination of Gaussian 09 at Sat Oct 5 22:12:16 2013.

Item	Value	Threshold	Converged?
Maximum Force	0.000024	0.000450	YES
RMS Force	0.000003	0.000300	YES
Maximum Displacement	0.001122	0.001800	YES
RMS Displacement	0.000192	0.001200	YES

Predicted change in Energy = -3.365820D-09

Optimization completed.

-- Stationary point found.

```
Link 1: N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UM062X/6-31G(d) Freq
Job cpu time: 1 days 7 hours 5 minutes 19.8 seconds.
File lengths (MBytes): RWF= 7684 Int= 0 D2E= 0 Chk= 78 Scr= 1
Normal termination of Gaussian 09 at Sun Oct 6 00:09:28 2013.
Item                    Value       Threshold   Converged?
Maximum Force           0.000024    0.000450    YES
RMS Force               0.000003    0.000300    YES
Maximum Displacement    0.002293    0.001800    NO
RMS Displacement        0.000421    0.001200    YES
Predicted change in Energy = -1.806644D-08

Values come from Link 1:
HF = -2337.9289835 hartrees (-1467073.81643608 kcal/mol)
Imaginary Frequencies: 1 (-408.6019 1/cm)
Zero-point correction = 0.627069 (Hartree/Particle)

Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
Sum of electronic and thermal Free Energies =
   -2337.376333 hartrees (-1466727.02272083 kcal/mol)

Comments:

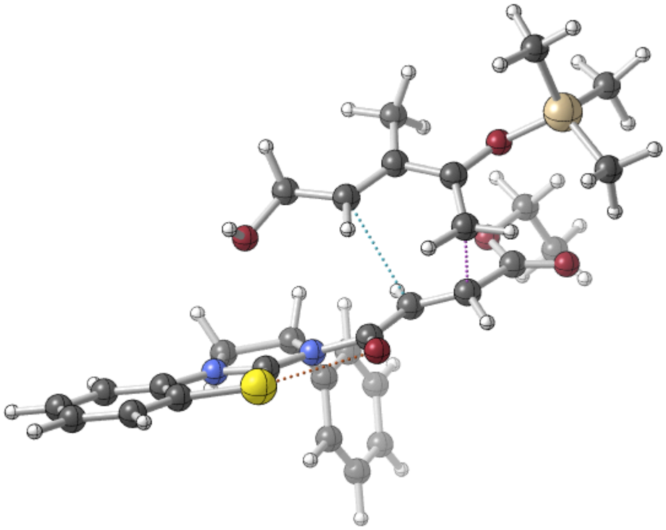
Coordinates (from last standard orientation):
---------------------------------------------------------------------
 Center      Atomic      Coordinates (Angstroms)
 Number      Number      X          Y          Z
---------------------------------------------------------------------
    1      6         6.011641   0.729163   0.255205
    2      6         4.681109   0.851146  -0.130982
    3      6         4.238845   1.915587  -0.927217
    4      6         5.127429   2.891388  -1.363734
```

5	6	6.460553	2.773854	-0.982110
6	6	6.894456	1.709117	-0.183475
7	6	2.448520	0.374371	-0.309824
8	6	3.494545	-1.183271	1.038554
9	6	2.015532	-1.614280	0.795617
10	6	1.857478	-2.902071	0.018827
11	6	1.284281	-4.010427	0.641746
12	6	2.295382	-3.004451	-1.304845
13	6	1.149375	-5.213346	-0.048813
14	6	2.157894	-4.204314	-1.994990
15	6	1.584804	-5.310898	-1.367620
16	6	0.100803	-0.179761	-0.290546
17	6	-0.874580	-1.039450	0.289809
18	6	-2.205520	-0.839067	-0.055543
19	6	-0.565119	0.961361	2.369900
20	6	-3.157981	0.528074	1.164183
21	6	0.813746	1.050217	2.965953
22	6	-2.421514	1.694247	0.978363
23	6	-5.656825	2.995900	0.413861
24	6	-4.433059	1.432199	-1.995072
25	6	-3.921916	4.448483	-1.679842
26	6	-1.123375	1.915352	1.584407
27	6	-3.158267	-1.941041	0.294901
28	6	-5.228982	-2.942795	-0.257776
29	6	-4.829547	-4.231696	-0.945119
30	6	-0.394959	3.167914	1.175762
31	1	6.336245	-0.101197	0.873592
32	1	4.793118	3.718627	-1.981249
33	1	7.173215	3.522145	-1.312383
34	1	7.939854	1.644614	0.099652
35	1	4.206275	-1.950353	0.729145

36	1	3.666948	-0.896836	2.078838
37	1	0.937449	-3.929739	1.669354
38	1	2.742445	-2.145680	-1.802076
39	1	0.697859	-6.069725	0.442537
40	1	2.496792	-4.276180	-3.024014
41	1	1.476016	-6.246220	-1.908290
42	1	1.499509	-1.673057	1.755284
43	1	-0.600109	-1.824888	0.982612
44	1	-1.139210	0.096376	2.689144
45	1	-4.162110	0.474117	0.754439
46	1	-3.014716	-0.034577	2.078733
47	1	-2.425115	-0.293648	-0.968920
48	1	1.542995	1.392596	2.223622
49	1	0.821975	1.794102	3.777550
50	1	-5.861671	2.070981	0.961670
51	1	-5.460122	3.787720	1.145157
52	1	-6.568628	3.268251	-0.130842
53	1	-3.532067	1.324703	-2.609858
54	1	-4.641081	0.467743	-1.519914
55	1	-5.267338	1.655265	-2.671723
56	1	-3.730917	5.263659	-0.973625
57	1	-3.057736	4.368033	-2.347876
58	1	-4.790120	4.727346	-2.287485
59	1	-6.149140	-2.532363	-0.676249
60	1	-5.351937	-3.078894	0.819036
61	1	-5.620219	-4.976737	-0.816084
62	1	-4.682851	-4.064894	-2.015948
63	1	-3.905461	-4.630308	-0.518323
64	1	0.772698	-0.447154	4.217842
65	1	-0.238701	3.170590	0.092242
66	1	-0.988660	4.054301	1.421154

```
    67          1             0.572245    3.261908    1.673292
    68          8            -0.108835    0.779965   -1.033128
    69          8            -2.785073    2.635499    0.109384
    70          8            -2.975446   -2.740483    1.185108
    71          8            -4.241620   -1.914191   -0.486339
    72          8             1.285065   -0.203221    3.429524
    73          7             3.623440    0.002858    0.182099
    74          7             1.462132   -0.447311    0.045747
    75         16             2.495052    1.813505   -1.251580
    76         14            -4.233484    2.843921   -0.787396
---------------------------------------------------------------------
```

ExoBottom TSS (asymmetric reaction; leads to *exo* cycloadduct):



Charge = 1 Multiplicity = 1

mem = 55GB

Dipole moment (field-independent basis, Debye):

X = –8.3541 Y = –2.6696 Z = 6.9204 Tot = 11.1718

Link 0: opt=(calcfc,ts,noeigen) freq=noraman M062X/6-31g(d) scrf=(smd,solvent= dichloromethane)

Job cpu time: 1 days 4 hours 58 minutes 5.1 seconds.

File lengths (MBytes): RWF= 4155 Int= 0 D2E= 0 Chk= 50 Scr= 1

Normal termination of Gaussian 09 at Sun Sep 22 12:21:14 2013.

Item	Value	Threshold	Converged?
Maximum Force	0.000401	0.000450	YES
RMS Force	0.000080	0.000300	YES
Maximum Displacement	0.000633	0.001800	YES
RMS Displacement	0.000128	0.001200	YES

Predicted change in Energy = 1.881745D-05

Optimization completed.

```
        -- Stationary point found.

Link 1: N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
Job cpu time: 0 days 16 hours 23 minutes 9.4 seconds.
File lengths (MBytes): RWF= 4181 Int= 0 D2E= 0 Chk= 65 Scr= 1
Normal termination of Gaussian 09 at Sun Sep 22 13:23:07 2013.
Item                      Value        Threshold    Converged?
Maximum Force             0.000401     0.000450     YES
RMS Force                 0.000080     0.000300     YES
Maximum Displacement      0.000584     0.001800     YES
RMS Displacement          0.000082     0.001200     YES
Predicted change in Energy = -4.003895D-07
Optimization completed.
        -- Stationary point found.

Values come from Link 1:
HF = -2337.9292947 hartrees (-1467074.0117172 kcal/mol)
Imaginary Frequencies: 1 (-395.0181 1/cm)
Zero-point correction = 0.627771 (Hartree/Particle)

Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
Sum of electronic and thermal Free Energies =
   -2337.374439 hartrees (-1466725.83421689 kcal/mol)

Comments:

Coordinates (from last standard orientation):
---------------------------------------------------------------------
 Center        Atomic         Coordinates (Angstroms)
 Number        Number         X          Y          Z
---------------------------------------------------------------------
```

1	6	-6.221235	-0.868759	1.043138
2	6	-5.083461	-0.928456	0.245046
3	6	-4.952277	-1.871346	-0.782465
4	6	-5.968435	-2.783912	-1.041659
5	6	-7.108731	-2.730357	-0.245492
6	6	-7.231491	-1.787076	0.781862
7	6	-2.999579	-0.423752	-0.553690
8	6	-3.519924	0.920433	1.250457
9	6	-2.088525	1.268488	0.730754
10	6	-1.920608	2.710779	0.310756
11	6	-1.086379	3.552900	1.044547
12	6	-2.617734	3.213872	-0.790410
13	6	-0.950415	4.892587	0.684607
14	6	-2.478050	4.549616	-1.152366
15	6	-1.645261	5.391231	-0.413938
16	6	-0.707662	0.020478	-1.109161
17	6	1.661999	0.381631	-1.354445
18	6	0.482998	0.646915	-0.653930
19	6	0.606811	-1.552235	1.259747
20	6	2.320754	-1.497322	-1.067275
21	6	1.945484	-1.378162	1.396819
22	6	2.806515	-1.433869	0.234913
23	6	-0.386872	-1.427162	2.384921
24	6	5.543461	-1.768905	-2.083400
25	6	5.684681	-3.516334	0.449776
26	6	6.838887	-0.619006	0.440947
27	6	2.593440	-1.019608	2.708516
28	6	2.921049	1.103170	-0.985275
29	6	4.057199	2.229312	0.757220
30	6	4.151971	3.646503	0.229999
31	1	-6.306579	-0.132512	1.835837

32	1	-5.873672	-3.517143	-1.836252
33	1	-7.914164	-3.434114	-0.426472
34	1	-8.131542	-1.770286	1.387234
35	1	-4.202163	1.770542	1.185761
36	1	-3.498870	0.520454	2.265087
37	1	-0.539872	3.157305	1.897816
38	1	-3.265650	2.557890	-1.368123
39	1	-0.298831	5.542352	1.260964
40	1	-3.018102	4.935287	-2.011792
41	1	-1.537861	6.433677	-0.698001
42	1	-1.351324	1.011504	1.494841
43	1	1.587254	0.156804	-2.415338
44	1	0.489786	1.253706	0.240510
45	1	0.184770	-1.909952	0.323831
46	1	3.038739	-1.573014	-1.876237
47	1	1.354091	-1.946696	-1.267955
48	1	-0.207664	-2.208498	3.137546
49	1	-0.268744	-0.465823	2.897205
50	1	6.578389	-1.924043	-2.414764
51	1	4.937962	-2.568331	-2.522600
52	1	5.206589	-0.806701	-2.482986
53	1	5.821573	-3.521280	1.536489
54	1	4.785332	-4.099265	0.218564
55	1	6.538594	-4.033596	-0.002362
56	1	7.834990	-1.056720	0.306964
57	1	6.820460	0.333482	-0.099973
58	1	6.701716	-0.415714	1.508192
59	1	-1.944906	-2.404751	1.737113
60	1	3.072322	-0.036805	2.643577
61	1	1.872776	-1.003650	3.528043
62	1	3.376435	-1.742828	2.958805

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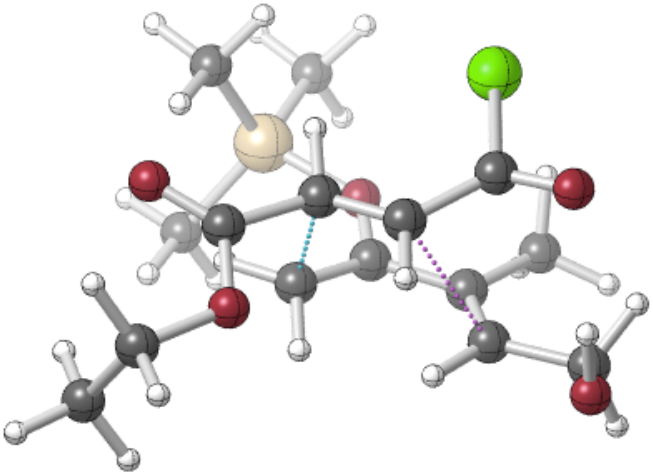
    63          1           4.930192    1.630246    0.486579
    64          1           3.940354    2.216376    1.842314
    65          1           3.246287    4.207816    0.478541
    66          1           5.007789    4.151286    0.688061
    67          1           4.286082    3.649963   -0.854219
    68          8          -0.796949   -0.820217   -2.008391
    69          8           4.090614   -1.148400    0.470204
    70          8          -1.728591   -1.476428    1.923734
    71          8           2.873061    1.571780    0.263779
    72          8           3.885932    1.193474   -1.712832
    73          7          -3.946555   -0.130966    0.324095
    74          7          -1.911405    0.331306   -0.412556
    75         16          -3.388583   -1.723662   -1.610891
    76         14           5.534737   -1.776596   -0.214599
---------------------------------------------------------------------
```

EndoTop TSS (background reaction; leads to enantiomer of *endo* cycloadduct)



Charge = 0 Multiplicity = 1

HF = -1712.0020168 hartrees (-1074298.38556217 kcal/mol)

Imaginary Frequencies: 1 (-367.8342 1/cm)

Zero-point correction = 0.385144 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-1711.674659 hartrees (-1074092.96526909 kcal/mol)

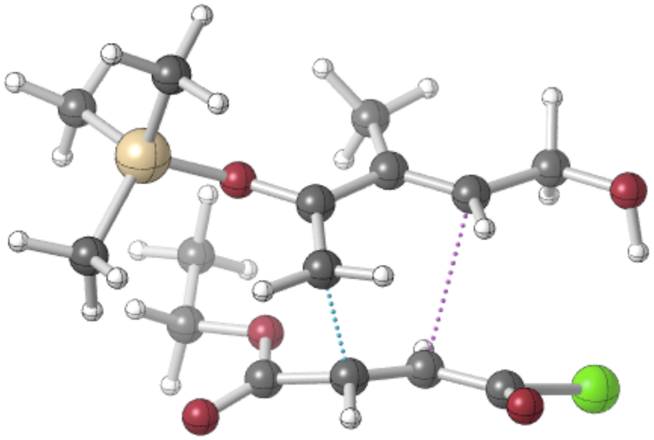
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.076063	1.207211	-1.334218
2	6	-1.896097	-0.116505	-0.837998
3	6	-0.715221	-0.846522	-0.891264
4	6	-1.508005	1.341130	1.492633
5	6	0.381392	-0.733495	0.897915

6	6	-2.638916	2.324655	1.611478
7	6	0.739783	0.608183	0.971809
8	6	4.539213	1.548485	-0.295813
9	6	2.931618	-0.784604	-1.489580
10	6	3.913553	-0.899430	1.469268
11	6	-0.201299	1.657391	1.288986
12	6	0.294000	3.077842	1.215079
13	6	-0.767943	-2.338458	-0.787996
14	6	-1.895911	-4.189418	0.151935
15	6	-0.966863	-4.620068	1.267853
16	17	-0.581647	1.953102	-2.107716
17	1	-2.793754	-0.555576	-0.414438
18	1	-1.811728	0.312341	1.656705
19	1	1.155845	-1.469231	0.703680
20	1	-0.437507	-1.087580	1.512035
21	1	0.092249	-0.508735	-1.531568
22	1	-2.492900	3.163756	0.917046
23	1	-2.661969	2.742260	2.626930
24	1	5.482969	1.139207	-0.673492
25	1	4.145489	2.236455	-1.051522
26	1	4.762118	2.128835	0.605984
27	1	2.216397	-1.600978	-1.340632
28	1	2.536432	-0.120168	-2.266994
29	1	3.858140	-1.224960	-1.878932
30	1	4.898070	-1.314702	1.222961
31	1	4.021964	-0.311151	2.387287
32	1	0.573162	3.343953	0.190283
33	1	-0.458514	3.784351	1.569509
34	1	1.188910	3.196659	1.833584
35	1	-3.972161	1.608643	0.424338
36	1	-2.941987	-4.358978	0.411039

```
    37        1          -1.670245   -4.702945   -0.785216
    38        1          -1.199212   -4.079790    2.190339
    39        1          -1.088871   -5.691090    1.455139
    40        1           0.076183   -4.433895    0.997531
    41        1           3.243475   -1.738419    1.681344
    42        8          -3.075956    1.884332   -1.337814
    43        8           1.935831    1.048263    0.572760
    44        8          -3.885875    1.697387    1.389480
    45        8          -1.804700   -2.765473   -0.063167
    46        8           0.056830   -3.067766   -1.293931
    47       14           3.325496    0.181906    0.062077
---------------------------------------------------------------------
```

ExoBottom TSS (background reaction; leads to enantiomer of *exo* cycloadduct)



Charge = 0 Multiplicity = 1

HF = -1711.9989996 hartrees (-1074296.492239 kcal/mol)

Imaginary Frequencies: 1 (-386.7660 1/cm)

Zero-point correction = 0.383850 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-1711.672772 hartrees (-1074091.78115772 kcal/mol)

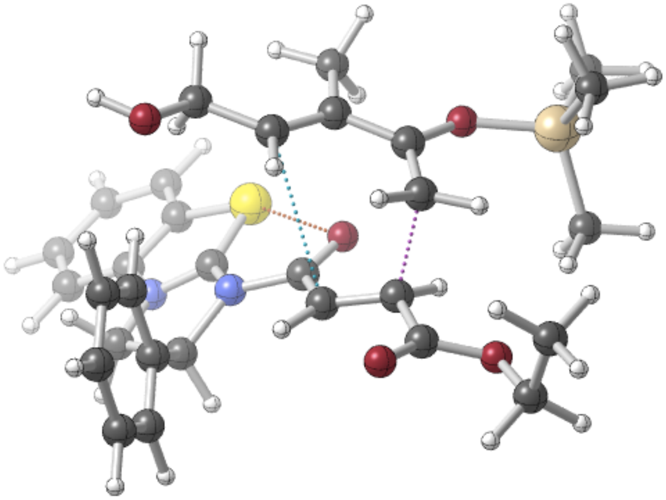
Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.773704	-1.406040	-1.011874
2	6	-1.912111	-1.171218	-0.240667
3	6	-1.713875	1.648816	0.116832
4	6	0.206660	0.314481	-1.574844
5	6	-0.433220	1.476396	0.535003

6	6	0.541508	0.880781	-0.349278
7	6	-2.833457	2.185973	0.969347
8	6	-0.006883	1.754847	1.952040
9	6	0.409067	-2.075201	-0.390224
10	6	1.707907	-2.294000	1.558896
11	1	-0.908098	-1.666488	-2.058315
12	1	-3.037176	1.499367	1.805153
13	1	-2.530835	3.141808	1.414705
14	1	-4.444986	1.600225	0.060433
15	1	0.948774	2.285864	1.977636
16	1	-0.747884	2.351397	2.487499
17	1	0.130068	0.813135	2.495863
18	1	1.616322	-3.379379	1.664415
19	8	1.753589	0.694239	0.186771
20	8	-3.997218	2.447184	0.214779
21	8	0.520928	-1.799109	0.910063
22	8	1.191861	-2.761040	-1.010218
23	1	-1.902443	-1.242330	0.837146
24	6	1.826305	-1.599104	2.894445
25	1	2.692427	-1.993707	3.434048
26	1	1.964707	-0.523141	2.752839
27	1	0.933692	-1.768374	3.503903
28	1	2.570370	-2.085955	0.918946
29	6	-3.116833	-0.857670	-0.918598
30	17	-4.577000	-0.811753	0.281692
31	8	-3.354400	-0.620458	-2.066275
32	14	3.298211	0.834114	-0.545806
33	6	3.646554	-0.576064	-1.721619
34	1	4.729906	-0.637418	-1.885288
35	1	3.311203	-1.538055	-1.320144
36	1	3.177225	-0.436264	-2.701178

```
   37          6              4.433765    0.768079    0.931857
   38          1              4.155640    1.523376    1.675137
   39          1              4.396648   -0.214568    1.416044
   40          1              5.472404    0.952771    0.635236
   41          6              3.322728    2.479816   -1.426888
   42          1              2.559067    2.515959   -2.212252
   43          1              3.135933    3.306723   -0.733117
   44          1              4.295910    2.648132   -1.901979
   45          1              1.000495   -0.101969   -2.188723
   46          1             -0.649063    0.688740   -2.124678
   47          1             -1.980799    1.516468   -0.928344
---------------------------------------------------------------------
```

EndoBottom TSS (asymmetric reaction; leads to enantiomer of *endo* cycloadduct)



Charge = 1 Multiplicity = 1

HF = -2337.9215634 hartrees (-1467069.16024913 kcal/mol)

Imaginary Frequencies: 1 (-411.3635 1/cm)

Zero-point correction = 0.626765 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-2337.369239 hartrees (-1466722.57116489 kcal/mol)

Coordinates (from last standard orientation):

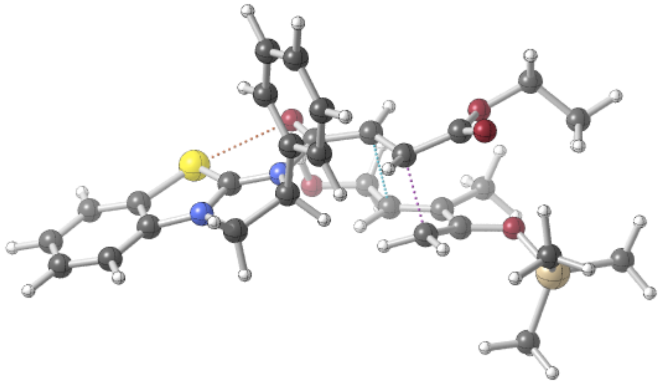
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	6.243099	-0.617570	-0.881687
2	6	4.881202	-0.876343	-0.766347
3	6	4.389159	-2.175111	-0.587697
4	6	5.256763	-3.260418	-0.528746
5	6	6.620297	-3.008335	-0.642463

6	6	7.104724	-1.705798	-0.815553
7	6	2.626519	-0.483094	-0.641321
8	6	3.772619	1.502996	-0.851492
9	6	2.247644	1.757736	-1.013762
10	6	1.777263	2.945914	-0.213394
11	6	1.532121	4.151811	-0.869682
12	6	1.605067	2.859059	1.168244
13	6	1.124551	5.270009	-0.144576
14	6	1.176638	3.969462	1.888004
15	6	0.942051	5.178509	1.233194
16	6	0.279295	0.026971	-0.685641
17	6	-0.714520	1.041035	-0.680999
18	6	-2.023352	0.645570	-0.929095
19	6	-0.617942	0.064704	2.416406
20	6	-3.045879	0.036371	0.766609
21	6	0.625531	0.131875	3.255322
22	6	-2.349819	-1.105872	1.141843
23	6	-4.257051	-2.242394	-1.759462
24	6	-5.595179	-2.410713	1.041973
25	6	-3.858562	-4.744503	0.005155
26	6	-1.129280	-1.090903	1.940966
27	6	-3.011768	1.739057	-1.204744
28	6	-5.097513	2.226833	-2.207441
29	6	-6.057774	2.227911	-1.036079
30	6	-0.455758	-2.422706	2.142981
31	1	6.607871	0.395383	-1.016500
32	1	4.881932	-4.270122	-0.395437
33	1	7.318473	-3.837358	-0.595236
34	1	8.173469	-1.539512	-0.900565
35	1	4.158125	1.905526	0.089098
36	1	4.346614	1.891892	-1.692681

37	1	1.653476	4.213161	-1.948373
38	1	1.779013	1.919394	1.683964
39	1	0.936218	6.206913	-0.659844
40	1	1.013904	3.877260	2.956910
41	1	0.609449	6.045719	1.795728
42	1	2.003004	1.902381	-2.070929
43	1	-0.488144	2.075696	-0.464295
44	1	-1.118684	1.017650	2.264539
45	1	-4.031364	-0.080691	0.323817
46	1	-2.900543	0.948086	1.333127
47	1	-2.194561	-0.291485	-1.451955
48	1	0.578332	-0.621406	4.054524
49	1	1.510710	-0.110918	2.641866
50	1	-4.406340	-1.157616	-1.794099
51	1	-3.357365	-2.484409	-2.336099
52	1	-5.108636	-2.711166	-2.267847
53	1	-5.389821	-2.594140	2.102429
54	1	-5.881307	-1.360715	0.926195
55	1	-6.463011	-3.020895	0.764239
56	1	-2.944667	-5.013026	-0.535591
57	1	-3.767575	-5.118281	1.030682
58	1	-4.695546	-5.267866	-0.470608
59	1	-5.572497	1.863616	-3.119776
60	1	-4.676862	3.217902	-2.388432
61	1	-6.887690	2.911182	-1.239557
62	1	-6.468622	1.226567	-0.874553
63	1	-5.554815	2.560310	-0.123240
64	1	1.506628	1.462059	4.368529
65	1	-1.092741	-3.099877	2.722222
66	1	-0.277911	-2.893201	1.171782
67	1	0.500390	-2.323870	2.659869

```
    68          8            0.075124   -1.186896   -0.751647
    69          8           -2.696216   -2.314278    0.715262
    70          8           -2.915272    2.867229   -0.780156
    71          8           -4.017741    1.299640   -1.967537
    72          8            0.719714    1.434164    3.801706
    73          7            3.833583    0.039606   -0.809060
    74          7            1.656437    0.438910   -0.608732
    75         16            2.618116   -2.196500   -0.484525
    76         14           -4.134619   -2.902929   -0.017933
 ---------------------------------------------------------------------
```

ExoTop TSS (asymmetric reaction; leads to enantiomer of *exo* cycloadduct)



Charge = 1 Multiplicity = 1

HF = -2337.9166877 hartrees (-1467066.10069863 kcal/mol)

Imaginary Frequencies: 1 (-416.3988 1/cm)

Zero-point correction = 0.627953 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-2337.361318 hartrees (-1466717.60065818 kcal/mol)

Coordinates (from last standard orientation):

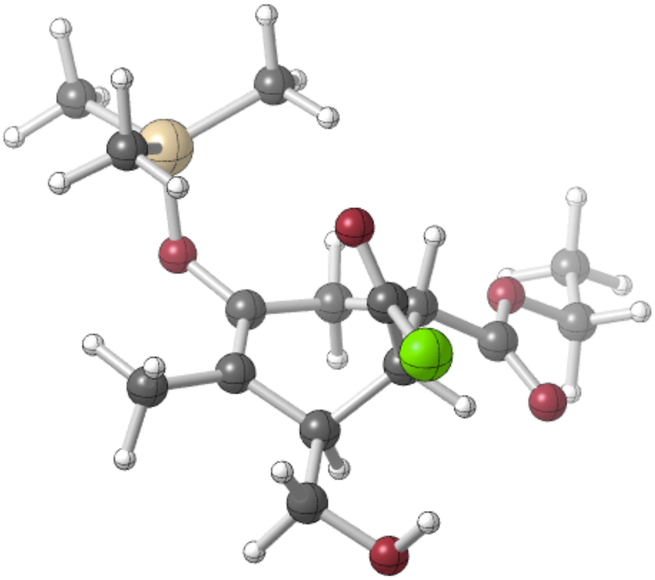
Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	6	-5.889345	-0.097916	2.085546
2	6	-4.971356	-0.405723	1.086367
3	6	-5.258980	-1.333089	0.077906
4	6	-6.489715	-1.979866	0.038473
5	6	-7.411501	-1.677668	1.034521
6	6	-7.114787	-0.750760	2.042551
7	6	-3.019651	-0.378880	-0.112886

8	6	-2.862870	1.019253	1.714416
9	6	-1.625010	1.220535	0.788868
10	6	-1.595134	2.577671	0.115485
11	6	-0.940912	3.626664	0.766177
12	6	-2.242457	2.814172	-1.098544
13	6	-0.934654	4.901971	0.208882
14	6	-2.232007	4.091006	-1.655405
15	6	-1.580534	5.135894	-1.003775
16	6	-0.940393	-0.273747	-1.300884
17	6	0.432067	0.093779	-1.383417
18	6	1.224308	0.812311	-0.488336
19	6	1.044092	-2.588595	-0.535804
20	6	1.829361	-0.337350	1.116465
21	6	0.510543	-3.568575	-1.547942
22	6	2.740094	-1.213640	0.531204
23	6	6.728796	-0.818338	1.442639
24	6	4.433730	-1.510184	3.404705
25	6	4.721484	1.365853	2.284833
26	6	2.351133	-2.261880	-0.387638
27	6	3.436300	-2.859871	-1.244682
28	6	2.563238	1.292232	-0.966272
29	6	4.319652	0.940577	-2.513646
30	6	5.527887	0.627318	-1.656941
31	1	-5.648145	0.621772	2.861174
32	1	-6.720180	-2.698150	-0.741594
33	1	-8.377818	-2.170702	1.028460
34	1	-7.855134	-0.538629	2.806575
35	1	-3.392831	1.954195	1.901940
36	1	-2.602916	0.532866	2.657279
37	1	-0.429467	3.441535	1.708533
38	1	-2.748081	2.007189	-1.624011

39	1	-0.418481	5.710110	0.717623
40	1	-2.731690	4.266136	-2.603179
41	1	-1.570181	6.128737	-1.442959
42	1	-0.723649	1.065503	1.381858
43	1	0.896000	-0.302998	-2.278010
44	1	0.295165	-2.218157	0.159442
45	1	2.205314	0.416336	1.803538
46	1	0.817404	-0.674386	1.309197
47	1	0.798604	1.531516	0.200189
48	1	0.897610	-4.571453	-1.324345
49	1	0.873567	-3.308861	-2.553760
50	1	7.390222	-0.766358	2.315594
51	1	6.818956	-1.822934	1.015329
52	1	7.098168	-0.098302	0.705368
53	1	3.375470	-1.359267	3.644742
54	1	4.589049	-2.574924	3.199661
55	1	5.015961	-1.251459	4.296774
56	1	5.623358	1.770120	2.760578
57	1	4.549450	1.926280	1.359478
58	1	4.287174	-3.170471	-0.631729
59	1	3.079638	-3.728396	-1.801387
60	1	3.806176	-2.115805	-1.959750
61	1	-1.231577	-2.828297	-1.910843
62	1	4.351814	0.400166	-3.461258
63	1	4.238474	2.011637	-2.715344
64	1	5.587467	-0.443055	-1.442486
65	1	6.433659	0.930944	-2.191761
66	1	5.482170	1.175362	-0.712105
67	1	3.881175	1.559578	2.960411
68	8	-1.505180	-0.987605	-2.143616
69	8	4.051708	-0.983555	0.601940

```
     70          8           -0.897123   -3.651525   -1.514275
     71          8            3.088864    0.499427   -1.899936
     72          8            3.090525    2.297722   -0.543708
     73          7           -3.689497    0.111179    0.918120
     74          7           -1.768381    0.110557   -0.200291
     75         16           -3.907830   -1.506994   -1.055043
     76         14            4.974136   -0.458734    1.956874
---------------------------------------------------------------------
```

Endo cycloadduct (background reaction):



Charge = 0 Multiplicity = 1

mem = 57GB

```
Link 0: opt freq=noraman M062X/6-31g(d) scrf=(smd,solvent=dichloromethane)
Job cpu time: 0 days 5 hours 19 minutes 13.0 seconds.
File lengths (MBytes): RWF= 404 Int= 0 D2E= 0 Chk= 17 Scr= 1
Normal termination of Gaussian 09 at Thu Oct 10 13:36:14 2013.
Item                    Value       Threshold   Converged?
Maximum Force           0.000017    0.000450    YES
RMS Force               0.000003    0.000300    YES
Maximum Displacement    0.001359    0.001800    YES
RMS Displacement        0.000361    0.001200    YES
Predicted change in Energy = -1.496742D-08
Optimization completed.
     -- Stationary point found.
```

```
Link 1: N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
Job cpu time: 0 days 3 hours 17 minutes 47.3 seconds.
File lengths (MBytes): RWF= 1057 Int= 0 D2E= 0 Chk= 24 Scr= 1
Normal termination of Gaussian 09 at Thu Oct 10 13:48:51 2013.
Item                    Value       Threshold   Converged?
Maximum Force           0.000017    0.000450    YES
RMS Force               0.000003    0.000300    YES
Maximum Displacement    0.002665    0.001800    NO
RMS Displacement        0.000692    0.001200    YES
Predicted change in Energy = -3.061451D-08

Values come from Link 1:
HF = -1712.0754828 hartrees (-1074344.48621183 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.390001 (Hartree/Particle)

Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
Sum of electronic and thermal Free Energies =
   -1711.742319 hartrees (-1074135.42259569 kcal/mol)

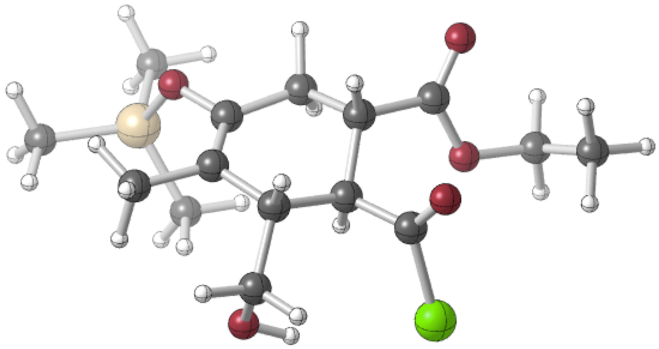
Comments:

Coordinates (from last standard orientation):
---------------------------------------------------------------------
 Center      Atomic       Coordinates (Angstroms)
 Number      Number       X          Y          Z
---------------------------------------------------------------------
    1         6        -0.154183   1.654713   1.284790
    2         6        -1.206319  -0.366778   0.284203
    3         6        -1.038176   1.161296   0.170868
    4         6        -0.411956   1.530950  -1.212825
```

5	6	-0.337104	-1.164872	-0.727313
6	6	0.938948	0.851693	-1.345586
7	6	0.950168	-0.458169	-1.065573
8	6	-0.388476	3.033571	-1.507435
9	6	4.242242	-2.865825	-0.407324
10	6	1.955515	-2.244303	1.582018
11	6	3.894524	-0.025527	0.772197
12	6	2.171050	1.628411	-1.716439
13	6	-2.668149	-0.748346	0.114379
14	6	-4.157389	-2.569606	-0.030194
15	6	-4.077929	-4.078198	-0.057167
16	17	-0.507604	3.385832	1.775369
17	1	-0.926280	-0.689798	1.293380
18	1	-2.014393	1.644019	0.253315
19	1	-1.125896	1.098392	-1.930569
20	1	-0.132886	-2.160942	-0.330634
21	1	-0.913003	-1.304686	-1.652668
22	1	0.352713	3.555023	-0.888705
23	1	-0.091092	3.173181	-2.551224
24	1	4.830785	-2.488525	-1.250793
25	1	4.940535	-3.146944	0.389188
26	1	3.724387	-3.773486	-0.735777
27	1	1.451631	-3.177051	1.306548
28	1	2.571057	-2.447089	2.466849
29	1	1.196811	-1.509015	1.874054
30	1	4.473085	-0.233234	1.680761
31	1	4.585965	0.366337	0.018716
32	1	3.168801	0.758445	1.016270
33	1	-1.800207	3.852636	-0.444575
34	1	2.027145	2.196038	-2.643174
35	1	2.447284	2.349884	-0.936424

36	1	3.014369	0.950356	-1.863961
37	1	-4.566480	-2.164464	-0.959821
38	1	-4.768758	-2.205407	0.800728
39	1	-3.657501	-4.462744	0.876141
40	1	-5.080698	-4.495892	-0.182771
41	1	-3.455159	-4.417640	-0.889609
42	8	0.713842	1.084506	1.853374
43	8	2.070541	-1.240047	-1.154997
44	8	-1.670391	3.617610	-1.376130
45	8	-2.813512	-2.074625	0.136142
46	8	-3.589837	0.023334	-0.021830
47	14	3.029666	-1.581915	0.198529

Exo cycloadduct (background reaction):



Charge = 0 Multiplicity = 1

mem = 57GB

```
Link 0: opt freq=noraman M062X/6-31g(d) scrf=(smd,solvent=dichloromethane)
Job cpu time: 0 days 4 hours 44 minutes 50.9 seconds.
File lengths (MBytes): RWF= 397 Int= 0 D2E= 0 Chk= 17 Scr= 1
Normal termination of Gaussian 09 at Wed Oct 9 23:02:15 2013.
Item                    Value       Threshold   Converged?
Maximum Force           0.000027    0.000450    YES
RMS Force               0.000005    0.000300    YES
Maximum Displacement    0.001382    0.001800    YES
RMS Displacement        0.000303    0.001200    YES
Predicted change in Energy = -3.280765D-08
Optimization completed.
     -- Stationary point found.
```

```
Link 1: N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
Job cpu time: 0 days 3 hours 14 minutes 57.0 seconds.
File lengths (MBytes): RWF= 1053 Int= 0 D2E= 0 Chk= 24 Scr= 1
Normal termination of Gaussian 09 at Wed Oct 9 23:14:42 2013.
Item                    Value       Threshold   Converged?
```

```
Maximum Force              0.000027     0.000450     YES
RMS Force                  0.000005     0.000300     YES
Maximum Displacement       0.004768     0.001800     NO
RMS Displacement           0.000868     0.001200     YES
Predicted change in Energy = -8.778539D-08

Values come from Link 1:
HF = -1712.084226 hartrees (-1074349.97265726 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.390590 (Hartree/Particle)

Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
Sum of electronic and thermal Free Energies =
    -1711.750175 hartrees (-1074140.35231425 kcal/mol)

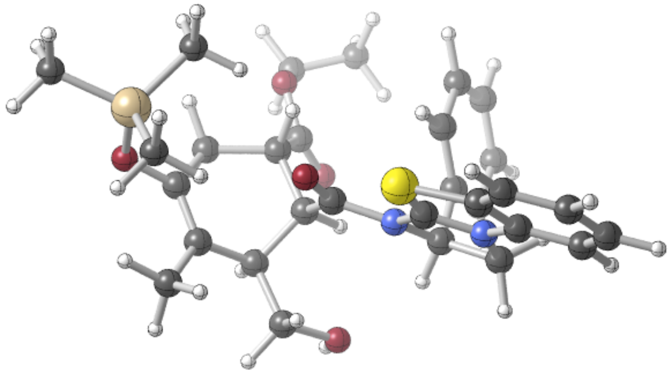
Comments:

Coordinates (from last standard orientation):
---------------------------------------------------------------------
 Center       Atomic        Coordinates (Angstroms)
 Number       Number        X          Y          Z
---------------------------------------------------------------------
     1        6          2.458361   1.137674  -0.327573
     2        6          0.956213  -0.714155  -1.023078
     3        6          1.038896   0.628876  -0.290363
     4        6          0.081069   1.639775  -0.960971
     5        6         -0.428060  -1.315693  -0.762797
     6        6         -1.307717   1.030291  -1.070545
     7        6         -1.510775  -0.285126  -0.917866
     8        6          0.042787   2.968180  -0.190641
     9        6         -2.759394  -0.115094   1.900776
```

10	6	-4.154620	-2.645268	0.810024
11	6	-5.294975	0.121478	0.138509
12	6	-2.456600	1.970451	-1.314018
13	6	2.019638	-1.712619	-0.611649
14	6	3.623292	-2.263366	1.045691
15	6	4.931117	-1.861185	0.395701
16	17	2.981276	1.956372	1.215116
17	1	1.083031	-0.549144	-2.098364
18	1	0.736874	0.492146	0.752601
19	1	0.471026	1.871758	-1.964506
20	1	-0.471567	-1.744199	0.249886
21	1	-0.618055	-2.136592	-1.462855
22	1	1.036196	3.436290	-0.201538
23	1	-0.633114	3.661676	-0.696579
24	1	-3.393645	-0.045222	2.792612
25	1	-1.895139	-0.737611	2.161559
26	1	-2.387769	0.889764	1.668287
27	1	-3.248011	-3.237272	0.980076
28	1	-4.790583	-2.742931	1.697627
29	1	-4.691549	-3.089675	-0.035482
30	1	-6.030437	-0.046381	0.934248
31	1	-5.103618	1.198135	0.083477
32	1	-5.752219	-0.191607	-0.807193
33	1	0.277966	2.495300	1.689644
34	1	-3.342110	1.421831	-1.641931
35	1	-2.713827	2.538307	-0.410005
36	1	-2.202725	2.700096	-2.092298
37	1	3.365649	-3.303192	0.833575
38	1	3.645654	-2.109367	2.125586
39	1	5.164139	-0.815054	0.615215
40	1	5.741757	-2.485191	0.783783

```
    41          1             4.882019   -1.993821   -0.688556
    42          8             3.221124    1.070365   -1.230973
    43          8            -2.768338   -0.833614   -0.913111
    44          8            -0.444244    2.821705    1.130299
    45          8             2.550630   -1.416270    0.582227
    46          8             2.319567   -2.680943   -1.268526
    47         14            -3.734068   -0.852259    0.481974
---------------------------------------------------------------------
```

Endo cycloadduct (asymmetric reaction):



Charge = 1 Multiplicity = 1

mem = 57GB

Link 0: opt freq=noraman M062X/6-31g(d) scrf=(smd,solvent=dichloromethane)

Job cpu time: 3 days 23 hours 33 minutes 21.5 seconds.

File lengths (MBytes): RWF= 1103 Int= 0 D2E= 0 Chk= 40 Scr= 1

Normal termination of Gaussian 09 at Fri Oct 11 03:46:42 2013.

Item	Value	Threshold	Converged?
Maximum Force	0.000017	0.000450	YES
RMS Force	0.000002	0.000300	YES
Maximum Displacement	0.000690	0.001800	YES
RMS Displacement	0.000144	0.001200	YES

Predicted change in Energy = -9.200397D-09

Optimization completed.

-- Stationary point found.

Link 1: N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

Job cpu time: 0 days 17 hours 45 minutes 55.8 seconds.

File lengths (MBytes): RWF= 4190 Int= 0 D2E= 0 Chk= 53 Scr= 1

Normal termination of Gaussian 09 at Fri Oct 11 04:53:46 2013.

Item	Value	Threshold	Converged?

```
Maximum Force            0.000017     0.000450     YES
RMS Force                0.000002     0.000300     YES
Maximum Displacement     0.002979     0.001800     NO
RMS Displacement         0.000389     0.001200     YES
Predicted change in Energy = -2.034819D-08
```

Values come from Link 1:

HF = -2338.0058055 hartrees (-1467122.0230093 kcal/mol)

Imaginary Frequencies: none found

Zero-point correction = 0.633959 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies =

-2337.442357 hartrees (-1466768.45344107 kcal/mol)

Comments:

Coordinates (from last standard orientation):

```
---------------------------------------------------------------------
 Center      Atomic        Coordinates (Angstroms)
 Number      Number        X          Y          Z
---------------------------------------------------------------------
    1        6         -6.028443  -0.351319  -0.080054
    2        6         -4.690019  -0.723403  -0.157688
    3        6         -4.288515  -1.921822  -0.761050
    4        6         -5.226731  -2.788241  -1.313068
    5        6         -6.565766  -2.422412  -1.236920
    6        6         -6.959804  -1.222396  -0.629220
    7        6         -2.425956  -0.625474   0.121761
    8        6         -3.429889   1.213020   1.094257
    9        6         -1.882555   1.407563   1.092278
```

10	6	-1.424117	2.527680	0.182443
11	6	-1.435982	3.826881	0.693744
12	6	-1.030764	2.307182	-1.138233
13	6	-1.080916	4.901352	-0.115480
14	6	-0.660789	3.384321	-1.943236
15	6	-0.695461	4.681438	-1.437213
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22	6	3.239903	-1.310369	0.779558
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46	1	4.057026	0.651383	0.876117
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52	1	4.791916	-4.779467	-2.495951
53	1	1.998490	-1.506515	-2.077925
54	1	3.642734	-1.340536	-2.742409
55	1	2.580315	-2.640742	-3.300945
56	1	2.421812	-5.077173	0.192118
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   74       7          -1.390714    0.079285    0.623290
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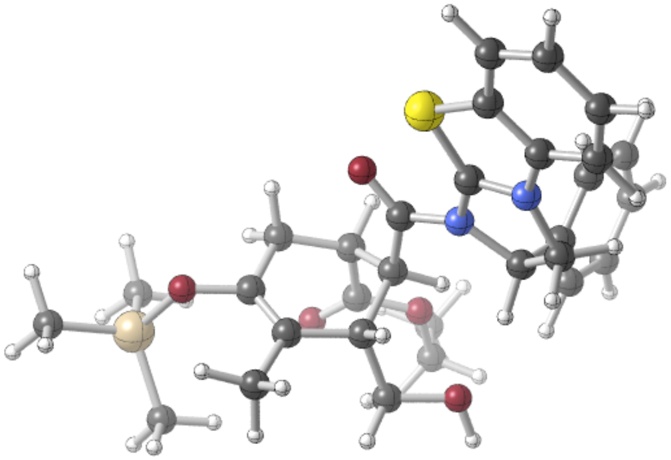
***Exo* cycloadduct (asymmetric reaction):**



Charge = 1 Multiplicity = 1

mem = 57GB

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Job cpu time: 1 days 0 hours 46 minutes 21.8 seconds.

File lengths (MBytes): RWF= 1059 Int= 0 D2E= 0 Chk= 39 Scr= 1

Normal termination of Gaussian 09 at Wed Oct 9 03:00:00 2013.

Item	Value	Threshold	Converged?
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Maximum Displacement	0.000175	0.001800	YES
RMS Displacement	0.000032	0.001200	YES

Predicted change in Energy = -5.731885D-10

Optimization completed.

-- Stationary point found.

Link 1: N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

Job cpu time: 0 days 16 hours 35 minutes 4.4 seconds.

File lengths (MBytes): RWF= 4176 Int= 0 D2E= 0 Chk= 52 Scr= 1

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Maximum Displacement        0.000596     0.001800     YES
RMS Displacement            0.000083     0.001200     YES
Predicted change in Energy = -1.789859D-09
Optimization completed.
      -- Stationary point found.

Values come from Link 1:
HF = -2338.0127968 hartrees (-1467126.41011997 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.634114 (Hartree/Particle)

Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
Sum of electronic and thermal Free Energies =
   -2337.450449 hartrees (-1466773.53125199 kcal/mol)

Comments:

Coordinates (from last standard orientation):
---------------------------------------------------------------------
 Center        Atomic         Coordinates (Angstroms)
 Number        Number         X          Y          Z
---------------------------------------------------------------------
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    4        6          -5.797449   -3.166676   -0.981947
    5        6          -7.022732   -3.060955   -0.332668
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     72          8            3.918635    1.542970   -0.597645
     73          7           -3.874246   -0.555150    0.592352
     74          7           -1.767443   -0.114299    0.077601
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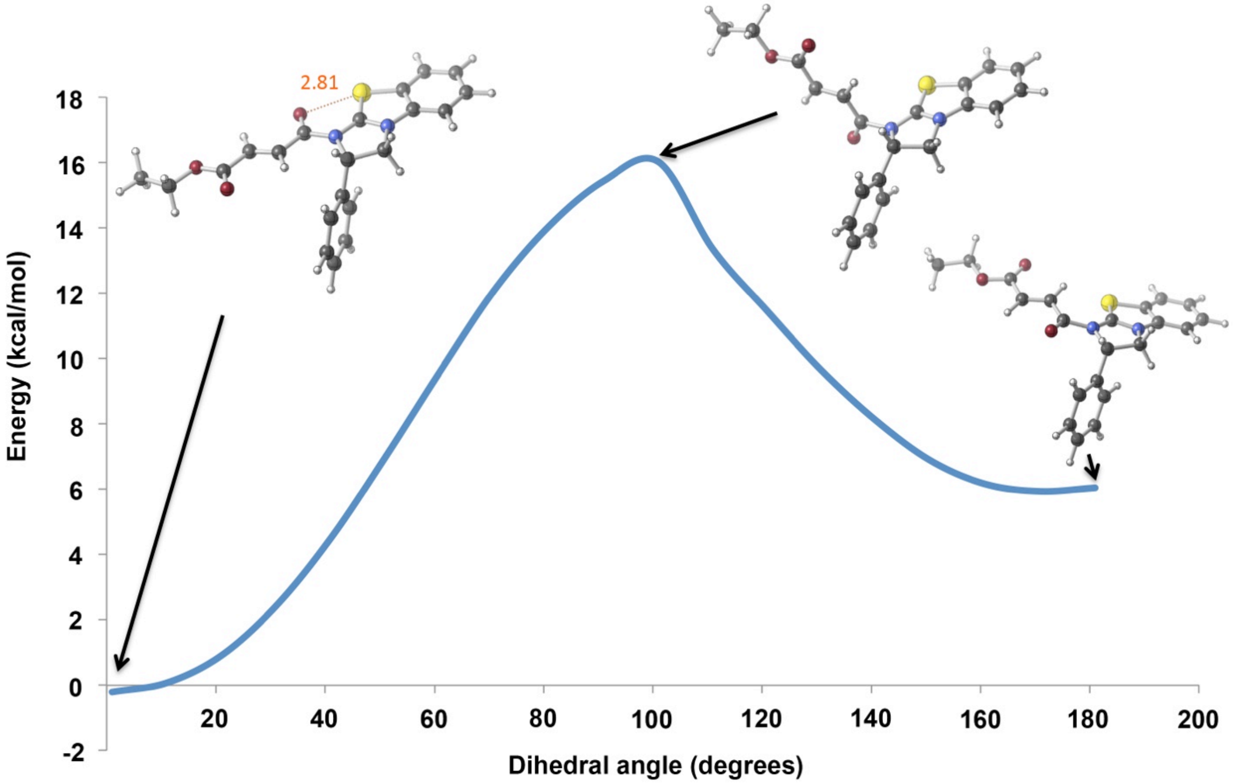


Figure S4. Dihedral angle scan of the O–C–N–C angle at 10-degree increments for 18 steps shows the lowest energy conformation where the sulfur atom is in close proximity to the oxygen atom. Selected distance is shown in Angstroms.

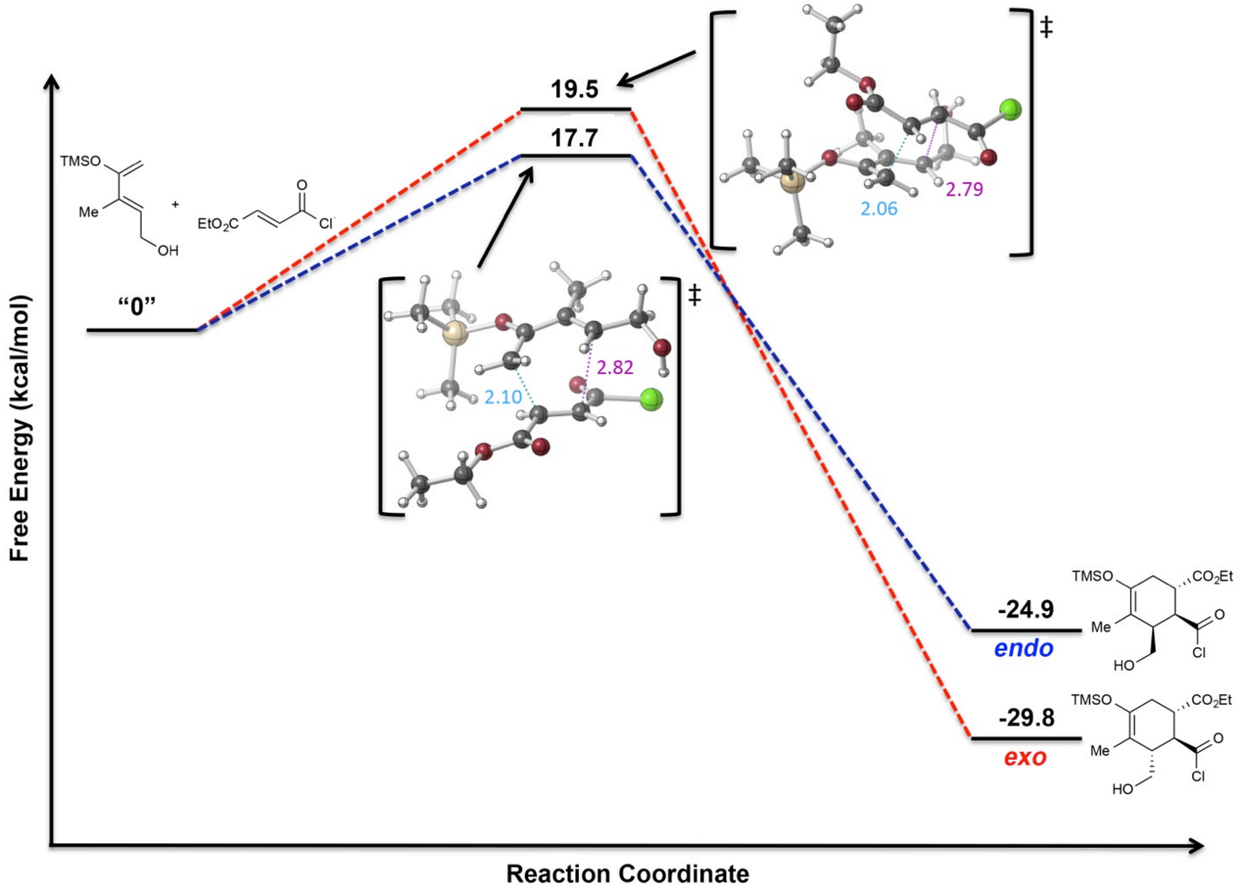


Figure S5. Reaction coordinate of the background reaction proceeding directly with ethyl fumaroyl chloride. Minima and transition state structures were optimized at the M06-2X/6-31G(d) level with an implicit solvent model (SMD(dichloromethane)). The TIPS group was truncated to a TMS group. Energies are Gibbs Free Energies in kcal/mol relative to the reactants. Selected distances are in Angstroms.

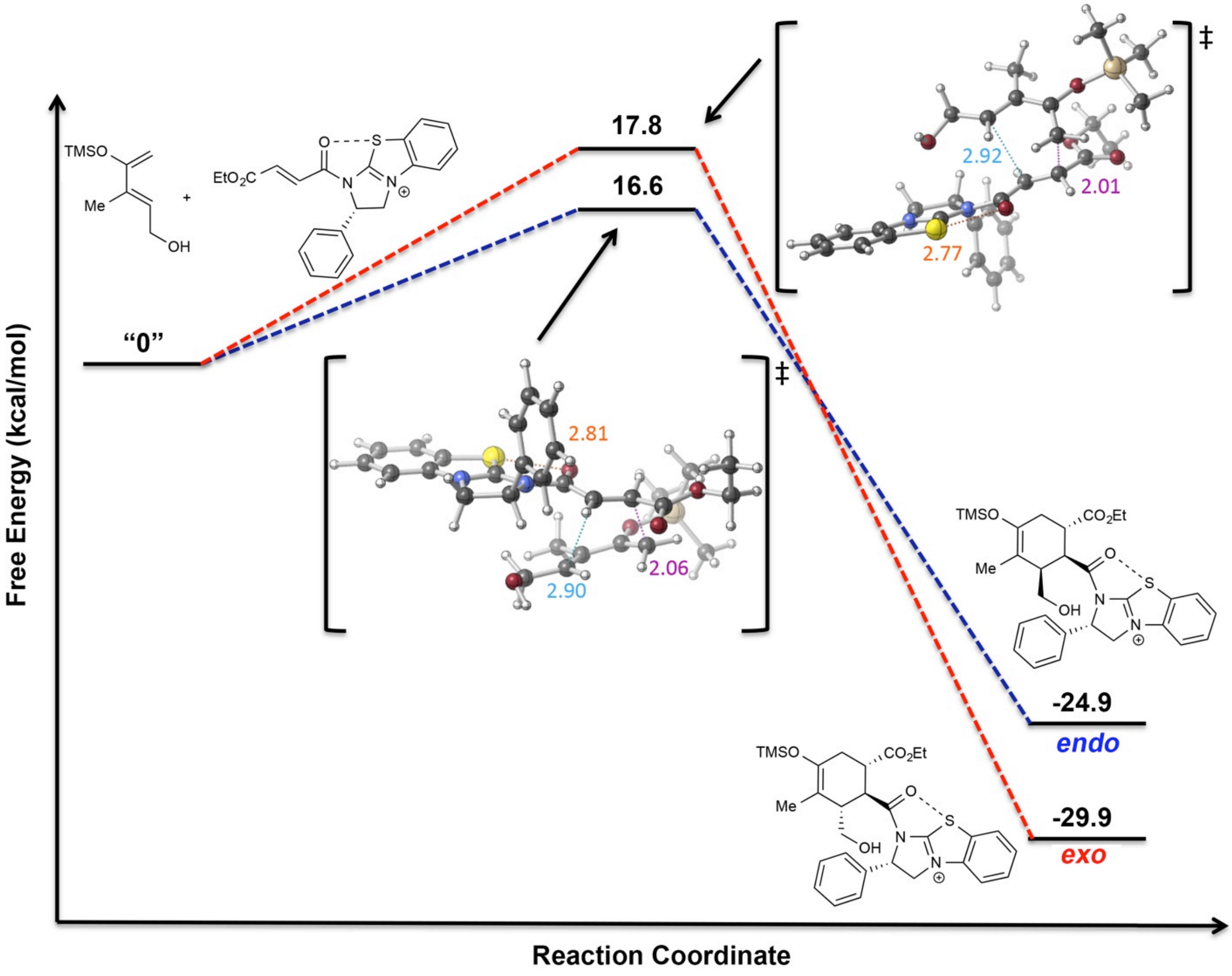


Figure S6. Reaction coordinates for the asymmetric Diels-Alder cycloaddition. Minima and transition state structures were optimized at the M06-2X/6-31G(d) level with an implicit solvent model (SMD(dichloromethane)). The TIPS group was truncated to a TMS group. Silyloxydiene and acylammonium cation energies were calculated for the reactants. Energies are Gibbs Free Energies in kcal/mol relative to the reactants. Selected distances are in Angstroms.

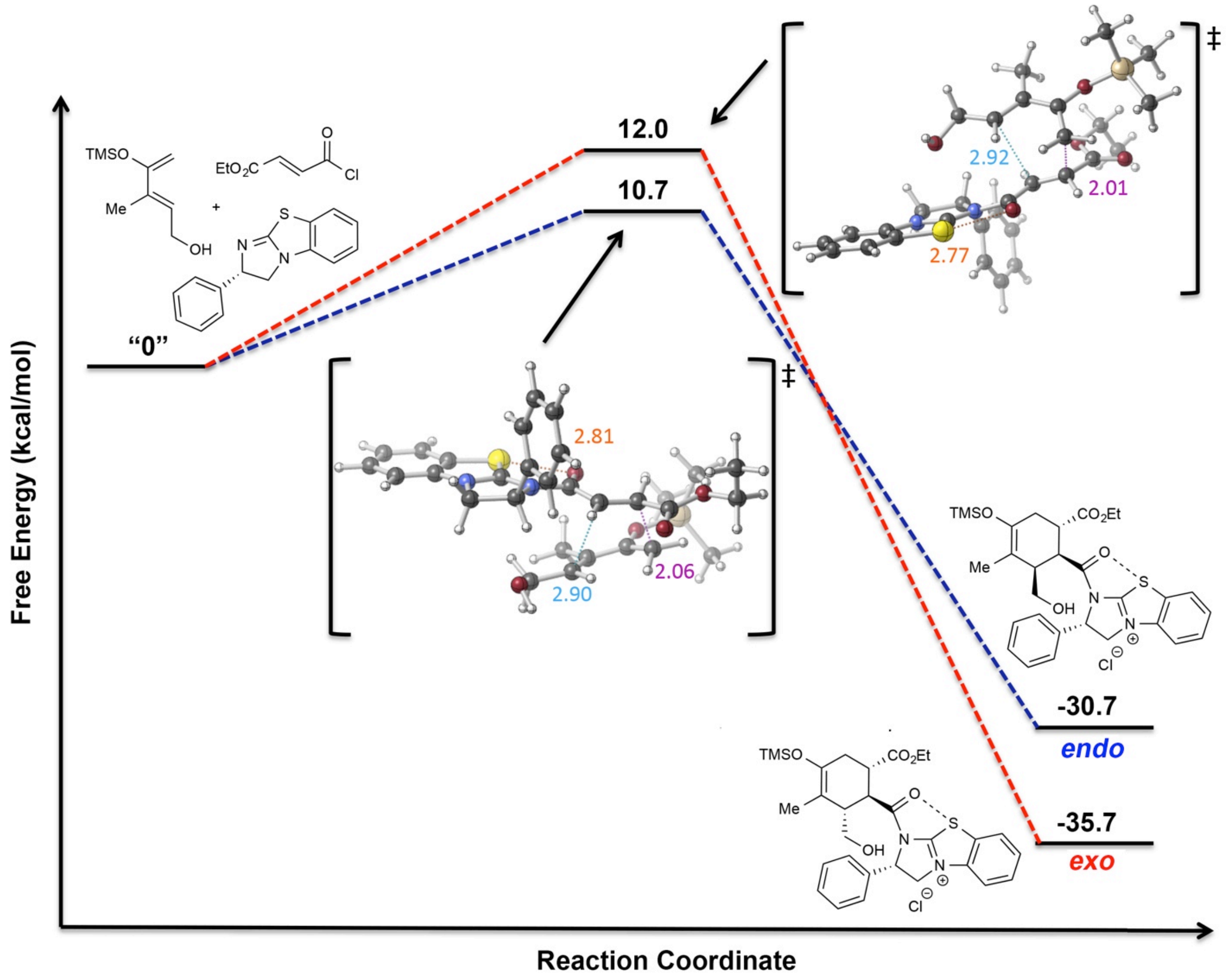


Figure S7. Reaction coordinates for the asymmetric Diels-Alder cycloaddition. Minima and transition state structures were optimized at the M06-2X/6-31G(d) level with an implicit solvent model (SMD(dichloromethane)). The TIPS group was truncated to a TMS group. Silyloxydiene, ethyl fumaroyl chloride and (*S*)-(–)-BTM energies were calculated for the reactants. Energies are Gibbs Free Energies in kcal/mol relative to the reactants. Selected distances are in Angstroms.

Intrinsic Reaction Coordinate: The following IRC was generated at the uM062X/6-31g(d) level with "guess=(mix,always)" keywords to assure that diradical processes were not missed and using the SMD(dichloromethane) continuum model. The IRC is for the *endo* Diels-Alder cycloadduct. This model has been truncated. The TIPS group was truncated to a TMS group, the ethyl ester moiety was removed from the acylammonium, and the alcohol tether was removed from the silyloxydiene. Note that there is a likely "hidden intermediate" in the area of the plateau.[16]

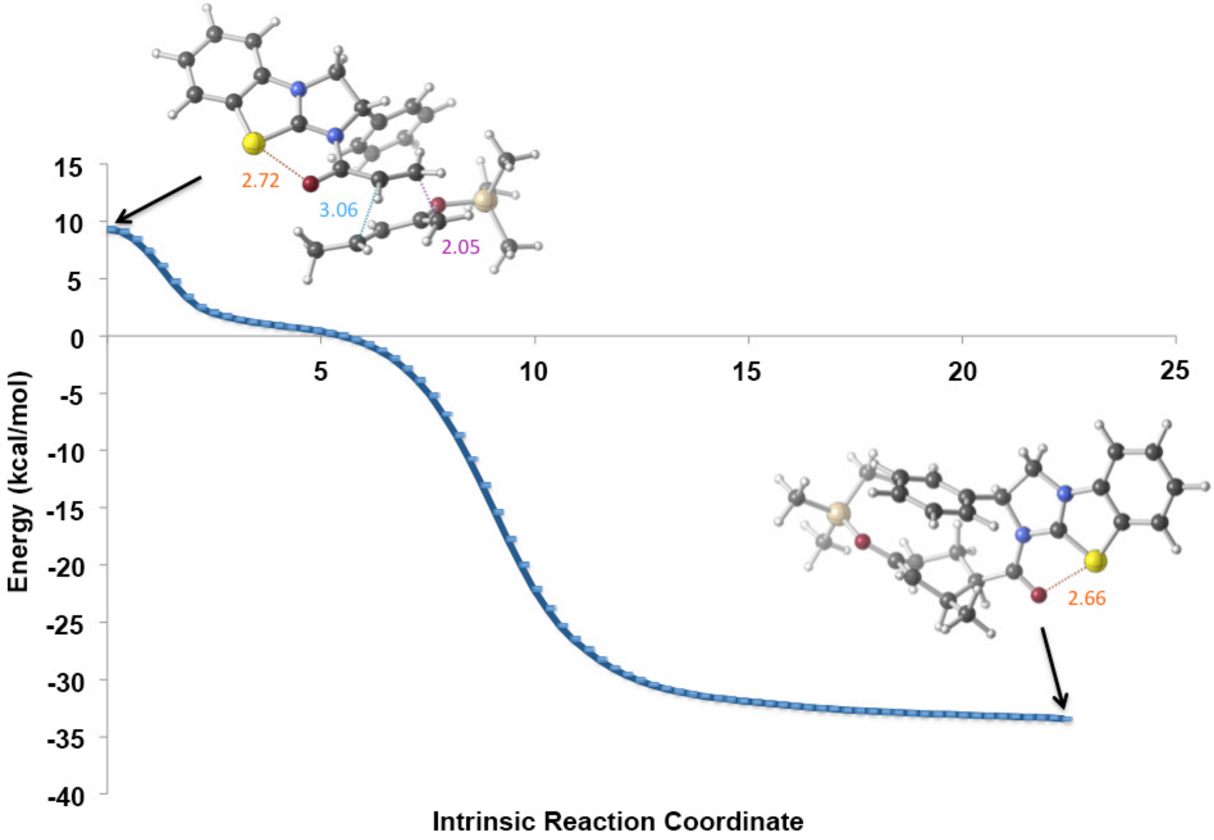


Figure S8. Total energy along IRC (*EndoTop*) generated at the uM062X/6-31g(d) level with an implicit solvent model (SMD(dichloromethane)) for the *endo* cycloadduct of the asymmetric Diels-Alder reaction. The TIPS group was truncated to a TMS group, the ethyl ester moiety was removed from the acylammonium, and the alcohol tether was removed from the silyloxydiene. Selected distances are in Angstroms.

NBO Analysis: All NBO calculations were done at the M06-2X/6-31G(d) level with the following keywords in the route card: pop(nbo6read) scf(tight) int(finegrid) iop(3/32=2). The keywords “E2PERT=0.1” and “STERIC=0.1” were used to compute all favorable (lone pair$_N$ ↔ S*$_{SC}$) and unfavorable (lone pair$_N$ ↔ lone pair$_S$) interactions that were 0.1 kcal/mol or higher in energy.

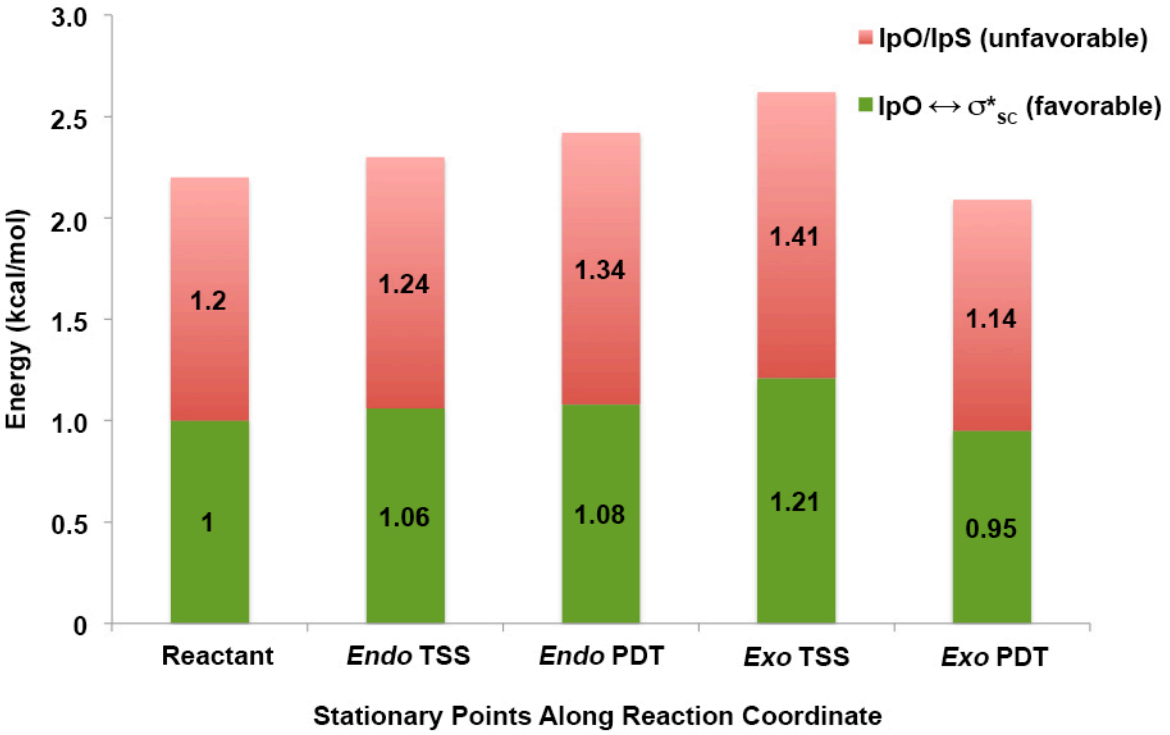
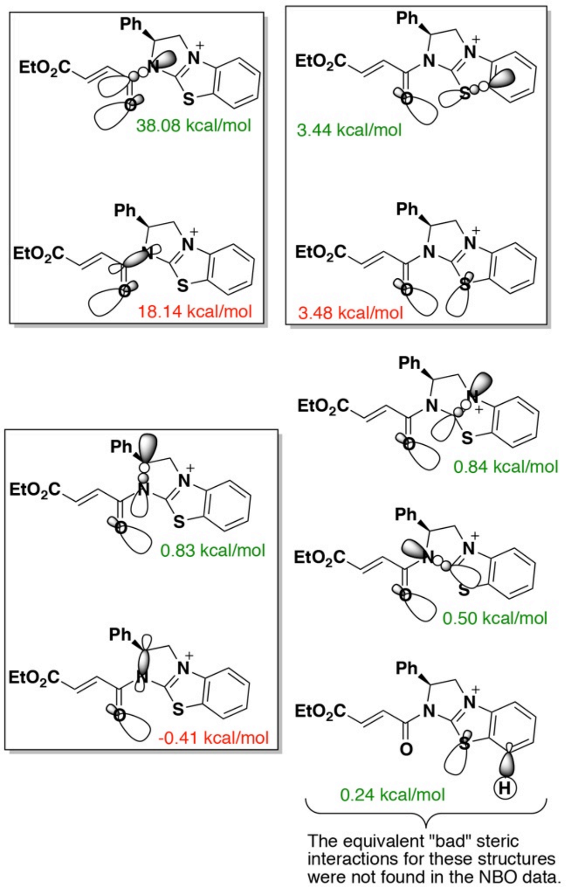
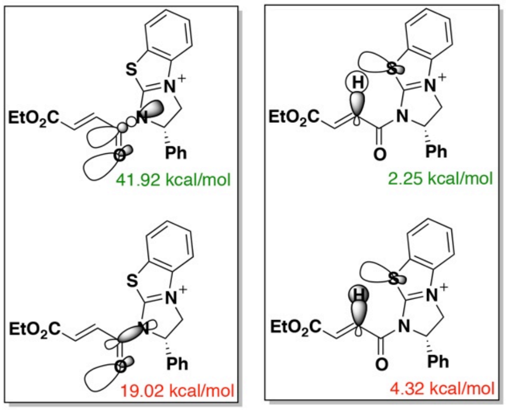


Figure S9. Natural bonding orbital (NBO) interactions generated at the M06-2X/6-31G(d) level. Favorable (lone pair$_N$ ↔ σ*$_{SC}$) and unfavorable (lone pair$_N$ ↔ lone pair$_S$) interactions tracked along the reaction coordinate (reactant → TS → product).





Type of NBO Interaction	Conformer	Energy (kcal/mol)
Good	0 degrees	43.93
Bad		21.21
Net Good		22.72
Good	180 degrees	44.17
Bad		23.34
Net Good		20.83

Figure S10. Relevant NBO interactions in the acylammonium cation. “Good” donor-acceptor interaction energies are shown in green, and “bad” filled-filled interaction energies are shown in red. The orbital interactions favor the 0-degree conformer (where the sulfur atom is in close proximity to the oxygen atom) by 1.89 kcal/mol.

Spin density maps: Spin density maps of the silyloxydiene **2c** and dienophiles (ethyl fumaroyl chloride **1a** and (*S*)-(–)-BTM catalyst-bound acylammonium cation) were generated using Spartan10. Optimizations were carried out using Spartan10, Truhlar M05-2X functional and 6-31+G(d) basis set.[17] The silyloxydiene **2c** was optimized as a radical cation and the dienophiles as radical anions.

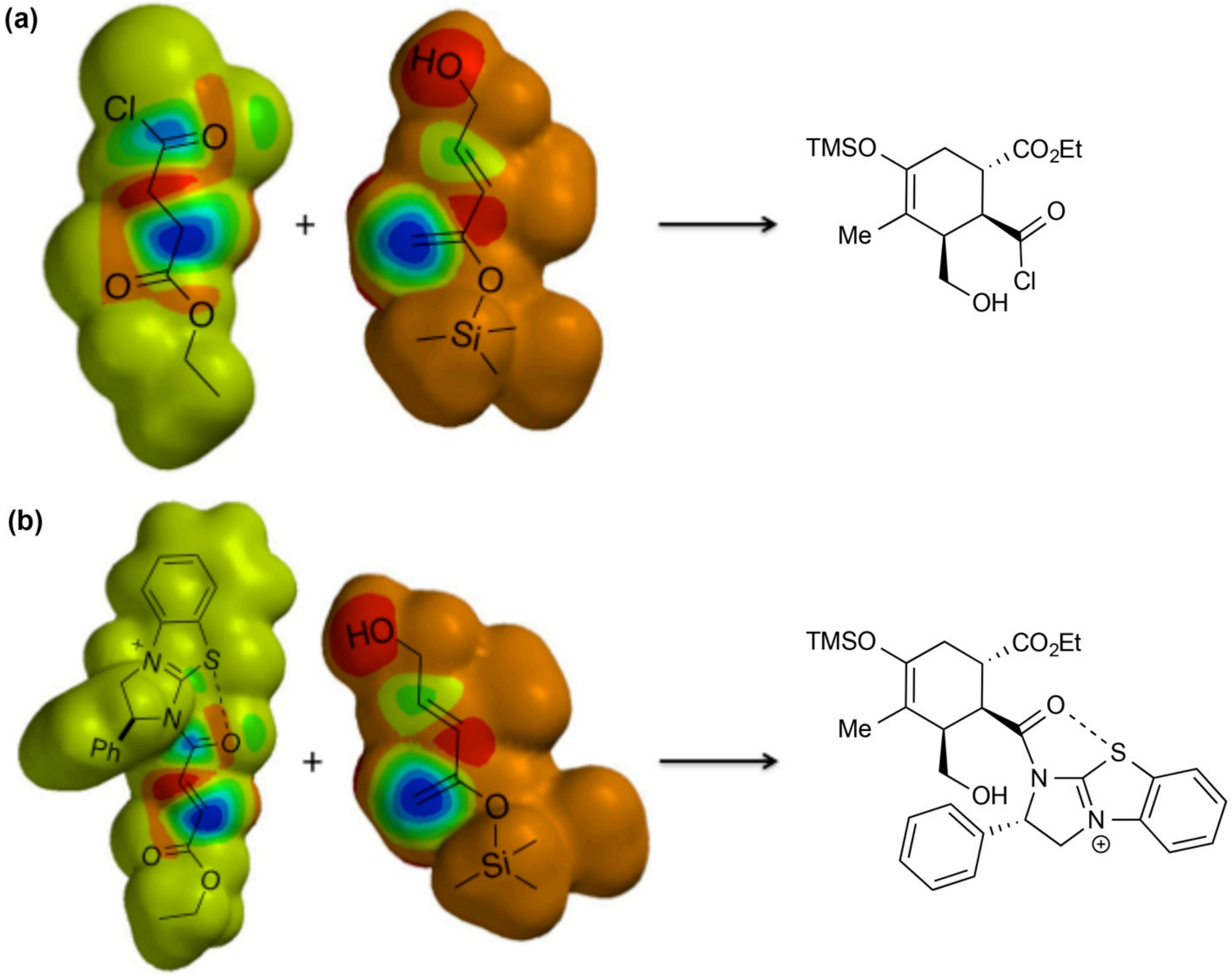
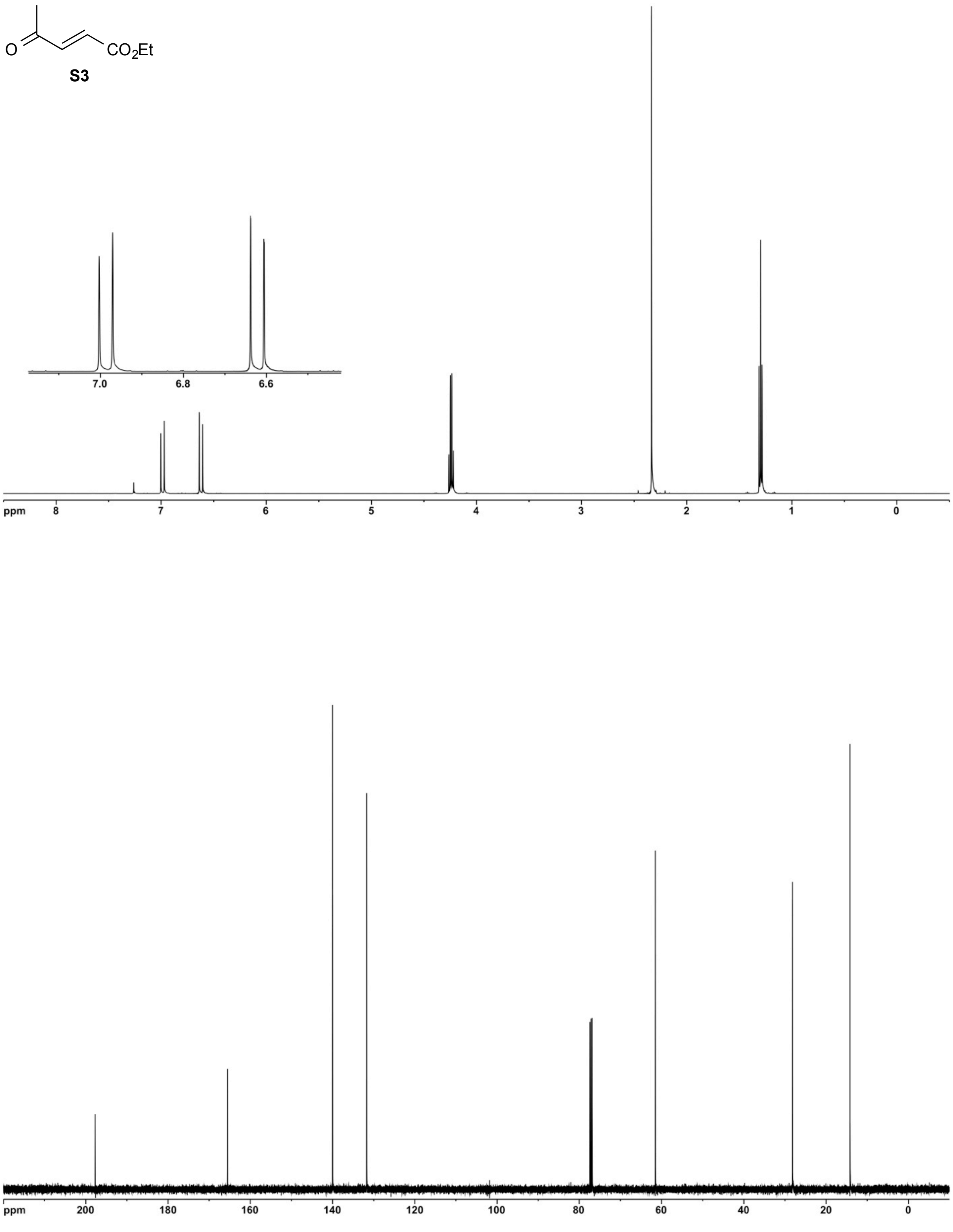
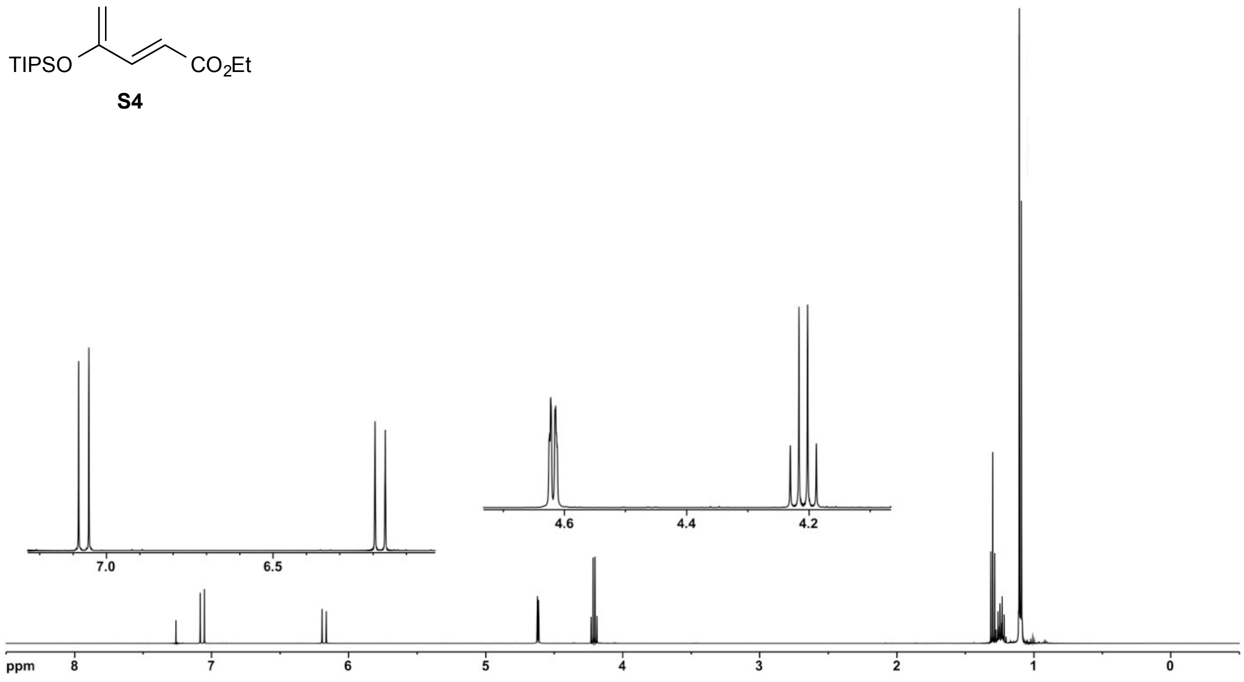
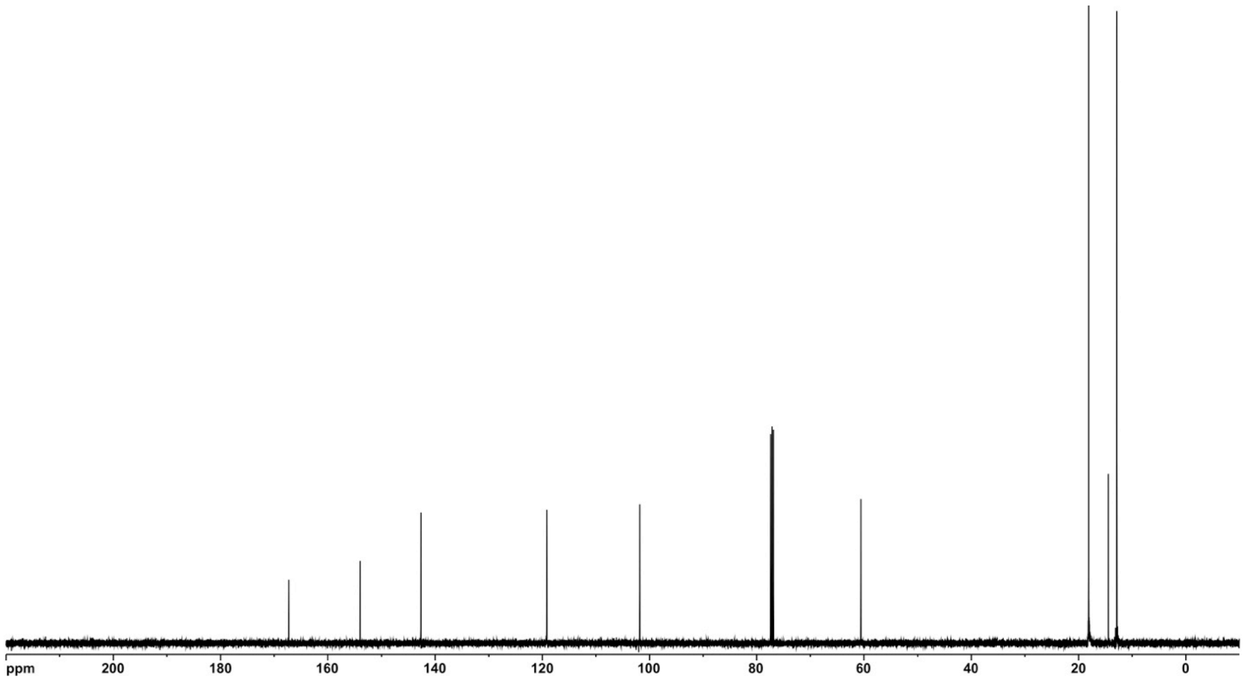


Figure S11. Spin density maps of the (a) background Diels-Alder cycloaddition and (b) asymmetric Diels-Alder cycloaddition leading to the preferred *endo* cycloadduct. The blue regions represent the reactive sites (highest spin density). The new bond occurs preferentially at these reactive sites. The above maps correctly predict the site of the first bond formations that occur in the Diels-Alder reaction.

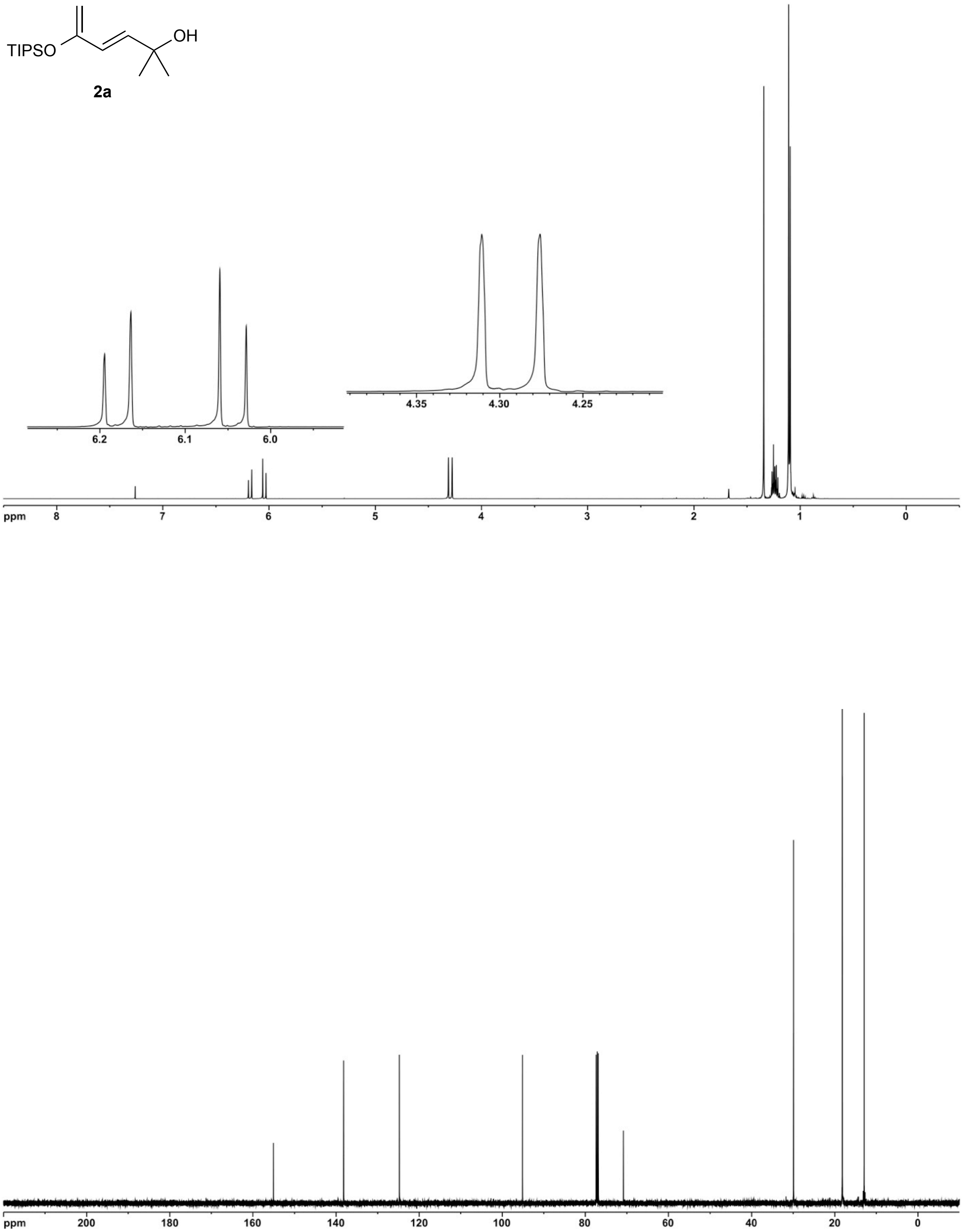


^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of ketoester **S3** in CDCl$_3$

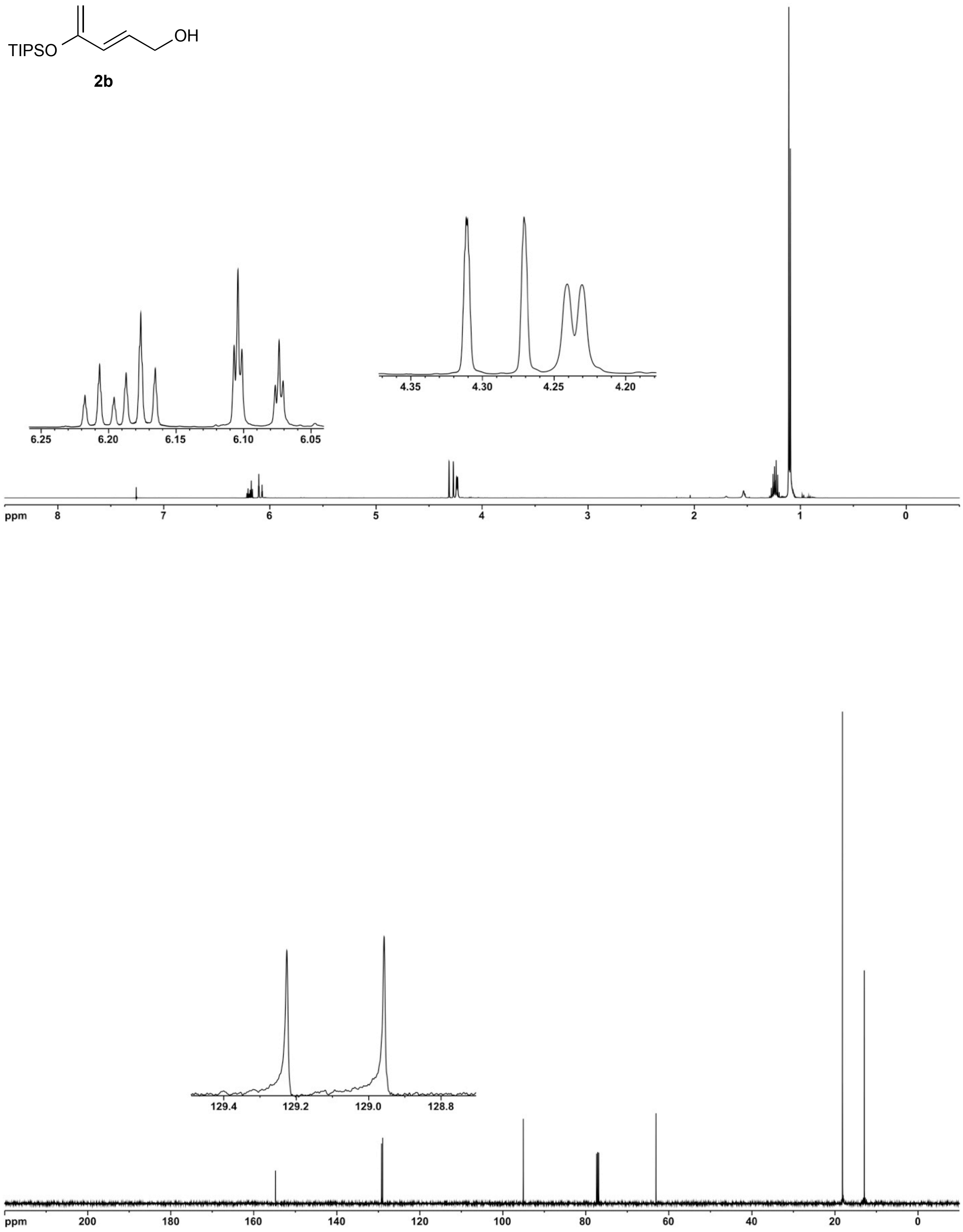




^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of diene **S4** in $CDCl_3$

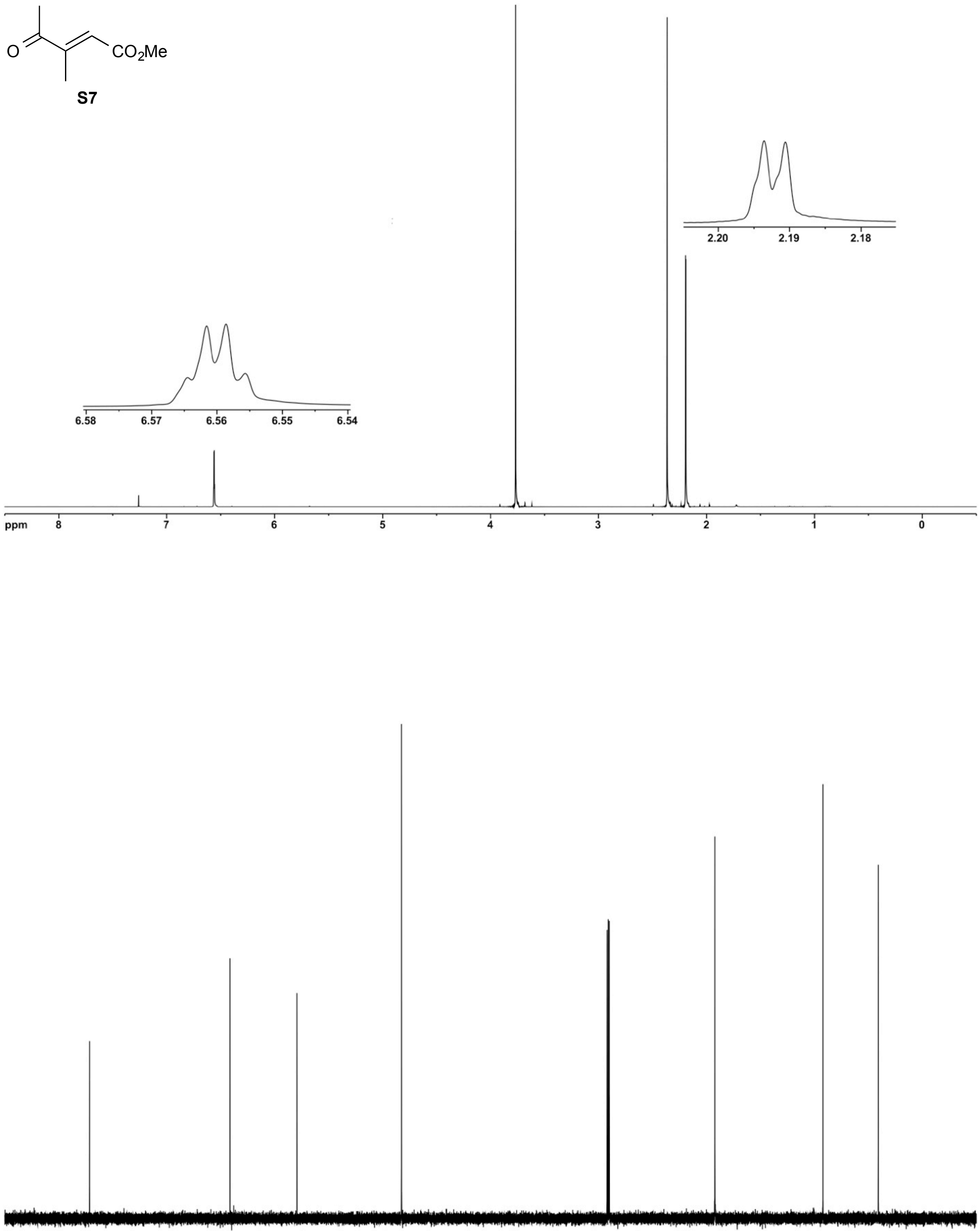

2a

^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of silyloxydiene alcohol **2a** in $CDCl_3$

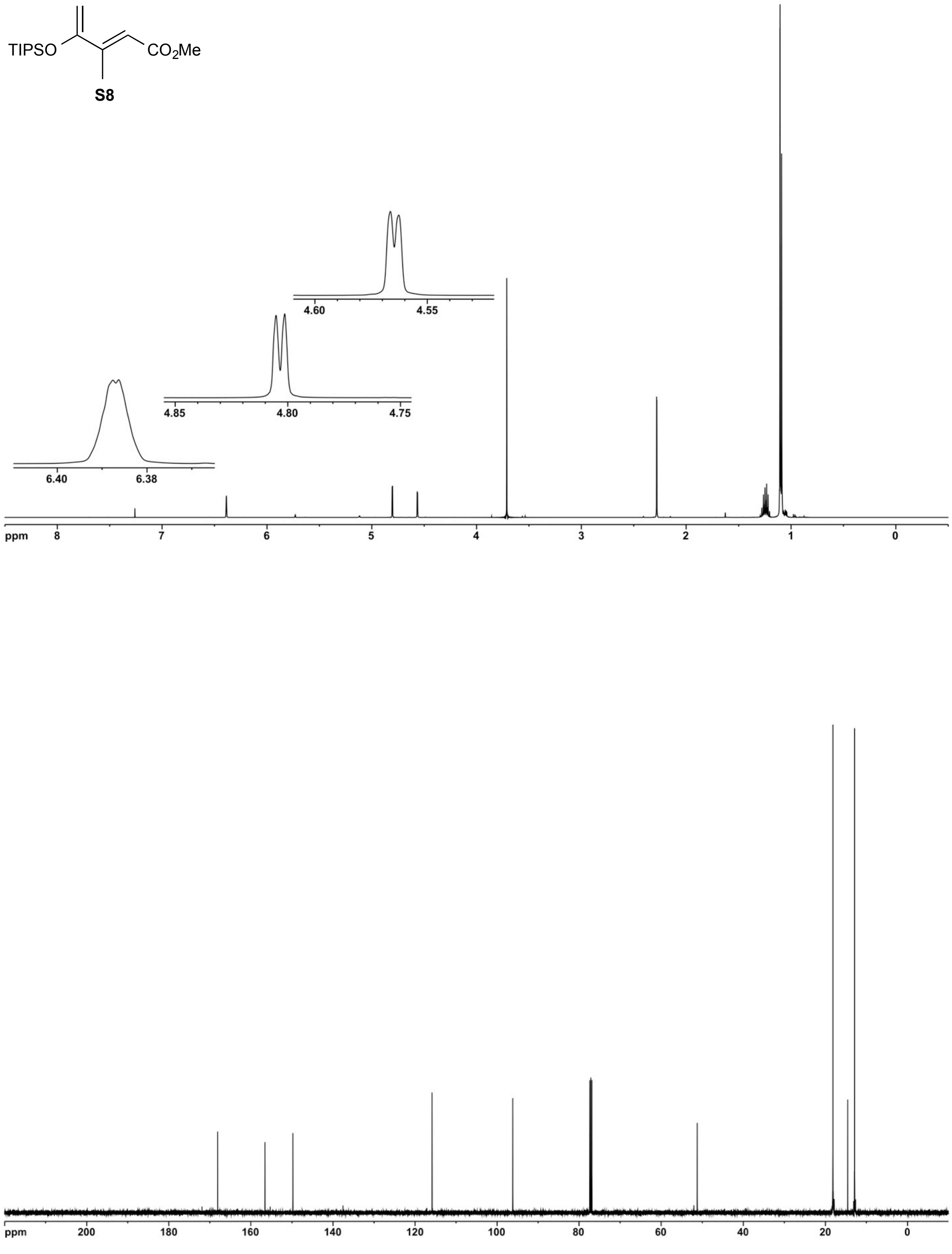


2b

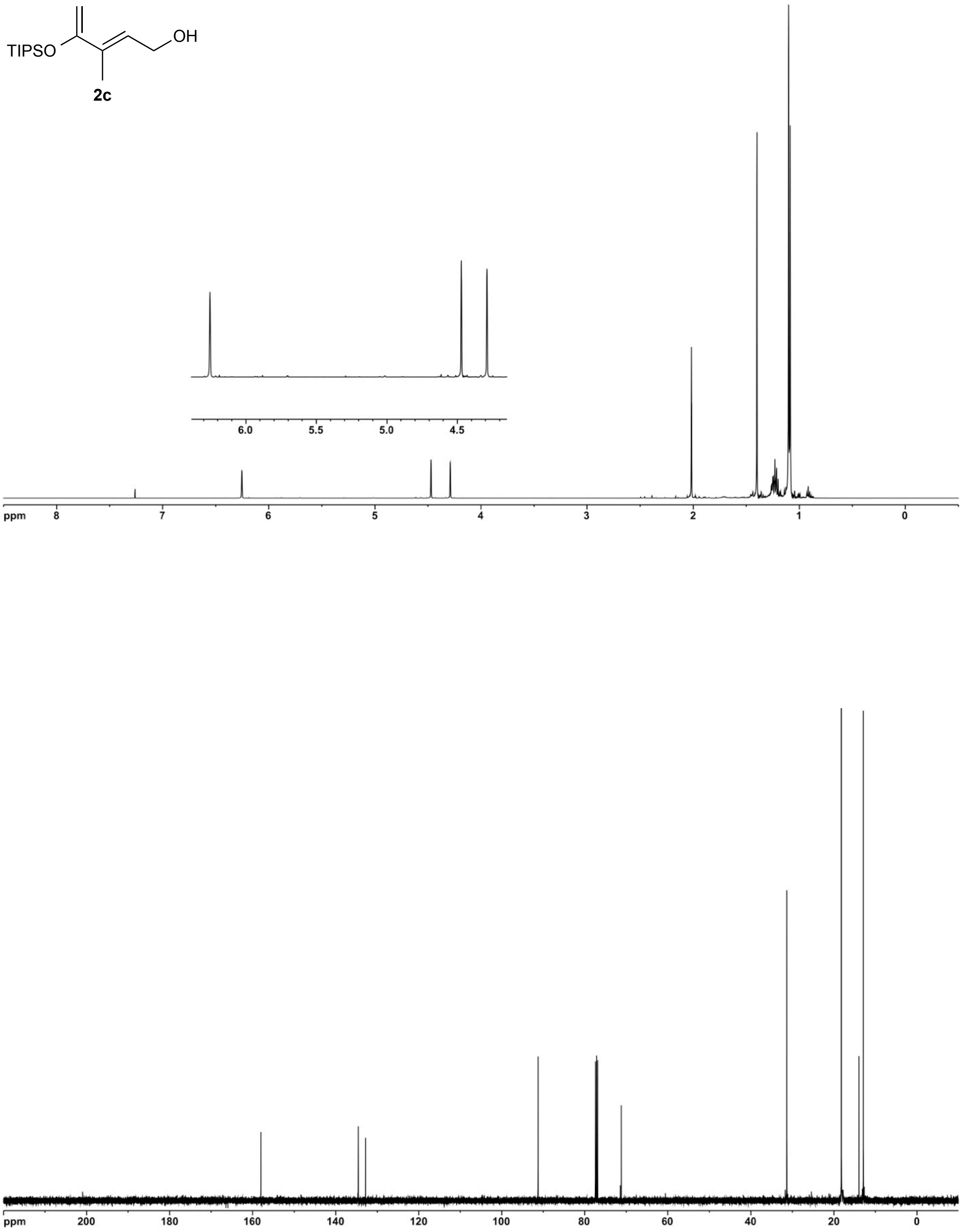
^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of silyloxydiene alcohol **2b** in $CDCl_3$



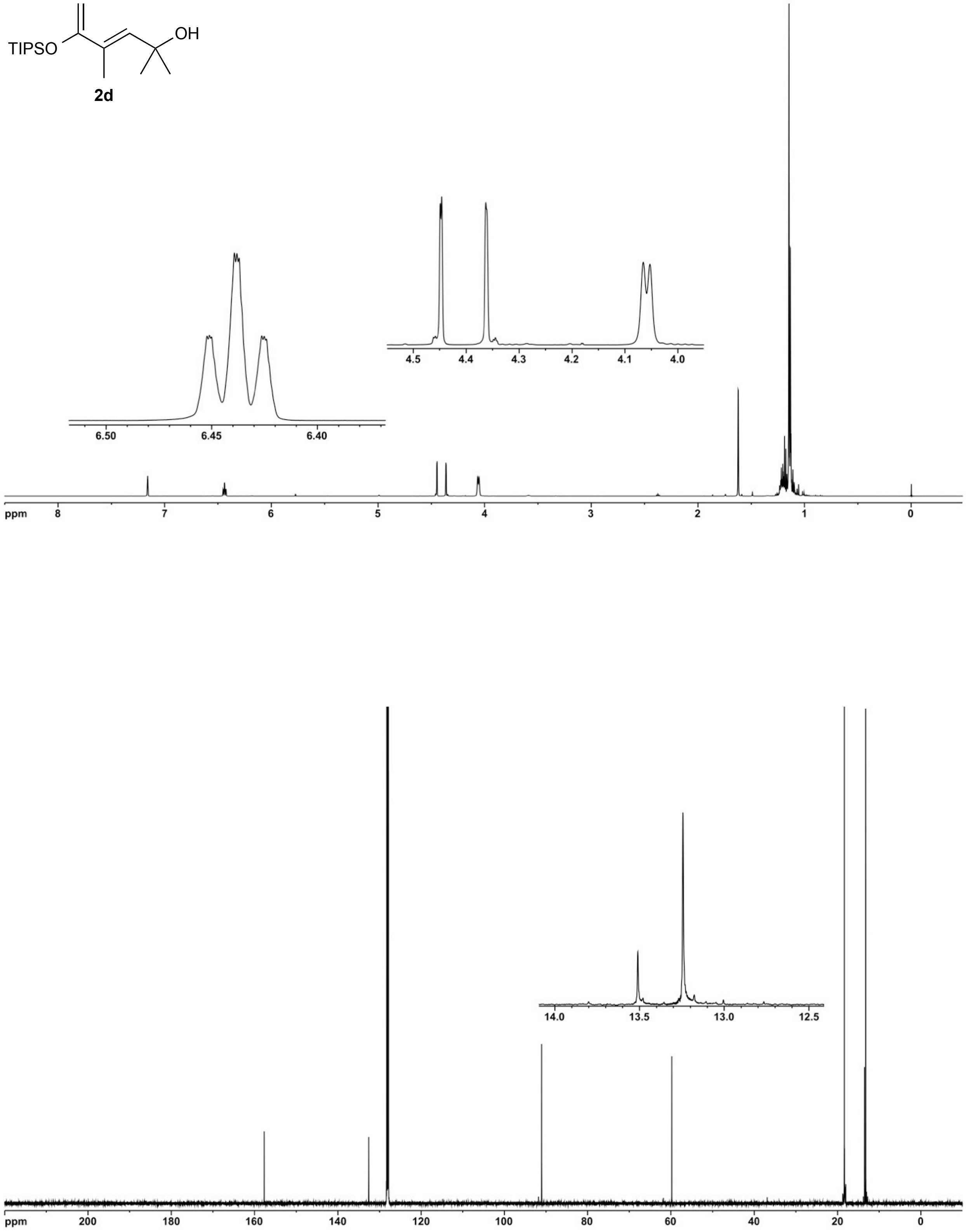
^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of ketoester **S7** in $CDCl_3$



^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of diene **S8** in $CDCl_3$

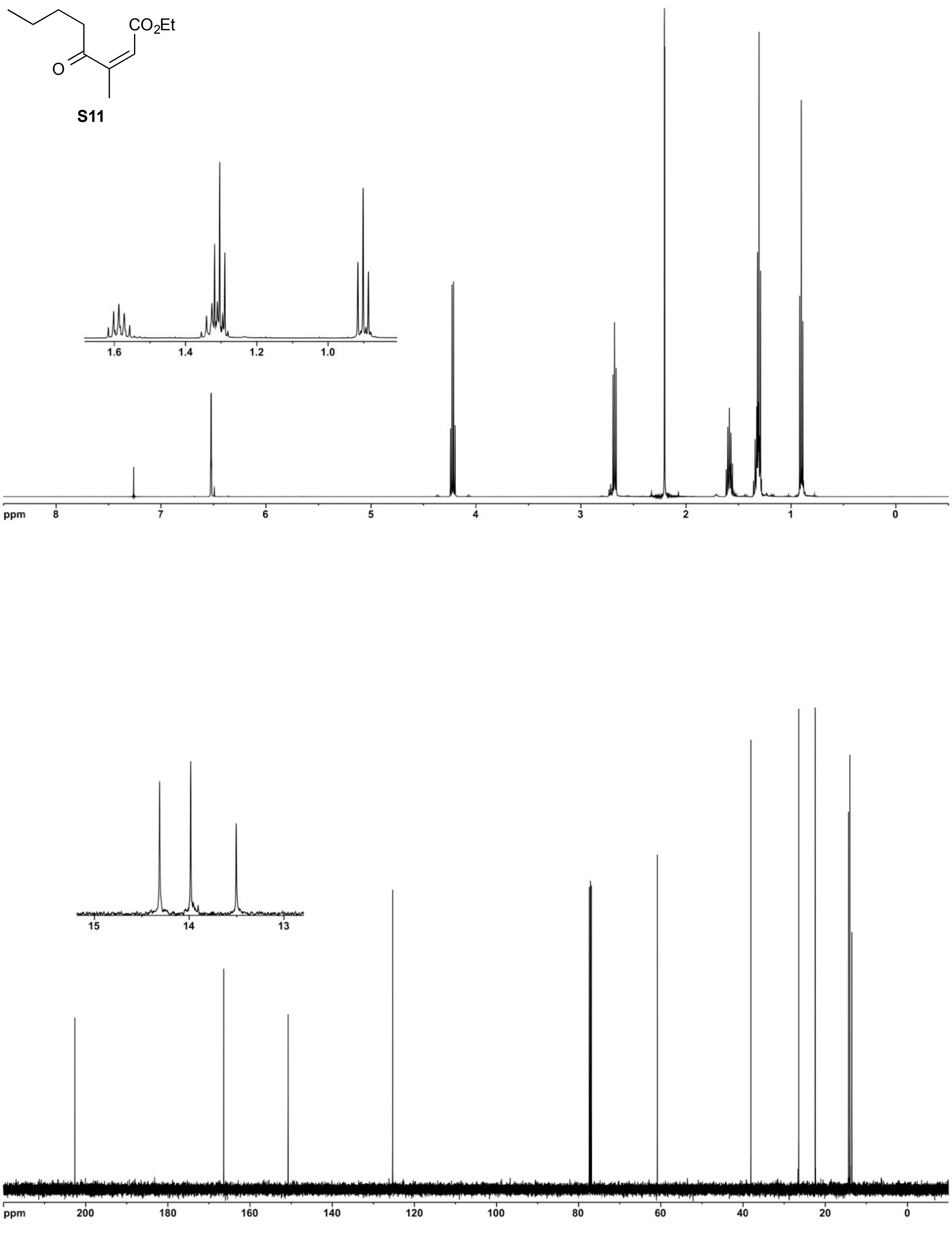


^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of silyloxydiene alcohol **2c** in $CDCl_3$

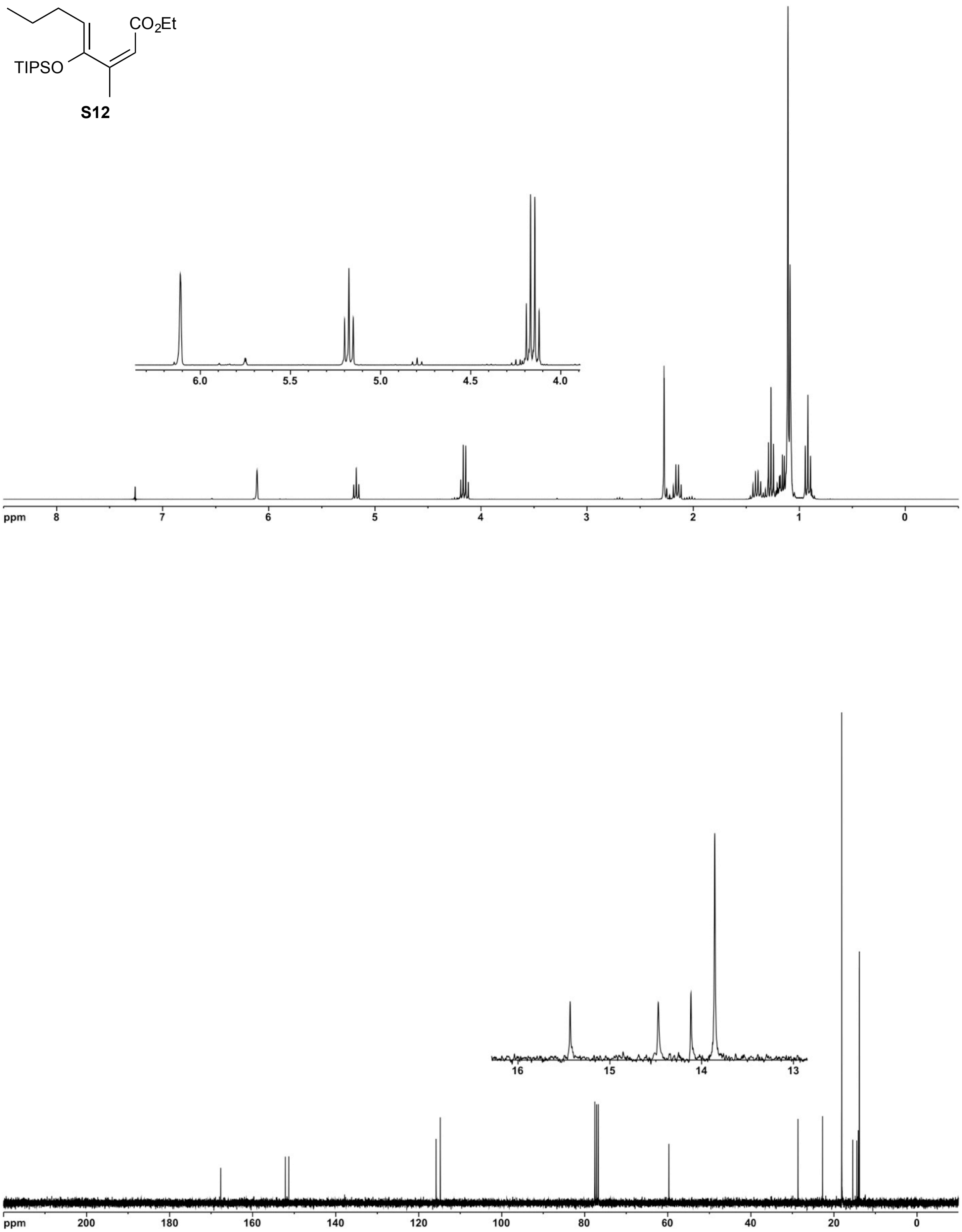


2d

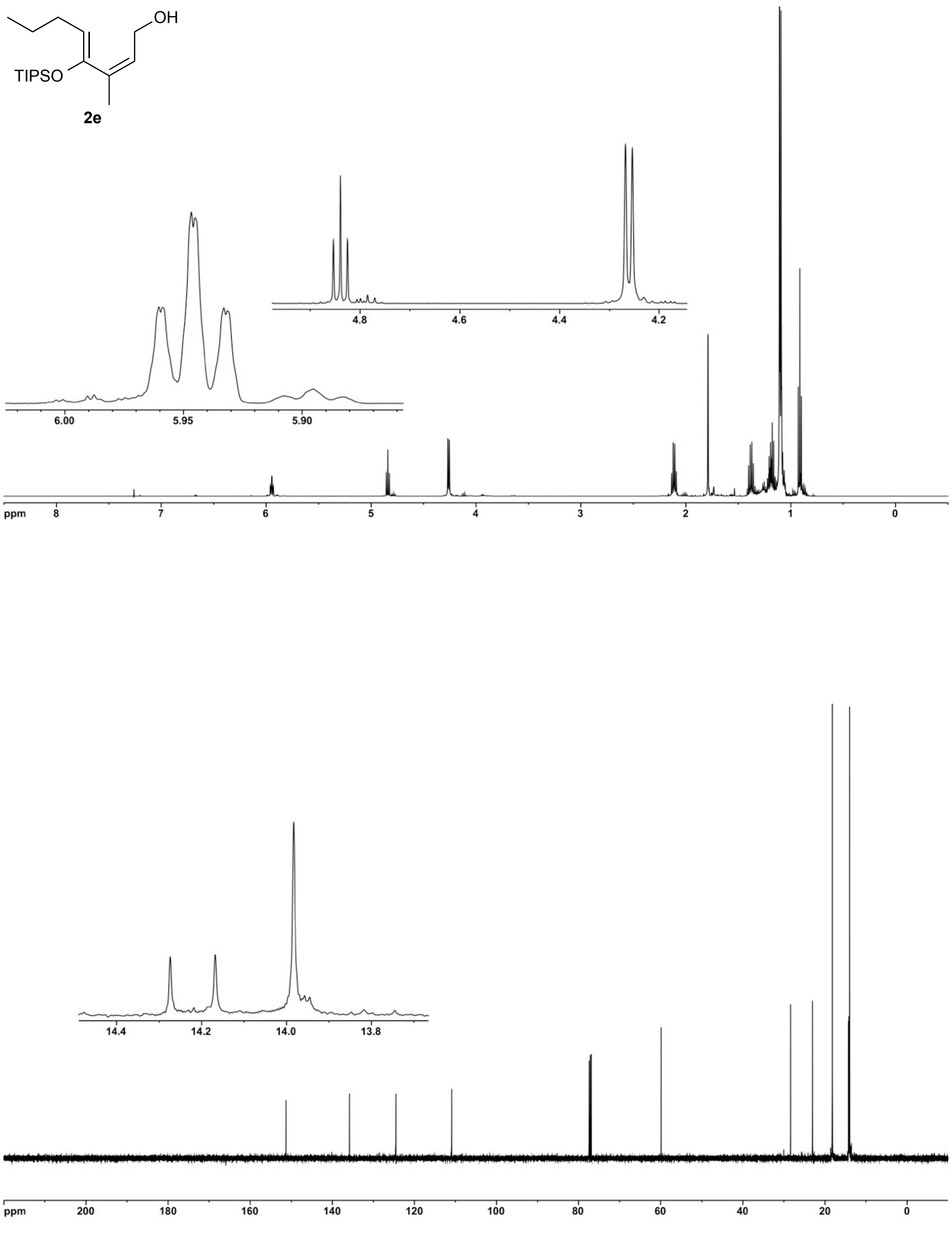
^1H (500 MHz) and ^{13}C NMR (125 MHz) spectra of silyloxydiene alcohol **2d** in C_6D_6



^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of ketoester **S11** in $CDCl_3$

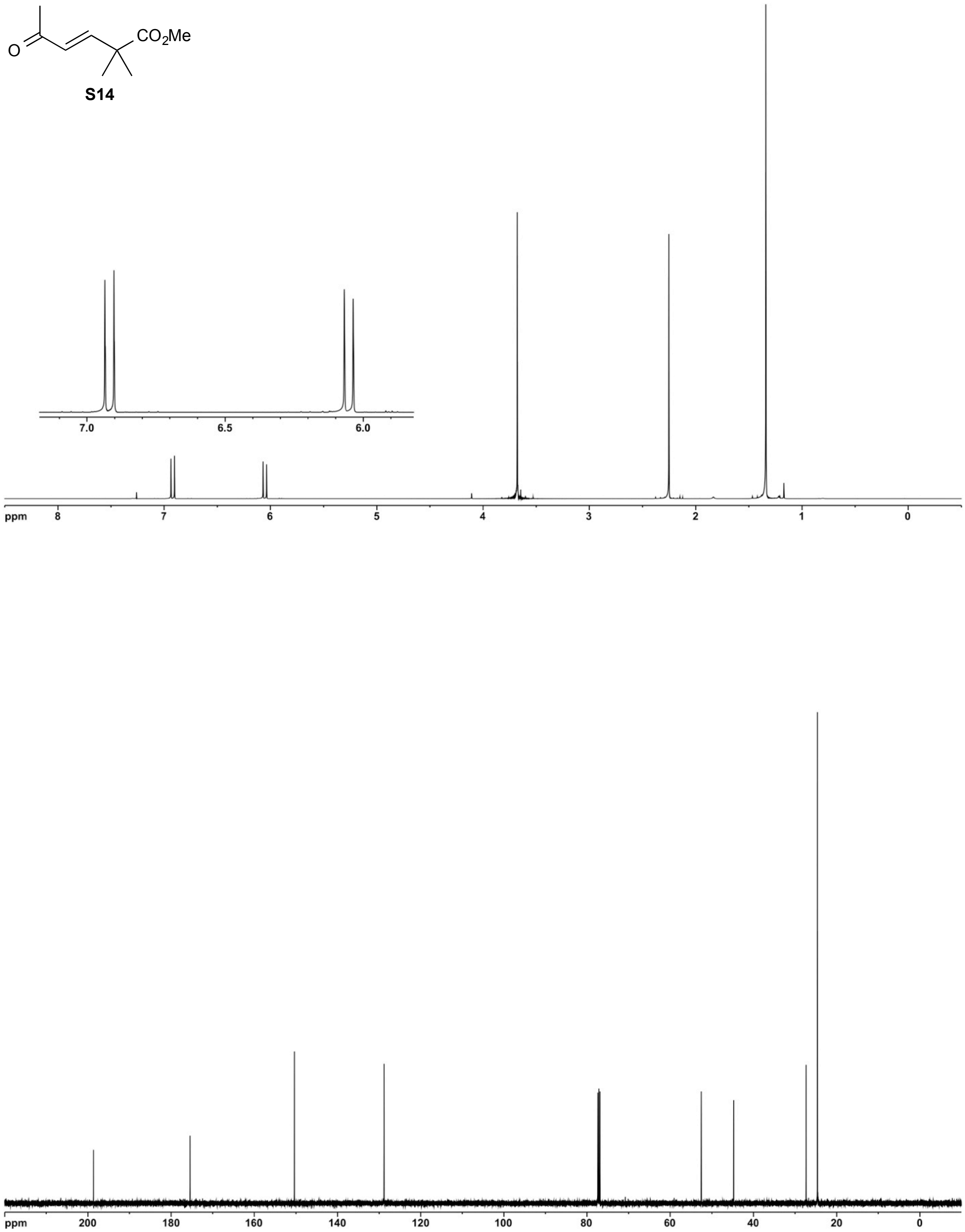


^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of diene **S12** in $CDCl_3$



2e

^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of silyloxydiene alcohol **2e** in $CDCl_3$



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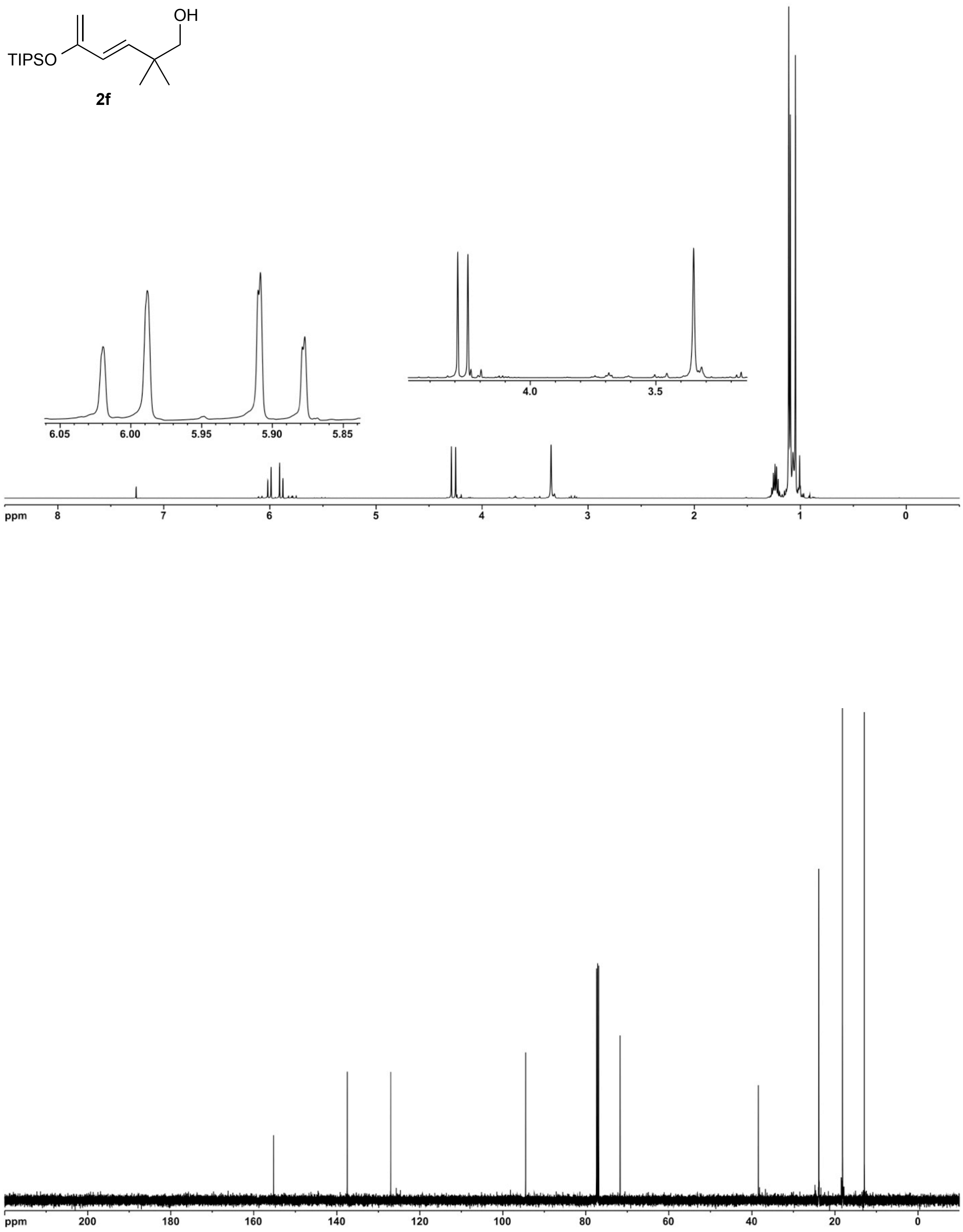
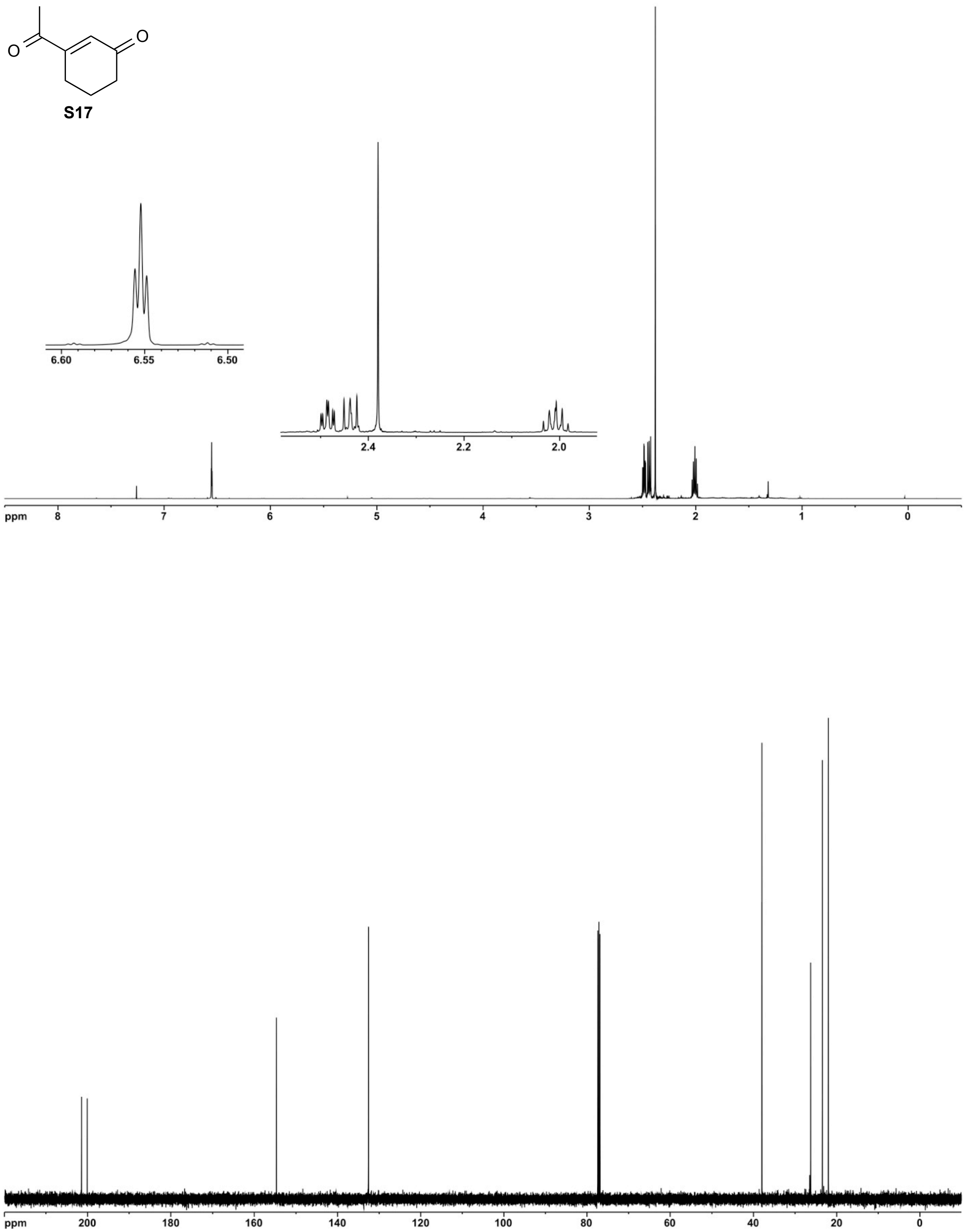
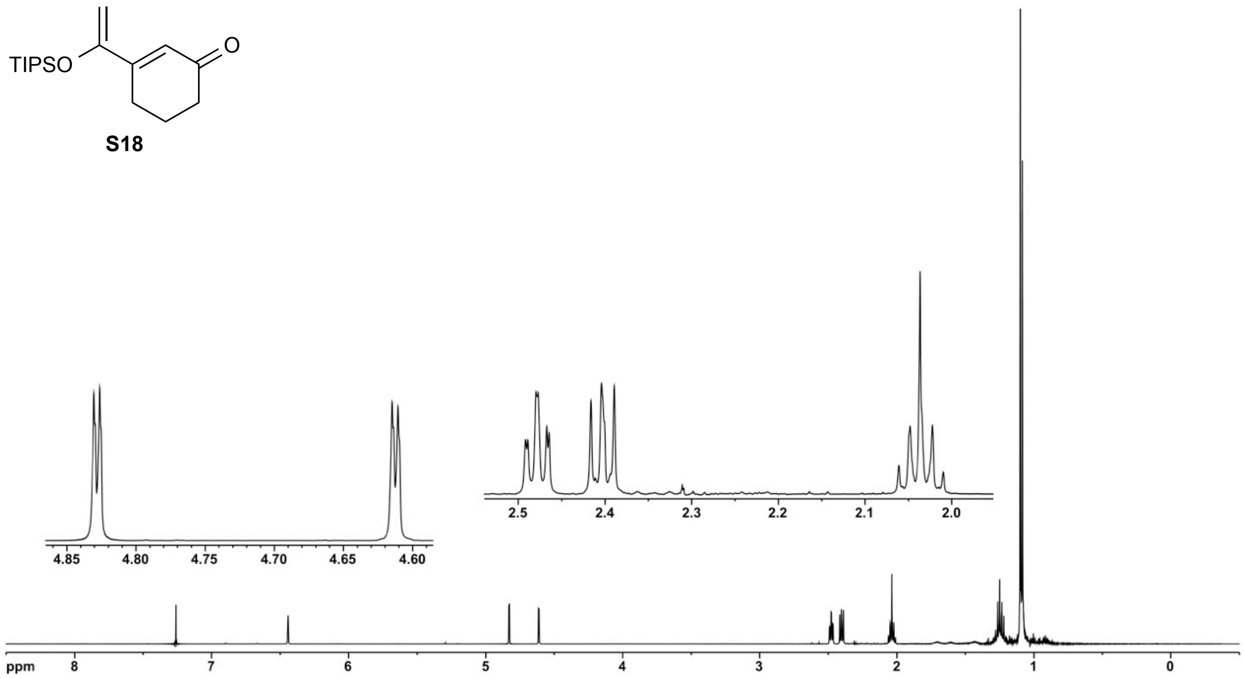


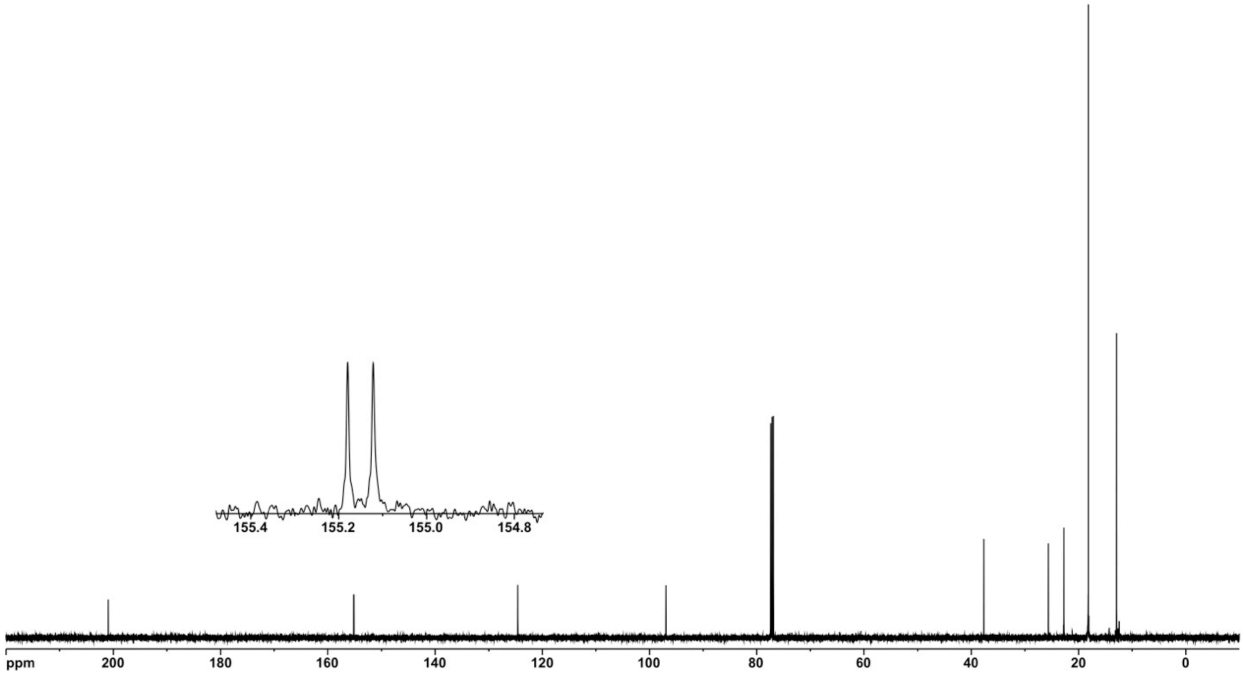
^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of silyloxydiene alcohol **2f** in $CDCl_3$



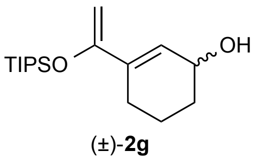
^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of diketone **S17** in $CDCl_3$



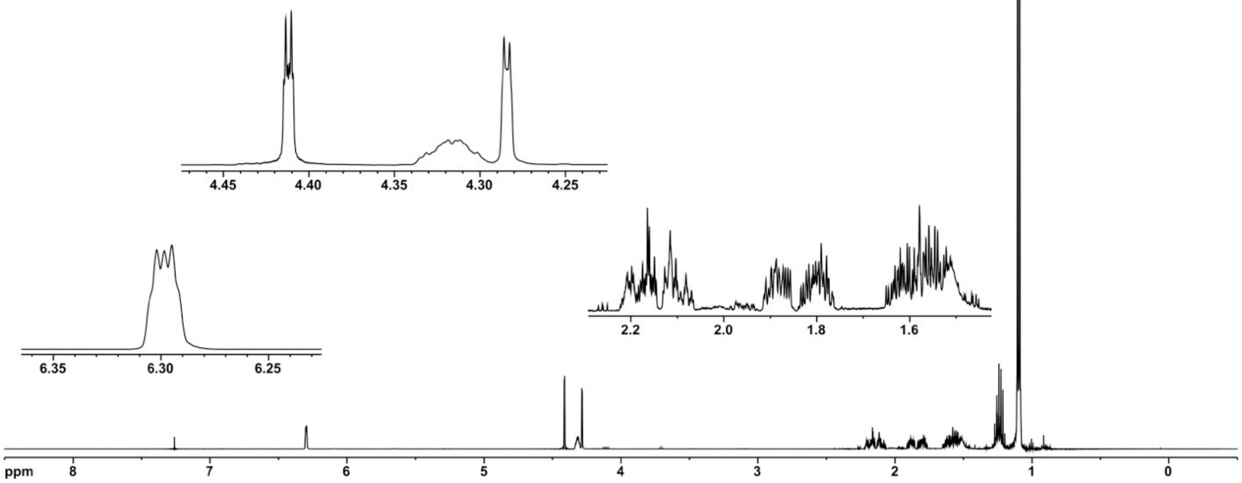
S18

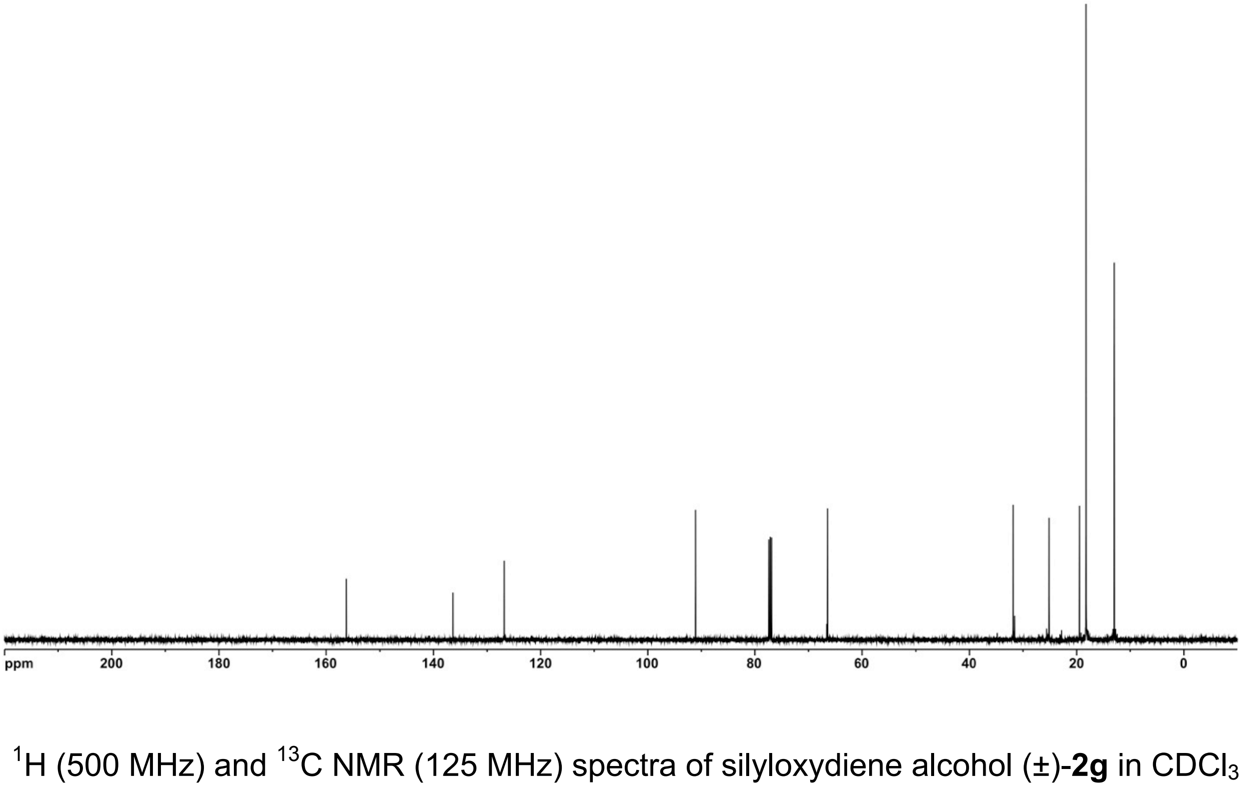


^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of diene **S18** in $CDCl_3$

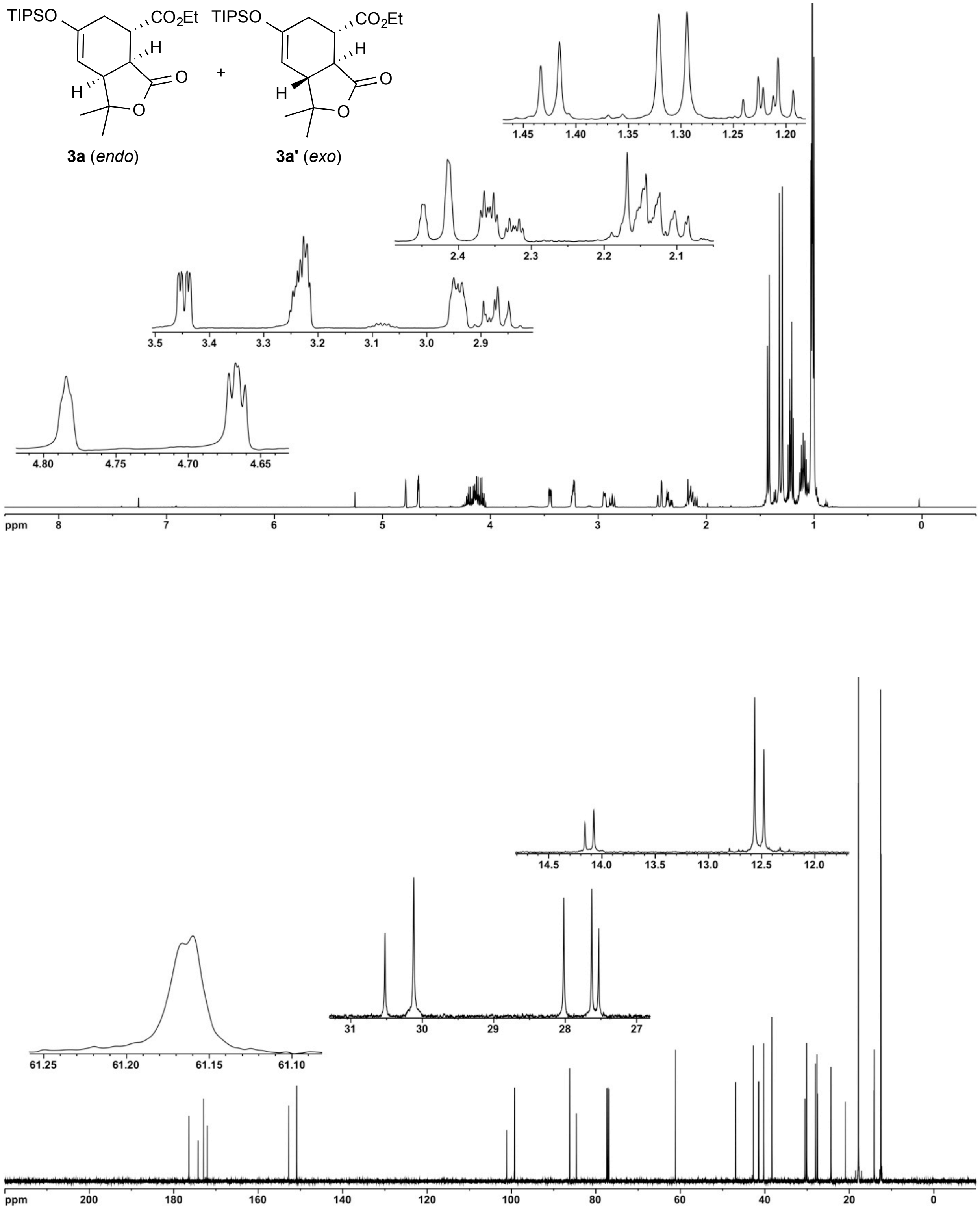


(±)-**2g**



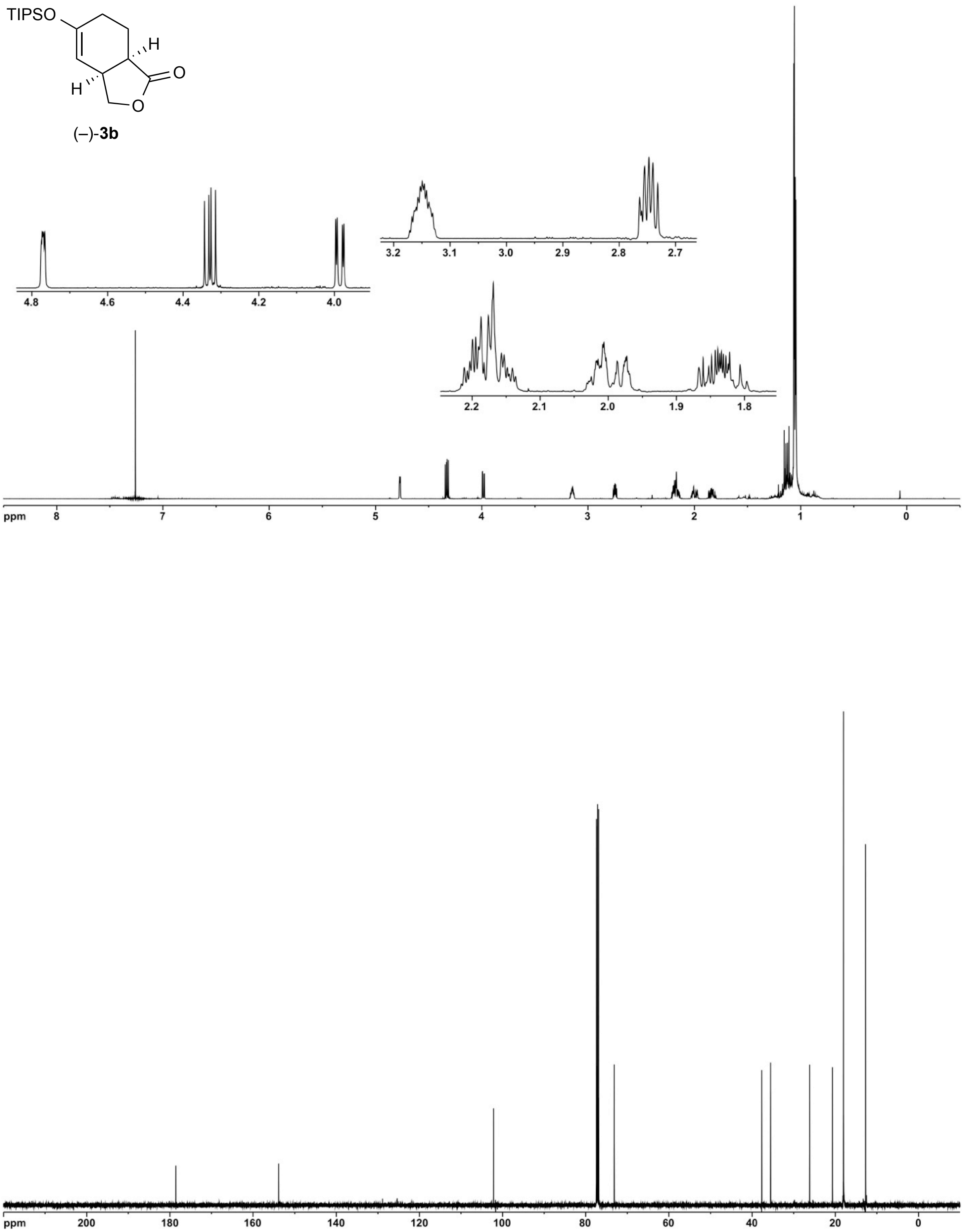


^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of silyloxydiene alcohol (±)-**2g** in $CDCl_3$



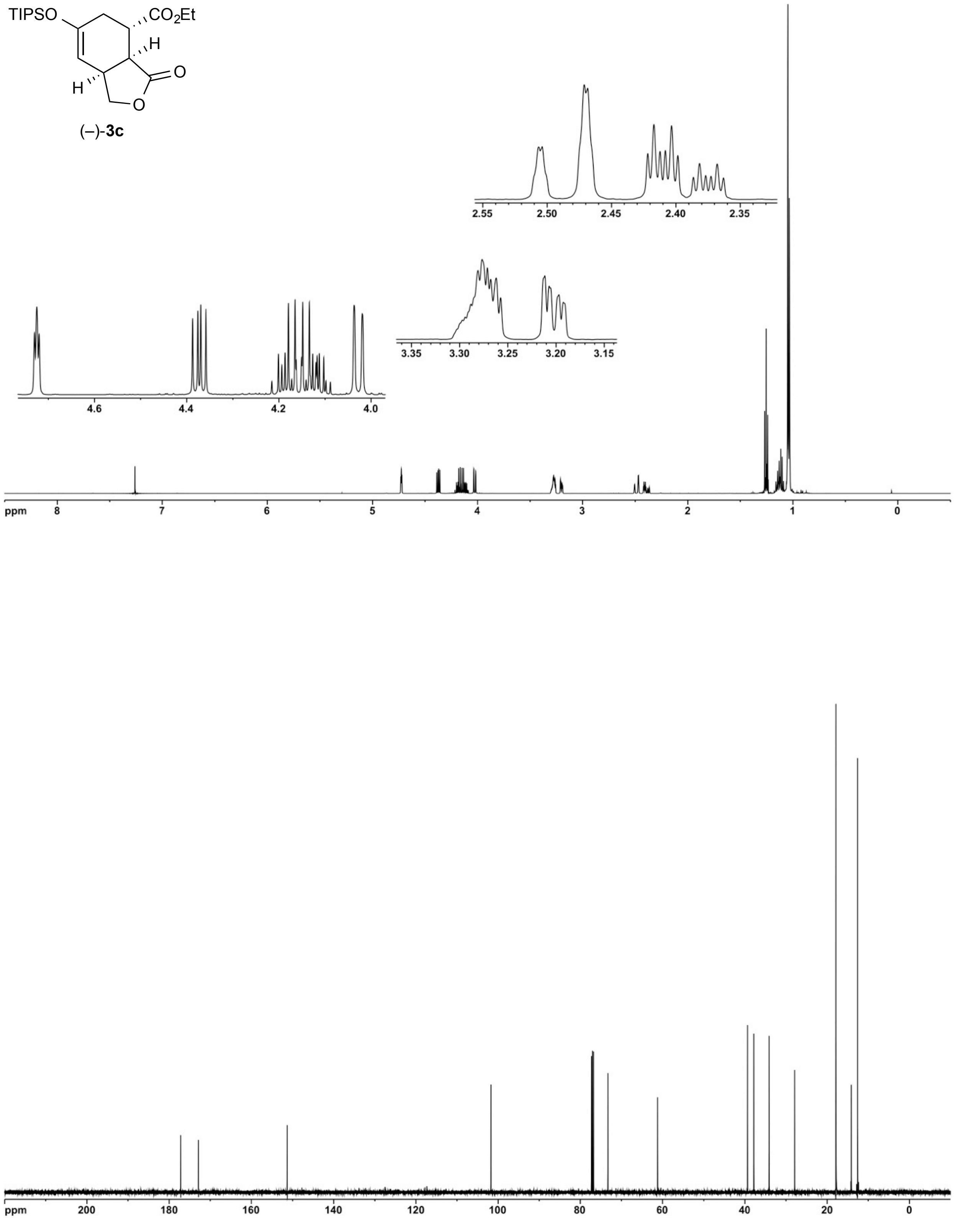
3a (*endo*) **3a'** (*exo*)

^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of bicyclic γ-lactones **3a** and **3a'**
(1.5:1 mixture of *endo/exo* diastereomers) in $CDCl_3$



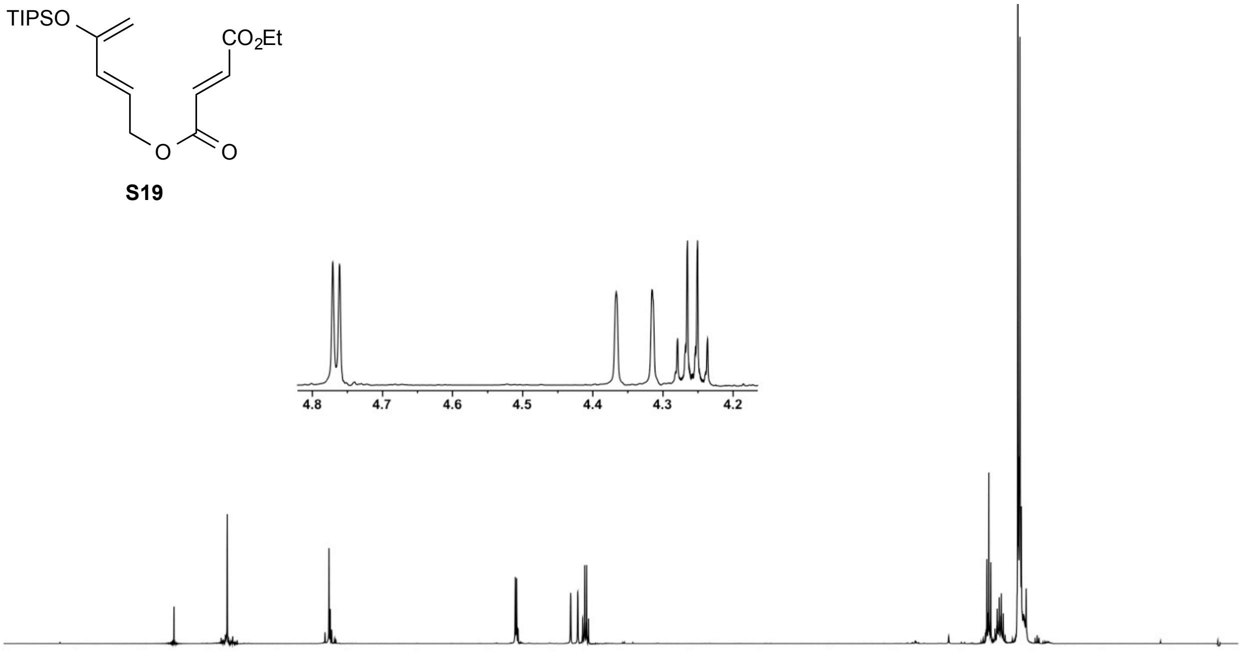
(–)-**3b**

^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of bicyclic γ-lactone (–)-**3b** in $CDCl_3$

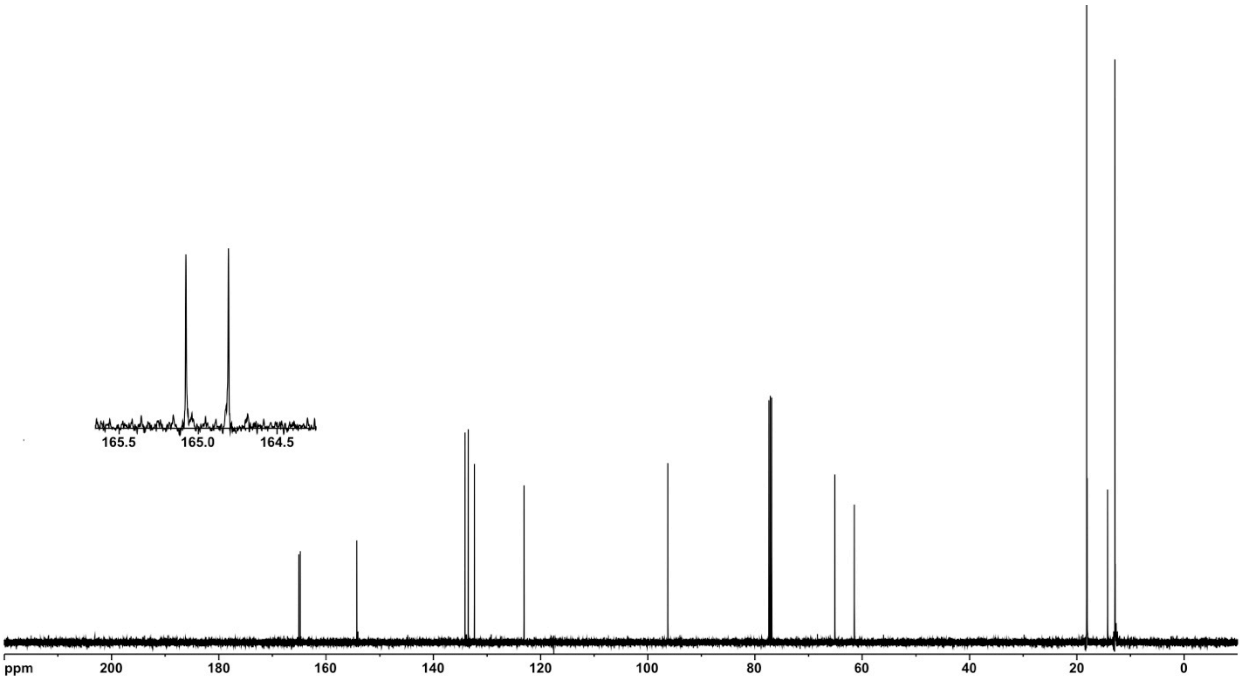


(–)-**3c**

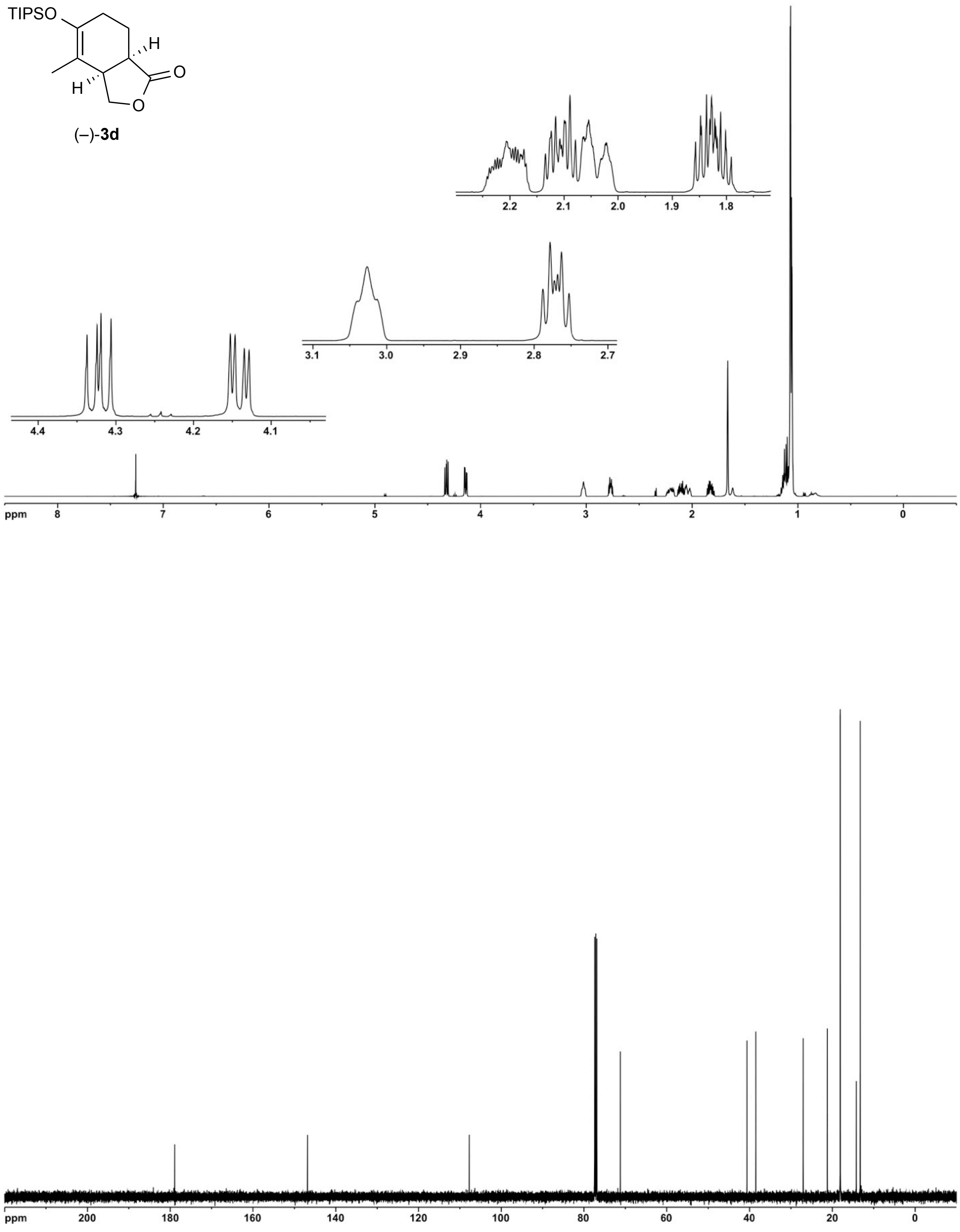
^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of bicyclic γ-lactone (–)-**3c** in $CDCl_3$



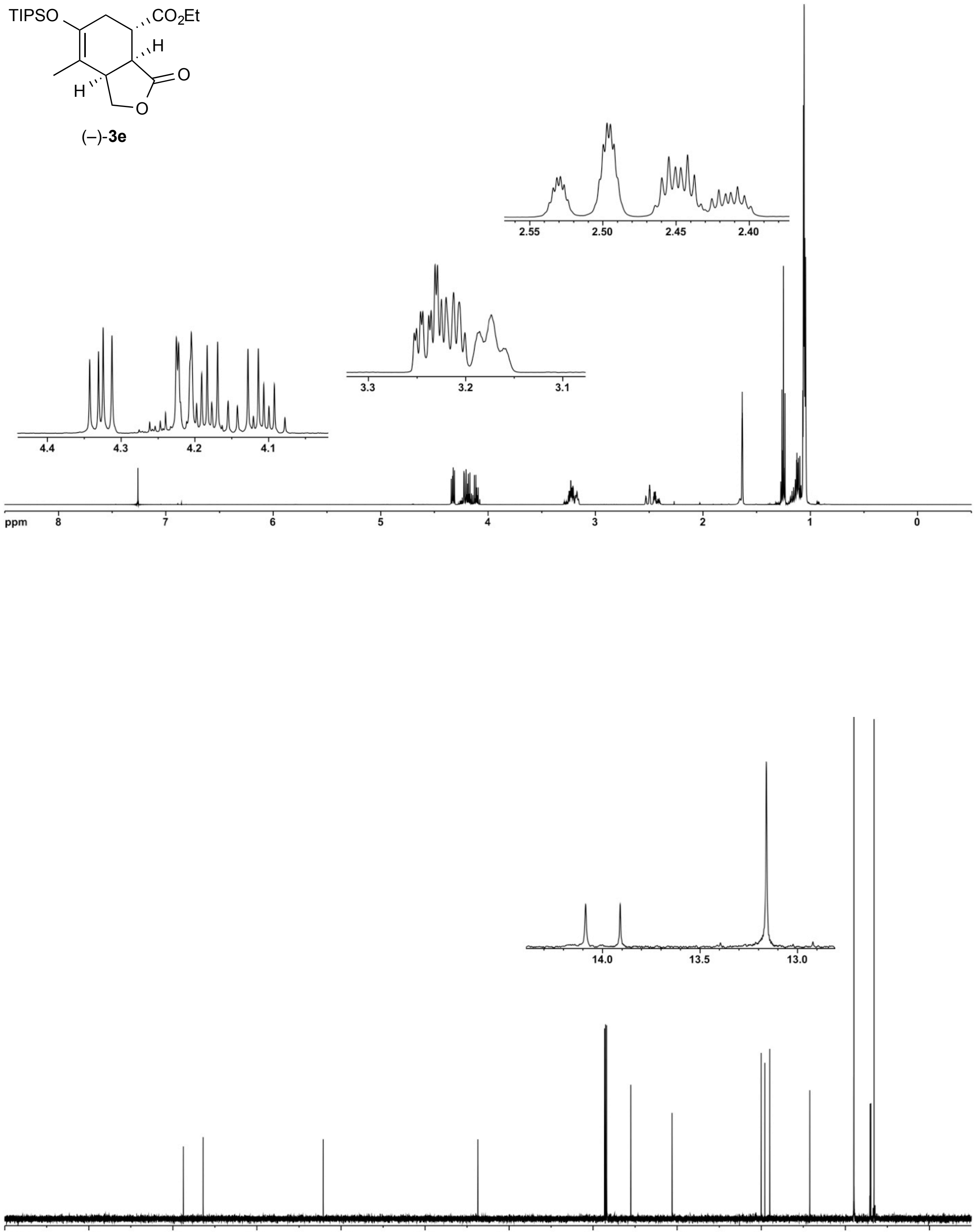
S19



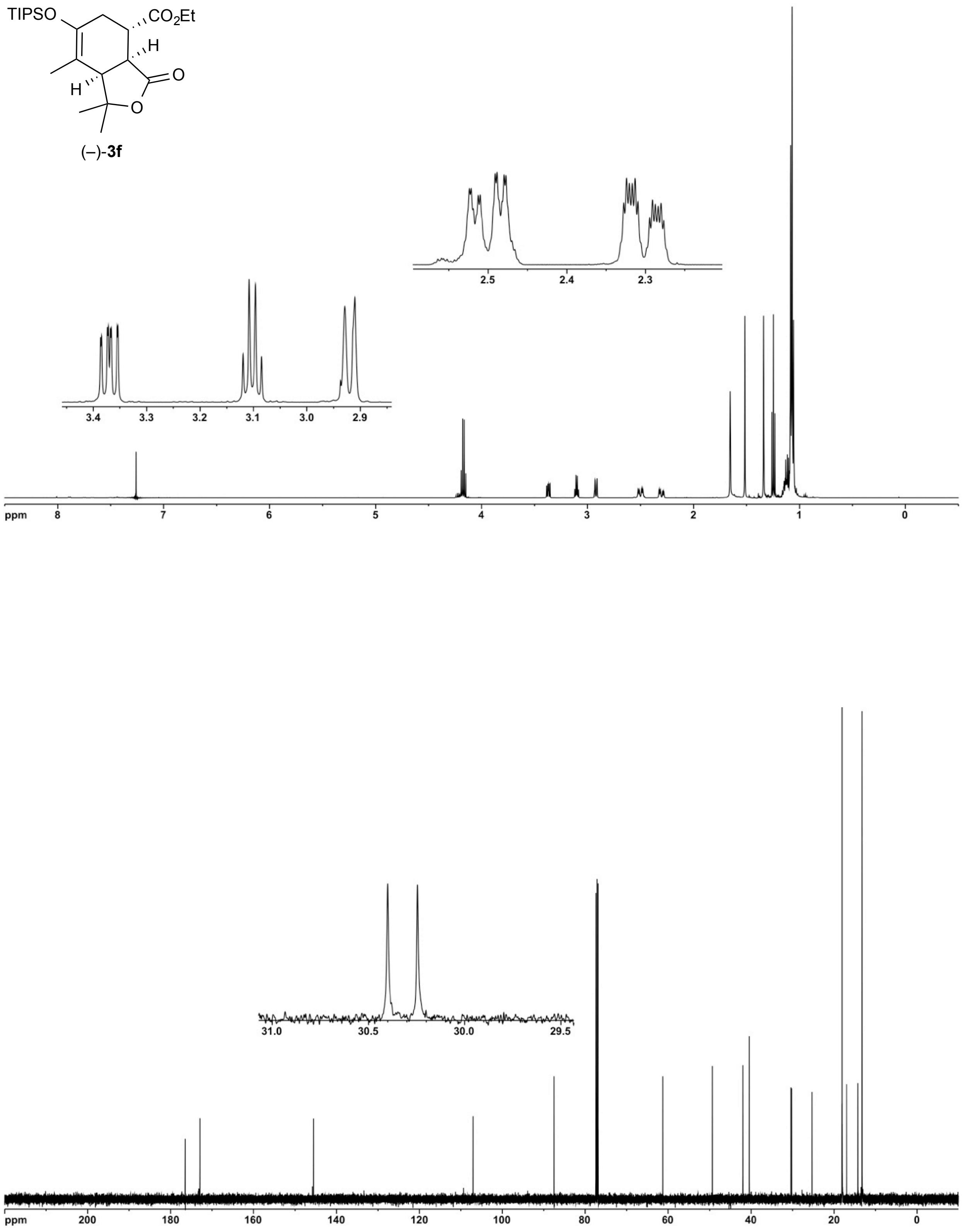
^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of ester **S19** in CDCl$_3$



^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of bicyclic γ-lactone (–)-**3d** in $CDCl_3$

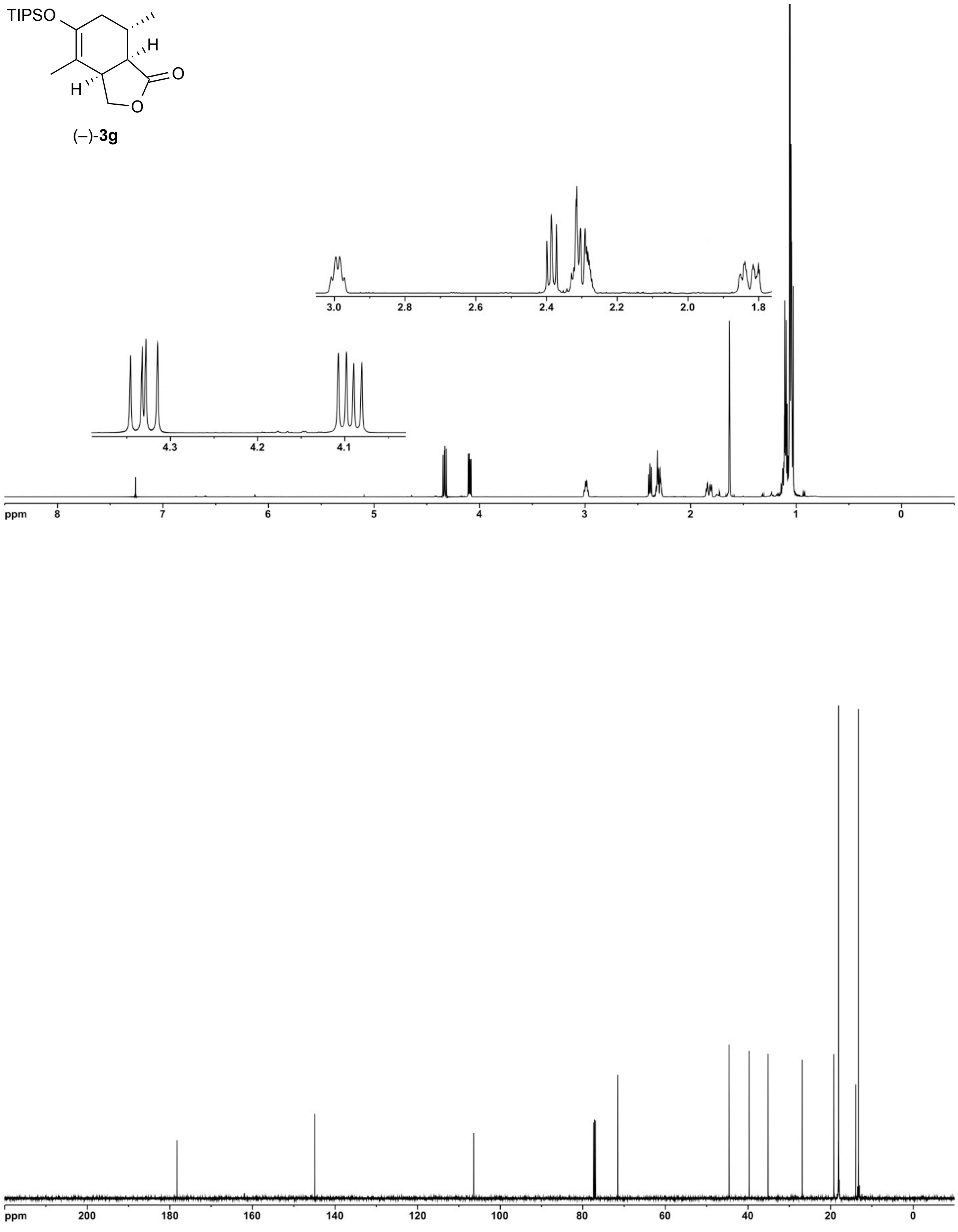


^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of bicyclic γ-lactone (–)-**3e** in CDCl$_3$

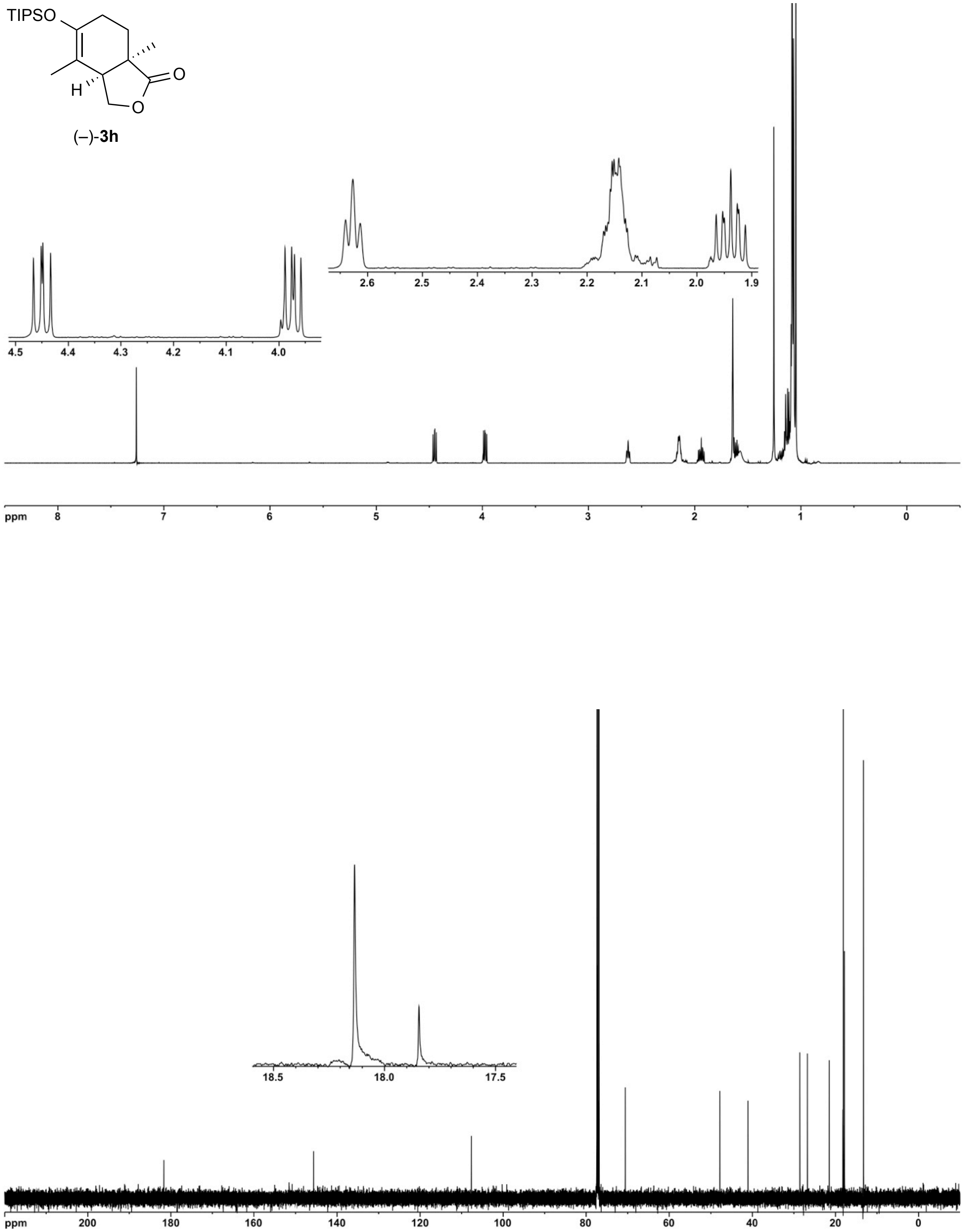


(–)-**3f**

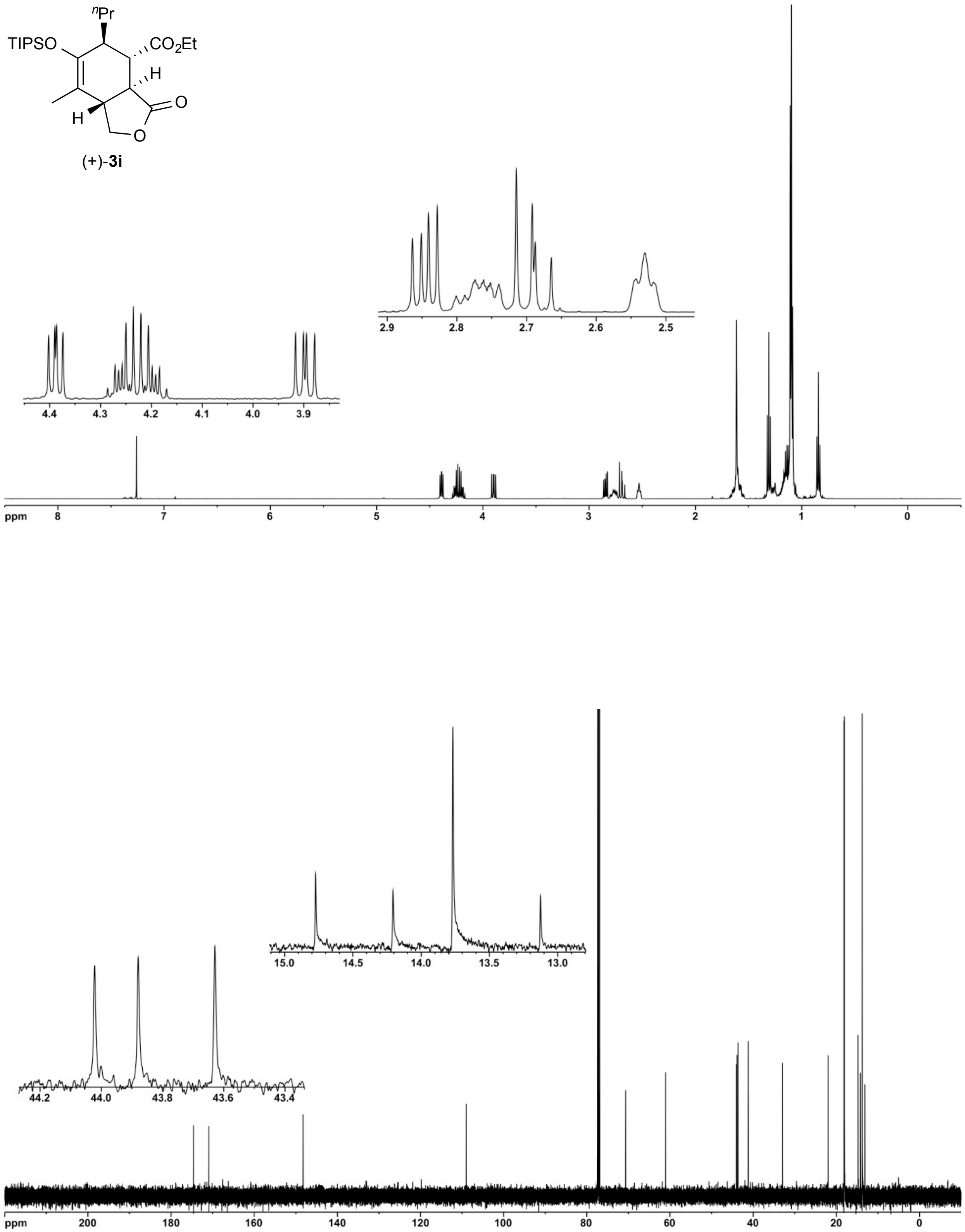
^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of bicyclic γ-lactone (–)-**3f** in $CDCl_3$



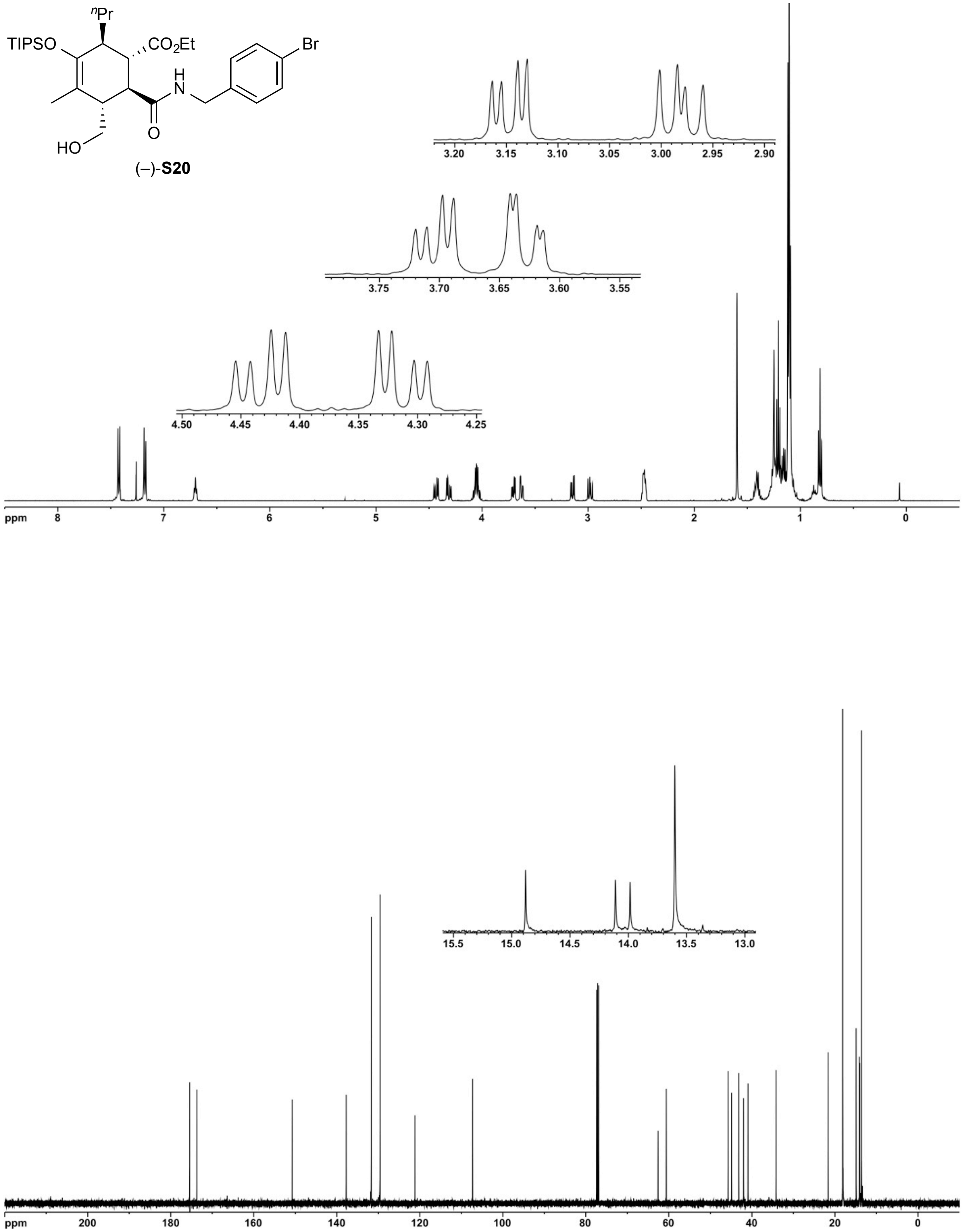
^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of bicyclic γ-lactone (–)-**3g** in $CDCl_3$



^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of bicyclic γ-lactone (–)-**3h** in $CDCl_3$

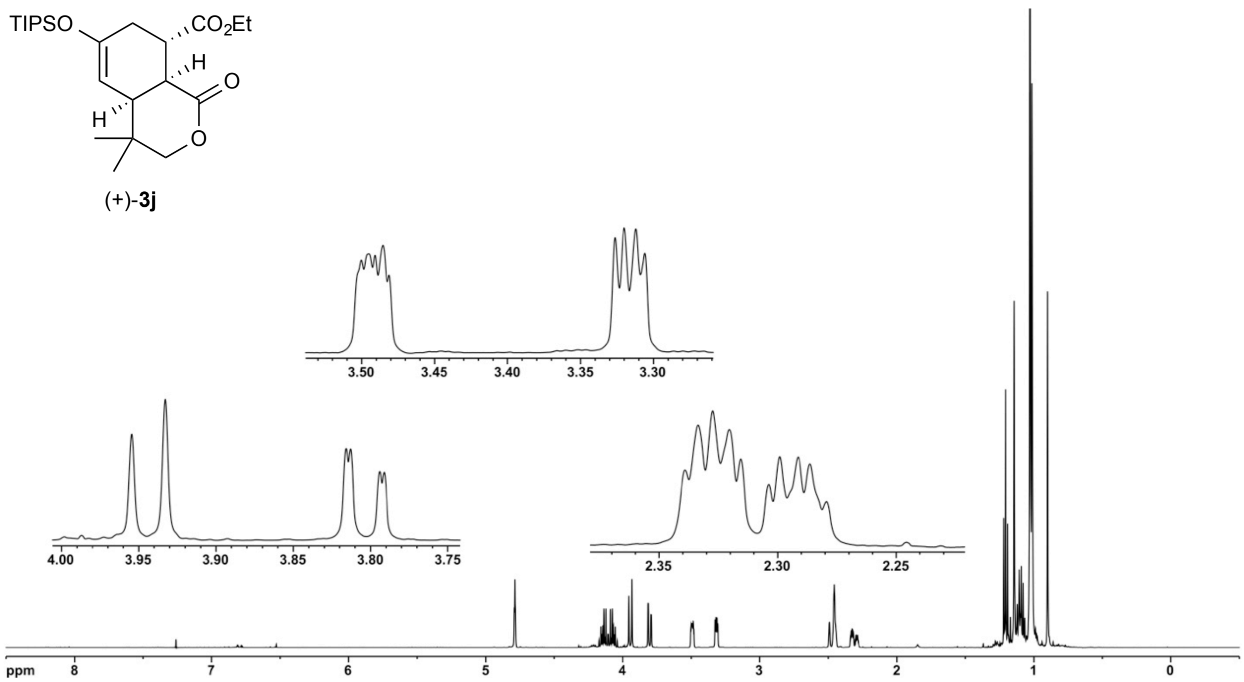

(+)-**3i**

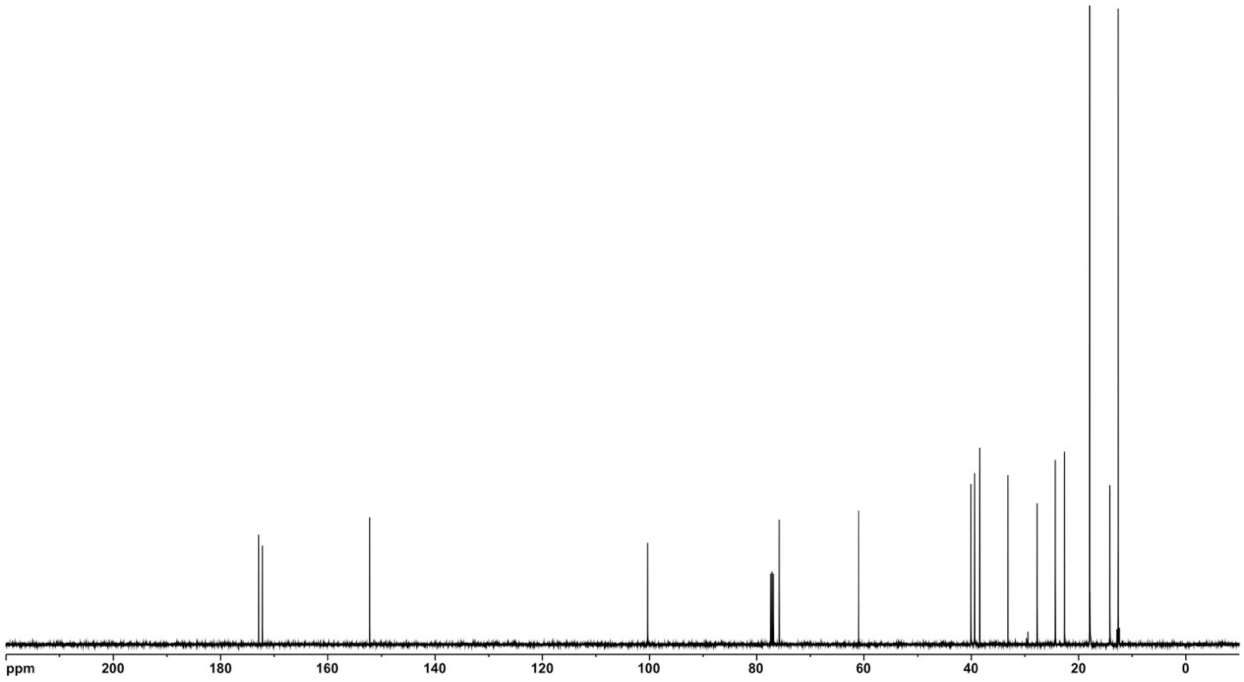
^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of bicyclic γ-lactone (+)-**3i** in CDCl$_3$



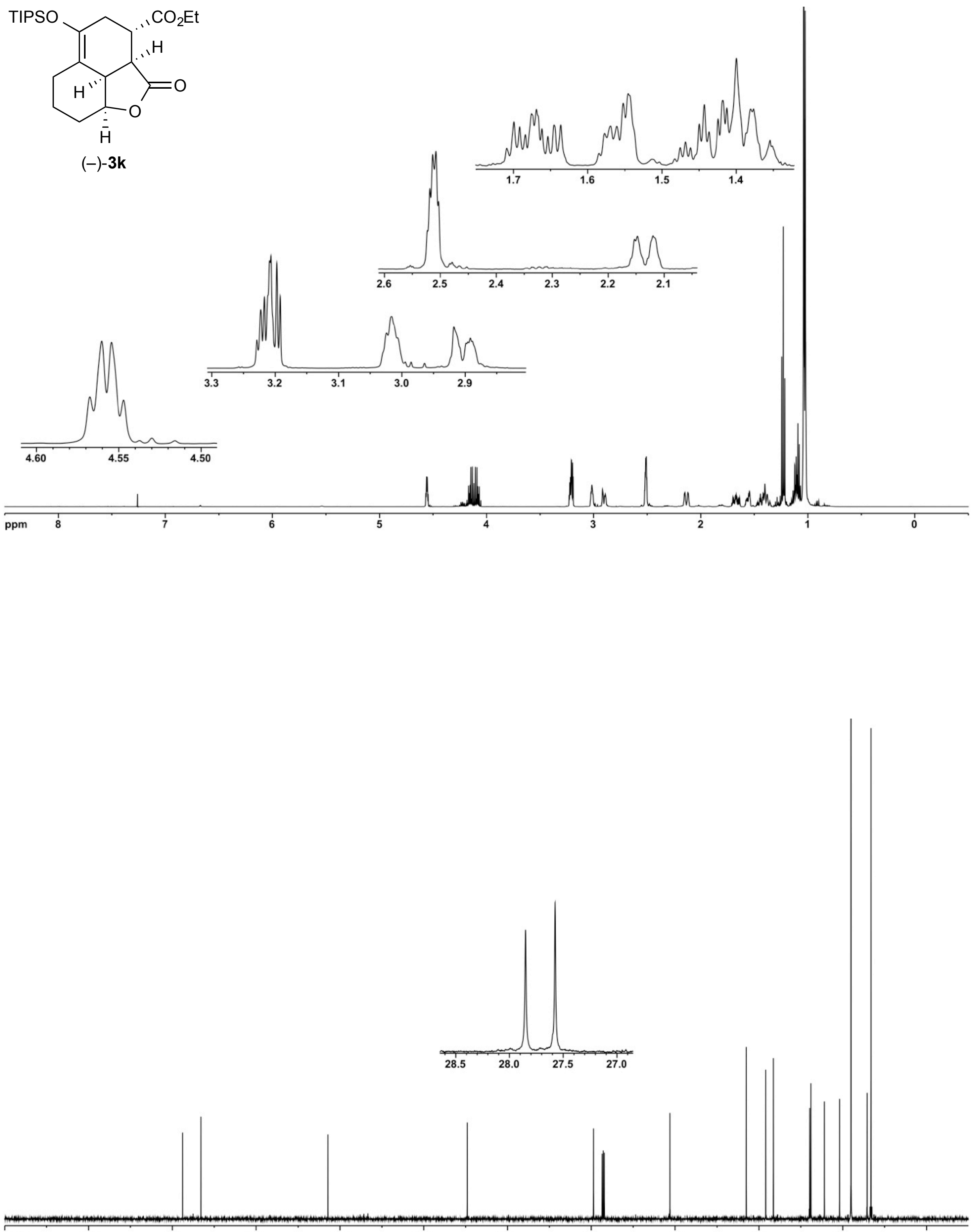
(–)-**S20**

^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of amide (–)-**S20** in $CDCl_3$



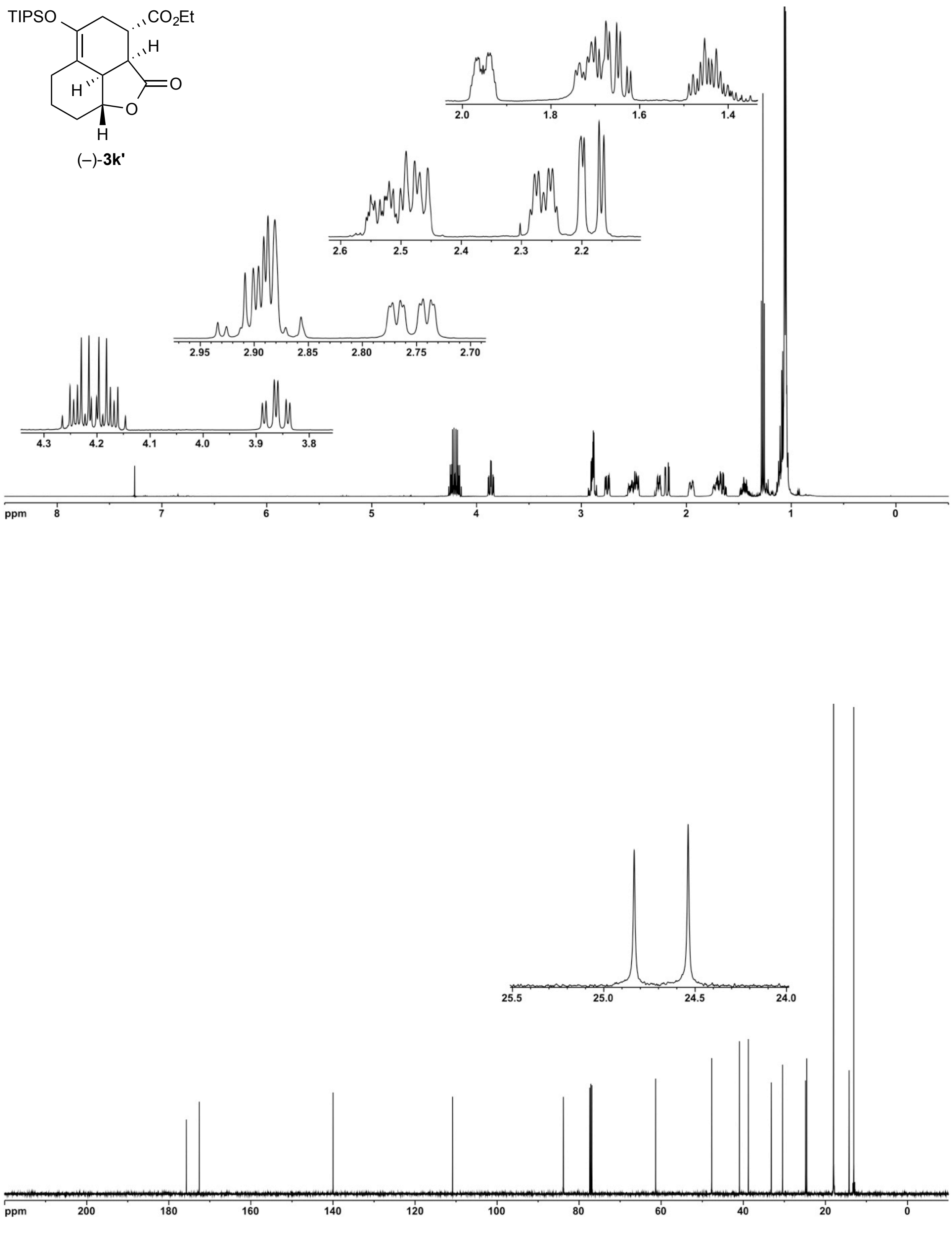


^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of bicyclic δ-lactone (+)-**3j** in $CDCl_3$



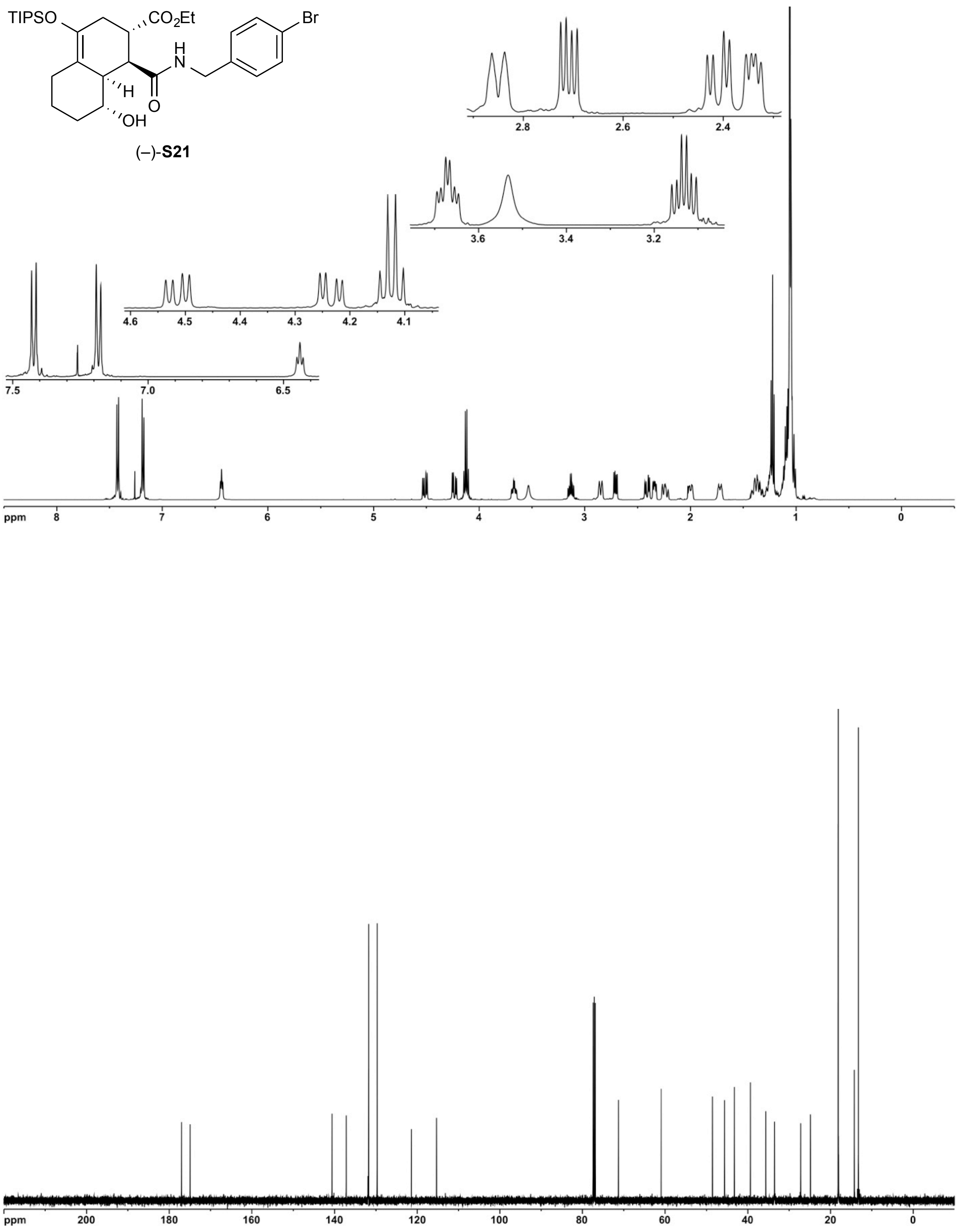
(–)-**3k**

^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of tricyclic γ-lactone (–)-**3k** in $CDCl_3$

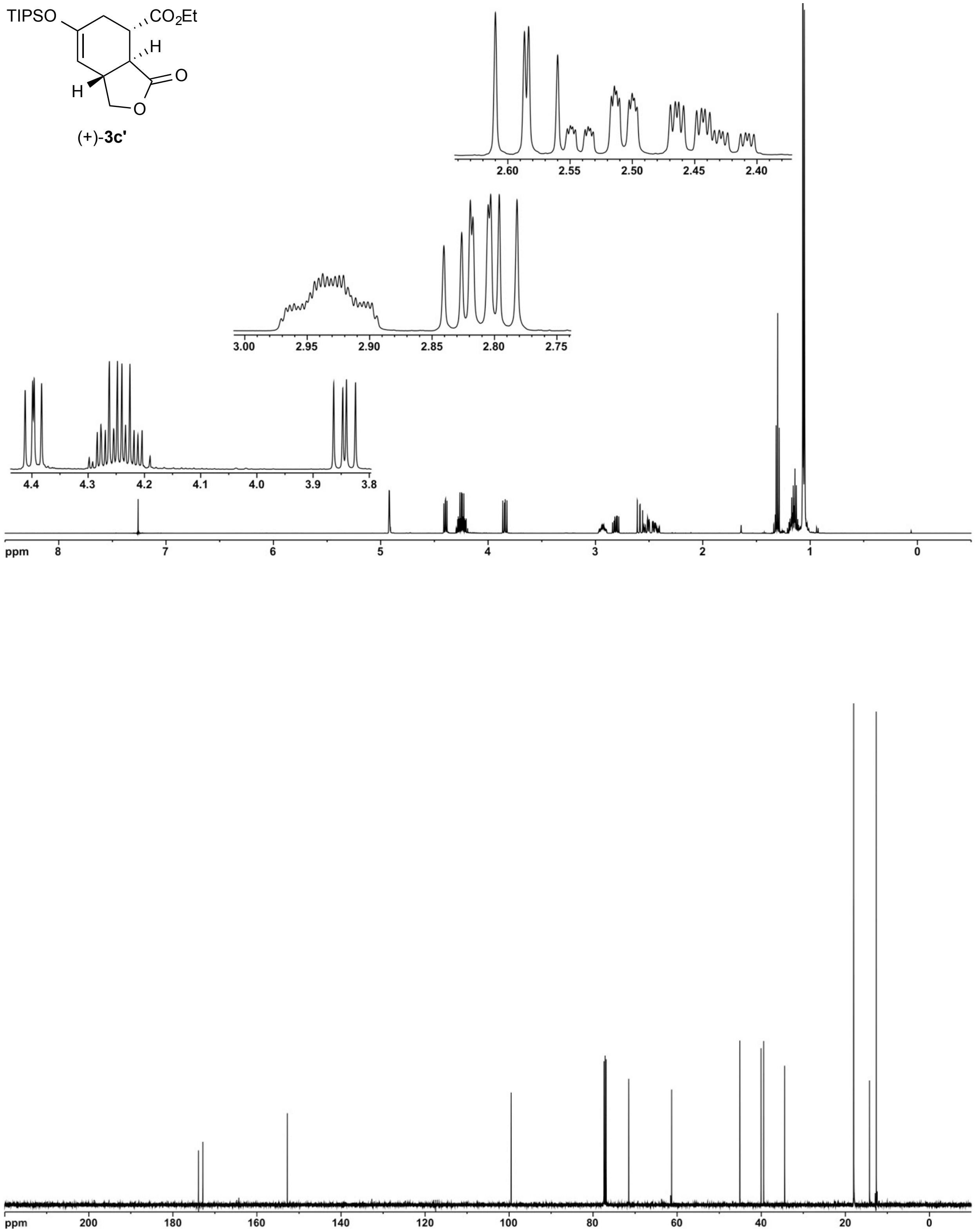


(–)-**3k'**

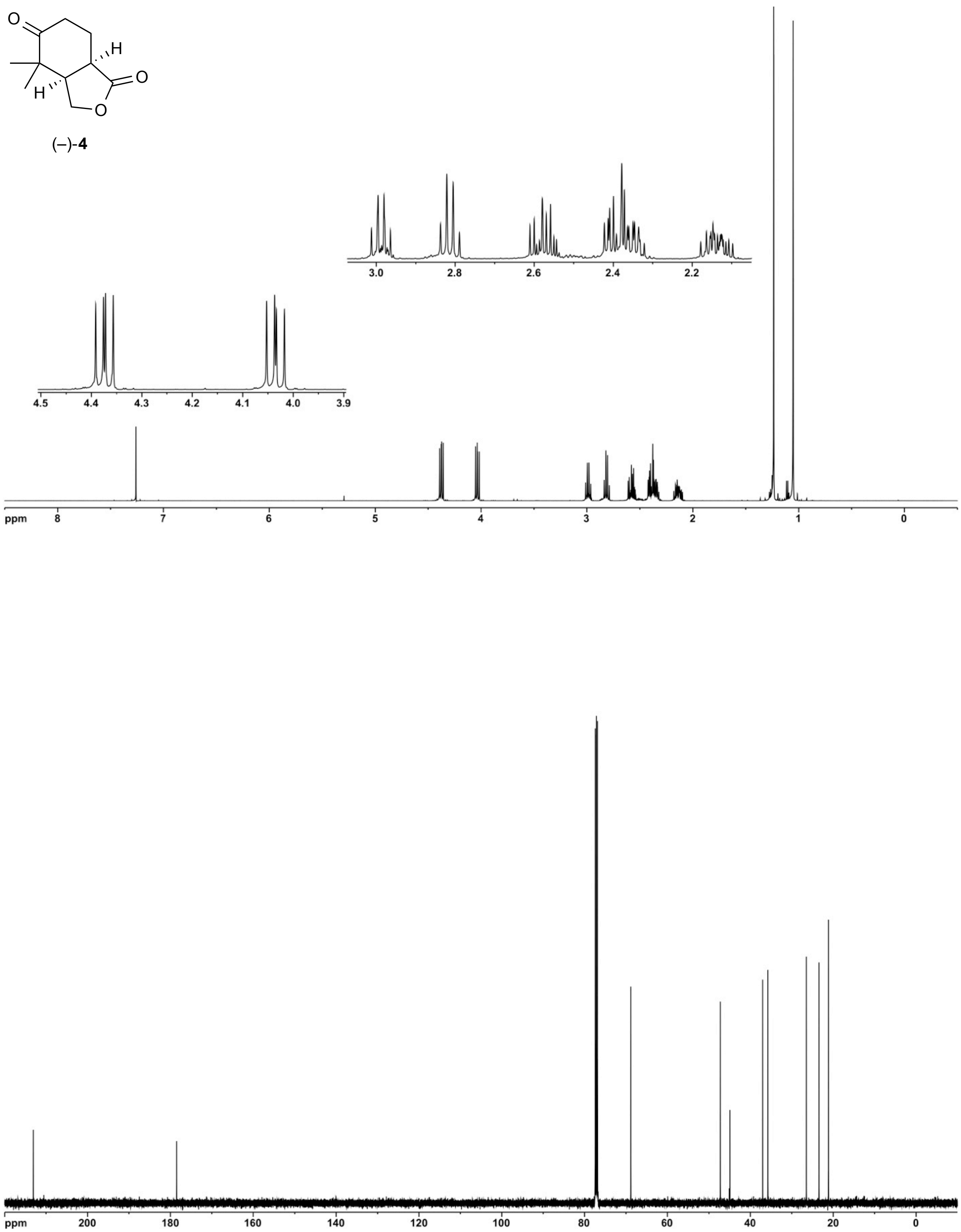
^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of tricyclic γ-lactone (–)-**3k'** in $CDCl_3$



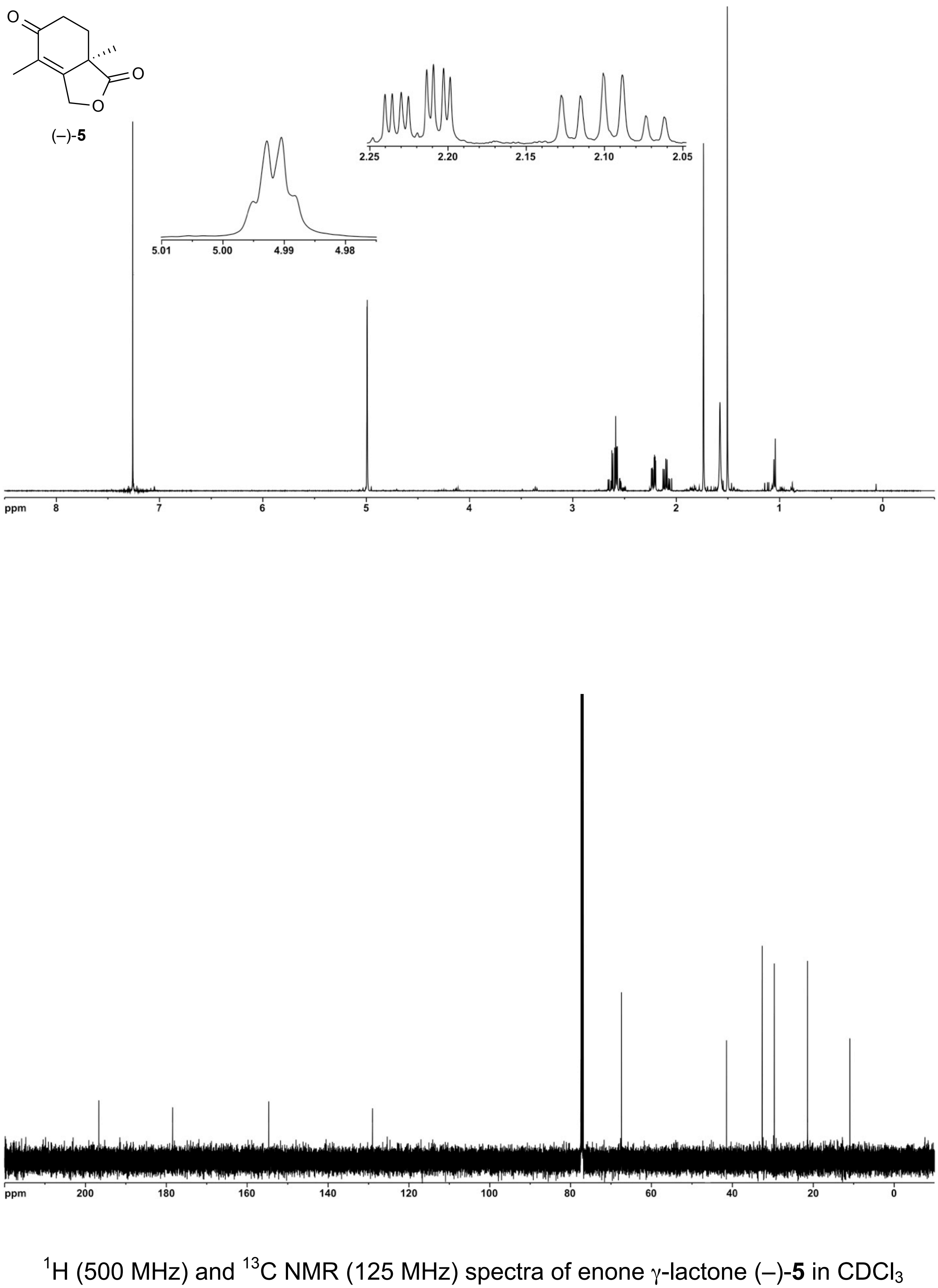
^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of bicyclic amide (–)-**S21** in $CDCl_3$



^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of bicyclic γ-lactone (+)-**3c’** in $CDCl_3$



^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of α,α-dimethyl ketone (–)-**4** in $CDCl_3$

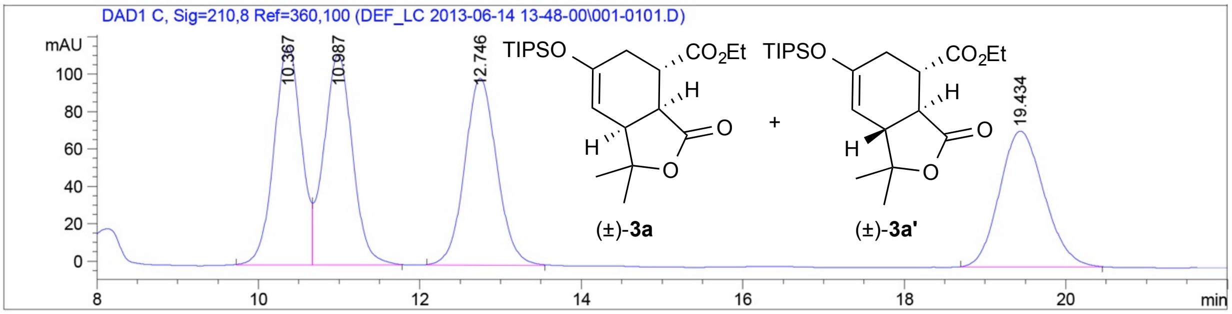


^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra of enone γ-lactone (–)-**5** in $CDCl_3$

Figure S12. Chiral HPLC determination of enantiomeric excess of bicyclic γ-lactones 3a and 3a':

Chiral HPLC analysis of bicyclic γ-lactone 3a and 3a': Chiralcel OD-H column: hexanes:^{i}PrOH = 95:05, flow rate 0.5 mL/min, λ = 210 nm: t_{major} = 10.3 min, t_{minor} = 10.9 min; 99% *ee*; t_{minor} = 12.7 min, t_{major} = 19.4 min; 99% *ee*.

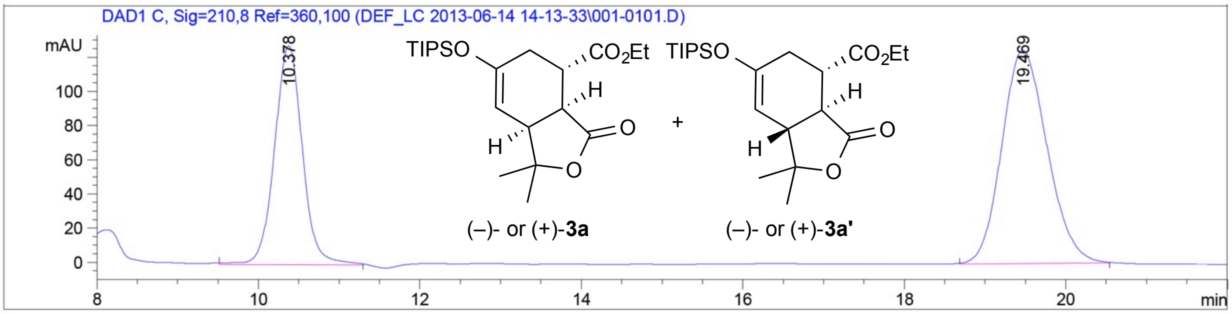
Table S1, entry 11:



```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.367 BV    0.3620 2754.59033  117.28511  24.8423
   2  10.987 VB    0.3772 2763.33936  112.26688  24.9212
   3  12.746 BB    0.4276 2769.97803   99.87013  24.9811
   4  19.434 BB    0.5993 2800.39136   72.71989  25.2554

Totals :                  1.10883e4   402.14201
```



```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

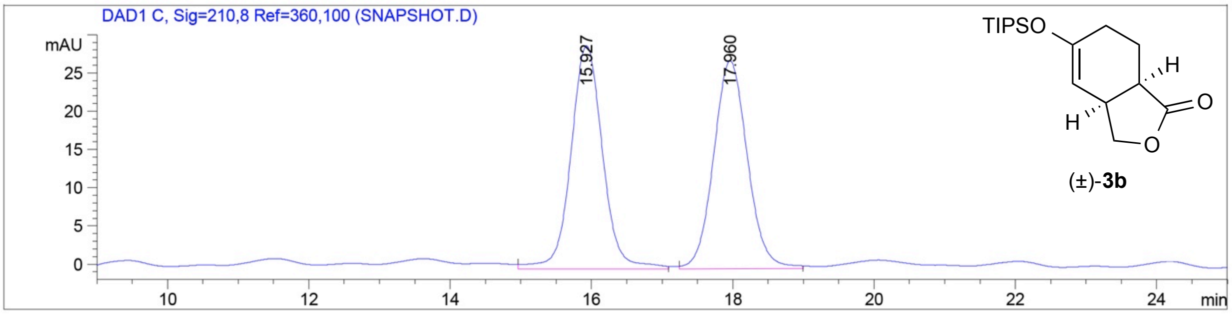
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.378 MM    0.4019 3085.39746  127.96414  38.8161
   2  19.469 BB    0.6070 4863.35352  124.70683  61.1839

Totals :                  7948.75098  252.67097
```

Figure S13. Chiral HPLC determinations of enantiomeric excess of bicyclic lactones 3b-j:

Determination of enantiomeric excess of bicyclic γ-lactone (–)-3b:

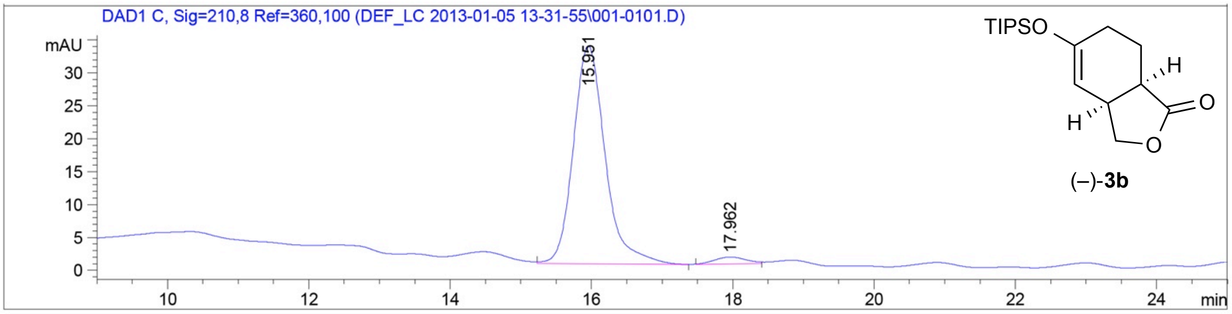
Chiral HPLC analysis of bicyclic γ-lactone (–)-3b: Chiralcel OD-H column: hexanes:^{i}PrOH = 98:02, flow rate 0.5 mL/min, λ = 210 nm: t_{major} = 15.9 min, t_{minor} = 17.9 min; 94% *ee*.



```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  15.927 VB    0.4815  914.27545   29.18653  50.2026
   2  17.960 BB    0.5175  906.89441   27.16312  49.7974

Totals :                  1821.16986   56.34965
```



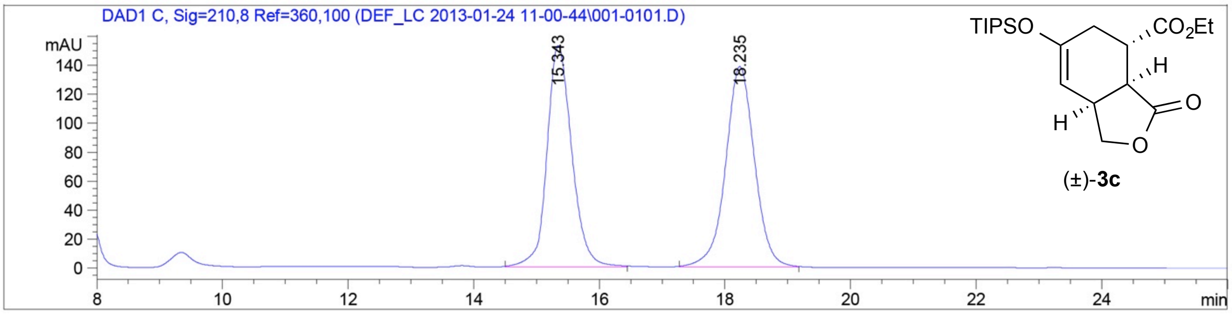
```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  15.951 MM    0.5203 1032.26636   33.06614  97.0640
   2  17.962 MM    0.5113   31.22353    1.01772   2.9360

Totals :                  1063.48989   34.08386
```

Determination of enantiomeric excess of bicyclic γ-lactone (–)-3c:

Chiral HPLC analysis of bicyclic γ-lactone (–)-3c: Chiralcel OD-H column: hexanes:^{i}PrOH = 95:05, flow rate 0.5 mL/min, λ = 210 nm: t_{minor} = 15.4 min, t_{major} = 18.1 min; 99% *ee* (using 20 mol% (*S*)-(–)-BTM), 98% *ee* (using 10 mol% (*S*)-(–)-BTM).

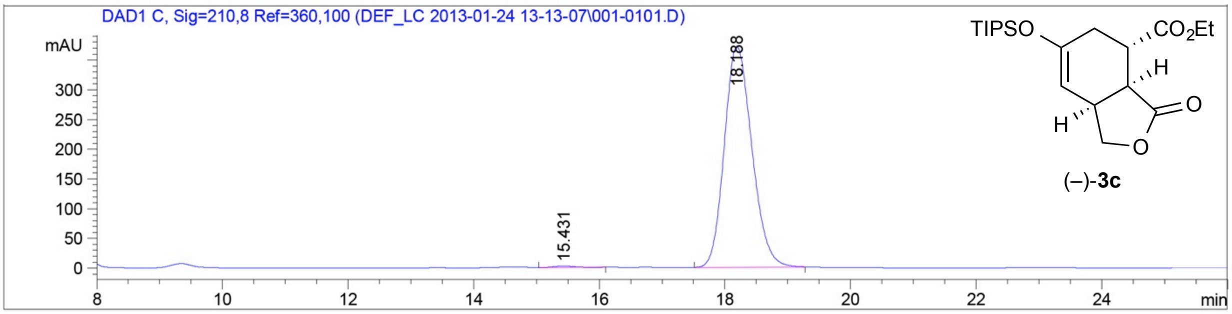


```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  15.343 MM    0.4858 4449.61182  152.66600  50.1120
   2  18.235 BB    0.4896 4429.72021  138.32141  49.8880

Totals :                  8879.33203  290.98741
```

Using 20 mol% (*S*)-(–)-BTM:

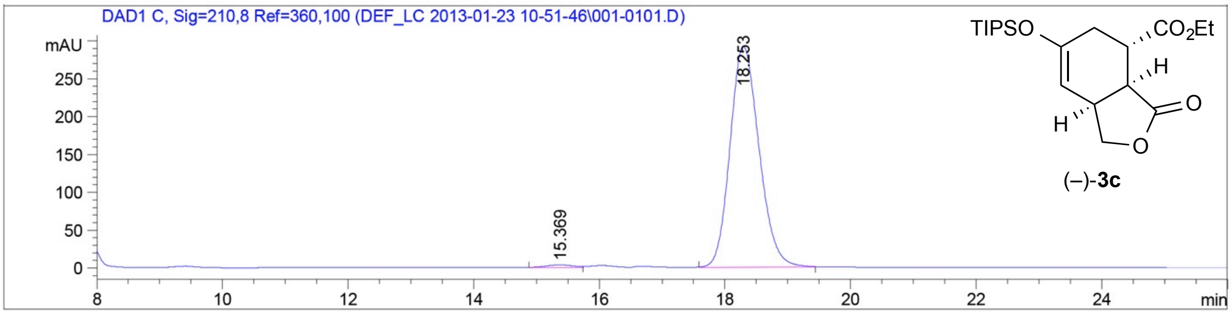


```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  15.431 BB    0.3303   52.56739    2.53123   0.4602
   2  18.188 BB    0.4743 1.13713e4  372.35049  99.5398

Totals :                  1.14239e4  374.88173
```

Using 10 mol% (*S*)-(–)-BTM:



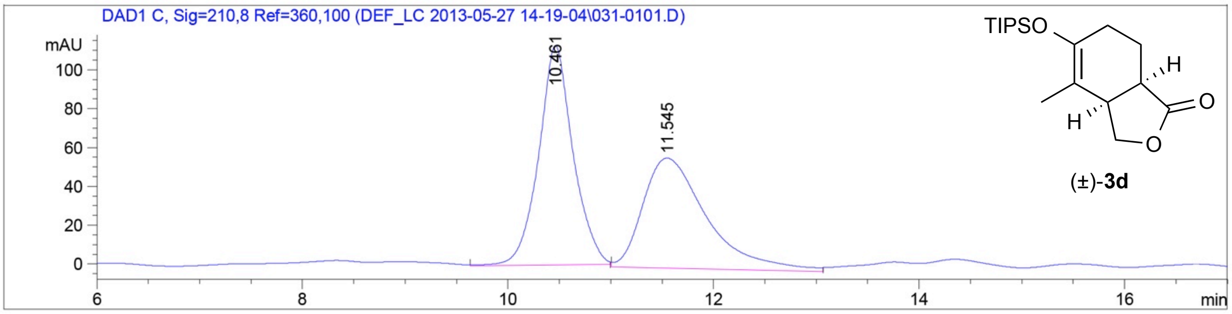
```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  15.369 BV    0.4333   99.30708    3.37506   1.0494
   2  18.253 BB    0.4961 9363.54004  292.00168  98.9506

Totals :                  9462.84712  295.37674
```

Determination of enantiomeric excess of bicyclic γ-lactone (–)-3d:

Chiral HPLC analysis of bicyclic γ-lactone (–)-3d: Chiralcel AS-H column: hexanes:^{i}PrOH = 99:01, flow rate 1.0 mL/min, λ = 210 nm: t_{major} = 10.3 min, t_{minor} = 11.5 min; 99% *ee*.

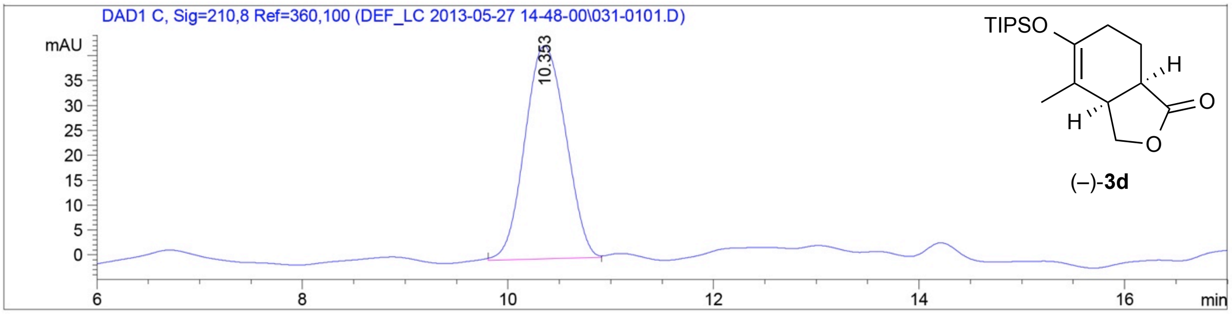


(±)-**3d**

```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.461 MM     0.3872 2622.94019  112.89551  51.7560
   2  11.545 MM     0.7187 2444.95142   56.69883  48.2440

Totals :                   5067.89160  169.59433
```



(–)-**3d**

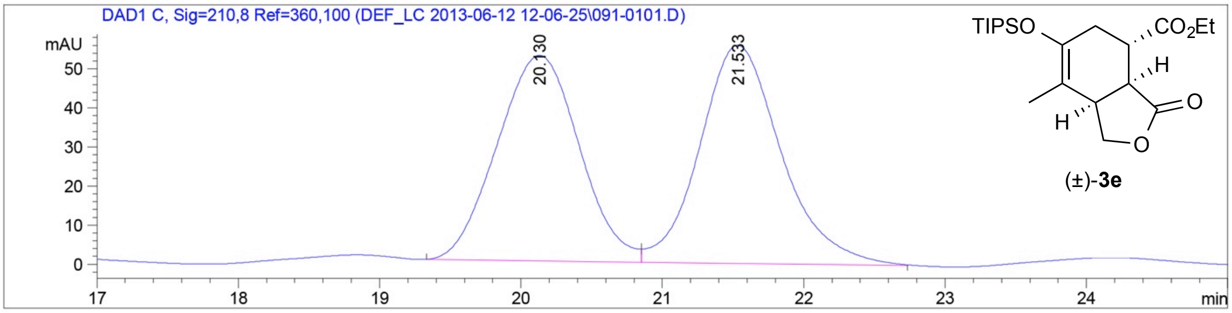
```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.353 BV     0.4441 1179.79602   42.73602 100.0000


Totals :                   1179.79602   42.73602
```

Determination of enantiomeric excess of bicyclic γ-lactone (–)-3e:

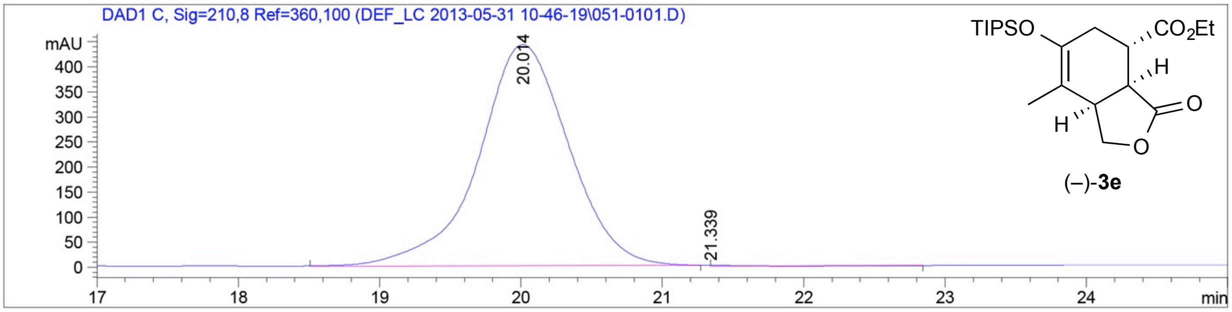
Chiral HPLC analysis of bicyclic γ-lactone (–)-3e: Chiralcel OD-H column: hexanes:^{i}PrOH = 98:02, flow rate 0.4 mL/min, λ = 210 nm: t_{major} = 20.0 min, t_{minor} = 21.3 min; 99% *ee*.



```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  20.130 BV    0.6185 2121.67554   52.60606  48.6533
   2  21.533 VB    0.6094 2239.12891   55.88930  51.3467

Totals :                  4360.80444  108.49536
```



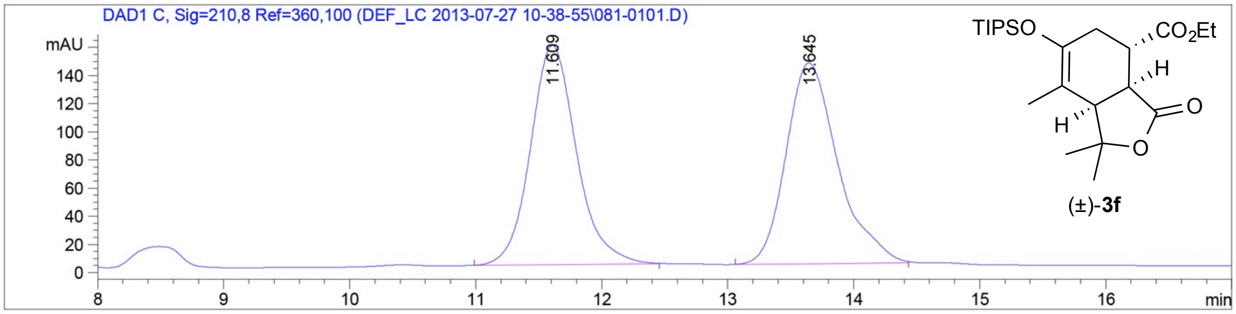
```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  20.014 BB    0.6478 1.96563e4  441.19595  99.8988
   2  21.339 MM    0.1555   19.91752    1.55744   0.1012

Totals :                  1.96762e4   442.75339
```

Determination of enantiomeric excess of bicyclic γ-lactone (–)-3f:

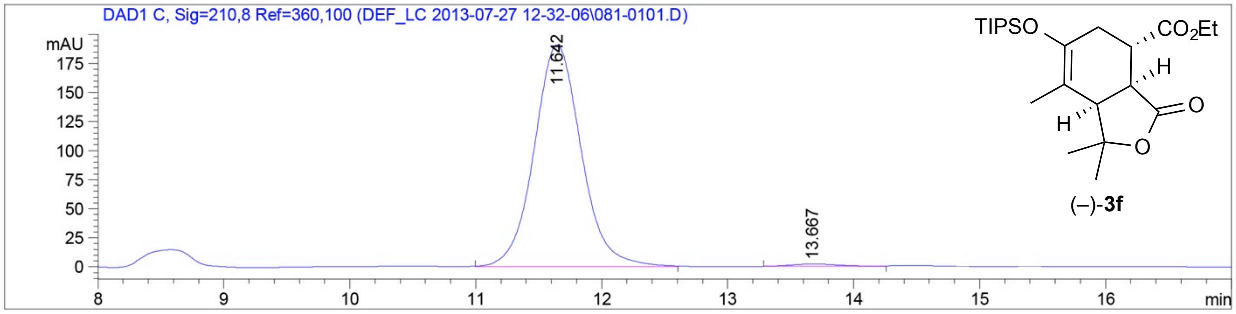
Chiral HPLC analysis of bicyclic γ-lactone (–)-3f: Chiralcel OD-H column: hexanes:^{i}PrOH = 95:05, flow rate 0.5 mL/min, λ = 210 nm: t_{major} = 11.6 min, t_{minor} = 13.6 min; 98% *ee*.



```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  11.609 BB    0.3884 3964.71484  156.04489  50.1639
   2  13.645 BV    0.4256 3938.81152  142.89645  49.8361

Totals :                  7903.52637  298.94135
```



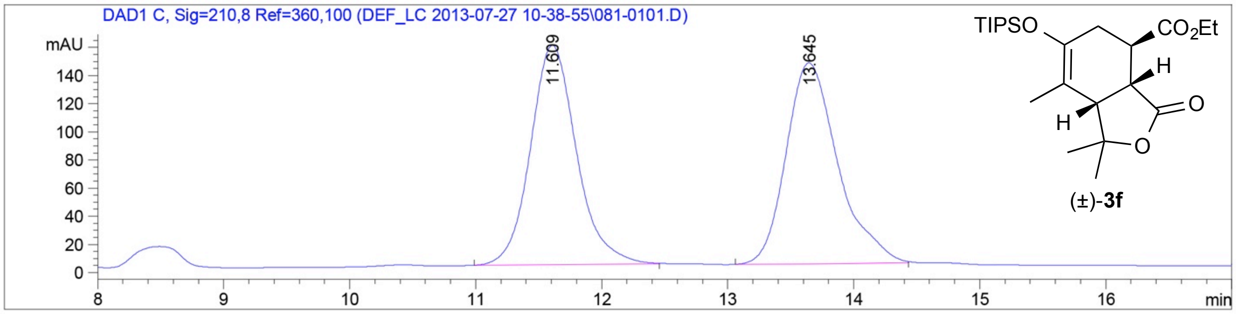
```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  11.642 BB    0.3965 4945.87793  190.72485  99.0991
   2  13.667 BB    0.2957   44.95997    1.87553   0.9009

Totals :                  4990.83790  192.60038
```

Determination of enantiomeric excess of bicyclic γ-lactone (+)-3f:

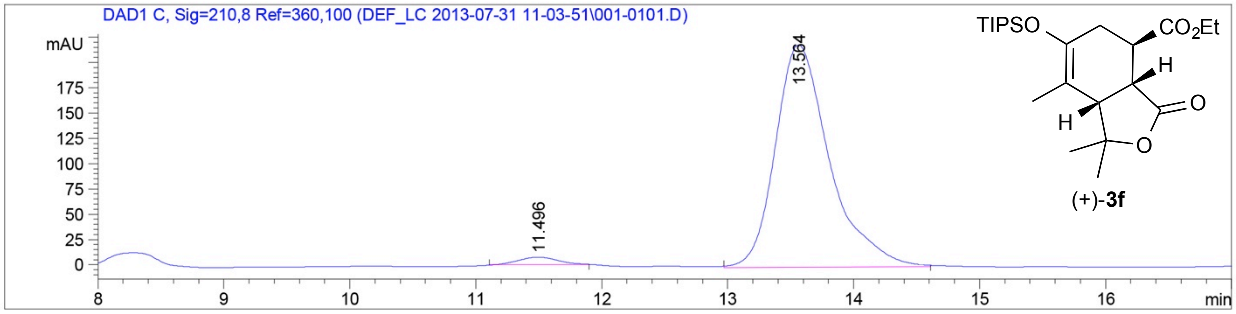
Chiral HPLC analysis of bicyclic γ-lactone (+)-3f: Chiralcel OD-H column: hexanes:^{i}PrOH = 95:05, flow rate 0.5 mL/min, λ = 210 nm: t_{minor} = 11.4 min, t_{major} = 13.5 min; 96% *ee*.



```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  11.609 BB     0.3884 3964.71484  156.04489  50.1639
   2  13.645 BV     0.4256 3938.81152  142.89645  49.8361

Totals :                   7903.52637  298.94135
```



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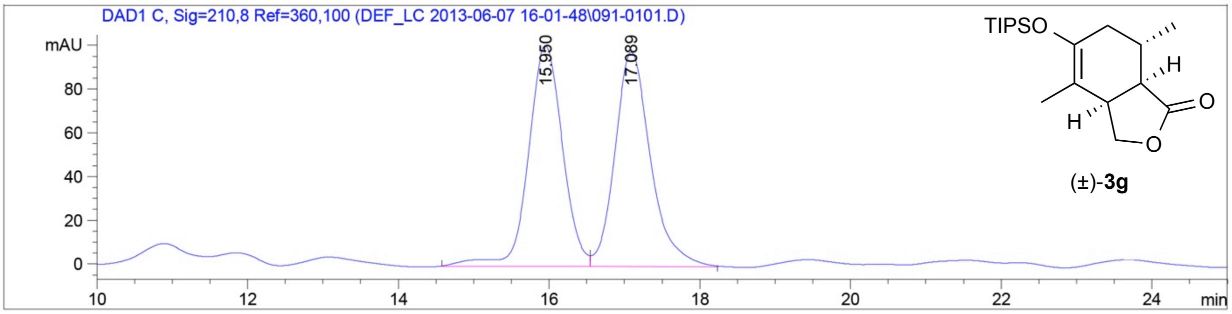
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  11.496 MM     0.3682  165.08434    7.47177   2.1938
   2  13.564 MM     0.5582 7359.91846  219.76448  97.8062

Totals :                   7525.00279  227.23625
```

Determination of enantiomeric excess of bicyclic γ-lactone (–)-3g:

Chiral HPLC analysis of bicyclic γ-lactone (–)-3g: Chiralcel OD-H column: hexanes:^{i}PrOH = 98:02, flow rate 0.5 mL/min, λ = 210 nm: t_{minor} = 16.0 min, t_{major} = 17.0 min; 95% *ee*.



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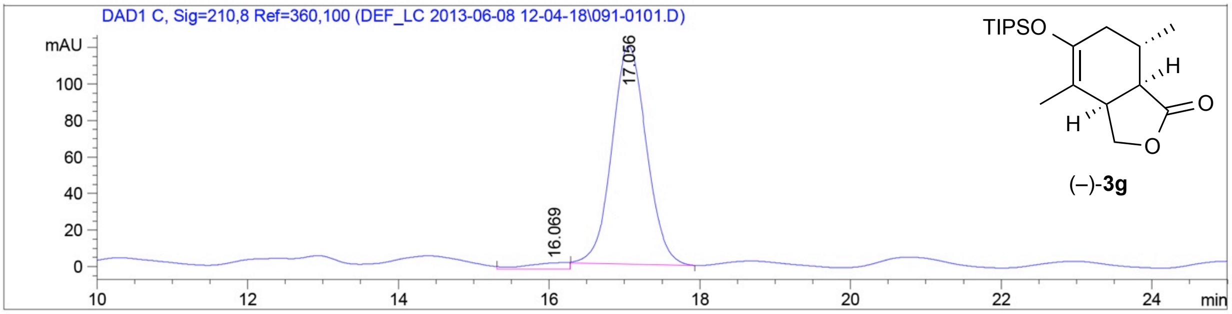
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  15.950 BV    0.4880 3186.13794  101.00188  49.7150
   2  17.089 VB    0.5011 3222.66260   98.14114  50.2850

Totals :                  6408.80054  199.14302
```



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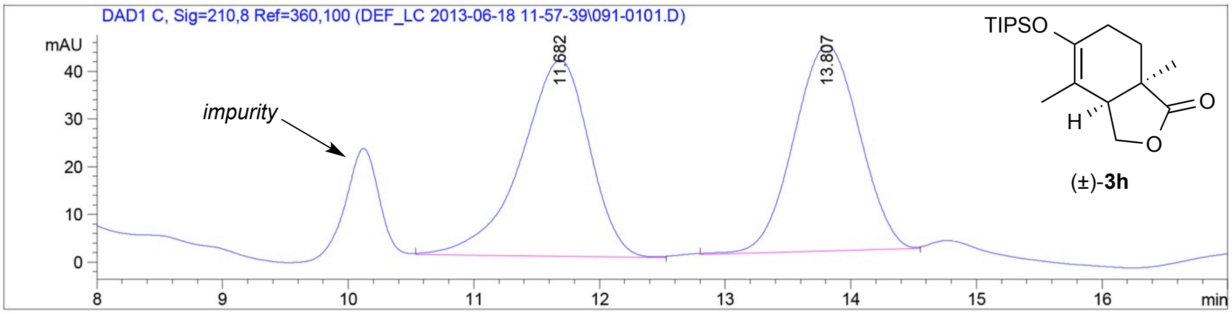
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  16.069 MM    0.6625   87.59249    2.20367   2.2516
   2  17.056 BB    0.4934 3802.59204  119.45309  97.7484

Totals :                  3890.18453  121.65676
```

Determination of enantiomeric excess of bicyclic γ-lactone (–)-3h:

Chiral HPLC analysis of bicyclic γ-lactone (–)-3h: Chiralcel AS-H column: hexanes:^{i}PrOH = 98:02, flow rate 0.5 mL/min, λ = 210 nm: t_{major} = 11.8 min, t_{minor} = 14.0 min; 91% *ee*.



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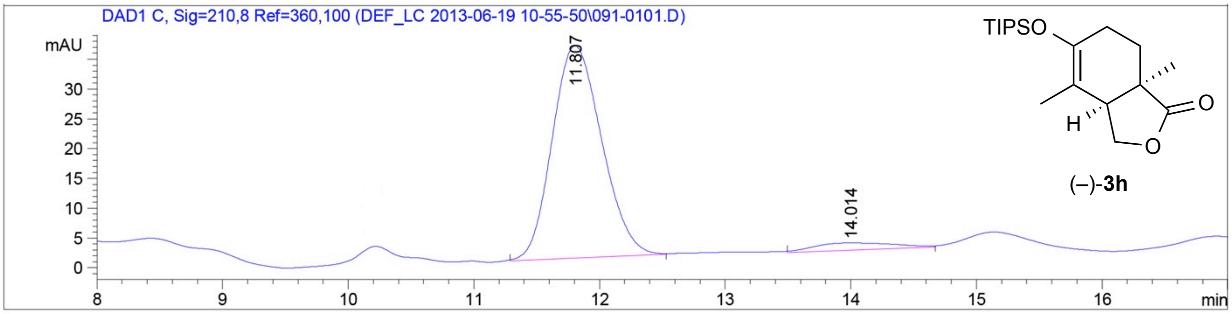
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  11.682 MM     0.6297 1554.04358   41.13143  49.8886
   2  13.807 MM     0.6046 1560.98486   43.03236  50.1114

Totals :                   3115.02844   84.16378
```



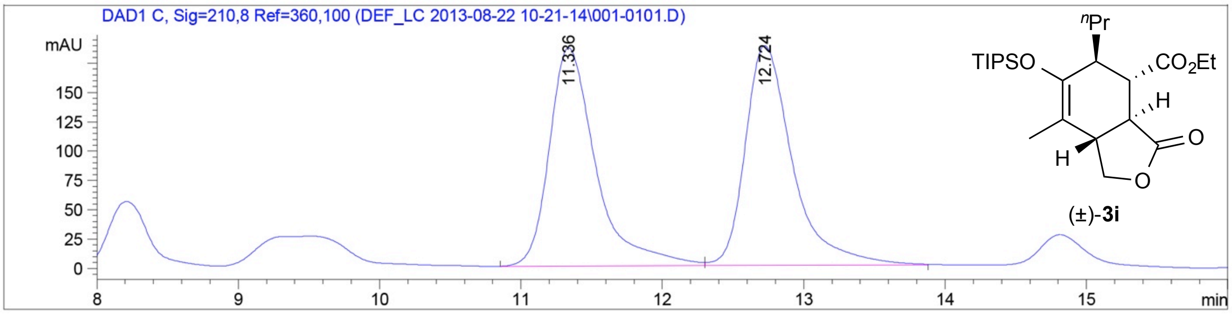
```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  11.807 BB     0.5004 9266.48242  290.29224  95.5840
   2  14.014 BB     0.7472  428.11127    9.54867   4.4160

Totals :                   9694.59369  299.84090
```

Determination of enantiomeric excess of bicyclic γ-lactone (+)-3i:

Chiral HPLC analysis of bicyclic γ-lactone (+)-3i: Chiralcel AD-H column: hexanes:^{i}PrOH = 95:05, flow rate 0.5 mL/min, λ = 210 nm: t_{major} = 11.4 min, t_{minor} = 12.8 min; 99% *ee* (using 20 mol% (*S*)-(–)-BTM), 97% *ee* (using 5 mol% (*S*)-(–)-BTM).

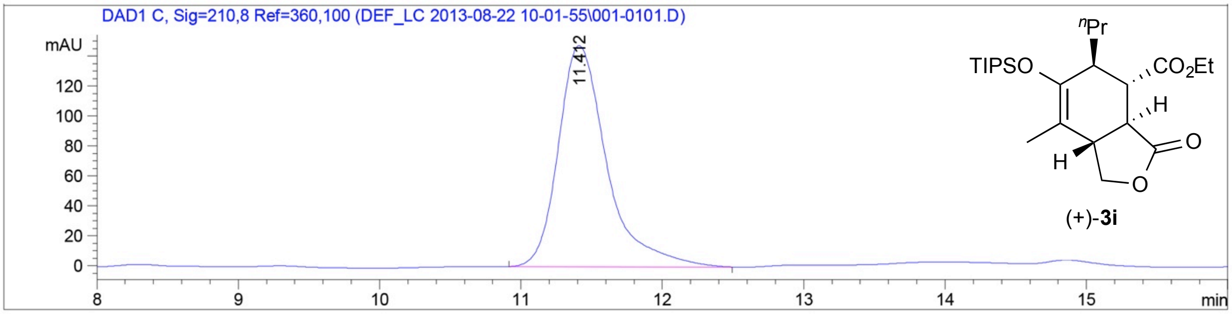


```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  11.336 BV    0.3475 4267.38916  186.10463  49.4355
   2  12.724 VB    0.3557 4364.84277  187.40324  50.5645

Totals :                  8632.23193  373.50787
```

Using 20 mol% (*S*)-(–)-BTM:

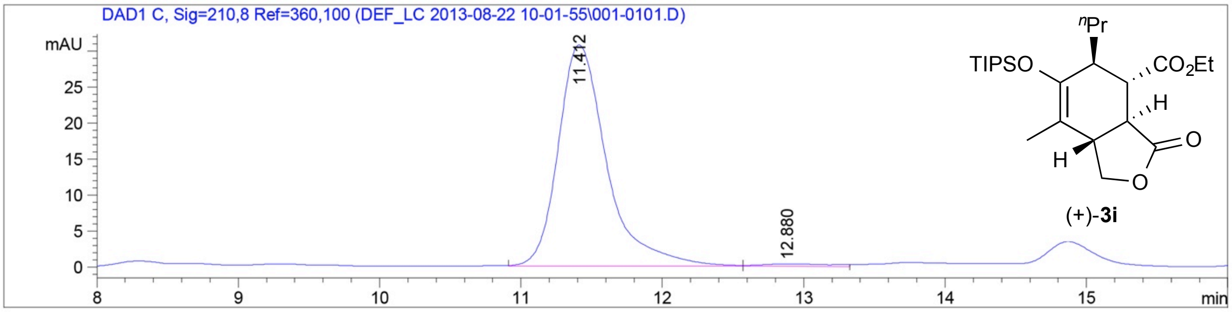


```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  11.412 BB    0.3652 3537.73755  147.84750 100.0000

Totals :                  3537.73755  147.84750
```

Using 5 mol% (*S*)-(–)-BTM:



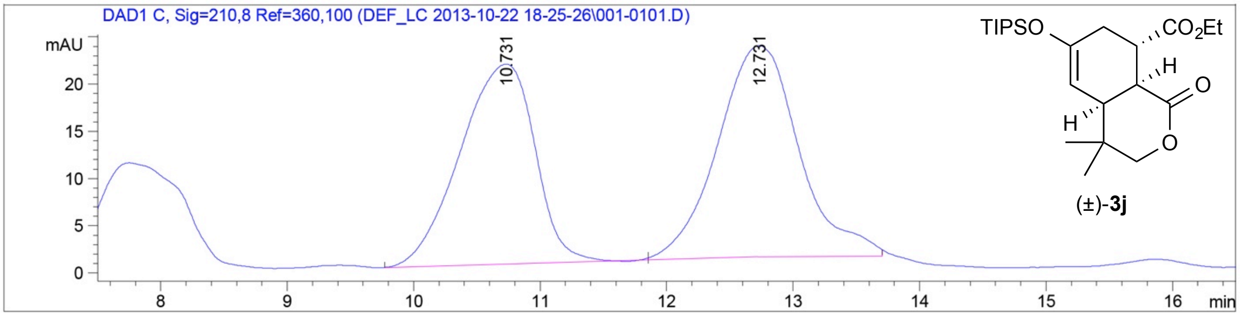
```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  11.412 BV    0.3628  733.42120   30.69212  98.4827
   2  12.880 VB    0.3948   11.29927 3.44362e-1   1.5173

Totals :                   744.72048   31.03648
```

Determination of enantiomeric excess of bicyclic δ-lactone (+)-3j:

Chiral HPLC analysis of bicyclic δ-lactone (+)-3j: Chiralcel OD-H column: hexanes:^{i}PrOH = 95:05, flow rate 0.5 mL/min, λ = 210 nm: t_{minor} = 10.7 min, t_{major} = 12.5 min; 92% *ee*.



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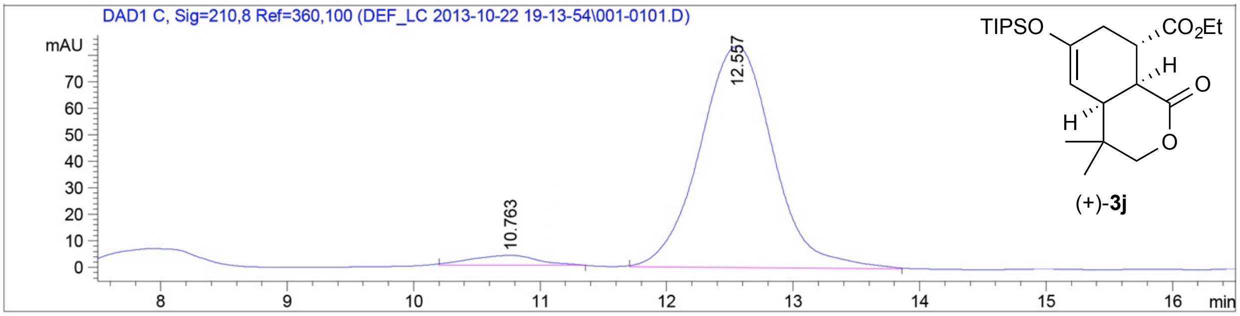
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.731 BB     0.6469  868.67236   21.16243  48.0105
   2  12.731 BV     0.6094  940.66602   22.33294  51.9895

Totals :                   1809.33838   43.49536
```



```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

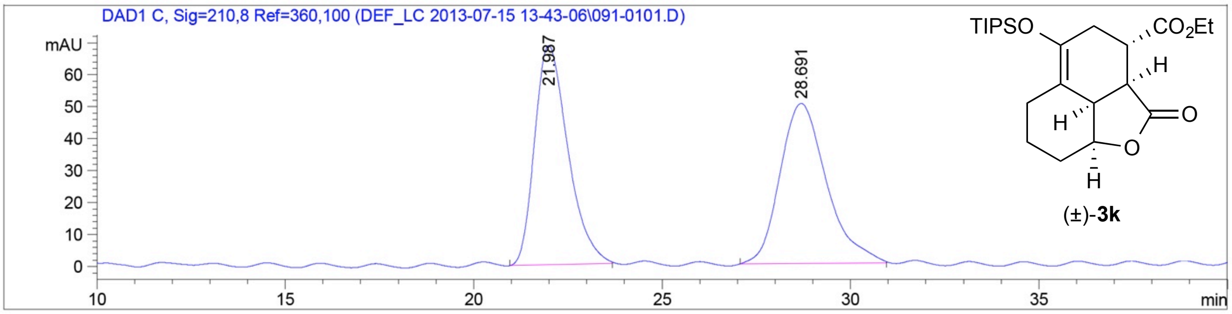
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.763 MM     0.5989  131.20264    3.65145   3.7611
   2  12.557 BB     0.6211 3357.17163   83.48924  96.2389

Totals :                   3488.37427   87.14069
```

Figure S14. Chiral HPLC determinations of enantiomeric excess of lactones 3k, 3k' and 3c':

Determination of enantiomeric excess of tricyclic γ-lactone (–)-3k:

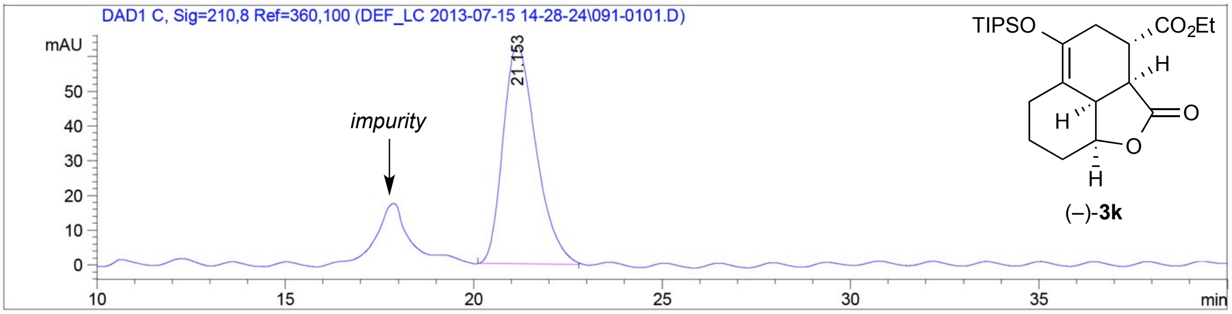
Chiral HPLC analysis of tricyclic γ-lactone (–)-3k: Chiralcel AS-H column: hexanes:^{i}PrOH = 97:03, flow rate 0.5 mL/min, λ = 210 nm: t_{major} = 21.1 min, t_{minor} = 28.6 min; 99% *ee*.



```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  21.987 BB    0.9366 4223.71094   68.57260  49.4877
   2  28.691 BB    1.2717 4311.16748   50.10910  50.5123

Totals :                  8534.87842  118.68170
```



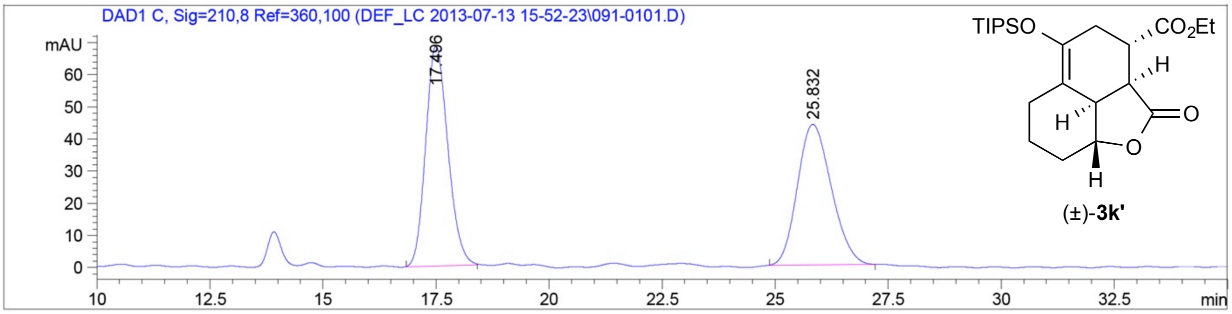
```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  21.153 BB    0.9376 3851.73779   62.79996 100.0000

Totals :                  3851.73779   62.79996
```

Determination of enantiomeric excess of tricyclic γ-lactone (–)-3k’:

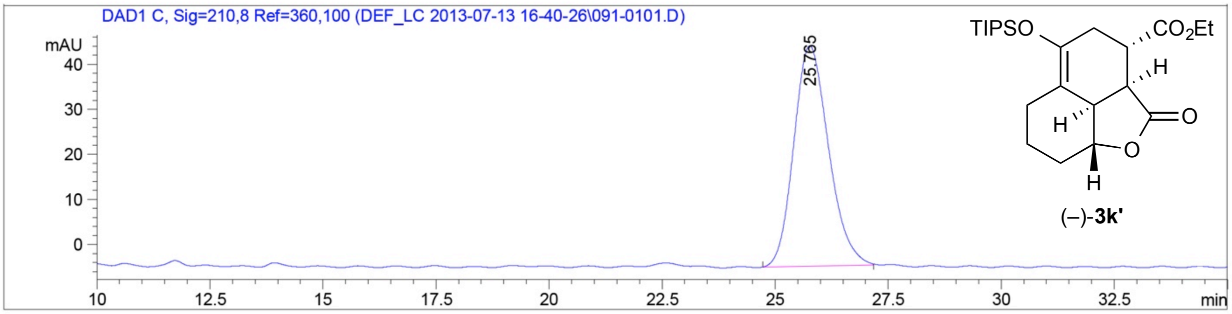
Chiral HPLC analysis of tricyclic γ-lactone (–)-3k’: Chiralcel OD-H column: hexanes:^{i}PrOH = 95:05, flow rate 0.5 mL/min, λ = 210 nm: t_{minor} = 17.4 min, t_{major} = 25.7 min; 99% *ee*.



```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  17.496 BB    0.5305 2341.91187   68.56427  50.6538
   2  25.832 BB    0.8102 2281.45386   43.76495  49.3462

Totals :                  4623.36572  112.32922
```



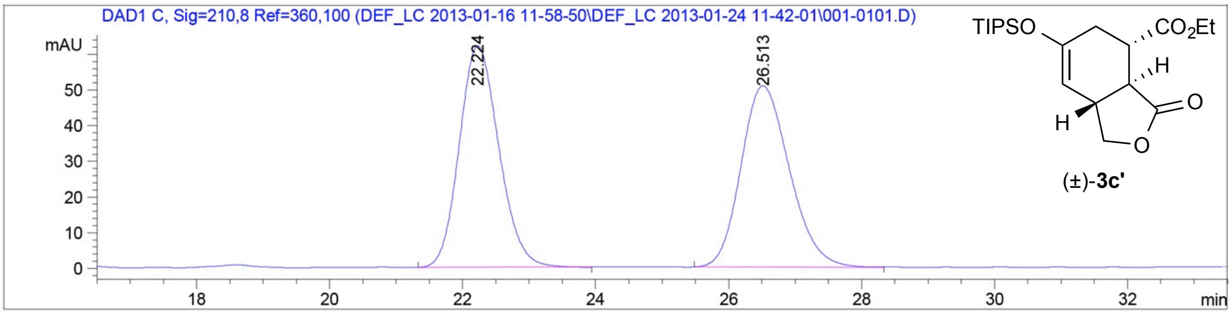
```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  25.765 BB    0.8166 2615.85327   48.86073 100.0000

Totals :                  2615.85327   48.86073
```

Determination of enantiomeric excess of bicyclic γ-lactone (+)-3c':

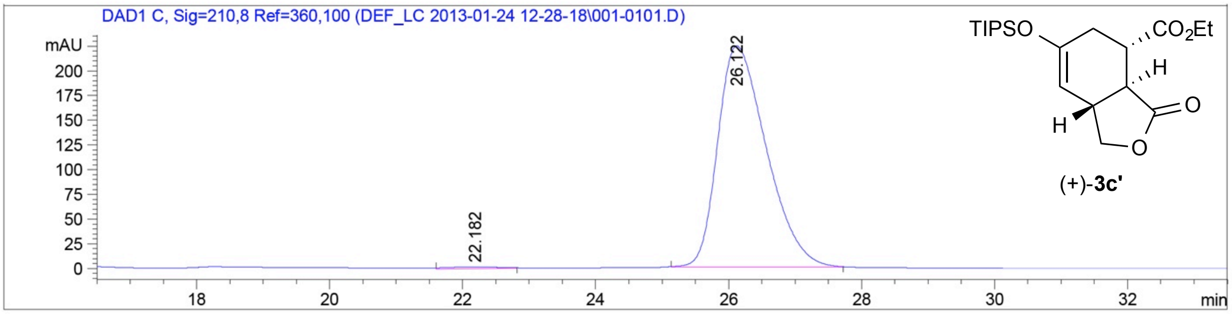
Chiral HPLC analysis of bicyclic γ-lactone (+)-3c': Chiralcel OD-H column: hexanes:^{i}PrOH = 95:05, flow rate 0.5 mL/min, λ = 210 nm: t_{minor} = 22.1 min, t_{major} = 26.1 min; 99% *ee*.



```
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  22.224 BB    0.6433 2574.76782   62.15416  49.9667
   2  26.513 BB    0.7918 2578.20190   50.82896  50.0333

Totals :                  5152.96973  112.98312
```



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Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  22.182 MM    0.8519   85.42705    1.67124   0.7437
   2  26.122 BB    0.7879 1.14013e4  223.98254  99.2563

Totals :                  1.14867e4  225.65378
```

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