

## Supporting Information

### **Highly efficient synthesis of substituted 3,4-dihydropyrimidin-2-(1H)-ones (DHPMs) catalyzed by Hf(OTf)<sub>4</sub>: Mechanistic insights into reaction pathways under metal Lewis acid catalysis and solvent-free conditions**

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## 1. The NMR spectra of DHPMs 1–14 and 20

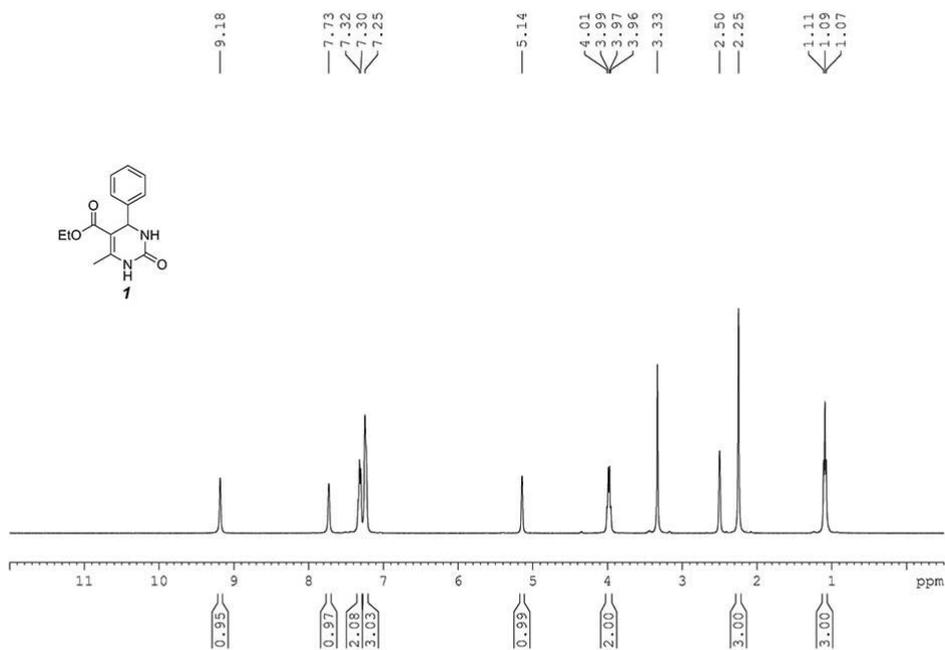


Figure S1. <sup>1</sup>H-NMR of **1**

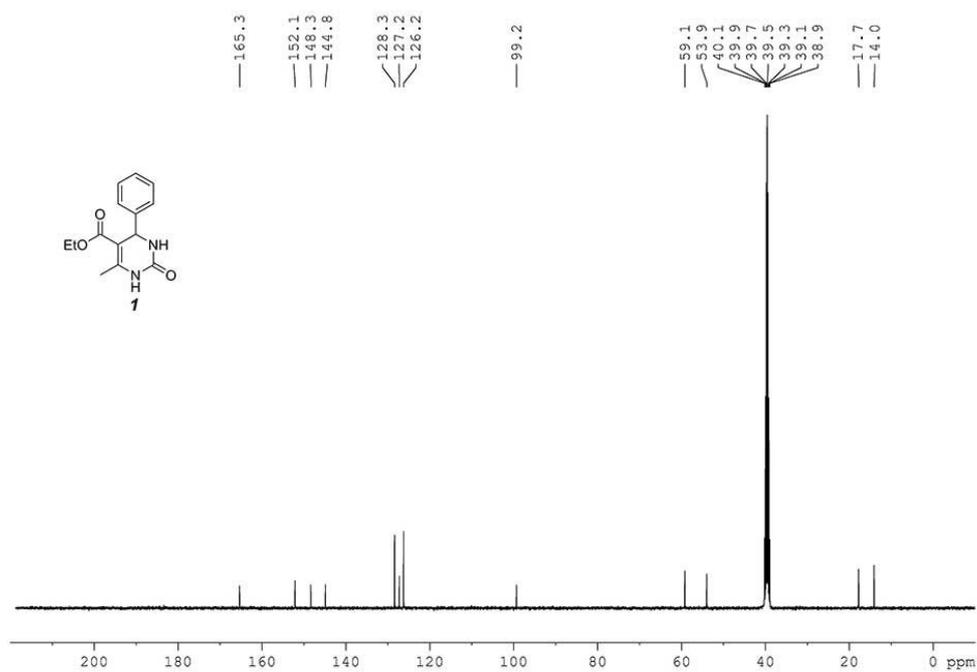


Figure S2. <sup>13</sup>C-NMR of **1**

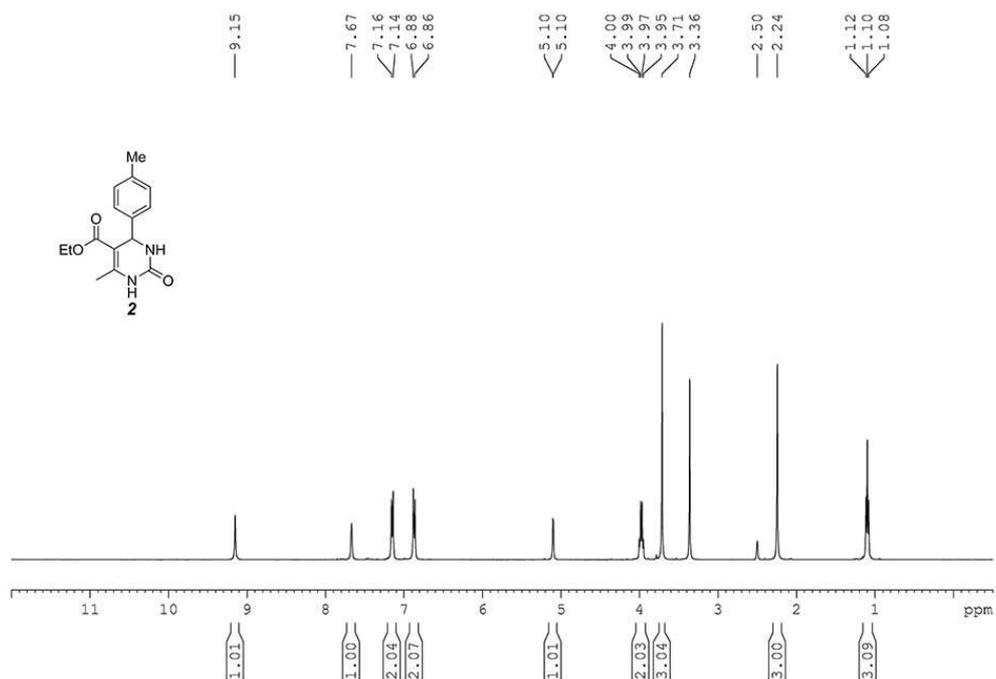


Figure S3. <sup>1</sup>H-NMR of **2**

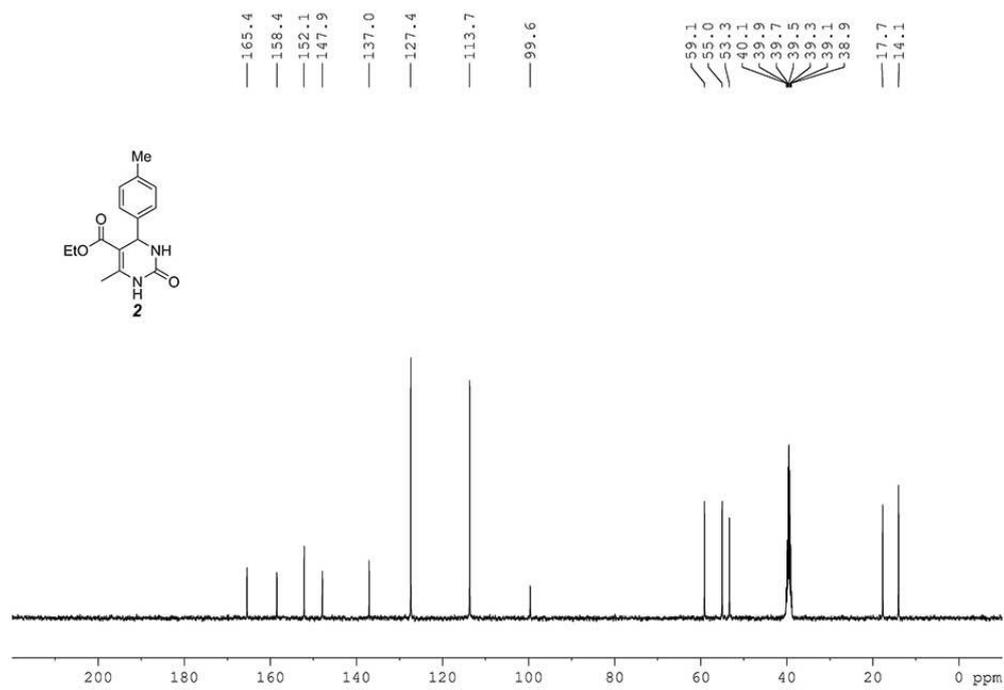


Figure S4. <sup>13</sup>C-NMR of **2**

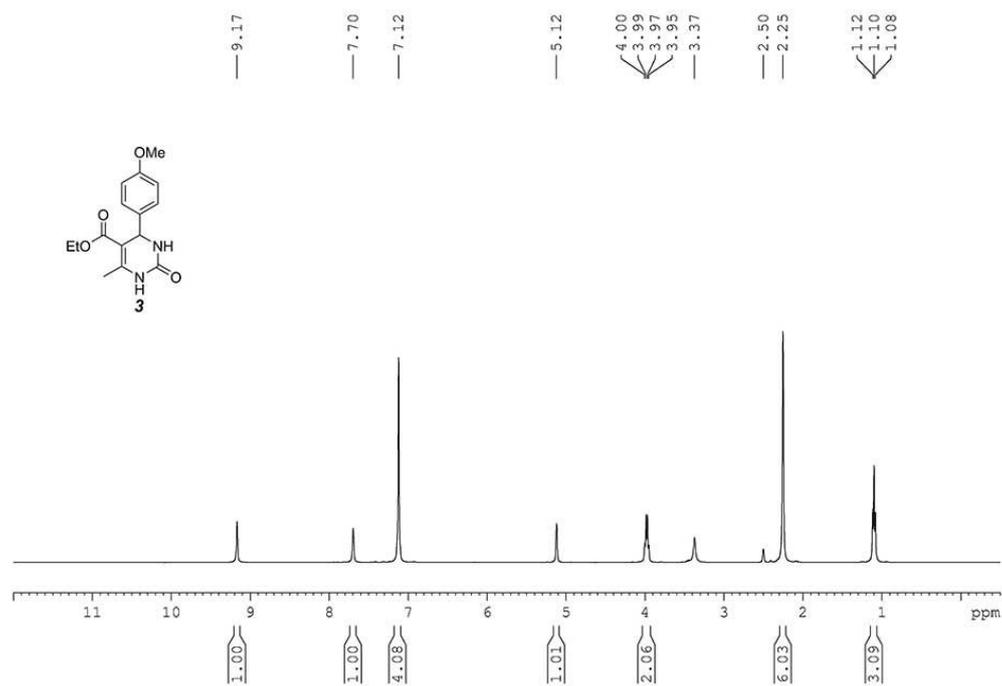


Figure S5. <sup>1</sup>H-NMR of **3**

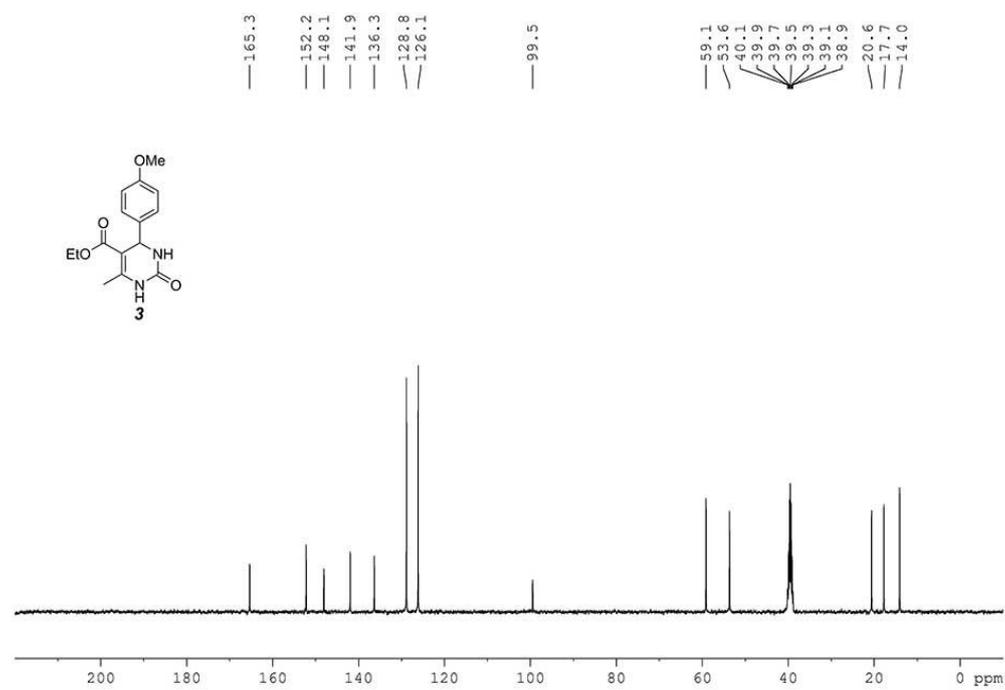


Figure S6. <sup>13</sup>C-NMR of **3**

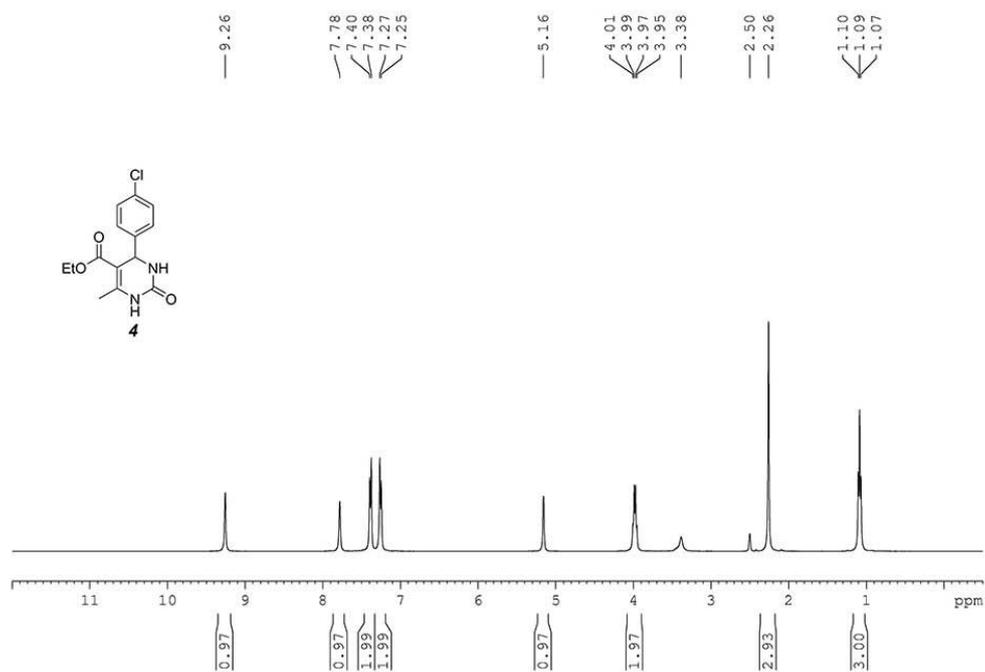


Figure S7. <sup>1</sup>H-NMR of **4**

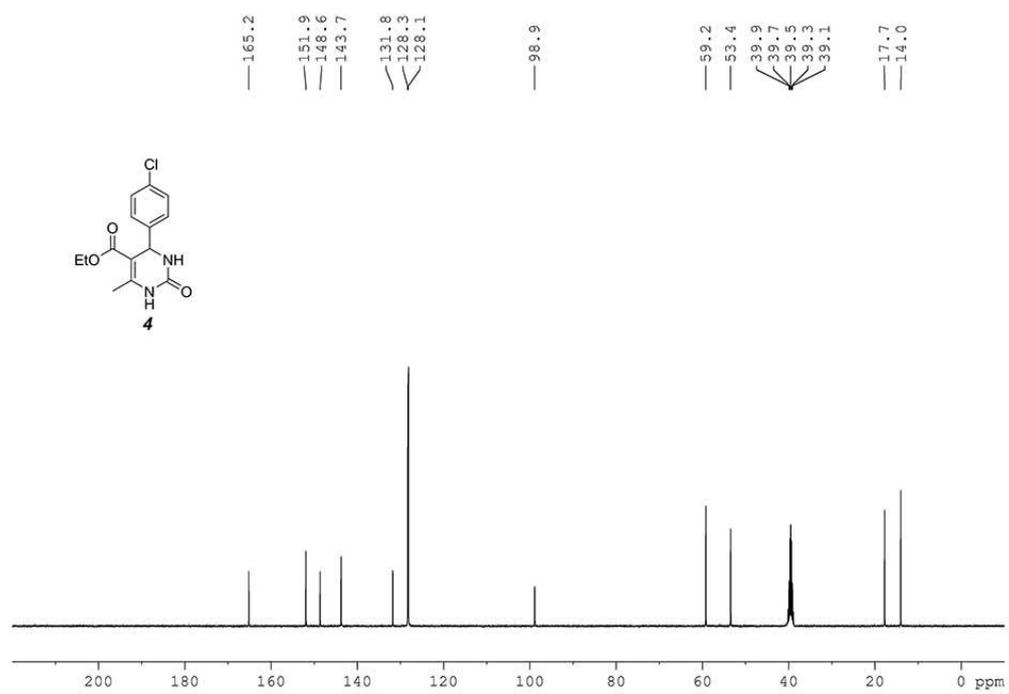


Figure S8. <sup>13</sup>C-NMR of **4**

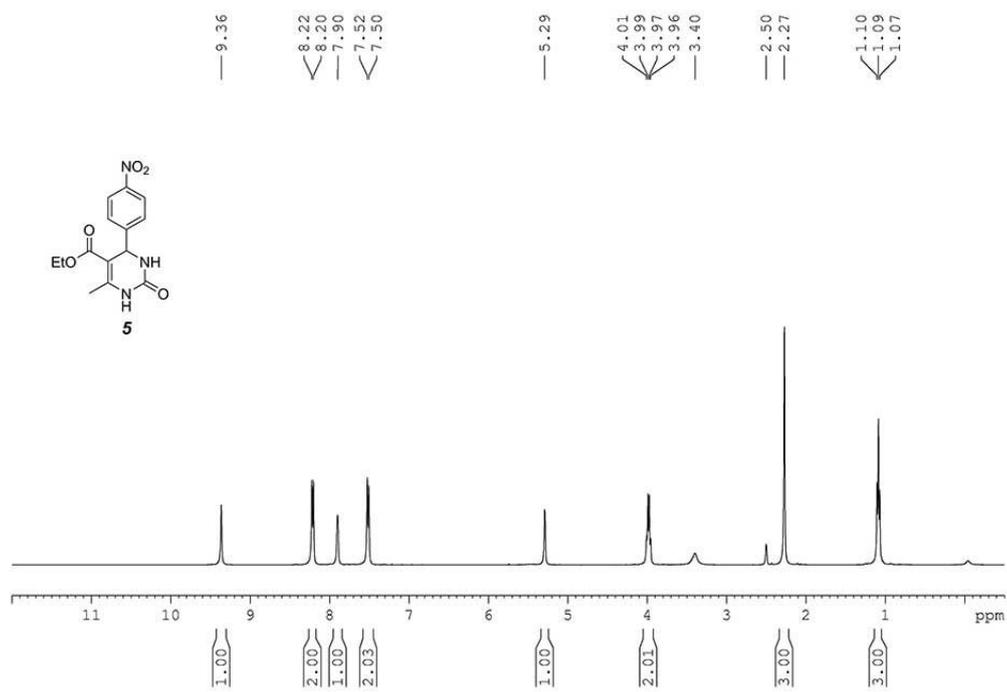


Figure S9. <sup>1</sup>H-NMR of **5**

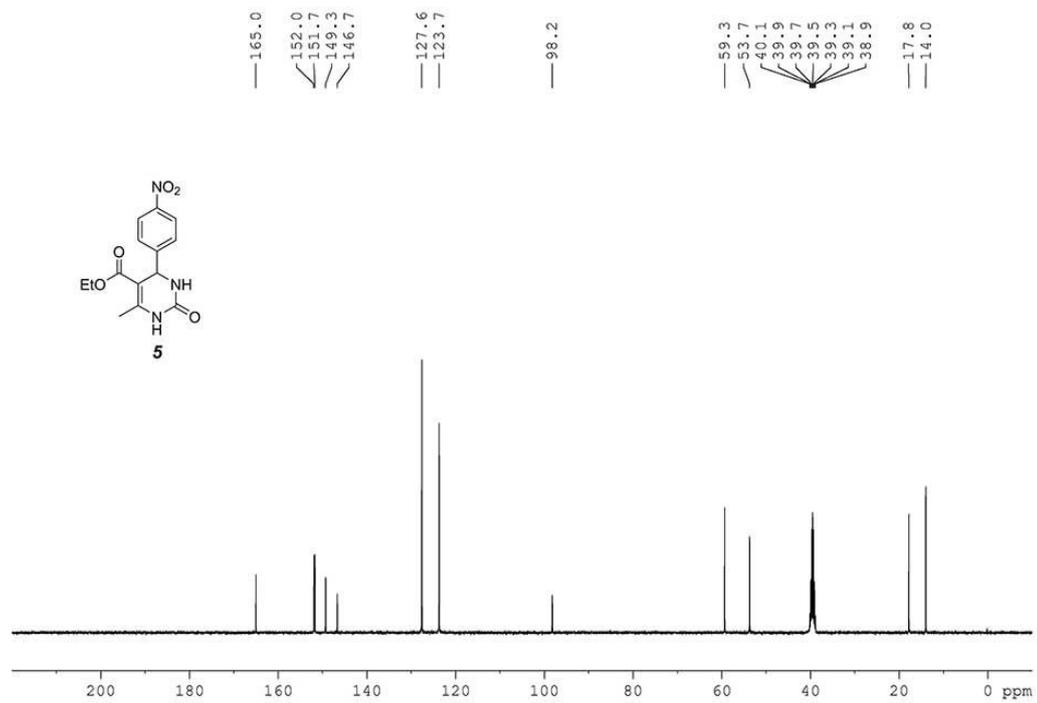


Figure S10. <sup>13</sup>C-NMR of **5**

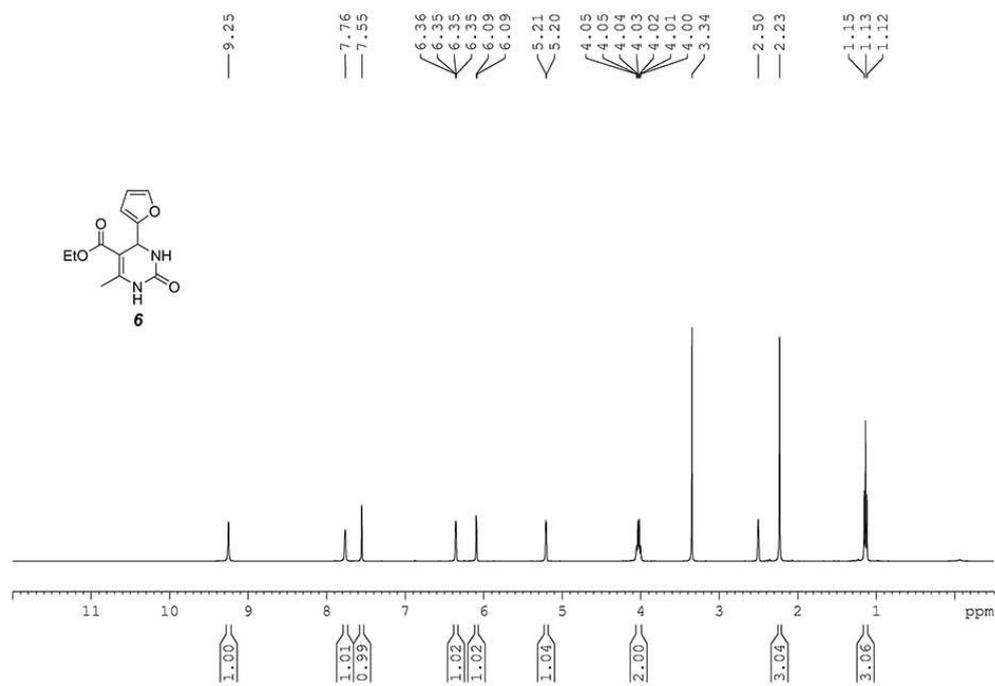


Figure S11. <sup>1</sup>H-NMR of **6**

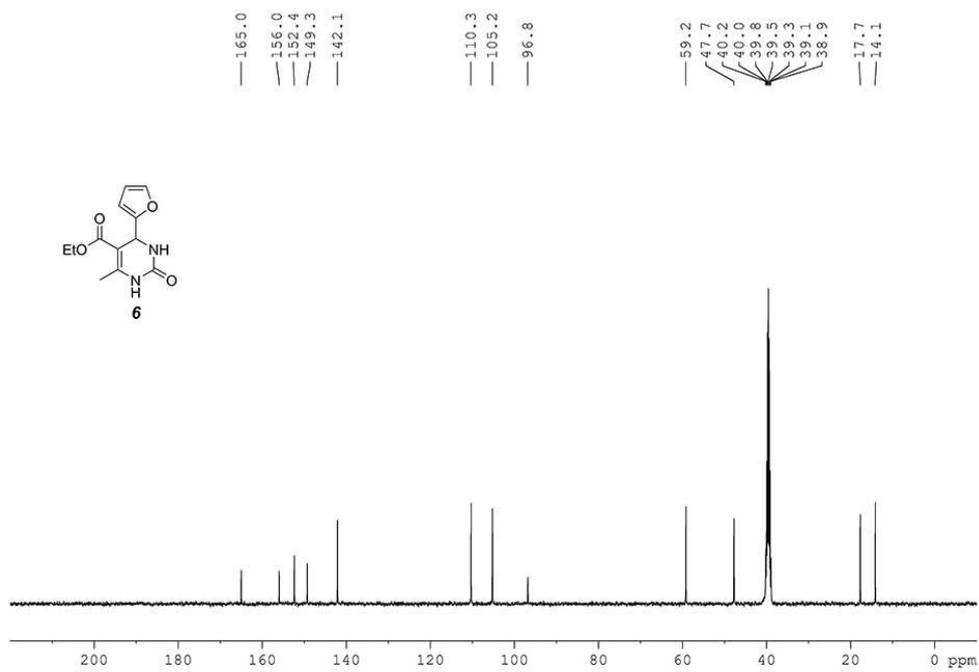


Figure S12. <sup>13</sup>C-NMR of **6**

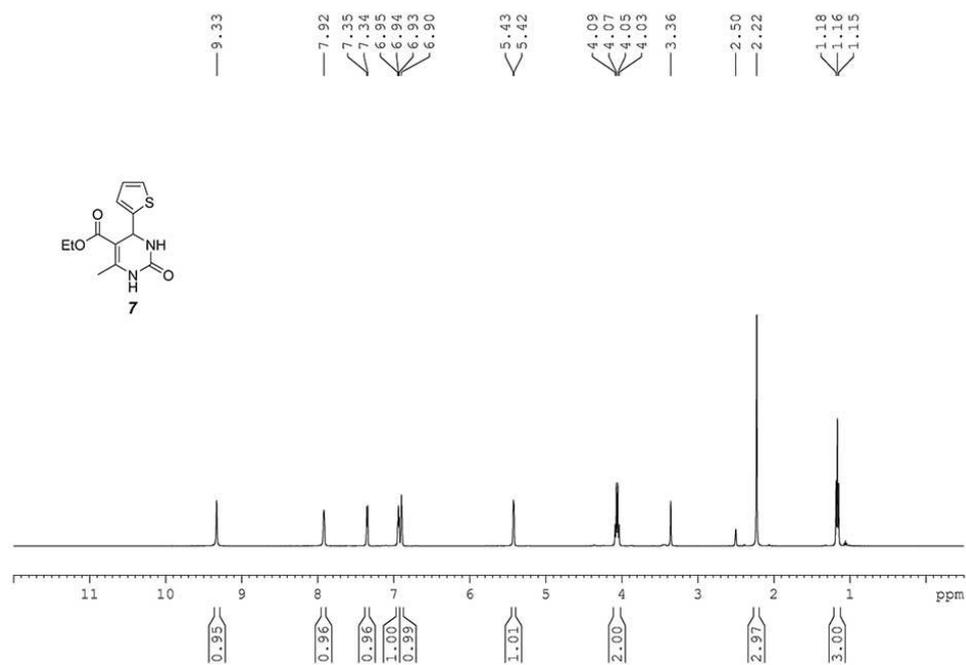


Figure S13. <sup>1</sup>H-NMR of 7

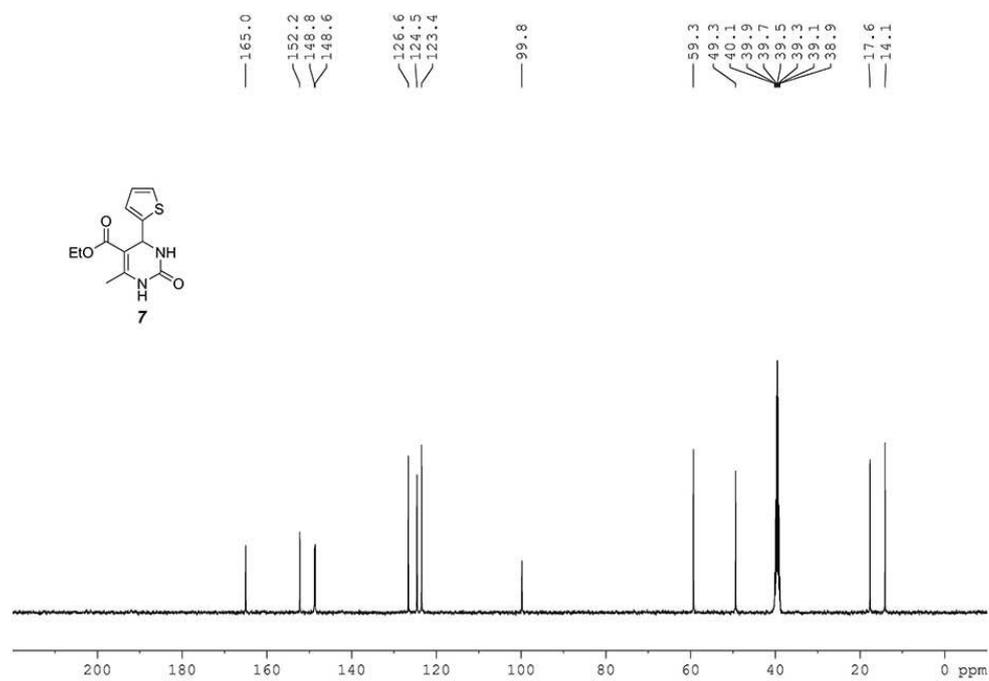


Figure S14. <sup>13</sup>C-NMR of 7

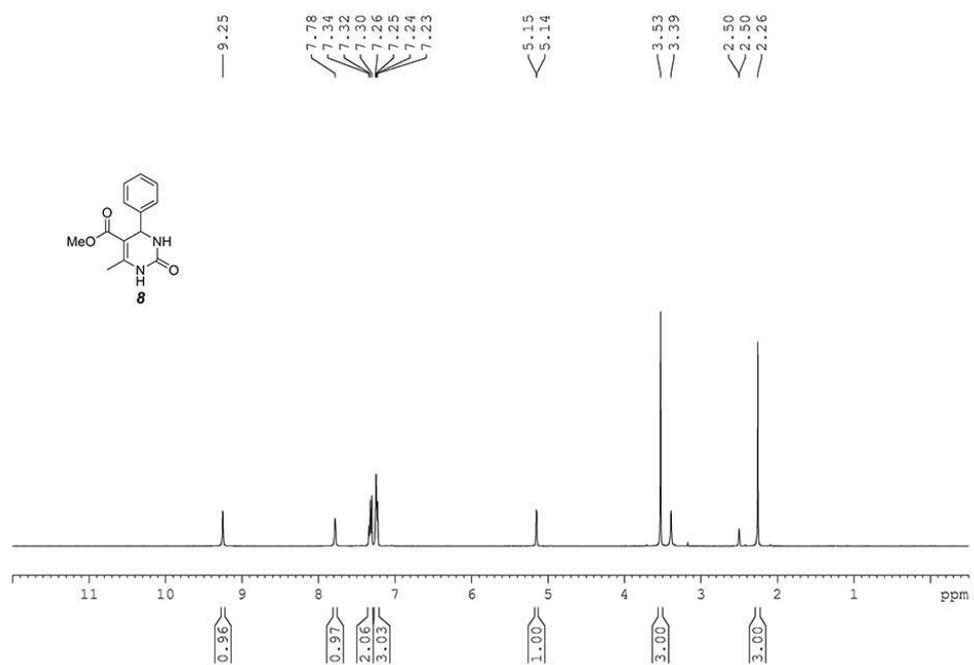


Figure S15. <sup>1</sup>H-NMR of **8**

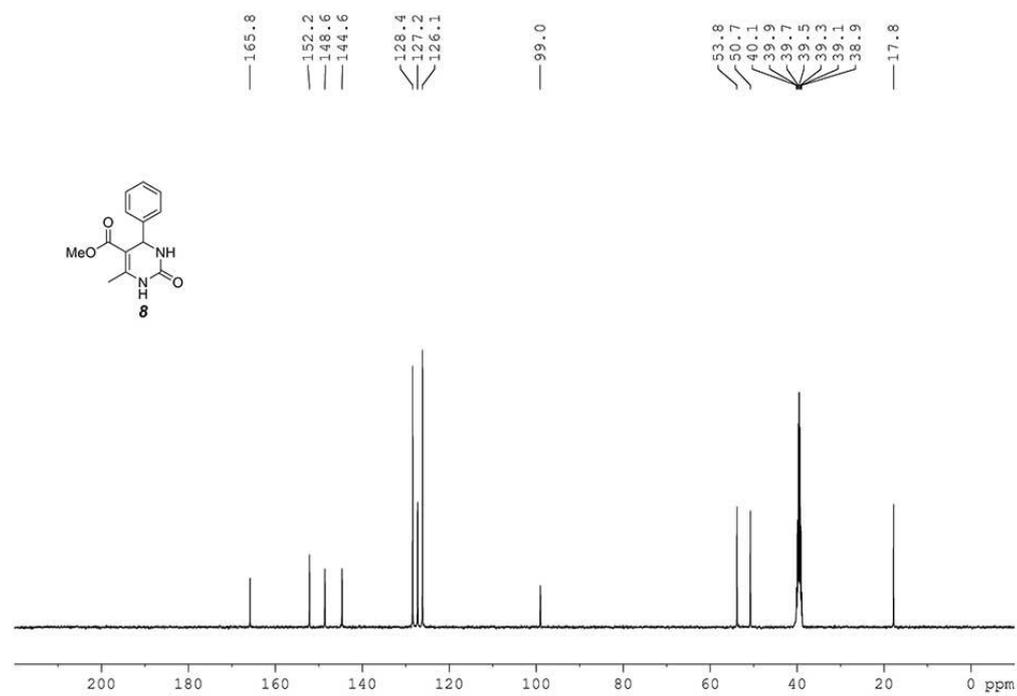


Figure S16. <sup>13</sup>C-NMR of **8**

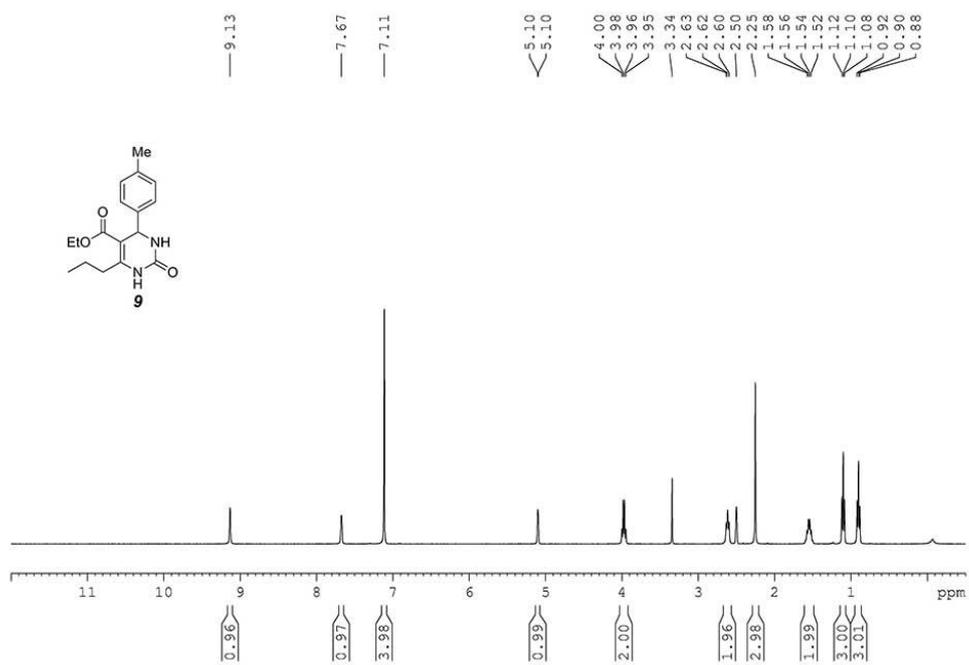


Figure S17. <sup>1</sup>H-NMR of **9**

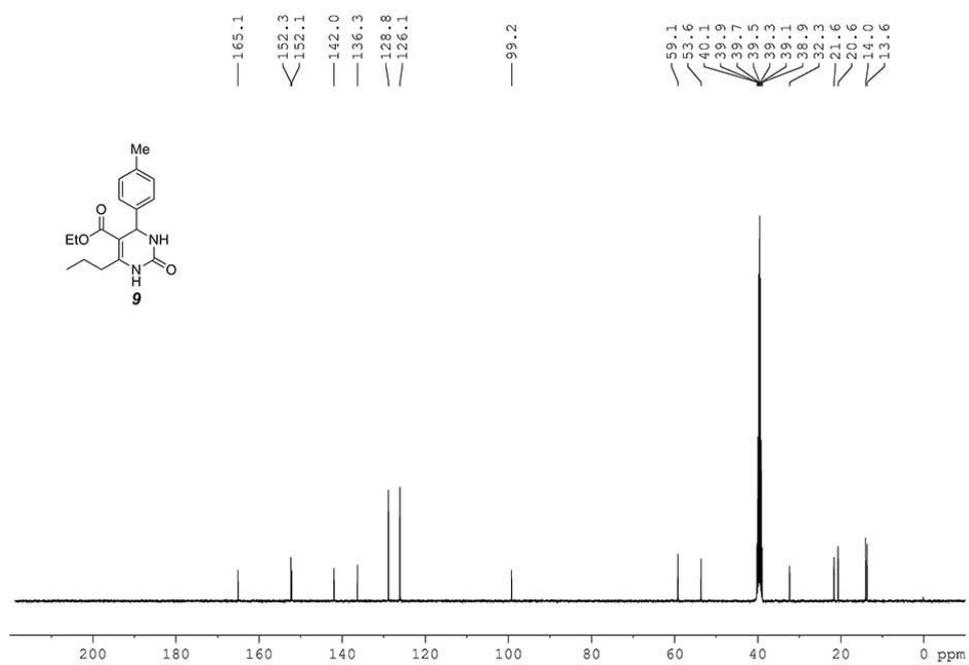


Figure S18. <sup>13</sup>C-NMR of **9**

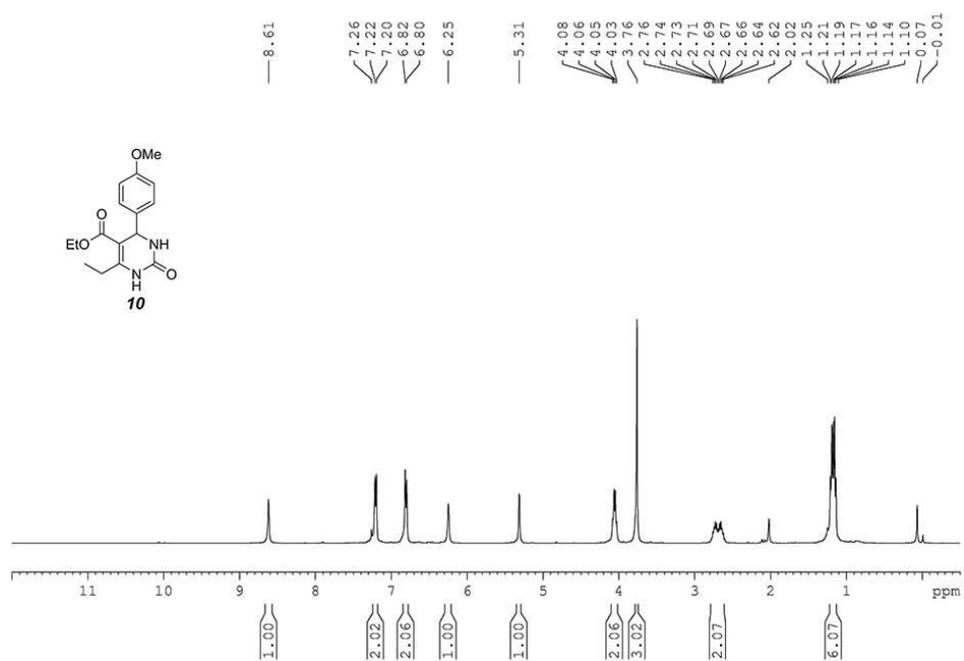


Figure S19. <sup>1</sup>H-NMR of **10**

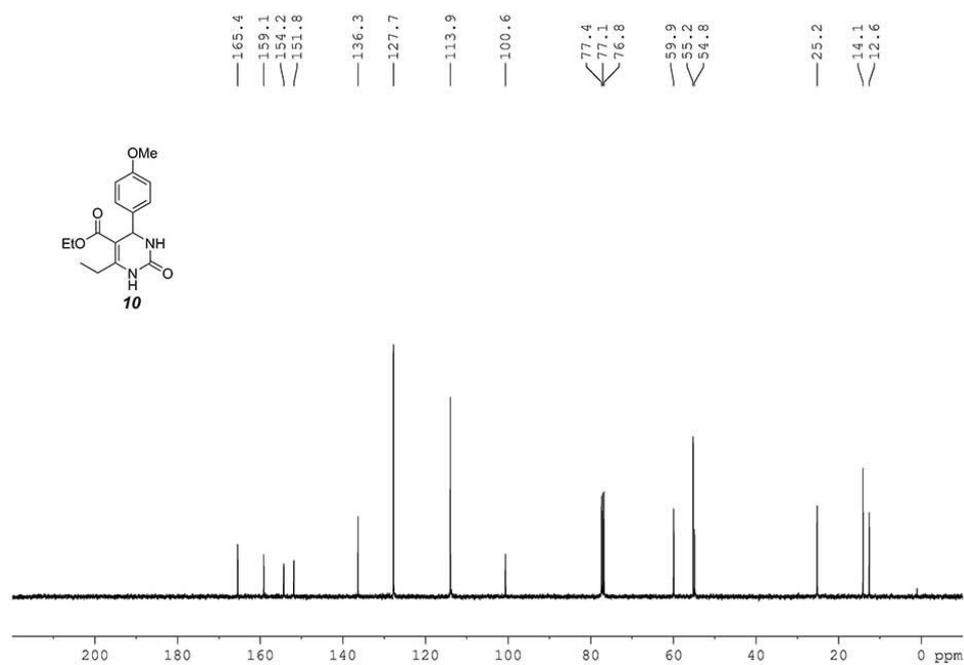


Figure S20. <sup>13</sup>C-NMR of **10**

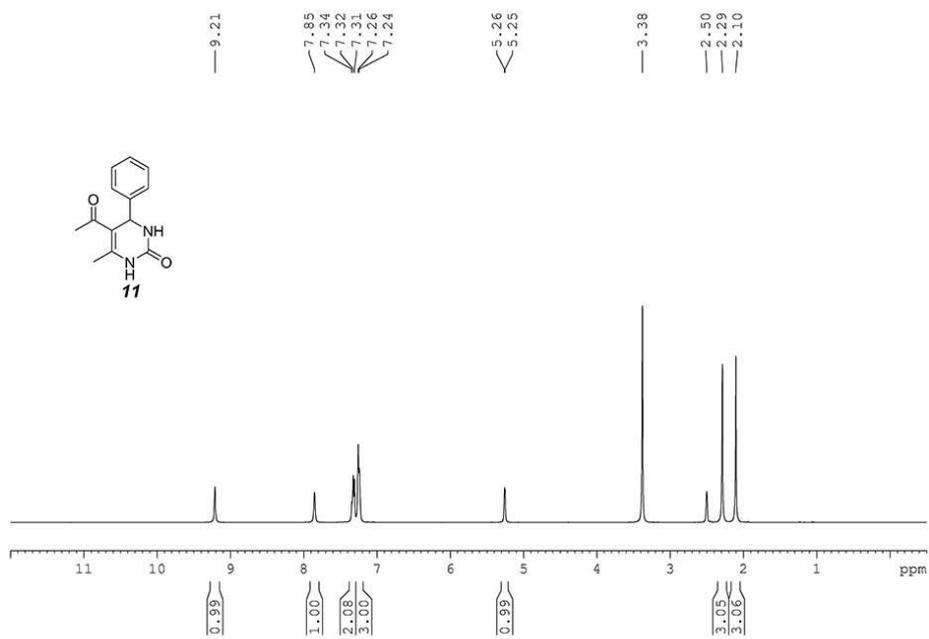


Figure S21. <sup>1</sup>H-NMR of **11**

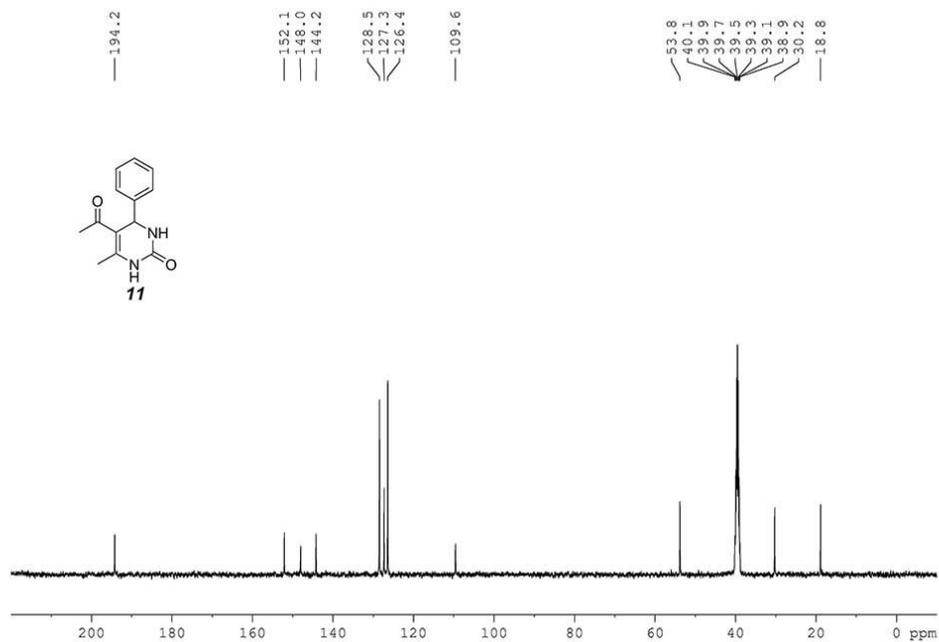


Figure S22. <sup>13</sup>C-NMR of **11**

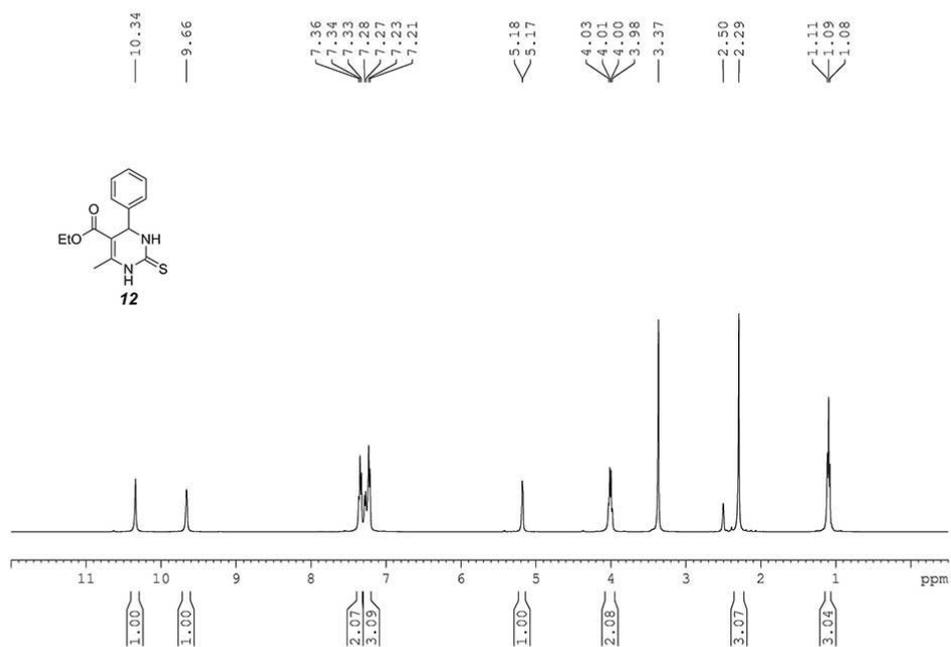


Figure S23. <sup>1</sup>H-NMR of **12**

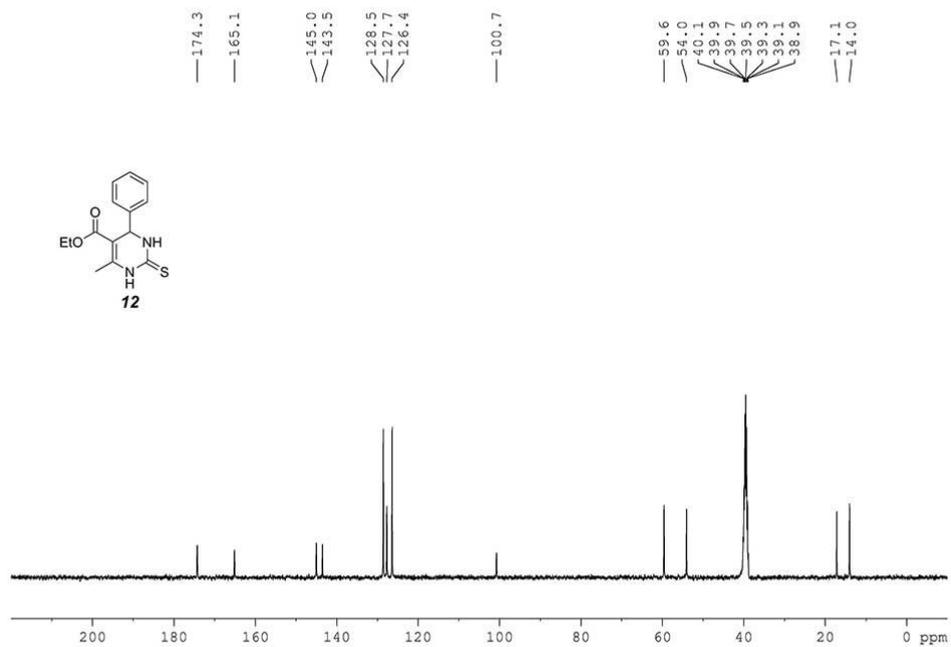


Figure S24. <sup>13</sup>C-NMR of **12**

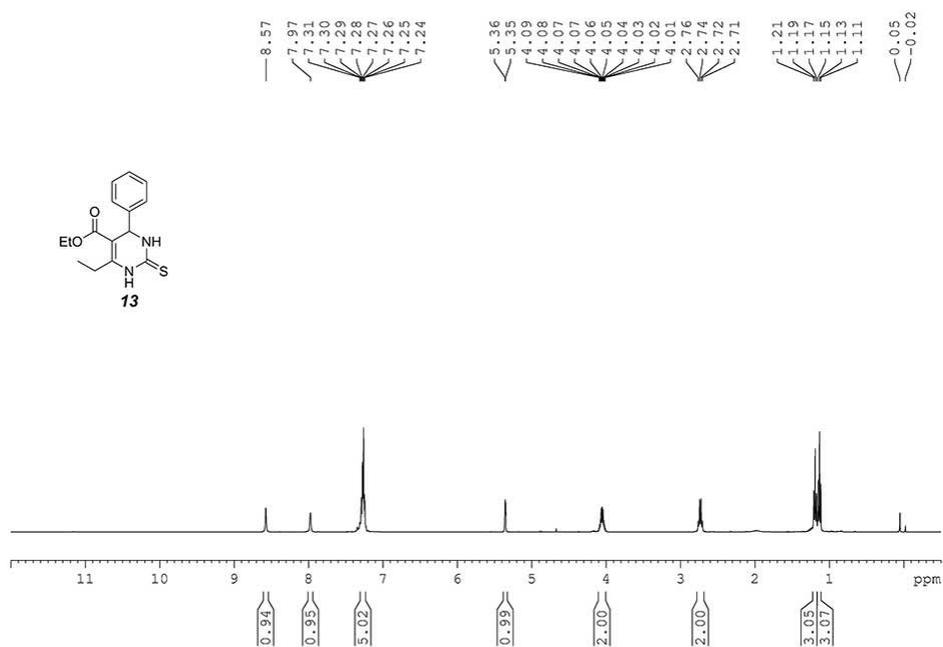


Figure S25. <sup>1</sup>H-NMR of **13**

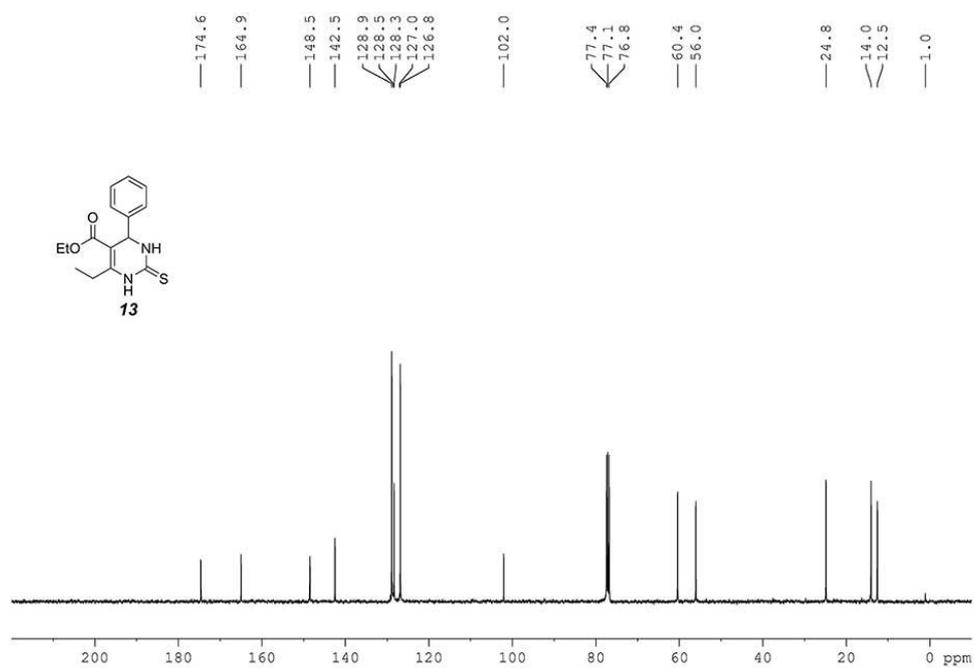


Figure S26. <sup>13</sup>C-NMR of **13**

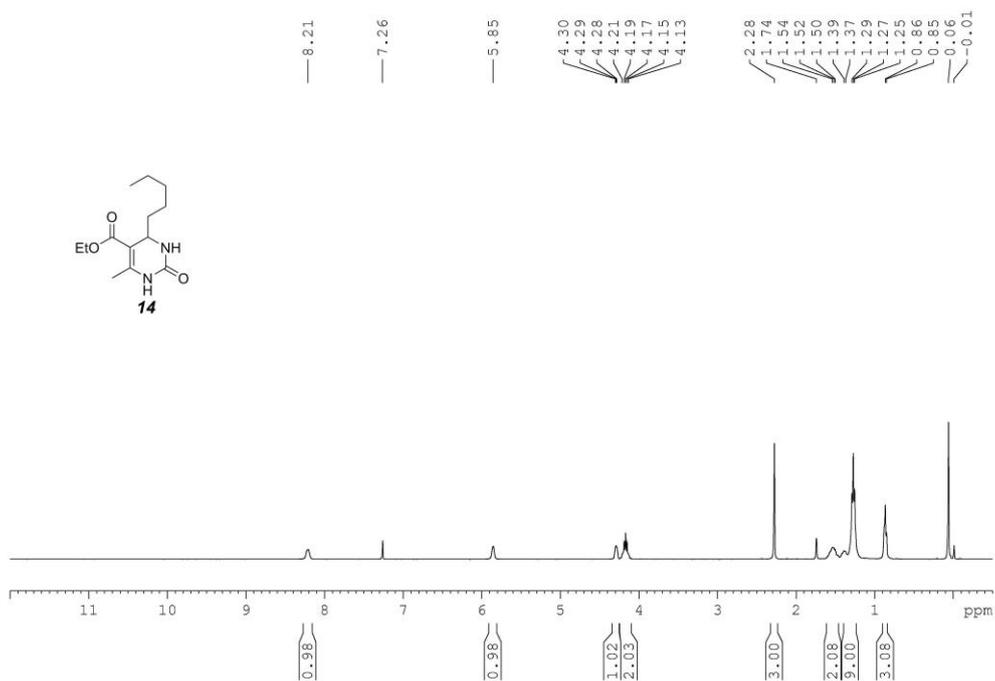


Figure S27.  $^1\text{H-NMR}$  of **14**

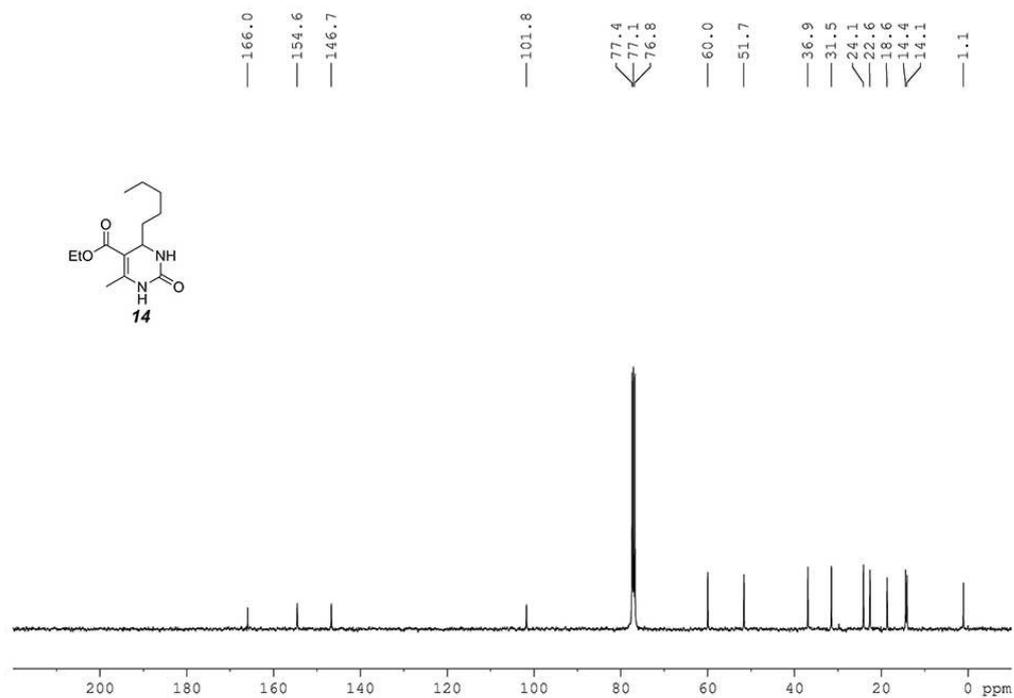


Figure S28.  $^{13}\text{C-NMR}$  of **14**

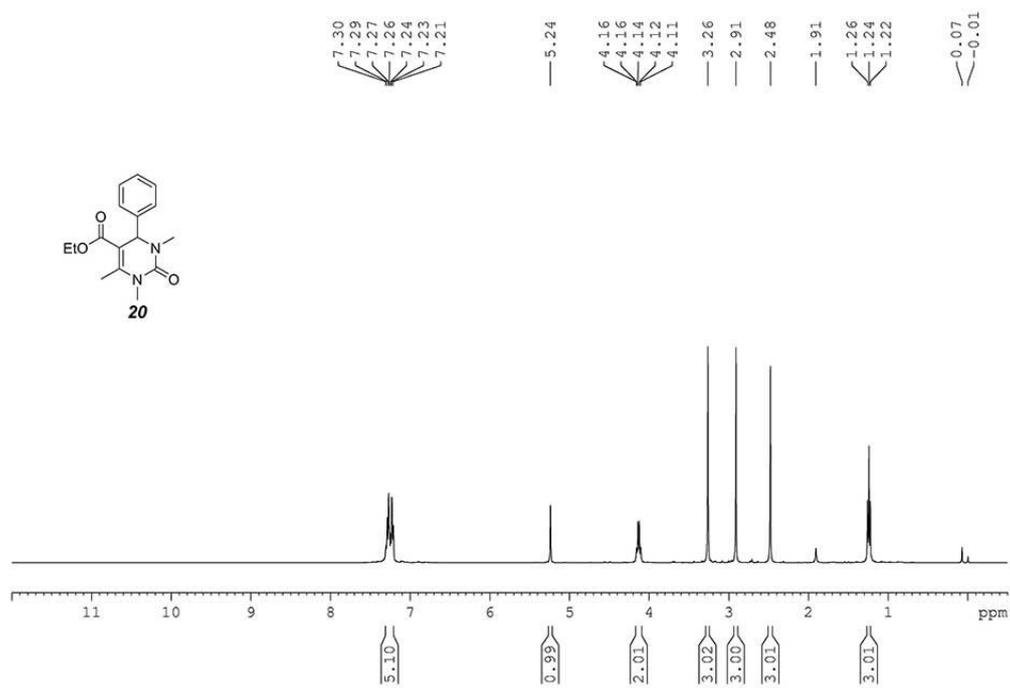


Figure S29. <sup>1</sup>H-NMR of **20**

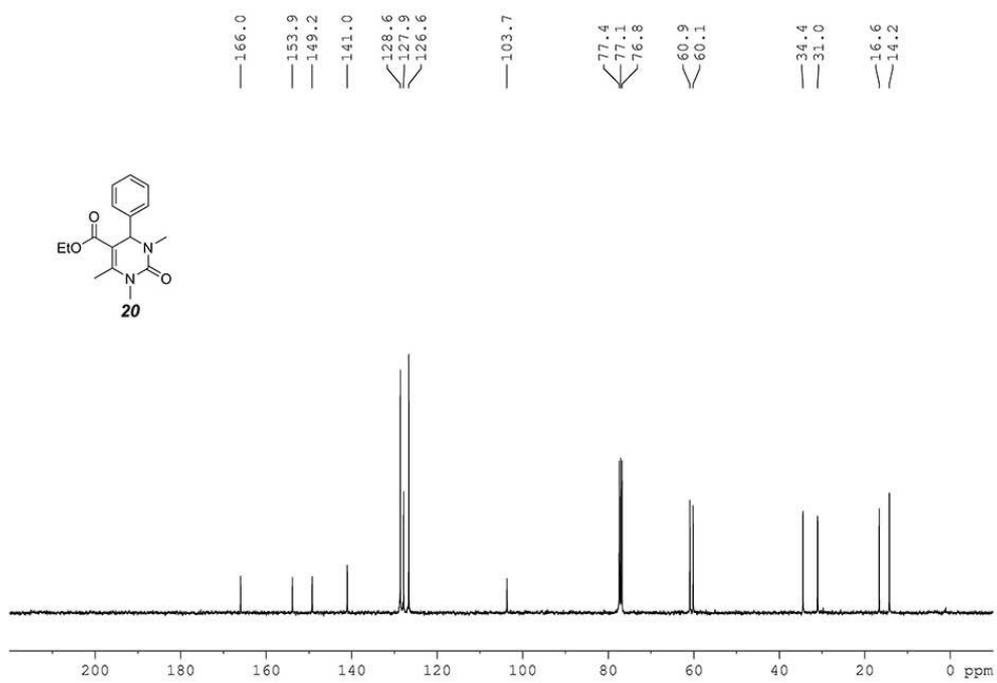


Figure S30. <sup>13</sup>C-NMR of **20**

## 2. The NMR spectra of compounds (15-17, 19, and 21).

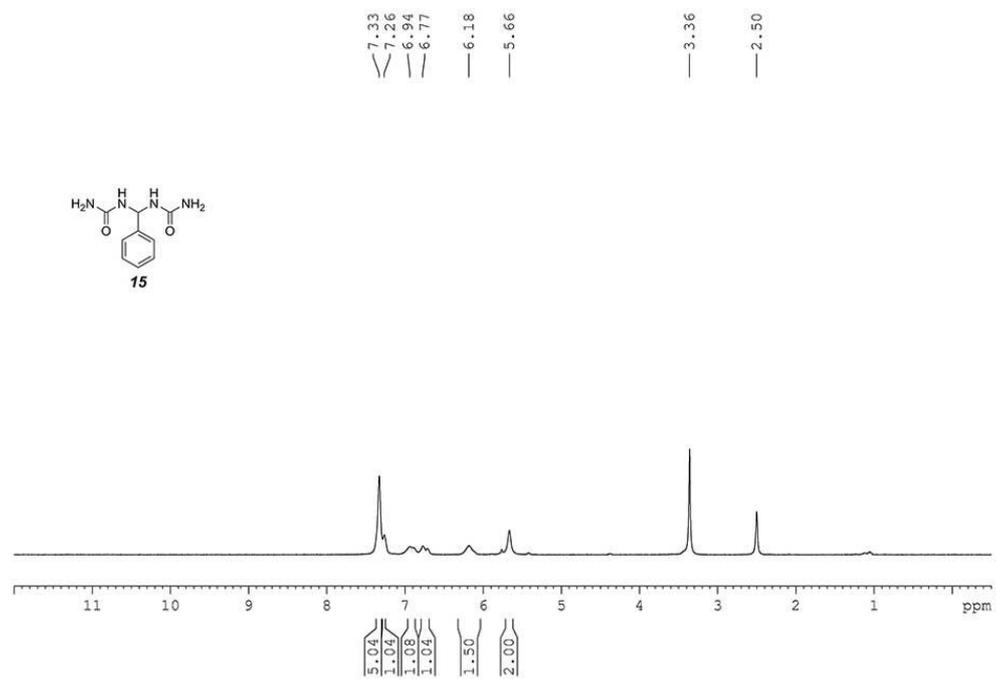


Figure S31. <sup>1</sup>H-NMR of **15**

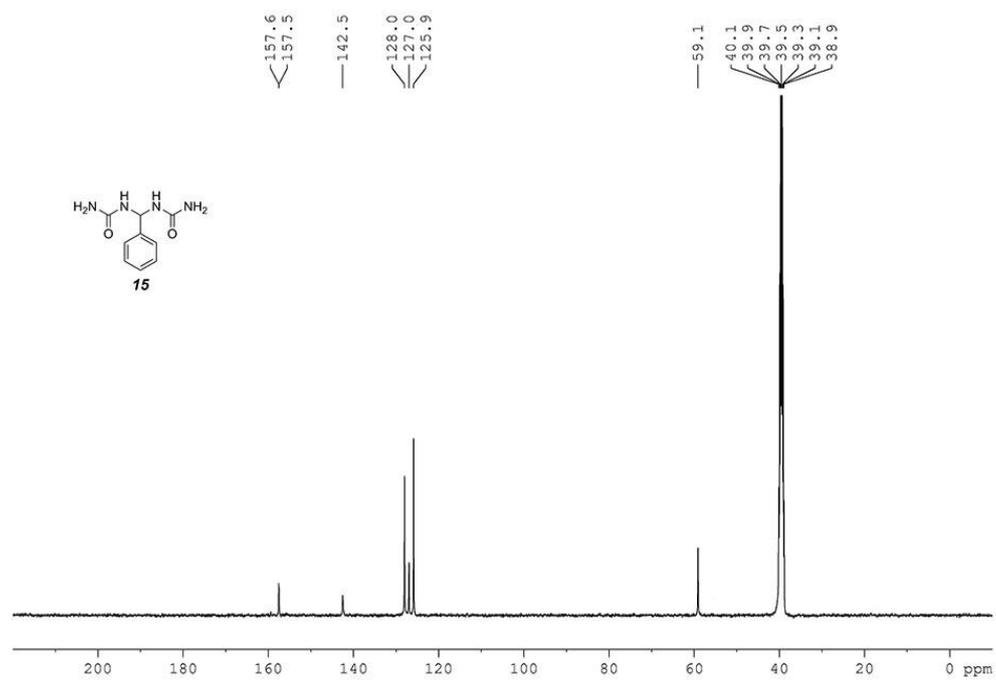


Figure S32. <sup>13</sup>C-NMR of **15**

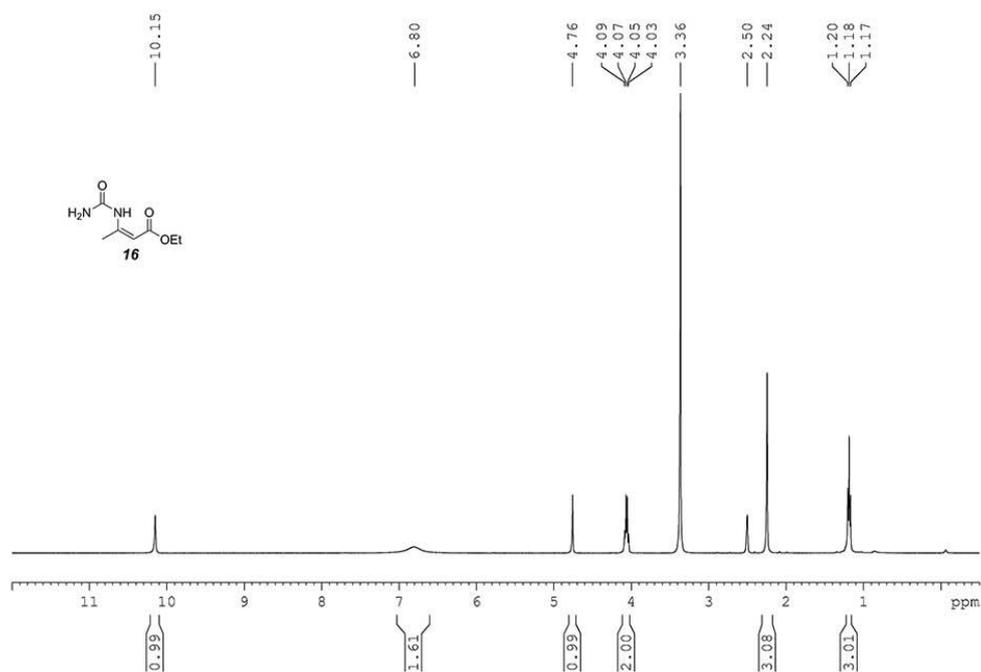


Figure S33. <sup>1</sup>H-NMR of **16**

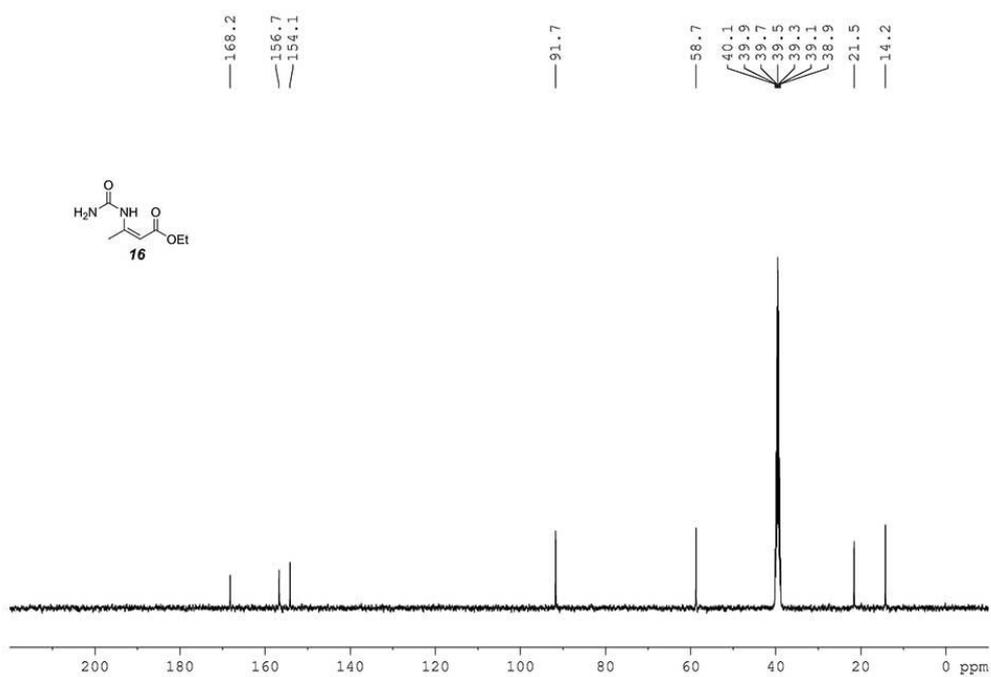


Figure S34. <sup>13</sup>C-NMR of **16**

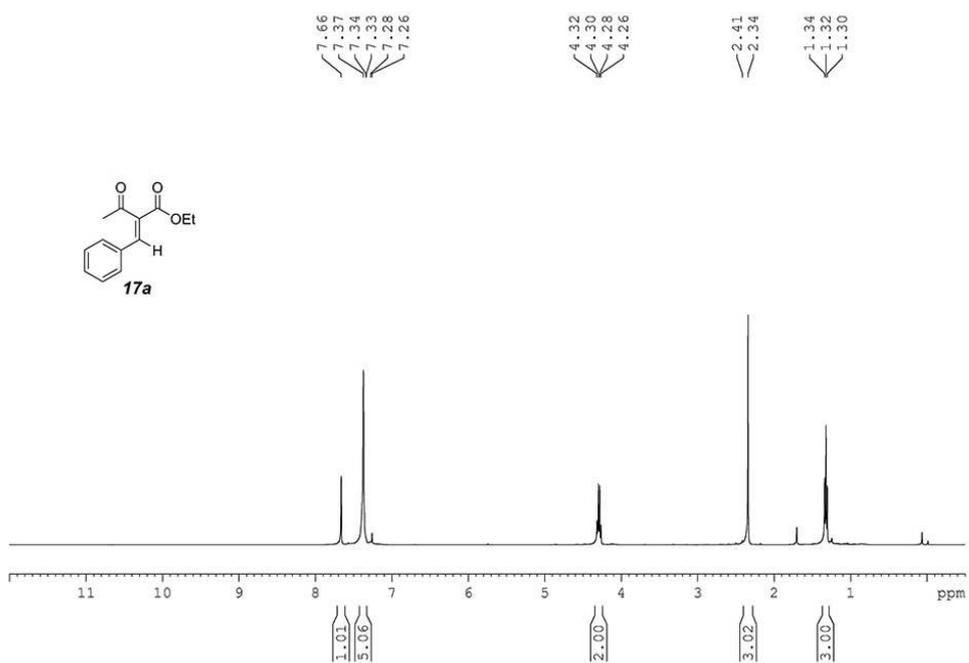


Figure S35. <sup>1</sup>H-NMR of **17a**

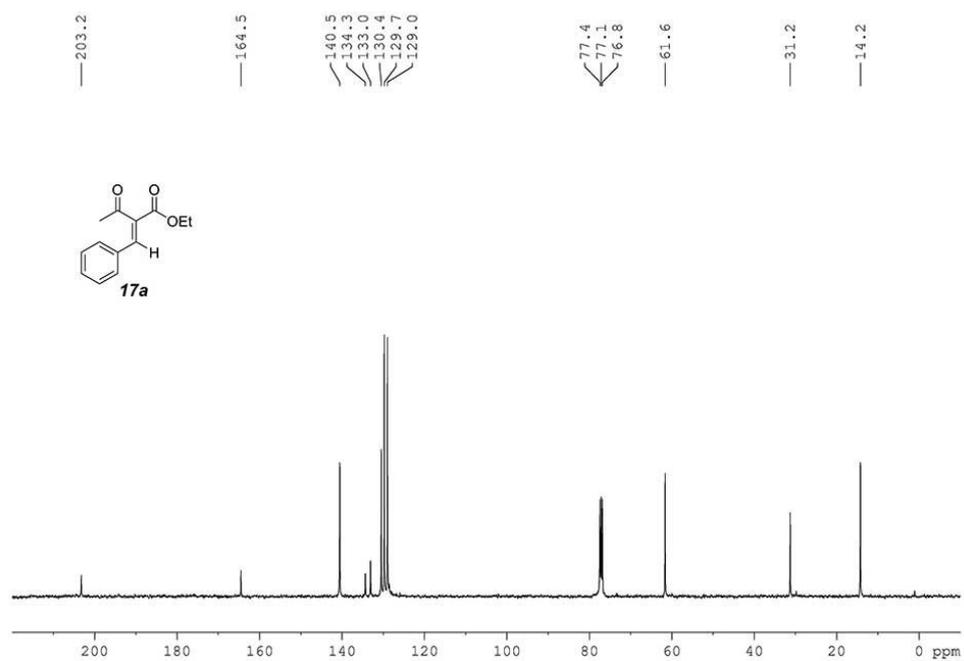


Figure S36. <sup>13</sup>C-NMR of **17a**

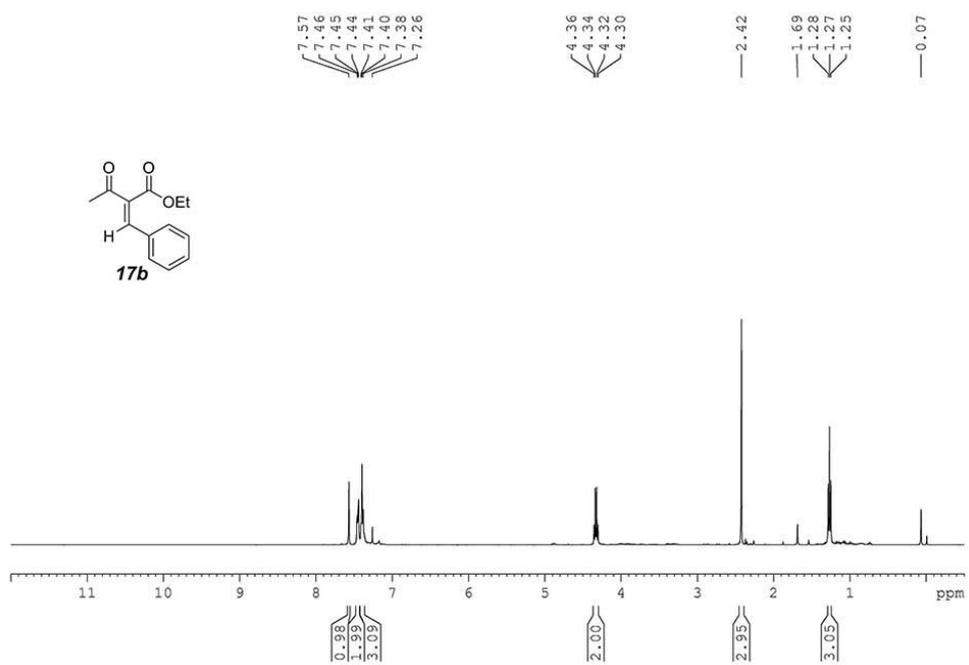


Figure S37. <sup>1</sup>H-NMR of **17b**

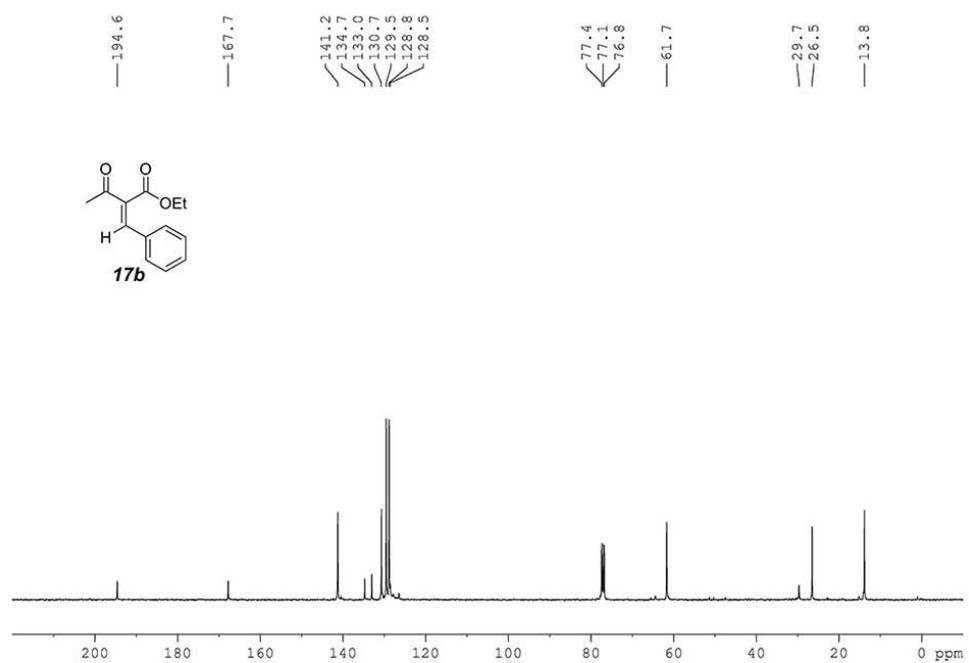


Figure S38. <sup>13</sup>C-NMR of **17b**

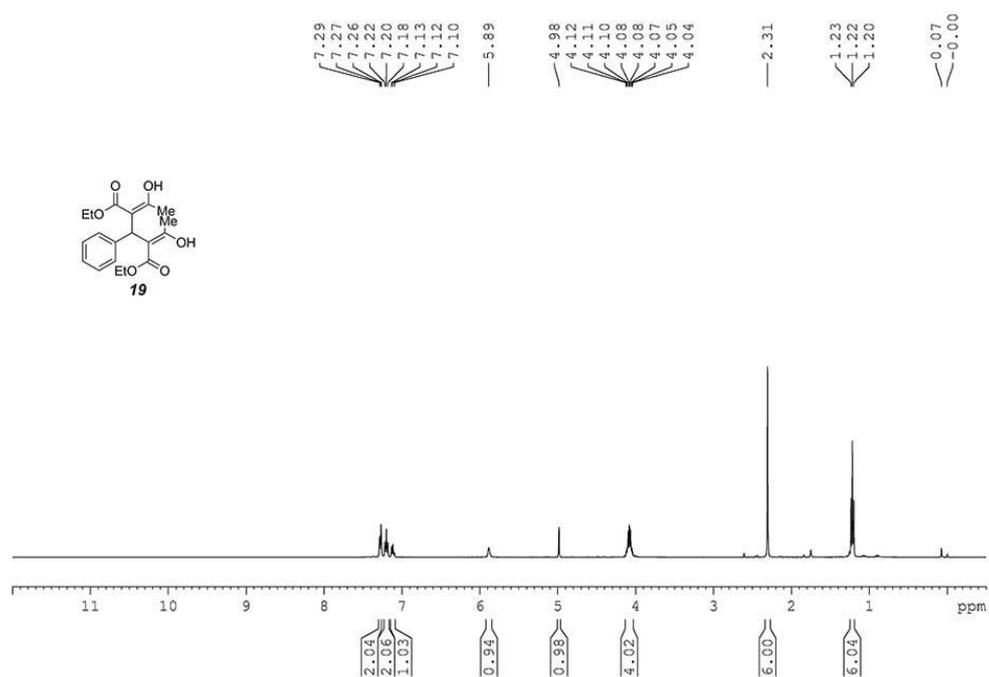


Figure S39. <sup>1</sup>H-NMR of **19**

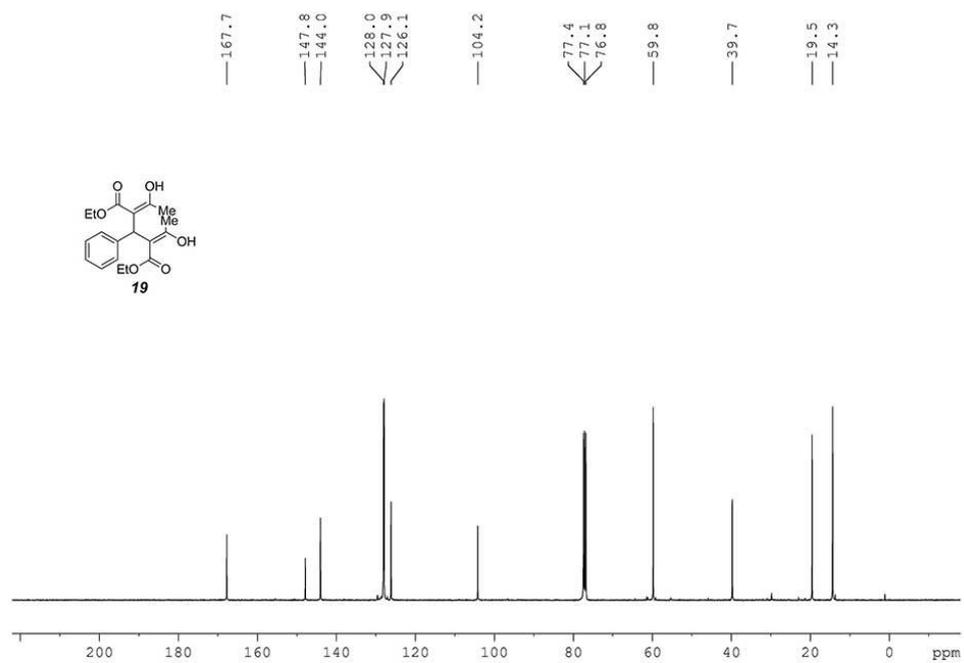


Figure S40. <sup>13</sup>C-NMR of **19**

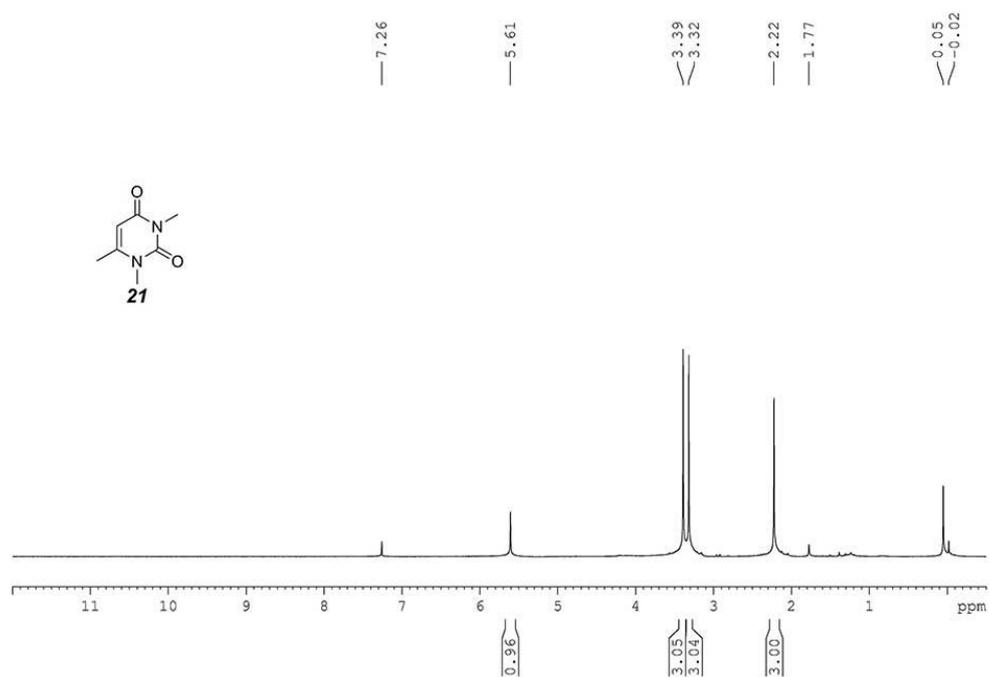


Figure S41. <sup>1</sup>H-NMR of **21**

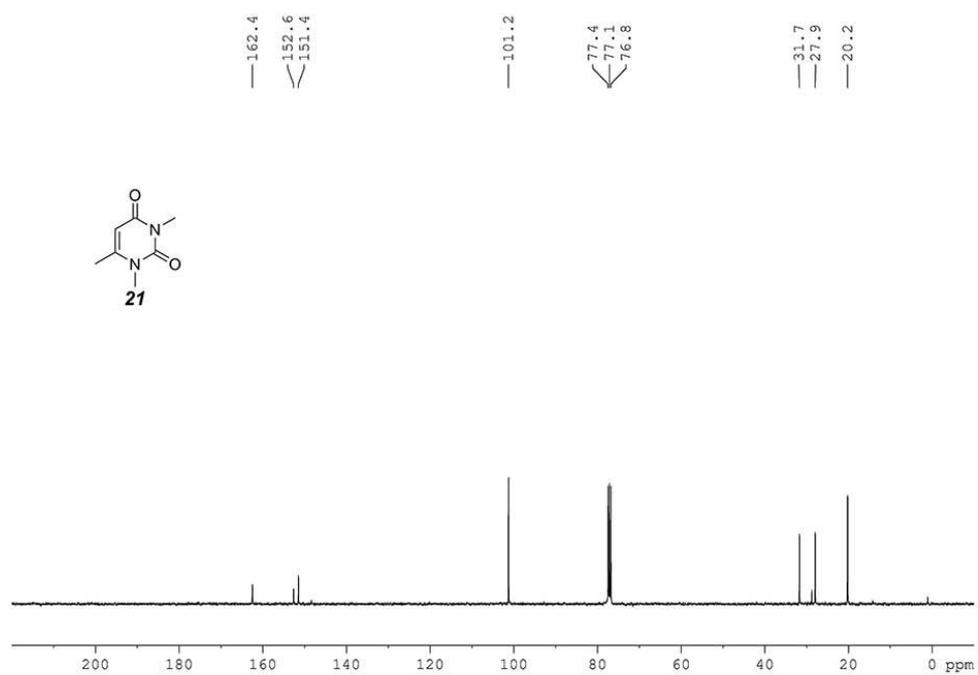


Figure S42. <sup>13</sup>C-NMR of **21**

### 3. The $^1\text{H-NMR}$ tracing of the H-D exchange reactions of methyl acetoacetate in $\text{MeOH-}d_4$

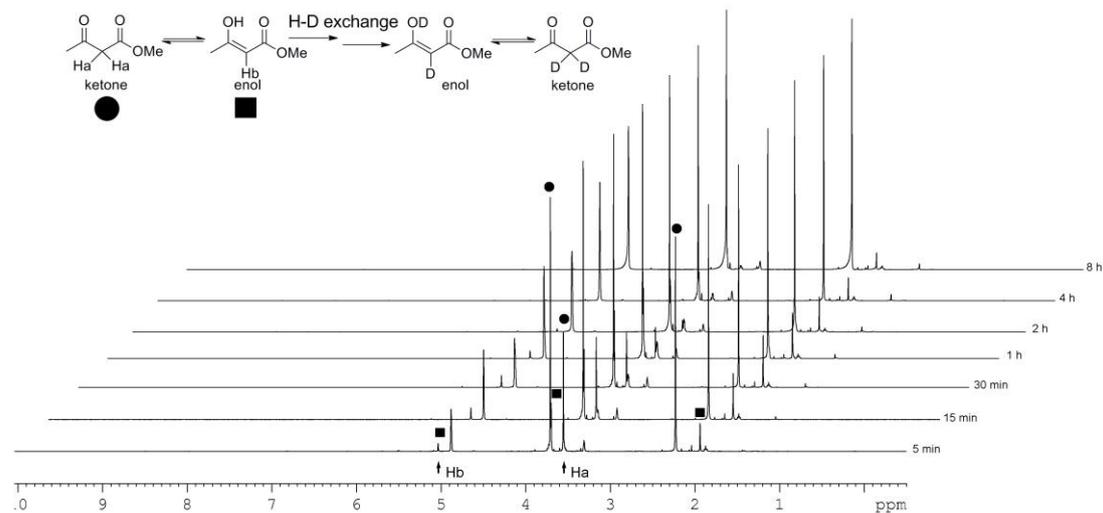


Figure S43.  $^1\text{H-NMR}$  of H-D exchange reaction of methyl acetoacetate in  $\text{MeOH-}d_4$  without  $\text{Hf(OTf)}_4$

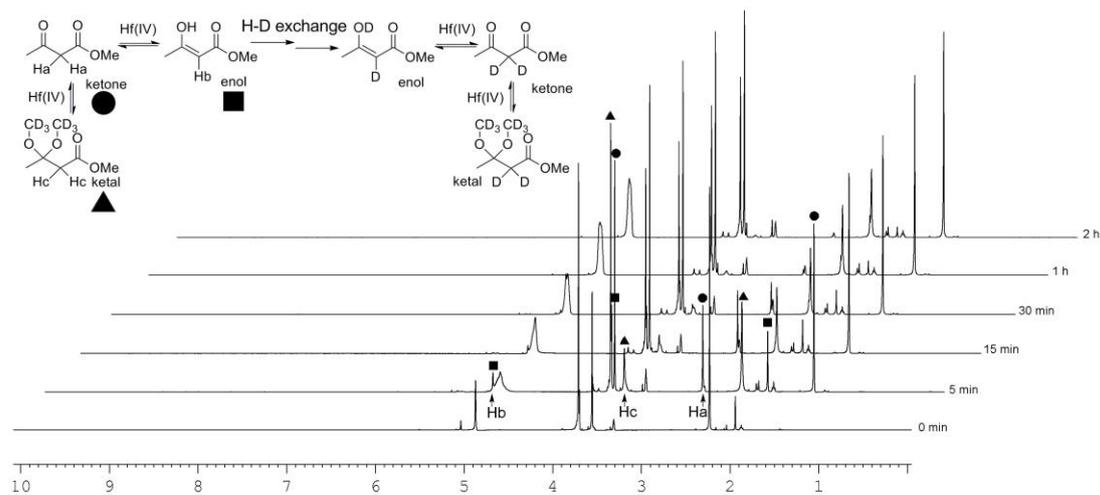


Figure S44.  $^1\text{H-NMR}$  of H-D exchange reaction of methyl acetoacetate in  $\text{MeOH-}d_4$  with 5 mol%  $\text{Hf(OTf)}_4$