

## Supplementary data

### Substrate and product role in the Shvo's catalyzed selective hydrogenation of the platform bio-based chemical 5-hydroxymethylfurfural

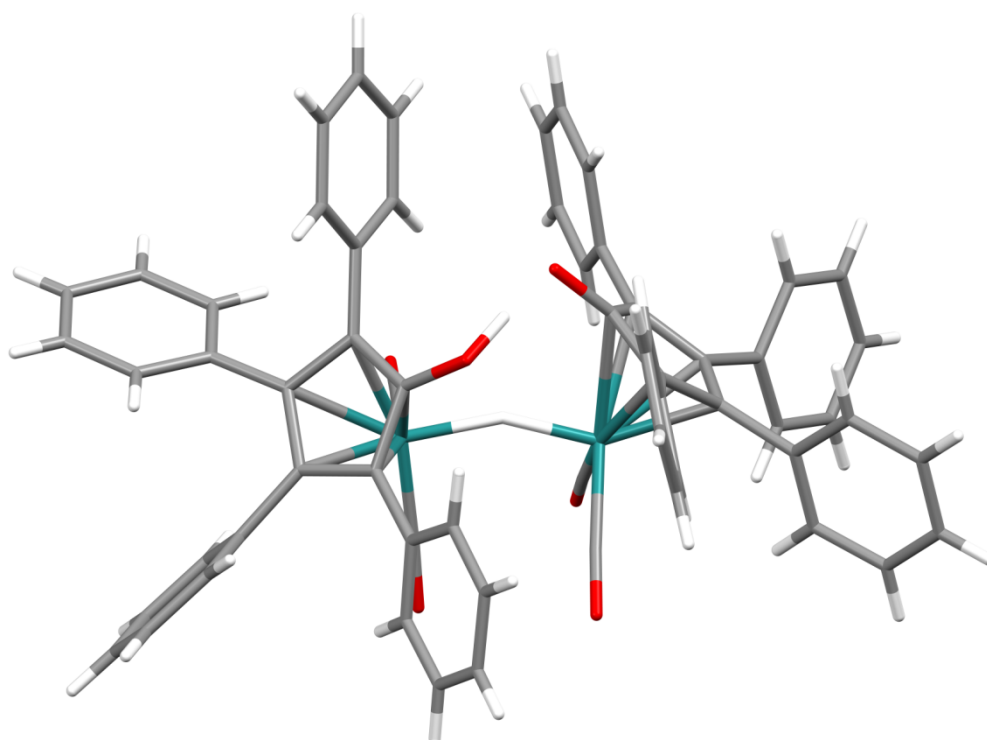
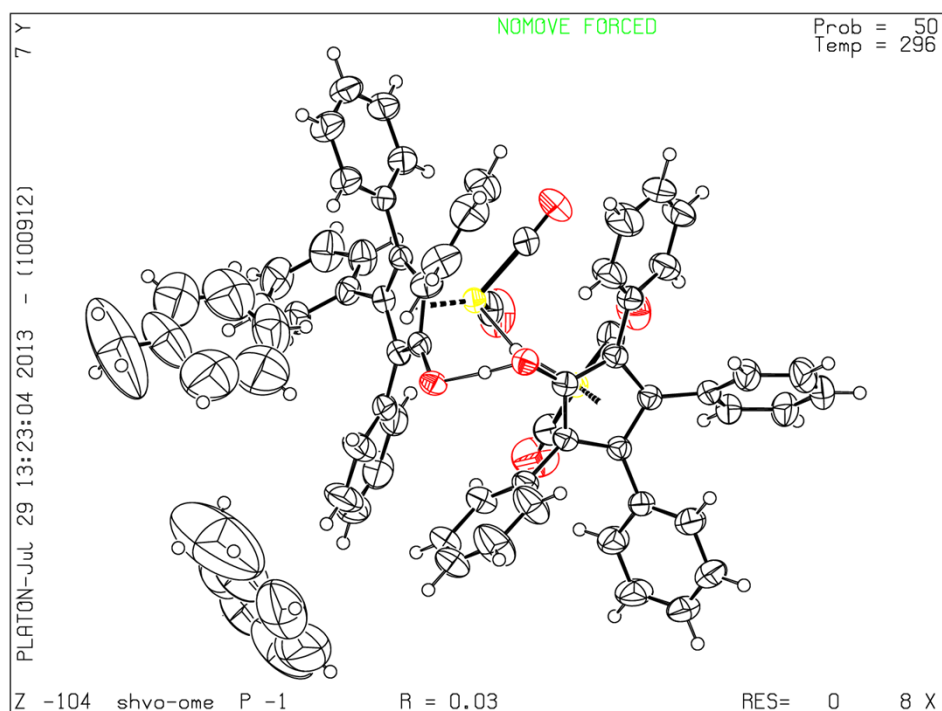
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**Table S1:** crystal data for Shvo catalyst **1**.

|                                       |                                                                |
|---------------------------------------|----------------------------------------------------------------|
| CCDC number                           | 953038                                                         |
| formula                               | C <sub>76</sub> H <sub>58</sub> O <sub>6</sub> Ru <sub>2</sub> |
| fw                                    | 1269.3                                                         |
| T, K                                  | 295(2)                                                         |
| λ, Å                                  | 0.71073                                                        |
| crystal system                        | triclinic                                                      |
| space group                           | P $\bar{1}$                                                    |
| a, Å                                  | 13.2876(12)                                                    |
| b, Å                                  | 15.3866(14)                                                    |
| c, Å                                  | 17.1807(15)                                                    |
| α, deg                                | 63.4230(10)                                                    |
| β, deg                                | 80.9220(10)                                                    |
| γ, deg                                | 81.2740(10)                                                    |
| V, Å <sup>3</sup>                     | 3089.0(5)                                                      |
| Z                                     | 2                                                              |
| D <sub>c</sub> , g cm <sup>-3</sup>   | 1.365                                                          |
| μ, mm <sup>-1</sup>                   | 0.543                                                          |
| F(000)                                | 1300                                                           |
| crystal size, mm                      | 0.3 × 0.15 × 0.15                                              |
| θ limits, deg                         | 1.49–28.00                                                     |
| reflections collected                 | 36149                                                          |
| independent reflections               | 14393 (R <sub>int</sub> = 0.0220)                              |
| data/restraints/params                | 14393/744/6                                                    |
| goodness on fit on F <sup>2</sup>     | 1.025                                                          |
| R <sub>1</sub> (I > 2σ(I))            | 0.0311                                                         |
| wR2 (all data)                        | 0.0892                                                         |
| diff peak and hole, e Å <sup>-3</sup> | 0.055 and −0.375                                               |
|                                       |                                                                |

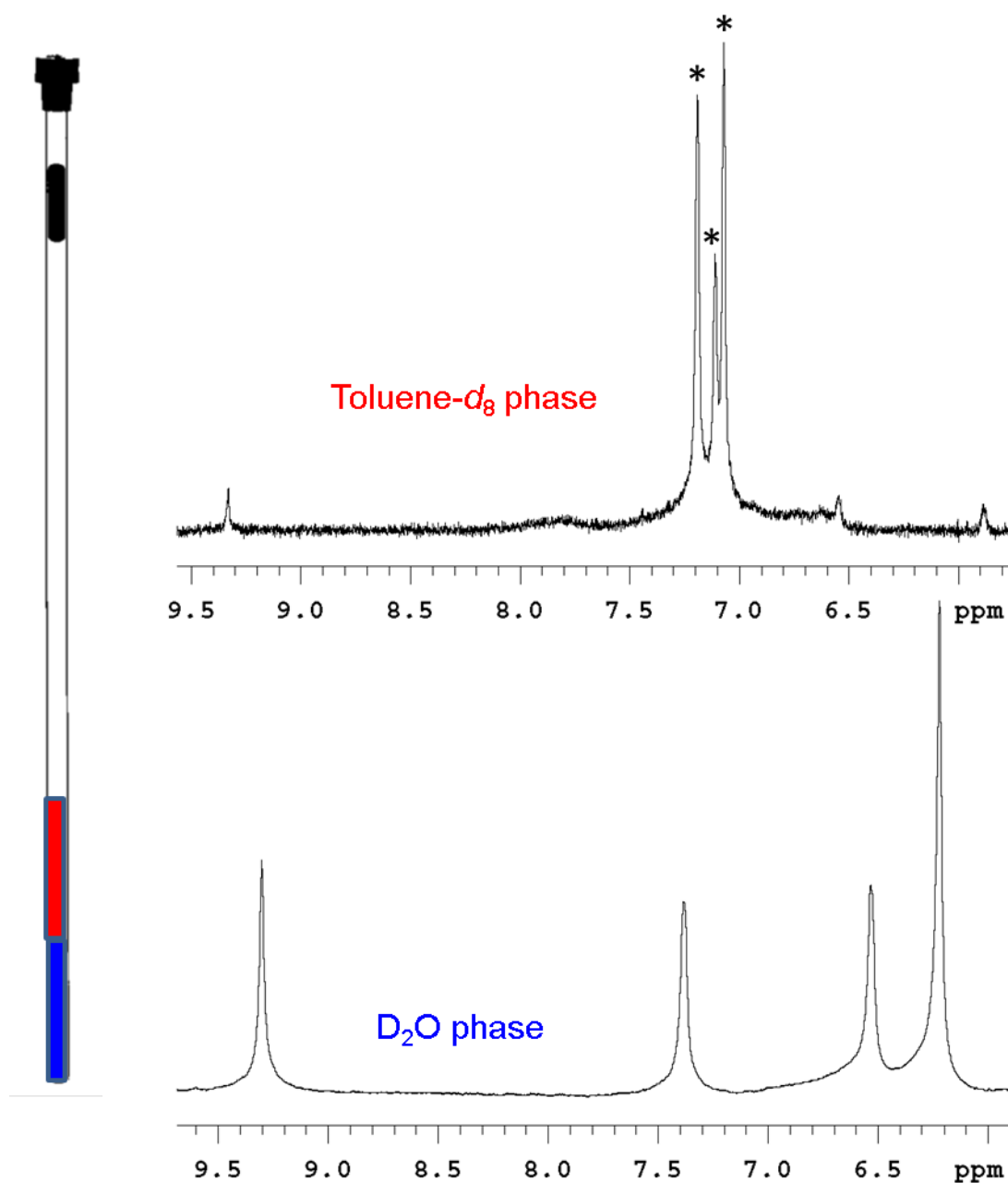


**Figure S1** ORTEP representation and stick figure of the X-ray structure of Shvo catalyst (toluene molecules were removed in the stick representation).

## IN SITU NMR EXPERIMENTS

### Toluene- $d_8$ /D $_2$ O HMF and BHMF distribution experiment

In a NMR tube, HMF (4,159 mg, 0,00785 mmol) and BHMF (4,233 mg, 0,00785 mmol) were dissolved in a mixture of 0.2 mL of toluene- $d_8$  and 0,2 mL of D $_2$ O. Spectra recorded using Varian Inova 300 ( $^1\text{H}$ , 300.1;  $^{13}\text{C}$ , 75.5 MHz) spectrometer on the D $_2$ O and toluene- $d_8$  phases (Figure S2) show that the large amount of HMF and BHMF reside in the aqueous phase.



**Figure S2** Distribution of HMF and BHMF in biphasic toluene- $d_8$ /D $_2$ O solution.

**General procedure for *in situ* NMR minute-by-minute monitoring of the catalytic hydrogenation of HMF to BHMF.**

In a J. Young valve equipped NMR tube, catalyst **1** (e.g. 0,0676 mg, 0,0628  $\mu\text{mol}$ ) and the substrate HMF (e.g. 250 eq., 1,98 mg, 0,0157 mmol) were added and dissolved in 0.7 mL of toluene- $\text{d}_8$  under nitrogen atmosphere. The samples solutions have been frozen in liquid nitrogen, the nitrogen inside the tube removed under vacuum and restored with 3 bar of  $\text{H}_2$ . The *in situ* experiments have been performed in a Varian Inova 600 ( $^1\text{H}$ , 599.7,  $^{13}\text{C}$ , 150.8 MHz) spectrometers at 90°C. A spectrum was acquired and recorded every 60 seconds.

**Table S2** *In situ* NMR experiment. Reaction conditions: catalyst **1** (0,0676 mg, 0,0628  $\mu\text{mol}$ ), HMF (250 eq., 1,98 mg, 0,0157 mmol), toluene- $\text{d}_8$  (0.7 mL), 90°C,  $p(\text{H}_2)$  (3 bar). Spectra acquired every 60 seconds. An absolute error of 1% affect the NMR integrations. This Table correspond to Figure 6 (BHMF yield vs time) in the manuscript.

| Min | HMF integration | BHMF integration | BHMF integration/2 | HMF integration+<br>(BHMF integration/2) | BHMF yield |
|-----|-----------------|------------------|--------------------|------------------------------------------|------------|
| 0   | 100             | 0                | 0                  | 100                                      | 0          |
| 1   | 99,1            | 0,9              | 0,5                | 99,6                                     | 0,5        |
| 2   | 98,6            | 1,4              | 0,7                | 99,3                                     | 0,7        |
| 3   | 97,2            | 2,8              | 1,4                | 98,6                                     | 1,4        |
| 4   | 96,5            | 3,5              | 1,8                | 98,3                                     | 1,8        |
| 5   | 95,5            | 4,5              | 2,3                | 97,8                                     | 2,3        |
| 6   | 94,5            | 5,5              | 2,8                | 97,3                                     | 2,8        |
| 7   | 93,6            | 6,4              | 3,2                | 96,8                                     | 3,3        |
| 8   | 92,7            | 7,3              | 3,7                | 96,4                                     | 3,8        |
| 9   | 91,7            | 8,3              | 4,2                | 95,9                                     | 4,3        |
| 10  | 90,6            | 9,4              | 4,7                | 95,3                                     | 4,9        |
| 11  | 90,1            | 9,9              | 5,0                | 95,1                                     | 5,2        |
| 12  | 89,4            | 10,6             | 5,3                | 94,7                                     | 5,6        |
| 13  | 88,3            | 11,7             | 5,9                | 94,2                                     | 6,2        |
| 14  | 87,5            | 12,5             | 6,3                | 93,8                                     | 6,7        |
| 15  | 86,7            | 13,3             | 6,7                | 93,4                                     | 7,1        |
| 16  | 85,8            | 14,2             | 7,1                | 92,9                                     | 7,6        |
| 17  | 84,9            | 15,1             | 7,6                | 92,5                                     | 8,2        |
| 18  | 84,4            | 15,6             | 7,8                | 92,2                                     | 8,5        |
| 19  | 83,5            | 16,5             | 8,3                | 91,8                                     | 9,0        |
| 20  | 82,6            | 17,4             | 8,7                | 91,3                                     | 9,5        |
| 21  | 82,0            | 18,0             | 9,0                | 91,0                                     | 9,9        |
| 22  | 81,2            | 18,8             | 9,4                | 90,6                                     | 10,4       |
| 23  | 80,5            | 19,5             | 9,8                | 90,3                                     | 10,8       |

|    |      |      |      |      |      |
|----|------|------|------|------|------|
| 24 | 79,7 | 20,3 | 10,2 | 89,9 | 11,3 |
| 25 | 78,7 | 21,3 | 10,7 | 89,4 | 11,9 |
| 26 | 78,2 | 21,8 | 10,9 | 89,1 | 12,2 |
| 27 | 77,4 | 22,6 | 11,3 | 88,7 | 12,7 |
| 28 | 76,7 | 23,3 | 11,7 | 88,4 | 13,2 |
| 29 | 76,0 | 24,0 | 12,0 | 88,0 | 13,6 |
| 30 | 75,2 | 24,8 | 12,4 | 87,6 | 14,2 |
| 31 | 74,7 | 25,3 | 12,7 | 87,4 | 14,5 |
| 32 | 73,8 | 26,2 | 13,1 | 86,9 | 15,1 |
| 33 | 73,1 | 26,9 | 13,5 | 86,6 | 15,5 |
| 34 | 72,5 | 27,5 | 13,8 | 86,3 | 15,9 |
| 35 | 72,0 | 28,0 | 14,0 | 86,0 | 16,3 |
| 36 | 71,2 | 28,8 | 14,4 | 85,6 | 16,8 |
| 37 | 70,7 | 29,3 | 14,7 | 85,4 | 17,2 |
| 38 | 70,0 | 30,0 | 15,0 | 85,0 | 17,6 |
| 39 | 68,9 | 31,1 | 15,6 | 84,5 | 18,4 |
| 40 | 68,7 | 31,3 | 15,7 | 84,4 | 18,6 |
| 41 | 67,8 | 32,2 | 16,1 | 83,9 | 19,2 |
| 42 | 67,4 | 32,6 | 16,3 | 83,7 | 19,5 |
| 43 | 66,8 | 33,2 | 16,6 | 83,4 | 19,9 |
| 44 | 66,0 | 34,0 | 17,0 | 83,0 | 20,5 |
| 45 | 65,5 | 34,5 | 17,3 | 82,8 | 20,8 |
| 46 | 64,8 | 35,2 | 17,6 | 82,4 | 21,4 |
| 47 | 64,2 | 35,8 | 17,9 | 82,1 | 21,8 |
| 48 | 63,7 | 36,3 | 18,2 | 81,9 | 22,2 |
| 49 | 63,0 | 37,0 | 18,5 | 81,5 | 22,7 |
| 50 | 62,4 | 37,6 | 18,8 | 81,2 | 23,2 |
| 51 | 61,9 | 38,1 | 19,1 | 81,0 | 23,5 |
| 52 | 61,2 | 38,8 | 19,4 | 80,6 | 24,1 |
| 53 | 60,7 | 39,3 | 19,7 | 80,4 | 24,5 |
| 54 | 60,1 | 39,9 | 20,0 | 80,1 | 24,9 |
| 55 | 59,5 | 40,5 | 20,3 | 79,8 | 25,4 |
| 56 | 59,0 | 41,0 | 20,5 | 79,5 | 25,8 |
| 57 | 58,6 | 41,4 | 20,7 | 79,3 | 26,1 |
| 58 | 57,9 | 42,1 | 21,1 | 79,0 | 26,7 |
| 59 | 57,4 | 42,6 | 21,3 | 78,7 | 27,1 |
| 60 | 56,9 | 43,1 | 21,6 | 78,5 | 27,5 |
| 61 | 56,3 | 43,7 | 21,9 | 78,2 | 28,0 |
| 62 | 55,7 | 44,3 | 22,2 | 77,9 | 28,5 |
| 63 | 55,4 | 44,6 | 22,3 | 77,7 | 28,7 |
| 64 | 54,8 | 45,2 | 22,6 | 77,4 | 29,2 |
| 65 | 54,3 | 45,7 | 22,9 | 77,2 | 29,6 |
| 66 | 53,6 | 46,4 | 23,2 | 76,8 | 30,2 |
| 67 | 53,3 | 46,7 | 23,4 | 76,7 | 30,5 |
| 68 | 52,9 | 47,1 | 23,6 | 76,5 | 30,8 |

|     |      |      |      |      |      |
|-----|------|------|------|------|------|
| 69  | 52,2 | 47,8 | 23,9 | 76,1 | 31,4 |
| 70  | 52,1 | 47,9 | 24,0 | 76,1 | 31,5 |
| 71  | 51,5 | 48,5 | 24,3 | 75,8 | 32,0 |
| 72  | 50,9 | 49,1 | 24,6 | 75,5 | 32,5 |
| 73  | 50,5 | 49,5 | 24,8 | 75,3 | 32,9 |
| 74  | 49,8 | 50,2 | 25,1 | 74,9 | 33,5 |
| 75  | 49,6 | 50,4 | 25,2 | 74,8 | 33,7 |
| 76  | 49,0 | 51,0 | 25,5 | 74,5 | 34,2 |
| 77  | 48,5 | 51,5 | 25,8 | 74,3 | 34,7 |
| 78  | 48,2 | 51,8 | 25,9 | 74,1 | 35,0 |
| 79  | 47,7 | 52,3 | 26,2 | 73,9 | 35,4 |
| 80  | 47,2 | 52,8 | 26,4 | 73,6 | 35,9 |
| 81  | 46,6 | 53,4 | 26,7 | 73,3 | 36,4 |
| 82  | 46,3 | 53,7 | 26,9 | 73,2 | 36,7 |
| 83  | 45,9 | 54,1 | 27,1 | 73,0 | 37,1 |
| 84  | 45,4 | 54,6 | 27,3 | 72,7 | 37,6 |
| 85  | 45,3 | 54,7 | 27,4 | 72,7 | 37,6 |
| 86  | 44,5 | 55,5 | 27,8 | 72,3 | 38,4 |
| 87  | 44,3 | 55,7 | 27,9 | 72,2 | 38,6 |
| 88  | 43,9 | 56,1 | 28,1 | 72,0 | 39,0 |
| 89  | 43,3 | 56,7 | 28,4 | 71,7 | 39,6 |
| 90  | 43,4 | 56,6 | 28,3 | 71,7 | 39,5 |
| 91  | 42,6 | 57,4 | 28,7 | 71,3 | 40,3 |
| 92  | 42,2 | 57,8 | 28,9 | 71,1 | 40,6 |
| 93  | 41,9 | 58,1 | 29,1 | 71,0 | 40,9 |
| 94  | 41,5 | 58,5 | 29,3 | 70,8 | 41,3 |
| 95  | 41,3 | 58,7 | 29,4 | 70,7 | 41,5 |
| 96  | 41,0 | 59,0 | 29,5 | 70,5 | 41,8 |
| 97  | 40,4 | 59,6 | 29,8 | 70,2 | 42,5 |
| 98  | 40,2 | 59,8 | 29,9 | 70,1 | 42,7 |
| 99  | 39,6 | 60,4 | 30,2 | 69,8 | 43,3 |
| 100 | 39,5 | 60,5 | 30,3 | 69,8 | 43,4 |
| 101 | 39,1 | 60,9 | 30,5 | 69,6 | 43,8 |
| 102 | 38,7 | 61,3 | 30,7 | 69,4 | 44,2 |
| 103 | 38,4 | 61,6 | 30,8 | 69,2 | 44,5 |
| 104 | 37,9 | 62,1 | 31,1 | 69,0 | 45,0 |
| 105 | 37,6 | 62,4 | 31,2 | 68,8 | 45,3 |
| 106 | 37,1 | 62,9 | 31,5 | 68,6 | 45,9 |
| 107 | 36,9 | 63,1 | 31,6 | 68,5 | 46,1 |
| 108 | 36,5 | 63,5 | 31,8 | 68,3 | 46,5 |
| 109 | 36,3 | 63,7 | 31,9 | 68,2 | 46,7 |
| 110 | 36,0 | 64,0 | 32,0 | 68,0 | 47,1 |
| 111 | 35,6 | 64,4 | 32,2 | 67,8 | 47,5 |
| 112 | 35,2 | 64,8 | 32,4 | 67,6 | 47,9 |
| 113 | 34,9 | 65,1 | 32,6 | 67,5 | 48,3 |

|     |      |      |      |      |      |
|-----|------|------|------|------|------|
| 114 | 34,7 | 65,3 | 32,7 | 67,4 | 48,5 |
| 115 | 34,4 | 65,6 | 32,8 | 67,2 | 48,8 |
| 116 | 34,0 | 66,0 | 33,0 | 67,0 | 49,3 |
| 117 | 33,7 | 66,3 | 33,2 | 66,9 | 49,6 |
| 118 | 33,3 | 66,7 | 33,4 | 66,7 | 50,0 |
| 119 | 33,1 | 66,9 | 33,5 | 66,6 | 50,3 |
| 120 | 32,7 | 67,3 | 33,7 | 66,4 | 50,7 |
| 121 | 32,5 | 67,5 | 33,8 | 66,3 | 50,9 |
| 122 | 32,3 | 67,7 | 33,9 | 66,2 | 51,2 |
| 123 | 32,0 | 68,0 | 34,0 | 66,0 | 51,5 |
| 124 | 31,5 | 68,5 | 34,3 | 65,8 | 52,1 |
| 125 | 31,5 | 68,5 | 34,3 | 65,8 | 52,1 |
| 126 | 31,1 | 68,9 | 34,5 | 65,6 | 52,6 |
| 127 | 30,8 | 69,2 | 34,6 | 65,4 | 52,9 |
| 128 | 30,6 | 69,5 | 34,7 | 65,3 | 53,2 |
| 129 | 30,4 | 69,6 | 34,8 | 65,2 | 53,4 |
| 130 | 29,7 | 70,3 | 35,2 | 64,9 | 54,2 |
| 131 | 30,1 | 69,9 | 35,0 | 65,1 | 53,7 |
| 132 | 29,6 | 70,4 | 35,2 | 64,8 | 54,3 |
| 133 | 29,0 | 71,0 | 35,5 | 64,5 | 55,0 |
| 134 | 28,8 | 71,2 | 35,6 | 64,4 | 55,3 |
| 135 | 28,7 | 71,3 | 35,7 | 64,4 | 55,4 |
| 136 | 28,5 | 71,5 | 35,8 | 64,3 | 55,6 |
| 137 | 28,5 | 71,5 | 35,8 | 64,3 | 55,6 |
| 138 | 28,1 | 71,9 | 36,0 | 64,1 | 56,1 |
| 139 | 27,7 | 72,3 | 36,2 | 63,9 | 56,6 |
| 140 | 27,4 | 72,6 | 36,3 | 63,7 | 57,0 |
| 141 | 27,0 | 73,0 | 36,5 | 63,5 | 57,5 |
| 142 | 27,0 | 73,0 | 36,5 | 63,5 | 57,5 |
| 143 | 26,8 | 73,2 | 36,6 | 63,4 | 57,7 |
| 144 | 26,4 | 73,6 | 36,8 | 63,2 | 58,2 |
| 145 | 26,2 | 73,8 | 36,9 | 63,1 | 58,5 |
| 146 | 25,9 | 74,1 | 37,1 | 63,0 | 58,9 |
| 147 | 25,8 | 74,2 | 37,1 | 62,9 | 59,0 |
| 148 | 25,5 | 74,5 | 37,3 | 62,8 | 59,4 |
| 149 | 25,6 | 74,4 | 37,2 | 62,8 | 59,2 |
| 150 | 25,1 | 74,9 | 37,5 | 62,6 | 59,9 |
| 151 | 24,9 | 75,1 | 37,6 | 62,5 | 60,1 |
| 152 | 24,5 | 75,5 | 37,8 | 62,3 | 60,6 |
| 153 | 24,7 | 75,3 | 37,7 | 62,4 | 60,4 |
| 154 | 24,3 | 75,7 | 37,9 | 62,2 | 60,9 |
| 155 | 23,9 | 76,1 | 38,1 | 62,0 | 61,4 |
| 156 | 23,8 | 76,2 | 38,1 | 61,9 | 61,6 |
| 157 | 23,6 | 76,4 | 38,2 | 61,8 | 61,8 |
| 158 | 23,5 | 76,5 | 38,3 | 61,8 | 61,9 |

|     |      |      |      |      |      |
|-----|------|------|------|------|------|
| 159 | 22,8 | 77,2 | 38,6 | 61,4 | 62,9 |
| 160 | 22,9 | 77,1 | 38,6 | 61,5 | 62,7 |
| 161 | 22,7 | 77,3 | 38,7 | 61,4 | 63,0 |
| 162 | 22,3 | 77,7 | 38,9 | 61,2 | 63,5 |
| 163 | 22,1 | 77,9 | 39,0 | 61,1 | 63,8 |
| 164 | 22,2 | 77,8 | 38,9 | 61,1 | 63,7 |
| 165 | 21,7 | 78,3 | 39,2 | 60,9 | 64,3 |
| 166 | 22,0 | 78,0 | 39,0 | 61,0 | 63,9 |
| 167 | 21,6 | 78,4 | 39,2 | 60,8 | 64,5 |
| 168 | 21,6 | 78,4 | 39,2 | 60,8 | 64,5 |
| 169 | 21,0 | 79,0 | 39,5 | 60,5 | 65,3 |
| 170 | 21,1 | 78,9 | 39,5 | 60,6 | 65,2 |
| 171 | 20,6 | 79,4 | 39,7 | 60,3 | 65,8 |
| 172 | 20,5 | 79,5 | 39,8 | 60,3 | 66,0 |
| 173 | 20,4 | 79,6 | 39,8 | 60,2 | 66,1 |
| 174 | 20,0 | 80,0 | 40,0 | 60,0 | 66,7 |
| 175 | 20,1 | 79,9 | 40,0 | 60,1 | 66,5 |
| 176 | 19,8 | 80,2 | 40,1 | 59,9 | 66,9 |
| 177 | 19,8 | 80,2 | 40,1 | 59,9 | 66,9 |
| 178 | 19,9 | 80,1 | 40,1 | 60,0 | 66,8 |
| 179 | 19,5 | 80,5 | 40,3 | 59,8 | 67,4 |
| 180 | 18,9 | 81,1 | 40,6 | 59,5 | 68,2 |
| 181 | 18,8 | 81,2 | 40,6 | 59,4 | 68,4 |
| 182 | 18,9 | 81,1 | 40,6 | 59,5 | 68,2 |
| 183 | 18,5 | 81,5 | 40,8 | 59,3 | 68,8 |
| 184 | 18,1 | 81,9 | 41,0 | 59,1 | 69,3 |
| 185 | 18,2 | 81,8 | 40,9 | 59,1 | 69,2 |
| 186 | 18,0 | 82,0 | 41,0 | 59,0 | 69,5 |
| 187 | 17,6 | 82,4 | 41,2 | 58,8 | 70,1 |
| 188 | 17,6 | 82,4 | 41,2 | 58,8 | 70,1 |
| 189 | 17,7 | 82,3 | 41,2 | 58,9 | 69,9 |
| 190 | 17,6 | 82,4 | 41,2 | 58,8 | 70,1 |
| 191 | 17,5 | 82,5 | 41,3 | 58,8 | 70,2 |
| 192 | 17,0 | 83,0 | 41,5 | 58,5 | 70,9 |
| 193 | 17,0 | 83,0 | 41,5 | 58,5 | 70,9 |
| 194 | 16,9 | 83,1 | 41,6 | 58,5 | 71,1 |
| 195 | 16,6 | 83,4 | 41,7 | 58,3 | 71,5 |
| 196 | 17,0 | 83,0 | 41,5 | 58,5 | 70,9 |
| 197 | 16,5 | 83,5 | 41,8 | 58,3 | 71,7 |
| 198 | 16,5 | 83,5 | 41,8 | 58,3 | 71,7 |
| 199 | 16,0 | 84,0 | 42,0 | 58,0 | 72,4 |
| 200 | 16,5 | 83,5 | 41,8 | 58,3 | 71,7 |
| 201 | 15,9 | 84,1 | 42,1 | 58,0 | 72,6 |
| 202 | 16,0 | 84,0 | 42,0 | 58,0 | 72,4 |
| 203 | 15,7 | 84,3 | 42,2 | 57,9 | 72,9 |

|     |      |      |      |      |      |
|-----|------|------|------|------|------|
| 204 | 15,6 | 84,4 | 42,2 | 57,8 | 73,0 |
| 205 | 15,8 | 84,2 | 42,1 | 57,9 | 72,7 |
| 206 | 16,0 | 84,0 | 42,0 | 58,0 | 72,4 |
| 207 | 14,8 | 85,2 | 42,6 | 57,4 | 74,2 |
| 208 | 15,1 | 84,9 | 42,5 | 57,6 | 73,8 |
| 209 | 15,0 | 85,0 | 42,5 | 57,5 | 73,9 |
| 210 | 14,6 | 85,4 | 42,7 | 57,3 | 74,5 |
| 211 | 15,4 | 84,6 | 42,3 | 57,7 | 73,3 |
| 212 | 15,0 | 85,0 | 42,5 | 57,5 | 73,9 |
| 213 | 15,6 | 84,4 | 42,2 | 57,8 | 73,0 |
| 214 | 14,6 | 85,4 | 42,7 | 57,3 | 74,5 |
| 215 | 14,5 | 85,5 | 42,8 | 57,3 | 74,7 |
| 216 | 13,9 | 86,1 | 43,1 | 57,0 | 75,6 |
| 217 | 14,3 | 85,7 | 42,9 | 57,2 | 75,0 |
| 218 | 13,9 | 86,1 | 43,1 | 57,0 | 75,6 |
| 219 | 13,9 | 86,1 | 43,1 | 57,0 | 75,6 |
| 220 | 13,4 | 86,6 | 43,3 | 56,7 | 76,4 |
| 221 | 13,7 | 86,3 | 43,2 | 56,9 | 75,9 |
| 222 | 13,3 | 86,7 | 43,4 | 56,7 | 76,5 |
| 223 | 14,0 | 86,0 | 43,0 | 57,0 | 75,4 |
| 224 | 13,8 | 86,2 | 43,1 | 56,9 | 75,7 |
| 225 | 13,1 | 86,9 | 43,5 | 56,6 | 76,8 |
| 226 | 13,0 | 87,0 | 43,5 | 56,5 | 77,0 |
| 227 | 13,3 | 86,7 | 43,4 | 56,7 | 76,5 |
| 228 | 13,4 | 86,6 | 43,3 | 56,7 | 76,4 |
| 229 | 12,7 | 87,3 | 43,7 | 56,4 | 77,5 |
| 230 | 12,9 | 87,1 | 43,6 | 56,5 | 77,1 |
| 231 | 13,3 | 86,7 | 43,4 | 56,7 | 76,5 |
| 232 | 12,8 | 87,2 | 43,6 | 56,4 | 77,3 |
| 233 | 12,7 | 87,3 | 43,7 | 56,4 | 77,5 |
| 234 | 12,4 | 87,6 | 43,8 | 56,2 | 77,9 |
| 235 | 12,7 | 87,3 | 43,7 | 56,4 | 77,5 |
| 236 | 12,2 | 87,8 | 43,9 | 56,1 | 78,3 |
| 237 | 12,2 | 87,8 | 43,9 | 56,1 | 78,3 |
| 238 | 12,0 | 88,0 | 44,0 | 56,0 | 78,6 |
| 239 | 12,4 | 87,6 | 43,8 | 56,2 | 77,9 |
| 240 | 12,2 | 87,8 | 43,9 | 56,1 | 78,3 |
| 241 | 11,9 | 88,1 | 44,1 | 56,0 | 78,7 |
| 242 | 12,2 | 87,8 | 43,9 | 56,1 | 78,3 |
| 243 | 11,9 | 88,1 | 44,1 | 56,0 | 78,7 |
| 244 | 11,8 | 88,2 | 44,1 | 55,9 | 78,9 |
| 245 | 11,6 | 88,4 | 44,2 | 55,8 | 79,2 |
| 246 | 11,3 | 88,7 | 44,4 | 55,7 | 79,7 |
| 247 | 11,1 | 88,9 | 44,5 | 55,6 | 80,0 |
| 248 | 12,2 | 87,8 | 43,9 | 56,1 | 78,3 |

|     |      |      |      |      |      |
|-----|------|------|------|------|------|
| 249 | 11,1 | 88,9 | 44,5 | 55,6 | 80,0 |
| 250 | 11,3 | 88,7 | 44,4 | 55,7 | 79,7 |
| 251 | 11,6 | 88,4 | 44,2 | 55,8 | 79,2 |
| 252 | 11,1 | 88,9 | 44,5 | 55,6 | 80,0 |
| 253 | 10,9 | 89,1 | 44,6 | 55,5 | 80,3 |
| 254 | 11,1 | 88,9 | 44,5 | 55,6 | 80,0 |
| 255 | 10,8 | 89,2 | 44,6 | 55,4 | 80,5 |
| 256 | 10,6 | 89,4 | 44,7 | 55,3 | 80,8 |
| 257 | 11,2 | 88,8 | 44,4 | 55,6 | 79,9 |
| 258 | 10,8 | 89,2 | 44,6 | 55,4 | 80,5 |
| 259 | 10,5 | 89,5 | 44,8 | 55,3 | 81,0 |
| 260 | 10,8 | 89,2 | 44,6 | 55,4 | 80,5 |
| 261 | 11,0 | 89,0 | 44,5 | 55,5 | 80,2 |
| 262 | 10,8 | 89,2 | 44,6 | 55,4 | 80,5 |
| 263 | 10,2 | 89,8 | 44,9 | 55,1 | 81,5 |
| 264 | 10,3 | 89,7 | 44,9 | 55,2 | 81,3 |
| 265 | 10,6 | 89,4 | 44,7 | 55,3 | 80,8 |
| 266 | 10,4 | 89,6 | 44,8 | 55,2 | 81,2 |
| 267 | 9,9  | 90,1 | 45,1 | 55,0 | 82,0 |
| 268 | 9,9  | 90,1 | 45,1 | 55,0 | 82,0 |
| 269 | 10,2 | 89,8 | 44,9 | 55,1 | 81,5 |
| 270 | 9,8  | 90,2 | 45,1 | 54,9 | 82,1 |
| 271 | 10,0 | 90,0 | 45,0 | 55,0 | 81,8 |
| 272 | 9,6  | 90,4 | 45,2 | 54,8 | 82,5 |
| 273 | 10,0 | 90,0 | 45,0 | 55,0 | 81,8 |
| 274 | 10,0 | 90,0 | 45,0 | 55,0 | 81,8 |
| 275 | 9,6  | 90,4 | 45,2 | 54,8 | 82,5 |
| 276 | 9,3  | 90,7 | 45,4 | 54,7 | 83,0 |
| 277 | 9,6  | 90,4 | 45,2 | 54,8 | 82,5 |
| 278 | 9,4  | 90,6 | 45,3 | 54,7 | 82,8 |
| 279 | 9,7  | 90,3 | 45,2 | 54,9 | 82,3 |
| 280 | 9,5  | 90,5 | 45,3 | 54,8 | 82,6 |
| 281 | 9,6  | 90,4 | 45,2 | 54,8 | 82,5 |
| 282 | 8,9  | 91,1 | 45,6 | 54,5 | 83,7 |
| 283 | 9,3  | 90,7 | 45,4 | 54,7 | 83,0 |
| 284 | 9,4  | 90,6 | 45,3 | 54,7 | 82,8 |
| 285 | 8,9  | 91,1 | 45,6 | 54,5 | 83,7 |
| 286 | 9,2  | 90,8 | 45,4 | 54,6 | 83,2 |
| 287 | 9,3  | 90,7 | 45,4 | 54,7 | 83,0 |
| 288 | 8,8  | 91,2 | 45,6 | 54,4 | 83,8 |
| 289 | 9,2  | 90,8 | 45,4 | 54,6 | 83,2 |
| 290 | 8,6  | 91,4 | 45,7 | 54,3 | 84,2 |
| 291 | 9,0  | 91,0 | 45,5 | 54,5 | 83,5 |
| 292 | 8,9  | 91,1 | 45,6 | 54,5 | 83,7 |
| 293 | 8,6  | 91,4 | 45,7 | 54,3 | 84,2 |

|     |     |      |      |      |      |
|-----|-----|------|------|------|------|
| 294 | 8,5 | 91,5 | 45,8 | 54,3 | 84,3 |
| 295 | 9,0 | 91,0 | 45,5 | 54,5 | 83,5 |
| 296 | 8,6 | 91,4 | 45,7 | 54,3 | 84,2 |
| 297 | 8,6 | 91,4 | 45,7 | 54,3 | 84,2 |
| 298 | 8,3 | 91,7 | 45,9 | 54,2 | 84,7 |
| 299 | 8,4 | 91,6 | 45,8 | 54,2 | 84,5 |
| 300 | 8,3 | 91,7 | 45,9 | 54,2 | 84,7 |
| 301 | 7,9 | 92,1 | 46,1 | 54,0 | 85,4 |
| 302 | 7,6 | 92,4 | 46,2 | 53,8 | 85,9 |
| 303 | 8,3 | 91,7 | 45,9 | 54,2 | 84,7 |
| 304 | 8,2 | 91,8 | 45,9 | 54,1 | 84,8 |
| 305 | 8,0 | 92,0 | 46,0 | 54,0 | 85,2 |
| 306 | 8,1 | 91,9 | 46,0 | 54,1 | 85,0 |
| 307 | 7,9 | 92,1 | 46,1 | 54,0 | 85,4 |
| 308 | 8,0 | 92,0 | 46,0 | 54,0 | 85,2 |
| 309 | 8,2 | 91,8 | 45,9 | 54,1 | 84,8 |
| 310 | 7,9 | 92,1 | 46,1 | 54,0 | 85,4 |
| 311 | 7,9 | 92,1 | 46,1 | 54,0 | 85,4 |
| 312 | 7,9 | 92,1 | 46,1 | 54,0 | 85,4 |
| 313 | 7,6 | 92,4 | 46,2 | 53,8 | 85,9 |
| 314 | 7,7 | 92,3 | 46,2 | 53,9 | 85,7 |
| 315 | 7,9 | 92,1 | 46,1 | 54,0 | 85,4 |
| 316 | 7,6 | 92,4 | 46,2 | 53,8 | 85,9 |
| 317 | 7,9 | 92,1 | 46,1 | 54,0 | 85,4 |
| 318 | 7,6 | 92,4 | 46,2 | 53,8 | 85,9 |
| 319 | 7,1 | 92,9 | 46,5 | 53,6 | 86,7 |
| 320 | 7,0 | 93,0 | 46,5 | 53,5 | 86,9 |
| 321 | 7,3 | 92,7 | 46,4 | 53,7 | 86,4 |
| 322 | 7,6 | 92,4 | 46,2 | 53,8 | 85,9 |
| 323 | 7,4 | 92,6 | 46,3 | 53,7 | 86,2 |
| 324 | 7,5 | 92,5 | 46,3 | 53,8 | 86,0 |
| 325 | 7,4 | 92,6 | 46,3 | 53,7 | 86,2 |
| 326 | 7,5 | 92,5 | 46,3 | 53,8 | 86,0 |
| 327 | 7,5 | 92,5 | 46,3 | 53,8 | 86,0 |
| 328 | 7,6 | 92,4 | 46,2 | 53,8 | 85,9 |
| 329 | 7,5 | 92,5 | 46,3 | 53,8 | 86,0 |
| 330 | 7,0 | 93,0 | 46,5 | 53,5 | 86,9 |
| 331 | 7,0 | 93,0 | 46,5 | 53,5 | 86,9 |
| 332 | 7,2 | 92,8 | 46,4 | 53,6 | 86,6 |
| 333 | 7,3 | 92,7 | 46,4 | 53,7 | 86,4 |
| 334 | 7,0 | 93,0 | 46,5 | 53,5 | 86,9 |
| 335 | 7,2 | 92,8 | 46,4 | 53,6 | 86,6 |
| 336 | 7,3 | 92,7 | 46,4 | 53,7 | 86,4 |
| 337 | 7,0 | 93,0 | 46,5 | 53,5 | 86,9 |
| 338 | 6,8 | 93,2 | 46,6 | 53,4 | 87,3 |

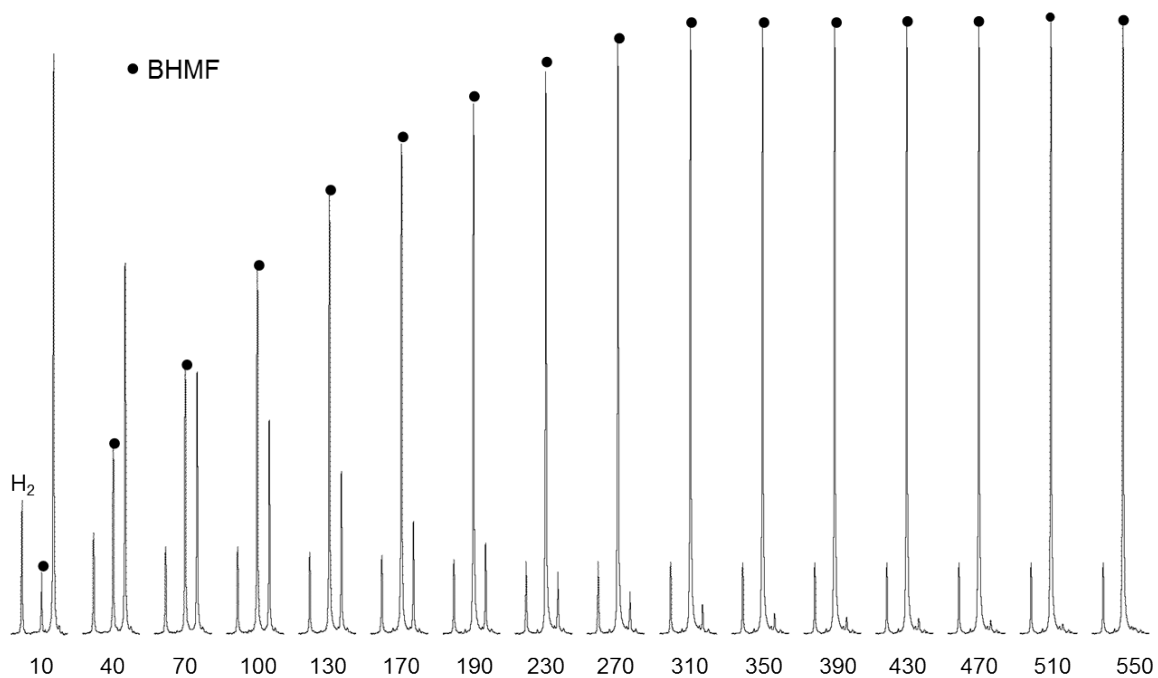
|     |     |      |      |      |      |
|-----|-----|------|------|------|------|
| 339 | 6,8 | 93,2 | 46,6 | 53,4 | 87,3 |
| 340 | 7,4 | 92,6 | 46,3 | 53,7 | 86,2 |
| 341 | 7,0 | 93,0 | 46,5 | 53,5 | 86,9 |
| 342 | 6,9 | 93,1 | 46,6 | 53,5 | 87,1 |
| 343 | 6,5 | 93,5 | 46,8 | 53,3 | 87,8 |
| 344 | 7,2 | 92,8 | 46,4 | 53,6 | 86,6 |
| 345 | 6,7 | 93,3 | 46,7 | 53,4 | 87,4 |
| 346 | 6,7 | 93,3 | 46,7 | 53,4 | 87,4 |
| 347 | 6,4 | 93,6 | 46,8 | 53,2 | 88,0 |
| 348 | 7,0 | 93,0 | 46,5 | 53,5 | 86,9 |
| 349 | 6,8 | 93,2 | 46,6 | 53,4 | 87,3 |
| 350 | 6,7 | 93,3 | 46,7 | 53,4 | 87,4 |
| 351 | 6,7 | 93,3 | 46,7 | 53,4 | 87,4 |
| 352 | 6,7 | 93,3 | 46,7 | 53,4 | 87,4 |
| 353 | 6,9 | 93,1 | 46,6 | 53,5 | 87,1 |
| 354 | 6,3 | 93,7 | 46,9 | 53,2 | 88,1 |
| 355 | 6,5 | 93,5 | 46,8 | 53,3 | 87,8 |
| 356 | 6,2 | 93,8 | 46,9 | 53,1 | 88,3 |
| 357 | 6,5 | 93,5 | 46,8 | 53,3 | 87,8 |
| 358 | 6,5 | 93,5 | 46,8 | 53,3 | 87,8 |
| 359 | 6,6 | 93,4 | 46,7 | 53,3 | 87,6 |
| 360 | 6,5 | 93,5 | 46,8 | 53,3 | 87,8 |
| 361 | 6,7 | 93,3 | 46,7 | 53,4 | 87,4 |
| 362 | 6,2 | 93,8 | 46,9 | 53,1 | 88,3 |
| 363 | 6,4 | 93,6 | 46,8 | 53,2 | 88,0 |
| 364 | 6,0 | 94,0 | 47,0 | 53,0 | 88,7 |
| 365 | 6,2 | 93,8 | 46,9 | 53,1 | 88,3 |
| 366 | 6,1 | 93,9 | 47,0 | 53,1 | 88,5 |
| 367 | 6,1 | 93,9 | 47,0 | 53,1 | 88,5 |
| 368 | 6,1 | 93,9 | 47,0 | 53,1 | 88,5 |
| 369 | 6,4 | 93,6 | 46,8 | 53,2 | 88,0 |
| 370 | 6,0 | 94,0 | 47,0 | 53,0 | 88,7 |
| 371 | 6,0 | 94,0 | 47,0 | 53,0 | 88,7 |
| 372 | 6,0 | 94,0 | 47,0 | 53,0 | 88,7 |
| 373 | 6,1 | 93,9 | 47,0 | 53,1 | 88,5 |
| 374 | 5,9 | 94,1 | 47,1 | 53,0 | 88,9 |
| 375 | 6,1 | 93,9 | 47,0 | 53,1 | 88,5 |
| 376 | 5,9 | 94,1 | 47,1 | 53,0 | 88,9 |
| 377 | 5,7 | 94,3 | 47,2 | 52,9 | 89,2 |
| 378 | 5,9 | 94,1 | 47,1 | 53,0 | 88,9 |
| 379 | 6,2 | 93,8 | 46,9 | 53,1 | 88,3 |
| 380 | 6,1 | 93,9 | 47,0 | 53,1 | 88,5 |
| 381 | 5,9 | 94,1 | 47,1 | 53,0 | 88,9 |
| 382 | 6,1 | 93,9 | 47,0 | 53,1 | 88,5 |
| 383 | 5,9 | 94,1 | 47,1 | 53,0 | 88,9 |

|     |     |      |      |      |      |
|-----|-----|------|------|------|------|
| 384 | 5,9 | 94,1 | 47,1 | 53,0 | 88,9 |
| 385 | 5,9 | 94,1 | 47,1 | 53,0 | 88,9 |
| 386 | 5,7 | 94,3 | 47,2 | 52,9 | 89,2 |
| 387 | 5,5 | 94,5 | 47,3 | 52,8 | 89,6 |
| 388 | 5,9 | 94,1 | 47,1 | 53,0 | 88,9 |
| 389 | 6,0 | 94,0 | 47,0 | 53,0 | 88,7 |
| 390 | 5,5 | 94,5 | 47,3 | 52,8 | 89,6 |
| 391 | 5,7 | 94,3 | 47,2 | 52,9 | 89,2 |
| 392 | 5,7 | 94,3 | 47,2 | 52,9 | 89,2 |
| 393 | 5,9 | 94,1 | 47,1 | 53,0 | 88,9 |
| 394 | 5,5 | 94,5 | 47,3 | 52,8 | 89,6 |
| 395 | 5,4 | 94,6 | 47,3 | 52,7 | 89,8 |
| 396 | 5,6 | 94,4 | 47,2 | 52,8 | 89,4 |
| 397 | 5,7 | 94,3 | 47,2 | 52,9 | 89,2 |
| 398 | 5,9 | 94,1 | 47,1 | 53,0 | 88,9 |
| 399 | 5,7 | 94,3 | 47,2 | 52,9 | 89,2 |
| 400 | 5,6 | 94,4 | 47,2 | 52,8 | 89,4 |
| 401 | 6,0 | 94,0 | 47,0 | 53,0 | 88,7 |
| 402 | 5,5 | 94,5 | 47,3 | 52,8 | 89,6 |
| 403 | 5,4 | 94,6 | 47,3 | 52,7 | 89,8 |
| 404 | 5,7 | 94,3 | 47,2 | 52,9 | 89,2 |
| 405 | 5,5 | 94,5 | 47,3 | 52,8 | 89,6 |
| 406 | 5,2 | 94,8 | 47,4 | 52,6 | 90,1 |
| 407 | 5,5 | 94,5 | 47,3 | 52,8 | 89,6 |
| 408 | 5,5 | 94,5 | 47,3 | 52,8 | 89,6 |
| 409 | 5,5 | 94,5 | 47,3 | 52,8 | 89,6 |
| 410 | 5,6 | 94,4 | 47,2 | 52,8 | 89,4 |
| 411 | 5,2 | 94,8 | 47,4 | 52,6 | 90,1 |
| 412 | 5,7 | 94,3 | 47,2 | 52,9 | 89,2 |
| 413 | 5,5 | 94,5 | 47,3 | 52,8 | 89,6 |
| 414 | 5,4 | 94,6 | 47,3 | 52,7 | 89,8 |
| 415 | 5,0 | 95,0 | 47,5 | 52,5 | 90,5 |
| 416 | 5,5 | 94,5 | 47,3 | 52,8 | 89,6 |
| 417 | 5,5 | 94,5 | 47,3 | 52,8 | 89,6 |
| 418 | 5,7 | 94,3 | 47,2 | 52,9 | 89,2 |
| 419 | 5,2 | 94,8 | 47,4 | 52,6 | 90,1 |
| 420 | 5,4 | 94,6 | 47,3 | 52,7 | 89,8 |
| 421 | 5,4 | 94,6 | 47,3 | 52,7 | 89,8 |
| 422 | 5,6 | 94,4 | 47,2 | 52,8 | 89,4 |
| 423 | 5,8 | 94,2 | 47,1 | 52,9 | 89,0 |
| 424 | 5,5 | 94,5 | 47,3 | 52,8 | 89,6 |
| 425 | 5,3 | 94,7 | 47,4 | 52,7 | 89,9 |
| 426 | 5,5 | 94,5 | 47,3 | 52,8 | 89,6 |
| 427 | 5,4 | 94,6 | 47,3 | 52,7 | 89,8 |
| 428 | 5,4 | 94,6 | 47,3 | 52,7 | 89,8 |

|     |     |      |      |      |      |
|-----|-----|------|------|------|------|
| 429 | 5,0 | 95,0 | 47,5 | 52,5 | 90,5 |
| 430 | 5,1 | 94,9 | 47,5 | 52,6 | 90,3 |
| 431 | 5,2 | 94,8 | 47,4 | 52,6 | 90,1 |
| 432 | 5,2 | 94,8 | 47,4 | 52,6 | 90,1 |
| 433 | 5,9 | 94,1 | 47,1 | 53,0 | 88,9 |
| 434 | 4,9 | 95,1 | 47,6 | 52,5 | 90,7 |
| 435 | 4,9 | 95,1 | 47,6 | 52,5 | 90,7 |
| 436 | 5,4 | 94,6 | 47,3 | 52,7 | 89,8 |
| 437 | 5,6 | 94,4 | 47,2 | 52,8 | 89,4 |
| 438 | 4,8 | 95,2 | 47,6 | 52,4 | 90,8 |
| 439 | 5,5 | 94,5 | 47,3 | 52,8 | 89,6 |
| 440 | 5,0 | 95,0 | 47,5 | 52,5 | 90,5 |
| 441 | 5,1 | 94,9 | 47,5 | 52,6 | 90,3 |
| 442 | 5,1 | 94,9 | 47,5 | 52,6 | 90,3 |
| 443 | 5,1 | 94,9 | 47,5 | 52,6 | 90,3 |
| 444 | 5,5 | 94,5 | 47,3 | 52,8 | 89,6 |
| 445 | 5,2 | 94,8 | 47,4 | 52,6 | 90,1 |
| 446 | 4,9 | 95,1 | 47,6 | 52,5 | 90,7 |
| 447 | 4,9 | 95,1 | 47,6 | 52,5 | 90,7 |
| 448 | 5,0 | 95,0 | 47,5 | 52,5 | 90,5 |
| 449 | 5,1 | 94,9 | 47,5 | 52,6 | 90,3 |
| 450 | 4,7 | 95,3 | 47,7 | 52,4 | 91,0 |
| 451 | 4,7 | 95,3 | 47,7 | 52,4 | 91,0 |
| 452 | 4,4 | 95,6 | 47,8 | 52,2 | 91,6 |
| 453 | 5,2 | 94,8 | 47,4 | 52,6 | 90,1 |
| 454 | 4,5 | 95,5 | 47,8 | 52,3 | 91,4 |
| 455 | 4,5 | 95,5 | 47,8 | 52,3 | 91,4 |
| 456 | 5,4 | 94,6 | 47,3 | 52,7 | 89,8 |
| 457 | 4,4 | 95,6 | 47,8 | 52,2 | 91,6 |
| 458 | 5,4 | 94,6 | 47,3 | 52,7 | 89,8 |
| 459 | 4,7 | 95,3 | 47,7 | 52,4 | 91,0 |
| 460 | 4,6 | 95,4 | 47,7 | 52,3 | 91,2 |
| 461 | 4,5 | 95,5 | 47,8 | 52,3 | 91,4 |
| 462 | 4,5 | 95,5 | 47,8 | 52,3 | 91,4 |
| 463 | 4,6 | 95,4 | 47,7 | 52,3 | 91,2 |
| 464 | 4,9 | 95,1 | 47,6 | 52,5 | 90,7 |
| 465 | 4,1 | 95,9 | 48,0 | 52,1 | 92,1 |
| 466 | 4,9 | 95,1 | 47,6 | 52,5 | 90,7 |
| 467 | 4,9 | 95,1 | 47,6 | 52,5 | 90,7 |
| 468 | 4,1 | 95,9 | 48,0 | 52,1 | 92,1 |
| 469 | 3,9 | 96,1 | 48,1 | 52,0 | 92,5 |
| 470 | 4,4 | 95,6 | 47,8 | 52,2 | 91,6 |
| 471 | 4,0 | 96,0 | 48,0 | 52,0 | 92,3 |
| 472 | 4,9 | 95,1 | 47,6 | 52,5 | 90,7 |
| 473 | 3,8 | 96,2 | 48,1 | 51,9 | 92,7 |

|     |     |      |      |      |      |
|-----|-----|------|------|------|------|
| 474 | 3,7 | 96,3 | 48,2 | 51,9 | 92,9 |
| 475 | 4,9 | 95,1 | 47,6 | 52,5 | 90,7 |
| 476 | 5,0 | 95,0 | 47,5 | 52,5 | 90,5 |
| 477 | 4,9 | 95,1 | 47,6 | 52,5 | 90,7 |
| 478 | 3,8 | 96,2 | 48,1 | 51,9 | 92,7 |
| 479 | 3,5 | 96,5 | 48,3 | 51,8 | 93,2 |
| 480 | 3,7 | 96,3 | 48,2 | 51,9 | 92,9 |
| 481 | 3,6 | 96,4 | 48,2 | 51,8 | 93,1 |
| 482 | 4,1 | 95,9 | 48,0 | 52,1 | 92,1 |
| 483 | 3,4 | 96,6 | 48,3 | 51,7 | 93,4 |
| 484 | 3,7 | 96,3 | 48,2 | 51,9 | 92,9 |
| 485 | 3,8 | 96,2 | 48,1 | 51,9 | 92,7 |
| 486 | 3,7 | 96,3 | 48,2 | 51,9 | 92,9 |
| 487 | 4,1 | 95,9 | 48,0 | 52,1 | 92,1 |
| 488 | 3,4 | 96,6 | 48,3 | 51,7 | 93,4 |
| 489 | 3,3 | 96,7 | 48,4 | 51,7 | 93,6 |
| 490 | 3,3 | 96,7 | 48,4 | 51,7 | 93,6 |
| 491 | 3,2 | 96,8 | 48,4 | 51,6 | 93,8 |
| 492 | 3,1 | 96,9 | 48,5 | 51,6 | 94,0 |
| 493 | 3,1 | 96,9 | 48,5 | 51,6 | 94,0 |
| 494 | 3,0 | 97,0 | 48,5 | 51,5 | 94,2 |
| 495 | 3,6 | 96,4 | 48,2 | 51,8 | 93,1 |
| 496 | 2,6 | 97,4 | 48,7 | 51,3 | 94,9 |
| 497 | 3,6 | 96,4 | 48,2 | 51,8 | 93,1 |
| 498 | 2,4 | 97,6 | 48,8 | 51,2 | 95,3 |
| 499 | 3,3 | 96,7 | 48,4 | 51,7 | 93,6 |
| 500 | 3,0 | 97,0 | 48,5 | 51,5 | 94,2 |
| 501 | 2,5 | 97,5 | 48,8 | 51,3 | 95,1 |
| 502 | 2,0 | 98,0 | 49,0 | 51,0 | 96,1 |
| 503 | 2,8 | 97,2 | 48,6 | 51,4 | 94,6 |
| 504 | 2,3 | 97,7 | 48,9 | 51,2 | 95,5 |
| 505 | 2,5 | 97,5 | 48,8 | 51,3 | 95,1 |
| 506 | 2,5 | 97,5 | 48,8 | 51,3 | 95,1 |
| 507 | 2,2 | 97,8 | 48,9 | 51,1 | 95,7 |
| 508 | 2,0 | 98,0 | 49,0 | 51,0 | 96,1 |
| 509 | 1,9 | 98,1 | 49,1 | 51,0 | 96,3 |
| 510 | 2,3 | 97,7 | 48,9 | 51,2 | 95,5 |
| 511 | 1,8 | 98,2 | 49,1 | 50,9 | 96,5 |
| 512 | 1,8 | 98,2 | 49,1 | 50,9 | 96,5 |
| 513 | 1,8 | 98,2 | 49,1 | 50,9 | 96,5 |
| 514 | 1,6 | 98,4 | 49,2 | 50,8 | 96,9 |
| 515 | 2,0 | 98,0 | 49,0 | 51,0 | 96,1 |
| 516 | 1,4 | 98,6 | 49,3 | 50,7 | 97,2 |
| 517 | 2,6 | 97,4 | 48,7 | 51,3 | 94,9 |
| 518 | 1,5 | 98,5 | 49,3 | 50,8 | 97,0 |

|     |     |      |      |      |      |
|-----|-----|------|------|------|------|
| 519 | 1,2 | 98,8 | 49,4 | 50,6 | 97,6 |
| 520 | 1,3 | 98,7 | 49,4 | 50,7 | 97,4 |
| 521 | 1,2 | 98,8 | 49,4 | 50,6 | 97,6 |
| 522 | 1,0 | 99,0 | 49,5 | 50,5 | 98,0 |
| 523 | 0,8 | 99,2 | 49,6 | 50,4 | 98,4 |
| 524 | 1,0 | 99,0 | 49,5 | 50,5 | 98,0 |
| 525 | 1,0 | 99,0 | 49,5 | 50,5 | 98,0 |
| 526 | 1,6 | 98,4 | 49,2 | 50,8 | 96,9 |
| 527 | 0,6 | 99,4 | 49,7 | 50,3 | 98,8 |
| 528 | 1,2 | 98,8 | 49,4 | 50,6 | 97,6 |
| 529 | 1,5 | 98,5 | 49,3 | 50,8 | 97,0 |
| 530 | 0,5 | 99,5 | 49,8 | 50,3 | 99,0 |

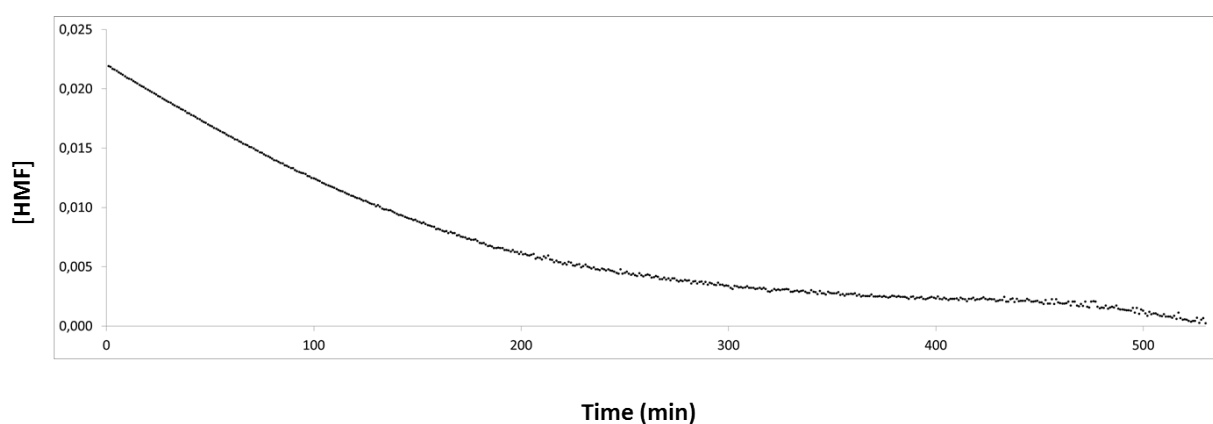


**Figure S3** Selected records of *in situ* NMR minute-by-minute monitoring of the Shvo's catalyzed hydrogenation of HMF.

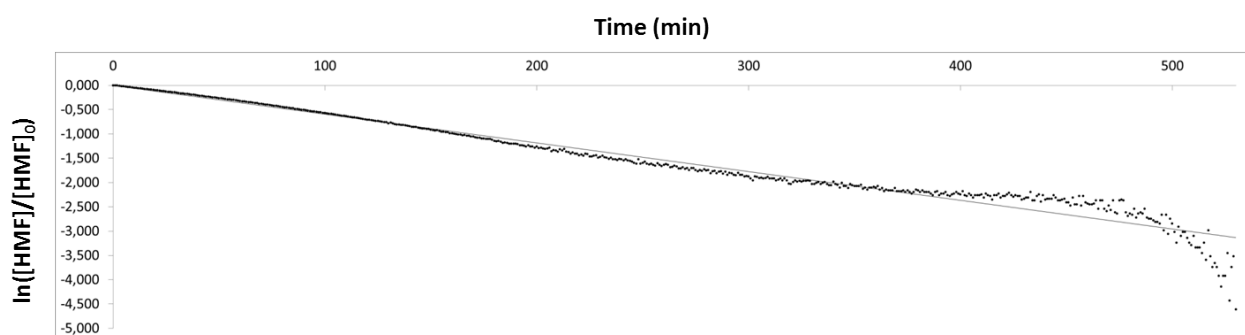
**Table S3** *In situ* NMR experiment. Reaction conditions: catalyst **1** (0,0676 mg, 0,0628  $\mu$ mol), HMF (250 eq., 1,98 mg, 0,0157 mmol), toluene- $d_8$  (0,7 mL), 90°C,  $p(H_2)$  (3 bar). Spectra acquired every 60 seconds. This table correspond to Figure 7 ( $\ln([HMF]/[HMF]_0)$  vs time) in the manuscript.

| Min | HMF conversion | [HMF]  | [HMF]/[HMF] <sub>0</sub> | $\ln([HMF]/[HMF]_0)$ |
|-----|----------------|--------|--------------------------|----------------------|
| 0   | 0              | 0,0220 | 1,000                    | 0,000                |
| 1   | 0,5            | 0,0219 | 0,995                    | -0,005               |
| 2   | 0,7            | 0,0218 | 0,993                    | -0,007               |
| 3   | 1,4            | 0,0217 | 0,986                    | -0,014               |
| 4   | 1,8            | 0,0216 | 0,982                    | -0,018               |
| 5   | 2,3            | 0,0215 | 0,977                    | -0,023               |
| 6   | 2,8            | 0,0214 | 0,972                    | -0,029               |
| 7   | 3,3            | 0,0213 | 0,967                    | -0,034               |
| 8   | 3,8            | 0,0212 | 0,962                    | -0,039               |
| 9   | 4,3            | 0,0210 | 0,957                    | -0,044               |
| 10  | 4,9            | 0,0209 | 0,951                    | -0,051               |
| 11  | 5,2            | 0,0209 | 0,948                    | -0,053               |
| 12  | 5,6            | 0,0208 | 0,944                    | -0,058               |
| 13  | 6,2            | 0,0206 | 0,938                    | -0,064               |
| 14  | 6,7            | 0,0205 | 0,933                    | -0,069               |
| 15  | 7,1            | 0,0204 | 0,929                    | -0,074               |
| 16  | 7,6            | 0,0203 | 0,924                    | -0,080               |
| 17  | 8,2            | 0,0202 | 0,918                    | -0,085               |
| 18  | 8,5            | 0,0201 | 0,915                    | -0,088               |
| 19  | 9,0            | 0,0200 | 0,910                    | -0,094               |
| 20  | 9,5            | 0,0199 | 0,905                    | -0,100               |
| 21  | 9,9            | 0,0198 | 0,901                    | -0,104               |
| 22  | 10,4           | 0,0197 | 0,896                    | -0,110               |
| 23  | 10,8           | 0,0196 | 0,892                    | -0,114               |
| 24  | 11,3           | 0,0195 | 0,887                    | -0,120               |
| 25  | 11,9           | 0,0194 | 0,881                    | -0,127               |
| 26  | 12,2           | 0,0193 | 0,878                    | -0,130               |
| 27  | 12,7           | 0,0192 | 0,873                    | -0,136               |
| 28  | 13,2           | 0,0191 | 0,868                    | -0,141               |
| 29  | 13,6           | 0,0190 | 0,864                    | -0,147               |
| 30  | 14,2           | 0,0189 | 0,858                    | -0,153               |
| 31  | 14,5           | 0,0188 | 0,855                    | -0,156               |
| 32  | 15,1           | 0,0187 | 0,849                    | -0,163               |
| 33  | 15,5           | 0,0186 | 0,845                    | -0,169               |
| 34  | 15,9           | 0,0185 | 0,841                    | -0,174               |
| 35  | 16,3           | 0,0184 | 0,837                    | -0,178               |
| 36  | 16,8           | 0,0183 | 0,832                    | -0,184               |
| 37  | 17,2           | 0,0182 | 0,828                    | -0,188               |
| 38  | 17,6           | 0,0181 | 0,824                    | -0,194               |
| 39  | 18,4           | 0,0179 | 0,816                    | -0,204               |

|    |      |        |       |        |
|----|------|--------|-------|--------|
| 40 | 18,6 | 0,0179 | 0,814 | -0,205 |
| 41 | 19,2 | 0,0178 | 0,808 | -0,213 |
| 42 | 19,5 | 0,0177 | 0,805 | -0,217 |
| 43 | 19,9 | 0,0176 | 0,801 | -0,222 |
| 44 | 20,5 | 0,0175 | 0,795 | -0,229 |
| 45 | 20,8 | 0,0174 | 0,792 | -0,234 |
| 46 | 21,4 | 0,0173 | 0,786 | -0,240 |
| 47 | 21,8 | 0,0172 | 0,782 | -0,246 |
| 48 | 22,2 | 0,0171 | 0,778 | -0,251 |
| 49 | 22,7 | 0,0170 | 0,773 | -0,257 |
| 50 | 23,2 | 0,0169 | 0,768 | -0,263 |



**Figure S4** *In situ* NMR experiment. [HMF] vs time. Reaction conditions: catalyst **1** (0,0676 mg, 0,0628  $\mu$ mol), HMF (250 eq., 1,98 mg, 0,0157 mmol), toluene- $d_8$  (0,7 mL), 90°C,  $p(H_2)$  (3 bar).



**Figure S5** *In situ* NMR experiment.  $\ln([HMF]/[HMF]_0)$  vs time. Reaction conditions: catalyst **1** (0,0676 mg, 0,0628  $\mu$ mol), HMF (250 eq., 1,98 mg, 0,0157 mmol), toluene- $d_8$  (0,7 mL), 90°C,  $p(H_2)$  (3 bar).

**Table S6** Selected data and TOF calculation for the *in situ* NMR experiments with variable substrate concentration. Reaction conditions: catalyst **1** (0,0676 mg, 0,0628  $\mu$ mol), toluene- $d_8$  (0,7 mL), 90°C,  $p(H_2)$  (3 bar), substrate: A) HMF (1000 eq., 7,92 mg, 0,0628 mmol); B) HMF (250 eq., 1,98 mg, 0,0157 mmol); C) HMF (125 eq., 0,99 mg, 0,00785 mmol); D) HMF (62,5 eq., 0,50 mg, 0,00393 mmol).

| HMF (mmol) | HMF/1 | Min | HMF integration | BHMF integration | BHMF integration/2 | HMF integration+ (BHMF integration/2) | yield | TOF ( $\text{min}^{-1}$ ) |
|------------|-------|-----|-----------------|------------------|--------------------|---------------------------------------|-------|---------------------------|
| A) 0,0628  | 1000  | 10  | 97,0            | 3,0              | 1,5                | 98,5                                  | 1,5   | 1,54                      |
| A) 0,0628  | 1000  | 20  | 94,0            | 6,0              | 3,0                | 97,0                                  | 3,1   | 1,56                      |
| A) 0,0628  | 1000  | 30  | 90,9            | 9,1              | 4,5                | 95,5                                  | 4,8   | 1,58                      |
| A) 0,0628  | 1000  | 40  | 87,9            | 12,1             | 6,0                | 94,0                                  | 6,4   | 1,60                      |
| A) 0,0628  | 1000  | 50  | 84,9            | 15,1             | 7,6                | 92,4                                  | 8,2   | 1,64                      |
| A) 0,0628  | 1000  | 60  | 82,0            | 18,0             | 9,0                | 91,0                                  | 9,9   | 1,65                      |
| B) 0,0157  | 250   | 10  | 90,1            | 9,9              | 5,0                | 95,1                                  | 5,2   | 1,30                      |
| B) 0,0157  | 250   | 20  | 82,0            | 18,0             | 9,0                | 91,0                                  | 9,9   | 1,24                      |
| B) 0,0157  | 250   | 30  | 74,7            | 25,3             | 12,7               | 87,4                                  | 14,5  | 1,21                      |
| B) 0,0157  | 250   | 40  | 67,8            | 32,2             | 16,1               | 83,9                                  | 19,2  | 1,20                      |
| B) 0,0157  | 250   | 50  | 61,9            | 38,1             | 19,1               | 81,0                                  | 23,5  | 1,18                      |
| B) 0,0157  | 250   | 60  | 56,3            | 43,7             | 21,9               | 78,2                                  | 28,0  | 1,16                      |
| C) 0,00785 | 125   | 10  | 82,4            | 17,6             | 8,8                | 91,2                                  | 9,6   | 1,21                      |
| C) 0,00785 | 125   | 20  | 67,3            | 32,7             | 16,3               | 83,7                                  | 19,5  | 1,22                      |
| C) 0,00785 | 125   | 30  | 54,8            | 45,3             | 22,6               | 77,4                                  | 29,2  | 1,22                      |
| C) 0,00785 | 125   | 40  | 44,7            | 55,3             | 27,7               | 72,3                                  | 38,2  | 1,19                      |
| C) 0,00785 | 125   | 50  | 36,4            | 63,7             | 31,8               | 68,2                                  | 46,7  | 1,17                      |
| C) 0,00785 | 125   | 60  | 29,3            | 70,7             | 35,4               | 64,6                                  | 54,7  | 1,14                      |
| D) 0,00393 | 62,5  | 10  | 77,3            | 22,7             | 11,3               | 88,7                                  | 12,8  | 0,80                      |
| D) 0,00393 | 62,5  | 20  | 60,9            | 39,1             | 19,6               | 80,5                                  | 24,3  | 0,76                      |
| D) 0,00393 | 62,5  | 30  | 47,5            | 52,5             | 26,3               | 73,7                                  | 35,6  | 0,74                      |
| D) 0,00393 | 62,5  | 40  | 37,1            | 62,9             | 31,5               | 68,5                                  | 45,9  | 0,72                      |
| D) 0,00393 | 62,5  | 50  | 28,4            | 71,6             | 35,8               | 64,2                                  | 55,8  | 0,70                      |
| D) 0,00393 | 62,5  | 60  | 22,2            | 77,8             | 38,9               | 61,1                                  | 63,7  | 0,66                      |

**Table S7** Data at 10 minutes from Table S6 corresponding to Figure 8 in the manuscript.

| HMF (mmol) | HMF/1 | Min | HMF integration | BHMF integration | BHMF integration/2 | HMF integration+ (BHMF integration/2) | yield | TOF ( $\text{min}^{-1}$ ) |
|------------|-------|-----|-----------------|------------------|--------------------|---------------------------------------|-------|---------------------------|
| A) 0,0628  | 1000  | 10  | 97,0            | 3,0              | 1,5                | 98,5                                  | 1,5   | 1,54                      |
| B) 0,0157  | 250   | 10  | 90,1            | 9,9              | 5,0                | 95,1                                  | 5,2   | 1,30                      |
| C) 0,00785 | 125   | 10  | 82,4            | 17,6             | 8,8                | 91,2                                  | 9,6   | 1,21                      |
| D) 0,00393 | 62,5  | 10  | 77,3            | 22,7             | 11,3               | 88,7                                  | 12,8  | 0,80                      |

**Table S8** *In situ* NMR experiment. Reaction conditions: catalyst **1** (0,0676 mg, 0,0628  $\mu$ mol), HMF (125 eq., 0,99 mg, 0,00785 mmol), toluene- $d_8$  (0,7 mL), 90°C,  $p(H_2)$  (3 bar). Spectra acquired every 60 seconds. An absolute error of 1% affect the NMR integrations.

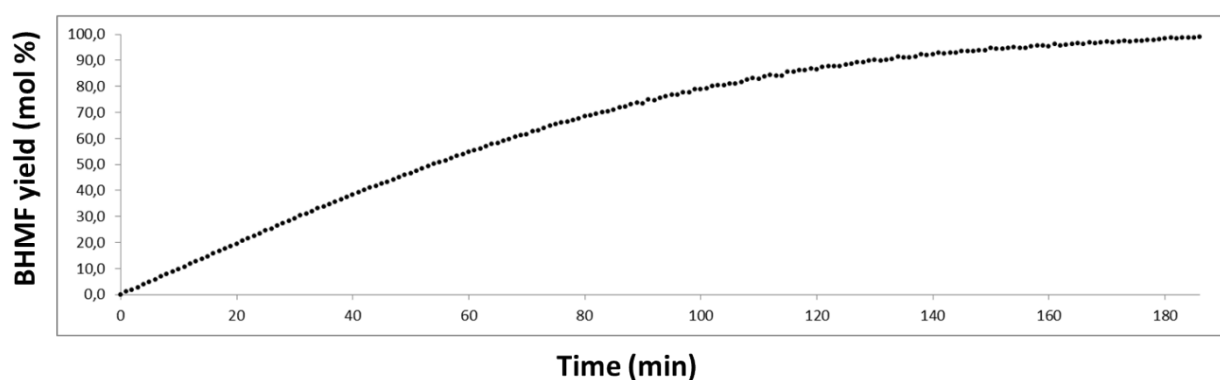
| Min | HMF integration | BHMF integration | BHMF integration/2 | HMF integration+ (BHMF integration/2) | yield |
|-----|-----------------|------------------|--------------------|---------------------------------------|-------|
| 0   | 100,0           | 0,0              | 0,0                | 0,0                                   | 0,0   |
| 1   | 97,7            | 2,3              | 1,1                | 98,9                                  | 1,2   |
| 2   | 96,4            | 3,6              | 1,8                | 98,2                                  | 1,8   |
| 3   | 94,9            | 5,1              | 2,6                | 97,4                                  | 2,6   |
| 4   | 92,8            | 7,2              | 3,6                | 96,4                                  | 3,7   |
| 5   | 91,2            | 8,8              | 4,4                | 95,6                                  | 4,6   |
| 6   | 89,1            | 10,9             | 5,5                | 94,5                                  | 5,8   |
| 7   | 87,4            | 12,6             | 6,3                | 93,7                                  | 6,7   |
| 8   | 85,6            | 14,4             | 7,2                | 92,8                                  | 7,8   |
| 9   | 84,0            | 16,0             | 8,0                | 92,0                                  | 8,7   |
| 10  | 82,4            | 17,6             | 8,8                | 91,2                                  | 9,6   |
| 11  | 80,7            | 19,3             | 9,6                | 90,4                                  | 10,7  |
| 12  | 79,1            | 20,9             | 10,5               | 89,6                                  | 11,7  |
| 13  | 77,4            | 22,6             | 11,3               | 88,7                                  | 12,7  |
| 14  | 75,8            | 24,2             | 12,1               | 87,9                                  | 13,8  |
| 15  | 74,5            | 25,5             | 12,8               | 87,3                                  | 14,6  |
| 16  | 72,9            | 27,1             | 13,6               | 86,4                                  | 15,7  |
| 17  | 71,4            | 28,6             | 14,3               | 85,7                                  | 16,7  |
| 18  | 70,2            | 29,9             | 14,9               | 85,1                                  | 17,5  |
| 19  | 68,6            | 31,4             | 15,7               | 84,3                                  | 18,6  |
| 20  | 67,3            | 32,7             | 16,3               | 83,7                                  | 19,5  |
| 21  | 65,9            | 34,2             | 17,1               | 82,9                                  | 20,6  |
| 22  | 64,6            | 35,4             | 17,7               | 82,3                                  | 21,5  |
| 23  | 63,3            | 36,7             | 18,3               | 81,7                                  | 22,5  |
| 24  | 62,1            | 37,9             | 19,0               | 81,0                                  | 23,4  |
| 25  | 60,6            | 39,4             | 19,7               | 80,3                                  | 24,5  |
| 26  | 59,6            | 40,4             | 20,2               | 79,8                                  | 25,3  |
| 27  | 58,1            | 41,9             | 20,9               | 79,1                                  | 26,5  |
| 28  | 57,0            | 43,0             | 21,5               | 78,5                                  | 27,4  |
| 29  | 55,9            | 44,1             | 22,0               | 78,0                                  | 28,3  |
| 30  | 54,8            | 45,3             | 22,6               | 77,4                                  | 29,2  |
| 31  | 53,6            | 46,4             | 23,2               | 76,8                                  | 30,2  |
| 32  | 52,7            | 47,3             | 23,7               | 76,3                                  | 31,0  |
| 33  | 51,8            | 48,3             | 24,1               | 75,9                                  | 31,8  |
| 34  | 50,3            | 49,7             | 24,9               | 75,1                                  | 33,1  |
| 35  | 49,7            | 50,3             | 25,1               | 74,9                                  | 33,6  |
| 36  | 48,5            | 51,5             | 25,7               | 74,3                                  | 34,6  |
| 37  | 47,5            | 52,6             | 26,3               | 73,7                                  | 35,6  |
| 38  | 46,5            | 53,5             | 26,8               | 73,2                                  | 36,5  |

|    |      |      |      |      |      |
|----|------|------|------|------|------|
| 39 | 45,6 | 54,4 | 27,2 | 72,8 | 37,4 |
| 40 | 44,7 | 55,3 | 27,7 | 72,3 | 38,2 |
| 41 | 43,7 | 56,3 | 28,2 | 71,9 | 39,2 |
| 42 | 42,8 | 57,2 | 28,6 | 71,4 | 40,1 |
| 43 | 41,8 | 58,2 | 29,1 | 70,9 | 41,0 |
| 44 | 41,3 | 58,7 | 29,4 | 70,6 | 41,6 |
| 45 | 40,3 | 59,7 | 29,9 | 70,1 | 42,6 |
| 46 | 39,6 | 60,5 | 30,2 | 69,8 | 43,3 |
| 47 | 38,7 | 61,3 | 30,6 | 69,4 | 44,2 |
| 48 | 37,8 | 62,2 | 31,1 | 68,9 | 45,1 |
| 49 | 37,0 | 63,0 | 31,5 | 68,5 | 45,9 |
| 50 | 36,4 | 63,7 | 31,8 | 68,2 | 46,7 |
| 51 | 35,6 | 64,4 | 32,2 | 67,8 | 47,5 |
| 52 | 34,8 | 65,2 | 32,6 | 67,4 | 48,3 |
| 53 | 34,0 | 66,1 | 33,0 | 67,0 | 49,3 |
| 54 | 33,1 | 66,9 | 33,5 | 66,6 | 50,3 |
| 55 | 32,6 | 67,4 | 33,7 | 66,3 | 50,8 |
| 56 | 32,0 | 68,0 | 34,0 | 66,0 | 51,5 |
| 57 | 31,3 | 68,7 | 34,4 | 65,6 | 52,3 |
| 58 | 30,6 | 69,4 | 34,7 | 65,3 | 53,1 |
| 59 | 30,1 | 69,9 | 35,0 | 65,0 | 53,8 |
| 60 | 29,3 | 70,7 | 35,4 | 64,6 | 54,7 |
| 61 | 28,7 | 71,3 | 35,6 | 64,4 | 55,4 |
| 62 | 28,3 | 71,8 | 35,9 | 64,1 | 55,9 |
| 63 | 27,4 | 72,6 | 36,3 | 63,7 | 57,0 |
| 64 | 26,7 | 73,3 | 36,6 | 63,4 | 57,8 |
| 65 | 26,5 | 73,5 | 36,7 | 63,3 | 58,1 |
| 66 | 25,8 | 74,2 | 37,1 | 62,9 | 59,0 |
| 67 | 25,2 | 74,8 | 37,4 | 62,6 | 59,8 |
| 68 | 24,7 | 75,3 | 37,7 | 62,3 | 60,4 |
| 69 | 24,2 | 75,8 | 37,9 | 62,1 | 61,0 |
| 70 | 23,8 | 76,2 | 38,1 | 61,9 | 61,6 |
| 71 | 22,9 | 77,1 | 38,5 | 61,5 | 62,7 |
| 72 | 22,6 | 77,4 | 38,7 | 61,3 | 63,1 |
| 73 | 22,1 | 77,9 | 39,0 | 61,0 | 63,8 |
| 74 | 21,4 | 78,6 | 39,3 | 60,7 | 64,7 |
| 75 | 21,0 | 79,1 | 39,5 | 60,5 | 65,4 |
| 76 | 20,5 | 79,5 | 39,8 | 60,2 | 66,0 |
| 77 | 20,1 | 79,9 | 39,9 | 60,1 | 66,5 |
| 78 | 19,7 | 80,3 | 40,2 | 59,8 | 67,1 |
| 79 | 19,5 | 80,5 | 40,3 | 59,7 | 67,4 |
| 80 | 18,6 | 81,4 | 40,7 | 59,3 | 68,6 |
| 81 | 18,6 | 81,4 | 40,7 | 59,3 | 68,7 |
| 82 | 18,1 | 81,9 | 40,9 | 59,1 | 69,3 |
| 83 | 17,7 | 82,3 | 41,1 | 58,9 | 69,9 |
| 84 | 17,4 | 82,7 | 41,3 | 58,7 | 70,4 |

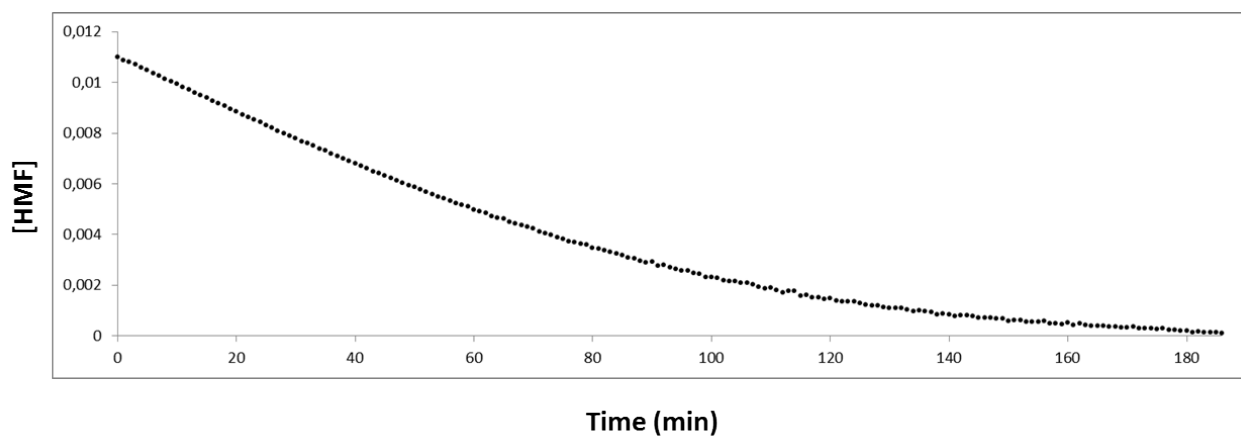
|     |      |      |      |      |      |
|-----|------|------|------|------|------|
| 85  | 17,0 | 83,0 | 41,5 | 58,5 | 71,0 |
| 86  | 16,4 | 83,6 | 41,8 | 58,2 | 71,8 |
| 87  | 16,1 | 83,9 | 42,0 | 58,0 | 72,3 |
| 88  | 15,5 | 84,5 | 42,2 | 57,8 | 73,1 |
| 89  | 15,2 | 84,8 | 42,4 | 57,6 | 73,7 |
| 90  | 15,3 | 84,7 | 42,4 | 57,6 | 73,5 |
| 91  | 14,4 | 85,6 | 42,8 | 57,2 | 74,8 |
| 92  | 14,6 | 85,4 | 42,7 | 57,3 | 74,6 |
| 93  | 13,9 | 86,1 | 43,0 | 57,0 | 75,5 |
| 94  | 13,7 | 86,4 | 43,2 | 56,8 | 76,0 |
| 95  | 13,2 | 86,8 | 43,4 | 56,6 | 76,7 |
| 96  | 13,2 | 86,8 | 43,4 | 56,6 | 76,7 |
| 97  | 12,7 | 87,3 | 43,7 | 56,3 | 77,5 |
| 98  | 12,5 | 87,5 | 43,8 | 56,3 | 77,8 |
| 99  | 11,8 | 88,3 | 44,1 | 55,9 | 79,0 |
| 100 | 11,8 | 88,2 | 44,1 | 55,9 | 78,8 |
| 101 | 11,6 | 88,5 | 44,2 | 55,8 | 79,3 |
| 102 | 11,1 | 88,9 | 44,5 | 55,5 | 80,0 |
| 103 | 10,9 | 89,1 | 44,6 | 55,4 | 80,4 |
| 104 | 10,9 | 89,1 | 44,6 | 55,4 | 80,4 |
| 105 | 10,6 | 89,4 | 44,7 | 55,3 | 80,8 |
| 106 | 10,6 | 89,4 | 44,7 | 55,3 | 80,8 |
| 107 | 10,2 | 89,8 | 44,9 | 55,1 | 81,5 |
| 108 | 9,7  | 90,3 | 45,2 | 54,8 | 82,4 |
| 109 | 9,2  | 90,8 | 45,4 | 54,6 | 83,1 |
| 110 | 9,4  | 90,6 | 45,3 | 54,7 | 82,7 |
| 111 | 8,9  | 91,1 | 45,6 | 54,5 | 83,7 |
| 112 | 8,4  | 91,6 | 45,8 | 54,2 | 84,5 |
| 113 | 8,7  | 91,3 | 45,6 | 54,4 | 84,0 |
| 114 | 8,7  | 91,3 | 45,6 | 54,4 | 84,0 |
| 115 | 7,8  | 92,2 | 46,1 | 53,9 | 85,6 |
| 116 | 7,8  | 92,2 | 46,1 | 53,9 | 85,5 |
| 117 | 7,4  | 92,6 | 46,3 | 53,7 | 86,3 |
| 118 | 7,4  | 92,6 | 46,3 | 53,7 | 86,3 |
| 119 | 7,1  | 92,9 | 46,5 | 53,5 | 86,8 |
| 120 | 7,3  | 92,7 | 46,4 | 53,7 | 86,4 |
| 121 | 6,7  | 93,3 | 46,6 | 53,4 | 87,4 |
| 122 | 6,5  | 93,5 | 46,8 | 53,3 | 87,8 |
| 123 | 6,5  | 93,5 | 46,7 | 53,3 | 87,7 |
| 124 | 6,5  | 93,5 | 46,8 | 53,2 | 87,8 |
| 125 | 6,2  | 93,8 | 46,9 | 53,1 | 88,4 |
| 126 | 6,0  | 94,0 | 47,0 | 53,0 | 88,8 |
| 127 | 5,8  | 94,2 | 47,1 | 52,9 | 89,1 |
| 128 | 5,7  | 94,3 | 47,1 | 52,9 | 89,1 |
| 129 | 5,4  | 94,6 | 47,3 | 52,7 | 89,7 |
| 130 | 5,2  | 94,8 | 47,4 | 52,6 | 90,1 |

|     |     |      |      |      |      |
|-----|-----|------|------|------|------|
| 131 | 5,3 | 94,7 | 47,4 | 52,6 | 90,0 |
| 132 | 5,3 | 94,7 | 47,4 | 52,6 | 90,0 |
| 133 | 4,9 | 95,1 | 47,5 | 52,5 | 90,6 |
| 134 | 4,5 | 95,5 | 47,7 | 52,3 | 91,3 |
| 135 | 4,8 | 95,2 | 47,6 | 52,4 | 90,9 |
| 136 | 4,7 | 95,3 | 47,7 | 52,3 | 91,1 |
| 137 | 4,5 | 95,5 | 47,8 | 52,3 | 91,4 |
| 138 | 4,0 | 96,0 | 48,0 | 52,0 | 92,3 |
| 139 | 4,2 | 95,8 | 47,9 | 52,1 | 91,9 |
| 140 | 4,0 | 96,0 | 48,0 | 52,0 | 92,4 |
| 141 | 3,7 | 96,3 | 48,1 | 51,9 | 92,8 |
| 142 | 3,8 | 96,2 | 48,1 | 51,9 | 92,7 |
| 143 | 3,8 | 96,2 | 48,1 | 51,9 | 92,8 |
| 144 | 3,7 | 96,3 | 48,1 | 51,9 | 92,8 |
| 145 | 3,4 | 96,6 | 48,3 | 51,7 | 93,4 |
| 146 | 3,4 | 96,6 | 48,3 | 51,7 | 93,4 |
| 147 | 3,4 | 96,6 | 48,3 | 51,7 | 93,4 |
| 148 | 3,2 | 96,8 | 48,4 | 51,6 | 93,8 |
| 149 | 3,2 | 96,9 | 48,4 | 51,6 | 93,9 |
| 150 | 2,8 | 97,2 | 48,6 | 51,4 | 94,6 |
| 151 | 2,9 | 97,1 | 48,6 | 51,4 | 94,4 |
| 152 | 2,8 | 97,2 | 48,6 | 51,4 | 94,5 |
| 153 | 2,7 | 97,3 | 48,7 | 51,3 | 94,8 |
| 154 | 2,6 | 97,4 | 48,7 | 51,3 | 94,9 |
| 155 | 2,7 | 97,4 | 48,7 | 51,3 | 94,8 |
| 156 | 2,7 | 97,3 | 48,6 | 51,4 | 94,7 |
| 157 | 2,3 | 97,7 | 48,8 | 51,2 | 95,5 |
| 158 | 2,3 | 97,7 | 48,9 | 51,1 | 95,6 |
| 159 | 2,2 | 97,8 | 48,9 | 51,1 | 95,7 |
| 160 | 2,4 | 97,6 | 48,8 | 51,2 | 95,3 |
| 161 | 1,9 | 98,1 | 49,0 | 51,0 | 96,2 |
| 162 | 2,2 | 97,8 | 48,9 | 51,1 | 95,7 |
| 163 | 2,0 | 98,0 | 49,0 | 51,0 | 96,0 |
| 164 | 1,9 | 98,1 | 49,1 | 50,9 | 96,3 |
| 165 | 1,8 | 98,2 | 49,1 | 50,9 | 96,5 |
| 166 | 1,9 | 98,1 | 49,1 | 50,9 | 96,3 |
| 167 | 1,6 | 98,4 | 49,2 | 50,8 | 96,8 |
| 168 | 1,7 | 98,3 | 49,2 | 50,9 | 96,7 |
| 169 | 1,5 | 98,5 | 49,2 | 50,8 | 97,0 |
| 170 | 1,5 | 98,5 | 49,3 | 50,8 | 97,0 |
| 171 | 1,6 | 98,4 | 49,2 | 50,8 | 96,8 |
| 172 | 1,4 | 98,6 | 49,3 | 50,7 | 97,2 |
| 173 | 1,3 | 98,7 | 49,3 | 50,7 | 97,4 |
| 174 | 1,4 | 98,6 | 49,3 | 50,7 | 97,2 |
| 175 | 1,3 | 98,8 | 49,4 | 50,6 | 97,5 |
| 176 | 1,3 | 98,7 | 49,3 | 50,7 | 97,4 |

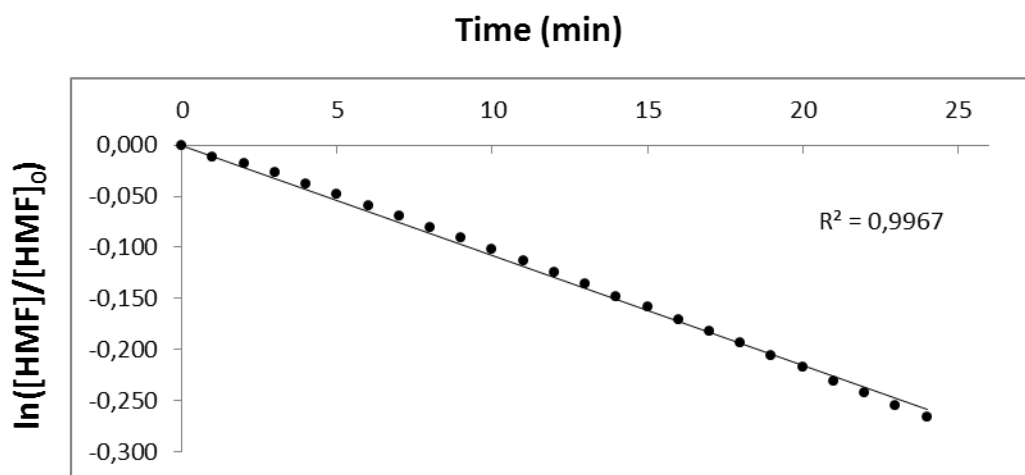
|     |     |      |      |      |      |
|-----|-----|------|------|------|------|
| 177 | 1,1 | 98,9 | 49,5 | 50,6 | 97,8 |
| 178 | 1,1 | 98,9 | 49,5 | 50,6 | 97,8 |
| 179 | 1,0 | 99,0 | 49,5 | 50,5 | 98,0 |
| 180 | 0,9 | 99,1 | 49,6 | 50,5 | 98,2 |
| 181 | 0,7 | 99,3 | 49,7 | 50,4 | 98,6 |
| 182 | 0,8 | 99,2 | 49,6 | 50,4 | 98,4 |
| 183 | 0,7 | 99,3 | 49,7 | 50,4 | 98,6 |
| 184 | 0,7 | 99,3 | 49,7 | 50,4 | 98,6 |
| 185 | 0,6 | 99,4 | 49,7 | 50,3 | 98,8 |
| 186 | 0,5 | 99,5 | 49,8 | 50,3 | 99,0 |



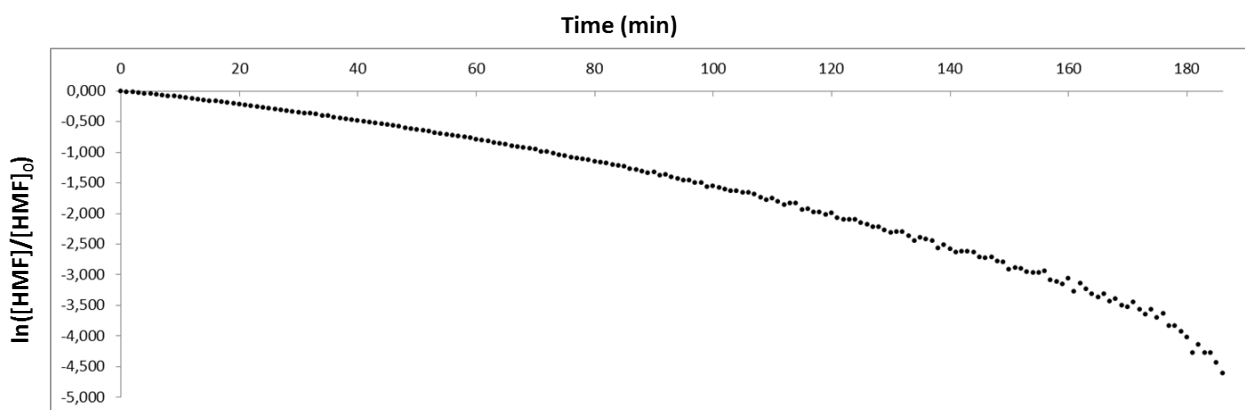
**Figure S6** *In situ* NMR experiment (BHMF yield vs time). Reaction conditions: catalyst **1** (0,0676 mg, 0,0628  $\mu\text{mol}$ ), HMF (125 eq., 0,99 mg, 0,00785 mmol), toluene- $\text{d}_8$  (0,7 mL), 90°C,  $p(\text{H}_2)$  (3 bar).



**Figure S7** *In situ* NMR experiment. [HMF] vs time. Reaction conditions: catalyst **1** (0,0676 mg, 0,0628  $\mu\text{mol}$ ), HMF (125 eq., 0,99 mg, 0,00785 mmol), toluene- $\text{d}_8$  (0,7 mL), 90°C,  $p(\text{H}_2)$  (3 bar).



**Figure S8** *In situ* NMR experiment.  $\ln([HMF]/[HMF]_0)$  vs time. Beginning of the reaction (0-23 min, up to 23 % yield). Reaction conditions: catalyst **1** (0,0676 mg, 0,0628  $\mu\text{mol}$ ), HMF (125 eq., 0,99 mg, 0,00785 mmol), toluene- $d_8$  (0,7 mL), 90°C,  $p(\text{H}_2)$  (3 bar).



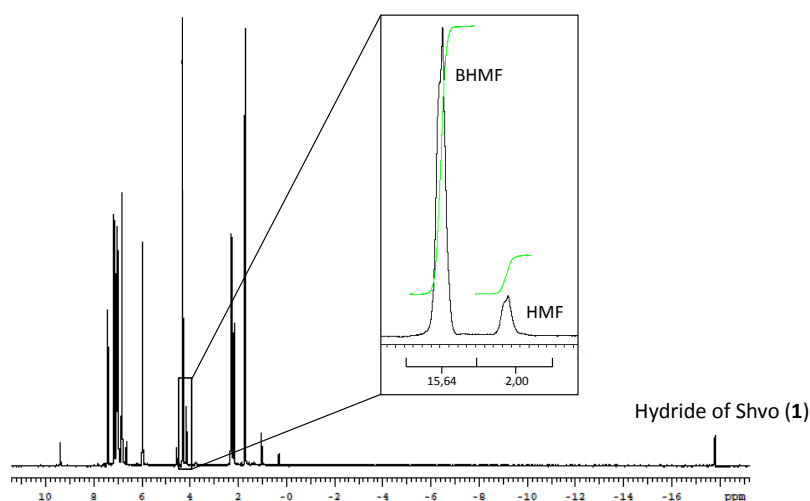
**Figure S9** *In situ* NMR experiment.  $\ln([HMF]/[HMF]_0)$  vs time. Reaction conditions: catalyst **1** (0,0676 mg, 0,0628  $\mu\text{mol}$ ), HMF (125 eq., 0,99 mg, 0,00785 mmol), toluene- $d_8$  (0,7 mL), 90°C,  $p(\text{H}_2)$  (3 bar).

***In situ* NMR reactions of catalyst **1** with HMF or BHMF under nitrogen or hydrogen atmosphere with a substrate/**1** ratio = 4.**

### General procedure

In a J. Young valve equipped NMR tube, catalyst **1** (e.g. 15.0 mg, 13.8  $\mu\text{mol}$ ) and the substrate HMF or BHMF (e.g. 4 eq., 55.2  $\mu\text{mol}$ ) were added and dissolved in 0.7 mL of toluene- $d_8$  under nitrogen atmosphere. The experiments were kept at 90°C for the time requested. For the experiments under hydrogen, before heating, the samples solutions have been frozen in liquid nitrogen, the nitrogen inside the tube removed under vacuum and restored with 3 bar of  $\text{H}_2$ .

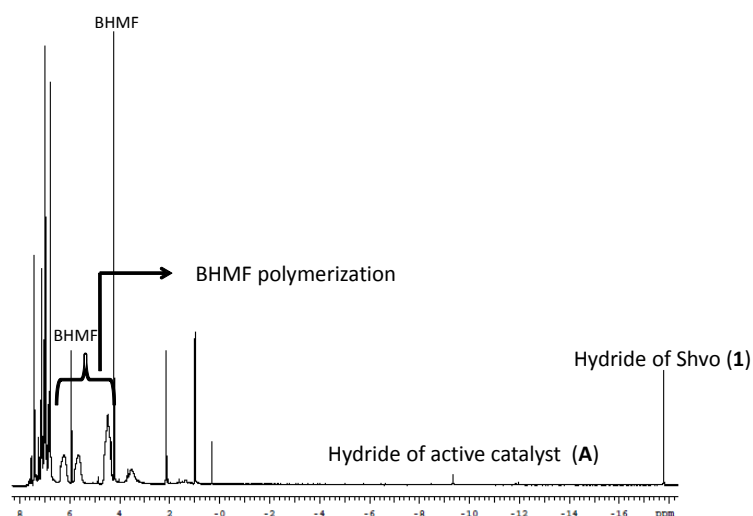
*Reaction between HMF and catalyst **1**:  $\text{H}_2$  atmosphere (3 bar).* The sample has been warmed to 90°C and the spectra registered every ten minutes. The reaction is selective toward the formation of BHMF, conversions have been followed by integration of the  $^1\text{H}$ -NMR signals of HMF and BHMF<sup>1</sup> as reported as an example in Figure S10.



**Figure S10** Selected *in situ* NMR spectrum. Reaction conditions (HMF/**1** = 4, T = 90 °C, P( $\text{H}_2$ ) = 3 bar, reaction time = 30 min). BHMF yield = HMF conversion = 80% (calculated from integration reported in the enlargement).

During the experiment the signal of the dimeric catalyst precursor **1** is always observable in the hydride region ( $\delta = -17.82$  ppm in toluene- $d_8$  – Figure S10) while the monomer **A** ( $\delta = -9.37$  ppm) appears only after the end of the reaction (Figure S11); this is in line with the findings by Casey and co-workers.<sup>2</sup> Leaving the reaction mixture at 90°C for 24h new signals in the region of BHMF arose at 6.31 and 5.85 ppm (CH furan) and 4.60 ppm ( $\text{CH}_2\text{OH}$ ) (Figure S11). They do not correspond to ruthenium complexes, in that the CO region of the  $^{13}\text{C}$ -NMR spectrum accounts only for the

presence of the dimeric precursor **1**. Therefore, the observed  $^1\text{H}$  NMR resonances are the consequence of a further transformation of BHMF, probably due to consecutive polymerization favoured by the temperature.<sup>3</sup>



**Figure S11** Selected *in situ* NMR spectrum. Reaction conditions (HMF/**1** = 4, T = 90 °C, P(H<sub>2</sub>) = 3 bar, reaction time = 24h).

It is important to underline that these by-products were not observed in all the experiments carried out in batch reactor, because in these cases reactions have been always stopped before, or as soon as, the complete conversion was reached.

*Reaction between HMF or BHMF and catalyst 1: N<sub>2</sub> atmosphere.* The reaction has been also performed in absence of H<sub>2</sub> (reaction conditions: catalyst **1**: 15.0 mg, 13.8  $\mu\text{mol}$ , HMF: 6.96 mg, 55.2  $\mu\text{mol}$ , T = 90 °C, HMF/**1** = 4). The toluene-d<sub>8</sub> solution has been monitored *in situ* for 90 min, then the tube has been kept at 90 °C in a silicon bath and the reaction mixture checked at room temperature at defined reaction times. The conversion of 23% was selective toward the formation of BHMF. Principal pattern of signals from  $^1\text{H}$ -NMR spectrum remained almost unchanged for 100 hours. Nevertheless, several signals arising from side reactions due to the prolonged reaction time, appeared in the region of CH<sub>2</sub> and CH from BHMF and HMF, and in the aldehyde region around 9 ppm.

The reaction between Shvo complex **1** and BHMF under inert atmosphere has been also performed (reaction conditions: catalyst **1**: 15.0 mg, 13.8  $\mu\text{mol}$ , BHMF: 7.05 mg, 55.2  $\mu\text{mol}$ , T = 90°C, BHMF/**1** = 4) and resulted in its partial dehydrogenation to HMF. The conversion was stabilized at 25% and the selectivity complete.

The above described  $^1\text{H}$ -NMR experiments under nitrogen atmosphere, which are actually stoichiometric reactions, are in line with what reported for the reactivity of Shvo complex **1** with other substrates,<sup>2</sup> confirming that complex **1**, once activated by the temperature, works as a reducing agent in the form of the 18 electron species (**A**), or as an oxidative agent in the form of the 16 electron species (**B**).

*Reaction between BHMF and catalyst 1:  $\text{H}_2$  atmosphere.* The present NMR experiment (reaction conditions:  $\text{P}(\text{H}_2) = 3\text{bar}$ ,  $T = 90\text{ }^\circ\text{C}$ ,  $\text{BHMF}/\mathbf{1} = 4$ , toluene- $d_8 = 0,6\text{ mL}$ , catalyst **1**: 15.0 mg, 13.8  $\mu\text{mol}$ , BHMF: 7.05 mg, 55.2  $\mu\text{mol}$ ) allowed to verify that  $\text{H}_2$  atmosphere suppresses the dehydrogenation.<sup>2</sup> After 150 h at  $90^\circ\text{C}$ , no HMF was detectable in the  $^1\text{H}$ -NMR spectrum.

## CALCULATIONS

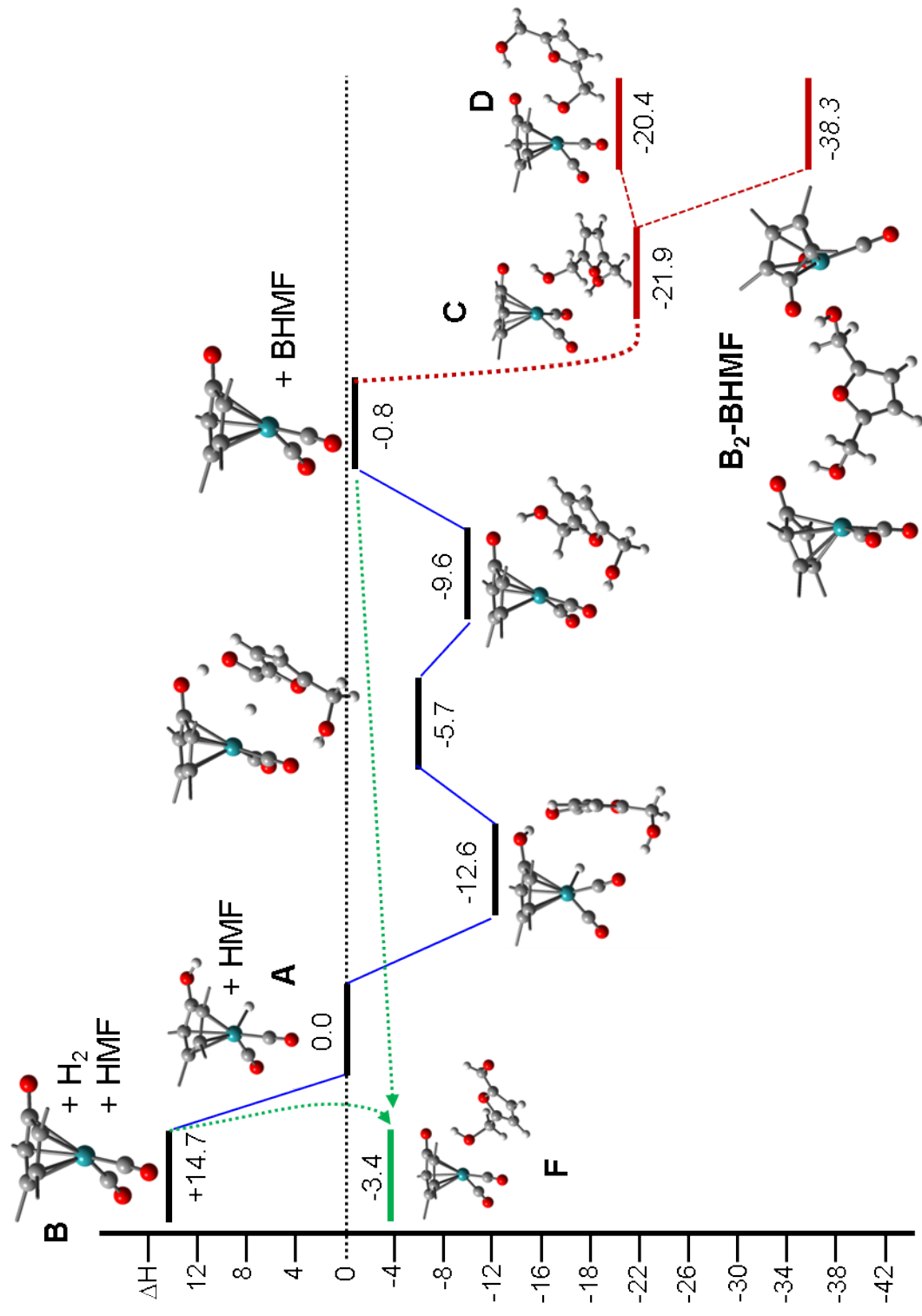
All the calculations were performed using Gaussian 09 rev A.02. All the geometries were optimized at the B3LYP/LANL2DZ level. Vibrational analysis were done on all the optimized geometries.

**Table S9 – calculations in gas phase**

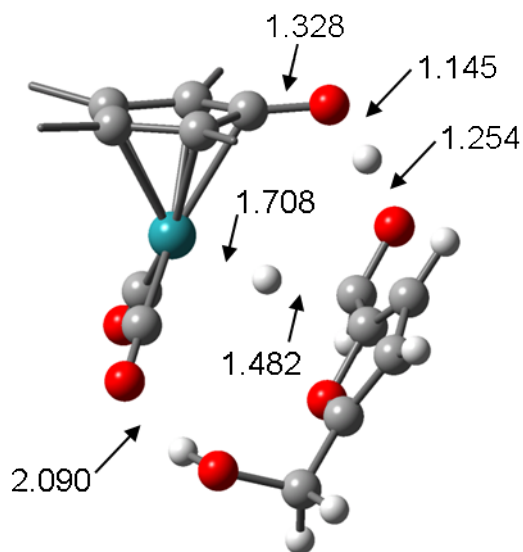
|                                             | Internal<br>energy (E) | thermal<br>corrected<br>enthalpy (H°) | Free Gibbs<br>energy<br>(G°) | $\Delta H^\circ$<br>(kcal/mol)                         | $\Delta G^\circ$<br>(kcal/mol)                         |
|---------------------------------------------|------------------------|---------------------------------------|------------------------------|--------------------------------------------------------|--------------------------------------------------------|
| <b>HMF</b>                                  | -457.812637            | -457.691367                           | -457.734494                  |                                                        |                                                        |
| <b>BHMF</b>                                 | -459.022477            | -458.877073                           | -458.922119                  |                                                        |                                                        |
| <b>H<sub>2</sub></b>                        | -1.174416              | -1.161007                             | -1.175801                    |                                                        |                                                        |
| <b>Catalyst B</b>                           | -1512.728885           | -1512.280247                          | -1512.374037                 |                                                        |                                                        |
| <b>F</b>                                    | -1970.576502           | -1970.005085                          | -1970.122125                 |                                                        |                                                        |
| <b>Catalyst A</b>                           | -1513.942887           | -1513.473822                          | -1513.568382                 |                                                        |                                                        |
| <b>B+H<sub>2</sub>+HMF</b>                  | -1971.715938           | -1971.131621                          | -1971.284332                 | 20.4                                                   | 11.6                                                   |
| <b>A+HMF</b>                                | -1971.755524           | -1971.165189                          | -1971.302876                 | <b>0.00</b>                                            | <b>0.00</b>                                            |
| <b>GS-preTS</b>                             | -1971.775296           | -1971.182702                          | -1971.299538                 | -11.0                                                  | 2.1                                                    |
| <b>TS</b>                                   | -1971.758111           | -1971.170817                          | -1971.283502                 | -3.5                                                   | 12.2                                                   |
| <b>GS-postTS</b>                            | -1971.771046           | -1971.176295                          | -1971.291057                 | -7.0                                                   | 7.4                                                    |
| <b>C</b>                                    | -1971.791488           | -1971.195401                          | -1971.312309                 | -19.0                                                  | -5.9                                                   |
| <b>C'</b>                                   | -1971.787918           | -1971.191704                          | -1971.311324                 | -16.6                                                  | -5.3                                                   |
| <b>D</b>                                    | -1971.790665           | -1971.194150                          | -1971.309141                 | -18.2                                                  | -3.9                                                   |
| <b>B<sub>2</sub>-BHMF</b>                   | -3484.552017           | -3483.505227                          | -3483.697854                 | <b>-20.9</b><br>(vs C'+B)<br><b>-42.4</b><br>(HBMF+2B) | <b>-7.8</b><br>(vs C'+B)<br><b>-17.4</b><br>( HBMF+2B) |
| <b>B<sub>2</sub>-BHMF</b><br><b>Cpoise3</b> | -3484.537022           | -3483.489858                          | -3483.683023                 | <b>-11.2</b><br>(vs C'+B)<br><b>-32.8</b><br>(HBMF+2B) | <b>+1.5</b><br>(vs C'+B)<br><b>-8.0</b><br>( HBMF+2B)  |
| <b>B<sub>2</sub>-BHMF</b><br><b>Cpoise2</b> | -3484.544551           | -3483.497614                          | -3483.690831                 | <b>-16.1</b><br>(vs C'+B)<br><b>-37.7</b><br>(HBMF+2B) | <b>-3.4</b><br>(vs C'+B)<br><b>-13.0</b><br>( HBMF+2B) |
| <b>C' + B</b>                               | -3484.516803           | -3483.471951                          | -3483.685361                 |                                                        |                                                        |
| <b>BHMF + 2B</b>                            | -3484.480247           | -3483.437567                          | -3483.670193                 |                                                        |                                                        |

Table S10 – calculations with solvent (PCM-B3LYP/LanL2DZ)

|                            | Internal<br>energy (E) | Thermal<br>corrected<br>enthalpy (H°) | Free Gibbs<br>energy<br>(G°) | $\Delta H^\circ$<br>(kcal/mol)                         | $\Delta G^\circ$<br>(kcal/mol)                       |
|----------------------------|------------------------|---------------------------------------|------------------------------|--------------------------------------------------------|------------------------------------------------------|
| <b>HMF</b>                 | -457.819377            | -457.698110                           | -457.741337                  |                                                        |                                                      |
| <b>BHMF</b>                | -459.029208            | -458.883845                           | -458.928927                  |                                                        |                                                      |
| <b>H<sub>2</sub></b>       | -1.174460              | -1.161007                             | -1.175801                    |                                                        |                                                      |
| <b>Catalyst B</b>          | -1512.737863           | -1512.289379                          | -1512.382942                 |                                                        |                                                      |
| <b>F</b>                   | -1970.588423           | -1970.016943                          | -1970.134629                 |                                                        |                                                      |
| <b>Catalyst A</b>          | -1513.982887           | -1513.473823                          | -1513.568386                 |                                                        |                                                      |
| <b>B+H<sub>2</sub>+HMF</b> | -1971.731700           | -1971.148496                          | -1971.300080                 | <b>+14.7</b>                                           | <b>+6.0</b>                                          |
| <b>A+HMF</b>               | -1971.802264           | -1971.171933                          | -1971.309723                 | <b>0.00</b>                                            | <b>0.00</b>                                          |
| <b>GS-preTS</b>            | -1971.784207           | -1971.191993                          | -1971.309708                 | -12.6                                                  | +0.0                                                 |
| <b>TS</b>                  | -1971.768036           | -1971.180988                          | -1971.295070                 | -5.7                                                   | +9.2                                                 |
| <b>GS-postTS</b>           | -1971.781780           | -1971.187171                          | -1971.301493                 | -9.6                                                   | +5.2                                                 |
| <b>C</b>                   | -1971.802795           | -1971.206857                          | -1971.323886                 | -21.9                                                  | -8.9                                                 |
| <b>C'</b>                  | -1971.799644           | -1971.203656                          | -1971.323861                 | -19.9                                                  | -8.9                                                 |
| <b>D</b>                   | -1971.800798           | -1971.204523                          | -1971.319240                 | -20.4                                                  | -6.0                                                 |
| <b>B<sub>2</sub>-BHMF</b>  | -3484.568796           | -3483.522324                          | -3483.714842                 | <b>-18.4</b><br>(vs C'+B)<br><b>-37.5</b><br>(HBMF+2B) | <b>-5.0</b><br>(vs C'+B)<br><b>-12.</b><br>(HBMF+2B) |
| <b>C' + B</b>              | -3484.537507           | -3483.493035                          | -3483.706803                 | <b>+18.4</b><br>(vs B <sub>2</sub> -BHMF)              | <b>+5.0</b><br>(vs B <sub>2</sub> -BHMF)             |
| <b>BHMF + 2B</b>           | -3484.498934           | -3483.462603                          | -3483.694811                 | <b>+37.5</b><br>(vs B <sub>2</sub> -BHMF)              | <b>+12.6</b><br>(vs B <sub>2</sub> -BHMF)            |



### Transition state for hydrogenation of HMF



B3LYP/LanL2DZ - gas phase

E = -1971.758111

H° = -1971.170817

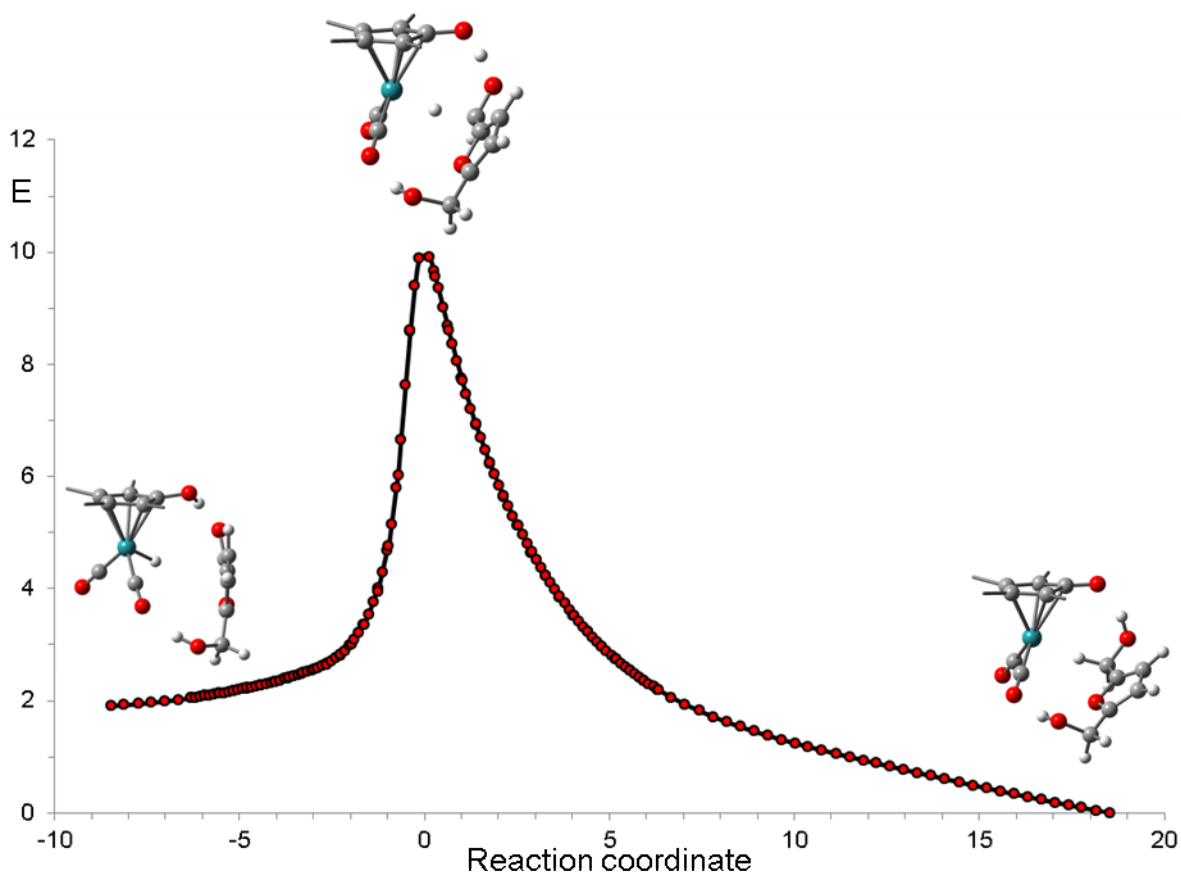
G° = -1971.283502

B3LYP/LanL2DZ - toluene

E = -1971.768036

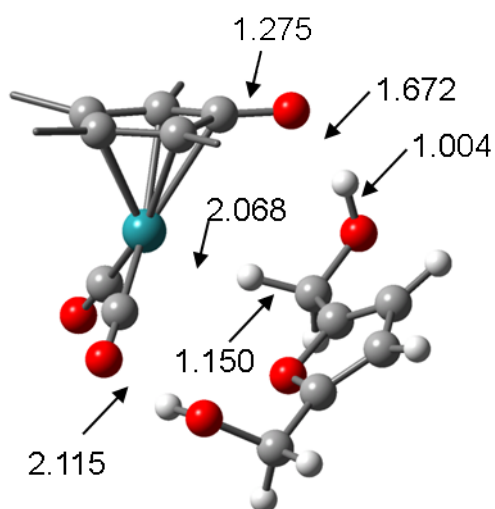
H° = -1971.180988

G° = -1971.295070



IRC profile starting from the above transition state. Two IRC calculations were run with different energy steps (0.1 Bohr and 50 points for the first. 0.3 Bohr and 50 points for the second job).

**Ground state found by IRC in the forward direction**

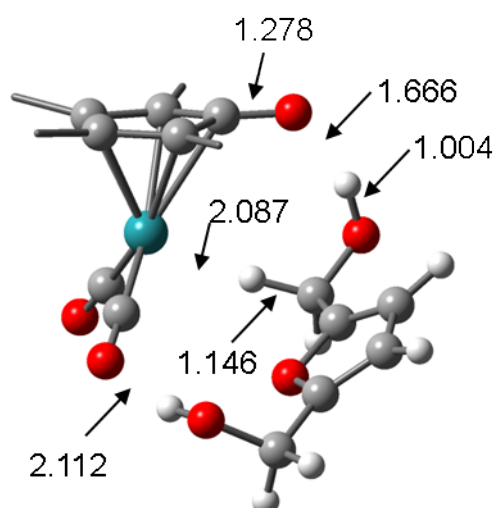


B3LYP/LanL2DZ - gas phase

E = -1971.771046

H° = -1971.176295

G° = -1971.291057



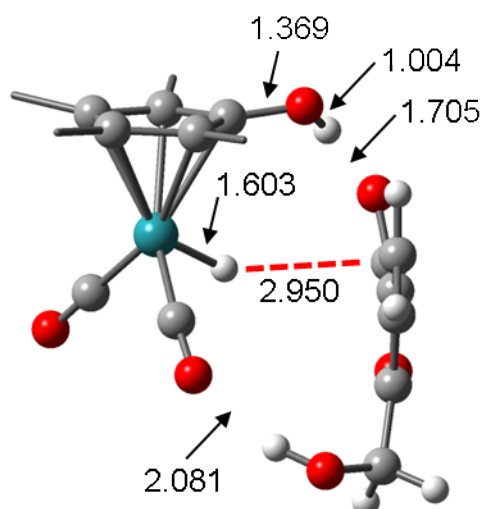
B3LYP/LanL2DZ - toluene PCM

E = -1971.781780

H° = -1971.187171

G° = -1971.301493

**Ground state found by IRC in the backward direction**

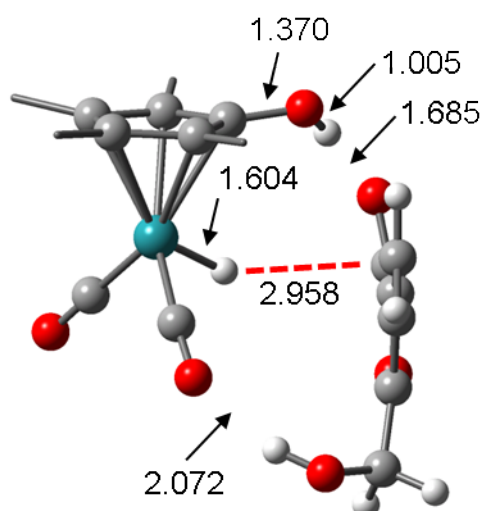


B3LYP/LanL2DZ - gas phase

E = -1971.775296

H° = -1971.182702

G° = -1971.299538



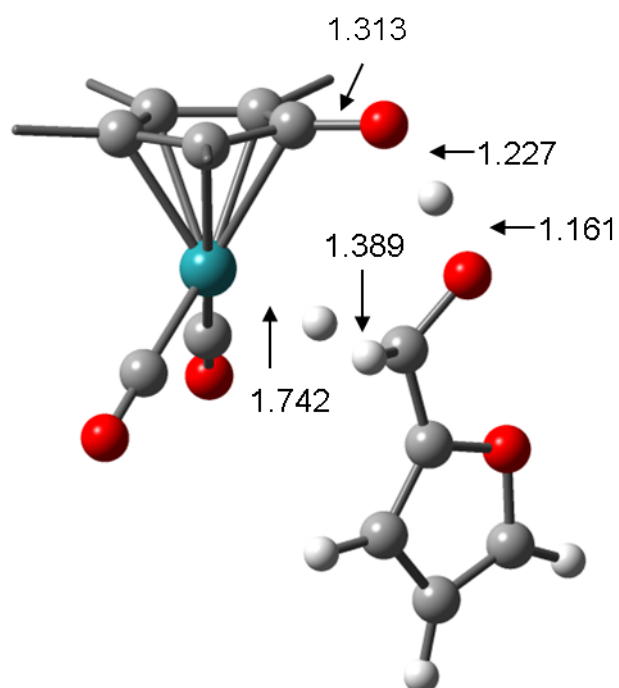
B3LYP/LanL2DZ - toluene PCM

E = -1971.784207

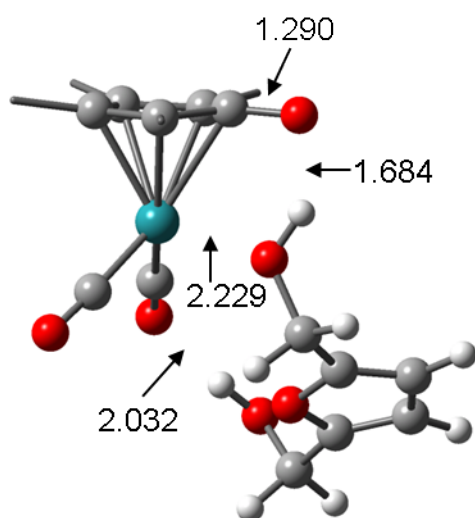
H° = -1971.191993

G° = -1971.309708

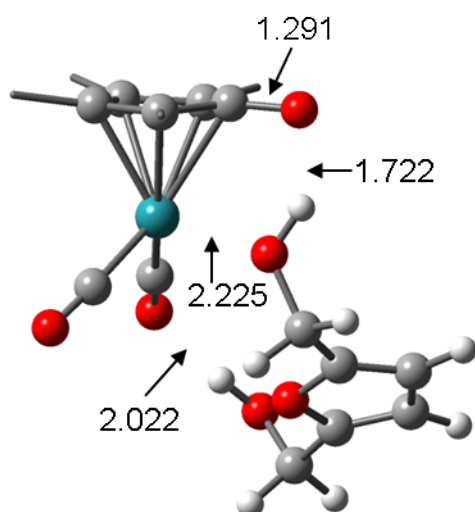
**Transition state for the hydrogenation of furfural.**



### Intermediate C

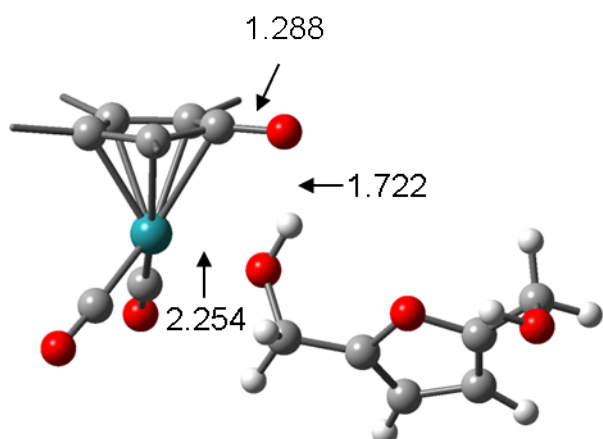


B3LYP/LanL2DZ - gas phase  
E = -1971.791488  
H° = -1971.195401  
G° = -1971.312309



B3LYP/LanL2DZ - toluene PCM  
E = -1971.802795  
H° = -1971.206857  
G° = -1971.323886

### Intermediate C'

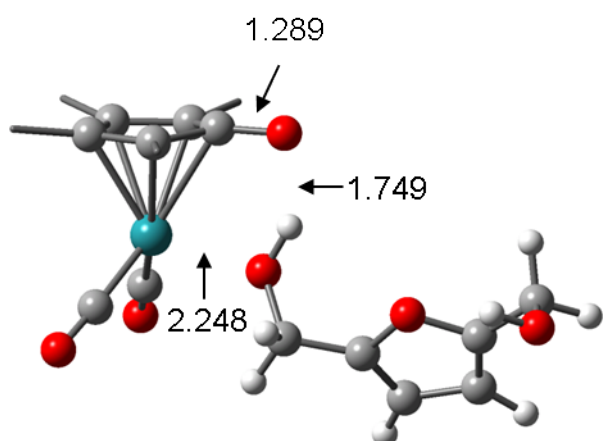


B3LYP/LanL2DZ - gas phase

E = -1971.787918

H° = -1971.191704

G° = -1971.311324



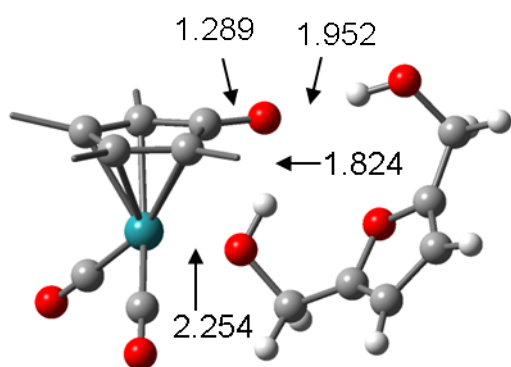
B3LYP/LanL2DZ - toluene PCM

E = -1971.799644

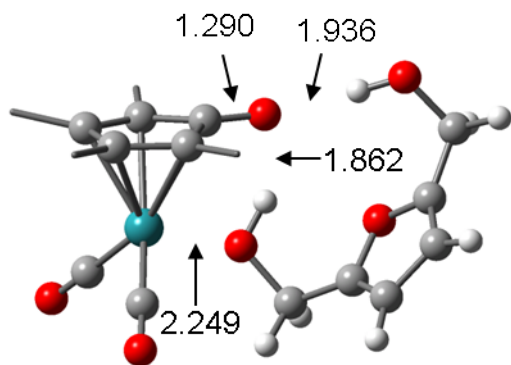
H° = -1971.203656

G° = -1971.323861

### Intermediate D

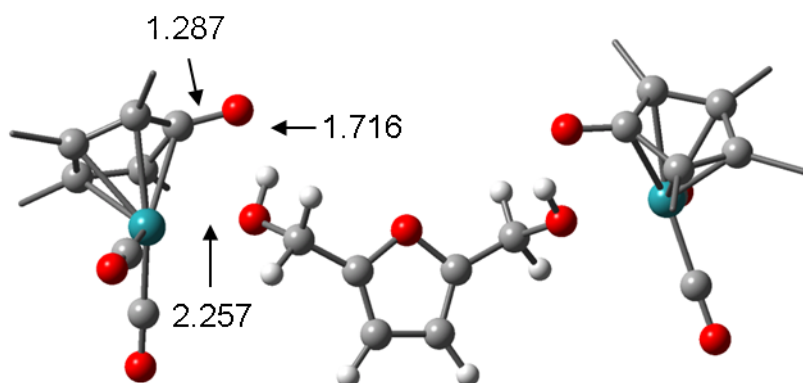


B3LYP/LanL2DZ - gas phase  
E = -1971.790665  
H° = -1971.194150  
G° = -1971.309141



B3LYP/LanL2DZ - toluene PCM  
E = -1971.800798  
H° = -1971.204523  
G° = -1971.319240

### Dimer B<sub>2</sub>-BHMF



B3LYP/LanL2DZ - gas phase

E = -3484.552017

H° = -3483.505227

G° = -3483.697854

B3LYP/LanL2DZ - gas phase

counterpoise BHMF + 2 B

BSSE = 0.014581

E = -3484.537022

H° = -3483.489858

G° = -3483.683023

B3LYP/LanL2DZ - gas phase

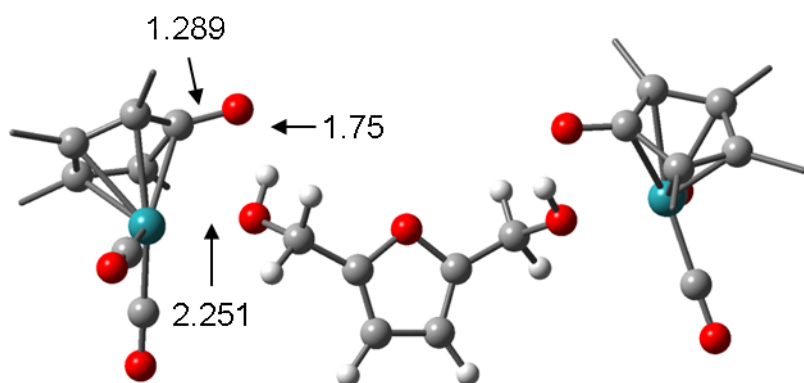
counterpoise C + B

BSSE = 0.007272

E = -3484.544551

H° = -3483.497614

G° = -3483.690831



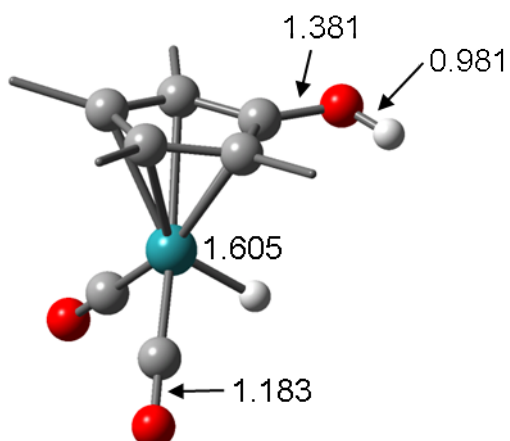
B3LYP/LanL2DZ - toluene PCM

E = -3484.568796

H° = -3483.522324

G° = -3483.714842

## Catalyst A

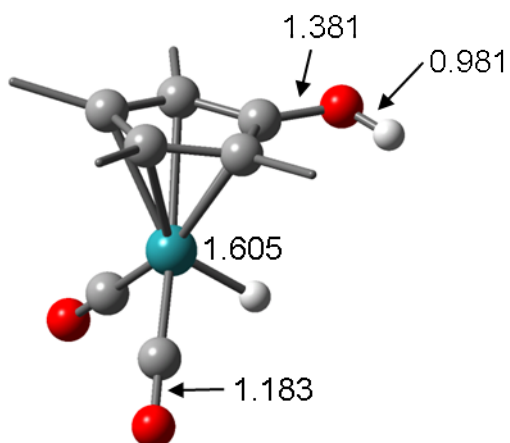


B3LYP/LanL2DZ - gasphase

E = -1513.942887

H° = -1513.473822

G° = -1513.568382



B3LYP/LanL2DZ - toluene PCM

E = -1513.982887

H° = -1513.473823

G° = -1513.568386

**HMF** - B3LYP/LanL2DZ - toluene PCM

E = -457.819377

H° = -457.698110

G° = -457.741337

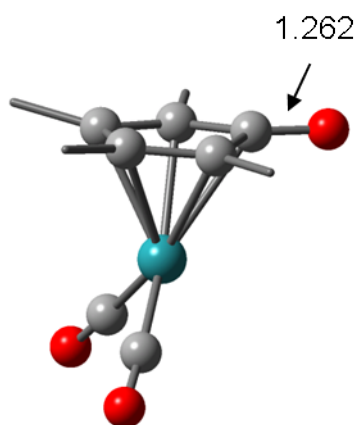
**HMF** + A B3LYP/LanL2DZ - toluene PCM

E = -1971.802264

H° = -1971.171933

G° = -1971.309723

## Catalyst B

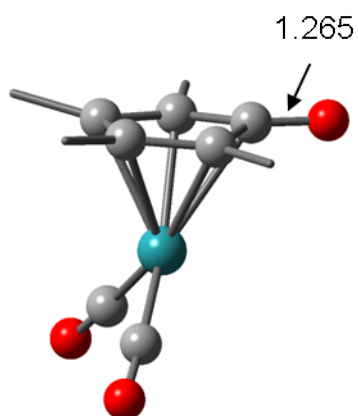


B3LYP/LanL2DZ - gas phase

E = -1512.728885

H° = -1512.280247

G° = -1512.374037



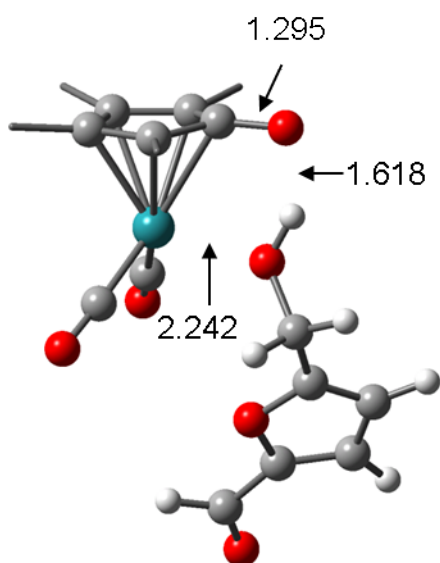
B3LYP/LanL2DZ - toluene PCM

E = -1512.737863

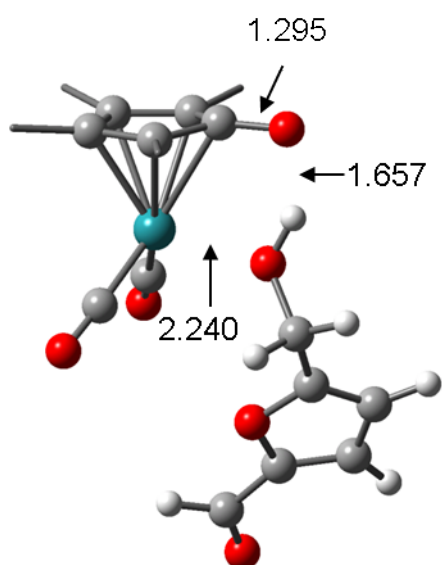
H° = -1512.289379

G° = -1512.382942

## Intermediate F



B3LYP/LanL2DZ - gas phase  
E = -1970.576502  
H° = -1970.005085  
G° = -1970.122125



B3LYP/LanL2DZ - toluene PCM  
E = -1970.588423  
H° = -1970.016943  
G° = -1970.134629

# Compound HMF-PCM

Method: opt freq b3lyp/lanl2dz srcf(solvent=toluene)

SCF Done: E(RB3LYP) = -457.819377346 A.U. after 1 cycles  
Lowest frequency = 48.6889

Zero-point correction= 0.111991  
(Hartree/Particle)  
Thermal correction to Energy= 0.120323  
Thermal correction to Enthalpy= 0.121268  
Thermal correction to Gibbs Free Energy= 0.078040  
Sum of electronic and zero-point Energies= -457.707386  
Sum of electronic and thermal Energies= -457.699054  
Sum of electronic and thermal Enthalpies= -457.698110  
Sum of electronic and thermal Free Energies= -457.741337

## Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 6                | 0              | -1.150850               | 0.002094  | 0.038984  |
| 2                | 6                | 0              | -0.927198               | 1.351200  | -0.196235 |
| 3                | 8                | 0              | 0.083421                | -0.624149 | 0.311787  |
| 4                | 6                | 0              | 0.484897                | 1.574962  | -0.074444 |
| 5                | 1                | 0              | -1.689823               | 2.079409  | -0.428816 |
| 6                | 6                | 0              | 1.071373                | 0.359190  | 0.233982  |
| 7                | 1                | 0              | 1.006720                | 2.511760  | -0.201194 |
| 8                | 6                | 0              | 2.479333                | -0.087419 | 0.465688  |
| 9                | 1                | 0              | 3.128003                | 0.786420  | 0.550799  |
| 10               | 1                | 0              | 2.544191                | -0.673261 | 1.393382  |
| 11               | 8                | 0              | 3.023619                | -0.858758 | -0.659792 |
| 12               | 1                | 0              | 2.534925                | -1.703913 | -0.757660 |
| 13               | 6                | 0              | -2.333792               | -0.841864 | 0.060951  |
| 14               | 8                | 0              | -3.498270               | -0.422659 | -0.153934 |
| 15               | 1                | 0              | -2.136755               | -1.904863 | 0.285436  |

# Compound BHMf-PCM

Method: opt freq b3lyp/lanl2dz srcf(solvent=toluene)

SCF Done: E(RB3LYP) = -459.029208402 A.U. after 1 cycles  
Lowest frequency = 47.7726

Zero-point correction= 0.135297  
(Hartree/Particle)  
Thermal correction to Energy= 0.144419  
Thermal correction to Enthalpy= 0.145363  
Thermal correction to Gibbs Free Energy= 0.100282  
Sum of electronic and zero-point Energies= -458.893912  
Sum of electronic and thermal Energies= -458.884789  
Sum of electronic and thermal Enthalpies= -458.883845  
Sum of electronic and thermal Free Energies= -458.928927

## Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 6                | 0              | -2.393541               | -0.362797 | -0.579214 |
| 2                | 1                | 0              | -2.244591               | -1.142570 | -1.339953 |
| 3                | 1                | 0              | -3.111085               | 0.368574  | -0.956670 |
| 4                | 8                | 0              | -3.040206               | -0.947022 | 0.608661  |
| 5                | 1                | 0              | -2.455085               | -1.628493 | 1.003469  |
| 6                | 6                | 0              | -1.102165               | 0.319818  | -0.274278 |
| 7                | 6                | 0              | -0.703000               | 1.632977  | -0.171606 |
| 8                | 8                | 0              | 0.000016                | -0.514887 | 0.000106  |
| 9                | 6                | 0              | 0.702955                | 1.633026  | 0.171525  |
| 10               | 1                | 0              | -1.332786               | 2.497798  | -0.320540 |
| 11               | 6                | 0              | 1.102200                | 0.319894  | 0.274234  |
| 12               | 1                | 0              | 1.332706                | 2.497890  | 0.320360  |
| 13               | 6                | 0              | 2.393629                | -0.362626 | 0.579165  |
| 14               | 1                | 0              | 3.111217                | 0.368868  | 0.956301  |
| 15               | 1                | 0              | 2.244810                | -1.142176 | 1.340160  |
| 16               | 8                | 0              | 3.040113                | -0.947195 | -0.608635 |
| 17               | 1                | 0              | 2.454947                | -1.628803 | -1.003139 |

# Catalyst B - PCM

Method: opt freq b3lyp/lanl2dz srcf(solvent=toluene)

SCF Done: E(RB3LYP) = -1512.73786326 A.U. after 1 cycles  
 Lowest frequency = 27.4578

Zero-point correction= 0.417925  
 (Hartree/Particle)  
 Thermal correction to Energy= 0.447540  
 Thermal correction to Enthalpy= 0.448484  
 Thermal correction to Gibbs Free Energy= 0.354921  
 Sum of electronic and zero-point Energies= -1512.319938  
 Sum of electronic and thermal Energies= -1512.290323  
 Sum of electronic and thermal Enthalpies= -1512.289379  
 Sum of electronic and thermal Free Energies= -1512.382942

## Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 44               | 0              | 0.001121                | -0.750949 | 1.402478  |
| 2                | 6                | 0              | -1.214390               | -0.890514 | -0.559682 |
| 3                | 6                | 0              | -0.730920               | 0.455394  | -0.398571 |
| 4                | 6                | 0              | 0.752757                | 0.427000  | -0.426826 |
| 5                | 6                | 0              | 1.185704                | -0.929102 | -0.608635 |
| 6                | 6                | 0              | -0.036823               | -1.777520 | -0.830983 |
| 7                | 6                | 0              | -1.359681               | -0.451430 | 2.688236  |
| 8                | 8                | 0              | -2.228552               | -0.228386 | 3.459293  |
| 9                | 8                | 0              | -0.071085               | -3.023984 | -1.041843 |
| 10               | 6                | 0              | 1.355591                | -0.316031 | 2.664615  |
| 11               | 8                | 0              | 2.208216                | 0.020570  | 3.411702  |
| 12               | 6                | 0              | 2.569018                | -1.445539 | -0.745472 |
| 13               | 6                | 0              | 2.834700                | -2.502599 | -1.652245 |
| 14               | 6                | 0              | 3.650735                | -0.908533 | -0.002586 |
| 15               | 6                | 0              | 4.141448                | -2.995418 | -1.817355 |
| 16               | 1                | 0              | 2.019062                | -2.940093 | -2.216224 |
| 17               | 6                | 0              | 4.953453                | -1.402550 | -0.167952 |
| 18               | 1                | 0              | 3.477711                | -0.106859 | 0.708244  |
| 19               | 6                | 0              | 5.207517                | -2.449014 | -1.078042 |
| 20               | 1                | 0              | 4.323564                | -3.806018 | -2.518632 |
| 21               | 1                | 0              | 5.766592                | -0.977071 | 0.414760  |
| 22               | 1                | 0              | 6.216878                | -2.833263 | -1.203456 |
| 23               | 6                | 0              | 1.610178                | 1.642744  | -0.438190 |
| 24               | 6                | 0              | 2.508513                | 1.838930  | -1.513543 |
| 25               | 6                | 0              | 1.514862                | 2.633644  | 0.563947  |
| 26               | 6                | 0              | 3.293248                | 3.002965  | -1.583613 |
| 27               | 1                | 0              | 2.590600                | 1.085423  | -2.292062 |
| 28               | 6                | 0              | 2.305104                | 3.793331  | 0.497446  |
| 29               | 1                | 0              | 0.829507                | 2.492318  | 1.395037  |
| 30               | 6                | 0              | 3.196705                | 3.983861  | -0.576798 |
| 31               | 1                | 0              | 3.977908                | 3.140704  | -2.416588 |
| 32               | 1                | 0              | 2.225522                | 4.543772  | 1.279627  |
| 33               | 1                | 0              | 3.807991                | 4.881407  | -0.627771 |
| 34               | 6                | 0              | -2.607885               | -1.355088 | -0.770338 |
| 35               | 6                | 0              | -3.062761               | -2.546468 | -0.157966 |
| 36               | 6                | 0              | -3.483830               | -0.664488 | -1.641969 |
| 37               | 6                | 0              | -4.363096               | -3.024757 | -0.392929 |
| 38               | 1                | 0              | -2.396222               | -3.099533 | 0.497745  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 39 | 6 | 0 | -4.784198 | -1.143853 | -1.878728 |
| 40 | 1 | 0 | -3.149120 | 0.239446  | -2.141979 |
| 41 | 6 | 0 | -5.231596 | -2.323923 | -1.252885 |
| 42 | 1 | 0 | -4.695348 | -3.940658 | 0.089391  |
| 43 | 1 | 0 | -5.442996 | -0.600718 | -2.552015 |
| 44 | 1 | 0 | -6.237510 | -2.693751 | -1.436257 |
| 45 | 6 | 0 | -1.549298 | 1.698300  | -0.438455 |
| 46 | 6 | 0 | -1.261647 | 2.680650  | -1.416591 |
| 47 | 6 | 0 | -2.653164 | 1.900209  | 0.420567  |
| 48 | 6 | 0 | -2.056906 | 3.834520  | -1.529502 |
| 49 | 1 | 0 | -0.424985 | 2.540563  | -2.094213 |
| 50 | 6 | 0 | -3.442000 | 3.057336  | 0.314281  |
| 51 | 1 | 0 | -2.900325 | 1.157227  | 1.170992  |
| 52 | 6 | 0 | -3.148188 | 4.030426  | -0.661582 |
| 53 | 1 | 0 | -1.822481 | 4.576301  | -2.288641 |
| 54 | 1 | 0 | -4.283350 | 3.196745  | 0.987974  |
| 55 | 1 | 0 | -3.759878 | 4.925315  | -0.744117 |

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# Intermediate F - PCM

Method: opt freq b3lyp/lanl2dz srcf(solvent=toluene)

SCF Done: E(RB3LYP) = -1970.58842338 A.U. after 1 cycles  
 Lowest frequency = 5.1177

Zero-point correction= 0.531654  
 (Hartree/Particle)  
 Thermal correction to Energy= 0.570537  
 Thermal correction to Enthalpy= 0.571481  
 Thermal correction to Gibbs Free Energy= 0.453794  
 Sum of electronic and zero-point Energies= -1970.056770  
 Sum of electronic and thermal Energies= -1970.017887  
 Sum of electronic and thermal Enthalpies= -1970.016943  
 Sum of electronic and thermal Free Energies= -1970.134629

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 44               | 0              | 0.357623                | -0.305360 | -0.299098 |
| 2                | 6                | 0              | -0.457703               | 1.154223  | 1.291499  |
| 3                | 6                | 0              | -1.370890               | 1.160536  | 0.160984  |
| 4                | 6                | 0              | -1.928801               | -0.186359 | 0.017628  |
| 5                | 6                | 0              | -1.381991               | -1.027509 | 1.070415  |
| 6                | 6                | 0              | -0.544708               | -0.171534 | 1.948177  |
| 7                | 6                | 0              | 1.499322                | 0.806934  | -1.324177 |
| 8                | 8                | 0              | 2.191432                | 1.524635  | -1.959446 |
| 9                | 8                | 0              | 0.179713                | -0.571049 | 2.945122  |
| 10               | 6                | 0              | 0.387348                | -1.631379 | -1.655711 |
| 11               | 8                | 0              | 0.347413                | -2.450800 | -2.507509 |
| 12               | 6                | 0              | -1.727707               | -2.436611 | 1.386577  |
| 13               | 6                | 0              | -1.828470               | -2.841600 | 2.740941  |
| 14               | 6                | 0              | -1.979255               | -3.398315 | 0.377406  |
| 15               | 6                | 0              | -2.179751               | -4.162732 | 3.072238  |
| 16               | 1                | 0              | -1.622313               | -2.123803 | 3.527222  |
| 17               | 6                | 0              | -2.330879               | -4.716351 | 0.708983  |
| 18               | 1                | 0              | -1.901200               | -3.120501 | -0.668949 |
| 19               | 6                | 0              | -2.434058               | -5.107327 | 2.059453  |
| 20               | 1                | 0              | -2.253365               | -4.451834 | 4.117932  |
| 21               | 1                | 0              | -2.520344               | -5.436295 | -0.083428 |
| 22               | 1                | 0              | -2.704907               | -6.128776 | 2.315598  |
| 23               | 6                | 0              | -3.024744               | -0.554322 | -0.921906 |
| 24               | 6                | 0              | -4.236853               | -1.058695 | -0.394510 |
| 25               | 6                | 0              | -2.915725               | -0.358780 | -2.316156 |
| 26               | 6                | 0              | -5.316033               | -1.357494 | -1.244543 |
| 27               | 1                | 0              | -4.335109               | -1.213997 | 0.676495  |
| 28               | 6                | 0              | -3.993211               | -0.660336 | -3.166181 |
| 29               | 1                | 0              | -1.988145               | 0.025530  | -2.731939 |
| 30               | 6                | 0              | -5.198566               | -1.160105 | -2.634464 |
| 31               | 1                | 0              | -6.241031               | -1.744028 | -0.824046 |
| 32               | 1                | 0              | -3.891815               | -0.507635 | -4.237606 |
| 33               | 1                | 0              | -6.031360               | -1.394687 | -3.292787 |
| 34               | 6                | 0              | 0.199891                | 2.327749  | 1.925602  |
| 35               | 6                | 0              | 1.590019                | 2.343602  | 2.176429  |
| 36               | 6                | 0              | -0.580292               | 3.429054  | 2.350434  |
| 37               | 6                | 0              | 2.188495                | 3.435576  | 2.829918  |
| 38               | 1                | 0              | 2.200851                | 1.504779  | 1.854354  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 39 | 6 | 0 | 0.017235  | 4.521936  | 3.002894  |
| 40 | 1 | 0 | -1.652862 | 3.428386  | 2.174893  |
| 41 | 6 | 0 | 1.404964  | 4.530042  | 3.245332  |
| 42 | 1 | 0 | 3.260449  | 3.433122  | 3.012412  |
| 43 | 1 | 0 | -0.596810 | 5.360826  | 3.321669  |
| 44 | 1 | 0 | 1.867651  | 5.374975  | 3.749767  |
| 45 | 6 | 0 | -1.837281 | 2.374700  | -0.565606 |
| 46 | 6 | 0 | -3.225153 | 2.641477  | -0.647875 |
| 47 | 6 | 0 | -0.934865 | 3.317436  | -1.107901 |
| 48 | 6 | 0 | -3.695609 | 3.814695  | -1.263622 |
| 49 | 1 | 0 | -3.937022 | 1.938736  | -0.225838 |
| 50 | 6 | 0 | -1.404214 | 4.486798  | -1.728444 |
| 51 | 1 | 0 | 0.133997  | 3.141941  | -1.046982 |
| 52 | 6 | 0 | -2.787526 | 4.741269  | -1.810642 |
| 53 | 1 | 0 | -4.765165 | 4.002096  | -1.315916 |
| 54 | 1 | 0 | -0.693014 | 5.195978  | -2.143932 |
| 55 | 1 | 0 | -3.150566 | 5.646347  | -2.291231 |
| 56 | 6 | 0 | 2.908942  | -2.177136 | 0.927946  |
| 57 | 1 | 0 | 3.144336  | -2.601669 | 1.908676  |
| 58 | 1 | 0 | 2.478443  | -2.956955 | 0.291244  |
| 59 | 8 | 0 | 1.893085  | -1.122064 | 1.113219  |
| 60 | 1 | 0 | 1.472443  | -1.079351 | 2.041708  |
| 61 | 6 | 0 | 4.143555  | -1.613758 | 0.314446  |
| 62 | 6 | 0 | 5.362280  | -1.204439 | 0.830177  |
| 63 | 8 | 0 | 4.134589  | -1.417181 | -1.065272 |
| 64 | 6 | 0 | 6.152329  | -0.729044 | -0.268733 |
| 65 | 1 | 0 | 5.651716  | -1.239469 | 1.870169  |
| 66 | 6 | 0 | 5.381827  | -0.865695 | -1.414810 |
| 67 | 1 | 0 | 7.157004  | -0.335136 | -0.233642 |
| 68 | 6 | 0 | 5.599013  | -0.570626 | -2.823288 |
| 69 | 8 | 0 | 6.668157  | -0.096108 | -3.278422 |
| 70 | 1 | 0 | 4.742004  | -0.797501 | -3.480527 |

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# Catalyst A - PCM

Method: opt freq b3lyp/lanl2dz srcf(solvent=toluene)

SCF Done: E(RB3LYP) = -1513.94288715 A.U. after 1 cycles  
 Lowest frequency = 27.0953

Zero-point correction= 0.437982  
 (Hartree/Particle)  
 Thermal correction to Energy= 0.468120  
 Thermal correction to Enthalpy= 0.469064  
 Thermal correction to Gibbs Free Energy= 0.374502  
 Sum of electronic and zero-point Energies= -1513.504905  
 Sum of electronic and thermal Energies= -1513.474767  
 Sum of electronic and thermal Enthalpies= -1513.473823  
 Sum of electronic and thermal Free Energies= -1513.568386

## Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 44               | 0              | -0.012187               | -0.704742 | 1.484449  |
| 2                | 6                | 0              | -1.191182               | -0.857362 | -0.559111 |
| 3                | 6                | 0              | -0.703960               | 0.529791  | -0.431027 |
| 4                | 6                | 0              | 0.736156                | 0.500116  | -0.411843 |
| 5                | 6                | 0              | 1.169471                | -0.902246 | -0.528938 |
| 6                | 6                | 0              | -0.028743               | -1.689249 | -0.684573 |
| 7                | 6                | 0              | -1.414052               | -0.528648 | 2.724230  |
| 8                | 8                | 0              | -2.307885               | -0.443897 | 3.494362  |
| 9                | 6                | 0              | 1.269464                | -0.248614 | 2.779092  |
| 10               | 8                | 0              | 2.091725                | 0.023116  | 3.585706  |
| 11               | 6                | 0              | 2.540403                | -1.431059 | -0.764082 |
| 12               | 6                | 0              | 2.785157                | -2.203446 | -1.928278 |
| 13               | 6                | 0              | 3.617348                | -1.180921 | 0.116272  |
| 14               | 6                | 0              | 4.067874                | -2.717319 | -2.196040 |
| 15               | 1                | 0              | 1.982170                | -2.370579 | -2.643375 |
| 16               | 6                | 0              | 4.899621                | -1.683802 | -0.157154 |
| 17               | 1                | 0              | 3.451028                | -0.596291 | 1.015675  |
| 18               | 6                | 0              | 5.130790                | -2.459520 | -1.310789 |
| 19               | 1                | 0              | 4.235967                | -3.306750 | -3.094318 |
| 20               | 1                | 0              | 5.714595                | -1.477534 | 0.532087  |
| 21               | 1                | 0              | 6.122930                | -2.853849 | -1.515940 |
| 22               | 6                | 0              | 1.646263                | 1.678183  | -0.404648 |
| 23               | 6                | 0              | 2.627368                | 1.809095  | -1.415513 |
| 24               | 6                | 0              | 1.533614                | 2.700041  | 0.565528  |
| 25               | 6                | 0              | 3.471061                | 2.933577  | -1.455902 |
| 26               | 1                | 0              | 2.727259                | 1.035586  | -2.172093 |
| 27               | 6                | 0              | 2.374422                | 3.823977  | 0.524901  |
| 28               | 1                | 0              | 0.790548                | 2.607793  | 1.353239  |
| 29               | 6                | 0              | 3.348143                | 3.946501  | -0.486074 |
| 30               | 1                | 0              | 4.219721                | 3.016542  | -2.240201 |
| 31               | 1                | 0              | 2.273811                | 4.598119  | 1.281580  |
| 32               | 1                | 0              | 4.001848                | 4.814986  | -0.514949 |
| 33               | 6                | 0              | -2.580162               | -1.321598 | -0.814538 |
| 34               | 6                | 0              | -3.088237               | -2.474463 | -0.173138 |
| 35               | 6                | 0              | -3.396137               | -0.653940 | -1.757280 |
| 36               | 6                | 0              | -4.381004               | -2.942762 | -0.458452 |
| 37               | 1                | 0              | -2.466836               | -2.998674 | 0.547350  |
| 38               | 6                | 0              | -4.691401               | -1.121673 | -2.041288 |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 39 | 1 | 0 | -3.019420 | 0.224769  | -2.272222 |
| 40 | 6 | 0 | -5.190517 | -2.266820 | -1.392677 |
| 41 | 1 | 0 | -4.756478 | -3.828741 | 0.047841  |
| 42 | 1 | 0 | -5.305793 | -0.594601 | -2.767436 |
| 43 | 1 | 0 | -6.193076 | -2.627155 | -1.611098 |
| 44 | 6 | 0 | -1.554070 | 1.751245  | -0.493316 |
| 45 | 6 | 0 | -1.265098 | 2.748994  | -1.454778 |
| 46 | 6 | 0 | -2.680625 | 1.927647  | 0.342054  |
| 47 | 6 | 0 | -2.073903 | 3.893233  | -1.570740 |
| 48 | 1 | 0 | -0.409053 | 2.627167  | -2.112316 |
| 49 | 6 | 0 | -3.490782 | 3.069269  | 0.225712  |
| 50 | 1 | 0 | -2.925107 | 1.174841  | 1.085270  |
| 51 | 6 | 0 | -3.190904 | 4.059498  | -0.730180 |
| 52 | 1 | 0 | -1.832375 | 4.649503  | -2.313853 |
| 53 | 1 | 0 | -4.351122 | 3.185242  | 0.880188  |
| 54 | 1 | 0 | -3.816545 | 4.944555  | -0.817790 |
| 55 | 1 | 0 | 0.124200  | -2.191136 | 2.075601  |
| 56 | 8 | 0 | -0.106005 | -3.038590 | -0.971188 |
| 57 | 1 | 0 | 0.767005  | -3.476540 | -0.874610 |

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# **Intermediate A/HMF (pre-TS) - PCM**

Method: opt freq b3lyp/lanl2dz srcf(solvent=toluene)

SCF Done: E(RB3LYP) = -1971.78420712 A.U. after 1 cycles  
 Lowest frequency = 15.0309

Zero-point correction= 0.551550  
 (Hartree/Particle)  
 Thermal correction to Energy= 0.591270  
 Thermal correction to Enthalpy= 0.592214  
 Thermal correction to Gibbs Free Energy= 0.474499  
 Sum of electronic and zero-point Energies= -1971.232657  
 Sum of electronic and thermal Energies= -1971.192938  
 Sum of electronic and thermal Enthalpies= -1971.191993  
 Sum of electronic and thermal Free Energies= -1971.309708

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 44               | 0              | -0.030087               | -0.308950 | -1.014547 |
| 2                | 1                | 0              | -0.882012               | -1.664718 | -1.108744 |
| 3                | 6                | 0              | 1.341497                | -1.043392 | 0.723612  |
| 4                | 6                | 0              | 1.947474                | 0.181278  | 0.195144  |
| 5                | 6                | 0              | 1.032278                | 1.277704  | 0.414023  |
| 6                | 6                | 0              | -0.145294               | 0.748485  | 1.115276  |
| 7                | 6                | 0              | 0.083225                | -0.658366 | 1.337876  |
| 8                | 6                | 0              | -1.515062               | 0.458962  | -1.859053 |
| 9                | 8                | 0              | -2.498750               | 0.887810  | -2.371200 |
| 10               | 8                | 0              | -0.724296               | -1.429782 | 2.132243  |
| 11               | 1                | 0              | -0.962720               | -2.346892 | 1.796225  |
| 12               | 6                | 0              | -2.734133               | -3.512251 | 0.272484  |
| 13               | 8                | 0              | -1.791392               | -3.644591 | 1.110874  |
| 14               | 1                | 0              | -2.923963               | -4.304178 | -0.466920 |
| 15               | 6                | 0              | 0.697773                | -0.840588 | -2.663931 |
| 16               | 8                | 0              | 1.147041                | -1.195993 | -3.700461 |
| 17               | 6                | 0              | 2.025804                | -2.343997 | 0.963489  |
| 18               | 6                | 0              | 1.525199                | -3.565126 | 0.463221  |
| 19               | 1                | 0              | 0.639648                | -3.563526 | -0.165282 |
| 20               | 6                | 0              | 2.167251                | -4.780718 | 0.763259  |
| 21               | 1                | 0              | 1.765797                | -5.711598 | 0.370646  |
| 22               | 6                | 0              | 3.324062                | -4.792774 | 1.565617  |
| 23               | 1                | 0              | 3.822154                | -5.731741 | 1.795074  |
| 24               | 6                | 0              | 3.832601                | -3.578629 | 2.069253  |
| 25               | 1                | 0              | 4.724834                | -3.577040 | 2.690778  |
| 26               | 6                | 0              | 3.187367                | -2.365882 | 1.773017  |
| 27               | 1                | 0              | 3.581518                | -1.433911 | 2.169842  |
| 28               | 6                | 0              | 3.343195                | 0.275712  | -0.315745 |
| 29               | 6                | 0              | 3.874518                | -0.680787 | -1.211823 |
| 30               | 1                | 0              | 3.244275                | -1.484512 | -1.579929 |
| 31               | 6                | 0              | 5.211667                | -0.607833 | -1.634313 |
| 32               | 1                | 0              | 5.596465                | -1.351454 | -2.327642 |
| 33               | 6                | 0              | 6.050705                | 0.421711  | -1.163659 |
| 34               | 1                | 0              | 7.085711                | 0.479093  | -1.491631 |
| 35               | 6                | 0              | 5.536555                | 1.373590  | -0.262675 |
| 36               | 1                | 0              | 6.174402                | 2.169783  | 0.113325  |
| 37               | 6                | 0              | 4.196736                | 1.300664  | 0.158153  |
| 38               | 1                | 0              | 3.818125                | 2.036251  | 0.860603  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 39 | 6 | 0 | 1.304810  | 2.715745  | 0.139956  |
| 40 | 6 | 0 | 1.327895  | 3.636689  | 1.214220  |
| 41 | 1 | 0 | 1.115945  | 3.290493  | 2.222590  |
| 42 | 6 | 0 | 1.625118  | 4.993006  | 0.991151  |
| 43 | 1 | 0 | 1.636513  | 5.686689  | 1.828389  |
| 44 | 6 | 0 | 1.907485  | 5.451745  | -0.310634 |
| 45 | 1 | 0 | 2.136822  | 6.500293  | -0.484296 |
| 46 | 6 | 0 | 1.886538  | 4.541908  | -1.386487 |
| 47 | 1 | 0 | 2.100088  | 4.885840  | -2.395513 |
| 48 | 6 | 0 | 1.585060  | 3.187256  | -1.162370 |
| 49 | 1 | 0 | 1.561024  | 2.491481  | -1.997192 |
| 50 | 6 | 0 | -1.272574 | 1.536686  | 1.678707  |
| 51 | 6 | 0 | -1.875857 | 2.595140  | 0.959246  |
| 52 | 1 | 0 | -1.536023 | 2.826833  | -0.045812 |
| 53 | 6 | 0 | -2.913795 | 3.351537  | 1.526893  |
| 54 | 1 | 0 | -3.364723 | 4.158539  | 0.954860  |
| 55 | 6 | 0 | -3.371090 | 3.066572  | 2.829473  |
| 56 | 1 | 0 | -4.173830 | 3.653431  | 3.269386  |
| 57 | 6 | 0 | -2.777204 | 2.016120  | 3.555911  |
| 58 | 1 | 0 | -3.118595 | 1.788762  | 4.563052  |
| 59 | 6 | 0 | -1.738700 | 1.256505  | 2.986449  |
| 60 | 1 | 0 | -1.290559 | 0.444690  | 3.549393  |
| 61 | 6 | 0 | -3.585950 | -2.356972 | 0.188408  |
| 62 | 6 | 0 | -3.781606 | -1.232037 | 0.985412  |
| 63 | 8 | 0 | -4.380068 | -2.233481 | -0.975068 |
| 64 | 6 | 0 | -4.711100 | -0.387821 | 0.306427  |
| 65 | 1 | 0 | -3.290123 | -1.038843 | 1.926751  |
| 66 | 6 | 0 | -5.042992 | -1.015335 | -0.887629 |
| 67 | 1 | 0 | -5.070730 | 0.576209  | 0.631259  |
| 68 | 6 | 0 | -5.839200 | -0.577234 | -2.083295 |
| 69 | 1 | 0 | -5.654137 | -1.277531 | -2.909712 |
| 70 | 1 | 0 | -6.911630 | -0.570582 | -1.866079 |
| 71 | 8 | 0 | -5.527895 | 0.799399  | -2.457097 |
| 72 | 1 | 0 | -4.559109 | 0.911398  | -2.588100 |

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# **Transition state for hydrogenation A/HMF - PCM**

Method: opt(ts,noeigen,modred,calcf) freq b3lyp/lanl2dz  
srcf(solvent=toluene)

SCF Done: E(RB3LYP) = -1971.76803649 A.U. after 21 cycles  
Lowest frequency = -837.0226

Zero-point correction= 0.547604  
(Hartree/Particle)  
Thermal correction to Energy= 0.586104  
Thermal correction to Enthalpy= 0.587048  
Thermal correction to Gibbs Free Energy= 0.472966  
Sum of electronic and zero-point Energies= -1971.220433  
Sum of electronic and thermal Energies= -1971.181932  
Sum of electronic and thermal Enthalpies= -1971.180988  
Sum of electronic and thermal Free Energies= -1971.295070

## Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 44               | 0              | 0.075828                | -0.472255 | -0.913820 |
| 2                | 1                | 0              | -0.955787               | -1.832470 | -0.878788 |
| 3                | 6                | 0              | 1.643279                | -0.904553 | 0.767240  |
| 4                | 6                | 0              | 1.874590                | 0.448097  | 0.261731  |
| 5                | 6                | 0              | 0.689514                | 1.247908  | 0.540847  |
| 6                | 6                | 0              | -0.288918               | 0.402792  | 1.218587  |
| 7                | 6                | 0              | 0.339626                | -0.904675 | 1.426470  |
| 8                | 6                | 0              | -1.233855               | 0.378694  | -1.967873 |
| 9                | 8                | 0              | -2.088159               | 0.906886  | -2.596560 |
| 10               | 8                | 0              | -0.209434               | -1.924618 | 2.076164  |
| 11               | 1                | 0              | -0.716047               | -2.761130 | 1.480571  |
| 12               | 6                | 0              | -1.782329               | -2.984302 | -0.447378 |
| 13               | 8                | 0              | -1.217355               | -3.524176 | 0.620926  |
| 14               | 1                | 0              | -1.593827               | -3.481730 | -1.406780 |
| 15               | 6                | 0              | 0.917063                | -1.220091 | -2.435925 |
| 16               | 8                | 0              | 1.457501                | -1.695154 | -3.373063 |
| 17               | 6                | 0              | 2.628647                | -2.011113 | 0.893093  |
| 18               | 6                | 0              | 2.266178                | -3.348623 | 0.612199  |
| 19               | 1                | 0              | 1.265474                | -3.577496 | 0.257095  |
| 20               | 6                | 0              | 3.188377                | -4.392899 | 0.795418  |
| 21               | 1                | 0              | 2.891087                | -5.415058 | 0.574109  |
| 22               | 6                | 0              | 4.487616                | -4.121269 | 1.265622  |
| 23               | 1                | 0              | 5.200475                | -4.930524 | 1.405579  |
| 24               | 6                | 0              | 4.854392                | -2.793803 | 1.557701  |
| 25               | 1                | 0              | 5.852161                | -2.572064 | 1.928980  |
| 26               | 6                | 0              | 3.932832                | -1.748531 | 1.375702  |
| 27               | 1                | 0              | 4.225386                | -0.731192 | 1.617983  |
| 28               | 6                | 0              | 3.168977                | 0.975151  | -0.254428 |
| 29               | 6                | 0              | 3.877556                | 0.338352  | -1.298237 |
| 30               | 1                | 0              | 3.459939                | -0.540416 | -1.778768 |
| 31               | 6                | 0              | 5.122280                | 0.828340  | -1.725440 |
| 32               | 1                | 0              | 5.648007                | 0.324921  | -2.532836 |
| 33               | 6                | 0              | 5.687556                | 1.963535  | -1.112373 |
| 34               | 1                | 0              | 6.650945                | 2.343201  | -1.444021 |
| 35               | 6                | 0              | 4.994906                | 2.601696  | -0.066294 |
| 36               | 1                | 0              | 5.421609                | 3.476919  | 0.417473  |
| 37               | 6                | 0              | 3.747324                | 2.112413  | 0.358499  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 38 | 1 | 0 | 3.225293  | 2.611528  | 1.169463  |
| 39 | 6 | 0 | 0.577098  | 2.717084  | 0.326607  |
| 40 | 6 | 0 | 0.298398  | 3.554693  | 1.432048  |
| 41 | 1 | 0 | 0.126562  | 3.114892  | 2.410776  |
| 42 | 6 | 0 | 0.241814  | 4.950433  | 1.275260  |
| 43 | 1 | 0 | 0.025044  | 5.579890  | 2.134874  |
| 44 | 6 | 0 | 0.460547  | 5.530711  | 0.010958  |
| 45 | 1 | 0 | 0.412891  | 6.610040  | -0.111584 |
| 46 | 6 | 0 | 0.737080  | 4.702869  | -1.094726 |
| 47 | 1 | 0 | 0.904333  | 5.140905  | -2.075540 |
| 48 | 6 | 0 | 0.795857  | 3.308218  | -0.937330 |
| 49 | 1 | 0 | 1.008306  | 2.673770  | -1.793828 |
| 50 | 6 | 0 | -1.591566 | 0.807803  | 1.807076  |
| 51 | 6 | 0 | -2.469366 | 1.700693  | 1.147736  |
| 52 | 1 | 0 | -2.213906 | 2.089390  | 0.166827  |
| 53 | 6 | 0 | -3.677447 | 2.093730  | 1.743263  |
| 54 | 1 | 0 | -4.339218 | 2.773345  | 1.212764  |
| 55 | 6 | 0 | -4.034771 | 1.603300  | 3.015023  |
| 56 | 1 | 0 | -4.969547 | 1.910809  | 3.478193  |
| 57 | 6 | 0 | -3.172421 | 0.710090  | 3.678874  |
| 58 | 1 | 0 | -3.437526 | 0.323593  | 4.660358  |
| 59 | 6 | 0 | -1.963414 | 0.311717  | 3.080724  |
| 60 | 1 | 0 | -1.309972 | -0.388102 | 3.590440  |
| 61 | 6 | 0 | -3.093049 | -2.336145 | -0.317724 |
| 62 | 6 | 0 | -3.926539 | -2.083652 | 0.756375  |
| 63 | 8 | 0 | -3.657161 | -1.794505 | -1.482136 |
| 64 | 6 | 0 | -5.058791 | -1.356870 | 0.245569  |
| 65 | 1 | 0 | -3.743703 | -2.382445 | 1.777085  |
| 66 | 6 | 0 | -4.868015 | -1.184922 | -1.111655 |
| 67 | 1 | 0 | -5.896855 | -0.985207 | 0.815932  |
| 68 | 6 | 0 | -5.599468 | -0.451690 | -2.190130 |
| 69 | 1 | 0 | -5.526509 | -1.009844 | -3.134876 |
| 70 | 1 | 0 | -6.652420 | -0.349163 | -1.917080 |
| 71 | 8 | 0 | -5.129103 | 0.925416  | -2.369840 |
| 72 | 1 | 0 | -4.178294 | 0.940976  | -2.618922 |

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**Intermediate B/BHMF (post-TS) - PCM**

Method: opt freq b3lyp/lanl2dz srcf(solvent=toluene)

SCF Done: E(RB3LYP) = -1971.78177983 A.U. after 2 cycles  
Lowest frequency = 26.2124

Zero-point correction= 0.554381  
(Hartree/Particle)  
Thermal correction to Energy= 0.593664  
Thermal correction to Enthalpy= 0.594608  
Thermal correction to Gibbs Free Energy= 0.480287  
Sum of electronic and zero-point Energies= -1971.227399  
Sum of electronic and thermal Energies= -1971.188116  
Sum of electronic and thermal Enthalpies= -1971.187171  
Sum of electronic and thermal Free Energies= -1971.301493

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 44               | 0              | 0.139296                | -0.440064 | -0.923142 |
| 2                | 1                | 0              | -1.098779               | -2.120120 | -0.902832 |
| 3                | 6                | 0              | 1.657458                | -0.939319 | 0.757168  |
| 4                | 6                | 0              | 1.886905                | 0.410983  | 0.293099  |
| 5                | 6                | 0              | 0.678074                | 1.212833  | 0.579915  |
| 6                | 6                | 0              | -0.292980               | 0.366780  | 1.228625  |
| 7                | 6                | 0              | 0.346628                | -0.961359 | 1.463775  |
| 8                | 6                | 0              | -1.148372               | 0.482142  | -1.967793 |
| 9                | 8                | 0              | -1.955307               | 1.099750  | -2.574071 |
| 10               | 8                | 0              | -0.189908               | -1.973906 | 2.029941  |
| 11               | 1                | 0              | -1.057513               | -3.139041 | 1.213832  |
| 12               | 6                | 0              | -1.832305               | -2.965063 | -0.654262 |
| 13               | 8                | 0              | -1.394792               | -3.721948 | 0.468574  |
| 14               | 1                | 0              | -1.796480               | -3.618906 | -1.533176 |
| 15               | 6                | 0              | 1.026838                | -1.083684 | -2.476359 |
| 16               | 8                | 0              | 1.610191                | -1.462272 | -3.430857 |
| 17               | 6                | 0              | 2.631175                | -2.057321 | 0.857554  |
| 18               | 6                | 0              | 2.241557                | -3.382325 | 0.550985  |
| 19               | 1                | 0              | 1.232406                | -3.585398 | 0.204641  |
| 20               | 6                | 0              | 3.146776                | -4.447334 | 0.699070  |
| 21               | 1                | 0              | 2.829596                | -5.458568 | 0.456938  |
| 22               | 6                | 0              | 4.455392                | -4.209088 | 1.163163  |
| 23               | 1                | 0              | 5.154921                | -5.033632 | 1.277405  |
| 24               | 6                | 0              | 4.848021                | -2.895289 | 1.485113  |
| 25               | 1                | 0              | 5.852121                | -2.700901 | 1.854265  |
| 26               | 6                | 0              | 3.943700                | -1.829285 | 1.336308  |
| 27               | 1                | 0              | 4.256572                | -0.824018 | 1.602109  |
| 28               | 6                | 0              | 3.182262                | 0.974159  | -0.176877 |
| 29               | 6                | 0              | 3.927418                | 0.381647  | -1.221463 |
| 30               | 1                | 0              | 3.538109                | -0.486509 | -1.742121 |
| 31               | 6                | 0              | 5.175858                | 0.903512  | -1.597024 |
| 32               | 1                | 0              | 5.730521                | 0.436922  | -2.406802 |
| 33               | 6                | 0              | 5.708927                | 2.022554  | -0.926889 |
| 34               | 1                | 0              | 6.675853                | 2.425519  | -1.217415 |
| 35               | 6                | 0              | 4.980171                | 2.614243  | 0.122520  |
| 36               | 1                | 0              | 5.382753                | 3.475117  | 0.649990  |
| 37               | 6                | 0              | 3.726344                | 2.097083  | 0.492426  |
| 38               | 1                | 0              | 3.177267                | 2.560860  | 1.306161  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 39 | 6 | 0 | 0.574902  | 2.684451  | 0.387589  |
| 40 | 6 | 0 | 0.259565  | 3.500143  | 1.499761  |
| 41 | 1 | 0 | 0.057025  | 3.043421  | 2.464491  |
| 42 | 6 | 0 | 0.210475  | 4.898579  | 1.366695  |
| 43 | 1 | 0 | -0.031970 | 5.512765  | 2.230125  |
| 44 | 6 | 0 | 0.468702  | 5.500872  | 0.119718  |
| 45 | 1 | 0 | 0.424831  | 6.582049  | 0.015390  |
| 46 | 6 | 0 | 0.780503  | 4.693499  | -0.992276 |
| 47 | 1 | 0 | 0.977977  | 5.149547  | -1.958866 |
| 48 | 6 | 0 | 0.837077  | 3.296349  | -0.858135 |
| 49 | 1 | 0 | 1.076963  | 2.678179  | -1.718860 |
| 50 | 6 | 0 | -1.615783 | 0.744421  | 1.785720  |
| 51 | 6 | 0 | -2.496230 | 1.623715  | 1.110079  |
| 52 | 1 | 0 | -2.224292 | 2.029455  | 0.141064  |
| 53 | 6 | 0 | -3.730401 | 1.980244  | 1.673524  |
| 54 | 1 | 0 | -4.395500 | 2.644377  | 1.128649  |
| 55 | 6 | 0 | -4.110638 | 1.468968  | 2.930681  |
| 56 | 1 | 0 | -5.067567 | 1.744899  | 3.367140  |
| 57 | 6 | 0 | -3.245893 | 0.591148  | 3.611720  |
| 58 | 1 | 0 | -3.530722 | 0.186392  | 4.579895  |
| 59 | 6 | 0 | -2.012415 | 0.226265  | 3.043574  |
| 60 | 1 | 0 | -1.359709 | -0.462601 | 3.568395  |
| 61 | 6 | 0 | -3.189963 | -2.360035 | -0.473103 |
| 62 | 6 | 0 | -4.143399 | -2.422764 | 0.515053  |
| 63 | 8 | 0 | -3.636487 | -1.520056 | -1.503945 |
| 64 | 6 | 0 | -5.242885 | -1.578373 | 0.093462  |
| 65 | 1 | 0 | -4.072333 | -2.997376 | 1.425481  |
| 66 | 6 | 0 | -4.913112 | -1.041152 | -1.129104 |
| 67 | 1 | 0 | -6.155484 | -1.390296 | 0.639932  |
| 68 | 6 | 0 | -5.568536 | -0.091047 | -2.075537 |
| 69 | 1 | 0 | -5.536237 | -0.489496 | -3.100151 |
| 70 | 1 | 0 | -6.611869 | 0.046906  | -1.783048 |
| 71 | 8 | 0 | -4.985842 | 1.260025  | -2.052290 |
| 72 | 1 | 0 | -4.051241 | 1.233634  | -2.354041 |

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# Intermediate C - PCM

Method: opt freq b3lyp/lanl2dz srcf(solvent=toluene)

SCF Done: E(RB3LYP) = -1971.80279532 A.U. after 1 cycles  
 Lowest frequency = 5.7619

Zero-point correction= 0.555768  
 (Hartree/Particle)  
 Thermal correction to Energy= 0.594994  
 Thermal correction to Enthalpy= 0.595938  
 Thermal correction to Gibbs Free Energy= 0.478909  
 Sum of electronic and zero-point Energies= -1971.247027  
 Sum of electronic and thermal Energies= -1971.207802  
 Sum of electronic and thermal Enthalpies= -1971.206857  
 Sum of electronic and thermal Free Energies= -1971.323886

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 44               | 0              | 0.118104                | -0.485141 | -0.558258 |
| 2                | 6                | 0              | -0.023798               | 0.818544  | 1.341280  |
| 3                | 6                | 0              | -1.022250               | 1.281771  | 0.389265  |
| 4                | 6                | 0              | -1.976501               | 0.193449  | 0.161706  |
| 5                | 6                | 0              | -1.579579               | -0.944499 | 0.970043  |
| 6                | 6                | 0              | -0.426237               | -0.526540 | 1.816024  |
| 7                | 6                | 0              | 1.451689                | 0.422997  | -1.536407 |
| 8                | 8                | 0              | 2.292252                | 1.020999  | -2.120717 |
| 9                | 8                | 0              | 0.243639                | -1.280387 | 2.621928  |
| 10               | 6                | 0              | -0.419759               | -1.451580 | -2.102431 |
| 11               | 8                | 0              | -0.805245               | -2.026422 | -3.061422 |
| 12               | 6                | 0              | -2.281702               | -2.242677 | 1.129108  |
| 13               | 6                | 0              | -2.337231               | -2.852015 | 2.407240  |
| 14               | 6                | 0              | -2.916453               | -2.897118 | 0.044682  |
| 15               | 6                | 0              | -3.016541               | -4.069402 | 2.594748  |
| 16               | 1                | 0              | -1.839332               | -2.375691 | 3.244486  |
| 17               | 6                | 0              | -3.593954               | -4.112068 | 0.232733  |
| 18               | 1                | 0              | -2.882246               | -2.460552 | -0.948657 |
| 19               | 6                | 0              | -3.649530               | -4.705975 | 1.510093  |
| 20               | 1                | 0              | -3.048739               | -4.518605 | 3.584526  |
| 21               | 1                | 0              | -4.073279               | -4.595635 | -0.614990 |
| 22               | 1                | 0              | -4.173180               | -5.647938 | 1.654606  |
| 23               | 6                | 0              | -3.235368               | 0.319950  | -0.624063 |
| 24               | 6                | 0              | -4.470305               | 0.057321  | 0.014217  |
| 25               | 6                | 0              | -3.240417               | 0.751876  | -1.968554 |
| 26               | 6                | 0              | -5.682249               | 0.225008  | -0.678398 |
| 27               | 1                | 0              | -4.482442               | -0.274759 | 1.048754  |
| 28               | 6                | 0              | -4.451270               | 0.915973  | -2.662098 |
| 29               | 1                | 0              | -2.297457               | 0.953141  | -2.469709 |
| 30               | 6                | 0              | -5.678045               | 0.654088  | -2.020132 |
| 31               | 1                | 0              | -6.622891               | 0.018873  | -0.173883 |
| 32               | 1                | 0              | -4.437061               | 1.244897  | -3.698040 |
| 33               | 1                | 0              | -6.614776               | 0.779317  | -2.557558 |
| 34               | 6                | 0              | 1.020840                | 1.632250  | 2.017825  |
| 35               | 6                | 0              | 2.362191                | 1.193700  | 2.083461  |
| 36               | 6                | 0              | 0.667887                | 2.836124  | 2.672535  |
| 37               | 6                | 0              | 3.329536                | 1.942423  | 2.776773  |
| 38               | 1                | 0              | 2.649652                | 0.270907  | 1.587496  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 39 | 6 | 0 | 1.634125  | 3.585677  | 3.366449  |
| 40 | 1 | 0 | -0.361435 | 3.183108  | 2.644081  |
| 41 | 6 | 0 | 2.970174  | 3.142454  | 3.421065  |
| 42 | 1 | 0 | 4.358400  | 1.592647  | 2.810319  |
| 43 | 1 | 0 | 1.345066  | 4.508962  | 3.862941  |
| 44 | 1 | 0 | 3.718345  | 3.722565  | 3.955977  |
| 45 | 6 | 0 | -1.195894 | 2.689581  | -0.068622 |
| 46 | 6 | 0 | -2.434523 | 3.338630  | 0.152321  |
| 47 | 6 | 0 | -0.139780 | 3.429352  | -0.646202 |
| 48 | 6 | 0 | -2.612429 | 4.687401  | -0.202675 |
| 49 | 1 | 0 | -3.256313 | 2.794105  | 0.607504  |
| 50 | 6 | 0 | -0.317990 | 4.775401  | -1.006222 |
| 51 | 1 | 0 | 0.823014  | 2.958992  | -0.815128 |
| 52 | 6 | 0 | -1.555934 | 5.411503  | -0.787502 |
| 53 | 1 | 0 | -3.571093 | 5.167979  | -0.024186 |
| 54 | 1 | 0 | 0.506651  | 5.324750  | -1.452950 |
| 55 | 1 | 0 | -1.693641 | 6.453182  | -1.066629 |
| 56 | 6 | 0 | 2.356475  | -3.030269 | -0.086210 |
| 57 | 1 | 0 | 2.377894  | -3.865647 | 0.620819  |
| 58 | 1 | 0 | 1.953436  | -3.377359 | -1.041405 |
| 59 | 8 | 0 | 1.389737  | -2.029872 | 0.415515  |
| 60 | 1 | 0 | 1.212984  | -2.028295 | 1.410617  |
| 61 | 6 | 0 | 3.721184  | -2.463003 | -0.253421 |
| 62 | 6 | 0 | 4.875826  | -2.502147 | 0.498303  |
| 63 | 8 | 0 | 3.949040  | -1.684450 | -1.400767 |
| 64 | 6 | 0 | 5.866794  | -1.710774 | -0.195596 |
| 65 | 1 | 0 | 5.005529  | -3.028134 | 1.433210  |
| 66 | 6 | 0 | 5.276831  | -1.222908 | -1.341830 |
| 67 | 1 | 0 | 6.883395  | -1.525865 | 0.118913  |
| 68 | 6 | 0 | 5.724620  | -0.329254 | -2.453364 |
| 69 | 1 | 0 | 6.815893  | -0.279553 | -2.458096 |
| 70 | 1 | 0 | 5.381970  | -0.729729 | -3.418482 |
| 71 | 8 | 0 | 5.283160  | 1.061820  | -2.298975 |
| 72 | 1 | 0 | 4.301823  | 1.115565  | -2.322519 |

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# Intermediate C' - PCM

Method: opt freq b3lyp/lanl2dz srcf(solvent=toluene)

SCF Done: E(RB3LYP) = -1971.79964367 A.U. after 1 cycles  
 Lowest frequency = 6.4959

Zero-point correction= 0.555253  
 (Hartree/Particle)  
 Thermal correction to Energy= 0.595044  
 Thermal correction to Enthalpy= 0.595988  
 Thermal correction to Gibbs Free Energy= 0.475782  
 Sum of electronic and zero-point Energies= -1971.244391  
 Sum of electronic and thermal Energies= -1971.204600  
 Sum of electronic and thermal Enthalpies= -1971.203656  
 Sum of electronic and thermal Free Energies= -1971.323861

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 44               | 0              | -0.197837               | -0.069389 | 1.063736  |
| 2                | 6                | 0              | -0.669055               | -1.203084 | -0.890001 |
| 3                | 6                | 0              | -1.902754               | -0.615016 | -0.394569 |
| 4                | 6                | 0              | -1.744477               | 0.841426  | -0.387877 |
| 5                | 6                | 0              | -0.419814               | 1.164807  | -0.891986 |
| 6                | 6                | 0              | 0.223352                | -0.101945 | -1.333673 |
| 7                | 6                | 0              | -0.398425               | -1.428936 | 2.369135  |
| 8                | 8                | 0              | -0.540297               | -2.292455 | 3.165168  |
| 9                | 8                | 0              | 1.424765                | -0.236070 | -1.782079 |
| 10               | 6                | 0              | -0.251482               | 1.273756  | 2.402299  |
| 11               | 8                | 0              | -0.333918               | 2.131198  | 3.213921  |
| 12               | 6                | 0              | 0.154432                | 2.509827  | -1.150613 |
| 13               | 6                | 0              | 0.963972                | 2.714142  | -2.295886 |
| 14               | 6                | 0              | -0.090079               | 3.613198  | -0.295790 |
| 15               | 6                | 0              | 1.499328                | 3.983326  | -2.580959 |
| 16               | 1                | 0              | 1.178739                | 1.877222  | -2.950992 |
| 17               | 6                | 0              | 0.444211                | 4.879401  | -0.581695 |
| 18               | 1                | 0              | -0.697940               | 3.487016  | 0.594689  |
| 19               | 6                | 0              | 1.241892                | 5.073369  | -1.727735 |
| 20               | 1                | 0              | 2.116546                | 4.118064  | -3.466043 |
| 21               | 1                | 0              | 0.241713                | 5.710833  | 0.089067  |
| 22               | 1                | 0              | 1.656738                | 6.054077  | -1.947902 |
| 23               | 6                | 0              | -2.839263               | 1.811053  | -0.105280 |
| 24               | 6                | 0              | -3.205248               | 2.739867  | -1.107712 |
| 25               | 6                | 0              | -3.564959               | 1.792723  | 1.105846  |
| 26               | 6                | 0              | -4.275020               | 3.628528  | -0.901981 |
| 27               | 1                | 0              | -2.656506               | 2.764813  | -2.045231 |
| 28               | 6                | 0              | -4.631799               | 2.683336  | 1.313255  |
| 29               | 1                | 0              | -3.290808               | 1.084205  | 1.882780  |
| 30               | 6                | 0              | -4.992477               | 3.604882  | 0.310200  |
| 31               | 1                | 0              | -4.544151               | 4.336091  | -1.682205 |
| 32               | 1                | 0              | -5.177973               | 2.658417  | 2.252766  |
| 33               | 1                | 0              | -5.817301               | 4.294525  | 0.471599  |
| 34               | 6                | 0              | -0.424142               | -2.626160 | -1.244396 |
| 35               | 6                | 0              | 0.748678                | -3.292885 | -0.822544 |
| 36               | 6                | 0              | -1.336541               | -3.318631 | -2.075484 |
| 37               | 6                | 0              | 0.998657                | -4.620612 | -1.212127 |
| 38               | 1                | 0              | 1.461265                | -2.774253 | -0.187528 |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 39 | 6 | 0 | -1.087833 | -4.646824 | -2.464372 |
| 40 | 1 | 0 | -2.236450 | -2.817987 | -2.421992 |
| 41 | 6 | 0 | 0.080854  | -5.304589 | -2.033401 |
| 42 | 1 | 0 | 1.905305  | -5.118409 | -0.876604 |
| 43 | 1 | 0 | -1.800986 | -5.163752 | -3.102090 |
| 44 | 1 | 0 | 0.273874  | -6.331652 | -2.334090 |
| 45 | 6 | 0 | -3.182891 | -1.343424 | -0.166578 |
| 46 | 6 | 0 | -4.349186 | -0.919886 | -0.848141 |
| 47 | 6 | 0 | -3.258252 | -2.495450 | 0.648101  |
| 48 | 6 | 0 | -5.558113 | -1.624497 | -0.710311 |
| 49 | 1 | 0 | -4.312191 | -0.045815 | -1.490976 |
| 50 | 6 | 0 | -4.466806 | -3.196856 | 0.791030  |
| 51 | 1 | 0 | -2.375253 | -2.848123 | 1.170099  |
| 52 | 6 | 0 | -5.623888 | -2.764366 | 0.113417  |
| 53 | 1 | 0 | -6.442481 | -1.283220 | -1.242486 |
| 54 | 1 | 0 | -4.503696 | -4.077845 | 1.426610  |
| 55 | 1 | 0 | -6.559184 | -3.307371 | 0.224601  |
| 56 | 6 | 0 | 3.091492  | 0.366815  | 1.584887  |
| 57 | 1 | 0 | 3.087092  | 1.437278  | 1.345365  |
| 58 | 1 | 0 | 2.806102  | 0.220213  | 2.627396  |
| 59 | 8 | 0 | 2.022344  | -0.294196 | 0.789239  |
| 60 | 1 | 0 | 2.188227  | -0.260871 | -0.208080 |
| 61 | 6 | 0 | 4.424137  | -0.238821 | 1.333485  |
| 62 | 6 | 0 | 5.196295  | -1.167835 | 1.996040  |
| 63 | 8 | 0 | 5.095465  | 0.164804  | 0.165052  |
| 64 | 6 | 0 | 6.403870  | -1.352398 | 1.223499  |
| 65 | 1 | 0 | 4.937366  | -1.660926 | 2.921873  |
| 66 | 6 | 0 | 6.312823  | -0.536075 | 0.117355  |
| 67 | 1 | 0 | 7.230910  | -2.004899 | 1.461234  |
| 68 | 6 | 0 | 7.198217  | -0.248277 | -1.049940 |
| 69 | 1 | 0 | 8.029996  | -0.955606 | -1.057607 |
| 70 | 1 | 0 | 6.635588  | -0.346847 | -1.989044 |
| 71 | 8 | 0 | 7.828300  | 1.080199  | -0.983088 |
| 72 | 1 | 0 | 7.138796  | 1.776754  | -1.028301 |

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# Intermediate D - PCM

Method: opt freq b3lyp/lanl2dz srcf(solvent=toluene)

SCF Done: E(RB3LYP) = -1971.80079831 A.U. after 19 cycles  
 Lowest frequency = 21.1191

Zero-point correction= 0.556271  
 (Hartree/Particle)  
 Thermal correction to Energy= 0.595331  
 Thermal correction to Enthalpy= 0.596275  
 Thermal correction to Gibbs Free Energy= 0.481558  
 Sum of electronic and zero-point Energies= -1971.244527  
 Sum of electronic and thermal Energies= -1971.205467  
 Sum of electronic and thermal Enthalpies= -1971.204523  
 Sum of electronic and thermal Free Energies= -1971.319240

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 44               | 0              | -0.252234               | -0.159763 | 1.317563  |
| 2                | 6                | 0              | -0.877741               | -1.200879 | -0.637866 |
| 3                | 6                | 0              | -1.779462               | -0.086204 | -0.411001 |
| 4                | 6                | 0              | -0.987917               | 1.145598  | -0.417148 |
| 5                | 6                | 0              | 0.401413                | 0.803023  | -0.700915 |
| 6                | 6                | 0              | 0.464984                | -0.653086 | -0.972499 |
| 7                | 6                | 0              | -1.297677               | -1.049903 | 2.627060  |
| 8                | 8                | 0              | -1.970478               | -1.604305 | 3.425909  |
| 9                | 8                | 0              | 1.515622                | -1.362864 | -1.211283 |
| 10               | 6                | 0              | 0.183819                | 1.213531  | 2.552371  |
| 11               | 8                | 0              | 0.434054                | 2.101243  | 3.293388  |
| 12               | 6                | 0              | 1.520148                | 1.749033  | -0.947579 |
| 13               | 6                | 0              | 2.411499                | 1.508128  | -2.020414 |
| 14               | 6                | 0              | 1.708546                | 2.915187  | -0.166247 |
| 15               | 6                | 0              | 3.451012                | 2.410703  | -2.308698 |
| 16               | 1                | 0              | 2.297279                | 0.618388  | -2.628195 |
| 17               | 6                | 0              | 2.744321                | 3.817224  | -0.455245 |
| 18               | 1                | 0              | 1.044383                | 3.124784  | 0.666373  |
| 19               | 6                | 0              | 3.622270                | 3.571036  | -1.530815 |
| 20               | 1                | 0              | 4.123765                | 2.200779  | -3.136285 |
| 21               | 1                | 0              | 2.866462                | 4.707904  | 0.156499  |
| 22               | 1                | 0              | 4.424845                | 4.269936  | -1.754744 |
| 23               | 6                | 0              | -1.557824               | 2.521903  | -0.373064 |
| 24               | 6                | 0              | -1.338759               | 3.388961  | -1.469284 |
| 25               | 6                | 0              | -2.359796               | 2.968366  | 0.700014  |
| 26               | 6                | 0              | -1.912435               | 4.672378  | -1.490930 |
| 27               | 1                | 0              | -0.724031               | 3.059744  | -2.302515 |
| 28               | 6                | 0              | -2.931311               | 4.251963  | 0.679853  |
| 29               | 1                | 0              | -2.532689               | 2.311634  | 1.548445  |
| 30               | 6                | 0              | -2.710999               | 5.109839  | -0.416021 |
| 31               | 1                | 0              | -1.733841               | 5.326848  | -2.340408 |
| 32               | 1                | 0              | -3.543795               | 4.580931  | 1.515493  |
| 33               | 1                | 0              | -3.151336               | 6.103766  | -0.430355 |
| 34               | 6                | 0              | -1.252679               | -2.617926 | -0.896994 |
| 35               | 6                | 0              | -0.727834               | -3.677172 | -0.124411 |
| 36               | 6                | 0              | -2.105969               | -2.925877 | -1.982794 |
| 37               | 6                | 0              | -1.051293               | -5.012853 | -0.424783 |
| 38               | 1                | 0              | -0.071191               | -3.455777 | 0.712853  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 39 | 6 | 0 | -2.431132 | -4.260226 | -2.283459 |
| 40 | 1 | 0 | -2.511195 | -2.121982 | -2.592202 |
| 41 | 6 | 0 | -1.904591 | -5.309945 | -1.505179 |
| 42 | 1 | 0 | -0.638788 | -5.816455 | 0.180494  |
| 43 | 1 | 0 | -3.088589 | -4.479495 | -3.121336 |
| 44 | 1 | 0 | -2.154110 | -6.342383 | -1.738126 |
| 45 | 6 | 0 | -3.265913 | -0.172380 | -0.397220 |
| 46 | 6 | 0 | -4.019412 | 0.671013  | -1.248786 |
| 47 | 6 | 0 | -3.951607 | -1.137472 | 0.375502  |
| 48 | 6 | 0 | -5.419266 | 0.557839  | -1.316407 |
| 49 | 1 | 0 | -3.515295 | 1.408219  | -1.865419 |
| 50 | 6 | 0 | -5.350257 | -1.245905 | 0.314090  |
| 51 | 1 | 0 | -3.396599 | -1.806830 | 1.024246  |
| 52 | 6 | 0 | -6.092252 | -0.397813 | -0.531770 |
| 53 | 1 | 0 | -5.979329 | 1.213463  | -1.978394 |
| 54 | 1 | 0 | -5.857531 | -1.990962 | 0.921477  |
| 55 | 1 | 0 | -7.175046 | -0.482641 | -0.579881 |
| 56 | 6 | 0 | 2.746617  | -1.437130 | 2.421938  |
| 57 | 1 | 0 | 2.528820  | -0.724737 | 3.218132  |
| 58 | 1 | 0 | 2.863303  | -2.441361 | 2.845169  |
| 59 | 8 | 0 | 1.551273  | -1.488120 | 1.526219  |
| 60 | 1 | 0 | 1.822235  | -1.729932 | 0.589130  |
| 61 | 6 | 0 | 3.923244  | -1.013548 | 1.614125  |
| 62 | 6 | 0 | 4.791136  | 0.052849  | 1.571042  |
| 63 | 8 | 0 | 4.121748  | -1.811833 | 0.477105  |
| 64 | 6 | 0 | 5.548226  | -0.065153 | 0.339995  |
| 65 | 1 | 0 | 4.865636  | 0.846540  | 2.300118  |
| 66 | 6 | 0 | 5.098223  | -1.188864 | -0.317655 |
| 67 | 1 | 0 | 6.294309  | 0.625758  | -0.023412 |
| 68 | 6 | 0 | 5.245443  | -1.778706 | -1.683094 |
| 69 | 1 | 0 | 6.134041  | -1.374247 | -2.174125 |
| 70 | 1 | 0 | 5.341759  | -2.872056 | -1.613263 |
| 71 | 8 | 0 | 4.111135  | -1.436517 | -2.549376 |
| 72 | 1 | 0 | 3.249320  | -1.496306 | -2.062487 |

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# Intermediate B<sub>2</sub>-BHMF - PCM

Method: opt freq b3lyp/lanl2dz srcf(solvent=toluene)

SCF Done: E(RB3LYP) = -3484.56879640 A.U. after 1 cycles  
 Lowest frequency = 3.9278

Zero-point correction= 0.975049  
 (Hartree/Particle)  
 Thermal correction to Energy= 1.045528  
 Thermal correction to Enthalpy= 1.046472  
 Thermal correction to Gibbs Free Energy= 0.853955  
 Sum of electronic and zero-point Energies= -3483.593747  
 Sum of electronic and thermal Energies= -3483.523268  
 Sum of electronic and thermal Enthalpies= -3483.522324  
 Sum of electronic and thermal Free Energies= -3483.714842

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 44               | 0              | 5.393499                | 0.560905  | -0.945852 |
| 2                | 6                | 0              | 5.925594                | -1.456480 | 0.043269  |
| 3                | 6                | 0              | 7.064858                | -0.565126 | 0.180991  |
| 4                | 6                | 0              | 6.650631                | 0.585140  | 0.988583  |
| 5                | 6                | 0              | 5.259256                | 0.406634  | 1.369502  |
| 6                | 6                | 0              | 4.822395                | -0.932233 | 0.888984  |
| 7                | 6                | 0              | 5.927310                | 0.277196  | -2.741547 |
| 8                | 8                | 0              | 6.280108                | 0.079062  | -3.853452 |
| 9                | 8                | 0              | 3.636572                | -1.430274 | 0.977169  |
| 10               | 6                | 0              | 5.291519                | 2.433334  | -1.232749 |
| 11               | 8                | 0              | 5.270869                | 3.608101  | -1.373976 |
| 12               | 6                | 0              | 4.439680                | 1.266688  | 2.260574  |
| 13               | 6                | 0              | 3.520927                | 0.666065  | 3.156931  |
| 14               | 6                | 0              | 4.549432                | 2.679519  | 2.258059  |
| 15               | 6                | 0              | 2.746956                | 1.453512  | 4.028276  |
| 16               | 1                | 0              | 3.406429                | -0.412010 | 3.157684  |
| 17               | 6                | 0              | 3.777136                | 3.464052  | 3.128916  |
| 18               | 1                | 0              | 5.236616                | 3.170256  | 1.575885  |
| 19               | 6                | 0              | 2.870780                | 2.855799  | 4.020996  |
| 20               | 1                | 0              | 2.045743                | 0.971936  | 4.705484  |
| 21               | 1                | 0              | 3.877666                | 4.546467  | 3.107326  |
| 22               | 1                | 0              | 2.268639                | 3.464436  | 4.691221  |
| 23               | 6                | 0              | 7.573608                | 1.640189  | 1.492823  |
| 24               | 6                | 0              | 7.709924                | 1.819642  | 2.889469  |
| 25               | 6                | 0              | 8.361788                | 2.425603  | 0.623683  |
| 26               | 6                | 0              | 8.616406                | 2.763644  | 3.403016  |
| 27               | 1                | 0              | 7.110023                | 1.222082  | 3.570505  |
| 28               | 6                | 0              | 9.265818                | 3.371288  | 1.136548  |
| 29               | 1                | 0              | 8.262655                | 2.297124  | -0.450827 |
| 30               | 6                | 0              | 9.397906                | 3.544372  | 2.528659  |
| 31               | 1                | 0              | 8.708904                | 2.890384  | 4.478779  |
| 32               | 1                | 0              | 9.862060                | 3.970660  | 0.453269  |
| 33               | 1                | 0              | 10.095586               | 4.277662  | 2.925560  |
| 34               | 6                | 0              | 5.911847                | -2.827630 | -0.530774 |
| 35               | 6                | 0              | 4.901065                | -3.228232 | -1.433937 |
| 36               | 6                | 0              | 6.874331                | -3.781165 | -0.122161 |
| 37               | 6                | 0              | 4.858067                | -4.545327 | -1.924066 |
| 38               | 1                | 0              | 4.154654                | -2.507058 | -1.754477 |

|    |    |   |           |           |           |
|----|----|---|-----------|-----------|-----------|
| 39 | 6  | 0 | 6.833029  | -5.098018 | -0.613411 |
| 40 | 1  | 0 | 7.650533  | -3.495471 | 0.582463  |
| 41 | 6  | 0 | 5.824561  | -5.486173 | -1.517132 |
| 42 | 1  | 0 | 4.074095  | -4.835908 | -2.619302 |
| 43 | 1  | 0 | 7.581735  | -5.817279 | -0.289957 |
| 44 | 1  | 0 | 5.791529  | -6.504858 | -1.896305 |
| 45 | 6  | 0 | 8.466536  | -0.878558 | -0.217255 |
| 46 | 6  | 0 | 9.488582  | -0.830360 | 0.761138  |
| 47 | 6  | 0 | 8.801431  | -1.303926 | -1.522522 |
| 48 | 6  | 0 | 10.809332 | -1.189703 | 0.439408  |
| 49 | 1  | 0 | 9.252266  | -0.519718 | 1.774184  |
| 50 | 6  | 0 | 10.121694 | -1.657362 | -1.846512 |
| 51 | 1  | 0 | 8.034313  | -1.363329 | -2.287184 |
| 52 | 6  | 0 | 11.133245 | -1.601463 | -0.867398 |
| 53 | 1  | 0 | 11.579493 | -1.147050 | 1.205468  |
| 54 | 1  | 0 | 10.358265 | -1.977439 | -2.857982 |
| 55 | 1  | 0 | 12.154867 | -1.875735 | -1.118567 |
| 56 | 6  | 0 | 2.120206  | 0.857779  | -1.665912 |
| 57 | 1  | 0 | 1.829918  | 1.513517  | -0.836535 |
| 58 | 1  | 0 | 2.542649  | 1.452414  | -2.476736 |
| 59 | 8  | 0 | 3.231725  | -0.018901 | -1.212401 |
| 60 | 1  | 0 | 2.993133  | -0.596507 | -0.417100 |
| 61 | 6  | 0 | 0.958090  | 0.074259  | -2.161237 |
| 62 | 6  | 0 | 0.568445  | -0.375016 | -3.405781 |
| 63 | 8  | 0 | 0.023279  | -0.355168 | -1.205594 |
| 64 | 6  | 0 | -0.660799 | -1.110227 | -3.229968 |
| 65 | 1  | 0 | 1.094437  | -0.203890 | -4.333716 |
| 66 | 6  | 0 | -0.965109 | -1.082339 | -1.884911 |
| 67 | 1  | 0 | -1.243505 | -1.592081 | -4.001489 |
| 68 | 6  | 0 | -2.091908 | -1.615806 | -1.074298 |
| 69 | 1  | 0 | -2.609393 | -2.399275 | -1.628939 |
| 70 | 1  | 0 | -1.740775 | -2.016635 | -0.116312 |
| 71 | 8  | 0 | -3.114296 | -0.575217 | -0.799639 |
| 72 | 1  | 0 | -2.869405 | 0.046945  | -0.042254 |
| 73 | 44 | 0 | -5.361547 | -0.698681 | -0.843379 |
| 74 | 6  | 0 | -5.634579 | 1.445451  | -0.038631 |
| 75 | 6  | 0 | -6.925930 | 0.777092  | -0.012864 |
| 76 | 6  | 0 | -6.832892 | -0.361496 | 0.904702  |
| 77 | 6  | 0 | -5.490862 | -0.400790 | 1.458004  |
| 78 | 6  | 0 | -4.760167 | 0.804035  | 0.975309  |
| 79 | 6  | 0 | -5.580030 | -0.440614 | -2.707327 |
| 80 | 8  | 0 | -5.731932 | -0.252997 | -3.865645 |
| 81 | 8  | 0 | -3.524086 | 1.091047  | 1.201138  |
| 82 | 6  | 0 | -5.592509 | -2.571939 | -1.037677 |
| 83 | 8  | 0 | -5.784724 | -3.736185 | -1.129440 |
| 84 | 6  | 0 | -4.957164 | -1.321549 | 2.493139  |
| 85 | 6  | 0 | -4.092453 | -0.814776 | 3.494876  |
| 86 | 6  | 0 | -5.292279 | -2.697710 | 2.527252  |
| 87 | 6  | 0 | -3.590507 | -1.656541 | 4.503786  |
| 88 | 1  | 0 | -3.807752 | 0.231294  | 3.471697  |
| 89 | 6  | 0 | -4.791225 | -3.536700 | 3.535086  |
| 90 | 1  | 0 | -5.943524 | -3.117460 | 1.766642  |
| 91 | 6  | 0 | -3.937294 | -3.020784 | 4.531102  |
| 92 | 1  | 0 | -2.928067 | -1.247640 | 5.262969  |
| 93 | 1  | 0 | -5.062124 | -4.589674 | 3.540654  |
| 94 | 1  | 0 | -3.546363 | -3.671646 | 5.309465  |
| 95 | 6  | 0 | -7.985396 | -1.202894 | 1.332226  |
| 96 | 6  | 0 | -8.311274 | -1.268071 | 2.707361  |
| 97 | 6  | 0 | -8.799386 | -1.889441 | 0.404668  |
| 98 | 6  | 0 | -9.427625 | -2.003204 | 3.142936  |

|     |   |   |            |           |           |
|-----|---|---|------------|-----------|-----------|
| 99  | 1 | 0 | -7.694849  | -0.743961 | 3.432542  |
| 100 | 6 | 0 | -9.913263  | -2.626960 | 0.840082  |
| 101 | 1 | 0 | -8.556520  | -1.848038 | -0.653755 |
| 102 | 6 | 0 | -10.233057 | -2.686913 | 2.211077  |
| 103 | 1 | 0 | -9.664495  | -2.043855 | 4.203169  |
| 104 | 1 | 0 | -10.527101 | -3.152990 | 0.113387  |
| 105 | 1 | 0 | -11.093812 | -3.259374 | 2.547858  |
| 106 | 6 | 0 | -5.305183  | 2.747685  | -0.676468 |
| 107 | 6 | 0 | -4.153354  | 2.896525  | -1.481699 |
| 108 | 6 | 0 | -6.109256  | 3.884794  | -0.425372 |
| 109 | 6 | 0 | -3.817091  | 4.147352  | -2.028958 |
| 110 | 1 | 0 | -3.524062  | 2.033614  | -1.680864 |
| 111 | 6 | 0 | -5.774453  | 5.135757  | -0.973218 |
| 112 | 1 | 0 | -6.990967  | 3.793058  | 0.203003  |
| 113 | 6 | 0 | -4.626687  | 5.272670  | -1.778302 |
| 114 | 1 | 0 | -2.927906  | 4.243030  | -2.647457 |
| 115 | 1 | 0 | -6.404126  | 5.998772  | -0.770097 |
| 116 | 1 | 0 | -4.366745  | 6.240081  | -2.201495 |
| 117 | 6 | 0 | -8.187010  | 1.301427  | -0.610081 |
| 118 | 6 | 0 | -9.310759  | 1.510580  | 0.225240  |
| 119 | 6 | 0 | -8.278529  | 1.673824  | -1.970000 |
| 120 | 6 | 0 | -10.494915 | 2.067742  | -0.288846 |
| 121 | 1 | 0 | -9.259005  | 1.245765  | 1.276895  |
| 122 | 6 | 0 | -9.462895  | 2.225705  | -2.485836 |
| 123 | 1 | 0 | -7.427288  | 1.536759  | -2.628235 |
| 124 | 6 | 0 | -10.578214 | 2.424451  | -1.648287 |
| 125 | 1 | 0 | -11.346597 | 2.220633  | 0.369251  |
| 126 | 1 | 0 | -9.513105  | 2.501332  | -3.536068 |
| 127 | 1 | 0 | -11.494711 | 2.851350  | -2.048067 |

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# HMF – gas phase

Method: opt freq b3lyp/lanl2dz

SCF Done: E(RB3LYP) = -457.812636737 A.U. after 2 cycles  
Lowest frequency = 52.3727

Zero-point correction= 0.112020  
(Hartree/Particle)  
Thermal correction to Energy= 0.120326  
Thermal correction to Enthalpy= 0.121270  
Thermal correction to Gibbs Free Energy= 0.078142  
Sum of electronic and zero-point Energies= -457.700617  
Sum of electronic and thermal Energies= -457.692311  
Sum of electronic and thermal Enthalpies= -457.691367  
Sum of electronic and thermal Free Energies= -457.734494

## Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 6                | 0              | -1.147505               | 0.000173  | 0.039668  |
| 2                | 6                | 0              | -0.931245               | 1.348996  | -0.195993 |
| 3                | 8                | 0              | 0.089073                | -0.620629 | 0.309801  |
| 4                | 6                | 0              | 0.481227                | 1.579356  | -0.078030 |
| 5                | 1                | 0              | -1.701375               | 2.069887  | -0.426458 |
| 6                | 6                | 0              | 1.073700                | 0.367320  | 0.229578  |
| 7                | 1                | 0              | 0.998749                | 2.518178  | -0.208368 |
| 8                | 6                | 0              | 2.481776                | -0.079479 | 0.459745  |
| 9                | 1                | 0              | 3.135776                | 0.792783  | 0.522355  |
| 10               | 1                | 0              | 2.549618                | -0.645522 | 1.400589  |
| 11               | 8                | 0              | 3.017711                | -0.874514 | -0.650075 |
| 12               | 1                | 0              | 2.496319                | -1.698911 | -0.756402 |
| 13               | 6                | 0              | -2.333238               | -0.845678 | 0.062957  |
| 14               | 8                | 0              | -3.493359               | -0.423750 | -0.150614 |
| 15               | 1                | 0              | -2.134784               | -1.909390 | 0.287830  |

# BHMF – gas phase

Method: opt freq b3lyp/lanl2dz

SCF Done: E(RB3LYP) = -459.022476645 A.U. after 15 cycles  
Lowest frequency = 42.1046

Zero-point correction= 0.135387 (Hartree/Particle)  
Thermal correction to Energy= 0.144460  
Thermal correction to Enthalpy= 0.145404  
Thermal correction to Gibbs Free Energy= 0.100358  
Sum of electronic and zero-point Energies= -458.887089  
Sum of electronic and thermal Energies= -458.878017  
Sum of electronic and thermal Enthalpies= -458.877073  
Sum of electronic and thermal Free Energies= -458.922119

## Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 6                | 0              | -2.391395               | -0.364425 | -0.576472 |
| 2                | 1                | 0              | -2.240282               | -1.138203 | -1.344067 |
| 3                | 1                | 0              | -3.116555               | 0.363941  | -0.945911 |
| 4                | 8                | 0              | -3.028196               | -0.957334 | 0.608923  |
| 5                | 1                | 0              | -2.420747               | -1.608965 | 1.020130  |
| 6                | 6                | 0              | -1.101752               | 0.323734  | -0.275245 |
| 7                | 6                | 0              | -0.703279               | 1.636575  | -0.172147 |
| 8                | 8                | 0              | 0.000559                | -0.510374 | -0.000122 |
| 9                | 6                | 0              | 0.702523                | 1.637284  | 0.171077  |
| 10               | 1                | 0              | -1.333594               | 2.501214  | -0.319725 |
| 11               | 6                | 0              | 1.102234                | 0.324869  | 0.274603  |
| 12               | 1                | 0              | 1.332075                | 2.502560  | 0.318210  |
| 13               | 6                | 0              | 2.392247                | -0.362181 | 0.576460  |
| 14               | 1                | 0              | 3.117737                | 0.367639  | 0.942419  |
| 15               | 1                | 0              | 2.242222                | -1.133203 | 1.347044  |
| 16               | 8                | 0              | 3.027303                | -0.959667 | -0.607651 |
| 17               | 1                | 0              | 2.418342                | -1.611125 | -1.016948 |

### Catalyst B – gas phase

Method: opt freq b3lyp/lanl2dz

SCF Done: E(RB3LYP) = -1512.72888478 A.U. after 20 cycles  
Lowest frequency = 24.6157

|                                              |                             |
|----------------------------------------------|-----------------------------|
| Zero-point correction=                       | 0.418053 (Hartree/Particle) |
| Thermal correction to Energy=                | 0.447694                    |
| Thermal correction to Enthalpy=              | 0.448638                    |
| Thermal correction to Gibbs Free Energy=     | 0.354848                    |
| Sum of electronic and zero-point Energies=   | -1512.310832                |
| Sum of electronic and thermal Energies=      | -1512.281191                |
| Sum of electronic and thermal Enthalpies=    | -1512.280247                |
| Sum of electronic and thermal Free Energies= | -1512.374037                |

#### Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 44               | 0              | 0.002150                | -0.755792 | 1.386299  |
| 2                | 6                | 0              | -1.219367               | -0.885530 | -0.580641 |
| 3                | 6                | 0              | -0.739181               | 0.457407  | -0.407069 |
| 4                | 6                | 0              | 0.746235                | 0.434990  | -0.433426 |
| 5                | 6                | 0              | 1.186802                | -0.916683 | -0.622270 |
| 6                | 6                | 0              | -0.033197               | -1.769711 | -0.848572 |
| 7                | 6                | 0              | -1.349391               | -0.477851 | 2.687465  |
| 8                | 8                | 0              | -2.212546               | -0.264712 | 3.466768  |
| 9                | 8                | 0              | -0.062609               | -3.012766 | -1.063204 |
| 10               | 6                | 0              | 1.373200                | -0.380259 | 2.648960  |
| 11               | 8                | 0              | 2.240410                | -0.081956 | 3.394081  |
| 12               | 6                | 0              | 2.572204                | -1.428802 | -0.752010 |
| 13               | 6                | 0              | 2.839540                | -2.513880 | -1.624588 |
| 14               | 6                | 0              | 3.654453                | -0.862420 | -0.031557 |
| 15               | 6                | 0              | 4.148580                | -3.002094 | -1.781076 |
| 16               | 1                | 0              | 2.022142                | -2.979715 | -2.162485 |
| 17               | 6                | 0              | 4.958783                | -1.353103 | -0.188362 |
| 18               | 1                | 0              | 3.479878                | -0.041995 | 0.657158  |
| 19               | 6                | 0              | 5.214929                | -2.425234 | -1.066813 |
| 20               | 1                | 0              | 4.331628                | -3.835130 | -2.455448 |
| 21               | 1                | 0              | 5.771732                | -0.905602 | 0.378142  |
| 22               | 1                | 0              | 6.226215                | -2.807006 | -1.185455 |
| 23               | 6                | 0              | 1.592054                | 1.658657  | -0.439151 |
| 24               | 6                | 0              | 2.488515                | 1.870136  | -1.512930 |
| 25               | 6                | 0              | 1.488082                | 2.642331  | 0.568930  |
| 26               | 6                | 0              | 3.262580                | 3.041302  | -1.575607 |
| 27               | 1                | 0              | 2.580105                | 1.119411  | -2.293246 |
| 28               | 6                | 0              | 2.267529                | 3.809337  | 0.509573  |
| 29               | 1                | 0              | 0.804677                | 2.487473  | 1.399267  |
| 30               | 6                | 0              | 3.156938                | 4.014848  | -0.563082 |
| 31               | 1                | 0              | 3.947279                | 3.189756  | -2.406920 |
| 32               | 1                | 0              | 2.181350                | 4.553913  | 1.296840  |
| 33               | 1                | 0              | 3.760490                | 4.918124  | -0.608072 |
| 34               | 6                | 0              | -2.608760               | -1.363014 | -0.781360 |
| 35               | 6                | 0              | -3.005272               | -2.620311 | -0.264981 |
| 36               | 6                | 0              | -3.542260               | -0.620412 | -1.544074 |
| 37               | 6                | 0              | -4.303625               | -3.109101 | -0.483300 |
| 38               | 1                | 0              | -2.291539               | -3.217282 | 0.294306  |
| 39               | 6                | 0              | -4.839926               | -1.112390 | -1.764877 |
| 40               | 1                | 0              | -3.254574               | 0.332934  | -1.975563 |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 41 | 6 | 0 | -5.229152 | -2.356192 | -1.231764 |
| 42 | 1 | 0 | -4.589805 | -4.075714 | -0.076159 |
| 43 | 1 | 0 | -5.542316 | -0.528491 | -2.355069 |
| 44 | 1 | 0 | -6.233959 | -2.735328 | -1.402613 |
| 45 | 6 | 0 | -1.551385 | 1.705867  | -0.432696 |
| 46 | 6 | 0 | -1.294085 | 2.668090  | -1.438434 |
| 47 | 6 | 0 | -2.612520 | 1.937420  | 0.470640  |
| 48 | 6 | 0 | -2.079778 | 3.829291  | -1.538352 |
| 49 | 1 | 0 | -0.485361 | 2.506541  | -2.145212 |
| 50 | 6 | 0 | -3.392259 | 3.101762  | 0.376282  |
| 51 | 1 | 0 | -2.834173 | 1.211488  | 1.245259  |
| 52 | 6 | 0 | -3.130987 | 4.052956  | -0.629156 |
| 53 | 1 | 0 | -1.868451 | 4.555698  | -2.319066 |
| 54 | 1 | 0 | -4.201613 | 3.263382  | 1.083618  |
| 55 | 1 | 0 | -3.735997 | 4.953408  | -0.701826 |

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### Intermediate F - gas phase

Method: opt freq b3lyp/lanl2dz

SCF Done: E(RB3LYP) = -1970.57650176 A.U. after 1 cycles  
Lowest frequency = 7.1363

Zero-point correction= 0.531645 (Hartree/Particle)  
Thermal correction to Energy= 0.570473  
Thermal correction to Enthalpy= 0.571417  
Thermal correction to Gibbs Free Energy= 0.454377  
Sum of electronic and zero-point Energies= -1970.044857  
Sum of electronic and thermal Energies= -1970.006029  
Sum of electronic and thermal Enthalpies= -1970.005085  
Sum of electronic and thermal Free Energies= -1970.122125

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 44               | 0              | 0.353425                | -0.318347 | -0.297998 |
| 2                | 6                | 0              | -0.430796               | 1.141639  | 1.312231  |
| 3                | 6                | 0              | -1.345234               | 1.176296  | 0.184053  |
| 4                | 6                | 0              | -1.928558               | -0.158775 | 0.026887  |
| 5                | 6                | 0              | -1.394520               | -1.022073 | 1.068008  |
| 6                | 6                | 0              | -0.536502               | -0.191923 | 1.951299  |
| 7                | 6                | 0              | 1.518427                | 0.773400  | -1.321343 |
| 8                | 8                | 0              | 2.228002                | 1.473553  | -1.955832 |
| 9                | 8                | 0              | 0.191154                | -0.620487 | 2.933095  |
| 10               | 6                | 0              | 0.355420                | -1.642419 | -1.657522 |
| 11               | 8                | 0              | 0.295511                | -2.461972 | -2.507111 |
| 12               | 6                | 0              | -1.754789               | -2.431447 | 1.365825  |
| 13               | 6                | 0              | -1.816478               | -2.863974 | 2.714096  |
| 14               | 6                | 0              | -2.053239               | -3.367641 | 0.345307  |
| 15               | 6                | 0              | -2.178059               | -4.186132 | 3.027949  |
| 16               | 1                | 0              | -1.567168               | -2.167494 | 3.506974  |
| 17               | 6                | 0              | -2.414282               | -4.686591 | 0.660715  |
| 18               | 1                | 0              | -2.002773               | -3.069493 | -0.697222 |
| 19               | 6                | 0              | -2.480538               | -5.104472 | 2.004968  |
| 20               | 1                | 0              | -2.221230               | -4.496779 | 4.069289  |
| 21               | 1                | 0              | -2.639235               | -5.386728 | -0.140290 |
| 22               | 1                | 0              | -2.759239               | -6.127064 | 2.248480  |
| 23               | 6                | 0              | -3.035342               | -0.492450 | -0.912485 |
| 24               | 6                | 0              | -4.253789               | -0.983775 | -0.387724 |
| 25               | 6                | 0              | -2.929614               | -0.276277 | -2.303700 |
| 26               | 6                | 0              | -5.341759               | -1.249316 | -1.237052 |
| 27               | 1                | 0              | -4.347704               | -1.157931 | 0.680856  |
| 28               | 6                | 0              | -4.016031               | -0.544491 | -3.152942 |
| 29               | 1                | 0              | -1.996600               | 0.098372  | -2.716183 |
| 30               | 6                | 0              | -5.227337               | -1.031163 | -2.623743 |
| 31               | 1                | 0              | -6.271232               | -1.627490 | -0.818451 |
| 32               | 1                | 0              | -3.916681               | -0.376211 | -4.222338 |
| 33               | 1                | 0              | -6.067215               | -1.240546 | -3.281785 |
| 34               | 6                | 0              | 0.252038                | 2.294852  | 1.956160  |
| 35               | 6                | 0              | 1.638372                | 2.268515  | 2.225444  |
| 36               | 6                | 0              | -0.499758               | 3.418694  | 2.372060  |
| 37               | 6                | 0              | 2.260347                | 3.341545  | 2.887011  |
| 38               | 1                | 0              | 2.227082                | 1.411160  | 1.911589  |
| 39               | 6                | 0              | 0.121650                | 4.492235  | 3.033146  |
| 40               | 1                | 0              | -1.569543               | 3.450312  | 2.182810  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 41 | 6 | 0 | 1.505217  | 4.458586  | 3.293129  |
| 42 | 1 | 0 | 3.329357  | 3.306715  | 3.083608  |
| 43 | 1 | 0 | -0.471165 | 5.348941  | 3.345072  |
| 44 | 1 | 0 | 1.986678  | 5.289023  | 3.804325  |
| 45 | 6 | 0 | -1.786329 | 2.405682  | -0.532848 |
| 46 | 6 | 0 | -3.167749 | 2.702478  | -0.616335 |
| 47 | 6 | 0 | -0.863162 | 3.333169  | -1.065981 |
| 48 | 6 | 0 | -3.611629 | 3.890203  | -1.223297 |
| 49 | 1 | 0 | -3.895238 | 2.010227  | -0.203501 |
| 50 | 6 | 0 | -1.306209 | 4.516942  | -1.677484 |
| 51 | 1 | 0 | 0.201423  | 3.133751  | -1.003699 |
| 52 | 6 | 0 | -2.683163 | 4.801605  | -1.760258 |
| 53 | 1 | 0 | -4.677063 | 4.100175  | -1.277165 |
| 54 | 1 | 0 | -0.578838 | 5.213996  | -2.085699 |
| 55 | 1 | 0 | -3.025892 | 5.718251  | -2.234139 |
| 56 | 6 | 0 | 2.876141  | -2.232162 | 0.912063  |
| 57 | 1 | 0 | 3.127411  | -2.660093 | 1.888429  |
| 58 | 1 | 0 | 2.430684  | -3.010328 | 0.281990  |
| 59 | 8 | 0 | 1.872987  | -1.173038 | 1.112198  |
| 60 | 1 | 0 | 1.442344  | -1.129595 | 2.043300  |
| 61 | 6 | 0 | 4.105333  | -1.678185 | 0.278537  |
| 62 | 6 | 0 | 5.353942  | -1.327965 | 0.763800  |
| 63 | 8 | 0 | 4.050294  | -1.416261 | -1.089038 |
| 64 | 6 | 0 | 6.115368  | -0.822438 | -0.343474 |
| 65 | 1 | 0 | 5.681621  | -1.418404 | 1.789182  |
| 66 | 6 | 0 | 5.297246  | -0.881822 | -1.461082 |
| 67 | 1 | 0 | 7.130987  | -0.456152 | -0.335736 |
| 68 | 6 | 0 | 5.471754  | -0.514951 | -2.862500 |
| 69 | 8 | 0 | 6.539458  | -0.055388 | -3.327007 |
| 70 | 1 | 0 | 4.580988  | -0.673022 | -3.495740 |

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### Catalyst A - gas phase

Method: opt freq b3lyp/lanl2dz

SCF Done: E(RB3LYP) = -1513.94288717 A.U. after 1 cycles  
Lowest frequency = 27.0904

Zero-point correction= 0.437984 (Hartree/Particle)  
Thermal correction to Energy= 0.468121  
Thermal correction to Enthalpy= 0.469065  
Thermal correction to Gibbs Free Energy= 0.374505  
Sum of electronic and zero-point Energies= -1513.504904  
Sum of electronic and thermal Energies= -1513.474766  
Sum of electronic and thermal Enthalpies= -1513.473822  
Sum of electronic and thermal Free Energies= -1513.568382

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 44               | 0              | -0.012158               | -0.704864 | 1.484346  |
| 2                | 6                | 0              | -1.191151               | -0.857410 | -0.559189 |
| 3                | 6                | 0              | -0.703973               | 0.529774  | -0.431012 |
| 4                | 6                | 0              | 0.736134                | 0.500168  | -0.411856 |
| 5                | 6                | 0              | 1.169501                | -0.902140 | -0.529146 |
| 6                | 6                | 0              | -0.028715               | -1.689224 | -0.684747 |
| 7                | 6                | 0              | -1.414017               | -0.528633 | 2.724128  |
| 8                | 8                | 0              | -2.307831               | -0.443783 | 3.494269  |
| 9                | 6                | 0              | 1.269459                | -0.249240 | 2.779175  |
| 10               | 8                | 0              | 2.091957                | 0.022149  | 3.585660  |
| 11               | 6                | 0              | 2.540439                | -1.430905 | -0.764224 |
| 12               | 6                | 0              | 2.785265                | -2.203815 | -1.928065 |
| 13               | 6                | 0              | 3.617406                | -1.180316 | 0.115998  |
| 14               | 6                | 0              | 4.068021                | -2.717707 | -2.195602 |
| 15               | 1                | 0              | 1.982320                | -2.371347 | -2.643114 |
| 16               | 6                | 0              | 4.899716                | -1.683185 | -0.157228 |
| 17               | 1                | 0              | 3.451073                | -0.595306 | 1.015155  |
| 18               | 6                | 0              | 5.130949                | -2.459406 | -1.310515 |
| 19               | 1                | 0              | 4.236117                | -3.307575 | -3.093594 |
| 20               | 1                | 0              | 5.714673                | -1.476515 | 0.531914  |
| 21               | 1                | 0              | 6.123105                | -2.853788 | -1.515479 |
| 22               | 6                | 0              | 1.646121                | 1.678328  | -0.404609 |
| 23               | 6                | 0              | 2.627072                | 1.809508  | -1.415578 |
| 24               | 6                | 0              | 1.533408                | 2.700079  | 0.565682  |
| 25               | 6                | 0              | 3.470613                | 2.934115  | -1.455922 |
| 26               | 1                | 0              | 2.726984                | 1.036114  | -2.172272 |
| 27               | 6                | 0              | 2.374048                | 3.824139  | 0.525092  |
| 28               | 1                | 0              | 0.790417                | 2.607633  | 1.353442  |
| 29               | 6                | 0              | 3.347670                | 3.946897  | -0.485955 |
| 30               | 1                | 0              | 4.219173                | 3.017273  | -2.240295 |
| 31               | 1                | 0              | 2.273394                | 4.598204  | 1.281844  |
| 32               | 1                | 0              | 4.001245                | 4.815484  | -0.514797 |
| 33               | 6                | 0              | -2.580138               | -1.321651 | -0.814560 |
| 34               | 6                | 0              | -3.088121               | -2.474554 | -0.173161 |
| 35               | 6                | 0              | -3.396234               | -0.654016 | -1.757231 |
| 36               | 6                | 0              | -4.380908               | -2.942897 | -0.458362 |
| 37               | 1                | 0              | -2.466669               | -2.998784 | 0.547271  |
| 38               | 6                | 0              | -4.691501               | -1.121781 | -2.041118 |
| 39               | 1                | 0              | -3.019589               | 0.224703  | -2.272205 |
| 40               | 6                | 0              | -5.190537               | -2.266954 | -1.392474 |
| 41               | 1                | 0              | -4.756298               | -3.828897 | 0.047955  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 42 | 1 | 0 | -5.305977 | -0.594727 | -2.767208 |
| 43 | 1 | 0 | -6.193111 | -2.627301 | -1.610807 |
| 44 | 6 | 0 | -1.554076 | 1.751246  | -0.493306 |
| 45 | 6 | 0 | -1.265011 | 2.748989  | -1.454724 |
| 46 | 6 | 0 | -2.680624 | 1.927708  | 0.342081  |
| 47 | 6 | 0 | -2.073760 | 3.893290  | -1.570679 |
| 48 | 1 | 0 | -0.408936 | 2.627157  | -2.112219 |
| 49 | 6 | 0 | -3.490709 | 3.069360  | 0.225744  |
| 50 | 1 | 0 | -2.925117 | 1.174872  | 1.085259  |
| 51 | 6 | 0 | -3.190754 | 4.059590  | -0.730144 |
| 52 | 1 | 0 | -1.832153 | 4.649556  | -2.313771 |
| 53 | 1 | 0 | -4.351053 | 3.185416  | 0.880201  |
| 54 | 1 | 0 | -3.816361 | 4.944675  | -0.817731 |
| 55 | 1 | 0 | 0.123819  | -2.191262 | 2.075455  |
| 56 | 8 | 0 | -0.105744 | -3.038530 | -0.971486 |
| 57 | 1 | 0 | 0.767282  | -3.476421 | -0.874717 |

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### Intermediate A/HMF - gas phase

Method: opt freq b3lyp/lanl2dz

SCF Done: E(RB3LYP) = -1971.77529771 A.U. after 1 cycles  
Lowest frequency = 18.2466

Zero-point correction= 0.552053 (Hartree/Particle)  
Thermal correction to Energy= 0.591652  
Thermal correction to Enthalpy= 0.592596  
Thermal correction to Gibbs Free Energy= 0.475759  
Sum of electronic and zero-point Energies= -1971.223245  
Sum of electronic and thermal Energies= -1971.183646  
Sum of electronic and thermal Enthalpies= -1971.182702  
Sum of electronic and thermal Free Energies= -1971.299538

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 44               | 0              | -0.022360               | -0.314151 | -1.017119 |
| 2                | 1                | 0              | -0.873106               | -1.669855 | -1.113670 |
| 3                | 6                | 0              | 1.358386                | -1.037296 | 0.723586  |
| 4                | 6                | 0              | 1.944295                | 0.200838  | 0.200858  |
| 5                | 6                | 0              | 1.010338                | 1.280232  | 0.422224  |
| 6                | 6                | 0              | -0.161207               | 0.726886  | 1.115524  |
| 7                | 6                | 0              | 0.091428                | -0.676362 | 1.334343  |
| 8                | 6                | 0              | -1.501836               | 0.452283  | -1.871037 |
| 9                | 8                | 0              | -2.484403               | 0.882314  | -2.384535 |
| 10               | 8                | 0              | -0.711183               | -1.459914 | 2.119989  |
| 11               | 1                | 0              | -0.921601               | -2.383863 | 1.789272  |
| 12               | 6                | 0              | -2.708264               | -3.541502 | 0.240808  |
| 13               | 8                | 0              | -1.760081               | -3.682065 | 1.069049  |
| 14               | 1                | 0              | -2.905496               | -4.326520 | -0.505473 |
| 15               | 6                | 0              | 0.716428                | -0.857520 | -2.660423 |
| 16               | 8                | 0              | 1.172952                | -1.220828 | -3.689444 |
| 17               | 6                | 0              | 2.063032                | -2.327605 | 0.958787  |
| 18               | 6                | 0              | 1.548773                | -3.560781 | 0.503872  |
| 19               | 1                | 0              | 0.638674                | -3.577388 | -0.088044 |
| 20               | 6                | 0              | 2.208337                | -4.766747 | 0.801966  |
| 21               | 1                | 0              | 1.794261                | -5.706773 | 0.445891  |
| 22               | 6                | 0              | 3.397045                | -4.758036 | 1.555406  |
| 23               | 1                | 0              | 3.908804                | -5.690284 | 1.782802  |
| 24               | 6                | 0              | 3.919365                | -3.532316 | 2.013262  |
| 25               | 1                | 0              | 4.836301                | -3.514220 | 2.597656  |
| 26               | 6                | 0              | 3.256441                | -2.328949 | 1.720565  |
| 27               | 1                | 0              | 3.661722                | -1.387756 | 2.082571  |
| 28               | 6                | 0              | 3.338418                | 0.324142  | -0.308824 |
| 29               | 6                | 0              | 3.886456                | -0.613896 | -1.213832 |
| 30               | 1                | 0              | 3.270696                | -1.425782 | -1.588383 |
| 31               | 6                | 0              | 5.221400                | -0.512462 | -1.635996 |
| 32               | 1                | 0              | 5.618975                | -1.242560 | -2.336569 |
| 33               | 6                | 0              | 6.041492                | 0.527553  | -1.156577 |
| 34               | 1                | 0              | 7.075130                | 0.606992  | -1.484707 |
| 35               | 6                | 0              | 5.510762                | 1.461532  | -0.247230 |
| 36               | 1                | 0              | 6.133978                | 2.266449  | 0.135051  |
| 37               | 6                | 0              | 4.173175                | 1.360301  | 0.173571  |
| 38               | 1                | 0              | 3.780501                | 2.083446  | 0.881358  |
| 39               | 6                | 0              | 1.258058                | 2.724091  | 0.156765  |
| 40               | 6                | 0              | 1.243660                | 3.642562  | 1.233131  |
| 41               | 1                | 0              | 1.019441                | 3.289207  | 2.236356  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 42 | 6 | 0 | 1.516697  | 5.004952  | 1.018463  |
| 43 | 1 | 0 | 1.498400  | 5.696563  | 1.857446  |
| 44 | 6 | 0 | 1.811994  | 5.472807  | -0.276633 |
| 45 | 1 | 0 | 2.022340  | 6.526485  | -0.443883 |
| 46 | 6 | 0 | 1.828266  | 4.565858  | -1.354459 |
| 47 | 1 | 0 | 2.052110  | 4.916781  | -2.358929 |
| 48 | 6 | 0 | 1.550987  | 3.205127  | -1.139167 |
| 49 | 1 | 0 | 1.555963  | 2.510647  | -1.975381 |
| 50 | 6 | 0 | -1.303674 | 1.491281  | 1.681110  |
| 51 | 6 | 0 | -1.928066 | 2.539885  | 0.965601  |
| 52 | 1 | 0 | -1.590765 | 2.783396  | -0.037517 |
| 53 | 6 | 0 | -2.983358 | 3.270467  | 1.534481  |
| 54 | 1 | 0 | -3.450162 | 4.070536  | 0.965228  |
| 55 | 6 | 0 | -3.437291 | 2.969234  | 2.834177  |
| 56 | 1 | 0 | -4.253374 | 3.536724  | 3.275290  |
| 57 | 6 | 0 | -2.821828 | 1.929148  | 3.557048  |
| 58 | 1 | 0 | -3.159959 | 1.689993  | 4.562692  |
| 59 | 6 | 0 | -1.765788 | 1.195300  | 2.986799  |
| 60 | 1 | 0 | -1.301647 | 0.389136  | 3.545152  |
| 61 | 6 | 0 | -3.559686 | -2.384401 | 0.168702  |
| 62 | 6 | 0 | -3.739509 | -1.258419 | 0.967084  |
| 63 | 8 | 0 | -4.357420 | -2.252009 | -0.991480 |
| 64 | 6 | 0 | -4.661209 | -0.402537 | 0.291645  |
| 65 | 1 | 0 | -3.236779 | -1.069904 | 1.903292  |
| 66 | 6 | 0 | -5.004744 | -1.025967 | -0.901001 |
| 67 | 1 | 0 | -5.003285 | 0.568570  | 0.614323  |
| 68 | 6 | 0 | -5.799328 | -0.574468 | -2.093626 |
| 69 | 1 | 0 | -5.589197 | -1.251093 | -2.934880 |
| 70 | 1 | 0 | -6.874573 | -0.599504 | -1.889098 |
| 71 | 8 | 0 | -5.520342 | 0.816337  | -2.423941 |
| 72 | 1 | 0 | -4.556366 | 0.951254  | -2.567541 |

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### Transition state - gas phase

Method: opt(ts,noeigen,modred) freq b3lyp/lanl2dz

SCF Done: E(RB3LYP) = -1971.75811123 A.U. after 1 cycles

Lowest frequency = -828.9675

Zero-point correction= 0.548023 (Hartree/Particle)  
Thermal correction to Energy= 0.586350  
Thermal correction to Enthalpy= 0.587294  
Thermal correction to Gibbs Free Energy= 0.474609  
Sum of electronic and zero-point Energies= -1971.210088  
Sum of electronic and thermal Energies= -1971.171761  
Sum of electronic and thermal Enthalpies= -1971.170817  
Sum of electronic and thermal Free Energies= -1971.283502

#### Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 44               | 0              | 0.075828                | -0.472255 | -0.913820 |
| 2                | 1                | 0              | -0.955787               | -1.832470 | -0.878788 |
| 3                | 6                | 0              | 1.643279                | -0.904553 | 0.767240  |
| 4                | 6                | 0              | 1.874590                | 0.448097  | 0.261731  |
| 5                | 6                | 0              | 0.689514                | 1.247908  | 0.540847  |
| 6                | 6                | 0              | -0.288918               | 0.402792  | 1.218587  |
| 7                | 6                | 0              | 0.339626                | -0.904675 | 1.426470  |
| 8                | 6                | 0              | -1.233855               | 0.378694  | -1.967873 |
| 9                | 8                | 0              | -2.088159               | 0.906886  | -2.596560 |
| 10               | 8                | 0              | -0.209434               | -1.924618 | 2.076164  |
| 11               | 1                | 0              | -0.716047               | -2.761130 | 1.480571  |
| 12               | 6                | 0              | -1.782329               | -2.984302 | -0.447378 |
| 13               | 8                | 0              | -1.217355               | -3.524176 | 0.620926  |
| 14               | 1                | 0              | -1.593827               | -3.481730 | -1.406780 |
| 15               | 6                | 0              | 0.917063                | -1.220091 | -2.435925 |
| 16               | 8                | 0              | 1.457501                | -1.695154 | -3.373063 |
| 17               | 6                | 0              | 2.628647                | -2.011113 | 0.893093  |
| 18               | 6                | 0              | 2.266178                | -3.348623 | 0.612199  |
| 19               | 1                | 0              | 1.265474                | -3.577496 | 0.257095  |
| 20               | 6                | 0              | 3.188377                | -4.392899 | 0.795418  |
| 21               | 1                | 0              | 2.891087                | -5.415058 | 0.574109  |
| 22               | 6                | 0              | 4.487616                | -4.121269 | 1.265622  |
| 23               | 1                | 0              | 5.200475                | -4.930524 | 1.405579  |
| 24               | 6                | 0              | 4.854392                | -2.793803 | 1.557701  |
| 25               | 1                | 0              | 5.852161                | -2.572064 | 1.928980  |
| 26               | 6                | 0              | 3.932832                | -1.748531 | 1.375702  |
| 27               | 1                | 0              | 4.225386                | -0.731192 | 1.617983  |
| 28               | 6                | 0              | 3.168977                | 0.975151  | -0.254428 |
| 29               | 6                | 0              | 3.877556                | 0.338352  | -1.298237 |
| 30               | 1                | 0              | 3.459939                | -0.540416 | -1.778768 |
| 31               | 6                | 0              | 5.122280                | 0.828340  | -1.725440 |
| 32               | 1                | 0              | 5.648007                | 0.324921  | -2.532836 |
| 33               | 6                | 0              | 5.687556                | 1.963535  | -1.112373 |
| 34               | 1                | 0              | 6.650945                | 2.343202  | -1.444021 |
| 35               | 6                | 0              | 4.994906                | 2.601696  | -0.066294 |
| 36               | 1                | 0              | 5.421609                | 3.476919  | 0.417473  |
| 37               | 6                | 0              | 3.747324                | 2.112413  | 0.358499  |
| 38               | 1                | 0              | 3.225293                | 2.611528  | 1.169463  |
| 39               | 6                | 0              | 0.577098                | 2.717084  | 0.326607  |
| 40               | 6                | 0              | 0.298398                | 3.554693  | 1.432048  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 41 | 1 | 0 | 0.126562  | 3.114892  | 2.410776  |
| 42 | 6 | 0 | 0.241814  | 4.950433  | 1.275260  |
| 43 | 1 | 0 | 0.025044  | 5.579890  | 2.134874  |
| 44 | 6 | 0 | 0.460547  | 5.530711  | 0.010958  |
| 45 | 1 | 0 | 0.412890  | 6.610040  | -0.111584 |
| 46 | 6 | 0 | 0.737080  | 4.702869  | -1.094726 |
| 47 | 1 | 0 | 0.904333  | 5.140905  | -2.075540 |
| 48 | 6 | 0 | 0.795857  | 3.308218  | -0.937330 |
| 49 | 1 | 0 | 1.008306  | 2.673770  | -1.793828 |
| 50 | 6 | 0 | -1.591566 | 0.807803  | 1.807076  |
| 51 | 6 | 0 | -2.469366 | 1.700693  | 1.147736  |
| 52 | 1 | 0 | -2.213906 | 2.089390  | 0.166827  |
| 53 | 6 | 0 | -3.677447 | 2.093730  | 1.743263  |
| 54 | 1 | 0 | -4.339218 | 2.773345  | 1.212764  |
| 55 | 6 | 0 | -4.034771 | 1.603300  | 3.015023  |
| 56 | 1 | 0 | -4.969547 | 1.910809  | 3.478193  |
| 57 | 6 | 0 | -3.172421 | 0.710090  | 3.678874  |
| 58 | 1 | 0 | -3.437526 | 0.323593  | 4.660358  |
| 59 | 6 | 0 | -1.963414 | 0.311717  | 3.080724  |
| 60 | 1 | 0 | -1.309972 | -0.388102 | 3.590440  |
| 61 | 6 | 0 | -3.093049 | -2.336145 | -0.317724 |
| 62 | 6 | 0 | -3.926539 | -2.083652 | 0.756375  |
| 63 | 8 | 0 | -3.657161 | -1.794505 | -1.482136 |
| 64 | 6 | 0 | -5.058791 | -1.356870 | 0.245569  |
| 65 | 1 | 0 | -3.743703 | -2.382445 | 1.777085  |
| 66 | 6 | 0 | -4.868015 | -1.184922 | -1.111655 |
| 67 | 1 | 0 | -5.896855 | -0.985208 | 0.815932  |
| 68 | 6 | 0 | -5.599468 | -0.451690 | -2.190130 |
| 69 | 1 | 0 | -5.526509 | -1.009844 | -3.134876 |
| 70 | 1 | 0 | -6.652420 | -0.349164 | -1.917080 |
| 71 | 8 | 0 | -5.129103 | 0.925416  | -2.369840 |
| 72 | 1 | 0 | -4.178294 | 0.940976  | -2.618922 |

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### Intermediate B/BHMF - gas phase

Method: opt freq b3lyp/lanl2dz

SCF Done: E(RB3LYP) = -1971.77104651 A.U. after 1 cycles  
Lowest frequency = 24.9100

Zero-point correction= 0.554502 (Hartree/Particle)  
Thermal correction to Energy= 0.593808  
Thermal correction to Enthalpy= 0.594752  
Thermal correction to Gibbs Free Energy= 0.479989  
Sum of electronic and zero-point Energies= -1971.216544  
Sum of electronic and thermal Energies= -1971.177239  
Sum of electronic and thermal Enthalpies= -1971.176295  
Sum of electronic and thermal Free Energies= -1971.291057

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 44               | 0              | 0.139634                | -0.429724 | -0.928429 |
| 2                | 1                | 0              | -1.083367               | -2.096496 | -0.896259 |
| 3                | 6                | 0              | 1.646218                | -0.943839 | 0.761957  |
| 4                | 6                | 0              | 1.884368                | 0.405283  | 0.298377  |
| 5                | 6                | 0              | 0.678451                | 1.213890  | 0.578567  |
| 6                | 6                | 0              | -0.300733               | 0.373307  | 1.221983  |
| 7                | 6                | 0              | 0.330506                | -0.958360 | 1.463997  |
| 8                | 6                | 0              | -1.145659               | 0.496734  | -1.971732 |
| 9                | 8                | 0              | -1.950814               | 1.120433  | -2.573915 |
| 10               | 8                | 0              | -0.214989               | -1.962932 | 2.030274  |
| 11               | 1                | 0              | -1.064236               | -3.149322 | 1.214441  |
| 12               | 6                | 0              | -1.808462               | -2.957943 | -0.663436 |
| 13               | 8                | 0              | -1.369471               | -3.723024 | 0.449184  |
| 14               | 1                | 0              | -1.754868               | -3.599460 | -1.550744 |
| 15               | 6                | 0              | 1.032796                | -1.072125 | -2.479854 |
| 16               | 8                | 0              | 1.622311                | -1.448608 | -3.431022 |
| 17               | 6                | 0              | 2.610639                | -2.069458 | 0.863880  |
| 18               | 6                | 0              | 2.199927                | -3.395183 | 0.588474  |
| 19               | 1                | 0              | 1.181063                | -3.596136 | 0.270010  |
| 20               | 6                | 0              | 3.096533                | -4.466684 | 0.737590  |
| 21               | 1                | 0              | 2.762349                | -5.478131 | 0.520265  |
| 22               | 6                | 0              | 4.416098                | -4.236023 | 1.171912  |
| 23               | 1                | 0              | 5.108434                | -5.066664 | 1.287303  |
| 24               | 6                | 0              | 4.829200                | -2.922050 | 1.463933  |
| 25               | 1                | 0              | 5.842072                | -2.732831 | 1.811630  |
| 26               | 6                | 0              | 3.934479                | -1.848854 | 1.313895  |
| 27               | 1                | 0              | 4.263751                | -0.843312 | 1.557749  |
| 28               | 6                | 0              | 3.184076                | 0.964065  | -0.166700 |
| 29               | 6                | 0              | 3.928682                | 0.373427  | -1.212485 |
| 30               | 1                | 0              | 3.536780                | -0.491530 | -1.736413 |
| 31               | 6                | 0              | 5.179756                | 0.891712  | -1.583178 |
| 32               | 1                | 0              | 5.733913                | 0.425581  | -2.393757 |
| 33               | 6                | 0              | 5.716239                | 2.005521  | -0.907975 |
| 34               | 1                | 0              | 6.685527                | 2.405621  | -1.195185 |
| 35               | 6                | 0              | 4.987847                | 2.596021  | 0.141761  |
| 36               | 1                | 0              | 5.392328                | 3.454022  | 0.672810  |
| 37               | 6                | 0              | 3.731677                | 2.082101  | 0.507331  |
| 38               | 1                | 0              | 3.181094                | 2.545948  | 1.320199  |
| 39               | 6                | 0              | 0.583360                | 2.686384  | 0.387253  |
| 40               | 6                | 0              | 0.256183                | 3.502237  | 1.495677  |
| 41               | 1                | 0              | 0.035793                | 3.044082  | 2.455857  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 42 | 6 | 0 | 0.212729  | 4.900702  | 1.363579  |
| 43 | 1 | 0 | -0.041010 | 5.514486  | 2.224244  |
| 44 | 6 | 0 | 0.488949  | 5.503582  | 0.121278  |
| 45 | 1 | 0 | 0.448978  | 6.585119  | 0.017410  |
| 46 | 6 | 0 | 0.811925  | 4.696530  | -0.987214 |
| 47 | 1 | 0 | 1.022307  | 5.152961  | -1.951055 |
| 48 | 6 | 0 | 0.862110  | 3.299381  | -0.854187 |
| 49 | 1 | 0 | 1.109480  | 2.680431  | -1.712296 |
| 50 | 6 | 0 | -1.622867 | 0.757970  | 1.775755  |
| 51 | 6 | 0 | -2.503264 | 1.630796  | 1.092415  |
| 52 | 1 | 0 | -2.233284 | 2.025022  | 0.118072  |
| 53 | 6 | 0 | -3.737599 | 1.991950  | 1.651880  |
| 54 | 1 | 0 | -4.405782 | 2.642847  | 1.095002  |
| 55 | 6 | 0 | -4.115855 | 1.493749  | 2.914363  |
| 56 | 1 | 0 | -5.073159 | 1.773035  | 3.348287  |
| 57 | 6 | 0 | -3.251340 | 0.622136  | 3.603170  |
| 58 | 1 | 0 | -3.536527 | 0.225787  | 4.574890  |
| 59 | 6 | 0 | -2.019193 | 0.249958  | 3.037908  |
| 60 | 1 | 0 | -1.369049 | -0.439878 | 3.564876  |
| 61 | 6 | 0 | -3.174292 | -2.370845 | -0.488268 |
| 62 | 6 | 0 | -4.144059 | -2.477726 | 0.479542  |
| 63 | 8 | 0 | -3.612060 | -1.501822 | -1.498290 |
| 64 | 6 | 0 | -5.245193 | -1.632112 | 0.066425  |
| 65 | 1 | 0 | -4.079331 | -3.083475 | 1.369976  |
| 66 | 6 | 0 | -4.899778 | -1.050513 | -1.131260 |
| 67 | 1 | 0 | -6.168502 | -1.470435 | 0.603246  |
| 68 | 6 | 0 | -5.550205 | -0.075820 | -2.057189 |
| 69 | 1 | 0 | -5.512611 | -0.450843 | -3.091299 |
| 70 | 1 | 0 | -6.595952 | 0.052142  | -1.767300 |
| 71 | 8 | 0 | -4.973718 | 1.273051  | -1.996196 |
| 72 | 1 | 0 | -4.045673 | 1.263077  | -2.317846 |

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### Intermediate C - gas phase

Method: opt freq b3lyp/lanl2dz

SCF Done: E(RB3LYP) = -1971.79148796 A.U. after 1 cycles  
Lowest frequency = 7.8302

Zero-point correction= 0.555975 (Hartree/Particle)  
Thermal correction to Energy= 0.595143  
Thermal correction to Enthalpy= 0.596087  
Thermal correction to Gibbs Free Energy= 0.479179  
Sum of electronic and zero-point Energies= -1971.235513  
Sum of electronic and thermal Energies= -1971.196345  
Sum of electronic and thermal Enthalpies= -1971.195401  
Sum of electronic and thermal Free Energies= -1971.312309

#### Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 44               | 0              | 0.108221                | -0.485458 | -0.566572 |
| 2                | 6                | 0              | -0.016192               | 0.808562  | 1.344541  |
| 3                | 6                | 0              | -1.015929               | 1.282225  | 0.399959  |
| 4                | 6                | 0              | -1.977884               | 0.200169  | 0.169786  |
| 5                | 6                | 0              | -1.583835               | -0.944830 | 0.968467  |
| 6                | 6                | 0              | -0.421341               | -0.539633 | 1.809326  |
| 7                | 6                | 0              | 1.443266                | 0.420451  | -1.545118 |
| 8                | 8                | 0              | 2.284902                | 1.019879  | -2.125994 |
| 9                | 8                | 0              | 0.252947                | -1.306790 | 2.597104  |
| 10               | 6                | 0              | -0.443981               | -1.444649 | -2.111186 |
| 11               | 8                | 0              | -0.839951               | -2.015507 | -3.067550 |
| 12               | 6                | 0              | -2.286625               | -2.243224 | 1.120477  |
| 13               | 6                | 0              | -2.314069               | -2.875292 | 2.388467  |
| 14               | 6                | 0              | -2.945876               | -2.877376 | 0.038633  |
| 15               | 6                | 0              | -2.992348               | -4.093908 | 2.568485  |
| 16               | 1                | 0              | -1.791873               | -2.417314 | 3.221155  |
| 17               | 6                | 0              | -3.621593               | -4.093756 | 0.220155  |
| 18               | 1                | 0              | -2.930737               | -2.424047 | -0.947717 |
| 19               | 6                | 0              | -3.650884               | -4.709451 | 1.487540  |
| 20               | 1                | 0              | -3.002806               | -4.561194 | 3.550453  |
| 21               | 1                | 0              | -4.119677               | -4.561762 | -0.625636 |
| 22               | 1                | 0              | -4.173579               | -5.652893 | 1.627000  |
| 23               | 6                | 0              | -3.240540               | 0.340402  | -0.607596 |
| 24               | 6                | 0              | -4.473210               | 0.078908  | 0.035317  |
| 25               | 6                | 0              | -3.251646               | 0.783436  | -1.948216 |
| 26               | 6                | 0              | -5.688046               | 0.259700  | -0.648165 |
| 27               | 1                | 0              | -4.480069               | -0.265754 | 1.065850  |
| 28               | 6                | 0              | -4.465517               | 0.960627  | -2.632478 |
| 29               | 1                | 0              | -2.310091               | 0.983059  | -2.452665 |
| 30               | 6                | 0              | -5.689571               | 0.700782  | -1.985563 |
| 31               | 1                | 0              | -6.626792               | 0.053101  | -0.139999 |
| 32               | 1                | 0              | -4.455495               | 1.297900  | -3.665909 |
| 33               | 1                | 0              | -6.628904               | 0.835965  | -2.516292 |
| 34               | 6                | 0              | 1.037460                | 1.611153  | 2.019943  |
| 35               | 6                | 0              | 2.371717                | 1.153239  | 2.091967  |
| 36               | 6                | 0              | 0.700926                | 2.823772  | 2.666416  |
| 37               | 6                | 0              | 3.347900                | 1.892185  | 2.782026  |
| 38               | 1                | 0              | 2.645808                | 0.222152  | 1.604433  |
| 39               | 6                | 0              | 1.676135                | 3.562800  | 3.358035  |
| 40               | 1                | 0              | -0.323101               | 3.185730  | 2.633215  |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 41 | 6 | 0 | 3.004998  | 3.100817  | 3.417924  |
| 42 | 1 | 0 | 4.371638  | 1.527817  | 2.819106  |
| 43 | 1 | 0 | 1.399367  | 4.493187  | 3.848479  |
| 44 | 1 | 0 | 3.760652  | 3.673467  | 3.950615  |
| 45 | 6 | 0 | -1.181554 | 2.692985  | -0.051995 |
| 46 | 6 | 0 | -2.416660 | 3.348857  | 0.166976  |
| 47 | 6 | 0 | -0.119110 | 3.428785  | -0.622840 |
| 48 | 6 | 0 | -2.584890 | 4.699874  | -0.182996 |
| 49 | 1 | 0 | -3.243926 | 2.806749  | 0.615179  |
| 50 | 6 | 0 | -0.287919 | 4.776906  | -0.977732 |
| 51 | 1 | 0 | 0.841430  | 2.952898  | -0.789117 |
| 52 | 6 | 0 | -1.522249 | 5.419680  | -0.760749 |
| 53 | 1 | 0 | -3.541564 | 5.185443  | -0.006418 |
| 54 | 1 | 0 | 0.542023  | 5.322868  | -1.419021 |
| 55 | 1 | 0 | -1.652543 | 6.463484  | -1.036065 |
| 56 | 6 | 0 | 2.347081  | -3.034044 | -0.093468 |
| 57 | 1 | 0 | 2.371060  | -3.871464 | 0.612286  |
| 58 | 1 | 0 | 1.951806  | -3.383280 | -1.051580 |
| 59 | 8 | 0 | 1.373782  | -2.042746 | 0.404113  |
| 60 | 1 | 0 | 1.188063  | -2.037598 | 1.402354  |
| 61 | 6 | 0 | 3.710427  | -2.461343 | -0.257625 |
| 62 | 6 | 0 | 4.861759  | -2.485834 | 0.500035  |
| 63 | 8 | 0 | 3.938413  | -1.691838 | -1.409601 |
| 64 | 6 | 0 | 5.850152  | -1.694462 | -0.196878 |
| 65 | 1 | 0 | 4.991072  | -3.001130 | 1.441112  |
| 66 | 6 | 0 | 5.262105  | -1.221061 | -1.350138 |
| 67 | 1 | 0 | 6.863540  | -1.497852 | 0.120672  |
| 68 | 6 | 0 | 5.707881  | -0.333498 | -2.468869 |
| 69 | 1 | 0 | 6.799979  | -0.292774 | -2.482243 |
| 70 | 1 | 0 | 5.355418  | -0.740790 | -3.428530 |
| 71 | 8 | 0 | 5.283902  | 1.058660  | -2.318288 |
| 72 | 1 | 0 | 4.303618  | 1.127179  | -2.337002 |

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### Intermediate C' - gas phase

Method: opt freq b3lyp/lanl2dz

SCF Done: E(RB3LYP) = -1971.78791851 A.U. after 1 cycles  
Lowest frequency = 7.7529

Zero-point correction= 0.555575 (Hartree/Particle)  
Thermal correction to Energy= 0.595270  
Thermal correction to Enthalpy= 0.596215  
Thermal correction to Gibbs Free Energy= 0.476594  
Sum of electronic and zero-point Energies= -1971.232344  
Sum of electronic and thermal Energies= -1971.192648  
Sum of electronic and thermal Enthalpies= -1971.191704  
Sum of electronic and thermal Free Energies= -1971.311324

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 44               | 0              | -0.210078               | -0.084679 | 1.068537  |
| 2                | 6                | 0              | -0.705570               | -1.213949 | -0.885131 |
| 3                | 6                | 0              | -1.920777               | -0.582080 | -0.397700 |
| 4                | 6                | 0              | -1.715308               | 0.869174  | -0.399337 |
| 5                | 6                | 0              | -0.377604               | 1.145807  | -0.892961 |
| 6                | 6                | 0              | 0.227410                | -0.145205 | -1.324688 |
| 7                | 6                | 0              | -0.445177               | -1.445033 | 2.368949  |
| 8                | 8                | 0              | -0.610503               | -2.310842 | 3.156755  |
| 9                | 8                | 0              | 1.428498                | -0.318028 | -1.755502 |
| 10               | 6                | 0              | -0.244104               | 1.260076  | 2.406786  |
| 11               | 8                | 0              | -0.314220               | 2.120447  | 3.215910  |
| 12               | 6                | 0              | 0.251537                | 2.467201  | -1.143940 |
| 13               | 6                | 0              | 1.100340                | 2.633065  | -2.266855 |
| 14               | 6                | 0              | 0.026647                | 3.583861  | -0.300755 |
| 15               | 6                | 0              | 1.690414                | 3.879454  | -2.542631 |
| 16               | 1                | 0              | 1.305260                | 1.782431  | -2.907259 |
| 17               | 6                | 0              | 0.616468                | 4.826638  | -0.578106 |
| 18               | 1                | 0              | -0.607983               | 3.485273  | 0.574517  |
| 19               | 6                | 0              | 1.451038                | 4.983377  | -1.702886 |
| 20               | 1                | 0              | 2.336699                | 3.985355  | -3.410871 |
| 21               | 1                | 0              | 0.428225                | 5.668878  | 0.083449  |
| 22               | 1                | 0              | 1.908323                | 5.946622  | -1.916776 |
| 23               | 6                | 0              | -2.780669               | 1.874180  | -0.129069 |
| 24               | 6                | 0              | -3.098633               | 2.820450  | -1.131374 |
| 25               | 6                | 0              | -3.525652               | 1.874999  | 1.070282  |
| 26               | 6                | 0              | -4.139836               | 3.744401  | -0.937158 |
| 27               | 1                | 0              | -2.531832               | 2.832934  | -2.058394 |
| 28               | 6                | 0              | -4.563902               | 2.800686  | 1.265936  |
| 29               | 1                | 0              | -3.287156               | 1.153287  | 1.846820  |
| 30               | 6                | 0              | -4.876612               | 3.739146  | 0.263075  |
| 31               | 1                | 0              | -4.371125               | 4.465877  | -1.716975 |
| 32               | 1                | 0              | -5.124947               | 2.790136  | 2.197043  |
| 33               | 1                | 0              | -5.679198               | 4.456657  | 0.415877  |
| 34               | 6                | 0              | -0.502553               | -2.646092 | -1.227492 |
| 35               | 6                | 0              | 0.667835                | -3.329941 | -0.827309 |
| 36               | 6                | 0              | -1.449044               | -3.331390 | -2.025182 |
| 37               | 6                | 0              | 0.881634                | -4.666625 | -1.204860 |
| 38               | 1                | 0              | 1.406828                | -2.816333 | -0.219206 |
| 39               | 6                | 0              | -1.235836               | -4.668658 | -2.402121 |
| 40               | 1                | 0              | -2.347811               | -2.818346 | -2.355945 |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 41 | 6 | 0 | -0.069718 | -5.343158 | -1.992614 |
| 42 | 1 | 0 | 1.787107  | -5.177526 | -0.885966 |
| 43 | 1 | 0 | -1.975155 | -5.179739 | -3.014461 |
| 44 | 1 | 0 | 0.095747  | -6.377779 | -2.284187 |
| 45 | 6 | 0 | -3.227528 | -1.263661 | -0.173884 |
| 46 | 6 | 0 | -4.371039 | -0.810997 | -0.874707 |
| 47 | 6 | 0 | -3.351719 | -2.399125 | 0.657346  |
| 48 | 6 | 0 | -5.604701 | -1.471384 | -0.740367 |
| 49 | 1 | 0 | -4.296787 | 0.053166  | -1.527964 |
| 50 | 6 | 0 | -4.584969 | -3.056382 | 0.796186  |
| 51 | 1 | 0 | -2.487113 | -2.773567 | 1.194572  |
| 52 | 6 | 0 | -5.718574 | -2.595515 | 0.098909  |
| 53 | 1 | 0 | -6.471226 | -1.107555 | -1.287077 |
| 54 | 1 | 0 | -4.658709 | -3.925978 | 1.444302  |
| 55 | 1 | 0 | -6.673265 | -3.104590 | 0.207328  |
| 56 | 6 | 0 | 3.078805  | 0.350220  | 1.562889  |
| 57 | 1 | 0 | 3.072608  | 1.409993  | 1.277269  |
| 58 | 1 | 0 | 2.794844  | 0.249864  | 2.611651  |
| 59 | 8 | 0 | 2.012917  | -0.346326 | 0.799576  |
| 60 | 1 | 0 | 2.172864  | -0.342520 | -0.202544 |
| 61 | 6 | 0 | 4.414948  | -0.259405 | 1.338419  |
| 62 | 6 | 0 | 5.195360  | -1.150946 | 2.041216  |
| 63 | 8 | 0 | 5.079062  | 0.091367  | 0.150108  |
| 64 | 6 | 0 | 6.401105  | -1.364803 | 1.273200  |
| 65 | 1 | 0 | 4.942885  | -1.602077 | 2.989945  |
| 66 | 6 | 0 | 6.299641  | -0.603369 | 0.129872  |
| 67 | 1 | 0 | 7.233888  | -1.998808 | 1.539193  |
| 68 | 6 | 0 | 7.171697  | -0.364149 | -1.058829 |
| 69 | 1 | 0 | 8.027898  | -1.041397 | -1.025062 |
| 70 | 1 | 0 | 6.607415  | -0.546702 | -1.985376 |
| 71 | 8 | 0 | 7.754779  | 0.983443  | -1.084961 |
| 72 | 1 | 0 | 7.038755  | 1.652602  | -1.133258 |

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### Intermediate D - gas phase

Method: opt freq b3lyp/lanl2dz

SCF Done: E(RB3LYP) = -1971.79064461 A.U. after 1 cycles  
Lowest frequency = 21.3529

Zero-point correction= 0.556493 (Hartree/Particle)  
Thermal correction to Energy= 0.595551  
Thermal correction to Enthalpy= 0.596495  
Thermal correction to Gibbs Free Energy= 0.481503  
Sum of electronic and zero-point Energies= -1971.234152  
Sum of electronic and thermal Energies= -1971.195094  
Sum of electronic and thermal Enthalpies= -1971.194150  
Sum of electronic and thermal Free Energies= -1971.309141

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 44               | 0              | -0.262614               | -0.157967 | 1.321702  |
| 2                | 6                | 0              | -0.886489               | -1.203602 | -0.633886 |
| 3                | 6                | 0              | -1.780475               | -0.081809 | -0.413553 |
| 4                | 6                | 0              | -0.980585               | 1.145099  | -0.424462 |
| 5                | 6                | 0              | 0.407545                | 0.792905  | -0.696594 |
| 6                | 6                | 0              | 0.463172                | -0.666890 | -0.959183 |
| 7                | 6                | 0              | -1.308508               | -1.054770 | 2.628248  |
| 8                | 8                | 0              | -1.981341               | -1.616577 | 3.420712  |
| 9                | 8                | 0              | 1.511832                | -1.384271 | -1.176666 |
| 10               | 6                | 0              | 0.170169                | 1.218409  | 2.554871  |
| 11               | 8                | 0              | 0.422048                | 2.107710  | 3.292872  |
| 12               | 6                | 0              | 1.538117                | 1.728815  | -0.927656 |
| 13               | 6                | 0              | 2.462916                | 1.464455  | -1.965860 |
| 14               | 6                | 0              | 1.708313                | 2.906848  | -0.159354 |
| 15               | 6                | 0              | 3.515965                | 2.357038  | -2.234355 |
| 16               | 1                | 0              | 2.370522                | 0.562903  | -2.559133 |
| 17               | 6                | 0              | 2.757382                | 3.798261  | -0.429720 |
| 18               | 1                | 0              | 1.019628                | 3.133103  | 0.648739  |
| 19               | 6                | 0              | 3.667917                | 3.529665  | -1.472127 |
| 20               | 1                | 0              | 4.214156                | 2.125742  | -3.034759 |
| 21               | 1                | 0              | 2.864437                | 4.698466  | 0.171063  |
| 22               | 1                | 0              | 4.480575                | 4.221449  | -1.682366 |
| 23               | 6                | 0              | -1.544279               | 2.524114  | -0.393183 |
| 24               | 6                | 0              | -1.308312               | 3.384865  | -1.490761 |
| 25               | 6                | 0              | -2.356641               | 2.979706  | 0.667840  |
| 26               | 6                | 0              | -1.876403               | 4.670053  | -1.525903 |
| 27               | 1                | 0              | -0.681380               | 3.049447  | -2.312439 |
| 28               | 6                | 0              | -2.922428               | 4.265165  | 0.634020  |
| 29               | 1                | 0              | -2.541089               | 2.327522  | 1.517337  |
| 30               | 6                | 0              | -2.686019               | 5.116047  | -0.463354 |
| 31               | 1                | 0              | -1.683669               | 5.320002  | -2.375933 |
| 32               | 1                | 0              | -3.543048               | 4.601158  | 1.460961  |
| 33               | 1                | 0              | -3.121907               | 6.111892  | -0.487949 |
| 34               | 6                | 0              | -1.266455               | -2.620377 | -0.883618 |
| 35               | 6                | 0              | -0.707455               | -3.677106 | -0.132111 |
| 36               | 6                | 0              | -2.155072               | -2.932728 | -1.938945 |
| 37               | 6                | 0              | -1.031978               | -5.013832 | -0.423250 |
| 38               | 1                | 0              | -0.023495               | -3.451896 | 0.681732  |
| 39               | 6                | 0              | -2.481147               | -4.268520 | -2.230080 |
| 40               | 1                | 0              | -2.586653               | -2.131090 | -2.532971 |

|    |   |   |           |           |           |
|----|---|---|-----------|-----------|-----------|
| 41 | 6 | 0 | -1.920372 | -5.315298 | -1.473113 |
| 42 | 1 | 0 | -0.592784 | -5.815524 | 0.165752  |
| 43 | 1 | 0 | -3.165943 | -4.491057 | -3.045029 |
| 44 | 1 | 0 | -2.170558 | -6.349257 | -1.699104 |
| 45 | 6 | 0 | -3.268004 | -0.155100 | -0.404946 |
| 46 | 6 | 0 | -4.010270 | 0.681247  | -1.272848 |
| 47 | 6 | 0 | -3.965921 | -1.100182 | 0.380878  |
| 48 | 6 | 0 | -5.410486 | 0.580033  | -1.344700 |
| 49 | 1 | 0 | -3.496418 | 1.405445  | -1.897125 |
| 50 | 6 | 0 | -5.364923 | -1.196533 | 0.314773  |
| 51 | 1 | 0 | -3.419782 | -1.763203 | 1.043409  |
| 52 | 6 | 0 | -6.095397 | -0.356326 | -0.548021 |
| 53 | 1 | 0 | -5.961682 | 1.230812  | -2.019058 |
| 54 | 1 | 0 | -5.881408 | -1.926788 | 0.932493  |
| 55 | 1 | 0 | -7.178876 | -0.432003 | -0.599433 |
| 56 | 6 | 0 | 2.752696  | -1.408450 | 2.414819  |
| 57 | 1 | 0 | 2.537272  | -0.685212 | 3.202588  |
| 58 | 1 | 0 | 2.879415  | -2.405881 | 2.852325  |
| 59 | 8 | 0 | 1.550758  | -1.479718 | 1.532343  |
| 60 | 1 | 0 | 1.815637  | -1.720751 | 0.590254  |
| 61 | 6 | 0 | 3.921454  | -0.989965 | 1.593681  |
| 62 | 6 | 0 | 4.768823  | 0.091278  | 1.518351  |
| 63 | 8 | 0 | 4.128713  | -1.812973 | 0.477251  |
| 64 | 6 | 0 | 5.521040  | -0.044850 | 0.287359  |
| 65 | 1 | 0 | 4.830227  | 0.907016  | 2.224017  |
| 66 | 6 | 0 | 5.087981  | -1.193032 | -0.338836 |
| 67 | 1 | 0 | 6.248110  | 0.652732  | -0.100606 |
| 68 | 6 | 0 | 5.227761  | -1.804835 | -1.696673 |
| 69 | 1 | 0 | 6.114224  | -1.409308 | -2.199418 |
| 70 | 1 | 0 | 5.323965  | -2.897462 | -1.608518 |
| 71 | 8 | 0 | 4.094439  | -1.470265 | -2.560971 |
| 72 | 1 | 0 | 3.232113  | -1.567741 | -2.082489 |

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### B<sub>2</sub>-HBMF Dimer—ground state

Method: opt freq b3lyp/lanl2dz

SCF Done: E(RB3LYP) = -3484.55201684 A.U. after 25 cycles

Conv g = 0.6109D-08 -V/T = 2.0427

Lowest frequency:+4.87

Zero-point correction= 0.975429 (Hartree/Particle)  
Thermal correction to Energy= 1.045845  
Thermal correction to Enthalpy= 1.046790  
Thermal correction to Gibbs Free Energy= 0.854162  
Sum of electronic and zero-point Energies= -3483.576588  
Sum of electronic and thermal Energies= -3483.506171  
Sum of electronic and thermal Enthalpies= -3483.505227  
Sum of electronic and thermal Free Energies= -3483.697854

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 44               | 0              | 5.404295                | 0.535114  | -0.972131 |
| 2                | 6                | 0              | 5.948901                | -1.456027 | 0.066011  |
| 3                | 6                | 0              | 7.061054                | -0.534588 | 0.224760  |
| 4                | 6                | 0              | 6.595434                | 0.616356  | 1.004192  |
| 5                | 6                | 0              | 5.197095                | 0.413289  | 1.339598  |
| 6                | 6                | 0              | 4.805557                | -0.943652 | 0.864152  |
| 7                | 6                | 0              | 5.983491                | 0.219355  | -2.749555 |
| 8                | 8                | 0              | 6.364690                | -0.002452 | -3.846708 |
| 9                | 8                | 0              | 3.627403                | -1.460896 | 0.914645  |
| 10               | 6                | 0              | 5.284421                | 2.401260  | -1.294801 |
| 11               | 8                | 0              | 5.250439                | 3.572937  | -1.454599 |
| 12               | 6                | 0              | 4.319254                | 1.272777  | 2.173604  |
| 13               | 6                | 0              | 3.351682                | 0.671199  | 3.016556  |
| 14               | 6                | 0              | 4.414018                | 2.686899  | 2.161606  |
| 15               | 6                | 0              | 2.517355                | 1.459937  | 3.828450  |
| 16               | 1                | 0              | 3.245307                | -0.407686 | 3.016943  |
| 17               | 6                | 0              | 3.580912                | 3.471513  | 2.973520  |
| 18               | 1                | 0              | 5.135552                | 3.178316  | 1.516301  |
| 19               | 6                | 0              | 2.627070                | 2.862778  | 3.813644  |
| 20               | 1                | 0              | 1.778564                | 0.978108  | 4.464359  |
| 21               | 1                | 0              | 3.670840                | 4.554819  | 2.945288  |
| 22               | 1                | 0              | 1.976939                | 3.471813  | 4.437235  |
| 23               | 6                | 0              | 7.480011                | 1.696914  | 1.522345  |
| 24               | 6                | 0              | 7.553086                | 1.911098  | 2.918752  |
| 25               | 6                | 0              | 8.293686                | 2.474295  | 0.669866  |
| 26               | 6                | 0              | 8.422837                | 2.880064  | 3.448035  |
| 27               | 1                | 0              | 6.929200                | 1.322859  | 3.586309  |
| 28               | 6                | 0              | 9.160643                | 3.445000  | 1.198491  |
| 29               | 1                | 0              | 8.241909                | 2.319083  | -0.404391 |
| 30               | 6                | 0              | 9.230130                | 3.651967  | 2.590070  |
| 31               | 1                | 0              | 8.465822                | 3.033997  | 4.523515  |
| 32               | 1                | 0              | 9.776853                | 4.037932  | 0.527238  |
| 33               | 1                | 0              | 9.899247                | 4.405181  | 2.999052  |
| 34               | 6                | 0              | 5.985012                | -2.834771 | -0.487546 |
| 35               | 6                | 0              | 4.993099                | -3.281065 | -1.389762 |
| 36               | 6                | 0              | 6.975220                | -3.750701 | -0.060400 |
| 37               | 6                | 0              | 4.996124                | -4.605067 | -1.860908 |
| 38               | 1                | 0              | 4.223950                | -2.590154 | -1.722445 |
| 39               | 6                | 0              | 6.979249                | -5.074645 | -0.532480 |

|     |    |   |            |           |           |
|-----|----|---|------------|-----------|-----------|
| 40  | 1  | 0 | 7.737521   | -3.430584 | 0.644504  |
| 41  | 6  | 0 | 5.989850   | -5.507985 | -1.435727 |
| 42  | 1  | 0 | 4.225648   | -4.930851 | -2.555780 |
| 43  | 1  | 0 | 7.748845   | -5.764569 | -0.194065 |
| 44  | 1  | 0 | 5.991985   | -6.532595 | -1.800481 |
| 45  | 6  | 0 | 8.482631   | -0.818820 | -0.122361 |
| 46  | 6  | 0 | 9.467504   | -0.746960 | 0.891807  |
| 47  | 6  | 0 | 8.873703   | -1.236968 | -1.413868 |
| 48  | 6  | 0 | 10.806273  | -1.077370 | 0.618669  |
| 49  | 1  | 0 | 9.187653   | -0.438357 | 1.894579  |
| 50  | 6  | 0 | 10.212007  | -1.561788 | -1.688951 |
| 51  | 1  | 0 | 8.135766   | -1.312631 | -2.205250 |
| 52  | 6  | 0 | 11.185820  | -1.483408 | -0.674448 |
| 53  | 1  | 0 | 11.547422  | -1.016072 | 1.411838  |
| 54  | 1  | 0 | 10.491671  | -1.877235 | -2.690961 |
| 55  | 1  | 0 | 12.221695  | -1.735633 | -0.888241 |
| 56  | 6  | 0 | 2.135822   | 0.807679  | -1.700222 |
| 57  | 1  | 0 | 1.850373   | 1.448977  | -0.857126 |
| 58  | 1  | 0 | 2.552124   | 1.417848  | -2.503272 |
| 59  | 8  | 0 | 3.248330   | -0.075679 | -1.272521 |
| 60  | 1  | 0 | 3.015359   | -0.665333 | -0.480034 |
| 61  | 6  | 0 | 0.966101   | 0.037633  | -2.200284 |
| 62  | 6  | 0 | 0.570166   | -0.401761 | -3.446442 |
| 63  | 8  | 0 | 0.029711   | -0.387726 | -1.246119 |
| 64  | 6  | 0 | -0.665449  | -1.126164 | -3.271762 |
| 65  | 1  | 0 | 1.097094   | -0.232422 | -4.374207 |
| 66  | 6  | 0 | -0.966244  | -1.101499 | -1.925851 |
| 67  | 1  | 0 | -1.255709  | -1.596709 | -4.044610 |
| 68  | 6  | 0 | -2.097366  | -1.622934 | -1.112737 |
| 69  | 1  | 0 | -2.623611  | -2.402392 | -1.665757 |
| 70  | 1  | 0 | -1.744603  | -2.028628 | -0.156679 |
| 71  | 8  | 0 | -3.105999  | -0.574545 | -0.833558 |
| 72  | 1  | 0 | -2.861029  | 0.033794  | -0.060144 |
| 73  | 44 | 0 | -5.360476  | -0.678556 | -0.872658 |
| 74  | 6  | 0 | -5.611159  | 1.443107  | 0.007318  |
| 75  | 6  | 0 | -6.904910  | 0.780266  | 0.022954  |
| 76  | 6  | 0 | -6.809694  | -0.389239 | 0.901726  |
| 77  | 6  | 0 | -5.462733  | -0.456681 | 1.438059  |
| 78  | 6  | 0 | -4.727675  | 0.758148  | 0.984767  |
| 79  | 6  | 0 | -5.586878  | -0.350856 | -2.725985 |
| 80  | 8  | 0 | -5.743655  | -0.116611 | -3.874305 |
| 81  | 8  | 0 | -3.485273  | 1.021486  | 1.197349  |
| 82  | 6  | 0 | -5.606761  | -2.542888 | -1.126032 |
| 83  | 8  | 0 | -5.806147  | -3.702452 | -1.250914 |
| 84  | 6  | 0 | -4.917794  | -1.419749 | 2.427481  |
| 85  | 6  | 0 | -4.000171  | -0.965883 | 3.407517  |
| 86  | 6  | 0 | -5.290160  | -2.786910 | 2.436328  |
| 87  | 6  | 0 | -3.485950  | -1.850016 | 4.372551  |
| 88  | 1  | 0 | -3.682167  | 0.070723  | 3.397719  |
| 89  | 6  | 0 | -4.775670  | -3.667256 | 3.400474  |
| 90  | 1  | 0 | -5.980203  | -3.167039 | 1.689166  |
| 91  | 6  | 0 | -3.871038  | -3.203694 | 4.376672  |
| 92  | 1  | 0 | -2.782991  | -1.481607 | 5.116032  |
| 93  | 1  | 0 | -5.075700  | -4.712345 | 3.386921  |
| 94  | 1  | 0 | -3.470134  | -3.886984 | 5.121666  |
| 95  | 6  | 0 | -7.965455  | -1.233094 | 1.315258  |
| 96  | 6  | 0 | -8.277616  | -1.336716 | 2.691146  |
| 97  | 6  | 0 | -8.795435  | -1.884356 | 0.376982  |
| 98  | 6  | 0 | -9.396330  | -2.073516 | 3.116457  |
| 99  | 1  | 0 | -7.645454  | -0.843428 | 3.424512  |
| 100 | 6  | 0 | -9.911728  | -2.623568 | 0.802237  |
| 101 | 1  | 0 | -8.562237  | -1.813556 | -0.682043 |
| 102 | 6  | 0 | -10.218139 | -2.721035 | 2.173636  |

|     |   |   |            |           |           |
|-----|---|---|------------|-----------|-----------|
| 103 | 1 | 0 | -9.621770  | -2.144552 | 4.177734  |
| 104 | 1 | 0 | -10.537811 | -3.122320 | 0.066639  |
| 105 | 1 | 0 | -11.080953 | -3.295267 | 2.502484  |
| 106 | 6 | 0 | -5.276756  | 2.763447  | -0.587923 |
| 107 | 6 | 0 | -4.099773  | 2.940995  | -1.349760 |
| 108 | 6 | 0 | -6.097603  | 3.888030  | -0.336067 |
| 109 | 6 | 0 | -3.757189  | 4.206653  | -1.855563 |
| 110 | 1 | 0 | -3.455723  | 2.088856  | -1.546754 |
| 111 | 6 | 0 | -5.755317  | 5.153991  | -0.841934 |
| 112 | 1 | 0 | -6.998308  | 3.775058  | 0.260890  |
| 113 | 6 | 0 | -4.583702  | 5.319084  | -1.605216 |
| 114 | 1 | 0 | -2.848792  | 4.324196  | -2.441689 |
| 115 | 1 | 0 | -6.398472  | 6.007070  | -0.638451 |
| 116 | 1 | 0 | -4.318189  | 6.298450  | -1.996596 |
| 117 | 6 | 0 | -8.170004  | 1.326947  | -0.545671 |
| 118 | 6 | 0 | -9.285253  | 1.514264  | 0.305740  |
| 119 | 6 | 0 | -8.273574  | 1.739399  | -1.892951 |
| 120 | 6 | 0 | -10.472197 | 2.089827  | -0.180050 |
| 121 | 1 | 0 | -9.224775  | 1.215874  | 1.348004  |
| 122 | 6 | 0 | -9.460795  | 2.309683  | -2.380302 |
| 123 | 1 | 0 | -7.428891  | 1.619461  | -2.562747 |
| 124 | 6 | 0 | -10.567112 | 2.487132  | -1.526907 |
| 125 | 1 | 0 | -11.317480 | 2.224694  | 0.490372  |
| 126 | 1 | 0 | -9.519823  | 2.616225  | -3.421583 |
| 127 | 1 | 0 | -11.486085 | 2.928431  | -1.905206 |

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**B<sub>2</sub>-HBMF Dimer – ground state**  
**2-fragment counterpoise correction**

**Method: B3LYP/LANL2DZ counterpoise=2**

|           |             |                |            |           |
|-----------|-------------|----------------|------------|-----------|
| SCF Done: | E(RB3LYP) = | -3484.55182367 | A.U. after | 22 cycles |
|           | Conv        | = 0.7733D-08   | -V/T =     | 2.0427    |
| SCF Done: | E(RB3LYP) = | -1971.79067319 | A.U. after | 21 cycles |
|           | Conv        | = 0.3578D-08   | -V/T =     | 2.0383    |
| SCF Done: | E(RB3LYP) = | -1512.72852689 | A.U. after | 21 cycles |
|           | Conv        | = 0.4213D-08   | -V/T =     | 2.0486    |
| SCF Done: | E(RB3LYP) = | -1971.78603784 | A.U. after | 21 cycles |
|           | Conv        | = 0.5462D-08   | -V/T =     | 2.0383    |
| SCF Done: | E(RB3LYP) = | -1512.72588970 | A.U. after | 20 cycles |
|           | Conv        | = 0.6997D-08   | -V/T =     | 2.0486    |

Counterpoise: corrected energy = -3484.544551135750  
Counterpoise: BSSE energy = 0.007272538902

Lowest frequency: +3.55

**Thermochemistry**

|                                              |                             |
|----------------------------------------------|-----------------------------|
| Zero-point correction=                       | 0.975506 (Hartree/Particle) |
| Thermal correction to Energy=                | 1.045993                    |
| Thermal correction to Enthalpy=              | 1.046938                    |
| Thermal correction to Gibbs Free Energy=     | 0.853720                    |
| Sum of electronic and zero-point Energies=   | -3483.569045                |
| Sum of electronic and thermal Energies=      | -3483.498558                |
| Sum of electronic and thermal Enthalpies=    | -3483.497614                |
| Sum of electronic and thermal Free Energies= | -3483.690831                |

**XYZ coordinates**

Charge = 0 Multiplicity = 1 in supermolecule  
Charge = 0 Multiplicity = 1 in fragment 1.  
Charge = 0 Multiplicity = 1 in fragment 2.

|                |         |          |          |
|----------------|---------|----------|----------|
| Ru(Fragment=1) | 5.39513 | 0.5814   | -0.91272 |
| C(Fragment=1)  | 5.90698 | -1.43596 | 0.08994  |
| C(Fragment=1)  | 7.03936 | -0.54074 | 0.25435  |
| C(Fragment=1)  | 6.6034  | 0.60791  | 1.05392  |
| C(Fragment=1)  | 5.20378 | 0.42821  | 1.39807  |
| C(Fragment=1)  | 4.78074 | -0.9132  | 0.90581  |
| C(Fragment=1)  | 5.9561  | 0.2829   | -2.69902 |
| O(Fragment=1)  | 6.32594 | 0.07148  | -3.8021  |
| O(Fragment=1)  | 3.59318 | -1.40778 | 0.95845  |
| C(Fragment=1)  | 5.30912 | 2.45429  | -1.20586 |
| O(Fragment=1)  | 5.29699 | 3.62876  | -1.34752 |
| C(Fragment=1)  | 4.35153 | 1.29174  | 2.2541   |
| C(Fragment=1)  | 3.3801  | 0.69607  | 3.0968   |
| C(Fragment=1)  | 4.47523 | 2.70361  | 2.26429  |
| C(Fragment=1)  | 2.57061 | 1.48798  | 3.93044  |
| H(Fragment=1)  | 3.25133 | -0.38026 | 3.08015  |
| C(Fragment=1)  | 3.6668  | 3.4914   | 3.09782  |
| H(Fragment=1)  | 5.20004 | 3.19084  | 1.61946  |
| C(Fragment=1)  | 2.70932 | 2.88834  | 3.9379   |
| H(Fragment=1)  | 1.82873 | 1.01066  | 4.56619  |
| H(Fragment=1)  | 3.77876 | 4.57297  | 3.0865   |
| H(Fragment=1)  | 2.07875 | 3.50005  | 4.57876  |
| C(Fragment=1)  | 7.51411 | 1.66287  | 1.5795   |
| C(Fragment=1)  | 7.60529 | 1.85504  | 2.97798  |

|                 |          |          |          |
|-----------------|----------|----------|----------|
| C (Fragment=1)  | 8.33498  | 2.43589  | 0.73     |
| C (Fragment=1)  | 8.50021  | 2.79805  | 3.51223  |
| H (Fragment=1)  | 6.97601  | 1.27005  | 3.64332  |
| C (Fragment=1)  | 9.22716  | 3.38066  | 1.26359  |
| H (Fragment=1)  | 8.26868  | 2.29725  | -0.34577 |
| C (Fragment=1)  | 9.31489  | 3.56555  | 2.65727  |
| H (Fragment=1)  | 8.55708  | 2.9353   | 4.58932  |
| H (Fragment=1)  | 9.84878  | 3.97058  | 0.59468  |
| H (Fragment=1)  | 10.00364 | 4.29863  | 3.07026  |
| C (Fragment=1)  | 5.90994  | -2.8055  | -0.48718 |
| C (Fragment=1)  | 4.9092   | -3.21116 | -1.39873 |
| C (Fragment=1)  | 6.87697  | -3.7524  | -0.07498 |
| C (Fragment=1)  | 4.88079  | -4.52633 | -1.89327 |
| H (Fragment=1)  | 4.15843  | -2.49531 | -1.72076 |
| C (Fragment=1)  | 6.84971  | -5.06746 | -0.57059 |
| H (Fragment=1)  | 7.64567  | -3.4629  | 0.63627  |
| C (Fragment=1)  | 5.85148  | -5.46047 | -1.48262 |
| H (Fragment=1)  | 4.10408  | -4.82091 | -2.59508 |
| H (Fragment=1)  | 7.60182  | -5.78182 | -0.24377 |
| H (Fragment=1)  | 5.82936  | -6.47825 | -1.86541 |
| C (Fragment=1)  | 8.45163  | -0.85002 | -0.10885 |
| C (Fragment=1)  | 9.44729  | -0.80912 | 0.89643  |
| C (Fragment=1)  | 8.82172  | -1.26321 | -1.40818 |
| C (Fragment=1)  | 10.77626 | -1.16431 | 0.60706  |
| H (Fragment=1)  | 9.18345  | -0.50517 | 1.9049   |
| C (Fragment=1)  | 10.15026 | -1.6129  | -1.69939 |
| H (Fragment=1)  | 8.07494  | -1.31588 | -2.19311 |
| C (Fragment=1)  | 11.13506 | -1.56492 | -0.69362 |
| H (Fragment=1)  | 11.52596 | -1.12649 | 1.39363  |
| H (Fragment=1)  | 10.41378 | -1.9241  | -2.70709 |
| H (Fragment=1)  | 12.16339 | -1.8364  | -0.9199  |
| C (Fragment=1)  | 2.12331  | 0.91366  | -1.62274 |
| H (Fragment=1)  | 1.80938  | 1.50765  | -0.7555  |
| H (Fragment=1)  | 2.55905  | 1.56827  | -2.37897 |
| O (Fragment=1)  | 3.22731  | 0.01324  | -1.20848 |
| H (Fragment=1)  | 2.9877   | -0.58702 | -0.42634 |
| C (Fragment=1)  | 0.97445  | 0.16721  | -2.20046 |
| C (Fragment=1)  | 0.60775  | -0.18143 | -3.48344 |
| O (Fragment=1)  | 0.02576  | -0.33923 | -1.29939 |
| C (Fragment=1)  | -0.62201 | -0.93077 | -3.38807 |
| H (Fragment=1)  | 1.15009  | 0.06296  | -4.38528 |
| C (Fragment=1)  | -0.9491  | -1.01066 | -2.05052 |
| H (Fragment=1)  | -1.19056 | -1.34987 | -4.20527 |
| C (Fragment=1)  | -2.08361 | -1.6142  | -1.29847 |
| H (Fragment=1)  | -2.59823 | -2.34114 | -1.92836 |
| H (Fragment=1)  | -1.7331  | -2.10803 | -0.3835  |
| O (Fragment=1)  | -3.10911 | -0.61175 | -0.93755 |
| H (Fragment=1)  | -2.83824 | -0.00349 | -0.17741 |
| Ru (Fragment=2) | -5.38977 | -0.73877 | -0.90456 |
| C (Fragment=2)  | -5.62067 | 1.40459  | -0.07179 |
| C (Fragment=2)  | -6.9118  | 0.74329  | -0.00527 |
| C (Fragment=2)  | -6.79121 | -0.40731 | 0.89668  |
| C (Fragment=2)  | -5.43253 | -0.45625 | 1.40472  |
| C (Fragment=2)  | -4.71212 | 0.75085  | 0.90676  |
| C (Fragment=2)  | -5.68936 | -0.47142 | -2.75789 |
| O (Fragment=2)  | -5.89227 | -0.27515 | -3.90645 |
| O (Fragment=2)  | -3.47071 | 1.03041  | 1.08857  |
| C (Fragment=2)  | -5.61894 | -2.61447 | -1.09167 |
| O (Fragment=2)  | -5.80327 | -3.78032 | -1.1728  |
| C (Fragment=2)  | -4.8645  | -1.39322 | 2.40626  |
| C (Fragment=2)  | -3.92409 | -0.91498 | 3.35265  |
| C (Fragment=2)  | -5.23634 | -2.75969 | 2.45941  |
| C (Fragment=2)  | -3.38692 | -1.77432 | 4.32763  |

|                |           |          |          |
|----------------|-----------|----------|----------|
| H (Fragment=2) | -3.60626  | 0.12075  | 3.30865  |
| C (Fragment=2) | -4.6991   | -3.61514 | 3.43349  |
| H (Fragment=2) | -5.94338  | -3.15912 | 1.73879  |
| C (Fragment=2) | -3.77165  | -3.1272  | 4.37576  |
| H (Fragment=2) | -2.66606  | -1.38719 | 5.04395  |
| H (Fragment=2) | -4.99894  | -4.66019 | 3.45369  |
| H (Fragment=2) | -3.35272  | -3.79149 | 5.128    |
| C (Fragment=2) | -7.93383  | -1.24411 | 1.35883  |
| C (Fragment=2) | -8.21994  | -1.30524 | 2.74289  |
| C (Fragment=2) | -8.77575  | -1.93101 | 0.45742  |
| C (Fragment=2) | -9.32595  | -2.03452 | 3.21225  |
| H (Fragment=2) | -7.57751  | -0.78469 | 3.44797  |
| C (Fragment=2) | -9.87953  | -2.66249 | 0.92674  |
| H (Fragment=2) | -8.56148  | -1.89301 | -0.60724 |
| C (Fragment=2) | -10.16062 | -2.71681 | 2.30591  |
| H (Fragment=2) | -9.53153  | -2.07276 | 4.27923  |
| H (Fragment=2) | -10.51551 | -3.18874 | 0.21934  |
| H (Fragment=2) | -11.01375 | -3.28498 | 2.66881  |
| C (Fragment=2) | -5.30867  | 2.71455  | -0.70196 |
| C (Fragment=2) | -4.18613  | 2.87062  | -1.54497 |
| C (Fragment=2) | -6.09671  | 3.85132  | -0.40403 |
| C (Fragment=2) | -3.86344  | 4.12782  | -2.08467 |
| H (Fragment=2) | -3.56868  | 2.00746  | -1.77699 |
| C (Fragment=2) | -5.77522  | 5.10864  | -0.94389 |
| H (Fragment=2) | -6.95597  | 3.75351  | 0.254    |
| C (Fragment=2) | -4.65714  | 5.25252  | -1.78775 |
| H (Fragment=2) | -2.99621  | 4.22891  | -2.73296 |
| H (Fragment=2) | -6.3924   | 5.97152  | -0.70435 |
| H (Fragment=2) | -4.40744  | 6.22532  | -2.20509 |
| C (Fragment=2) | -8.18822  | 1.27634  | -0.56002 |
| C (Fragment=2) | -9.30078  | 1.44898  | 0.29802  |
| C (Fragment=2) | -8.30333  | 1.69411  | -1.90514 |
| C (Fragment=2) | -10.49626 | 2.01375  | -0.17967 |
| H (Fragment=2) | -9.23227  | 1.14861  | 1.33896  |
| C (Fragment=2) | -9.49902  | 2.25286  | -2.38428 |
| H (Fragment=2) | -7.46015  | 1.58744  | -2.57916 |
| C (Fragment=2) | -10.60289 | 2.41463  | -1.52447 |
| H (Fragment=2) | -11.33913 | 2.13757  | 0.49592  |
| H (Fragment=2) | -9.56669  | 2.56295  | -3.42396 |
| H (Fragment=2) | -11.52869 | 2.84715  | -1.89622 |

#####

### B<sub>2</sub>-HBMF Dimer – ground state 3-fragment counterpoise correction

#### Method: B3LYP/LANL2Z counterpoise = 3

|           |             |                |            |           |
|-----------|-------------|----------------|------------|-----------|
| SCF Done: | E(RB3LYP) = | -3484.55160283 | A.U. after | 22 cycles |
|           | Conv        | = 0.5340D-08   | -V/T =     | 2.0427    |
|           |             |                |            |           |
| SCF Done: | E(RB3LYP) = | -1512.72871115 | A.U. after | 21 cycles |
|           | Conv        | = 0.4359D-08   | -V/T =     | 2.0486    |
|           |             |                |            |           |
| SCF Done: | E(RB3LYP) = | -1512.72859098 | A.U. after | 21 cycles |
|           | Conv        | = 0.4616D-08   | -V/T =     | 2.0486    |
|           |             |                |            |           |
| SCF Done: | E(RB3LYP) = | -459.028199632 | A.U. after | 11 cycles |
|           | Conv        | = 0.2992D-08   | -V/T =     | 2.0058    |

SCF Done: E(RB3LYP) = -1512.72612801 A.U. after 19 cycles  
Convrg = 0.9814D-08 -V/T = 2.0486

SCF Done: E(RB3LYP) = -1512.72602517 A.U. after 20 cycles  
Convrg = 0.6622D-08 -V/T = 2.0486

SCF Done: E(RB3LYP) = -459.018767302 A.U. after 15 cycles  
Convrg = 0.3715D-08 -V/T = 2.0057

Counterpoise: corrected energy = -3484.537021543276

Counterpoise: BSSE energy = 0.014581286216

Lowest frequency: 3.95

### Thermochemistry

|                                              |                             |
|----------------------------------------------|-----------------------------|
| Zero-point correction=                       | 0.975737 (Hartree/Particle) |
| Thermal correction to Energy=                | 1.046220                    |
| Thermal correction to Enthalpy=              | 1.047164                    |
| Thermal correction to Gibbs Free Energy=     | 0.853999                    |
| Sum of electronic and zero-point Energies=   | -3483.561285                |
| Sum of electronic and thermal Energies=      | -3483.490802                |
| Sum of electronic and thermal Enthalpies=    | -3483.489858                |
| Sum of electronic and thermal Free Energies= | -3483.683023                |

### XYZ coordinates

Charge = 0 Multiplicity = 1 in supermolecule  
Charge = 0 Multiplicity = 1 in fragment 1.  
Charge = 0 Multiplicity = 1 in fragment 2.  
Charge = 0 Multiplicity = 1 in fragment 3.

|                |          |          |          |
|----------------|----------|----------|----------|
| Ru(Fragment=1) | 5.43376  | 0.70241  | -0.72811 |
| C(Fragment=1)  | 5.78759  | -1.35269 | 0.27251  |
| C(Fragment=1)  | 7.02388  | -0.59308 | 0.32725  |
| C(Fragment=1)  | 6.78819  | 0.60851  | 1.1355   |
| C(Fragment=1)  | 5.41189  | 0.59378  | 1.59629  |
| C(Fragment=1)  | 4.79846  | -0.6962  | 1.16811  |
| C(Fragment=1)  | 5.81736  | 0.32505  | -2.5464  |
| O(Fragment=1)  | 6.07303  | 0.06248  | -3.67098 |
| O(Fragment=1)  | 3.57404  | -1.05252 | 1.33075  |
| C(Fragment=1)  | 5.53144  | 2.57135  | -1.04647 |
| O(Fragment=1)  | 5.63126  | 3.73921  | -1.20731 |
| C(Fragment=1)  | 4.74055  | 1.55805  | 2.50388  |
| C(Fragment=1)  | 3.79181  | 1.08574  | 3.44511  |
| C(Fragment=1)  | 5.01955  | 2.9472   | 2.47067  |
| C(Fragment=1)  | 3.15538  | 1.974    | 4.33034  |
| H(Fragment=1)  | 3.5449   | 0.0302   | 3.46637  |
| C(Fragment=1)  | 4.38346  | 3.83141  | 3.35529  |
| H(Fragment=1)  | 5.73168  | 3.34196  | 1.75276  |
| C(Fragment=1)  | 3.44749  | 3.35014  | 4.29254  |
| H(Fragment=1)  | 2.42923  | 1.59049  | 5.04321  |
| H(Fragment=1)  | 4.61304  | 4.8933   | 3.30931  |
| H(Fragment=1)  | 2.95134  | 4.03657  | 4.97464  |
| C(Fragment=1)  | 7.85144  | 1.55796  | 1.56838  |
| C(Fragment=1)  | 8.0813   | 1.74068  | 2.9523   |
| C(Fragment=1)  | 8.67606  | 2.23679  | 0.6451   |
| C(Fragment=1)  | 9.11491  | 2.58114  | 3.40032  |
| H(Fragment=1)  | 7.45123  | 1.2276   | 3.67385  |
| C(Fragment=1)  | 9.70685  | 3.07987  | 1.09286  |
| H(Fragment=1)  | 8.50589  | 2.10623  | -0.42013 |
| C(Fragment=1)  | 9.93211  | 3.25517  | 2.47217  |
| H(Fragment=1)  | 9.27755  | 2.71177  | 4.4674   |
| H(Fragment=1)  | 10.32965 | 3.59845  | 0.36825  |
| H(Fragment=1)  | 10.72888 | 3.90928  | 2.81803  |
| C(Fragment=1)  | 5.59173  | -2.72606 | -0.2617  |

|                 |          |          |          |
|-----------------|----------|----------|----------|
| C (Fragment=1)  | 4.48812  | -3.03656 | -1.08738 |
| C (Fragment=1)  | 6.47157  | -3.76871 | 0.11402  |
| C (Fragment=1)  | 4.27374  | -4.35184 | -1.53413 |
| H (Fragment=1)  | 3.80019  | -2.24831 | -1.37915 |
| C (Fragment=1)  | 6.25809  | -5.08413 | -0.33299 |
| H (Fragment=1)  | 7.31789  | -3.55285 | 0.76042  |
| C (Fragment=1)  | 5.15816  | -5.38191 | -1.16024 |
| H (Fragment=1)  | 3.41951  | -4.5716  | -2.17023 |
| H (Fragment=1)  | 6.94512  | -5.8724  | -0.03392 |
| H (Fragment=1)  | 4.99204  | -6.39971 | -1.50568 |
| C (Fragment=1)  | 8.35589  | -1.06588 | -0.1455  |
| C (Fragment=1)  | 9.44175  | -1.1022  | 0.76171  |
| C (Fragment=1)  | 8.55497  | -1.55782 | -1.45512 |
| C (Fragment=1)  | 10.69252 | -1.60746 | 0.36597  |
| H (Fragment=1)  | 9.30975  | -0.74151 | 1.77713  |
| C (Fragment=1)  | 9.80537  | -2.05788 | -1.85266 |
| H (Fragment=1)  | 7.73463  | -1.55426 | -2.16489 |
| C (Fragment=1)  | 10.88172 | -2.08444 | -0.94452 |
| H (Fragment=1)  | 11.51384 | -1.62611 | 1.07821  |
| H (Fragment=1)  | 9.93704  | -2.42704 | -2.86659 |
| H (Fragment=1)  | 11.84999 | -2.47138 | -1.2529  |
| C (Fragment=3)  | 2.10143  | 1.31586  | -1.2908  |
| H (Fragment=3)  | 1.71394  | 1.87855  | -0.43231 |
| H (Fragment=3)  | 2.59071  | 2.00203  | -1.98348 |
| O (Fragment=3)  | 3.1714   | 0.40686  | -0.82485 |
| H (Fragment=3)  | 2.91382  | -0.15617 | -0.02648 |
| C (Fragment=3)  | 1.00682  | 0.58936  | -1.99137 |
| C (Fragment=3)  | 0.72369  | 0.33379  | -3.31662 |
| O (Fragment=3)  | 0.02204  | -0.0068  | -1.18947 |
| C (Fragment=3)  | -0.48778 | -0.45047 | -3.35201 |
| H (Fragment=3)  | 1.30909  | 0.66075  | -4.16352 |
| C (Fragment=3)  | -0.8889  | -0.64226 | -2.04669 |
| H (Fragment=3)  | -0.99625 | -0.81849 | -4.23112 |
| C (Fragment=3)  | -2.04693 | -1.32961 | -1.41193 |
| H (Fragment=3)  | -2.48411 | -2.04128 | -2.11369 |
| H (Fragment=3)  | -1.74101 | -1.85653 | -0.49939 |
| O (Fragment=3)  | -3.14114 | -0.39041 | -1.07999 |
| H (Fragment=3)  | -2.92551 | 0.23002  | -0.3119  |
| Ru (Fragment=2) | -5.40311 | -0.71549 | -1.04523 |
| C (Fragment=2)  | -5.82198 | 1.39311  | -0.19745 |
| C (Fragment=2)  | -7.04828 | 0.61745  | -0.13348 |
| C (Fragment=2)  | -6.82324 | -0.5228  | 0.76187  |
| C (Fragment=2)  | -5.46407 | -0.45394 | 1.26549  |
| C (Fragment=2)  | -4.85626 | 0.81659  | 0.77466  |
| C (Fragment=2)  | -5.72493 | -0.45798 | -2.89611 |
| O (Fragment=2)  | -5.94332 | -0.26853 | -4.04298 |
| O (Fragment=2)  | -3.6444  | 1.20486  | 0.95645  |
| C (Fragment=2)  | -5.46702 | -2.60249 | -1.2492  |
| O (Fragment=2)  | -5.54796 | -3.77921 | -1.34156 |
| C (Fragment=2)  | -4.80967 | -1.34326 | 2.25787  |
| C (Fragment=2)  | -3.91278 | -0.78952 | 3.20533  |
| C (Fragment=2)  | -5.05548 | -2.73829 | 2.30012  |
| C (Fragment=2)  | -3.29516 | -1.60462 | 4.17061  |
| H (Fragment=2)  | -3.69063 | 0.27115  | 3.16953  |
| C (Fragment=2)  | -4.43834 | -3.54949 | 3.26466  |
| H (Fragment=2)  | -5.72652 | -3.19394 | 1.57847  |
| C (Fragment=2)  | -3.55497 | -2.98726 | 4.20795  |
| H (Fragment=2)  | -2.60848 | -1.15963 | 4.88682  |
| H (Fragment=2)  | -4.64157 | -4.61766 | 3.27657  |
| H (Fragment=2)  | -3.07346 | -3.61721 | 4.95218  |
| C (Fragment=2)  | -7.88637 | -1.46012 | 1.22017  |
| C (Fragment=2)  | -8.1567  | -1.56267 | 2.60499  |
| C (Fragment=2)  | -8.67392 | -2.20431 | 0.31494  |

|                |           |          |          |
|----------------|-----------|----------|----------|
| C (Fragment=2) | -9.19401  | -2.38854 | 3.07133  |
| H (Fragment=2) | -7.55589  | -0.99835 | 3.31305  |
| C (Fragment=2) | -9.70833  | -3.03262 | 0.78125  |
| H (Fragment=2) | -8.47204  | -2.13536 | -0.75056 |
| C (Fragment=2) | -9.97423  | -3.12778 | 2.16124  |
| H (Fragment=2) | -9.38834  | -2.45693 | 4.13892  |
| H (Fragment=2) | -10.3025  | -3.6019  | 0.07081  |
| H (Fragment=2) | -10.77386 | -3.77039 | 2.52175  |
| C (Fragment=2) | -5.62885  | 2.72813  | -0.82247 |
| C (Fragment=2) | -4.51436  | 2.99216  | -1.64954 |
| C (Fragment=2) | -6.52733  | 3.78359  | -0.53834 |
| C (Fragment=2) | -4.30758  | 4.27426  | -2.18723 |
| H (Fragment=2) | -3.81272  | 2.19321  | -1.87194 |
| C (Fragment=2) | -6.32169  | 5.06572  | -1.07645 |
| H (Fragment=2) | -7.38303  | 3.60363  | 0.10677  |
| C (Fragment=2) | -5.21078  | 5.31702  | -1.90439 |
| H (Fragment=2) | -3.44501  | 4.45829  | -2.82342 |
| H (Fragment=2) | -7.02358  | 5.86441  | -0.84784 |
| H (Fragment=2) | -5.05074  | 6.30904  | -2.32048 |
| C (Fragment=2) | -8.37037  | 1.03671  | -0.67921 |
| C (Fragment=2) | -9.48409  | 1.11961  | 0.19058  |
| C (Fragment=2) | -8.53532  | 1.4332   | -2.02539 |
| C (Fragment=2) | -10.72831 | 1.57794  | -0.27637 |
| H (Fragment=2) | -9.37888  | 0.83116  | 1.23197  |
| C (Fragment=2) | -9.7792   | 1.88626  | -2.4937  |
| H (Fragment=2) | -7.69416  | 1.39136  | -2.70906 |
| C (Fragment=2) | -10.88311 | 1.96005  | -1.62206 |
| H (Fragment=2) | -11.57134 | 1.63381  | 0.40799  |
| H (Fragment=2) | -9.88436  | 2.18249  | -3.5343  |
| H (Fragment=2) | -11.84621 | 2.31045  | -1.98542 |

### A + furfural Transition State

#### Method: B3LYP/LANL2DZ

SCF Done: E(RB3LYP) = -1857.23122719 A.U. after 19 cycles  
Convrg = 0.8288D-08 -V/T = 2.0403  
Lowest frequency: -836.13  
Second frequency: +8.13

#### Thermochemistry

Zero-point correction= 0.514771 (Hartree/Particle)  
Thermal correction to Energy= 0.551046  
Thermal correction to Enthalpy= 0.551990  
Thermal correction to Gibbs Free Energy= 0.440947  
Sum of electronic and zero-point Energies= -1856.716456  
Sum of electronic and thermal Energies= -1856.680181  
Sum of electronic and thermal Enthalpies= -1856.679237  
Sum of electronic and thermal Free Energies= -1856.790281

#### XYZ coordinates

Charge = 0 Multiplicity = 1

|    |          |          |          |
|----|----------|----------|----------|
| Ru | 0.45198  | -0.19786 | -0.74095 |
| C  | -0.01299 | 1.19118  | 1.07259  |
| C  | -1.22544 | 1.07605  | 0.26901  |
| C  | -1.63403 | -0.32685 | 0.26394  |
| C  | -0.68751 | -1.08904 | 1.07484  |
| C  | 0.25974  | -0.12743 | 1.65763  |
| C  | 1.16177  | 1.0109   | -2.01817 |
| O  | 1.61821  | 1.77899  | -2.79078 |
| C  | 0.36952  | -1.60166 | -2.00731 |
| O  | 0.32655  | -2.5057  | -2.76889 |
| C  | -0.7651  | -2.52183 | 1.46013  |
| C  | -0.39189 | -2.91234 | 2.77037  |
| C  | -1.21784 | -3.51959 | 0.56261  |
| C  | -0.4834  | -4.25732 | 3.17031  |
| H  | -0.02038 | -2.16475 | 3.46254  |
| C  | -1.30789 | -4.86134 | 0.96428  |
| H  | -1.49962 | -3.25163 | -0.45109 |
| C  | -0.9428  | -5.23864 | 2.27193  |
| H  | -0.19243 | -4.53631 | 4.18025  |
| H  | -1.65733 | -5.61028 | 0.25769  |
| H  | -1.01037 | -6.27881 | 2.58177  |
| C  | -2.90272 | -0.85437 | -0.31182 |
| C  | -3.86644 | -1.41646 | 0.55803  |
| C  | -3.19549 | -0.77117 | -1.6904  |
| C  | -5.09567 | -1.88103 | 0.05897  |
| H  | -3.65164 | -1.49145 | 1.621    |
| C  | -4.42427 | -1.23552 | -2.18979 |
| H  | -2.45976 | -0.34367 | -2.36646 |
| C  | -5.3802  | -1.79191 | -1.3176  |
| H  | -5.82462 | -2.31274 | 0.74048  |
| H  | -4.6328  | -1.1657  | -3.25448 |
| H  | -6.3297  | -2.1536  | -1.70478 |
| C  | 0.66739  | 2.42761  | 1.54164  |
| C  | 2.0768   | 2.53089  | 1.54015  |
| C  | -0.0922  | 3.49029  | 2.08572  |
| C  | 2.70969  | 3.67528  | 2.05516  |
| H  | 2.68273  | 1.71966  | 1.14677  |
| C  | 0.54141  | 4.63433  | 2.59998  |

|   |          |          |          |
|---|----------|----------|----------|
| H | -1.17603 | 3.41965  | 2.11335  |
| C | 1.94604  | 4.73313  | 2.58464  |
| H | 3.79513  | 3.73566  | 2.04705  |
| H | -0.05819 | 5.44142  | 3.01436  |
| H | 2.43737  | 5.61763  | 2.98339  |
| C | -1.99759 | 2.20872  | -0.31128 |
| C | -3.39764 | 2.28317  | -0.11732 |
| C | -1.35709 | 3.26194  | -1.00632 |
| C | -4.13477 | 3.37424  | -0.61056 |
| H | -3.91117 | 1.49724  | 0.42685  |
| C | -2.09319 | 4.34852  | -1.50248 |
| H | -0.28375 | 3.23158  | -1.16297 |
| C | -3.48745 | 4.41075  | -1.30805 |
| H | -5.20936 | 3.41211  | -0.44947 |
| H | -1.58032 | 5.14334  | -2.03805 |
| H | -4.05769 | 5.25277  | -1.69288 |
| C | 6.04129  | -0.36699 | -1.67724 |
| C | 5.52519  | -1.2501  | -2.60294 |
| O | 5.23202  | -0.33688 | -0.54453 |
| C | 4.33584  | -1.81312 | -2.01718 |
| H | 5.94105  | -1.47674 | -3.57325 |
| C | 4.19346  | -1.2473  | -0.7609  |
| H | 3.67907  | -2.54669 | -2.46339 |
| C | 3.13034  | -1.37321 | 0.25242  |
| H | 2.66135  | -2.36842 | 0.25268  |
| H | 2.07258  | -0.69942 | -0.3453  |
| O | 3.32834  | -0.79859 | 1.44768  |
| H | 6.90894  | 0.2725   | -1.65377 |
| O | 1.23632  | -0.41022 | 2.48828  |
| H | 2.36908  | -0.65689 | 2.08573  |

## References

<sup>1</sup> HMF - <sup>1</sup>H-NMR (toluene-*d*<sub>8</sub>): C(O)H 9.25 ppm, CH furan 6.50 and 5.83 ppm, CH<sub>2</sub>OH 4.00 ppm) BHMF - <sup>1</sup>H-NMR (tolulene-*d*<sub>8</sub>): CH furan 5.89 ppm, CH<sub>2</sub>OH 4.18 ppm). All the other signals registered are ascribable to Shvo complex **1** and toluene-*d*<sub>8</sub>.

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