

# Organocatalytic Asymmetric Michael Addition Reaction of Aldehydes to 2-Furanones: Experimental, Applications and DFT Studies †

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## 1. General methods

$^1\text{H}$  NMR spectra and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AVANCE III 400 (400MHz) or Bruker AVANCE III 600 (600MHz) spectrometer in needful D-reagents with tetramethylsilane (TMS) as an internal reference. Data for  $^1\text{H}$  NMR were reported as follows: chemical shift (ppm), and multiplicity (s= singlet, d= doublet, t= triplet, dd= double of doublet, br= broad, m= multiplet), coupling constants (Hz) and integration; Data for  $^{13}\text{C}$  NMR were reported as ppm. HPLC analyses were performed using a Daicel ChiralPak OD or AD column purchased. Crystal structure determination of Michael product **3aa** was carried out on a Rigaku MicroMax 002+ diffractometer. HRMS of Michael products were carried out AB SCIEX X500R QTOF.

### 1.1 Materials

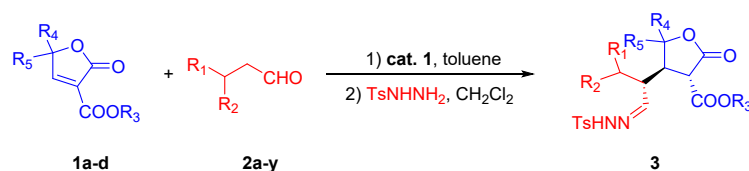
Unless otherwise stated, all reagents were purchased from commercial suppliers, including, aldehydes and catalysts **I**, **II**, **V** and **VI**. Ethyl 5, 5-disubstituted-2-oxo-2,5-dihydrofuran-3-carboxylates **1a-c** were prepared according to literature procedures and all the spectral data of **1a-c** matches with the desired compounds<sup>[1]</sup>. Catalysts **III**<sup>[2]</sup> and **IV**<sup>[2]</sup> were prepared according to the literature procedures and all the spectral data matches with the desired compounds. All the reactions were monitored by thin layer chromatography (TLC) on GF254 silica gel plates.

### Reference

- [1] W. Wang, J. Wang, S. Zhou, Q. Sun, Z. Ge, X. Wang and R. Li. *Chem. Commun.*, 2013, **49**, 1333.  
[2] C. B. Tripathi, S. Kayal and S. Mukherjee, *Org. Lett.*, 2012, **14**, 3296.

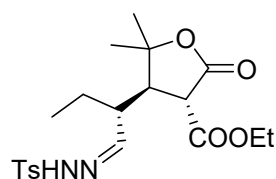
## 2. Synthesis and characterization of compounds 3-11

### 2.1 General procedure for the organocatalytic Michael addition reactions

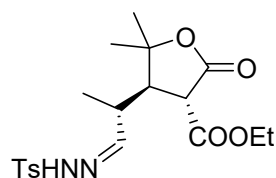


To a suspension of catalyst **I** (20% mol, Pyrrolidine is used for the preparation of racemic samples) and 2-furanone **1** (1.0 mmol) in toluene was added aldehyde **2** (2.0 mmol) and stirred at room temperature for 12h under  $\text{N}_2$ . Then  $\text{NH}_4\text{Cl}$  was added to the reaction mixture, extracted with ethyl acetate and concentrated in vacuo. The residue was purified by flash column chromatography (EtOAc: petroleum =1:5) to afford the Michael adduct. *p*-toluenesulfonyl hydrazide  $\text{TsNHNH}_2$  (1.5 mmol) and anhydrous  $\text{MgSO}_4$  (5 mmol) was added to a solution of above purified product in dichloromethane (10 mL) at  $0^\circ\text{C}$ . The resulting mixture was left with stirring for 24h. The reaction was concentrated under reduced pressure and purified by flash column chromatography (EtOAc:petroleum = 1:2) to afford hydrazine **3**.

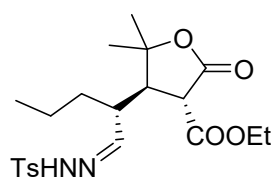
## 2.2 Scope of the Michael addition reaction



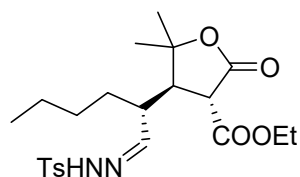
**(3*S*,4*R*)-ethyl-5,5-dimethyl-2-oxo-4-((*R*)-1-(2-tosylhydrazinyl)butan-2-yl)tetrahydrofuran-3-carboxylate 3aa:** Obtained in 87% yield. white solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 – 7.72 (m, 3H), 7.39 – 7.29 (m, 2H), 6.91 – 6.72 (m, 1H), 4.37 – 4.04 (m, 2H), 3.52 – 3.28 (m, 1H), 2.89 – 2.66 (m, 1H), 2.43 (d,  $J = 3.6$  Hz, 3H), 1.38 – 1.05 (m, 11H), 0.66 (m, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.0, 168.3, 151.76, 144.5, 135.3, 129.8, 128.0, 85.7, 62.5, 52.2, 51.2, 44.4, 27.8, 24.1, 22.9, 21.6, 14.0, 11.3. HPLC(CHIRAL-AD-H, 228nm, hexane: *i*-PrOH =85:15, 1.0mL/min,  $t_{\text{R1}}$ (minor) = 21.857 min,  $t_{\text{R1}}$ (major) = 26.117 min,  $t_{\text{R2}}$ (major) = 33.801 min,  $t_{\text{R2}}$ (minor) = 46.868 min ). dr= 8.3:1. 99%/96% ee. ES-HRMS: Calcd for  $\text{C}_{21}\text{H}_{31}\text{N}_2\text{O}_6\text{S}$  [M+H], 439.1903, Found 439.1896.



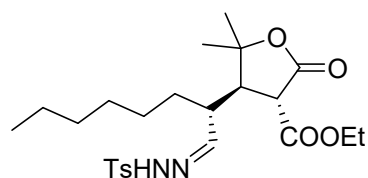
**(3*S*,4*R*)-ethyl-5,5-dimethyl-2-oxo-4-((*R*)-1-(2-tosylhydrazinyl)propan-2-yl)tetrahydrofuran-3-carboxylate 3ab:** Obtained in 88% yield, white solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (s, 1H), 7.81 (d,  $J = 8.2$  Hz, 2H), 7.33 (d,  $J = 8.1$  Hz, 2H), 6.90 (d,  $J = 7.9$  Hz, 1H), 4.26 (q,  $J = 7.1$  Hz, 2H), 3.41 (d,  $J = 12.0$  Hz, 1H), 2.73 (t,  $J = 11.4$  Hz, 1H), 2.60 – 2.48 (m, 1H), 2.44 (s, 3H), 1.30 (t,  $J = 7.1$  Hz, 3H), 1.06 (d,  $J = 8.6$  Hz, 6H), 0.98 (d,  $J = 6.8$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.8, 168.2, 152.3, 144.6, 135.2, 129.8, 128.1, 85.5, 62.5, 52.1, 52.0, 37.6, 29.7, 27.7, 22.9, 21.6, 16.9, 14.0. HPLC(CHIRAL-AD-H, 254nm, hexane: *i*-PrOH =90:10, 2.0mL/min,  $t_{\text{R1}}$ (minor) = 40.310 min,  $t_{\text{R1}}$ (major) = 54.120 min ). dr>9.2:1. 86 %/n.d. ee. ES-HRMS: Calcd for  $\text{C}_{19}\text{H}_{27}\text{N}_2\text{O}_6\text{S}$  [M+H], 411.1590, Found 411.1580.



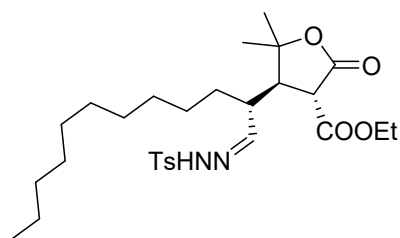
**(3*S*,4*R*)-ethyl-5,5-dimethyl-2-oxo-4-((*R,E*)-1-(2-tosylhydrazono)pentan-2-yl)tetrahydrofuran-3-carboxylate 3ac.** Obtained in 85% yield, white solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 – 8.11 (m, 1H), 7.86 (t,  $J = 9.0$  Hz, 2H), 7.38 (dd,  $J = 8.0, 3.5$  Hz, 2H), 6.86 (dd,  $J = 15.2, 8.2$  Hz, 1H), 4.44 – 4.13 (m, 2H), 3.49 (dd,  $J = 15.3, 12.1$  Hz, 1H), 2.92 – 2.75 (m, 1H), 2.50 (d,  $J = 2.5$  Hz, 3H), 2.48 – 2.39 (m, 1H), 1.48 – 1.28 (m, 9H), 1.16 (d,  $J = 6.4$  Hz, 3H), 1.09 – 0.92 (m, 2H), 0.86 – 0.77 (m, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.0, 169.6, 168.3, 168.1, 152.1, 151.7, 144.5, 144.4, 135.2, 135.1, 129.8, 129.7, 128.1, 127.9, 85.7, 85.3, 62.6, 62.4, 52.2, 51.9, 51.4, 51.1, 42.8, 42.8, 33.2, 33.1, 29.1, 27.8, 23.0, 22.7, 21.6, 20.0, 20.0, 14.1, 14.0, 13.7, 13.5. HPLC(CHIRAL-AD-H, 228nm, hexane: *i*-PrOH =90:10, 1.0mL/min,  $t_{\text{R1}}$ (minor) = 28.225 min,  $t_{\text{R1}}$ (major) = 36.245 min,  $t_{\text{R2}}$ (major) = 48.591 min,  $t_{\text{R2}}$ (minor) = 56.932 min ). dr= 5.4:1. 93 %/6 % ee. ES-HRMS: Calcd for  $\text{C}_{21}\text{H}_{31}\text{N}_2\text{O}_6\text{S}$  [M+H], 439.1903, Found 439.1896.



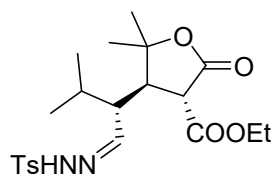
**(3S,4R)-ethyl-5,5-dimethyl-2-oxo-4-((R,E)-1-(2-tosylhydrazono)hexan-2-yl)tetrahydrofuran-3-carboxylate 3ad.** Obtained in 82% yield, white solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J = 8.5$  Hz, 1H), 7.80 (dd,  $J = 11.5, 5.9$  Hz, 2H), 7.31 (t,  $J = 6.3$  Hz, 2H), 6.79 (dd,  $J = 12.7, 8.2$  Hz, 1H), 4.39 – 4.13 (m, 2H), 3.43 (dd,  $J = 17.4, 12.1$  Hz, 1H), 2.80 – 2.69 (m, 1H), 2.41 (s, 3H), 2.40 – 2.30 (m, 1H), 1.54 (s, 3H), 1.41 – 1.05 (m, 10H), 0.97 – 0.83 (m, 2H), 0.73 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.6, 168.1, 152.1, 144.4, 135.1, 129.7, 127.9, 85.3, 62.6, 51.9, 51.1, 43.1, 30.9, 29.1, 29.1, 22.7, 22.2, 21.6, 14.1, 13.8. HPLC(CHIRAL-AD-H, 228nm, hexane: i-PrOH =90:10, 1.0mL/min,  $t_{\text{R1}}$ (minor) = 22.126 min,  $t_{\text{R1}}$ (major) = 27.062 min,  $t_{\text{R2}}$ (major) = 35.431 min,  $t_{\text{R2}}$ (minor) = 46.065 min ). dr= 4.4:1. 91 %/35 % ee. ES-HRMS: Calcd for  $\text{C}_{22}\text{H}_{33}\text{N}_2\text{O}_6\text{S}$  [M+H], 453.2059, Found 453.2051.



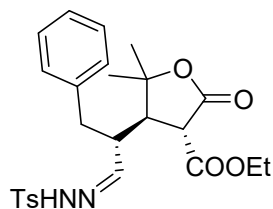
**(3S,4R)-ethyl-5,5-dimethyl-2-oxo-4-((R,E)-1-(2-tosylhydrazono)octan-2-yl)tetrahydrofuran-3-carboxylate 3ae.** Obtained in 80% yield, white solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.15 (s, 1H), 7.77 (d,  $J = 8.3$  Hz, 2H), 7.35 – 7.23 (m, 2H), 6.80 (d,  $J = 8.1$  Hz, 1H), 4.31 – 4.11 (m, 2H), 3.47 (d,  $J = 12.3$  Hz, 1H), 2.77 (dd,  $J = 12.2, 9.3$  Hz, 1H), 2.41 (s, 3H), 2.34 (dd,  $J = 14.8, 6.2$  Hz, 1H), 1.53 (s, 3H), 1.31 (t,  $J = 7.1$  Hz, 11H), 1.25 – 1.02 (m, 5H), 0.86 (dt,  $J = 14.6, 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  170.1, 168.4, 151.9, 144.5, 135.3, 129.8, 128.0, 85.8, 62.4, 52.3, 51.5, 43.1, 31.5, 31.1, 29.0, 27.8, 26.7, 22.9, 22.5, 21.6, 14.0. HPLC(CHIRAL-AD-H, 254nm, hexane: i-PrOH =90:10, 2.0mL/min,  $t_{\text{R1}}$ (minor) = 10.289 min,  $t_{\text{R1}}$ (major) = 11.483 min,  $t_{\text{R2}}$ (minor) = 15.872 min,  $t_{\text{R2}}$ (major) = 21.764 min ). dr= 2.3:1. 92 %/29 % ee. ES-HRMS: Calcd for  $\text{C}_{24}\text{H}_{37}\text{N}_2\text{O}_6\text{S}$  [M+H], 481.2372, Found 481.2378.



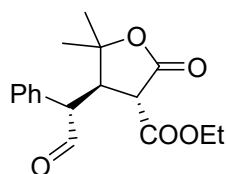
**(3S,4R)-ethyl-5,5-dimethyl-2-oxo-4-((R,E)-1-(2-tosylhydrazono)dodecan-2-yl)tetrahydrofuran-3-carboxylate 3af.** Obtained in 79% yield, white oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 – 7.75 (m, 2H), 7.34 – 7.27 (m, 2H), 6.85 – 6.77 (m, 1H), 4.38 – 4.07 (m, 2H), 3.62 – 3.27 (m, 1H), 2.85 – 2.70 (m, 1H), 2.47 – 2.29 (m, 4H), 1.61 – 0.80 (m, 30H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.7, 168.2, 152.2, 144.3, 135.2, 129.7, 127.8, 85.5, 62.7, 51.9, 51.2, 43.0, 31.9, 31.2, 29.6, 29.4, 29.3, 29.2, 29.0, 27.0, 22.7, 21.6, 14.1, 14.0. HPLC(CHIRAL-OD-H, 254 nm, hexane: i-PrOH =95:5, 2.0mL/min,  $t_{\text{R1}}$ (major) = 10.257 min,  $t_{\text{R1}}$ (minor) = 13.346 min,  $t_{\text{R2}}$ (major) = 21.540 min,  $t_{\text{R2}}$ (minor) = 32.443 min ). dr= 5.4:1. 78 %/21 % ee. ES-HRMS: Calcd for  $\text{C}_{28}\text{H}_{45}\text{N}_2\text{O}_6\text{S}$  [M+H], 537.2998, Found 537.2977.



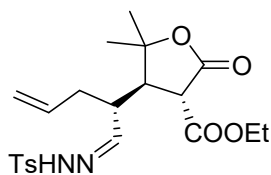
**(3*S*,4*R*)-ethyl-5,5-dimethyl-4-((*R,E*)-3-methyl-1-(2-tosylhydrazono)butan-2-yl)-2-oxotetrahydrofuran-3-carboxylate 3ag.** Obtained in 53% yield, white solid.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 – 7.69 (m, 2H), 7.23 (d,  $J = 8.0$  Hz, 2H), 6.81 (d,  $J = 8.5$  Hz, 1H), 4.24 – 4.03 (m, 2H), 3.29 (d,  $J = 12.3$  Hz, 1H), 2.91 (dd,  $J = 12.2, 9.2$  Hz, 1H), 2.35 (s, 3H), 2.21 – 2.17 (m, 1H), 1.77 – 1.66 (m, 1H), 1.47 (s, 3H), 1.25 (t,  $J = 7.1$  Hz, 3H), 1.14 (s, 3H), 0.78 (d,  $J = 6.8$  Hz, 3H), 0.62 (d,  $J = 6.7$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.8, 167.2, 149.2, 143.3, 134.2, 128.6, 126.8, 84.6, 61.6, 50.7, 47.4, 47.3, 27.5, 27.4, 21.5, 20.5, 20.3, 16.0, 13.0. HPLC(CHIRAL-AD-H, 228 nm, hexane: *i*-PrOH =90:10, 1.0mL/min,  $t_{\text{R1}}$ (minor) = 28.455 min,  $t_{\text{R1}}$ (major) = 41.080 min). dr = >20:1. 95 %/n.d. ee. ES-HRMS: Calcd for  $\text{C}_{21}\text{H}_{31}\text{N}_2\text{O}_6\text{S}$  [ $\text{M}+\text{H}$ ], 439.1903, Found 439.1910.



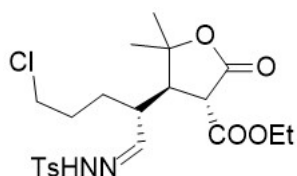
**(3*S*,4*R*)-ethyl-5,5-dimethyl-2-oxo-4-((*R,E*)-1-phenyl-3-(2-tosylhydrazono)propan-2-yl)tetrahydrofuran-3-carboxylate 3ah.** Obtained in 84% yield, white solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 – 8.00 (m, 1H), 7.64 (dd,  $J = 10.5, 8.4$  Hz, 2H), 7.23 (d,  $J = 8.2$  Hz, 2H), 7.12 – 7.07 (m, 3H), 6.94 – 6.86 (m, 3H), 4.35 – 4.14 (m, 2H), 3.56 (d,  $J = 12.2$  Hz, 1H), 3.04 – 2.87 (m, 1H), 2.88 – 2.56 (m, 3H), 2.51 – 2.37 (m, 3H), 1.50 (s, 3H), 1.38 – 1.24 (m, 6H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.9, 169.8, 168.3, 168.2, 151.0, 150.5, 144.2, 144.1, 137.3, 136.9, 135.3, 135.2, 129.7, 129.7, 128.8, 128.8, 128.5, 127.8, 127.6, 126.6, 126.6, 86.0, 85.5, 62.8, 62.6, 52.3, 51.5, 51.3, 50.8, 44.2, 43.8, 37.8, 37.6, 28.5, 27.9, 23.2, 22.7, 21.6, 14.0. HPLC(CHIRAL-AD-H, 210 nm, hexane: *i*-PrOH =80:20, 2.0mL/min,  $t_{\text{R1}}$ (major) =6.328min,  $t_{\text{R1}}$ (minor) = 7.987 min,  $t_{\text{R2}}$ (major) = 16.498 min,  $t_{\text{R2}}$ (minor) = 50.885min). dr= 1.5:1. 88 %/78 % ee. ES-HRMS: Calcd for  $\text{C}_{25}\text{H}_{30}\text{N}_2\text{NaO}_7\text{S}$  [ $\text{M}+\text{Na}$ ], 509.1722, Found 509.1607.



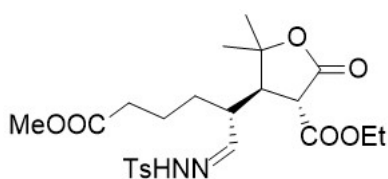
**ethyl (3*S*,4*R*)-5,5-dimethyl-2-oxo-4-((*S*)-2-oxo-1-phenylethyl)tetrahydrofuran-3-carboxylate 3ai.** Obtained in 82% yield, white oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.72 (d,  $J = 1.2$  Hz, 1H), 9.51 (d,  $J = 2.4$  Hz, 1H), 7.48 – 7.17 (m, 10H), 4.40 – 4.25 (m, 2H), 3.89 – 3.46 (m, 7H), 3.34 (d,  $J = 9.4$  Hz, 1H), 1.65 (s, 3H), 1.40 (s, 3H), 1.36 (t,  $J = 7.1$  Hz, 3H), 1.31 (s, 3H), 1.03 – 0.95 (m, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.8, 197.2, 169.8, 169.8, 167.9, 167.3, 132.9, 131.7, 130.1, 129.7, 129.5, 129.4, 128.9, 85.8, 85.6, 62.5, 62.0, 60.1, 59.9, 52.7, 52.0, 49.2, 49.1, 28.8, 28.3, 24.0, 23.2, 14.1, 13.7. HPLC(CHIRAL-AD-H, 210 nm, hexane: *i*-PrOH =80:20, 2.0mL/min,  $t_{\text{R1}}$ (minor) = 14.845 min,  $t_{\text{R1}}$ (major) = 16.001 min,  $t_{\text{R2}}$ (minor) = 21.856 min,  $t_{\text{R2}}$ (major) = 22.325 min). dr= 1:1.2. 92 %/69 % ee. ESI-HRMS: Calcd for  $\text{C}_{17}\text{H}_{20}\text{NaO}_5$  [ $\text{M}+\text{Na}$ ], 327.1208, Found 327.1133.



**(3*S*,4*R*)-ethyl-5,5-dimethyl-2-oxo-4-((*R,E*)-1-(2-tosylhydrazono)pent-4-en-2-yl)tetrahydrofuran-3-carboxylate 3aj.** Obtained in 89% yield, white solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.29 (d,  $J = 101.5$  Hz, 1H), 7.78 (t,  $J = 8.6$  Hz, 2H), 7.31 (dd,  $J = 8.1, 3.6$  Hz, 2H), 6.84 (t,  $J = 8.6$  Hz, 1H), 5.48 – 5.28 (m, 1H), 4.94 – 4.79 (m, 2H), 4.31 – 4.10 (m, 2H), 3.46 (dd,  $J = 12.0, 9.4$  Hz, 1H), 2.88 – 2.74 (m, 1H), 2.55 – 2.46 (m, 1H), 2.42 (d,  $J = 2.5$  Hz, 3H), 2.32 – 1.93 (m, 2H), 1.30 (td,  $J = 7.1, 2.1$  Hz, 3H), 1.27 – 1.18 (m, 3H), 1.08 (d,  $J = 4.3$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.9, 169.7, 168.2, 168.1, 151.3, 151.3, 144.5, 144.4, 135.3, 135.2, 133.6, 133.5, 129.8, 129.7, 128.1, 127.9, 118.1, 85.8, 85.4, 62.6, 62.5, 52.2, 51.4, 50.8, 50.5, 42.5, 42.2, 35.7, 35.5, 28.8, 27.8, 23.0, 22.8, 21.6, 21.6, 14.0, 14.0. HPLC(CHIRAL-AD-H, 254 nm, hexane: *i*-PrOH =90:10, 2.0mL/min,  $t_{\text{R1}}$ (minor) = 18.911 min,  $t_{\text{R1}}$ (major) = 21.988 min,  $t_{\text{R2}}$ (major) = 42.280 min,  $t_{\text{R2}}$ (minor) = 49.230 min ). dr = 1.2:1. 87 %/82 % ee. ES-HRMS: Calcd for  $\text{C}_{21}\text{H}_{29}\text{N}_2\text{O}_6\text{S}$  [M+H], 437.1746, Found 437.1722.

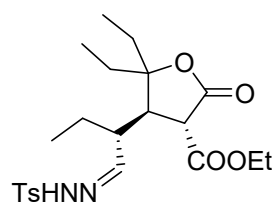


**(3*S*,4*R*)-ethyl-4-((*R,E*)-5-chloro-1-(2-tosylhydrazono)pentan-2-yl)-5,5-dimethyl-2-oxotetrahydrofuran-3-carboxylate 3ak.** Obtained in 82% yield, white oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.38 (s, 1H), 7.90 – 7.73 (m, 2H), 7.32 (d,  $J = 8.1$  Hz, 2H), 6.85 (d,  $J = 8.1$  Hz, 1H), 4.44 – 4.00 (m, 2H), 3.71 – 3.23 (m, 3H), 2.94 – 2.61 (m, 1H), 2.48 – 2.24 (m, 4H), 1.85 – 1.17 (m, 13H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.6, 168.1, 151.3, 144.5, 135.1, 129.8, 127.9, 85.5, 62.7, 51.8, 51.3, 43.7, 42.1, 29.2, 29.1, 27.9, 22.7, 21.6, 14.0. HPLC(CHIRAL-OD-H, 210 nm, hexane: *i*-PrOH =95:5, 2.0mL/min,  $t_{\text{R1}}$ (major) = 30.074 min,  $t_{\text{R1}}$ (minor) = 37.612 min, dr = 5.9:1, 82%/-- ee. ES-HRMS: Calcd for  $\text{C}_{21}\text{H}_{29}\text{ClN}_2\text{NaO}_6\text{S}$  [M+Na], 495.1333, Found 495.1334.

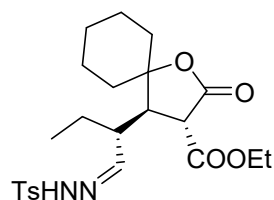


**(3*S*,4*R*)-ethyl-4-((*R,E*)-6-methoxy-6-oxo-1-(2-tosylhydrazono)hexan-2-yl)-5,5-dimethyl-2-oxotetrahydrofuran-3-carboxylate 3al.** Obtained in 68% yield, white oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.64 (m, 1H), 7.79 (t,  $J = 7.9$  Hz, 2H), 7.31 (dd,  $J = 8.1, 3.5$  Hz, 2H), 6.88 (dd,  $J = 8.0, 5.5$  Hz, 1H), 4.36 – 4.06 (m, 2H), 3.65 (d,  $J = 1.9$  Hz, 3H), 3.45 (dd,  $J = 19.6, 12.1$  Hz, 1H), 2.83 – 2.67 (m, 1H), 2.42 (m, 4H), 2.15 (dt,  $J = 9.6, 6.7$  Hz, 2H), 2.06 – 2.01 (m, 1H), 1.43 – 1.19 (m, 9H), 1.06 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.4, 170.0, 169.7, 168.4, 168.1, 151.5, 151.4, 144.5, 144.3, 135.3, 135.2, 129.8, 129.7, 128.0, 127.8, 85.8, 85.6, 62.7, 62.5, 52.2, 51.7, 51.7, 51.3, 51.2, 42.7, 42.6, 33.2, 32.8, 30.3, 30.2, 29.0, 27.7, 22.8, 22.7, 22.0, 21.9, 21.6, 14.0, 14.0. HPLC(CHIRAL-AD-H, 254 nm, hexane: *i*-PrOH =95:5, 1.0mL/min,  $t_{\text{R1}}$ (major) = 8.838 min,  $t_{\text{R1}}$ (minor) = 9.227 min. dr= 1.5:1. 92%/n.d. ee. ES-HRMS:

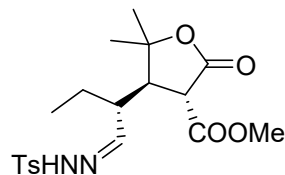
Calcd for C<sub>23</sub>H<sub>33</sub>N<sub>2</sub>O<sub>8</sub>S [M+H], 497.1958, Found 497.1925.



**(3S,4R)-ethyl-5,5-diethyl-2-oxo-4-((R,E)-1-(2-tosylhydrazono)butan-2-yl)tetrahydrofuran-3-carboxylate 3am.** Obtained in 52% yield, white oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.21 – 7.85 (m, 1H), 7.84 – 7.77 (m, 2H), 7.34 – 7.28 (m, 2H), 6.80 (d, *J* = 8.1 Hz, 1H), 4.40 – 4.07 (m, 2H), 3.52 – 3.22 (m, 1H), 3.14 – 2.95 (m, 1H), 2.43 (d, *J* = 3.1 Hz, 3H), 2.40 – 2.27 (m, 1H), 1.68 – 1.28 (m, 9H), 1.02 – 0.61 (m, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.47, 170.09, 168.56, 168.35, 152.26, 151.69, 144.52, 144.46, 135.31, 135.11, 129.75, 129.66, 127.98, 127.91, 89.34, 89.28, 62.49, 62.38, 52.20, 51.68, 46.40, 46.31, 43.99, 43.70, 29.70, 28.48, 28.40, 28.19, 24.58, 24.29, 22.70, 21.59, 14.12, 14.05, 13.99, 11.51, 11.27, 7.78, 7.74, 7.55, 7.24. HPLC(CHIRAL-AD-H, 254 nm, hexane: *i*-PrOH =80:20, 1.0mL/min, *t*<sub>R1</sub>(minor) = 26.804 min, *t*<sub>R1</sub>(major) =32.155min, *t*<sub>R2</sub>(minor) =73.729 min, *t*<sub>R2</sub>(major) =113.252 min ). *dr* = 2.2:1. 93 %/79 % ee. ES-HRMS: Calcd for C<sub>22</sub>H<sub>32</sub>N<sub>2</sub>NaO<sub>7</sub>S [M+Na], 475.1879, Found 475.1769.

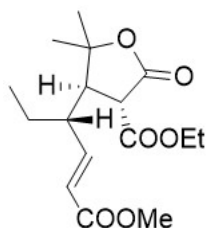


**(3S,4R)-ethyl-2-oxo-4-((R,E)-1-(2-tosylhydrazono)butan-2-yl)-1-oxaspiro[4.5]decane-3-carboxylate 3an.** Obtained in 65% yield, white oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.18 – 7.90 (m, 1H), 7.81 (dd, *J* = 16.3, 8.2 Hz, 2H), 7.36 – 7.28 (m, 2H), 6.83 (t, *J* = 8.3 Hz, 1H), 4.39 – 4.06 (m, 2H), 3.43 (d, *J* = 12.0 Hz, 1H), 2.67 (dd, *J* = 21.7, 11.0 Hz, 1H), 2.41 (s, 3H), 2.40 – 2.22 (m, 1H), 1.80 – 1.14 (m, 13H), 0.91 – 0.80 (m, 2H), 0.65 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.2, 170.0, 168.5, 168.4, 152.1, 151.9, 144.5, 144.4, 135.3, 135.2, 129.7, 128.0, 127.9, 87.4, 87.1, 62.5, 62.4, 51.8, 51.6, 51.4, 50.9, 44.0, 43.7, 37.5, 37.0, 31.7, 31.7, 29.7, 25.0, 24.9, 24.5, 24.2, 22.6, 22.6, 21.6, 21.4, 21.3, 14.0, 14.0, 11.4, 11.2. HPLC(CHIRAL-AD-H, 229 nm, hexane: *i*-PrOH =70:30, 1.0mL/min, *t*<sub>R1</sub>(minor) = 6.784 min, *t*<sub>R1</sub>(major) = 8.562 min, *t*<sub>R2</sub>(minor) = 9.910 min, *t*<sub>R2</sub>(major) = 12.682 min ). *dr* = 2.6:1. 87 %/48 % ee. ES-HRMS: Calcd for C<sub>23</sub>H<sub>33</sub>N<sub>2</sub>O<sub>6</sub>S [M+H], 465.2059, Found 465.2036.



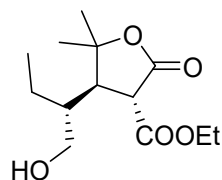
**(3S,4R)-methyl-5,5-dimethyl-2-oxo-4-((R,E)-1-(2-tosylhydrazono)butan-2-yl)tetrahydrofuran-3-carboxylate 3ao.** Obtained in 80% yield, white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.09 (s, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.42 – 7.15 (m, 2H), 6.81 (d, *J* = 8.1 Hz, 1H), 3.70 (s, 3H), 3.44 (d, *J* = 12.3 Hz, 1H), 2.79 (dd, *J* = 12.2, 9.3 Hz, 1H), 2.42 (s, 3H), 2.30 (ddd, *J* = 12.9, 10.2, 3.9 Hz, 1H), 1.53 (s, 3H), 1.32 – 1.20 (m, 5H), 0.66 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 169.5, 168.5, 152.0, 144.5, 135.2, 129.7, 127.8, 85.5, 53.3, 51.7, 50.9, 44.7, 29.1, 24.3, 22.7, 21.6, 11.4. HPLC(CHIRAL-OD-H, 254nm, hexane: *i*-PrOH =90:10, 2.0mL/min, *t*<sub>R1</sub>(major) = 9.691 min, *t*<sub>R1</sub>(minor) = 14.033 min, *t*<sub>R2</sub>(minor) =

18.038 min,  $t_{R2}$ (major) = 24.733 min ).  $dr > 20:1$ . 99%/35% ee. ES-HRMS: Calcd for  $C_{19}H_{26}N_2NaO_6S$  [M+Na], 433.1409, Found 433.1403.



To a round-bottom flask, (*S*)-2-(2,5-dioxo-1-phenylpyrrolidin-3-yl)-2-methylpropanal (81 mg, 0.33 mmol) was dissolved in dichloromethane (10 mL). After the addition of methyl 2-(triphenylphosphoranylidene)acetate (121 mg, 0.36 mmol), the reaction mixture was stirred for 48 h at 50 °C in a pressure vessel. The solvent was evaporated and the crude product was purified using flash column chromatography eluting with petroleum ether (40-60 °C)/ethyl acetate (7:3) to afford the desired product.

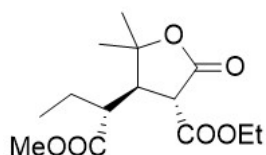
**(3*S*,4*R*)-ethyl-4-((*S*,*E*)-6-methoxy-6-oxohex-4-en-3-yl)-5,5-dimethyl-2-oxotetrahydrofuran-3-carboxylate 5.** Obtained in 83% yield, white oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.64 (dd,  $J = 15.7, 10.4$  Hz, 1H, minor isomer), 6.54 (dd,  $J = 15.6, 10.4$  Hz, 1H, major isomer), 5.86 (d,  $J = 15.6$  Hz, 1H, major isomer), 5.85 (d,  $J = 15.7$  Hz, 1H, minor isomer), 4.35 – 4.08 (m, 2H, major isomer+ minor isomer), 3.77 (s, 3H, minor isomer), 3.73 (s, 3H, major isomer), 3.47 (d,  $J = 12.0$  Hz, 1H, minor isomer), 3.34 (d,  $J = 12.2$  Hz, 1H, major isomer), 2.86 (ddd,  $J = 12.2, 10.1, 7.6$  Hz, 1H, major isomer+ minor isomer), 2.27 – 2.12 (m, 1H, major isomer+ minor isomer), 1.38 – 1.22 (m, 1H, major isomer+ minor isomer), 0.86 (t,  $J = 7.4$  Hz, 3H, major isomer), 0.81 (t,  $J = 7.4$  Hz, 3H, minor isomer).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.1, 169.9, 168.3, 167.7, 166.0, 165.9, 149.2, 148.0, 123.4, 123.3, 85.9, 85.7, 62.4, 62.3, 53.0, 52.9, 52.6, 51.8, 51.8, 51.6, 45.6, 45.2, 29.3, 28.4, 25.6, 25.4, 22.9, 22.8, 14.0, 13.9, 11.7, 11.5. ES-HRMS: Calcd for  $C_{16}H_{25}O_6$  [M+H], 313.1651, Found 313.1617.



To a stirring solution of the Michael addition product **4aa** (1 mmol) was added  $\text{NaBH}_4$  (2 mmol). The solution was stirred for 4 h at room temperature, quenched with HCl (1 mL, 1 M). The reaction mixture was extracted with EtOAc (3 x 15 mL). The combined organic layers were dried over  $\text{MgSO}_4$  and the solvents were evaporated in vacuo. The crude product was purified using flash column chromatography eluting with petroleum ether (40-60 °C)/ethyl acetate (1:1) to afford the desired product.

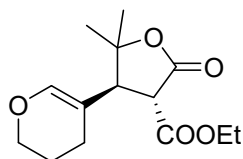
**(3*S*,4*R*)-ethyl-4-((*R*)-1-hydroxybutan-2-yl)-5,5-dimethyl-2-oxotetrahydrofuran-3-carboxylate 6.** Obtained in 73% yield, white oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.30 (q,  $J = 7.1$  Hz, 2H), 3.73 – 3.66 (m, 1H), 3.61 (d,  $J = 12.1$  Hz, 1H), 3.47 (d,  $J = 11.8$  Hz, 1H), 2.84 (dd,  $J = 12.1, 9.2$  Hz, 1H), 1.79 (dd,  $J = 6.8, 4.5$  Hz, 1H), 1.60 (s, 3H), 1.53 – 1.46 (m, 2H), 1.34 (m, 6H), 0.96 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.3, 169.3, 86.2, 62.5, 61.8, 52.5, 49.5, 42.2, 29.3, 22.8, 22.2, 14.0, 11.0. ES-HRMS: Calcd for  $C_{13}H_{23}O_5$  [M+H], 259.1545, Found 259.1516.





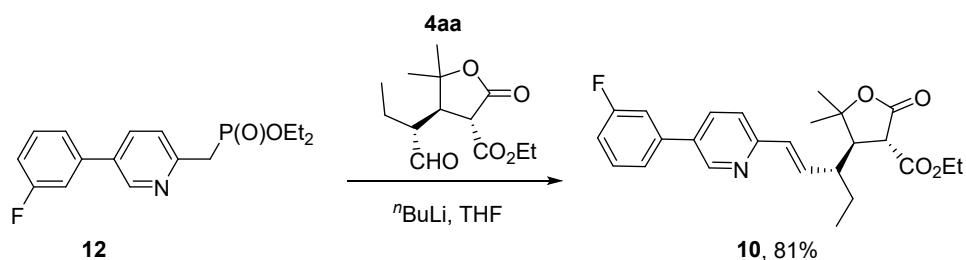
A solution of the Michael addition product **4aa** (1 mmol) in  $\text{CH}_2\text{Cl}_2$  was stirred at room temperature for 2 days and the crude acid was obtained. Then, to a stirring solution of the crude acid in MeOH (4 mL) and EtOH (4 mL) was added a solution of trimethylsilyldiazomethane (2.0 M in diethyl ether) dropwise until the yellow colour persisted. The reaction mixture was stirred for 1.5 h at room temperature. Then, it was quenched with dropwise addition of glacial acetic acid until the yellow colour disappeared. The reaction mixture was diluted with a solution of saturated aq.  $\text{NaHCO}_3$  (15 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layers were dried over  $\text{MgSO}_4$  and the solvents were evaporated in vacuo. The crude product was purified using flash column chromatography eluting with petroleum ether (40-60 °C)/ethyl acetate (3:2) to afford the desired product.

**(3*S*,4*R*)-ethyl-4-((*R*)-1-methoxy-1-oxobutan-2-yl)-5,5-dimethyl-2-oxotetrahydrofuran-3-carboxylate **7**.** Obtained in 95% yield. white oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.35 – 4.18 (m, 2H), 3.85 (d,  $J = 11.6$  Hz, 1H), 3.67 (s, 3H), 2.95 (dd,  $J = 11.6, 7.5$  Hz, 1H), 2.46 (ddd,  $J = 10.2, 7.5, 4.9$  Hz, 1H), 1.71 – 1.59 (m, 2H), 1.57 (s, 3H), 1.36 – 1.29 (m, 6H), 0.92 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.9, 170.3, 167.9, 85.5, 62.2, 51.8, 51.4, 50.6, 46.9, 28.7, 25.2, 22.7, 14.0, 11.9. ES-HRMS: Calcd for  $\text{C}_{14}\text{H}_{23}\text{O}_6$   $[\text{M}+\text{H}]$ , 287.1495, Found 287.1457.

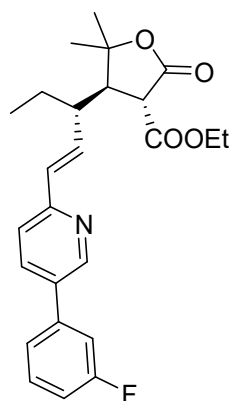


The Michael addition product **8** (304mg, 1mmol) was dissolved in 3ml DMF, and NaH(64.8mg 2.7mmol) was added to the solution under  $\text{N}_2$  atmosphere, This mixture was stirred for 8 h and then  $\text{NH}_4\text{Cl}$ (sat.) was added. The mixture was extracted (EtOAc), dried( $\text{Na}_2\text{SO}_4$ ), concentrated in Vacuo, and then chromatographed (8/1 Petroleum ether/EtOAc) to give (190 mg, 71%) of **8**.

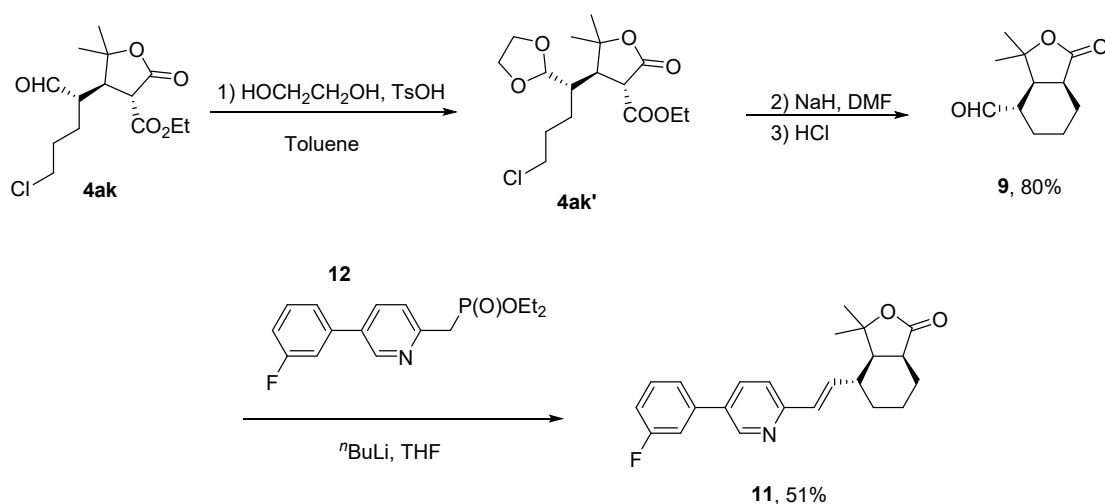
**ethyl (3*S*,4*S*)-4-(3,4-dihydro-2H-pyran-5-yl)-5,5-dimethyl-2-oxotetrahydrofuran-3-carboxylate **8**,** Obtained in 71% yield. white oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.38 (s, 1H), 4.28 (td,  $J = 14.1, 6.8$  Hz, 3H), 4.06 – 3.96 (m, 1H), 3.91 (ddd,  $J = 10.9, 7.0, 4.0$  Hz, 1H), 3.73 (d,  $J = 13.0$  Hz, 1H), 3.18 (d,  $J = 13.0$  Hz, 1H), 2.13 – 1.94 (m, 2H), 1.92 – 1.81 (m, 2H), 1.53 (s, 3H), 1.31 (t,  $J = 7.1$  Hz, 3H), 1.27 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5, 167.6, 143.0, 105.5, 86.5, 65.6, 62.1, 53.4, 49.3, 27.6, 23.1, 22.6, 21.9, 14.1. ES-HRMS: Calcd for  $\text{C}_{14}\text{H}_{21}\text{O}_5$   $[\text{M}+\text{H}]$ , 269.1389, Found 269.1832.



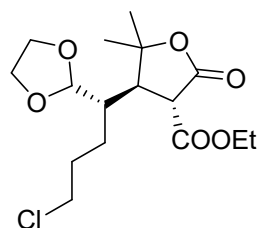
Phosphonate **12** (380 mg, 1mmol) was dissolved in THF (4.0 mL) and cooled to 0 °C. *n*-BuLi (0.6mL of 2.5 M solution in hexanes, 1mmol) was added and the mixture stirred for 10 min. This solution was then added to a solution of aldehyde **4aa** (128.0 mg, 0.5mmol) in THF (4.0 mL) at 0 °C. This mixture was stirred for 2 h and then NH<sub>4</sub>Cl (sat.) was added. The mixture was extracted (EtOAc), dried (Na<sub>2</sub>SO<sub>4</sub>), concentrated in Vacuo, and then chromatographed (8/1)Petroleum ether/EtOAc) to the title compound **10**.(172.0mg, 81% ).



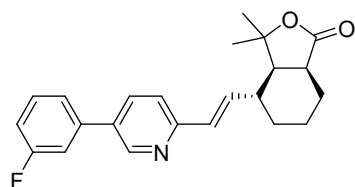
**ethyl (3S,4R)-4-((S,E)-1-(5-(3-fluorophenyl)pyridin-2-yl)pent-1-en-3-yl)-5,5-dimethyl-2-oxotetrahydrofuran-3-carboxylate 10**, Obtained in 81% yield. white oil. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.76 (d, *J* = 2.1 Hz, 1H), 7.82 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.45 (td, *J* = 7.9, 6.0 Hz, 1H), 7.35 (dd, *J* = 10.6, 8.2 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.10 (td, *J* = 8.3, 2.2 Hz, 1H), 6.56 (d, *J* = 15.6 Hz, 1H), 6.36 (dd, *J* = 15.6, 10.0 Hz, 1H), 4.00 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.75 (dq, *J* = 10.7, 7.2 Hz, 1H), 3.46 (d, *J* = 12.2 Hz, 1H), 2.92 (dd, *J* = 12.2, 9.9 Hz, 1H), 2.36 – 2.20 (m, 1H), 1.71 (ddt, *J* = 14.8, 7.5, 3.7 Hz, 1H), 1.65 (s, 3H), 1.49 – 1.42 (m, 1H), 1.40 (s, 3H), 0.93 (t, *J* = 7.2 Hz, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 170.3, 168.0, 163.3 (d, *J* = 247.1 Hz), 154.2, 147.8, 139.8, 135.7, 134.7, 133.8, 131.8, 130.7 (d, *J* = 8.2 Hz), 122.5 (d, *J* = 3.2 Hz), 120.9, 115.0 (d, *J* = 20.9 Hz), 113.80 (d, *J* = 22.3 Hz), 85.9, 62.0, 53.4, 52.7, 46.6, 29.4, 26.0, 22.9, 13.6, 12.0. ES-HRMS: Calcd for C<sub>25</sub>H<sub>29</sub>FN<sub>2</sub>O<sub>4</sub> [M+H], 426.2081, Found 426.2012.



Aldehyde **4ak** (304 mg), ethylene glycol(186mg, 3 mmol) and *p*-toluenesulfonic acid (36 mg, 0.15 mmol) in toluene (15 mL) were heated at reflux for 12 hours. The reaction was cooled to RT and quenched with saturated aqueous sodium bicarbonate solution (20 mL). The resulting mixture was extracted with EtOAc (2 x 50 mL). The combined organic extracts were washed with saturated aqueous sodium bicarbonate solution (50 mL), water (50 mL), brine (100 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), The residue was distilled under reduced pressure, and then purified by Flash Chromatography (8/1 Petroleum ether/EtOAc) to prepare 313mg(89.9%) of **4ak'** which is a protection product of aldehyde **4ak**.



**ethyl (3S,4R)-4-((S)-4-chloro-1-(1,3-dioxolan-2-yl)butyl)-5,5-dimethyl-2-oxotetrahydrofuran-3-carboxylate **4ak'****. Obtained in 90% yield. white oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 4.65 (d, *J* = 4.5 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.97 – 3.65 (m, 5H), 3.57 – 3.41 (m, 2H), 2.82 (dd, *J* = 11.8, 7.3 Hz, 1H), 1.93 – 1.70 (m, 3H), 1.69 – 1.53 (m, 2H), 1.52 (s, 3H), 1.29 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.9, 168.2, 104.5, 86.0, 64.6, 64.5, 61.8, 51.5, 48.4, 45.1, 40.1, 29.6, 28.9, 26.6, 23.3, 14.2. ES-HRMS: Calcd for C<sub>16</sub>H<sub>26</sub>ClO<sub>6</sub> [M+H], 349.1418, Found 349.1407.



Step 1: Compound **4ak'**(313mg 0.90mmol) was desolved in 3mL dry DMF, and add the solution to the sealing tube, added NaH(64.8mg 2.7mmol) was added to the solution under N<sub>2</sub> atmosphere. The mixture was stirred for 8 h and then HCl(1.5 M)(sat.) was added. The mixture was extracted with EtOAc(2x100mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated in vacuo. 10mL Ethyl acetate was added to the resulted product, and followed by 2 drops HCl (12 M). the resulting mixture was stirred for 4 h at room temperature. and then NaHCO<sub>3</sub>(sat.) was added. The mixture was extracted (EtOAc), dried(Na<sub>2</sub>SO<sub>4</sub>), concentrated in Vacuo, and then chromatographed (8/1 Petroleum ether/EtOAc) to give (149.0mg) of **9** (compound **9** is un stable in atmosphere and was used directly for the next step).

Phosphonate **12** (380mg, 1mmol) was dissolved in THF (4.0 mL) and cooled to 0 °C. *n*-BuLi (0.6mL of 2.5 M solution in hexanes, 1mmol) was added and the mixture stirred for 10 min. This solution was then added to a solution of the resulting product from above step (149.0 mg, 0.56mmol) in THF (4.0 mL) at 0 °C. This mixture was stirred for 2 h and then NH<sub>4</sub>Cl (sat.) was added. The mixture was extracted (EtOAc), dried (Na<sub>2</sub>SO<sub>4</sub>), concentrated in Vacuo, and then chromatographed (8/1)Petroleum ether/EtOAc) to give 224.74mg(total yield 51% ) of **11**.

**(3aR,4R,7aS)-4-((E)-2-(5-(3-fluorophenyl)pyridin-2-yl)vinyl)-3,3-dimethylhexahydroisobenzofuran-1(3H)-one **11**** Obtained in 51% yield. white oil. <sup>1</sup>H NMR (400

MHz, Chloroform-*d*)  $\delta$  8.77 (d,  $J = 2.0$  Hz, 1H), 7.82 (dt,  $J = 8.1, 2.6$  Hz, 1H), 7.44 (td,  $J = 8.0, 6.0$  Hz, 1H), 7.39 – 7.24 (m, 4H), 7.14 – 7.06 (m, 1H), 6.59 (s, 1H), 2.41 – 2.16 (m, 3H), 2.06 – 1.95 (m, 1H), 1.91 – 1.83 (m, 1H), 1.75 (dd,  $J = 13.5, 10.8$  Hz, 1H), 1.43 (s, 3H), 1.35 (s, 3H), 1.34 – 1.22 (m, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  176.1, 163.3 (d,  $J = 246.7$  Hz), 154.4, 148.0, 139.9, 137.0, 134.9, 133.8 (d,  $J = 1.7$  Hz), 130.7 (d,  $J = 8.4$  Hz), 129.7, 122.6 (d,  $J = 2.9$  Hz), 121.3, 114.9 (d,  $J = 21.1$  Hz), 113.8 (d,  $J = 22.5$  Hz), 85.8, 56.1, 43.7, 43.7, 32.9, 28.8, 25.3, 25.2, 20.6. ES-HRMS: Calcd for  $\text{C}_{23}\text{H}_{25}\text{FNO}_2$  [M+H], 266.1869, Found 366.1813.

### 3. Determination of the configuration of products 3

#### 3.1 Determination of the absolute configuration of products 3aa

Figure S1. X-ray structure of 3aa

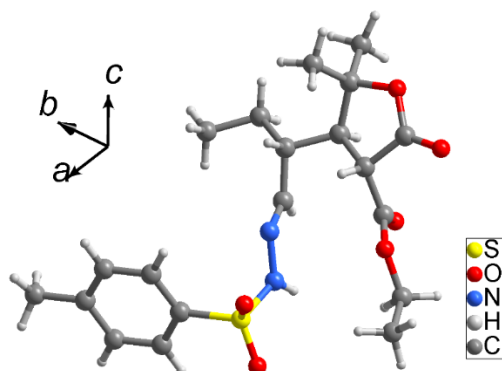


Table S1 Crystal data and structure refinement for 3aa.	
Identification code	<b>3aa</b>
CCDC	1970628
Empirical formula	C <sub>20</sub> H <sub>28</sub> N <sub>2</sub> O <sub>6</sub> S
Formula weight	424.50
Temperature/K	296.15
Crystal system	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a/Å	8.1166(3)
b/Å	13.9920(6)
c/Å	19.8075(9)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	2249.49(16)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.253
μ/mm <sup>-1</sup>	1.593
F(000)	904.0
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	7.736 to 133.144
Index ranges	-7 ≤ h ≤ 9, -16 ≤ k ≤ 16, -22 ≤ l ≤ 23
Reflections collected	10404
Independent reflections	3894 [R <sub>int</sub> = 0.1263, R <sub>sigma</sub> = 0.1278]
Data/restraints/parameters	3894/0/267

Goodness-of-fit on $F^2$	0.990
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0927$ , $wR_2 = 0.2105$
Final R indexes [all data]	$R_1 = 0.1173$ , $wR_2 = 0.2395$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.60/-0.71
Flack parameter	0.05(2)

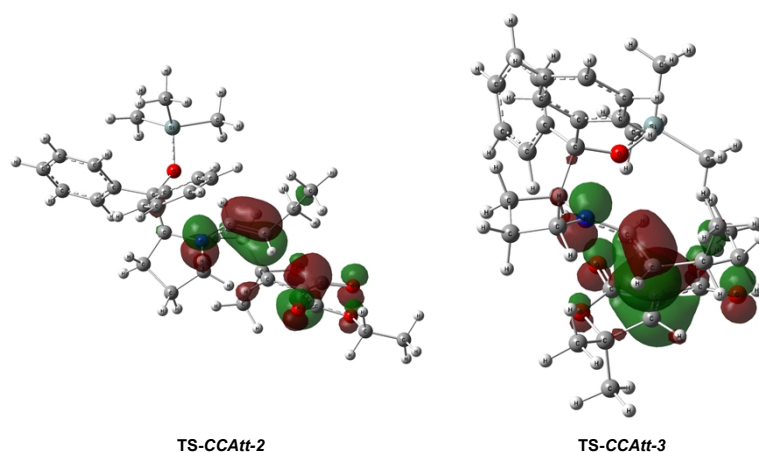
## 4. DFT calculations

### 4.1 Computational Information

To explain the high enantioselectivity and diastereoselectivity, DFT<sup>1</sup> studies have been performed with the Gaussian09 program<sup>2</sup> using the M06<sup>3</sup> method. The 6-31+G\*\* basis set was considered for the system. Ultrafine integral grid was used to get more accurate results. The structures were optimized with SMD<sup>4</sup> method in toluene ( $\epsilon=2.3741$ ). Harmonic vibrational frequency calculations show that all structures were shown to be stationary points (with no imaginary frequency) or transition states (with one imaginary frequency). The 3D molecular figures were prepared using CYLView.<sup>5</sup>

In a reaction, the translational and rotational entropy loss in the transition states will be overestimated significantly for the unequal number of molecules between the reactant and the product. In this study, the entropic corrections were made to the calculated free energies based on “the theory of free volume”.<sup>6</sup> For 2-to-1 (or 1-to-2) reactions, a correction of -2.6 (or 2.6) kcal/mol was made.

HOMO of TS-CCAtt-2 and TS-CCAtt-3



**Figure S2.** HOMO of TS-CCAtt-2 and TS-CCAtt-3. The contours are generated with a uniform value of 0.04. The selected bond lengths are in Å. Calculated at the M06/6-31+G\*\* level.

### 4.2. Calculated total energies and cartesian coordinates

#### INT1

##### *E-s-trans*

E(RM06)= -1353.21305068 Hartree

Sum of electronic and thermal Free Energies= -1352.760642 Hartree

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C,0,2.6009524305,-1.0950563544,0.6776211574  
C,0,3.9221479553,-1.2889565866,0.4919023795  
C,0,0.564297049,0.1784454027,1.331719614  
C,0,0.5134585999,1.3656988894,2.3040776884  
C,0,1.7405508706,2.2169161707,1.9729055547  
C,0,2.7689609102,1.2063877873,1.4857300963  
C,0,-0.3391165525,0.3054468511,0.0596001481  
C,0,-1.8323624394,0.3236325769,0.3926337103  
C,0,0.0873535497,1.5355953938,-0.7349295063  
O,0,-0.0720616999,-0.8259430186,-0.7578184565  
Si,0,-0.6387769759,-2.3996446876,-0.8247966748

C,0,-2.3591563454,-2.5476356236,-1.5523435398  
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***E-s-cis***

E(RM06)= -1353.20859880 Hartree

Sum of electronic and thermal Free Energies= -1352.755180 Hartree

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**Z-s-trans**

E(RM06)= -1353.20887343 Hartree

Sum of electronic and thermal Free Energies= -1352.755884 Hartree

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Si,0,-1.4212943719,2.405392542,0.1052875646  
O,0,-0.5138989684,1.0971768845,-0.4119130677  
C,0,-1.7233729586,2.4283908367,1.9553008948  
H,0,-0.7883330417,2.4909615144,2.5255524623  
H,0,-2.3237827567,3.3150181599,2.204037532  
H,0,-2.2769800668,1.5504224081,2.3099600205  
C,0,-3.0612066678,2.5001679797,-0.7942035537  
H,0,-3.7617210874,1.7179718944,-0.475482219  
H,0,-3.535091427,3.4715466893,-0.5948171252  
H,0,-2.9268974687,2.4140623133,-1.8800152352  
C,0,-0.3332484901,3.8482316597,-0.3737527253  
H,0,-0.164475884,3.8763591172,-1.4577762089  
H,0,-0.7840494024,4.8046628086,-0.0780773483  
H,0,0.6478755654,3.7716165601,0.1135753139  
C,0,2.2244541068,0.781641255,-1.447895653  
H,0,1.5009272388,1.3416466057,-2.0450981187  
C,0,3.3883610609,1.3809456022,-1.1258896884  
H,0,3.5521142722,2.3608053573,-1.5781203934  
C,0,4.4655350366,0.8958019408,-0.2025228433  
H,0,4.1374523358,0.0015302032,0.3433757826  
H,0,4.6365628445,1.6632911519,0.5697358082  
C,0,5.790480516,0.6206485228,-0.9078880944  
H,0,6.5779452013,0.3340106675,-0.1994620358  
H,0,5.6880779127,-0.186256709,-1.6460090877  
H,0,6.1373665219,1.5101287639,-1.4499845448

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**Z-s-cis**

E(RM06)= -1353.20378157 Hartree

Sum of electronic and thermal Free Energies= -1352.750129 Hartree

N,0,1.7671682792,0.607709412,0.7606103232  
C,0,2.7611063811,-0.3302745757,0.5369544889  
C,0,2.854999617,-1.6604886421,0.7467705244  
C,0,0.45047028,0.3327147116,1.3221432005  
C,0,0.1874549311,1.5270413587,2.2433306575  
C,0,1.015803458,2.6698667747,1.6549204153  
C,0,2.233074564,1.9625089698,1.0822278911  
C,0,-0.6372098051,0.0803662032,0.2210833976  
C,0,-1.9619874893,-0.3959714779,0.8347081257  
C,0,-0.7839398595,1.3271377785,-0.6463054231  
O,0,-0.0984847728,-0.9718478286,-0.5528759927  
Si,0,-0.6512170154,-2.1190357599,-1.6328782516  
C,0,-1.6669109514,-1.4025234922,-3.0377394591  
C,0,0.9369963697,-2.8239027433,-2.323479521  
C,0,-1.626458409,-3.4690635852,-0.7747500318  
C,0,-3.148750936,-0.3082683381,0.095888718  
C,0,-4.3427826872,-0.8438601847,0.5685055539  
C,0,-4.3818593911,-1.486103076,1.8029311891  
C,0,-3.2130553084,-1.5872997903,2.549988109  
C,0,-2.019438954,-1.0533833345,2.069403002  
C,0,0.0952953607,1.5153868861,-1.7175175718  
C,0,0.0675591716,2.6864836861,-2.4699163866  
C,0,-0.8428795281,3.6955598406,-2.1654703854  
C,0,-1.7260859632,3.519733854,-1.1034902933  
C,0,-1.6927592812,2.3484369382,-0.3508764531  
H,0,3.647162235,0.146904565,0.1094241755  
H,0,3.8120571071,-2.0838128346,0.4385322313  
H,0,0.5057707211,-0.5938555721,1.8998337784  
H,0,0.5562876789,1.2782191592,3.2484129335  
H,0,-0.8766100317,1.7707732653,2.3419843382  
H,0,0.4618787067,3.1883198708,0.8641069437  
H,0,1.2928350121,3.4159398516,2.406989729  
H,0,3.0442713033,1.9142556069,1.8286060364  
H,0,2.6336248991,2.4607581884,0.1869981469  
H,0,-1.1437532882,-0.5823910749,-3.5454579677  
H,0,-1.8419763419,-2.1921246854,-3.7825659139  
H,0,-2.6492790834,-1.0333748725,-2.7200462593  
H,0,0.7334509173,-3.5526393981,-3.1195191186  
H,0,1.5209845284,-3.3274428263,-1.542427563  
H,0,1.5673775849,-2.0284453966,-2.7424841072

H,0,-1.0696665484,-3.8882251088,0.0737551107  
H,0,-2.5976447827,-3.1184537577,-0.4036070696  
H,0,-1.8165410882,-4.2888558276,-1.4817798111  
H,0,-3.1439794842,0.1884153409,-0.8719779991  
H,0,-5.2452949454,-0.7569630458,-0.0328664635  
H,0,-5.3131995383,-1.9043894896,2.1777771133  
H,0,-3.2227942617,-2.0880756085,3.515654249  
H,0,-1.1296278793,-1.1674975498,2.6844330986  
H,0,0.8137837064,0.7328828424,-1.9526277259  
H,0,0.7632117718,2.8103473113,-3.2975096312  
H,0,-0.8675753625,4.6099827873,-2.7542141612  
H,0,-2.4459887574,4.2970437872,-0.8558777067  
H,0,-2.3857298172,2.2376837903,0.481141711  
C,0,1.8918015764,-2.6247989501,1.3769277311  
H,0,0.8620116914,-2.3979957173,1.0725332478  
H,0,2.100840378,-3.6345649047,0.9928498591  
C,0,1.9819705832,-2.6616527474,2.9021856657  
H,0,1.2742020019,-3.3843607593,3.3300674128  
H,0,2.9903709998,-2.9397466872,3.23448059  
H,0,1.7650781571,-1.6754194972,3.3379533495

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**1a**

E(RM06)= -650.756842330 Hartree

Sum of electronic and thermal Free Energies= -650.596747 Hartree

C,0,-2.4911480761,-0.1193139439,0.024264466  
O,0,-1.9217561559,1.2076378901,-0.0447045918  
C,0,-0.173796596,-0.2756665188,-0.0277762769  
C,0,-1.2925078875,-1.0063450876,0.0263621438  
H,0,-1.3538277276,-2.0908336782,0.0673181136  
C,0,-0.5637809599,1.1600391822,-0.0699114308  
O,0,0.1098946738,2.1553080712,-0.1200122351  
C,0,-3.355310922,-0.334547166,-1.205915325  
H,0,-3.7870196636,-1.3418551579,-1.1952796371  
H,0,-4.1722748183,0.3950711638,-1.2161987007  
H,0,-2.7670496401,-0.2151228412,-2.1223484617  
C,0,-3.2873632998,-0.2281533512,1.3128928986  
H,0,-4.1017445817,0.5044724363,1.306203345  
H,0,-3.720101229,-1.2302764212,1.4102497351  
H,0,-2.6500919424,-0.0349505455,2.1828301818  
C,0,1.1856864834,-0.8600250043,-0.0445533324  
O,0,1.3817082356,-2.0581174784,-0.0904824792  
O,0,2.1415977699,0.0596363579,0.0009529384  
C,0,3.5005741749,-0.4259011649,-0.0145610706  
H,0,3.6276954699,-1.1340441649,0.8128509001

H,0,3.6612476393,-0.9749088166,-0.9506214497  
C,0,4.4050494252,0.7677592185,0.1105573188  
H,0,5.4508638565,0.442561708,0.0974486376  
H,0,4.2521611514,1.4673472658,-0.7177752425  
H,0,4.22396762,1.3029810468,1.0486765546

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## INT2

E(RM06)= -2003.98536542 Hartree

Sum of electronic and thermal Free Energies= -2003.345834 Hartree

C,0,0.5622421346,-0.4628219011,-2.9595715041  
C,0,-0.0694998895,0.7400377087,-2.2476832214  
C,0,-0.3054668112,0.3093779465,-0.7977906814  
C,0,1.1563912981,-1.329481249,-1.8479052566  
H,0,-0.189154845,-1.0291723682,-3.5203701242  
H,0,1.3283710539,-0.1425284528,-3.6731161905  
H,0,-0.9845200308,1.0829243138,-2.7425351956  
H,0,0.637175171,1.580661572,-2.2387455416  
H,0,-0.0747876116,1.1313559711,-0.1044979151  
H,0,2.2600350167,-1.3300009555,-1.8564532126  
H,0,0.8360513711,-2.3828584195,-1.9305913167  
N,0,0.689305474,-0.7347982556,-0.6082501541  
C,0,-1.7573759261,-0.1323128111,-0.4050645632  
C,0,-2.0869564442,-1.4567113243,-1.0855531636  
C,0,-2.54522341,-1.5035529176,-2.4062478299  
C,0,-1.8396039071,-2.6641076884,-0.4286209157  
C,0,-2.7501017336,-2.7202578142,-3.0509016217  
H,0,-2.7461075418,-0.5780099337,-2.9441358924  
C,0,-2.0443703996,-3.8835377196,-1.0690276137  
H,0,-1.4662888097,-2.6465810147,0.5929350375  
C,0,-2.4976014816,-3.9174208129,-2.3848240761  
H,0,-3.1084414061,-2.7305256566,-4.0781992984  
H,0,-1.8398941593,-4.809698471,-0.5354453739  
H,0,-2.6573262936,-4.8686359852,-2.8878866608  
C,0,-2.7930656588,0.9604839805,-0.6839229049  
C,0,-4.1488768749,0.6419666598,-0.8157777792  
C,0,-2.4408125872,2.3139558613,-0.6894846212  
C,0,-5.1151747862,1.6354695221,-0.9518099204  
H,0,-4.4593479721,-0.4011014346,-0.8154175229  
C,0,-3.4001983398,3.3119545608,-0.8320563873  
H,0,-1.3995079609,2.6082537124,-0.5907895351  
C,0,-4.7451487101,2.9773755862,-0.962325138  
H,0,-6.1617014319,1.3556757465,-1.0526922923  
H,0,-3.0915259257,4.3557167564,-0.843042951  
H,0,-5.4976241385,3.7547848285,-1.0731676106

Si,0,-2.6940116716,-0.3042119841,2.313084469  
O,0,-1.664115303,-0.3159800755,0.99697598  
C,0,-4.1128623559,-1.520037467,2.1533828843  
H,0,-3.7580559957,-2.5504495301,2.0256039113  
H,0,-4.7124267589,-1.4892191911,3.0742675183  
H,0,-4.7853146633,-1.2862869865,1.3186964164  
C,0,-3.3754625341,1.4026763218,2.6748153533  
H,0,-4.1144439539,1.7318616229,1.9337863849  
H,0,-3.8730829398,1.3902991152,3.6547835401  
H,0,-2.578348031,2.1559218958,2.7204313608  
C,0,-1.5544123841,-0.8392552293,3.6949017427  
H,0,-0.7062007838,-0.1491191652,3.79907804  
H,0,-2.0836433037,-0.8718966315,4.6564400365  
H,0,-1.1505848181,-1.8423765416,3.5017124082  
C,0,1.0783237366,-1.2275724562,0.6104008025  
H,0,0.7381548868,-0.6319124621,1.4588624548  
C,0,1.843526012,-2.3179950057,0.8265152098  
H,0,2.1432416327,-2.9533219683,-0.0108775513  
C,0,2.2599308394,-2.7572599341,2.1973932395  
H,0,1.9739290761,-1.9837695063,2.9275491904  
C,0,5.2162584242,-0.1240444561,-0.2868825979  
O,0,4.7068317243,0.5233210638,-1.4769209791  
C,0,3.3704929237,1.1728787947,0.2672016847  
C,0,4.2578623406,0.3073696092,0.7722641034  
H,0,4.3252671258,-0.018247718,1.8074884032  
C,0,3.6329098803,1.3042252869,-1.1877761714  
O,0,3.059998726,1.9386960854,-2.0373012038  
C,0,6.6128032121,0.4162231635,-0.0180472274  
H,0,7.0237131957,-0.0264169218,0.8966290451  
H,0,7.2736598907,0.1635174855,-0.8545918443  
H,0,6.5943399317,1.505699204,0.0977578063  
C,0,5.226452434,-1.6229294839,-0.5176891713  
H,0,5.8756614585,-1.861591358,-1.3675500063  
H,0,5.6131279277,-2.1365628742,0.3703677361  
H,0,4.2160158186,-1.9943240502,-0.7213111739  
C,0,2.328591656,1.8376894734,1.0730510218  
O,0,2.0825938166,1.5305491532,2.2225959638  
O,0,1.7156165472,2.8209306608,0.4141619217  
C,0,0.7023280234,3.5404637717,1.1434764013  
H,0,-0.1125135587,2.8422976877,1.3873196485  
H,0,1.1266719213,3.8893438568,2.0921810955  
C,0,0.2447266291,4.6771270254,0.2723072874  
H,0,-0.5847816407,5.2047559775,0.7563243313  
H,0,1.0554947696,5.3928754118,0.0997006314

H,0,-0.095313959,4.3170528414,-0.7065566732  
C,0,1.6564390553,-4.1002277146,2.5974226615  
H,0,1.9403908451,-4.8858782212,1.8844683775  
H,0,1.9880229911,-4.4193741602,3.5939173715  
H,0,0.5594130521,-4.0491748519,2.6034155895  
H,0,3.3588239399,-2.8393518057,2.2606609133

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**TS-CCAtt-endo**

E(RM06)= -2003.96930771 Hartree

Sum of electronic and thermal Free Energies= -2003.328367 Hartree

C,0,-0.8506107627,1.1749247052,2.3623922256  
C,0,0.3429862645,1.6958570898,1.5443578619  
C,0,0.5201504232,0.7469835626,0.351096154  
C,0,-1.1452126045,-0.2197789733,1.8222411617  
H,0,-0.63779793,1.1497989179,3.4362846721  
H,0,-1.7251024548,1.8181432925,2.2099856473  
H,0,1.2573138532,1.7487783162,2.1427870047  
H,0,0.1546056552,2.7153409647,1.1876273406  
H,0,0.4071549512,1.2639224702,-0.6114863908  
H,0,-2.2155422331,-0.4486380421,1.8079960294  
H,0,-0.6374657507,-1.013942208,2.3928409256  
N,0,-0.6120920645,-0.1796598857,0.4593395319  
C,0,1.8998725634,0.0052553542,0.2788891528  
C,0,1.9669274585,-1.0287998948,1.4044303341  
C,0,2.2689422288,-0.6793903464,2.726591377  
C,0,1.6025317217,-2.3535258316,1.1475833842  
C,0,2.2019629568,-1.6185349923,3.7524745218  
H,0,2.5679429518,0.3374708797,2.9717801423  
C,0,1.5331636166,-3.2961458925,2.1697937538  
H,0,1.3552277321,-2.6469564746,0.1302876987  
C,0,1.8297090977,-2.9322105258,3.4801379715  
H,0,2.4451018087,-1.3180334946,4.7692956344  
H,0,1.2416712877,-4.3184776569,1.9369044043  
H,0,1.776613267,-3.665899906,4.28122292  
C,0,3.0527907395,1.013480466,0.277121306  
C,0,4.2923504454,0.7186197294,0.852044033  
C,0,2.9272164483,2.220124899,-0.4225514703  
C,0,5.3631348837,1.6049408343,0.7509924812  
H,0,4.4327606916,-0.2179515823,1.387323103  
C,0,3.9901730908,3.1111141674,-0.5195911966  
H,0,1.9941235649,2.4708068701,-0.9231199478  
C,0,5.2148860232,2.8090468879,0.0708209507  
H,0,6.3156230036,1.3485670116,1.209725753  
H,0,3.8610432669,4.0425346376,-1.0664008243



H,0,6.0471278871,3.5051504062,-0.0038997259  
Si,0,3.0397738655,-1.2757790695,-2.0035667919  
O,0,1.8684842782,-0.6482123122,-0.9759131021  
C,0,4.2939419492,-2.3492684587,-1.1198055158  
H,0,3.8303686057,-3.1884225258,-0.5868957823  
H,0,4.9863423189,-2.7694161966,-1.86295786  
H,0,4.8976081408,-1.7825047016,-0.4000683988  
C,0,3.930875433,0.0665505159,-2.9528655592  
H,0,4.642341162,0.625049864,-2.3322239002  
H,0,4.4976638819,-0.3908888421,-3.7760020854  
H,0,3.2268720385,0.7832477821,-3.3941553204  
C,0,2.0075064095,-2.3067036907,-3.1723965573  
H,0,1.2824134313,-1.6839494978,-3.7120288641  
H,0,2.6375865289,-2.8064752358,-3.9198591663  
H,0,1.4488177638,-3.0837740844,-2.6332099135  
C,0,-0.9901968231,-0.980130391,-0.5380157291  
H,0,-0.4492779804,-0.8237893786,-1.4710303364  
C,0,-2.0760348965,-1.8386648579,-0.5117199418  
H,0,-2.4288490826,-2.1628531179,0.4677087842  
C,0,-2.2664570369,-2.8213852072,-1.6369154418  
H,0,-3.3191781373,-2.838172406,-1.9627321132  
H,0,-1.6943211866,-2.4803859808,-2.5134283943  
C,0,-4.9051196358,-0.7788195766,-0.1760425795  
O,0,-4.9775097535,0.1117324576,0.9579190964  
C,0,-3.3248835649,0.9189843011,-0.3953397345  
C,0,-3.6342095307,-0.3446823111,-0.8914635369  
H,0,-3.5159700374,-0.5916616328,-1.9445335633  
C,0,-4.1114277281,1.1659285849,0.8028585826  
O,0,-4.1049963398,2.0700173102,1.6105700778  
C,0,-6.0834379905,-0.4731445283,-1.099234743  
H,0,-6.0764544038,-1.1490399026,-1.9636588988  
H,0,-7.024961779,-0.6123237135,-0.5559056057  
H,0,-6.0404623021,0.5588937284,-1.4648039691  
C,0,-5.030151126,-2.1884737529,0.3661225722  
H,0,-6.0244478259,-2.3102586251,0.8106787484  
H,0,-4.924125104,-2.9349602712,-0.4293361658  
H,0,-4.2938479976,-2.392459791,1.1490413451  
C,0,-2.3666895201,1.7927465553,-1.0281690794  
O,0,-1.7333136401,1.4932191255,-2.0360630785  
O,0,-2.2282497895,2.986676223,-0.4179918784  
C,0,-1.3078941521,3.9057731585,-1.012860535  
H,0,-0.297600409,3.4682855828,-0.9982678269  
H,0,-1.5752619865,4.0612966261,-2.0658377201  
C,0,-1.3745261368,5.1830146727,-0.219560931

H,0,-0.670193694,5.9173011627,-0.6260294988  
H,0,-2.3813656533,5.6126625469,-0.2567400063  
H,0,-1.1223638169,5.0075955952,0.8328694306  
C,0,-1.8526670872,-4.2365203412,-1.2546500335  
H,0,-2.4357686535,-4.5948554745,-0.3951529164  
H,0,-2.0075080394,-4.9423796095,-2.0794888195  
H,0,-0.7935535132,-4.2780223293,-0.9677375389

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**TS-CCAtt-2**

E(RM06)= -2003.96080594 Hartree

Sum of electronic and thermal Free Energies= -2003.321629 Hartree

C,0,-0.2317995702,1.7100938623,-2.5377682586  
C,0,1.1665012263,1.0928620323,-2.4833946417  
C,0,1.1391567903,0.1131530926,-1.3010532924  
C,0,-0.6718160653,1.7021267912,-1.0849016201  
H,0,-0.2378329968,2.7113168546,-2.978982664  
H,0,-0.9116852742,1.07811363,-3.1261215866  
H,0,1.9126138018,1.8768900265,-2.3162317317  
H,0,1.4426774964,0.5881822246,-3.4142301397  
H,0,1.0683478873,-0.9280392767,-1.6456229649  
H,0,-1.7554593661,1.7444681347,-0.9449730771  
H,0,-0.2251984046,2.5344176107,-0.5164108557  
N,0,-0.1208683742,0.4311950033,-0.6090489828  
C,0,2.3763799391,0.1592690648,-0.3399632364  
C,0,2.3369329259,1.466962918,0.4533839686  
C,0,2.8253759299,2.6739790876,-0.0622418136  
C,0,1.6931929189,1.5005965336,1.6936987931  
C,0,2.6680470439,3.869691091,0.6345431335  
H,0,3.3532326389,2.6912411124,-1.0136290061  
C,0,1.5314231321,2.6931569141,2.3927667284  
H,0,1.3059724682,0.5763829579,2.1158675589  
C,0,2.0150956348,3.8862624876,1.8636085653  
H,0,3.0622454528,4.7910930559,0.2116608122  
H,0,1.0208303703,2.6864564698,3.3535236565  
H,0,1.8900010904,4.8199595354,2.406907629  
C,0,3.6820146712,-0.075829524,-1.1045040748  
C,0,4.8927517197,0.467523814,-0.663178787  
C,0,3.7203621772,-0.9621649624,-2.1875197313  
C,0,6.0951311526,0.1575472667,-1.2943653339  
H,0,4.9044675163,1.1426483526,0.1895121013  
C,0,4.9176611648,-1.2698499621,-2.8255523387  
H,0,2.8095836289,-1.4414096044,-2.5398635208  
C,0,6.1122265109,-0.7069719278,-2.3841067578  
H,0,7.0206904127,0.597698826,-0.9299598343

H,0,4.9157625279,-1.9585411471,-3.6674381486  
H,0,7.0491357063,-0.9463953914,-2.8815743502  
Si,0,3.1044831528,-1.841154231,1.5833752732  
O,0,2.1584752243,-0.9401547604,0.525767939  
C,0,4.1841658236,-0.7959794029,2.6993138089  
H,0,3.604204455,-0.0954649158,3.3125149449  
H,0,4.7294543916,-1.4616590638,3.3832543562  
H,0,4.9341791414,-0.2206574839,2.1427107834  
C,0,4.1664870932,-3.0745669538,0.6620963749  
H,0,5.0115144386,-2.6000477967,0.1472680403  
H,0,4.5811071929,-3.8025022491,1.3733402851  
H,0,3.5851275876,-3.6343890366,-0.0814770371  
C,0,1.7926345923,-2.7231437506,2.5831425321  
H,0,1.1426147868,-3.3289114004,1.9373768746  
H,0,2.2410439776,-3.3978740465,3.3239487798  
H,0,1.1605662996,-2.0086046556,3.1282940008  
C,0,-0.6827641343,-0.3607454374,0.3123492831  
H,0,-0.0935347841,-1.2465023859,0.5492224221  
C,0,-1.9324685105,-0.1983958138,0.8870697327  
H,0,-2.3856524715,0.7946331943,0.8213901329  
C,0,-2.2996424766,-0.9672168763,2.1252877707  
H,0,-3.3330675279,-1.3404064517,2.0378057119  
H,0,-1.6544488426,-1.8530432871,2.2293849467  
C,0,-3.1115155207,-2.292604371,-1.0854712469  
O,0,-4.2194249092,-2.9074948902,-0.3998547078  
C,0,-4.4972638706,-0.6491342462,-0.1915209384  
C,0,-3.2123222774,-0.8282674979,-0.7022497559  
H,0,-2.7421302827,-0.1035401992,-1.364893714  
C,0,-5.0923437268,-1.950530091,0.0687536311  
O,0,-6.139125523,-2.2823427554,0.5793016097  
C,0,-3.358117011,-2.4063407708,-2.5887662314  
H,0,-2.5301647894,-1.9510054975,-3.1483011271  
H,0,-3.4314392264,-3.4620621151,-2.8740118313  
H,0,-4.2887932009,-1.9032623863,-2.8743651747  
C,0,-1.8611458337,-3.0576963072,-0.7085496431  
H,0,-1.9636899077,-4.0995784356,-1.0342274681  
H,0,-0.9828096593,-2.6311630567,-1.2098244845  
H,0,-1.6972106291,-3.0555575611,0.3730146684  
C,0,-5.0321546136,0.6639403191,0.0892799165  
O,0,-4.3981122333,1.6999737746,-0.095708164  
O,0,-6.2834699862,0.6601936615,0.5720734315  
C,0,-6.8570830179,1.9406628272,0.8651818058  
H,0,-6.2177171222,2.4639925493,1.587812746  
H,0,-6.8766654856,2.5443615418,-0.0514854705

C,0,-8.2394322668,1.7002189387,1.4091157685  
H,0,-8.7215842256,2.6560723406,1.6429483228  
H,0,-8.8619547059,1.1704118771,0.6800144676  
H,0,-8.2026323226,1.0991782046,2.3240064919  
C,0,-2.2061080028,-0.1094691639,3.382075963  
H,0,-2.8692743992,0.7624470787,3.3047596616  
H,0,-2.5001527542,-0.6729350756,4.2756628612  
H,0,-1.1858458208,0.266688698,3.5386583082

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### TS-CCAtt-3

E(RM06)= -2003.95482598 Hartree

Sum of electronic and thermal Free Energies= -2003.310975 Hartree

C,0,-0.9256125457,-3.2406873726,-2.0065318728  
C,0,-1.6072626236,-1.8773441052,-2.1334212836  
C,0,-0.9425812754,-0.9779540376,-1.0835950622  
C,0,-0.5326931581,-3.3008120491,-0.5405560353  
H,0,-1.5770517556,-4.0693661792,-2.3006819453  
H,0,-0.0261960913,-3.2770422019,-2.6348881064  
H,0,-2.6801449985,-1.9752335675,-1.9390941377  
H,0,-1.5013133025,-1.4510470823,-3.1353630666  
H,0,-0.222400264,-0.291635868,-1.548464843  
H,0,0.2837748906,-3.9920572565,-0.3154838209  
H,0,-1.3895961714,-3.5720833869,0.0966102687  
N,0,-0.1529302886,-1.9167905006,-0.2504604036  
C,0,-1.905347806,-0.0882062622,-0.2343457533  
C,0,-2.7417935866,-0.9830179484,0.6832850571  
C,0,-3.8976227799,-1.6431772832,0.2480243123  
C,0,-2.2913506006,-1.2445474692,1.9809842378  
C,0,-4.5696403382,-2.5398303861,1.0753346134  
H,0,-4.3006674343,-1.4472113888,-0.7431784755  
C,0,-2.9585376445,-2.1417701831,2.8107108764  
H,0,-1.4012523324,-0.7351350617,2.3437249178  
C,0,-4.1000186615,-2.7985299432,2.3598789271  
H,0,-5.4690641491,-3.0319627331,0.7115744181  
H,0,-2.581730646,-2.3250653257,3.8150675889  
H,0,-4.6248108765,-3.4978703745,3.0067490331  
C,0,-2.7234360641,0.8303546498,-1.1455671735  
C,0,-3.999310191,1.2707209353,-0.7801105804  
C,0,-2.1469413057,1.3720220091,-2.3015910598  
C,0,-4.6901903154,2.198738398,-1.5559851375  
H,0,-4.4640959366,0.8925487764,0.1279122959  
C,0,-2.8390808643,2.2900773941,-3.084607696  
H,0,-1.1311220024,1.1095765787,-2.5908805356  
C,0,-4.1165395164,2.7052955592,-2.7180842128

H,0,-5.6812437614,2.5240746222,-1.2467466096  
H,0,-2.3668704697,2.693876341,-3.9772877996  
H,0,-4.6561885821,3.4263947377,-3.3278494242  
Si,0,-1.0866517494,2.2151512683,1.2690143203  
O,0,-1.033290582,0.6983825162,0.5503552794  
C,0,-2.6065169594,2.4533264735,2.3376703023  
H,0,-2.7470736052,1.6343767237,3.0544914068  
H,0,-2.4912864988,3.3823743247,2.913694223  
H,0,-3.5243827792,2.5512109304,1.7448055537  
C,0,-0.9516192323,3.5863114893,0.0091008826  
H,0,-1.8635060323,3.7061743795,-0.5890463417  
H,0,-0.7640768335,4.5414294096,0.5199053276  
H,0,-0.1135226751,3.3924964324,-0.674422571  
C,0,0.4584519183,2.1588294144,2.3181271866  
H,0,1.3326357093,2.0129695929,1.6683452511  
H,0,0.6035636805,3.0931021138,2.8770693719  
H,0,0.4279626501,1.3361620437,3.0462153959  
C,0,0.8640820422,-1.5172223106,0.5050895944  
H,0,0.8717151583,-0.4346544471,0.6672131812  
C,0,1.9513793213,-2.2231873884,1.0170512223  
H,0,1.9996866042,-3.2991782425,0.8255445239  
C,0,2.4920312506,-1.8080624236,2.3664079834  
H,0,3.5272554451,-2.1613913743,2.4762730007  
H,0,2.5460791487,-0.71224538,2.4253771488  
C,0,3.3788247819,-1.8140041514,-1.6225324816  
O,0,2.4753729169,-0.8964647278,-2.2775724693  
C,0,3.2031384372,0.1190764932,-0.3581818287  
C,0,3.4661056968,-1.2513926154,-0.2230596044  
H,0,4.229921907,-1.6310454073,0.4548180542  
C,0,2.4320530631,0.2944758679,-1.5752214279  
O,0,1.764473187,1.2127421549,-2.007860579  
C,0,4.7551510288,-1.6876894032,-2.2801659203  
H,0,5.4770780293,-2.3585303477,-1.7985713229  
H,0,4.6795738764,-1.9639008583,-3.3383862086  
H,0,5.1354423209,-0.6633976128,-2.2124589704  
C,0,2.8743845573,-3.2253636741,-1.8097948283  
H,0,2.891695547,-3.486638163,-2.8744103447  
H,0,3.5256470382,-3.9286380841,-1.2761299605  
H,0,1.855637009,-3.352260672,-1.4446958922  
C,0,3.6272536038,1.1219729365,0.5886998192  
O,0,4.2693020092,0.8889040081,1.6065943715  
O,0,3.2802201848,2.3779061614,0.2332854506  
C,0,3.7282252538,3.4238256725,1.1029055948  
H,0,3.4292329105,3.1935304338,2.1343245153

H,0,4.8257593137,3.4599991012,1.0842265024  
C,0,3.1153499009,4.7088457942,0.6161186111  
H,0,3.4429010311,5.543825471,1.2456367657  
H,0,3.4083041464,4.9203039575,-0.4181259312  
H,0,2.0203196035,4.6593998801,0.6531248071  
C,0,1.6508751218,-2.3509007717,3.5154897105  
H,0,1.5782996741,-3.4461880699,3.4770746342  
H,0,2.0780932443,-2.0784482945,4.4884018488  
H,0,0.6263568182,-1.9548082198,3.4761836132

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### INT3

E(RM06)= -2003.98674107 Hartree

Sum of electronic and thermal Free Energies= -2003.342056 Hartree

C,0,-0.9237419715,1.1304196367,2.3750160802  
C,0,0.3740734721,1.6261734367,1.726549833  
C,0,0.550537491,0.8172799837,0.4351001145  
C,0,-1.0865680151,-0.2846861757,1.851224547  
H,0,-0.8808687536,1.1521426476,3.4678354811  
H,0,-1.7845310807,1.7332451756,2.0585551956  
H,0,1.2267466051,1.4785035926,2.3959620219  
H,0,0.3326499196,2.6984260396,1.5055267813  
H,0,0.3503861869,1.4217716767,-0.4585535738  
H,0,-2.1193356939,-0.6342037927,1.8465881574  
H,0,-0.4594365046,-1.0064669347,2.3948332692  
N,0,-0.5509660361,-0.1799347024,0.4769468992  
C,0,1.933793017,0.1233870549,0.2165380801  
C,0,2.0980337821,-1.0022096233,1.2415023639  
C,0,2.5078101806,-0.7644550825,2.5592607269  
C,0,1.7227065906,-2.3037021974,0.8990975342  
C,0,2.5188228997,-1.7889424881,3.5025898159  
H,0,2.8393856222,0.2264874902,2.8619352002  
C,0,1.7304328099,-3.3310049596,1.8383724004  
H,0,1.4158089061,-2.5120436608,-0.1224096771  
C,0,2.1226880122,-3.0761266818,3.1493948649  
H,0,2.8433890462,-1.576327369,4.5186941554  
H,0,1.4287336342,-4.3330560356,1.5393315688  
H,0,2.1298128973,-3.8749404368,3.8872284436  
C,0,3.0587175491,1.1605023902,0.2462724007  
C,0,4.3571001564,0.8030601245,0.6232542116  
C,0,2.8470608633,2.4588933079,-0.2302677368  
C,0,5.4052226765,1.7168562072,0.5465222804  
H,0,4.5591055802,-0.2033917287,0.9838825762  
C,0,3.8897959829,3.376998792,-0.3018369204  
H,0,1.8613736082,2.771659124,-0.5681495883

C,0,5.1746252274,3.0105460046,0.0889184989  
H,0,6.4049893475,1.4126164532,0.8480707405  
H,0,3.6956319566,4.3810866284,-0.6718278619  
H,0,5.9903671084,3.7275059109,0.0337787071  
Si,0,2.9289847055,-0.8834461708,-2.2751630236  
O,0,1.8303333585,-0.4208935633,-1.0853504652  
C,0,4.1596025498,-2.1500811669,-1.6536887029  
H,0,3.6717052913,-3.0749399596,-1.3215537996  
H,0,4.8445007055,-2.413596292,-2.4718033931  
H,0,4.772603717,-1.7732546347,-0.825596639  
C,0,3.8370246097,0.5730708077,-3.0144010057  
H,0,4.5991912677,0.9850559234,-2.3417006171  
H,0,4.3491806988,0.2435340056,-3.9294694365  
H,0,3.150105181,1.3812775983,-3.2943698859  
C,0,1.798775278,-1.6473518853,-3.5532772031  
H,0,1.0603279725,-0.9201751782,-3.9151616783  
H,0,2.3724528715,-1.9965173901,-4.4218863563  
H,0,1.2550168969,-2.5121149073,-3.148417496  
C,0,-1.0197146021,-0.7330692431,-0.5945556507  
H,0,-0.4877379851,-0.5031290721,-1.5161734367  
C,0,-2.2126959582,-1.5948940674,-0.6376589072  
H,0,-2.2889578506,-2.1279788087,0.3209414576  
C,0,-2.0966746491,-2.6041833298,-1.7804345213  
H,0,-3.0827414611,-3.0532765254,-1.954690758  
H,0,-1.8518898924,-2.0546473168,-2.703478521  
C,0,-4.7900909481,-1.2897132703,-0.1459404562  
O,0,-4.8917221157,-0.5843049707,1.1093631257  
C,0,-3.4807296026,0.649372328,-0.1806204969  
C,0,-3.5176387356,-0.6978186322,-0.815468128  
H,0,-3.6617809604,-0.6366037736,-1.9057527142  
C,0,-4.2478427589,0.6460707125,1.019676656  
O,0,-4.3837215272,1.4461884496,1.9312985575  
C,0,-6.0077234051,-0.937256143,-0.9904254835  
H,0,-5.9966679972,-1.4953636885,-1.9358956796  
H,0,-6.9267392269,-1.1895746365,-0.448420703  
H,0,-6.0266354773,0.1339915655,-1.2221735199  
C,0,-4.8196548264,-2.7663957202,0.1947572977  
H,0,-5.7434849908,-2.9803567125,0.7448050443  
H,0,-4.8192683608,-3.3893696433,-0.7073311965  
H,0,-3.9853404373,-3.0716547905,0.836767903  
C,0,-2.6610787142,1.6638217397,-0.7097673974  
O,0,-1.9090505835,1.5008002727,-1.6900914918  
O,0,-2.7004755499,2.8589991612,-0.0601168592  
C,0,-1.8313793457,3.8765560754,-0.5453721123

H,0,-0.7923106508,3.5086071549,-0.5512781489  
H,0,-2.0856481008,4.1211135546,-1.5857130457  
C,0,-1.9850852776,5.0694345954,0.3613855324  
H,0,-1.3305881176,5.8846497941,0.0321295076  
H,0,-3.0183536882,5.433172492,0.3563899293  
H,0,-1.7264396874,4.8133434154,1.3959185175  
C,0,-1.0739438493,-3.6956373461,-1.5198191541  
H,0,-1.3120627589,-4.2472693794,-0.59926904  
H,0,-1.0348616872,-4.4182345701,-2.3427810213  
H,0,-0.0624793976,-3.2813686656,-1.3997519748

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**ee-TS-CCAtt-endo**

E(RM06)= -2003.96868864 Hartree

Sum of electronic and thermal Free Energies= -2003.325830 Hartree

C,0,-1.4464030603,2.6235244475,-0.8434751418  
C,0,-0.4156433818,1.708044382,-1.5100218864  
C,0,-0.0124519246,0.6483097984,-0.4636611821  
C,0,-1.1985326699,2.442516894,0.643766533  
H,0,-1.3383957291,3.667555044,-1.1562315708  
H,0,-2.4614115519,2.2944732953,-1.0995364033  
H,0,0.4590964662,2.2814553747,-1.8307798879  
H,0,-0.8274627573,1.2277427439,-2.4028802922  
H,0,-0.351331423,-0.3554012624,-0.7478079045  
H,0,-2.0871813919,2.5914167763,1.2671918709  
H,0,-0.4011722023,3.1068201873,1.0100959489  
N,0,-0.767612127,1.044087054,0.7396555254  
C,0,1.5390026208,0.5302052552,-0.2595033284  
C,0,2.0168751956,1.7317611124,0.5563886479  
C,0,2.294162097,2.9772544315,-0.020057468  
C,0,2.0686291216,1.6306489032,1.950712249  
C,0,2.6210272601,4.0785611281,0.7679070922  
H,0,2.2696687077,3.1014597636,-1.100323194  
C,0,2.3939274624,2.7291071801,2.7412582697  
H,0,1.8402862368,0.6766741451,2.4226790845  
C,0,2.6716514676,3.9605276868,2.1534509224  
H,0,2.8389475044,5.0313033511,0.2902329515  
H,0,2.4266564582,2.6200405855,3.8233107931  
H,0,2.928176027,4.819449583,2.7693510139  
C,0,2.2281783872,0.347922761,-1.6178609276  
C,0,3.5124687956,0.83864412,-1.8679021376  
C,0,1.6298842739,-0.4522501078,-2.6011388324  
C,0,4.1724513884,0.5591798439,-3.0633336605  
H,0,4.0186156908,1.4450509799,-1.1207702882  
C,0,2.2818235589,-0.7263534241,-3.7982150683



H,0,0.6426839422,-0.8840701597,-2.4432961558  
C,0,3.5571445237,-0.2197545103,-4.0371534377  
H,0,5.1719452153,0.9557597407,-3.2285271482  
H,0,1.7878687164,-1.3434873618,-4.5451258599  
H,0,4.0674650706,-0.4342126307,-4.9733529176  
Si,0,3.1018193301,-1.6200473577,0.7313297564  
O,0,1.7362062493,-0.6652343242,0.4833621814  
C,0,4.628812239,-0.6486604187,1.2160423644  
H,0,4.4715480201,-0.0598590948,2.1282006557  
H,0,5.4380995563,-1.3648055352,1.4194171875  
H,0,4.9855538946,0.0283381334,0.4310319866  
C,0,3.4858420716,-2.7023178039,-0.7452426577  
H,0,3.9146679439,-2.1400225428,-1.5835613852  
H,0,4.2209618678,-3.4621393075,-0.4438052246  
H,0,2.5962803764,-3.2305286412,-1.1118744449  
C,0,2.6032607623,-2.686967994,2.1841734661  
H,0,1.656701191,-3.2171491172,2.0150088752  
H,0,3.3751716882,-3.4430480962,2.3817779544  
H,0,2.4998857338,-2.0787599801,3.092342211  
C,0,-1.1323961848,0.2769337748,1.7708725171  
H,0,-1.7686180715,0.7995094051,2.4890909086  
C,0,-0.9527800893,-1.0841758145,1.9317241041  
H,0,-0.1046350053,-1.5326343284,1.424379137  
C,0,-1.3821279646,-1.7026810949,3.2375913557  
H,0,-2.3846896357,-1.3298668904,3.501331194  
H,0,-1.4888932199,-2.7913976656,3.1068808097  
C,0,-1.9834395472,-2.8822197419,-0.3686007204  
O,0,-1.9043386642,-2.2184410611,-1.650108236  
C,0,-3.0730483729,-0.8274811383,-0.2686125133  
C,0,-2.5382385316,-1.8125852558,0.5566960319  
H,0,-3.0328285529,-2.118190423,1.4759819176  
C,0,-2.622039565,-1.0454648041,-1.6317980695  
O,0,-2.7481648199,-0.3961283608,-2.6483971529  
C,0,-0.6158124773,-3.467188534,-0.0843790873  
H,0,-0.590263113,-3.9259939907,0.9118694151  
H,0,-0.3942585895,-4.2460406742,-0.8236296417  
H,0,0.1672875311,-2.7044080771,-0.1486648267  
C,0,-3.0190037716,-3.9996509993,-0.474458804  
H,0,-2.7159874641,-4.7136809475,-1.2486695883  
H,0,-3.1015893273,-4.5345114236,0.4799618448  
H,0,-4.0052948055,-3.5997259182,-0.7351532806  
C,0,-3.8934778526,0.2421786749,0.2438122838  
O,0,-4.061713015,0.4438068927,1.4429703432  
O,0,-4.4632416373,1.0084471464,-0.7047766781

C,0,-5.2649664198,2.1019111714,-0.2417817027  
H,0,-6.0815050524,1.7129247543,0.3800247076  
H,0,-4.6530118887,2.7536213847,0.3977610961  
C,0,-5.776282695,2.8295625185,-1.4556676172  
H,0,-6.3985286246,3.6781895817,-1.1507054328  
H,0,-4.9483015135,3.210662482,-2.0644308577  
H,0,-6.381261959,2.1674085647,-2.0844960185  
C,0,-0.4232078447,-1.4313321538,4.3909910513  
H,0,-0.3261017353,-0.3530683617,4.5760456401  
H,0,-0.7682948689,-1.9005085149,5.3207656483  
H,0,0.5795467705,-1.8201553766,4.1731446705

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**dr1-TS-CCAtt-endo**

E(RM06)= -2003.96618239 Hartree

Sum of electronic and thermal Free Energies= -2003.324698 Hartree

C,0,0.9991250775,-2.5579781566,-0.4886388195  
C,0,-0.2605426271,-2.0023949908,-1.1602645848  
C,0,-0.5416410377,-0.6305733769,-0.5200395953  
C,0,1.1046177056,-1.8004736889,0.8229745227  
H,0,0.9453202083,-3.6405910631,-0.3294492599  
H,0,1.872111418,-2.3428049357,-1.1153262496  
H,0,-1.1103201536,-2.6770554601,-1.0248010715  
H,0,-0.1080459353,-1.8953450855,-2.2382694038  
H,0,-0.3859560301,0.1774513325,-1.2494430743  
H,0,2.1294378222,-1.6969598538,1.1879144083  
H,0,0.5069399741,-2.2698128842,1.6219385457  
N,0,0.515411173,-0.4938130831,0.5041367346  
C,0,-1.9873850021,-0.4530766195,0.0588307891  
C,0,-2.1499663558,-1.3422612288,1.2930764434  
C,0,-2.4706532776,-2.7007357842,1.1922969162  
C,0,-1.9070841236,-0.8154483044,2.5646492171  
C,0,-2.5119044437,-3.5134271632,2.3221543347  
H,0,-2.715367803,-3.134939599,0.2250051401  
C,0,-1.9461100486,-1.6257753472,3.6962358523  
H,0,-1.6919724826,0.2457537454,2.6641335305  
C,0,-2.240148932,-2.981397118,3.5798196948  
H,0,-2.7671093178,-4.5655931714,2.2162863992  
H,0,-1.748746903,-1.1912249889,4.6742200188  
H,0,-2.2716806467,-3.6154826533,4.4629478335  
C,0,-3.0653986271,-0.7101511963,-0.9950729826  
C,0,-4.387432034,-0.8955850234,-0.5731742586  
C,0,-2.8158051782,-0.6354465434,-2.367998235  
C,0,-5.4232250722,-1.0258569737,-1.4906306627  
H,0,-4.6081129981,-0.9292839756,0.4928579277

C,0,-3.8522033391,-0.7644922993,-3.2914183056  
H,0,-1.8082925255,-0.4722768953,-2.7433115329  
C,0,-5.1584147337,-0.9643239022,-2.8574773024  
H,0,-6.4416398093,-1.171100535,-1.1368848925  
H,0,-3.630127979,-0.7087653377,-4.3548071933  
H,0,-5.9658372058,-1.0680912266,-3.5787815442  
Si,0,-2.5075397682,2.3533075192,-0.2125327476  
O,0,-2.1143309277,0.8875420198,0.5051340163  
C,0,-4.3262481999,2.5101202075,-0.617629399  
H,0,-4.9585747775,2.22924445,0.2342015848  
H,0,-4.5410597084,3.5620418304,-0.855395953  
H,0,-4.6283816133,1.9087236207,-1.4834240713  
C,0,-1.5002914614,2.7144164417,-1.7508952673  
H,0,-1.9028750035,2.1932863096,-2.6291924974  
H,0,-1.5556611297,3.7921316285,-1.9631994768  
H,0,-0.4365751416,2.4553862075,-1.6673700656  
C,0,-2.0994652268,3.5547468397,1.1662395268  
H,0,-1.0876522998,3.4083892035,1.5673892773  
H,0,-2.1738562851,4.5944321658,0.8209024086  
H,0,-2.8020709392,3.4275232283,2.0001572423  
C,0,0.7608028101,0.6426352062,1.1651849516  
H,0,0.0395966513,1.4339352982,0.9706648971  
C,0,1.8789066496,0.9321678643,1.9283909835  
H,0,2.5345158809,0.1052853839,2.2123727208  
C,0,1.8717348827,2.0776999489,2.9035659681  
H,0,2.8668940428,2.5493026021,2.9328620752  
H,0,1.1706763304,2.8558772818,2.5715635113  
C,0,2.7096526428,2.5910832837,-0.5884809084  
O,0,2.0453656678,1.8940742246,-1.6662041973  
C,0,3.3118204817,0.3539287418,-0.555050258  
C,0,3.213246564,1.4596771289,0.2853965848  
H,0,3.9453013931,1.6722640042,1.0633822702  
C,0,2.4913947646,0.5900456496,-1.730315086  
O,0,2.1491294747,-0.119811743,-2.6531675482  
C,0,1.7543572182,3.6212089641,-0.026900639  
H,0,2.2358591916,4.1884160835,0.7779877532  
H,0,1.4825703511,4.3270265598,-0.8210448223  
H,0,0.8316933173,3.1813826244,0.3574299934  
C,0,3.9264987105,3.3154169119,-1.1702600653  
H,0,3.5926847598,4.0511158891,-1.9110781469  
H,0,4.4754015785,3.8427253597,-0.3804597414  
H,0,4.6106943762,2.6134202264,-1.6583510954  
C,0,4.0548194799,-0.8300244799,-0.1930854221  
O,0,4.5449851588,-1.0119833203,0.9162629464

O,0,4.1599125519,-1.7314707479,-1.1851207279  
C,0,4.7974519941,-2.9720253104,-0.8532312021  
H,0,5.8265879741,-2.7748116563,-0.5278346393  
H,0,4.2682879947,-3.4289263255,-0.0047651623  
C,0,4.7478157039,-3.8423586956,-2.0792958351  
H,0,5.2289557937,-4.8054846005,-1.8762463116  
H,0,3.7124966304,-4.0324933981,-2.3851263767  
H,0,5.2680370024,-3.3679054903,-2.9184727566  
C,0,1.4952638085,1.6269290021,4.3109964785  
H,0,2.1766833213,0.8460716109,4.6717089849  
H,0,1.5320949601,2.4588469417,5.0248296226  
H,0,0.4790925225,1.2108715988,4.3298420631

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**dr2-TS-CCAtt-endo**

E(RM06)= -2003.96010246 Hartree

Sum of electronic and thermal Free Energies= -2003.317093 Hartree

C,0,-2.2108259217,1.8813382811,2.3614561599  
C,0,-0.9161160408,2.3934883784,1.7124550362  
C,0,-0.3440644065,1.2411557022,0.8632943137  
C,0,-2.1870888366,0.3739032329,2.161224962  
H,0,-2.2796705511,2.1479985048,3.4215088331  
H,0,-3.077798652,2.3134072493,1.8484843692  
H,0,-0.192123119,2.7231036051,2.4638161797  
H,0,-1.12440814,3.2588279991,1.0722216551  
H,0,-0.2186097883,1.5258067513,-0.1831892911  
H,0,-3.1831332226,-0.0563486054,2.0127296318  
H,0,-1.7049448806,-0.150191113,2.9986364882  
N,0,-1.3950094305,0.2095512726,0.9338254699  
C,0,1.068130081,0.7209889109,1.3077122234  
C,0,0.935310718,-0.1102811592,2.5825897482  
C,0,0.802777371,0.4833338753,3.8438920898  
C,0,0.8426693806,-1.5016780266,2.4981365958  
C,0,0.5871425145,-0.2888429228,4.9818480045  
H,0,0.8747608012,1.5639331713,3.9498654844  
C,0,0.6265775814,-2.2777883053,3.6344357945  
H,0,0.9360153562,-1.9785220309,1.5245410689  
C,0,0.4957069828,-1.6748453623,4.8823602085  
H,0,0.4933067101,0.197915034,5.9501934256  
H,0,0.5603417582,-3.3597955471,3.5409912966  
H,0,0.3298507511,-2.2794994729,5.7710733988  
C,0,2.0454505088,1.8955277574,1.4421560992  
C,0,3.1116563917,1.8653456022,2.3453775399  
C,0,1.9640186826,2.983929079,0.5659124837  
C,0,4.0587582091,2.8872150413,2.3780474391

H,0,3.2152782869,1.0303856629,3.0349258376  
C,0,2.9016889168,4.009437258,0.5982702257  
H,0,1.1613461995,3.035858935,-0.1668872572  
C,0,3.9564721541,3.9666443411,1.5068443412  
H,0,4.8785022242,2.8350732049,3.0913940249  
H,0,2.8091044508,4.8432827624,-0.0957221774  
H,0,4.6918212058,4.7674584245,1.5333330527  
Si,0,3.0290218669,-0.5046685969,-0.3334258854  
O,0,1.4942189745,-0.1073673632,0.2370244239  
C,0,4.1835308965,-1.1289726658,1.0067588629  
H,0,3.6947573249,-1.8456260147,1.6789305575  
H,0,5.0203413191,-1.6522894341,0.5222743733  
H,0,4.612253389,-0.3243950558,1.6151837038  
C,0,3.8359790764,0.8967064191,-1.2747647627  
H,0,4.2427285632,1.6850665114,-0.6304756732  
H,0,4.6679467623,0.4884510434,-1.8664153836  
H,0,3.1288375463,1.3558172571,-1.9782907304  
C,0,2.6906801513,-1.8935537486,-1.5338248639  
H,0,2.0418584884,-1.5516319993,-2.3502660212  
H,0,3.6327649112,-2.238716452,-1.9809645887  
H,0,2.2158589812,-2.7538058256,-1.0459460696  
C,0,-1.7237107756,-0.7321699015,0.0428556633  
H,0,-2.4706171963,-1.4273171413,0.4350689158  
C,0,-1.3782698436,-0.8815768038,-1.289428697  
H,0,-0.4886479075,-0.3649130519,-1.6582991154  
C,0,-1.7350773602,-2.1767149597,-1.9761571811  
H,0,-2.6471198268,-2.5885856943,-1.5200829071  
H,0,-1.9855312455,-1.9804960727,-3.0310572706  
C,0,-4.1364376282,0.5031120465,-1.9398308243  
O,0,-4.3521488542,1.5449618851,-0.9640730618  
C,0,-2.2674184478,1.8735194971,-1.8308694356  
C,0,-2.6504908662,0.5965830472,-2.2344573787  
H,0,-2.2750774599,0.1475656017,-3.1526925378  
C,0,-3.302915919,2.4364120668,-0.9830235766  
O,0,-3.3719923063,3.4685595861,-0.3494265374  
C,0,-4.8808194005,0.8880786702,-3.2205108361  
H,0,-4.7426703655,0.1188352487,-3.9903890945  
H,0,-5.9521486661,0.9796638203,-3.0085897106  
H,0,-4.5214674436,1.8441720471,-3.616280203  
C,0,-4.7301435455,-0.7728908861,-1.3873791606  
H,0,-5.8060807756,-0.6272790429,-1.2375782718  
H,0,-4.5968844758,-1.6012512041,-2.0917817637  
H,0,-4.29523889,-1.0471121427,-0.4230332135  
C,0,-1.027249553,2.4771476459,-2.2615137864

O,0,-0.1997841113,1.9065599882,-2.9628618032  
O,0,-0.8517702629,3.7358526952,-1.8148483852  
C,0,0.2917055693,4.4415805574,-2.3138585946  
H,0,1.199904545,3.8477395426,-2.1397615326  
H,0,0.1908757881,4.5576469993,-3.4011379225  
C,0,0.3361502972,5.7685802165,-1.6054929202  
H,0,1.2030500237,6.3484033038,-1.9420869304  
H,0,-0.5681717734,6.3521117637,-1.8086194582  
H,0,0.4083131311,5.6304811991,-0.5193170588  
C,0,-0.6395883977,-3.2328179166,-1.9266076724  
H,0,-0.3692712433,-3.4733210323,-0.8895514944  
H,0,-0.9639382213,-4.1609008298,-2.4135903786  
H,0,0.2681266404,-2.8903766958,-2.4355885533

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H<sub>2</sub>O

E(RM06)= -76.4024626846 Hartree

Sum of electronic and thermal Free Energies= -76.398617 Hartree

O,0,0.,0.,0.1104077121  
H,0,0.,0.7661240253,-0.472744856  
H,0,0.,-0.7661240253,-0.472744856

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**TS-Hyd**

E(RM06)= -2080.36814761 Hartree

Sum of electronic and thermal Free Energies= -2079.702150 Hartree

C,0,0.7790307029,-2.2926979,3.0704193284  
C,0,1.85705316,-1.2712713139,2.7087666314  
C,0,1.3087079325,-0.527489636,1.4821487929  
C,0,0.1937725719,-2.6526163767,1.7155907822  
H,0,1.1810272918,-3.1621713551,3.6001116885  
H,0,0.0002805553,-1.839619395,3.6962109634  
H,0,2.7893266824,-1.790713673,2.4655655888  
H,0,2.0799547691,-0.5828438387,3.5300498027  
H,0,0.8855181918,0.4440410073,1.7778577161  
H,0,-0.8127992202,-3.0768929777,1.7612588331  
H,0,0.8485885045,-3.3565297467,1.180878581  
N,0,0.1783656478,-1.360598464,1.0102865708  
C,0,2.2963877957,-0.2104619508,0.3180204514  
C,0,2.8707572784,-1.5043679193,-0.2653391865  
C,0,3.9551435836,-2.1602651176,0.331614755  
C,0,2.292008194,-2.0873449432,-1.3940027102  
C,0,4.4252372909,-3.3715372339,-0.1654669183  
H,0,4.4633058131,-1.7095795372,1.1820320863  
C,0,2.7665719917,-3.2959590554,-1.900898153  
H,0,1.4612034577,-1.5832386271,-1.8822143939

C,0,3.8282506595,-3.9491049978,-1.2836511316  
H,0,5.2706206157,-3.8575941904,0.3165849587  
H,0,2.2996395557,-3.7274322495,-2.7841945855  
H,0,4.1987204299,-4.8927027448,-1.6777434101  
C,0,3.4022552321,0.7503158874,0.7675899055  
C,0,4.5515030201,0.8856665555,-0.0204038239  
C,0,3.2749078445,1.5834983384,1.8829739095  
C,0,5.5365784772,1.8161533765,0.2913854786  
H,0,4.6793056458,0.2516160387,-0.8959087558  
C,0,4.2648594204,2.5086046183,2.2076441457  
H,0,2.3938983123,1.5356136761,2.5179891736  
C,0,5.39954822,2.6307547597,1.4127919878  
H,0,6.4164901886,1.8998624125,-0.3427305331  
H,0,4.1407500939,3.140734411,3.0839741095  
H,0,6.1712517591,3.3546978255,1.6635332669  
Si,0,1.5436071545,1.7429027517,-1.6698527602  
O,0,1.4783042785,0.4047744178,-0.6556574565  
C,0,2.9376645083,1.6230323098,-2.92020231  
H,0,3.0354150642,0.6050511487,-3.3205489934  
H,0,2.7167748826,2.2875922883,-3.7671303715  
H,0,3.9085695675,1.9262882727,-2.5112789317  
C,0,1.6624297845,3.3331823495,-0.6935643886  
H,0,2.6596226918,3.5009194878,-0.2678855704  
H,0,1.430274326,4.1851406725,-1.347324122  
H,0,0.9286745315,3.3404419849,0.1238144491  
C,0,-0.0962790602,1.648434095,-2.5553800595  
H,0,-0.9272294276,1.7258129533,-1.8401560288  
H,0,-0.1933704047,2.4780417176,-3.268702922  
H,0,-0.1983572777,0.712835689,-3.1220450578  
C,0,-0.9587674484,-0.7447535661,0.6624810274  
H,0,-0.8154038031,0.2939960672,0.3491047424  
C,0,-2.0908710777,-1.4378585817,-0.0550589571  
H,0,-2.4429242004,-2.2741290822,0.569309146  
C,0,-1.5340360199,-1.9729135907,-1.3959585103  
H,0,-2.329743175,-1.8981629683,-2.1475576868  
H,0,-0.7498683065,-1.2820587597,-1.7447182636  
C,0,-4.6225242853,-1.1653671584,-0.6896999204  
O,0,-5.4364828145,-0.9827523899,0.4963285009  
C,0,-3.6963335407,0.491449701,0.7483289945  
C,0,-3.2671896465,-0.4675686241,-0.3557531078  
H,0,-2.9476573066,0.1141072021,-1.2356821685  
C,0,-5.0295056837,0.114691022,1.2052390412  
O,0,-5.7260168465,0.5522227687,2.0960197375  
C,0,-5.3066597656,-0.4276473433,-1.8298439294

H,0,-4.7665412944,-0.5875184096,-2.7721825728  
H,0,-6.3364286045,-0.7832011044,-1.9529319376  
H,0,-5.3379610561,0.6518613574,-1.6336585739  
C,0,-4.639601822,-2.6602045758,-0.9452407197  
H,0,-5.6827948617,-2.9825240503,-1.0420582538  
H,0,-4.1228197818,-2.9276599705,-1.8730779203  
H,0,-4.2011896546,-3.2252075929,-0.1157303113  
C,0,-3.2311915656,1.8587005345,0.6650965634  
O,0,-2.1728212251,2.1841463976,0.1221948587  
O,0,-4.0120554145,2.7647130465,1.2796114471  
C,0,-3.5383164988,4.1163204488,1.2896512711  
H,0,-2.5597419541,4.1530252977,1.7870263716  
H,0,-3.3897316883,4.4569303146,0.2570522924  
C,0,-4.5646149101,4.9470693326,2.0119003239  
H,0,-4.2402835194,5.9930808116,2.0509024254  
H,0,-5.5325856467,4.9061630922,1.5006679982  
H,0,-4.708721572,4.5907027607,3.0376548969  
C,0,-1.0081295566,-3.396426075,-1.3738591932  
H,0,-1.766604049,-4.0964818862,-0.9983531122  
H,0,-0.7330924537,-3.7224592138,-2.3844816262  
H,0,-0.115240534,-3.5014887725,-0.7489051313  
O,0,-1.8396141381,-0.3877763497,2.2762305391  
H,0,-1.3948192494,0.3532325401,2.7141071099  
H,0,-2.7756684884,0.0485955181,1.805636696

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**TS-Hyd-water**

E(RM06)= -2156.79410650 Hartree

Sum of electronic and thermal Free Energies= -2156.103266 Hartree

C,0,0.8953081243,-0.7713107277,-0.9127971465  
H,0,1.2757697706,-0.4754837117,0.0680306014  
C,0,1.9468133461,-1.4180932695,-1.7865943826  
H,0,1.5786012681,-1.4228767585,-2.8252564044  
C,0,2.1343793319,-2.8671909079,-1.2702397345  
H,0,3.1888155129,-3.1357691798,-1.4082068234  
H,0,1.988066174,-2.8589013227,-0.1781999239  
C,0,4.287243779,-1.0572163089,-2.8999279367  
O,0,4.2527786458,0.1118286592,-3.7564700284  
C,0,3.3899555879,0.8096490417,-1.7580374538  
C,0,3.3299049487,-0.7077701658,-1.7145286508  
H,0,3.7894749702,-1.0592534203,-0.7758286621  
C,0,3.938339891,1.2334057343,-3.0318674938  
O,0,4.0880362606,2.3321489114,-3.526502983  
C,0,5.7086211698,-1.2071285201,-2.3799204794  
H,0,5.80500727,-2.1222620171,-1.781120362



H,0,6.4161995935,-1.2616352774,-3.2156318269  
H,0,5.9882525561,-0.3545868844,-1.7483536009  
C,0,3.9460038466,-2.2163952586,-3.8174398924  
H,0,4.6592679085,-2.214629183,-4.6498154778  
H,0,4.0294219385,-3.1850655979,-3.3135160264  
H,0,2.9445316001,-2.1231706067,-4.2504610762  
C,0,3.4851974212,1.553301354,-0.5484622159  
O,0,3.1000821454,1.131057426,0.5627733724  
O,0,3.9809296793,2.8003150418,-0.6690955376  
C,0,4.0891267651,3.5806810906,0.5234301243  
H,0,3.0895274484,3.7435674616,0.9529104945  
H,0,4.6757163843,3.0309250646,1.2702971816  
C,0,4.7386976942,4.8854427585,0.1479256278  
H,0,4.8388865671,5.5240690213,1.0326470718  
H,0,5.7365884646,4.7180142515,-0.2711583274  
H,0,4.1439575471,5.4202504096,-0.6003432994  
C,0,1.2737346127,-3.9487396307,-1.8983029178  
H,0,1.3409124821,-3.9320593191,-2.9945891231  
H,0,1.6088628658,-4.9395467979,-1.5665003373  
H,0,0.2184269432,-3.860554698,-1.6174144961  
O,0,0.7315858205,0.8422033888,-1.6377387306  
H,0,0.5140114452,1.4414700916,-0.881193227  
H,0,1.7160836385,1.0595780392,-1.8648141514  
O,0,0.5545355048,2.1143381185,0.7662990077  
H,0,1.4841429497,1.8513792237,0.9541729836  
H,0,0.4882864399,3.0580671446,0.9486078427  
C,0,-2.3696719708,-1.6849015698,3.7447961779  
C,0,-1.9796201505,-0.9270582602,2.633854228  
C,0,-2.2299165289,0.4493443853,2.6663255483  
C,0,-2.8587897495,1.040424003,3.7599090629  
C,0,-3.239931886,0.2717723483,4.854788476  
C,0,-2.9880308899,-1.0974663453,4.8438541965  
C,0,-1.1933367783,-1.5993940096,1.4987719403  
O,0,0.1872217297,-1.5997827185,1.8142995596  
Si,0,1.1203334497,-1.5626038993,3.2111744934  
C,0,0.9541875568,0.0655424924,4.1159365627  
C,0,-1.2736424019,-0.7579988301,0.1881752661  
C,0,-2.634692068,-0.6821076232,-0.5076483294  
C,0,-2.5370807239,-1.6644640553,-1.6722468592  
C,0,-1.1013273558,-1.4976762223,-2.1264364374  
N,0,-0.3643762047,-1.2638341221,-0.8688444289  
H,0,-2.7746361019,0.335608345,-0.8975725606  
C,0,-1.662881369,-3.0336595936,1.2547082542  
C,0,-3.0226215203,-3.37033324,1.2531290551

C,0,-3.4420592256,-4.6640261115,0.9618431949  
C,0,-2.5074917586,-5.6553246972,0.668960159  
C,0,-1.1536367777,-5.3372995271,0.679979703  
C,0,-0.7381882418,-4.0385241472,0.9691406806  
C,0,0.753411144,-2.9963865817,4.3639329692  
C,0,2.8522935887,-1.7335905036,2.5328276994  
H,0,-0.9235408516,0.2418828814,0.4691554447  
H,0,-3.7707192823,-2.617940224,1.4956742576  
H,0,-4.5042104952,-4.8992235579,0.9714706272  
H,0,-2.833157852,-6.6686547724,0.4452067387  
H,0,-0.4104841806,-6.1019451561,0.4616253293  
H,0,0.3226670244,-3.7987626696,0.9777729566  
H,0,-1.9263298436,1.0928109316,1.8447324624  
H,0,-3.043510448,2.1123875103,3.7545952363  
H,0,-3.7279964965,0.7350955522,5.7091296927  
H,0,-3.2764371388,-1.715348135,5.6915096179  
H,0,-2.1878038005,-2.757729555,3.7540280522  
H,0,-0.1249995371,-2.8227541243,4.9967042905  
H,0,0.6000725405,-3.9343125556,3.8142746699  
H,0,1.6136306318,-3.1449436544,5.0316119305  
H,0,3.5849930623,-1.6900934328,3.3501532775  
H,0,2.9936286591,-2.692503572,2.01559066  
H,0,3.0854098542,-0.9175101675,1.8338121332  
H,0,-0.0014211189,0.1669346378,4.6447018932  
H,0,1.7585622364,0.1536692131,4.8596087463  
H,0,1.0509671308,0.9102428975,3.4208438002  
H,0,-0.7117393052,-2.3686058613,-2.6611592421  
H,0,-0.9935825613,-0.6166848567,-2.7769111982  
H,0,-3.4722568813,-0.8857423647,0.1664859314  
H,0,-3.2501298796,-1.4470139697,-2.4732863401  
H,0,-2.7112401663,-2.6945217798,-1.334233478

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#### INT4

E(RM06)= -2080.42163672 Hartree

Sum of electronic and thermal Free Energies= -2079.750613 Hartree

C,0,-0.7429147897,-0.5647835474,-3.6202931562  
C,0,-1.8890804569,0.0691675842,-2.8402926605  
C,0,-1.3749467088,0.1439091339,-1.3924774509  
C,0,-0.1640597607,-1.5261593343,-2.5939195948  
H,0,-1.0782828362,-1.0600352054,-4.5385496006  
H,0,0.0100338795,0.1851422778,-3.8983576555  
H,0,-2.7696319795,-0.5788209782,-2.9064593704  
H,0,-2.1849956813,1.0503511022,-3.2265810829  
H,0,-0.9683904035,1.1539755645,-1.2004887998

H,0,0.8742477593,-1.805561236,-2.8007224507  
H,0,-0.7611251898,-2.453455729,-2.5640620637  
N,0,-0.270293089,-0.8272900894,-1.3063371211  
C,0,-2.4262709566,-0.0718666525,-0.2569223478  
C,0,-3.0618320149,-1.4603416947,-0.360252866  
C,0,-4.1204749995,-1.7142891622,-1.2417402702  
C,0,-2.585947963,-2.5212399029,0.4117424029  
C,0,-4.6584534925,-2.9907460939,-1.3736523633  
H,0,-4.5557690474,-0.9002276885,-1.8187165569  
C,0,-3.127247083,-3.7996290515,0.289233343  
H,0,-1.7875272232,-2.3370475514,1.1252739344  
C,0,-4.1587927138,-4.0438050686,-0.6114226892  
H,0,-5.4809085524,-3.1574594478,-2.0660269708  
H,0,-2.7386661335,-4.6079797621,0.9057496038  
H,0,-4.5810188639,-5.0415259786,-0.708689827  
C,0,-3.5019189567,1.0201256735,-0.2371820459  
C,0,-4.6365853033,0.8323462762,0.5626732668  
C,0,-3.3702302834,2.2415554338,-0.9026311108  
C,0,-5.6009687358,1.8248204029,0.6950203437  
H,0,-4.7653432573,-0.1101725035,1.0935155148  
C,0,-4.340122312,3.235681333,-0.7843186986  
H,0,-2.5004572397,2.4472951085,-1.5207929956  
C,0,-5.4582236774,3.0339010754,0.0170485335  
H,0,-6.4693356805,1.6500216941,1.3268010819  
H,0,-4.2122031371,4.1750215136,-1.3179641549  
H,0,-6.2141706713,3.8100259071,0.1123129345  
Si,0,-1.6176922424,0.8741548205,2.3529732449  
O,0,-1.6693844636,-0.0162173851,0.9383405642  
C,0,-2.9955046711,0.3842181423,3.5281551476  
H,0,-3.1636352026,-0.7011896511,3.51036036  
H,0,-2.7182226812,0.657588842,4.5556478968  
H,0,-3.9461601765,0.8817434033,3.3014543486  
C,0,-1.6276291043,2.7227458032,2.0570993668  
H,0,-2.6078002432,3.1077855504,1.7508970319  
H,0,-1.3411161674,3.2337422243,2.9870602608  
H,0,-0.8890458973,3.0051735657,1.2940862446  
C,0,0.0277192043,0.3843950634,3.0934819133  
H,0,0.8634364851,0.7520891867,2.4814339818  
H,0,0.1395771873,0.8212613758,4.0953073031  
H,0,0.1177433295,-0.7055871378,3.1936111535  
C,0,0.9555997011,-0.3021878035,-0.7582515073  
H,0,0.6659345476,0.3424481208,0.0869930292  
C,0,1.9139689902,-1.3821677863,-0.2340787295  
H,0,2.2894529573,-1.924403616,-1.1187118922

C,0,1.1376594323,-2.3535833836,0.6807231342  
H,0,1.672586462,-2.4834090788,1.6280699233  
H,0,0.1838414767,-1.8811546364,0.9455963596  
C,0,4.2849338849,-1.798353481,0.7996135435  
O,0,5.4080826358,-0.9094482715,1.1173008618  
C,0,3.8943259247,0.3685537796,-0.105249541  
C,0,3.1269002964,-0.7985520059,0.5187894932  
H,0,2.7685865864,-0.4422530573,1.5005360666  
C,0,5.2312438545,0.3166934685,0.6144415622  
O,0,6.0381619052,1.2019414885,0.7469378278  
C,0,4.1404387293,-2.6800000185,2.0232969739  
H,0,3.4609811936,-3.5182088914,1.8379058992  
H,0,5.1207410483,-3.100291128,2.2770988353  
H,0,3.7779952864,-2.1109959509,2.887340137  
C,0,4.7064694019,-2.619532505,-0.4065612168  
H,0,5.647884209,-3.1343389819,-0.1832881728  
H,0,3.9550773409,-3.3801537835,-0.64719652  
H,0,4.8628797196,-2.0003298262,-1.2980485091  
C,0,3.2675254916,1.7284996684,0.0581351996  
O,0,2.4853091524,2.0216160233,0.9386371789  
O,0,3.7190582852,2.5852317336,-0.8548837283  
C,0,3.2298580392,3.9356244229,-0.7597389941  
H,0,2.1334857178,3.9165583381,-0.8291293219  
H,0,3.4915214578,4.3353658918,0.2271358735  
C,0,3.8556961033,4.7239677502,-1.8763393994  
H,0,3.5093028365,5.7623589598,-1.8389383664  
H,0,4.9474642258,4.7244720031,-1.7911432974  
H,0,3.5868631454,4.3084911657,-2.8538294298  
C,0,0.8723846768,-3.7179812141,0.0673669763  
H,0,1.8060928907,-4.2225068047,-0.2208100887  
H,0,0.351660046,-4.3783285019,0.771950985  
H,0,0.2492512851,-3.6407417981,-0.8319354025  
O,0,1.6975387766,0.4735635458,-1.711198242  
H,0,1.172863616,1.2477885859,-1.9515077662  
H,0,4.0939328678,0.2120143729,-1.1741276078

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**ee-TS-Hyd-water**

E(RM06)= -2156.79019421 Hartree

Sum of electronic and thermal Free Energies= -2156.096962 Hartree

C,0,1.4977428122,-3.3557051608,1.810997615  
C,0,2.0676382252,-1.9648791245,2.1665184469  
C,0,1.3724547773,-0.9539873146,1.245544601  
C,0,0.4411469015,-3.1147056328,0.7272541206  
H,0,2.2720228996,-4.0455879412,1.4589562929

H,0,1.0352968125,-3.8109833446,2.6946593715  
H,0,3.1578507077,-1.9195434671,2.096395776  
H,0,1.8191706592,-1.708442208,3.2030912619  
H,0,1.0298054698,-0.0764049568,1.8056117268  
H,0,-0.4714328175,-3.6963422661,0.8818794691  
H,0,0.8209925379,-3.3546945331,-0.2761373172  
N,0,0.1685101501,-1.6835833069,0.8395979034  
C,0,2.2093231159,-0.374795637,0.0550607565  
C,0,2.6227547737,-1.4708482592,-0.9292674989  
C,0,3.6007232106,-2.4157106963,-0.5895305359  
C,0,2.0114776636,-1.5921739763,-2.1789763387  
C,0,3.9270121826,-3.4584176696,-1.449421282  
H,0,4.1333260671,-2.3348342754,0.3550502668  
C,0,2.337584322,-2.6333530733,-3.0465567736  
H,0,1.2660934931,-0.8669725601,-2.4921383224  
C,0,3.2899749743,-3.5782355607,-2.6826550786  
H,0,4.6909842981,-4.1748999824,-1.155221862  
H,0,1.8394678815,-2.7001771836,-4.0111446814  
H,0,3.5449840677,-4.3926307064,-3.3566722385  
C,0,3.4074816331,0.4141223097,0.5992878191  
C,0,4.6190470706,0.4691720146,-0.098270429  
C,0,3.288164032,1.1777391843,1.768601844  
C,0,5.6809813206,1.2449139794,0.3596495348  
H,0,4.7404342047,-0.0922084874,-1.0221933119  
C,0,4.3525173764,1.9437086776,2.2340506598  
H,0,2.3473857726,1.2183493928,2.3135519994  
C,0,5.5553412199,1.9796855972,1.5343815002  
H,0,6.6093737635,1.2703966917,-0.2067613732  
H,0,4.2310670606,2.5263839375,3.144598094  
H,0,6.3854070644,2.5812816572,1.8978666901  
Si,0,1.5244744351,2.0317234148,-1.3621095444  
O,0,1.3049120871,0.5245754281,-0.600198633  
C,0,2.9179546913,2.0135796532,-2.6114306213  
H,0,2.9294016514,1.0971016391,-3.2151140659  
H,0,2.7709021127,2.8567827127,-3.301032621  
H,0,3.9051914273,2.1365657105,-2.1517239111  
C,0,1.7460943537,3.4095289794,-0.1208417953  
H,0,2.8008376231,3.5726404278,0.1342927411  
H,0,1.3575715926,4.3468094123,-0.5452358809  
H,0,1.2007020477,3.2021787776,0.8102271724  
C,0,-0.0914533378,2.2361385916,-2.2821881967  
H,0,-0.9802811575,2.2804059658,-1.6362664295  
H,0,-0.058222359,3.1841731958,-2.8369328498  
H,0,-0.2530009652,1.4476773431,-3.0307760672

C,0,-0.9995314982,-1.0549455255,0.6364935642  
H,0,-0.9739761055,-0.0309116717,1.0129901337  
C,0,-2.3274517481,-1.7425140473,0.8426094808  
H,0,-2.3208864219,-2.6257983124,0.1916768636  
C,0,-2.4210309811,-2.2541912338,2.294799947  
H,0,-3.4361534861,-2.6551133733,2.4277910786  
H,0,-1.7437626782,-3.109714052,2.4284627996  
C,0,-4.602775354,-1.5820959493,-0.434837316  
O,0,-5.2241482532,-0.5254339648,-1.1984689633  
C,0,-3.3707569512,0.4614907336,-0.2652416559  
C,0,-3.5663410799,-0.854780137,0.477760414  
H,0,-4.0719317925,-0.6415926346,1.4354033159  
C,0,-4.4651969807,0.6174052693,-1.2076077312  
O,0,-4.7930454947,1.5416247869,-1.9233665033  
C,0,-4.0260819561,-2.5436597797,-1.4666104368  
H,0,-3.7045217488,-3.4934836191,-1.0229023416  
H,0,-4.8122859108,-2.7725798699,-2.194962376  
H,0,-3.1807119507,-2.1061162507,-2.0113248357  
C,0,-5.6951512838,-2.2639832163,0.3635706608  
H,0,-6.4499436342,-2.6968858726,-0.3042395577  
H,0,-5.2758699702,-3.0751086381,0.973619811  
H,0,-6.1924601376,-1.5503110412,1.0304889358  
C,0,-2.8315645559,1.5860503123,0.4346729574  
O,0,-2.3198756931,1.5136053906,1.5670843411  
O,0,-2.851170216,2.7582252968,-0.2281555792  
C,0,-2.2032187121,3.8635199297,0.4108280313  
H,0,-2.6801066846,4.06003007,1.3797272486  
H,0,-1.1518044503,3.6027881625,0.6105036176  
C,0,-2.307760301,5.0449311255,-0.5152831569  
H,0,-1.821957109,5.9177926631,-0.06442705  
H,0,-1.819629666,4.8366905708,-1.4747371077  
H,0,-3.3547153757,5.2952728029,-0.7169505339  
C,0,-2.1326164199,-1.2246232745,3.378040665  
H,0,-2.7398481879,-0.3203050797,3.2596502883  
H,0,-2.3332320844,-1.6476867018,4.3689339138  
H,0,-1.0805633946,-0.9074415227,3.3656429949  
O,0,-1.1073991668,-0.6785884607,-1.0799404512  
H,0,-1.9443689783,-0.0682978338,-1.078819882  
H,0,-0.2976863715,-0.1248305672,-1.1661610298  
O,0,0.1256143342,1.930497014,2.759133456  
H,0,-0.7650366649,1.8768121022,2.3536923412  
H,0,-0.0283072837,2.2073902908,3.6678980881

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**dr1-TS-Hyd-water**

E(RM06)= -2156.78838550 Hartree

Sum of electronic and thermal Free Energies= -2156.094885 Hartree

C,0,-1.5075643474,-2.8176971067,-1.8730637072  
C,0,-2.5476253186,-2.0670997197,-1.0557596558  
C,0,-1.7167261613,-1.2385407763,-0.0676992416  
C,0,-0.5065043297,-3.205662901,-0.8052414233  
H,0,-1.9185183547,-3.6834870657,-2.4020966653  
H,0,-1.043992651,-2.1532439921,-2.6158108366  
H,0,-3.185527569,-2.785218664,-0.528445726  
H,0,-3.20150215,-1.4424798491,-1.668519664  
H,0,-1.4637956078,-0.2764119933,-0.5407532129  
H,0,0.4854825783,-3.4546337322,-1.1927911306  
H,0,-0.8828471504,-4.0684144601,-0.2391221943  
N,0,-0.4542615218,-2.0175671948,0.0712467687  
C,0,-2.3567543159,-0.89401872,1.314845771  
C,0,-2.3209408927,-2.1232508204,2.2278417182  
C,0,-3.1963019902,-3.1991316484,2.0369618651  
C,0,-1.3964689411,-2.2089530188,3.2699416399  
C,0,-3.1241604467,-4.3357692118,2.8369211512  
H,0,-3.9743627357,-3.1450529595,1.2785976123  
C,0,-1.3254789934,-3.3423047232,4.0772872821  
H,0,-0.7312397165,-1.3687891075,3.4537232902  
C,0,-2.1821561855,-4.4164092084,3.8596434963  
H,0,-3.8201594568,-5.154742993,2.6680216054  
H,0,-0.5927132846,-3.3812060602,4.8814729564  
H,0,-2.1277620669,-5.3018484949,4.4889308616  
C,0,-3.7796368497,-0.3395200771,1.1821747924  
C,0,-4.6461157024,-0.4012023171,2.279489831  
C,0,-4.215439459,0.3475954825,0.0448007321  
C,0,-5.9111084723,0.1745750664,2.2335940931  
H,0,-4.3233546937,-0.9031606838,3.1897052098  
C,0,-5.482585871,0.9241524725,-0.0078942115  
H,0,-3.5636043702,0.4606873825,-0.8179860975  
C,0,-6.3394617718,0.8339918167,1.0842879811  
H,0,-6.5635019393,0.1082097027,3.1014038923  
H,0,-5.795475235,1.4493048884,-0.907703463  
H,0,-7.3296995409,1.2818402899,1.0437866147  
Si,0,-1.4877463011,1.7838337212,1.8224883769  
O,0,-1.5303065692,0.0979131933,1.9167172194  
C,0,-3.0244208835,2.6112521296,2.5001869223  
H,0,-3.2583206404,2.2576477442,3.5124108112  
H,0,-2.8206907787,3.6895456953,2.568646572  
H,0,-3.9151412944,2.4829332153,1.8747818952  
C,0,-1.1541299297,2.3699698637,0.0736194494

H,0,-1.9951526715,2.2088830073,-0.6123550949  
H,0,-0.9620706947,3.4518865273,0.0997158143  
H,0,-0.2576034378,1.9024863836,-0.3566494954  
C,0,-0.0475940267,2.2613866634,2.9063673065  
H,0,0.9208244525,2.0163979882,2.4523971144  
H,0,-0.0648117101,3.3491992378,3.0603335667  
H,0,-0.1062410263,1.7859842328,3.8940776931  
C,0,0.7093837879,-1.3467401104,0.2759158947  
H,0,0.5413715691,-0.4332866993,0.8538950223  
C,0,1.9951230312,-2.084259064,0.6335507987  
H,0,2.2736218042,-2.7009858202,-0.2362381469  
C,0,1.8268957416,-3.0462342951,1.830640879  
H,0,2.8061400408,-3.0992575343,2.3276786677  
H,0,1.135194879,-2.6216486807,2.5663747001  
C,0,3.2905045017,-0.1997561618,2.0855101213  
O,0,3.0985929762,1.1310666131,1.540742345  
C,0,3.5652919228,-0.1838170567,-0.2662861013  
C,0,3.2304439063,-1.1551120717,0.850913145  
H,0,4.0542598174,-1.8773900771,0.9599955827  
C,0,3.5004183803,1.1755044857,0.2240269723  
O,0,3.655386145,2.2504158843,-0.3199054525  
C,0,2.2720625974,-0.3354820487,3.2007719058  
H,0,2.4305478524,-1.251858224,3.7779481593  
H,0,2.397664621,0.5128926774,3.8842674244  
H,0,1.2368074009,-0.3155868246,2.8418342648  
C,0,4.6930892638,-0.2407019613,2.6768974797  
H,0,4.8110533552,0.548384377,3.4289912657  
H,0,4.8822284299,-1.2106086982,3.1553072044  
H,0,5.451327692,-0.0886071961,1.8987348487  
C,0,4.2888077693,-0.6358412008,-1.4068774596  
O,0,4.3856190739,-1.8371381867,-1.7268885948  
O,0,4.8378581922,0.3251688642,-2.1709516901  
C,0,5.4925381095,-0.0988494027,-3.3705804869  
H,0,6.2720799006,-0.8304435448,-3.1235669129  
H,0,4.7651462664,-0.6052427454,-4.0217903591  
C,0,6.0635059082,1.12875869,-4.0283933616  
H,0,6.5832341566,0.8527888651,-4.9527653391  
H,0,5.2747563354,1.8472629841,-4.2758899012  
H,0,6.7800906756,1.6282441954,-3.3674872339  
C,0,1.3856082191,-4.4670527022,1.5187454691  
H,0,1.9598601449,-4.9020796239,0.6897408451  
H,0,1.5399213578,-5.1066111235,2.3962129871  
H,0,0.3214452744,-4.529908413,1.272519833  
O,0,1.0987174568,-0.5509435777,-1.2011302394



H,0,2.0546462949,-0.1883613995,-0.9988668907  
H,0,1.2661732002,-1.2415137609,-1.897208892  
O,0,2.0234806925,-2.4599470242,-2.9002814322  
H,0,2.9594130818,-2.4005966703,-2.5954595728  
H,0,2.0397952681,-2.4164084118,-3.8621745652

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**dr2-TS-Hyd-water**

E(RM06)= -2156.78229860 Hartree

Sum of electronic and thermal Free Energies= -2156.091334 Hartree

C,0,-1.4803644461,2.0235207301,3.2083725363  
C,0,-2.3649168036,0.802818502,2.8993952447  
C,0,-1.8001542302,0.1463089597,1.6355621192  
C,0,-0.2405167832,1.8780410867,2.32238033  
H,0,-1.9967058311,2.9631851048,2.9874748878  
H,0,-1.210988965,2.0489707171,4.2700877611  
H,0,-3.4229745691,1.0623242065,2.7969782622  
H,0,-2.298003601,0.0752850697,3.7183926632  
H,0,-1.8021274422,-0.948433184,1.7291732973  
H,0,0.7034739491,1.9375443112,2.8700792844  
H,0,-0.2108711512,2.6531574625,1.5432794711  
N,0,-0.3889418137,0.5624983238,1.68941389  
C,0,-2.5055582857,0.4297464019,0.2764516206  
C,0,-2.4212986163,1.9128640635,-0.0868265821  
C,0,-3.2438559682,2.8593894261,0.5346446126  
C,0,-1.4861972759,2.3583119578,-1.0227112431  
C,0,-3.1136943515,4.2154517822,0.2516049673  
H,0,-4.0087350776,2.5380160312,1.2400438011  
C,0,-1.3580293046,3.7154597845,-1.3127788788  
H,0,-0.8426514467,1.6310130381,-1.5100344975  
C,0,-2.1638635565,4.6508274934,-0.670508898  
H,0,-3.7644431677,4.9332669907,0.746585144  
H,0,-0.6225560305,4.039115822,-2.0466423105  
H,0,-2.0643934442,5.7103671653,-0.8955765748  
C,0,-3.9544786047,-0.0723447411,0.2787129112  
C,0,-4.8453741986,0.4088419185,-0.6873873622  
C,0,-4.4020632446,-1.0847141437,1.1340948564  
C,0,-6.1344245273,-0.1021519206,-0.7995827513  
H,0,-4.5246136281,1.1945834168,-1.3693804596  
C,0,-5.6958267706,-1.5911974594,1.0335359107  
H,0,-3.7479663592,-1.5041215657,1.8951109775  
C,0,-6.5672752616,-1.104643747,0.064150017  
H,0,-6.8021425853,0.2884197232,-1.5645114802  
H,0,-6.0187339082,-2.3757418814,1.7142731118  
H,0,-7.5757389471,-1.5033949614,-0.0176867844

Si,0,-1.9630655474,-1.3172393956,-1.9678615899  
O,0,-1.7381979281,-0.3215681072,-0.6360786398  
C,0,-2.8813249318,-0.4723213736,-3.3660279913  
H,0,-2.5234148632,0.5526624673,-3.5286495209  
H,0,-2.7036769795,-1.0313615985,-4.2953943571  
H,0,-3.9654651715,-0.4380157766,-3.2059882849  
C,0,-2.8426286926,-2.8932221104,-1.467776969  
H,0,-3.9120360004,-2.7400003167,-1.2749855267  
H,0,-2.7514173,-3.6429089793,-2.2655843544  
H,0,-2.3907335091,-3.3225327466,-0.5624971833  
C,0,-0.2064826532,-1.6683437213,-2.4779161417  
H,0,0.3650833147,-2.1858434294,-1.6945882413  
H,0,-0.1663576889,-2.3043829324,-3.3720741121  
H,0,0.3252566477,-0.7375425489,-2.714983115  
C,0,0.60864205,-0.1517030005,1.1569449996  
H,0,0.2342747628,-1.022743391,0.6177754351  
C,0,1.9268897887,-0.3651919273,1.8766285464  
H,0,2.4060238464,0.6098178764,2.0519481164  
C,0,1.6311706987,-1.010133583,3.2562328577  
H,0,0.7400930541,-1.6518580767,3.1925932887  
H,0,2.4678577989,-1.6868349161,3.4790724852  
C,0,2.742575287,-2.702815638,0.7538372721  
O,0,2.6304023457,-2.73249762,-0.6871347506  
C,0,3.4914392373,-0.6749967419,-0.2132071374  
C,0,3.0035697607,-1.2009224136,1.1176822684  
H,0,3.8403907235,-1.1872631644,1.83514279  
C,0,3.2715500656,-1.6461548997,-1.2523170358  
O,0,3.4844003338,-1.6409664559,-2.4496237102  
C,0,3.9746296027,-3.518941661,1.1236078118  
H,0,4.0863248928,-3.5816546863,2.2141860895  
H,0,3.8910952335,-4.5357785521,0.7217644946  
H,0,4.8821682013,-3.061144928,0.7112833818  
C,0,1.5050759978,-3.420233005,1.2654860332  
H,0,1.4628382215,-4.4041718978,0.7831136616  
H,0,1.5463217865,-3.5838079298,2.3468334555  
H,0,0.5680068465,-2.9068549753,1.0208124948  
C,0,4.3288295224,0.4664744906,-0.2747847213  
O,0,4.5174985618,1.2411692238,0.6872977658  
O,0,4.8975173997,0.713096932,-1.4735277882  
C,0,5.7036534427,1.8880764677,-1.5750121297  
H,0,5.0982448714,2.7730157428,-1.3297874615  
H,0,6.5179385957,1.8397605051,-0.8404656676  
C,0,6.2267728335,1.9554817666,-2.9850562658  
H,0,6.8585857971,2.8422671771,-3.1093401195

H,0,6.8253603254,1.0695799178,-3.2227994689  
H,0,5.4052933682,2.0118637978,-3.7076372706  
C,0,1.4731657481,-0.0612069263,4.4342482439  
H,0,0.5252471145,0.4877330266,4.4137427305  
H,0,1.4919399134,-0.6228269119,5.3755964344  
H,0,2.2905489182,0.6705186325,4.4720576726  
O,0,1.1360398077,0.7413805154,-0.3666573244  
H,0,1.9870546342,0.2636813816,-0.6090819849  
H,0,1.451777306,1.6328177552,-0.068248657  
O,0,2.4044498409,2.9502035875,0.6267390237  
H,0,3.2784569079,2.5057424234,0.7279634419  
H,0,2.5617348266,3.7721611058,0.1505846705

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### **TS-Decom**

E(RM06)= -2156.80044977 Hartree

Sum of electronic and thermal Free Energies= -2156.105657 Hartree

C,0,-1.3012663874,-1.0816843169,-1.5516706193  
H,0,-1.4424844029,-1.5019459607,-2.5608973832  
C,0,-2.1589298268,-1.8871128101,-0.5360574604  
H,0,-1.4995918493,-2.1143772719,0.3146156383  
C,0,-2.5782768327,-3.2122077787,-1.214797803  
H,0,-1.69743902,-3.6624196003,-1.6955835846  
H,0,-2.8917900141,-3.9430525065,-0.4563091148  
C,0,-4.0218785332,-1.9295006426,1.2612785796  
O,0,-4.6373917591,-0.8783109787,2.0646703185  
C,0,-3.1856421186,0.2487157518,0.6130543482  
C,0,-3.3855375152,-1.1641025513,0.0568862702  
H,0,-4.1640786993,-1.0721465202,-0.7136887049  
C,0,-4.1411609937,0.3328912162,1.7886177977  
O,0,-4.4570209631,1.3199788579,2.4042699275  
C,0,-5.1650903125,-2.8549784708,0.8974580358  
H,0,-4.8161393537,-3.7318530606,0.3426431486  
H,0,-5.6552115109,-3.2106666324,1.8114115507  
H,0,-5.912266958,-2.3292308843,0.2919571463  
C,0,-3.022671364,-2.6137866887,2.1790307736  
H,0,-3.5353074023,-2.9370739442,3.0924624155  
H,0,-2.580372064,-3.5009147667,1.7090169888  
H,0,-2.2115699736,-1.9321197869,2.4685107975  
C,0,-3.5908371191,1.3366544097,-0.3618167086  
O,0,-4.5084537296,1.2279131833,-1.1471224402  
O,0,-2.8727170963,2.4419963973,-0.1951361859  
C,0,-3.1700314239,3.532280709,-1.0843427744  
H,0,-3.0653837767,3.173541845,-2.1163503508  
H,0,-4.2140792888,3.8347777122,-0.9376750035

C,0,-2.2073121876,4.6434923483,-0.768312951  
H,0,-2.3936318114,5.4985674499,-1.4272407945  
H,0,-2.3206832974,4.9782851384,0.2684295494  
H,0,-1.1713352823,4.3169129097,-0.9132508429  
C,0,-3.6616412071,-3.0810263686,-2.2792725641  
H,0,-3.4384069493,-2.2824135248,-2.9993555566  
H,0,-3.75623525,-4.0143599499,-2.8456892325  
H,0,-4.6471147506,-2.85982026,-1.8558380932  
O,0,-1.5082110565,0.2649488079,-1.6113789082  
H,0,-0.9805594234,0.6746265089,-0.8037927345  
H,0,-2.1651665269,0.4487811367,0.9789781708  
O,0,-0.0337389108,0.6772584259,0.329026498  
H,0,0.3438618656,-0.5310217602,-0.4033610823  
H,0,0.5468756985,1.4427760007,0.3473999824  
C,0,3.3040383561,-4.5759399811,1.0070624213  
C,0,2.0471978164,-4.2076451199,0.5183653777  
C,0,1.06661236,-5.2060306852,0.4336219564  
C,0,1.340157825,-6.5212239962,0.7937953307  
C,0,2.6019125001,-6.8718245739,1.266557771  
C,0,3.5802608621,-5.8901767179,1.3784505611  
C,0,1.6910625582,-2.7384652286,0.2333690885  
O,0,0.9243417772,-2.2453612415,1.3084673001  
Si,0,1.0661344233,-2.2866982496,2.9878337241  
C,0,0.330489661,-3.8789719875,3.6463708791  
C,0,0.6973113898,-2.6723662632,-0.9660207344  
C,0,1.1826142237,-3.2207935533,-2.3145357804  
C,0,1.1937788618,-2.0337941864,-3.2899874787  
C,0,1.0234265948,-0.8047601507,-2.411512578  
N,0,0.2222739061,-1.2772530473,-1.2411316839  
H,0,0.510562874,-4.0157418302,-2.6602114871  
C,0,2.9074883656,-1.841459195,-0.0176986265  
C,0,3.9508567277,-2.2218297243,-0.872765215  
C,0,4.9925027323,-1.3478289304,-1.169341281  
C,0,5.0185202095,-0.0719056298,-0.6114207351  
C,0,3.9945037796,0.3147956157,0.247062596  
C,0,2.9500777747,-0.5602308908,0.5379162067  
C,0,2.8310623666,-2.1667721147,3.6080542003  
C,0,0.0923317661,-0.779167721,3.5261197177  
H,0,-0.1642369867,-3.2279126468,-0.6095446606  
H,0,3.9706358633,-3.2179441515,-1.309363487  
H,0,5.7906541258,-1.6711404412,-1.8340444074  
H,0,5.8330654642,0.6113439935,-0.8406073764  
H,0,3.9987300177,1.3078222645,0.6916842688  
H,0,2.1298784019,-0.2258968791,1.1693227337

H,0,0.0558310544,-4.9702204985,0.1032710403  
H,0,0.5577785159,-7.2724922188,0.7121631605  
H,0,2.8166727959,-7.8989717735,1.5519523653  
H,0,4.5680211335,-6.1421949815,1.7579490532  
H,0,4.0855234843,-3.8274149407,1.1119187049  
H,0,3.4598514634,-3.0056074503,3.2861440273  
H,0,3.3257441707,-1.2322176768,3.3173061869  
H,0,2.7971607124,-2.1919727073,4.7070381088  
H,0,0.7168926142,-0.1141793824,4.1380374356  
H,0,-0.2225907104,-0.2064179363,2.6397472528  
H,0,-0.7920243326,-1.0342512613,4.1240082411  
H,0,0.9626475252,-4.7485694263,3.4225819078  
H,0,0.2305790304,-3.8124804678,4.7387190602  
H,0,-0.6698277508,-4.0713639069,3.2366318338  
H,0,1.9823846631,-0.4368918773,-2.0305039534  
H,0,0.4998287954,0.0302182716,-2.8831277679  
H,0,2.1685784943,-3.6843162404,-2.2197844623  
H,0,0.3664826679,-2.1123707486,-4.0055973349  
H,0,2.1184027328,-1.9779771967,-3.873789506

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#### 4aa

E(RM06)= -883.106895795 Hartree

Sum of electronic and thermal Free Energies= -882.836736 Hartree

C,0,1.4325131469,1.5352420991,0.3451498745  
O,0,0.3397443877,2.4914861976,0.1449833379  
C,0,-0.3007825108,0.5571510928,-0.9897290387  
C,0,0.7572659063,0.1755817365,0.0427609772  
H,0,0.225959968,-0.1354921044,0.9581758024  
C,0,-0.6399261975,1.9929955947,-0.6177866578  
O,0,-1.6183763291,2.6201835679,-0.9294354515  
C,0,1.8597216885,1.7110649761,1.7856000351  
H,0,2.6963468877,1.0507704649,2.0353088762  
H,0,2.1815214698,2.7445636065,1.9576166574  
H,0,1.0293867888,1.4915547875,2.4662728564  
C,0,2.5315006198,1.9201241111,-0.626912402  
H,0,2.818953411,2.9634096437,-0.4559242524  
H,0,3.4226092166,1.2975589671,-0.4873281283  
H,0,2.2074222075,1.8284445375,-1.6705717015  
C,0,-1.5455178182,-0.3008711666,-0.9847833216  
O,0,-1.960285472,-0.8773408553,-0.0018313109  
O,0,-2.1154659342,-0.3314105455,-2.18039947  
C,0,-3.3101981727,-1.1356218997,-2.3040515237  
H,0,-3.0486128506,-2.1703064158,-2.0502797299  
H,0,-4.0448941988,-0.7810356397,-1.5722747899

C,0,-3.799871471,-0.9990088703,-3.7179380902  
H,0,-4.7063529516,-1.5983312408,-3.8542059167  
H,0,-4.0412161959,0.0433777874,-3.9515364475  
H,0,-3.0478575249,-1.3507242876,-4.4322712815  
H,0,0.110354779,0.5730961182,-2.010944919  
C,0,1.6701426126,-0.9750841099,-0.405713661  
H,0,2.1581679792,-0.7087098116,-1.3573198037  
C,0,2.7201753183,-1.3824774859,0.6316207009  
H,0,2.2152203675,-1.6013261408,1.5859994403  
H,0,3.3896019664,-0.5354238261,0.8253344891  
C,0,3.5453488876,-2.5788000104,0.1820373476  
H,0,4.336691418,-2.8076541664,0.9036220854  
H,0,2.9365759808,-3.4858602453,0.0711623157  
H,0,4.0228276059,-2.3866196723,-0.7874593799  
C,0,0.7923387914,-2.172148806,-0.6862353494  
H,0,0.4012907562,-2.6876018469,0.2241775866  
O,0,0.5028769658,-2.5694018212,-1.7925886656

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**Cat**

E(RM06)= -1197.30062441 Hartree

Sum of electronic and thermal Free Energies= -1196.930423 Hartree

C,0,1.3080912673,-2.965862599,-1.9501142569  
C,0,1.8856223028,-1.7223837783,-2.6251555325  
N,0,1.4960198905,-0.6444338095,-1.7212931424  
C,0,0.1107940889,-0.9200627032,-1.3589795423  
C,0,0.1077085479,-2.4404289471,-1.1401099299  
H,0,1.024684354,-3.7291876632,-2.6823870784  
H,0,2.0520023383,-3.4174493174,-1.2829724663  
H,0,1.4425171606,-1.5970530043,-3.6317459623  
H,0,2.9760445929,-1.7577159645,-2.7448175084  
H,0,-0.5830380515,-0.6887164799,-2.1924933292  
H,0,0.2304918083,-2.66320065,-0.0739194242  
H,0,-0.8450804268,-2.879399204,-1.4556614325  
C,0,-0.3423616652,-0.1144828738,-0.1239753313  
C,0,-0.3960240812,1.398486488,-0.3646914306  
C,0,-0.3055955294,1.9952570542,-1.622054766  
C,0,-0.3499199102,3.383541028,-1.7599383074  
C,0,-0.503488439,4.1949637522,-0.6421726576  
C,0,-0.62679226,3.6076933143,0.6171873535  
C,0,-0.5757848237,2.2262402048,0.7498934276  
H,0,-0.2043533044,1.387657737,-2.5197418561  
H,0,-0.2664330054,3.8269932652,-2.7499080224  
H,0,-0.5364834132,5.2766777924,-0.7497585356  
H,0,-0.7636723811,4.230226112,1.4987713677

H,0,-0.6685570144,1.7695996112,1.7345441465  
C,0,-1.7462748826,-0.5896672651,0.2605557873  
C,0,-1.9699435075,-1.3100176165,1.4335218145  
C,0,-3.247400551,-1.7678388101,1.7520488463  
C,0,-4.3186233178,-1.5140920308,0.9013815272  
C,0,-4.1048233768,-0.7888624047,-0.2692739436  
C,0,-2.8306411712,-0.3272337642,-0.5827688479  
H,0,-1.1324773479,-1.5069705736,2.0976714597  
H,0,-3.4027661572,-2.3272362745,2.6724739353  
H,0,-5.315191928,-1.8719124327,1.1505421492  
H,0,-4.9354431062,-0.5738152103,-0.9383259725  
H,0,-2.6840578786,0.2571389936,-1.4907208189  
O,0,0.5116466684,-0.378775911,0.960506552  
Si,0,2.1333512246,-0.0992799727,1.2884169986  
C,0,2.1020079125,0.1833180557,3.1450363426  
H,0,3.1191864776,0.2918355992,3.5454609347  
H,0,1.6254809568,-0.6572528598,3.6666840564  
H,0,1.543821551,1.0933909248,3.4020162352  
C,0,2.896587932,1.420850907,0.4974714047  
H,0,2.2874297193,2.3222611469,0.643406  
H,0,3.0861290701,1.2990407696,-0.5741202211  
H,0,3.8653766242,1.5986644368,0.9871226397  
C,0,3.188377312,-1.6145829655,0.9698969551  
H,0,2.6948541364,-2.5260918753,1.3321216445  
H,0,4.1383460865,-1.5196564746,1.5148737599  
H,0,3.4150889233,-1.739683767,-0.0945439656  
H,0,1.616006584,0.2713100097,-2.1454830563

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**TS-HDA**

E(RM06)= -2003.97757424 Hartree

Sum of electronic and thermal Free Energies= -2003.331245 Hartree

C,0,-0.8911437115,1.5680460786,2.100524624  
C,0,0.5165314489,1.8293366904,1.558052627  
C,0,0.6896244929,0.8816533779,0.356472587  
C,0,-1.1619790616,0.12877066,1.6966279984  
H,0,-0.9618373112,1.7195274599,3.1821424632  
H,0,-1.6293130489,2.2275113856,1.6234274229  
H,0,1.2661163448,1.6228440185,2.3285495639  
H,0,0.6574419095,2.8752346769,1.2612566315  
H,0,0.659854354,1.4353635395,-0.5907018489  
H,0,-2.2254981301,-0.1083320029,1.6373691805  
H,0,-0.6809876252,-0.5783178637,2.3903913631  
N,0,-0.5073303117,0.0214805312,0.3821280213  
C,0,2.0054058747,0.0435596768,0.3203720018

C,0,1.9742723945,-0.9949384058,1.4434869418  
C,0,2.3219963751,-0.6808681314,2.7630822937  
C,0,1.486224076,-2.2779251891,1.1851148517  
C,0,2.1681197424,-1.6114437851,3.7877686687  
H,0,2.7371802438,0.2954616614,3.004724415  
C,0,1.3306820687,-3.2119969258,2.2056236452  
H,0,1.222095851,-2.544168148,0.1658081058  
C,0,1.6644215648,-2.8804055271,3.5157955235  
H,0,2.449125483,-1.3404256398,4.8031109625  
H,0,0.9458834807,-4.2027529402,1.9710057528  
H,0,1.5435073895,-3.6067711873,4.316156316  
C,0,3.2378886008,0.9503952829,0.3662752833  
C,0,4.4614744258,0.468446445,0.8435172889  
C,0,3.2111002569,2.2396936175,-0.1774851336  
C,0,5.6132942116,1.2487918646,0.7945310517  
H,0,4.5209491213,-0.5352175574,1.2598524067  
C,0,4.3577321117,3.0271364494,-0.2211889602  
H,0,2.2902786253,2.6471623037,-0.5895024407  
C,0,5.5653040146,2.5356503291,0.266496056  
H,0,6.5503121669,0.8474088981,1.1742896791  
H,0,4.3055046462,4.0274181315,-0.6451502441  
H,0,6.4622187002,3.1496828205,0.232446806  
Si,0,3.1035360918,-1.1607506563,-2.0319444159  
O,0,1.9490752788,-0.6136999637,-0.9389687414  
C,0,4.3506217044,-2.3325244714,-1.2692775655  
H,0,3.8731425885,-3.0802025905,-0.6230534185  
H,0,4.8573894088,-2.8755254312,-2.0799802765  
H,0,5.1249601559,-1.8191450132,-0.6876267784  
C,0,3.9884142129,0.2456038185,-2.8922024774  
H,0,4.7010864718,0.7655129085,-2.240822886  
H,0,4.552394748,-0.1578596078,-3.7448703346  
H,0,3.2813538852,0.9866797012,-3.2865376356  
C,0,2.080111867,-2.1073929007,-3.2809946419  
H,0,1.1964313232,-1.5427947963,-3.6065034344  
H,0,2.6838441151,-2.3195985751,-4.1738347088  
H,0,1.7430343186,-3.0720517415,-2.8805406357  
C,0,-1.1075863542,-0.3468662856,-0.7650592614  
H,0,-0.4030669684,-0.486435779,-1.5849208441  
C,0,-2.2681693476,-1.3197858949,-0.7056545952  
H,0,-2.195243404,-1.8155194734,0.2729911172  
C,0,-2.1099347834,-2.3921588375,-1.786296353  
H,0,-3.0562500721,-2.9474610804,-1.8649554442  
H,0,-1.9744586512,-1.8914340182,-2.758958581  
C,0,-4.8483946627,-1.2510693548,-0.0442081319



O,0,-5.2559418789,-0.2304573973,0.9049722441  
C,0,-3.6982555547,0.788978702,-0.3933706013  
C,0,-3.6556400136,-0.6330607822,-0.8380643257  
H,0,-3.8938800765,-0.6951787681,-1.9144476936  
C,0,-4.6582126293,0.9818008916,0.6550684566  
O,0,-4.9565161492,1.955933317,1.3190304968  
C,0,-6.0260007222,-1.4884420402,-0.9726803727  
H,0,-5.7984441132,-2.2898575069,-1.6880201267  
H,0,-6.9160500713,-1.77503888,-0.4003399044  
H,0,-6.2592654435,-0.5779597843,-1.5386225769  
C,0,-4.5518753843,-2.4915140035,0.7749235008  
H,0,-5.4663841076,-2.8177481212,1.2837886608  
H,0,-4.2041833478,-3.3187810451,0.142971414  
H,0,-3.7989275515,-2.298108524,1.54771819  
C,0,-2.7224818683,1.6301199551,-0.8686396684  
O,0,-1.7499246865,1.1460315987,-1.5704815647  
O,0,-2.7383957322,2.9393370728,-0.5949399332  
C,0,-1.6252416789,3.733528144,-1.0239790678  
H,0,-0.6857314038,3.2455892021,-0.7274778569  
H,0,-1.6284899522,3.7994457772,-2.1200650642  
C,0,-1.7700158466,5.0853008185,-0.379504773  
H,0,-0.9450487281,5.7382769881,-0.6854373397  
H,0,-2.7123570981,5.5611068721,-0.6708706255  
H,0,-1.7570883669,4.9998047025,0.7135144586  
C,0,-0.9733998606,-3.3610108015,-1.519655082  
H,0,-1.1226626492,-3.8877343936,-0.5658644777  
H,0,-0.8920208076,-4.1158663736,-2.310339151  
H,0,-0.0091253706,-2.8395936566,-1.4619933888

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#### **INT-HDA**

E(RM06)= -2003.98917102 Hartree

Sum of electronic and thermal Free Energies= -2003.342585 Hartree

C,0,-0.0710525148,1.3821313095,-3.0985070768  
C,0,-1.3184870273,1.5921339686,-2.247332679  
C,0,-1.0048786993,0.8729940128,-0.9287140083  
C,0,0.3561165227,-0.0172989626,-2.6848502468  
H,0,-0.2680326461,1.4711994131,-4.1725435877  
H,0,0.7097189912,2.1054166298,-2.8300977628  
H,0,-2.1790409678,1.1346827867,-2.7485714169  
H,0,-1.56125585,2.6479497682,-2.0860054876  
H,0,-0.6017773506,1.6003384948,-0.2099524976  
H,0,1.4098387032,-0.2351029503,-2.8893625473  
H,0,-0.2473006829,-0.7729301931,-3.2149393752  
N,0,0.0736684232,-0.090777184,-1.2422010494

C,0,-2.2031987137,0.1908743691,-0.2026291897  
C,0,-2.7427184575,-0.9590903732,-1.0539845113  
C,0,-3.640507791,-0.7449500288,-2.1082373826  
C,0,-2.2903619942,-2.2621963963,-0.838904507  
C,0,-4.0580090692,-1.7923963223,-2.9243867996  
H,0,-4.0430912157,0.2498377446,-2.2891136937  
C,0,-2.7118432131,-3.3153152224,-1.6474342049  
H,0,-1.592713102,-2.4504191343,-0.026470077  
C,0,-3.5931849391,-3.0854538326,-2.6989646635  
H,0,-4.7583691902,-1.595435121,-3.7332379197  
H,0,-2.3422216719,-4.3206160424,-1.4540950877  
H,0,-3.9214979363,-3.9063050969,-3.3325739677  
C,0,-3.2851437479,1.2091640425,0.1815035316  
C,0,-4.6140085261,0.8081778507,0.3624995065  
C,0,-2.9601932792,2.5340856284,0.4959822484  
C,0,-5.5830485346,1.6958404073,0.8221493586  
H,0,-4.9024295777,-0.218383112,0.1466382103  
C,0,-3.9266441794,3.428600665,0.9468360043  
H,0,-1.9361720809,2.8884531039,0.4062031832  
C,0,-5.2451581804,3.014424174,1.1111406959  
H,0,-6.6070329713,1.3520064804,0.9524763485  
H,0,-3.6421979551,4.4528737761,1.1778363891  
H,0,-6.000820336,3.7116691213,1.4655721296  
Si,0,-2.1779402762,-0.7018724935,2.5204350509  
O,0,-1.6200881702,-0.3261787304,0.9851044614  
C,0,-3.7438562351,-1.7326068328,2.5314143719  
H,0,-3.7334807295,-2.5153668438,1.7623130561  
H,0,-3.8312930513,-2.2299762455,3.5077346317  
H,0,-4.6474706268,-1.1273955043,2.3931679405  
C,0,-2.4255073159,0.8376125268,3.5551192865  
H,0,-3.3159833074,1.4042720927,3.255100762  
H,0,-2.5505448613,0.5593027979,4.610811836  
H,0,-1.5589388536,1.5082979826,3.4893218549  
C,0,-0.7654029431,-1.7151817143,3.2118898235  
H,0,0.1842422242,-1.1663906498,3.1625797723  
H,0,-0.9459837268,-1.9669801959,4.2654738686  
H,0,-0.6420514064,-2.6590525218,2.6642007284  
C,0,1.1732914997,-0.0494565793,-0.3603471006  
H,0,0.7806684603,0.0228937526,0.6643890924  
C,0,2.1719759566,-1.2080485775,-0.4193551668  
H,0,2.6821060424,-1.1803108805,-1.3963812433  
C,0,1.4613321327,-2.5544887528,-0.2408863362  
H,0,2.1378176081,-3.2407117794,0.2849471235  
H,0,0.6024582047,-2.4133720954,0.4346729521

C,0,4.5183459645,-1.7654032586,0.7077370659  
O,0,5.4844843726,-0.8330678467,1.2787144965  
C,0,3.7391378863,0.450632216,0.6127767289  
C,0,3.2015275671,-0.9459444519,0.6819761595  
H,0,2.6953455833,-1.1226105216,1.6511160537  
C,0,5.1040346071,0.4682317372,1.0909590382  
O,0,5.8688689944,1.3784770937,1.3268572366  
C,0,4.50314725,-2.9565475201,1.6416486631  
H,0,3.8641142495,-3.7597650752,1.2573883155  
H,0,5.5178166511,-3.3577918881,1.7491519146  
H,0,4.1421464529,-2.6693414191,2.6360941812  
C,0,5.028340747,-2.1478221202,-0.6692333519  
H,0,6.0369294497,-2.5678083575,-0.5812833399  
H,0,4.3843194891,-2.9033250806,-1.1367560817  
H,0,5.0827206818,-1.2760440682,-1.3328816065  
C,0,3.0754726886,1.4397387367,-0.0393566293  
O,0,1.8859891472,1.2478212635,-0.5947818059  
O,0,3.573466939,2.6582461518,-0.1891509022  
C,0,2.8624393426,3.6189600899,-0.9897013029  
H,0,2.8277412581,3.2621849612,-2.0280217621  
H,0,1.8307559649,3.7083328596,-0.6255021104  
C,0,3.6073834951,4.9199021625,-0.8747253999  
H,0,3.108144701,5.6881695315,-1.4750142637  
H,0,3.6396844398,5.2607844966,0.1653563513  
H,0,4.6368577365,4.8166445728,-1.2329056136  
C,0,1.0107094647,-3.211160317,-1.5341701519  
H,0,1.8582914857,-3.3554092922,-2.2188619283  
H,0,0.573929533,-4.199045508,-1.3433649614  
H,0,0.2551691839,-2.6118708566,-2.053070371

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### TS-2+2

E(RM06)= -2003.98177027 Hartree

Sum of electronic and thermal Free Energies= -2003.337449 Hartree

C,0,0.6804471922,-0.3614844744,-3.0321983006  
C,0,-0.6410952807,0.2283288174,-2.5474800461  
C,0,-0.5864987466,0.1359172131,-1.0202895482  
C,0,0.9388228844,-1.4729449439,-2.0340446229  
H,0,0.6287603581,-0.7330925062,-4.0593733854  
H,0,1.4899283978,0.3797414305,-2.9701910518  
H,0,-1.4791562541,-0.3545903494,-2.9433912042  
H,0,-0.7766701991,1.2627098327,-2.8758077574  
H,0,-0.2332287061,1.079490021,-0.5861225094  
H,0,1.979393256,-1.7965422242,-1.9849285685  
H,0,0.2923164933,-2.3464622307,-2.2029672051

N,0,0.5232732855,-0.8425290079,-0.7645245462  
C,0,-1.886289844,-0.2423262129,-0.2508152798  
C,0,-2.3546809312,-1.6413334542,-0.6597920974  
C,0,-3.0942771454,-1.8662683626,-1.8267345806  
C,0,-1.9897626878,-2.7457594392,0.1131674887  
C,0,-3.4227878712,-3.1587876751,-2.2259290162  
H,0,-3.4411988377,-1.0249852557,-2.4239588837  
C,0,-2.316878718,-4.0403111012,-0.2830206608  
H,0,-1.4526547033,-2.5811406458,1.0440405452  
C,0,-3.0270998978,-4.2531422003,-1.4604034083  
H,0,-4.0000442369,-3.3086213276,-3.1355666067  
H,0,-2.0186551022,-4.8830922881,0.3376053458  
H,0,-3.2854274139,-5.2624836001,-1.7721333994  
C,0,-2.9640628518,0.824089409,-0.4556604763  
C,0,-4.2830668564,0.5277371701,-0.0948408224  
C,0,-2.672599613,2.1263725818,-0.8715198272  
C,0,-5.2782044562,1.4977784005,-0.1488810445  
H,0,-4.5353681215,-0.4778883169,0.2384414226  
C,0,-3.668048465,3.0982665732,-0.9380675194  
H,0,-1.6595381464,2.4160102332,-1.1406579134  
C,0,-4.9745937411,2.789063519,-0.5747756109  
H,0,-6.2949350109,1.2418537626,0.1410115267  
H,0,-3.411224961,4.102694421,-1.268224227  
H,0,-5.751512917,3.5485309921,-0.6221031046  
Si,0,-1.9173127354,0.3900434322,2.5819498958  
O,0,-1.4954384436,-0.2870823175,1.1010056552  
C,0,-3.5523044771,-0.3007609198,3.1829172711  
H,0,-3.6402571992,-1.3716275851,2.9555830078  
H,0,-3.6241888927,-0.1880468591,4.2732705657  
H,0,-4.4134951317,0.2158959449,2.7420562371  
C,0,-1.9280557782,2.2545393067,2.5485097308  
H,0,-2.7282946924,2.6760941717,1.9276593352  
H,0,-2.0635261338,2.6352786507,3.5704406683  
H,0,-0.9579826273,2.6228836675,2.1862152071  
C,0,-0.5165364568,-0.2135164354,3.6632811503  
H,0,0.4252152081,0.2686055399,3.3635861659  
H,0,-0.6934336121,0.0383258717,4.7171232531  
H,0,-0.3979894407,-1.3043120945,3.5968559981  
C,0,1.1961275496,-0.8233652578,0.335733262  
H,0,0.7932425296,-0.1832149761,1.1221346885  
C,0,2.498962206,-1.4648848398,0.6220345162  
H,0,2.7997265809,-2.1015269915,-0.2190196881  
C,0,2.4252724578,-2.3103321056,1.894263052  
H,0,3.4508275239,-2.5626746992,2.1947307535

H,0,2.0162424566,-1.6884736802,2.705997886  
C,0,4.8910460488,-0.5407437562,0.1646041153  
O,0,4.760079074,-0.1517752127,-1.2209167263  
C,0,3.0786871385,0.9172215437,-0.1056076191  
C,0,3.4901379275,-0.2546094939,0.7516600532  
H,0,3.5616938647,0.0035365962,1.8198776138  
C,0,3.7883468047,0.8431929411,-1.3422414068  
O,0,3.6846079074,1.4247159217,-2.4108551606  
C,0,5.9215721536,0.3641276781,0.8267817863  
H,0,6.105288199,0.0477315866,1.8615854375  
H,0,6.8680139415,0.3149544726,0.2754446293  
H,0,5.5836238669,1.4064202495,0.8394419119  
C,0,5.3927274636,-1.9701335741,0.183217069  
H,0,6.3656425448,-2.0155156445,-0.3202247447  
H,0,5.5341270544,-2.3216828018,1.2127661818  
H,0,4.7263914161,-2.6657555389,-0.3390119341  
C,0,2.1303137737,1.873129337,0.3207224194  
O,0,1.5489605977,1.8601145588,1.4217726722  
O,0,1.8326078844,2.8407900733,-0.5955405414  
C,0,0.8529798697,3.7977486732,-0.2041049273  
H,0,-0.026331506,3.2853254581,0.2158369246  
H,0,1.2531620163,4.435640785,0.5966657341  
C,0,0.4865343503,4.6011745086,-1.4245830515  
H,0,-0.2904457298,5.33418514,-1.1755005062  
H,0,1.3543148736,5.1380641255,-1.8227400566  
H,0,0.1048118522,3.9507639702,-2.222495765  
C,0,1.6047269714,-3.5755587499,1.7184568729  
H,0,2.0333913469,-4.2186326786,0.9377972986  
H,0,1.5583191272,-4.1615010699,2.6430843599  
H,0,0.5708281241,-3.3485256831,1.421328644

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### **INT-CB**

E(RM06)= -2004.00132470 Hartree

Sum of electronic and thermal Free Energies = -2003.353905 Hartree

C,0,0.3033489966,-1.4464296966,-3.2673086278  
C,0,-0.8830183911,-0.6190833634,-2.7867072507  
C,0,-0.5507713661,-0.2870394747,-1.3299153807  
C,0,0.6986762405,-2.2231085437,-2.0198877663  
H,0,0.0492178937,-2.1004250981,-4.1089285863  
H,0,1.1265549311,-0.791612617,-3.5713405755  
H,0,-1.7986916619,-1.2196038658,-2.8464780629  
H,0,-1.0446110071,0.2869350494,-3.3808207457  
H,0,-0.0014763459,0.6674839305,-1.2935412449  
H,0,1.7585958487,-2.5034133163,-2.0194170146

H,0,0.1152730536,-3.1584094337,-1.9389548302  
N,0,0.3713796376,-1.3429440541,-0.8947306898  
C,0,-1.7859612216,-0.114101538,-0.388507145  
C,0,-2.5173997493,-1.4504481657,-0.279510424  
C,0,-3.4979798,-1.8529992647,-1.1932416794  
C,0,-2.1277390649,-2.3654271288,0.7032419585  
C,0,-4.0766029532,-3.1183409725,-1.1202833191  
H,0,-3.8290228189,-1.1700991672,-1.9733669225  
C,0,-2.7013646591,-3.6313056412,0.7798381837  
H,0,-1.3600415835,-2.0787012427,1.418712861  
C,0,-3.68041914,-4.0149871603,-0.1326520686  
H,0,-4.8418894873,-3.399988317,-1.8404339195  
H,0,-2.3751951369,-4.3216832068,1.5557910683  
H,0,-4.1317005746,-5.0029206778,-0.0735527302  
C,0,-2.6628090448,1.0649270353,-0.8315762275  
C,0,-4.0323210356,1.1081359776,-0.5516589914  
C,0,-2.0773153492,2.2154406534,-1.3768137557  
C,0,-4.7912942714,2.2457968332,-0.8185371404  
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C,0,-2.8310893982,3.3521258901,-1.6505545156  
H,0,-1.0100519101,2.2434704024,-1.5856191054  
C,0,-4.1953369894,3.3738883693,-1.3728136271  
H,0,-5.8543599687,2.2463683524,-0.5867250891  
H,0,-2.3444267318,4.2268092003,-2.0779960531  
H,0,-4.7861813242,4.2624330026,-1.5834873238  
Si,0,-1.8097098269,0.8311617161,2.320036432  
O,0,-1.2246991869,0.2295866512,0.8694562149  
C,0,-3.5554912561,0.2873789827,2.7460260879  
H,0,-3.7388817444,-0.7760464339,2.5469900144  
H,0,-3.7033409775,0.4512148587,3.8233719381  
H,0,-4.3196452508,0.8748273836,2.2229217269  
C,0,-1.7326633104,2.700492727,2.3326625205  
H,0,-2.2712829727,3.1427496788,1.4835596797  
H,0,-2.1860521396,3.090292106,3.2545938319  
H,0,-0.6879425515,3.0372086748,2.3046287672  
C,0,-0.6202431646,0.1355796287,3.5854688125  
H,0,0.4132890827,0.3919619193,3.3170925203  
H,0,-0.8232532151,0.5572440334,4.5793160307  
H,0,-0.704372718,-0.9565537499,3.6670167254  
C,0,1.3286122354,-0.9709360354,0.0851393465  
H,0,0.7997363655,-0.6539024101,0.9943305526  
C,0,2.4891576383,-1.8735427864,0.5219120299  
H,0,2.9200995304,-2.4039996882,-0.3412527448  
C,0,2.2410838772,-2.8521609739,1.6504552753

H,0,3.20800059,-3.2261419816,2.0224010277  
H,0,1.7772659214,-2.3101464779,2.490855565  
C,0,4.6939709754,-0.4601692393,0.1788280056  
O,0,4.389762655,-0.2562001536,-1.2388265834  
C,0,2.3924137584,0.2288067065,-0.1046152183  
C,0,3.3137935801,-0.5991126303,0.806658147  
H,0,3.2879751177,-0.3007166677,1.8623417058  
C,0,3.1383449494,0.2227602112,-1.4214960773  
O,0,2.7401327468,0.5425305106,-2.5136228629  
C,0,5.4042680521,0.7850133533,0.6763474902  
H,0,5.6883740763,0.6666016933,1.7288809127  
H,0,6.3112213001,0.9689387963,0.0891392905  
H,0,4.7643576583,1.6744014968,0.596319422  
C,0,5.5759289459,-1.6813306095,0.2877523726  
H,0,6.5216094109,-1.5208055272,-0.242737882  
H,0,5.8062417005,-1.8794446677,1.3419004641  
H,0,5.0970398915,-2.5706348396,-0.1356301294  
C,0,1.9056906146,1.5574011762,0.3921121981  
O,0,1.6617331159,1.7643465383,1.5642464308  
O,0,1.7517670695,2.4649158768,-0.5761494363  
C,0,1.2625190019,3.7656840479,-0.1916012187  
H,0,0.8578728962,4.1839972148,-1.1189817523  
H,0,0.4411232552,3.6397850706,0.5237653377  
C,0,2.3707164884,4.6264096447,0.359446488  
H,0,1.9920222257,5.634551631,0.562053173  
H,0,2.7642920871,4.2180143202,1.2960281593  
H,0,3.1911105871,4.7105785116,-0.3624279063  
C,0,1.3607693784,-4.0164902854,1.2250996862  
H,0,1.8367399,-4.6004949158,0.4257506848  
H,0,1.1583264616,-4.6993436573,2.0584262069  
H,0,0.3962718363,-3.661378639,0.8376104808

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#### 4aa-INT2

E(RM06)= -883.108145700 Hartree

Sum of electronic and thermal Free Energies= -882.837808 Hartree

C,0,-1.3735771462,-1.5487696909,0.2477157749  
O,0,-0.2677256453,-2.4803525914,0.0156644684  
C,0,0.3557183442,-0.4802758373,-1.027030015  
C,0,-0.7186893282,-0.1672152122,0.0091255602  
H,0,-0.1974137165,0.1137569361,0.940343759  
C,0,0.6926006269,-1.9396673693,-0.739157941  
O,0,1.6665272061,-2.5425115936,-1.1093020552  
C,0,-1.8206768355,-1.7714658707,1.6746731772  
H,0,-2.6709754974,-1.1260306421,1.9245893538

H,0,-2.1456861061,-2.8089809019,1.8121783197  
H,0,-1.0053546376,-1.5673705287,2.3779111928  
C,0,-2.4644349513,-1.9078172245,-0.7432780326  
H,0,-2.7334723255,-2.9624193035,-0.6176369359  
H,0,-3.3660786669,-1.3073244891,-0.5777238888  
H,0,-2.1392287585,-1.7661223674,-1.7813229961  
C,0,1.6228136334,0.3362632231,-0.9186752177  
O,0,2.1150711704,0.6780536543,0.133435997  
O,0,2.1346229169,0.5988061464,-2.1175923981  
C,0,3.3952063661,1.3066655196,-2.1388627072  
H,0,3.2600097887,2.268008422,-1.6284228987  
H,0,4.1274715118,0.7225134993,-1.5696565  
C,0,3.791745692,1.4746675743,-3.5784567116  
H,0,4.7469826808,2.0067434805,-3.6388386351  
H,0,3.9108536286,0.5031214263,-4.0695673701  
H,0,3.0438034945,2.053721552,-4.1311526477  
H,0,-0.0293059315,-0.4254576646,-2.0563483468  
C,0,-1.6696533723,0.9689726244,-0.3791475674  
C,0,-0.9106054515,2.279629558,-0.6458869093  
H,0,-0.2098271492,2.1106933549,-1.4754557317  
H,0,-0.2966409663,2.5287696089,0.2331568838  
C,0,-1.8283575319,3.4397073415,-0.9967330208  
H,0,-1.2492706286,4.3217936326,-1.2897548576  
H,0,-2.4924229149,3.1825166197,-1.8319029769  
H,0,-2.4649385908,3.7343208297,-0.1530294505  
C,0,-2.645323345,1.2323178695,0.7359766325  
O,0,-3.8507671049,1.2004023338,0.6313893427  
H,0,-2.166332465,1.5025301159,1.7109909346  
H,0,-2.2489947734,0.7004198543,-1.2760302548

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#### 4aa-INT3

E(RM06)= -883.102327049 Hartree

Sum of electronic and thermal Free Energies= -882.831985 Hartree

C,0,-1.7449306686,1.3044643688,0.2465678543  
O,0,-0.7731385141,2.3935389826,0.1237770566  
C,0,0.4487888686,0.4500906753,-0.3067484148  
C,0,-1.0509129982,0.1289921696,-0.4857463231  
H,0,-1.25413978,0.2560542046,-1.5597096311  
C,0,0.455908471,1.960570383,-0.1932905855  
O,0,1.3843378136,2.7050760763,-0.3744075196  
C,0,-2.9932827586,1.8124541357,-0.4451939644  
H,0,-3.8116548656,1.088858696,-0.376214171  
H,0,-3.3263221647,2.7442131351,0.0262550315  
H,0,-2.7974712249,2.0147803133,-1.5043947315



C,0,-1.982981716,1.0820646787,1.7290972333  
H,0,-2.3068518375,2.0224479814,2.1891497436  
H,0,-2.7707032755,0.3381200565,1.8950294771  
H,0,-1.077045248,0.752188804,2.2516543179  
C,0,1.1025800325,-0.2400277773,0.8730757395  
O,0,1.2879857116,-1.4382931985,0.9098618423  
O,0,1.4237716341,0.5963323092,1.854138313  
C,0,2.0039653264,0.0174942592,3.0455902103  
H,0,1.3107818101,-0.7402046233,3.4324611524  
H,0,2.9342002663,-0.4896234838,2.7652899016  
C,0,2.2297748559,1.1383489684,4.020147641  
H,0,2.6710849711,0.743903886,4.9414837067  
H,0,2.911356632,1.8887748306,3.6065741902  
H,0,1.2865519999,1.6337142172,4.2766597938  
C,0,-1.4779924942,-1.2906741325,-0.1120979483  
H,0,-1.3304315431,-1.4773028675,0.962825847  
C,0,-2.9517321332,-1.5854784858,-0.4499871465  
H,0,-3.1277971744,-1.3220522712,-1.5040847348  
H,0,-3.5899325047,-0.9249267637,0.1502976578  
C,0,-3.3623922117,-3.0290582123,-0.1963870241  
H,0,-4.4431554195,-3.1521845564,-0.3233630074  
H,0,-2.8771473318,-3.727838631,-0.8887483808  
H,0,-3.1121841983,-3.344400795,0.8251951454  
C,0,-0.639133939,-2.3034955153,-0.865795273  
H,0,-0.4220130581,-3.251563985,-0.3292579032  
O,0,-0.2770811744,-2.1443177333,-2.011360073  
H,0,1.0247724009,0.1457298403,-1.1876919034

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#### 4aa-INT4

E(RM06)= -883.102877663 Hartree

Sum of electronic and thermal Free Energies= -882.830575 Hartree

C,0,2.0237048284,-0.6347337994,0.1234602511  
O,0,1.8868881155,-2.0782791354,-0.0719182634  
C,0,-0.1571318177,-1.1861966527,-0.8031496103  
C,0,0.8920427725,-0.0544474178,-0.7644516555  
H,0,1.3026618993,0.0054253269,-1.7865538248  
C,0,0.6776629424,-2.4259325028,-0.5236105314  
O,0,0.3395683618,-3.5680602989,-0.6970148239  
C,0,3.4090940328,-0.2778820567,-0.3722666019  
H,0,3.6186365311,0.7879748839,-0.2218925597  
H,0,4.1623157383,-0.8406155731,0.1903234514  
H,0,3.5253682104,-0.5132633506,-1.4365444504  
C,0,1.8894838474,-0.3651497779,1.6099130625  
H,0,2.6614032947,-0.9299408928,2.1447594126

H,0,2.0355514912,0.6978166181,1.8329009246  
 H,0,0.9140323265,-0.6779021647,1.9941995511  
 C,0,-1.2735535697,-1.0819251069,0.2187515452  
 O,0,-1.1891582765,-1.4305484009,1.3749475993  
 O,0,-2.3634144533,-0.5346243708,-0.3188717498  
 C,0,-3.4705422089,-0.2779732527,0.5746374567  
 H,0,-3.8156558446,-1.2338571713,0.9849499506  
 H,0,-3.1040108706,0.3334729868,1.4088238825  
 C,0,-4.5311747503,0.4233475525,-0.2262389303  
 H,0,-5.3848914481,0.6622322881,0.4163864688  
 H,0,-4.1490236955,1.3606565338,-0.6483388043  
 H,0,-4.8880902957,-0.205771973,-1.0486525683  
 C,0,0.3677670066,1.3379141933,-0.4013177248  
 C,0,-0.614995207,1.8643821951,-1.4662243331  
 H,0,-1.3393863013,1.0779592491,-1.707506856  
 H,0,-0.0556212623,2.0639139659,-2.3944645483  
 C,0,-1.3524342041,3.1133226378,-1.0142322425  
 H,0,-2.0740016665,3.440392238,-1.770897706  
 H,0,-1.9046232095,2.9279331369,-0.0827258946  
 H,0,-0.6725612994,3.9533121747,-0.8234963409  
 H,0,-0.6113239059,-1.2855553201,-1.7941597724  
 C,0,1.4934717506,2.3376902902,-0.3500860068  
 O,0,1.7546372273,3.0551031921,0.5880242449  
 H,0,2.0755325273,2.4157867737,-1.3032216778  
 H,0,-0.1192241169,1.3308093517,0.5876662061

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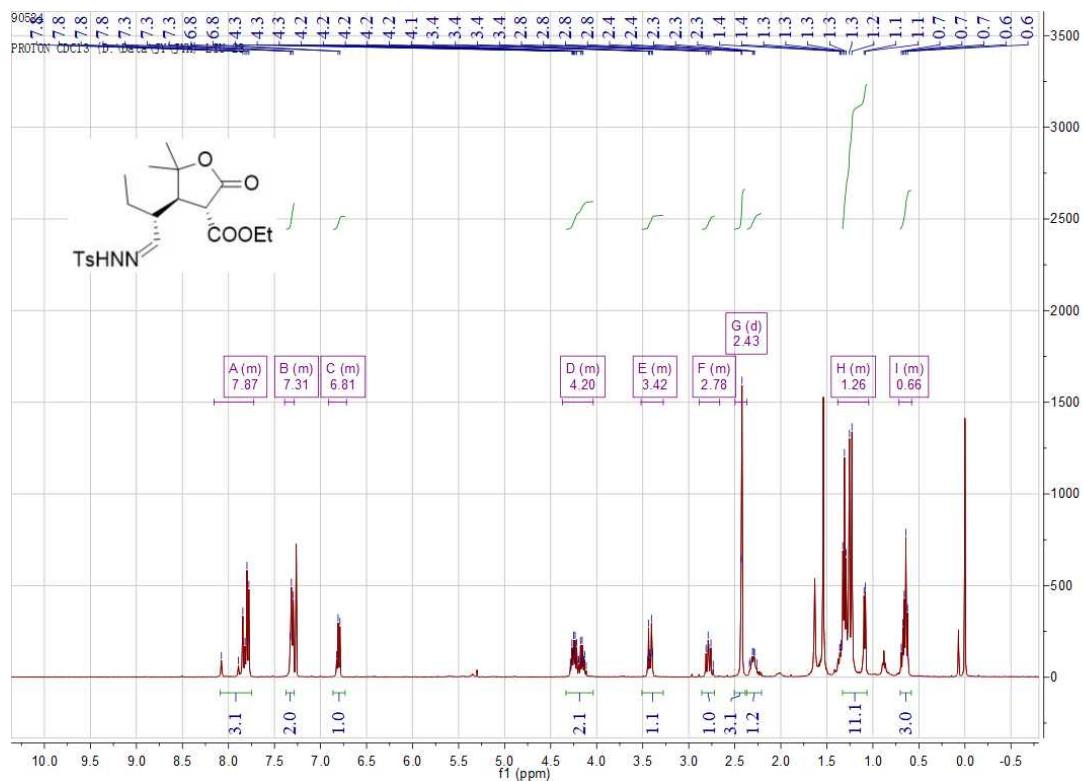
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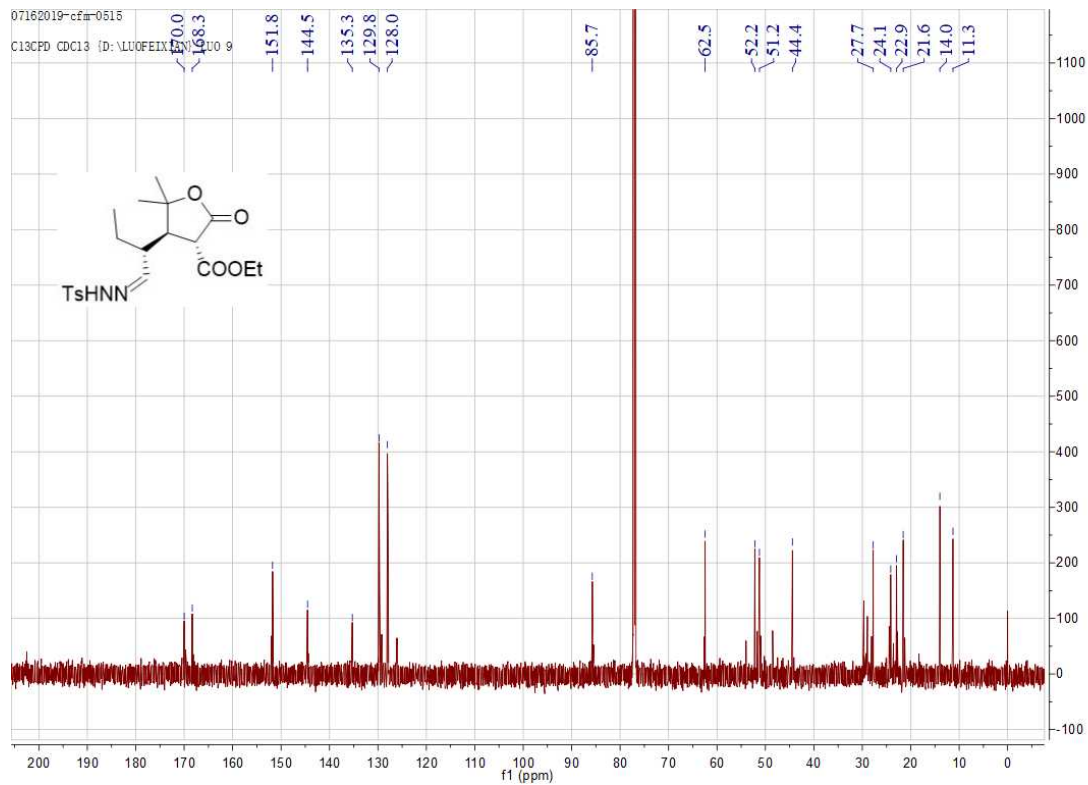
## 5. NMR Spectra for Michael Product 3-11

$^1\text{H}$  NMR of product **3aa** (400 MHz,  $\text{CDCl}_3$ )

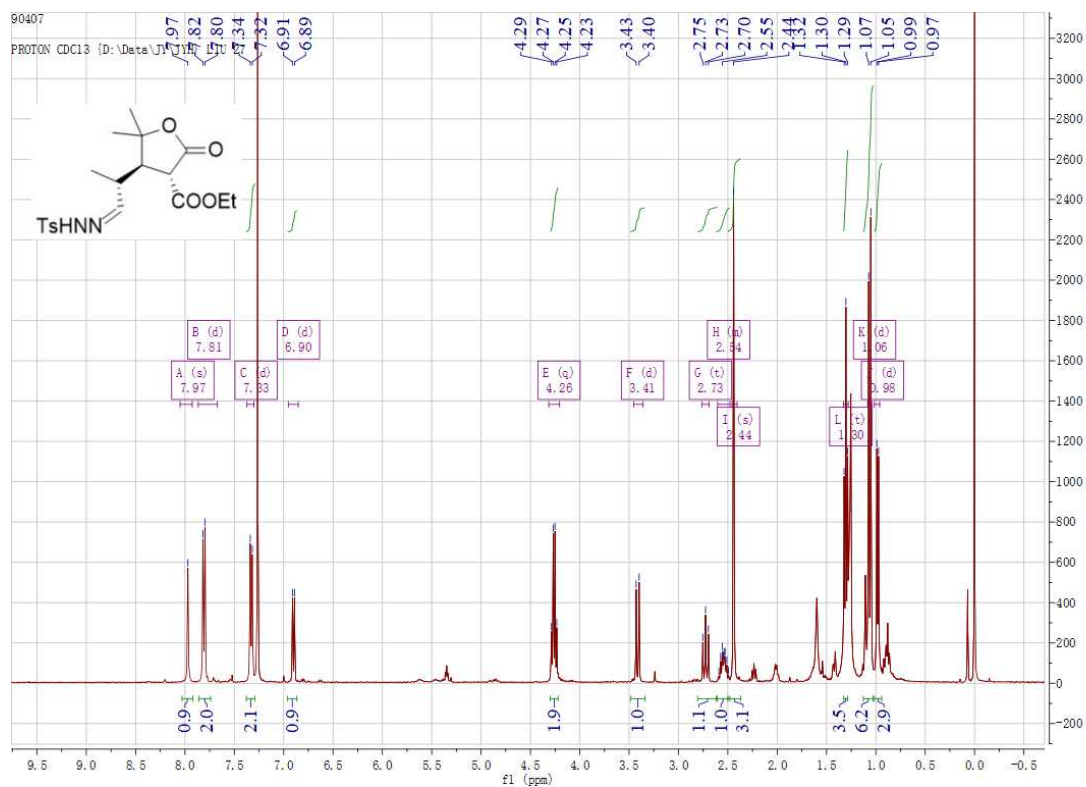
Mixture of two diastereoisomers



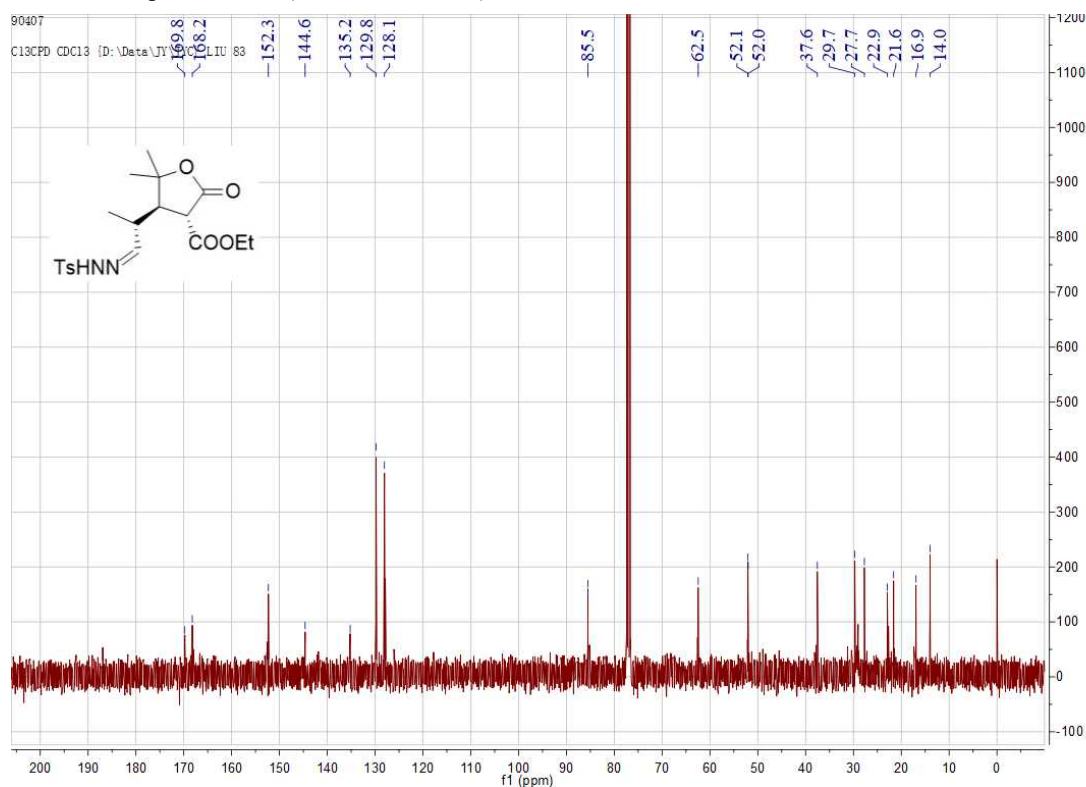
$^{13}\text{C}$  NMR of product **3aa** (100 MHz,  $\text{CDCl}_3$ )



$^1\text{H}$  NMR of product **3ab** (400 MHz,  $\text{CDCl}_3$ )

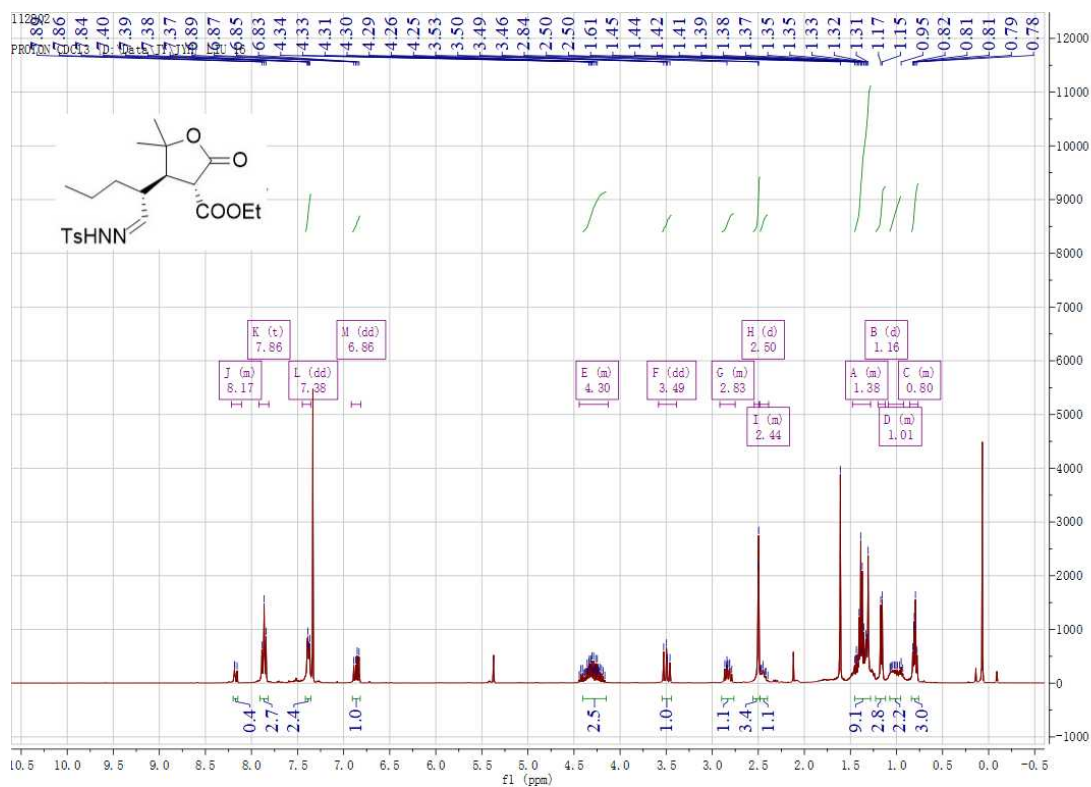


<sup>13</sup>C NMR of product **3ab** (100 MHz, CDCl<sub>3</sub>)

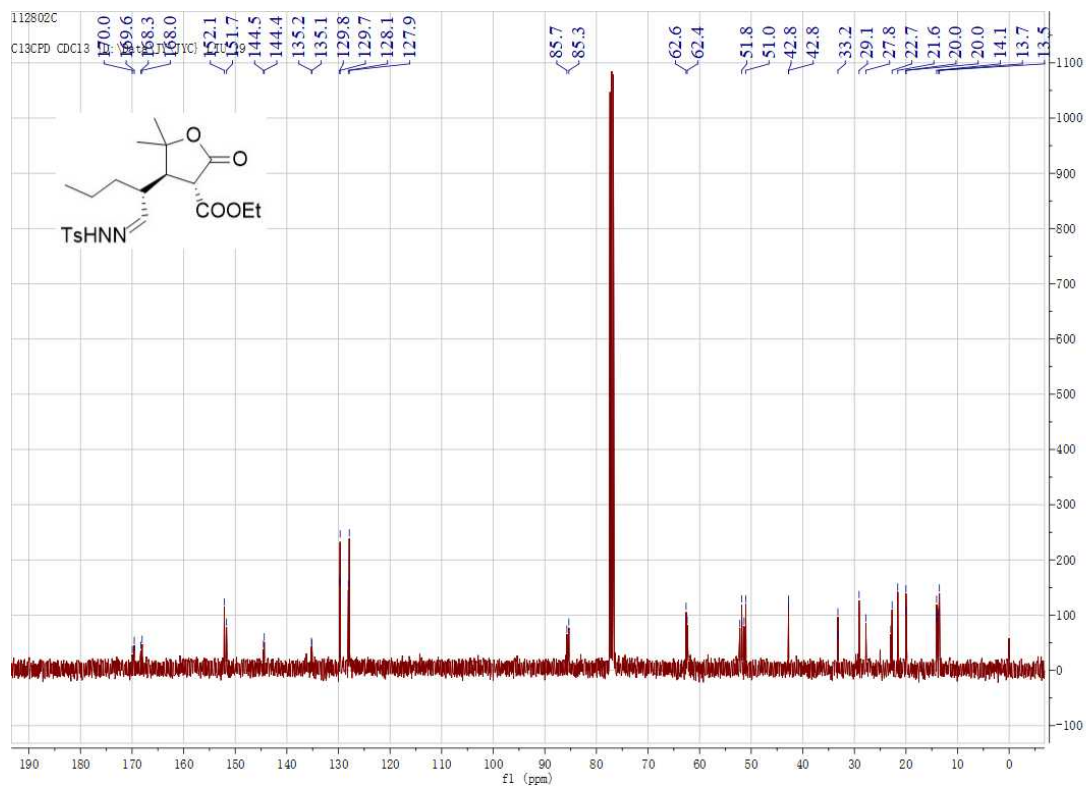


<sup>1</sup>H NMR of product **3ac** (400 MHz, CDCl<sub>3</sub>)

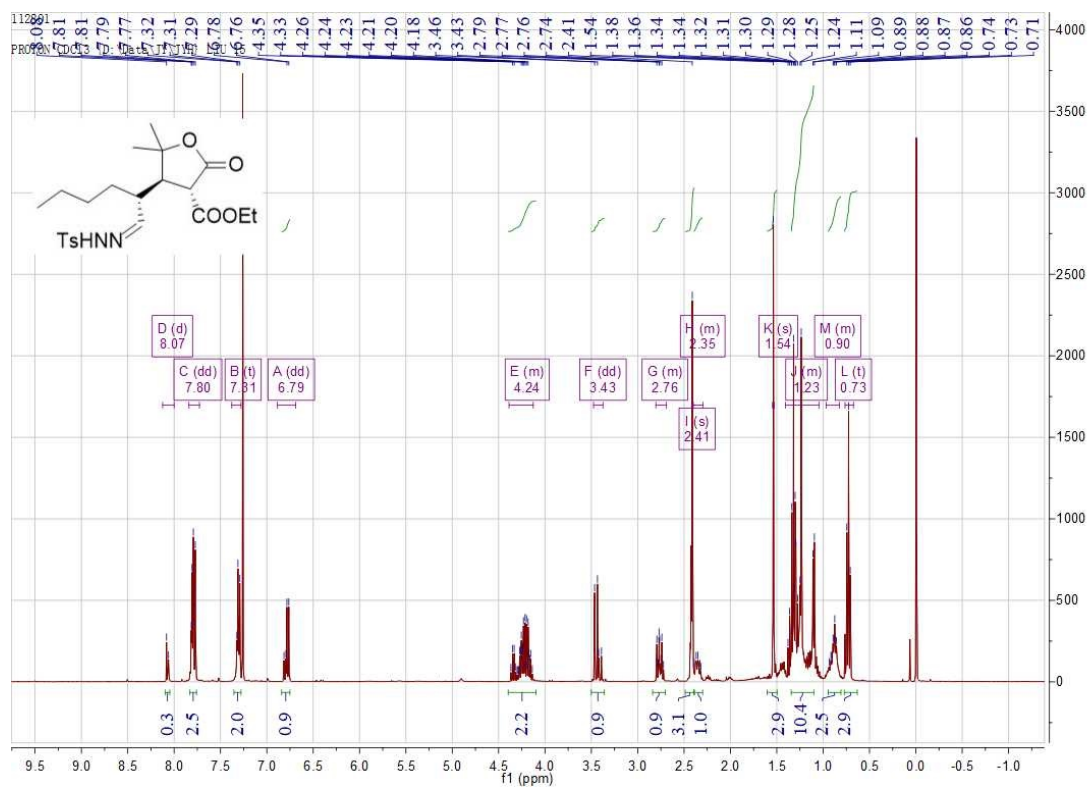
Mixture of two diastereoisomers



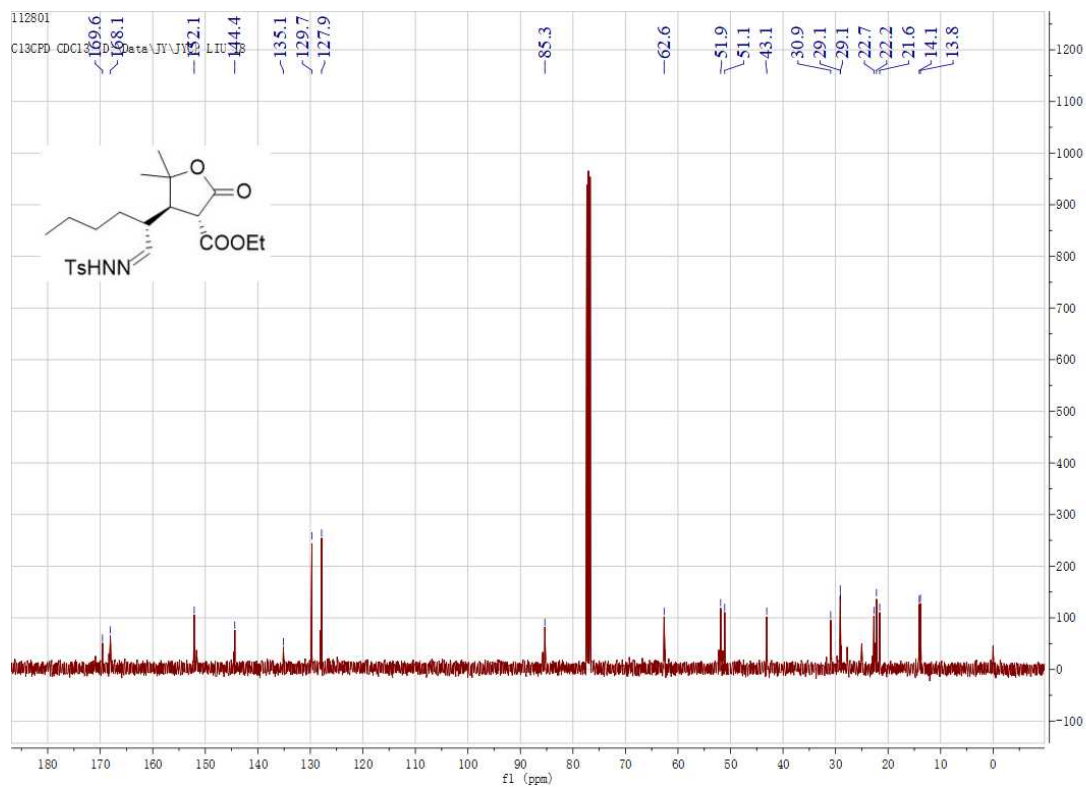
<sup>13</sup>C NMR of product 3ac (100 MHz, CDCl<sub>3</sub>)



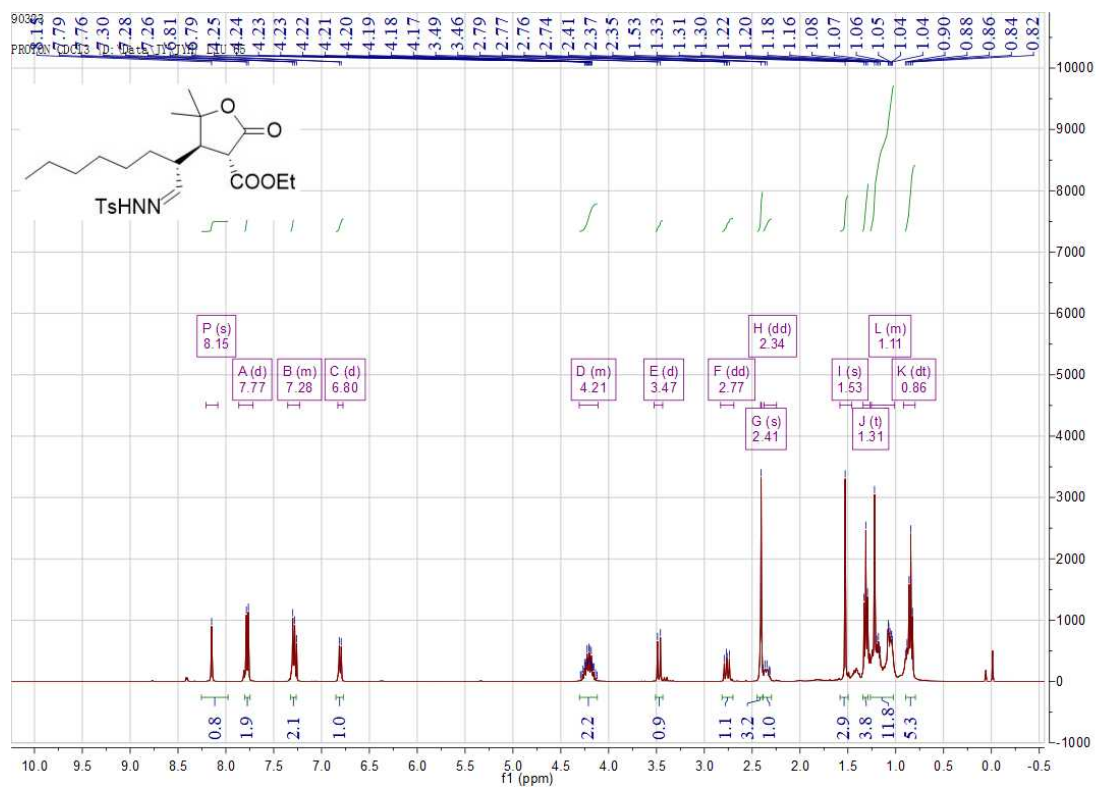
<sup>1</sup>H NMR of product 3ad (400 MHz, CDCl<sub>3</sub>)



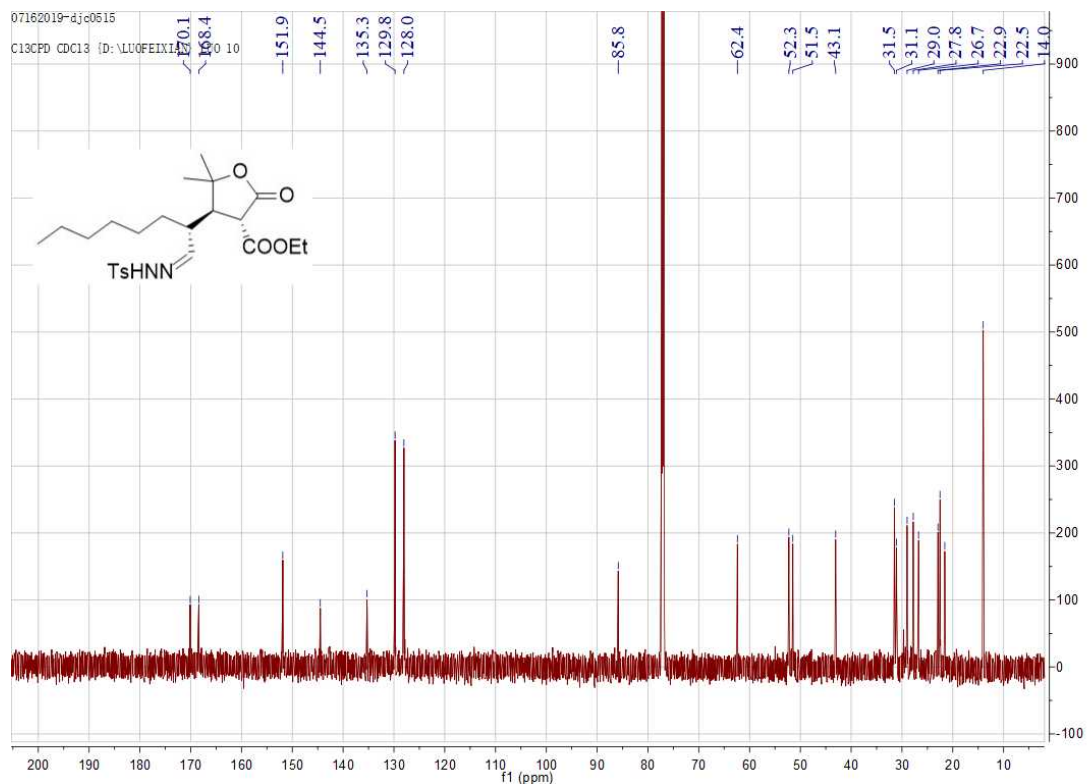
<sup>13</sup>C NMR of product **3ad** (100 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of product **3ae** (400 MHz, CDCl<sub>3</sub>)



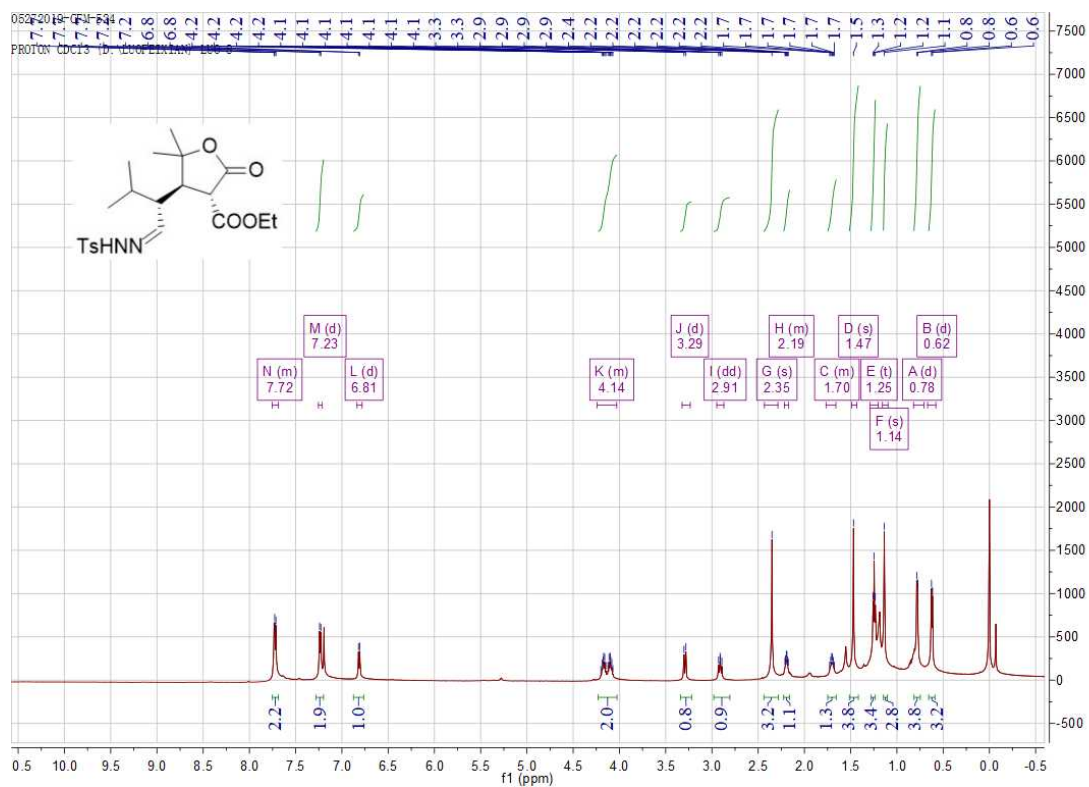
<sup>13</sup>C NMR of product **3ae** (100 MHz, CDCl<sub>3</sub>)



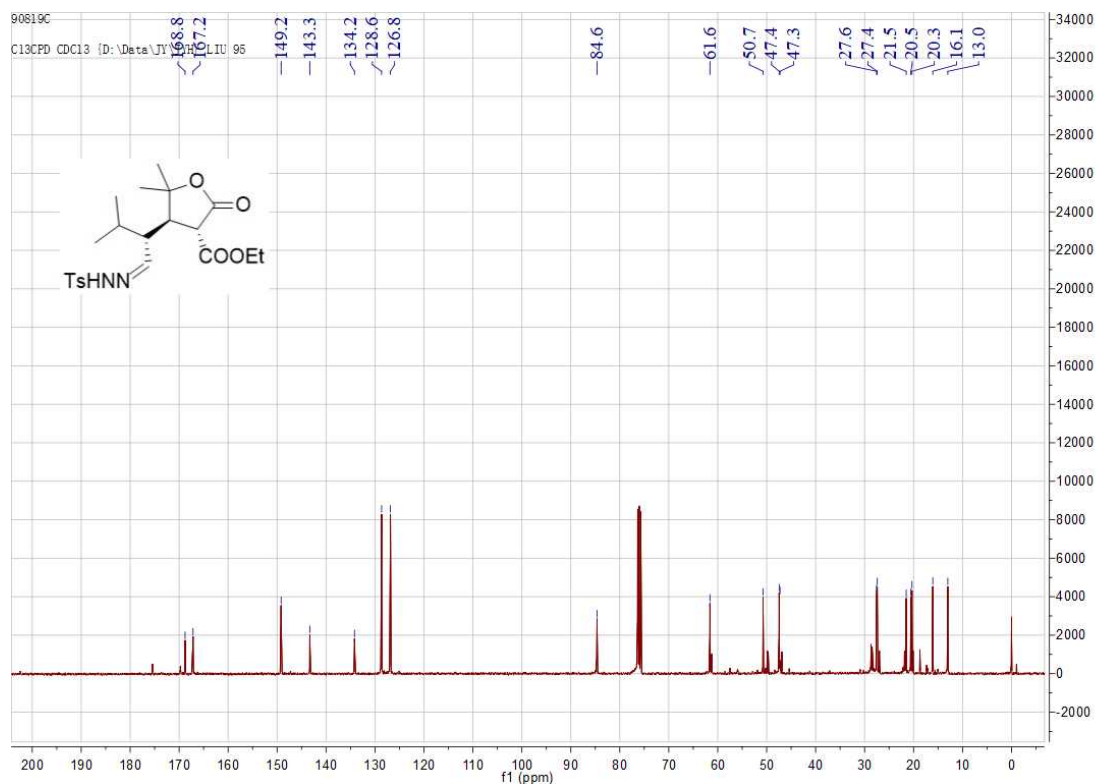
<sup>1</sup>H NMR of product **3af** (400 MHz, CDCl<sub>3</sub>)





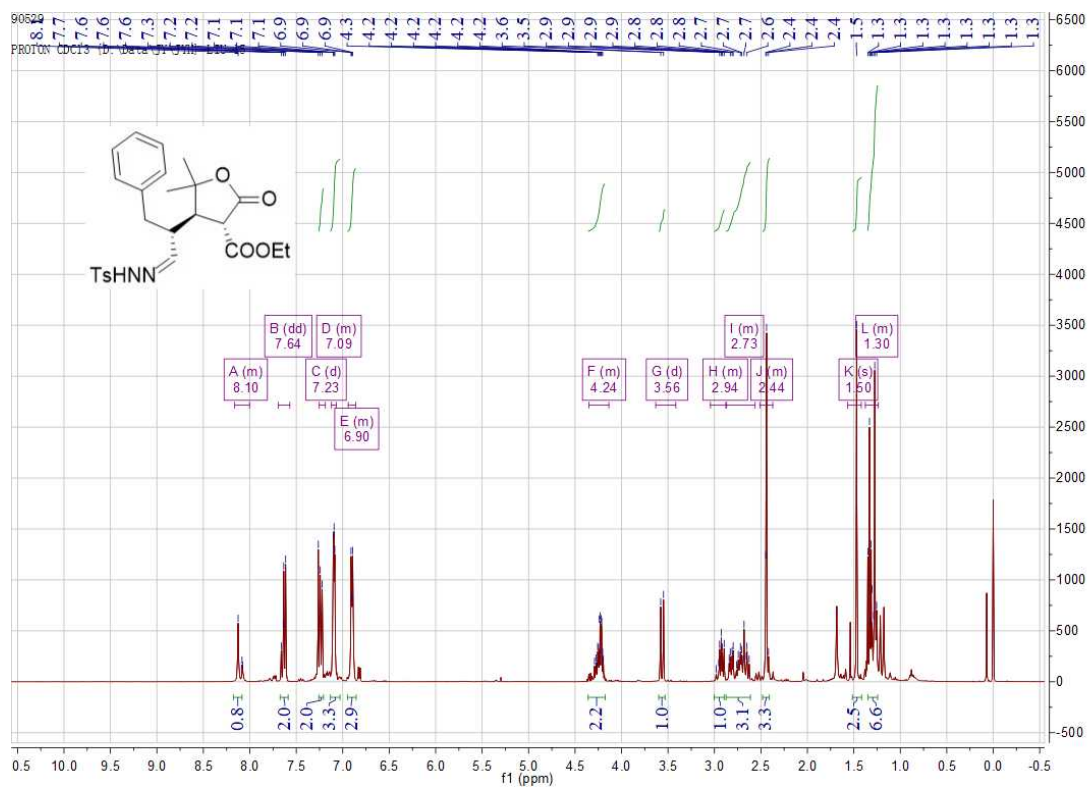


<sup>13</sup>C NMR of product **3a** (100 MHz, CDCl<sub>3</sub>)

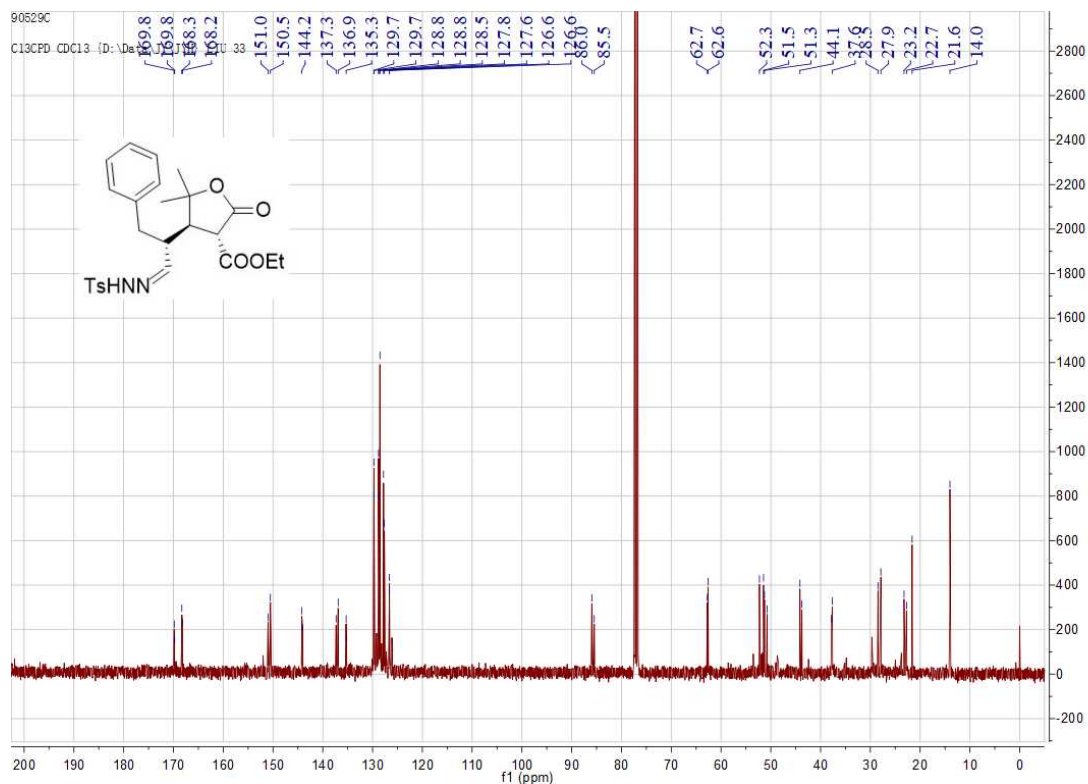


<sup>1</sup>H NMR of product **3ah** (400 MHz, CDCl<sub>3</sub>)

Mixture of two diastereoisomers

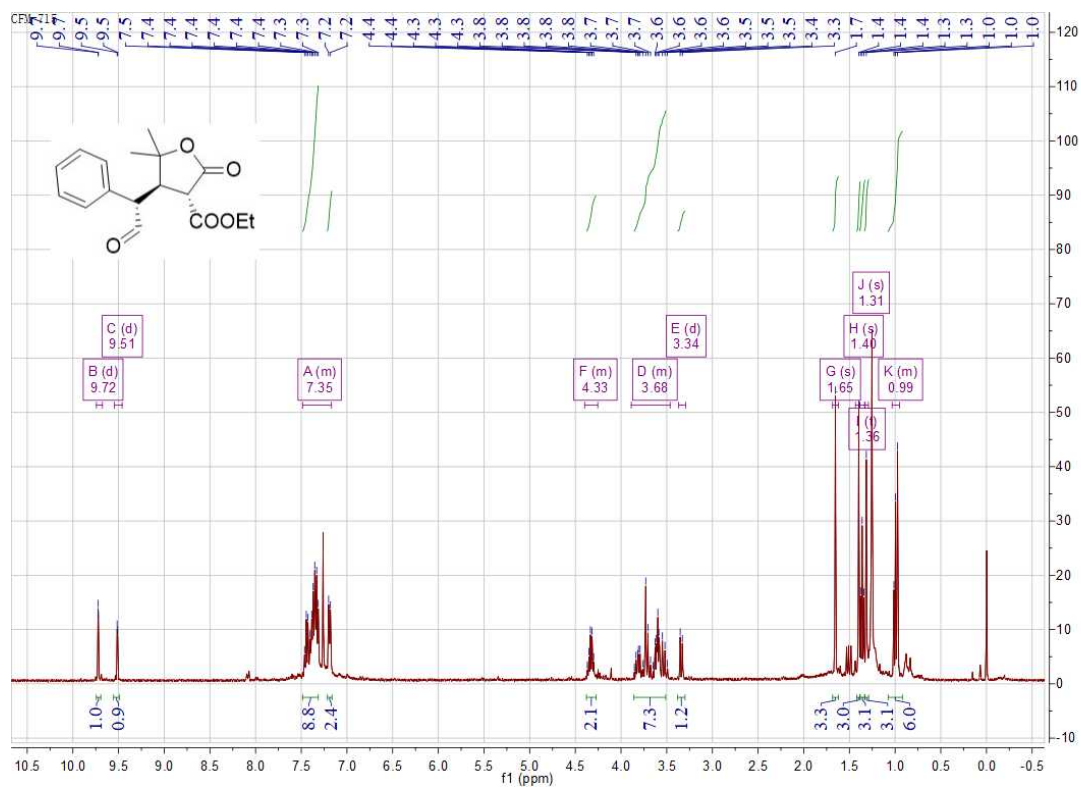


<sup>13</sup>C NMR of product **3ah** (100 MHz, CDCl<sub>3</sub>)

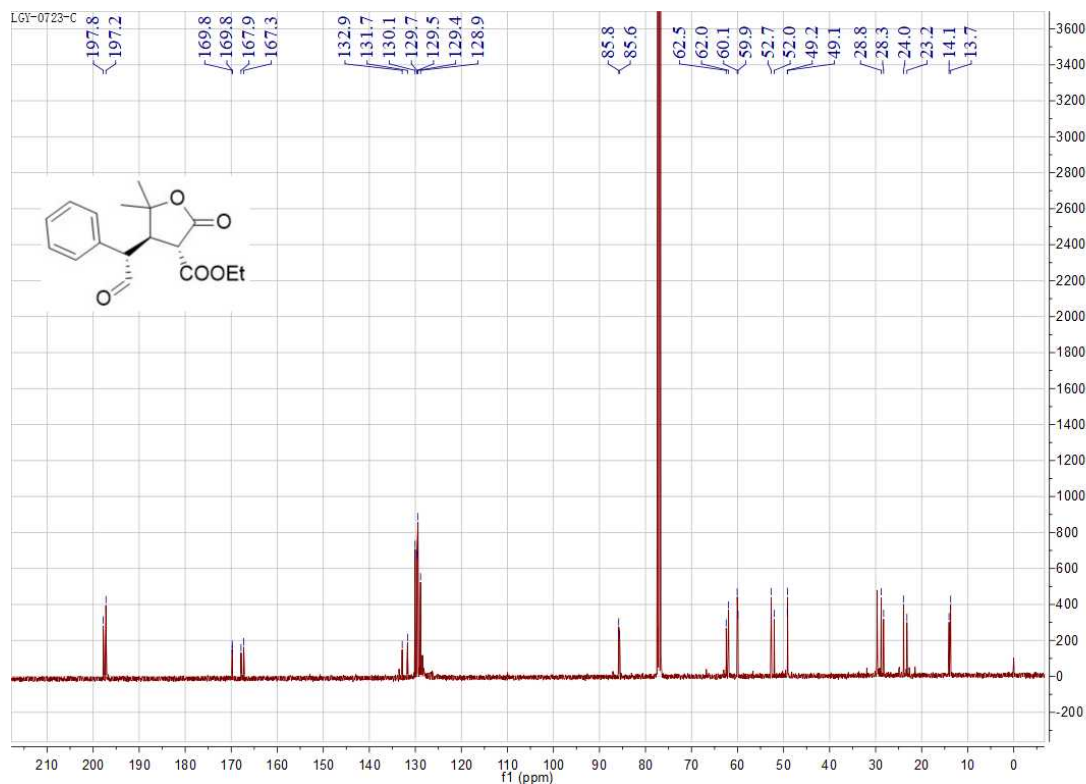


<sup>1</sup>H NMR of product **3ai** (400 MHz, CDCl<sub>3</sub>)

Mixture of two diastereoisomers

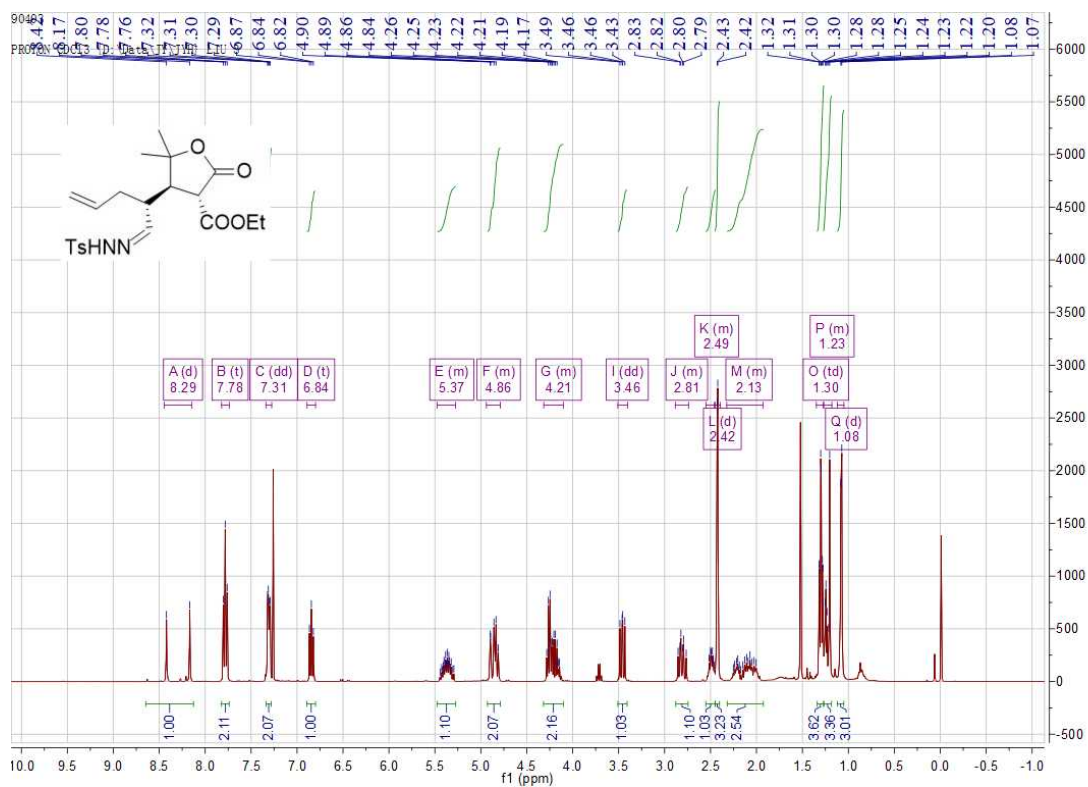


**<sup>13</sup>C NMR of product 3ai (100 MHz, CDCl<sub>3</sub>)**

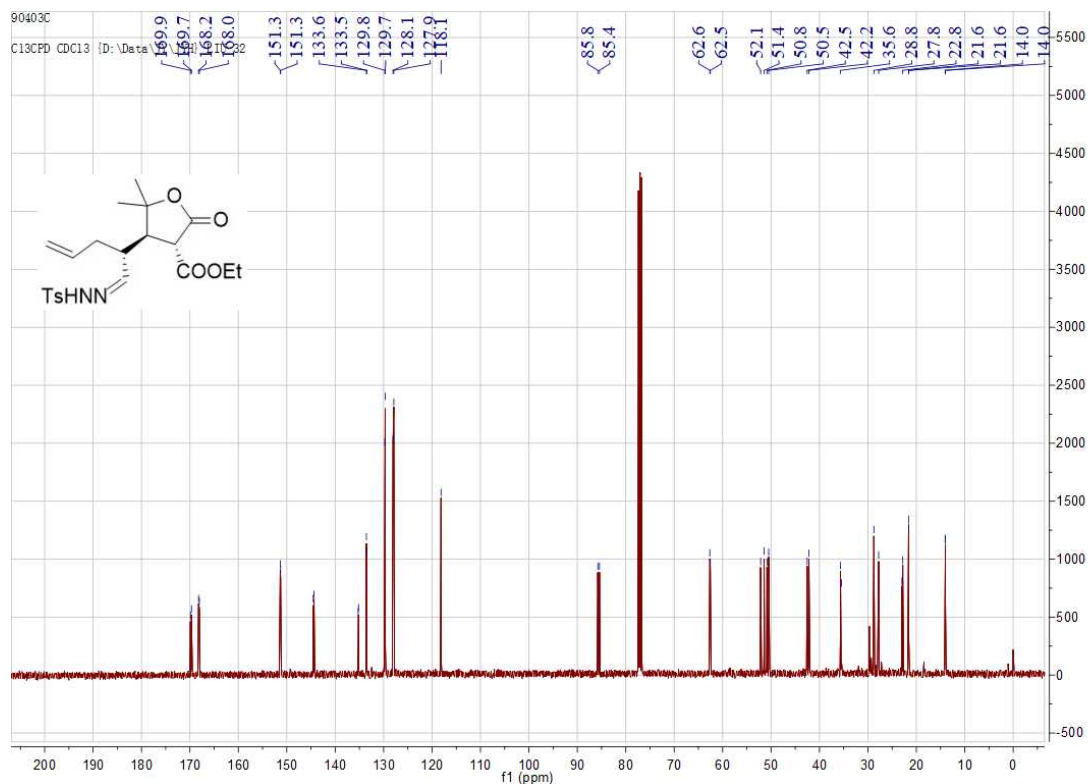


**<sup>1</sup>H NMR of product 3aj (400 MHz, CDCl<sub>3</sub>)**

Mixture of two diastereoisomers



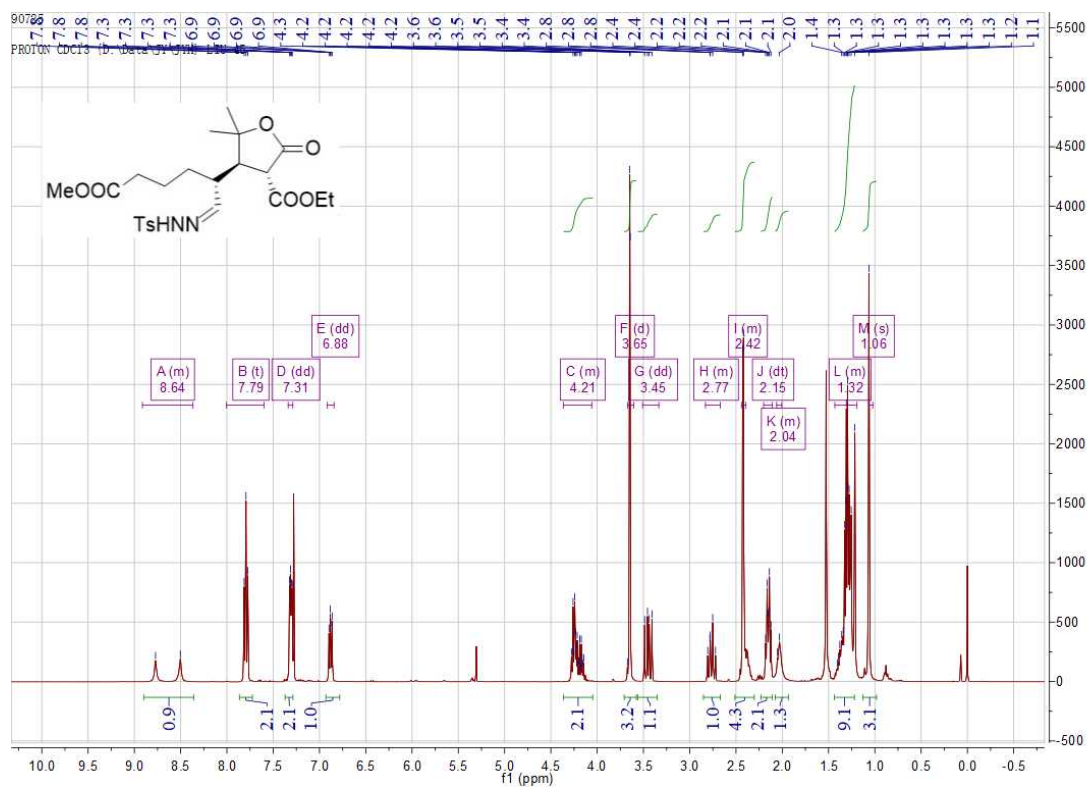
<sup>13</sup>C NMR of product **3aj** (100 MHz, CDCl<sub>3</sub>)



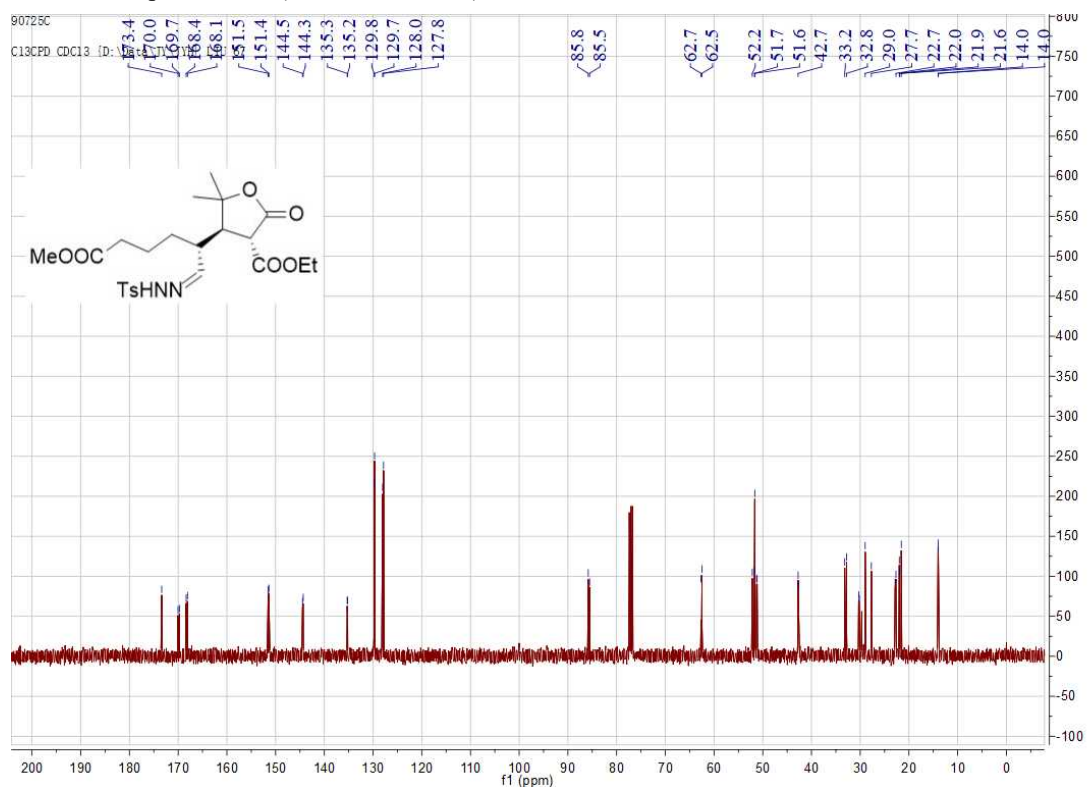
<sup>1</sup>H NMR of product **3ak** (400 MHz, CDCl<sub>3</sub>)





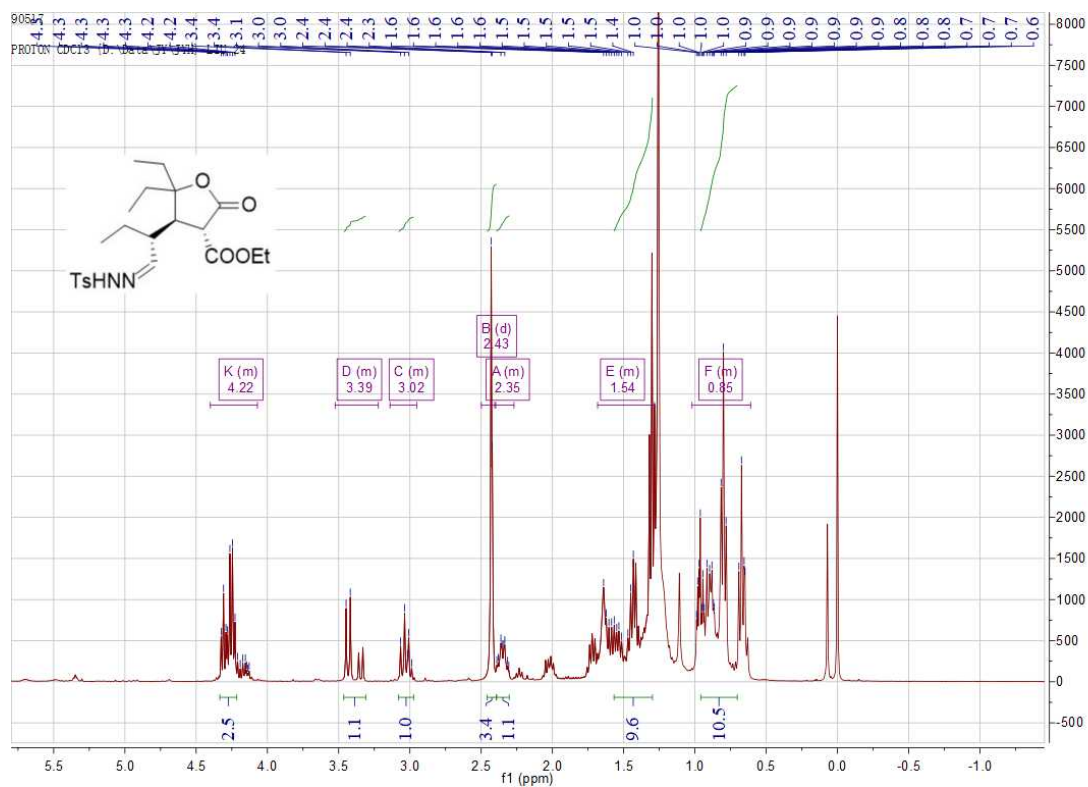


<sup>13</sup>C NMR of product **3al** (100 MHz, CDCl<sub>3</sub>)

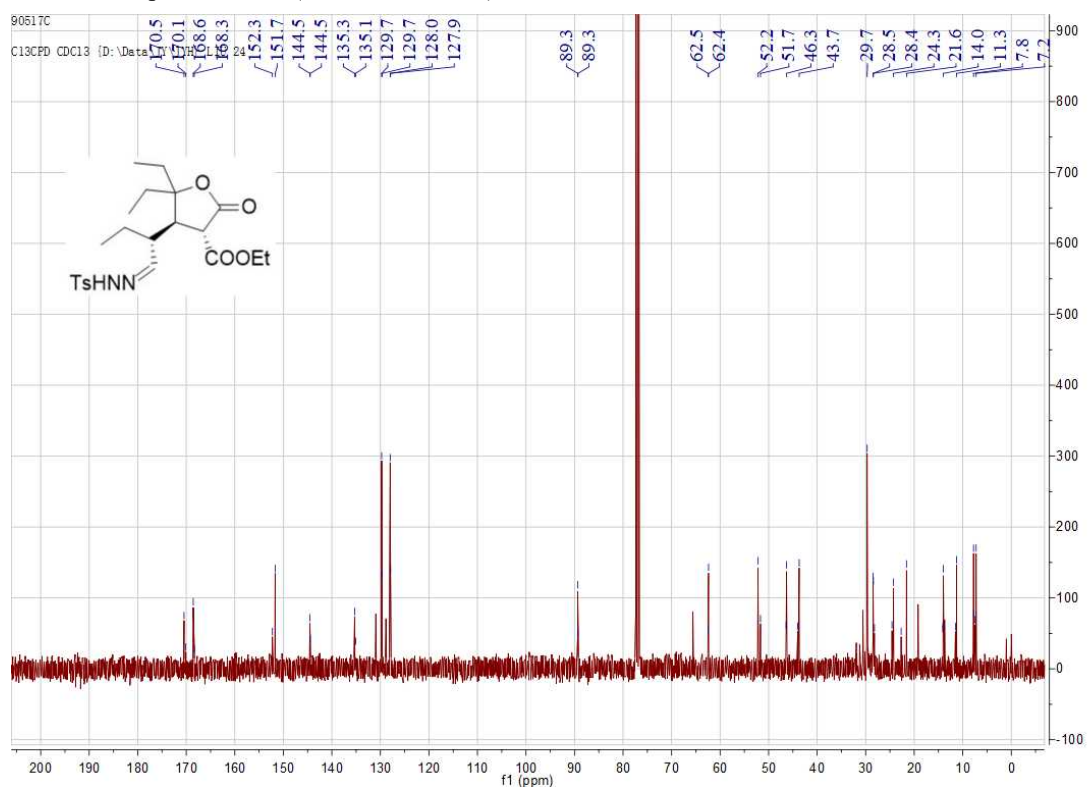


<sup>1</sup>H NMR of product **3am** (400 MHz, CDCl<sub>3</sub>)

Mixture of two diastereoisomers

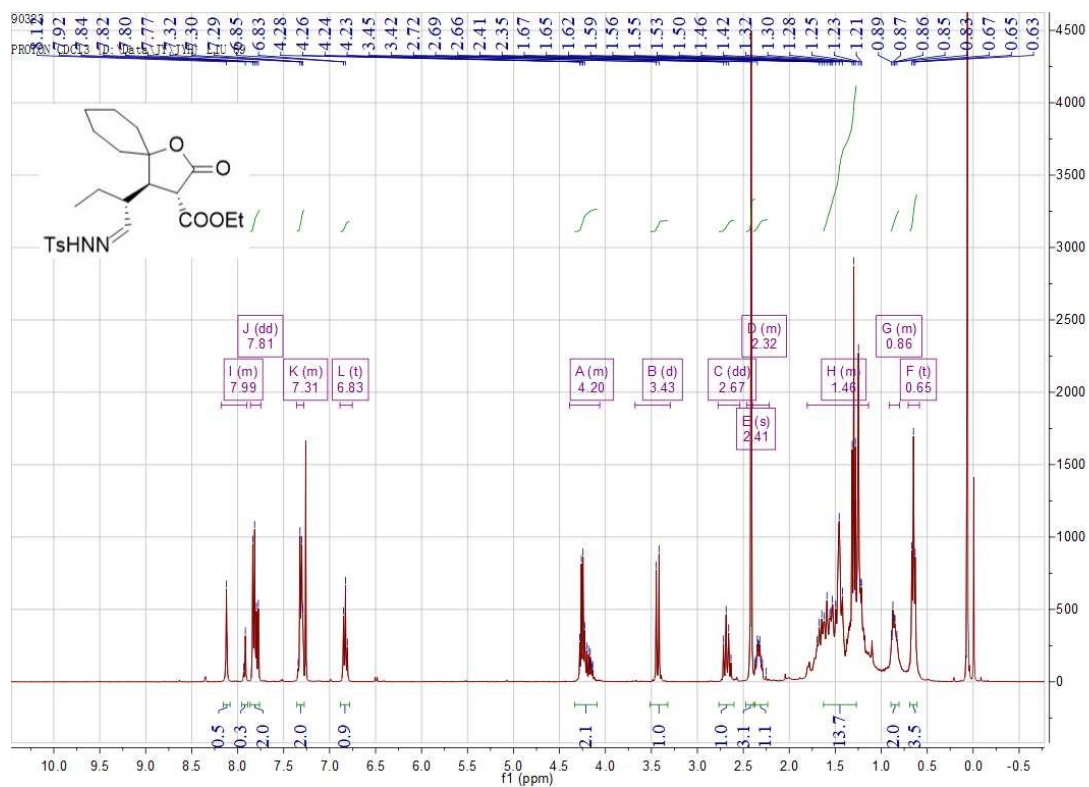


<sup>13</sup>C NMR of product **3am** (100 MHz, CDCl<sub>3</sub>)

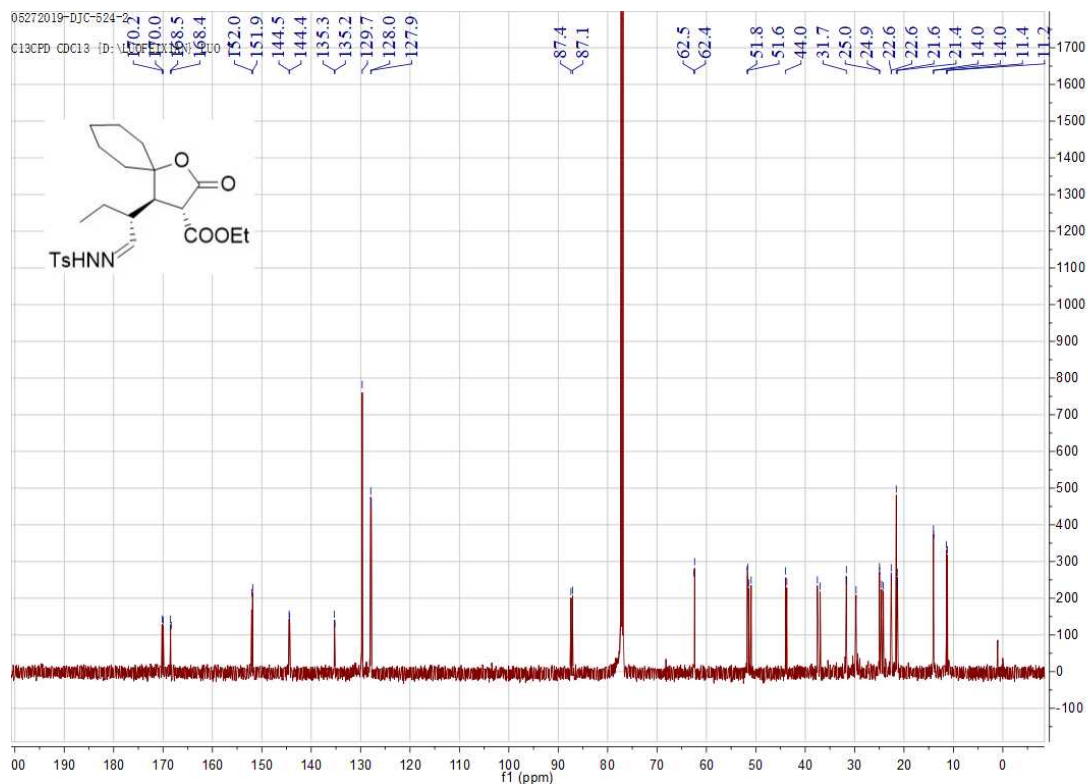


<sup>1</sup>H NMR of product **3an** (400 MHz, CDCl<sub>3</sub>)

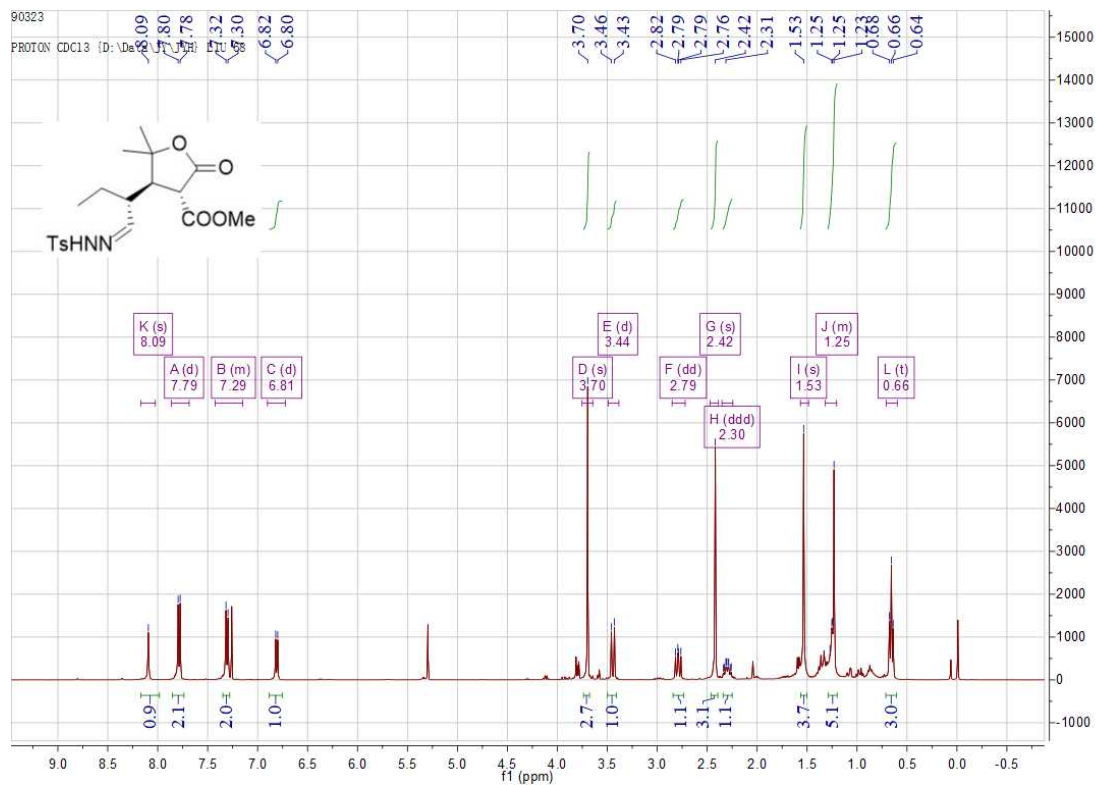




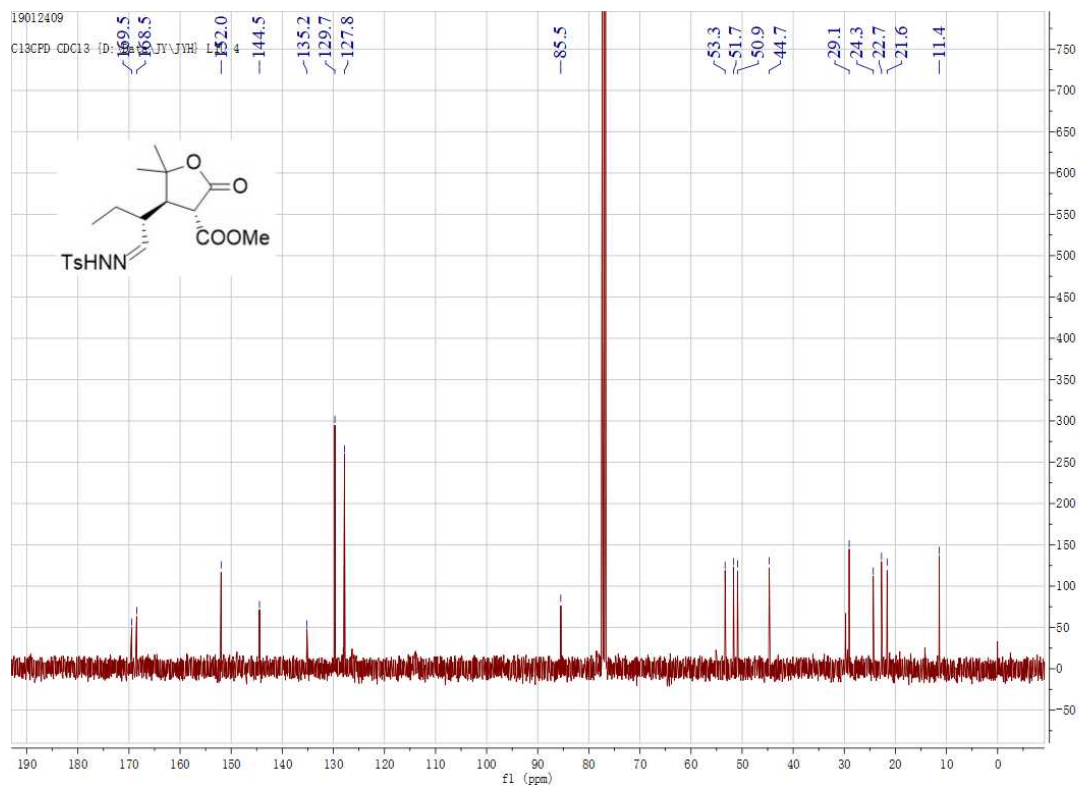
<sup>13</sup>C NMR of product **3an** (100 MHz, CDCl<sub>3</sub>)



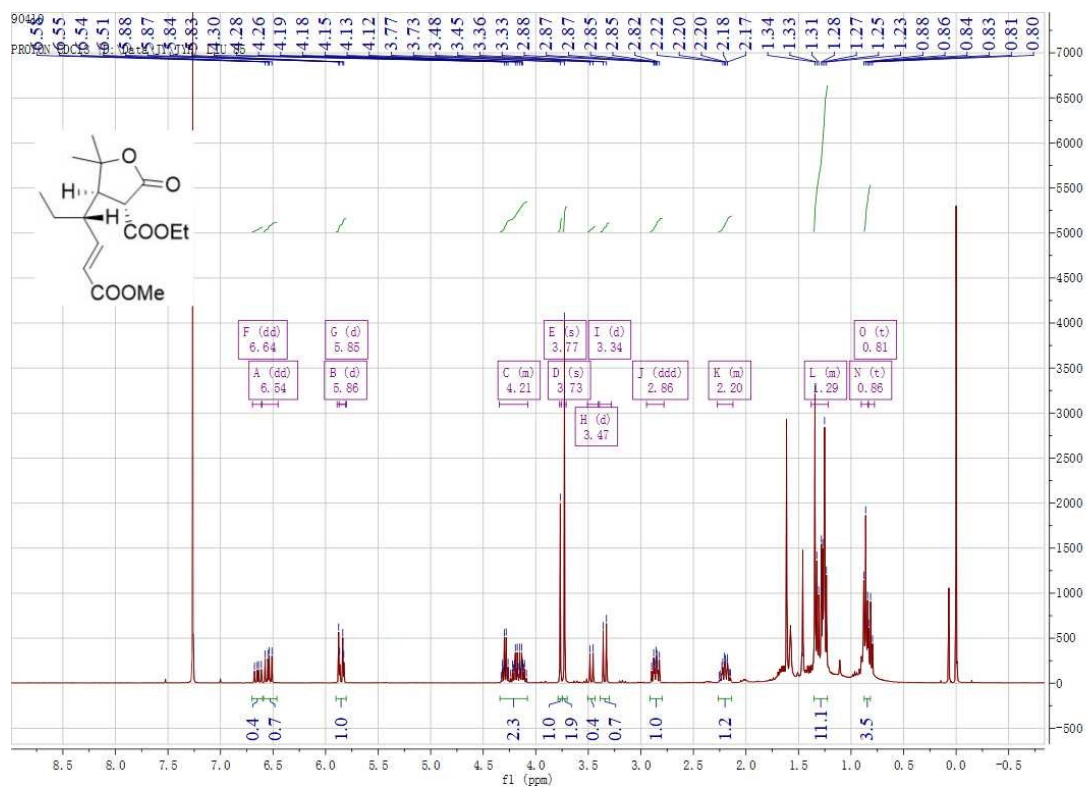
<sup>1</sup>H NMR of product **3ao** (400 MHz, CDCl<sub>3</sub>)



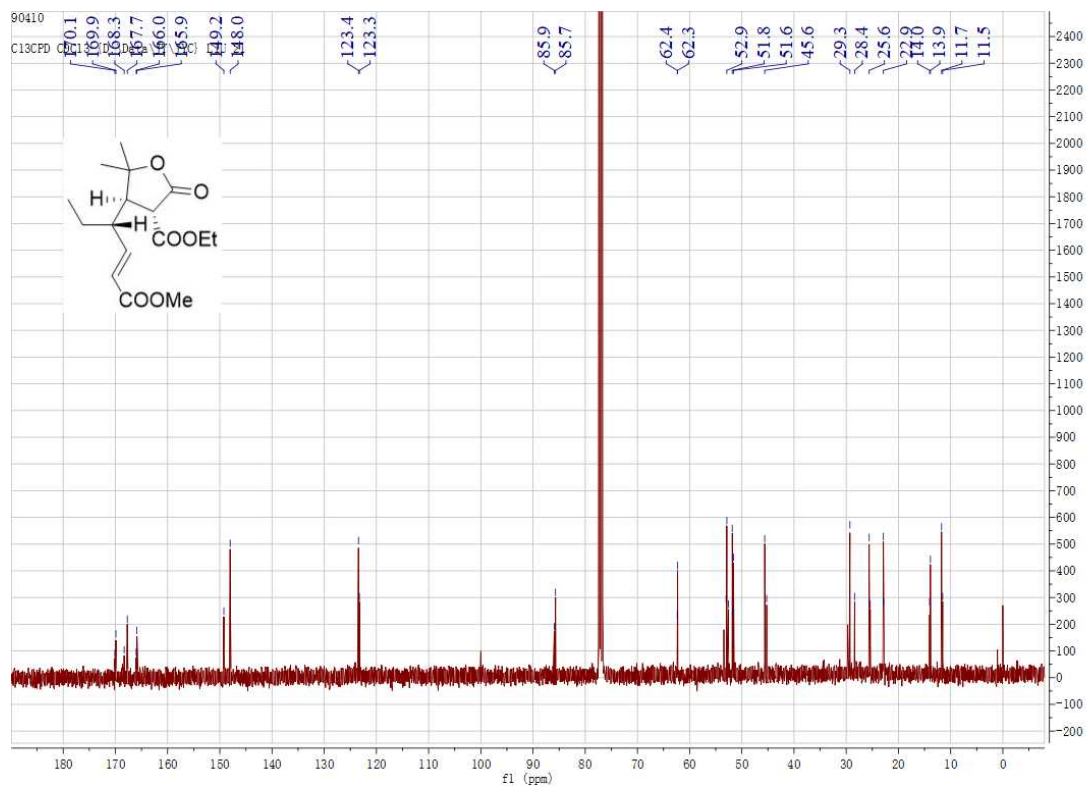
<sup>13</sup>C NMR of product **3ao** (100 MHz, CDCl<sub>3</sub>)



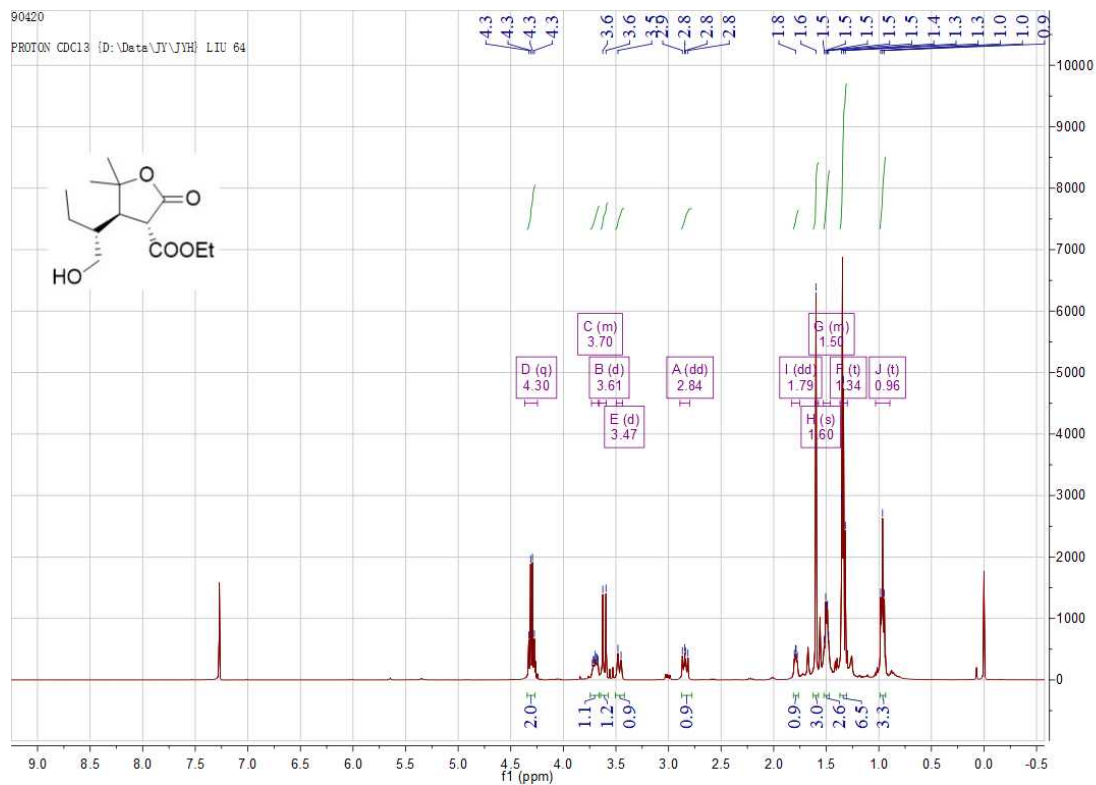
<sup>1</sup>H NMR of product **5** (400 MHz, CDCl<sub>3</sub>)



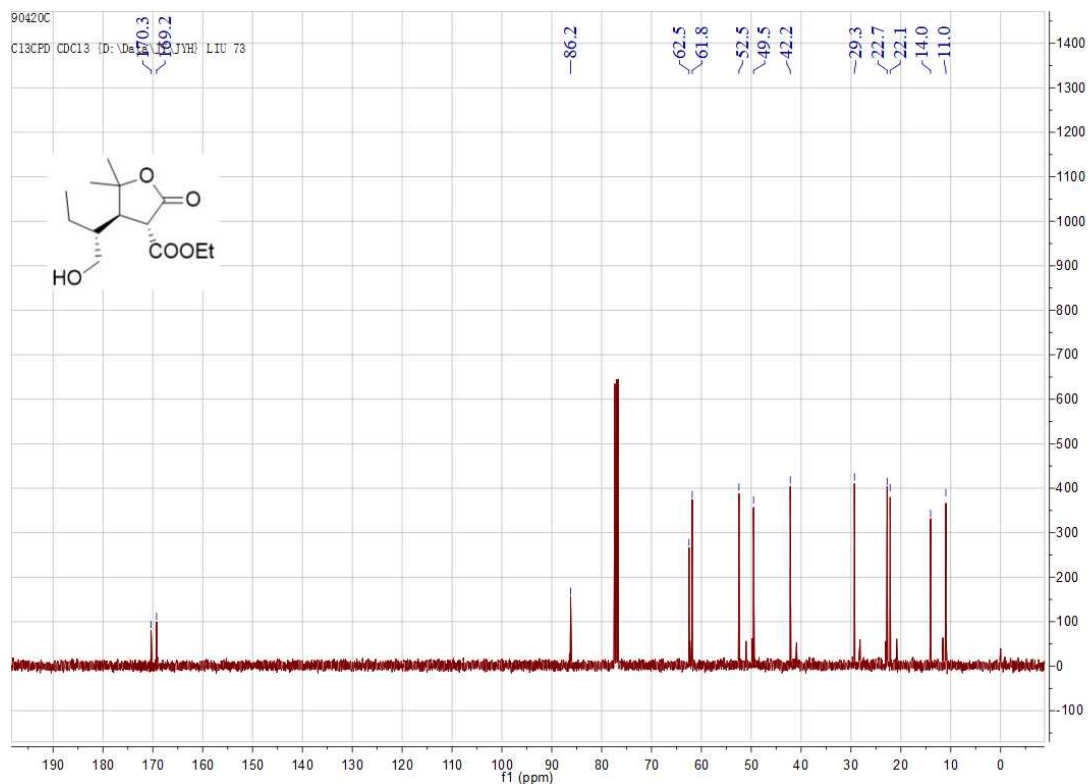
<sup>13</sup>C NMR of product 5 (100 MHz, CDCl<sub>3</sub>)



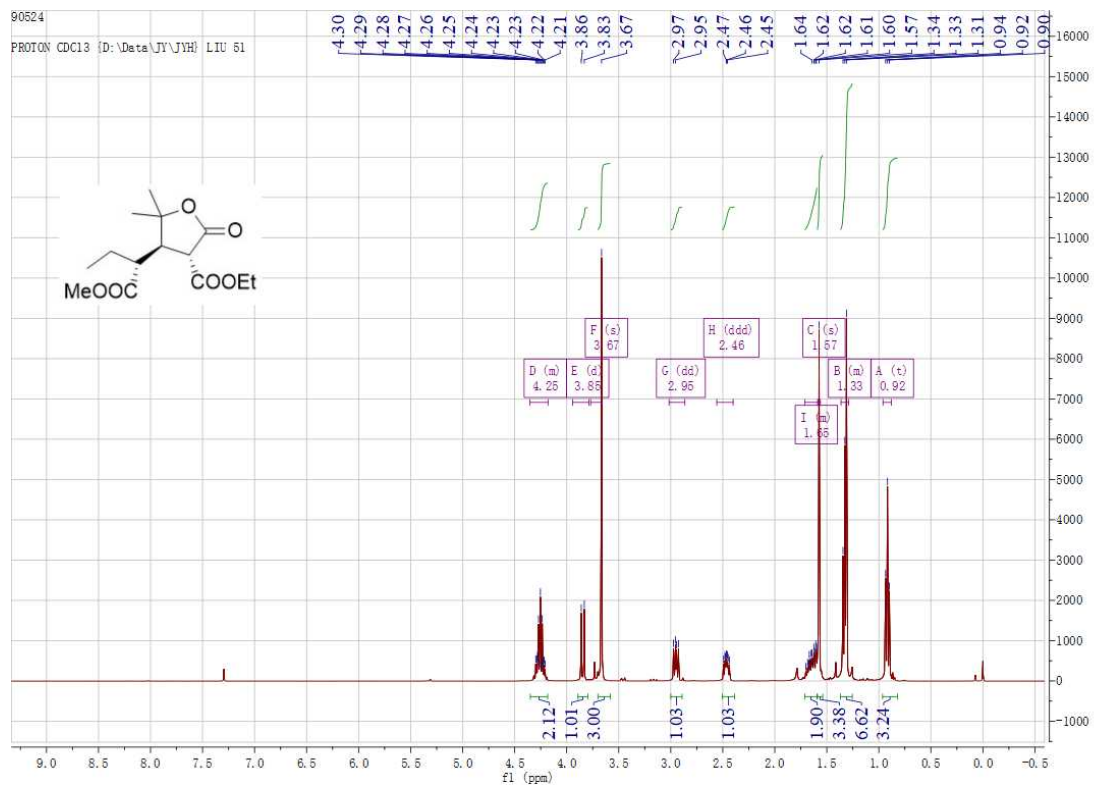
<sup>1</sup>H NMR of product 6 (400 MHz, CDCl<sub>3</sub>)



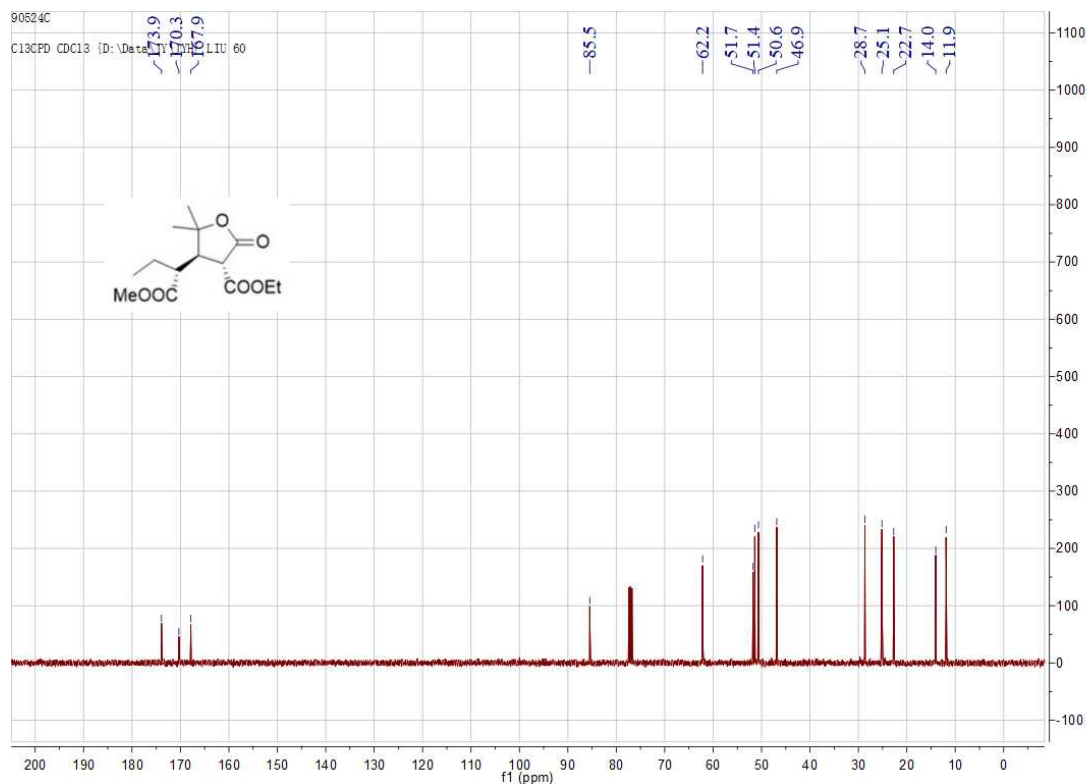
<sup>13</sup>C NMR of product 6 (100 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of product 7 (400 MHz, CDCl<sub>3</sub>)

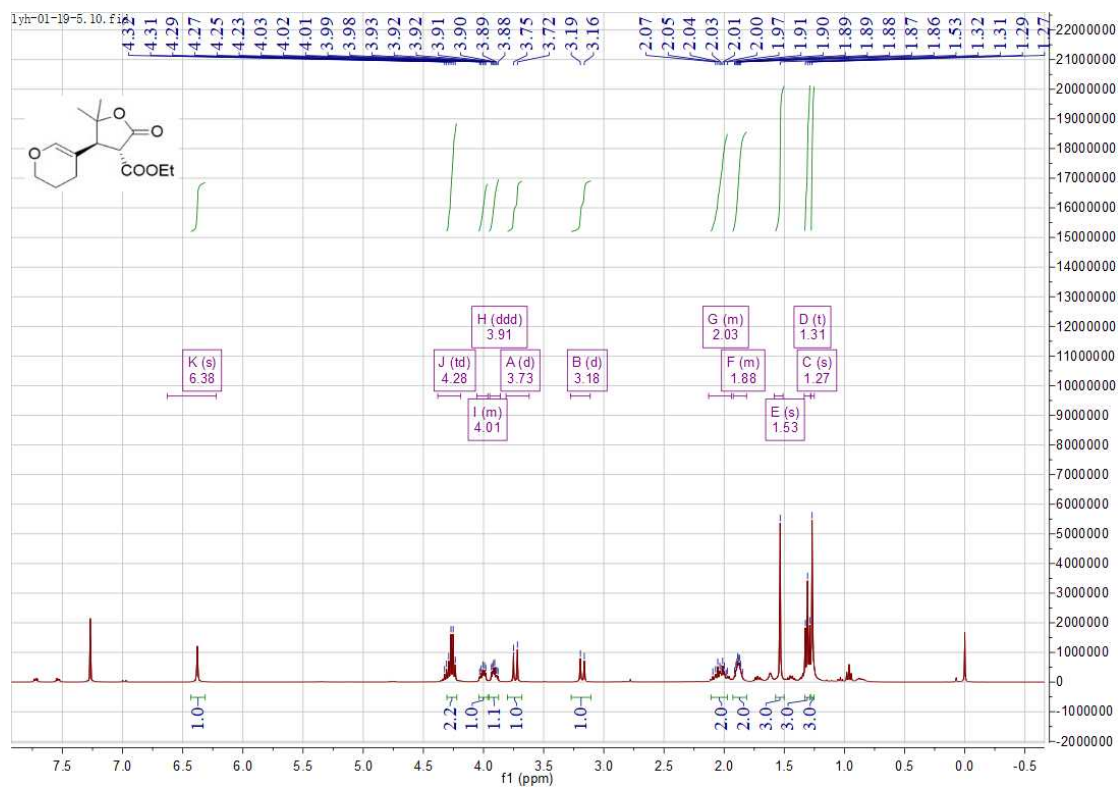


<sup>13</sup>C NMR of product 7 (100 MHz, CDCl<sub>3</sub>)

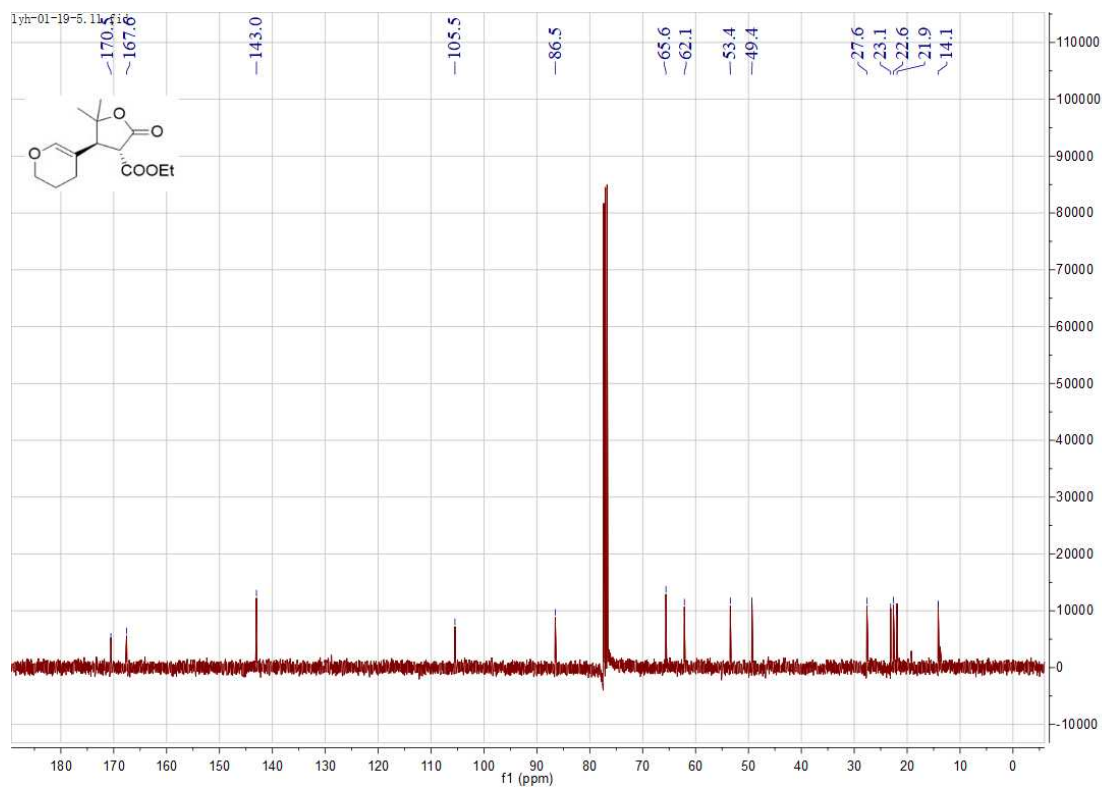




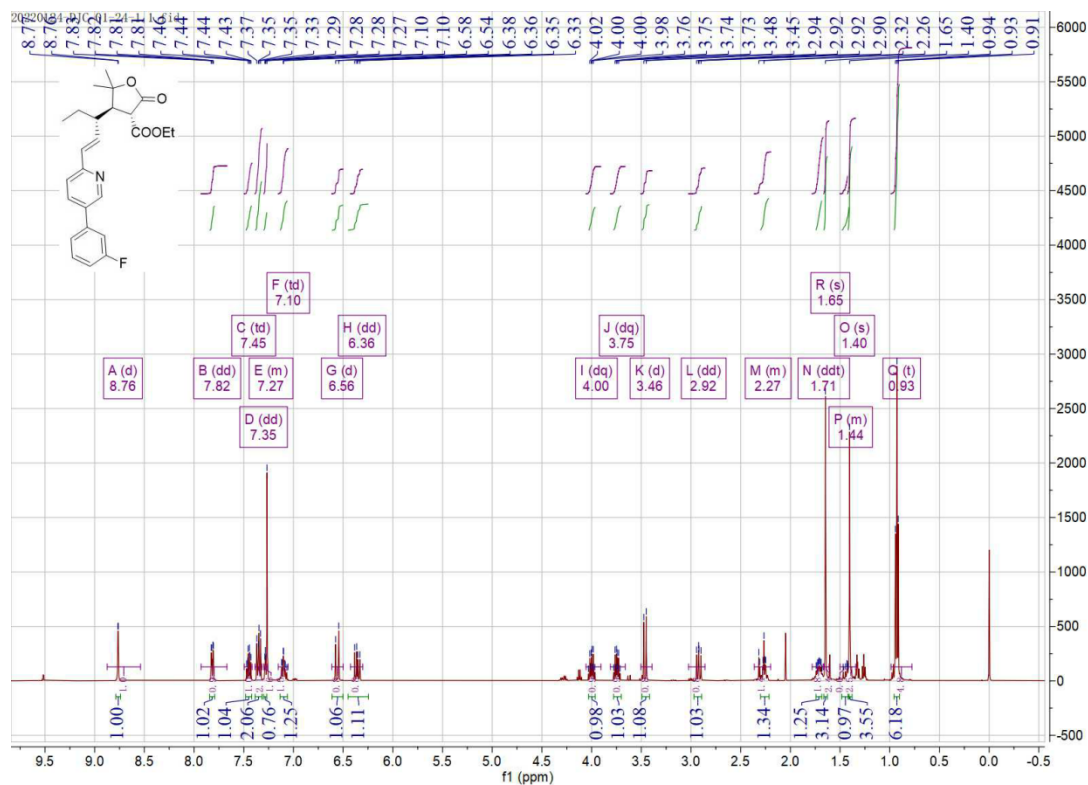
<sup>1</sup>H NMR of product **8** (400 MHz, CDCl<sub>3</sub>)



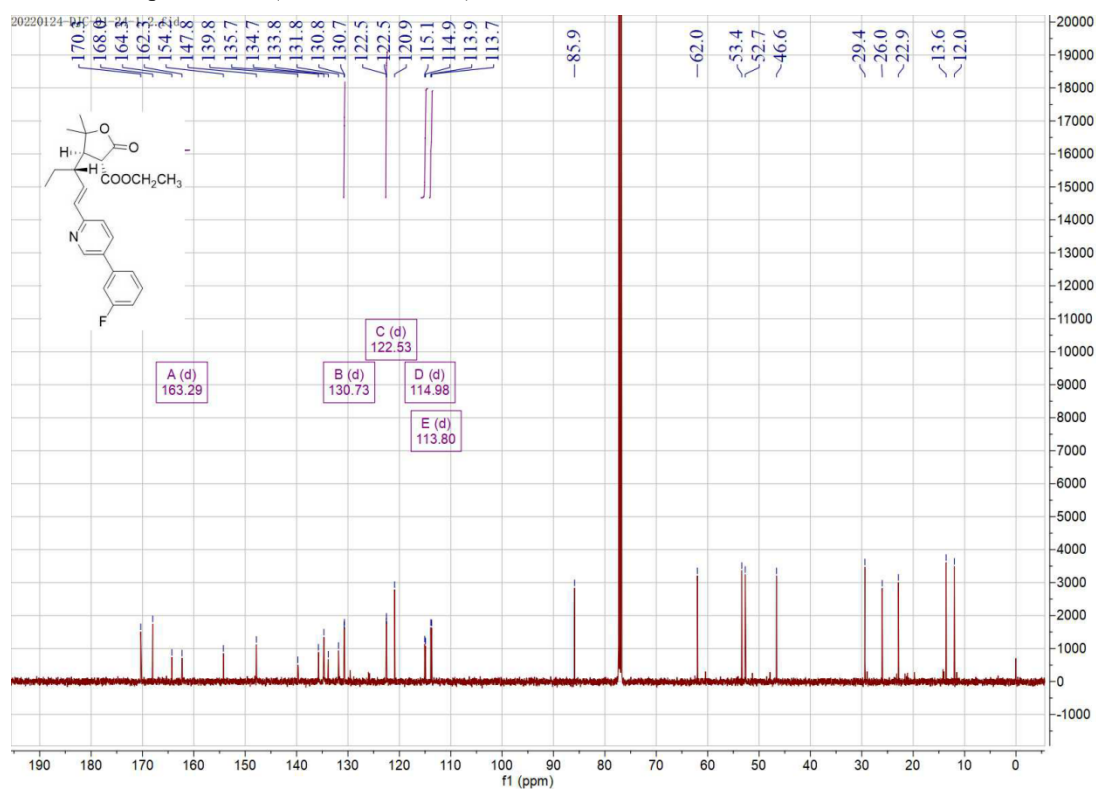
<sup>13</sup>C NMR of product **8** (100 MHz, CDCl<sub>3</sub>)



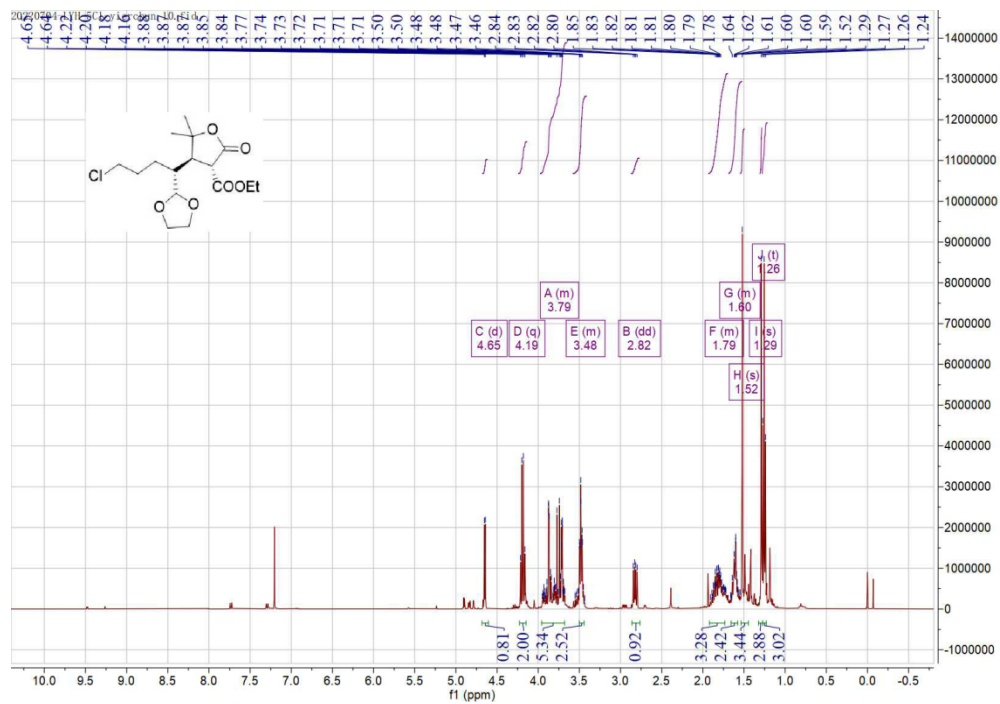
<sup>1</sup>H NMR of product **10** (400 MHz, CDCl<sub>3</sub>)



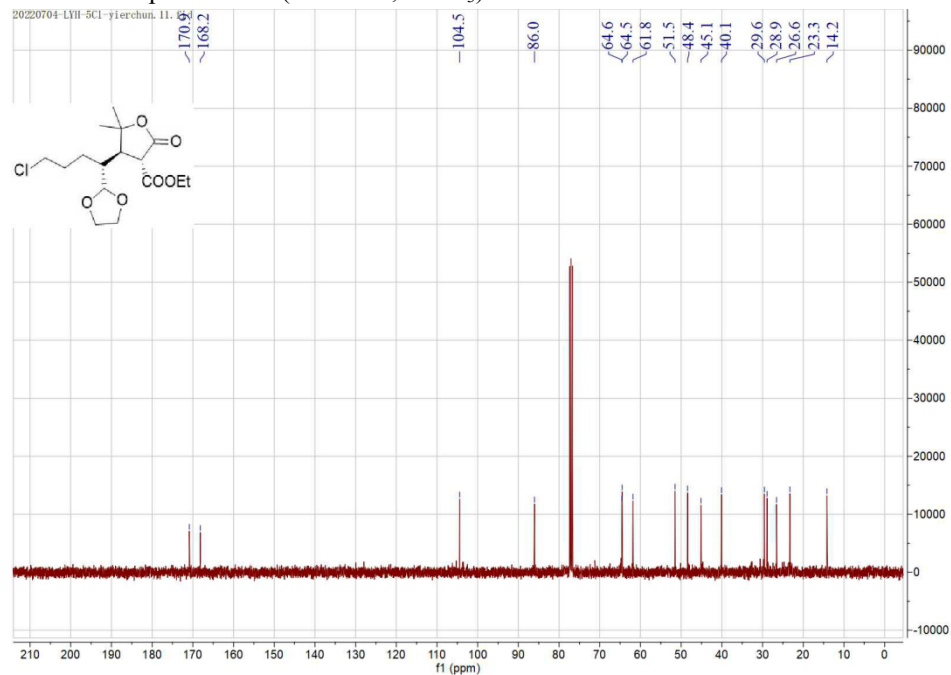
<sup>13</sup>C NMR of product **10** (100 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of product **4k'** (400 MHz, CDCl<sub>3</sub>)

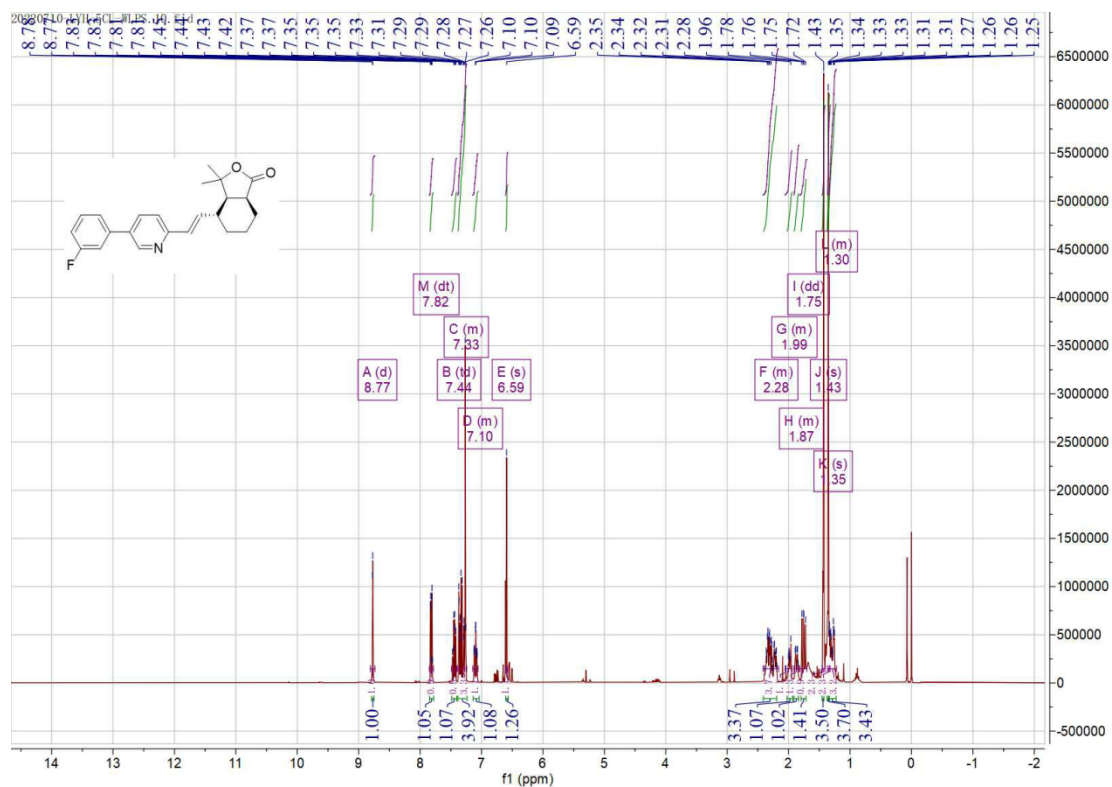


<sup>13</sup>C NMR of product 4k' (100 MHz, CDCl<sub>3</sub>)

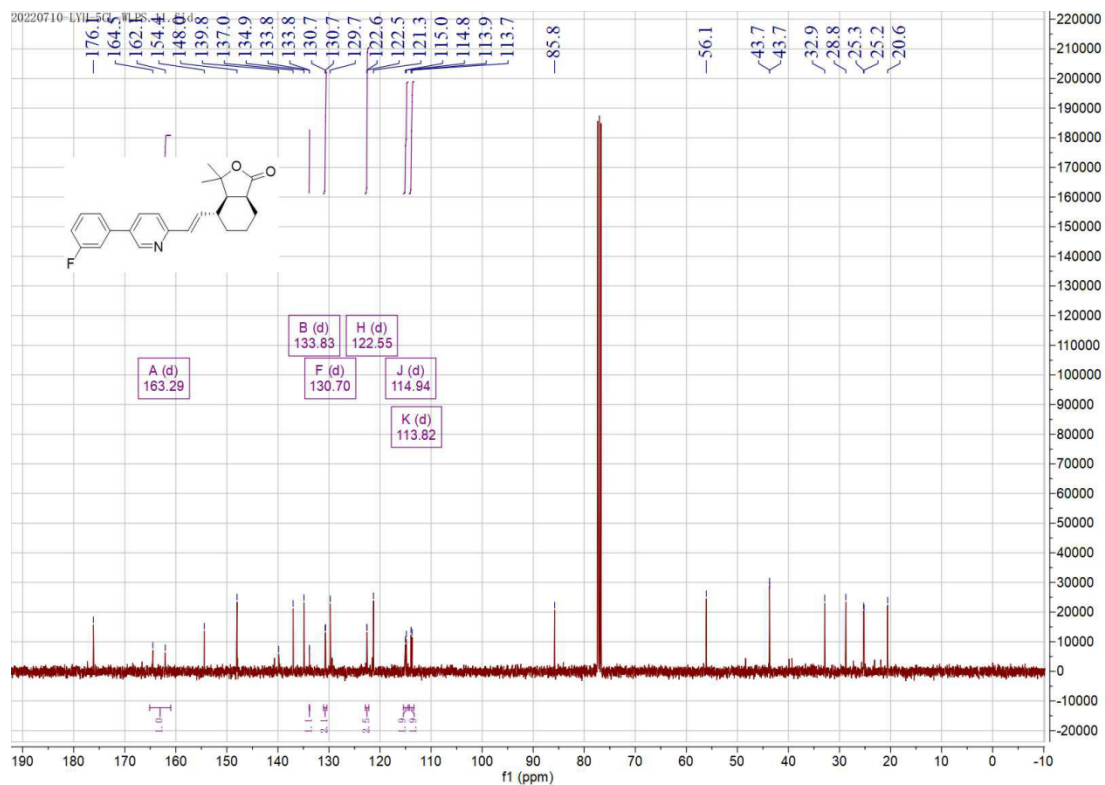


<sup>1</sup>H NMR of product 11 (400 MHz, CDCl<sub>3</sub>)

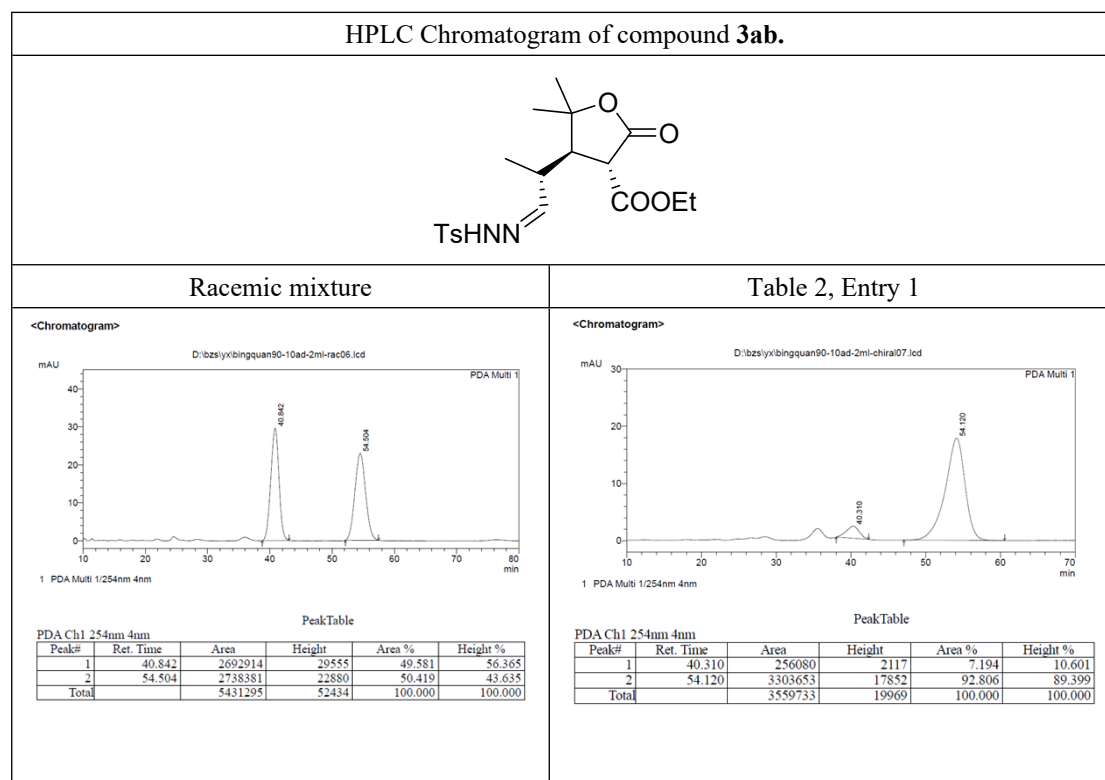
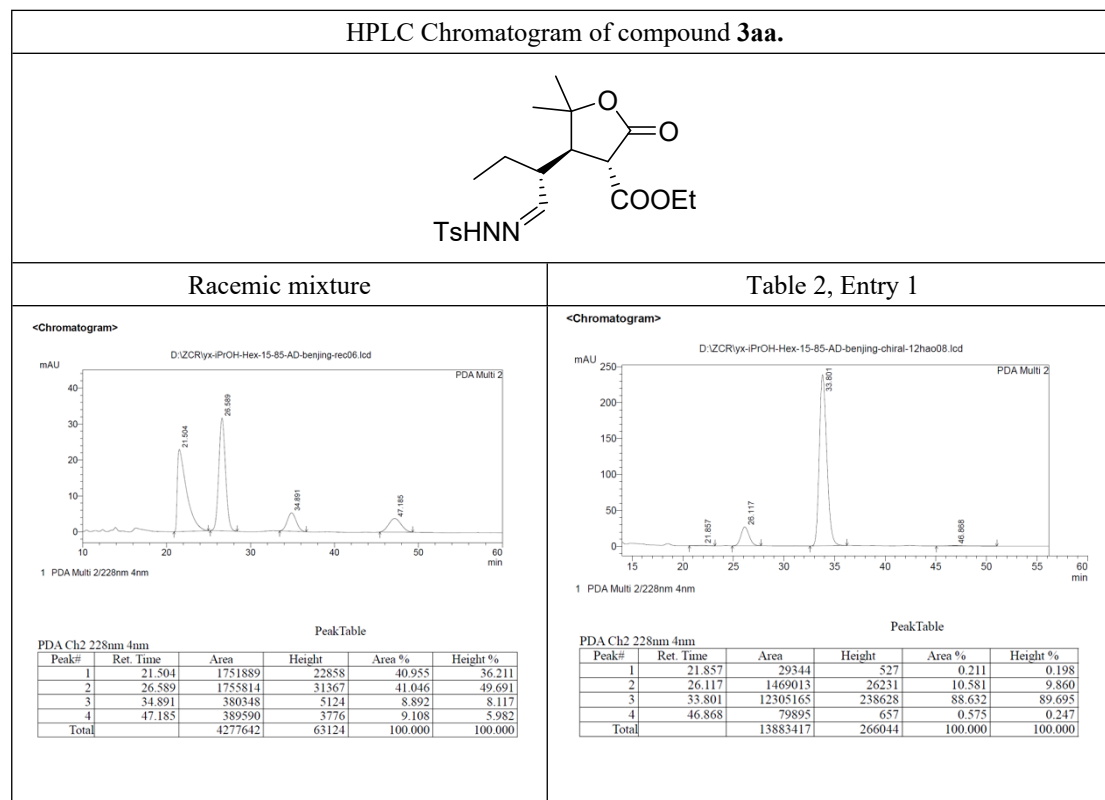




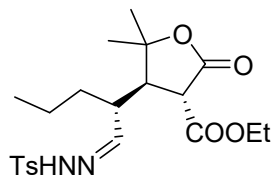
<sup>13</sup>C NMR of product **11** (100 MHz, CDCl<sub>3</sub>)



6. HPLC data for Michael Product 3a-3o

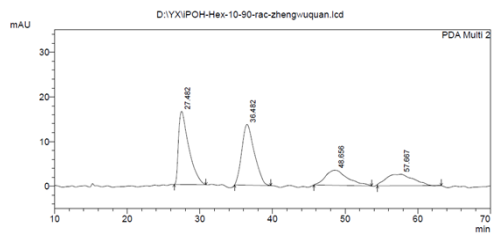


### HPLC Chromatogram of compound **3ac**.



Racemic mixture

<Chromatogram>



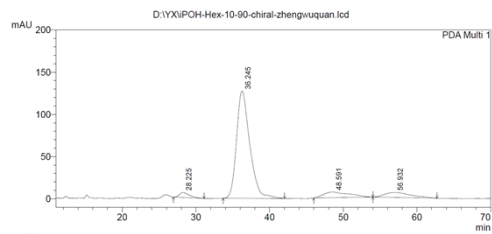
1 PDA Multi 2/228nm 4nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.482	1614722	16381	34.792	45.553
2	36.482	1635791	13605	35.246	37.832
3	48.656	719773	3396	15.509	9.443
4	57.667	670769	2579	14.453	7.173
Total		4641056	35961	100.000	100.000

Table 2, Entry 1

<Chromatogram>

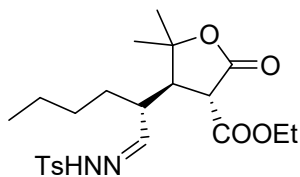


1 PDA Multi 1/228nm 4nm

PeakTable

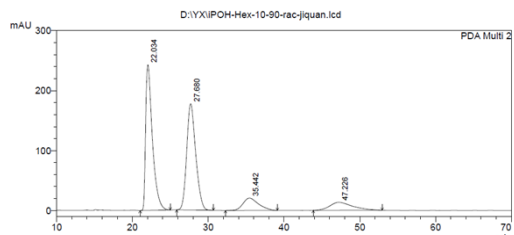
Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.225	557778	5955	2.866	4.091
2	36.245	15875068	127167	81.579	87.352
3	48.591	1602732	6682	8.236	4.590
4	56.932	1424118	5776	7.318	3.968
Total		19459696	145581	100.000	100.000

HPLC Chromatogram of compound 3ad.



Racemic mixture of 3d

<Chromatogram>



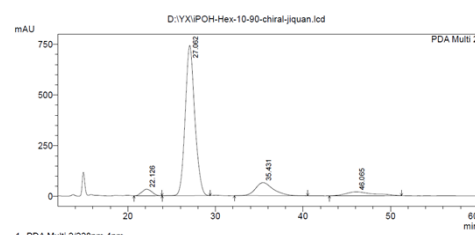
1 PDA Multi 2/228nm 4nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.034	15028954	242963	42.361	53.470
2	27.680	14649482	177384	41.292	39.038
3	35.442	2945901	20673	8.303	4.550
4	47.226	3853838	13368	8.044	2.942
Total		35478175	454388	100.000	100.000

Table 2, Entry 1

<Chromatogram>

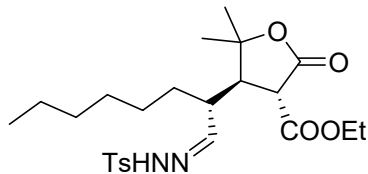


1 PDA Multi 2/228nm 4nm

PeakTable

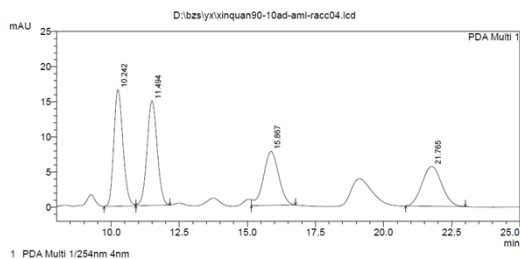
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.126	2573131	32804	3.551	3.823
2	27.062	56523260	741997	78.008	86.380
3	35.431	9029146	64553	12.461	7.524
4	46.065	4332774	19497	5.980	2.272
Total		72458311	857951	100.000	100.000

HPLC Chromatogram of compound 3ae.



### Racemic mixture

<Chromatogram>



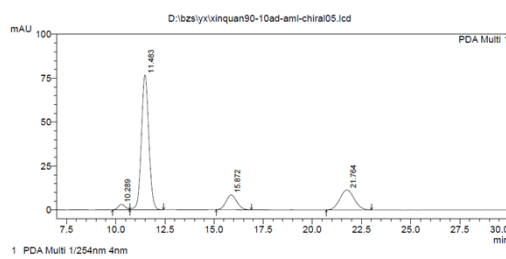
1 PDA Multi 1/254nm 4nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.242	387817	16610	28.472	37.022
2	11.494	387467	14901	28.447	33.214
3	15.897	300127	7671	22.035	17.098
4	21.765	285666	5683	21.046	12.666
Total		1362077	44865	100.000	100.000

### Table 2, Entry 1

<Chromatogram>

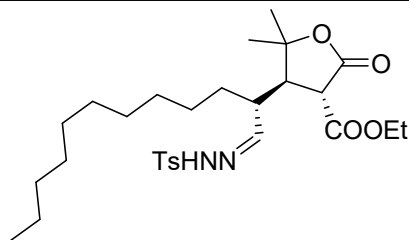


1 PDA Multi 1/254nm 4nm

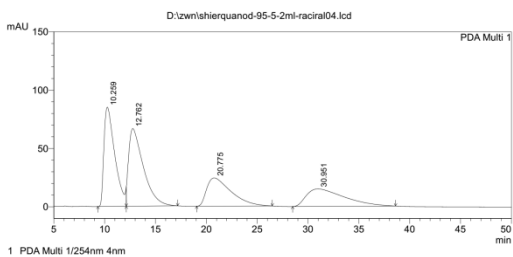
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.289	73744	3118	2.469	3.133
2	11.483	2015055	76684	67.475	77.048
3	15.872	320386	8374	10.728	8.413
4	21.764	577179	11352	19.327	11.406
Total		2986364	99528	100.000	100.000

### HPLC Chromatogram of compound 3af.



### Racemic mixture

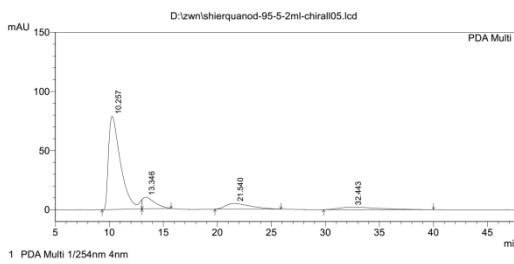


1 PDA Multi 1/254nm 4nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.289	6346283	85059	30.309	44.586
2	12.762	6095483	66531	31.977	38.874
3	20.775	4029596	24204	19.245	12.687
4	30.951	3867349	14979	18.470	7.852
Total		20938711	190773	100.000	100.000

### Table 2, Entry 1

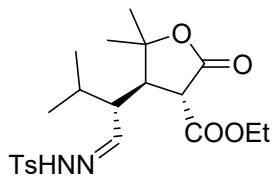


1 PDA Multi 1/254nm 4nm

PeakTable

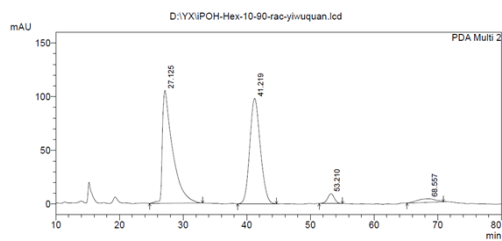
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.257	6196794	78931	75.050	82.508
2	13.346	767502	9898	9.295	10.346
3	21.540	781587	4791	9.466	5.008
4	32.443	510985	2045	6.189	2.138
Total		8256869	95665	100.000	100.000

### HPLC Chromatogram of compound 3ag.



Racemic mixture

<Chromatogram>



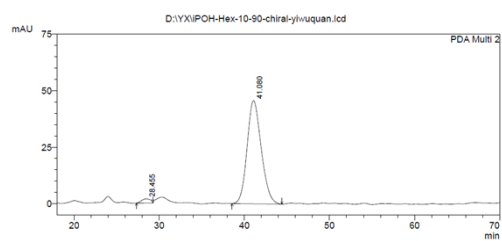
1 PDA Multi 2/228nm 4nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.125	11755649	105231	48.021	48.699
2	41.219	11343372	98284	46.336	45.484
3	53.210	686309	9172	2.803	4.245
4	68.557	695115	3397	2.839	1.572
Total		24480445	216083	100.000	100.000

Table 2, Entry 1

<Chromatogram>

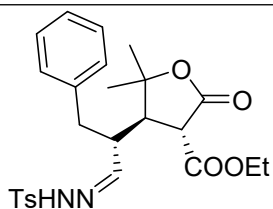


1 PDA Multi 2/228nm 4nm

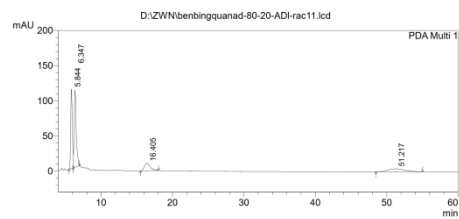
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.455	140840	1846	2.597	3.883
2	41.080	5281293	45685	97.403	96.117
Total		5422133	47531	100.000	100.000

HPLC Chromatogram of compound 3ah.



Racemic mixture



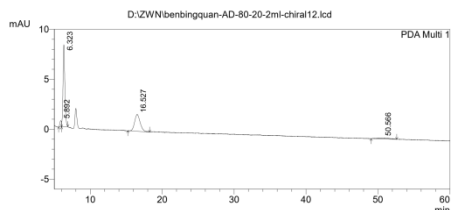
1 PDA Multi 1/254nm 4nm

1 PDA Multi 1/254nm,4nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.844	1737039	112937	33.272	47.579
2	6.347	2164964	109558	41.468	46.155
3	16.405	609804	10627	11.680	4.477
4	51.217	708992	4248	13.580	1.789
总计		5220799	237369	100.000	100.000

Table 2, Entry 2

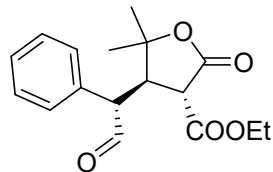


1 PDA Multi 1/254nm,4nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.892	9756	629	3.780	5.933
2	6.323	146457	8198	56.751	77.312
3	16.527	90791	1679	35.181	15.833
4	50.566	11065	98	4.288	0.921
总计		258069	10603	100.000	100.000

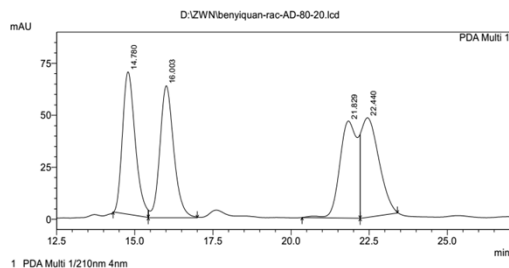
HPLC Chromatogram of compound 3ai.



Racemic mixture

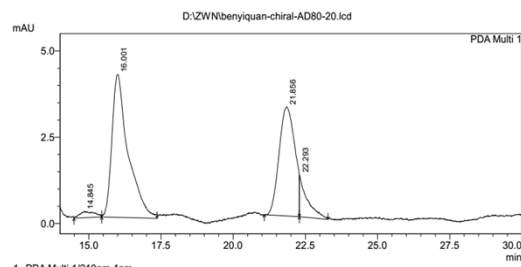
Table 2, Entry 2

<Chromatogram>



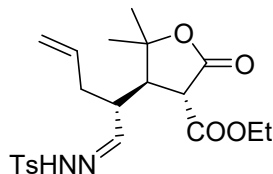
PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.780	1951010	68521	25.555	30.242
2	16.003	1963916	63441	25.724	28.000
3	21.829	1852270	46693	24.327	20.668
4	22.440	1862314	47918	24.393	21.149
Total		7634509	226572	100.000	100.000

<Chromatogram>



PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.845	6413	193	2.079	2.222
2	16.001	161010	4141	52.190	47.566
3	21.856	119087	3159	38.601	36.280
4	22.293	21996	1213	7.130	13.932
Total		308506	8707	100.000	100.000

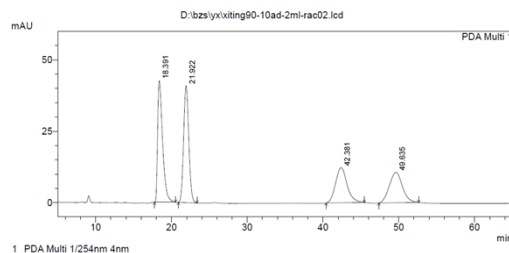
### HPLC Chromatogram of compound 3aj.



Racemic mixture

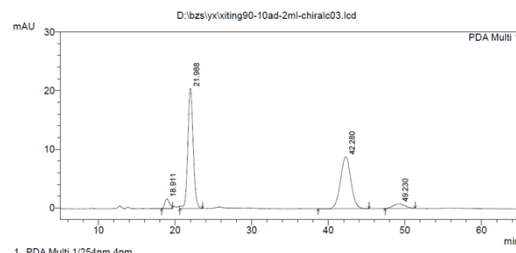
Table 2, Entry 1

<Chromatogram>



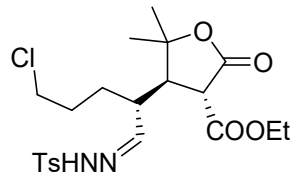
PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.391	1946307	42608	30.083	39.954
2	21.922	1936803	40988	29.937	38.435
3	42.381	1303773	12366	20.152	11.596
4	49.635	1282821	10681	19.828	10.015
Total		6469704	106642	100.000	100.000

<Chromatogram>



PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.911	71592	1630	3.593	5.142
2	21.988	1000346	20453	50.208	64.537
3	42.280	838091	8841	42.065	27.897
4	49.230	82365	768	4.134	2.424
Total		1992394	31692	100.000	100.000

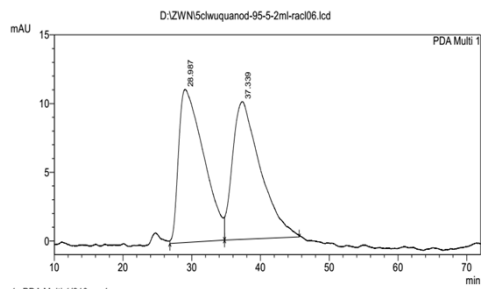
### HPLC Chromatogram of compound 3ak.



Racemic mixture

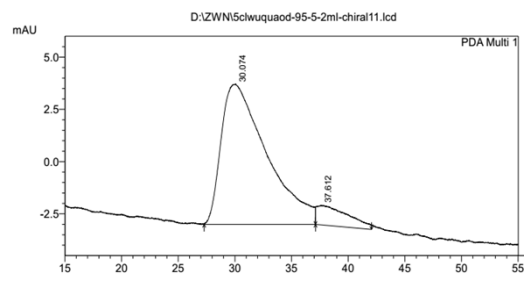
Table 2, Entry 1

<Chromatogram>



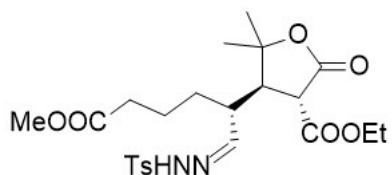
Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.987	2821282	11152	49.970	52.660
2	37.339	2824677	10025	50.030	47.340
Total		5645959	21177	100.000	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.074	1869670	6717	90.997	87.735
2	37.612	184986	939	9.003	12.265
Total		2054657	7656	100.000	100.000

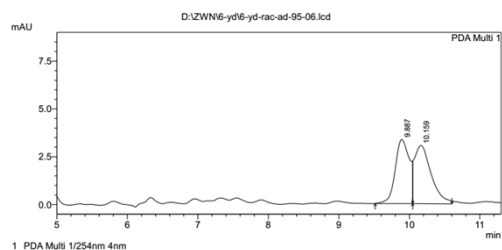
HPLC Chromatogram of compound 3a.



Racemic mixture

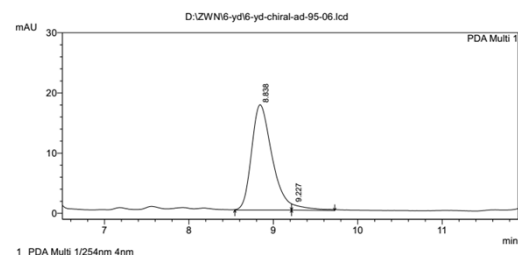
Table 2, Entry 1

<Chromatogram>



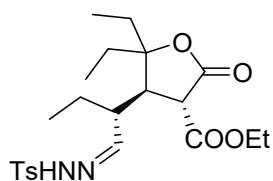
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.887	47646	3347	49.204	52.366
2	10.159	49186	3045	50.796	47.634
Total		96832	6392	100.000	100.000

<Chromatogram>

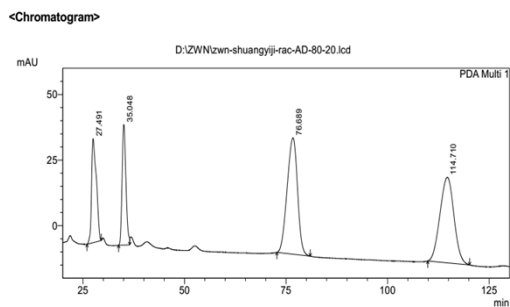


Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.838	299987	17500	96.160	94.885
2	9.227	11621	943	3.840	5.115
Total		302609	18445	100.000	100.000

### HPLC Chromatogram of compound **3am**.

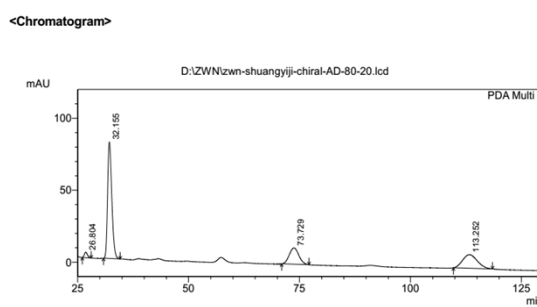


#### Racemic mixture



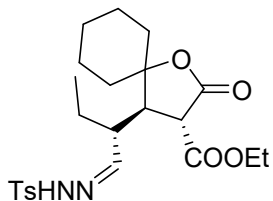
Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.491	3238450	39624	14.756	24.382
2	35.048	3038338	45937	13.799	28.266
3	76.689	7874210	443361	35.879	27.293
4	114.710	7805755	32599	35.567	20.059
Total		21946753	162515	100.000	100.000

#### Table 2, Entry 1

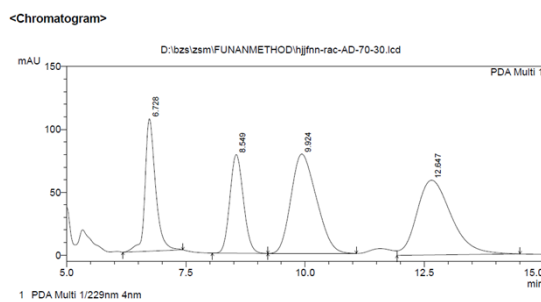


Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.804	188105	3870	2.005	3.659
2	32.155	5307401	81060	56.581	76.639
3	73.729	1711819	11379	18.249	10.758
4	113.252	2172858	9461	23.164	8.945
Total		9380183	105770	100.000	100.000

### HPLC Chromatogram of compound **3an**.

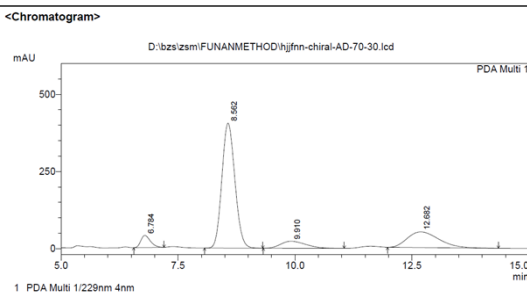


#### Racemic mixture



Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.728	1622844	105351	17.800	32.661
2	8.549	1558314	78574	17.092	24.360
3	9.924	2936254	79154	32.205	24.539
4	12.647	2999883	59479	32.903	18.440
Total		9117295	322557	100.000	100.000

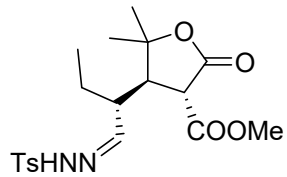
#### Table 2, Entry 1



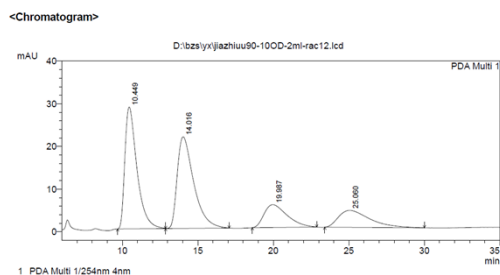
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.784	561701	39444	4.821	7.609
2	8.562	7858074	405356	67.440	78.193
3	9.910	843546	22763	7.239	4.391
4	12.682	2388671	50840	20.500	9.807
Total		11651992	518403	100.000	100.000

### HPLC Chromatogram of compound **3ao**.





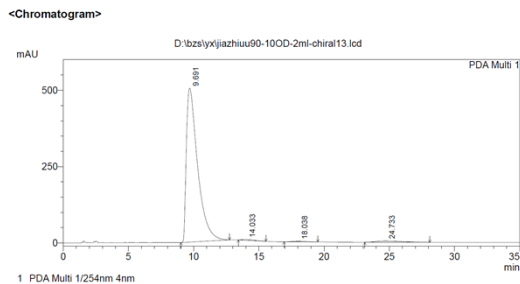
Racemic mixture



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.449	1589694	28564	36.417	48.126
2	14.016	1635619	21472	37.469	36.178
3	19.987	566808	5337	12.985	8.991
4	25.060	573136	3979	13.129	6.705
Total		4365257	59351	100.000	100.000

Table 2, Entry 1



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.691	30285778	503967	96.924	98.118
2	14.033	148036	2466	0.474	0.480
3	18.038	166221	2339	0.532	0.455
4	24.733	646951	4863	2.070	0.947
Total		31246986	513635	100.000	100.000