Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Lithium amidoborane, highly chemoselective reagent for reduction of α,β-unsaturated ketones to allylic alcohols

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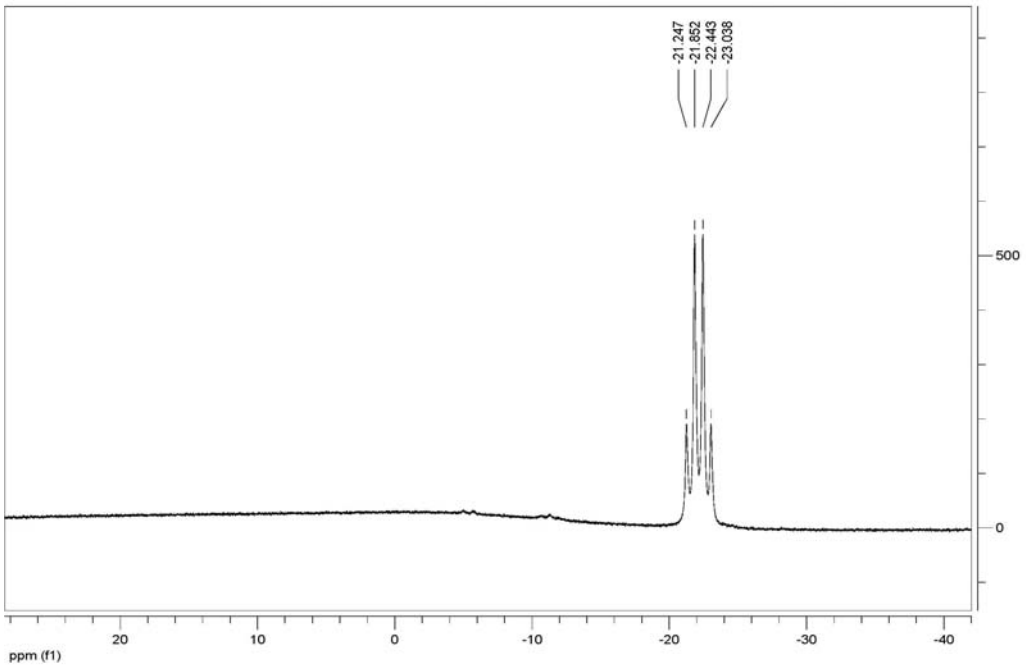
S1. Synthesis of α,β-unsaturated ketones (entry 3-6, entry 8, entry 9-14, Table 2)

In a 50 mL flask, corresponding aldehyde (10 mmol), corresponding ketone (10 mmol) and ethanol (20 ml) were placed, and the solution was stirred at room temperature. To the solution, NaOH aqueous solution (1.5M, 10ml) was slowly added. After 5 hrs, the reaction mixture was neutralized with 2M aqueous HCl solution. Crude α,β-unsaturated ketone was obtained after filtration. Then, the crude product was recrystallized from ethanol.

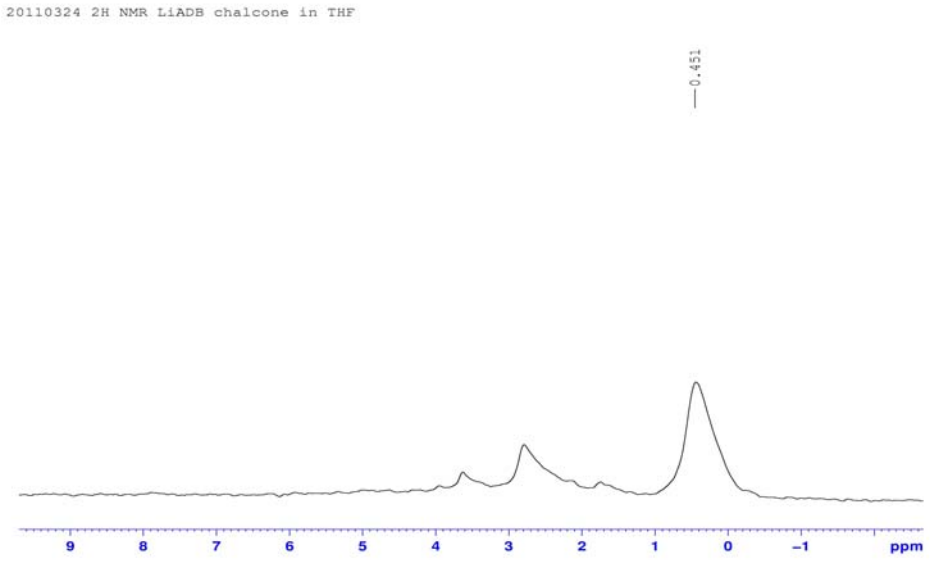
S2. Synthesis of α,β-unsaturated ketones (entry 2, entry 16)

In a 50 mL flask, corresponding aldehyde (10 mmol), corresponding ketone (10 mmol) and ethanol (20 ml) were placed, and the solution was stirred at room temperature. To the solution, NaOH aqueous solution (1.5M, 10ml) was added slowly. After 5 hrs, the reaction mixture was neutralized with 2M aqueous HCl solution. The solution was extracted with DCM (3 X 10 mL). The organic layer was washed with aqueous NaCl (2 X 10 mL) and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography with hexane/EtOAc (v/v,10/1) as an eluent to obtain α,β-unsaturated ketone.

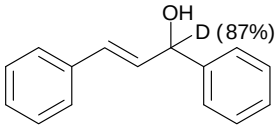
S3. ^{11}B NMR spectrum for synthesized LiAB



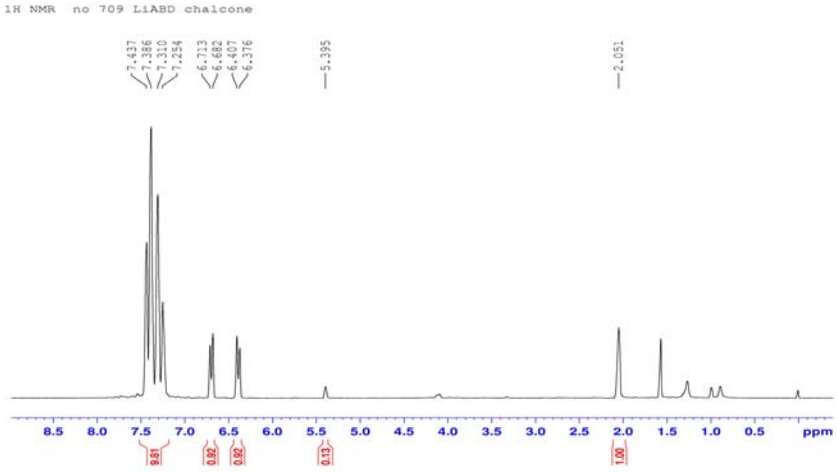
S4. ^{2}H NMR result for $LiND_2BH_3$ (LiA(D)B)reacting chalcone in THF

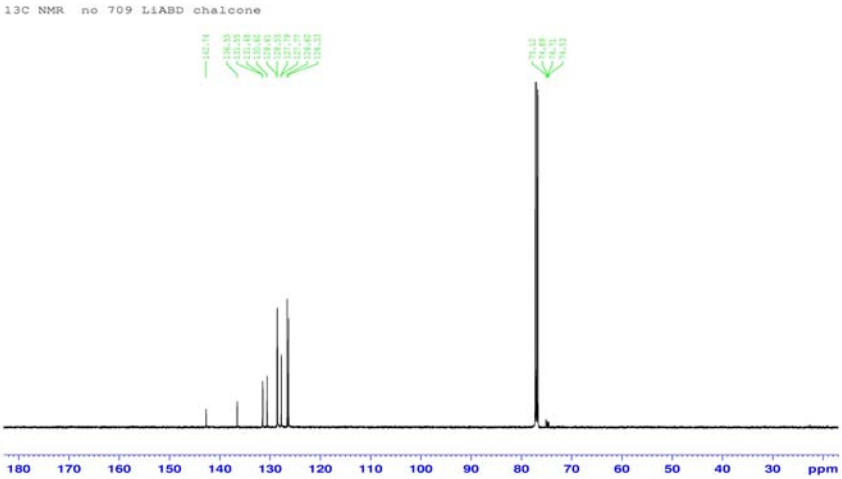


S5. Characterization data for the isolated product after $LiNH_2BD_3$ (LiAB(D)) reacting with chalcone

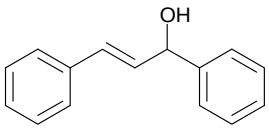


^{1}H NMR (500 MHz, $CDCl_3$, 25 ^oC; TMS): δ = 2.05 (s, 1H; OH), 5.39 (s, 0.13H; CH), 6.37-6.40 (m, 1H; CH), 6.69 (d, $^3J_{HH}$ = 15.80 Hz, 1H; CH), 7.24-7.43 ppm (m, 10H; ArH); ^{13}C NMR (126 MHz, $CDCl_3$, 25^{o}C; $CDCl_3$) : δ = 74.70 (t, J_{CD}= 22.08 Hz; CD), 126.32, 126.60, 127.76, 127.79, 128.54, 128.61, 130.59, 131.48, 131.54, 136.53, 142.78 ppm ; FT-IR (film): ν_{max} = 3348, 3077, 3059, 3026, 2128 (CD), 1600, 1493, 1448 cm^{-1}; MS (EI): m/z (%) 211 $[M]^+$ (10), 105 (100), 77 (40).

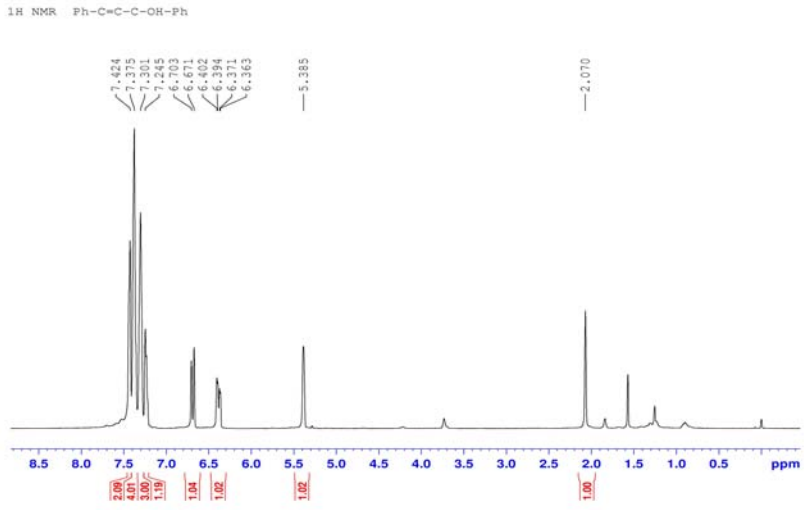


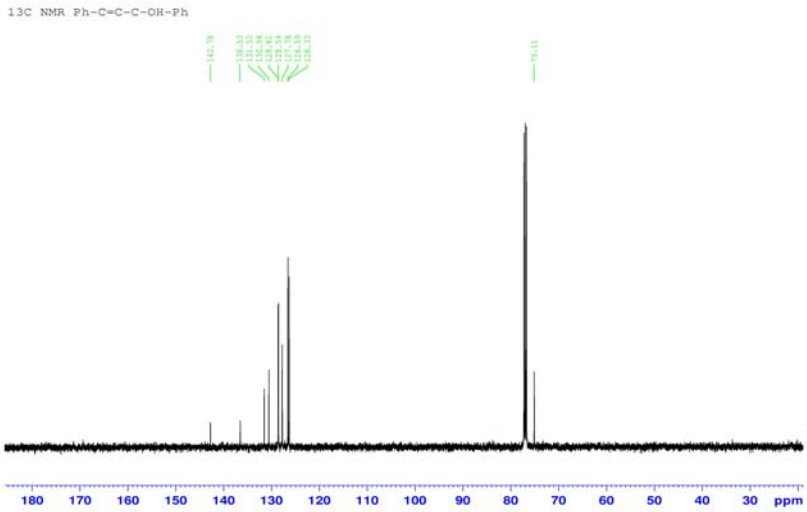


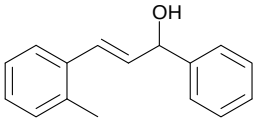
S6. ^{1}H and ^{13}C NMR spectra of products



(entry 1, Table 2):







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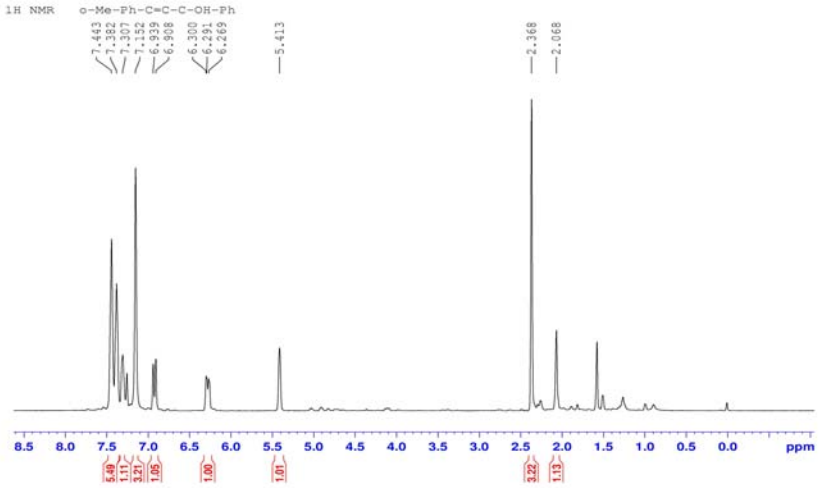

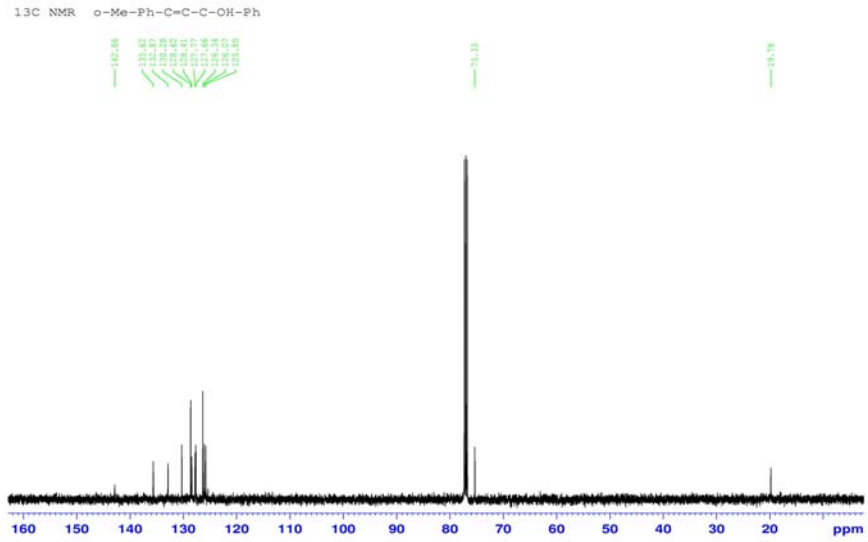

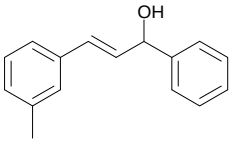

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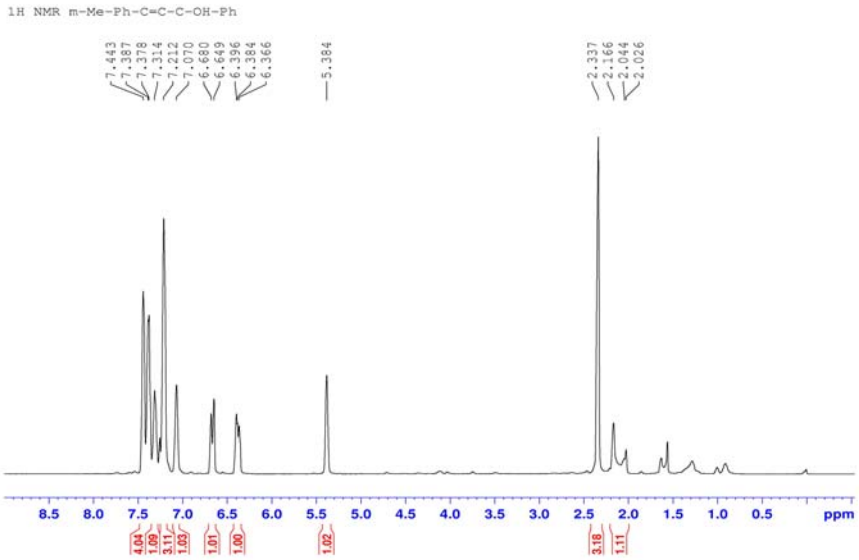

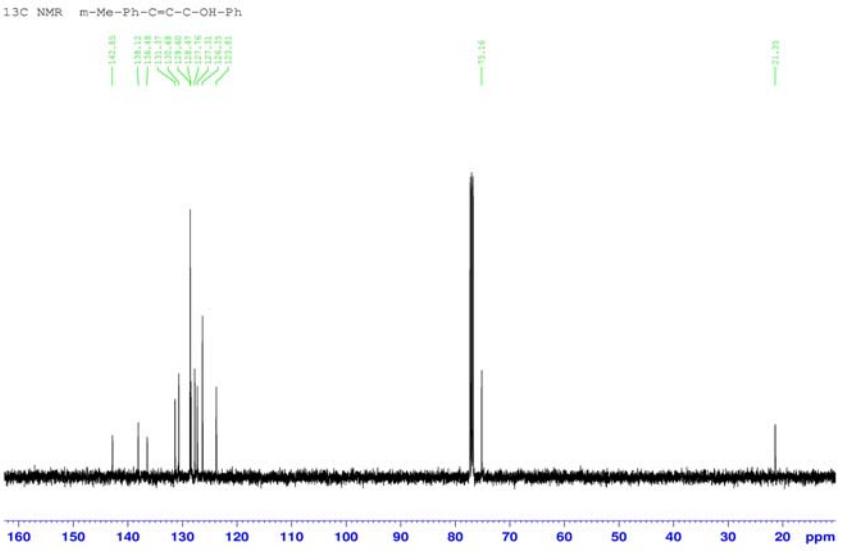

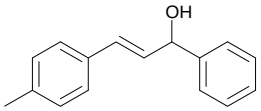

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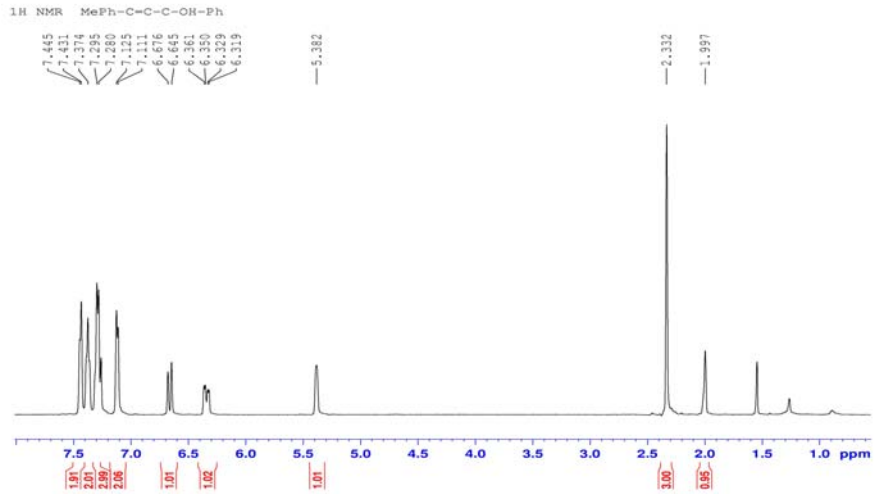

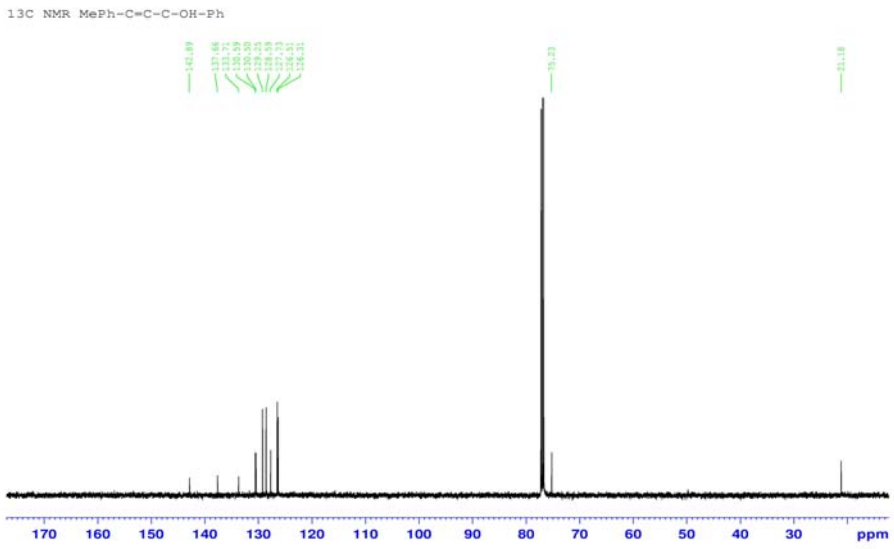

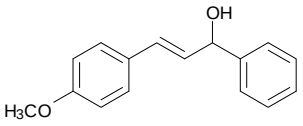

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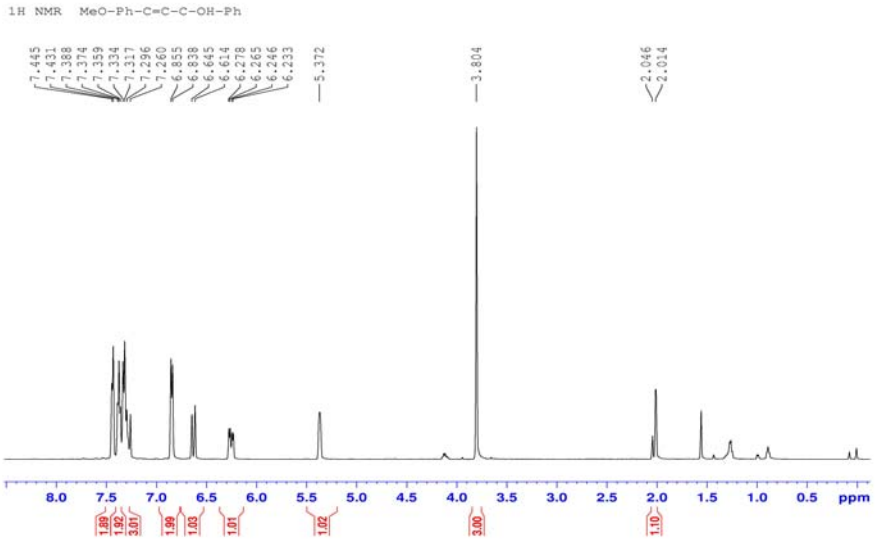

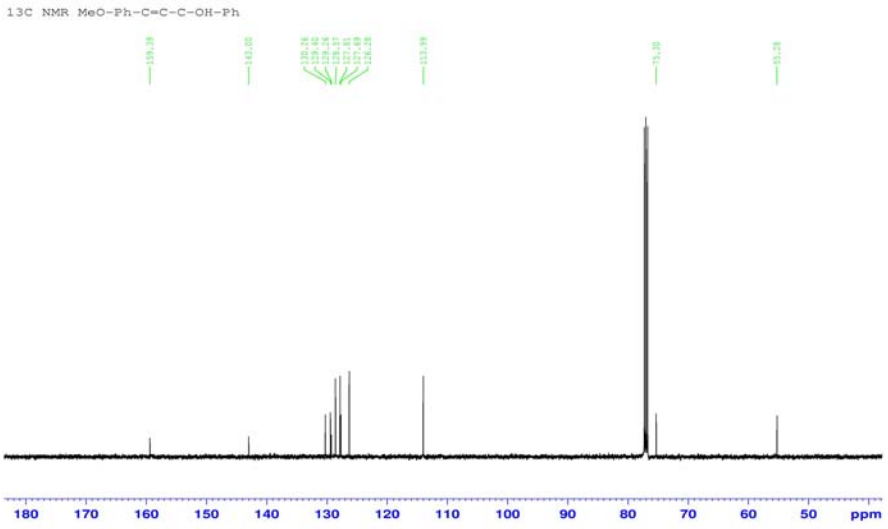

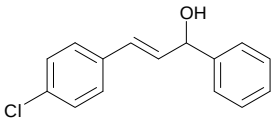

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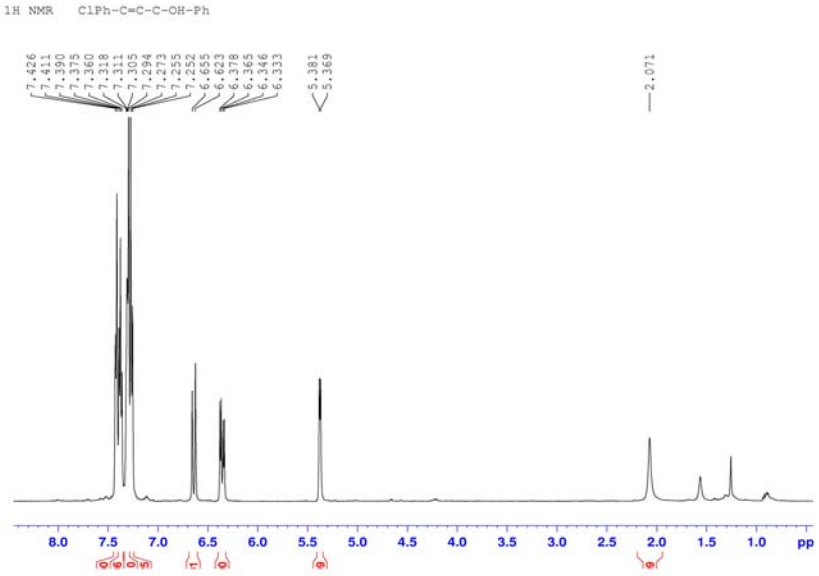

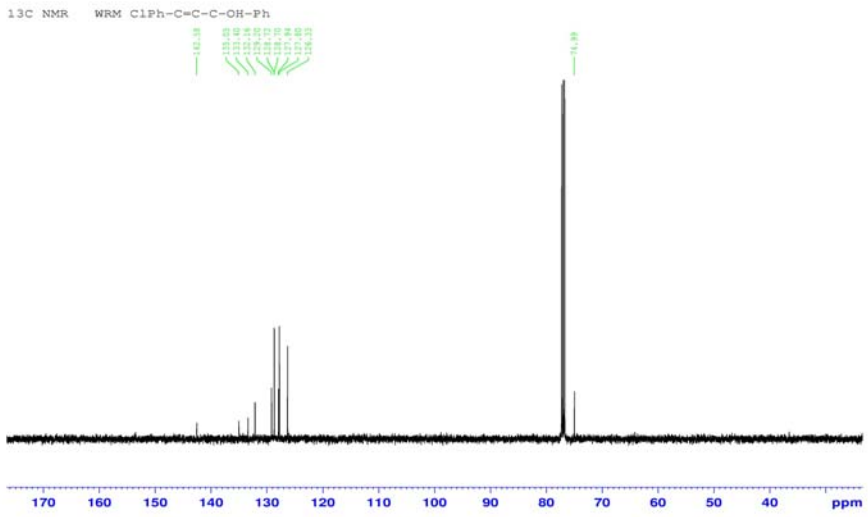

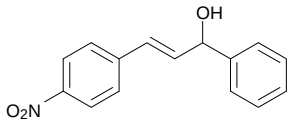

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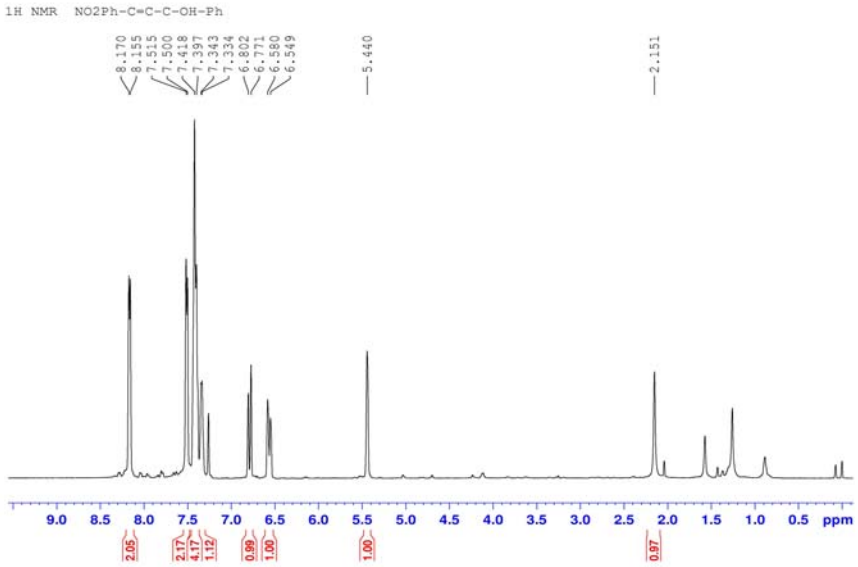

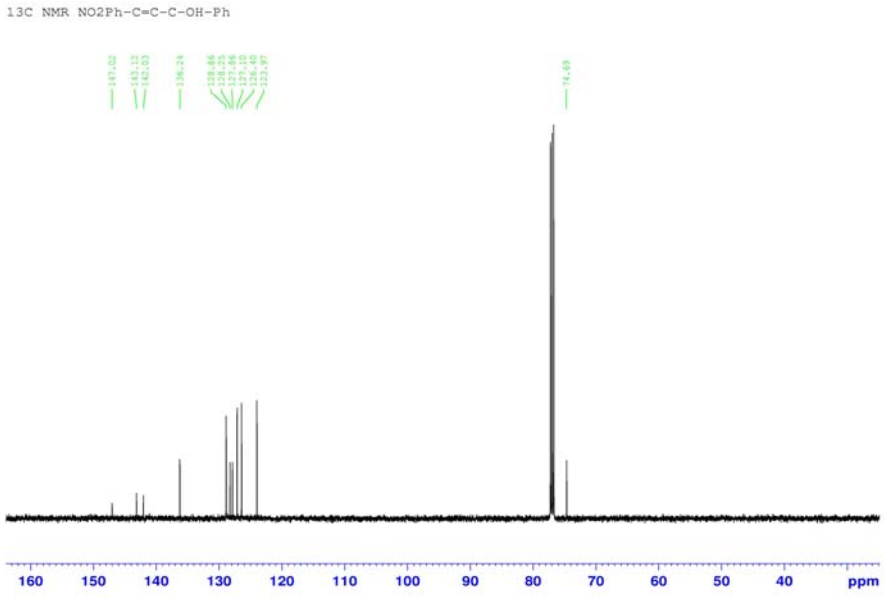

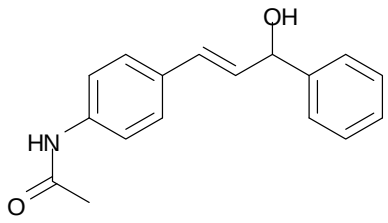

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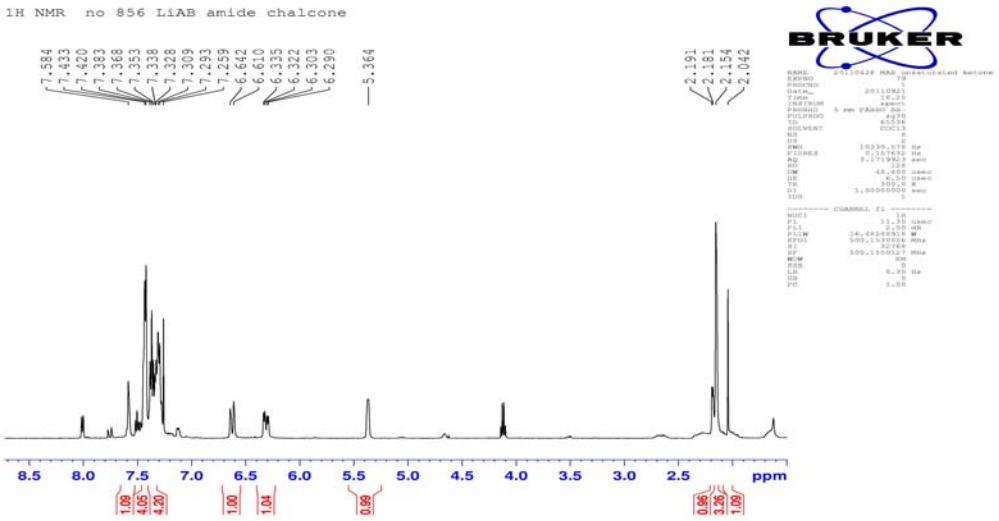

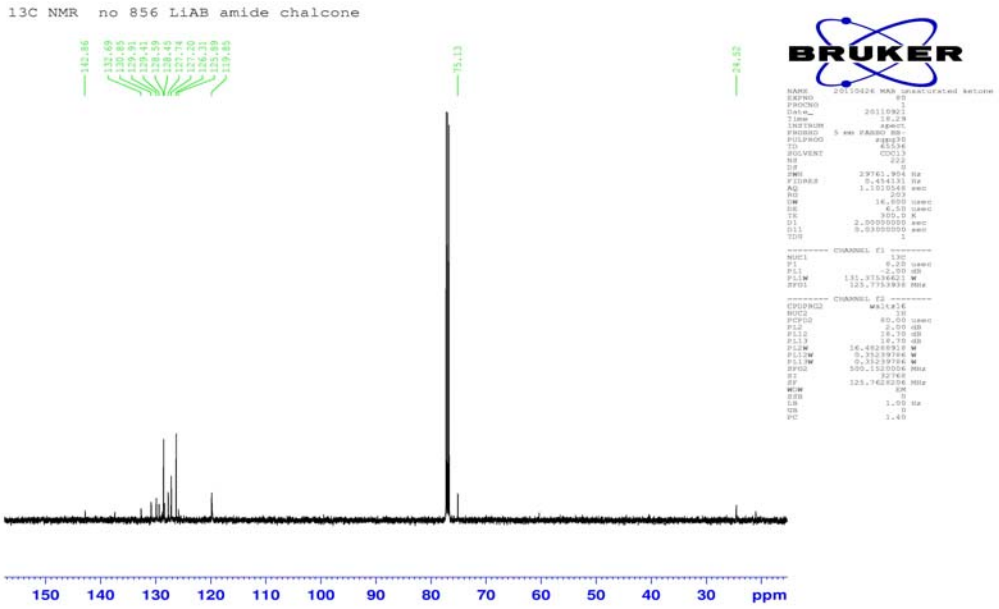

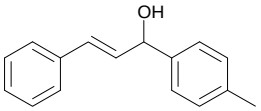

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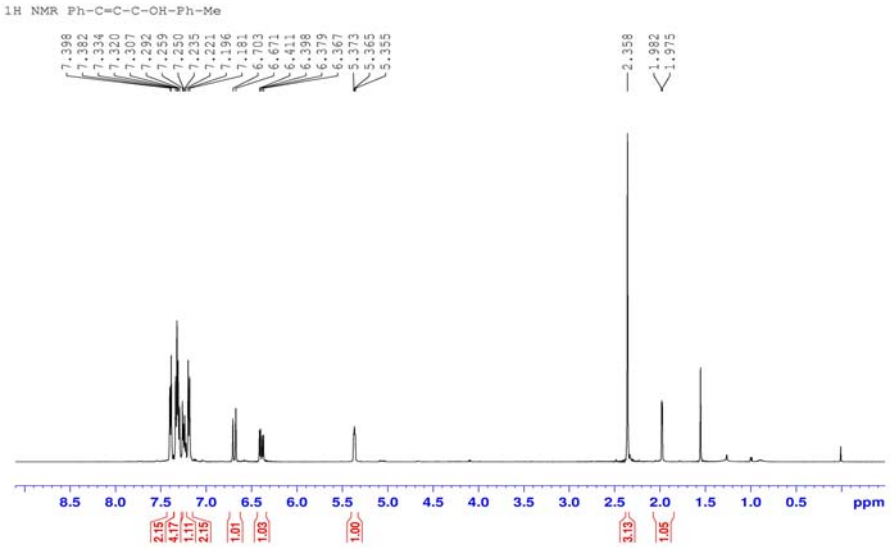

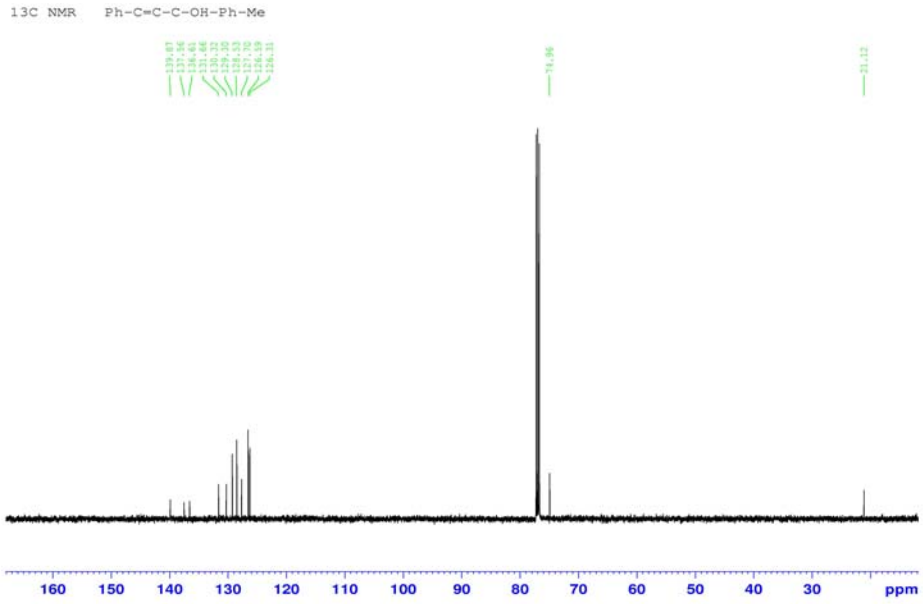

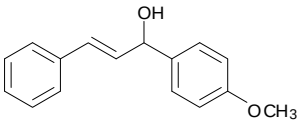

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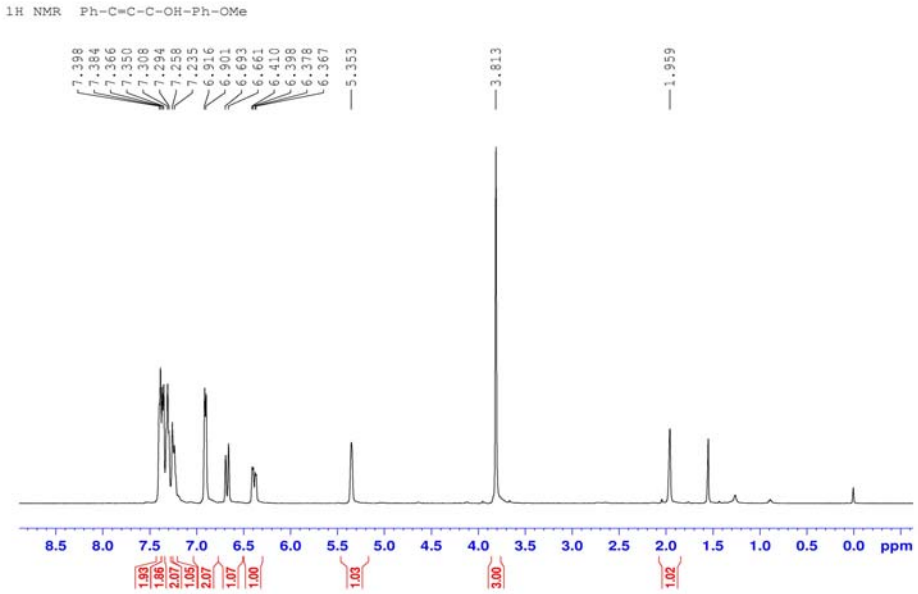

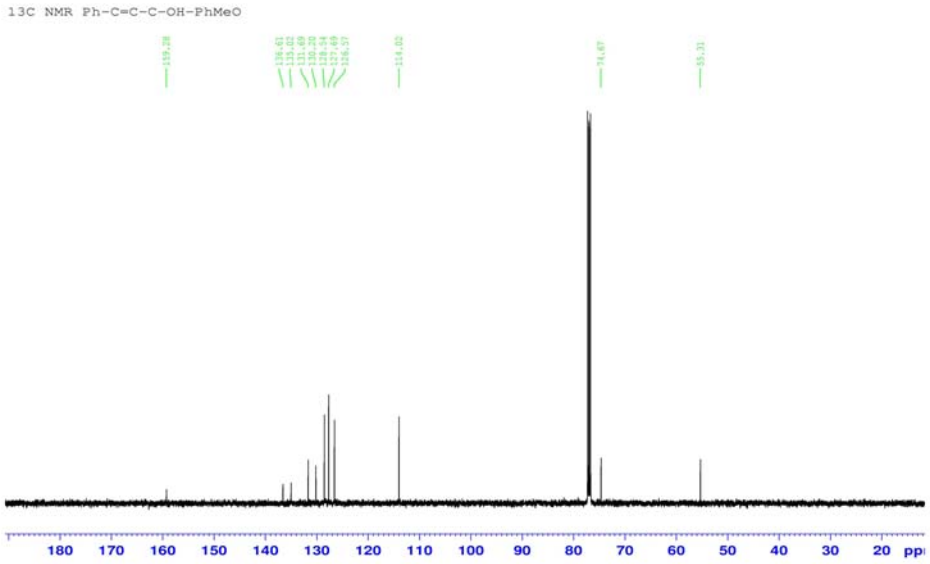

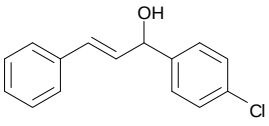

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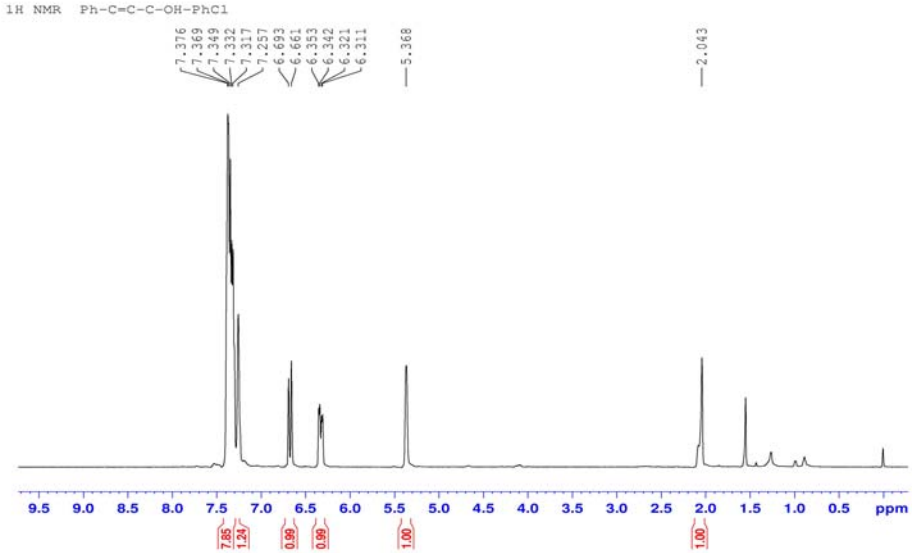

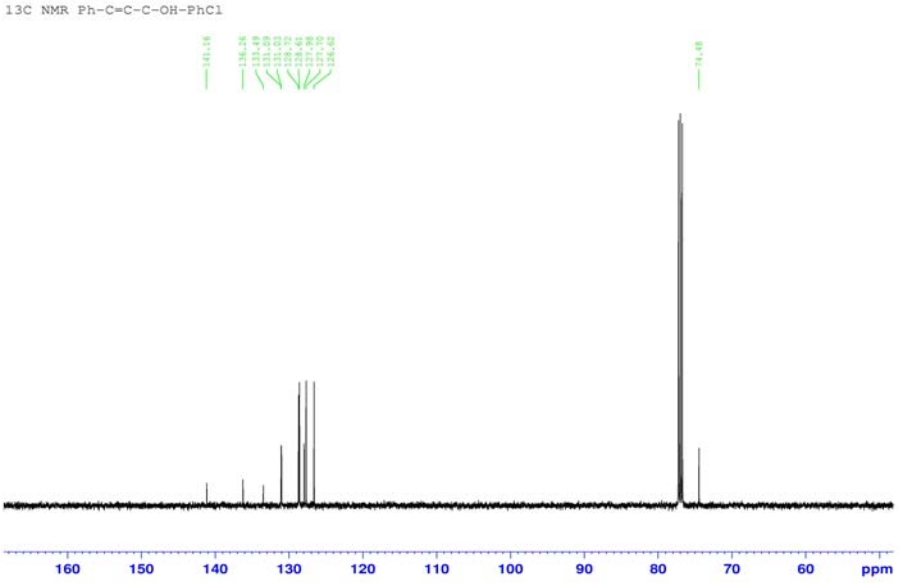

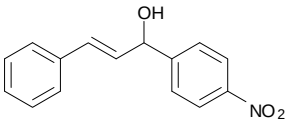

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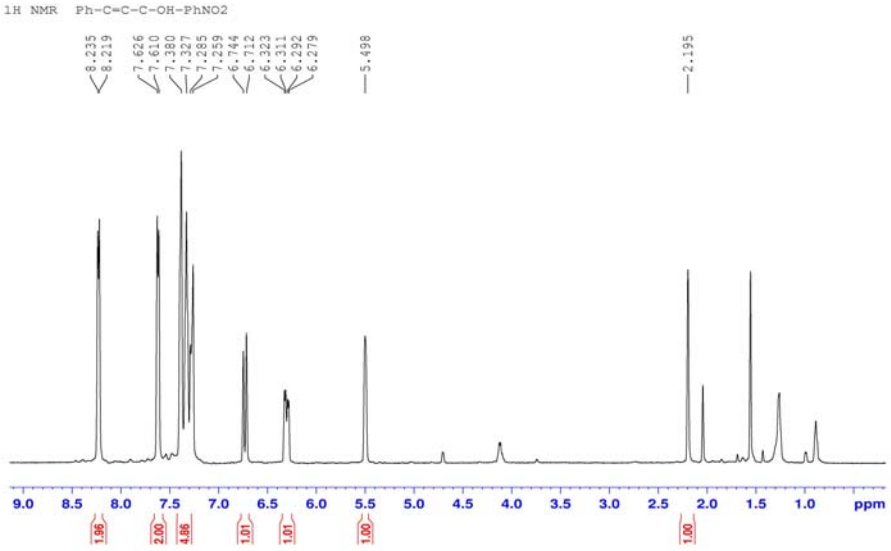

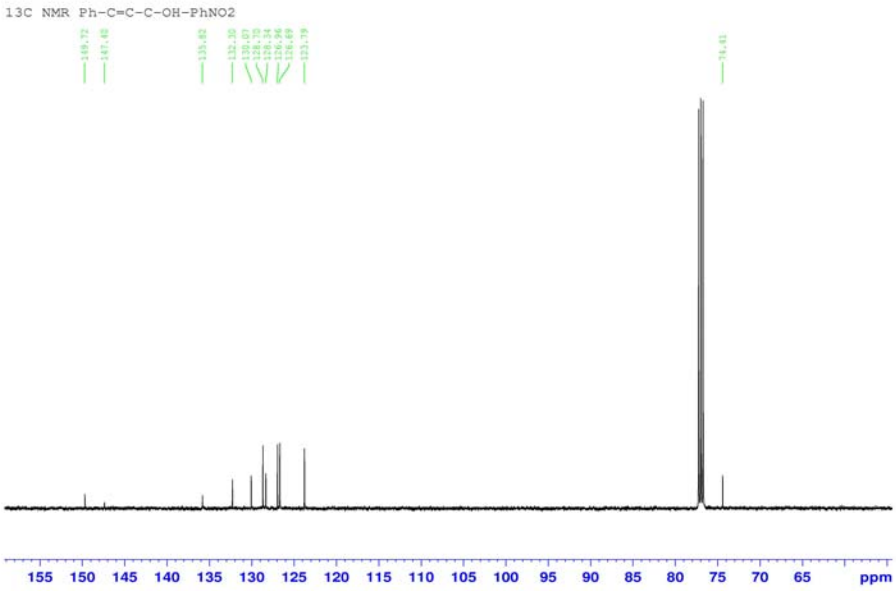

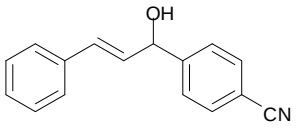

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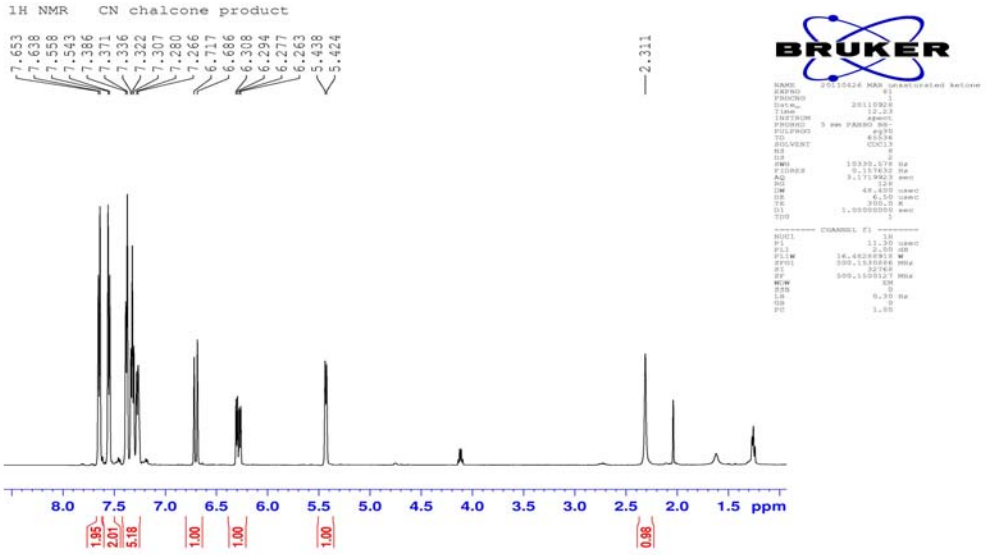

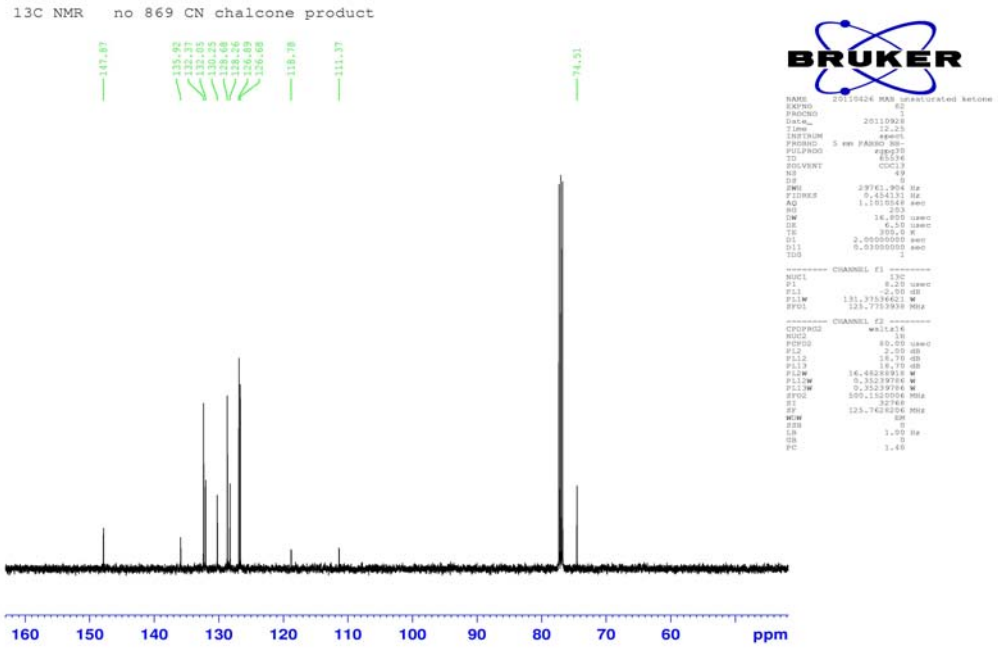

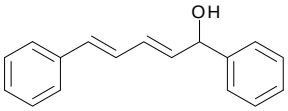

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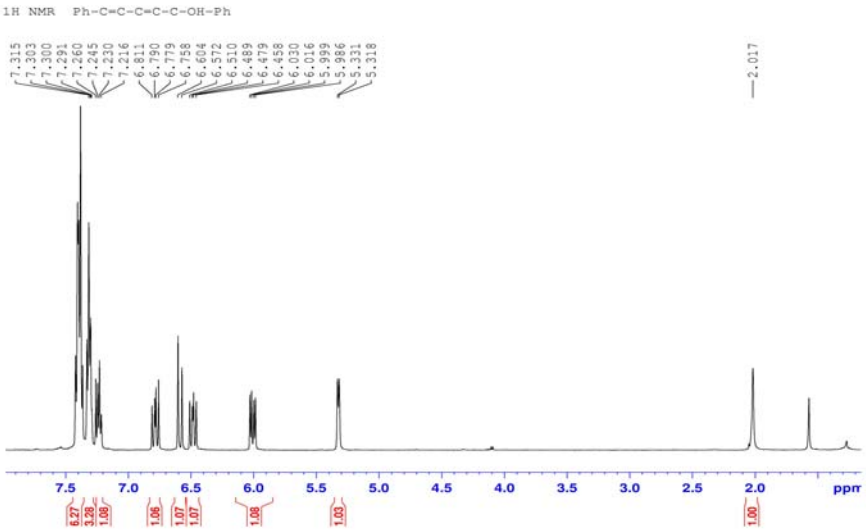

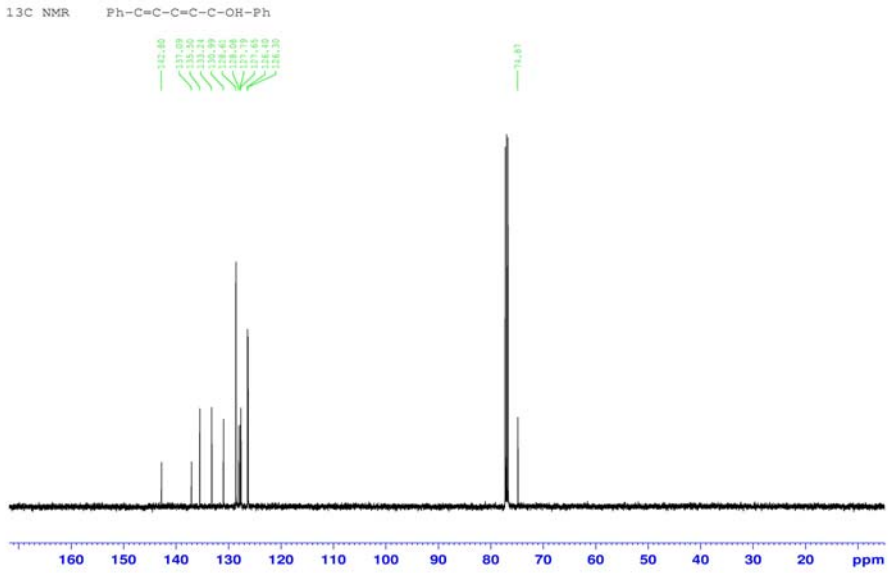

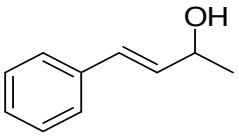

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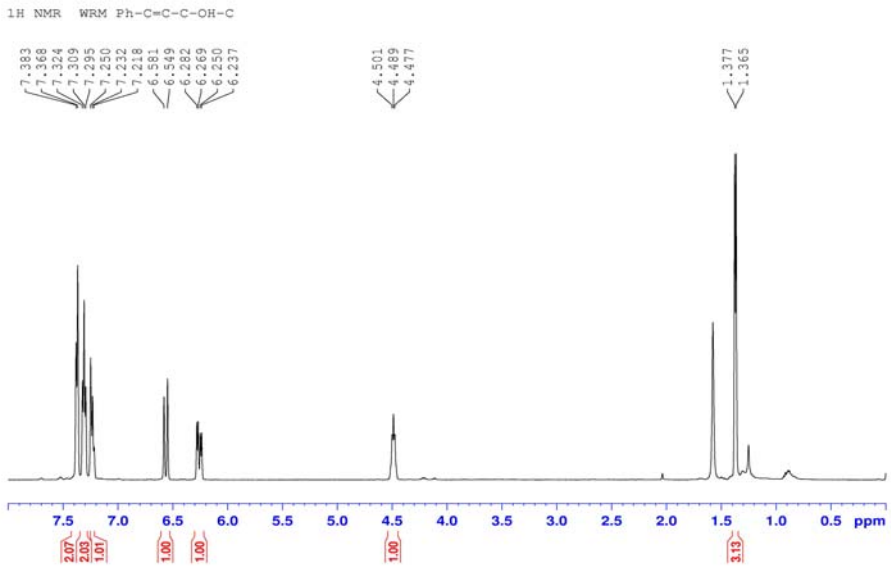
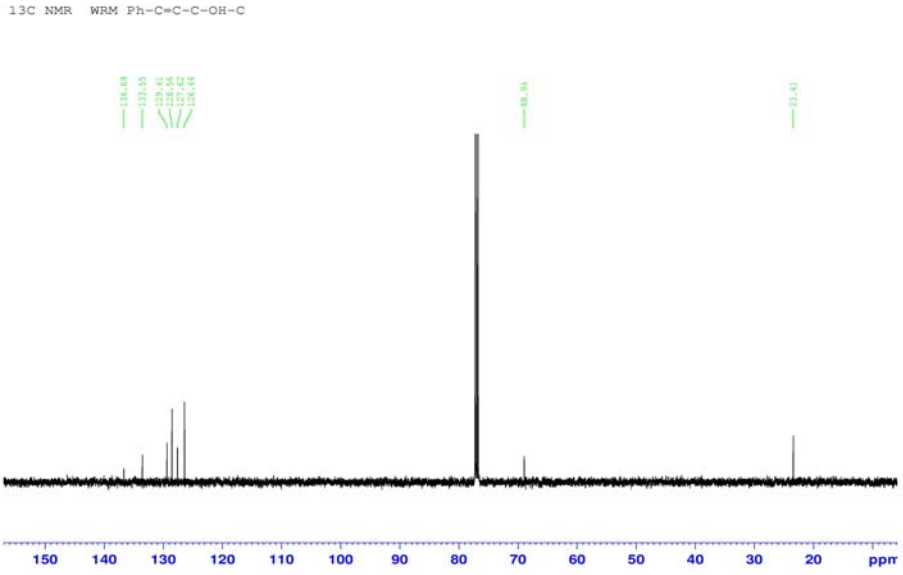
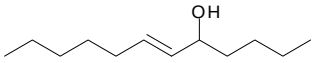
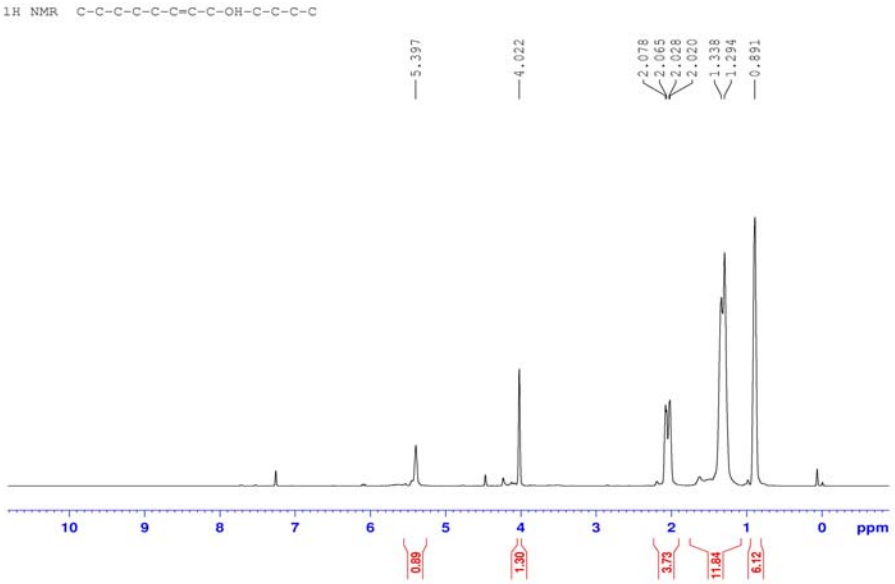
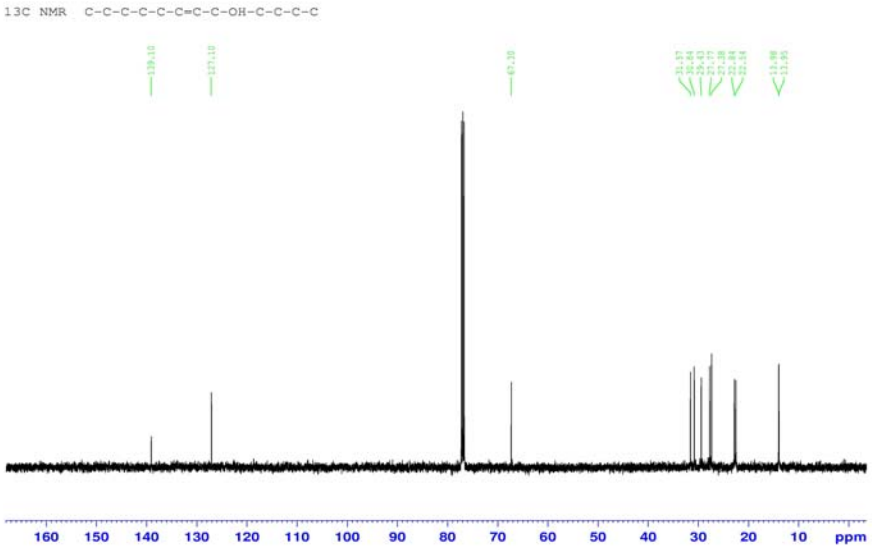


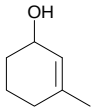




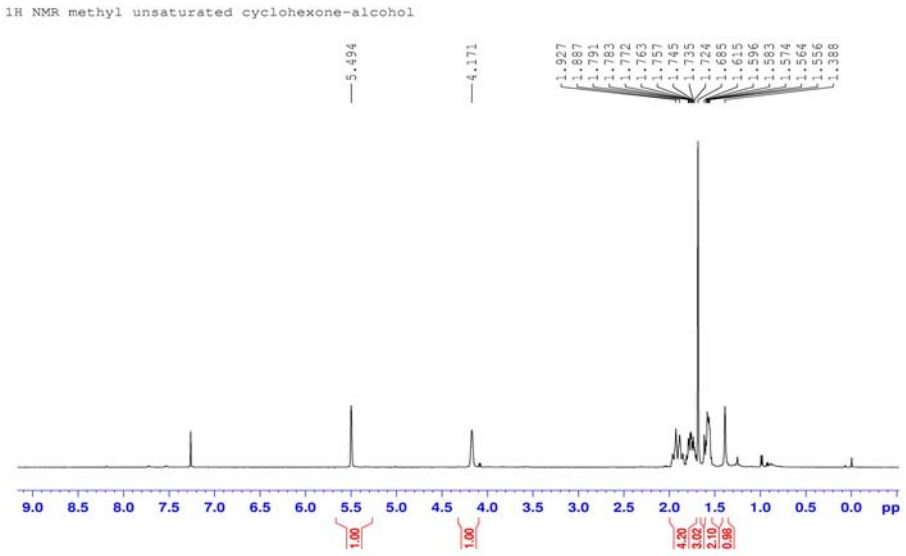
(entry 16, Table 2):

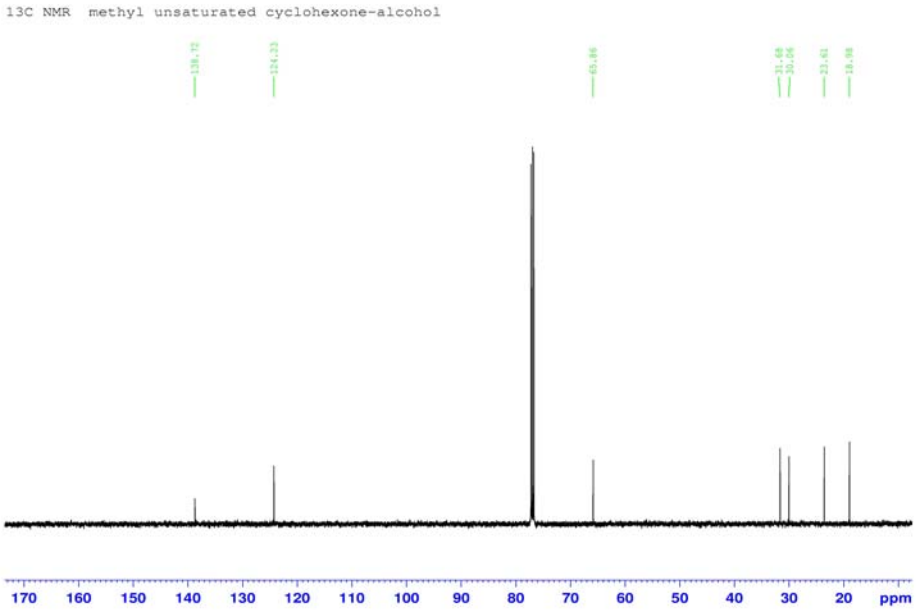


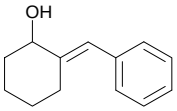




(entry 17, Table 2):







(entry 16, Table 2):