# Supporting Information

# An Unexpected Role of a Trace Amount of Water in Catalyzing Proton Transfer in Phosphine-Catalyzed (3 + 2) Cycloadditions of Allenoates and Alkenes

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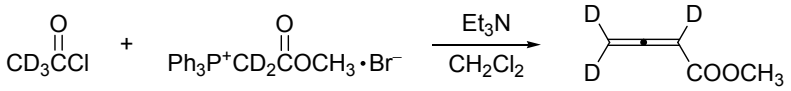
## Content

## 1. Experimental Details and Spectroscopic Data

**General.** Methyl 2,3–butadienoate (**1**),[1] deuterium labeled methyl 2,3–butadienoate (**8**),[1] and deuterium labeled dimethyl fumarate (**9**)[2] were prepared according to literature procedures. Triphenylphosphine catalyzed (3+2) cycloaddition reactions were performed according to Lu's procedure.[3] Benzene were refluxed with Na and benzophenone, and freshly distilled prior to use. All reactions were performed under nitrogen.

**Preparation of Methyl [2,4,4–$D_3$]Buta–2, 3–dienoate (8).**

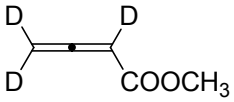



| | | | | |
|---|---|---|---|---|
| M | 81.5 | 417 | 101 | 101 |
| m (g) | 6.10 | 30.0 | 15.0 | 1.22 |
| n (mmol) | 74.8 | 71.9 | 149 | 12.1 |

Notes:

1. $Ph_3P^+CD_2COOCH_3 \bullet Br^-$ was prepared from $BrCD_2COOCH_3$ and $PPh_3$ in benzene with a quantitative yield.
2. $CH_2Cl_2$ and $Et_3N$ were refluxed with $CaH_2$ and freshly distilled prior to use. Pentane was refluxed with Na and benzophenone, and freshly distilled prior to use.
3. The rotary evaporation should be carried out with cooling in an ice-water bath.
4. After the addition of $Et_3N$, the reaction mixture was stirred for 2 hours. After the addition of $CD_3COCl$, stirring was continued over night.
5. Rapid distillation in a short-path distillation apparatus under reduced pressure gave the product as a colorless oil in 17% yield, bp 64–66 $^oC$ (18–20 mmHg).
6. The ratio of 2–D is about 95%, and the ratio of 4–D is more than 98% according to the $^1H$ NMR of the product.

**Methyl [2,4,4–$D_3$]Buta–2, 3–dienoate (8)**




Colorless oil. $^1H$ NMR (400 MHz, $C_6D_6$): $\delta$ 3.37 (s, 3H). $^{13}C$ NMR (100 MHz, $C_6D_6$): $\delta$ 51.2, 78.2 (quin, $J_{C–D}$ = 26 Hz), 87.5 (t, $J_{C–D}$ = 26 Hz), 165.1, 215.8. IR $\nu$ ($cm^{-1}$): 1719, 1924. MS (ESI) m/z: 102 $(M+H)^+$.

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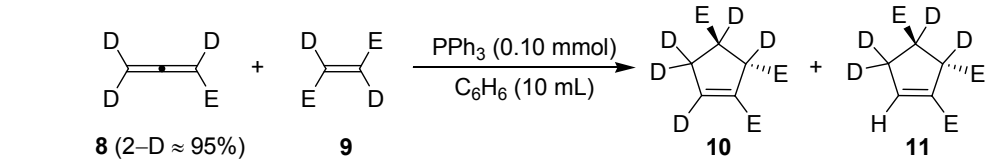
[1] Lang, R. W.; Hansen, H. *Organic Syntheses* **1990**, *Coll. Vol. 7*, p232.
[2] Lee, K. M.; Ramalingam, K.; Son, J. K.; Woodard, R. W. *J. Org. Chem.* **1989**, *54*, 3195-3198. The ratio of 2(3)–D is more than 98%.
[3] Zhang, C.; Lu, X. *J. Org. Chem.* **1995**, *60*, 2906-2908.

**$PPh_3$ Catalyzed (3+2) Cycloaddition Reactions.** For the reactions without additives, fumarate and $PPh_3$ was mixed in benzene, then 2,3−butadienoate was added through a syringe; for the reactions with water, water was added to the mixture through a syringe before the addition of 2,3−butadienoate. Experimental results were summarized in Scheme S1 and S2. The ratio of products **10** and **11** or **13** and **14** was determined by $^1$H NMR analysis. The amount of D or H incorporated into these molecules was measured based on the integrations of olefinic protons versus the protons in methoxyl groups.

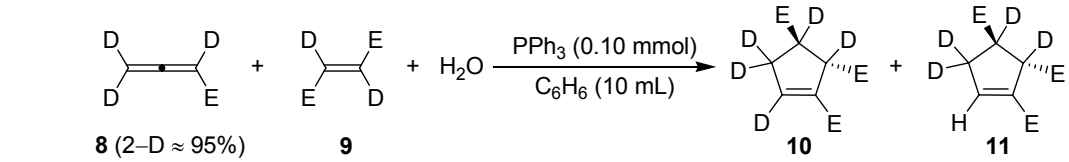
**Scheme S1** (E = $COOCH_3$).




**8** (2–D ≈ 95%) **9** **10** : **11**

75 : 25

| | | | | |
|---|---|---|---|---|
| M | 101 | 146 | | 246.75 |
| m (mg) | 101 | 292 | | 197 |
| n (mmol) | 1.00 | 2.00 | | 0.774 |
| Yield | | | | 77% |

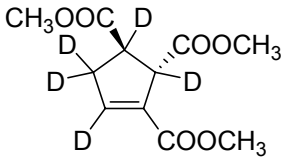



**8** (2–D ≈ 95%) **9** **10** **11**

12 : 88

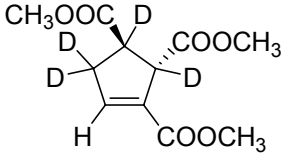
| | | | | |
|---|---|---|---|---|
| M | 101 | 146 | 18 | 246.12 |
| m (mg) | 101 | 292 | 18 | 56.3 |
| n (mmol) | 1.00 | 2.00 | 1.0 | 0.229 |
| Yield | | | | 23% |

***trans*−Trimethyl [1,2,4,5,5−$D_5$]Cyclopent−3−ene−1, 2, 3−tricarboxylate (10)**



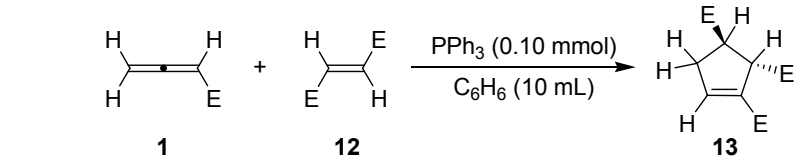
Colorless oil ($R_f$ = 0.15, PE/AcOEt = 6:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.74 (s, 6H), 3.75 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 35.1 (m), 45.9 (t, $J_{C-D}$ = 20 Hz), 51.5, 52.1 (t, $J_{C-D}$ = 21 Hz), 52.2, 133.5, 143.5 (t, $J_{C-D}$ = 26 Hz), 163.6, 173.3, 173.4. MS (ESI) m/z: 248 $(M+H)^+$.

***trans*–Trimethyl [1,2,5,5–$D_4$]Cyclopent–3–ene–1, 2, 3–tricarboxylate (11)**

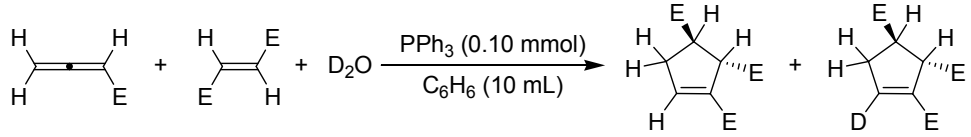


Colorless oil ($R_f$ = 0.15, PE/AcOEt = 6:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.74 (s, 6H), 3.75 (s, 3H), 6.84 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 35.2 (m), 45.9 (t, $J_{C–D}$ = 20 Hz), 51.6, 52.1 (t, $J_{C–D}$ = 21 Hz), 52.2, 133.7, 143.8, 163.7, 173.3, 173.4. MS (ESI) m/z: 247 $(M+H)^+$.

**Scheme S2** (E = $COOCH_3$).

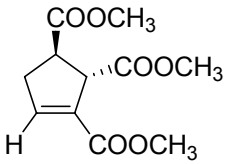


| | 1 | 12 | 13 |
|---|---|---|---|
| M | 98 | 144 | 242 |
| m (mg) | 98 | 288 | 158 |
| n (mmol) | 1.00 | 2.00 | 0.653 |
| Yield | | | 65% |



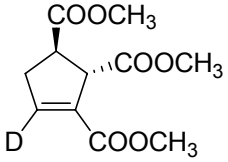
| | 1 | 12 | | 13 : 14 |
|---|---|---|---|---|
| | | | | 24 : 76 |
| M | 98 | 144 | 20 | 242.76 |
| m (mg) | 98 | 288 | 22 | 66.2 |
| n (mmol) | 1.00 | 2.00 | 1.1 | 0.273 |
| Yield | | | | 27% |

***trans*–Trimethyl Cyclopent–3–ene–1, 2, 3–tricarboxylate (13)**



Colorless oil ($R_f$ = 0.15, PE/AcOEt = 6:1). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.81-3.02 (m, 2H), 3.42 (ddd, $J$ = 9.0, 6.3, 6.0 Hz, 1H), 3.746 (s, 6H), 3.753 (s, 3H), 4.15 (m, 1H), 6.86 (dd, $J$ = 4.5, 2.4 Hz, 1H). $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ 36.0, 46.6, 51.7, 52.3, 52.5, 133.6, 143.9, 163.7, 173.4, 173.5. IR $\nu$ ($cm^{-1}$): 1734. MS (EI) m/z: 242 ($M^+$, 3), 210 (64), 182 (69), 151 (100). Calcd for $C_{11}H_{14}O_6$ (HRMS): 242.0790. Found: 242.0796.

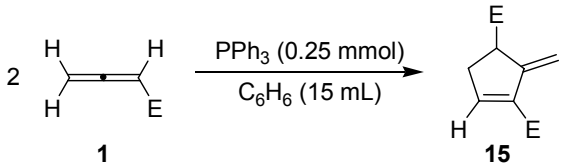
***trans*–Trimethyl [4–D]Cyclopent–3–ene–1, 2, 3–tricarboxylate (14)**




Colorless oil ($R_f$ = 0.15, PE/AcOEt = 6:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.86 (ddd, $J$ = 18.8, 6.1, 2.0 Hz, 1H), 2.95 (ddd, $J$ = 18.8, 9.2, 2.5 Hz, 1H), 3.41 (ddd, $J$ = 9.2, 6.1, 6.0 Hz, 1H), 3.74 (s, 6H), 3.75 (s, 3H), 4.14 (ddd, $J$ = 6.0, 2.2, 2.1 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 35.9, 46.6, 51.7, 52.4, 52.6, 133.6, 143.6 (t, $J_{C–D}$ = 26 Hz), 163.8, 173.4, 173.5. MS (ESI) m/z: 244 $(M+H)^+$.

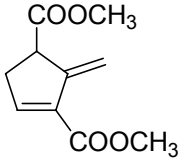
**Control Experiments.** The reaction of methyl 2,3–butadienoate (**1**) with 10 mol % of $PPh_3$ was conducted (Scheme S3). It was found that a self-condensation product **15** was isolated in 10% yield, together with some uncharacterized oligomers. This is in agreement with previous result.[3] Deuterium labeled 2,3–butadienoate **8** (2-D is about 95%) and (3+2) product **10** (4-D is about 75%) were also conducted in control experiments (0.1 equiv. $PPh_3$, 1 equiv. $H_2O$), respectively (Scheme S4). The $^1$H NMR indicated no deuterium and hydrogen exchange occurred. However, in the control experiment involving deuterium labeled 2,3–butadienoate **8**, most of **8** became messy after 5 hours (the reaction time for (3+2) cycloaddition reactions), and a little amount of self-condensation product **16** (in about 4% yield based on integrations of olefinic protons in the reaction mixtures) and uncharacterized oligomers were found. This may be the reason that the (3+2) reactions with 1 equiv. $H(D)_2O$ (Schemes S1 and S2) gave lower yields compared with those without additives.

**Scheme S3** (E = $COOCH_3$).



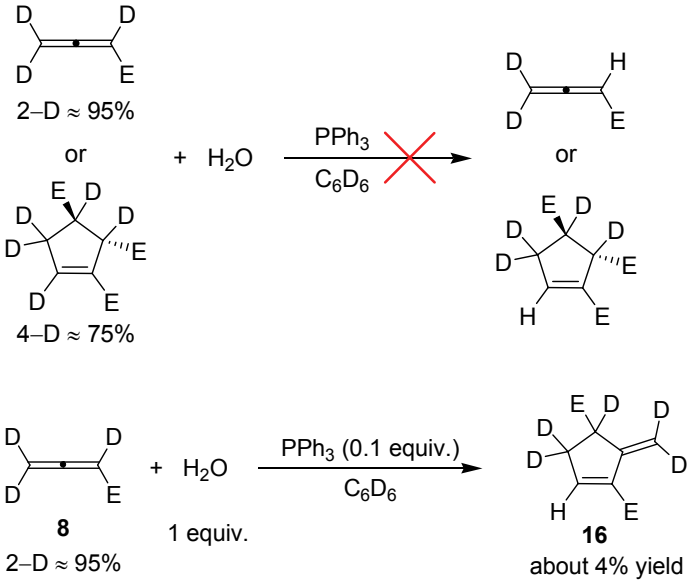

| | **1** | **15** |
|---|---|---|
| M | 98 | 196 |
| m (mg) | 245 | 24 |
| n (mmol) | 2.50 | 0.122 |
| Yield | | 10% |

**Dimethyl 2–*exo*–Methylene–3–cyclopentene–1, 3–dicarboxylate (15)**

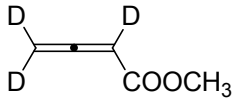



Colorless oil ($R_f$ = 0.27, PE/AcOEt = 6:1). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.75 (ddd, $J$ = 19.8, 8.7, 3.0 Hz, 1H), 3.00 (dt, $J$ = 19.8, 3.3 Hz, 1H), 3.75 (s, 3H), 3.76 (m, 1H), 3.79 (s, 3H), 5.31 (s, 1H), 5.89 (d, $J$ = 2.4 Hz, 1H), 7.09 (dd, $J$ = 4.2, 2.7 Hz, 1H). $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ 2.04 (ddd, $J$ = 19.8, 8.7, 3.0 Hz, 1H), 2.76 (dt, $J$ = 19.8, 3.3 Hz, 1H), 3.30 (s, 3H), 3.33 (s, 3H), 3.45 (m, 1H), 5.48 (s, 1H), 6.35 (d, $J$ = 2.4 Hz, 1H), 6.73 (dd, $J$ = 4.2, 2.7 Hz, 1H). $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ 33.8, 47.4, 51.4, 52.3, 109.3, 134.4, 145.9, 148.9, 163.8, 173.2. IR $\nu$ ($cm^{-1}$): 1724. MS (ESI) m/z: 197 $(M+H)^+$.

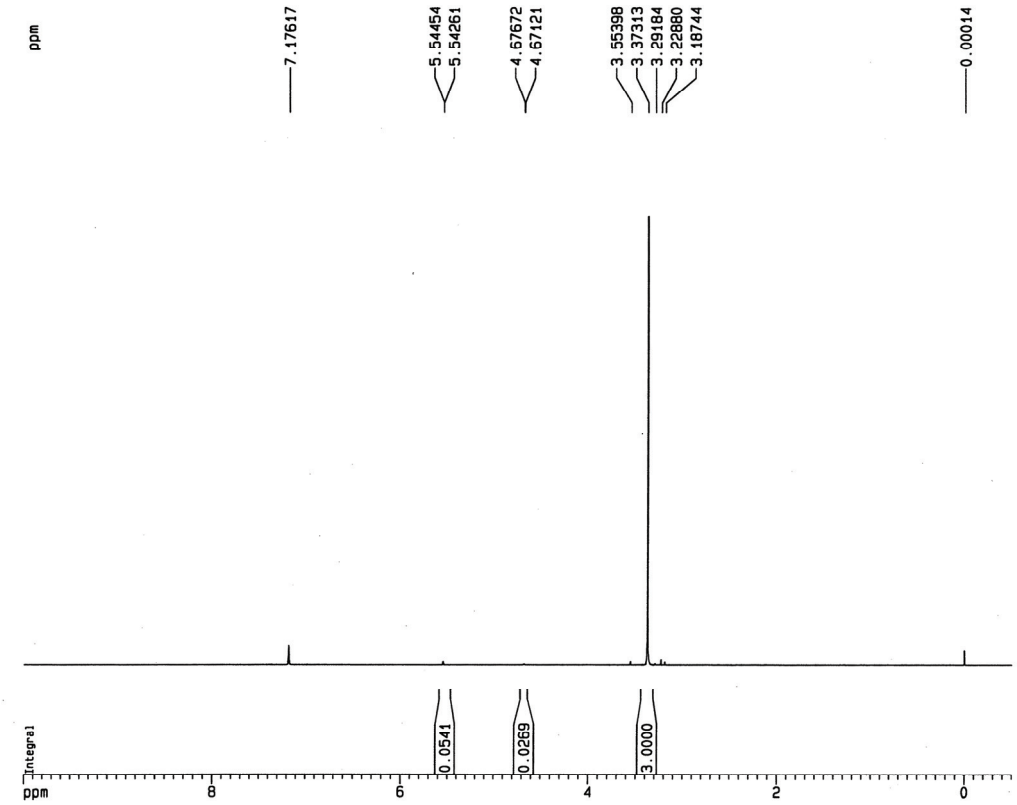
**Scheme S4** (E = $COOCH_3$).

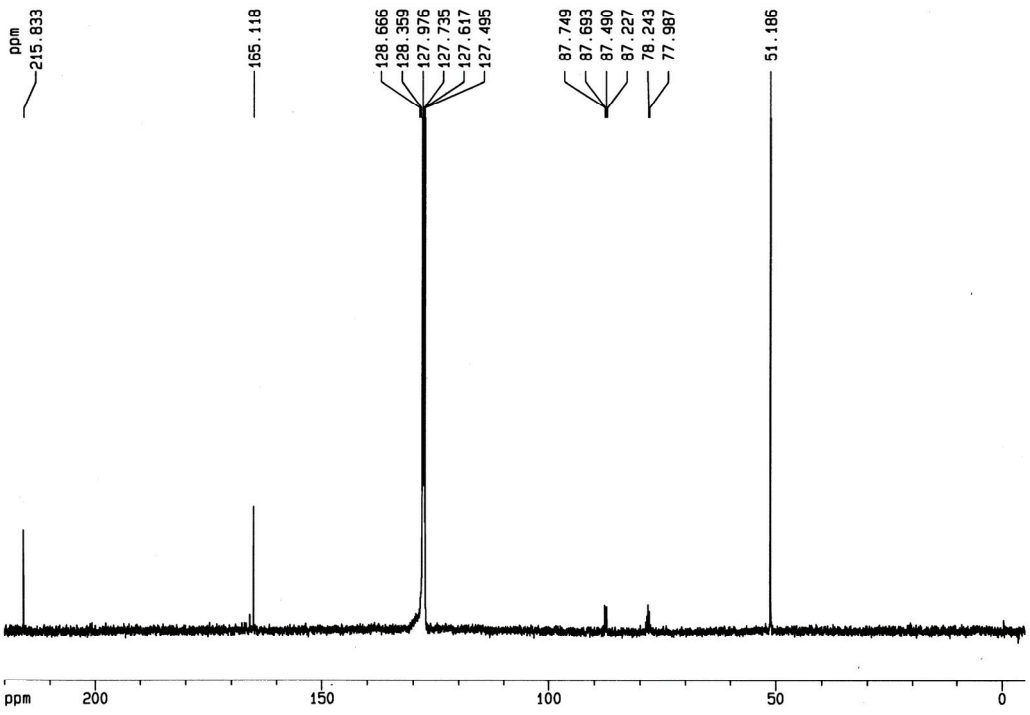


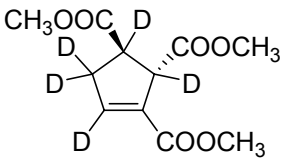
## 2. Copies of $^{1}H$, $^{13}C$ NMR，and Mass Spectra




**8**

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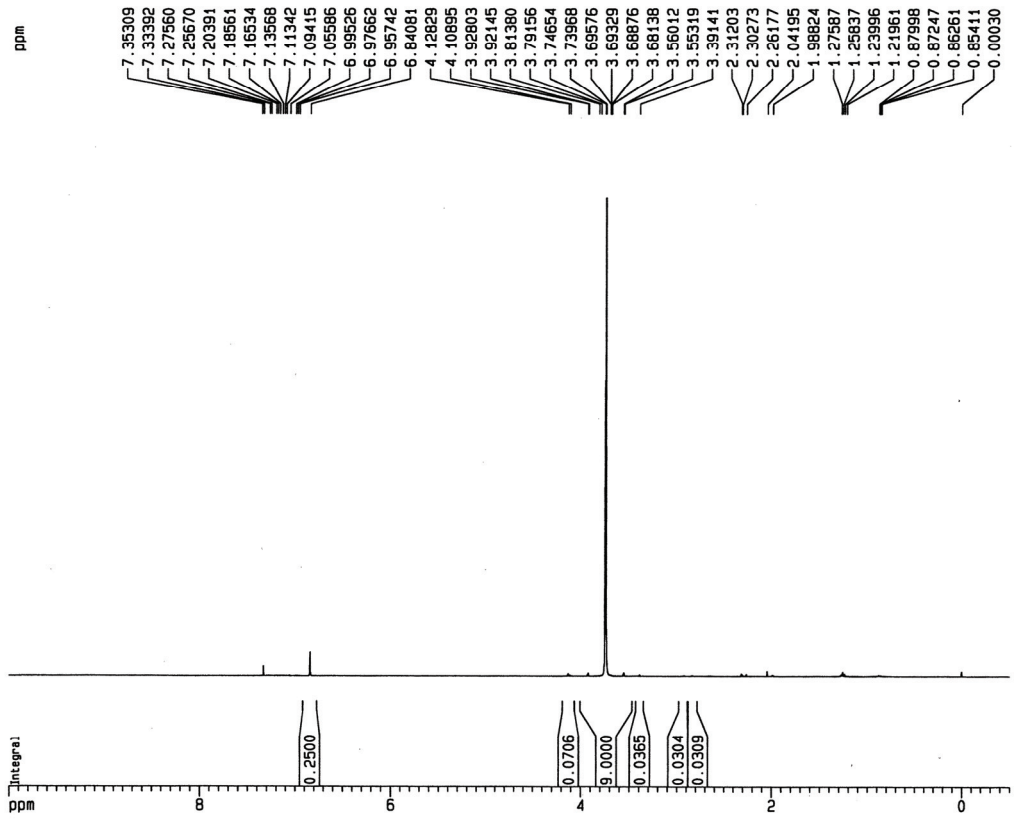
D
D
D
COOCH3
D
D
COOCH3

**10**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6.99526
6.97662
6.95742
6.84081
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3.92145
3.81380
3.79156
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3.39141
2.31203
2.30273
2.26177
2.04195
1.98824
1.27587
1.25837
1.23996
1.21961
0.87998
0.87247
0.86261
0.85411
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Integral
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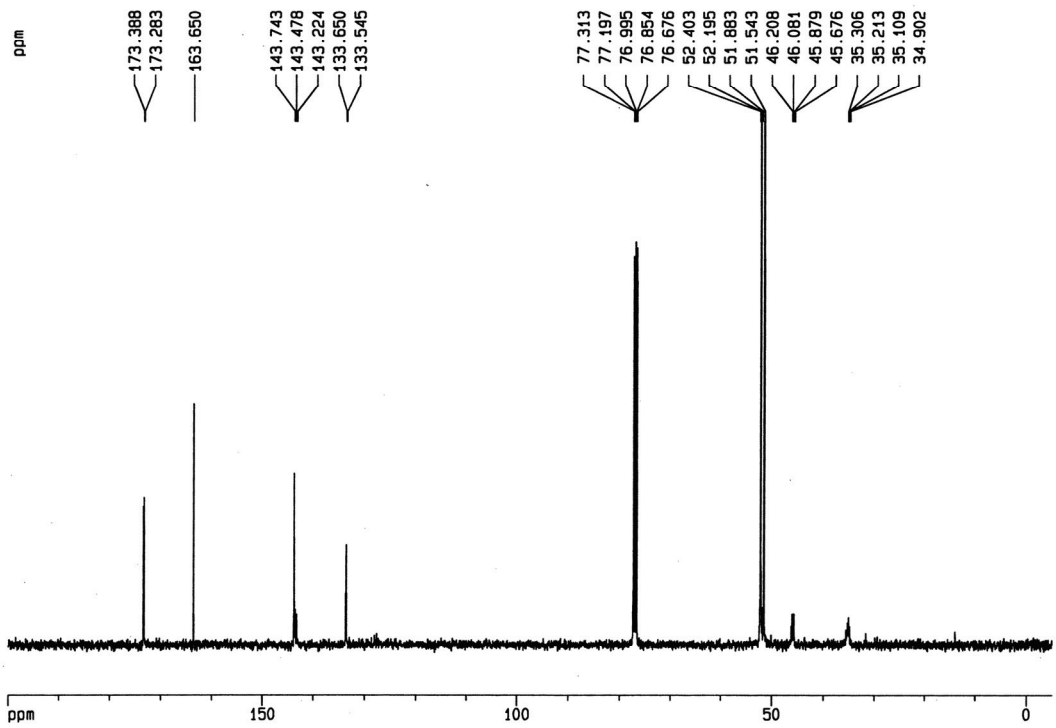
0.0309
ppm
8
6
4
2
0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143.478
143.224
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52.403
52.195
51.883
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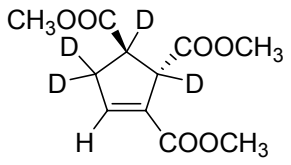
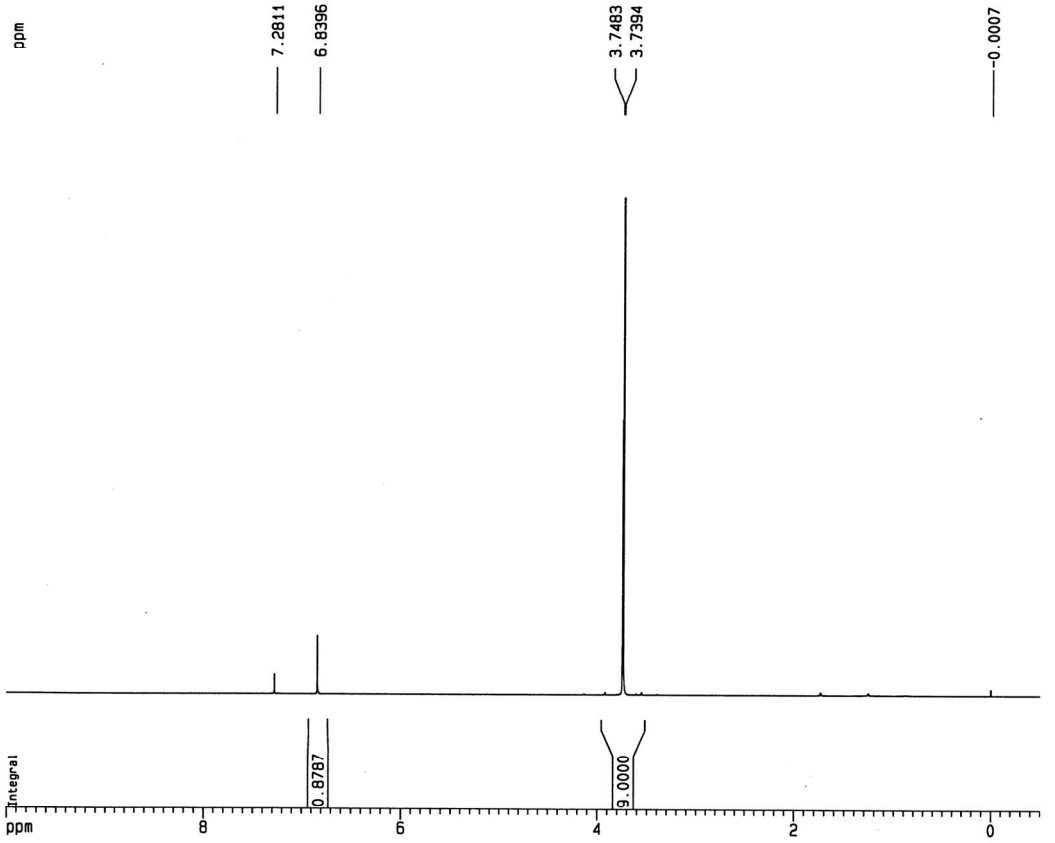
50
0


CH3OOC
D
D
COOCH3
D
D
H
COOCH3

**11**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6
4
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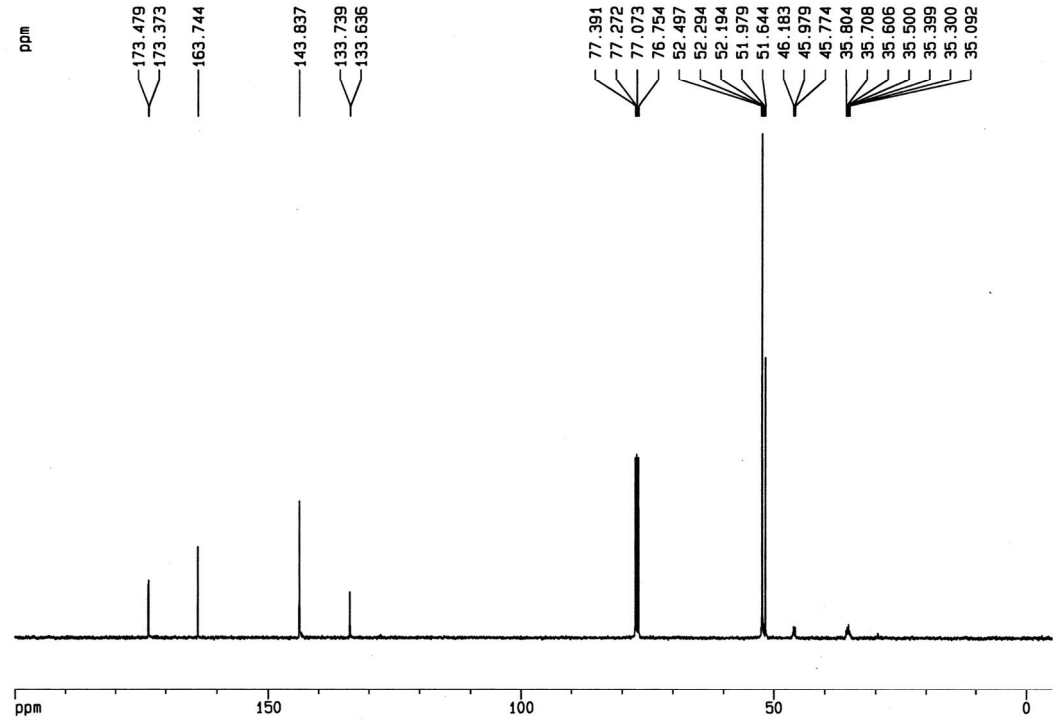
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133.739
133.636
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52.497
52.294
52.194
51.979
51.644
46.183
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35.300
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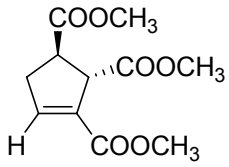
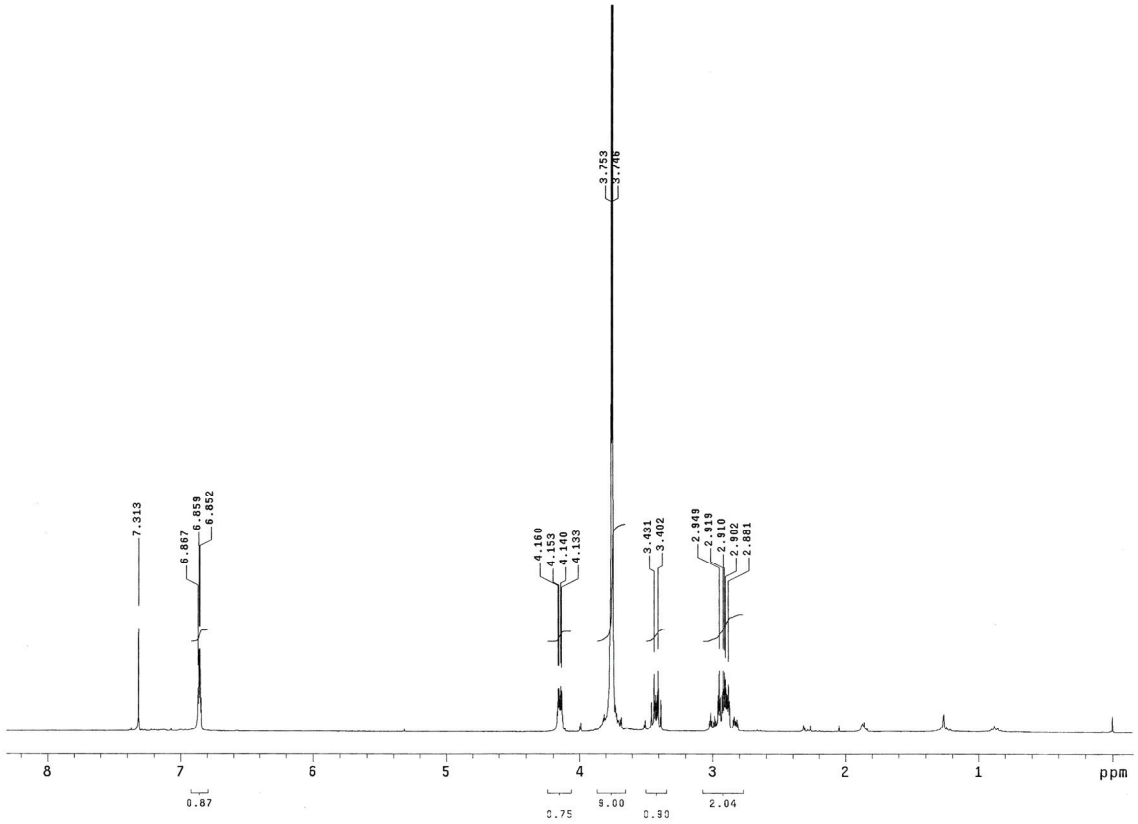
ppm
150
100
50
0


COOCH3
COOCH3
H
COOCH3

**13**


7.313
6.867
6.859
6.852
4.160
4.153
4.140
4.133
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3.746
3.431
3.402
2.943
2.919
2.910
2.902
2.881
8
7
6
5
4
3
2
1
ppm
0.87
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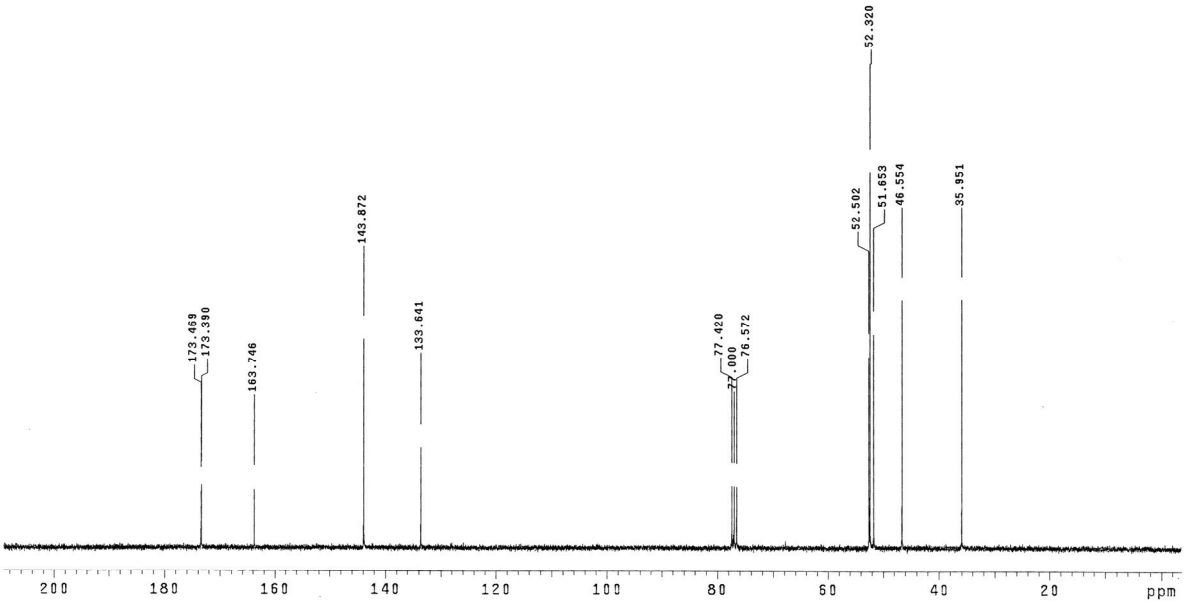
9.00
0.80
2.04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143.872
133.641
77.420
77.000
76.572
52.502
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51.653
46.554
35.951
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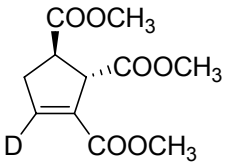
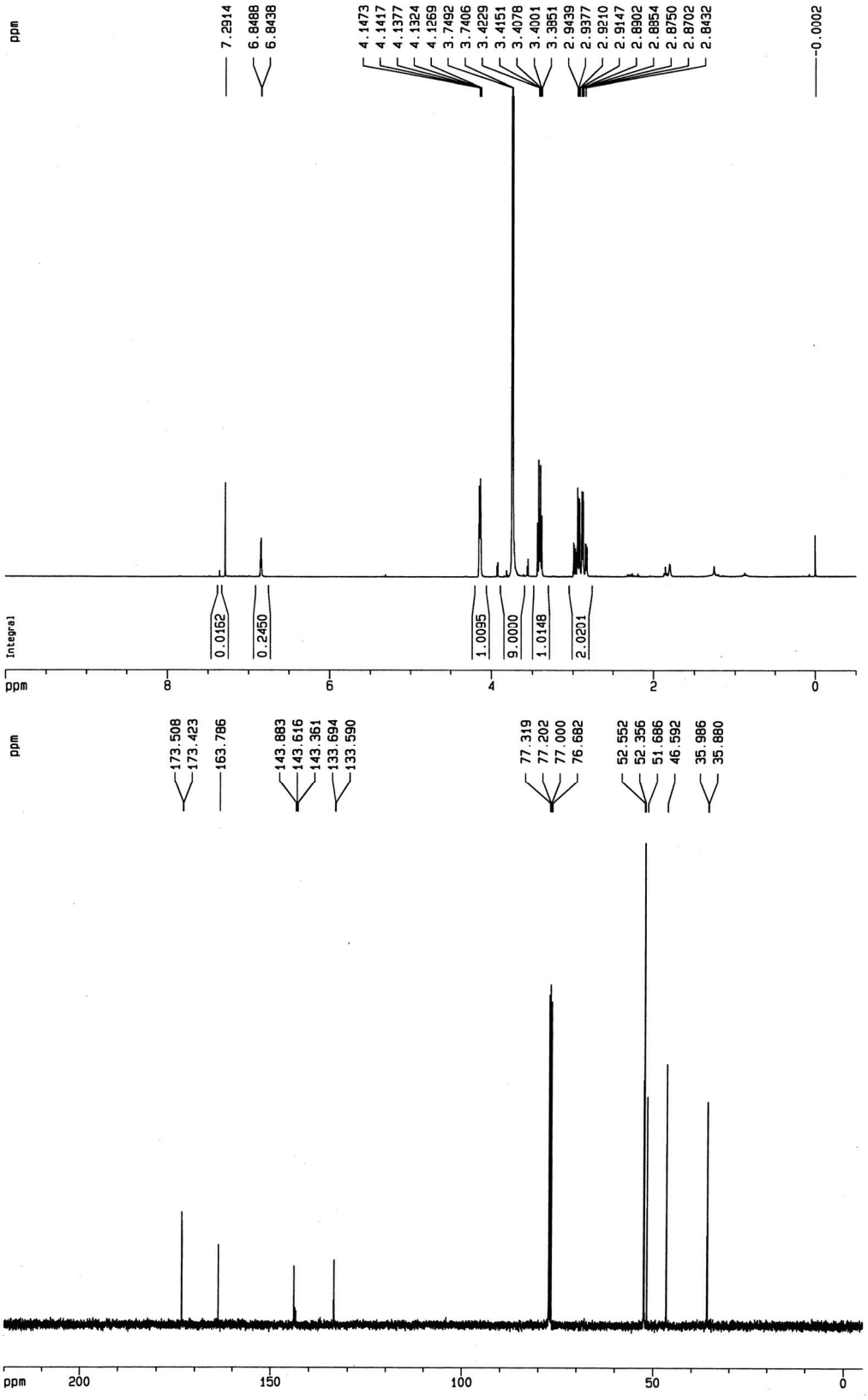
180
160
140
120
100
80
60
40
20
ppm


COOCH3
COOCH3
D
COOCH3

**14**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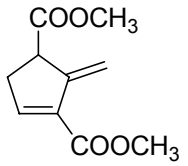
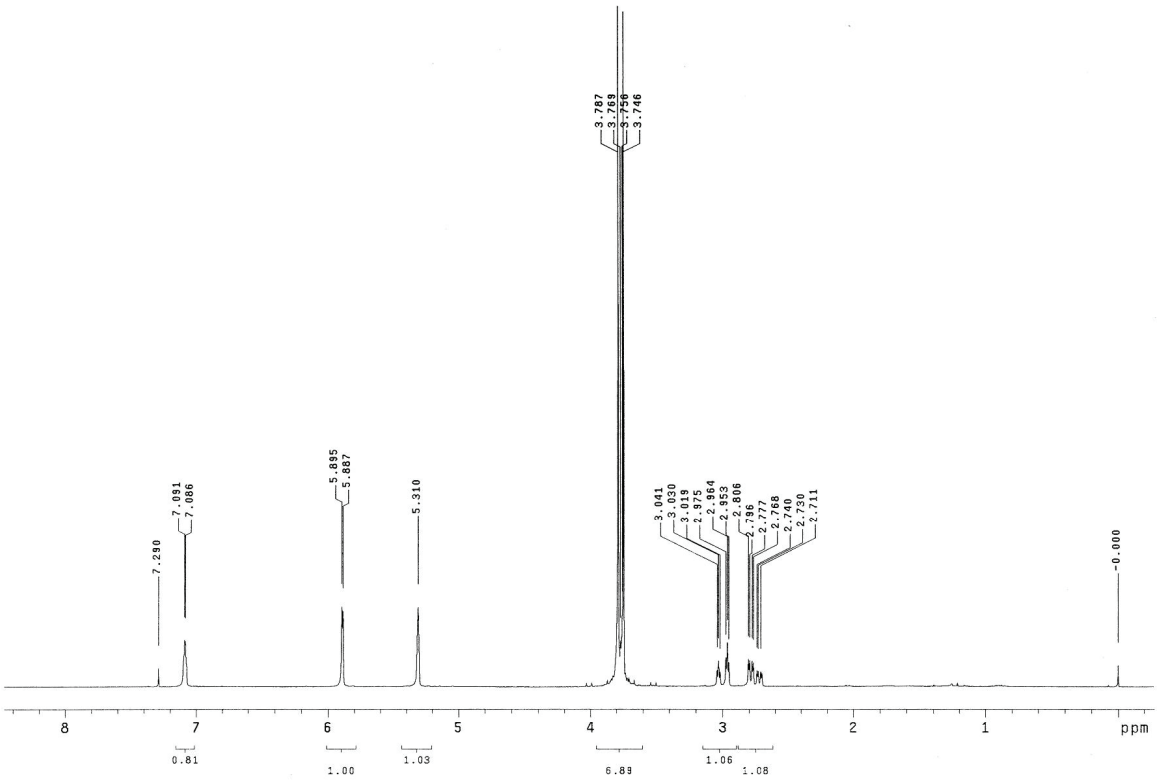
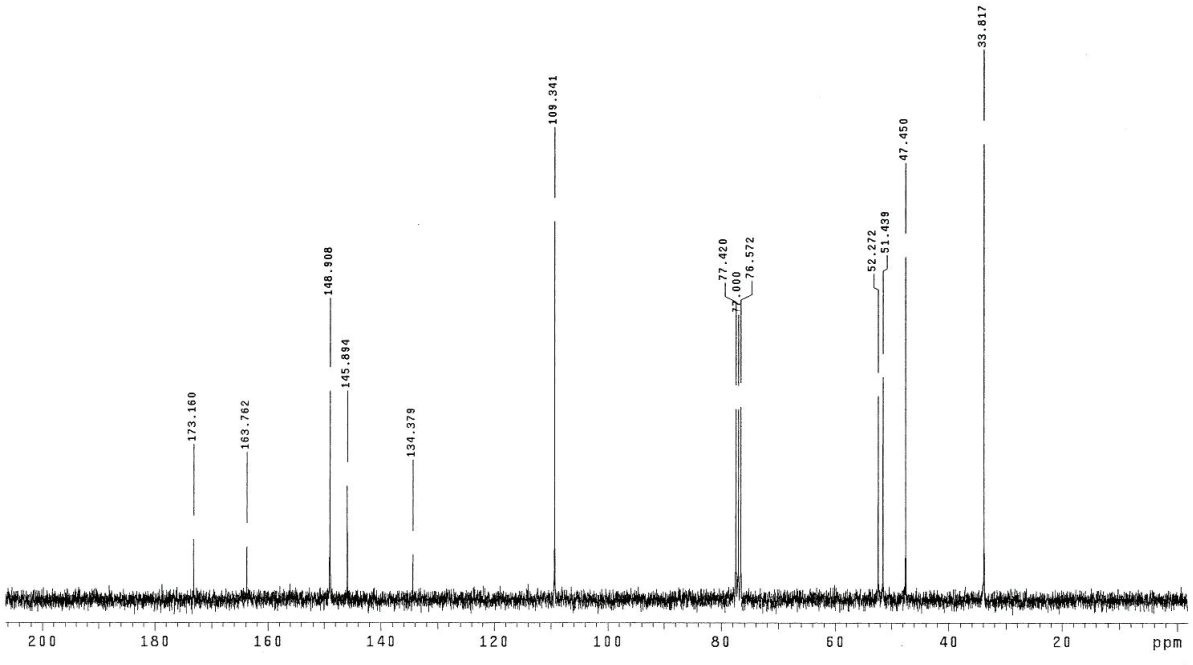
6.8438
4.1473
4.1417
4.1377
4.1324
4.1269
3.7492
3.7406
3.4229
3.4151
3.4078
3.4001
3.3851
2.9439
2.9377
2.9210
2.9147
2.8902
2.8854
2.8750
2.8702
2.8432
-0.0002
Integral
0.0162
0.2450
1.0095
9.0000
1.0148
2.0201
ppm
8
6
4
2
0
ppm
173.508
173.423
163.786
143.883
143.616
143.361
133.694
133.590
77.319
77.202
77.000
76.682
52.552
52.356
51.686
46.592
35.986
35.880
ppm
200
150
100
50
0

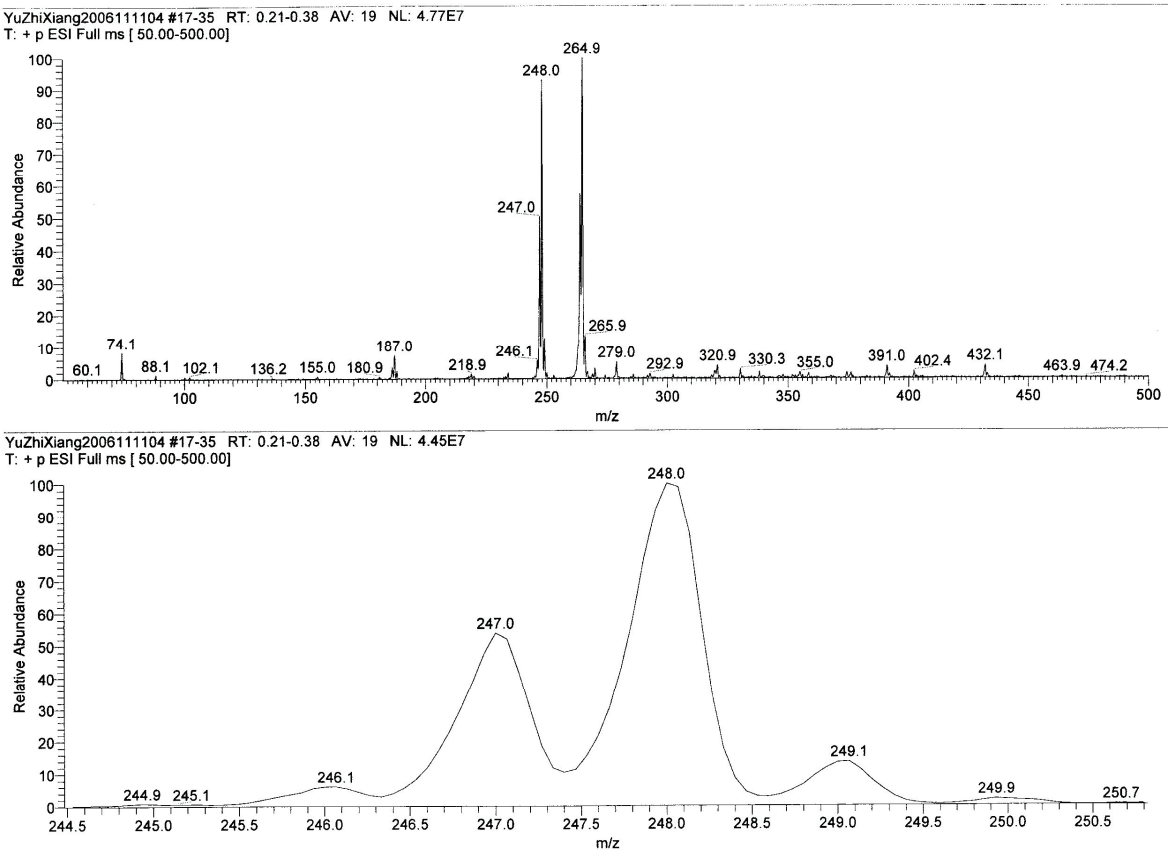

COOCH3
COOCH3

**15**

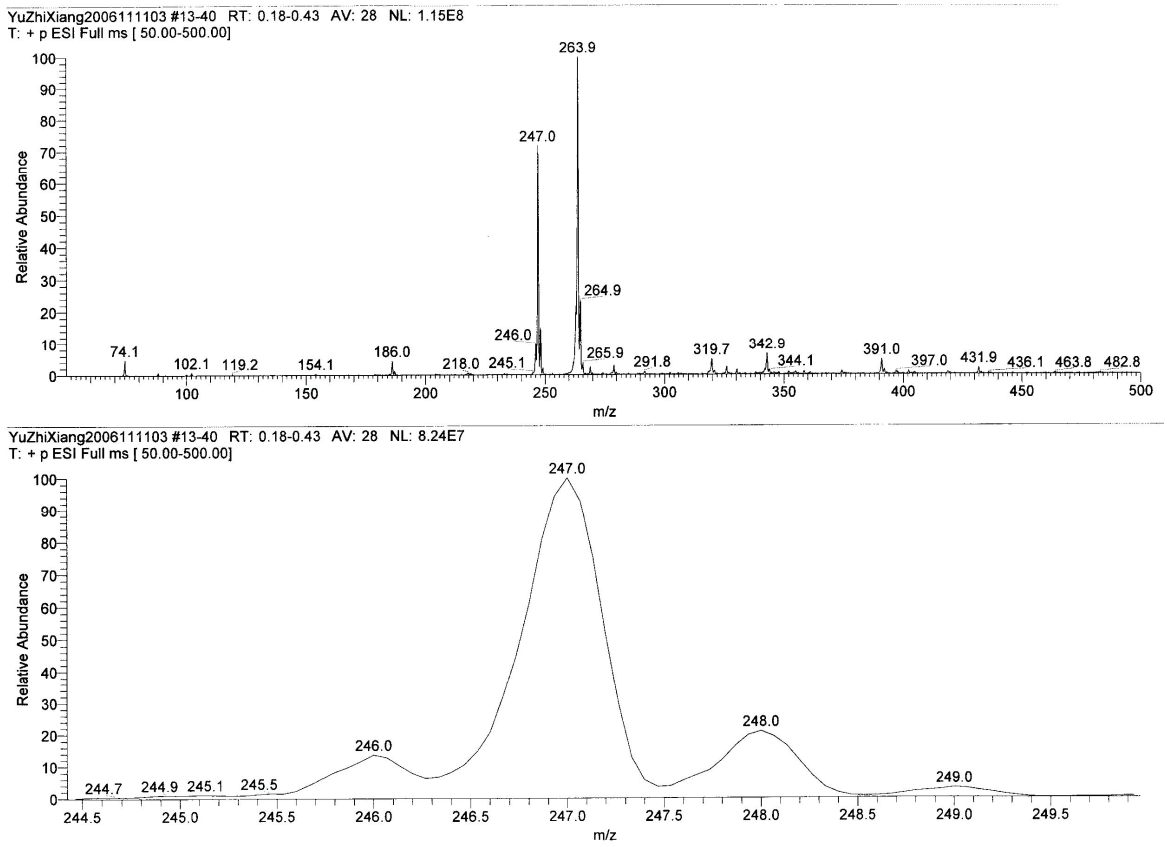

3.787
3.769
3.756
3.746
7.290
7.091
7.086
5.895
5.887
5.310
3.041
3.030
3.019
2.975
2.964
2.953
2.806
2.796
2.777
2.768
2.740
2.730
2.711
0.000
8
7
6
5
4
3
2
1
ppm
0.81
1.00
1.03
6.89
1.06
1.08


173.160
163.762
148.808
145.894
134.379
109.341
77.420
77.000
76.572
52.272
51.439
47.450
33.817
200
180
160
140
120
100
80
60
40
20
ppm

## MS for Reaction I (no additives) in Scheme 2




## MS for Reaction II (add 1 equiv. $H_2O$) in Scheme 2



## 3. Computational Details

All of the DFT calculations were performed with the Gaussian 03 program package.[4] The geometry optimization of all the minima and transition states involved were performed at the B3LYP[5] levels of theory with the 6-31+G* basis set[6] used. The vibrational frequencies were computed at the same level of theory to check whether the optimized geometrical structure is at an energy minimum or a transition state and to evaluate the zero-point vibration energy (ZPE). IRC calculations were used to confirm that each transition state is connected with its related reactant(s) and product(s). Solvent effects were computed by the CPCM[7] method at the B3LYP/6-31+G* level using the gas phase optimized structures. These methods have been shown to give very good solvation energies that are comparable with the experimentally measured ones.[7a,8] This solvation method has also been widely applied in studying organic and organometallic reaction mechanisms.[9] We have to mentioned that, even though the calculated relative free energies for bi- and tri-molecular reactions in solution are somehow overestimated, the main purpose of such calculations is to know how solvent affects a reaction (For example, such solvation calculations can provide such information as how solvent

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[4] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven,K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega,G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao,H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz,I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

[5] (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

[6] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

[7] (a) Takana, Y.; Houk, K. N. *J. Chem. Theory Comput.* **2005**, *1*, 70. (b) Dudding, T.; Kwon, O.; Mercier, E. *Org. Lett.* **2006**, *8*, 3643. (c) Klamt, A.; Schuurmann, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 799. (d) Andzelm, J.; Kolmel, C.; Klamt, A. *J. Chem. Phys.* **1995**, *103*, 9312-9320. (e) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995-2001. (f) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **2003**, *24*, 669-681.

[8] (a) Bahmanyar, S.; Houk, K. N. *J. Am. Soc. Chem.* **2001**, *123*, 12911. (b) Clemente, F. R.; Houk, K. N. *Angew. Chem. Int. Ed.* **2004**, *43*, 5766. (c) Dehestani, A.; Lam, W. H.; Hrovat, D. A.; Davidson, E. R.; Borden, W. T.; Mayer, J. M. *J. Am. Soc. Chem.* **2005**, *127*, 3423. (d) Oxgaard, J.; Goddard, W. A., III *J. Am. Soc. Chem.* **2004**, *126*, 442.

[9] (a) Yu, Z.-X.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **2003**, *125,* 15420. (b) Yu, Z.-X.; Houk, K. N. *J. Am. Chem. Soc.* **2003**, *125,* 13825. (c) Yu, Z.-X.; Wender, P. A.; Houk, K. N. *J. Am. Chem. Soc.* **2004**, *126,* 9154.

influces the reaction rate, regio- and stereo-selectivity, and so on).[9] Therefore, the present solvation calculations is very helpful for us to understand the solvent effects on the Lu (3+2) reaction. The natural bond orbital (NBO) technique was applied to calculate the Wiberg bond indices to analyze the intramolecular bondings and interactions. The charges reported are Mulliken atomic charges. $E_0$ is the ZPE corrected relative electronic energy in the gas phase. The $G_{solv}$ values in benzene were calculated by adding the solvation energies to the computed gas phase relative free energies ($G_{298}$).

The tunneling effect for the direct [1,2]-H shift converting **IN2** to **IN3** was evaluated by using the a model reaction (see Table S2). GAUSSRATE[10] was used as the interface between Gaussian 03 and POLYRATE[11] for the direct dynamics calculations. Transition states were located using canonical variational transition theory (CVT[12]), and quantum effects were calculated with the small curvature tunneling (SCT[13]) approximation.

[10] Corchado, J. C.; Chuang, Y. Y.; Coitino, E. L.; Ellinson, B. A.; Truhlar, D. G. *GAUSSRATE*, version 9.5; University of Minnesota: Minneapolis, MN, 2007.

[11] Corchado, J. C.; Chuang, Y. Y.; Fast, P. L.; Villa, J.; Hu, W. P.; Liu, Y. P.; Lynch, G. C.; Nguyen, K. A.; Jackels, C. F.; Melissas, V. S.; Lynch, B. J.; Rossi, I.; Coitiño, E. L.; Fernandez-Ramos, A.; Pu, J.; Albu, T. V.; Steckler, R.; Garrett, B. C.; Isaacson, A. D.; Truhlar, D. G. POLYRATE*version 9.5, University of Minnesota, Minneapolis, MN, 2006.

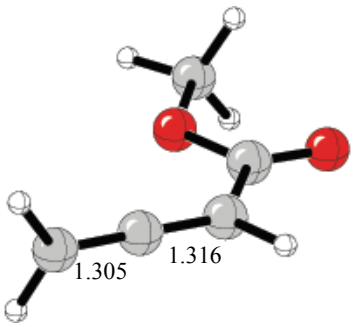
[12] Review: Truhlar, D. G.; Garrett, B. C. *Annu. Rev. Phys. Chem.* **1984**, *35*, 159.

[13] Lu, D. H.; Truong, T. N.; Melissas, V. S.; Lynch, G. C.; Liu, Y.-P.; Garrett, B. C.; Steckler, R.; Isaacson, A. D.; Rai, S. N.; Hancock, G. C.; Lauderdale, J. G.; Joseph, T.; Truhlar, D. G. *Comput. Phys. Commun.* **1992**, *71*, 235.

**4. Coordinates and Geometries of All Stationary Points** (Distances are in angstrom, values in box and parentheses are Mulliken charges and bond order, respectively)

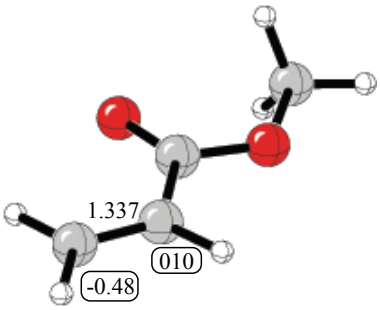
**4.1. Standard coordinate and geometry of 1:**

| | | | |
|---|---|---|---|
| 6 | 1.872747 | 0.130043 | -0.000103 |
| 6 | 2.885038 | -0.693058 | 0.000232 |
| 1 | 3.320267 | -1.054402 | 0.930193 |
| 1 | 3.320857 | -1.054400 | -0.929455 |
| 6 | 0.864078 | 0.974797 | -0.000526 |
| 1 | 1.036251 | 2.048757 | 0.000741 |
| 6 | -0.568363 | 0.585412 | 0.000013 |
| 8 | -1.477016 | 1.395538 | 0.000243 |
| 8 | -0.756465 | -0.751884 | -0.000220 |
| 6 | -2.127014 | -1.190238 | 0.000050 |
| 1 | -2.079608 | -2.279654 | -0.000192 |
| 1 | -2.644183 | -0.825826 | 0.891874 |
| 1 | -2.644658 | -0.825450 | -0.891345 |



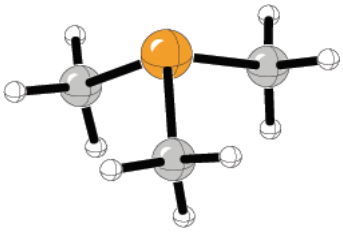

**4.2. Standard coordinate and geometry of 2:**

| | | | |
|---|---|---|---|
| 6 | -1.429575 | -0.583441 | 0.013633 |
| 1 | -0.967844 | -1.566590 | -0.025832 |
| 1 | -2.514012 | -0.532621 | 0.047433 |
| 6 | -0.679698 | 0.523382 | 0.019898 |
| 1 | -1.115592 | 1.517753 | 0.058877 |
| 6 | 0.803050 | 0.446716 | -0.026841 |
| 8 | 1.464419 | -0.573732 | -0.072137 |
| 8 | 1.346854 | 1.687312 | -0.011710 |
| 6 | 2.784285 | 1.743747 | -0.053380 |
| 1 | 3.032401 | 2.805289 | -0.034942 |
| 1 | 3.209950 | 1.231034 | 0.813460 |
| 1 | 3.156612 | 1.274400 | -0.968009 |




**4.3. Standard coordinate and geometry of phosphine $P(CH_3)_3$:**

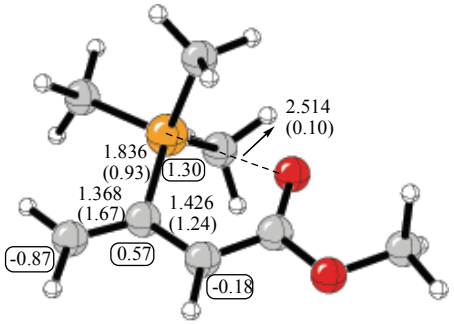
| | | | |
|---|---|---|---|
| 15 | -0.000524 | -0.000549 | -0.605642 |
| 6 | 0.459499 | 1.577630 | 0.279874 |
| 1 | 1.464428 | 1.892352 | -0.024061 |
| 1 | -0.235590 | 2.376423 | -0.003128 |
| 1 | 0.442065 | 1.467894 | 1.372459 |
| 6 | 1.138131 | -1.185734 | 0.280334 |
| 1 | 0.899553 | -2.214844 | -0.011709 |
| 1 | 2.175594 | -0.991610 | -0.015164 |
| 1 | 1.063949 | -1.104634 | 1.373003 |
| 6 | -1.596898 | -0.391177 | 0.280738 |



| | | | |
|---|---|---|---|
| 1 | -2.369749 | 0.326646 | -0.017192 |
| 1 | -1.945666 | -1.389199 | -0.008584 |
| 1 | -1.491116 | -0.359109 | 1.373332 |

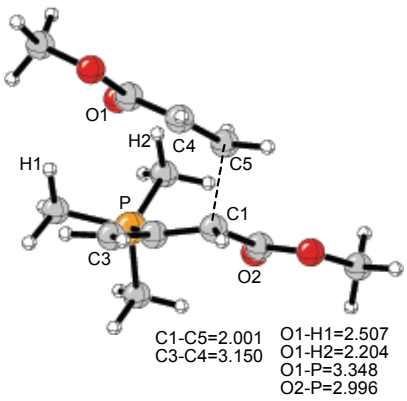
**4.4. Standard coordinate and geometry of 3:**

| | | | |
|---|---|---|---|
| 6 | 0.641936 | 1.330703 | -0.000034 |
| 6 | 1.566204 | 2.339819 | -0.000155 |
| 1 | 1.228317 | 3.373206 | -0.000216 |
| 1 | 2.636341 | 2.186230 | -0.000167 |
| 6 | -0.777436 | 1.472904 | 0.000082 |
| 1 | -1.211101 | 2.466873 | 0.000220 |
| 6 | -1.601841 | 0.347762 | -0.000053 |
| 8 | -1.175345 | -0.844999 | -0.000240 |
| 8 | -2.949878 | 0.592747 | 0.000093 |
| 6 | -3.802651 | -0.552552 | -0.000009 |
| 1 | -4.820137 | -0.155610 | -0.000078 |
| 1 | -3.639374 | -1.168646 | -0.890674 |
| 1 | -3.639526 | -1.168686 | 0.890661 |
| 15 | 1.296351 | -0.384892 | 0.000020 |
| 6 | 0.993646 | -1.329651 | -1.547003 |
| 1 | 0.531289 | -2.289787 | -1.311472 |
| 1 | 0.297384 | -0.767571 | -2.171865 |
| 1 | 1.936690 | -1.481674 | -2.081898 |
| 6 | 0.993318 | -1.329574 | 1.547023 |
| 1 | 0.296876 | -0.767487 | 2.171678 |
| 1 | 0.531077 | -2.289754 | 1.311444 |
| 1 | 1.936238 | -1.481511 | 2.082161 |
| 6 | 3.139656 | -0.261670 | 0.000206 |
| 1 | 3.506501 | 0.255190 | -0.890678 |
| 1 | 3.506311 | 0.255303 | 0.891102 |
| 1 | 3.542640 | -1.281126 | 0.000309 |




**4.5. Standard coordinate and geometry of TS1:**

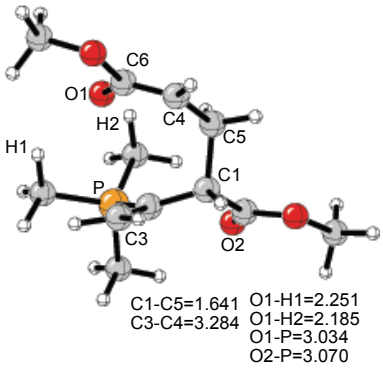
| | | | |
|---|---|---|---|
| 6 | -0.261143 | 0.348148 | 1.067606 |
| 6 | 0.694135 | 0.298497 | 2.033481 |
| 1 | 0.727373 | -0.545887 | 2.715089 |
| 1 | 1.445250 | 1.063315 | 2.186723 |
| 6 | -1.083508 | -0.825486 | 0.795566 |
| 1 | -1.110042 | -1.516711 | 1.634615 |
| 6 | -2.372922 | -0.699699 | 0.137919 |
| 8 | -2.749618 | 0.244857 | -0.565523 |
| 8 | -3.141903 | -1.809675 | 0.304602 |
| 6 | -4.403573 | -1.817675 | -0.379082 |
| 1 | -4.860447 | -2.776389 | -0.129349 |
| 1 | -5.034639 | -0.992595 | -0.035580 |



| | | | |
|---|---|---|---|
| 1 | -4.258913 | -1.732562 | -1.459892 |
| 15 | -0.252540 | 1.806872 | -0.018292 |
| 6 | -1.609631 | 2.954237 | 0.412250 |
| 1 | -2.565072 | 2.468797 | 0.204476 |
| 1 | -1.546657 | 3.207856 | 1.475046 |
| 1 | -1.520096 | 3.869396 | -0.183270 |
| 6 | -0.286842 | 1.492708 | -1.811380 |
| 1 | 0.568835 | 0.851608 | -2.045351 |
| 1 | -1.228160 | 1.018314 | -2.087680 |
| 1 | -0.188751 | 2.455512 | -2.325935 |
| 6 | 1.291959 | 2.745751 | 0.250453 |
| 1 | 1.383544 | 3.091172 | 1.283251 |
| 1 | 2.136296 | 2.103110 | -0.016061 |
| 1 | 1.278935 | 3.619300 | -0.409722 |
| 6 | 0.046630 | -1.991081 | -0.369450 |
| 1 | -0.584693 | -2.873527 | -0.282532 |
| 1 | -0.093095 | -1.456539 | -1.307234 |
| 6 | 1.369573 | -2.094415 | 0.105511 |
| 1 | 1.648186 | -2.867772 | 0.814417 |
| 6 | 2.378166 | -1.182471 | -0.310127 |
| 8 | 2.238849 | -0.181420 | -1.043574 |
| 8 | 3.629473 | -1.512521 | 0.173966 |
| 6 | 4.704711 | -0.667704 | -0.225966 |
| 1 | 5.607029 | -1.126564 | 0.185083 |
| 1 | 4.775727 | -0.603042 | -1.316577 |
| 1 | 4.587755 | 0.345328 | 0.178399 |

**4.6. Standard coordinate and geometry of IN1:**

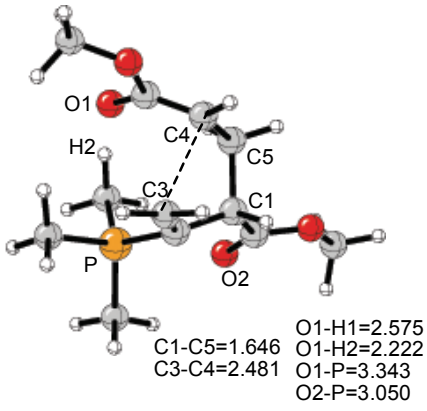
| | | | |
|---|---|---|---|
| 6 | -0.230773 | 0.316375 | 1.019066 |
| 6 | 0.539199 | 0.264032 | 2.124897 |
| 1 | 0.486266 | -0.596866 | 2.784690 |
| 1 | 1.248852 | 1.034541 | 2.406826 |
| 6 | -1.005995 | -0.910098 | 0.626818 |
| 1 | -1.110131 | -1.533934 | 1.518159 |
| 6 | -2.377301 | -0.655948 | 0.077641 |
| 8 | -2.724407 | 0.334350 | -0.556317 |
| 8 | -3.202024 | -1.699878 | 0.295101 |
| 6 | -4.519541 | -1.608621 | -0.278331 |
| 1 | -5.017363 | -2.538382 | -0.002044 |
| 1 | -5.054723 | -0.747749 | 0.131539 |
| 1 | -4.456231 | -1.512766 | -1.365425 |
| 15 | -0.070738 | 1.787769 | -0.037914 |
| 6 | -1.368751 | 3.003701 | 0.406177 |
| 1 | -2.350372 | 2.585886 | 0.174513 |
| 1 | -1.310781 | 3.228528 | 1.475745 |



| | | | |
|---|---|---|---|
| 1 | -1.217528 | 3.927589 | -0.163068 |
| 6 | -0.156020 | 1.538403 | -1.838090 |
| 1 | 0.659965 | 0.864666 | -2.113862 |
| 1 | -1.127738 | 1.126195 | -2.111530 |
| 1 | -0.024939 | 2.516823 | -2.314632 |
| 6 | 1.512712 | 2.627332 | 0.299314 |
| 1 | 1.572395 | 2.968847 | 1.336062 |
| 1 | 2.312422 | 1.916670 | 0.070199 |
| 1 | 1.586396 | 3.500697 | -0.357730 |
| 6 | -0.154879 | -1.842200 | -0.421687 |
| 1 | -0.759647 | -2.750358 | -0.525132 |
| 1 | -0.172261 | -1.313207 | -1.381771 |
| 6 | 1.221803 | -2.149494 | 0.010280 |
| 1 | 1.439352 | -3.073092 | 0.535950 |
| 6 | 2.249602 | -1.261660 | -0.280225 |
| 8 | 2.135934 | -0.131982 | -0.848489 |
| 8 | 3.517201 | -1.693188 | 0.109774 |
| 6 | 4.599964 | -0.829298 | -0.199147 |
| 1 | 5.502233 | -1.364776 | 0.109586 |
| 1 | 4.646989 | -0.604938 | -1.270944 |
| 1 | 4.534156 | 0.119536 | 0.350757 |

**4.7. Standard coordinate and geometry of TS2:**

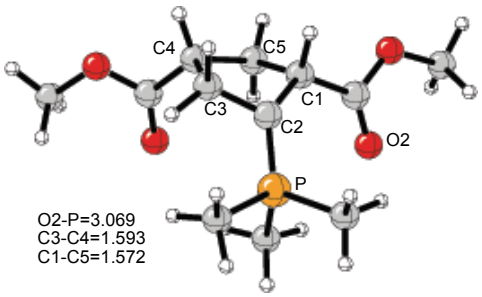
| | | | |
|---|---|---|---|
| 6 | -0.047434 | -0.346657 | -1.069559 |
| 6 | 0.823953 | 0.466996 | -1.767086 |
| 1 | 0.430409 | 1.194458 | -2.468202 |
| 1 | 1.885381 | 0.267386 | -1.870271 |
| 6 | -1.313079 | 0.382914 | -0.741401 |
| 1 | -1.671469 | 0.888631 | -1.644279 |
| 6 | -2.462270 | -0.404719 | -0.186773 |
| 8 | -2.388011 | -1.490846 | 0.372122 |
| 8 | -3.630086 | 0.255295 | -0.327711 |
| 6 | -4.794945 | -0.371541 | 0.240328 |
| 1 | -5.617999 | 0.313795 | 0.036267 |
| 1 | -4.974403 | -1.341384 | -0.231508 |
| 1 | -4.666029 | -0.510275 | 1.317039 |
| 15 | 0.616003 | -1.696236 | -0.114523 |
| 6 | -0.032846 | -3.308384 | -0.699179 |
| 1 | -1.113890 | -3.336223 | -0.548625 |
| 1 | 0.188889 | -3.423034 | -1.764729 |
| 1 | 0.435339 | -4.126791 | -0.140635 |
| 6 | 0.402359 | -1.672793 | 1.700244 |
| 1 | 0.836255 | -0.738729 | 2.069090 |
| 1 | -0.656722 | -1.738661 | 1.951937 |
| 1 | 0.933690 | -2.532612 | 2.124642 |



| | | | |
|---|---|---|---|
| 6 | 2.423062 | -1.795498 | -0.371766 |
| 1 | 2.670651 | -1.878212 | -1.433389 |
| 1 | 2.885117 | -0.902914 | 0.058904 |
| 1 | 2.799129 | -2.684251 | 0.145567 |
| 6 | -0.898319 | 1.615898 | 0.267631 |
| 1 | -1.756357 | 2.296276 | 0.280120 |
| 1 | -0.786350 | 1.183237 | 1.267552 |
| 6 | 0.345444 | 2.296430 | -0.160142 |
| 1 | 0.284025 | 3.183111 | -0.783469 |
| 6 | 1.569758 | 2.035572 | 0.494567 |
| 8 | 1.815691 | 1.094117 | 1.281548 |
| 8 | 2.574356 | 2.931567 | 0.155952 |
| 6 | 3.843413 | 2.709521 | 0.762958 |
| 1 | 4.289322 | 1.763719 | 0.430309 |
| 1 | 4.471891 | 3.544463 | 0.443049 |
| 1 | 3.766236 | 2.691484 | 1.855124 |

**4.8. Standard coordinate and geometry of IN2:**

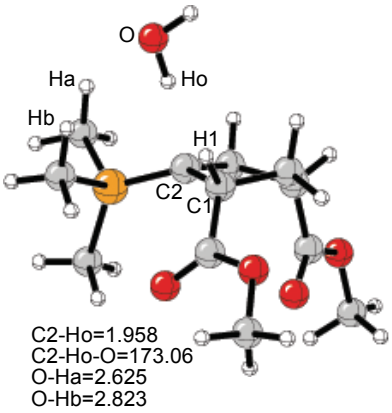
| | | | |
|---|---|---|---|
| 6 | -0.271989 | 0.475218 | 1.062367 |
| 6 | 1.061122 | -0.058519 | 1.551564 |
| 1 | 0.998458 | -0.364786 | 2.608266 |
| 1 | 1.896488 | 0.646391 | 1.492108 |
| 6 | -1.050289 | -0.797373 | 0.768926 |
| 1 | -1.318087 | -1.292815 | 1.715488 |
| 6 | -2.318716 | -0.713385 | -0.041400 |
| 8 | -2.580558 | 0.128010 | -0.885179 |
| 8 | -3.158240 | -1.735106 | 0.241742 |
| 6 | -4.371260 | -1.796128 | -0.529938 |
| 1 | -4.900401 | -2.677330 | -0.165607 |
| 1 | -4.969949 | -0.894876 | -0.372149 |
| 1 | -4.142668 | -1.895460 | -1.594632 |
| 15 | -0.356204 | 1.947703 | 0.191417 |
| 6 | -1.913350 | 2.885924 | 0.472191 |
| 1 | -2.761261 | 2.305561 | 0.102815 |
| 1 | -2.035227 | 3.063215 | 1.544758 |
| 1 | -1.880248 | 3.844151 | -0.059627 |
| 6 | -0.123789 | 2.082834 | -1.651636 |
| 1 | 0.817472 | 1.593364 | -1.921486 |
| 1 | -0.945717 | 1.563676 | -2.150451 |
| 1 | -0.104370 | 3.130407 | -1.978546 |
| 6 | 0.959029 | 3.065937 | 0.821765 |
| 1 | 0.935302 | 3.105142 | 1.913978 |
| 1 | 1.945598 | 2.725256 | 0.494489 |
| 1 | 0.793980 | 4.071515 | 0.421331 |
| 6 | -0.007214 | -1.727240 | 0.049480 |



| | | | |
|---|---|---|---|
| 1 | -0.259111 | -2.791069 | 0.135426 |
| 1 | 0.032265 | -1.462893 | -1.012423 |
| 6 | 1.343519 | -1.390284 | 0.723467 |
| 1 | 1.660371 | -2.185851 | 1.403700 |
| 6 | 2.454303 | -1.152410 | -0.266330 |
| 8 | 2.361968 | -0.523112 | -1.306789 |
| 8 | 3.631488 | -1.675221 | 0.164150 |
| 6 | 4.772962 | -1.440736 | -0.678193 |
| 1 | 4.968613 | -0.368454 | -0.770099 |
| 1 | 5.605799 | -1.941680 | -0.183041 |
| 1 | 4.606407 | -1.860899 | -1.673902 |

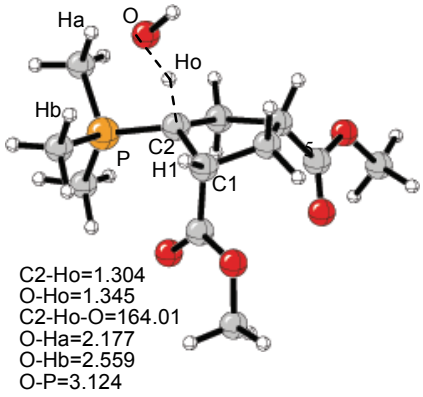
**4.9. Standard coordinate and geometry of 4:**

| | | | |
|---|---|---|---|
| 6 | 0.845933 | -0.592247 | 0.443264 |
| 6 | -0.152513 | -1.755914 | 0.296675 |
| 1 | 0.164750 | -2.656887 | 0.844727 |
| 1 | -0.334907 | -2.090214 | -0.737402 |
| 6 | 0.175932 | 0.583696 | 1.153865 |
| 1 | 0.824491 | 1.011955 | 1.938424 |
| 6 | -0.180270 | 1.812491 | 0.310103 |
| 8 | 0.334844 | 2.097824 | -0.756991 |
| 8 | -1.037680 | 2.638399 | 0.942777 |
| 6 | -1.408884 | 3.832656 | 0.232768 |
| 1 | -2.102515 | 4.357114 | 0.891393 |
| 1 | -0.528351 | 4.449110 | 0.030590 |
| 1 | -1.895540 | 3.569891 | -0.710022 |
| 15 | 2.095615 | -0.432825 | -0.727613 |
| 6 | 3.322159 | 0.828790 | -0.232035 |
| 1 | 2.861720 | 1.819073 | -0.268513 |
| 1 | 3.669977 | 0.614536 | 0.782796 |
| 1 | 4.173372 | 0.807301 | -0.920698 |
| 6 | 1.748764 | -0.089180 | -2.520338 |
| 1 | 1.051301 | -0.842718 | -2.903423 |
| 1 | 1.286867 | 0.895357 | -2.612876 |
| 1 | 2.670063 | -0.133520 | -3.114168 |
| 6 | 3.010075 | -2.024940 | -0.825017 |
| 1 | 3.417327 | -2.271896 | 0.159620 |
| 1 | 2.328231 | -2.824746 | -1.133933 |
| 1 | 3.820796 | -1.958952 | -1.558822 |
| 6 | -1.044556 | -0.075913 | 1.848009 |
| 1 | -0.717352 | -0.498046 | 2.805227 |
| 1 | -1.845793 | 0.637242 | 2.053249 |
| 6 | -1.483634 | -1.235634 | 0.933099 |
| 1 | -1.974877 | -2.034867 | 1.496478 |
| 6 | -2.442733 | -0.790637 | -0.150506 |



| | | | |
|---|---|---|---|
| 8 | -2.490865 | 0.316661 | -0.652603 |
| 8 | -3.253757 | -1.805235 | -0.539823 |
| 6 | -4.166007 | -1.509487 | -1.612683 |
| 1 | -3.616505 | -1.216242 | -2.511597 |
| 1 | -4.720177 | -2.433089 | -1.783763 |
| 1 | -4.843384 | -0.700473 | -1.325921 |
| 1 | 2.055782 | -1.159957 | 1.874050 |
| 8 | 2.765717 | -1.395218 | 2.546995 |
| 1 | 2.300042 | -1.664855 | 3.352530 |

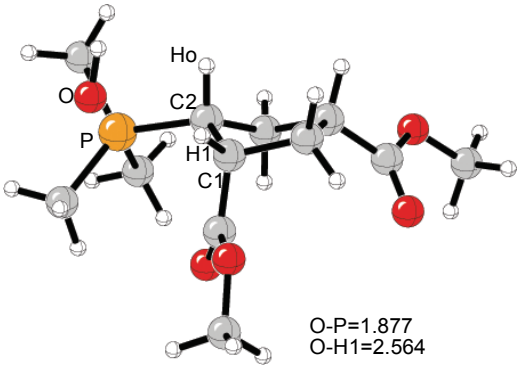
**4.10. Standard coordinate and geometry of TS3:**




| | | | |
|---|---|---|---|
| 6 | 0.637704 | -0.700384 | 0.587164 |
| 6 | -0.863298 | -1.012854 | 0.483384 |
| 1 | -1.125572 | -1.972293 | 0.942736 |
| 1 | -1.225632 | -1.035198 | -0.555507 |
| 6 | 0.764774 | 0.826953 | 0.585684 |
| 1 | 1.700756 | 1.139935 | 1.070050 |
| 6 | 0.745411 | 1.529433 | -0.768082 |
| 8 | 0.852213 | 0.979508 | -1.851667 |
| 8 | 0.663357 | 2.865742 | -0.636161 |
| 6 | 0.603719 | 3.629089 | -1.855604 |
| 1 | 0.545879 | 4.671191 | -1.540007 |
| 1 | 1.498823 | 3.456903 | -2.459546 |
| 1 | -0.284908 | 3.349352 | -2.427005 |
| 15 | 1.735953 | -1.732438 | -0.368322 |
| 6 | 3.435603 | -1.100309 | -0.193850 |
| 1 | 3.543612 | -0.142574 | -0.711331 |
| 1 | 3.617125 | -0.979060 | 0.880179 |
| 1 | 4.148868 | -1.816624 | -0.614261 |
| 6 | 1.412944 | -2.030364 | -2.150851 |
| 1 | 0.394843 | -2.413423 | -2.277399 |
| 1 | 1.503984 | -1.097797 | -2.708449 |
| 1 | 2.118056 | -2.778691 | -2.530436 |
| 6 | 1.715378 | -3.387608 | 0.403862 |
| 1 | 1.917098 | -3.241273 | 1.473275 |
| 1 | 0.731209 | -3.850498 | 0.275377 |
| 1 | 2.471917 | -4.029640 | -0.060002 |
| 6 | -0.431057 | 1.228623 | 1.493106 |
| 1 | -0.101315 | 1.166411 | 2.534028 |
| 1 | -0.771368 | 2.247828 | 1.301109 |
| 6 | -1.544192 | 0.174798 | 1.253797 |
| 1 | -1.940504 | -0.191803 | 2.204263 |
| 6 | -2.703950 | 0.715329 | 0.443039 |
| 8 | -2.638625 | 1.607447 | -0.381648 |
| 8 | -3.849655 | 0.046931 | 0.713124 |

| | | | |
|---|---|---|---|
| 6 | -5.006199 | 0.436838 | -0.050739 |
| 1 | -4.827218 | 0.284909 | -1.118686 |
| 1 | -5.814140 | -0.205754 | 0.300581 |
| 1 | -5.243546 | 1.488909 | 0.128533 |
| 1 | 1.126281 | -1.034887 | 1.749110 |
| 8 | 1.927276 | -1.469546 | 2.738496 |
| 1 | 1.738899 | -1.127272 | 3.625606 |

**4.11. Standard coordinate and geometry of 5:**

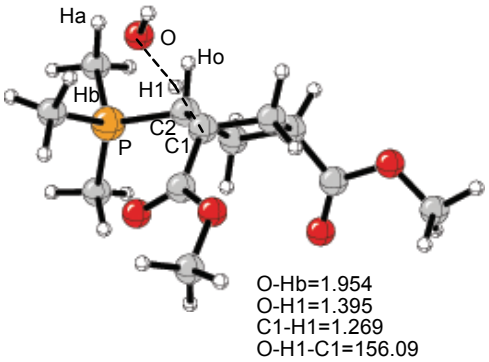



| | | | |
|---|---|---|---|
| 6 | 0.647078 | -0.570330 | 0.825798 |
| 6 | -0.551025 | -1.121001 | 0.030402 |
| 1 | -0.523827 | -2.205291 | -0.107724 |
| 1 | -0.601688 | -0.652882 | -0.955889 |
| 6 | 0.172696 | 0.832965 | 1.276125 |
| 1 | 0.744935 | 1.182715 | 2.136895 |
| 6 | 0.282816 | 1.899821 | 0.199638 |
| 8 | 0.492679 | 1.710946 | -0.984003 |
| 8 | 0.088277 | 3.128049 | 0.724028 |
| 6 | 0.097492 | 4.226426 | -0.207623 |
| 1 | -0.072800 | 5.117535 | 0.397137 |
| 1 | 1.062752 | 4.284221 | -0.717475 |
| 1 | -0.697908 | 4.102889 | -0.947441 |
| 15 | 2.411445 | -0.734023 | 0.162928 |
| 6 | 3.433501 | 0.659816 | -0.513255 |
| 1 | 3.073122 | 0.961615 | -1.497265 |
| 1 | 3.449713 | 1.502390 | 0.176973 |
| 1 | 4.458057 | 0.278983 | -0.601277 |
| 6 | 1.959831 | -1.368233 | -1.589752 |
| 1 | 1.390404 | -2.305279 | -1.567516 |
| 1 | 1.385813 | -0.624215 | -2.151297 |
| 1 | 2.890170 | -1.562576 | -2.141719 |
| 6 | 3.248629 | -2.329570 | 0.639767 |
| 1 | 4.288906 | -2.111053 | 0.896852 |
| 1 | 2.768199 | -2.742288 | 1.534405 |
| 1 | 3.211207 | -3.079278 | -0.154745 |
| 6 | -1.328772 | 0.601758 | 1.643865 |
| 1 | -1.424678 | 0.469297 | 2.726264 |
| 1 | -1.954984 | 1.452066 | 1.363919 |
| 6 | -1.771052 | -0.688818 | 0.901506 |
| 1 | -1.980802 | -1.489524 | 1.619453 |
| 6 | -3.016475 | -0.508603 | 0.054314 |
| 8 | -3.474329 | 0.549461 | -0.328991 |
| 8 | -3.559761 | -1.706560 | -0.265352 |
| 6 | -4.718918 | -1.667832 | -1.119601 |
| 1 | -4.472090 | -1.197720 | -2.075273 |

| | | | |
|---|---|---|---|
| 1 | -5.005334 | -2.709911 | -1.264572 |
| 1 | -5.526096 | -1.107885 | -0.639805 |
| 1 | 0.713630 | -1.153498 | 1.755790 |
| 8 | 2.975005 | -0.040350 | 1.813882 |
| 1 | 2.880183 | -0.649165 | 2.563684 |

**4.12. Standard coordinate and geometry of TS4:**

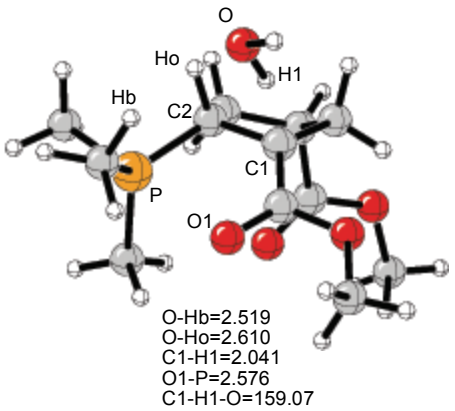
| | | | |
|---|---|---|---|
| 6 | -0.780105 | -0.801826 | -0.426714 |
| 6 | 0.449705 | -1.510625 | 0.180172 |
| 1 | 0.358460 | -2.603394 | 0.222298 |
| 1 | 0.649005 | -1.144920 | 1.192753 |
| 6 | -0.268945 | 0.581510 | -0.859168 |
| 1 | -1.130893 | 0.871768 | -1.744645 |
| 6 | -0.290014 | 1.591930 | 0.200430 |
| 8 | -1.044960 | 1.566942 | 1.180796 |
| 8 | 0.536356 | 2.643222 | -0.021420 |
| 6 | 0.472239 | 3.716388 | 0.929307 |
| 1 | 1.199067 | 4.452487 | 0.582198 |
| 1 | -0.531076 | 4.151398 | 0.951470 |
| 1 | 0.734446 | 3.361994 | 1.930290 |
| 15 | -2.348208 | -0.898770 | 0.529088 |
| 6 | -3.578162 | 0.361487 | 0.095451 |
| 1 | -3.413970 | 1.254827 | 0.699288 |
| 1 | -3.422300 | 0.605852 | -0.975660 |
| 1 | -4.580257 | -0.046048 | 0.268698 |
| 6 | -2.118478 | -1.035716 | 2.335426 |
| 1 | -1.477662 | -1.891305 | 2.570193 |
| 1 | -1.662468 | -0.118057 | 2.709697 |
| 1 | -3.095804 | -1.185228 | 2.807019 |
| 6 | -3.085344 | -2.498243 | 0.017871 |
| 1 | -3.332660 | -2.447940 | -1.047398 |
| 1 | -2.381074 | -3.320163 | 0.181959 |
| 1 | -3.999698 | -2.696422 | 0.586491 |
| 6 | 1.094172 | 0.247250 | -1.480853 |
| 1 | 0.982044 | 0.033736 | -2.549563 |
| 1 | 1.800438 | 1.075149 | -1.386203 |
| 6 | 1.602979 | -1.065930 | -0.753502 |
| 1 | 1.808115 | -1.831224 | -1.508520 |
| 6 | 2.893631 | -0.814793 | -0.001883 |
| 8 | 2.995018 | -0.547347 | 1.180545 |
| 8 | 3.960001 | -0.888277 | -0.832580 |
| 6 | 5.241028 | -0.590691 | -0.247345 |
| 1 | 5.461823 | -1.290394 | 0.563308 |
| 1 | 5.961288 | -0.700526 | -1.058700 |
| 1 | 5.253199 | 0.430125 | 0.144352 |



| | | | |
|---|---|---|---|
| 1 | -1.066650 | -1.302276 | -1.362920 |
| 8 | -2.256394 | 0.669718 | -2.542882 |
| 1 | -2.206667 | 1.183601 | -3.363562 |

**4.13. Standard coordinate and geometry of 6:**

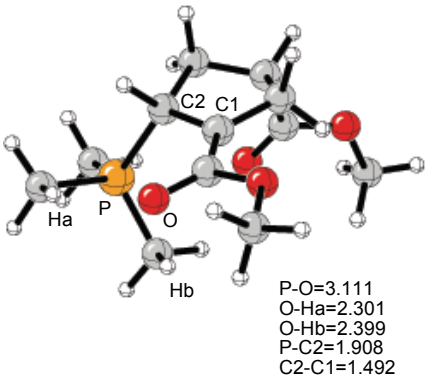
| | | | |
|---|---|---|---|
| 6 | 0.833376 | -0.799307 | 0.836214 |
| 6 | -0.202067 | -1.981291 | 0.703210 |
| 1 | 0.024523 | -2.761004 | 1.438731 |
| 1 | -0.192569 | -2.451745 | -0.284459 |
| 6 | 0.009726 | 0.439041 | 1.105914 |
| 1 | 1.392057 | 1.077016 | 2.465255 |
| 6 | 0.156818 | 1.538427 | 0.263811 |
| 8 | 1.106340 | 1.686308 | -0.560080 |
| 8 | -0.801067 | 2.525216 | 0.382013 |
| 6 | -0.632957 | 3.667420 | -0.457355 |
| 1 | -1.458942 | 4.336985 | -0.205149 |
| 1 | 0.324527 | 4.163223 | -0.265826 |
| 1 | -0.681797 | 3.394765 | -1.517164 |
| 15 | 2.065695 | -0.704407 | -0.543920 |
| 6 | 3.516528 | 0.346508 | -0.173733 |
| 1 | 3.438101 | 1.282949 | -0.724988 |
| 1 | 3.501129 | 0.583408 | 0.896668 |
| 1 | 4.440413 | -0.184719 | -0.425376 |
| 6 | 1.420322 | -0.553891 | -2.247330 |
| 1 | 0.362822 | -0.840170 | -2.240047 |
| 1 | 1.490534 | 0.485596 | -2.566692 |
| 1 | 1.977336 | -1.214478 | -2.920198 |
| 6 | 2.792251 | -2.404619 | -0.519081 |
| 1 | 3.204359 | -2.624736 | 0.471449 |
| 1 | 2.038449 | -3.159835 | -0.760117 |
| 1 | 3.600710 | -2.473440 | -1.254880 |
| 6 | -1.287679 | -0.012391 | 1.722938 |
| 1 | -1.198772 | -0.240337 | 2.797184 |
| 1 | -2.091905 | 0.719669 | 1.613600 |
| 6 | -1.593253 | -1.365130 | 0.984495 |
| 1 | -2.212541 | -2.019655 | 1.608430 |
| 6 | -2.359673 | -1.102361 | -0.296331 |
| 8 | -1.896098 | -1.104188 | -1.424180 |
| 8 | -3.660728 | -0.838127 | -0.045612 |
| 6 | -4.473792 | -0.504589 | -1.184943 |
| 1 | -4.475987 | -1.325960 | -1.906729 |
| 1 | -5.475124 | -0.339065 | -0.786007 |
| 1 | -4.096684 | 0.400835 | -1.668017 |
| 1 | 1.508804 | -1.041773 | 1.676515 |
| 8 | 2.224094 | 1.086039 | 3.008515 |



| | | | |
|---|---|---|---|
| 1 | 2.213308 | 1.932576 | 3.478892 |

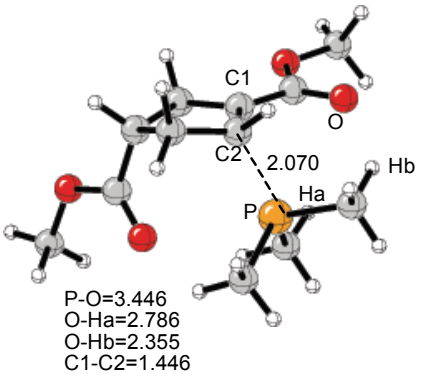
**4.14. Standard coordinate and geometry of IN3:**

| | | | |
|---|---|---|---|
| 15 | 0.816305 | 1.853873 | -0.051898 |
| 6 | 1.645465 | 2.855214 | -1.334897 |
| 1 | 1.947547 | 2.170091 | -2.132621 |
| 1 | 0.950586 | 3.603707 | -1.730996 |
| 1 | 2.519157 | 3.367272 | -0.917794 |
| 6 | 2.068770 | 0.784592 | 0.717933 |
| 1 | 2.861282 | 1.408733 | 1.145364 |
| 1 | 1.602613 | 0.187698 | 1.504221 |
| 1 | 2.476876 | 0.138488 | -0.062717 |
| 6 | 0.266309 | 3.053169 | 1.224478 |
| 1 | -0.486316 | 3.730405 | 0.807431 |
| 1 | -0.162595 | 2.509511 | 2.069453 |
| 1 | 1.118788 | 3.649731 | 1.568555 |
| 6 | -0.618434 | 0.902871 | -0.874018 |
| 6 | -1.961500 | 0.896196 | -0.090679 |
| 1 | -2.049328 | 1.668668 | 0.679167 |
| 1 | -2.766678 | 1.071029 | -0.814110 |
| 6 | -0.318404 | -0.537650 | -1.122687 |
| 6 | 0.776344 | -0.896500 | -1.894072 |
| 8 | 1.672925 | -0.107292 | -2.309223 |
| 6 | -1.402583 | -1.432142 | -0.573333 |
| 1 | -2.152643 | -1.735305 | -1.326422 |
| 1 | -1.028521 | -2.363092 | -0.130352 |
| 6 | -2.122317 | -0.529156 | 0.477958 |
| 1 | -3.176394 | -0.811342 | 0.578208 |
| 6 | -1.488624 | -0.674765 | 1.842675 |
| 8 | -0.689494 | 0.101092 | 2.346617 |
| 1 | -0.723067 | 1.508487 | -1.792672 |
| 8 | 0.865695 | -2.257245 | -2.178865 |
| 6 | 2.011699 | -2.660870 | -2.922597 |
| 1 | 2.939251 | -2.460025 | -2.373253 |
| 1 | 1.897227 | -3.737367 | -3.076265 |
| 1 | 2.063034 | -2.146437 | -3.888157 |
| 8 | -1.901233 | -1.794174 | 2.469834 |
| 6 | -1.315891 | -2.065039 | 3.756449 |
| 1 | -1.785154 | -2.988277 | 4.097278 |
| 1 | -0.234498 | -2.196019 | 3.661791 |
| 1 | -1.523159 | -1.246321 | 4.450812 |



**4.15. Standard coordinate and geometry of TS5:**

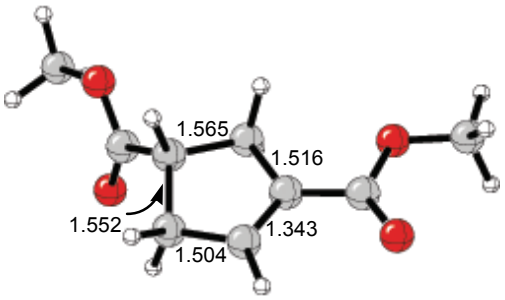
| | | | |
|---|---|---|---|
| 15 | -0.429071 | 1.998824 | -0.112469 |
| 6 | -2.018739 | 2.884116 | 0.111010 |
| 1 | -2.817634 | 2.135990 | 0.067006 |
| 1 | -2.039777 | 3.371344 | 1.092552 |
| 1 | -2.165213 | 3.644868 | -0.664042 |
| 6 | -0.454291 | 1.363802 | -1.823625 |
| 1 | -0.604226 | 2.187154 | -2.530369 |
| 1 | 0.493377 | 0.862911 | -2.034027 |
| 1 | -1.275984 | 0.648770 | -1.914645 |
| 6 | 0.870729 | 3.309068 | -0.059783 |
| 1 | 0.904094 | 3.758150 | 0.938547 |
| 1 | 1.840004 | 2.856424 | -0.281706 |
| 1 | 0.657096 | 4.099320 | -0.790653 |
| 6 | -0.495920 | 0.424136 | 1.228812 |
| 6 | 0.850460 | 0.183585 | 1.930357 |
| 1 | 1.517023 | 1.053257 | 1.952643 |
| 1 | 0.639250 | -0.088441 | 2.971940 |
| 6 | -0.860635 | -0.831175 | 0.609847 |
| 6 | -2.158743 | -1.052705 | 0.119651 |
| 8 | -3.074917 | -0.204597 | 0.033363 |
| 6 | 0.279827 | -1.825761 | 0.602437 |
| 1 | 0.071429 | -2.708314 | 1.225449 |
| 1 | 0.528297 | -2.222248 | -0.393979 |
| 6 | 1.488404 | -1.034173 | 1.218467 |
| 1 | 2.041939 | -1.665767 | 1.919205 |
| 6 | 2.449432 | -0.627883 | 0.126872 |
| 8 | 2.396828 | 0.406532 | -0.521783 |
| 1 | -1.257480 | 0.876033 | 1.873845 |
| 8 | -2.368607 | -2.354805 | -0.314742 |
| 6 | -3.675181 | -2.638189 | -0.813417 |
| 1 | -3.915872 | -2.011383 | -1.679099 |
| 1 | -3.655247 | -3.691163 | -1.105493 |
| 1 | -4.436843 | -2.474858 | -0.043563 |
| 8 | 3.390214 | -1.570086 | -0.089838 |
| 6 | 4.313296 | -1.322426 | -1.166495 |
| 1 | 4.985183 | -2.181060 | -1.172458 |
| 1 | 3.777654 | -1.246138 | -2.116717 |
| 1 | 4.869006 | -0.397933 | -0.988193 |




**4.16. Standard coordinate and geometry of 7:**

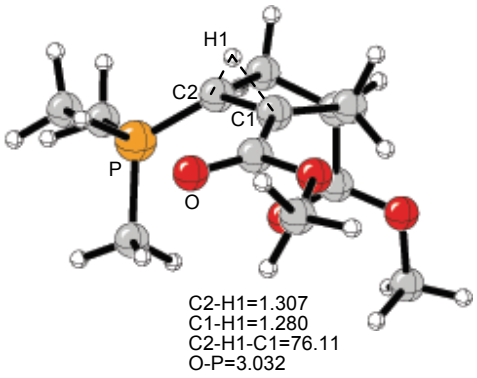
| | | | |
|---|---|---|---|
| 6 | 0.779013 | 1.820113 | -0.098274 |
| 6 | -0.719068 | 1.936884 | -0.160418 |
| 1 | -1.125042 | 2.227931 | 0.818847 |
| 1 | -1.059443 | 2.690426 | -0.881562 |

| | | | |
|---|---|---|---|
| 6 | 1.189477 | 0.541581 | -0.106795 |
| 6 | 2.610715 | 0.148462 | 0.004032 |
| 8 | 3.556842 | 0.914664 | 0.044274 |
| 6 | 0.025391 | -0.427426 | -0.177294 |
| 1 | 0.166078 | -1.221314 | -0.916914 |
| 1 | -0.122744 | -0.919922 | 0.793846 |
| 6 | -1.176770 | 0.505125 | -0.545976 |
| 1 | -1.332801 | 0.446177 | -1.627630 |
| 6 | -2.454743 | 0.068874 | 0.140965 |
| 8 | -2.816035 | 0.418991 | 1.247258 |
| 1 | 1.447746 | 2.671545 | -0.015095 |
| 8 | 2.747958 | -1.200732 | 0.055559 |
| 6 | 4.096374 | -1.689210 | 0.169880 |
| 1 | 4.560848 | -1.313538 | 1.085634 |
| 1 | 4.008526 | -2.775751 | 0.198944 |
| 1 | 4.690591 | -1.371356 | -0.691181 |
| 8 | -3.147575 | -0.808511 | -0.620232 |
| 6 | -4.353566 | -1.338780 | -0.036448 |
| 1 | -4.765326 | -2.012707 | -0.788102 |
| 1 | -4.123755 | -1.880197 | 0.885125 |
| 1 | -5.055151 | -0.530320 | 0.185187 |




**4.17. Standard coordinate and geometry of TS (1,2-H-shift):**

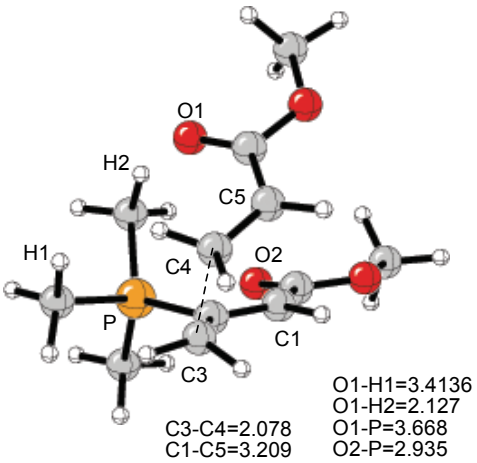
| | | | |
|---|---|---|---|
| 6 | 0.251611 | 0.651050 | -1.187045 |
| 6 | -1.089230 | 0.340527 | -1.861646 |
| 1 | -0.972574 | 0.245710 | -2.950822 |
| 1 | -1.843895 | 1.112423 | -1.691833 |
| 6 | 0.833355 | -0.784226 | -0.808129 |
| 1 | 1.231681 | -0.008943 | -1.745085 |
| 6 | 1.866381 | -0.933088 | 0.146766 |
| 8 | 2.543546 | -0.003579 | 0.633488 |
| 8 | 2.110061 | -2.244729 | 0.497502 |
| 6 | 3.200579 | -2.453276 | 1.397554 |
| 1 | 3.235717 | -3.531966 | 1.565969 |
| 1 | 4.142809 | -2.108390 | 0.959065 |
| 1 | 3.039803 | -1.927172 | 2.344130 |
| 15 | 0.503938 | 2.076468 | -0.207522 |
| 6 | 2.149049 | 2.834702 | -0.480006 |
| 1 | 2.913304 | 2.104752 | -0.204188 |
| 1 | 2.251229 | 3.099489 | -1.536748 |
| 1 | 2.254475 | 3.735776 | 0.135568 |
| 6 | 0.304956 | 2.019863 | 1.625137 |
| 1 | -0.660753 | 1.565890 | 1.863987 |
| 1 | 1.113177 | 1.409195 | 2.034807 |
| 1 | 0.351725 | 3.031918 | 2.045851 |



| | | | |
|---|---|---|---|
| 6 | -0.691179 | 3.354867 | -0.761250 |
| 1 | -0.667942 | 3.451994 | -1.850383 |
| 1 | -1.702719 | 3.087531 | -0.442914 |
| 1 | -0.423600 | 4.317887 | -0.314053 |
| 6 | -0.211747 | -1.827357 | -1.166067 |
| 1 | -0.006729 | -2.332347 | -2.119727 |
| 1 | -0.270354 | -2.610423 | -0.404369 |
| 6 | -1.543900 | -1.029626 | -1.309910 |
| 1 | -2.228903 | -1.548571 | -1.991138 |
| 6 | -2.264971 | -0.888550 | 0.017158 |
| 8 | -2.379543 | 0.136402 | 0.667448 |
| 8 | -2.798695 | -2.064397 | 0.416902 |
| 6 | -3.492584 | -2.056087 | 1.677685 |
| 1 | -4.329088 | -1.352418 | 1.649094 |
| 1 | -3.851883 | -3.076349 | 1.815727 |
| 1 | -2.811437 | -1.775373 | 2.485688 |

**4.18. Standard coordinate and geometry of γ-TS1:**

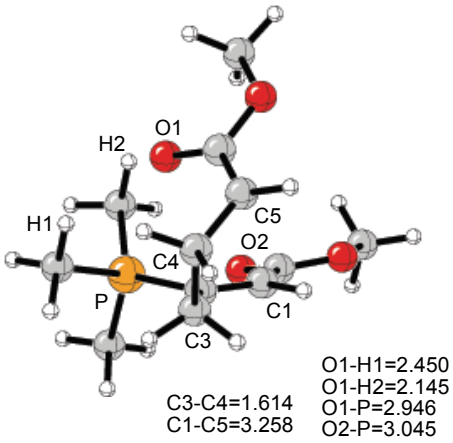
| | | | |
|---|---|---|---|
| 6 | 0.526638 | -1.108931 | 0.679254 |
| 6 | 0.661895 | -1.442616 | 2.032742 |
| 1 | 1.673230 | -1.504690 | 2.418840 |
| 1 | -0.063268 | -2.059369 | 2.546648 |
| 6 | 1.492694 | -0.350377 | 0.008031 |
| 1 | 2.337782 | 0.037301 | 0.558327 |
| 6 | 1.523898 | -0.255014 | -1.405085 |
| 8 | 0.733885 | -0.831901 | -2.207178 |
| 8 | 2.555310 | 0.538696 | -1.886724 |
| 6 | 2.632673 | 0.624931 | -3.351533 |
| 1 | 3.536689 | 1.200911 | -3.546754 |
| 1 | 2.696137 | -0.369551 | -3.801148 |
| 1 | 1.755322 | 1.133430 | -3.762031 |
| 15 | -1.021666 | -1.569246 | -0.145357 |
| 6 | -0.794877 | -3.139853 | -1.034932 |
| 1 | -0.098453 | -2.935578 | -1.852055 |
| 1 | -0.372212 | -3.892293 | -0.361300 |
| 1 | -1.750096 | -3.500093 | -1.433272 |
| 6 | -1.878873 | -0.399840 | -1.240286 |
| 1 | -2.033810 | 0.510751 | -0.654295 |
| 1 | -1.254302 | -0.213843 | -2.112739 |
| 1 | -2.839801 | -0.840778 | -1.532641 |
| 6 | -2.263994 | -1.870138 | 1.154089 |
| 1 | -1.958743 | -2.646304 | 1.859413 |
| 1 | -2.402874 | -0.914709 | 1.671257 |
| 1 | -3.206661 | -2.173155 | 0.684937 |
| 6 | 0.317379 | 0.420338 | 3.157375 |



| | | | |
|---|---|---|---|
| 1 | -0.714142 | 0.114683 | 3.282553 |
| 1 | 0.991595 | 0.163361 | 3.966894 |
| 6 | 0.573817 | 1.512143 | 2.362522 |
| 1 | 1.501332 | 2.064931 | 2.381310 |
| 6 | -0.415699 | 1.884728 | 1.402144 |
| 8 | -1.474991 | 1.250014 | 1.153679 |
| 8 | -0.112498 | 3.072398 | 0.748992 |
| 6 | -1.074545 | 3.503068 | -0.271141 |
| 1 | -2.100467 | 3.410682 | 0.094105 |
| 1 | -0.823372 | 4.543933 | -0.474838 |
| 1 | -0.968568 | 2.904776 | -1.182107 |

**4.19. Standard coordinate and geometry of γ-IN1:**

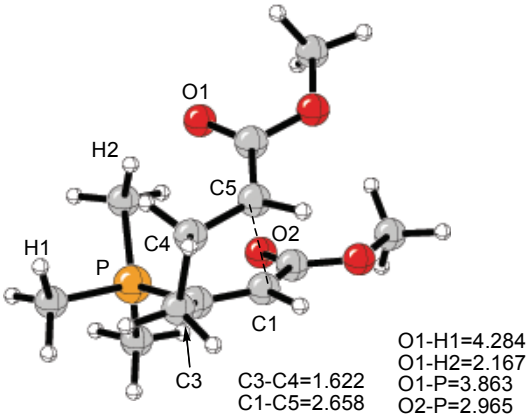
| | | | |
|---|---|---|---|
| 6 | -0.129563 | 0.791966 | -1.008397 |
| 6 | -1.258756 | 0.788956 | -1.995330 |
| 1 | -0.819535 | 0.595477 | -2.979303 |
| 1 | -1.758305 | 1.761870 | -2.061808 |
| 6 | 0.911876 | -0.057154 | -1.249904 |
| 1 | 0.862494 | -0.678114 | -2.138856 |
| 6 | 2.143406 | -0.163805 | -0.475901 |
| 8 | 2.503099 | 0.609707 | 0.411213 |
| 8 | 2.904852 | -1.203097 | -0.885000 |
| 6 | 4.159911 | -1.378680 | -0.208907 |
| 1 | 4.618964 | -2.249816 | -0.677245 |
| 1 | 4.791270 | -0.494429 | -0.335219 |
| 1 | 3.998067 | -1.557392 | 0.857819 |
| 15 | -0.288768 | 1.823631 | 0.477542 |
| 6 | 0.708061 | 3.345079 | 0.232705 |
| 1 | 1.765002 | 3.070428 | 0.187882 |
| 1 | 0.419351 | 3.834974 | -0.702274 |
| 1 | 0.545273 | 4.037096 | 1.066384 |
| 6 | 0.145366 | 1.188596 | 2.132581 |
| 1 | -0.461042 | 0.298294 | 2.310230 |
| 1 | 1.207962 | 0.954995 | 2.181583 |
| 1 | -0.098517 | 1.977817 | 2.854026 |
| 6 | -2.021706 | 2.374162 | 0.627019 |
| 1 | -2.355465 | 2.915930 | -0.260925 |
| 1 | -2.641559 | 1.487492 | 0.785770 |
| 1 | -2.098127 | 3.039236 | 1.493484 |
| 6 | -2.400865 | -0.327791 | -1.766505 |
| 1 | -3.112395 | 0.112188 | -1.056527 |
| 1 | -2.908863 | -0.410932 | -2.735038 |
| 6 | -1.935655 | -1.643546 | -1.283287 |
| 1 | -1.834417 | -2.499263 | -1.940993 |
| 6 | -1.624261 | -1.735250 | 0.066343 |



| | | | |
|---|---|---|---|
| 8 | -1.656756 | -0.754966 | 0.874359 |
| 8 | -1.248955 | -2.990223 | 0.523416 |
| 6 | -0.918242 | -3.089120 | 1.901172 |
| 1 | -1.738755 | -2.741770 | 2.539625 |
| 1 | -0.728153 | -4.150174 | 2.083627 |
| 1 | -0.017098 | -2.510233 | 2.143181 |

**4.20. Standard coordinate and geometry of γ-TS2:**

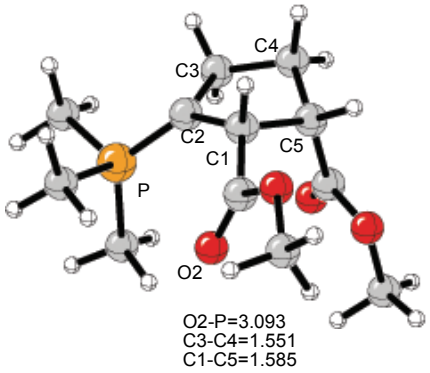
| | | | |
|---|---|---|---|
| 6 | -1.106371 | -0.128941 | -1.018337 |
| 6 | -1.360818 | -1.365272 | -1.830305 |
| 1 | -1.459518 | -1.075243 | -2.882766 |
| 1 | -2.245910 | -1.935795 | -1.549768 |
| 6 | 0.034263 | 0.513593 | -1.449292 |
| 1 | 0.368138 | 0.400222 | -2.469711 |
| 6 | 0.749093 | 1.489658 | -0.655598 |
| 8 | 0.395402 | 1.898515 | 0.468505 |
| 8 | 1.889549 | 1.920391 | -1.282376 |
| 6 | 2.847124 | 2.665048 | -0.442415 |
| 1 | 3.444035 | 3.258441 | -1.133680 |
| 1 | 2.315202 | 3.294323 | 0.273206 |
| 1 | 3.467681 | 1.937468 | 0.086194 |
| 15 | -1.849702 | 0.087462 | 0.585933 |
| 6 | -2.919219 | 1.566136 | 0.431147 |
| 1 | -2.259083 | 2.434729 | 0.330550 |
| 1 | -3.546060 | 1.488867 | -0.462159 |
| 1 | -3.551103 | 1.697233 | 1.316876 |
| 6 | -1.158541 | 0.303119 | 2.272020 |
| 1 | -0.545181 | -0.568815 | 2.489109 |
| 1 | -0.545603 | 1.201524 | 2.293319 |
| 1 | -2.004063 | 0.394834 | 2.965132 |
| 6 | -2.970482 | -1.329566 | 0.825440 |
| 1 | -3.665498 | -1.451597 | -0.008773 |
| 1 | -2.343775 | -2.222551 | 0.922261 |
| 1 | -3.543910 | -1.190315 | 1.747702 |
| 6 | -0.040567 | -2.350142 | -1.746158 |
| 1 | -0.305657 | -3.104247 | -0.999059 |
| 1 | 0.068871 | -2.826393 | -2.724503 |
| 6 | 1.190506 | -1.642201 | -1.321915 |
| 1 | 2.031982 | -1.454011 | -1.970274 |
| 6 | 1.264519 | -1.376836 | 0.044441 |
| 8 | 0.310151 | -1.604708 | 0.858532 |
| 8 | 2.442645 | -0.727757 | 0.472822 |
| 6 | 2.499518 | -0.421133 | 1.907058 |
| 1 | 3.557764 | -0.266049 | 2.126207 |
| 1 | 1.930239 | 0.487749 | 2.119804 |



| | | | |
|---|---|---|---|
| 1 | 2.100860 | -1.244602 | 2.504953 |

**4.21. Standard coordinate and geometry of γ-IN2:**

| | | | |
|---|---|---|---|
| 6 | -1.053591 | -0.468799 | -0.662730 |
| 6 | -1.144608 | -1.933575 | -1.160013 |
| 1 | -2.009586 | -2.128570 | -1.786835 |
| 1 | -1.147918 | -2.657456 | -0.352235 |
| 6 | 0.171799 | 0.153881 | -1.302806 |
| 1 | -0.014801 | 0.522206 | -2.312854 |
| 6 | 0.796415 | 1.308006 | -0.586883 |
| 8 | 0.345475 | 1.889364 | 0.377342 |
| 8 | 1.905177 | 1.733458 | -1.218665 |
| 6 | 2.679499 | 2.794854 | -0.605789 |
| 1 | 3.482415 | 2.996263 | -1.293905 |
| 1 | 2.069407 | 3.672558 | -0.458106 |
| 1 | 3.066582 | 2.463091 | 0.345422 |
| 15 | -2.055974 | 0.162100 | 0.510930 |
| 6 | -2.752434 | 1.812504 | 0.200012 |
| 1 | -1.951177 | 2.537955 | 0.170582 |
| 1 | -3.266596 | 1.811398 | -0.754663 |
| 1 | -3.451570 | 2.093949 | 0.981758 |
| 6 | -1.516205 | 0.279915 | 2.256370 |
| 1 | -1.207765 | -0.703547 | 2.598688 |
| 1 | -0.671108 | 0.951715 | 2.313483 |
| 1 | -2.310692 | 0.642451 | 2.903062 |
| 6 | -3.508566 | -0.920242 | 0.645900 |
| 1 | -4.014530 | -0.985655 | -0.309889 |
| 1 | -3.211785 | -1.919116 | 0.945001 |
| 1 | -4.201365 | -0.533834 | 1.385970 |
| 6 | 0.160253 | -2.129259 | -1.999161 |
| 1 | 0.562186 | -3.125565 | -1.893175 |
| 1 | -0.035348 | -1.931277 | -3.045877 |
| 6 | 1.117481 | -1.061100 | -1.456020 |
| 1 | 1.966230 | -0.843932 | -2.091276 |
| 6 | 1.603349 | -1.501476 | -0.099222 |
| 8 | 1.544530 | -2.610785 | 0.365224 |
| 8 | 2.172278 | -0.478649 | 0.586169 |
| 6 | 2.645546 | -0.743000 | 1.932912 |
| 1 | 3.009339 | 0.201600 | 2.298500 |
| 1 | 1.837332 | -1.105734 | 2.548744 |
| 1 | 3.434561 | -1.478949 | 1.912987 |



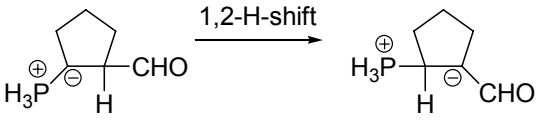
## 5. Tables of the Computed Energies, and Other Thermodynamic and Dynamic Parameters

**Table S1**.

| | $E_0$ | $H_{298}$ | $G_{298}$ | E | $G_s$ |
|---|---|---|---|---|---|
| **1** | -344.452669 | -344.444080 | -344.484881 | -344.5522379 | -344.547801 |
| **2** | -306.387307 | -306.379724 | -306.417722 | -306.4828479 | -306.479295 |
| **$P(CH_3)_3$** | -460.991549 | -460.983860 | -461.020947 | -461.1045377 | -461.098449 |
| **3** | -805.445884 | -805.430247 | -805.487499 | -805.6625508 | -805.654828 |
| **TS1** | -1111.825730 | -1111.803568 | -1111.874865 | -1112.1406334 | -1112.130713 |
| **IN1** | -1111.828366 | -1111.806079 | -1111.877653 | -1112.1447502 | -1112.137153 |
| **TS2** | -1111.825542 | -1111.804132 | -1111.873628 | -1112.1421321 | -1112.132818 |
| **IN2** | -1111.853634 | -1111.831966 | -1111.904043 | -1112.1730883 | -1112.161027 |
| **$H_2O$** | -76.401477 | -76.397698 | -76.419138 | -76.4225723 | -76.428114 |
| **4** | -1188.267271 | -1188.242425 | -1188.322123 | -1188.6104619 | -1188.598672 |
| **TS3** | -1188.260059 | -1188.235846 | -1188.316378 | -1188.5993233 | -1188.592728 |
| **5** | -1188.271926 | -1188.248730 | -1188.324880 | -1188.6189427 | -1188.610886 |
| **TS4** | -1188.258269 | -1188.234675 | -1188.310266 | -1188.5983769 | -1188.592672 |
| **6** | -1188.270258 | -1188.245629 | -1188.323827 | -1188.6140523 | -1188.603158 |
| **IN3** | -1111.863428 | -1111.841743 | -1111.912650 | -1112.1821417 | -1112.174055 |
| **TS5** | -1111.863191 | -1111.841676 | -1111.912668 | -1112.1809333 | -1112.171308 |
| **7** | -650.905011 | -650.890590 | -650.947189 | -651.1084185 | -651.103487 |
| **TS(**1,2-H-shift**)** | -1111.792211 | -1111.770760 | -1111.841389 | -1112.1068985 | -1112.094364 |
| **γ-TS1** | -1111.823436 | -1111.801146 | -1111.873854 | -1112.1380974 | -1112.127243 |
| **γ-IN1** | -1111.830599 | -1111.808464 | -1111.880033 | -1112.147683 | -1112.139215 |
| **γ-TS2** | -1111.828920 | -1111.807519 | -1111.877329 | -1112.1458874 | -1112.137094 |
| **γ-IN2** | -1111.850087 | -1111.828336 | -1111.899814 | -1112.1692102 | -1112.156971 |

$E_0$: Sum of electronic and zero-point energies
$H_{298}$: Sum of electronic and thermal enthalpies
$G_{298}$: Sum of electronic and thermal free energies
E: Electronic energies
$G_s$: Total free energy in solution

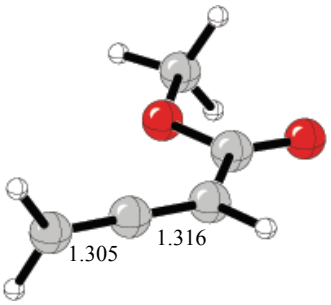
**Table S2**. In order to investigate the Hydrogen tunneling effect in the direct proton shift process converting **IN2** to **IN3**, dynamic parameters were calculated at the temperature of 298 K by using B3LYP/6-31G* method for the model reaction shown below.[10-13] The tunneling effect correction for this model reaction is only 0.0002 kcal/mol, suggesting that the tunneling effect in the direct proton shift process converting **IN2** to **IN3** is almost negligible. Similar negligible tunneling effect was also found by Doering (see. Doering, W. von E.; Zhao, X. *J. Am. Chem. Soc.* **2004**, *126*, 10028).



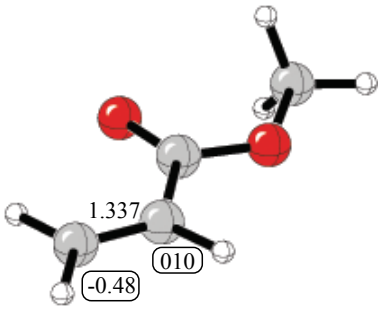

| | CVT | CVT+SCT |
|---|---|---|
| Rate Constants (sˆ-1) | 1.3686E-14 | 1.3684E-14 |
| Activation Energies (kcal/mol) | 35.6518 | 35.6516 |

## 6. Computed Structures of the Stationary Points in Figure 1

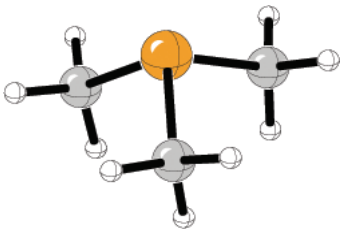
**Figure S1**



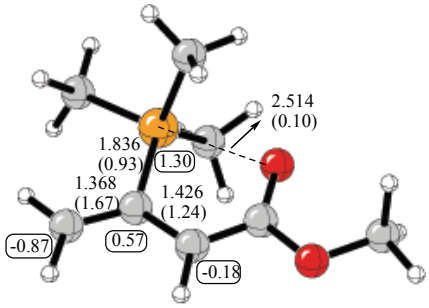

**1**



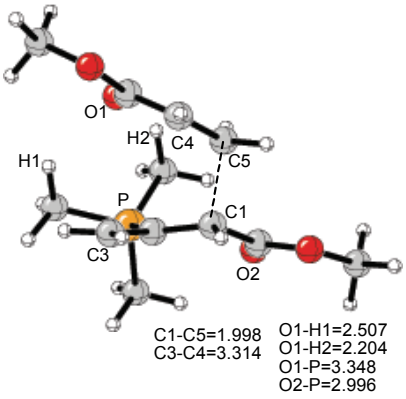

**2**



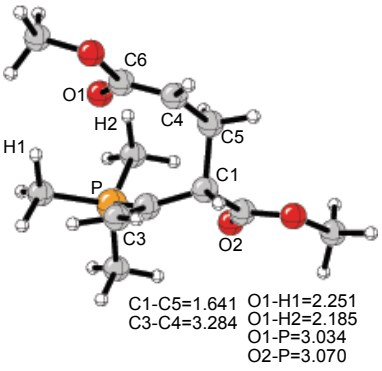
**$P(CH_3)_3$**



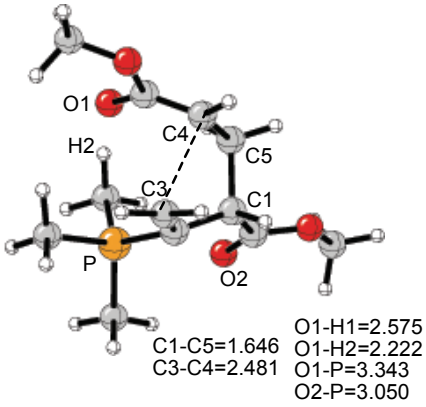

**3**



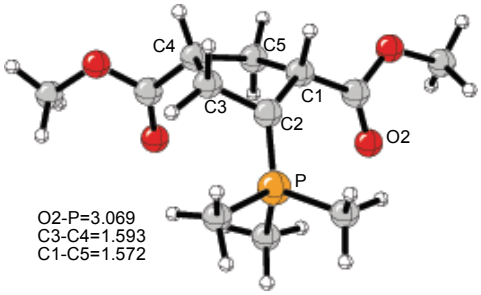

**TS1**



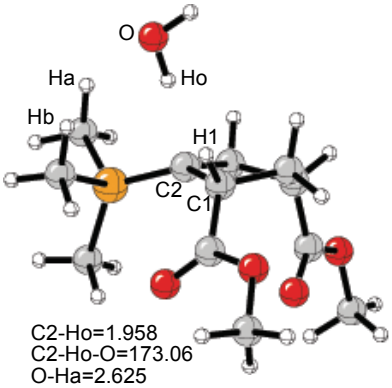

**IN1**




**TS2**

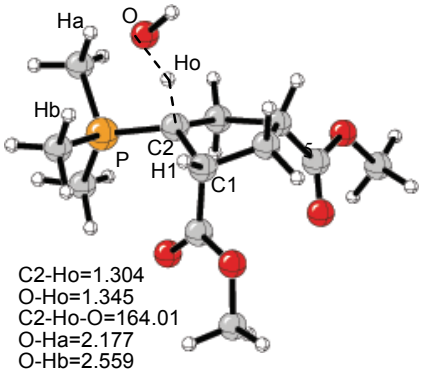



**IN2**



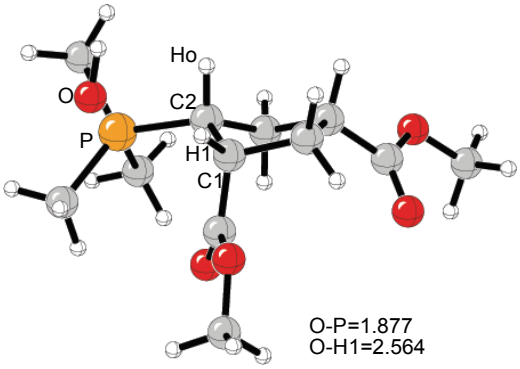

C2-Ho=1.958
C2-Ho-O=173.06
O-Ha=2.625
O-Hb=2.823

**4**



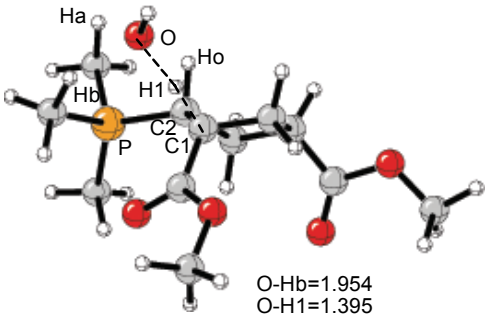

C2-Ho=1.304
O-Ho=1.345
C2-Ho-O=164.01
O-Ha=2.177
O-Hb=2.559
O-P=3.124

**TS3**



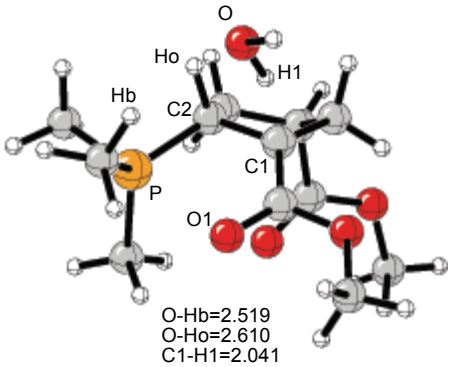

O-P=1.877
O-H1=2.564

**5**



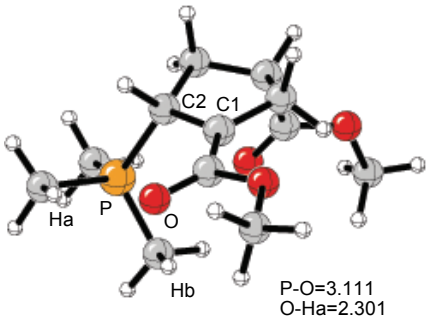

O-Hb=1.954
O-H1=1.395
C1-H1=1.269
O-H1-C1=156.09

**TS4**



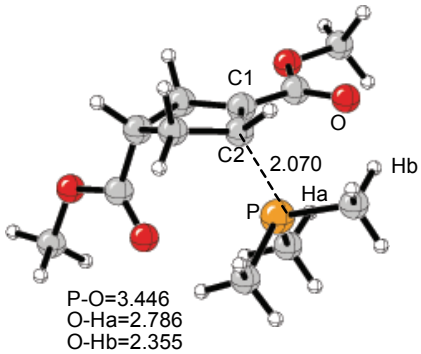

O-Hb=2.519
O-Ho=2.610
C1-H1=2.041
O1-P=2.576
C1-H1-O=159.07

**6**



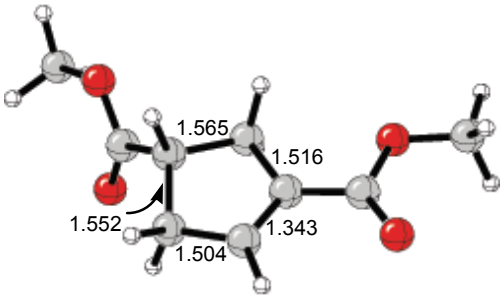

P-O=3.111
O-Ha=2.301
O-Hb=2.399
P-C2=1.908
C2-C1=1.492

**IN3**




P-O=3.446
O-Ha=2.786
O-Hb=2.355
C1-C2=1.446

**TS5**

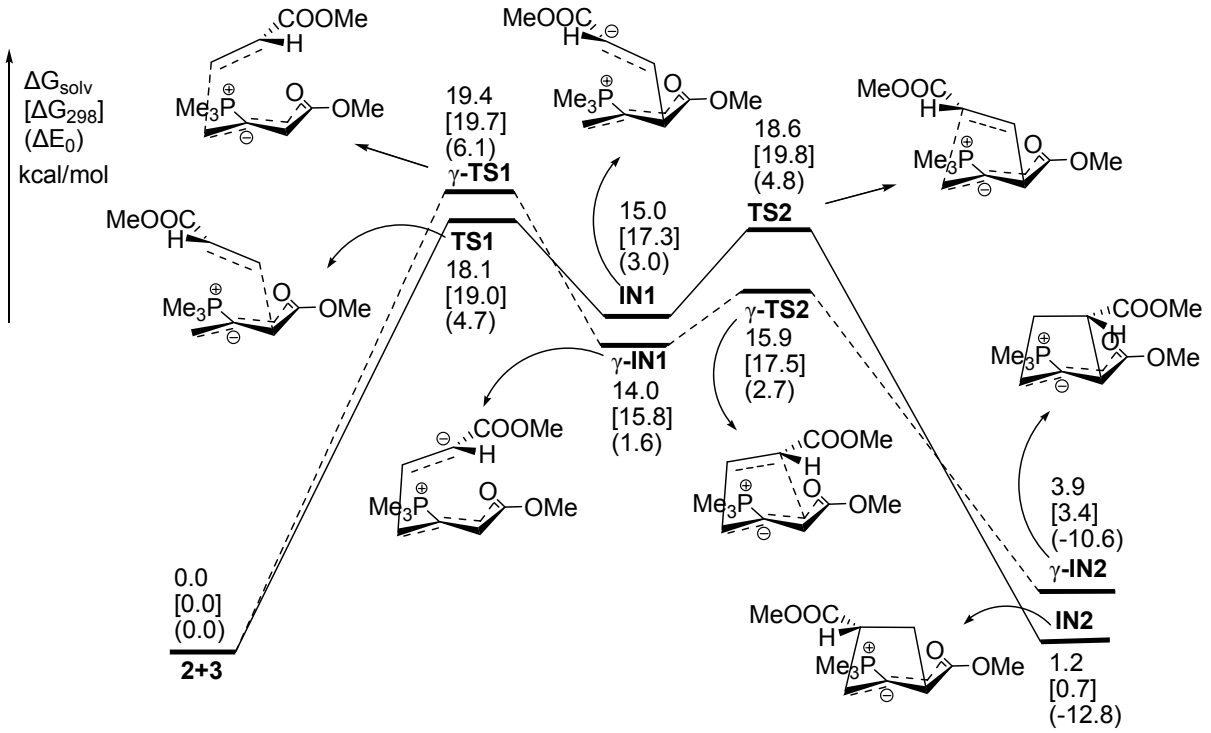



**7**

## 7. Comparison of Energy Surfaces for the Regiochemistry

As shown in Figure S2, for α-addition, the cyclization step (**TS2**) is the rate-determining step with an energy barrier of 18.6 kcal/mol starting from **2** and **3**. While for *γ*-addition, the first transition state (*γ*-**TS1**) is higher in energy than the second one (*γ*-**TS2**), and the activation barrier for this pathway is 19.4 kcal/mol. Thus the formation of the **IN2** through α-addition is more energetically favorable.

**Figure S2.**



## 8. Discussion of the Disfavored Intermolecular H-Shift Processes between two IN2 Molecules

The possibilities of intermolecular H-shift between two molecules of **IN2** have also been considered, however, much higher activation barriers were required for these pathways. Figure S3 shows the calculated potential energy surface at B3LYP/6-31+G*//B3LYP/3-21G* level for pathway 1, which is a stepwise H-donation and H-abstraction process and gives two **IN3** as the products. The activation barrier is 25.1 kcal/mol in terms of Δ*E* (electronic energy in the gas phase without ZPE correction), which is much higher than the water-assisted H-shift pathway. It's reasonable to consider that the barrier of this pathway will be much higher in terms of activation free energies. Figure S4 shows the calculated potential energy surface for pathway 2, which will generate one **IN3** and another **IN2** from the intermolecular H-exchange between two **IN2**, and the activation energy is calculated to be as high as 25.6 kcal/mol in terms of Δ*E* at B3LYP/6-31+G*//B3LYP/3-21G* level. Both on these results, we can rule out the possibilities of intermolecular proton shift between two **IN2** molecules.

**Figure S3**. The B3LYP/6-31+G*//B3LYP/3-21G* energies for the intermolecular H-exchange between two molecules of **IN2** to generate two molecules of **IN3** (pathway 1).

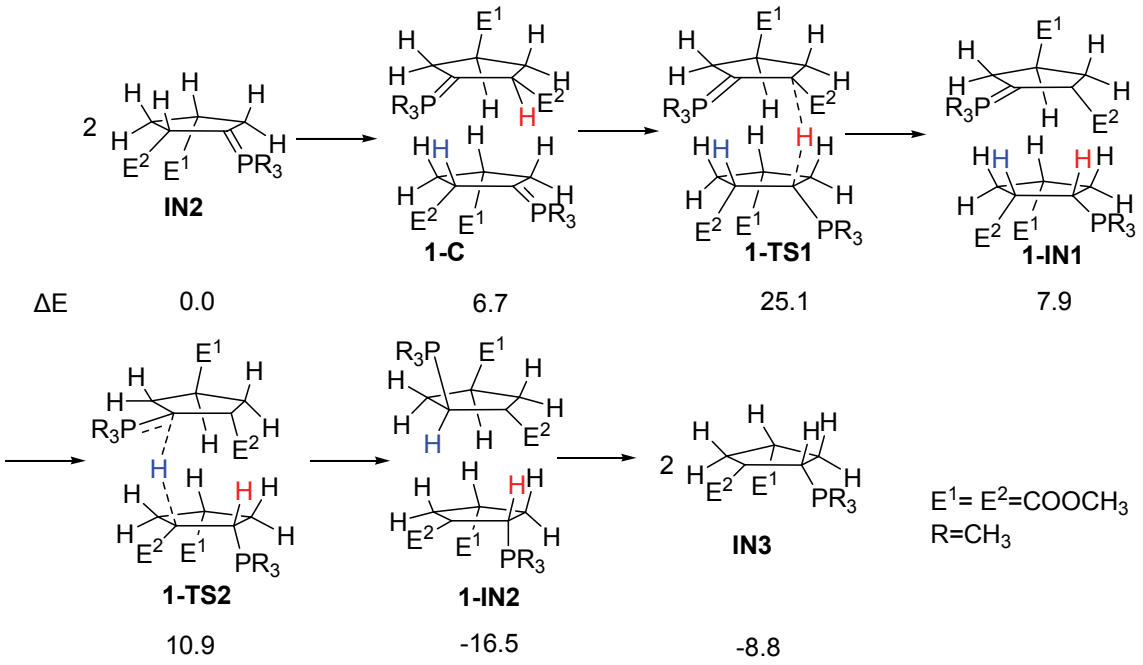


**Figure S4**. The B3LYP/6-31+G*//B3LYP/3-21G* energies for the intermolecular H-exchange between two molecules of **IN2** to generate one **IN3** and another **IN2** (pathway 2).