

# SUPPORTING INFORMATION

## Photochemistry of Dicarbonyl-Substituted Benzenes: Influence of Steric and Electronic Factors in the Cyclization and Diels-Alder Trapping Reactions of Photoenols

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Dedicated to Prof. Waldemar Adam on the occasion of his 70th birth anniversary

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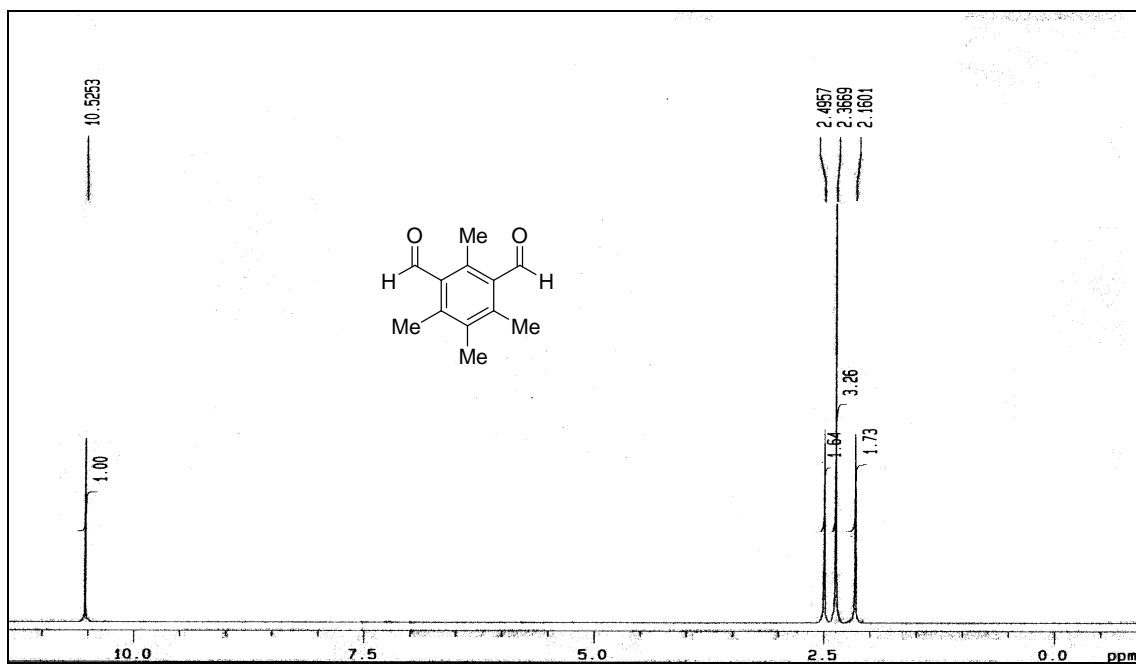


Figure S1.  $^1\text{H}$  NMR spectrum of 2, 4, 5, 6-Tetramethylisophthalaldehyde.

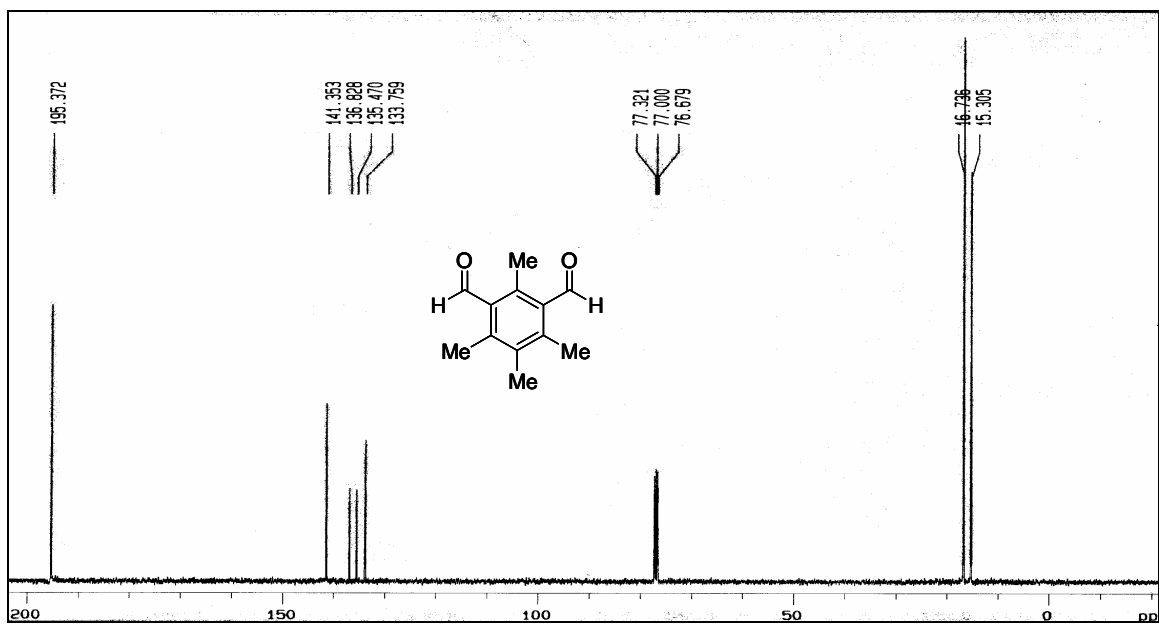


Figure S2.  $^{13}\text{C}$  NMR spectrum of 2, 4, 5, 6-Tetramethylisophthalaldehyde.

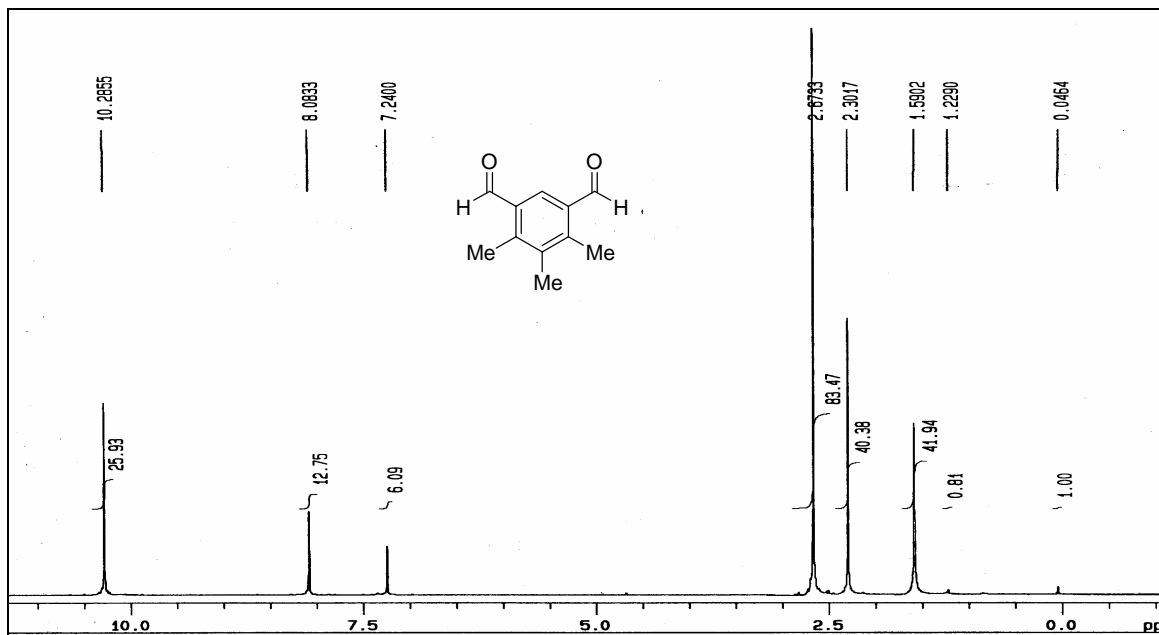


Figure S3.  $^1\text{H}$  NMR spectrum of 4, 5, 6-Trimethylisophthalaldehyde.

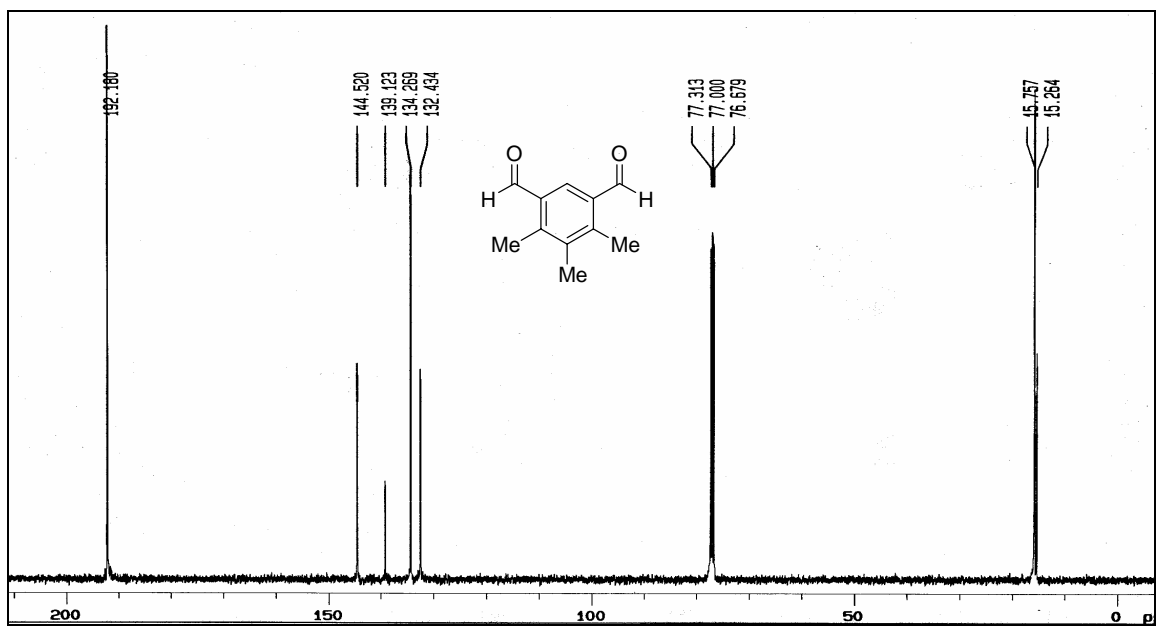


Figure S4.  $^{13}\text{C}$  NMR spectrum of 4, 5, 6-Trimethylisophthalaldehyde.

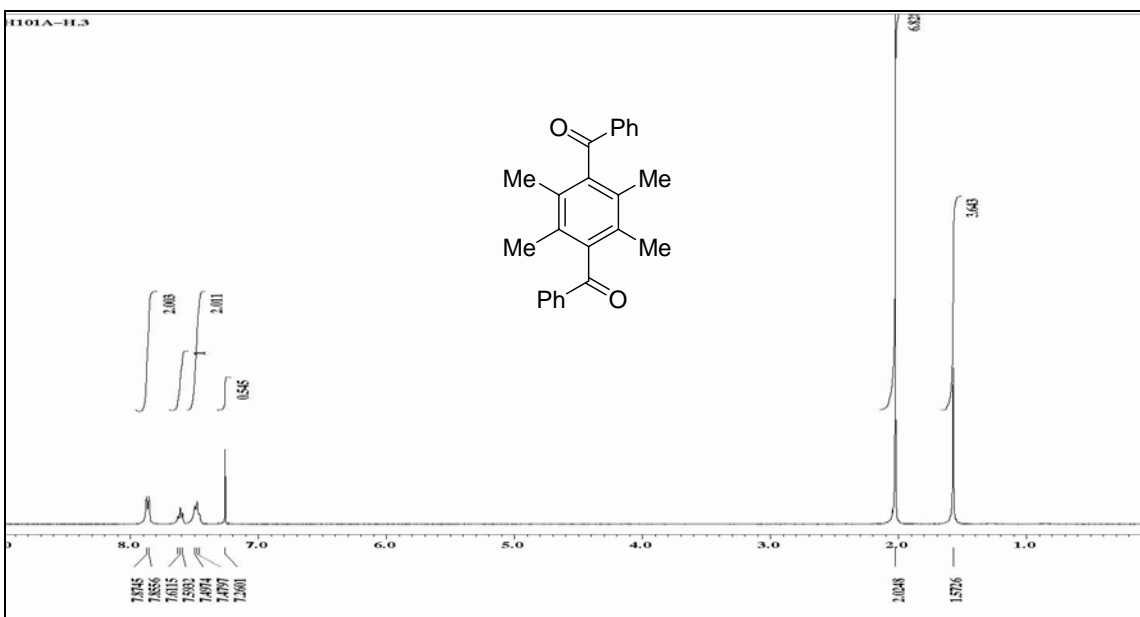


Figure S5.  $^1\text{H}$  NMR spectrum of ketone **1a**.

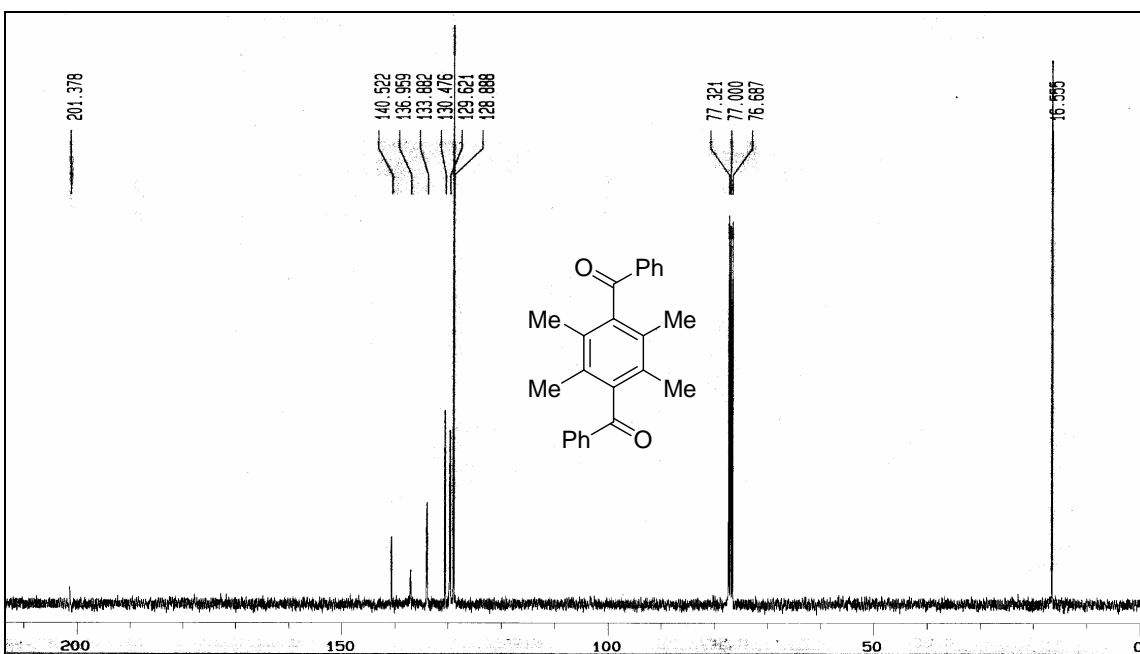


Figure S6.  $^{13}\text{C}$  NMR spectrum of ketone **1a**.

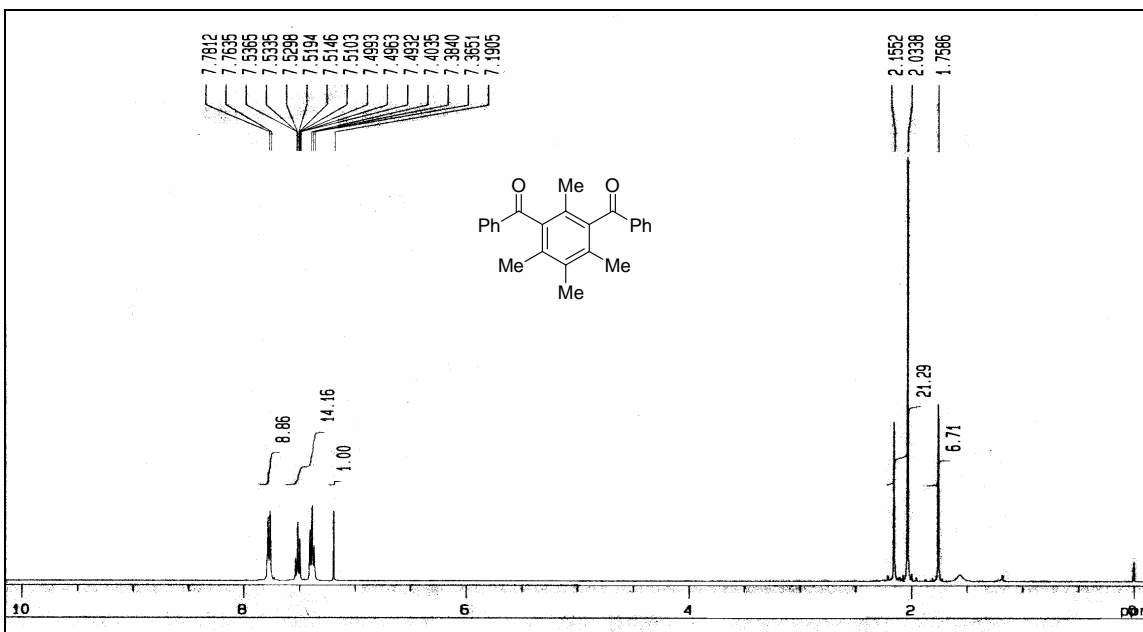


Figure S7.  $^1\text{H NMR}$  spectrum of ketone **2a**.

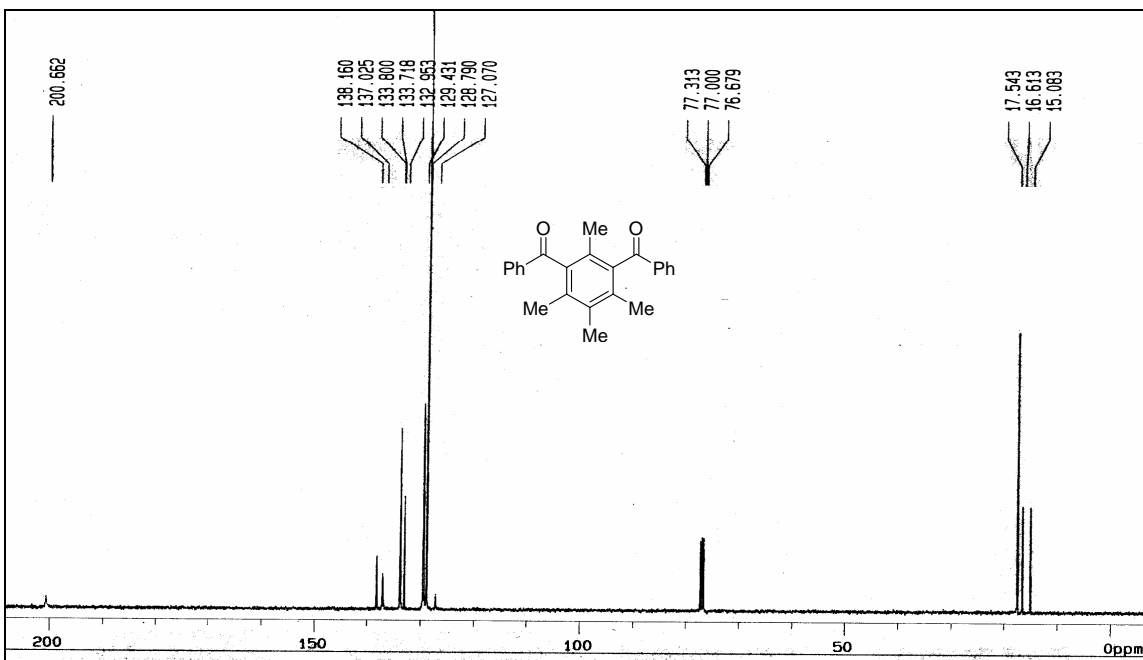


Figure S8.  $^{13}\text{C NMR}$  spectrum of ketone **2a**.

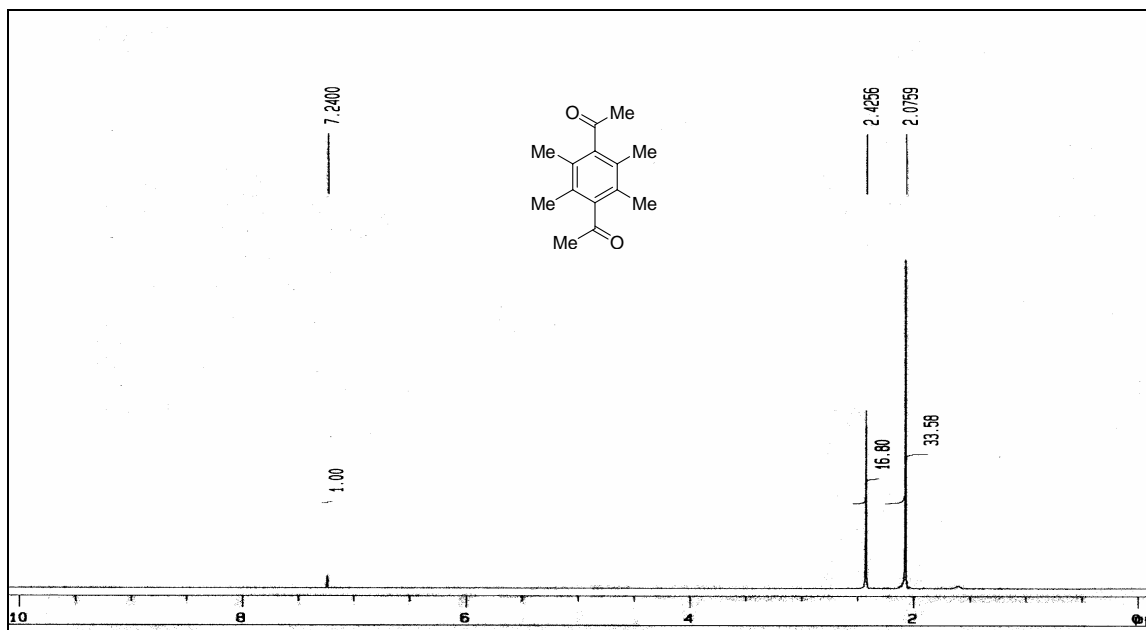


Figure S9.  $^1\text{H}$  NMR spectrum of ketone **1b**.

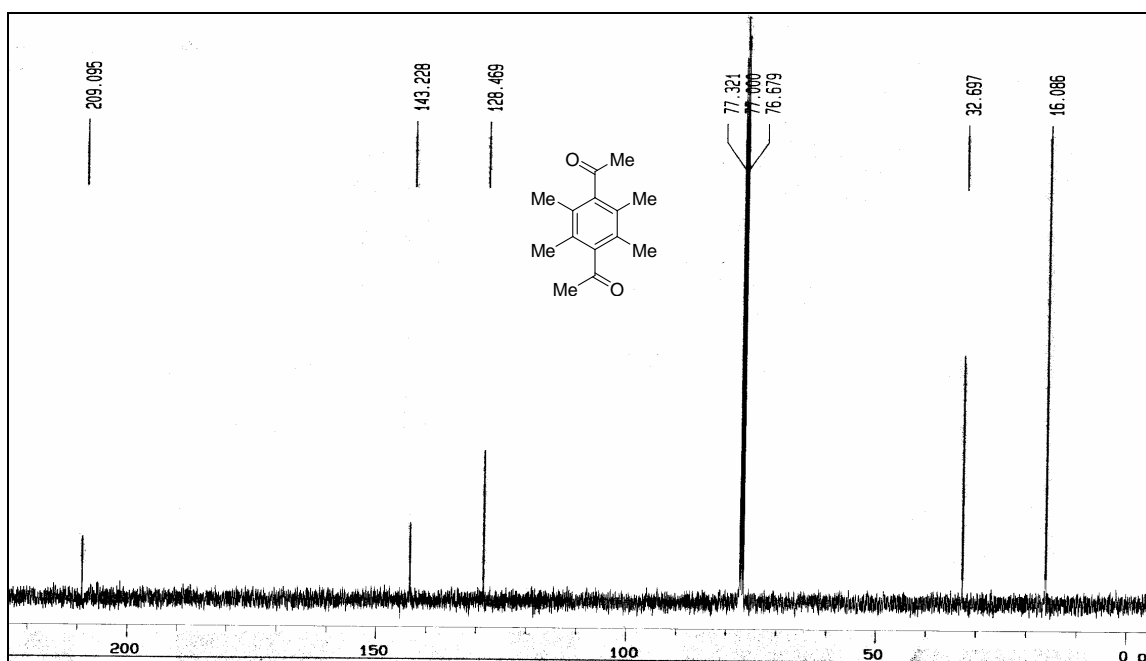


Figure S10.  $^{13}\text{C}$  NMR spectrum of ketone **1b**.

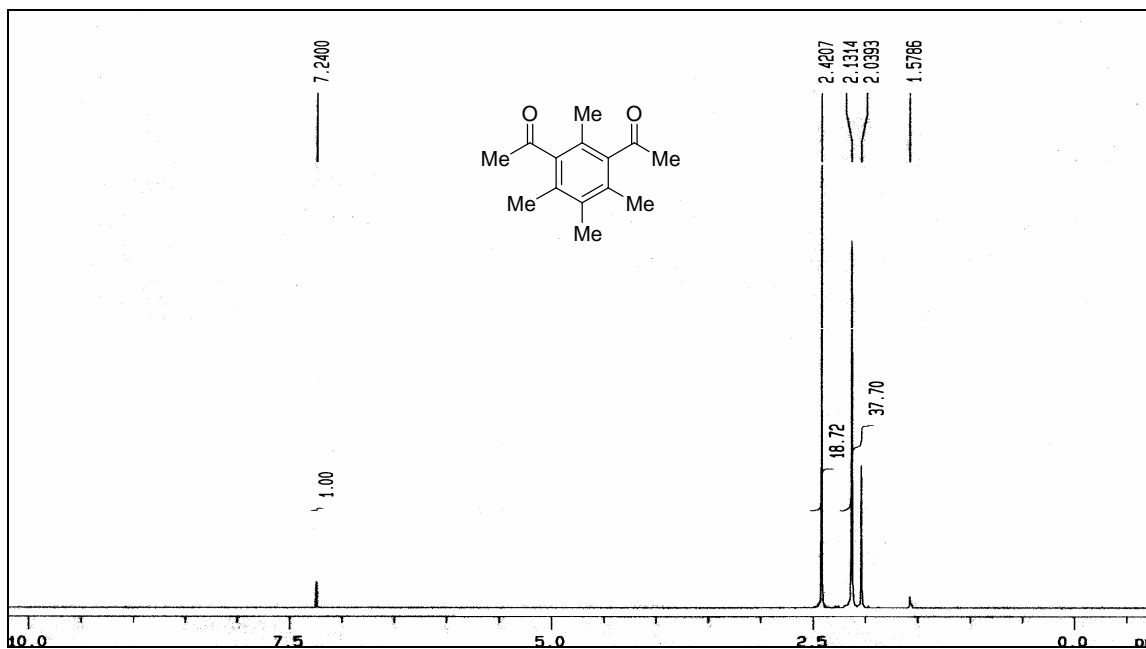


Figure S11. <sup>1</sup>H NMR spectrum of ketone **2b**.

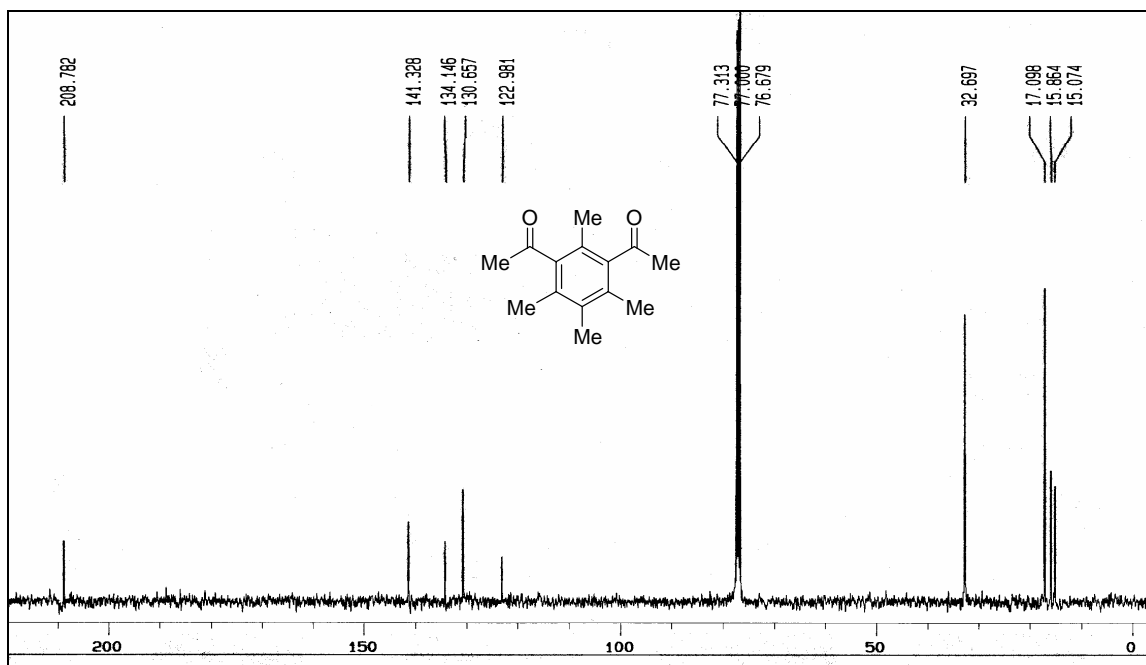


Figure S12. <sup>13</sup>C NMR spectrum of ketone **2b**.

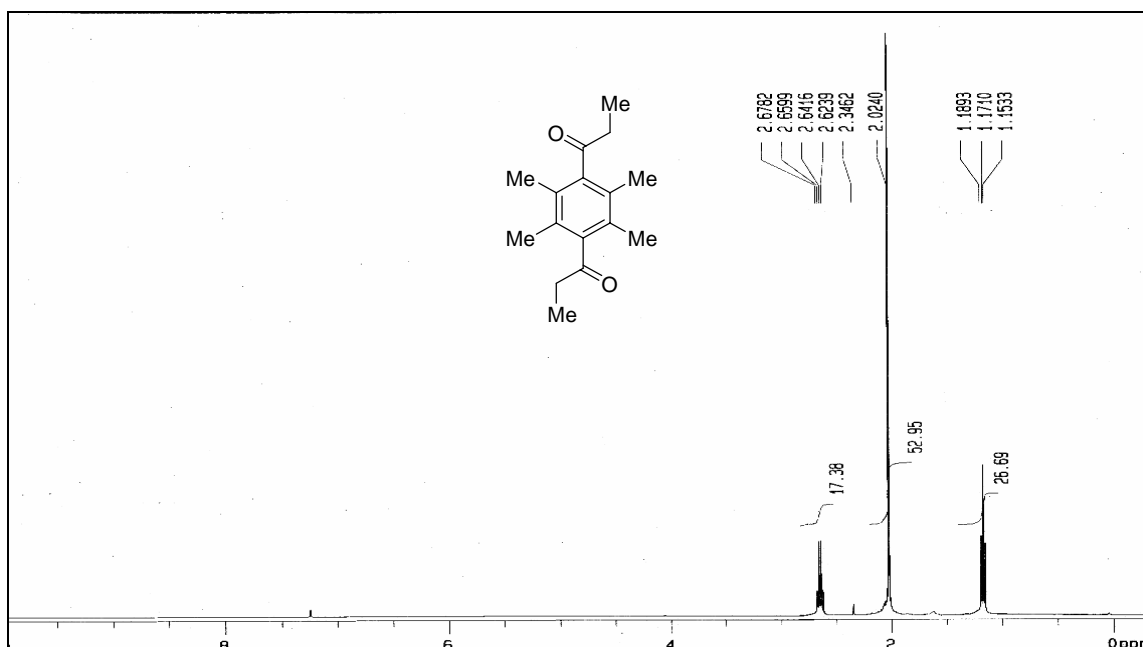


Figure S13. <sup>1</sup>H NMR spectrum of ketone **1c**.

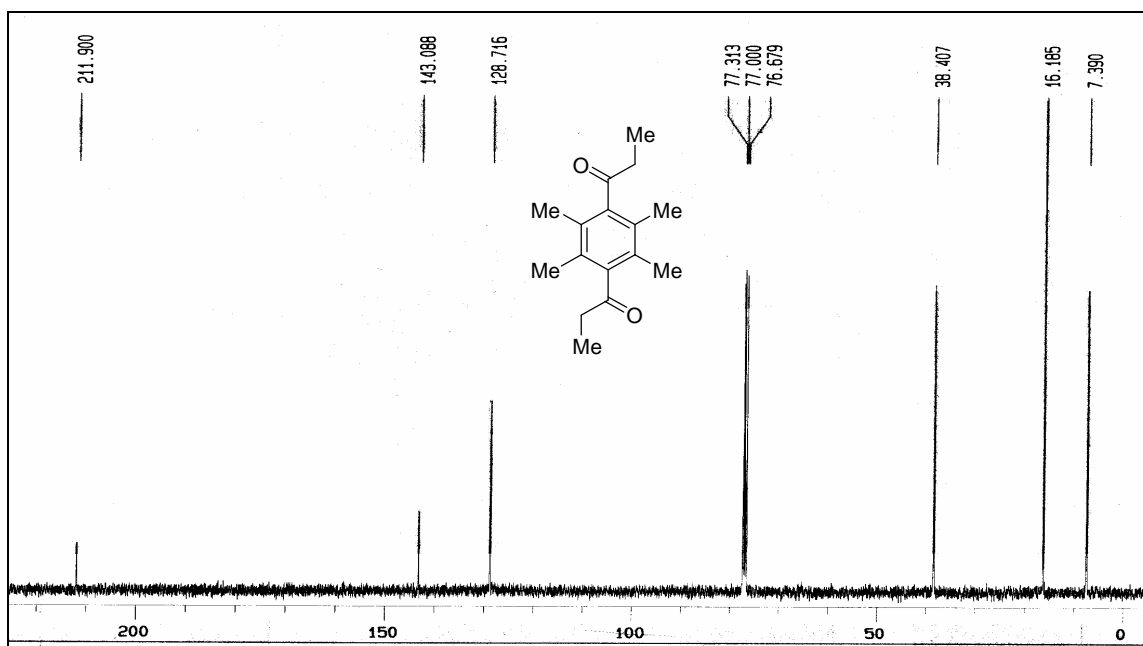


Figure S14. <sup>13</sup>C NMR spectrum of ketone **1c**.



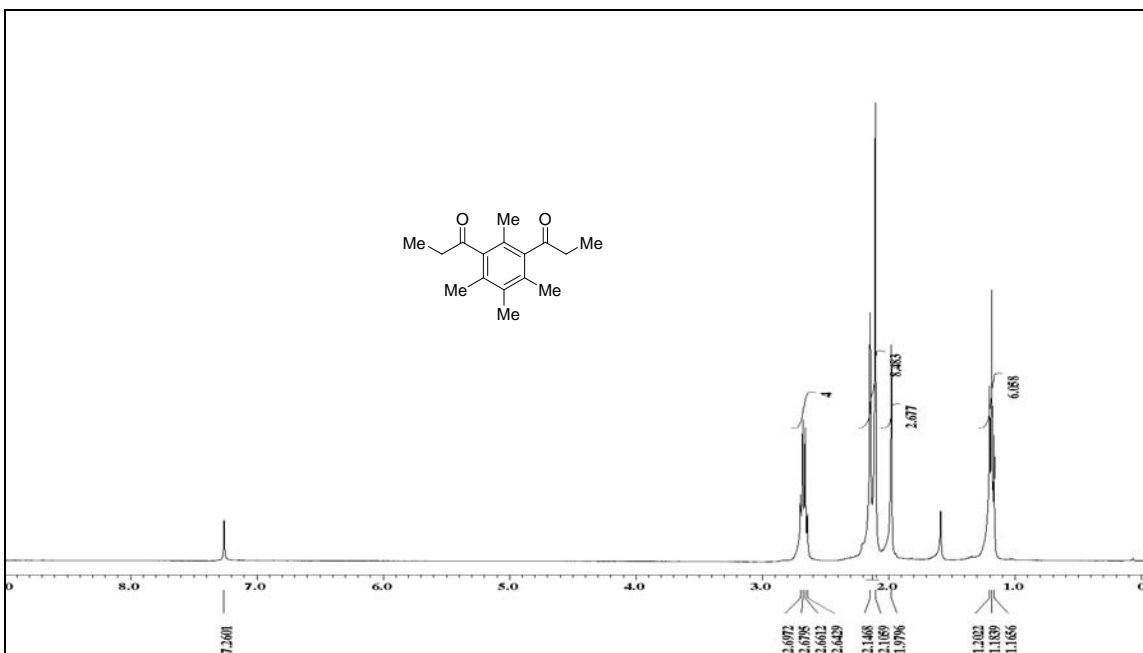


Figure S15. <sup>1</sup>H NMR spectrum of ketone **2c**.

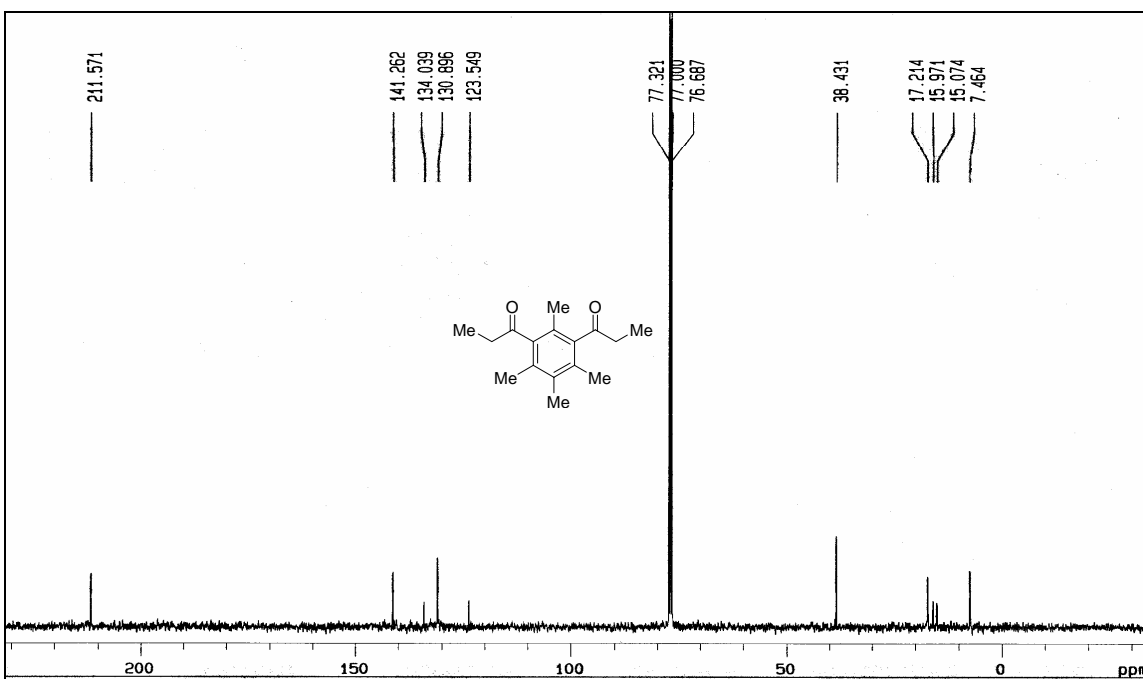


Figure S16. <sup>13</sup>C NMR spectrum of ketone **2c**.

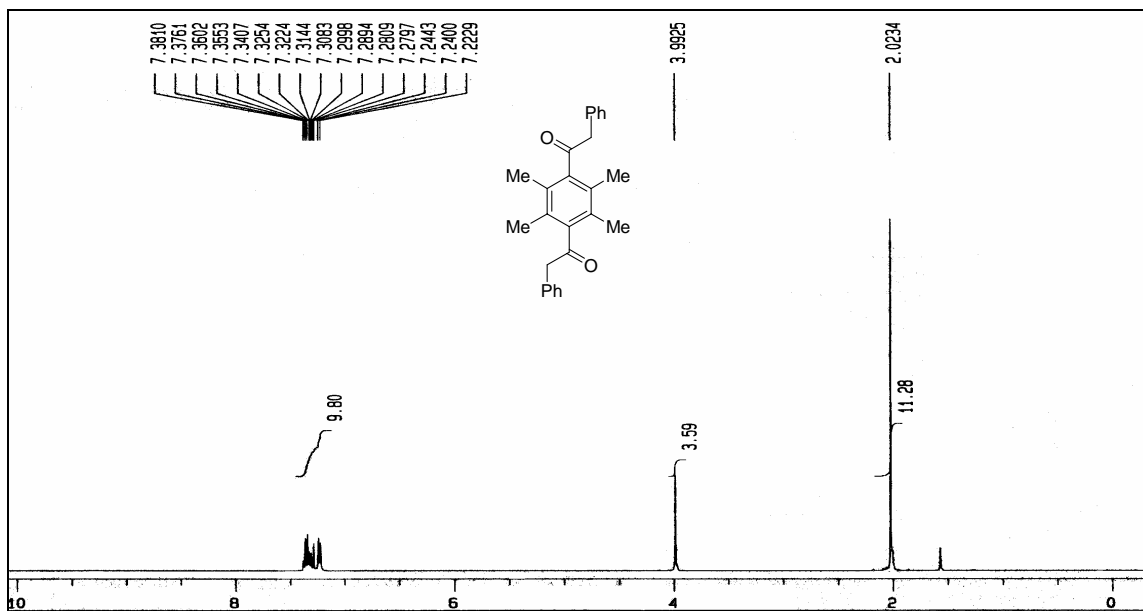


Figure S17.  $^1\text{H}$  NMR spectrum of ketone **1d**.

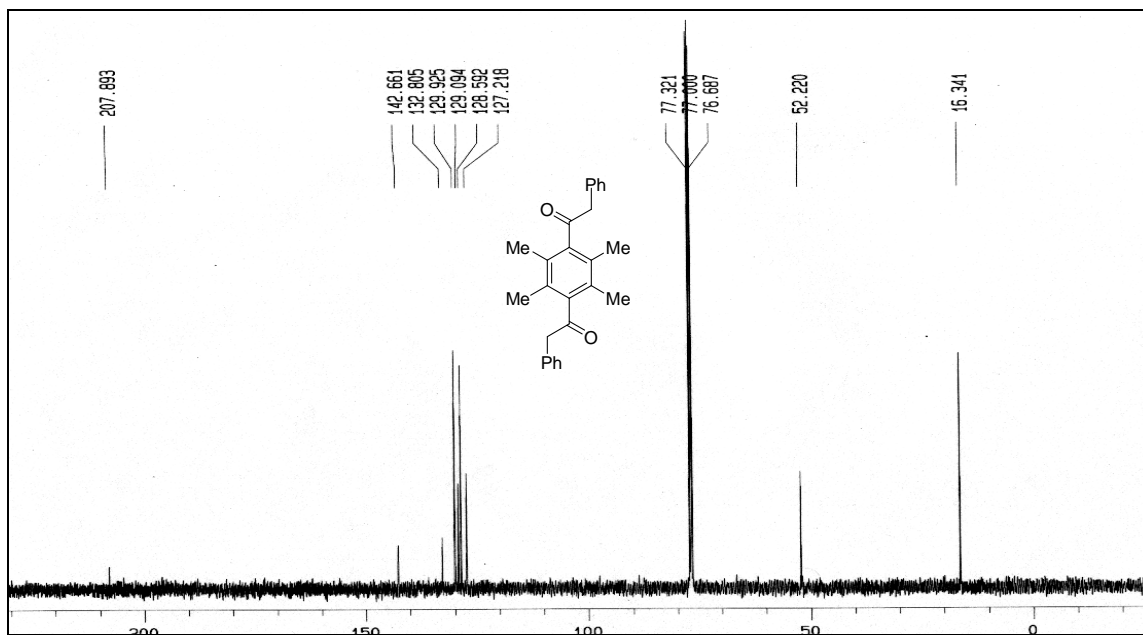


Figure S18.  $^{13}\text{C}$  NMR spectrum of ketone **1d**.

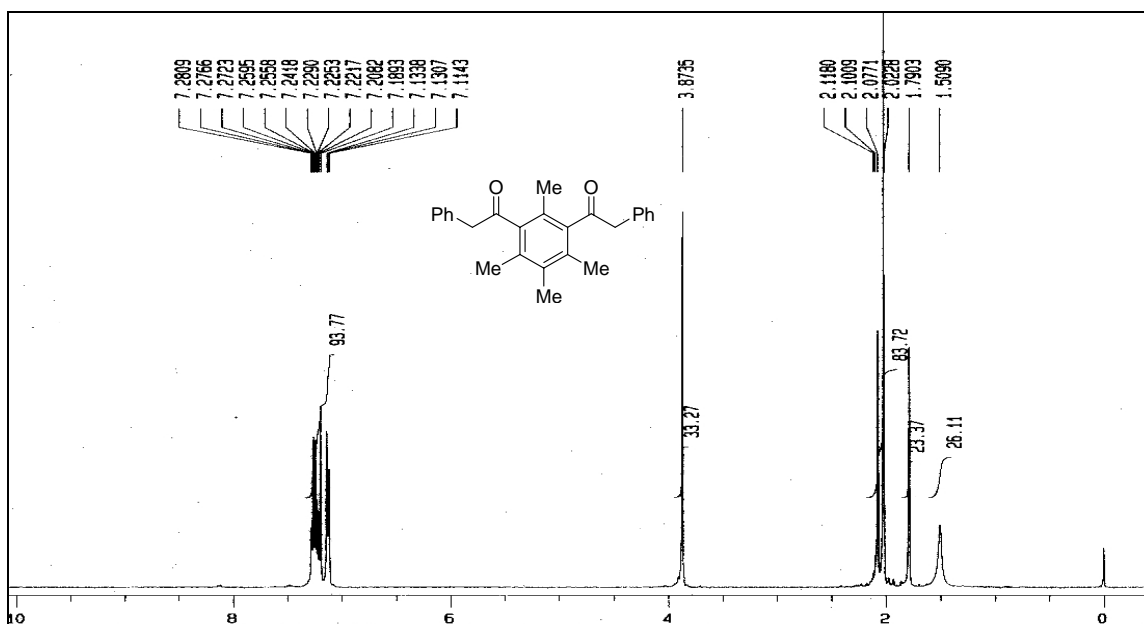


Figure S19.  $^1\text{H}$  NMR spectrum of ketone **2d**.

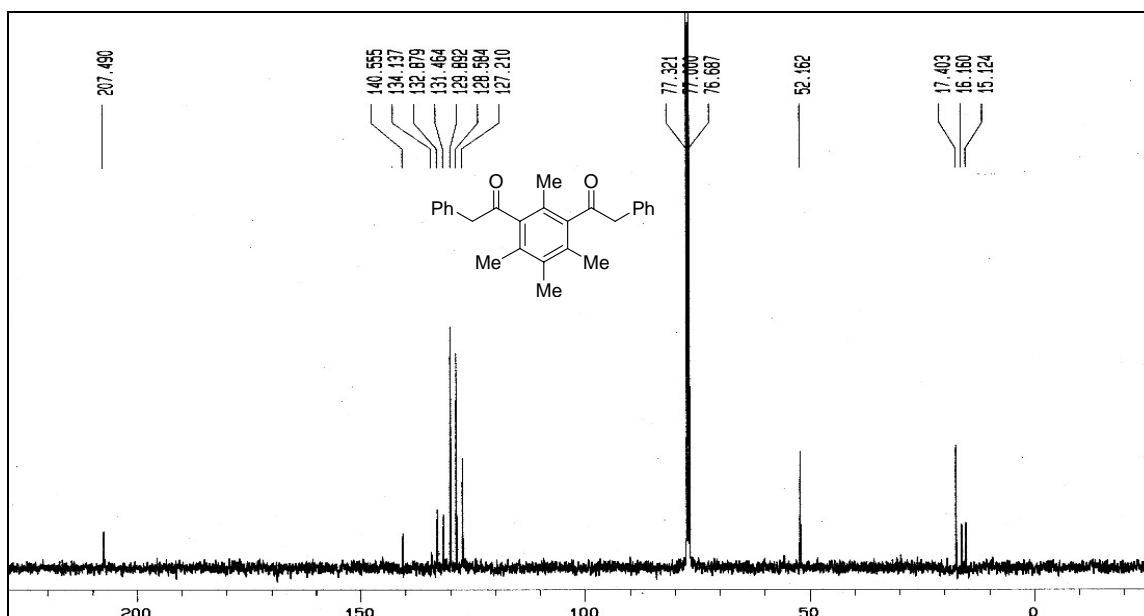


Figure S20.  $^{13}\text{C}$  NMR spectrum of ketone **2d**.

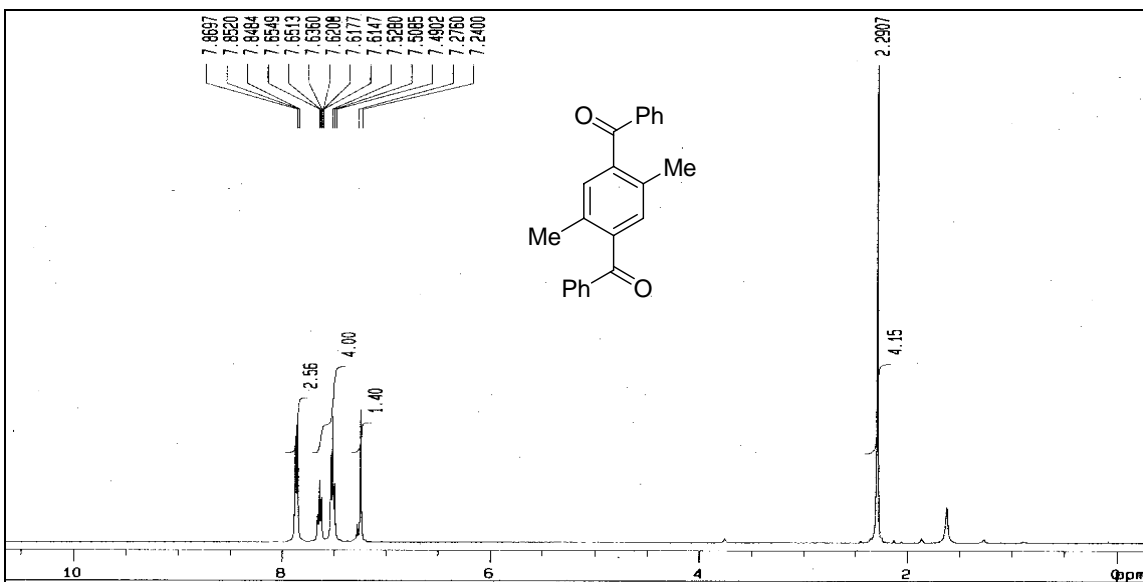


Figure S21. <sup>1</sup>H NMR spectrum of ketone 3.

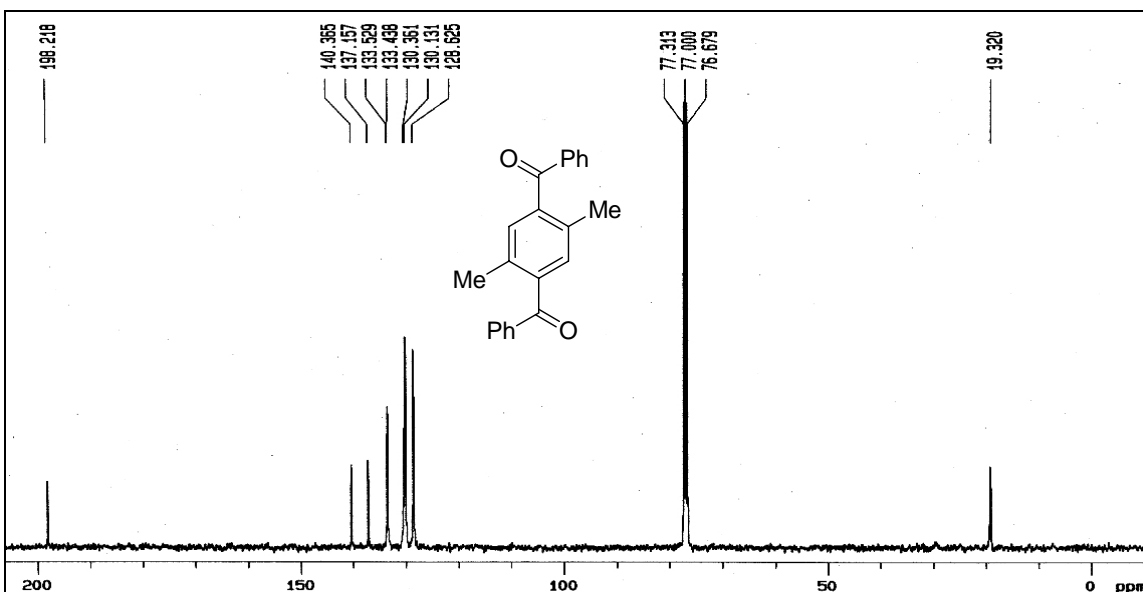


Figure 22. <sup>13</sup>C NMR spectrum of ketone 3.

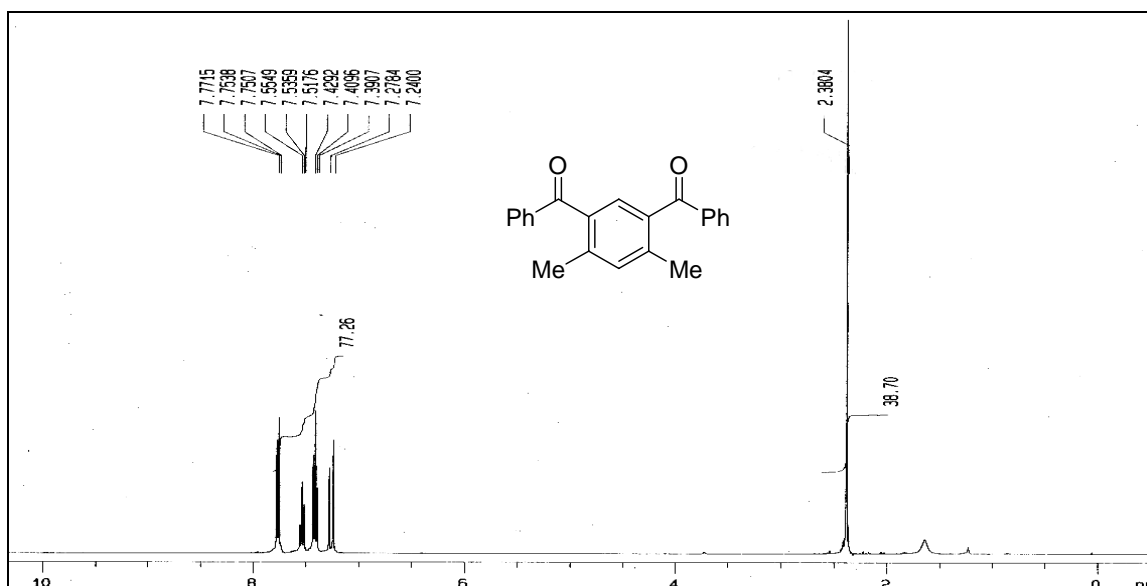


Figure S23.  $^1\text{H NMR}$  spectrum of ketone 4.

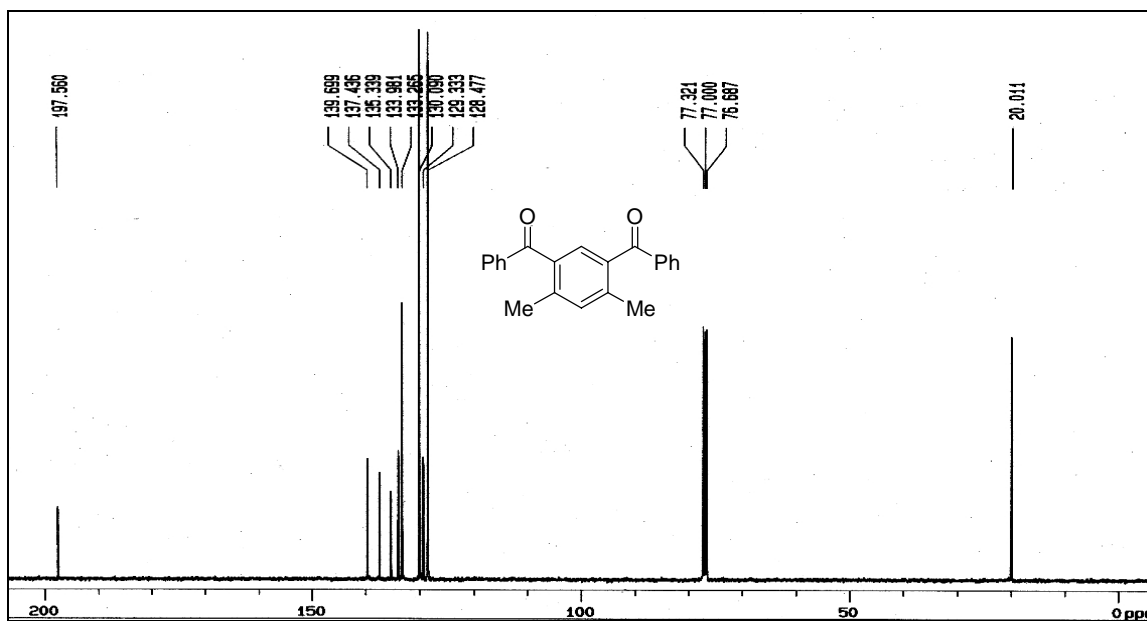


Figure S24.  $^{13}\text{C NMR}$  spectrum of ketone 4.

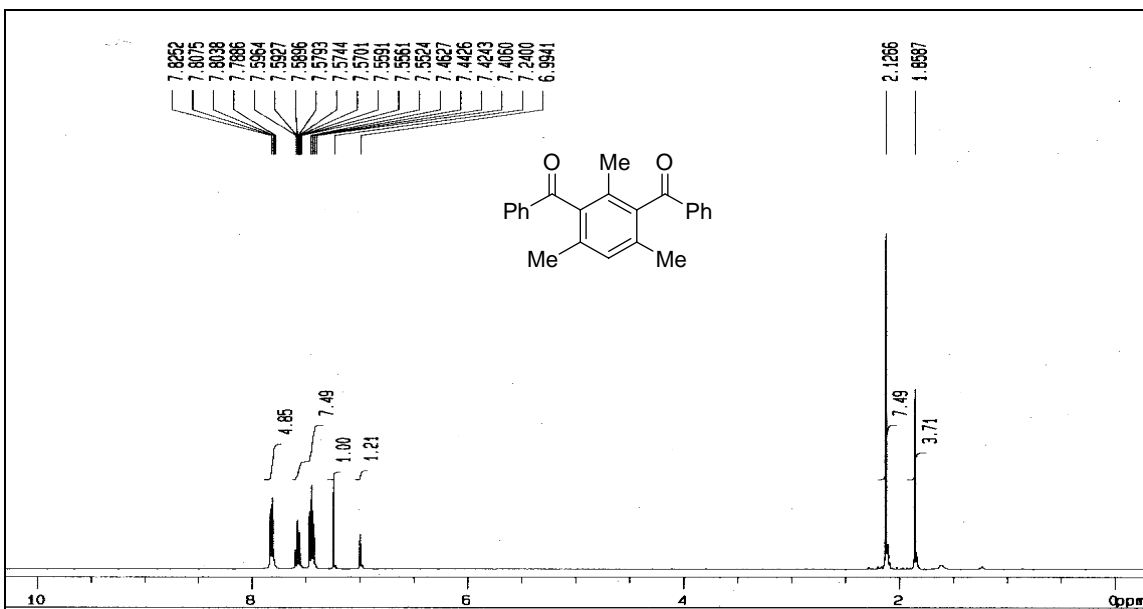


Figure S25. <sup>1</sup>H NMR spectrum of ketone 5.

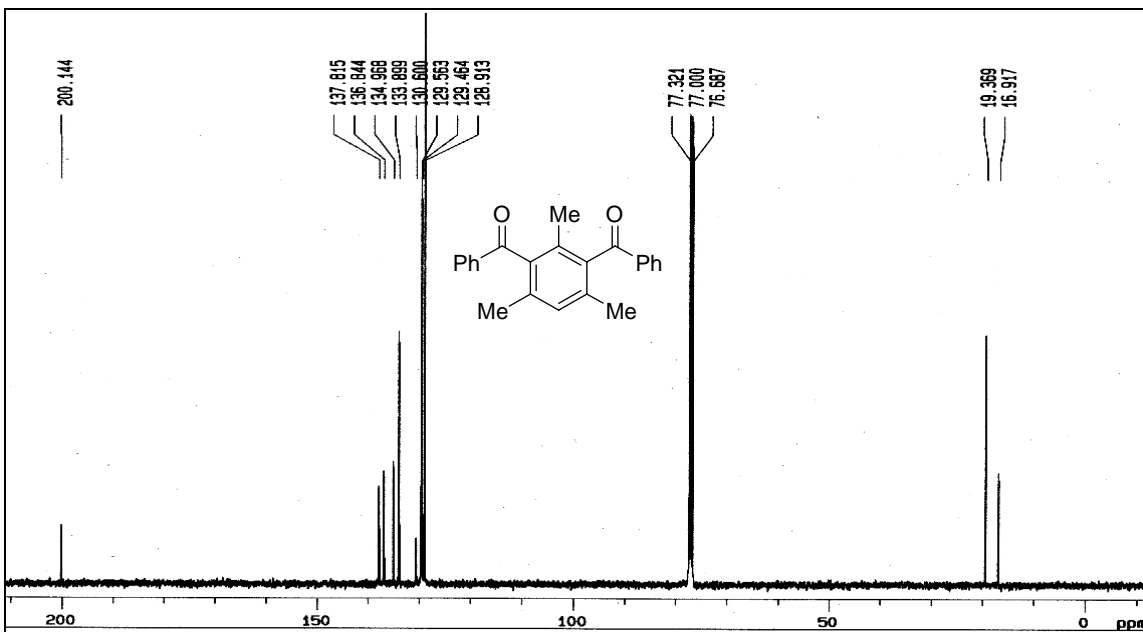


Figure S26. <sup>13</sup>C NMR spectrum of ketone 5.

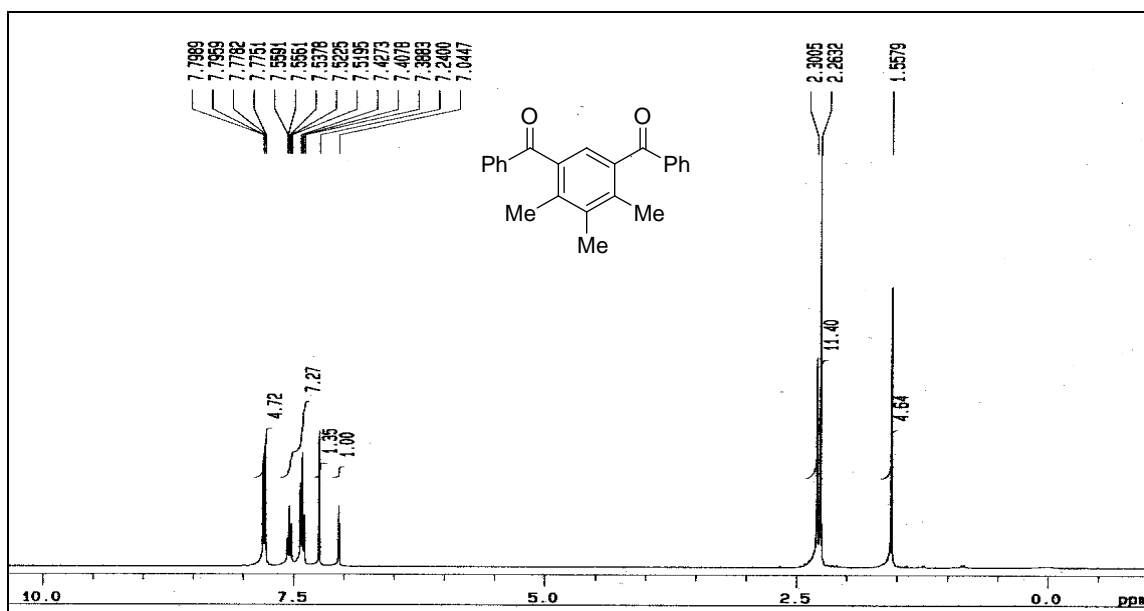


Figure S27.  $^1\text{H}$  NMR spectrum of ketone 6.

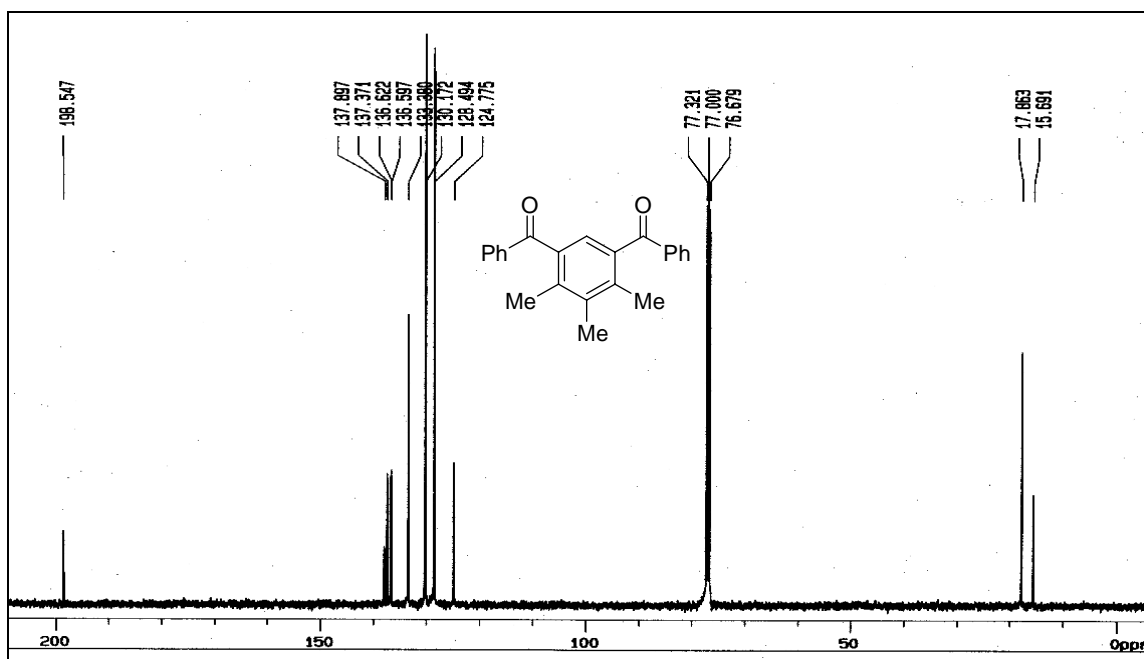


Figure S28.  $^{13}\text{C}$  NMR spectrum of ketone 6.

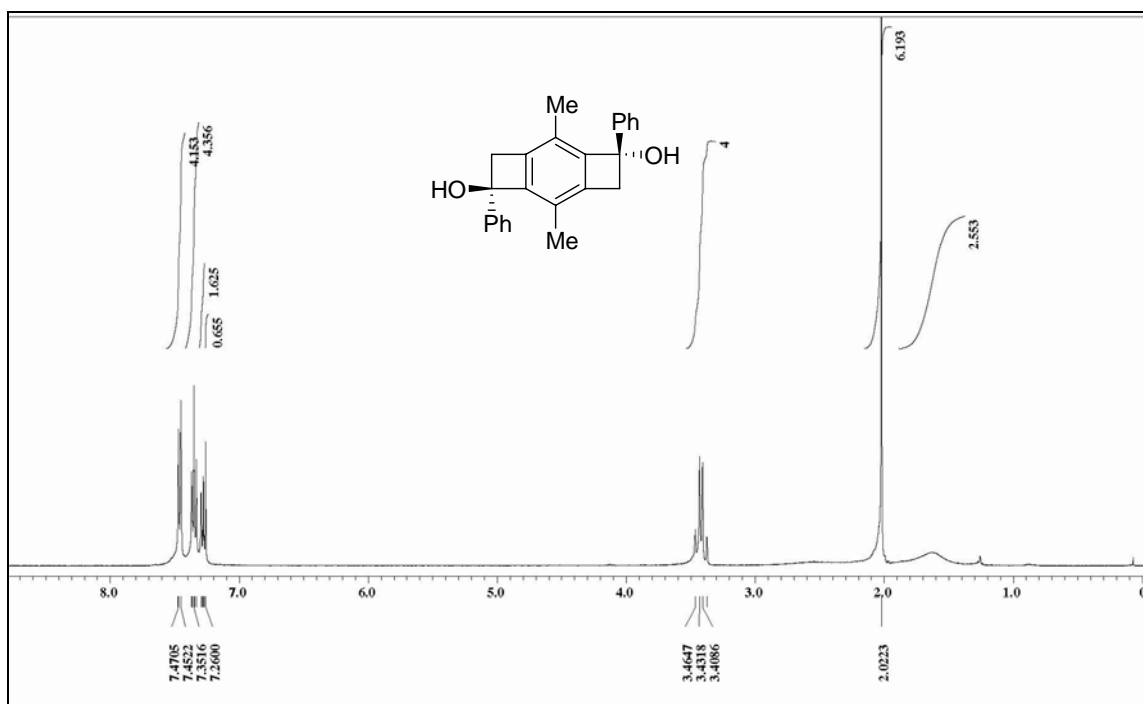


Figure S29.  $^1\text{H}$  NMR spectrum of *Anti* 1a-BCB.

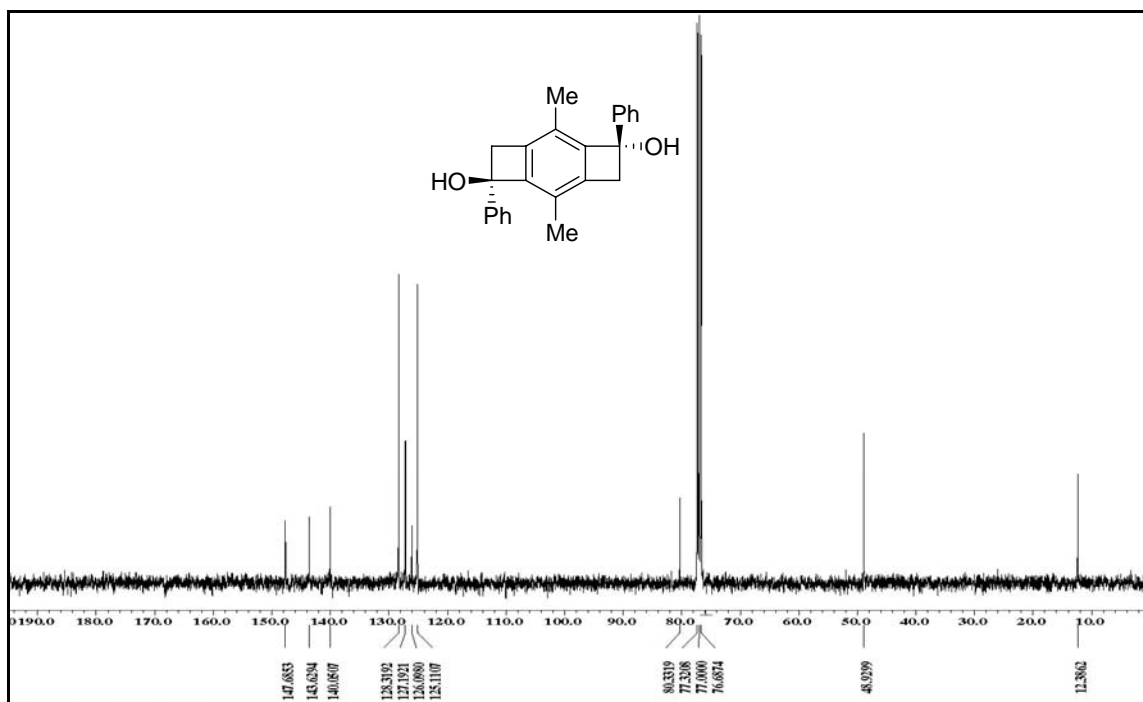


Figure S30.  $^{13}\text{C}$  NMR spectrum of *Anti* 1a-BCB.



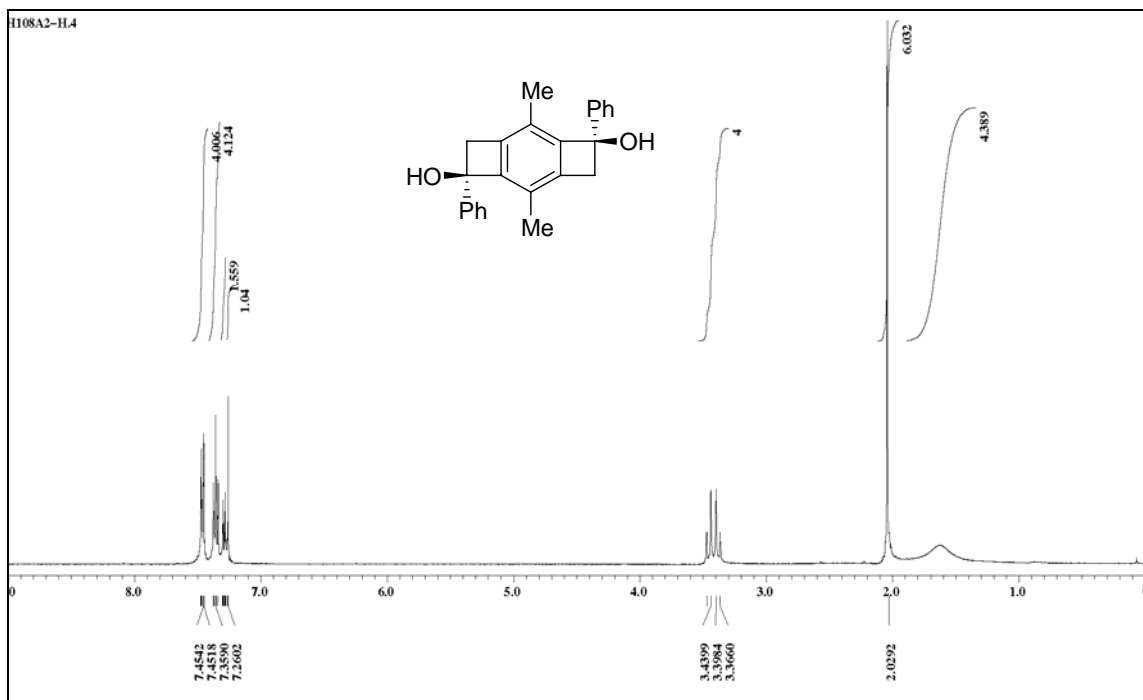


Figure S31.  $^1\text{H}$  NMR spectrum of *Syn 1a-BCB*.

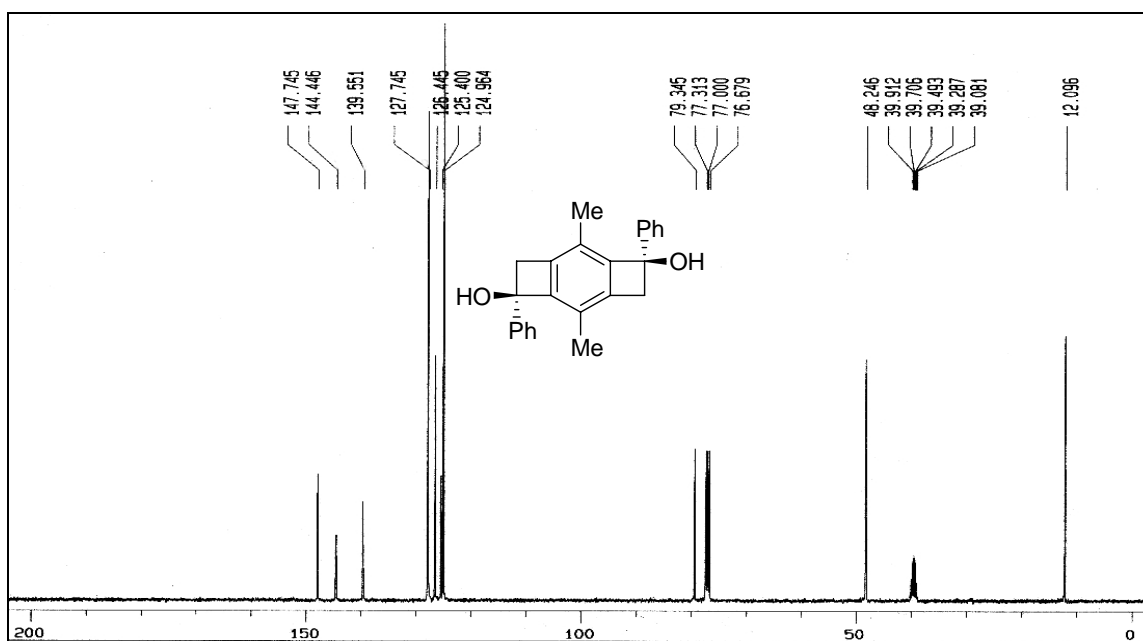


Figure S32.  $^{13}\text{C}$  NMR spectrum of *Syn 1a-BCB*.

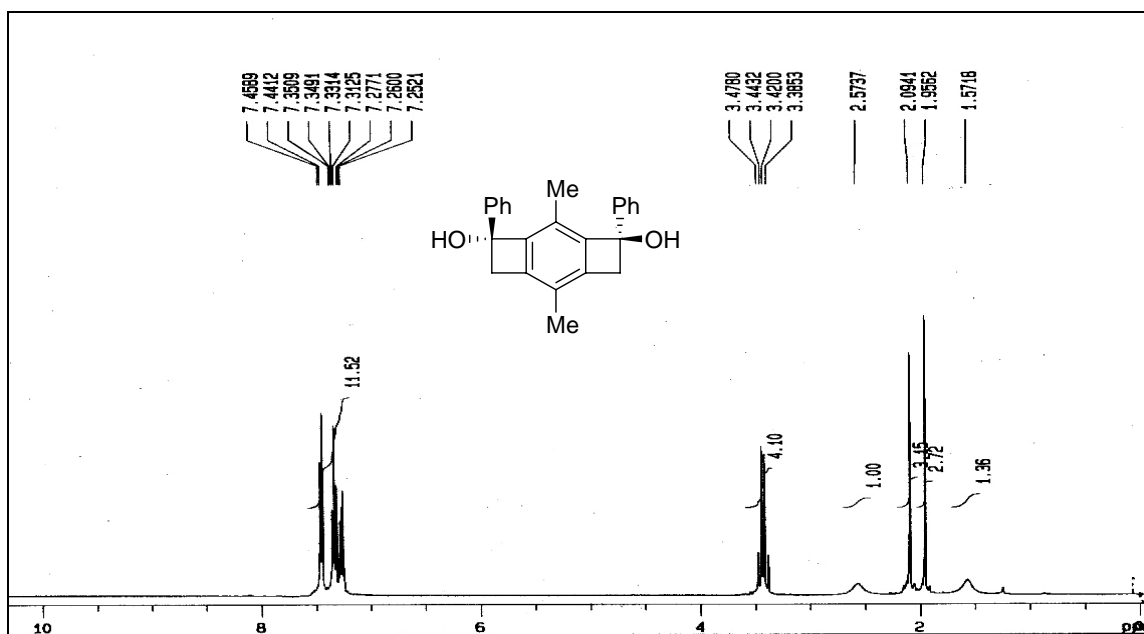


Figure S33. <sup>1</sup>H NMR spectrum of *Anti 2a-BCB*.

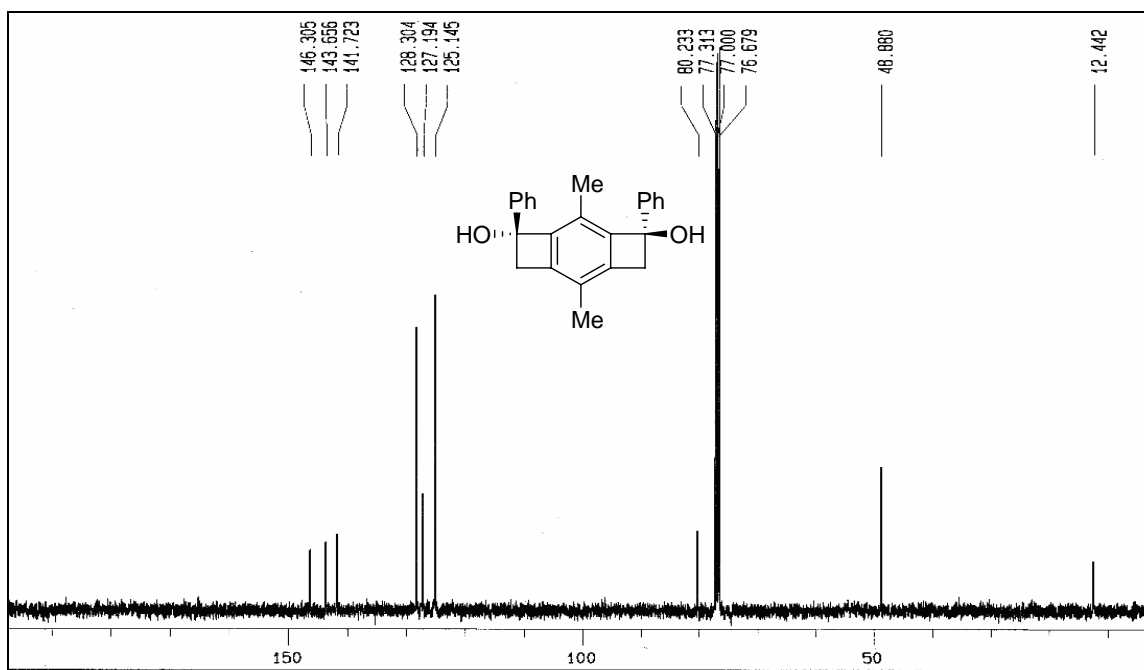


Figure S34. <sup>13</sup>C NMR spectrum of *Anti 2a-BCB*.

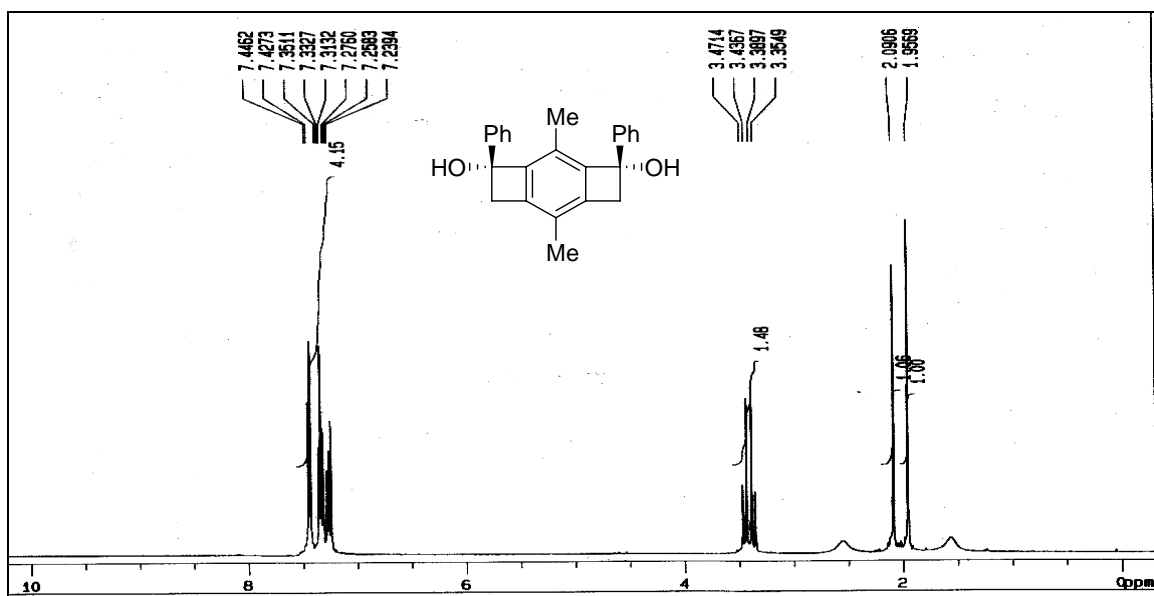


Figure S35. <sup>1</sup>H NMR spectrum of *Syn 2a-BCB*.

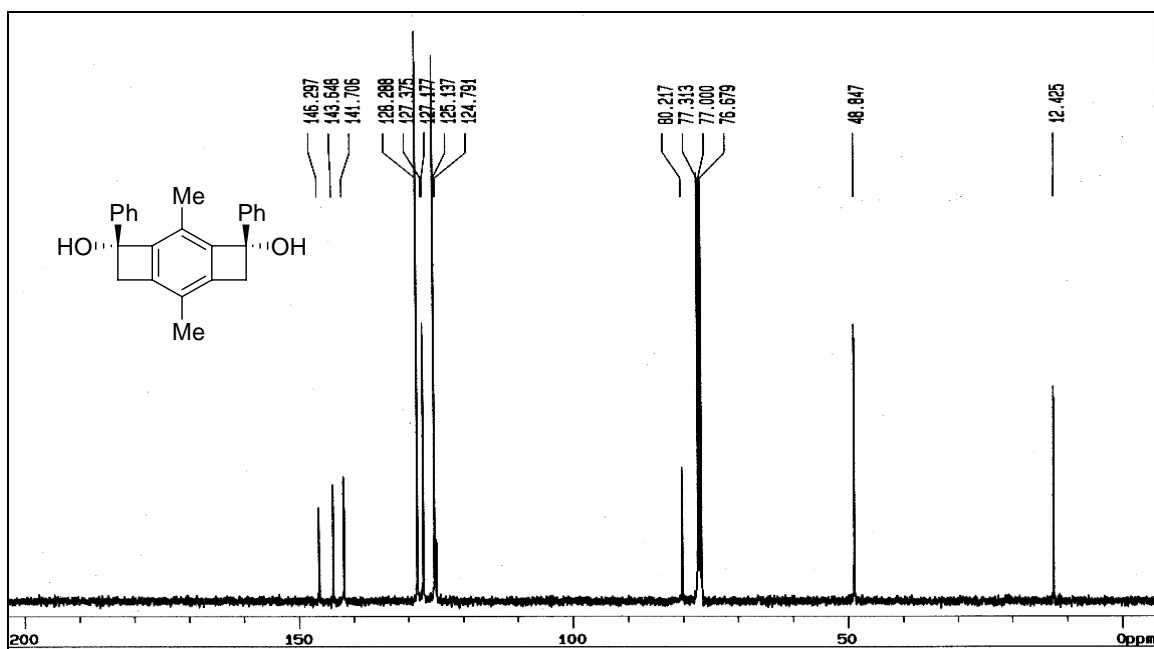
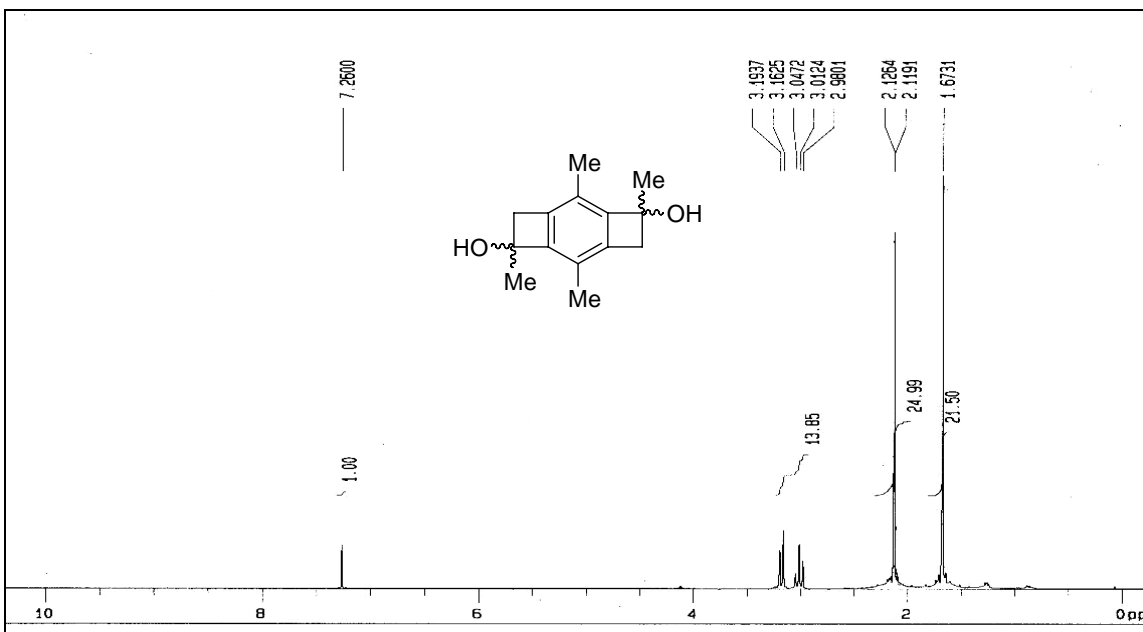
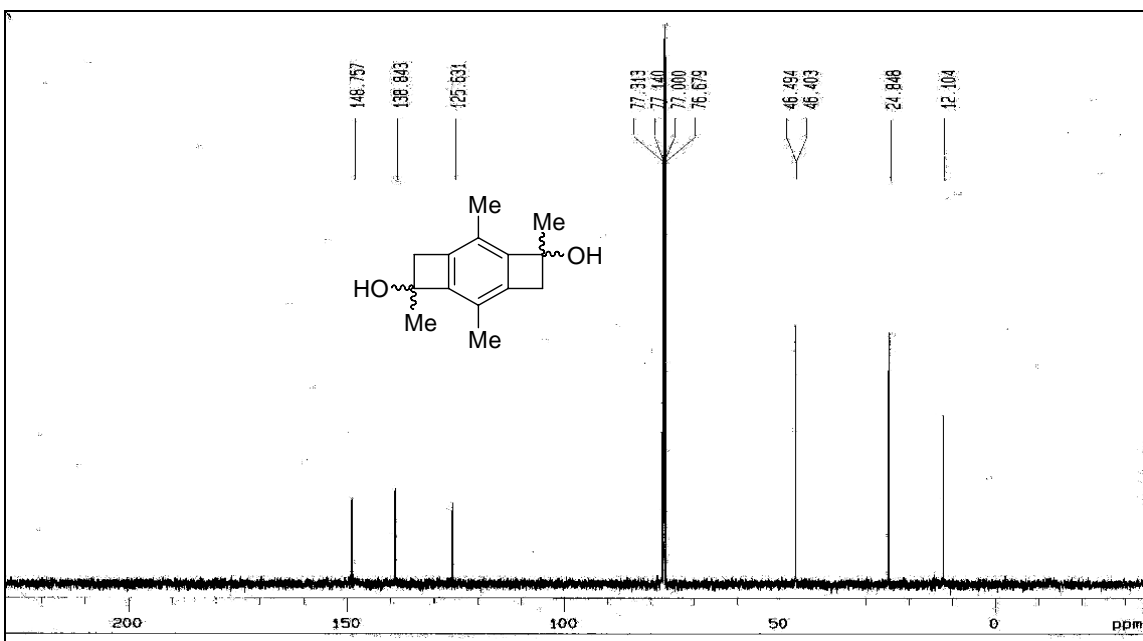


Figure S36. <sup>13</sup>C NMR spectrum of *Syn 2a-BCB*.



**Figure S37.  $^1\text{H}$  NMR spectrum of *Anti* + *Syn* 1b-BCB.**



**Figure S38.  $^{13}\text{C}$  NMR spectrum of *Anti* + *Syn* 1b-BCB.**

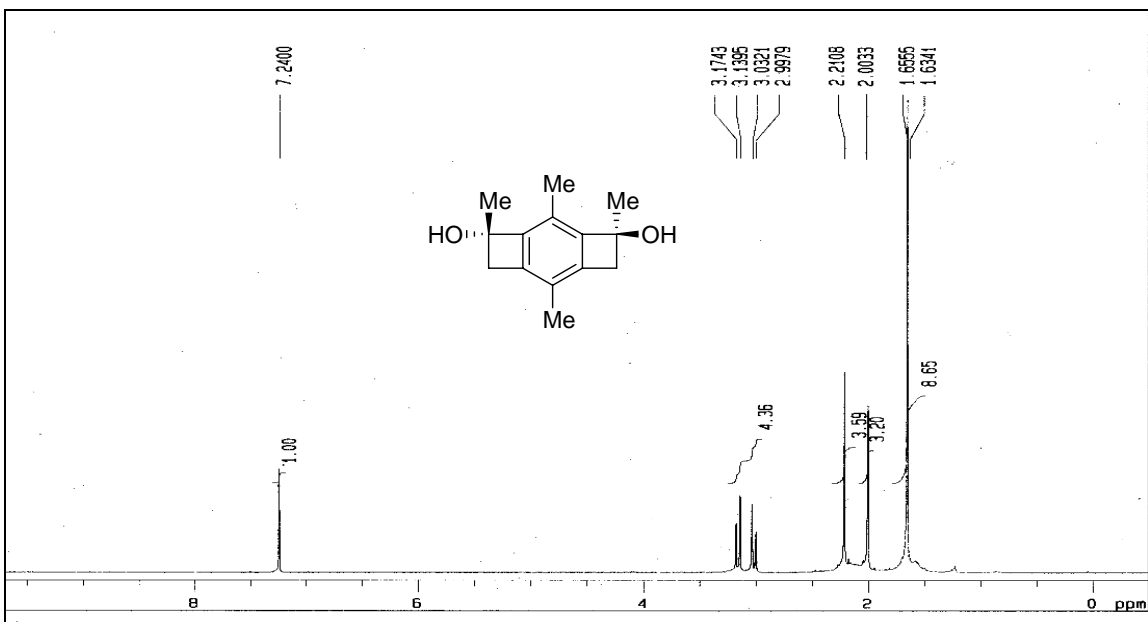


Figure S39.  $^1\text{H}$  NMR spectrum of *Anti* 2b-BCB.

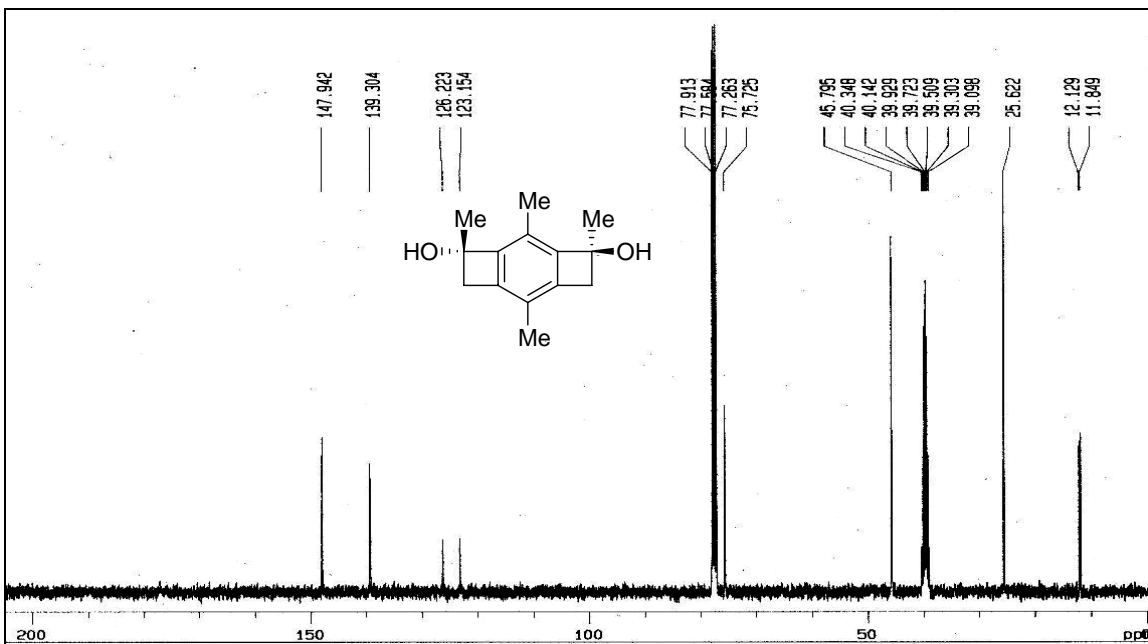


Figure S40.  $^{13}\text{C}$  NMR spectrum of *Anti* 2b-BCB.

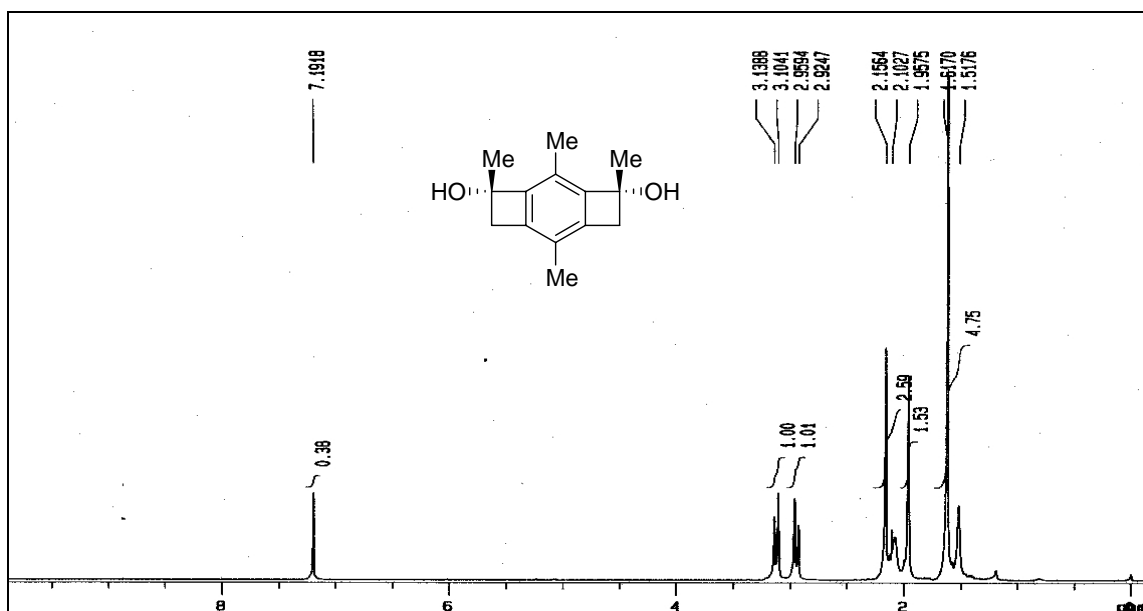


Figure S41.  $^1\text{H}$  NMR spectrum of *Syn 2b-BCB*.

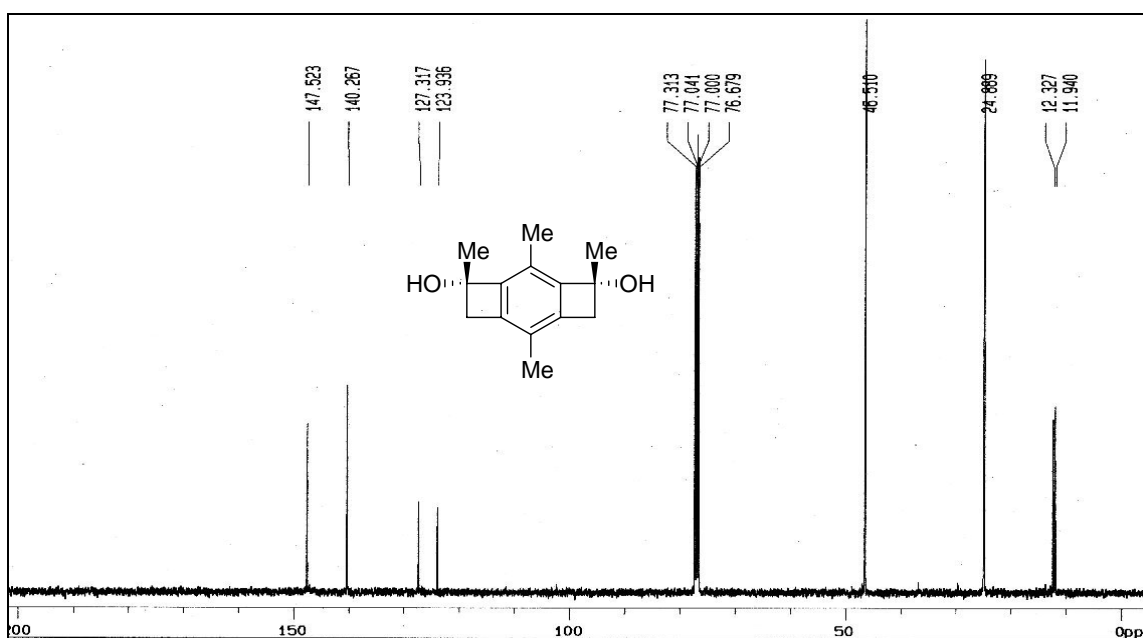


Figure S42.  $^{13}\text{C}$  NMR spectrum of *Syn 2b-BCB*.

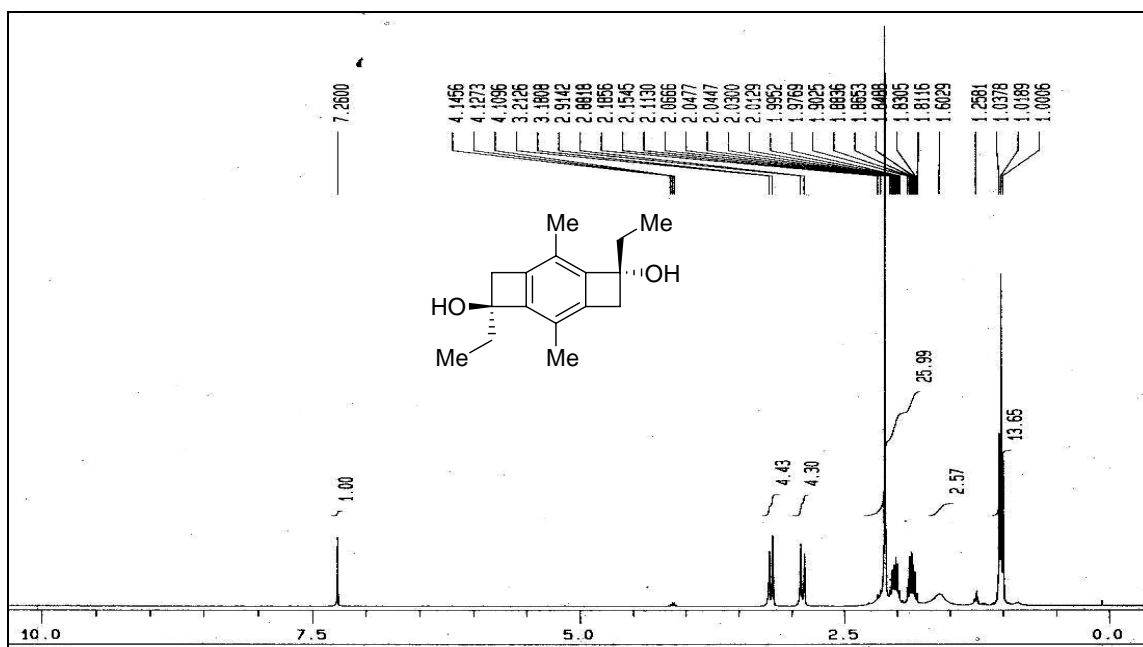


Figure S43.  $^1\text{H}$  NMR spectrum of *Anti* 1c-BCB.

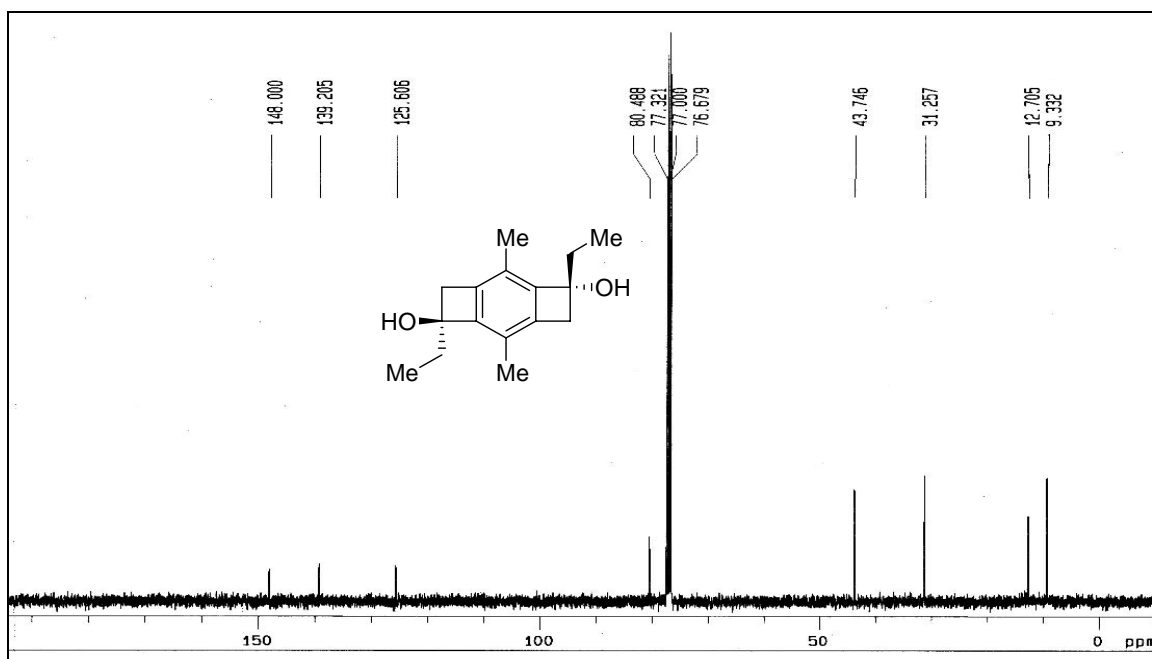


Figure S44.  $^{13}\text{C}$  NMR spectrum of *Anti* 1c-BCB.

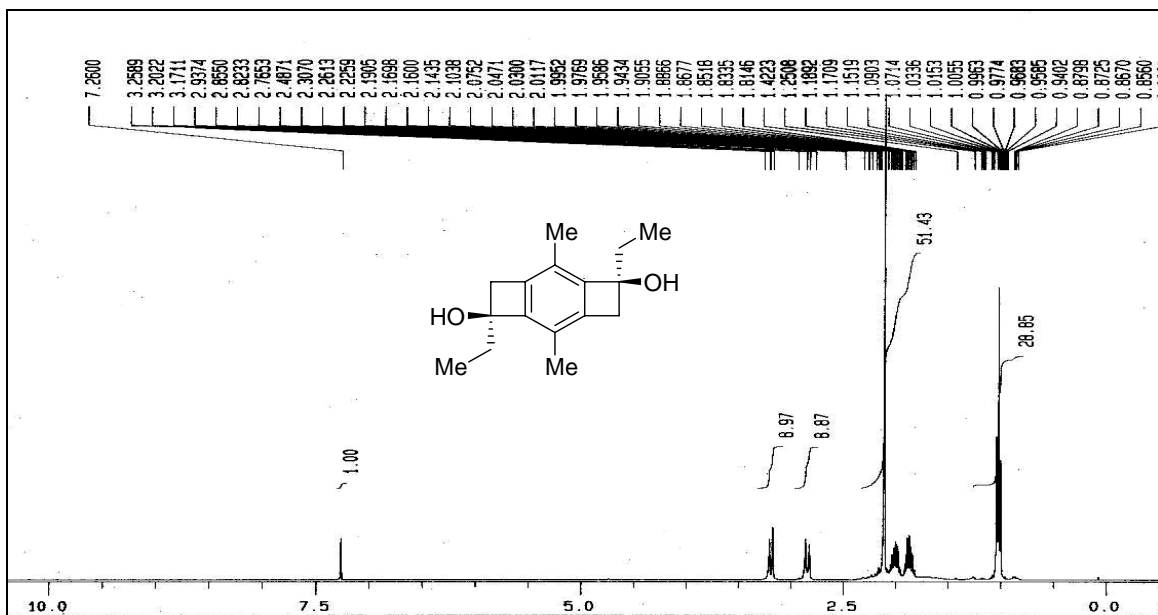


Figure S45.  $^1\text{H}$  NMR spectrum of *Syn 1c-BCB*.

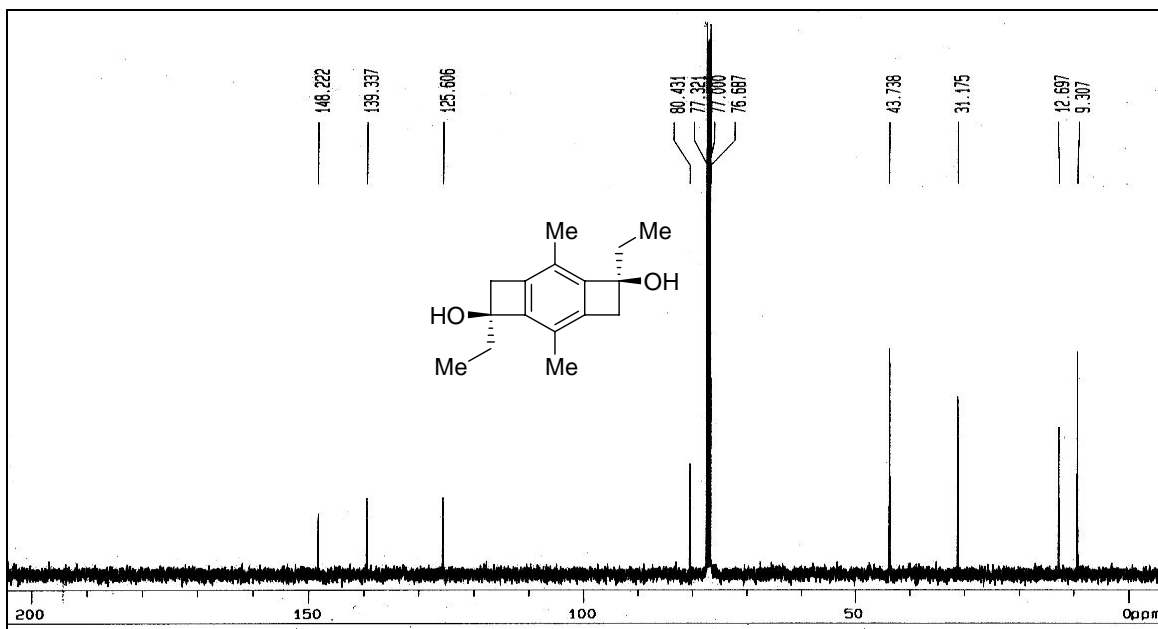


Figure S46.  $^{13}\text{C}$  NMR spectrum of *Syn 1c-BCB*.



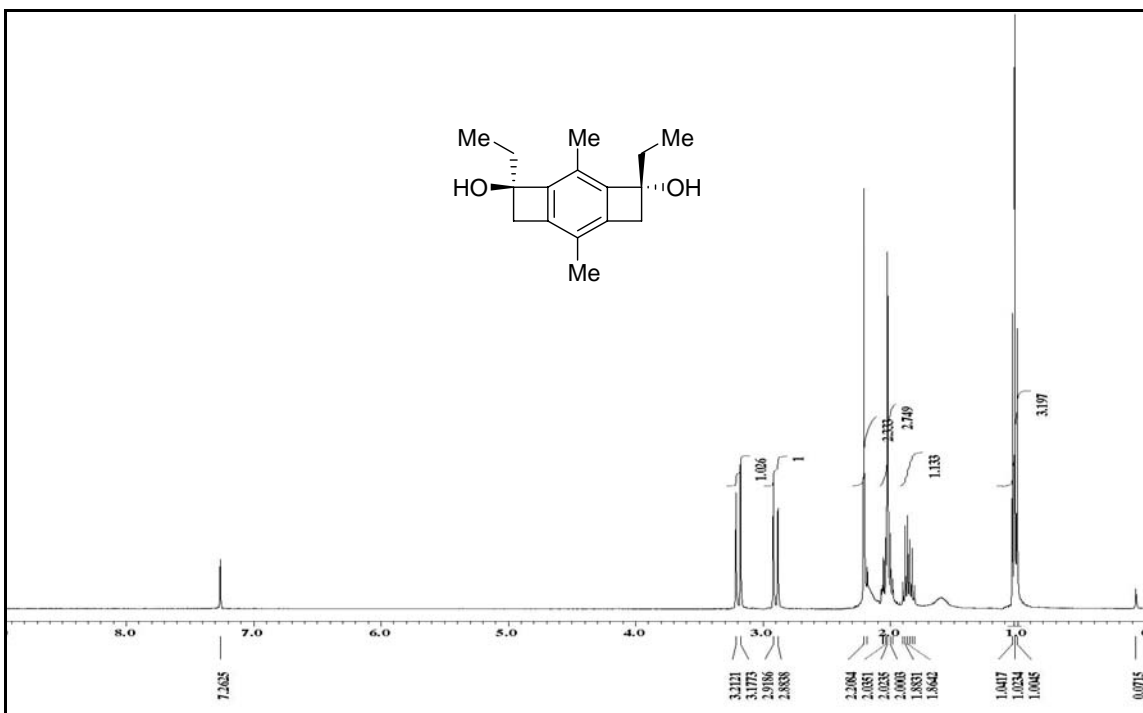


Figure S47. <sup>1</sup>H NMR spectrum of *Anti* 2c-BCB.

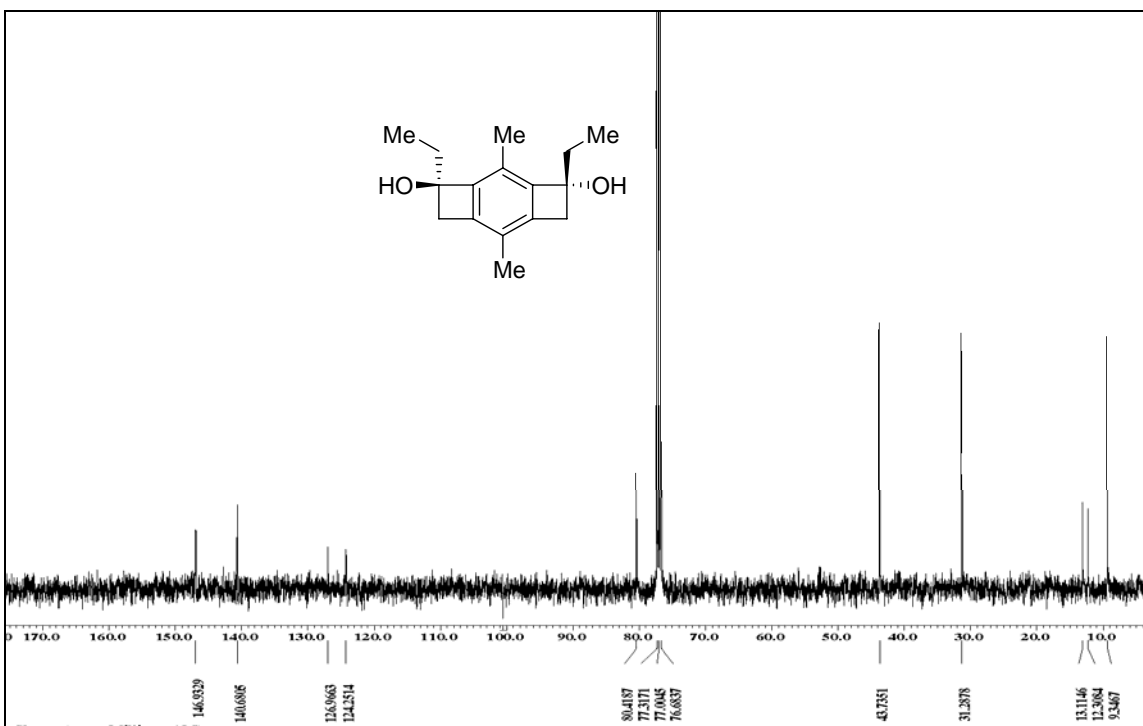


Figure S48. <sup>13</sup>C NMR spectrum of *Anti* 2c-BCB.

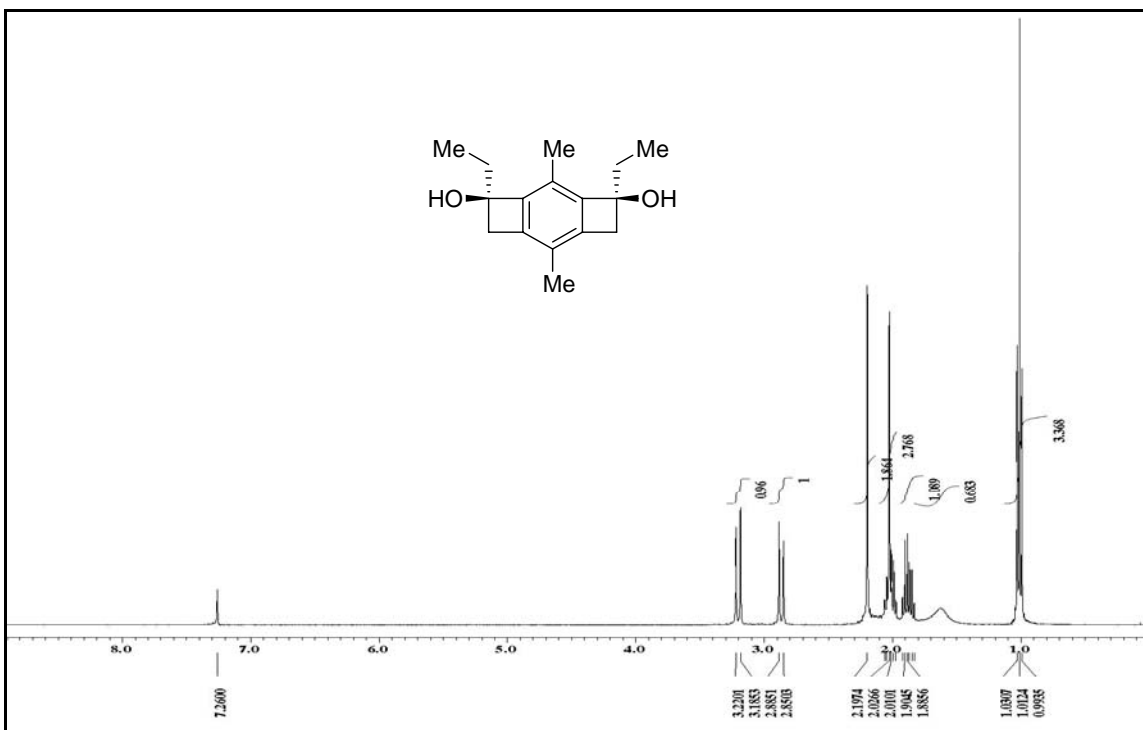


Figure S49.  $^1\text{H}$  NMR spectrum of *Syn 2c-BCB*.

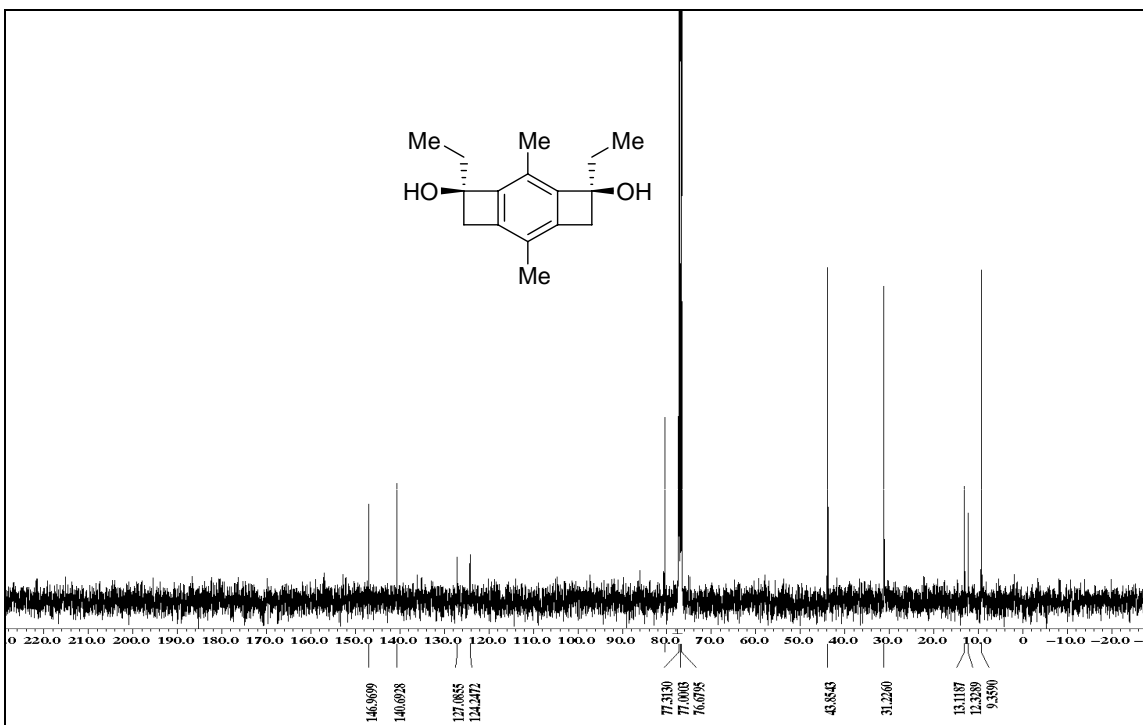


Figure S50.  $^{13}\text{C}$  NMR spectrum of *Syn 2c-BCB*.

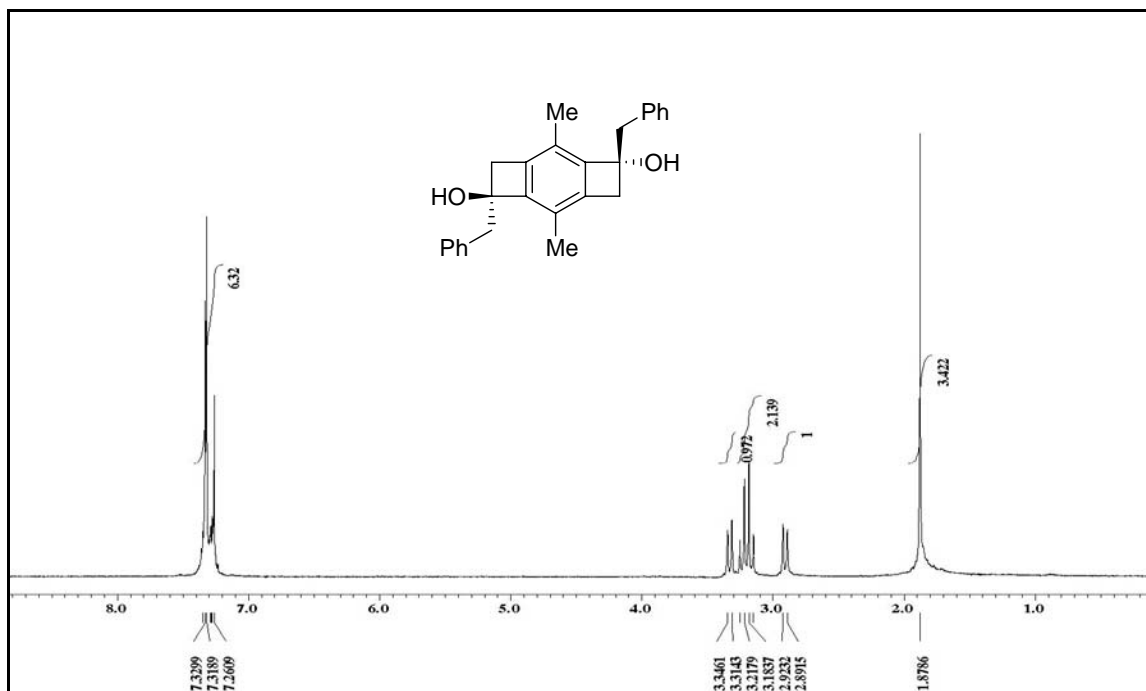


Figure S51. <sup>1</sup>H NMR spectrum of *Anti* 1d-BCB.

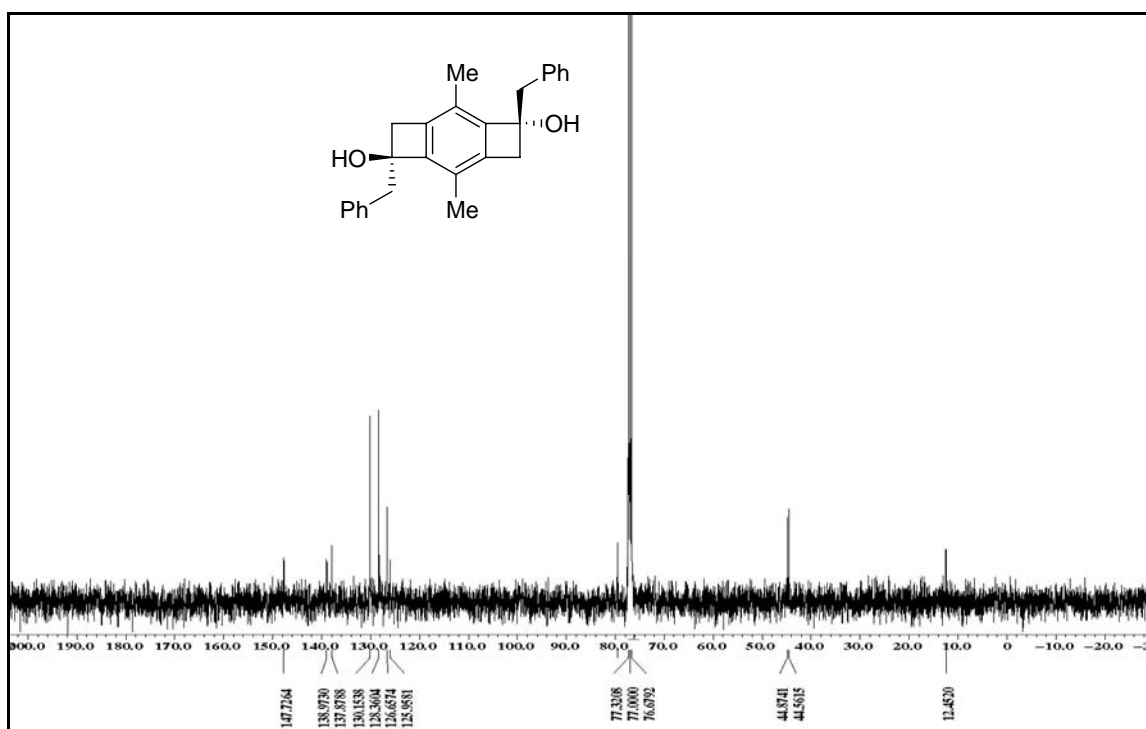


Figure S52. <sup>13</sup>C NMR spectrum of *Anti* 1d-BCB.

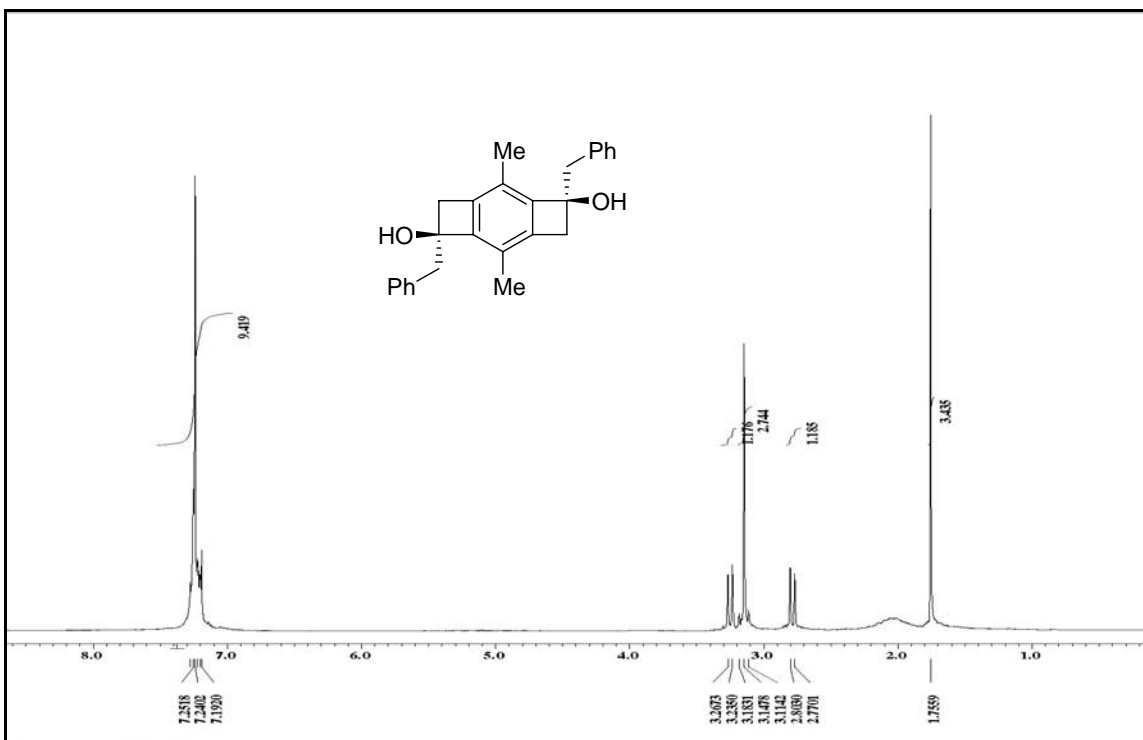


Figure S53.  $^1\text{H}$  NMR spectrum of *Syn 1d-BCB*.

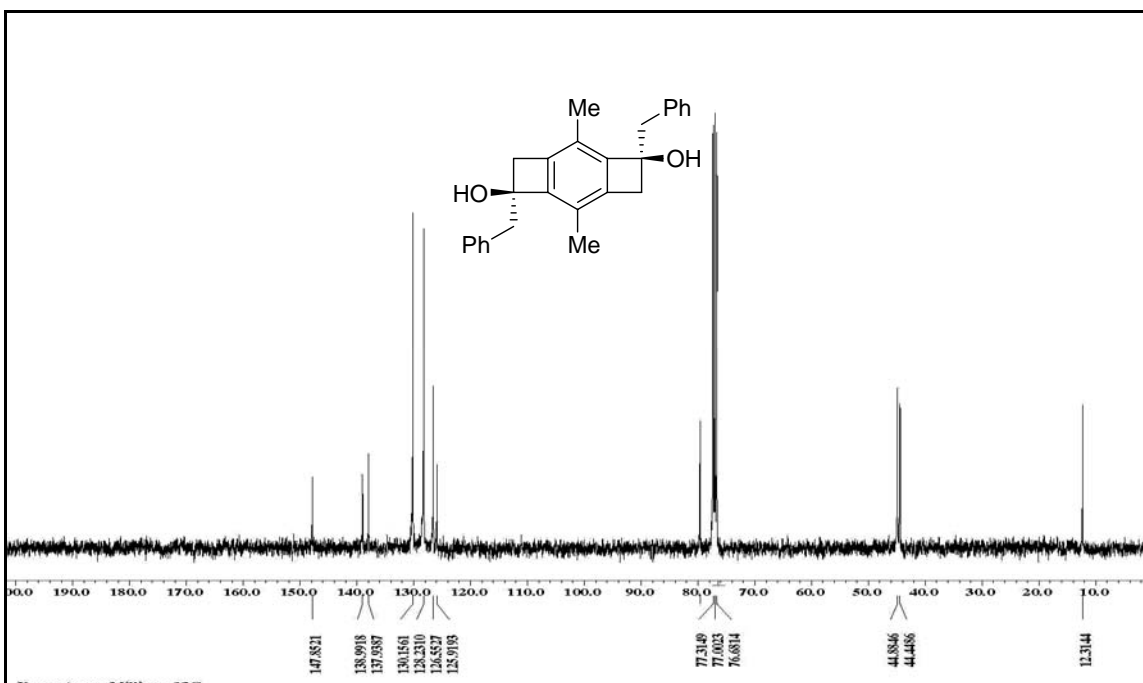


Figure 54.  $^{13}\text{C}$  NMR spectrum of *Syn 1d-BCB*.

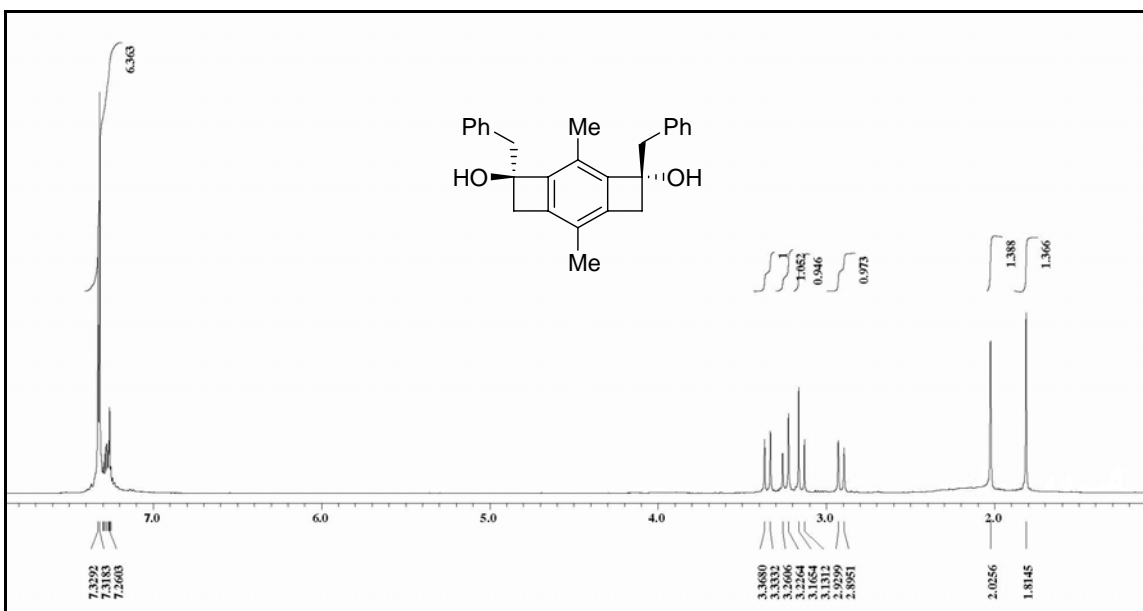


Figure S55. <sup>1</sup>H NMR spectrum of *Anti* 2d-BCB.

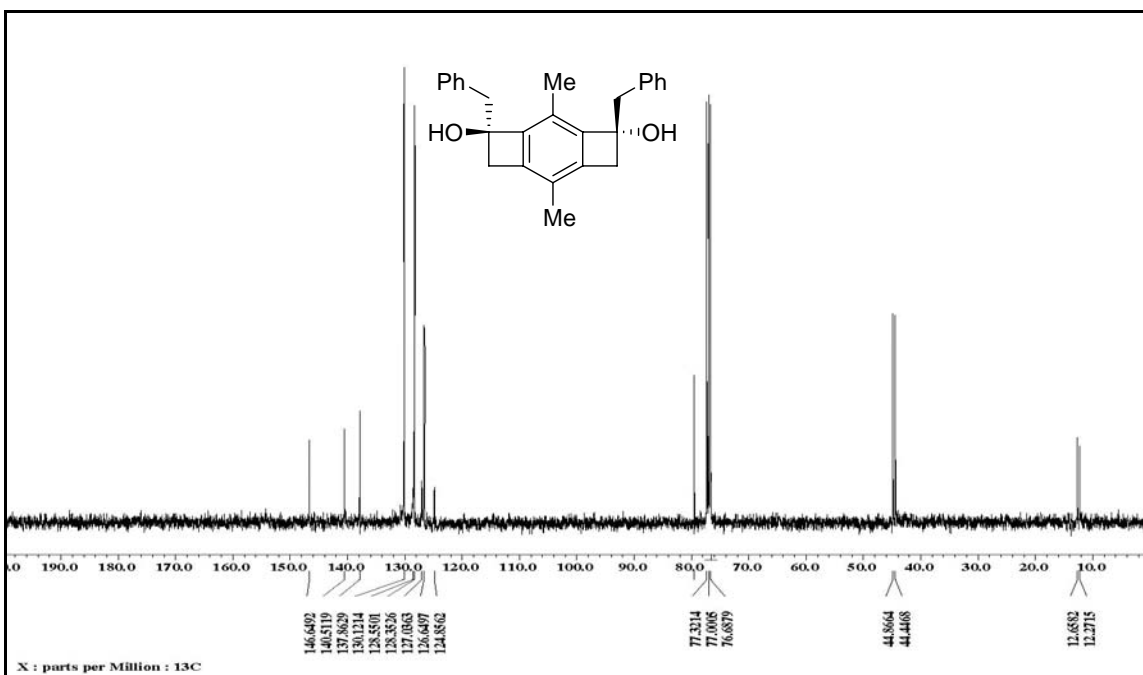


Figure S56. <sup>13</sup>C NMR spectrum of *Anti* 2d-BCB.

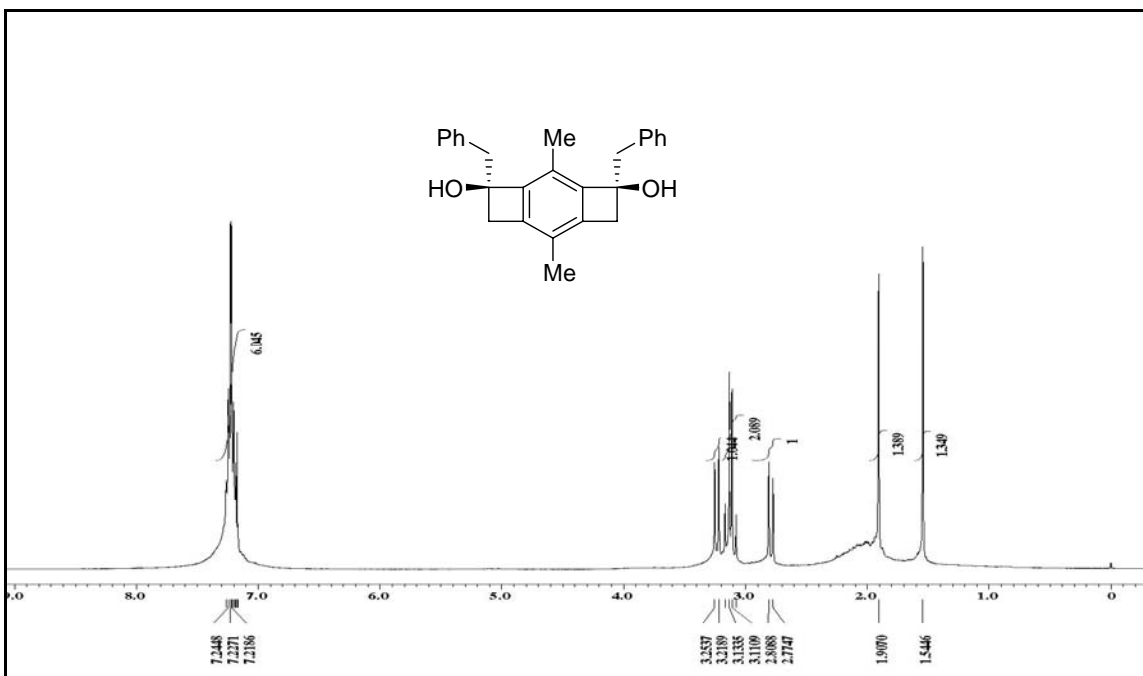


Figure S57. <sup>1</sup>H NMR spectrum of *Syn 2d-BCB*.

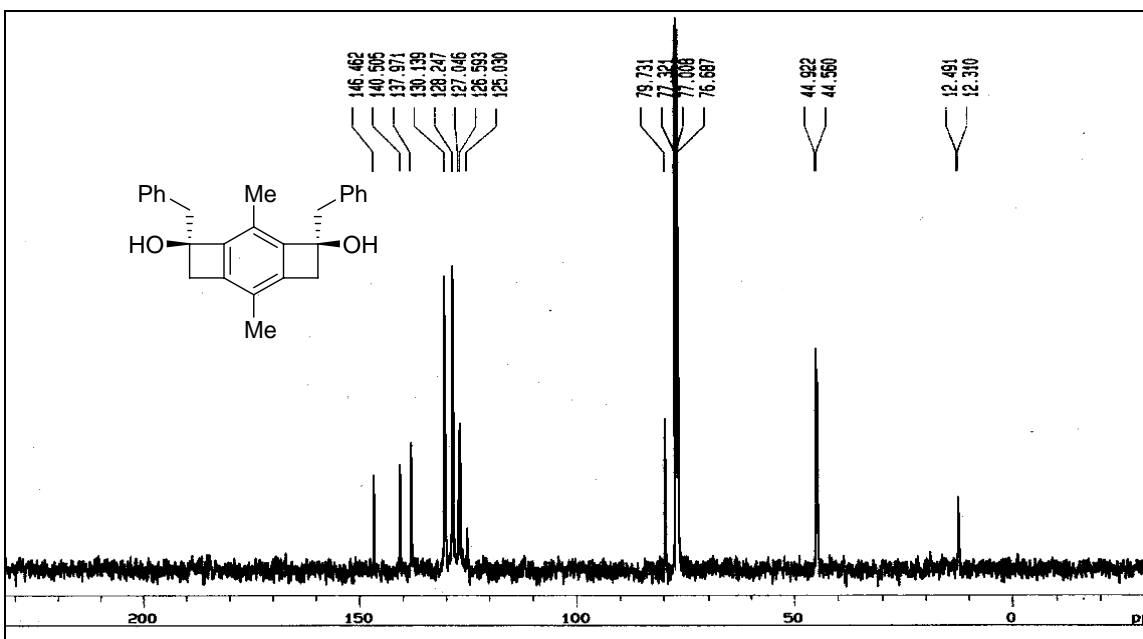
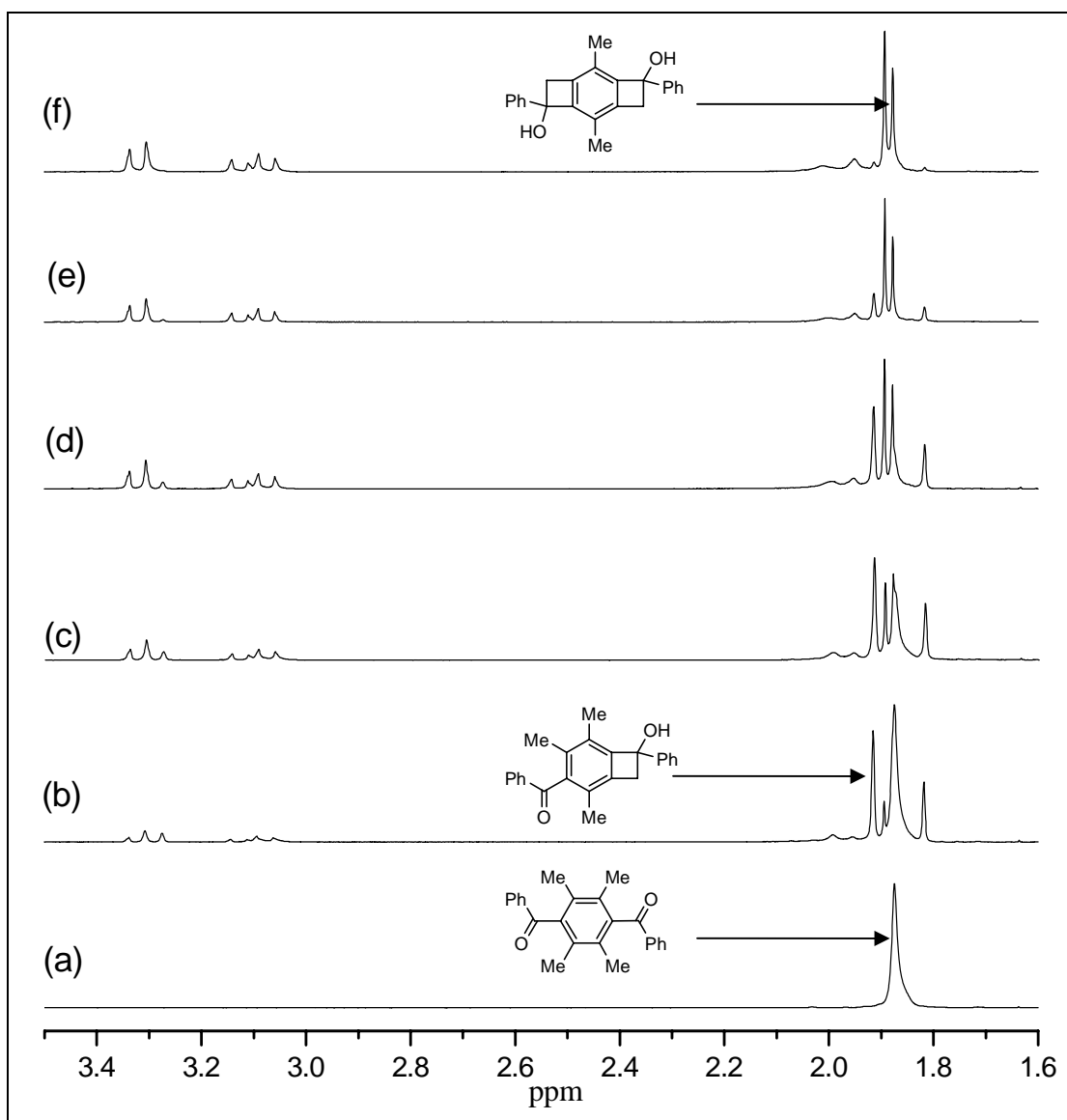
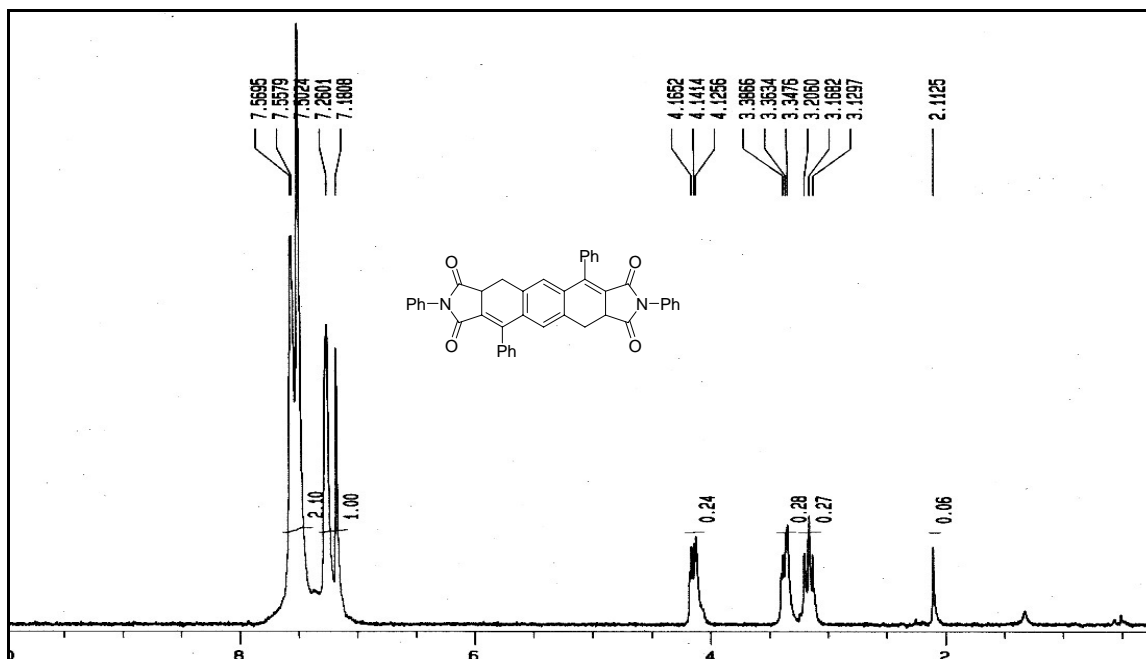


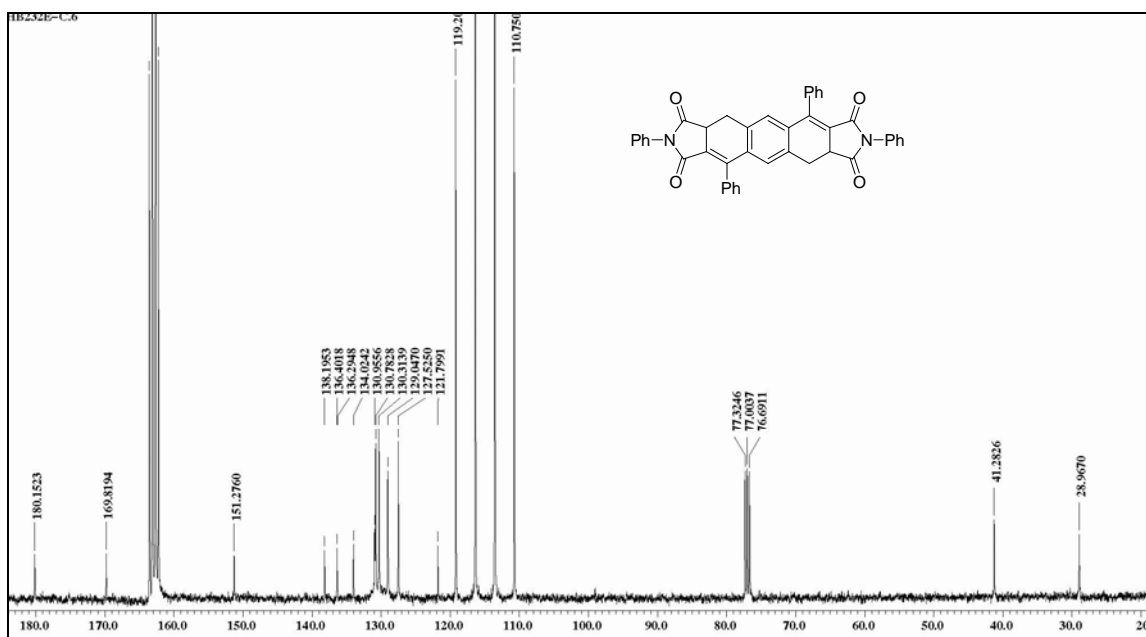
Figure S58. <sup>13</sup>C NMR spectrum of *Syn 2d-BCB*.



**Figure S59.**  $^1\text{H}$  NMR monitoring of the photolysis of ketone **1a** in  $\text{C}_6\text{D}_6$  in NMR tube under a  $\text{N}_2$  gas atmosphere: (a) 0.0 min; (b) 20 min; (c) 40 min; (d) 60 min; (e) 90 min; (f) 135 min.



**Figure S60.**  $^1\text{H}$  NMR spectrum of 3-DCA.



**Figure S61.**  $^{13}\text{C}$  NMR spectrum of 3-DCA.



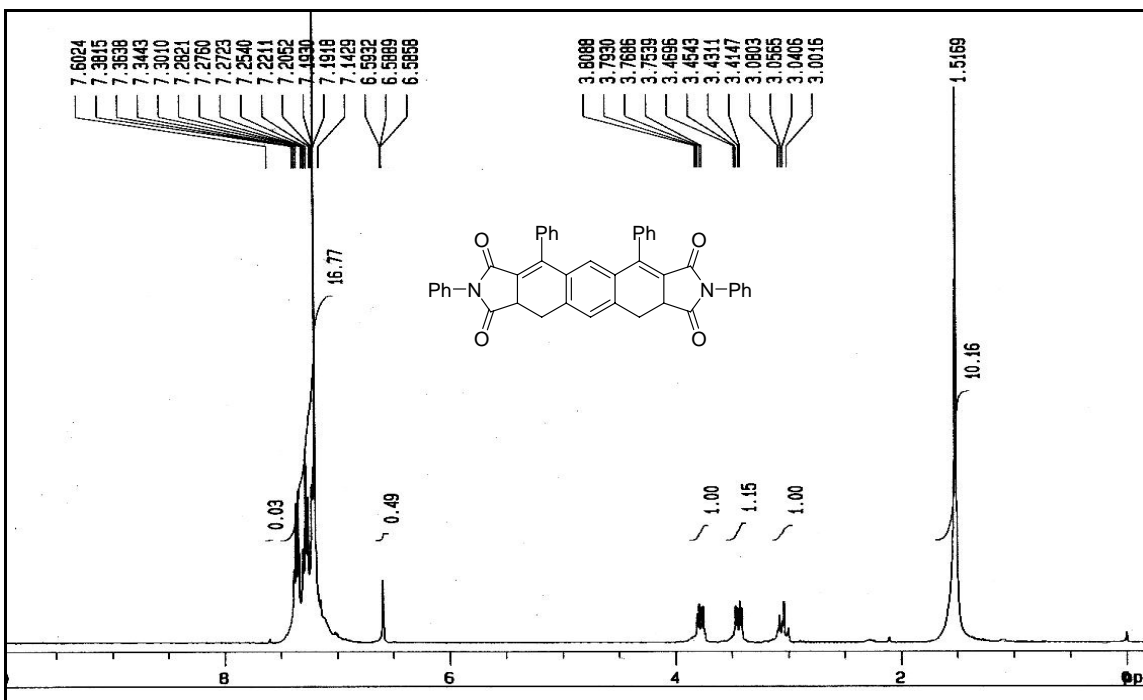


Figure S62. <sup>1</sup>H NMR spectrum of 4-DCA.

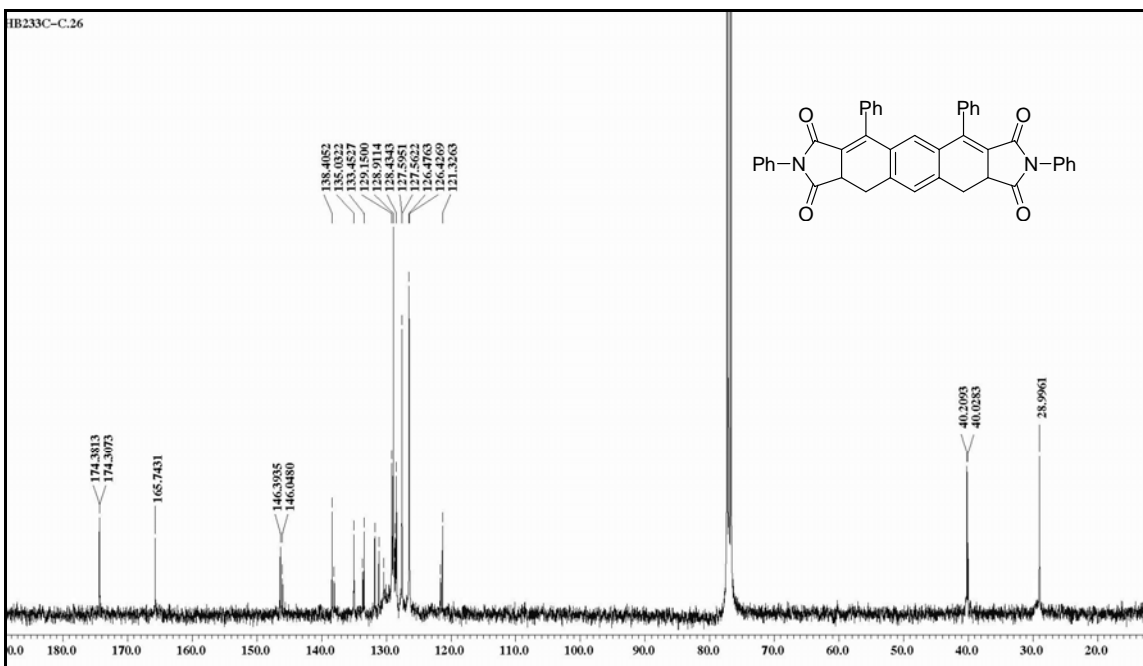


Figure S63. <sup>13</sup>C NMR spectrum of 4-DCA.

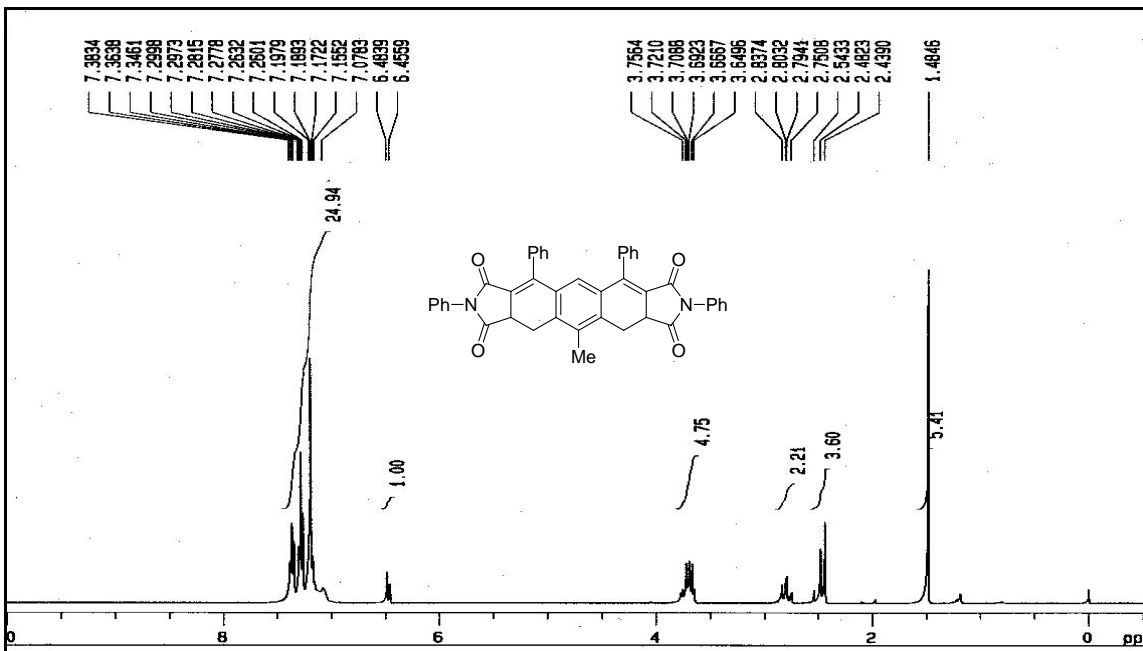


Figure S64. <sup>1</sup>H NMR spectrum of 6-DCA.

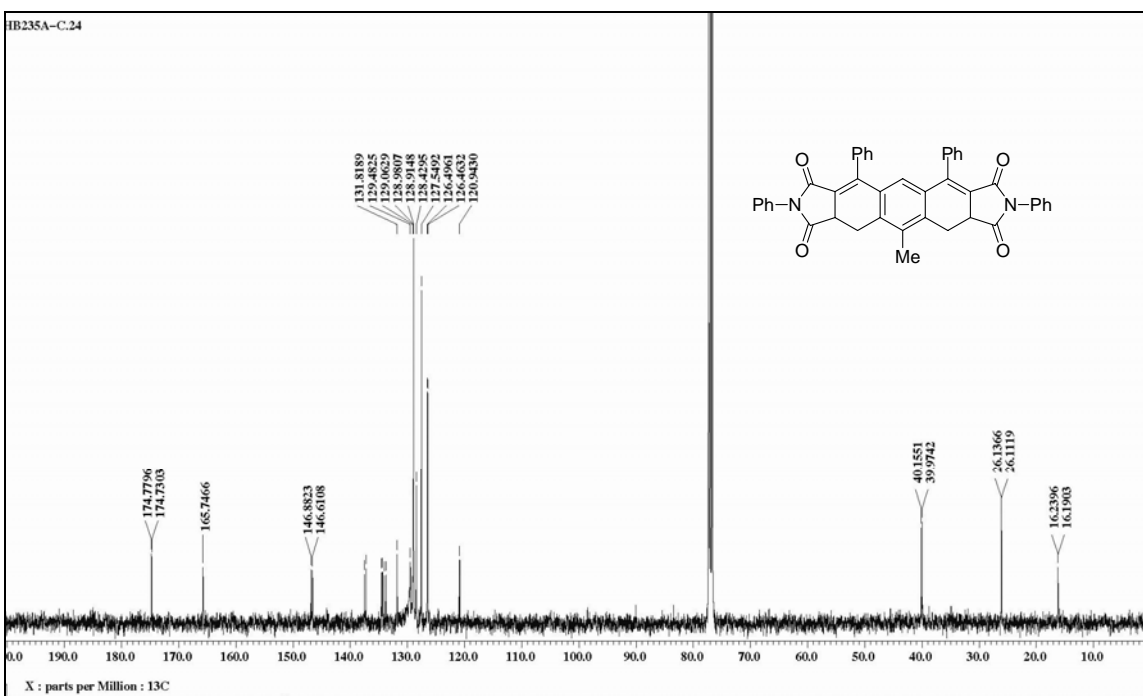


Figure S65. <sup>13</sup>C NMR spectrum of 6-DCA.

