



## Supporting Information

for

### **Why do thioureas and squaramides slow down the Ireland–Claisen rearrangement?**

Dominika Krištofiková, Juraj Filo, Mária Mečiarová and Radovan Šebesta

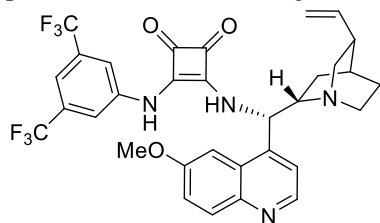
*Beilstein J. Org. Chem.* **2019**, *15*, 2948–2957. doi:10.3762/bjoc.15.290

### **Experimental procedures and characterization data for all compounds, copies of NMR spectra, details of DFT calculations**

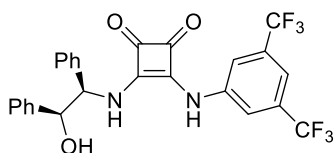
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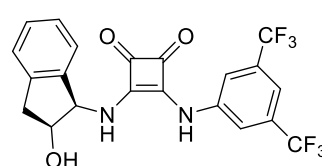
## pKa Values for catalysts



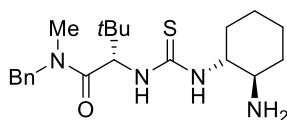
**C1**  
pKa(DMSO) 15.0  
(*Molecules* **2015**, 20, 15500)



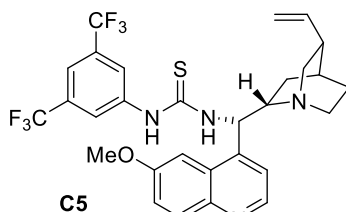
**C2**  
pKa(DMSO) 8.3-16.5  
(*Org. Lett.* **2014**, 16, 1786)



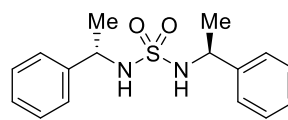
**C3**  
pKa(DMSO) 8.3-16.5  
(*Org. Lett.* **2014**, 16, 1786)



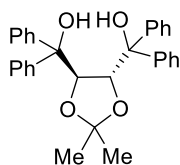
**C4**  
pKa(DMSO) 19.5-21.0  
(*Molecules* **2015**, 20, 15500)



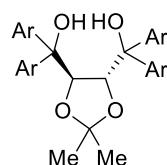
**C5**  
pKa(DMSO) 12.4  
(*Org. Lett.* **2014**, 16, 1786)



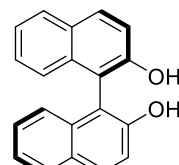
**C6**  
pKa(DMSO) 16.0-17.5  
(*J. Org. Chem.* **1990**, 55, 3330)



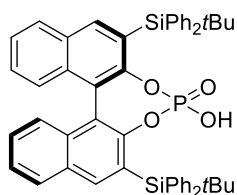
**C7**  
pKa(DMSO) 28.0  
(*Chem. Rev.* **2007**, 107, 5713)



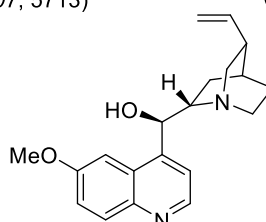
**C8** (Ar = 2-Naphthyl)  
pKa(DMSO) 28.0  
(*Chem. Rev.* **2007**, 107, 5713)



**C9**  
pKa(DMSO) 13.0  
(*Org. Chem. Front.* **2016**, 3, 1154)



**C10**  
pKa(H<sub>2</sub>O) 1.0  
(*Chem. Rev.* **2007**, 107, 5713)



**C11**

## Materials and methods

All commercially available chemicals were purchased from Sigma-Aldrich, Alfa Aesar or Merck and were used without further purification. Solvents were distilled and dried according to the standard procedures. All reactions were carried out in an inert atmosphere. Thin-layer chromatography was performed on silica gel 60, F-254 nm plates. Compounds were visualized with UV light (254 nm) and/or by treatment with  $\text{KMnO}_4$  and anisaldehyde solution. NMR spectra were recorded on Varian NMR System 300 (300 or 600 MHz for  $^1\text{H}$  and 75 or 151 MHz for  $^{13}\text{C}$ ). Chemical shifts ( $\delta$ ) are given in ppm relative to tetramethylsilane. Enantiomeric purity was determined by chiral HPLC column (OJ-H).

### Typical procedure for Ireland–Claisen rearrangement with $\text{Et}_3\text{N}$ as a base<sup>1</sup>

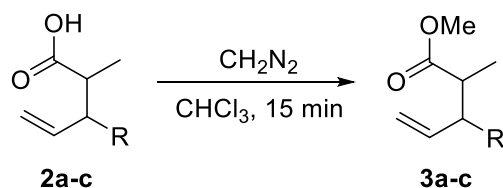
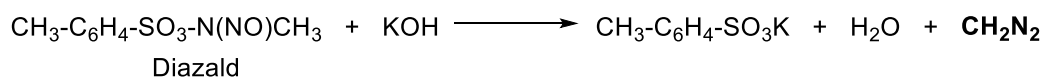
Ester **1** (2.34 mmol) was added into solution of  $\text{Et}_3\text{N}$  (1.6 mL, 11.51 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (2.2 mL) under a nitrogen atmosphere. The reaction mixture was cooled to  $-60\text{ }^\circ\text{C}$ . Then, trialkyl silyl triflate (3.7 mmol) was added dropwise. Next, an organocatalyst (10 mol %) was added in one portion. The reaction temperature was allowed to reach ambient temperature and the reaction mixture was stirred at this temperature for 24 h. After the reaction, the solvent was evaporated under reduced pressure. Diethyl ether (5 mL) and 1.3 M NaOH (7 mL) were added to the distillation residue. The aqueous layer was washed with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 8\text{ mL}$ ) and after that it was acidified with concentrated HCl. The products were extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 8\text{ mL}$ ). The organic phase was washed with water ( $3 \times 12\text{ mL}$ ), dried with anhydrous  $\text{MgSO}_4$  and the solvent was evaporated under reduced pressure.

### Synthesis of methyl esters for HPLC analysis<sup>2</sup>

A solution of diazald (1 g) in a mixture of 1,2-dimethoxyethane/diethyl ether 1:1 (3 mL) and a solution of KOH (1 g) in a mixture of water/methanol 1:1 (10 mL) were added in a vial. Diazomethane was generated on the interface and injected through a capillary into another vial containing a solution of acid **2a–c** in chloroform (1.5 mg/mL). Methyl esters **3a–c** were prepared in quantitative yields within 15–20 min.

<sup>1</sup> Araki, K.; Welch, J. T. *Tetrahedron Lett.* **1993**, 34, 2251–2254.

<sup>2</sup> Glastrup, J. J. *Chromatogr. A*, **1998**, 827, 133–136.

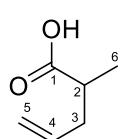


### Typical procedure for the Ireland–Claisen rearrangement with LDA as a base<sup>3</sup>

*n*-BuLi in hexanes (*c* 1.6 M, 2.7 mL, 4.32 mmol) was added over 15 min to a solution of dry diisopropylamine (0.47 g, 4.68 mmol) in anhydrous THF (8 mL) at 0 °C. The reaction mixture was stirred for 10 min and then cooled to −78 °C and ester **1a–c** (3.9 mmol) added dropwise within 3 min. The reaction mixture was stirred for another 5 min, then trialkylsilyl chloride (4.3 mmol) was added in one portion. The temperature was allowed to reach ambient temperature and the mixture was stirred at this temperature for 1 h. Then, methanol (1.2 mL) was added and the mixture stirred for another 10 min followed by extraction with 5% NaOH (3 × 10 mL). The aqueous solution was washed with diethyl ether (3 × 12 mL) and acidified with concentrated HCl. The products were isolated by extraction with CH<sub>2</sub>Cl<sub>2</sub> (3 × 12 mL) and subsequent solvent evaporation.

### Characterization data

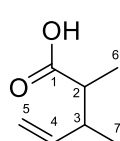
#### 2-Methylpent-4-enoic acid (**3a**)



Colourless oil, *R*<sub>F</sub> = 0.38 (hexanes/ethyl acetate 3:1)

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 1.19 (d, *J* = 7.0 Hz, 3H, **H**<sup>6</sup>); 2.21 (dt, *J* = 14.2; 7.2 Hz, 1H, **H**<sup>3</sup>); 2.45 (dt, *J* = 13.7; 6.8 Hz, 1H, **H**<sup>3</sup>); 2.56 (h, *J* = 7.0 Hz, 1H, **H**<sup>2</sup>); 5.06–5.111 (m, 2H, **H**<sup>5</sup>); 5.77 (ddt, *J* = 17.1; 10.2; 7.0 Hz, 1H, **H**<sup>4</sup>); 11.46 (brs, 1H, **H**<sup>OH</sup>). <sup>1</sup>H NMR spectrum corresponds with those in literature.<sup>4</sup>

#### 2,3-Dimethylpent-4-enoic acid (**3b**)



Colourless oil, *R*<sub>F</sub> = 0.05 (hexanes/ethyl acetate 9:1)

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 1.04 (d, *J* = 6.8 Hz, 0.7×3H, **H**<sup>7</sup>); 1.07 (d, *J* = 6.8 Hz, 0.3×3H, **H**<sup>7</sup>); 1.13 (d, *J* = 7.0 Hz, 3H, **H**<sup>6</sup>); 2.32–2.37 (m, 0.3×2H, **H**<sup>2,3</sup>);

<sup>3</sup> Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, 2868–2877.

<sup>4</sup> Kang, Y-B.; Chen, X-M.; Yao, C-Z.; Ning, X-S. *Chem. Commun.* **2016**, 52, 6193–6196.

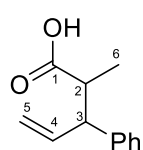
2.44–2.56 (m, 0.7×2H, **H**<sup>2,3</sup>); 5.01–5.07 (m, 2H, **H**<sup>5</sup>); 5.66 (ddd, *J* = 17.3; 10.2; 8.3 Hz, 0.3 ×1H, **H**<sup>4</sup>); 5.78 (ddd, *J* = 17.4; 10.3; 7.4 Hz, 0.7 ×1H, **H**<sup>4</sup>); 11.59 (brs, 1H, **H**<sup>OH</sup>). <sup>1</sup>H NMR spectrum corresponds with those in literature.<sup>5,6</sup>

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)

**Syn:** δ 13.3 (**C**<sup>6</sup>); 16.2 (**C**<sup>7</sup>); 40.3 (**C**<sup>3</sup>); 44.7 (**C**<sup>2</sup>); 114.8 (**C**<sup>5</sup>); 140.7 (**C**<sup>4</sup>); 182.4 (**C**<sup>1</sup>). <sup>13</sup>C NMR spectrum corresponds with those in literature.<sup>5</sup>

**Anti:** δ 14.5 (**C**<sup>6</sup>); 18.6 (**C**<sup>7</sup>); 41.0 (**C**<sup>3</sup>); 45.1 (**C**<sup>2</sup>); 115.5 (**C**<sup>5</sup>); 141.4 (**C**<sup>4</sup>); 182.7 (**C**<sup>1</sup>). <sup>13</sup>C NMR spectrum corresponds with those in literature.<sup>7</sup>

### 2-Methyl-3-phenylpent-4-enoic acid (3c)

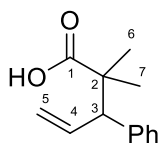


White solid, *R*<sub>F</sub> = 0.05 (hexanes/ethyl acetate 9:1)

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 1.02 (d, *J* = 6.9 Hz, 0.75×3H, **H**<sup>6</sup>); 1.26 (d, *J* = 7.0 Hz, 0.25×3H, **H**<sup>6</sup>); 2.82–2.90 (m, 1H, **H**<sup>2</sup>); 3.45–3.48 (m, 0.75×1H, **H**<sup>3</sup>); 3.56 (t, *J* = 9.3 Hz, 0.25×1H, **H**<sup>3</sup>); 5.05–5.17 (m, 2H, **H**<sup>5</sup>); 5.94 (m, 0.25×1H, **H**<sup>4</sup>); 6.04 (ddd, *J* = 17.1; 10.2; 8.2 Hz, 0.75×1H, **H**<sup>4</sup>); 7.19–7.34 (m, 5H, **H**<sup>Ar</sup>); 1.35 (bs, 1H, **H**<sup>OH</sup>). <sup>1</sup>H NMR spectrum corresponds with those in literature.<sup>8</sup>

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 15.5 (**C**<sup>6</sup>); 16.1 (**C**<sup>6</sup>); 44.9 (**C**<sup>2</sup>); 45.3 (**C**<sup>2</sup>); 53.3 (**C**<sup>3</sup>); 53.4 (**C**<sup>3</sup>); 115.9 (**C**<sup>5</sup>); 117.2 (**C**<sup>5</sup>); 126.8 (**C**<sup>Ar</sup>); 127.0 (**C**<sup>Ar</sup>); 127.8 (**C**<sup>Ar</sup>); 128.3 (**C**<sup>Ar</sup>); 128.7 (**C**<sup>Ar</sup>); 128.9 (**C**<sup>Ar</sup>); 138.3 (**C**<sup>4</sup>); 139.5 (**C**<sup>4</sup>); 141.1 (**C**<sup>7</sup>); 142.2 (**C**<sup>7</sup>); 182.2 (**C**<sup>1</sup>); 182.3 (**C**<sup>1</sup>). <sup>13</sup>C NMR spectrum corresponds with those in literature.<sup>8</sup>

### 2,2-Dimethyl-3-phenylpent-4-enoic acid (3d)



white solid, *R*<sub>F</sub> = 0.35 (hexanes/ethyl acetate 3:1)

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 1.15 (s, 3H, **H**<sup>6</sup>); 1.21 (s, 3H, **H**<sup>7</sup>); 3.65 (d, *J* = 9.5 Hz, 1H, **H**<sup>3</sup>); 5.15–5.18 (m, 2H, **H**<sup>5</sup>); 6.26 (dt, *J* = 16.7; 9.9 Hz, 1H, **H**<sup>4</sup>); 7.22–7.31 (m, 5H, **H**<sup>Ar</sup>); 11.25–11.84 (bs, 1H, **H**<sup>OH</sup>). <sup>1</sup>H NMR spectrum corresponds with those in literature.<sup>9</sup>

### 2-Ethyl-3-phenylpent-4-enoic acid (3e)

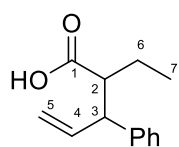
<sup>5</sup> Rye, C. E.; Barker, D. *J. Org. Chem.* **2011**, 76, 6636-6648.

<sup>6</sup> Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, 2868-2877.

<sup>7</sup> Yodwaree, S.; Soorukram, D.; Kuhakarn, Ch.; Tuchinda, P.; Reutrakul, V.; Pohmakotr, M. *Org. Biomol. Chem.* **2014**, 12, 6885-6894.

<sup>8</sup> Ishihara, J.; Watanabe, Y.; Koyama, N.; Nishino, Y.; Takahashi, K. *Tetrahedron*, **2011**, 67, 3659-3667.

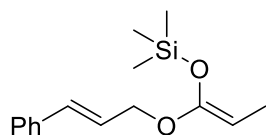
<sup>9</sup> Ishihara, J.; Koyama, N.; Nishino, Y.; Takahashi, K.; Hatakeyama, S. *SynLett* **2009**, 2351-2355.



Colorless oil,  $R_F = 0.26$  (hexanes/ethyl acetate 3:1)

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  0.84 (t,  $J = 7.4$  Hz,  $0.67 \times 3\text{H}$ ,  $\text{H}^7$ ); 0.96 (t,  $J = 6.2$  Hz,  $0.33 \times 3\text{H}$ ,  $\text{H}^7$ ); 1.26–1.33 (m,  $0.67 \times 1\text{H}$ ,  $\text{H}^6$ ); 1.42–1.49 (m,  $0.67 \times 1\text{H}$ ,  $\text{H}^6$ ); 1.59–1.64 (m,  $0.33 \times 1\text{H}$ ,  $\text{H}^6$ ); 1.76–1.82 (m,  $0.33 \times 1\text{H}$ ,  $\text{H}^6$ ); 2.65–2.71 (m, 1H,  $\text{H}^2$ ); 3.43–3.46 (m,  $0.67 \times 1\text{H}$ ,  $\text{H}^3$ ); 3.49 (t,  $J = 9.7$  Hz,  $0.33 \times 1\text{H}$ ,  $\text{H}^3$ ); 5.0–5.14 (m, 2H,  $\text{H}^5$ ); 5.9 (dt,  $J = 16.9$ ; 9.8 Hz,  $0.33 \times 1\text{H}$ ,  $\text{H}^4$ ); 6.0 (ddd,  $J = 17.4$ ; 9.9; 8.8 Hz,  $0.67 \times 1\text{H}$ ,  $\text{H}^4$ ); 7.17–7.33 (m, 5H,  $\text{H}^{\text{Ar}}$ ); 10.99–11.65 (bs, 1H,  $\text{H}^{\text{OH}}$ ).  $^1\text{H}$  NMR spectrum corresponds with those in literature.<sup>10</sup>

### (((Z)-1-(cinnamyloxy)prop-1-en-1-yl)oxy)trimethylsilane (2c)

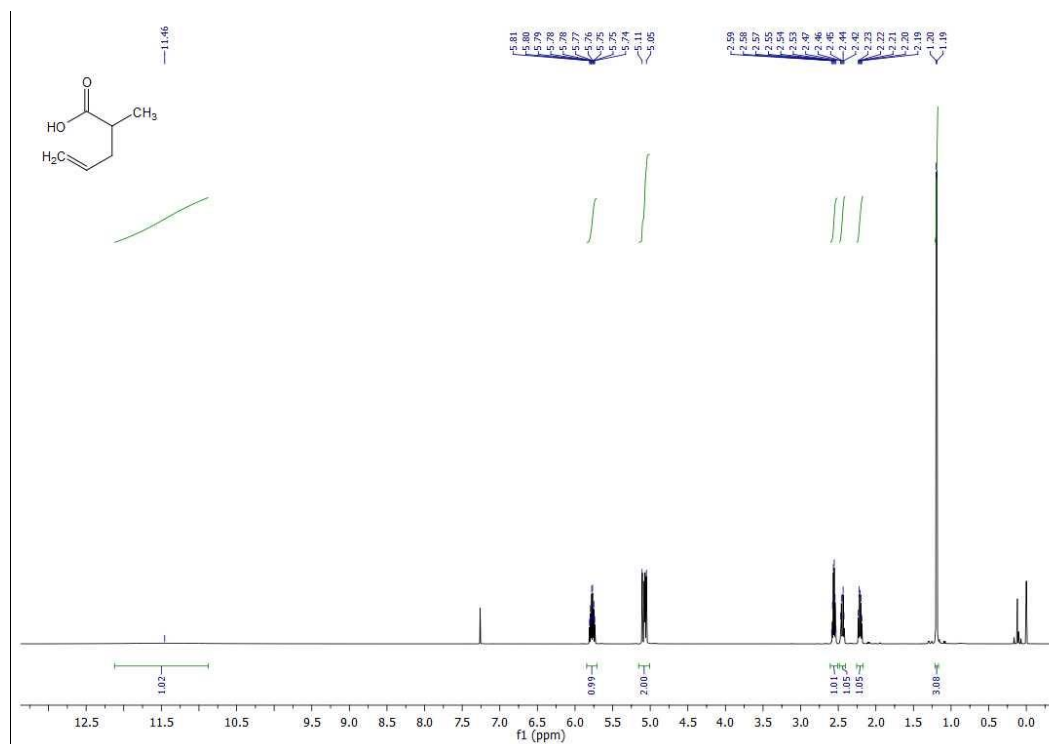


$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  0.09 (s, 9H); 1.21 (d,  $J = 7.1$  Hz, 3H); 2.10 (q,  $J = 7.1$  Hz, 1H); 4.71 (dd,  $J = 6.5$ ; 1.2 Hz, 2H); 6.29 (dt,  $J = 15.9$ ; 6.5 Hz, 1H); 6.65 (d,  $J = 15.9$  Hz, 1H); 7.24–7.39 (m, 5H).

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  2.6; 11.2; 30.5; 64.7; 124.1; 126.8; 128.2; 128.8; 134.0; 136.6; 176.3.

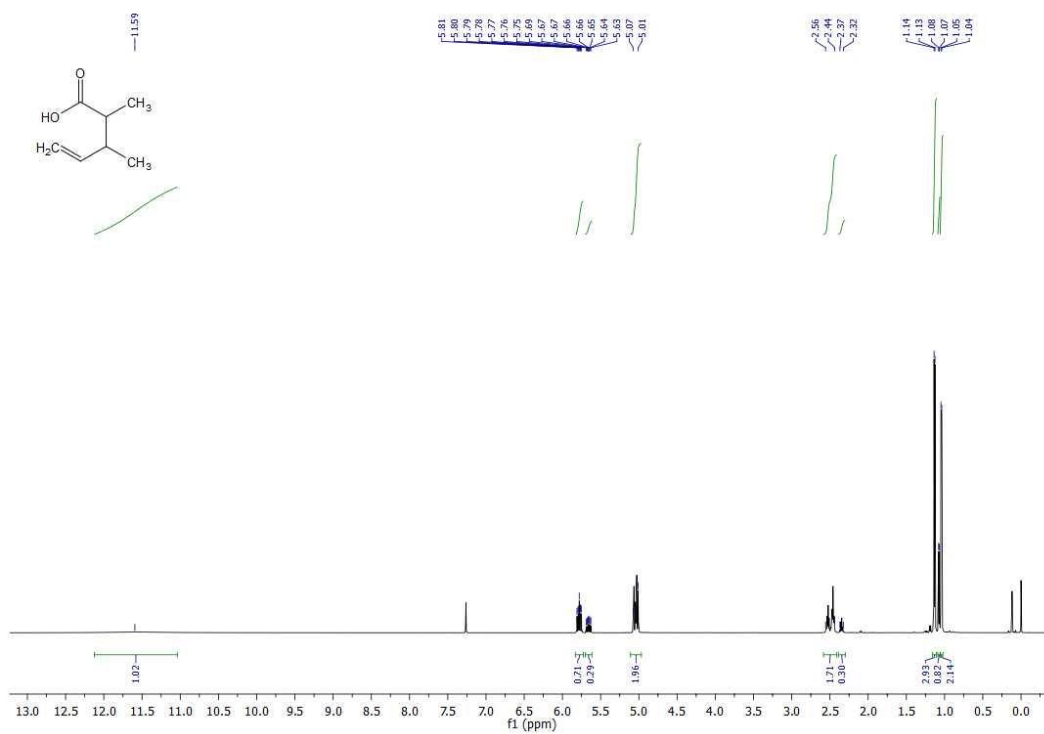
### Pictures of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

#### $^1\text{H}$ NMR of 3a

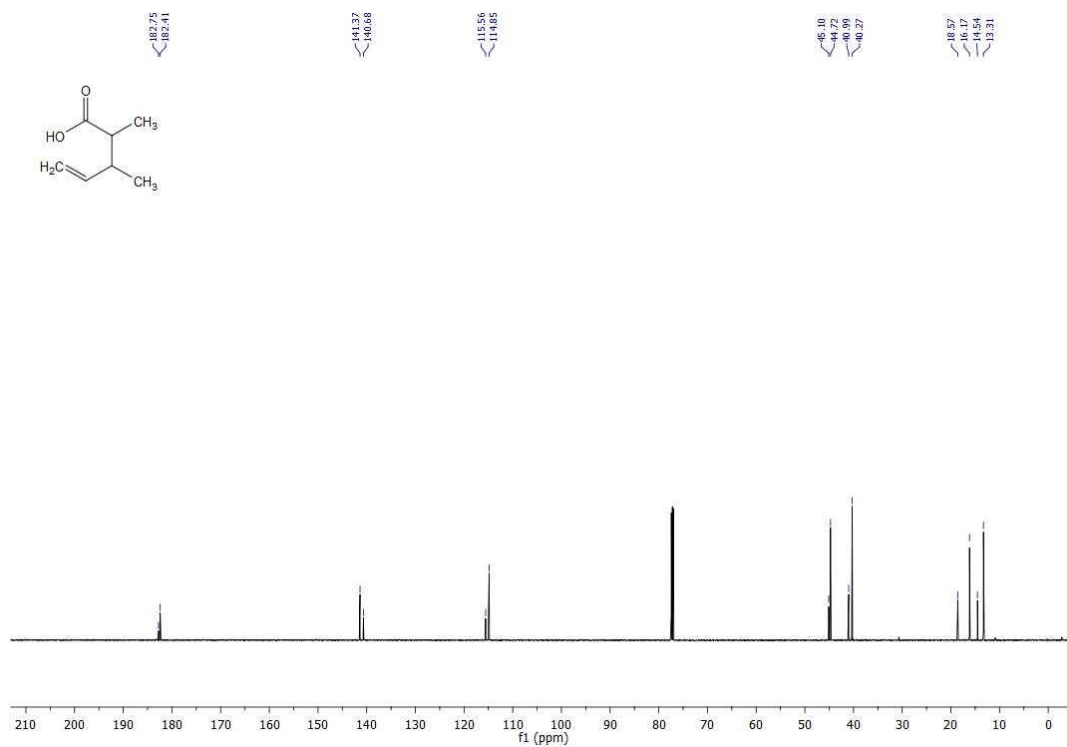


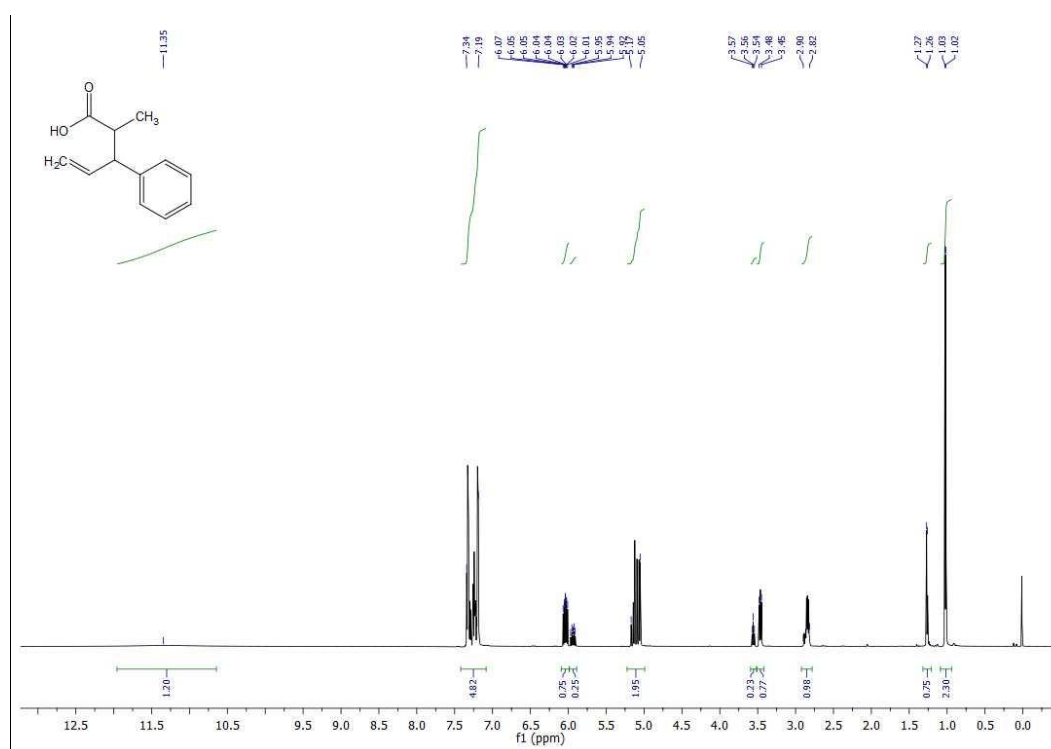
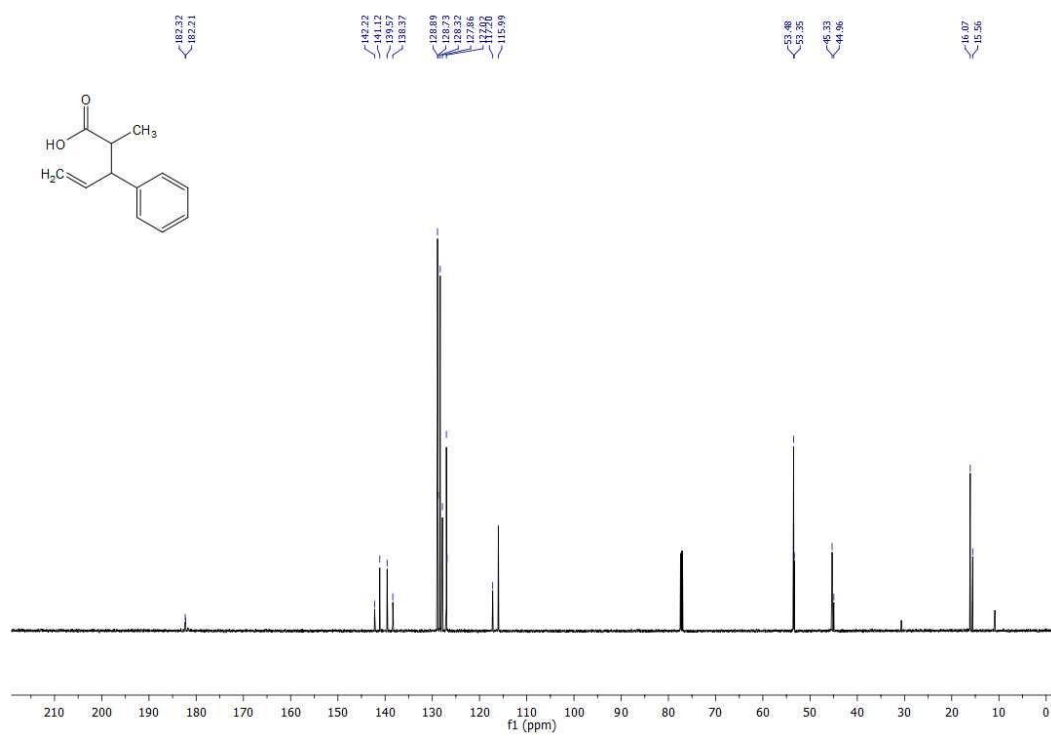
<sup>10</sup> Eriksson, M.; Hjelmencrantz, A.; Nilsson, M.; Olsson, T. *Tetrahedron* **1995**, *51*, 12631-12644.

# <sup>1</sup>H NMR of **3b**



# <sup>13</sup>C NMR of **3b**



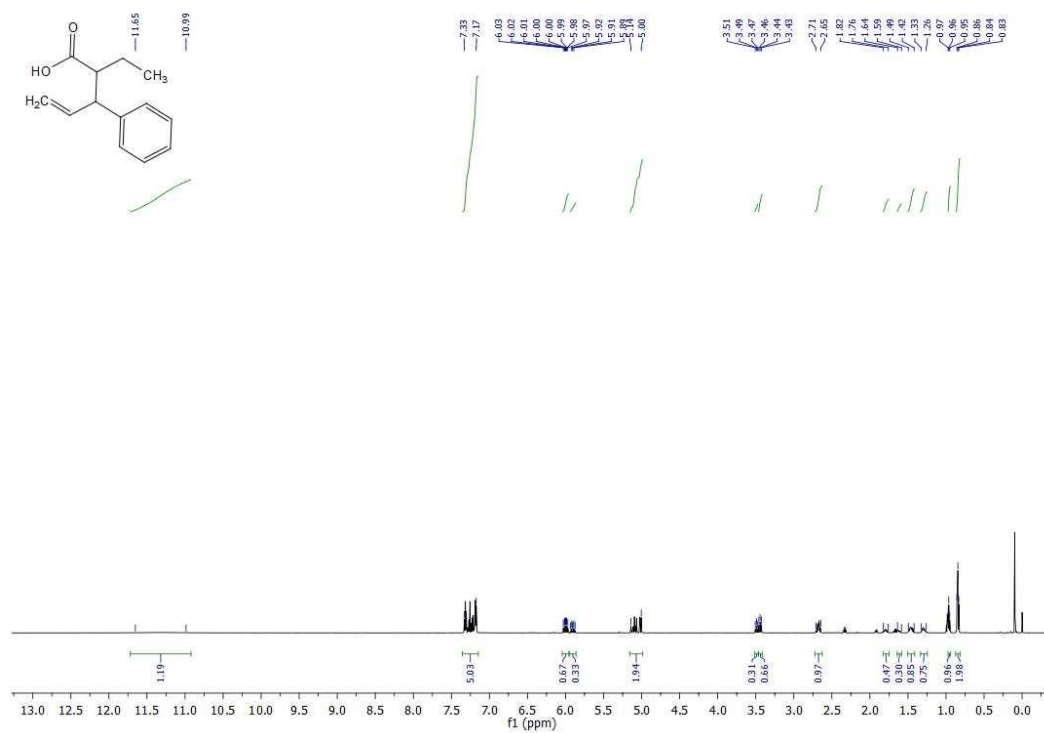
<sup>1</sup>H NMR of **3c** $^{13}\text{C}$  NMR of **3c**



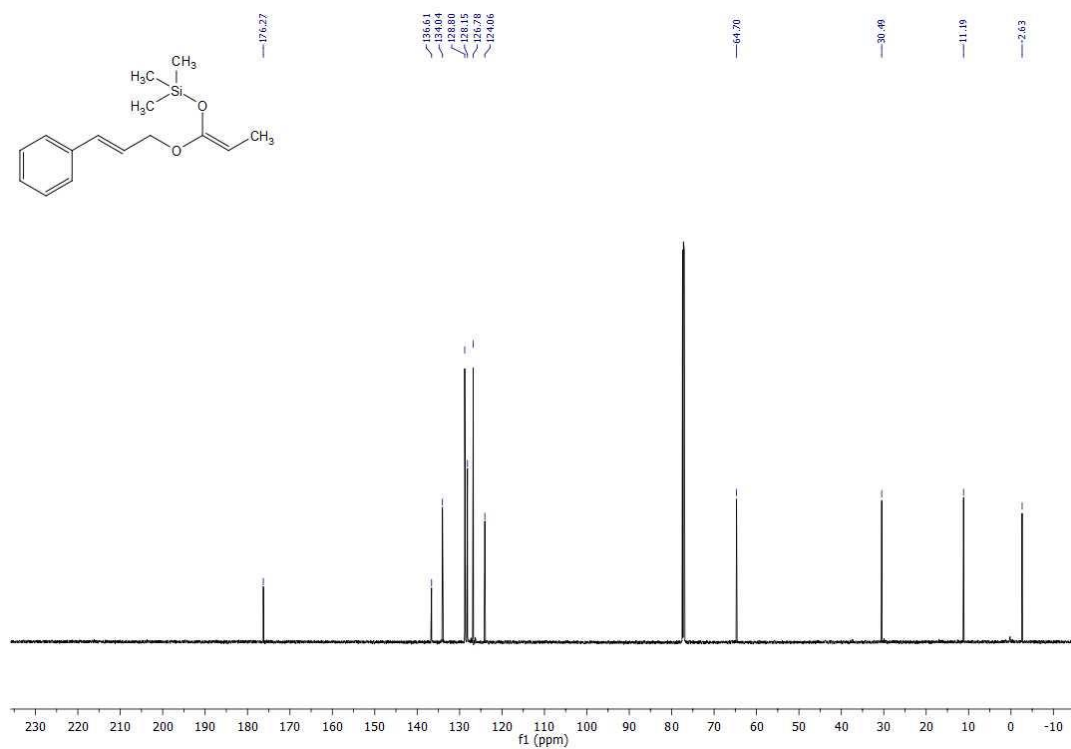
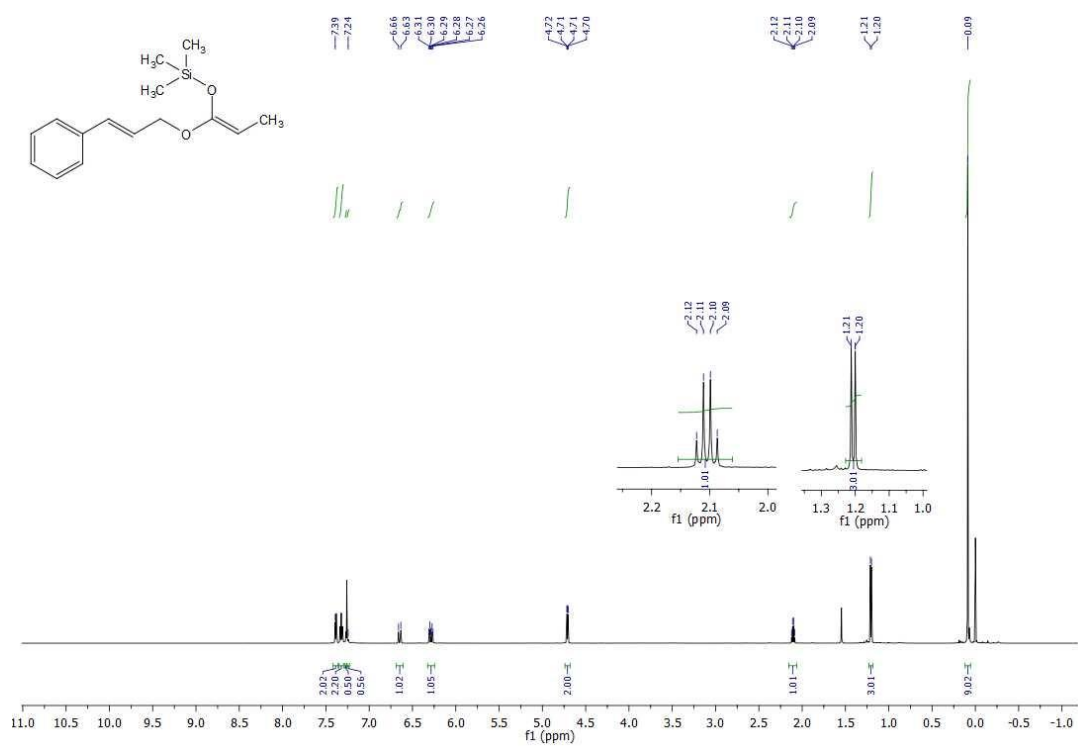
# <sup>1</sup>H NMR of **3d**



# <sup>1</sup>H NMR of **3e**



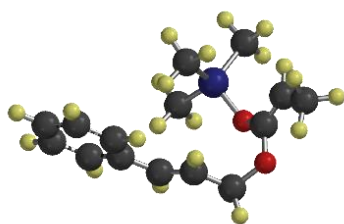
# <sup>1</sup>H NMR of 2c



## Computational details

The molecular models were built and optimized by AM1 method in Spartan 18 program package.<sup>11</sup> From the conformer distribution, several of the most stable conformers were selected and pre-optimized in Spartan at HF/3-21G level and then fully geometrically optimized at  $\omega$ B97X-D/6-31G\* level.<sup>12</sup> Transition states were optimized by  $\omega$ B97X-D/6-31G\* and were verified by visualization of their imaginary frequencies.

### (E)-Silyl ketene acetal 2c



Method:  $\omega$ B97X-D

Basis set: 6-31G\*

Energy: -1024.571296 hartrees

Zero Point Energy : 839.22 kJ/mol (ZPE)

Temperature Correction : 49.83 kJ/mol (vibration + gas law + rotation + translation)

Enthalpy Correction : 889.04 kJ/mol (ZPE + temperature correction)

Enthalpy : -1024.232678 au (Electronic Energy + Enthalpy Correction)

Entropy : 674.59 J/mol•K

Gibbs Energy : -1024.309284 au (Enthalpy - T\*Entropy)

Cv : 341.83 J/mol•K

#### Coordinates:

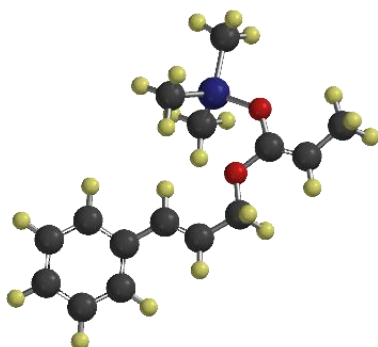
|   |           |           |           |   |           |           |           |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| C | -0.041081 | -1.472650 | -2.159880 | C | -1.928051 | 0.380800  | 0.626803  |
| C | -2.254786 | -1.054198 | -1.385021 | H | -3.192666 | -1.616749 | -1.431614 |
| C | -1.850092 | -0.814717 | 0.038777  | H | -1.475962 | -1.689001 | 0.568453  |

<sup>11</sup> Spartan '18, Wavefunction, Inc., Irvine, CA

<sup>12</sup> Shao, Y.; Gan, Z.; Epifanovsky, E.; Gilbert, A. T. B.; Wormit, M.; Kussmann, J.; Lange, A. W.; Behn, A.; Deng, J.; Feng, X.; Ghosh, D.; Goldey, M.; Horn, P. R.; Jacobson, L. D.; Kaliman, I.; Khaliullin, R. Z.; Kuś, T.; Landau, A.; Liu, J.; Proynov, E. I.; Rhee, Y. M.; Richard, R. M.; Rohrdanz, M. A.; Steele, R. P.; Sundstrom, E. J.; Woodcock, H. L.; Zimmerman, P. M.; Zuev, D.; Albrecht, B.; Alguire, E.; Austin, B.; Beran, G. J. O.; Bernard, Y. A.; Berquist, E.; Brandhorst, K.; Bravaya, K. B.; Brown, S. T.; Casanova, D.; Chang, C.-M.; Chen, Y.; Chien, S. H.; Closser, K. D.; Crittenden, D. L.; Diedenhofen, M.; DiStasio, R. A.; Do, H.; Dutoi, A. D.; Edgar, R. G.; Fatehi, S.; Fusti-Molnar, L.; Ghysels, A.; Golubeva-Zadorozhnaya, A.; Gomes, J.; Hanson-Heine, M. W. D.; Harbach, P. H. P.; Hauser, A. W.; Hohenstein, E. G.; Holden, Z. C.; Jagau, T.-C.; Ji, H.; Kaduk, B.; Khistyayev, K.; Kim, J.; Kim, J.; King, R. A.; Klunzinger, P.; Kosenkov, D.; Kowalczyk, T.; Krauter, C. M.; Lao, K. U.; Laurent, A. D.; Lawler, K. V.; Levchenko, S. V.; Lin, C. Y.; Liu, F.; Livshits, E.; Lochan, R. C.; Luenser, A.; Manohar, P.; Manzer, S. F.; Mao, S.-P.; Mardirossian, N.; Marenich, A. V.; Maurer, S. A.; Mayhall, N. J.; Neuscamman, E.; Oana, C. M.; Olivares-Amaya, R.; O'Neill, D. P.; Parkhill, J. A.; Perrine, T. M.; Peverati, R.; Prociuk, A.; Rehn, D. R.; Rosta, E.; Russ, N. J.; Sharada, S. M.; Sharma, S.; Small, D. W.; Sodt, A. *Mol. Phys.* **2015**, *113*, 184-215.

|    |           |           |           |   |           |           |           |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| H  | -2.396021 | -0.104209 | -1.911471 | H | 3.527222  | 1.615987  | -2.210073 |
| H  | -2.292496 | 1.216951  | 0.028691  | H | 1.009575  | 0.039061  | 0.912856  |
| O  | 0.098773  | -0.130618 | -2.186621 | H | 2.128295  | -1.037121 | 0.054774  |
| Si | 1.320020  | 0.783161  | -1.439204 | H | 2.677266  | 0.554771  | 0.613772  |
| C  | 2.783081  | 0.915464  | -2.607363 | H | -1.942081 | 2.819595  | 1.684015  |
| C  | 0.545499  | 2.467068  | -1.173907 | H | -1.256529 | 3.513746  | 3.952492  |
| C  | 1.828667  | 0.006904  | 0.187263  | H | 3.281040  | -0.048677 | -2.752692 |
| C  | -1.537301 | 0.730870  | 2.002127  | H | -1.029874 | -1.263044 | 2.661723  |
| C  | -0.753129 | 1.518866  | 4.583444  | H | -0.343121 | -0.569065 | 4.914661  |
| C  | -1.591014 | 2.073889  | 2.393831  | H | -0.451507 | 1.820186  | 5.581935  |
| C  | -1.081259 | -0.212842 | 2.933476  | O | -1.334391 | -1.884165 | -2.085744 |
| C  | -0.692875 | 0.177856  | 4.208121  | C | 0.950140  | -2.365873 | -2.257313 |
| C  | -1.204276 | 2.466492  | 3.670691  | C | 0.765034  | -3.851660 | -2.176783 |
| H  | -0.237034 | 2.412776  | -0.410378 | H | 1.949386  | -1.984882 | -2.443548 |
| H  | 0.100975  | 2.853156  | -2.097300 | H | -0.265150 | -4.104345 | -1.914663 |
| H  | 2.468781  | 1.280302  | -3.590993 | H | 0.995289  | -4.342164 | -3.131182 |
| H  | 1.293886  | 3.190817  | -0.830801 | H | 1.427754  | -4.292823 | -1.421413 |

### (Z)-Silyl ketene acetal 2c



Method:  $\omega$ B97X-D

Basis set: 6-31G\*

Energy: -1024.571293 hartrees

Zero Point Energy : 838.41 kJ/mol (ZPE)

Temperature Correction : 49.89 kJ/mol (vibration + gas law + rotation + translation)

Enthalpy Correction : 888.30 kJ/mol (ZPE + temperature correction)

Enthalpy : -1024.232958 au (Electronic Energy + Enthalpy Correction)

Entropy : 660.13 J/mol•K

Gibbs Energy : -1024.307922 au (Enthalpy - T\*Entropy)

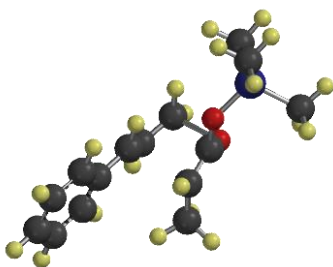
Cv : 342.24 J/mol•K

#### Coordinates:

|   |           |           |           |   |           |           |           |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| C | -0.950121 | -1.792969 | -1.668624 | H | -2.661619 | -1.341016 | 0.321812  |
| C | -2.184522 | -0.458813 | -0.131736 | H | -2.875732 | 0.920138  | 1.408801  |
| C | -1.966038 | 0.598556  | 0.904696  | H | -2.866888 | -0.089303 | -0.912808 |
| C | -0.782146 | 1.120201  | 1.228855  | H | 0.101905  | 0.742063  | 0.721796  |

|    |           |           |           |   |           |           |           |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| O  | 0.299660  | -2.025019 | -2.096409 | H | 1.581544  | 0.732020  | -3.030366 |
| Si | 1.730447  | -1.271617 | -1.576063 | H | 0.840863  | 1.059927  | -1.457053 |
| C  | 2.034338  | -1.620244 | 0.242549  | H | 2.607467  | 1.052114  | -1.624136 |
| C  | 3.036059  | -2.111942 | -2.622023 | H | 1.557845  | 1.678388  | 2.366086  |
| C  | 1.681304  | 0.565244  | -1.952123 | H | 2.059123  | 3.374018  | 4.091782  |
| C  | -0.535294 | 2.156937  | 2.245561  | H | 1.206254  | -1.272621 | 0.866747  |
| C  | 0.032193  | 4.089765  | 4.204669  | H | -2.550572 | 2.921269  | 2.340380  |
| C  | 0.763081  | 2.317488  | 2.743705  | H | -2.056308 | 4.595755  | 4.072518  |
| C  | -1.541785 | 2.998491  | 2.735960  | H | 0.249491  | 4.837420  | 4.961527  |
| C  | -1.262079 | 3.951066  | 3.707565  | O | -0.953665 | -0.826820 | -0.708820 |
| C  | 1.045359  | 3.270581  | 3.716142  | C | -2.017307 | -2.443035 | -2.146239 |
| H  | 2.853036  | -1.944903 | -3.688653 | C | -1.929906 | -3.500135 | -3.207439 |
| H  | 3.044812  | -3.192911 | -2.447460 | H | -2.318800 | -4.460878 | -2.846960 |
| H  | 2.152982  | -2.696138 | 0.412019  | H | -0.895691 | -3.653127 | -3.524267 |
| H  | 4.034253  | -1.724753 | -2.387119 | H | -2.517993 | -3.226906 | -4.092710 |
| H  | 2.952802  | -1.126504 | 0.582285  | H | -2.998335 | -2.201784 | -1.754450 |

### TS-(E)-uncatalyzed



Method:  $\omega$ B97X-D  
Basis set: 6-31G\*  
Energy: -1024.537184 hartrees

Imaginary vibration:  $-504\text{ cm}^{-1}$  (Uncorrected);  $-475\text{ cm}^{-1}$  (Corrected); Intensity 25.81

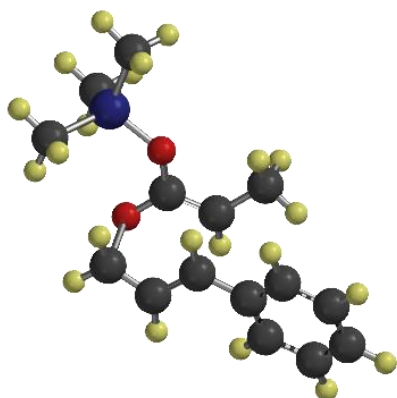
Zero Point Energy : 835.69 kJ/mol (ZPE)  
Temperature Correction : 50.40 kJ/mol (vibration + gas law + rotation + translation)  
Enthalpy Correction : 886.09 kJ/mol (ZPE + temperature correction)  
Enthalpy : -1024.199690 au (Electronic Energy + Enthalpy Correction)  
Entropy : 634.87 J/mol•K  
Gibbs Energy : -1024.271785 au (Enthalpy - T\*Entropy)  
Cv : 345.44 J/mol•K

### Coordinates:

|   |           |           |          |   |           |           |           |
|---|-----------|-----------|----------|---|-----------|-----------|-----------|
| C | -0.654372 | 0.970672  | 0.263163 | H | 0.269753  | 0.184463  | 3.357203  |
| C | 0.514761  | -0.025028 | 2.321985 | H | -0.435852 | -1.945538 | 2.335506  |
| C | 0.211184  | -1.276493 | 1.775401 | H | 1.371936  | 0.519695  | 1.938772  |
| C | 0.423663  | -1.480592 | 0.423500 | H | 1.144238  | -0.829471 | -0.068194 |

|    |           |           |           |   |           |           |           |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| O  | 0.320705  | 1.627286  | -0.432874 | H | -1.302296 | 4.312535  | -0.642586 |
| Si | 0.840443  | 3.195551  | -0.048692 | H | -1.239603 | 3.927389  | 1.086617  |
| C  | 1.970911  | 3.209186  | 1.448855  | H | -0.343929 | 5.321635  | 0.454111  |
| C  | 1.791578  | 3.718027  | -1.576282 | H | 1.301795  | -2.111653 | -2.008104 |
| C  | -0.651912 | 4.291961  | 0.238572  | H | 0.816737  | -4.138038 | -3.334438 |
| C  | 0.096473  | -2.703016 | -0.327951 | H | 1.421124  | 2.936476  | 2.354831  |
| C  | -0.467448 | -5.002898 | -1.837478 | H | -1.202475 | -3.584629 | 1.153959  |
| C  | 0.648931  | -2.880743 | -1.602951 | H | -1.689283 | -5.598177 | -0.168632 |
| C  | -0.751273 | -3.698961 | 0.173448  | H | -0.685237 | -5.893057 | -2.419612 |
| C  | -1.029371 | -4.837293 | -0.574345 | O | -0.734091 | 1.160081  | 1.526420  |
| C  | 0.373789  | -4.018700 | -2.350229 | C | -1.316272 | -0.044958 | -0.395147 |
| H  | 1.145461  | 3.713699  | -2.460429 | C | -2.519523 | -0.719680 | 0.183044  |
| H  | 2.629783  | 3.040361  | -1.770928 | H | -1.154197 | -0.123379 | -1.466592 |
| H  | 2.809455  | 2.513826  | 1.329110  | H | -2.575659 | -1.766784 | -0.135774 |
| H  | 2.198320  | 4.729124  | -1.459677 | H | -2.499554 | -0.676527 | 1.275033  |
| H  | 2.392359  | 4.211007  | 1.595324  | H | -3.441049 | -0.227361 | -0.153937 |

### TS-(Z)-uncatalyzed



Method:  $\omega$ B97X-D  
Basis set: 6-31G\*  
Energy: -1024.538466 hartrees

Imaginary vibration:  $-532\text{ cm}^{-1}$  (Uncorrected);  $-501\text{ cm}^{-1}$  (Corrected); Intensity 36.89

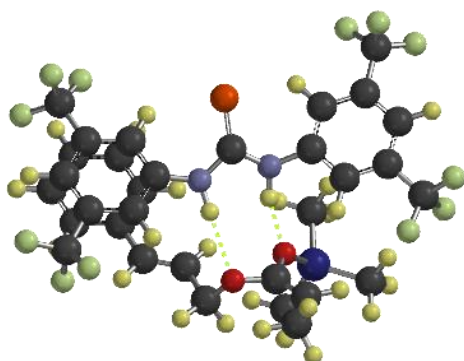
Zero Point Energy : 835.02 kJ/mol (ZPE)  
Temperature Correction : 50.43 kJ/mol (vibration + gas law + rotation + translation)  
Enthalpy Correction : 885.45 kJ/mol (ZPE + temperature correction)  
Enthalpy : -1024.201216 au (Electronic Energy + Enthalpy Correction)  
Entropy : 642.16 J/mol•K  
Gibbs Energy : -1024.274139 au (Enthalpy - T\*Entropy)  
Cv : 345.87 J/mol•K

### Coordinates:

|   |           |          |          |   |          |           |          |
|---|-----------|----------|----------|---|----------|-----------|----------|
| C | -0.701572 | 0.917252 | 0.370373 | C | 0.437292 | -0.070351 | 2.450043 |
|---|-----------|----------|----------|---|----------|-----------|----------|

|    |           |           |           |   |           |           |           |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| C  | 0.117906  | -1.331638 | 1.937587  | H | 2.671751  | 2.535695  | 1.511674  |
| C  | 0.336295  | -1.577471 | 0.593505  | H | 1.954534  | 4.902506  | -1.145980 |
| H  | 0.202660  | 0.167360  | 3.481422  | H | 2.217685  | 4.207776  | 1.862380  |
| H  | -0.552872 | -1.972438 | 2.503252  | H | -1.512790 | 4.289095  | -0.340489 |
| H  | 1.301559  | 0.452618  | 2.051361  | H | -1.424652 | 3.815963  | 1.365539  |
| H  | 1.105622  | -0.988099 | 0.096543  | H | -0.589728 | 5.277419  | 0.803965  |
| O  | 0.225507  | 1.667654  | -0.291016 | H | 1.526980  | -2.588522 | -1.570579 |
| Si | 0.676840  | 3.232813  | 0.183705  | H | 0.958495  | -4.651968 | -2.804952 |
| C  | 1.818466  | 3.204275  | 1.672406  | H | 1.285105  | 2.875455  | 2.569316  |
| C  | 1.596049  | 3.880875  | -1.315559 | H | -1.721814 | -3.311143 | 1.138683  |
| C  | -0.857356 | 4.248738  | 0.536165  | H | -2.283862 | -5.372426 | -0.085005 |
| C  | -0.036719 | -2.815651 | -0.112814 | H | -0.950312 | -6.057264 | -2.063268 |
| C  | -0.694105 | -5.153013 | -1.520178 | O | -0.816159 | 1.063715  | 1.638166  |
| C  | 0.695322  | -3.204827 | -1.239912 | C | -1.286541 | -0.128381 | -0.315232 |
| C  | -1.117935 | -3.611069 | 0.287415  | C | -1.223754 | -0.285553 | -1.803402 |
| C  | -1.440773 | -4.769182 | -0.407554 | H | -1.315803 | -1.339695 | -2.084218 |
| C  | 0.374496  | -4.365375 | -1.935782 | H | -0.280815 | 0.101680  | -2.198874 |
| H  | 0.947651  | 3.892851  | -2.197917 | H | -2.040218 | 0.258499  | -2.295506 |
| H  | 2.464810  | 3.255498  | -1.547331 | H | -2.067248 | -0.653672 | 0.222063  |

(*E*)-Silyl ketene acetal + Schreiner thiourea



Method:  $\omega$ B97X-D  
Basis set: 6-31G\*  
Energy: -3382.515231 hartrees

Zero Point Energy : 1456.94 kJ/mol (ZPE)  
Temperature Correction : 110.38 kJ/mol (vibration + gas law + rotation + translation)  
Enthalpy Correction : 1567.31 kJ/mol (ZPE + temperature correction)  
Enthalpy : -3381.918273 au (Electronic Energy + Enthalpy Correction)  
Entropy : 1302.40 J/mol•K  
Gibbs Energy : -3382.066173 au (Enthalpy - T\*Entropy)  
Cv : 807.25 J/mol•K

Energy ( $\omega$ B97X-D/6-31G\*\*//M06-2X/6-311+G\*\*): -3383.12863 au

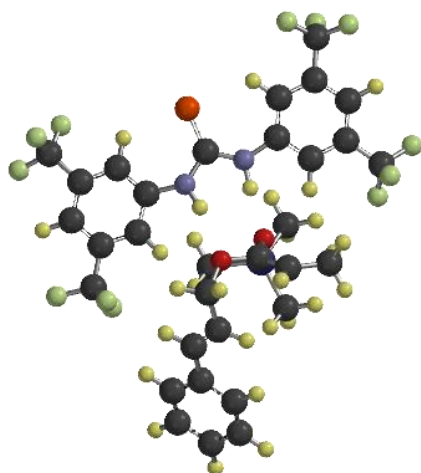
[E(E-enol): -1024.67643 au; E(**C12**): -2358.40134 au]

*Coordinates:*

|    |           |           |           |   |           |           |           |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| C  | 0.048666  | 2.554667  | 1.133876  | C | -3.986975 | -3.519191 | 0.941126  |
| C  | -0.500561 | 0.989848  | 2.834876  | C | -2.230773 | -2.908922 | -0.612488 |
| C  | -0.062715 | -0.391684 | 2.472813  | C | -3.189624 | -1.242816 | 0.840691  |
| C  | -0.759169 | -1.479176 | 2.815643  | C | -4.020781 | -2.210201 | 1.395621  |
| H  | -1.385187 | 0.960931  | 3.476395  | C | -3.091505 | -3.851451 | -0.072303 |
| H  | 0.832374  | -0.466214 | 1.860390  | C | 0.854360  | 1.235713  | -2.723494 |
| H  | 0.282084  | 1.555568  | 3.352092  | C | 2.277663  | 2.760686  | -4.586760 |
| H  | -1.653060 | -1.348481 | 3.425244  | C | 1.061160  | 2.600342  | -2.509269 |
| O  | 1.128530  | 1.858712  | 0.679676  | C | 1.363347  | 0.630835  | -3.871641 |
| Si | 2.794316  | 2.072596  | 0.999544  | C | 2.060570  | 1.404006  | -4.794920 |
| C  | 3.564476  | 0.785717  | -0.113556 | C | 1.776213  | 3.350168  | -3.431741 |
| C  | 3.356631  | 3.804720  | 0.581107  | C | 2.558199  | 0.769881  | -6.068509 |
| C  | 3.080078  | 1.717513  | 2.816565  | C | -3.076671 | -5.261881 | -0.598260 |
| C  | -0.494005 | -2.865203 | 2.404757  | C | -4.877496 | -1.838991 | 2.571257  |
| C  | -0.166467 | -5.523381 | 1.576848  | C | 2.054820  | 4.803724  | -3.166804 |
| C  | -1.269149 | -3.888695 | 2.958996  | F | 3.713536  | 1.326433  | -6.473913 |
| C  | 0.450406  | -3.197136 | 1.423854  | F | 1.898733  | 5.553298  | -4.265624 |
| C  | 0.611313  | -4.512630 | 1.014201  | F | 3.325051  | 4.984352  | -2.747720 |
| C  | -1.105651 | -5.208354 | 2.552186  | F | 2.772859  | -0.545689 | -5.921700 |
| H  | 2.896962  | 4.549616  | 1.238712  | F | 1.255267  | 5.307877  | -2.210666 |
| H  | 3.138792  | 4.077482  | -0.454821 | F | 1.674379  | 0.923801  | -7.066481 |
| H  | 3.359710  | 1.002511  | -1.167665 | F | -1.908800 | -5.576178 | -1.178089 |
| H  | 4.443115  | 3.874322  | 0.716115  | F | -4.039599 | -5.449187 | -1.516358 |
| H  | 4.651883  | 0.755755  | 0.016119  | F | -3.295203 | -6.157740 | 0.382609  |
| H  | 2.562050  | 2.447457  | 3.448996  | F | -4.156113 | -1.854660 | 3.719145  |
| H  | 2.737408  | 0.715843  | 3.097419  | F | -5.900343 | -2.684344 | 2.747663  |
| H  | 4.148360  | 1.783092  | 3.052585  | F | -5.380664 | -0.600577 | 2.457477  |
| H  | -2.026509 | -3.640525 | 3.697772  | H | -1.511032 | -3.195702 | -1.365721 |
| H  | -1.727546 | -5.987121 | 2.981721  | H | -3.226296 | -0.219240 | 1.200715  |
| H  | 3.174768  | -0.214341 | 0.106313  | H | -4.633775 | -4.272812 | 1.374175  |
| H  | 1.038432  | -2.417518 | 0.947757  | H | 0.434756  | 0.879851  | -0.768735 |
| H  | 1.333147  | -4.750115 | 0.238574  | H | -1.212906 | 0.116287  | 0.143914  |
| H  | -0.052274 | -6.548651 | 1.239650  | H | 1.212474  | -0.427058 | -4.037991 |
| O  | -0.904748 | 1.739048  | 1.661719  | H | 2.830753  | 3.347649  | -5.311136 |
| C  | -0.137534 | 3.864957  | 0.971118  | H | 0.644500  | 3.069778  | -1.624426 |
| C  | -0.799157 | -0.398008 | -1.788576 | H | 0.625716  | 4.411718  | 0.425356  |
| S  | -1.286254 | -1.145732 | -3.195163 | C | -1.340075 | 4.618907  | 1.450633  |
| N  | -1.364237 | -0.606339 | -0.555274 | H | -2.010428 | 3.972850  | 2.021752  |
| N  | 0.197914  | 0.531924  | -1.696972 | H | -1.045741 | 5.462678  | 2.085229  |
| C  | -2.281702 | -1.589950 | -0.155905 | H | -1.903257 | 5.032462  | 0.606183  |



**(Z)-Silyl ketene acetal + Schreiner thiourea**



Method:  $\omega$ B97X-D  
Basis set: 6-31G\*  
Energy: -3382.508748 hartrees

Zero Point Energy : 1455.81 kJ/mol (ZPE)  
Temperature Correction : 110.41 kJ/mol (vibration + gas law + rotation + translation)  
Enthalpy Correction : 1566.22 kJ/mol (ZPE + temperature correction)  
Enthalpy : -3381.912205 au (Electronic Energy + Enthalpy Correction)  
Entropy : 1292.42 J/mol•K  
Gibbs Energy : -3382.058971 au (Enthalpy - T\*Entropy)  
Cv : 807.58 J/mol•K

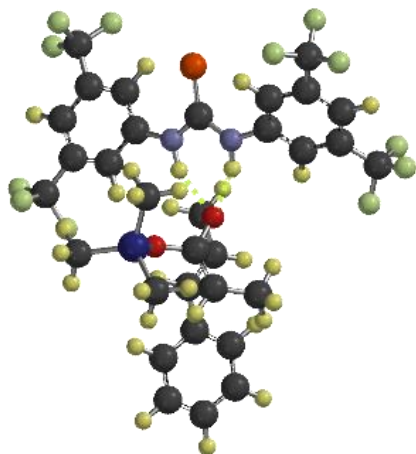
Energy ( $\omega$ B97X-D/6-31G\*\*/M06-2X/6-311+G\*\*): -3383.12077 au  
[E(Z-enol): -1024.67962 au; E(**C12**): -2358.39846 au]

**Coordinates:**

|    |           |           |           |   |           |           |          |
|----|-----------|-----------|-----------|---|-----------|-----------|----------|
| C  | 0.558330  | -1.649499 | -0.670085 | C | 2.553326  | -3.222766 | 3.960813 |
| C  | 2.867980  | -1.229669 | -0.121704 | C | 2.389298  | -3.670372 | 5.264775 |
| C  | 2.813914  | -1.968589 | 1.181846  | C | 2.816322  | -1.447093 | 6.088340 |
| C  | 3.007235  | -1.335894 | 2.343241  | H | -3.193315 | 0.327864  | 0.246580 |
| H  | 3.469825  | -0.322962 | -0.034941 | H | -3.647023 | -0.440092 | 1.773833 |
| H  | 2.524520  | -3.015485 | 1.148957  | H | -0.565704 | 1.494145  | 1.473183 |
| H  | 3.280142  | -1.835684 | -0.935461 | H | -3.503184 | -1.413939 | 0.301190 |
| H  | 3.284227  | -0.283850 | 2.307636  | H | -0.884007 | 0.740772  | 3.041294 |
| O  | -0.628008 | -1.060699 | -0.379116 | H | -1.303961 | -3.346054 | 1.583350 |
| Si | -1.259873 | -0.883687 | 1.215785  | H | 0.148245  | -2.612383 | 2.296154 |
| C  | -0.440724 | 0.573166  | 2.052732  | H | -1.409344 | -2.463360 | 3.116755 |
| C  | -3.066651 | -0.575450 | 0.854803  | H | 3.209937  | 0.044765  | 4.589287 |
| C  | -0.926064 | -2.477983 | 2.133061  | H | 2.920940  | -0.750499 | 6.914296 |
| C  | 2.852196  | -1.878875 | 3.700841  | H | 0.629363  | 0.397611  | 2.199293 |
| C  | 2.520058  | -2.784080 | 6.332934  | H | 2.454633  | -3.927213 | 3.139908 |
| C  | 2.981514  | -0.999824 | 4.782470  | H | 2.160857  | -4.715557 | 5.451224 |

|   |           |           |           |   |           |           |           |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| H | 2.390737  | -3.137530 | 7.351149  | C | -4.830426 | 1.146469  | -5.955047 |
| O | 1.563635  | -0.742586 | -0.492355 | C | 1.841252  | 6.691550  | -0.472562 |
| C | 0.671620  | -2.894908 | -1.130094 | C | 3.673217  | 2.721526  | 1.998236  |
| C | -0.479357 | -3.835822 | -1.330472 | C | -4.142524 | -2.979523 | -3.187282 |
| H | -0.298724 | -4.789813 | -0.822753 | F | -5.301272 | 0.301573  | -6.888649 |
| H | -0.629739 | -4.056103 | -2.393544 | F | -5.381074 | -3.321554 | -3.565700 |
| H | -1.417066 | -3.425578 | -0.948111 | F | -4.043204 | -3.216645 | -1.862681 |
| H | 1.660800  | -3.251073 | -1.401380 | F | -5.882872 | 1.828351  | -5.472429 |
| C | -0.826441 | 2.139104  | -2.194320 | F | -3.291062 | -3.827600 | -3.791914 |
| S | -1.338894 | 3.531339  | -2.950177 | F | -4.035748 | 2.032237  | -6.571985 |
| N | 0.250393  | 2.044103  | -1.341091 | F | 0.605345  | 7.140322  | -0.732548 |
| N | -1.410219 | 0.907752  | -2.315420 | F | 2.600892  | 6.969905  | -1.545074 |
| C | 1.041333  | 3.005086  | -0.696516 | F | 2.326255  | 7.409909  | 0.554451  |
| C | 2.735067  | 4.710982  | 0.771213  | F | 2.969075  | 2.154831  | 3.003080  |
| C | 1.006469  | 4.385752  | -0.910289 | F | 4.512183  | 3.603442  | 2.547116  |
| C | 1.932982  | 2.493894  | 0.253854  | F | 4.420053  | 1.731860  | 1.461244  |
| C | 2.764132  | 3.337106  | 0.973787  | H | 0.326950  | 4.804916  | -1.637909 |
| C | 1.849697  | 5.212893  | -0.174022 | H | 1.951952  | 1.424900  | 0.439398  |
| C | -2.453489 | 0.405104  | -3.106917 | H | 3.381264  | 5.372569  | 1.334121  |
| C | -4.476813 | -0.895558 | -4.559605 | H | -1.088422 | 0.210290  | -1.645411 |
| C | -2.823922 | -0.912030 | -2.805566 | H | 0.535925  | 1.099722  | -1.096658 |
| C | -3.106518 | 1.071804  | -4.145142 | H | -2.838652 | 2.089087  | -4.390803 |
| C | -4.102869 | 0.408056  | -4.858636 | H | -5.254576 | -1.392641 | -5.125380 |
| C | -3.825669 | -1.546870 | -3.517829 | H | -2.316418 | -1.436329 | -2.002856 |

TS-(*E*)-Schreiner thiourea-catalyzed



Method:  $\omega$ B97X-D  
Basis set: 6-31G\*  
Energy: -3382.470065 hartrees

Imaginary vibration:  $-408\text{ cm}^{-1}$  (Uncorrected);  $-385\text{ cm}^{-1}$  (Corrected); Intensity 37.41

Zero Point Energy : 1448.89 kJ/mol (ZPE)

Temperature Correction : 111.19 kJ/mol (vibration + gas law + rotation + translation)  
 Enthalpy Correction : 1560.08 kJ/mol (ZPE + temperature correction)  
 Enthalpy : -3381.875861 au (Electronic Energy + Enthalpy Correction)  
 Entropy : 1300.59 J/mol•K  
 Gibbs Energy : -3382.023555 au (Enthalpy - T\*Entropy)  
 Cv : 813.30 J/mol•K

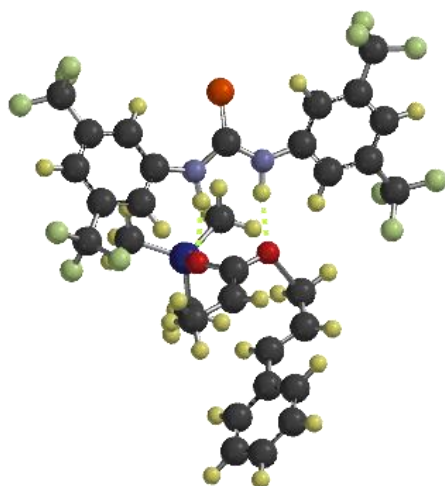
Energy ( $\omega$ B97X-D/6-31G\*\*//M06-2X/6-311+G\*\*): -3383.08386 au  
 [E(TS-E-enol): -1024.64305 au; E(C12): -2358.40080 au]

*Coordinates:*

|    |           |           |           |   |           |           |           |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| C  | -0.326768 | -0.991586 | -1.033402 | C | -1.051491 | -1.936324 | -1.713598 |
| C  | -0.060922 | -1.803823 | 1.482695  | C | -2.482907 | -2.243260 | -1.414616 |
| C  | -0.498567 | -3.031849 | 0.991603  | H | -0.634749 | -2.312028 | -2.643348 |
| C  | 0.096567  | -3.537544 | -0.147685 | H | -2.666321 | -3.323827 | -1.453378 |
| H  | -0.557516 | -1.336695 | 2.325649  | H | -2.765390 | -1.868701 | -0.428168 |
| H  | -1.437120 | -3.439686 | 1.354434  | H | -3.145192 | -1.779742 | -2.156299 |
| H  | 0.976553  | -1.519383 | 1.338501  | C | 0.071655  | 2.537481  | 1.549424  |
| H  | 1.051213  | -3.102044 | -0.439151 | S | 0.424161  | 3.942418  | 2.374050  |
| O  | 0.956300  | -0.718604 | -1.422850 | N | -1.125620 | 2.256748  | 0.937368  |
| Si | 1.396139  | 0.351489  | -2.674022 | N | 0.929417  | 1.486343  | 1.368401  |
| C  | 1.100958  | 2.100071  | -2.072734 | C | -2.327598 | 2.982620  | 0.942946  |
| C  | 3.202927  | -0.013012 | -2.970483 | C | -4.820104 | 4.261920  | 0.862604  |
| C  | 0.373202  | -0.019018 | -4.201608 | C | -2.397079 | 4.375812  | 0.900752  |
| C  | -0.255191 | -4.772573 | -0.853079 | C | -3.508215 | 2.236514  | 0.919989  |
| C  | -0.834248 | -7.121034 | -2.269082 | C | -4.740143 | 2.874549  | 0.875441  |
| C  | 0.574790  | -5.204912 | -1.896856 | C | -3.640807 | 4.996650  | 0.873969  |
| C  | -1.384178 | -5.538361 | -0.532548 | C | 2.236691  | 1.262208  | 1.816906  |
| C  | -1.668806 | -6.702828 | -1.235574 | C | 4.824633  | 0.528454  | 2.623336  |
| C  | 0.290585  | -6.368181 | -2.598784 | C | 2.974967  | 0.326405  | 1.084795  |
| H  | 3.339878  | -1.045250 | -3.310447 | C | 2.799270  | 1.826946  | 2.964218  |
| H  | 3.807133  | 0.122567  | -2.069131 | C | 4.084896  | 1.458288  | 3.344966  |
| H  | 1.755098  | 2.349555  | -1.230093 | C | 4.249385  | -0.039018 | 1.493391  |
| H  | 3.607512  | 0.649814  | -3.743821 | H | -1.490815 | 4.964208  | 0.889737  |
| H  | 1.295404  | 2.824847  | -2.872065 | H | -3.459024 | 1.151748  | 0.934549  |
| H  | 0.531120  | -1.046187 | -4.548887 | H | -5.781309 | 4.759782  | 0.828052  |
| H  | -0.698195 | 0.116143  | -4.020708 | H | 0.572882  | 0.744006  | 0.764600  |
| H  | 0.660369  | 0.653990  | -5.018033 | H | -1.223159 | 1.301311  | 0.596638  |
| H  | 1.451477  | -4.615860 | -2.154692 | H | 2.235137  | 2.535155  | 3.554049  |
| H  | 0.946875  | -6.689690 | -3.401420 | H | 5.817360  | 0.239920  | 2.945070  |
| H  | 0.065034  | 2.242996  | -1.742800 | H | 2.534888  | -0.130040 | 0.201922  |
| H  | -2.042504 | -5.230473 | 0.273707  | C | 4.692365  | 2.111232  | 4.560713  |
| H  | -2.544867 | -7.287976 | -0.973933 | C | 5.012783  | -1.030333 | 0.660064  |
| H  | -1.058884 | -8.032136 | -2.814800 | F | 3.769942  | 2.360840  | 5.502217  |
| O  | -0.685466 | -0.518617 | 0.111058  | F | 5.639990  | 1.337590  | 5.117235  |

|   |           |           |           |   |           |          |          |
|---|-----------|-----------|-----------|---|-----------|----------|----------|
| F | 5.573835  | -0.441363 | -0.414909 | F | -3.661311 | 6.970746 | 2.156500 |
| F | 4.207909  | -2.003333 | 0.190953  | F | -4.831131 | 6.963938 | 0.338857 |
| F | 6.001535  | -1.617727 | 1.347592  | F | -7.023242 | 2.675545 | 0.313408 |
| F | 5.269708  | 3.282466  | 4.248269  | F | -5.831186 | 0.864981 | 0.292990 |
| C | -3.700013 | 6.502381  | 0.898897  | F | -6.376042 | 1.782058 | 2.171742 |
| C | -5.997735 | 2.048813  | 0.909957  | F | -2.668732 | 7.051471 | 0.238786 |

### TS-(Z)-Schreiner thiourea-catalyzed



Method:  $\omega$ B97X-D  
Basis set: 6-31G\*  
Energy: -3382.466567 hartrees

Imaginary vibration:  $-446\text{ cm}^{-1}$  (Uncorrected);  $-420\text{ cm}^{-1}$  (Corrected); Intensity 28.45

Zero Point Energy : 1447.31 kJ/mol (ZPE)  
Temperature Correction : 111.58 kJ/mol (vibration + gas law + rotation + translation)  
Enthalpy Correction : 1558.89 kJ/mol (ZPE + temperature correction)  
Enthalpy : -3381.872818 au (Electronic Energy + Enthalpy Correction)  
Entropy : 1318.71 J/mol•K  
Gibbs Energy : -3382.022569 au (Enthalpy - T\*Entropy)  
Cv : 815.73 J/mol•K

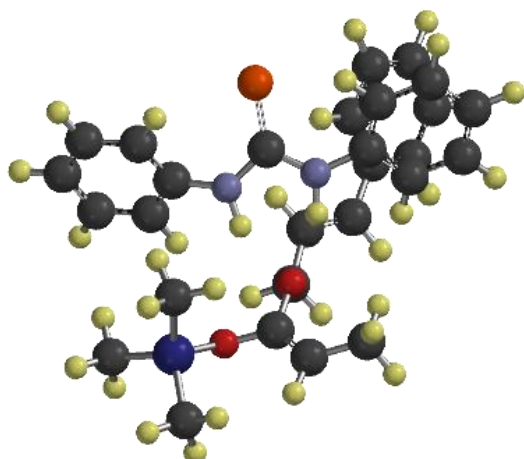
Energy ( $\omega$ B97X-D/6-31G\*\*//M06-2X/6-311+G\*\*): -3383.08112 au  
[E(TS-Z-enol): -1024.64378 au; E(C12): -2358.40001 au]

#### Coordinates:

|   |          |           |          |    |           |           |           |
|---|----------|-----------|----------|----|-----------|-----------|-----------|
| C | 0.150436 | -1.107572 | 0.052682 | H  | -0.403918 | -3.281922 | 2.902621  |
| C | 0.953432 | -1.673614 | 2.537597 | H  | 1.931834  | -1.413130 | 2.148898  |
| C | 0.441069 | -2.947928 | 2.307693 | H  | 1.689506  | -3.313734 | 0.637213  |
| C | 0.779053 | -3.619816 | 1.149379 | O  | 1.079907  | -0.554628 | -0.787941 |
| H | 0.646089 | -1.121160 | 3.417721 | Si | 2.651887  | 0.053054  | -0.564649 |

|   |           |           |           |   |           |           |           |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| C | 3.815719  | -1.378751 | -0.212019 | C | -1.514179 | 3.227366  | 5.128562  |
| C | 3.022401  | 0.823659  | -2.225001 | C | -1.929863 | 3.699348  | 2.779947  |
| C | 2.700122  | 1.330270  | 0.805451  | C | -0.492177 | 1.875187  | 3.413083  |
| C | 0.242636  | -4.920707 | 0.730340  | C | -0.704164 | 2.163561  | 4.751579  |
| C | -0.715080 | -7.413573 | -0.116972 | C | -2.113845 | 3.983178  | 4.129495  |
| C | 0.998750  | -5.721733 | -0.132915 | C | -0.635514 | 2.130505  | -2.501019 |
| C | -1.012913 | -5.382010 | 1.148811  | C | -0.894518 | 2.133664  | -5.286161 |
| C | -1.485669 | -6.617496 | 0.729270  | C | -0.849043 | 0.937901  | -3.190934 |
| C | 0.527922  | -6.962156 | -0.548982 | C | -0.528116 | 3.327768  | -3.207534 |
| H | 2.345846  | 1.660605  | -2.429417 | C | -0.671563 | 3.316326  | -4.590307 |
| H | 2.901159  | 0.093436  | -3.031992 | C | -0.972276 | 0.943839  | -4.573814 |
| H | 3.691981  | -2.171220 | -0.958741 | C | -0.625126 | 4.621999  | -5.340204 |
| H | 4.048639  | 1.205511  | -2.264242 | C | -2.953357 | 5.175959  | 4.509520  |
| H | 4.856154  | -1.036753 | -0.264994 | C | -0.001075 | 1.326897  | 5.783167  |
| H | 1.993956  | 2.145239  | 0.612547  | C | -1.144537 | -0.364661 | -5.294131 |
| H | 2.466315  | 0.909100  | 1.787789  | F | -0.201136 | 4.451371  | -6.604262 |
| H | 3.701543  | 1.773120  | 0.862706  | F | -1.713289 | -0.206086 | -6.497784 |
| H | 1.967640  | -5.367920 | -0.475499 | F | -1.914274 | -1.219443 | -4.593195 |
| H | 1.130926  | -7.574116 | -1.212161 | F | -1.837724 | 5.193731  | -5.403588 |
| H | 3.673496  | -1.821189 | 0.779886  | F | 0.037896  | -0.977333 | -5.487988 |
| H | -1.632795 | -4.762386 | 1.789992  | F | 0.199875  | 5.502075  | -4.752063 |
| H | -2.461960 | -6.959857 | 1.057733  | F | -3.945267 | 5.389227  | 3.633561  |
| H | -1.088182 | -8.378905 | -0.444067 | F | -2.212608 | 6.296346  | 4.553253  |
| O | 0.007427  | -0.598179 | 1.223178  | F | -3.509349 | 5.023136  | 5.723833  |
| C | -0.525667 | -2.222383 | -0.383466 | F | -0.070462 | 0.010540  | 5.480970  |
| C | -0.363599 | -2.821513 | -1.745954 | F | -0.523162 | 1.480138  | 7.006146  |
| H | -0.524388 | -3.903988 | -1.709000 | F | 1.306082  | 1.629992  | 5.860086  |
| H | 0.634790  | -2.629436 | -2.148104 | H | -2.425962 | 4.288091  | 2.022560  |
| H | -1.089885 | -2.414078 | -2.459414 | H | 0.147025  | 1.046955  | 3.129111  |
| H | -1.388653 | -2.507406 | 0.205950  | H | -1.684006 | 3.453514  | 6.173530  |
| C | -1.022155 | 2.802880  | -0.113422 | H | -0.045120 | 1.150249  | -0.833028 |
| S | -1.793229 | 4.254360  | -0.393615 | H | -0.446586 | 1.263310  | 1.090202  |
| N | -0.844678 | 2.204261  | 1.101608  | H | -0.337851 | 4.252781  | -2.681966 |
| N | -0.463298 | 2.033642  | -1.106188 | H | -1.000658 | 2.140143  | -6.363907 |
| C | -1.104012 | 2.635031  | 2.411352  | H | -0.924619 | 0.007519  | -2.638382 |

**(E)-Silyl ketene acetal + Ph-thiourea**



Method:  $\omega$ B97X-D  
Basis set: 6-31G\*  
Energy: -2034.684092 hartrees

Zero Point Energy : 1405.33 kJ/mol (ZPE)  
Temperature Correction : 80.72 kJ/mol (vibration + gas law + rotation + translation)  
Enthalpy Correction : 1486.05 kJ/mol (ZPE + temperature correction)  
Enthalpy : -2034.118085 au (Electronic Energy + Enthalpy Correction)  
Entropy : 1020.04 J/mol•K  
Gibbs Energy : -2034.233920 au (Enthalpy - T\*Entropy)  
Cv : 593.35 J/mol•K

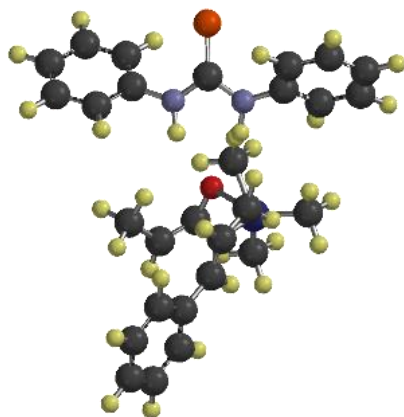
Energy ( $\omega$ B97X-D/6-31G\*\*/M06-2X/6-311+G\*\*): -2034.91230 au  
[E(E-enol): -1024.67697 au; E(Ph-thiourea): -1010.20040 au]

Coordinates:

|    |           |           |           |   |           |           |           |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| C  | 1.203842  | 0.271462  | -2.480163 | O | 0.715704  | -0.356354 | -1.359243 |
| C  | 1.627771  | -1.284211 | -0.722448 | C | 0.614160  | 0.106160  | -3.664752 |
| C  | 0.964102  | -1.780121 | 0.518654  | C | -0.572270 | -0.775208 | -3.916805 |
| C  | 0.515732  | -3.031343 | 0.651498  | C | -1.318845 | 0.874635  | 1.194071  |
| O  | 2.281576  | 1.036390  | -2.211083 | S | -2.007626 | 1.103576  | 2.701774  |
| Si | 2.422538  | 2.703171  | -2.548862 | N | -0.157405 | 1.473649  | 0.781182  |
| C  | 3.969601  | 3.212756  | -1.636641 | N | -1.802981 | 0.041805  | 0.224434  |
| C  | 2.628708  | 2.964789  | -4.396596 | C | 0.715883  | 2.299643  | 1.523406  |
| C  | 0.886745  | 3.572373  | -1.924334 | C | 2.560925  | 3.943284  | 2.828105  |
| C  | -0.247539 | -3.564965 | 1.790256  | C | 0.273454  | 3.413749  | 2.238022  |
| C  | -1.734713 | -4.642010 | 3.905264  | C | 2.083242  | 2.023585  | 1.450523  |
| C  | -0.287528 | -4.947248 | 2.003918  | C | 3.000910  | 2.843954  | 2.097975  |
| C  | -0.978926 | -2.729992 | 2.644047  | C | 1.197674  | 4.220822  | 2.891720  |
| C  | -1.715039 | -3.265343 | 3.691977  | C | -2.898766 | -0.851045 | 0.271160  |
| C  | -1.018539 | -5.483070 | 3.058192  | C | -4.994745 | -2.695537 | 0.206208  |

|   |           |           |           |   |           |           |           |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| C | -2.729679 | -2.091672 | -0.349068 | H | -0.356376 | -1.507218 | -4.703498 |
| C | -4.129615 | -0.524118 | 0.840101  | H | 1.831142  | -2.099507 | -1.426806 |
| C | -5.163994 | -1.453377 | 0.810628  | H | 0.712694  | -3.739778 | -0.155545 |
| C | -3.772648 | -3.007661 | -0.381632 | H | 0.265932  | -5.606610 | 1.339261  |
| H | -0.784707 | 3.637394  | 2.280736  | H | -2.315572 | -5.058943 | 4.722400  |
| H | 2.427256  | 1.165566  | 0.878643  | H | -2.285596 | -2.599617 | 4.332104  |
| H | 3.274068  | 4.580776  | 3.341182  | H | -1.005190 | -1.656984 | 2.480009  |
| H | -1.163095 | -0.147816 | -0.541572 | H | 0.822603  | -1.054165 | 1.317098  |
| H | 0.268945  | 1.071658  | -0.049384 | H | 4.824946  | 2.595610  | -1.932271 |
| H | -4.269492 | 0.442165  | 1.305205  | H | 1.686746  | 2.839188  | -4.940626 |
| H | -5.809416 | -3.413068 | 0.191548  | H | 1.025612  | 0.656682  | -4.504416 |
| H | -1.764205 | -2.343142 | -0.779670 | H | -1.437131 | -0.189664 | -4.251239 |
| H | -6.116811 | -1.195204 | 1.263011  | H | -0.866417 | -1.321413 | -3.017094 |
| H | -3.621980 | -3.972592 | -0.856156 | H | 0.838672  | 4.592594  | -2.322298 |
| H | 0.845285  | 5.082141  | 3.450975  | H | 3.363453  | 2.269849  | -4.817449 |
| H | 4.060578  | 2.613713  | 2.037289  | H | 2.984949  | 3.983500  | -4.590817 |
| H | 3.831066  | 3.118149  | -0.555253 | H | 0.875415  | 3.639040  | -0.831828 |
| H | 4.217468  | 4.258536  | -1.851880 | H | -0.022668 | 3.051402  | -2.244640 |
| H | -1.034561 | -6.557682 | 3.213962  | H | 2.564670  | -0.757089 | -0.512468 |

#### TS-(*E*)-Ph-thiourea-catalyzed



Method:  $\omega$ B97X-D

Basis set: 6-31G\*

Energy: -2034.645454 hartrees

Imaginary vibration:  $-435\text{ cm}^{-1}$  (Uncorrected);  $-410\text{ cm}^{-1}$  (Corrected); Intensity 31.39

Zero Point Energy : 1398.15 kJ/mol (ZPE)

Temperature Correction : 81.60 kJ/mol (vibration + gas law + rotation + translation)

Enthalpy Correction : 1479.75 kJ/mol (ZPE + temperature correction)

Enthalpy : -2034.081849 au (Electronic Energy + Enthalpy Correction)

Entropy : 967.88 J/mol•K

Gibbs Energy : -2034.191761 au (Enthalpy - T\*Entropy)

Cv : 600.21 J/mol•K

Energy ( $\omega$ B97X-D/6-31G\*\*//M06-2X/6-311+G\*\*): -2034.87339 au

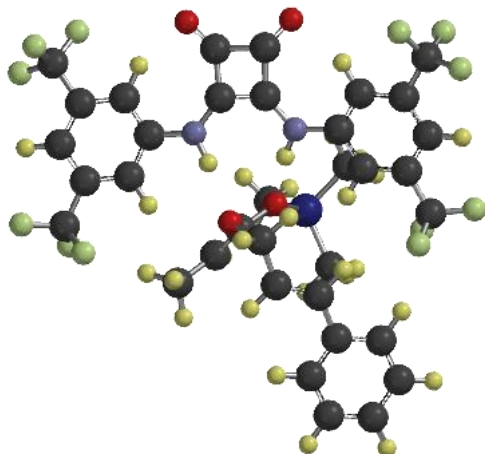
[E(TS-E-enol): -1024.64863 au; E(Ph-thiourea): -1010.20123 au]

*Coordinates:*

|    |           |           |           |   |           |           |           |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| C  | 0.527061  | -0.320423 | -1.204510 | C | -0.101221 | -1.303572 | -1.926917 |
| C  | 1.154097  | -1.297327 | 1.156729  | C | -1.415055 | -1.899819 | -1.539827 |
| C  | 0.891822  | -2.543251 | 0.580256  | H | 0.258231  | -1.472837 | -2.937316 |
| C  | 1.420755  | -2.823361 | -0.663295 | H | -1.436689 | -2.974249 | -1.757938 |
| H  | 0.680027  | -1.019400 | 2.092409  | H | -1.613946 | -1.752846 | -0.474735 |
| H  | 0.086869  | -3.147594 | 0.987617  | H | -2.234143 | -1.437632 | -2.105548 |
| H  | 2.109034  | -0.819566 | 0.964721  | C | -1.839669 | 2.022673  | 1.929050  |
| H  | 2.249199  | -2.202814 | -0.999660 | S | -2.814712 | 2.923204  | 2.943459  |
| O  | 1.667119  | 0.202738  | -1.719689 | N | -2.200107 | 1.570446  | 0.690338  |
| Si | 2.345860  | 1.718076  | -1.363323 | N | -0.560345 | 1.640840  | 2.228100  |
| C  | 3.503560  | 1.564550  | 0.105629  | C | -3.390428 | 1.850905  | -0.019601 |
| C  | 3.324913  | 2.111192  | -2.910051 | C | -5.675144 | 2.328368  | -1.550214 |
| C  | 1.007305  | 2.993870  | -1.068191 | C | -3.851817 | 3.156056  | -0.195303 |
| C  | 1.207114  | -4.038310 | -1.457968 | C | -4.070836 | 0.789788  | -0.616113 |
| C  | 0.891288  | -6.329211 | -3.045083 | C | -5.205201 | 1.029819  | -1.385060 |
| C  | 1.949757  | -4.206223 | -2.634656 | C | -4.995442 | 3.385807  | -0.949548 |
| C  | 0.296274  | -5.038439 | -1.094476 | C | 0.129122  | 1.793339  | 3.452937  |
| C  | 0.143017  | -6.174140 | -1.881208 | C | 1.633323  | 1.965903  | 5.796540  |
| C  | 1.795940  | -5.339218 | -3.421434 | C | 1.426697  | 2.302529  | 3.418732  |
| H  | 2.664138  | 2.181569  | -3.780490 | C | -0.419582 | 1.372430  | 4.665204  |
| H  | 4.065205  | 1.330481  | -3.115508 | C | 0.331352  | 1.470364  | 5.829885  |
| H  | 4.253136  | 0.783809  | -0.066193 | C | 2.179913  | 2.379029  | 4.586231  |
| H  | 3.858886  | 3.063089  | -2.813504 | H | -3.318653 | 3.978162  | 0.265627  |
| H  | 4.041003  | 2.506980  | 0.265776  | H | -3.714881 | -0.224713 | -0.461854 |
| H  | 0.285009  | 3.002681  | -1.891815 | H | -6.565825 | 2.517252  | -2.141273 |
| H  | 0.451005  | 2.824759  | -0.141706 | H | -0.023722 | 1.238737  | 1.465300  |
| H  | 1.453884  | 3.993596  | -1.010012 | H | -1.594199 | 0.863290  | 0.281002  |
| H  | 2.651839  | -3.431349 | -2.931770 | H | -1.430934 | 0.984825  | 4.686940  |
| H  | 2.382499  | -5.451318 | -4.327857 | H | 2.215085  | 2.033154  | 6.710447  |
| H  | 2.971999  | 1.326757  | 1.032759  | H | 1.830538  | 2.660316  | 2.475872  |
| H  | -0.291779 | -4.936890 | -0.188107 | H | -0.103264 | 1.148084  | 6.771119  |
| H  | -0.562473 | -6.943012 | -1.582304 | H | 3.189345  | 2.776848  | 4.548281  |
| H  | 0.770724  | -7.218228 | -3.655994 | H | -5.353201 | 4.403231  | -1.074936 |
| O  | 0.217731  | -0.040077 | 0.017785  | H | -5.728416 | 0.196271  | -1.843756 |



**(E)-Silyl ketene acetal + squaramide**



Method:  $\omega$ B97X-D  
Basis set: 6-31G\*  
Energy: -3248.981166 hartrees

Zero Point Energy : 1514.98 kJ/mol (ZPE)  
Temperature Correction : 116.52 kJ/mol (vibration + gas law + rotation + translation)  
Enthalpy Correction : 1631.50 kJ/mol (ZPE + temperature correction)  
Enthalpy : -3248.359763 au (Electronic Energy + Enthalpy Correction)  
Entropy : 1383.07 J/mol•K  
Gibbs Energy : -3248.516823 au (Enthalpy - T\*Entropy)  
Cv : 852.91 J/mol•K

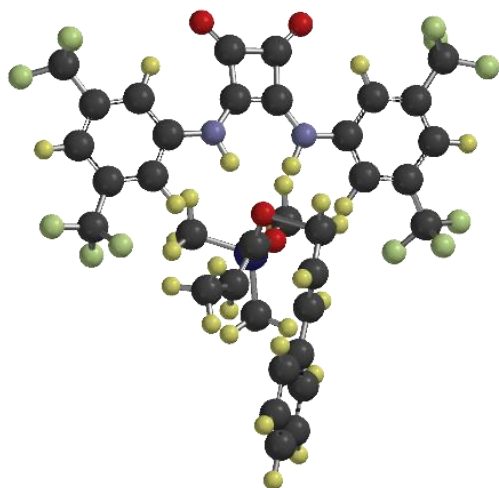
Energy ( $\omega$ B97X-D/6-31G\*\*/M06-2X/6-311+G\*\*): -3249.64000 au  
[E(E-enol): -1024.67824 au; E(squaramide): -2224.91638 au]

*Coordinates:*

|    |           |           |           |   |           |           |           |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| C  | -1.335377 | -0.341787 | 0.119867  | C | -1.877574 | -3.651286 | -3.732159 |
| C  | 0.278883  | -2.101318 | -0.064919 | C | -2.539499 | -3.959353 | -4.912915 |
| C  | -0.479386 | -2.585081 | -1.255677 | C | -0.982911 | -2.598588 | -6.146221 |
| C  | -0.058103 | -2.402945 | -2.510055 | H | 1.081939  | 2.409679  | -2.596676 |
| H  | 0.564433  | -2.917330 | 0.604413  | H | 0.884698  | 3.106642  | -0.977380 |
| H  | -1.425748 | -3.078166 | -1.043734 | H | -2.392581 | 2.977109  | 0.173898  |
| H  | 1.188151  | -1.567437 | -0.361282 | H | 0.048598  | 3.820811  | -2.358337 |
| H  | 0.890391  | -1.891218 | -2.669223 | H | -2.516928 | 3.820229  | -1.374416 |
| O  | -0.597917 | 0.653366  | -0.436608 | H | -0.768225 | 0.368218  | -3.614330 |
| Si | -1.133404 | 1.791119  | -1.617109 | H | -2.333154 | 0.011373  | -2.878607 |
| C  | -2.524945 | 2.830578  | -0.903598 | H | -2.129798 | 1.469133  | -3.866420 |
| C  | 0.365040  | 2.870924  | -1.912668 | H | 0.553792  | -1.646077 | -4.986368 |
| C  | -1.640041 | 0.820504  | -3.131420 | H | -0.628056 | -2.187275 | -7.086265 |
| C  | -0.761782 | -2.803912 | -3.738468 | H | -3.518242 | 2.401152  | -1.066208 |
| C  | -2.097648 | -3.430081 | -6.124260 | H | -2.226515 | -4.084694 | -2.799575 |
| C  | -0.317618 | -2.293270 | -4.963903 | H | -3.401803 | -4.618766 | -4.889797 |

|   |           |           |           |   |           |           |           |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| H | -2.617200 | -3.671630 | -7.046378 | F | 7.568497  | 1.190597  | -1.832183 |
| O | -0.539588 | -1.246257 | 0.771999  | F | 3.956829  | 0.241926  | -4.968444 |
| C | -2.663381 | -0.450096 | 0.141001  | F | 1.910011  | 0.466974  | -4.293210 |
| C | -3.419545 | -1.601533 | 0.730369  | F | 6.777099  | 3.108750  | -1.224497 |
| H | -3.248322 | 0.348820  | -0.299937 | F | 2.954323  | -1.394730 | -3.972562 |
| H | -4.068945 | -2.061971 | -0.024073 | F | 7.135539  | 1.573348  | 0.255206  |
| H | -2.748470 | -2.372777 | 1.115914  | F | -1.206850 | 3.074870  | 7.148956  |
| H | -4.064403 | -1.275204 | 1.552592  | F | -1.076200 | 1.278851  | 8.345600  |
| N | 0.196638  | 0.460534  | 3.040245  | F | -3.011726 | 2.094281  | 7.834877  |
| N | 2.114272  | 0.944135  | 0.674898  | F | -4.890547 | -1.197157 | 3.920772  |
| C | -0.770327 | 0.367741  | 4.049599  | F | -4.371852 | -2.188423 | 5.768712  |
| C | -2.793100 | 0.082352  | 5.961406  | F | -3.438391 | -2.799158 | 3.911825  |
| C | -0.779374 | 1.189005  | 5.177679  | H | 0.002664  | 1.924824  | 5.337259  |
| C | -1.769702 | -0.594124 | 3.880437  | H | -1.754147 | -1.238170 | 3.007327  |
| C | -2.767992 | -0.730417 | 4.834083  | H | -3.573331 | -0.026223 | 6.704838  |
| C | -1.792559 | 1.034145  | 6.117098  | H | 1.167229  | 0.732918  | 0.359206  |
| C | 3.083241  | 0.931592  | -0.330908 | H | 0.053282  | -0.174297 | 2.254640  |
| C | 4.911285  | 0.838495  | -2.458017 | H | 4.732060  | 1.716336  | 0.831028  |
| C | 2.685533  | 0.480152  | -1.591167 | H | 5.620028  | 0.805130  | -3.275709 |
| C | 4.406351  | 1.336395  | -0.133232 | H | 1.655271  | 0.178402  | -1.752764 |
| C | 5.298523  | 1.280531  | -1.196794 | C | 1.328471  | 1.195030  | 3.007765  |
| C | 3.592707  | 0.445651  | -2.640906 | C | 2.228684  | 1.362505  | 1.961961  |
| C | 6.704760  | 1.788016  | -0.993644 | C | 2.147984  | 2.025960  | 3.933831  |
| C | -1.770489 | 1.879410  | 7.365697  | C | 3.172234  | 2.148527  | 2.795575  |
| C | -3.865966 | -1.735719 | 4.613467  | O | 2.045605  | 2.458788  | 5.053500  |
| C | 3.116460  | -0.055346 | -3.974463 | O | 4.268311  | 2.636225  | 2.670058  |

#### TS-(E)-Ph-squaramide-catalyzed



Method:  $\omega$ B97X-D  
Basis set: 6-31G\*  
Energy: -3248.945799 hartrees

Imaginary vibration:  $-417\text{ cm}^{-1}$  (Uncorrected);  $-393\text{ cm}^{-1}$  (Corrected); Intensity 37.36

Zero Point Energy : 1507.02 kJ/mol (ZPE)  
 Temperature Correction : 117.46 kJ/mol (vibration + gas law + rotation + translation)  
 Enthalpy Correction : 1624.48 kJ/mol (ZPE + temperature correction)  
 Enthalpy : -3248.327067 au (Electronic Energy + Enthalpy Correction)  
 Entropy : 1340.16 J/mol•K  
 Gibbs Energy : -3248.479255 au (Enthalpy - T\*Entropy)  
 Cv : 859.97 J/mol•K

Energy ( $\omega$ B97X-D/6-31G\*\*//M06-2X/6-311+G\*\*): -3249.60586 au  
 [E(TS-E-enol): -1024.64290 au; E(squaramide): -2224.91621 au]

*Coordinates:*

|    |           |           |           |   |           |           |           |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| C  | -0.243101 | -0.843765 | -0.492015 | C | -2.007715 | -2.624473 | -0.137172 |
| C  | 1.326652  | -1.626672 | 1.491546  | H | -0.925911 | -2.149824 | -2.002257 |
| C  | 0.977522  | -2.916166 | 1.099586  | H | -1.994864 | -3.703107 | -0.330588 |
| C  | 1.043456  | -3.256218 | -0.239123 | H | -1.865279 | -2.461123 | 0.934276  |
| H  | 1.207385  | -1.314872 | 2.522883  | H | -3.006613 | -2.265707 | -0.409527 |
| H  | 0.435140  | -3.543892 | 1.799946  | N | -1.550184 | 1.706319  | 1.833112  |
| H  | 2.075652  | -1.081169 | 0.926267  | N | 1.423917  | 2.017684  | 1.066133  |
| H  | 1.648519  | -2.620578 | -0.883950 | C | -2.943989 | 1.637299  | 1.890861  |
| O  | 0.608037  | -0.163832 | -1.311174 | C | -5.729851 | 1.344298  | 1.871070  |
| Si | 0.275974  | 0.415623  | -2.883672 | C | -3.756910 | 2.703678  | 2.279899  |
| C  | -1.451113 | 1.138735  | -2.877056 | C | -3.525519 | 0.427037  | 1.508131  |
| C  | 1.587503  | 1.710989  | -3.169126 | C | -4.905788 | 0.289798  | 1.497959  |
| C  | 0.439155  | -0.993751 | -4.115392 | C | -5.137534 | 2.540375  | 2.262287  |
| C  | 0.650198  | -4.539720 | -0.828601 | C | 2.800457  | 2.117756  | 0.838208  |
| C  | -0.050704 | -6.969783 | -2.040645 | C | 5.557568  | 2.155345  | 0.341876  |
| C  | 0.994384  | -4.803520 | -2.161466 | C | 3.365844  | 1.225597  | -0.076242 |
| C  | -0.060567 | -5.515436 | -0.115731 | C | 3.615305  | 3.038691  | 1.500151  |
| C  | -0.406012 | -6.719108 | -0.717604 | C | 4.980443  | 3.045224  | 1.241724  |
| C  | 0.651010  | -6.007066 | -2.762530 | C | 4.733014  | 1.249984  | -0.314975 |
| H  | 2.593819  | 1.289972  | -3.083841 | C | 5.844781  | 4.075270  | 1.926006  |
| H  | 1.501692  | 2.526310  | -2.442526 | C | -5.999056 | 3.690219  | 2.721211  |
| H  | -1.529027 | 1.960762  | -2.156991 | C | -5.482557 | -1.012066 | 1.013928  |
| H  | 1.488374  | 2.142036  | -4.172452 | C | 5.322601  | 0.234254  | -1.254745 |
| H  | -1.706594 | 1.536735  | -3.865793 | F | 7.106872  | 3.636879  | 2.075050  |
| H  | 1.283060  | -1.641991 | -3.852557 | F | 6.478414  | 0.649960  | -1.787841 |
| H  | -0.462127 | -1.613902 | -4.169456 | F | 4.485704  | -0.049212 | -2.275997 |
| H  | 0.628053  | -0.601433 | -5.121292 | F | 5.901865  | 5.212464  | 1.215634  |
| H  | 1.541528  | -4.053391 | -2.727213 | F | 5.565379  | -0.931198 | -0.629183 |
| H  | 0.932301  | -6.196423 | -3.793718 | F | 5.377991  | 4.385661  | 3.142977  |
| H  | -2.206268 | 0.390240  | -2.614455 | F | -5.530383 | 4.864816  | 2.277730  |
| H  | -0.348048 | -5.337988 | 0.915609  | F | -6.043544 | 3.759248  | 4.061595  |
| H  | -0.954880 | -7.464832 | -0.150914 | F | -7.264875 | 3.568198  | 2.286851  |
| H  | -0.319532 | -7.912538 | -2.506983 | F | -5.303843 | -1.158624 | -0.316134 |
| O  | -0.139222 | -0.532467 | 0.753910  | F | -6.795975 | -1.112009 | 1.250444  |
| C  | -0.952716 | -1.932883 | -0.938311 | F | -4.882180 | -2.065976 | 1.596769  |

|   |           |          |          |   |           |           |           |
|---|-----------|----------|----------|---|-----------|-----------|-----------|
| C | -0.738105 | 2.772326 | 2.009434 | H | 6.624676  | 2.170615  | 0.157251  |
| C | 0.613098  | 2.894314 | 1.703027 | H | 2.723982  | 0.535725  | -0.615530 |
| C | -0.808360 | 4.146111 | 2.571544 | H | 0.978168  | 1.170558  | 0.713057  |
| C | 0.684683  | 4.275597 | 2.248082 | H | -1.094242 | 0.850810  | 1.512658  |
| O | -1.655248 | 4.863538 | 3.044630 | H | -2.890375 | -0.400677 | 1.208649  |
| O | 1.531320  | 5.121704 | 2.396974 | H | -6.806967 | 1.239844  | 1.853333  |
| H | 3.190263  | 3.760487 | 2.189192 | H | -3.319970 | 3.648305  | 2.593318  |

## Kinetic measurements

For kinetic measurements,  $^1\text{H}$  NMR spectra were recorded every 10 minutes for 15 hours. The relative concentrations of initial compound **2c**, product **3c** and unidentified by-product were determined through integration of selected signals (5.96 ppm, 6.31 ppm and 7.0 ppm, respectively) (Figure S6). Corresponding rate constants for initial compound consumption and product(s) formation were obtained by monoexponential fitting of the experimental data (equation S1).

$$y = A_1 e^{-x/t_1} + y_0 \quad (\text{S1})$$

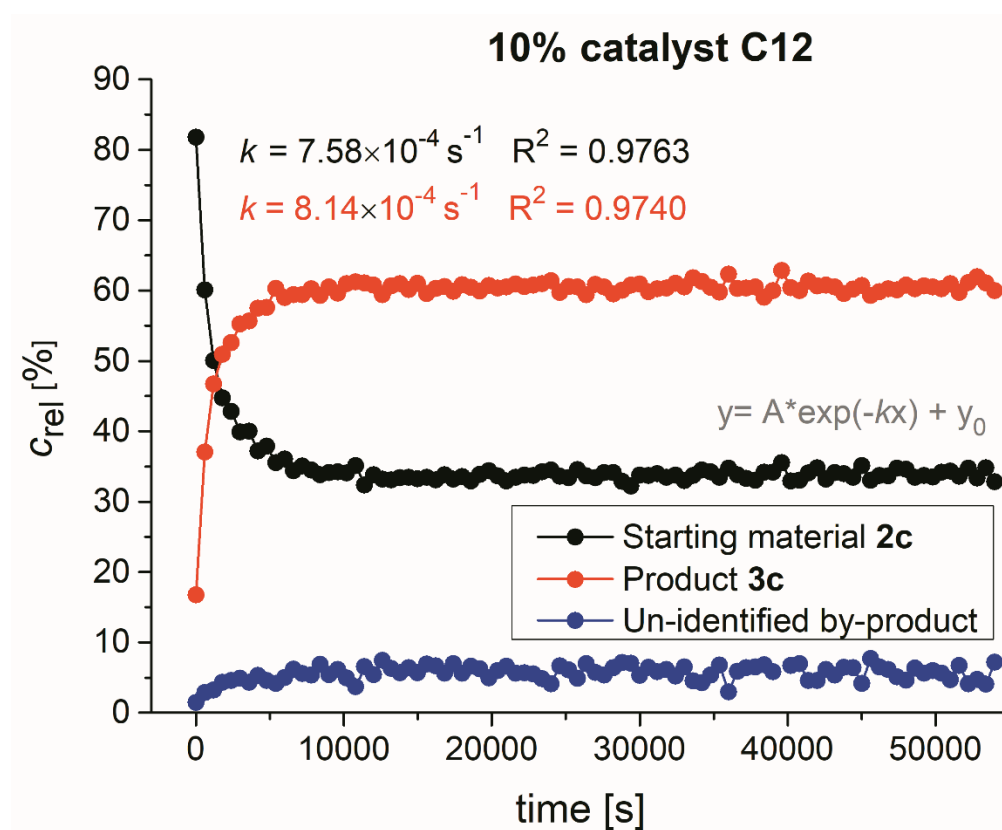


Figure S1.

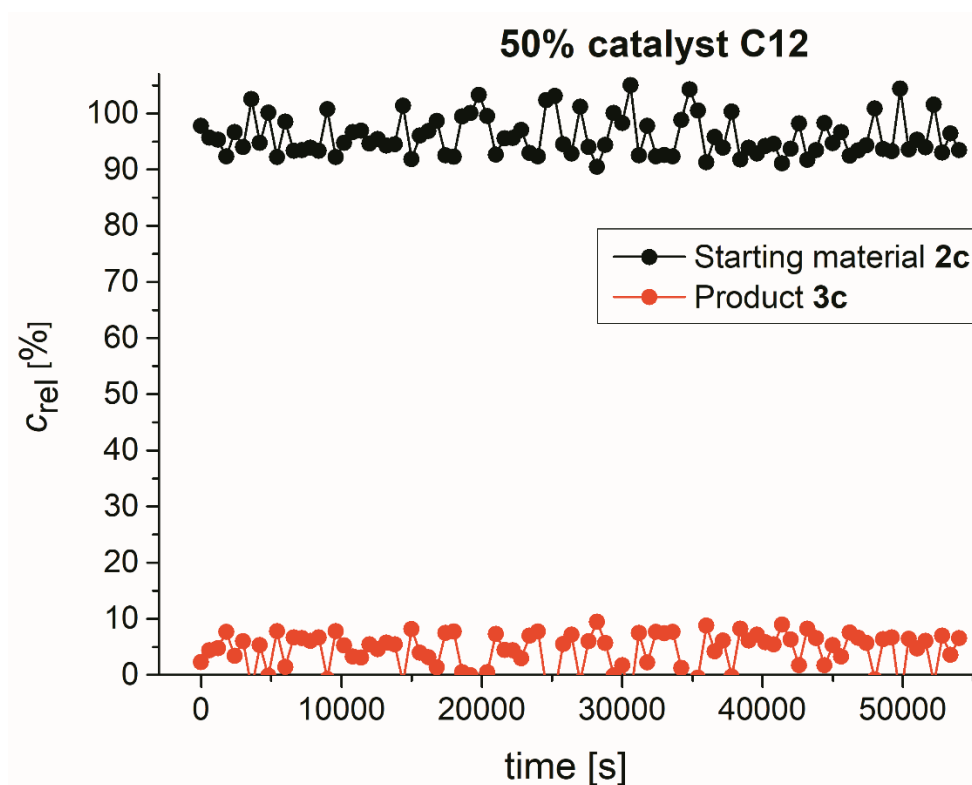


Figure S2.

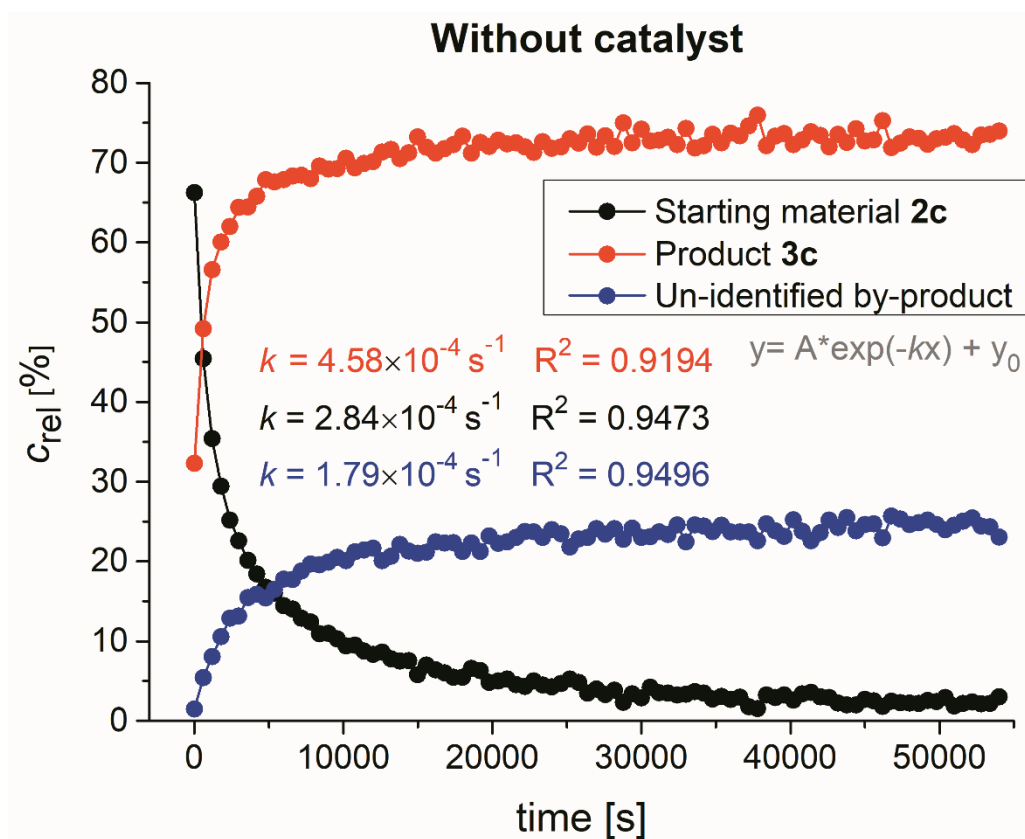


Figure S3.

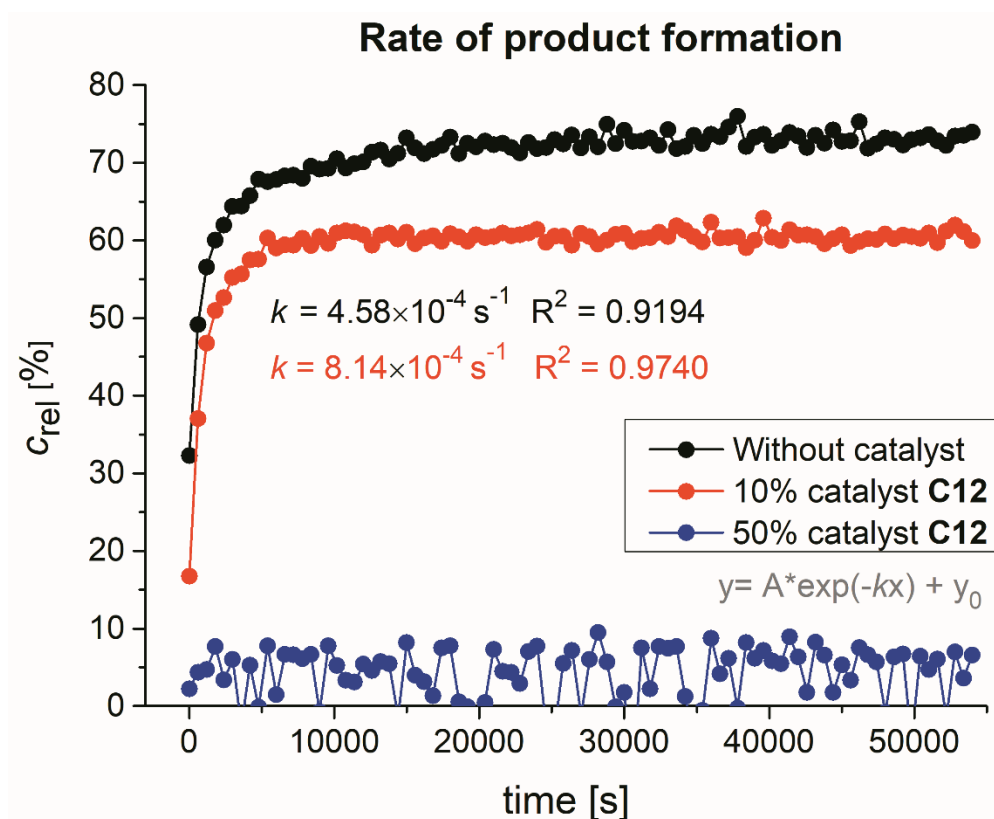


Figure S4.

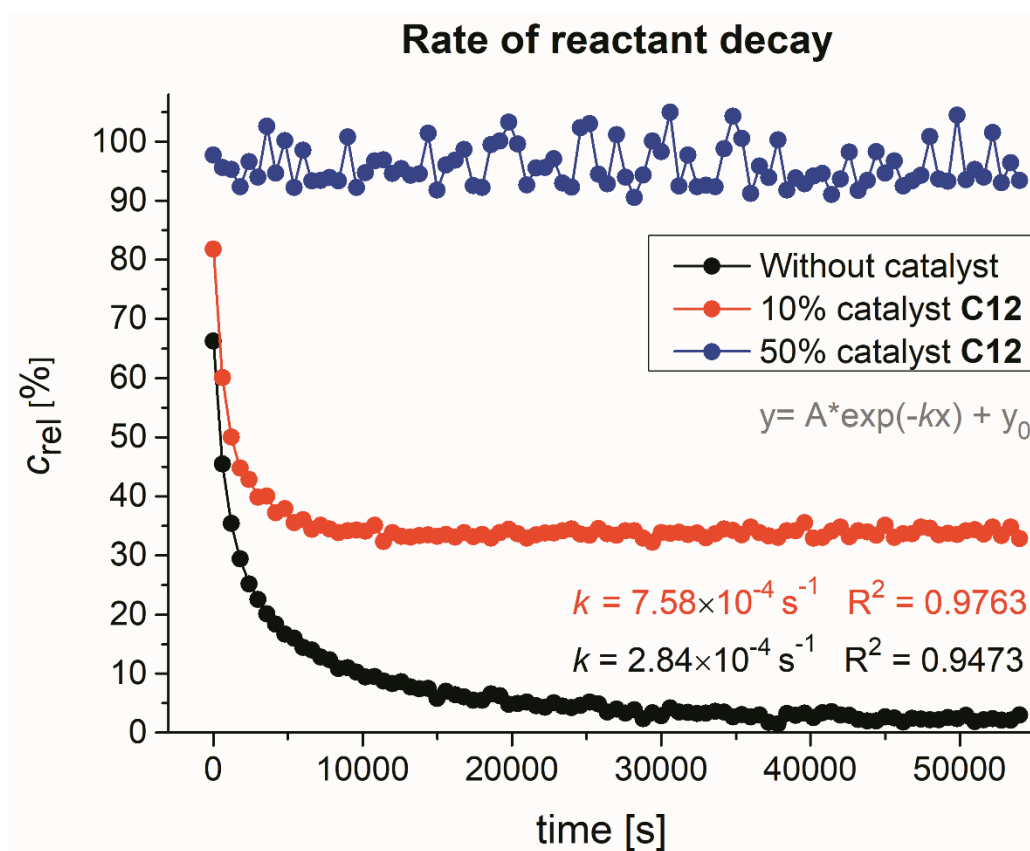


Figure S5.

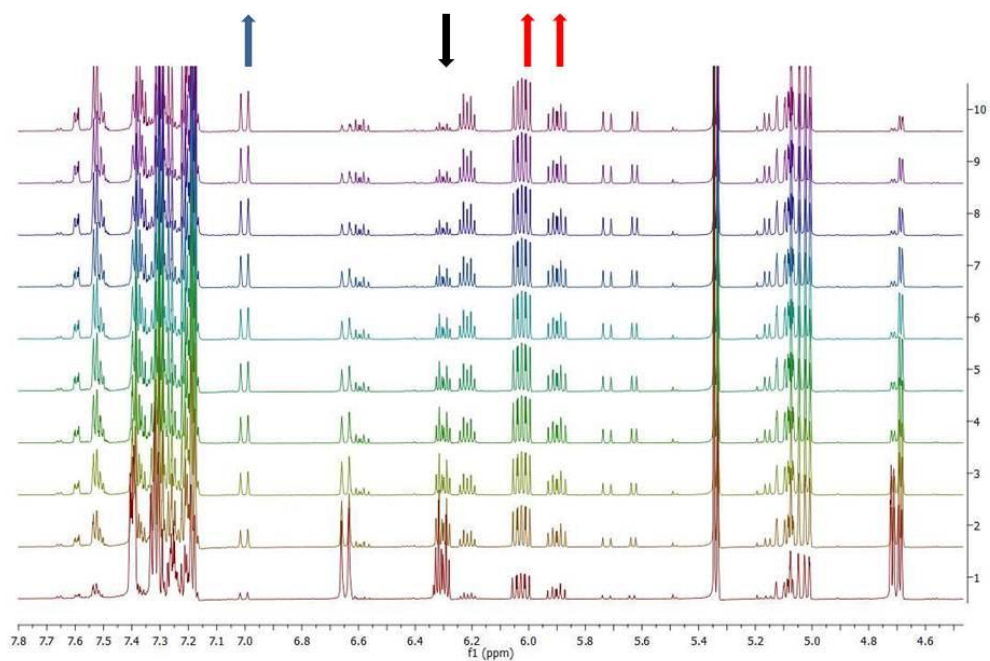


Figure S6