

**Dimethylberyllium + CO<sub>2</sub> → Fire!**

**A DFT and *ab initio* Study into the photon emission observed in a gas phase carbon dioxide activation reaction.**

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**Supporting Information**

**Table S1:** Calculated relative electronic energies, enthalpies, entropies, and free energies for intermediates in the reactions of **1/2** with CO<sub>2</sub>

Min. or TS	B3LYP/6-31G(d) U/H/S/G	M06/cc-pVQZ U/H/S/G	M06-2X/cc-pVQZ U/H/S/G	CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ U
3	-1.0/-0.1/-15.5 /4.5	-1.3/-0.4/-21.1 /5.9	-2.3/-1.4/-23.4 /5.1	-2.0
4	-1.3/-0.4/-17.1 /4.7	-1.8/-0.8/ -25.8/6.9	-2.9/-2.0/-25.7 /5.7	n.c.
TS35	9.2/9.6/-34.7 /20.0	11.8/12.1/-34.0 /22.2	7.2/7.6/ -36.3/17.9	9.5
TS46	7.7/7.9/-36.6 /18.8	8.4/8.5/ -39.6/20.3	4.5/4.7/ -37.8/16.0	n.c.
5	-43.0/-40.3/ -31.0/-31.1	-34.5/-32.0/ -30.0/-23.0	-44.5/-41.7/ -31.8/-32.8	-42.4
6	-48.1/-45.8/ -34.3/-35.5	-40.6/-38.5/ -37.1/-27.5	-50.5/-48.2/ -36.5/-37.3	n.c.
TS57	-27.4/-24.3/ -71.7/-2.6	-17.1/-14.4/ -68.9/0.7	-30.2/-27.0/ -71.7/-6.2	n.c.
TS68	-33.7/-30.8/ -72.3/-9.2	-25.2/-22.8/ -73.7/-0.9	-37.8/-35.2/ -74.2/-13.0	n.c.
7	-89.3/-83.9/ -66.6/-63.8	-72.3/-67.3/ -69.0/-46.7	-92.4/-86.8/ -71.8/-66.0	n.c.
8	-99.0/-94.0/ -72.7/-72.2	-83.5/-79.1/ -77.2/-56.1	-103.4/-98.6/ -76.6/-75.8	n.c.

Electronic energies, enthalpies, entropies, and free energies, relative to dialkylberyllium + 2 CO<sub>2</sub>, in kcal mol<sup>-1</sup> (entropies in cal mol<sup>-1</sup> K<sup>-1</sup>). n.c.: not calculated.

**Table S2:** Calculated relative electronic energies, enthalpies, entropies, and free energies for intermediates in the thermal decomposition reactions of **1/2**.

Min. or TS	B3LYP/6-31G(d) U/H/S/G	M06/cc-pVQZ U/H/S/G	M06-2X/cc-pVQZ U/H/S/G	CASSCF U/H/S/G	CCSD(T)/basis // M06-2X/cc- pVQZ U
<b>9</b> + C <sub>2</sub> H <sub>4</sub>	32.6/28.5/32.0/ 18.9	32.3/28.3/30.1 /19.3	35.4/31.4/30.6 /22.3	n.c.	33.3 <sup>d</sup>
<b>TS 2-9</b> + C <sub>2</sub> H <sub>4</sub>	35.7/32.5/ -3.4/33.5	33.6/30.5/ -5.7/32.2	34.4/31.5/ -5.4/33.1	n.c.	36.4 <sup>d</sup>
<b>10</b> + 2 C <sub>2</sub> H <sub>4</sub>	65.7/57.8/61.7/ 39.3	65.1/57.4/ 58.9/40.0	71.3/63.6/58.5/ 46.2	n.c.	66.5 <sup>d</sup>
<b>TS 9-10</b> + 2 C <sub>2</sub> H <sub>4</sub>	65.1/57.9/28.8/ 49.3	63.6/56.7/ 26.6/48.7	67.2/60.3/27.0/ 52.3	n.c.	67.5 <sup>d</sup>
<b>11</b> + H + 2 C <sub>2</sub> H <sub>4</sub>	163.7/151.8/ 89.1/125.0	165.7/154.1/ 86.6/128.4	167.8/156.2/86.3 /130.5	n.c.	163.5 <sup>d</sup>
<b>12</b> + H <sub>2</sub> + 2 C <sub>2</sub> H <sub>4</sub>	111.3/103.5/ 83.6/78.3	113.8/105.5/ 80.8/81.6	113.4/105.2/80.3 /81.5	87.6/77.5/ 60.7/57.8 <sup>a</sup>	102.7 <sup>d</sup>

<b>TS 10-12</b> + 2 C <sub>2</sub> H <sub>4</sub>	157.8/146.9/ 66.5/127.0	161.4/150.5/ 62.9/132.1	163.0/152.3/61.9 /133.9	158.6/146.3/ 60.0/128.0 <sup>b</sup>	174.8 <sup>d</sup>
<b>16</b> + C <sub>2</sub> H <sub>6</sub>	S: 87.3/85.6 /30.0/76.6 T: 72.5/70.7 /32.9/60.9	S: 90.5/88.7/ 29.6/79.9 T: 77.6/75.7/ 32.4/66.0	S: 93.3/91.7/29.7 /82.8 T: 78.5/76.7/32.7 /67.0	n.c.	S: 98.2 <sup>d</sup> T: 76.4 <sup>d</sup>
<b>TS 2-16</b> + C <sub>2</sub> H <sub>6</sub>	84.1/80.9/ -2.7/81.8	83.9/80.6/ -2.7/81.4	85.3/82.2/ -2.9/83.1	n.c.	83.2 <sup>d</sup>
<b>17</b> + C <sub>2</sub> H <sub>6</sub>	S: 77.3/72.4/ 32.5/62.6 T: 69.3/65.2 /32.7/55.5	S: 84.9/79.5/ 28.2/71.1 T: 70.2/66.1 /32.2/56.4	S: 90.4/85.6 /34.5/75.3 T: 77.3/73.2/32.8 /63.4	n.c.	S: 104.0 <sup>d</sup> T: 77.6 <sup>d</sup>
<b>TS 16-17</b>	S: 115.7/110.7 /29.8/101.7 T: 109.9/104.4 /33.2/94.5	S: 118.6/113.5 /29.6/104.5 T: 114.5/109.0 /32.5/99.3	S: 124.2/119.0 /31.0/109.7 T: 117.8/112.5 /33.0/102.7	n.c.	S: 124.5 <sup>d</sup> T: 118.8 <sup>d</sup>
<b>18</b> + C <sub>2</sub> H <sub>6</sub>	25.0/21.6/29.9 /2.7	26.8/23.4/29.5 /14.6	30.2/26.9/29.5 /18.1	n.c.	27.7 <sup>d</sup>
<b>TS 16-18</b>	102.5/97.3/ 27.1/89.1	102.3/97.3/ 26.2/90.0	105.4/100.4/ 26.5/92.5	n.c.	104.0 <sup>d</sup>
<b>TS 17-18</b>	98.6/91.9/30.2/ 82.8	96.0/89.3/ 30.0/80.4	101.9/95.2/30.1/ 86.2	n.c.	101.8 <sup>d</sup>
<b>10</b> + C <sub>2</sub> H <sub>6</sub> + C <sub>2</sub> H <sub>2</sub>	77.5/69.4/57.0/ 42.5	72.4/64.7/ 55.7/48.1	80.0/72.3/56.0 /55.6	n.c.	76.1 <sup>d</sup>
<b>TS 18-10</b>	68.6/61.2/28.5/ 42.7	65.8/58.7/27.6 /50.5	71.0/64.0/27.8 /55.7	n.c.	72.5 <sup>d</sup>
<b>12</b> + C <sub>4</sub> H <sub>10</sub>	44.3/45.6/16.8/ 40.6	46.4/47.6/16.1 /42.8	46.2/47.4/16.4 /42.6	n.c.	36.8 <sup>c</sup>
<b>TS 2-12</b> + C <sub>4</sub> H <sub>10</sub>	116.0/114.4/ -5.8/116.1	110.5/109.0/ -7.5/111.2	114.8/113.3/ -7.1/115.4	n.c.	144.7 <sup>d</sup>
<b>19</b> + C <sub>2</sub> H <sub>5</sub>	85.8/82.4/39.0/ 70.8	84.9/85.6/38.9 /74.0	89.8/86.5/38.9/ 74.8	n.c.	87.8 <sup>d</sup>
<b>13</b> + CH <sub>4</sub>	S: 97.4/95.6 /29.8/86.7 T: 83.3/81.3/ 32.2/71.7	S: 99.5/97.8/ 25.4/90.2 T: 88.6/86.5/ 28.0/78.1	S: 101.7/100.1/ 24.4/92.8 T: 88.9/87.0/ 26.9/79.0	S: 69.2/69.2 /0.3/68.9	S: 103.5 <sup>e</sup> T: 86.3 <sup>e</sup>
<b>13</b> × CH <sub>4</sub>	85.3/86.5/4.1/ 85.3	83.4/83.1/4.9/ 81.6	83.7/83.7/0.7/ 83.5	n.c.	64.6 <sup>e</sup>
<b>TS 1-13</b> + CH <sub>4</sub>	91.2/88.1/ -4.7/89.5	89.8/86.7/ -3.9/87.9	91.2/88.3/ -4.7/89.8	75.5/75.5/0.3 /75.1	89.6 <sup>e</sup>
<b>14</b> + CH <sub>4</sub>	S: 96.5/92.7/ 28.2/84.3 T: 87.6/83.7/ 30.6/74.6	S: 103.9/100.0 /24.4/92.7 T: 88.4/84.6/ 26.4/76.7	S: 108.0/104.2 /23.0/97.4 T: 93.6/89.7 /25.5/82.1	n.c.	S: 104.8 <sup>e</sup> T: 93.2 <sup>e</sup>
<b>TS 13-14</b> + CH <sub>4</sub>	S: 134.0/128.2 /30.4/119.1 T: 129.3/123.9/ 33.5/113.9	S: 137.2/131.5 /28.0/123.1 T: 134.3/128.9 /29.3/120.2	S: 141.5/136.5 /26.4/128.6 T: 135.9/130.7 /28.1/122.3	n.c.	S: 123.2 <sup>e</sup> T: 119.3 <sup>e</sup>
<b>15</b> + CH <sub>3</sub>	94.0/90.6/34.7/ 80.2	98.1/94.5/34.2 /84.3	97.8/94.4/33.2/ 84.5	n.c.	95.3 <sup>e</sup>
<b>12</b> + C <sub>2</sub> H <sub>6</sub>	53.0/55.0/14.6/ /14.6	57.4/59.4/15.4 /15.4	56.9/59.1/14.3/ /14.3	25.3/25.3/0.7 /0.7	48.9 <sup>e</sup>

	50.7	/54.8	54.8	/24.6 <sup>c</sup>	
<b>TS 1-12</b> + C <sub>2</sub> H <sub>6</sub>	125.6/124.3/ -5.2/125.9	123.3/122.0/ -6.8/124.1	126.4/125.3/ -8.1/127.7	n.c.	164.5 <sup>e</sup>

S: singlet state. T: triplet state. If not specified, the spin multiplicity is a singlet (or doublet for **15**, **19**, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>). <sup>a</sup>CASSCF(4,6)/SVP, complex of Be atom with H<sub>2</sub>. Energies / entropies for reaction up to **10** taken from M06-2X/cc-pVQZ. <sup>b</sup>CASSCF(4,6)/SVP. Energies / entropies for reaction up to **10** taken from M06-2X/cc-pVQZ. <sup>c</sup>CASSCF(4,6)/SVP, complex of Be atom with C<sub>2</sub>H<sub>6</sub>. n.c.: not calculated. <sup>d</sup>CCSD(T)/aug-cc-pVTZ//M06-2X-cc-pVQZ <sup>e</sup>CCSD(T)/aug-cc-pVQZ//M06-2X-cc-pVQZ

**Table S3:** Calculated relative electronic energies, enthalpies, entropies, and free energies for intermediates in the reactions of reactive species derived from **1/2** with CO<sub>2</sub>.

Min. or TS	B3LYP/6-31G(d) U / H / S / G	M06/cc-pVQZ U / H / S / G	M06-2X/cc-pVQZ U / H / S / G	CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ U
<b>10</b> x CO <sub>2</sub> + CO <sub>2</sub>	n.c.	n.c.	n.c.	-2.7 <sup>a</sup>
<b>19</b> + CO <sub>2</sub>	-45.3/-41.8/ -28.2/-33.3	-37.5/-34.2/ -28.1/-25.8	-45.4/-46.4/ -28.3/-37.9	-46.3
<b>TS 10-19</b> + CO <sub>2</sub>	-0.4/-0.3/ -27.2/7.9	2.7/3.0/ -27.6/11.2	-1.7/-1.4/ -27.4/6.8	0.5
<b>20</b>	-92.9/-85.7/ -64.0/-66.5	-76.8/-70.1/ -63.8/-51.1	-97.2/-94.6/ -64.3/-75.3	-94.7
<b>TS 19-20</b>	-37.6/-33.8/ -56.6/-16.8	-36.4/-32.8/ -63.1/-13.9	-49.1/-49.6/ -63.0/-30.8	-47.9
<b>21</b> + CO <sub>2</sub>	-44.4/-40.8/ -30.7/-31.6	-36.5/-33.1/ -30.5/-24.0	-48.9/-45.2/ -31.4/-35.8	n.c.
<b>TS 9-21</b> + CO <sub>2</sub>	1.1/1.4/ -30.8/10.5	4.0/4.3/ -31.2/13.6	-0.4/-0.1/ -31.3/9.2	n.c.
<b>23</b> + CO <sub>2</sub>	-48.8/-46.4/ -34.4/-36.1	-41.4/-39.1/ -36.3/-28.2	-51.3/-48.8/ -35.9/-38.1	n.c.
<b>TS 9-23</b> + CO <sub>2</sub>	6.1/6.5/ -34.4/16.8	8.2/8.5/ -35.3/19.0	4.1/4.6/ -35.4/15.1	n.c.
<b>22</b>	-95.7/-89.6/ -69.5/-69.3	-80.1/-74.4/ -71.6/-53.0	-102.5/-96.4/ -71.6/-75.0	n.c.
<b>TS 21-22</b>	-33.0/-29.1/ -66.2/-9.2	-24.2/-20.5/ -67.3/-0.4	-39.4/-35.3/ -67.8/-15.1	n.c.
<b>TS 23-22</b>	no barrier	no barrier	no barrier	n.c.
<b>24</b>	-18.3/-19.1/ -22.3/-12.4	-12.8/-13.5/ -23.6/-6.5	-19.6/-20.3/ -22.2/-13.7	-10.8
<b>TS 12-24</b>	14.6/13.1/ -20.4/19.2	19.8/18.2/ -20.7/24.4	20.5/18.9/ -20.8/25.1	15.4
<b>25</b>	-13.3/-13.6/ -20.7/-7.4	-8.1/-8.5/ -21.3/-2.1	-12.2/-12.5/ -21.1/-6.2	-4.9
<b>TS 12-25</b>	13.7/12.2/ -18.8/17.7	17.9/16.1/ -18.8/21.7	17.5/15.7/ -18.6/21.2	20.1
<b>26</b>	-2.8/-3.1/ -19.9/2.8	6.0/5.5/ -18.7/11.1	-1.5/-1.8/ -18.6/3.8	3.4
<b>27</b>	-21.3/-21.1/	-9.8/-9.8/-	-14.2/-14.1/	-11.6

	-20.0/-15.1	18.2/-4.4	-18.7/-8.5	
<b>TS 24-26</b>	5.9/4.4/ -17.8/9.7	14.2/12.5/ -18.6/18.1	6.5/5.0/ -18.9/10.7	11.5
<b>TS 25-27</b>	-12.9/-13.7/ -21.7/-7.2	-11.4/-12.5/ -21.4/-6.1	-10.3/-11.0/ -21.3/-4.7	-6.0
<b>28 + CO</b>	24.8/23.3/ 10.7/20.1	28.3/26.7/ 10.8/23.4	22.8/21.3/ 10.8/18.1	24.6
<b>13 x CO<sub>2</sub> + CO<sub>2</sub></b>	T: -1.2/-0.3/ -12.9/3.6 S: no min.	T: -1.1/0.0/ -17.3/-5.1 S: no min.	T: -2.0/-1.0/ -16.3/3.8 S: no min.	T: -0.9
<b>29 + CO<sub>2</sub></b>	-64.8/-61.9/ -37.7/-50.7	-63.3/-60.4/ -37.5/-49.2	-70.1/-67.2/ -37.7/-55.9	-66.4
<b>29 x CO<sub>2</sub></b>	-83.2/-79.0/ -63.1/-60.2	-80.6/-76.5/ -62.6/-57.8	-90.3/-86.1/ -64.3/-66.9	-85.4
<b>30</b>	-118.4/-113.0/ -74.8/-90.7	-109.6/-104.4/ -74.5/-82.1	-125.3/-119.9/ -74.8/-97.6	-119.3
<b>TS 29-30</b>	-82.2/-78.9/ -71.3/-57.7	-77.8/-74.7/ -72.2/-53.2	-88.2/-85.0/ -72.3/-63.3	-82.7
<b>31</b>	T: -33.3/-32.6/ -27.1/-24.5 S: -33.3/-32.6/ -27.1/-24.5	T: -27.0/26.4/ -23.1/-19.5 S: -27.4/-26.7/ -26.5/-18.8	T: -32.8/-32.1/ -23.0/-25.3 S: -33.9/-33.1/ -30.6/-24.0	T: -29.2 S: -28.6
<b>TS 13-31</b>	T: 0.2/0.2/ -24.9/7.6 S: no barrier	T: 0.9/0.8/ -24.9/8.2 S: no barrier	T: -0.7/-0.8/ -24.4/6.5 S: no barrier	T: 3.9 S: n.c.
<b>TS 31-29</b>	-5.3/-5.2/ -31.6/4.2	-9.4/-8.6/ -30.3/0.4	-10.0/-9.2/ -30.6/0.0	-7.5
<b>32</b>	T: -31.2/-30.5/ -21.4/-24.1 S: no min.	no min.	T: -31.5/-30.8/ -19.8/-24.9 S: no min.	T: -27.6
<b>33</b>	-21.0/-18.8/ -38.6/-7.3	-17.6/-15.3/ -38.7/-3.8	-26.3/-23.7/ -38.7/-12.2	-22.3
<b>TS 32-33</b>	12.0/13.0/ -36.0/-23.7	21.8/22.8/ -35.9/33.5	14.0/14.9/ -35.9/25.6	17.1
<b>34</b>	T: -32.3/-31.7/ -30.3/-22.6	T: -26.1/-25.4/ -30.1/-16.4	T: -33.9/-33.1/ -30.6/-24.0	T: -29.1
<b>TS 32-34</b>	T: -28.9/-28.9/ -29.8/-20.0	T: -23.5/-23.5/ -29.6/-14.7	T: -29.1/-29.1/ -30.6/-20.0	T: -25.6
<b>14 x CO<sub>2</sub> + CO<sub>2</sub></b>	T: -1.0/0.8/ -12.8/3.4 S: 8.0/9.9/ -16.3/13.5	T: -1.4/-0.8/ -18.0/4.6 S: 14.5/14.9/ -18.6/20.5	T: -2.7/-2.1/ -18.6/3.4 S: 12.3/12.9/ -20.6/19.1	T: -1.3 S: 27.2
<b>15 x CO<sub>2</sub></b>	-1.1/-0.2/ -11.4/3.2	-0.5/0.4/ -17.2/5.5	-1.8/-0.9/ -9.8/2.0	4.3
<b>35</b>	-34.9/-33.9/ -22.4/-27.2	-28.3/-27.5/ -22.5/-20.8	-34.7/-33.7/ -21.6/-27.3	-31.4
<b>TS 15-35</b>	0.9/0.8 -24.4/8.1	2.1/1.8/ -24.5/9.1	0.3/0.2/ -23.2/7.1	4.0
<b>36</b>	-33.1/-32.1/ -19.7/-26.2	no min.	-33.2/-32.3/ -20.3/-26.3	-29.8
<b>37</b>	No minimum	-27.3/-26.5/	No minimum	-47.2 <sup>b</sup>

		-26.6/-18.6		
<b>TS 35-37</b>	No stationary point	-27.2/-27.1/ -28.8/-18.5	No stationary point	n.c.
<b>38</b>	-32.8/-32.0/ -24.6/-24.7	-25.7/-25.1/ -22.9/-18.3	-33.8/-33.0/ -25.3/-25.5	-48.1
<b>TS 36-38</b>	-30.2/-30.0/ -29.7/-21.1	-23.9/-23.9/ -29.7/-15.0	-30.2/-30.0/ -29.7/-21.1	-27.3
<b>39 + CO</b>	-4.7/-6.4/ 9.3/-9.2	n.c.	3.1/1.4/ 7.1/-0.7	4.3
<b>TS 35-39</b>	no barrier	no barrier	no barrier	n.c.
<b>TS 36-39</b>	no barrier	no barrier	no barrier	n.c.

n.c.: not calculated no min.: no minimum <sup>a</sup>CCSD(T)/aug-cc-pVQZ//MP2/cc-pVTZ <sup>b</sup>CCSD(T)/aug-cc-pVQZ//M06/cc-pVQZ

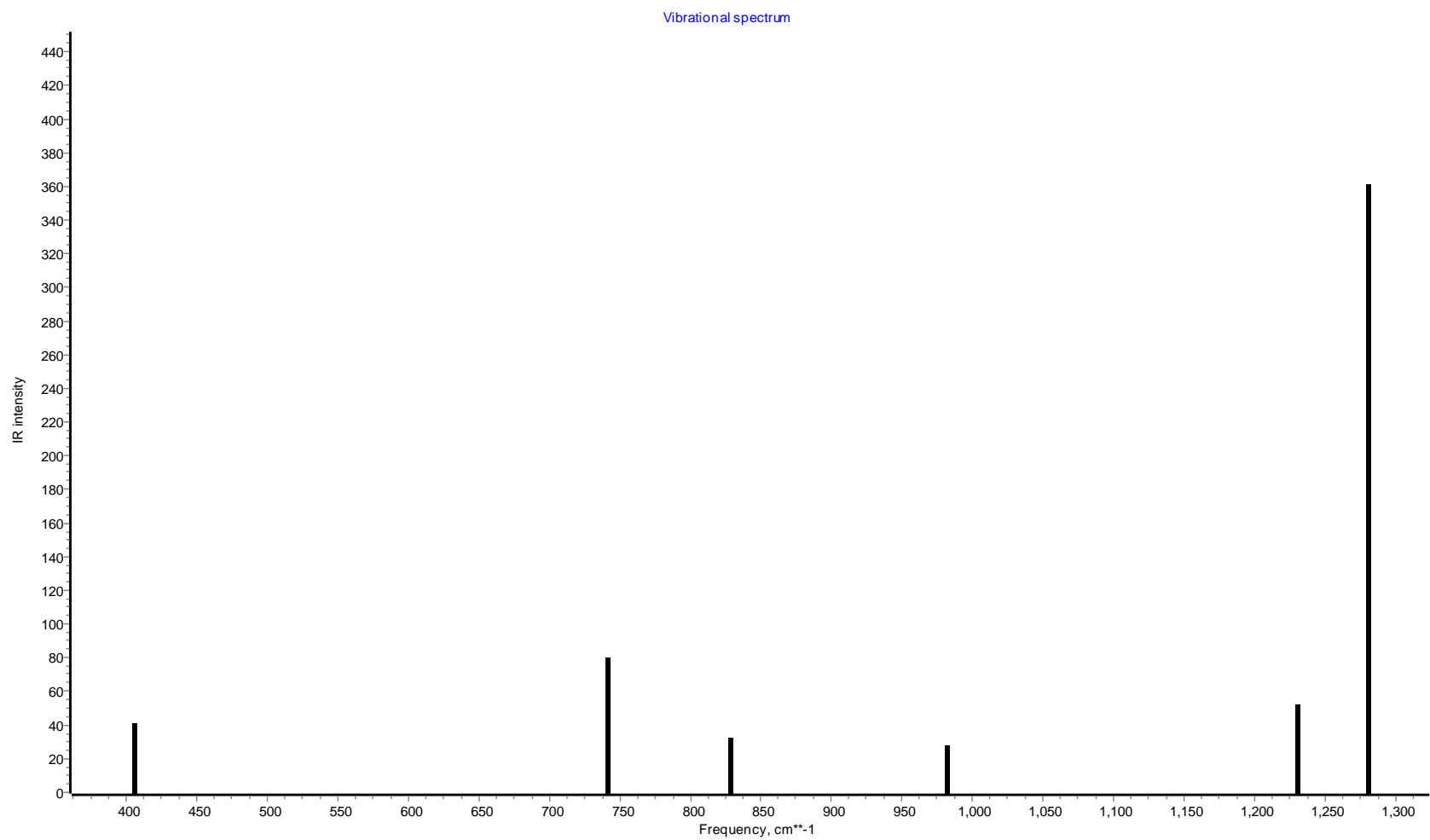


Figure S1: Calculated IR spectrum of 24 (M06-2X/cc-pVQZ), unscaled.

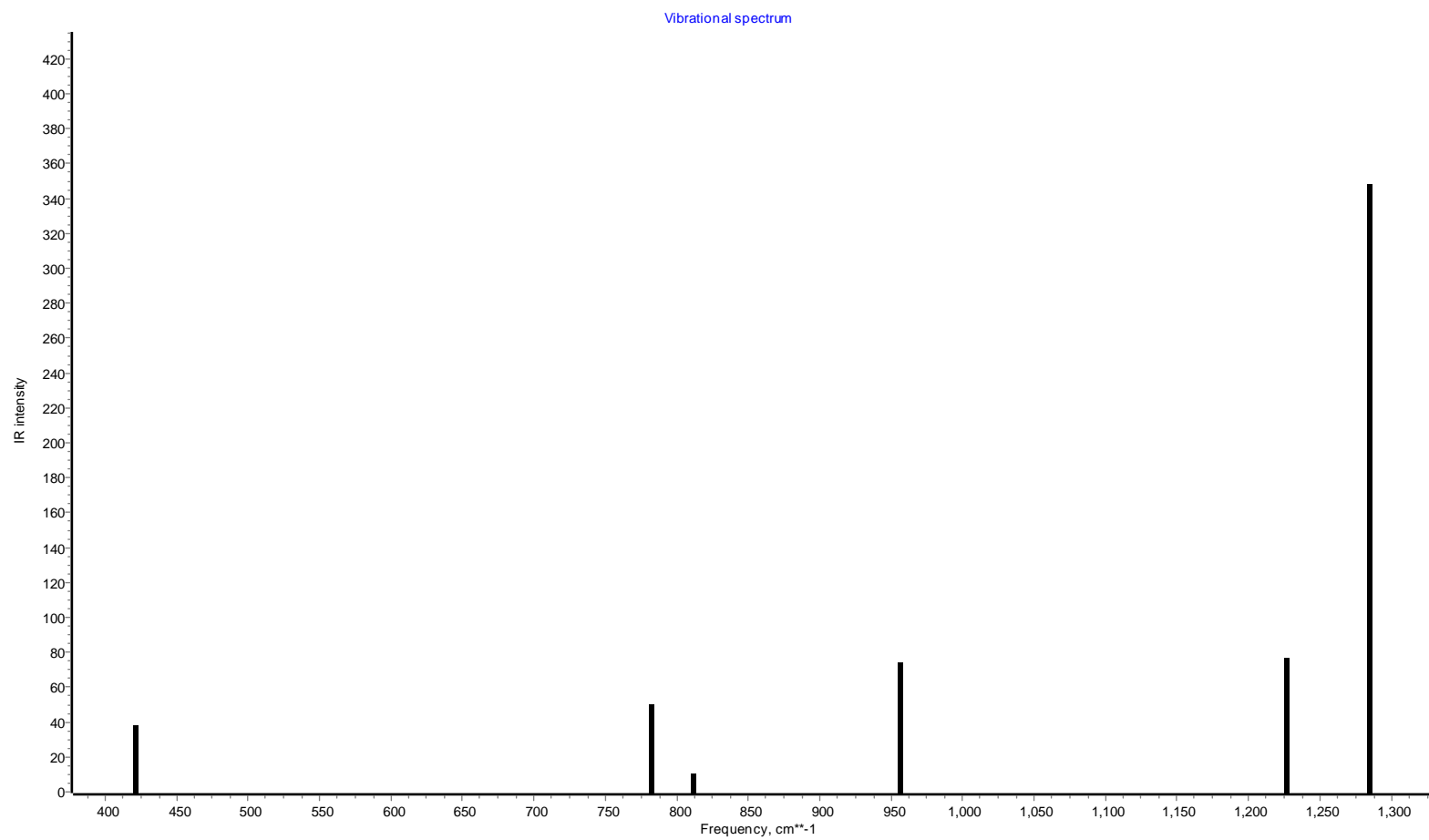


Figure S2: Calculated IR spectrum (M06/cc-pVQZ) of 24, unscaled.



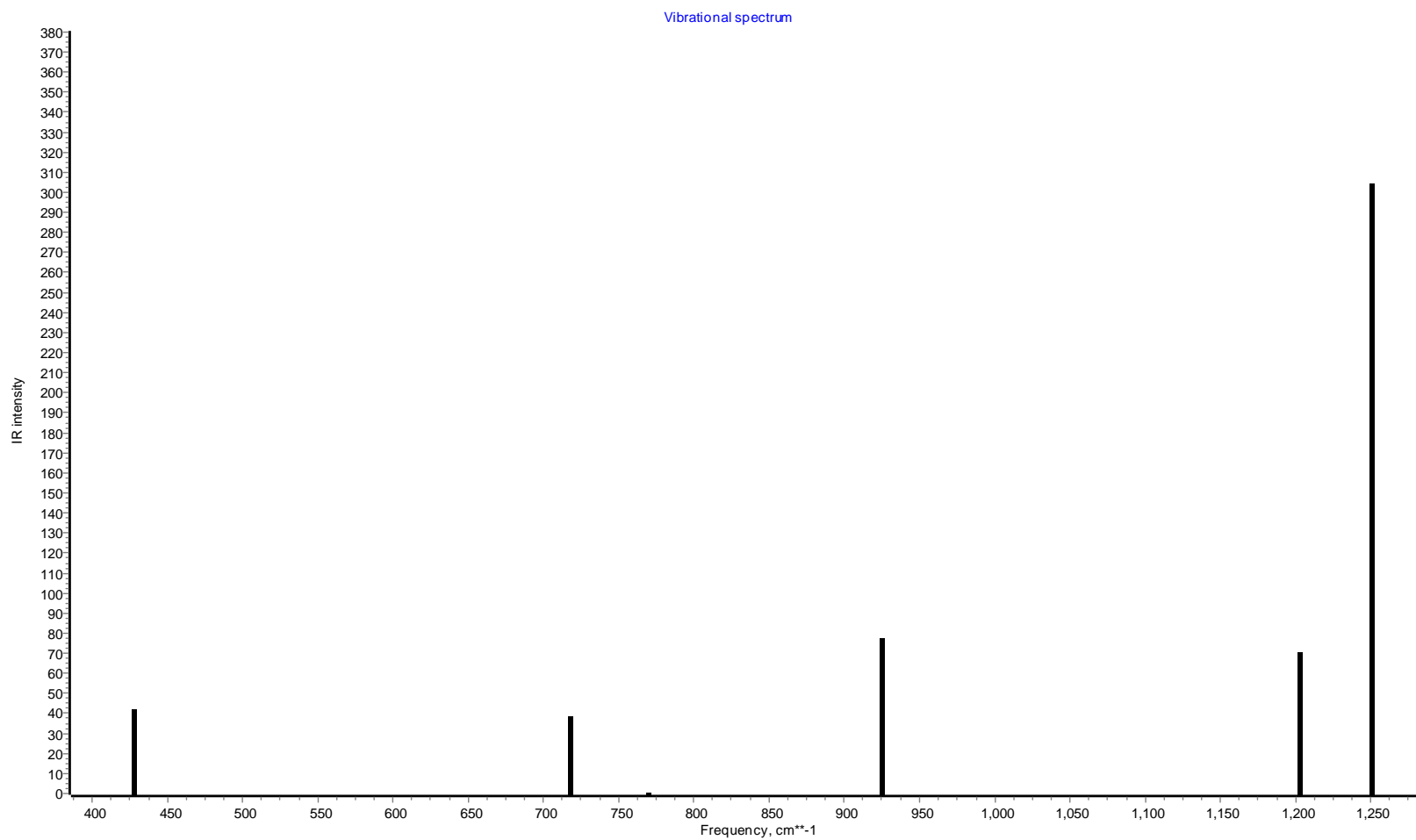


Figure S3: Calculated IR spectrum (B3LYP/6-31G(d)) of 24, unscaled.

## Calculations: Energies

**General remarks:** All stationary points were characterized by performing a vibrational analysis. All minima had exactly zero vibrational modes with imaginary frequency, and all transition states exactly one. In some cases, broken-symmetry wavefunctions were employed to achieve an approximate description of species with partial or full singlet diradical character. This is indicated via the Gaussian keyword `guess=(mix,always)`. The Cartesian coordinates are available via the `.xyz` file connected with this Supporting Information.

Dimethylberyllium 1, electronic energy (B3LYP/6-31(d))

E(B3LYP) = -94.5832837

Dimethylberyllium 1, electronic energy (M06/cc-pVQZ)

E(M06) = -94.5459235

Dimethylberyllium 1, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -94.5677262

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -94.397325335

Diethylberyllium 2, electronic energy (B3LYP/6-31G(d))

E(B3LYP) = -173.1970736

Diethylberyllium 2, electronic energy (M06/cc-pVQZ)

E(M06) = -173.1247695

Diethylberyllium 2, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -173.1708325

E(CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVQZ) = -172.842005297665

Complex 3 of dimethylberyllium with CO<sub>2</sub>, electronic energy (B3LYP / 6-31G(d))

E(B3LYP) = -283.1658514

Complex 3 of dimethylberyllium with CO<sub>2</sub>, electronic energy (M06 / cc-pVQZ)

E(M06) = -283.1388157

Complex 3 of dimethylberyllium with CO<sub>2</sub>, electronic energy (M06-2X / cc-pVQZ)

E(M06-2X) = -283.1747606

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -282.789708462146

Complex 4 of diethylberyllium with CO<sub>2</sub>, electronic energy (B3LYP / 6-31G(d))

E(B3LYP) = -361.7800403

Complex 4 of diethylberyllium with CO<sub>2</sub>, electronic energy (M06 / cc-pVQZ)

E(M06) = -361.7184656

Complex 4 of diethylberyllium with CO<sub>2</sub>, electronic energy (M06-2X / cc-pVQZ)

E(M06-2X) = -361.7787547

Transition state for formation of methylberyllium acetate 5 (B3LYP / 6-31G(d))

E(B3LYP) = -283.1494904

Transition state for formation of methylberyllium acetate 5, electronic energy (M06 / cc-pVQZ)

E(M06) = -283.1179149

Transition state for formation of methylberyllium acetate 5, electronic energy (M06-2X / cc-pVQZ)

E(M06-2X) = -283.1596668

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -282.771470506179

Transition state for formation of ethylberyllium propionate 6, electronic energy (B3LYP / 6-31G(d))

E(B3LYP) = -361.765681

Transition state for formation of ethylberyllium propionate 6,  
electronic energy (M06 / cc-pVQZ)

$$E(M06) = -361.7022303$$

Transition state for formation of ethylberyllium propionate 6,  
electronic energy (M06-2X / cc-pVQZ)

$$E(M06-2X) = -361.7669523$$

Methylberyllium acetate 5, electronic energy (B3LYP / 6-31G(d))

$$E(B3LYP) = -283.2327682$$

Methylberyllium acetate 5, electronic energy (M06/cc-pVQZ)

$$E(M06) = -283.1916438$$

Methylberyllium acetate 5, electronic energy (M06-2X/cc-pVQZ)

$$E(M06-2X) = -283.2419257$$

$$E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -282.854131767786$$

Ethylberyllium propionate 6, electronic energy (B3LYP / 6-31G(d))

$$E(B3LYP) = -361.854690$$

Ethylberyllium propionate 6, electronic energy (M06/cc-pVQZ)

$$E(M06) = -361.7803003$$

Ethylberyllium propionate 6, electronic energy (M06-2X/cc-pVQZ)

$$E(M06-2X) = -361.8547017$$

Transition state for formation of beryllium diacetate 7, electronic  
energy (B3LYP / 6-31G(d))

$$E(B3LYP) = -471.7888086$$

Transition state for formation of beryllium diacetate 7, electronic  
energy (M06 / cc-pVQZ)

$$E(M06) = -471.7547837$$

Transition state for formation of beryllium diacetate 7, electronic energy (M06-2X / cc-pVQZ)

$$E(\text{M06-2X}) = -471.8225379$$

Transition state for formation of beryllium dipropionate 8, electronic energy (B3LYP / 6-31G(d))

$$E(\text{B3LYP}) = -550.412209$$

Transition state for formation of beryllium dipropionate 8, electronic energy (M06 / cc-pVQZ)

$$E(\text{M06}) = -550.3464946$$

Transition state for formation of beryllium dipropionate 8, electronic energy (M06-2X / cc-pVQZ)

$$E(\text{M06-2X}) = -550.4378911$$

Beryllium diacetate 7 monomer, electronic energy (B3LYP / 6-31G(d))

$$E(\text{B3LYP}) = -471.8874713$$

Beryllium diacetate 7 monomer, electronic energy (M06/cc-pVQZ)

$$E(\text{M06}) = -471.842623$$

Beryllium diacetate 7 monomer, electronic energy (M06-2X/cc-pVQZ)

$$E(\text{M06-2X}) = -471.9215677$$

Beryllium dipropionate 8 monomer, electronic energy (B3LYP / 6-31G(d))

$$E(\text{B3LYP}) = -550.5162478$$

Beryllium dipropionate 8 monomer, electronic energy (M06 / cc-pVQZ)

$$E(\text{M06}) = -550.4394293$$

Beryllium dipropionate 8 monomer, electronic energy (M06-2X / cc-pVQZ)

$$E(\text{M06-2X}) = -550.5423146$$

Transition state for formation of ethylberyllium hydride 9,  
electronic energy (B3LYP / 6-31G(d))

E(B3LYP) = -173.1402035

Transition state for formation of ethylberyllium hydride 9,  
electronic energy (M06 / cc-pVQZ)

E(M06) = -173.0712166

Transition state for formation of ethylberyllium hydride 9,  
electronic energy (M06-2X / cc-pVQZ)

E(M06-2X) = -173.1159413

E(CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVQZ) = -172.783939488

Ethylberyllium hydride 9, electronic energy (B3LYP / 6-31G(d))

E(B3LYP) = -94.5576905

Ethylberyllium hydride 9, electronic energy (M06 / cc-pVQZ)

E(M06) = -94.5182071

Ethylberyllium hydride 9, electronic energy (M06-2X / cc-pVQZ)

E(M06-2X) = -94.536740

E(CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVQZ) = -94.345567396

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -94.368512718

Transition state for formation of beryllium dihydride 10, electronic  
energy (B3LYP / 6-31G(d))

E(B3LYP) = -94.5059541

Transition state for formation of beryllium dihydride 10, electronic  
energy (M06 / cc-pVQZ)

E(M06) = -94.4683678

Transition state for formation of beryllium dihydride 10, electronic  
energy (M06-2X / cc-pVQZ)

E(M06-2X) = -94.4861389

E(CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVQZ) = -94.291070516

Beryllium dihydride 10, electronic energy (B3LYP / 6-31G(d))

E(B3LYP) = -15.9174673

Beryllium dihydride 10, electronic energy (M06 / cc-pVQZ)

E(M06) = -15.9108397

Beryllium dihydride 10, electronic energy (M06-2X / cc-pVQZ)

E(M06-2X) = -15.9017934

E(CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVQZ) = -15.849257087

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -15.852369639

Beryllium dihydride 10, electronic energy (CASSCF(4,6) / SVP)

E(CASSCF) = -15.770682943

Beryllium monohydride 11, electronic energy (UB3LYP / 6-31G(d))

E(B3LYP) = -15.2610422

Beryllium monohydride 11, electronic energy (UM06 / cc-pVQZ)

E(M06) = -15.2504895

Beryllium monohydride 11, electronic energy (UM06-2X / cc-pVQZ)

E(M06-2X) = -15.2492315

E(CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVQZ) = -15.196519010

Transition state for cleavage of beryllium dihydride 10 into atomic beryllium 12 and dihydrogen (UB3LYP / 6-31G(d)) (guess=mix,always)

E(B3LYP) = -15.7706949

Transition state for cleavage of beryllium dihydride 10 into atomic beryllium 12 and dihydrogen (UM06 / cc-pVQZ) (guess=mix,always)

E(M06) = -15.7574638

Transition state for cleavage of beryllium dihydride 10 into atomic beryllium 12 and dihydrogen (UM06-2X / cc-pVQZ) (guess=mix,always)

E(M06-2X) = -15.7556552

E(CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVQZ) = -15.676727270

Transition state for cleavage of beryllium dihydride 10 into atomic beryllium 12 and dihydrogen (CASSCF(4,6)/SVP)

E(CASSCF) = -15.63154397

Atomic beryllium 12

E(UB3LYP/6-31G(d), guess=mix) = -14.6684425

E(UM06/cc-pVQZ, guess=mix) = -14.6609108

E(UM06-2X/cc-pVQZ, guess=mix) = -14.6651795

E(CCSD(T)/aug-cc-pVTZ) = -14.618454969

Complex of atomic beryllium 12 with dihydrogen, electronic energy (CASSCF(4,6)/SVP)

E(CASSCF) = -15.744739252

Transition state for cleavage of diethylberyllium 2 into *n*-butane and atomic beryllium 12, electronic energy (UB3LYP / 6-31G(d), guess=mix,always)

E(B3LYP) = -173.0122337

Transition state for cleavage of diethylberyllium 2 into *n*-butane and atomic beryllium 12, electronic energy (UM06 / cc-pVQZ, guess=mix,always)

E(M06) = -172.9486246

Transition state for cleavage of diethylberyllium 2 into *n*-butane and atomic beryllium 12, electronic energy (UM06-2X / cc-pVQZ, guess=mix,always)

E(M062X) = -172.9878886

Transition state for cleavage of dimethylberyllium 1 into ethane and atomic beryllium 12, electronic energy (UB3LYP / 6-31G(d), guess=mix,always)

E(B3LYP) = -94.3831223

Transition state for cleavage of dimethylberyllium 1 into ethane and atomic beryllium 12, electronic energy (UM06 / cc-pVQZ, guess=mix,always)

E(M06) = -94.3494789



Transition state for cleavage of dimethylberyllium 1 into ethane and atomic beryllium 12, electronic energy (UM06-2X / cc-pVQZ, guess=mix,always)

E(M06-2X) = -94.366239

E(CCSD(T)/aug-cc-pVQZ//UM062X/cc-pVQZ) = -94.135185169

Transition state for formation of methyleneberyllium 13, electronic energy (B3LYP/6-31G(d))

E(B3LYP) = -94.4379459

Transition state for formation of methyleneberyllium 13, electronic energy (M06/cc-pVQZ)

E(M06) = -94.4028794

Transition state for formation of methyleneberyllium 13, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -94.4223804

Triplet methyleneberyllium 13, electronic energy (UB3LYP / 6-31G(d))

E(B3LYP) = -53.9321891

Triplet methyleneberyllium 13, electronic energy (UM06 / cc-pVQZ)

E(M06) = -53.9063458

Triplet methyleneberyllium 13, electronic energy (UM06-2X / cc-pVQZ)

E(M06-2X) = -53.9211671

E(CCSD(T)/aug-cc-pVQZ//M062X/cc-pVQZ) = -53.808091787

Complex of singlet methyleneberyllium 13 with methane, electronic energy (B3LYP/6-31G(d))

E(B3LYP) = -94.4447739

Complex of singlet methyleneberyllium 13 with methane, electronic energy (M06/cc-pVQZ)

E(M06) = -94.4130373

Complex of singlet methyleneberyllium 13 with methane, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -94.4343261

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -94.294272775051

Transition state for formation of triplet beryllo-carbene 14, electronic energy (UB3LYP / 6-31G(d))

E(B3LYP) = -53.8588671

Transition state for formation of triplet beryllo-carbene 14, electronic energy (UM06 / cc-pVQZ)

E(M06) = -53.8335782

Transition state for formation of triplet beryllo-carbene 14, electronic energy (UM06-2X / cc-pVQZ)

E(M06-2X) = -53.8462661

E(CCSD(T)/aug-cc-pVQZ//M062X/cc-pVQZ) = -53.755448483

Triplet beryllo-carbene 14, electronic energy (UB3LYP / 6-31G(d))

E(B3LYP) = -53.9254057

Triplet beryllo-carbene 14, electronic energy (UM06 / cc-pVQZ)

E(M06) = -53.906639

Triplet beryllo-carbene 14, electronic energy (UM06-2X / cc-pVQZ)

E(M06-2X) = -53.9137312

E(CCSD(T)/aug-cc-pVQZ//M062X/cc-pVQZ) = -53.797034246

Methylberyllium radical 15, electronic energy (UB3LYP / 6-31G(d))

E(B3LYP) = -54.5951713

Methylberyllium radical 15, electronic energy (UM06 / cc-pVQZ)

E(M06) = -54.5699142

Methylberyllium radical 15, electronic energy (UM06-2X / cc-pVQZ)

E(M06-2X) = -54.5841441

E(CCSD(T)/aug-cc-pVQZ//M062X/cc-pVQZ) = -54.472121820

Transition state for formation of ethylideneberyllium 16, electronic energy (B3LYP/6-31G(d))

E(B3LYP) = -173.0630672

Transition state for formation of ethylideneberyllium 16, electronic energy (M06/cc-pVQZ)

E(M06) = -172.9911431

Transition state for formation of ethylideneberyllium 16, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -173.0348859

E(CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVQZ) = -172.709461872

Triplet ethylideneberyllium 16, electronic energy (UB3LYP/6-31G(d))

E(B3LYP) = -93.2510823

Triplet ethylideneberyllium 16, electronic energy (UM06/cc-pVQZ)

E(M06) = -93.2075437

Triplet ethylideneberyllium 16, electronic energy (UM06-2X/cc-pVQZ)

E(M06-2X) = -93.2337956

E(CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVQZ) = -93.040339051

Transition state for formation of triplet beryllo-carbene 17, electronic energy (UB3LYP/6-31G(d))

E(B3LYP) = -93.1915177

Transition state for formation of triplet beryllo-carbene 17, electronic energy (UM06/cc-pVQZ)

E(M06) = -93.1488063

Transition state for formation of triplet beryllo-carbene 17, electronic energy (UM06-2X/cc-pVQZ)

E(M06-2X) = -93.1710618

E(CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVQZ) = -92.972740565

Triplet beryllo-carbene 17, electronic energy (UB3LYP/6-31G(d))

E(B3LYP) = -93.2561854

Triplet beryllo-carbene 17, electronic energy (UM06/cc-pVQZ)

E(M06) = -93.219368

Triplet beryllo-carbene 17, electronic energy (UM06-2X/cc-pVQZ)

E(M06-2X) = -93.2357547

E(CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVQZ) = -93.038471980

Transition state 16 → vinylberyllium hydride 18, electronic energy  
(B3LYP / 6-31G(d))

E(B3LYP) = -93.2033329

Transition state 16 → vinylberyllium hydride 18, electronic energy  
(M06 / cc-pVQZ)

E(M06) = -93.1681571

Transition state 16 → vinylberyllium hydride 18, electronic energy  
(M06-2X / cc-pVQZ)

E(M06-2X) = -93.1909561

E(CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVQZ) = -92.996418176

Transition state 17 → vinylberyllium hydride 18, electronic energy  
(B3LYP / 6-31G(d))

E(B3LYP) = -93.2095954

Transition state 17 → vinylberyllium hydride 18, electronic energy  
(M06 / cc-pVQZ)

E(M06) = -93.1780689

Transition state 17 → vinylberyllium hydride 18, electronic energy  
(M06-2X / cc-pVQZ)

E(M06-2X) = -93.1965084

E(CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVQZ) = -92.999826538

Vinylberyllium hydride 18, electronic energy (B3LYP / 6-31G(d))

E(B3LYP) = -93.3268432

Vinylberyllium hydride 18, electronic energy (M06 / cc-pVQZ)

E(M06) = -93.2884255

Vinylberyllium hydride 18, electronic energy (M06 / cc-pVQZ)

E(M06-2X) = -93.3106964

E(CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVQZ) = -93.117936094

Transition state 18 → 10 + C<sub>2</sub>H<sub>2</sub>, electronic energy (B3LYP / 6-31G(d))

E(B3LYP) = -93.2572991

Transition state 18 → 10 + C<sub>2</sub>H<sub>2</sub>, electronic energy (M06 / cc-pVQZ)

E(M06) = -93.2262457

Transition state 18 → 10 + C<sub>2</sub>H<sub>2</sub>, electronic energy (M06-2X / cc-pVQZ)

E(M06-2X) = -93.2456442

E(CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVQZ) = -93.046564196

Transition state for formation of hydridoberyllium formate 19, electronic energy (B3LYP / 6-31G(d))

E(B3LYP) = -204.4990717

Transition state for formation of hydridoberyllium formate 19, electronic energy (M06 / cc-pVQZ)

E(M06) = -204.4972817

Transition state for formation of hydridoberyllium formate 19, electronic energy (M06-2X / cc-pVQZ)

E(M06-2X) = -204.5078245

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -204.240876636

Hydridoberyllium formate 19, electronic energy (B3LYP / 6-31G(d))

E(B3LYP) = -204.5705662

Hydridoberyllium formate 19, electronic energy (M06 / cc-pVQZ)

E(M06) = -204.5614522

Hydridoberyllium formate 19, electronic energy (M06-2X / cc-pVQZ)

E(M06-2X) = -204.584738

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -204.315402890

Transition state for formation of beryllium diformate 20, electronic energy (B3LYP / 6-31G(d))

E(B3LYP) = -393.1392753

Transition state for formation of beryllium diformate 20, electronic energy (M06 / cc-pVQZ)

E(M06) = -393.1505342

Transition state for formation of beryllium diformate 20, electronic energy (M06-2X / cc-pVQZ)

E(M06-2X) = -393.1939273

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -392.707180642668

Beryllium diformate 20, electronic energy (B3LYP / 6-31G(d))

E(B3LYP) = -393.2273714

Beryllium diformate 20, electronic energy (M06 / cc-pVQZ)

E(M06) = -393.2149134

Beryllium diformate 20, electronic energy (M06-2X / cc-pVQZ)

E(M06-2X) = -393.2707156

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -392.781796911294

Transition state for formation of ethylberyllium formate 21, electronic energy (B3LYP / 6-31G(d))

E(B3LYP) = -283.1368375

Transition state for formation of ethylberyllium formate 21, electronic energy (M06 / cc-pVQZ)

(M06) = -283.102611

Transition state for formation of ethylberyllium formate 21,  
electronic energy (M06-2X / cc-pVQZ)

E(M06-2X) = -283.1407483

Ethylberyllium formate 21, electronic energy (B3LYP / 6-31G(d))

E(B3LYP) = -283.2094406

Ethylberyllium formate 21, electronic energy (M06 / cc-pVQZ)

E(M06) = -283.1671771

Ethylberyllium formate 21, electronic energy (M06-2X / cc-pVQZ)

E(M06-2X) = -283.2179967

Transition state for formation of beryllium formate propionate 22  
from 21, electronic energy (B3LYP/6-31G(d))

E(B3LYP) = -471.7722698

Transition state for formation of beryllium formate propionate 22  
from 21, electronic energy (M06/cc-pVQZ)

E(M06) = -471.7384221

Transition state for formation of beryllium formate propionate 22  
from 21, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -471.8061756

Beryllium formate propionate 22, electronic energy (B3LYP / 6-  
31G(d))

E(B3LYP) = -471.8720898

Beryllium formate propionate 22, electronic energy (M06 / cc-pVQZ)

E(M06) = -471.8274284

Beryllium formate propionate 22, electronic energy (M06-2X / cc-  
pVQZ)

E(M06-2X) = -471.9067639

Transition state for formation of hydridoberyllium propionate 23,  
electronic energy (B3LYP/6-31G(d))

E(B3LYP) = -283.1288503

Transition state for formation of hydridoberyllium propionate 23,  
electronic energy (M06/cc-pVQZ)

E(M06) = -283.0960131

Transition state for formation of hydridoberyllium propionate 23,  
electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -283.1336173

Hydridoberyllium propionate 23, electronic energy (B3LYP / 6-31G(d))

E(B3LYP) = -283.2164444

Hydridoberyllium propionate 23, electronic energy (M06 / cc-pVQZ)

E(M06) = -283.1750106

Hydridoberyllium propionate 23, electronic energy (M06-2X / cc-pVQZ)

E(M06-2X) = -283.2219114

Transition state for the formation of 22 from 23

This reaction is barrierless at all levels of theory employed  
(B3LYP/6-31G(d); M06/cc-pVQZ; M06-2X/cc-pVQZ).

Transition state for formation of 2-berylla-1,3-dioxetane-4-ylidene  
24, electronic energy (UB3LYP / 6-31G(d); guess=(mix,always))

E(B3LYP) = -203.2261264

Transition state for formation of 2-berylla-1,3-dioxetane-4-ylidene  
24, electronic energy (UM06 / cc-pVQZ; guess=(mix,always))

E(M06) = -203.2200855

Transition state for formation of 2-berylla-1,3-dioxetane-4-ylidene  
24, electronic energy (UM06-2X / cc-pVQZ; guess=(mix,always))



E(M06-2X) = -203.2358411  
E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -202.983711176  
2-Berylla-1,3-dioxetane-4-ylidene 24, electronic energy (B3LYP/6-31G(d))

E(B3LYP) = -203.2785969

2-Berylla-1,3-dioxetane-4-ylidene 24, electronic energy (M06/cc-pVQZ)

E(M06) = -203.2721039

2-Berylla-1,3-dioxetane-4-ylidene 24, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -203.2998138

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -203.025334980

Transition state for formation of 2-beryllaoxirane-3-one 25, electronic energy (UB3LYP/6-31G(d); guess=(mix,always))

E(B3LYP) = -203.2274726

Transition state for formation of 2-beryllaoxirane-3-one 25, electronic energy (UM06/cc-pVQZ; guess=(mix,always))

E(M06) = -203.2231612

Transition state for formation of 2-beryllaoxirane-3-one 25, electronic energy (UM06-2X/cc-pVQZ; guess=(mix,always))

E(M06-2X) = -203.2405796

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -202.976176798

2-Beryllaoxirane-3-one 25, electronic energy (B3LYP/6-31G(d))

E(B3LYP) = -203.2705268

2-Beryllaoxirane-3-one 25, electronic energy (M06/cc-pVQZ)

E(M06) = -203.2645936

2-Beryllaoxirane-3-one 25, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -203.2880029

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -203.016060301

Transition state for the formation of oxoberylliumisocarbonyl 26 from 24, electronic energy (B3LYP / 6-31G(d))

E(B3LYP) = -203.239998

Transition state for the formation of oxoberylliumisocarbonyl 26 from 24, electronic energy (M06 / cc-pVQZ)

E(M06) = -203.2290882

Transition state for the formation of oxoberylliumisocarbonyl 26 from 24, electronic energy (M06-2X / cc-pVQZ)

E(M06-2X) = -203.2581907

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -202.989818468

Oxoberylliumisocarbonyl 26, electronic energy (B3LYP / 6-31G(d))

E(B3LYP) = -203.2538852

Oxoberylliumisocarbonyl 26, electronic energy (M06 / cc-pVQZ)

E(M06) = -203.2421821

Oxoberylliumisocarbonyl 26, electronic energy (M06-2X / cc-pVQZ)

E(M06-2X) = -203.2708966

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -203.002743765

Transition state for the formation of oxoberylliumcarbonyl 27 from 25, electronic energy (B3LYP/6-31G(d))

E(B3LYP) = -203.2699037

Transition state for the formation of oxoberylliumcarbonyl 27 from 25, electronic energy (M06/cc-pVQZ)

E(M06) = -203.2595129

Transition state for the formation of oxoberylliumcarbonyl 27 from 25, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -203.2850142

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -203.017726816

Oxoberylliumcarbonyl 27, electronic energy (B3LYP / 6-31G(d))

E(B3LYP) = -203.2832865

Oxoberylliumcarbonyl 27, electronic energy (M06 / cc-pVQZ)

E(M06) = -203.2673049

Oxoberylliumcarbonyl 27, electronic energy (M06-2X / cc-pVQZ)

E(M06-2X) = -203.2912042

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -203.026744785

Beryllium oxide monomer 28, electronic energy (B3LYP / 6-31G(d))

E(B3LYP) = -89.9003663

Beryllium oxide monomer 28, electronic energy (M06 / cc-pVQZ)

E(M06) = -89.9008574

Beryllium oxide monomer 28, electronic energy (M06-2X / cc-pVQZ)

E(M06-2X) = -89.9061491

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -89.778928440

Complex of triplet methyleneberyllium 13 with CO<sub>2</sub>, electronic energy (UB3LYP/6-31G(d))

E(B3LYP) = -242.5150384

Complex of triplet methyleneberyllium 13 with CO<sub>2</sub>, electronic energy (UM06/cc-pVQZ)

E(M06) = -242.498844

Complex of triplet methyleneberyllium 13 with CO<sub>2</sub>, electronic energy (UM06-2X/cc-pVQZ)

E(M06-2X) = -242.5277026

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -242.198789996

Beryllaoxetanone 29, electronic energy (B3LYP / 6-31G(d))

E(B3LYP) = -242.6163566

Beryllaoxetanone 29, electronic energy (M06 / cc-pVQZ)

E(M06) = -242.5979405

Beryllaoxetanone 29, electronic energy (M06-2X / cc-pVQZ)

E(M06-2X) = -242.6362658

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -242.303074185

Complex of beryllaoxetanone 29 with CO<sub>2</sub>, electronic energy (B3LYP/6-31G(d))

E(B3LYP) = -431.2265552

Complex of beryllaoxetanone 29 with CO<sub>2</sub>, electronic energy (M06/cc-pVQZ)

E(M06) = -431.216291

Complex of beryllaoxetanone 29 with CO<sub>2</sub>, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -431.2717718

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -430.722566324

Transition state for formation of beryllium malonate 30, electronic energy (B3LYP/6-31G(d))

E(B3LYP) = -431.2250713

Transition state for formation of beryllium malonate 30, electronic energy (M06/cc-pVQZ)

E(M06) = -431.2119112

Transition state for formation of beryllium malonate 30, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -431.2684797

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -430.718322745

Beryllium malonate 30, electronic energy (B3LYP/6-31G(d))

E(B3LYP) = -431.2826799

Beryllium malonate 30, electronic energy (M06/cc-pVQZ)

E(M06) = -431.2625345

Beryllium malonate 30, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -431.3275359

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -430.776649279

Transition state for formation of triplet diradical <sup>3</sup>31, electronic energy (UB3LYP / 6-31G(d))

E(B3LYP) = -242.5128206

Transition state for formation of triplet diradical <sup>3</sup>31, electronic energy (UM06/cc-pVQZ)

E(M06) = -242.4957759

Transition state for formation of triplet diradical <sup>3</sup>31, electronic energy (UM06-2X/cc-pVQZ)

E(M06-2X) = -242.5256084

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -242.191102083

Triplet diradical <sup>3</sup>31, electronic energy (UB3LYP / 6-31G(d))

E(B3LYP) = -242.5657007

Triplet diradical <sup>3</sup>31, electronic energy (UM06 / cc-pVQZ)

E(M06) = -242.5402393

Triplet diradical <sup>3</sup>31, electronic energy (UM06-2X / cc-pVQZ)

E(M06-2X) = -242.5768102

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -242.243936466

Singlet diradical <sup>1</sup>31, electronic energy (UB3LYP / 6-31G(d);  
guess=(mix,always))

E(B3LYP) = -242.5662254

Singlet diradical <sup>1</sup>31, electronic energy (UM06 / cc-pVQZ;  
guess=(mix,always))

E(M06) = -242.5407799

Singlet diradical <sup>1</sup>31, electronic energy (UM06-2X / cc-pVQZ;  
guess=(mix,always))

E(M06-2X) = -242.5772134

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -242.242933374

Transition state for formation of beryllaoxetanone 29 from singlet  
diradical <sup>1</sup>31, electronic energy (UB3LYP/6-31G(d);  
guess=(mix,always))

E(B3LYP) = -242.521517

Transition state for formation of beryllaoxetanone 29 from singlet  
diradical <sup>1</sup>31, electronic energy (UM06/cc-pVQZ; guess=(mix,always))

E(M06) = -242.5120996

Transition state for formation of beryllaoxetanone 29 from singlet  
diradical <sup>1</sup>31, electronic energy (UM06-2X/cc-pVQZ;  
guess=(mix,always))

E(M06-2X) = -242.5404797

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -242.209298887

Triplet diradical <sup>3</sup>32, electronic energy (UB3LYP / 6-31G(d))

E(B3LYP) = -242.5628411

Triplet diradical <sup>3</sup>32, electronic energy (UM06 / cc-pVQZ)

<sup>3</sup>32 is not a minimum structure at this level of theory. Attempts at  
optimization instead yielded <sup>3</sup>31.

Triplet diradical <sup>3</sup>32, electronic energy (UM06-2X / cc-pVQZ)

E(M06-2X) = -242.5746558

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -242.241296633

Singlet diradical <sup>1</sup>32, electronic energy

On the singlet spin manifold, this diradical is not a minimum  
structure at any of the three levels of theory employed.

Transition state (triplet) for formation of carbene 33, electronic  
energy (UB3LYP/6-31G(d))

E(B3LYP) = -242.4940008

Transition state (triplet) for formation of carbene 33, electronic energy (UM06/cc-pVQZ)

E(M06) = -242.4623946

Transition state (triplet) for formation of carbene 33, electronic energy (UM06-2X/cc-pVQZ)

E(M06-2X) = -242.5022902

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -242.170129512

Carbene 33, singlet ground state, electronic energy (B3LYP/6-31G(d))

E(B3LYP) = -242.5466704

Carbene 33, singlet ground state, electronic energy (M06/cc-pVQZ)

E(M06) = -242.5252579

Carbene 33, singlet ground state, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -242.5662505

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -242.232808727

Transition state (triplet) for formation of triplet diradical 34, electronic energy (UB3LYP/6-31G(d))

E(B3LYP) = -242.559245

Transition state (triplet) for formation of triplet diradical 34, electronic energy (UM06/cc-pVQZ)

E(M06) = -242.5345099

Transition state (triplet) for formation of triplet diradical 34, electronic energy (UM06-2X/cc-pVQZ)

E(M06-2X) = -242.5709336

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -242.238146881

Triplet diradical 34, electronic energy (UB3LYP/6-31G(d))

E(B3LYP) = -242.5646499

Triplet diradical 34, electronic energy (UM06/cc-pVQZ)

E(M06) = -242.5386528

Triplet diradical 34, electronic energy (UM06-2X/cc-pVQZ)

E(M06-2X) = -242.5784881

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -242.243757391

Complex of methylberyllium radical 15 with CO<sub>2</sub>, electronic energy (UB3LYP/6-31G(d))

E(B3LYP) = -243.1778332

Complex of methylberyllium radical 15 with CO<sub>2</sub>, electronic energy (UM06/cc-pVQZ)

E(M06) = -243.1614688

Complex of methylberyllium radical 15 with CO<sub>2</sub>, electronic energy (UM06-2X/cc-pVQZ)

E(M06-2X) = -243.1903635

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -242.862473258

Transition state for formation of *trans*-MeBeOCO radical 35, electronic energy (UB3LYP/6-31G(d))

E(B3LYP) = -243.1746995

Transition state for formation of *trans*-MeBeOCO radical 35, electronic energy (UM06/cc-pVQZ)

E(M06) = -243.1574132

Transition state for formation of *trans*-MeBeOCO radical 35, electronic energy (UM06-2X/cc-pVQZ)

E(M06-2X) = -243.1869509

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -242.855070556

*trans*-MeBeOCO radical 35, electronic energy (UB3LYP/6-31G(d))

E(B3LYP) = -243.2317673



*trans*-MeBeOCO radical 35, electronic energy (UM06/cc-pVQZ)

E(M06) = -243.2058757

*trans*-MeBeOCO radical 35, electronic energy (UM06-2X/cc-pVQZ)

E(M06-2X) = -243.2427572

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -242.911422335

*cis*-MeBeOCO radical 36, electronic energy (UM06-2X/cc-pVQZ)

E(M06-2X) = -243.2404673

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -242.908856853

This species is not a minimum structure at the M06/cc-pVQZ level of theory.

Transition state for formation of 37 (UM06/cc-pVQZ)

E(M06) = -243.2039888

E(CCSD(T)/aug-cc-pVQZ//M06/cc-pVQZ) = -242.937204333761

Radical 37, electronic energy (UM06/cc-pVQZ)

E(M06) = -243.2041646

E(CCSD(T)/aug-cc-pVQZ//M06/cc-pVQZ) = -242.936540834

Radical 37 is not a minimum structure at the UB3LYP/6-31G(d) and UM06-2X/cc-pVQZ levels of theory.

Transition state for formation of radical 38 (UB3LYP / 6-31G(d))

E(B3LYP) = -243.2242148

Transition state for formation of radical 38 (UM06 / cc-pVQZ)

E(M06) = -243.1988035

Transition state for formation of radical 38 (UM06-2X / cc-pVQZ)

E(M06-2X) = -243.2355546

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -242.904923749

Radical 38, electronic energy (UB3LYP/6-31G(d))

E(B3LYP) = -243.2283181

Radical 38, electronic energy (UM06/cc-pVQZ)

E(M06) = -243.2017049

Radical 38, electronic energy (UM06-2X/cc-pVQZ)

E(M06-2X) = -243.2414257

E(CCSD(T)/aug-cc-pVQZ//M06/cc-pVQZ) = -242.938071786

Methylberylliumoxy radical 39, electronic energy (UB3LYP / 6-31G(d))

E(B3LYP) = -129.8575166

Methylberylliumoxy radical 39, electronic energy (UM06 / cc-pVQZ)

This geometry optimization failed to converge.

Methylberylliumoxy radical 39, electronic energy (UM06-2X / cc-pVQZ)

E(M06-2X) = -129.8564156

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -129.664480038

Beryllium oxide cyclic dimer 40, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -180.0897157

Beryllium oxide cyclic trimer 41, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -270.2918065

Beryllium oxide cyclic tetramer 42, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -360.4563768

Beryllium oxide cubane tetramer 43, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -360.4005379

Methane, electronic energy (B3LYP/6-31G(d))

E(B3LYP) = -40.5183833

Methane, electronic energy (M06/cc-pVQZ)

E(M06) = -40.4983703

Methane, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -40.5048878

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -40.451712862

Ethane, electronic energy (B3LYP/6-31G(d))

E(B3LYP) = -79.8304206

Ethane, electronic energy (M06/cc-pVQZ)

E(M06) = -79.7935517

Ethane, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -79.8119074

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -79.700504139

E(CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVQZ) = -79.679857473

*n*-Butane, electronic energy (B3LYP/6-31G(d))

E(B3LYP) = -158.4580428

*n*-Butane, electronic energy (M06/cc-pVQZ)

E(M06) = -158.3899386

*n*-Butane, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -158.4320395

E(CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVQZ) = -158.164881117

Ethene, electronic energy (B3LYP/6-31G(d))

E(B3LYP) = -78.5874587

Ethene, electronic energy (M06/cc-pVQZ)

E(M06) = -78.5550494

Ethene, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -78.5776897

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -78.463383577

E(CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVQZ) = -78.443433867

Ethyne, electronic energy (B3LYP/6-31G(d))

E(B3LYP) = -77.325646

Ethyne, electronic energy (M06/cc-pVQZ)

E(M06) = -77.3049878

Ethyne, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -77.3295672

E(CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVQZ) = -77.191629462

Methyl, electronic energy (UB3LYP/6-31G(d))

E(B3LYP) = -39.8382919

Methyl, electronic energy (UM06/cc-pVQZ)

E(M06) = -39.8197387

Methyl, electronic energy (UM06-2X/cc-pVQZ)

E(M06-2X) = -39.8276864

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -39.773328742

Ethyl, electronic energy (UB3LYP/6-31G(d))

E(B3LYP) = -79.1578683

Ethyl, electronic energy (UM06/cc-pVQZ)

E(M06) = -79.1228066

Ethyl, electronic energy (UM06-2X/cc-pVQZ)

E(M06-2X) = -79.1411536

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -79.027582437

E(CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVQZ) = -79.007879046

Carbon dioxide, electronic energy (B3LYP/6-31G(d))

E(B3LYP) = -188.5809395

Carbon dioxide, electronic energy (M06/cc-pVQZ)

E(M06) = -188.590794

Carbon dioxide, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -188.6033635

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -188.389248151

Carbon monoxide, electronic energy (B3LYP/6-31G(d))

E(B3LYP) = -113.3094531

Carbon monoxide, electronic energy (M06/cc-pVQZ)

E(M06) = -113.3058097

Carbon monoxide, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -113.3261211

E(CCSD(T)/aug-cc-pVQZ//M06-2X/cc-pVQZ) = -113.190025922

Ketene, electronic energy (B3LYP/6-31G(d))

E(B3LYP) = -152.5984726

Ketene, electronic energy (M06/cc-pVQZ)

E(M06) = -152.5816318

Ketene, electronic energy (M06-2X/cc-pVQZ)

E(M06-2X) = -152.6063756