Supplementary Information for

Synthetic and Mechanistic Studies of Metal-Free Transfer Hydrogenations Applying Polarized Olefins as Hydrogen Acceptors and Amine Borane Adducts as Hydrogen Donors

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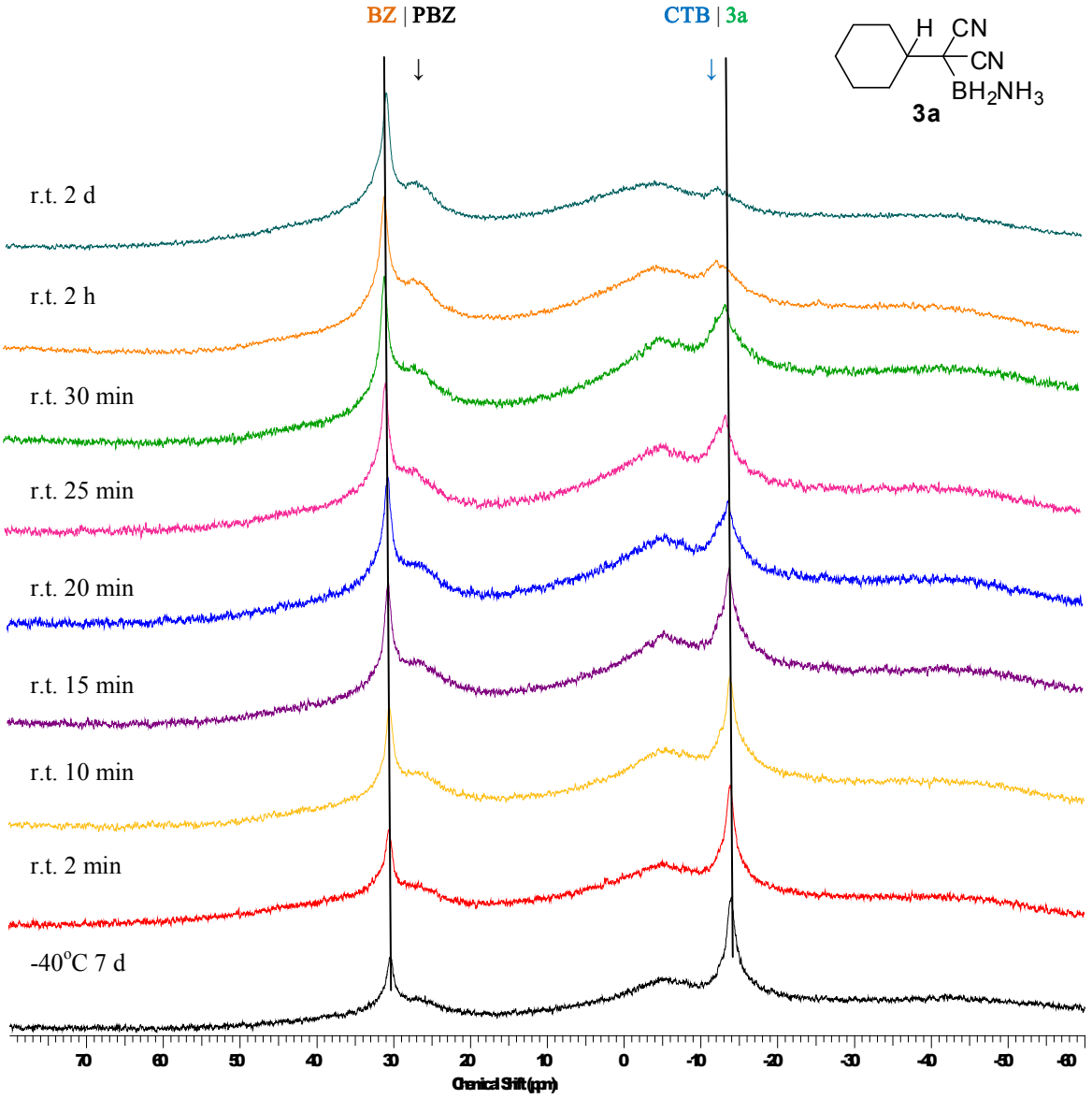
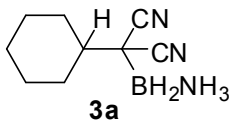
S1 *In situ* ^{11}B NMR spectra in THF-D_8 showing the decomposition of -2-cyclohexyl-malononitrile-2-boryl ammonia (**3a**) were pursued at room temperature to cyclotriborazane (**CTB**), borazine (**BZ**) and polyborazylene (**PBZ**). Initially **3a** was formed by keeping a NMR sample of 2-cyclohexylidenemalononitrile (**1a**) with ammonia borane (**AB**) (3:1 molar ratio) at -40°C over one week; by that time **AB** was completely consumed with concomitant formation of small amounts of **BZ**. (Fig. 3 in the main text)



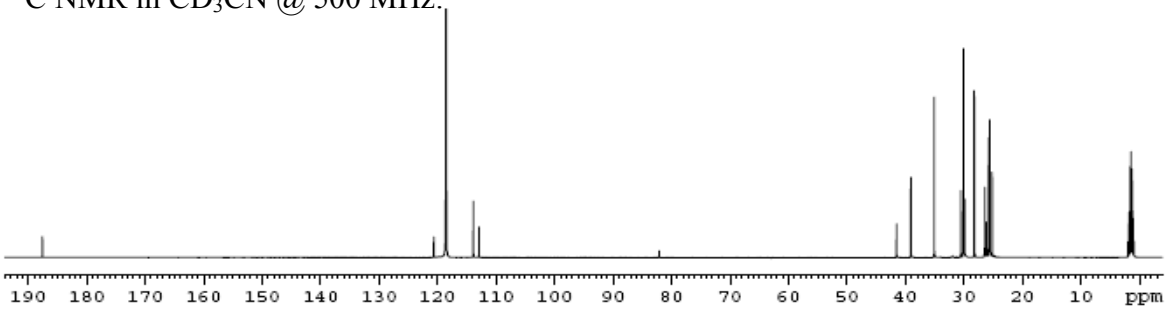
S2 Determination of the hydroboration intermediate **3a** in the reaction mixture.

^{1}H NMR in CD_3CN @ 500 MHz:

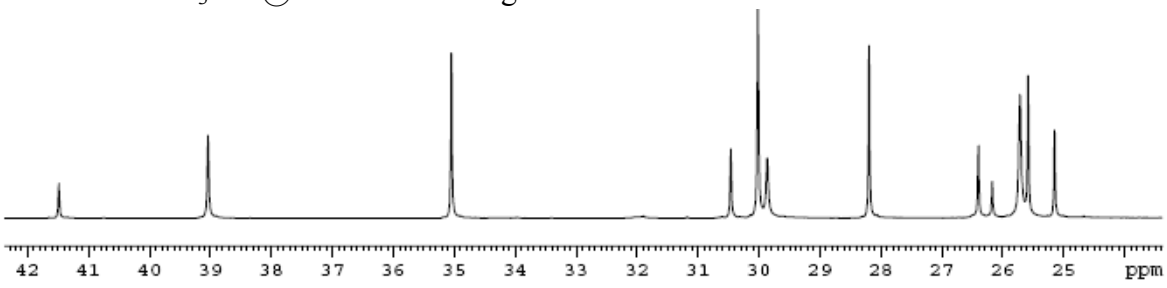


3a

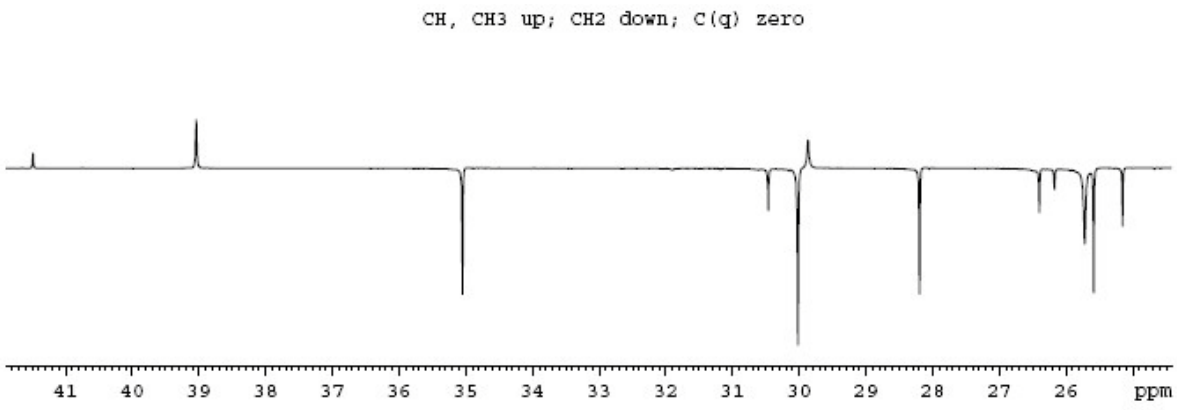
^{13}C NMR in CD_3CN @ 500 MHz:



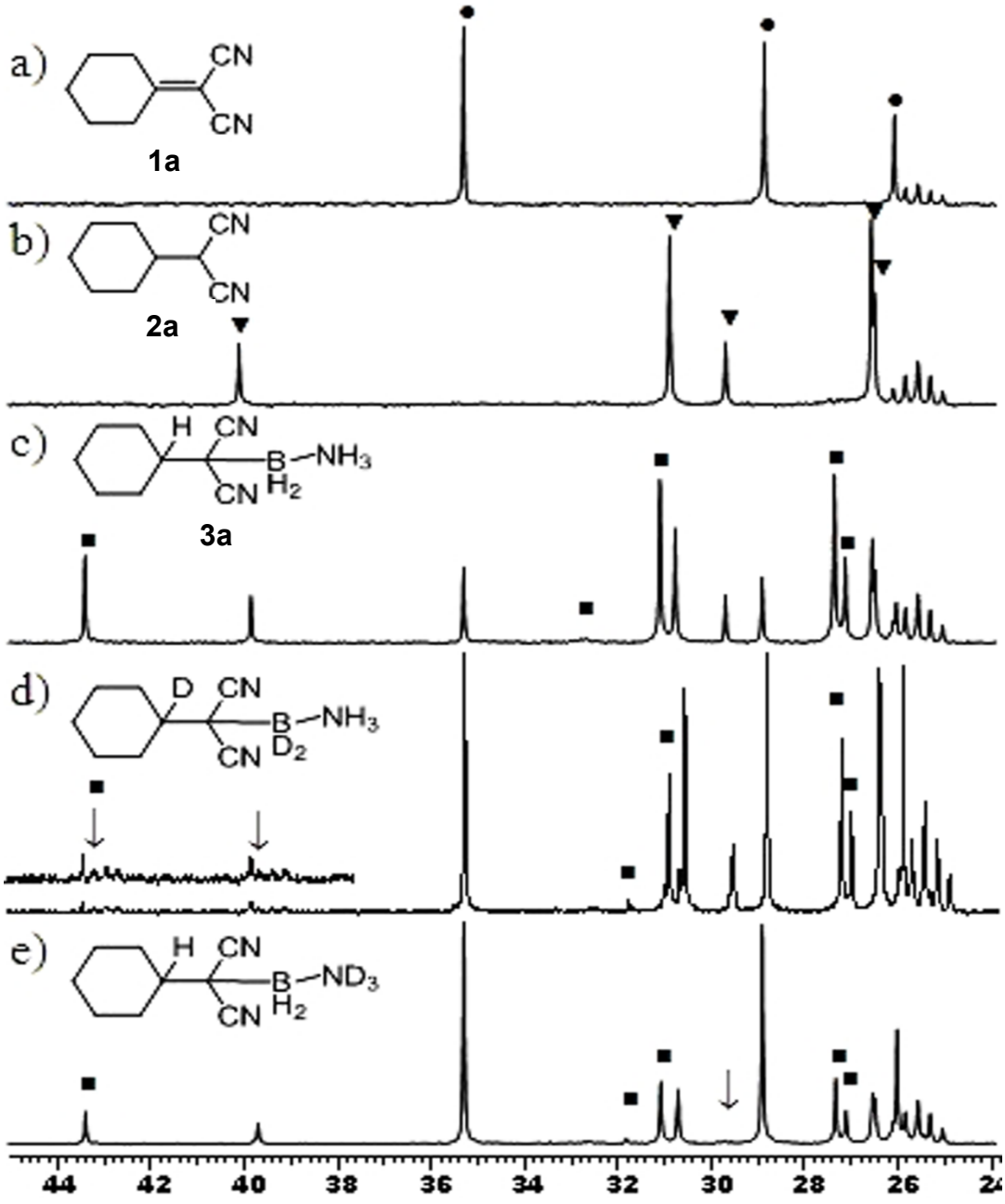
^{13}C NMR in CD_3CN @ 500 MHz: enlarged scale



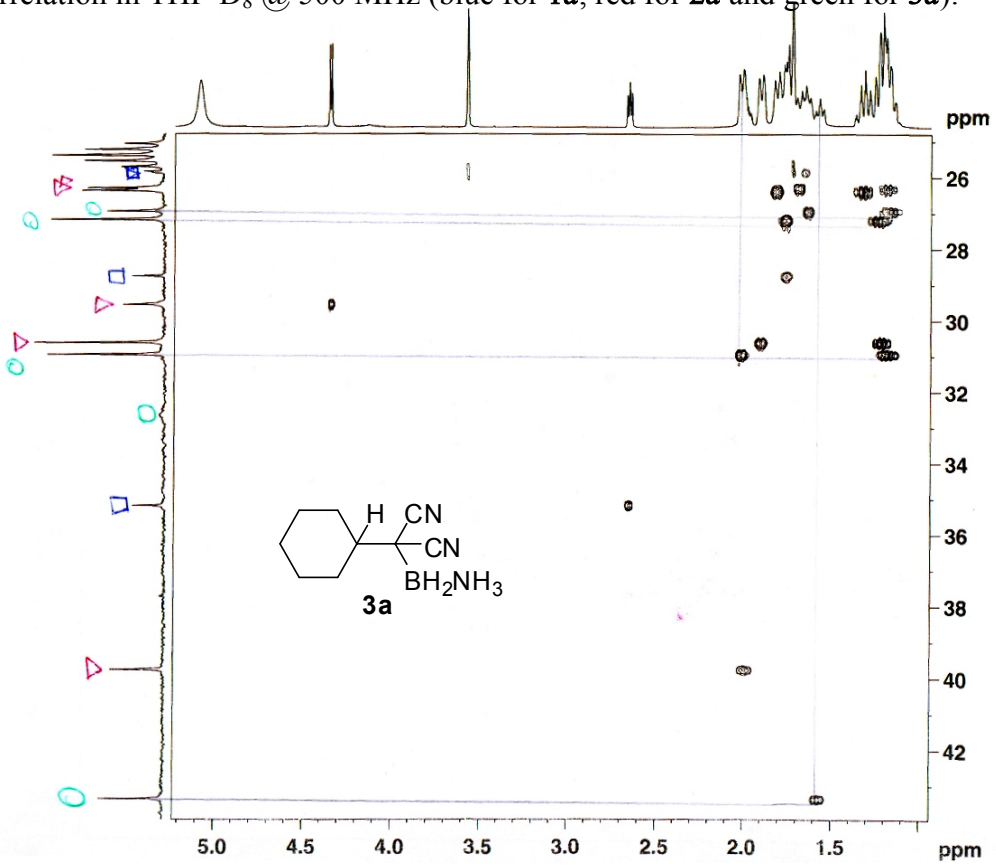
DEPT @ 500 MHz:



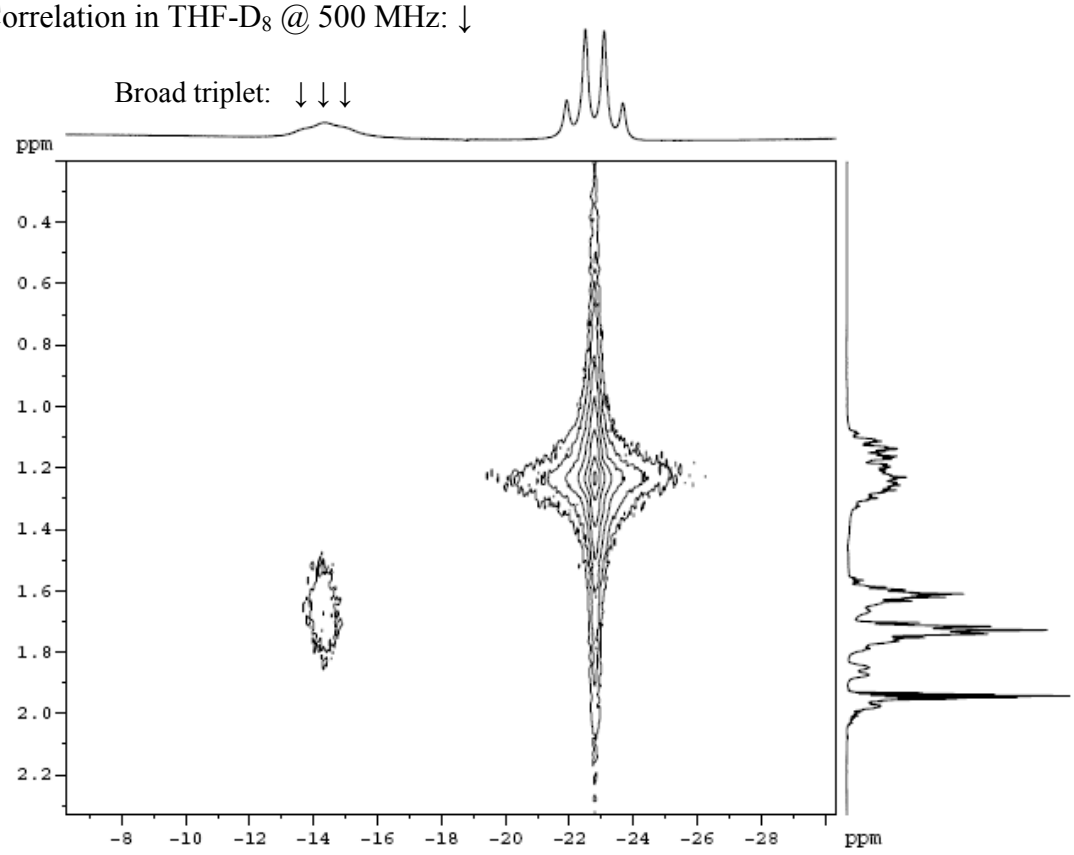
^{13}C NMR in THF-D_8 @ 500 MHz: enlarged scale



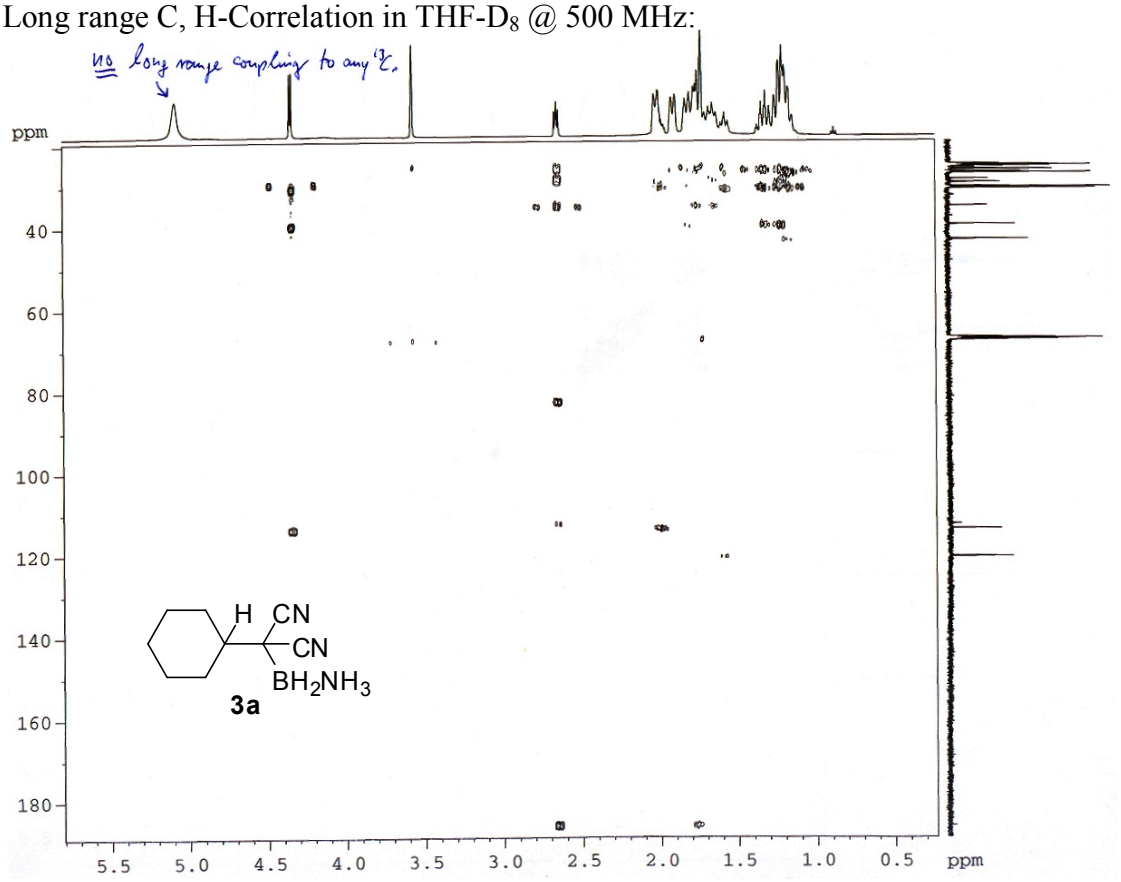
C, H-Correlation in THF-D_8 @ 500 MHz (blue for **1a**, red for **2a** and green for **3a**):



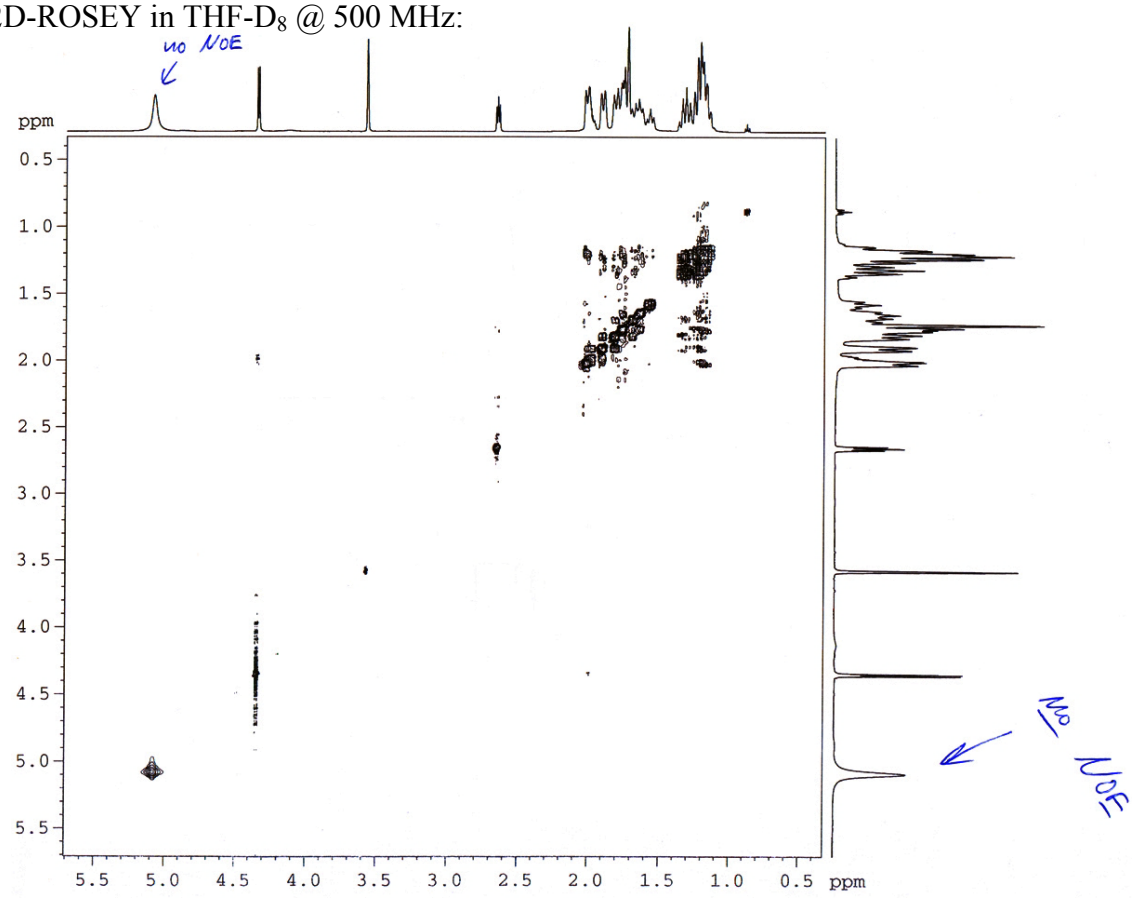
B, H-Correlation in THF-D_8 @ 500 MHz: ↓



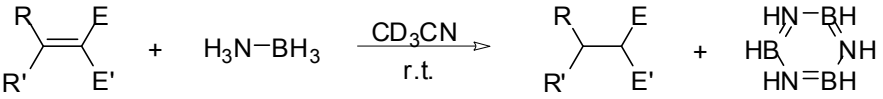
Long range C, H-Correlation in THF-D_8 @ 500 MHz:



2D-ROSEY in THF-D_8 @ 500 MHz:

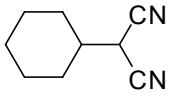


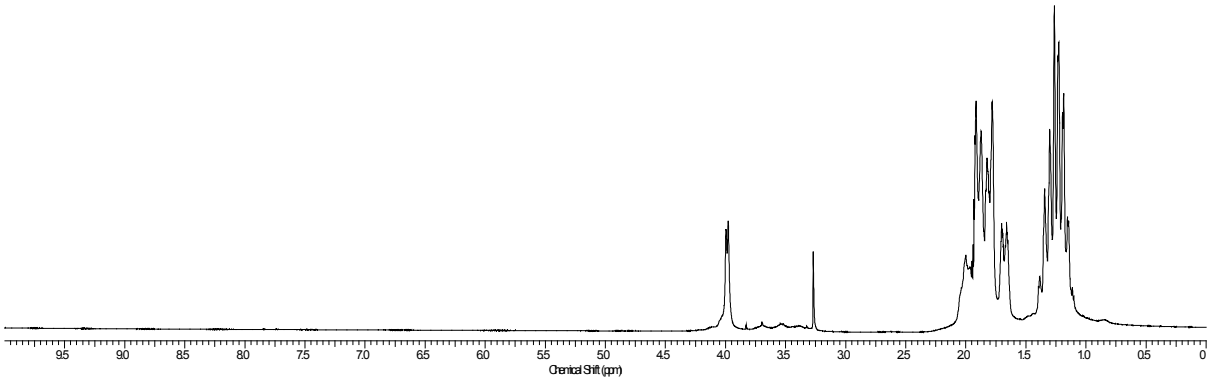
S3 *In situ* ^{1}H and ^{13}C NMR spectra for the transfer hydrogenation reactions.

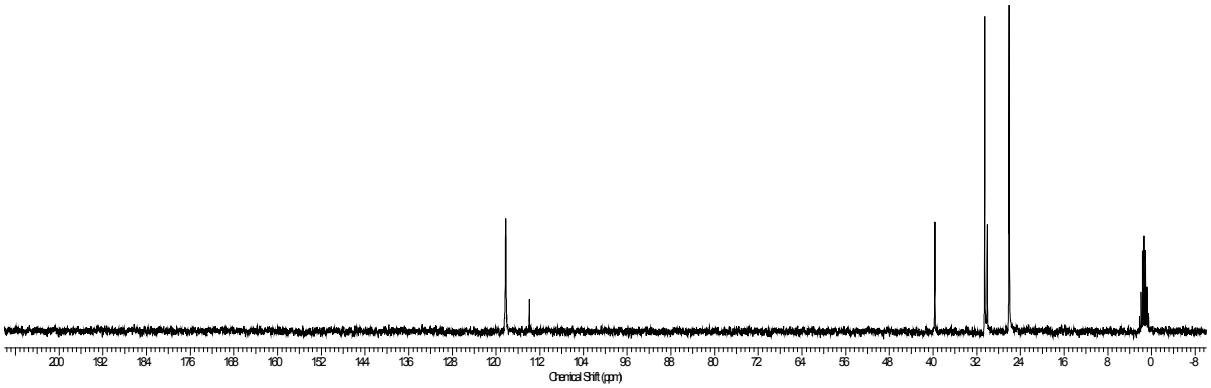


1 0.1 mmol **AB** 0.1 mmol **2** **BZ**

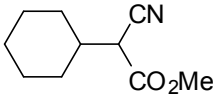
2a

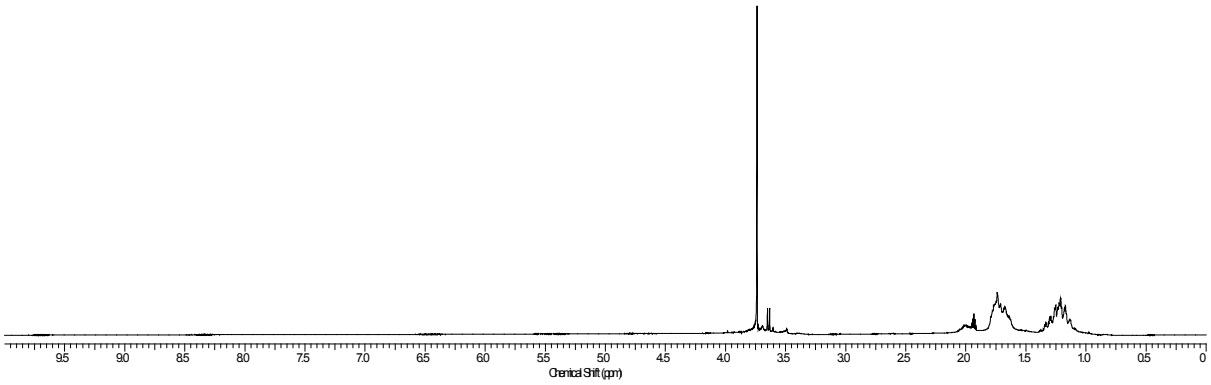


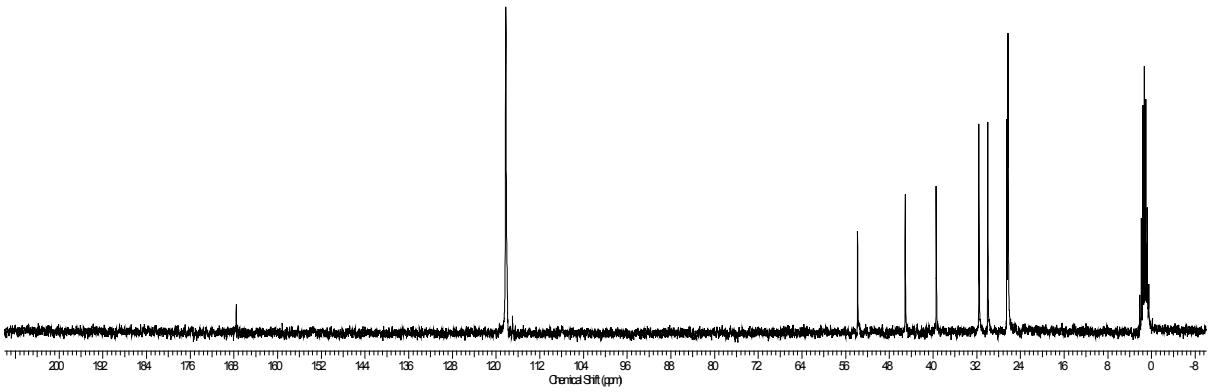


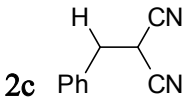


2b

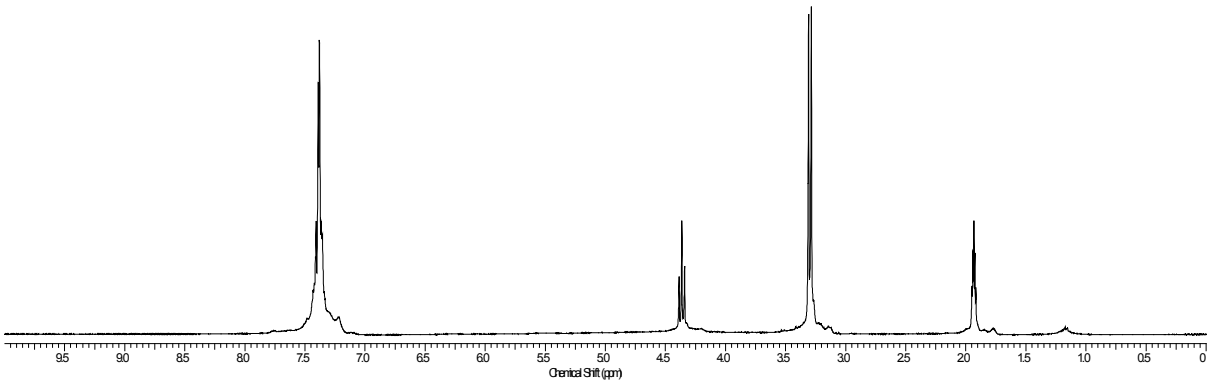


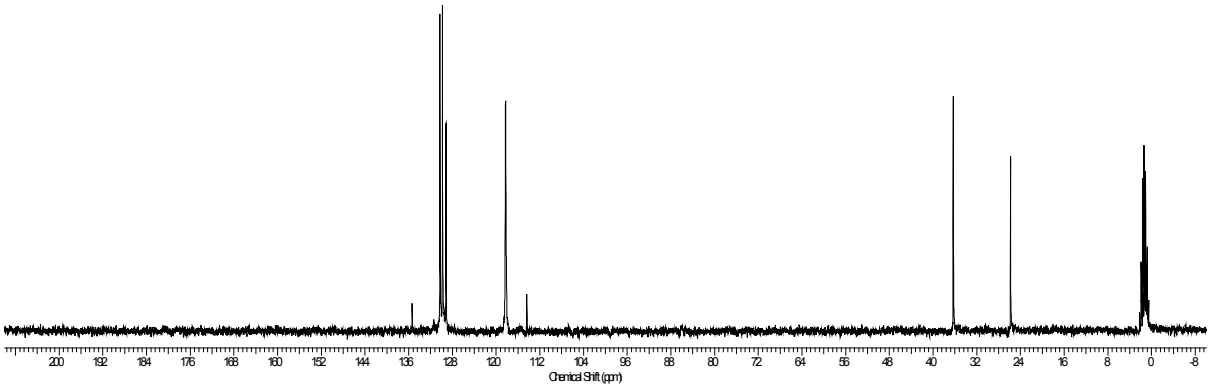


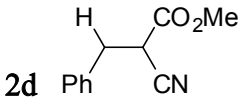




2c







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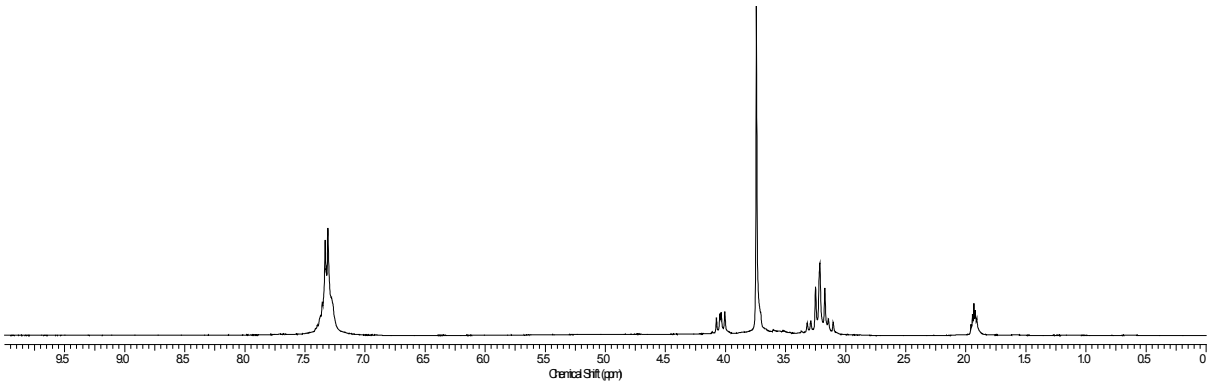

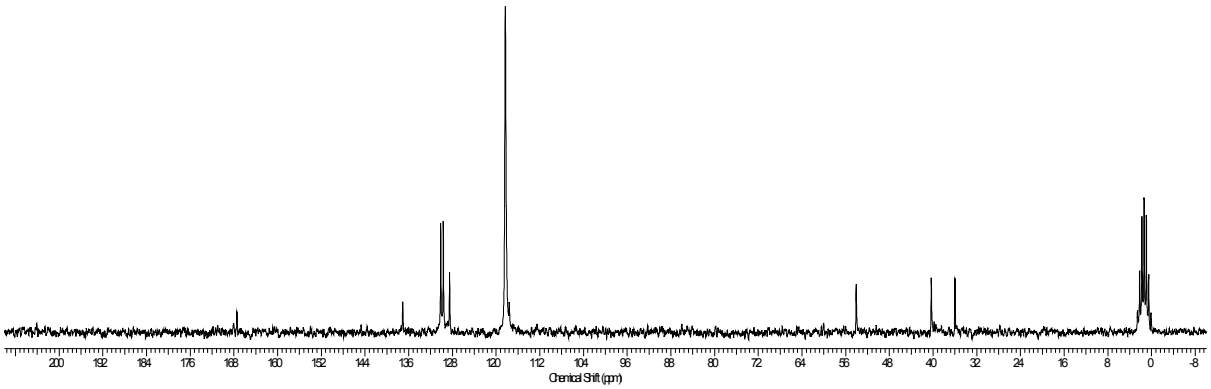

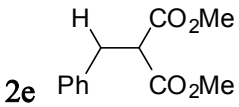

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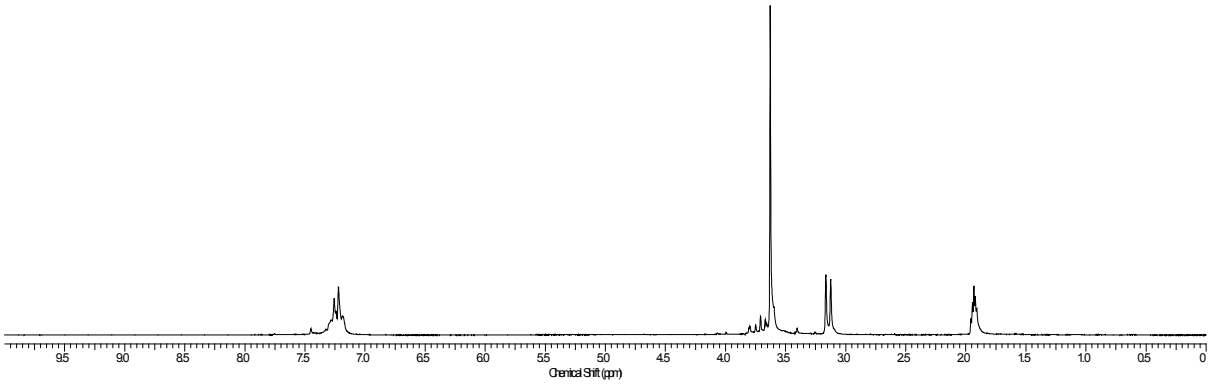

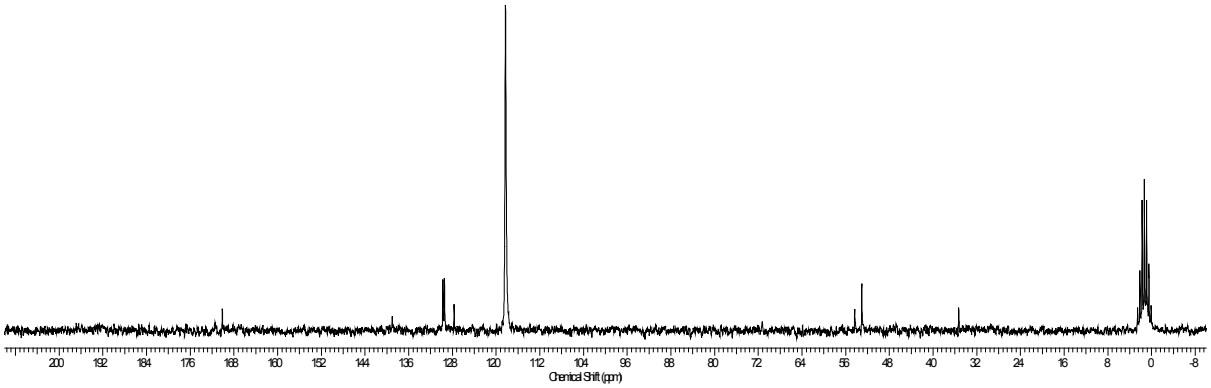

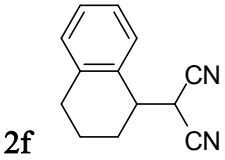

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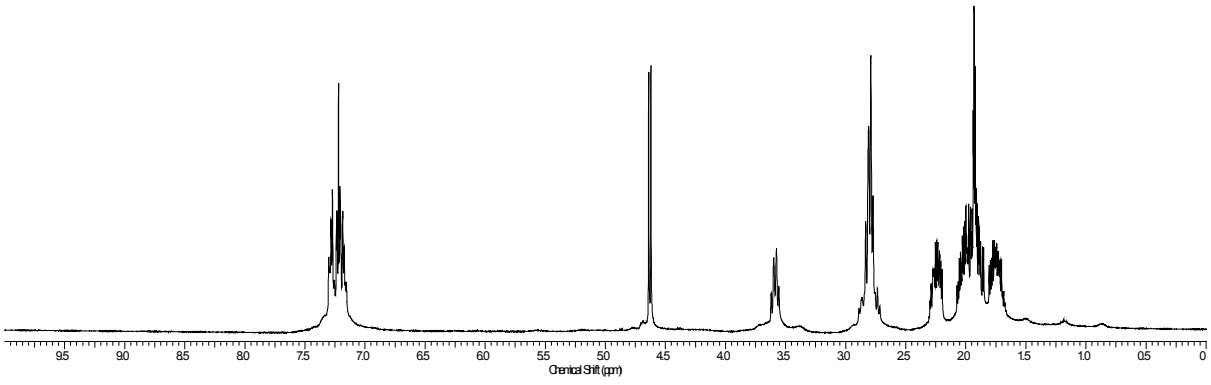

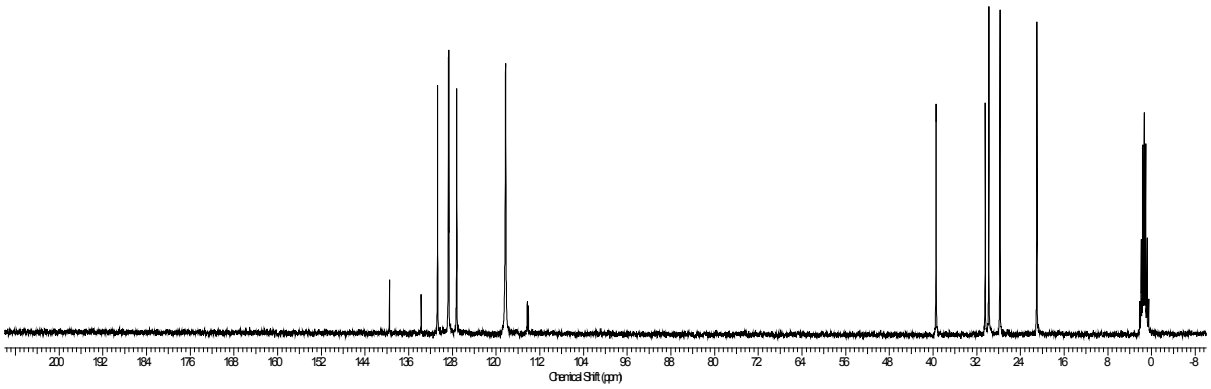

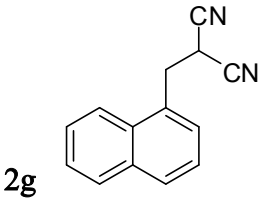

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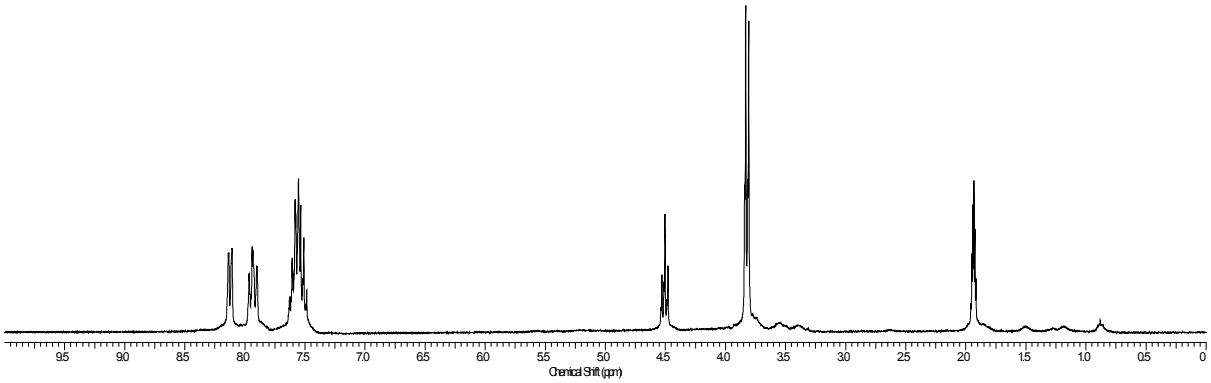

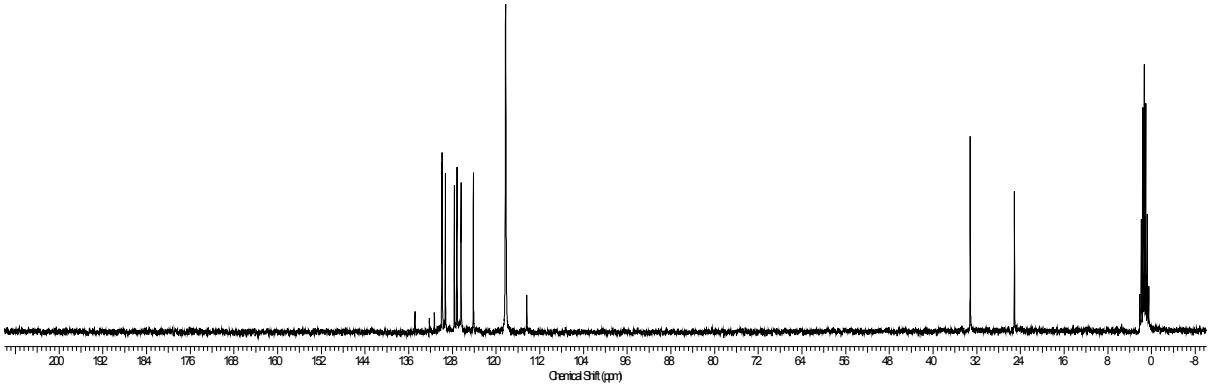

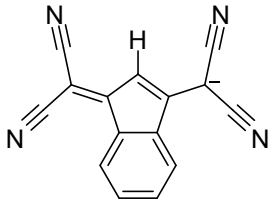

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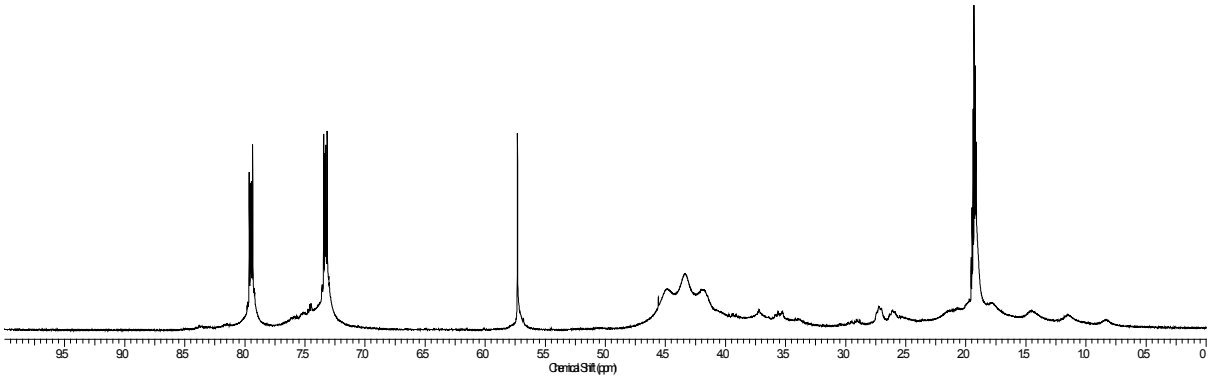

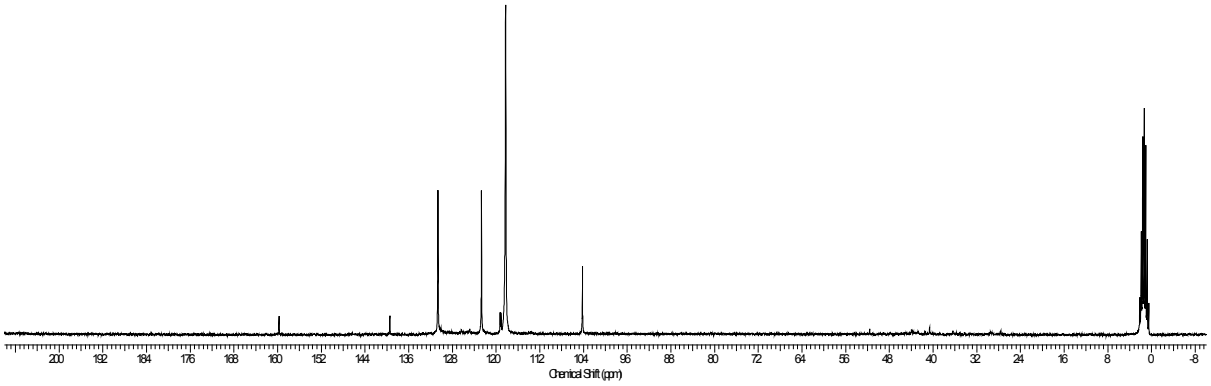

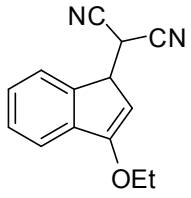

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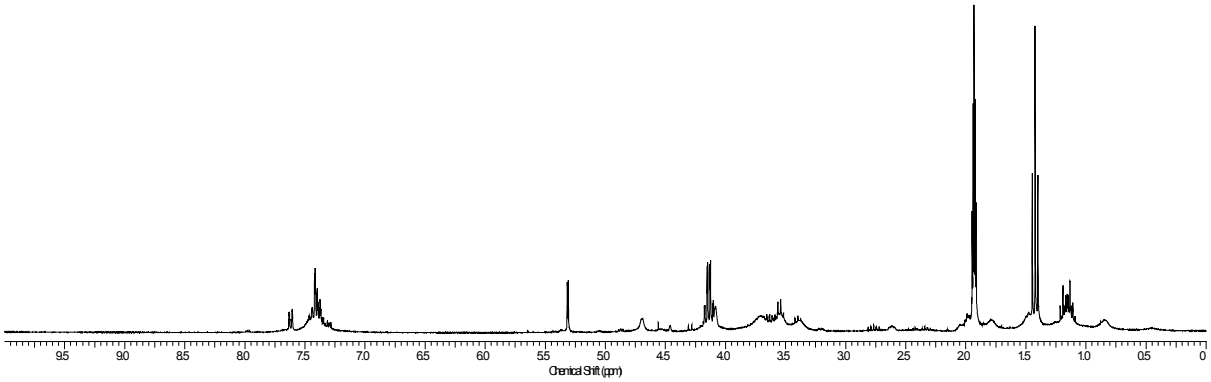

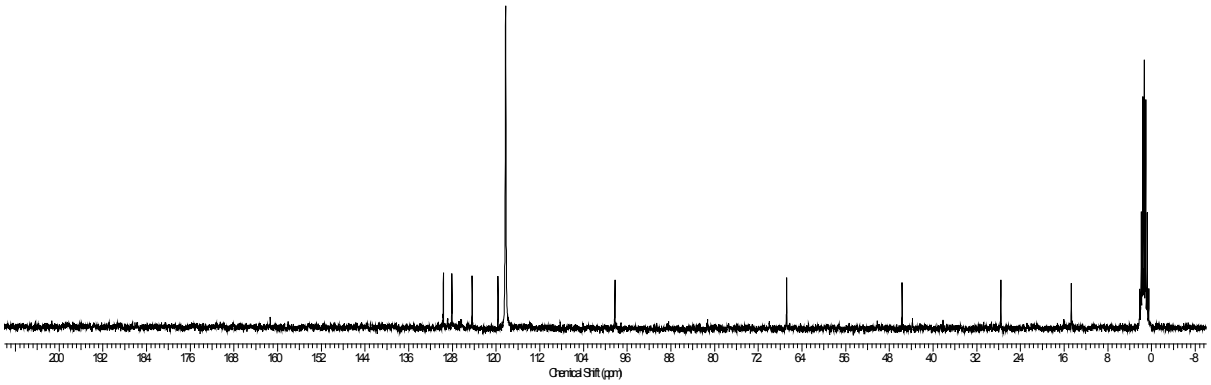

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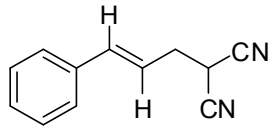

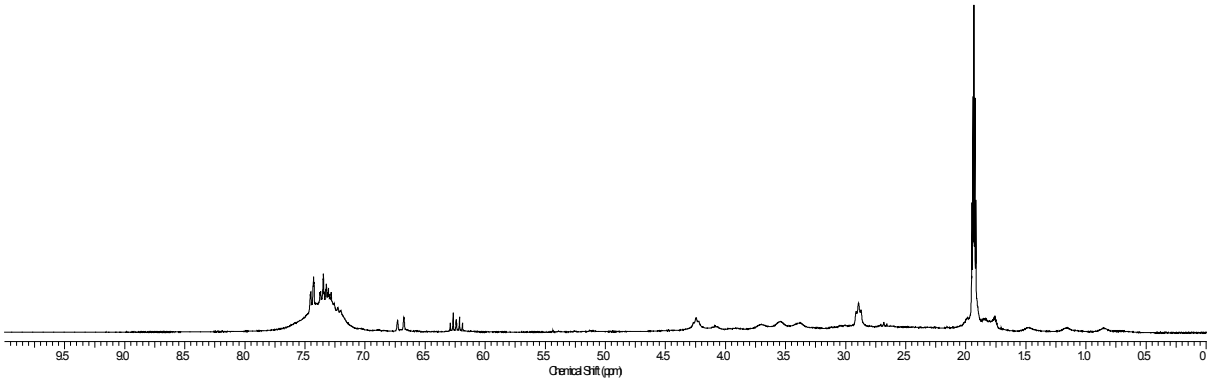

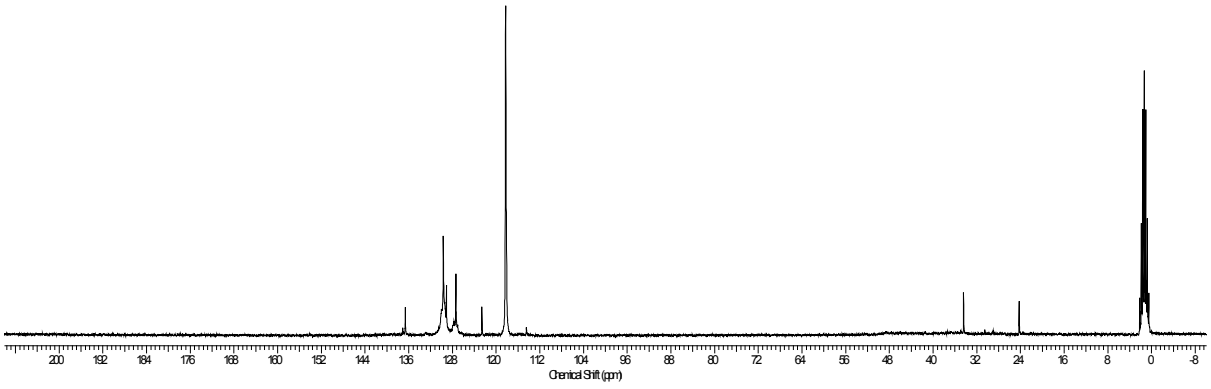

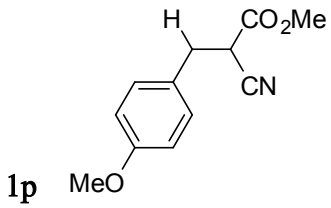

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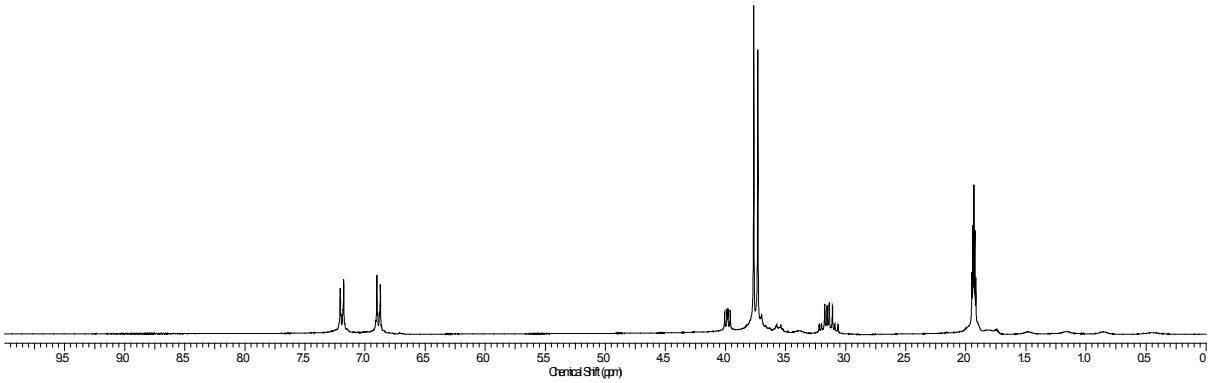

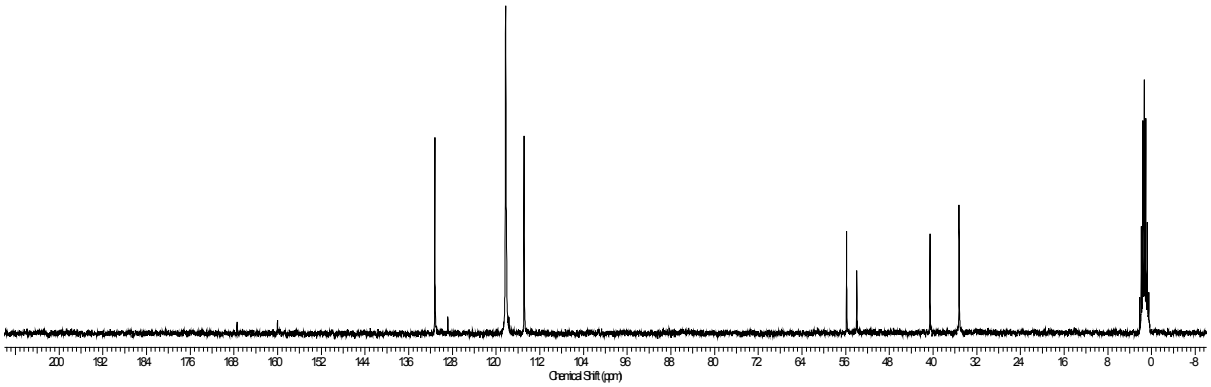

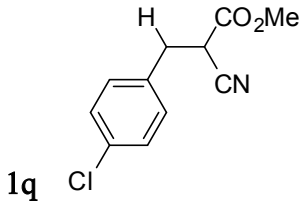

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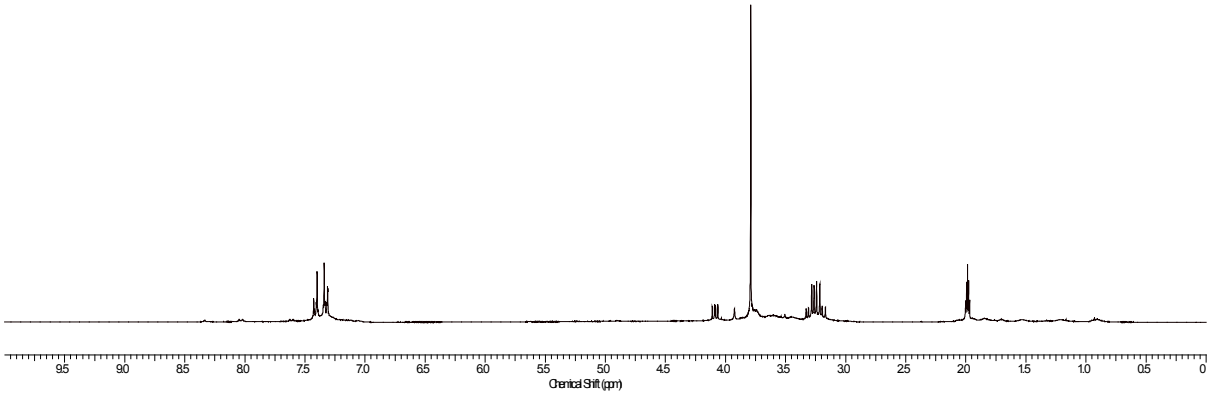

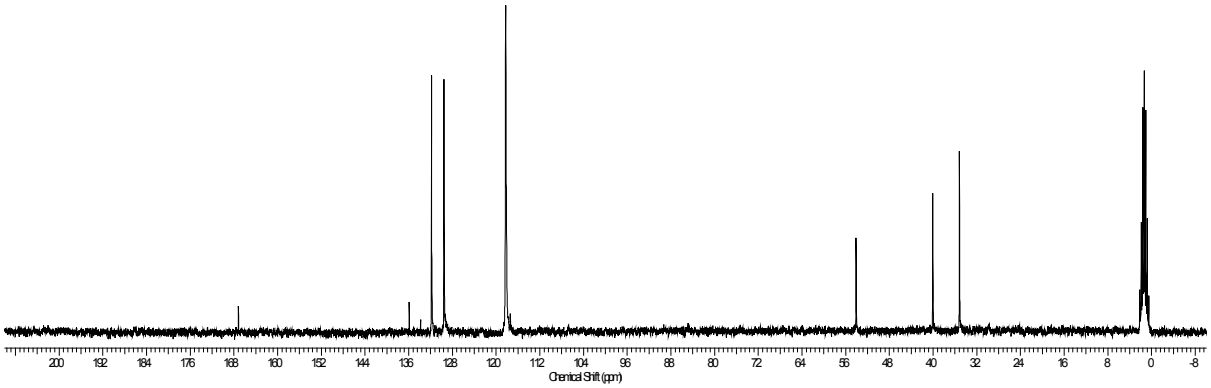

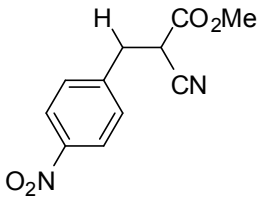

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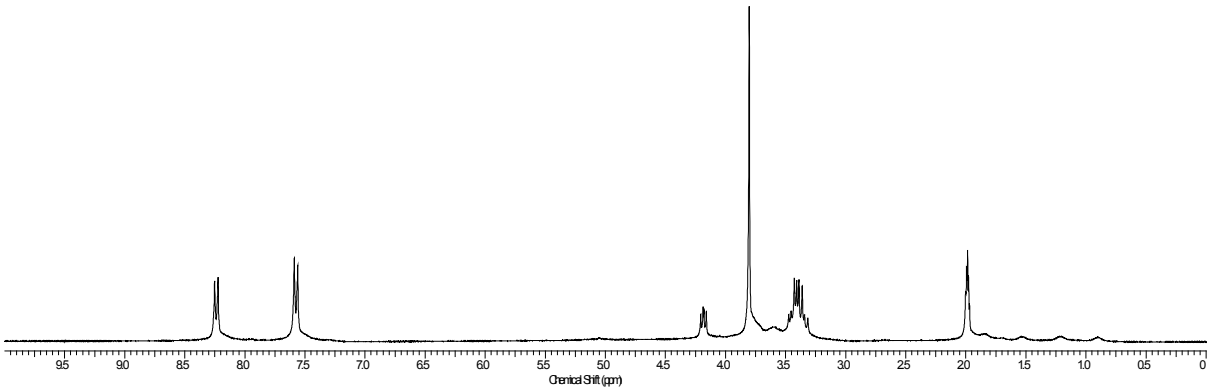

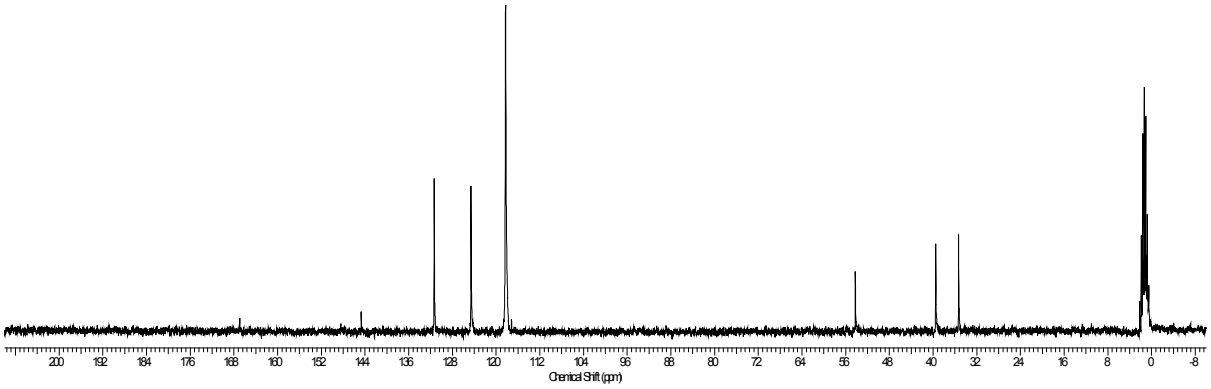

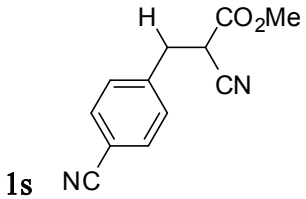

1s