

*Supporting Information for*

**A Crossed Molecular Beam and Ab-Initio Investigation on the Exclusive Methyl  
Loss Pathway in the Gas Phase Reaction of Boron Monoxide (BO; X<sup>2</sup>Σ<sup>+</sup>) with  
Dimethylacetylene (CH<sub>3</sub>CCCH<sub>3</sub>; X<sup>1</sup>A<sub>1g</sub>)**

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**Table S1:** Cartesian coordinates of structures optimized at B3LYP/cc-pVTZ (except  
i1 at CCSD/6-31G and p2 at MP2/cc-pVTZ)

i1 ( <sup>2</sup> A, C <sub>1</sub> )				i2 ( <sup>2</sup> A, C <sub>1</sub> )			
	X	Y	Z		X	Y	Z
C	1.220257	0.122643	-0.000072	C	-0.89917	-0.63039	0.000149
C	0.3621	1.005184	0.0006	C	0.08214	0.246105	0.000065
C	2.40755	-0.77383	0.000587	C	-2.35614	-0.75149	-0.00005
C	-0.77751	1.95968	-0.0005	C	-0.10836	1.760964	-0.000034
H	2.980035	-0.66764	0.936788	H	-2.69988	-1.29926	0.879972
H	2.107646	-1.83094	-0.09566	H	-2.84765	0.229956	-0.00146
H	3.079496	-0.5344	-0.84002	H	-2.69941	-1.30133	-0.87902
H	-0.75082	2.603557	-0.89507	H	-1.16418	2.025666	0.000123
H	-1.73416	1.412063	0.002802	H	0.358556	2.206104	0.879737
H	-0.74783	2.60904	0.890015	H	0.358503	2.206084	-0.87985
B	-1.14071	-1.59189	-0.0038	B	1.490328	-0.33132	0.00005
O	-2.31315	-1.18929	0.002057	O	2.616444	-0.77021	-0.000066

**Table S1** (continued)

i3 ( <sup>2</sup> A, C <sub>1</sub> )				ts-i2i3 ( <sup>2</sup> A, C <sub>1</sub> )			
	X	Y	Z		X	Y	Z
C	1.075975	0.543067	0.000091	C	1.04018	-0.1599	0.004993
C	-0.24073	0.541252	-0.00015	C	-0.11683	0.44607	0.000221
C	2.230394	-0.35521	0.000014	C	2.33523	-0.80213	-0.0034
C	-1.09329	1.796683	0.000065	C	-0.32801	1.958935	-0.00146
H	1.923297	-1.40935	-0.00028	H	2.30854	-1.78349	-0.49167
H	2.854648	-0.18488	-0.87968	H	3.093718	-0.20136	-0.51997
H	2.854453	-0.1853	0.879923	H	2.682971	-0.95726	1.02097
H	-0.46323	2.68402	0.000107	H	0.627051	2.481008	-0.01369
H	-1.73908	1.827616	-0.87899	H	-0.90623	2.263851	-0.87535
H	-1.73891	1.82742	0.879252	H	-0.88478	2.268732	0.884627
B	-0.89911	-0.83343	-0.00036	B	-1.31691	-0.49776	0.000081
O	-1.37872	-1.94339	0.000164	O	-2.24002	-1.28007	-0.00093
ts-i3p1 ( <sup>2</sup> A, C <sub>1</sub> )				ts-i3p3 ( <sup>2</sup> A, C <sub>1</sub> )			
	X	Y	Z		X	Y	Z
C	-1.01768	-0.34169	0.00000	C	-1.21919	-0.42824	-0.00018
C	0.080903	0.368077	0.00000	C	-0.01085	-0.19249	-0.00127
C	-2.14076	-1.01055	0.00000	C	-2.66635	-0.43377	0.000042
C	0.086575	1.889358	0.00000	C	0.545516	1.986583	0.000436
H	-2.58265	-1.35862	0.92517	H	-3.05197	-0.95459	-0.87851
H	-3.68871	0.440318	0.00000	H	-3.05143	-0.94345	0.885345
H	-2.58265	-1.35862	-0.92517	H	-3.06846	0.584272	-0.00601
H	-0.92978	2.276577	0.00000	H	-0.42958	2.411819	-0.18411
H	0.606628	2.270233	0.879857	H	0.93937	2.086352	1.001568
H	0.606628	2.270233	-0.87986	H	1.256744	2.035062	-0.812
B	1.392428	-0.40212	0.00000	B	1.400266	-0.62754	-0.00025
O	2.444267	-0.99508	0.00000	O	2.563653	-0.95928	0.000099

**Table S1** (continued)

ts-rp2 ( ${}^2A, C_1$ )				p1 ( ${}^1A, C_1$ )			
	X	Y	Z		X	Y	Z
C	-1.96514	-0.0339	0.000031	C	1.126788	-0.27598	-0.00113
C	-0.93011	0.583756	0.000029	C	-0.00469	0.384413	-0.00055
C	0.320737	1.271657	0.000015	C	2.243048	-0.93792	0.000563
C	-3.22139	-0.76443	0.000003	C	-0.07971	1.902198	0.000476
H	0.508476	1.860117	0.897246	H	2.727638	-1.22593	-0.9246
H	0.508277	1.860433	-0.89705	H	0.91807	2.335765	0.001251
H	-3.04223	-1.84159	-0.00191	B	-1.27951	-0.44298	-0.0015
H	-3.81472	-0.5271	0.884601	O	-2.3066	-1.07848	0.000751
H	-3.81631	-0.52425	-0.88276	H	-0.61565	2.262078	-0.8789
B	2.604719	-0.40266	-0.00029	H	2.724008	-1.22623	0.927555
O	3.773065	-0.70191	0.000139	H	-0.61636	2.260721	0.879998
H	1.223814	0.45843	-0.00024				
p2 ( ${}^2A, C_1$ )				p3 ( ${}^1A_1, C_{3v}$ )			
	X	Y	Z		X	Y	Z
C	-0.50861	-0.00019	-0.00242	C	-1.1029	-0.00111	0.00049
C	0.690839	-0.00011	-0.00033	C	0.104101	0.000068	-0.00084
C	2.079731	0.00008	0.000754	C	-2.55124	0.000343	0.000112
C	-1.96297	0.000133	0.000073	H	-2.93705	-0.65286	-0.78422
H	2.624271	0.928514	0.000653	H	-2.93741	-0.35158	0.958112
H	2.624597	-0.92816	0.0006	H	-2.93527	1.006739	-0.17396
H	-2.34351	-0.01842	1.020372	B	1.572392	0.000427	-0.00031
H	-2.34955	0.891808	-0.48913	O	2.780998	-0.00003	0.000379
H	-2.34978	-0.87326	-0.52098				
BO ( ${}^2\Sigma^+, C_{\infty v}$ )				CH <sub>3</sub> CCCH <sub>3</sub> ( ${}^1A_{1g}, D_{3d}$ )			
	X	Y	Z		X	Y	Z
B	-1.1029	0.0000	-0.74025	C	0.0000	0.0000	0.600493
O	0.104101	0.0000	0.462655	C	0.0000	0.0000	-0.60049
				C	0.0000	0.0000	-2.0574
				C	0.0000	0.0000	2.057398
				H	0.0000	-1.01813	-2.45197
				H	-0.88173	0.509066	-2.45197
				H	0.881729	0.509066	-2.45197
				H	0.0000	1.018133	2.451971
				H	-0.88173	-0.50907	2.451971
				H	0.881729	-0.50907	2.451971

**Table S2:** Relative energies in  $\text{kJ mol}^{-1}$ . Geometries are optimized at B3LYP / cc-pVTZ (except i1 at CCSD/6-31G and p2 at MP2/cc-pVTZ)

Structures	Relative Energy (kJ/mol)	
	B3LYP / cc-pVTZ	CCSD(T)/ cc-pVTZ
BO+C <sub>4</sub> H <sub>6</sub>	0.0	0.0
i1	-	-13.3
i2	-185.4	-179.2
i3	-189.7	-184.1
ts-i2i3	-171.7	-158.8
ts-i3p1	-28.4	-15.4
ts-rp2	-7.8	13.8
ts-i3p3	-77.2	-59.2
p1	-34.4	-29.2
p2	-	-73.0
p3	-121.5	-105.3

**Table S3:** Vibrational frequencies ( $\text{cm}^{-1}$ ) and infrared intensities ( $\text{km mol}^{-1}$ ) of the optimized structures of the  $\text{BOC}_4\text{H}_6$  PES calculated at B3LYP / cc-pVTZ (except i1 at CCSD/6-31G and p2 at MP2/cc-pVTZ)

$\text{BO } (^2\Sigma^+, C_{\infty v})$					
Normal modes	symmetry	Vibration mode	Frequency( $\text{cm}^{-1}$ )	Rel. inty	Inty ( $\text{km/mol}$ )
$\nu_1$	$\Sigma$	BO stretching	1918.8777	1.0000	42.2019
$\text{CH}_3\text{CCCH}_3 (^1\text{A}_{1g}, \text{D}_{3d})$					
Normal modes	symmetry	Vibration mode	Frequency( $\text{cm}^{-1}$ )	Rel. inty	Inty ( $\text{km/mol}$ )
$\nu_1$	$\text{A}_{1u}$	$\text{CH}_3$ rock + $\text{CH}_3$ rock	40.5229	0.0000	0.0000
$\nu_2$	$\text{E}_u$	CCCC wagging	203.0533	0.1783	11.5784
$\nu_3$	$\text{E}_u$	CCCC wagging	203.0557	0.1783	11.5789
$\nu_4$	$\text{E}_g$	CC twist	396.8454	0.0000	0.0000
$\nu_5$	$\text{E}_g$	CC twist	396.8464	0.0000	0.0000
$\nu_6$	$\text{A}_{1g}$	$\text{CH}_3(\text{CC})\text{CH}_3$ sym. str.	723.5814	0.0000	0.0000
$\nu_7$	$\text{E}_u$	HCH wagging	1054.6237	0.0284	1.8428
$\nu_8$	$\text{E}_u$	HCH twist	1054.6249	0.0284	1.8429
$\nu_9$	$\text{E}_g$	HCH wagging	1061.0520	0.0000	0.0000
$\nu_{10}$	$\text{E}_g$	HCH twist	1061.0530	0.0000	0.0000
$\nu_{11}$	$\text{A}_{2u}$	$\text{CH}_3(\text{CC})\text{CH}_3$ asym. str.	1166.2010	0.0003	0.0197
$\nu_{12}$	$\text{A}_{2u}$	$\text{CH}_3$ wagging	1417.8460	0.0577	3.7473
$\nu_{13}$	$\text{A}_{1g}$	$\text{CH}_3$ wagging	1421.3228	0.0000	0.0000
$\nu_{14}$	$\text{E}_g$	HCH scissor	1481.6328	0.0000	0.0000
$\nu_{15}$	$\text{E}_g$	HCH scissor	1481.6329	0.0000	0.0000
$\nu_{16}$	$\text{E}_u$	HCH scissor + CH rock	1481.9192	0.2105	13.6733
$\nu_{17}$	$\text{E}_u$	HCH scissor	1481.9193	0.2105	13.6755
$\nu_{18}$	$\text{A}_{1g}$	CC str.	2363.3183	0.0000	0.0000
$\nu_{19}$	$\text{A}_{1g}$	$\text{CH}_3$ sym. str.	3020.2634	0.0000	0.0000
$\nu_{20}$	$\text{A}_{2u}$	$\text{CH}_3$ sym. str.	3020.6426	1.0000	64.9548
$\nu_{21}$	$\text{E}_g$	HCH asym. str.	3073.1486	0.0000	0.0000
$\nu_{22}$	$\text{E}_g$	CH str. + HCH sym. str.	3073.1487	0.0000	0.0000
$\nu_{23}$	$\text{E}_u$	HCH asym. str.	3073.7004	0.3718	24.1506
$\nu_{24}$	$\text{E}_u$	CH str. + HCH sym. str.	3073.7005	0.3717	24.1450

**Table S3** (continued)

$i1 (^2A, C_1)$					
Normal modes	symmetry	Vibration mode	Frequency( $\text{cm}^{-1}$ )	Rel. inty	Inty (km/mol)
v <sub>1</sub>	A	CH <sub>3</sub> rock	17.1634	0.0039	0.2137
v <sub>2</sub>	A	CH <sub>3</sub> rock	64.7128	0.1967	10.7718
v <sub>3</sub>	A	BC scissor	70.9337	0.1356	7.4249
v <sub>4</sub>	A	OCH <sub>3</sub> scissor	92.6053	0.0284	1.5559
v <sub>5</sub>	A	CH <sub>3</sub> rock	98.5337	0.0722	3.9511
v <sub>6</sub>	A	BCH <sub>3</sub> scissor	160.5569	1.0000	54.7581
v <sub>7</sub>	A	CH <sub>3</sub> (CC)CH <sub>3</sub> wagging	185.7839	0.1805	9.8860
v <sub>8</sub>	A	H(CH <sub>2</sub> CCCH <sub>2</sub> )H scissor	211.9439	0.4236	23.1962
v <sub>9</sub>	A	CCCH <sub>3</sub> wagging	214.1076	0.0942	5.1561
v <sub>10</sub>	A	HCCC scissor	373.0468	0.0035	0.1929
v <sub>11</sub>	A	CH <sub>3</sub> (CC)CH <sub>3</sub> sym. str.	714.2485	0.0193	1.0577
v <sub>12</sub>	A	CH <sub>3</sub> twist. + CH <sub>3</sub> twist.	1071.2102	0.0046	0.2542
v <sub>13</sub>	A	CH <sub>3</sub> wagging	1083.4200	0.0252	1.3824
v <sub>14</sub>	A	CH <sub>3</sub> twist. + CH <sub>3</sub> twist.	1109.1477	0.0272	1.4870
v <sub>15</sub>	A	H(CH <sub>2</sub> CCCH <sub>2</sub> )H scissor	1111.4453	0.0196	1.0742
v <sub>16</sub>	A	CH <sub>3</sub> (CC)CH <sub>3</sub> asym. str.	1147.7702	0.1060	5.8026
v <sub>17</sub>	A	(CH <sub>3</sub> + CH <sub>3</sub> ) wagging	1474.7202	0.0098	0.5384
v <sub>18</sub>	A	(CH <sub>3</sub> + CH <sub>3</sub> ) wagging	1481.3472	0.0157	0.8596
v <sub>19</sub>	A	HCH scissor	1538.4540	0.0747	4.0881
v <sub>20</sub>	A	HCH scissor	1539.7978	0.1318	7.2164
v <sub>21</sub>	A	HCH scissor	1540.3557	0.0961	5.2640
v <sub>22</sub>	A	HCH scissor	1542.6360	0.1882	10.3039
v <sub>23</sub>	A	BO str.	1766.6075	0.8046	44.0572
v <sub>24</sub>	A	CC str.	2313.7119	0.1879	10.2908
v <sub>25</sub>	A	CH <sub>3</sub> sym. str.	3010.8154	0.4772	26.1315
v <sub>26</sub>	A	CH <sub>3</sub> sym. str.	3013.9735	0.4056	22.2080
v <sub>27</sub>	A	CH str. + HCH sym. str.	3073.5749	0.2811	15.3903
v <sub>28</sub>	A	HCH asym. str.	3078.7861	0.3195	17.4969
v <sub>29</sub>	A	HCH asym. str.	3082.0027	0.2946	16.1307
v <sub>30</sub>	A	CH str. + HCH sym. str.	3089.3556	0.1112	6.0878

**Table S3** (continued)

$i_2 (^2A, C_1)$					
Normal modes	symmetry	Vibration mode	Frequency( $\text{cm}^{-1}$ )	Rel. inty	Inty (km/mol)
v <sub>1</sub>	A	CH <sub>3</sub> rock	105.5143	0.0015	0.4884
v <sub>2</sub>	A	O(BCC)C scissor	116.1540	0.0059	1.8998
v <sub>3</sub>	A	CH <sub>3</sub> rock	139.9685	0.0006	0.2023
v <sub>4</sub>	A	CH <sub>3</sub> (CC)CH <sub>3</sub> wagging	160.9345	0.0000	0.0018
v <sub>5</sub>	A	CH <sub>3</sub> (CC)CH <sub>3</sub> scissor	209.1200	0.0119	3.8393
v <sub>6</sub>	A	CCC wagging	376.4533	0.0429	13.8385
v <sub>7</sub>	A	CCCH <sub>3</sub> scissor	431.0395	0.0127	4.1013
v <sub>8</sub>	A	B scissor	536.4192	0.0709	22.8538
v <sub>9</sub>	A	OBC wagging	554.7162	0.0688	22.1636
v <sub>10</sub>	A	HCCC scissor	677.2960	0.0107	3.4408
v <sub>11</sub>	A	CH rock + CH <sub>2</sub> wagging	932.0906	0.0126	4.0574
v <sub>12</sub>	A	CH <sub>2</sub> (CC)CH <sub>2</sub> twist.	1017.4145	0.0006	0.1924
v <sub>13</sub>	A	CH rock + CH <sub>2</sub> wagging	1017.5385	0.0070	2.2400
v <sub>14</sub>	A	CH <sub>2</sub> (CC)CH <sub>2</sub> twist.	1046.2926	0.0006	0.1928
v <sub>15</sub>	A	H(H <sub>2</sub> CCCH <sub>2</sub> )H scissor	1061.5672	0.0201	6.4687
v <sub>16</sub>	A	HCC scissor	1158.1723	0.0006	0.2021
v <sub>17</sub>	A	CH <sub>3</sub> wagging	1390.0675	0.0018	0.5744
v <sub>18</sub>	A	CH <sub>3</sub> wagging	1405.0660	0.0056	1.8091
v <sub>19</sub>	A	CH rock + HCH scissor	1452.3252	0.0243	7.8197
v <sub>20</sub>	A	HCH scissor	1463.1309	0.0441	14.1984
v <sub>21</sub>	A	CH rock + HCH scissor	1483.5610	0.0205	6.5918
v <sub>22</sub>	A	HCH scissor	1491.6091	0.0170	5.4804
v <sub>23</sub>	A	CC str.	1730.7026	0.1253	40.3602
v <sub>24</sub>	A	OBC asym. str.	2006.6654	1.0000	322.2296
v <sub>25</sub>	A	CH str. + HCH sym. str.	2973.5426	0.0479	15.4232
v <sub>26</sub>	A	CH <sub>3</sub> sym. str.	3032.3473	0.0530	17.0764
v <sub>27</sub>	A	CH str. + HCH sym. str.	3053.2117	0.0222	7.1584
v <sub>28</sub>	A	HCH asym. str.	3076.3089	0.0123	3.9735
v <sub>29</sub>	A	HCH asym. str.	3087.1970	0.0329	10.6064
v <sub>30</sub>	A	CH str. + HCH sym. str.	3114.0008	0.0431	13.8784

**Table S3** (continued)

$i3 (^2A, C_1)$					
Normal modes	symmetry	Vibration mode	Frequency( $\text{cm}^{-1}$ )	Rel. inty	Inty (km/mol)
v <sub>1</sub>	A	O(BCCC)H scissor	104.2153	0.0259	6.5615
v <sub>2</sub>	A	CH <sub>3</sub> (CC)CH <sub>3</sub> rock	136.8277	0.0049	1.2306
v <sub>3</sub>	A	CH <sub>3</sub> (CC)CH <sub>3</sub> rock	139.5327	0.0004	0.1088
v <sub>4</sub>	A	CH <sub>3</sub> (CC)CH <sub>3</sub> wagging	219.9955	0.0019	0.4833
v <sub>5</sub>	A	C(CC)C scissor	226.2133	0.0113	2.8497
v <sub>6</sub>	A	CCC wagging	296.4432	0.0633	16.0197
v <sub>7</sub>	A	B(CCC)H scissor	412.5232	0.0094	2.3788
v <sub>8</sub>	A	OBC wagging	563.7091	0.0692	17.5197
v <sub>9</sub>	A	B scissor	570.5060	0.0900	22.7815
v <sub>10</sub>	A	BC str.	647.5235	0.0071	1.8014
v <sub>11</sub>	A	CH rock + CH <sub>2</sub> wagging	916.8875	0.0041	1.0290
v <sub>12</sub>	A	HCH twist. + HCH twist.	1024.6998	0.0031	0.7914
v <sub>13</sub>	A	CH rock + CH <sub>2</sub> wagging	1043.3444	0.0037	0.9319
v <sub>14</sub>	A	HCH twist. + HCH twist.	1060.2710	0.0007	0.1657
v <sub>15</sub>	A	C(CC)C asym. str.	1086.0108	0.0281	7.1027
v <sub>16</sub>	A	HCC scissor	1163.3009	0.0032	0.8167
v <sub>17</sub>	A	CH <sub>3</sub> wagging	1401.6374	0.0139	3.5069
v <sub>18</sub>	A	CH <sub>3</sub> wagging	1408.4352	0.0024	0.5950
v <sub>19</sub>	A	CH rock + HCH scissor	1451.2435	0.0328	8.3040
v <sub>20</sub>	A	HCH scissor	1466.3204	0.0558	14.1316
v <sub>21</sub>	A	HCH scissor	1485.9839	0.0275	6.9496
v <sub>22</sub>	A	HCH scissor	1489.8642	0.0315	7.9808
v <sub>23</sub>	A	CCstr.	1723.5544	0.1427	36.1094
v <sub>24</sub>	A	OBC asym. str.	1994.7442	1.0000	253.1003
v <sub>25</sub>	A	CH str. + HCH sym. str.	2972.6147	0.0343	8.6753
v <sub>26</sub>	A	CH <sub>3</sub> sym. str.	3030.5252	0.0871	22.0469
v <sub>27</sub>	A	CH str. + HCH sym. str.	3054.0986	0.0265	6.7158
v <sub>28</sub>	A	HCH asym. str.	3076.5684	0.0191	4.8355
v <sub>29</sub>	A	HCH asym. str.	3082.8126	0.0491	12.4186
v <sub>30</sub>	A	CH str. + HCH sym. str.	3116.2455	0.0396	10.0334



**Table S3** (continued)

ts-i2i3 ( <sup>2</sup> A, C <sub>1</sub> )					
Normal modes	symmetry	Vibration mode	Frequency(cm <sup>-1</sup> )	Rel. inty	Inty (km/mol)
v <sub>1</sub>	A	CCCH <sub>3</sub> wagging	-260.3089	0.0441	12.7193
v <sub>2</sub>	A	CH <sub>3</sub> rock	35.3223	0.0026	0.7591
v <sub>3</sub>	A	O(BCCCH <sub>2</sub> )H scissor	119.4633	0.0198	5.7187
v <sub>4</sub>	A	CH <sub>3</sub> rock	126.5908	0.0020	0.5843
v <sub>5</sub>	A	CCCC wagging	183.6860	0.0001	0.0392
v <sub>6</sub>	A	CH <sub>3</sub> (C)C scissor	308.5065	0.0034	0.9757
v <sub>7</sub>	A	CCCH <sub>3</sub> wagging	349.0915	0.0505	14.5555
v <sub>8</sub>	A	OBC wagging	525.0211	0.0613	17.6674
v <sub>9</sub>	A	OBC wagging	558.4639	0.0648	18.6753
v <sub>10</sub>	A	CH <sub>3</sub> (CC)CH <sub>3</sub> sym. str.	622.3863	0.0041	1.1730
v <sub>11</sub>	A	HCH wagging	893.7439	0.0130	3.7354
v <sub>12</sub>	A	HCH twist.	983.2945	0.0037	1.0796
v <sub>13</sub>	A	HCH twist.	1025.9013	0.0004	0.1278
v <sub>14</sub>	A	HCH scissor	1031.2975	0.0084	2.4284
v <sub>15</sub>	A	CH <sub>3</sub> (CC)CH <sub>3</sub> asym. str.	1051.4133	0.0056	1.6046
v <sub>16</sub>	A	H(CH <sub>2</sub> )C scissor	1132.3529	0.0039	1.1134
v <sub>17</sub>	A	CH <sub>3</sub> wagging	1395.7805	0.0030	0.8623
v <sub>18</sub>	A	CH <sub>3</sub> wagging	1405.7515	0.0061	1.7525
v <sub>19</sub>	A	CH rock + HCH scissor	1445.3498	0.0273	7.8785
v <sub>20</sub>	A	HCH scissor	1465.9083	0.0358	10.3012
v <sub>21</sub>	A	CH rock + HCH scissor	1482.5794	0.0229	6.5954
v <sub>22</sub>	A	HCH scissor	1488.0309	0.0282	8.1318
v <sub>23</sub>	A	CCCH <sub>3</sub> asym. str.	1802.8133	0.0531	15.2870
v <sub>24</sub>	A	OBC asym. str.	1990.7428	1.0000	288.1382
v <sub>25</sub>	A	CH <sub>3</sub> sym. str.	2969.1739	0.1124	32.3753
v <sub>26</sub>	A	HCH asym. str.	2999.9711	0.0367	10.5668
v <sub>27</sub>	A	CH <sub>3</sub> sym. str.	3027.1811	0.0730	21.0341
v <sub>28</sub>	A	CH str. + HCH sym. str.	3061.4649	0.0124	3.5644
v <sub>29</sub>	A	HCH asym. str.	3083.4320	0.0439	12.6597
v <sub>30</sub>	A	CH str. + HCH sym. str.	3114.1160	0.0413	11.8875

**Table S3** (continued)

ts-i3p1 ( $^2A, C_1$ )					
Normal modes	symmetry	Vibration mode	Frequency( $\text{cm}^{-1}$ )	Rel. inty	Inty (km/mol)
v <sub>1</sub>	A	HCstr.	-425.3244	0.1227	37.0354
v <sub>2</sub>	A	O(BCC)C scissor	105.5384	0.0188	5.6719
v <sub>3</sub>	A	CH <sub>3</sub> rock	142.9957	0.0043	1.2906
v <sub>4</sub>	A	CH rock	159.5844	0.0117	3.5403
v <sub>5</sub>	A	H(CCCCH <sub>2</sub> )H scissor	186.9631	0.0039	1.1738
v <sub>6</sub>	A	CH rock	232.9895	0.0043	1.2899
v <sub>7</sub>	A	CH rock	279.6182	0.0167	5.0313
v <sub>8</sub>	A	CCC wagging	372.5468	0.0475	14.3363
v <sub>9</sub>	A	OBC wagging	500.5013	0.0648	19.5394
v <sub>10</sub>	A	BC twist.	558.2799	0.0608	18.3473
v <sub>11</sub>	A	BCC scissor	572.5767	0.0433	13.0556
v <sub>12</sub>	A	CH <sub>3</sub> (C)C scissor	667.7338	0.0187	5.6304
v <sub>13</sub>	A	HCH twist.	689.0730	0.0062	1.8751
v <sub>14</sub>	A	HCH wagging	894.1857	0.1280	38.6165
v <sub>15</sub>	A	HCH wagging	973.6821	0.0293	8.8432
v <sub>16</sub>	A	HCH twist.	1009.4419	0.0002	0.0604
v <sub>17</sub>	A	CH <sub>3</sub> twist.	1056.6001	0.0000	0.0027
v <sub>18</sub>	A	CH <sub>3</sub> C str.	1146.9044	0.0031	0.9355
v <sub>19</sub>	A	CCCH <sub>2</sub> sym. str.	1251.4465	0.0060	1.8045
v <sub>20</sub>	A	CH <sub>3</sub> wagging	1408.9435	0.0147	4.4464
v <sub>21</sub>	A	HCH scissor	1455.0608	0.0139	4.2000
v <sub>22</sub>	A	CH rock + HCH scissor	1486.3324	0.0238	7.1863
v <sub>23</sub>	A	HCH scissor	1496.2986	0.0186	5.5986
v <sub>24</sub>	A	CCCH <sub>2</sub> asym. str.	1993.4938	0.6834	206.2183
v <sub>25</sub>	A	OBC asym. str.	2013.6140	1.0000	301.7499
v <sub>26</sub>	A	CH <sub>3</sub> sym. str.	3035.9823	0.0580	17.5130
v <sub>27</sub>	A	HCH asym. str.	3090.6216	0.0321	9.6782
v <sub>28</sub>	A	CH str. + HCH sym. str.	3125.3479	0.0213	6.4299
v <sub>29</sub>	A	HCH sym. str.	3128.2299	0.0037	1.1173
v <sub>30</sub>	A	HCH asym. str.	3203.9608	0.0030	0.8989

**Table S3** (continued)

ts-i3p3 ( ${}^2A, C_1$ )					
Normal modes	symmetry	Vibration mode	Frequency( $\text{cm}^{-1}$ )	Rel. inty	Inty (km/mol)
v <sub>1</sub>	A	CH <sub>3</sub> C scissor	-457.0682	0.0490	16.7327
v <sub>2</sub>	A	CH <sub>3</sub> rock	44.0615	0.0004	0.1522
v <sub>3</sub>	A	CH <sub>3</sub> rock	60.2302	0.0004	0.1282
v <sub>4</sub>	A	O(BCC)CH <sub>3</sub> scissor	102.2881	0.0000	0.0086
v <sub>5</sub>	A	HCH <sub>2</sub> (CC)CH <sub>2</sub> H scissor	116.8520	0.0022	0.7662
v <sub>6</sub>	A	O(BCC)CH <sub>3</sub> wagging	135.3127	0.0001	0.0382
v <sub>7</sub>	A	CCC wagging	335.8804	0.0423	14.4455
v <sub>8</sub>	A	HCH twist.	369.2590	0.0317	10.8294
v <sub>9</sub>	A	OBC wagging	466.4102	0.0921	31.4437
v <sub>10</sub>	A	HCH twist.	509.8007	0.0681	23.2606
v <sub>11</sub>	A	HCH wagging	564.6313	0.0082	2.7857
v <sub>12</sub>	A	HCH twist.	566.7575	0.0178	6.0694
v <sub>13</sub>	A	B(CC)CH <sub>3</sub> sym. str.	627.9563	0.0172	5.8759
v <sub>14</sub>	A	CH <sub>3</sub> wagging	909.8527	0.0140	4.7817
v <sub>15</sub>	A	HCH wagging	1026.8432	0.0189	6.4544
v <sub>16</sub>	A	HCH scissor	1047.9378	0.0055	1.8949
v <sub>17</sub>	A	B(CC)CH <sub>3</sub> asym. str.	1095.0084	0.0023	0.7981
v <sub>18</sub>	A	CH <sub>3</sub> wagging	1409.4475	0.0075	2.5760
v <sub>19</sub>	A	HCH scissor	1421.1976	0.0092	3.1290
v <sub>20</sub>	A	CH rock + HCH scissor	1422.7698	0.0085	2.8899
v <sub>21</sub>	A	HCH scissor	1463.8629	0.0374	12.7855
v <sub>22</sub>	A	CH rock + HCH scissor	1464.4277	0.0253	8.6442
v <sub>23</sub>	A	OBC asym. str. + CCC asym. str.	1978.0423	0.4591	156.7942
v <sub>24</sub>	A	OBC asym. str. + CCC asym. str.	2141.4102	1.0000	341.5476
v <sub>25</sub>	A	CH <sub>3</sub> sym. str.	3005.4462	0.0450	15.3822
v <sub>26</sub>	A	CH str. + HCH sym. str.	3062.7161	0.0078	2.6627
v <sub>27</sub>	A	HCH asym. str.	3083.7886	0.0071	2.4081
v <sub>28</sub>	A	CH <sub>3</sub> sym. str.	3092.1202	0.0009	0.2935
v <sub>29</sub>	A	CH str. + HCH sym. str.	3247.8565	0.0087	2.9552
v <sub>30</sub>	A	HCH asym. str.	3252.2649	0.0111	3.8034

**Table S3** (continued)

ts-rp2 ( <sup>2</sup> A, C <sub>1</sub> )					
Normal modes	symmetry	Vibration mode	Frequency(cm <sup>-1</sup> )	Rel. inty	Inty (km/mol)
v <sub>1</sub>	A	BHC asym. str.	-405.6268	0.4169	195.6602
v <sub>2</sub>	A	CH <sub>3</sub> rock	21.2748	0.0009	0.4349
v <sub>3</sub>	A	OB rock	31.3692	0.0145	6.8197
v <sub>4</sub>	A	HBO wagging	33.4853	0.0201	9.4222
v <sub>5</sub>	A	HCH <sub>2</sub> (CCCH)B scissor	101.6796	0.0132	6.2019
v <sub>6</sub>	A	CCCC wagging	200.4916	0.0264	12.4056
v <sub>7</sub>	A	HCH <sub>2</sub> (CCC)H scissor	233.7498	0.0119	5.6056
v <sub>8</sub>	A	CCC wagging	381.2081	0.0000	0.0171
v <sub>9</sub>	A	CCC wagging	426.9772	0.0062	2.8914
v <sub>10</sub>	A	HCH <sub>2</sub> rock	432.0808	0.0002	0.1008
v <sub>11</sub>	A	CH <sub>3</sub> (CC)C sym. str.	742.2329	0.0056	2.6459
v <sub>12</sub>	A	BHC asym. str.	823.8847	1.0000	469.2827
v <sub>13</sub>	A	HCH wagging	1044.9109	0.0099	4.6623
v <sub>14</sub>	A	HCH twist.	1049.6177	0.0012	0.5473
v <sub>15</sub>	A	HCH twist.	1066.6733	0.0007	0.3273
v <sub>16</sub>	A	HCH wagging	1071.7783	0.0310	14.5449
v <sub>17</sub>	A	CH <sub>3</sub> (CC)C asym. str.	1191.3063	0.0069	3.2389
v <sub>18</sub>	A	HCH twist.	1327.3992	0.0010	0.4489
v <sub>19</sub>	A	HCH wagging	1399.4276	0.0651	30.5674
v <sub>20</sub>	A	CH <sub>3</sub> wagging	1417.9607	0.0039	1.8445
v <sub>21</sub>	A	HCH scissor	1459.1494	0.0212	9.9519
v <sub>22</sub>	A	CH rock + HCH scissor	1474.6644	0.0171	8.0155
v <sub>23</sub>	A	HCH scissor	1476.8403	0.0155	7.2536
v <sub>24</sub>	A	BO str.	1917.4500	0.3077	144.4125
v <sub>25</sub>	A	CC str.	2317.9964	0.2604	122.1936
v <sub>26</sub>	A	CH <sub>3</sub> sym. str.	3025.4606	0.0362	17.0012
v <sub>27</sub>	A	HCH sym. str.	3060.0929	0.0255	11.9873
v <sub>28</sub>	A	CH str. + HCH sym. str.	3079.4701	0.0171	8.0378
v <sub>29</sub>	A	HCH asym. str.	3085.0498	0.0142	6.6715
v <sub>30</sub>	A	HCH asym. str.	3118.4285	0.0041	1.9053

**Table S3** (continued)

p1 ( <sup>1</sup> A, C <sub>1</sub> )					
Normal modes	symmetry	Vibration mode	Frequency(cm <sup>-1</sup> )	Rel. inty	Inty (km/mol)
v <sub>1</sub>	A	OB(CC)C scissor	114.1491	0.0104	3.5750
v <sub>2</sub>	A	CH <sub>3</sub> rock	138.2513	0.0015	0.5077
v <sub>3</sub>	A	CH <sub>3</sub> (CC)CH <sub>2</sub> wagging	194.1494	0.0008	0.2707
v <sub>4</sub>	A	CH <sub>2</sub> H(CC)C scissor	215.7737	0.0100	3.4420
v <sub>5</sub>	A	CCCH <sub>2</sub> wagging	372.8974	0.0431	14.8894
v <sub>6</sub>	A	B scissor	498.3565	0.0482	16.6402
v <sub>7</sub>	A	CH <sub>2</sub> twist.	545.3442	0.0365	12.5893
v <sub>8</sub>	A	BCC scissor	572.0696	0.0223	7.7001
v <sub>9</sub>	A	CH <sub>2</sub> twist.	630.7658	0.0232	8.0113
v <sub>10</sub>	A	CH <sub>3</sub> CC scissor	672.0292	0.0100	3.4673
v <sub>11</sub>	A	CH <sub>2</sub> wagging	876.9321	0.1495	51.5931
v <sub>12</sub>	A	HCH wagging	975.6261	0.0262	9.0460
v <sub>13</sub>	A	CH <sub>2</sub> twist.	1004.6008	0.0002	0.0739
v <sub>14</sub>	A	CH <sub>3</sub> twist.	1059.0565	0.0000	0.0050
v <sub>15</sub>	A	H(CH <sub>2</sub> )C scissor	1158.0371	0.0017	0.5841
v <sub>16</sub>	A	CCC sym. str.	1265.3308	0.0008	0.2737
v <sub>17</sub>	A	CH <sub>3</sub> wagging	1410.8227	0.0051	1.7686
v <sub>18</sub>	A	HCH scissor	1458.8985	0.0098	3.3806
v <sub>19</sub>	A	HCH scissor	1486.1089	0.0205	7.0798
v <sub>20</sub>	A	HCH scissor	1498.0188	0.0181	6.2533
v <sub>21</sub>	A	BO str.	2012.5092	1.0000	345.1774
v <sub>22</sub>	A	CCC asym. str.	2029.3693	0.2659	91.7659
v <sub>23</sub>	A	CH <sub>3</sub> sym. str.	3034.0928	0.0579	19.9810
v <sub>24</sub>	A	CH <sub>3</sub> asym. str.	3087.4775	0.0310	10.6959
v <sub>25</sub>	A	CH str. + HCH sym. str.	3121.4793	0.0230	7.9475
v <sub>26</sub>	A	CH <sub>2</sub> sym. str.	3124.3059	0.0003	0.1016
v <sub>27</sub>	A	CH <sub>2</sub> asym. str.	3197.1424	0.0000	0.0004

**Table S3** (continued)

p2 ( <sup>2</sup> A, C <sub>1</sub> )					
Normal modes	symmetry	Vibration mode	Frequency(cm <sup>-1</sup> )	Rel. inty	Inty (km/mol)
v <sub>1</sub>	A	CH <sub>3</sub> rock + CH <sub>2</sub> rock	11.6318	0.0002	0.0131
v <sub>2</sub>	A	CCCC wagging	231.4199	0.1428	9.8006
v <sub>3</sub>	A	CCCC wagging	234.3984	0.1648	11.3133
v <sub>4</sub>	A	CCC wagging	455.5229	0.0008	0.0521
v <sub>5</sub>	A	CCC wagging	489.1534	0.0371	2.5443
v <sub>6</sub>	A	HCH wagging	607.7431	0.6902	47.3797
v <sub>7</sub>	A	CH <sub>3</sub> (CC)CH <sub>2</sub> sym. str.	796.0374	0.0228	1.5678
v <sub>8</sub>	A	HCH twist.	1064.2779	0.0100	0.6850
v <sub>9</sub>	A	CH <sub>3</sub> wagging	1066.1753	0.0237	1.6278
v <sub>10</sub>	A	CH <sub>3</sub> twist.	1075.5441	0.0117	0.8057
v <sub>11</sub>	A	CH <sub>3</sub> (CC)CH <sub>2</sub> asym. str.	1226.7406	0.0970	6.6586
v <sub>12</sub>	A	CH <sub>3</sub> wagging	1422.3379	0.0545	3.7401
v <sub>13</sub>	A	HCH scissor	1488.5319	0.0100	0.6877
v <sub>14</sub>	A	HCH scissor	1497.3595	0.1177	8.0796
v <sub>15</sub>	A	HCH scissor	1497.3820	0.1150	7.8921
v <sub>16</sub>	A	CC str.	2518.9362	1.0000	68.6490
v <sub>17</sub>	A	CH <sub>3</sub> sym. str.	3082.6149	0.2261	15.5228
v <sub>18</sub>	A	CH str. + HCH sym. str.	3163.3220	0.0527	3.6200
v <sub>19</sub>	A	HCH asym. str.	3173.1787	0.0536	3.6790
v <sub>20</sub>	A	CH <sub>2</sub> sym. str.	3227.2499	0.0821	5.6387
v <sub>21</sub>	A	CH <sub>2</sub> asym. str.	3337.4809	0.0008	0.0540

**Table S3** (continued)

p3 ( ${}^1A_1, C_{3v}$ )					
Normal modes	symmetry	Vibration mode	Frequency( $\text{cm}^{-1}$ )	Rel. inty	Inty (km/mol)
$\nu_1$	A	CCCBO wagging	124.2380	0.0005	0.1705
$\nu_2$	A	CCCBO wagging	124.5526	0.0005	0.1732
$\nu_3$	A	CCC wagging	368.5313	0.0420	14.1025
$\nu_4$	A	CCC wagging	368.7932	0.0421	14.1134
$\nu_5$	A	CBO wagging	526.3616	0.0955	32.0571
$\nu_6$	A	CBO wagging	526.3817	0.0955	32.0471
$\nu_7$	A	$\text{CH}_3(\text{CC})\text{BO}$ sym. str.	610.4125	0.0058	1.9626
$\nu_8$	A	HCH scissor	1049.7847	0.0061	2.0459
$\nu_9$	A	HCH wagging	1050.0259	0.0061	2.0464
$\nu_{10}$	A	$\text{OCCCH}_3$ asym. str.	1103.3084	0.0012	0.4087
$\nu_{11}$	A	$\text{CH}_3$ wagging	1413.6175	0.0000	0.0049
$\nu_{12}$	A	HCH scissor	1468.2738	0.0292	9.7834
$\nu_{13}$	A	HCH scissor	1468.4686	0.0292	9.7818
$\nu_{14}$	A	BO str. + CC str.	2011.6517	0.8596	288.4410
$\nu_{15}$	A	BCC asym. str.	2330.4716	1.0000	335.5485
$\nu_{16}$	A	$\text{CH}_3$ sym. str.	3031.4396	0.0121	4.0739
$\nu_{17}$	A	CH str. + HCH sym. str.	3092.7363	0.0049	1.6393
$\nu_{18}$	A	HCH asym. str.	3093.1367	0.0049	1.6299
HBO ( ${}^1\Sigma^+, C_{\infty v}$ )					
Normal modes	symmetry	Vibration mode	Frequency( $\text{cm}^{-1}$ )	Rel. inty	Inty (km/mol)
$\nu_1$	$\Pi$	H scissor	778.9805	0.2037	12.3311
$\nu_2$	$\Pi$	H scissor	778.9805	0.2037	12.3311
$\nu_3$	$\Sigma$	OB str.	1867.9283	1.0000	60.5290
$\nu_4$	$\Sigma$	BH str.	2895.6010	0.1505	9.1070